The effects of solvent changes and of electrolyte additions on the stabilities of initial and transition states in nucleophilic substitution reactions

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ABSTRACT

This thesis describes the effects of solvent changes and electrolyte additions on the stabilities of the initial and transition states in the solvolysis (or ionisation) of organic chlorides. Very little relevant information was available when the present work began, but many workers[1b,32,42,43,50a,e,f,j.] had studied the effects of changes in the reaction conditions on the rate coefficient.

The present experiments were carried out in aqueous acetone using 4-phenyl:4'-nitrodiphenylmethyl chloride (I), 4-nitrodiphenylmethyl chloride (II) and 4-nitrobenzyl chloride (III) as substrates. Compound (III) undergoes S_N2 solvolysis, while (I) and (II) react entirely by the unimolecular mechanism, S_N1.[17,86.]

The rate of solvolysis of compound (III) was less sensitive to solvent changes than that of compounds (I) and (II); in agreement with earlier views.[1]
In bimolecular solvolysis, compound (III), an increase in the water content reduced the stability of both the initial and transition states, though not to the same extent. However, the stability of the transition state in S_N1 reactions was almost independent of the solvent composition, although this did not apply to the corresponding entropy and enthalpy terms. These results show some differences from those obtained from a study of the effects of solvent changes in the solvolysis of tert.-butyl chloride in aqueous ethanol.[31,55b,g.,85.]

The effects of added electrolytes on the rate of ionisation of compound (III) in 70% (v/v) aqueous acetone depended markedly on their nature, in agreement with other recent reports of specific electrolyte effects.[50]

In general, the stability of the initial state was more sensitive to the nature of the electrolyte than the stability of the transition state. These results are qualitatively consistent with the view that two separate effects control the stabilities of these two states, and hence the rate; the ionic-strength effect,[1] which is independent of the nature of the electrolyte and the salt-induced medium effect.[50a,e.,58] The magnitude of the latter effect depends on the nature of the electrolyte, since it can be considered to arise from changes in the "effective" solvent composition caused by the varying degrees of solvation of different electrolytes. The smaller sensitivity of the transition state to the nature of the electrolyte is then consistent with its virtually constant stability as the composition of solvent is altered.

THE EFFECTS OF SOLVENT CHANGES AND OF ELECTROLYTE ADDITIONS ON THE STABILITIES OF INITIAL AND TRANSITION STATES IN NUCLEOPHILIC SUBSTITUTION REACTIONS.

A THESIS SUBMITTED FOR THE DEGREE OF DOCTOR OF
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HATFIELD COLLEGE

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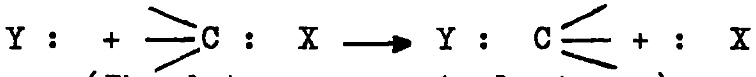
I. 1. Nucleophilic Substitution Reactions.

This thesis describes a kinetic study of the effects of electrolyte additions and changes in the solvent composition on the rates of solvolysis of organic halides. These reactions belong to the general class called nucleophilic substitution reactions (S_N), which are characterised by the fact that the electrons in the bond to be broken remain associated with the departing group, X, while the new bond is formed by co-ordination of the nucleophile, Y, with the substrate.



(The dots represent electrons)

There need be no restriction on the states of electrification of the substrate or the nucleophile provided that the electron displacements occur in the required manner. Thus all the following processes are nucleophilic substitutions:

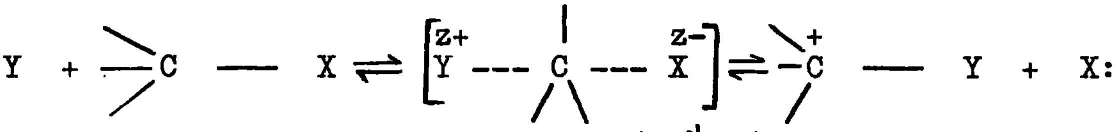
$$RCl + H_2O \longrightarrow ROH + H^+ + Cl^-$$

$$RCl + OH^- \longrightarrow ROH + Cl^-$$

$$RCl + NR'_3 \longrightarrow R'_3\overset{+}{N}R + Cl^-$$

$$R_4N^+ + OH^- \longrightarrow R_3N + ROH$$

Two mechanisms have been recognised for nucleophilic substitution reactions[1]. Fission of the C —— X bond may occur at the same time as the new bond C —— Y is formed:

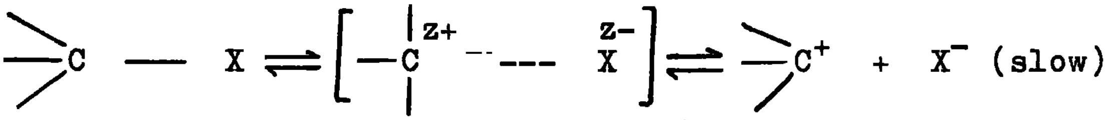


Transition state ($Z \ngtr 1$)

Two molecules then undergo covalency change on passage from the initial state to the transition state and the reaction is therefore regarded as bimolecular (S_N2). An example of reaction by this mechanism is afforded by the solvolysis of methyl bromide in aqueous ethanol[2]:

$$CH_3Br + H_2O \longrightarrow CH_3OH + H^+ + Br^- \qquad (S_N2)$$

Alternatively, the substrate may undergo a rate determining heterolysis without any participation by the nucleophile, Y. The carbonium ion formed in this ionisation then undergoes a rapid reaction with the nucleophile to form the products:



Transition state ($Z \ngtr 1$)

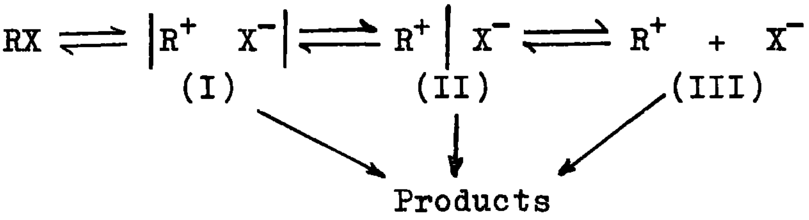
Since only one molecule is undergoing covalency change in the rate-determining step, the reaction is termed unimolecular[1,2] (S_N1). The large activation energy required for the gas phase heterolysis of the C —— X bond is reduced to an accessible value in solution by solvation of the polar transition state[2]. Mechanism S_N1 is known to operate in the solvolysis of <u>tert</u>.-butyl chloride in aqueous acetone[3]:

$$(CH_3)_3CCl + H_2O \longrightarrow (CH_3)_3COH + H^+ + Cl^- \qquad (S_N1)$$

I. 2. Ion-Pair Intermediates in S_N1 Reactions.

The detailed nature of the ionisation process in S_N1 reactions has been the subject of a great deal of controversy. It was originally thought that an optically active substrate would give a completely racemic product, since the ionisation should lead to a planar carbonium ion. However, shielding of the newly formed carbonium ion by the leaving group had to be invoked to account for the observed partial inversion in the S_N1 solvolysis of α- phenylethyl chloride[4].

On the basis of the simple reaction scheme for S_N1 heterolysis, the rate of racemisation should be equal to the rate of reaction. However, Winstein and his coworkers[5] showed that in a large number of cases the rate of racemisation of organic sulphonates was greater than the rate of acetolysis. These observations further strengthened the earlier objections of Hammett[6] and Winstein[7] that the original reaction scheme proposed by Hughes and Ingold was too simple to be of universal validity. Working independently, they both came to the conclusion that some form of metastable intermediate must be involved in the ionisation process. More recently, studies of the effect of added electrolytes on the acetolysis of organic sulphonates by Winstein and his coworkers[5] have led them to postulate that two separate types of ion-pair intermediates, in addition to the fully-developed carbonium ion, exist in S_N1 heterolysis:

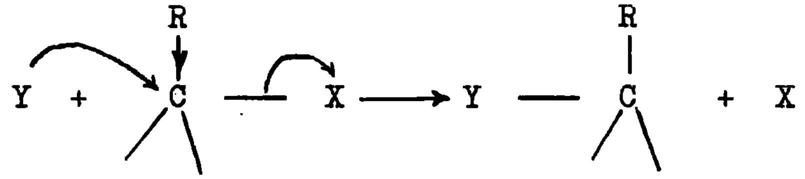


In the internal or intimate ion-pair (I), the two ions are considered to share a common solvation shell, while they are believed to be separated by at least one solvent molecule in the external or solvent-separated ion-pair (II). The internal ion-pair (I) can reform the original substrate with accompanying racemisation (internal return). The external ion-pair (II) can also return to the initial state <u>via</u>. the internal ion-pair (I) (external return), but it can also react with the nucleophile to give an inverted product, or it may form the fully developed carbonium ion (III). The internal ion-pair (I) is also susceptible to nucleophilic attack, but is considered to be far less reactive than (II).[5a,c,e] The principal evidence for the existence of the ion-pairs arose from the observation that the rate of racemisation was greater than the rate of solvolysis. The postulate of distinct internal and external ion-pairs is based on the "special salt effect" <u>i.e</u>. a marked increase in the rate of solvolysis on the addition of small amounts of electrolytes and a much smaller increase on further additions once the electrolyte concentration had exceeded some critical value. Under these conditions the rate of racemisation was still greater than the rate of solvolysis and it was therefore concluded that the rates of solvolysis in the presence of small concentrations of electrolytes arose from the resulting stabilisation of the external ion-pair (II), thus rendering it more likely to attack by nucleophiles and leading to a reduction in external return. No similar effect was postulated for the internal ion-pair (I). However, Hughes and his coworkers[8] have pointed out that the "special salt effect" may be explained if ion-pairing of the added electrolyte is assumed to occur in solvents of low dielectric constant. It is noteworthy that in the majority of cases where racemisation has been reported to occur more rapidly than reaction, poor ionising or non-hydroxylic solvents have been used e.g., acetic acid,[5,9] acetone,[10] nitromethane,[11] sulphur dioxide[11] and acetonitrile.[12] Nevertheless, excess racemisation has also been demonstrated for reactions carried out in aqueous solvents[13,14] e.g., for optically active substituted diphenylmethyl chlorides,[13] although the ratio of the two rates was closer to unity than in poorer ionising solvents. Ion-pair intermediates have been invoked in a few other S_N1 reactions in aqueous solvents,[14] but the bulk of the evidence for their existence is derived from work in acetic acid and other solvents of low dielectric constant. However, it has been recently reported that for the solvolysis of exo-norbornyl p-trifluoromethylthionbenzoate[15] in acetic acid the rate of racemisation is equal to the rate of acetolysis, indicating the absence of ion-pair return in this system. Kohnstam and his coworkers[16] concluded from their work on dichlorodiphenylmethane in aqueous acetone that any reaction between water or anions and any intermediate ion-pairs contributed nothing to the total rate of solvolysis. It will therefore be assumed that S_N1 reactions in aqueous solvents occur only via., the fully developed carbonium ion, as originally envisaged by Hughes, Ingold and their coworkers.[1b]

I. 3. Factors Controlling the Mechanism in Nucleophilic Substitution Reactions.

I. 3.1. Structural variations in the radical R.

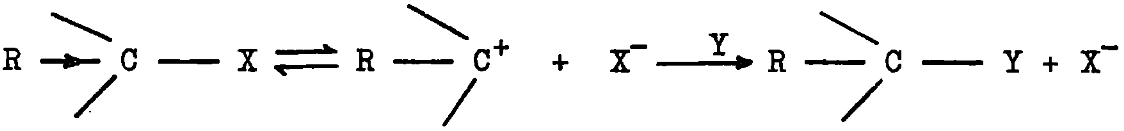
Bond-breaking and bond-making occur simultaneously when mechanism S_N2 is in operation;



If the nature of R is varied to allow an increased degree of electron release to the reaction centre, (as shown above) the bond-breaking process will be facilitated.
However, at the same time, the formation of the new bond (which involves co-ordination of the unshared electrons associated with Y) will become more difficult so that the effect of structural changes in R on the rate will depend on whether bond-making or bond-breaking is the predominant factor in the activation process. Analogous considerations apply to the introduction of electron-attracting groups. The kinetic effect of changes in the electron density at the central carbon atom in S_N2 reactions therefore represents the difference of two opposing effects and can thus be expected to be relatively small. Bond-breaking appears to be the predominant factor in reaction with weak nucleophiles, such as water, and the rate of hydrolysis of 4-substituted benzyl chlorides increases with increasing electron supply to the reaction centre.[17] Bond-formation appears to become progressively more important in the reactions of these compounds as the

nucleophilic power of the reagent (Y) is increased and a rate minimum has been observed in a series of substituted benzyl halides in which the electron-donating power of the group R increases.[18]

No such ambiguity arises in reaction by mechanism S_N1:



Here no contribution from the nucleophile is required until after the rate determining ionisation, and an increased degree of electron-release towards the reaction centre (as shown above) will facilitate the bond-breaking process and give rise to a large unambiguous acceleration of the reaction. The converse is true if R is electron attracting.

Thus the introduction of electron-releasing substituents can be expected to have only a small effect on the free energy of activation of a bimolecular reaction but will markedly reduce this parameter in reaction by the alternative unimolecular mechanism. As a result a transition from mechanism S_N2 to mechanism S_N1 can be expected by increasing the electron accession to the reaction centre of a compound, which reacts bimolecularly. This expected transition has been observed in the solvolysis of the α-methylated methyl halides:[2,3,19.]

$$CH_3X,\ CH_3CH_2X,\ (CH_3)_2CHX,\ (CH_3)_3CX$$

In this series the increased electron release towards the reaction centre is brought about by a purely inductive process,[1b,20.] and only the last member of the series reacts entirely by mechanism S_N1. A similar transition occurs in the solvolysis of the α-phenyl substituted methyl halides[21.] where the electron release occurs by a conjugative process:[1b,22.]

$$CH_3X,\ PhCH_2X,\ (Ph)_2CHX,\ Ph_3CX$$

In this series the last two members react by mechanism S_N1. It should however be stressed at this point that the nucleophilic power of the reagent (Y) could also affect the point of mechanistic transition, although in the presence of hydroxide ions <u>tert</u>.-butyl halides and diphenyl methyl halides have been shown to react by mechanism S_N1.[23.]

In both series the compounds which undergo S_N1 reactions also show considerable steric hinderance to S_N2 attack.[19b,24.] Since the central carbon atom is subjected to a shielding effect by the bulky groups which form the radical R, thus preventing easy approach by the nucleophile (Y) until the leaving group (X) has departed some distance from the central carbon atom. However, the fact that <u>tert</u>.-butyl chloride undergoes hydrolysis more rapidly than iso-propyl chloride[1b.] and diphenylmethyl chloride more rapidly than benzyl chloride[1b,17b.] suggests very strongly that polar rather than steric factors are responsible for the mechanistic change. Nevertheless, both <u>tert</u>.-butyl halides[25] and diphenylmethyl halides[26] have been reported to undergo reaction by mechanism S_N2. The effect of increasing electron supply to the reaction centre can be more clearly seen in the solvolytic reactions of a series of 4-substituted benzyl halides[17] in which the substituent is at a sufficient distance from the reaction centre to cause no significant effect on any steric hinderance to substitution, the substituents used being;

4-NO_2-; 4-H-; 4-Me-; 4-PhO-; 4-MeO-

In this series, only the phenoxy[17b] and methoxy[17a] compounds react entirely by mechanism S_N1.

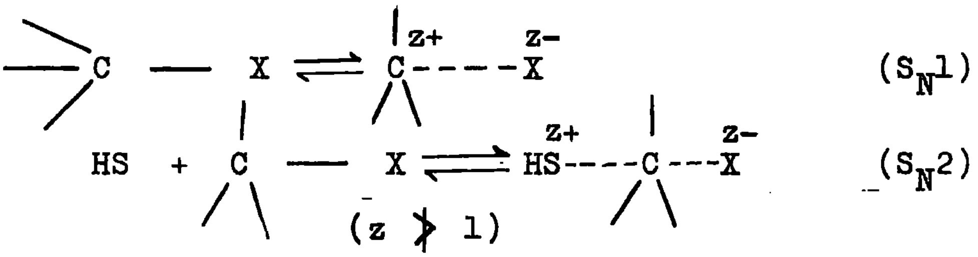
I. 3.2. Variations in the nature of the leaving group (X).

The predominant process in S_N1 reactions is bond breaking, whereas both bond-breaking and bond-making are of importance in the S_N2 reaction. It might therefore be thought that a change in the leaving group (X) such that the C —— X bond is more easily ionised should facilitate reaction by mechanism S_N1. This would result in a change of mechanism occuring at an earlier stage in a series of increasing electron release towards the reaction centre. However, this is not found in practice as little difference is observed in the point of mechanistic change for the reactions of the corresponding alkyl chlorides, bromides and sulphonates with aqueous acetone;[27,28,29.] this may be due to the great importance of bond-breaking in both the S_N1 and S_N2 solvolysis of these compounds. Moreover, the introduction of a "better" leaving group is probably only a small factor in determining the mechanism as this group has the same function to perform (namely to acquire completely the electrons it previously shared with the substrate) in reaction by either mechanism.

I. 3.3. Changes in the solvent composition.

Early discussions[1] of the effect of changes in the solvent composition on the rates of nucleophilic substitution reactions were limited to explanations involving only the effect of solvent changes on the stability of the transition state; it being assumed that the effect of these changes on the initial state was negligible. As a study of these effects on solvolytic reactions forms part of the present thesis, a detailed discussion is deferred (see sections I.6 and I.11) and only the earlier theories relevant to such reactions are considered here.

The energy of activation in the S_N solvolysis of a neutral substrate is considered to be reduced to accessible values by solvation of the polar transition state.[1b.] Hence, in a reaction which involves passage from an essentially non-polar initial state to a dipolar transition state, an increase in the solvating power of the solvent (HS) will increase the rate of both S_N1 and S_N2 reactions:[1b.]



However, the electric charges are more diffuse in the transition state of an S_N2 reaction than they are when mechanism S_N1 is in operation, and consequently the solvation requirements of the former are far less, i.e., the rate of an S_N2 reaction will be the less sensitive to solvent changes.[1b.] This can be clearly seen from the results in table I.

TABLE I

The rates of solvolysis of n-butyl bromide[31] and *tert*.-butyl bromide[1b.] in aqueous ethanol.

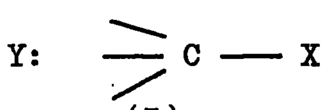
Solvent % (v/v) H_2O	n-Butyl bromide 10^6k_1 at 75.1°C	*tert*.-Butyl bromide 10^6k_1 at 25°C
	(S_N2)	(S_N1)
10.0	——	1.71
10.7	2.48	——
28.0	5.67	——
30.0	——	40.3
44.1	11.08	——
50.0	——	367

The precise meaning of the term "solvating power" is vague and it has been suggested that carboxylic acids which would solvate the incipient anion should be specially favourable to the operation of mechanism S_N1. Evidence for this has been obtained for the formolysis of alkyl halides.[30.] In solvent formic acid, the mechanism was shown to be closer to S_N1 than for the corresponding reaction in aqueous alcohol, but Fox[17c.] has recently shown that the point of mechanistic transition for a series of 4-substituted benzyl halides is not very different in formic acid and aqueous acetone.

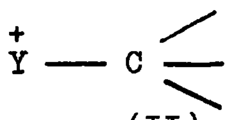
I. 4. The Border-Line Region

It can be concluded from the discussion in the last section that the most important factor controlling the mechanism of S_N reactions is the effect caused by structural variations in the radical R and it has also become apparent that a region of transition from reaction by mechanism S_N2 to mechanism S_N1 must exist. This region has often been called the border-line region.

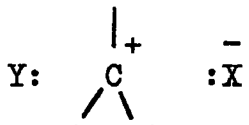
The precise nature of the reaction path in the region which marks the transition from mechanism S_N2 to mechanism S_N1 is of interest. In a nucleophilic substitution reaction the transition state can be regarded as a resonance hybrid of the following valence bond structures:[32b.]



(I)



(II)



(III)

If structure (II) makes any contribution to the transition state, the reaction must be regarded as bimolecular (S_N2), since covalent participation of the nucleophile (Y) is an essential feature of the activation process.[1b.]

Two alternatives have been proposed for the nature of the reaction path in the region of mechanistic change. All individual acts of substitution may proceed *via*. a single reaction path. The transition state is regarded as a resonance hybrid of all three cannonical forms; the reaction being termed S_N2 as covalent participation is evident. The greater the contribution from structure (III) relative to (II), the more does the reaction tend to show the characteristics of an S_N1 process. Alternatively, a variety of reaction paths may be available, some of which involve a contribution from structure (II) to the transition state structure while others do not. Hence, it is possible for reaction to occur by the concurrent operation of mechanisms S_N1 and S_N2. So far, no unambiguous experimental evidence in favour of either of these alternatives is available for solvolytic reactions, although both possibilities have been proposed.[14b,24f,26a,32,33] However, evidence for the concurrent operation of mechanisms S_N1 and S_N2 has been obtained for reactions involving more powerful nucleophiles than solvent molecules.[14b,26b,33b]

I. 5. Methods for the Recognition of Mechanism.

In the reaction between a substrate (RX) and a nucleophile (Y), the unimolecular mechanism of substitution leads to first-order kinetics;

$$\text{Rate} = k_1^{\text{obs.}}[\text{RX}] \qquad \text{-------} \qquad 1.1.$$

The bimolecular mechanism requires a second-order rate law, provided that the nucleophile is not present in much greater amounts than the substrate;

$$\text{Rate} = k_2^{\text{obs.}}[\text{RX}][\text{Y}] \qquad \text{-------} \qquad 1.2.$$

This is not true in solvolysis, where the solvent is present in large excess and first-order kinetics, as represented by equation 1.1., are therefore usually observed for reaction by both mechanisms. Slight deviations from the first-order rate law in solvolytic reactions are however found in certain special cases (see page 18). Indirect methods must therefore be employed to obtain information about the mechanism in solvolysis. Several methods are available for the recognition of mechanism, namely,

(i) Structural changes in the radical R.

(ii) Systematic changes in the substituting agent (Y).

(iii) The stereochemical course of the substitution.
(iv) The effect of electrolyte additions of the rate of reaction.
(v) The effect of solvent changes on the rate of reaction.
(vi) The value of the ratio of the heat capacity of activation ($\Delta C^{\ddagger}$) to the entropy of activation ($\Delta S^{\ddagger}$).

These methods have been extensively reviewed[34,35.] but as methods (iv) and (v) are concerned with the problems now under investigation, it is necessary to discuss them in more detail.

I. 6. The Effects of Solvent Changes on Rates of Solvolysis.

The formation of a highly polar transition state is an essential feature of the S_N solvolysis of a neutral substrate and thus, in polar solvents, the transition state will be stabilised by solvation. The importance of solvation in increasing the rate of reaction by increasing the stability of the transition state has been stressed in section I.3.3. The power to solvate a charged solute will, in general, increase with an increase in the molecular dipole moment of the solvent, but will decrease with increased shielding of the dipolar charge.[1b.] It must be emphasised, however, that the ionising or solvating power of a given solvent cannot be measured in terms of its dielectric constant alone. Indeed, the relationship between ionising power and other properties of the solvent is complex, and although the simple model of a solvent as a continous dielectric can often be used to predict the gross effect on the rate of a change in the solvent composition for reactions of various charge types,[2,36.] there is little doubt that such a model is severely restricted.[36-43] This is especially true for mixtures of water and inert solvents, where the actual water content is of far greater importance than any function of the dielectric constant.[37,38] Thus, it has been found that the rates of hydrolysis of several acid chlorides are almost equal in 95% aqueous acetone and 95% aqueous dioxan[38b] in spite of the considerable differences in dielectric constant and that the rate of reaction of 4-nitrobenzoyl chloride in 5% aqueous formic acid, which has a very high dielectric constant, is considerably less than in the above solvents.[38c] Although relationships between log $k_1^{obs.}$ and D,[39] 1/D[40] and (D-1)/(2D+1)[41] have been proposed and had some qualitative success, quantitative agreement cannot be expected for the reasons already put forward. The most recent test of the relationships between the rate and the dielectric constant was made by Hyne and his coworkers,[42] who found them completely inadequate to explain their own experimental observations. This failure of correlations based on the rate and the dielectric constant of the medium is hardly surprising, especially in mixed solvents which cannot be considered as continuous media. Some segregation of the solvent components will undoubtedly occur in the vicinity of the reactants and any approach which treats the medium as a continuous dielectric is therefore open to objections. This is particularly likely in hydroxylic solvents where there is always the possibility that hydrogen bonding will occur between the solvents, and the ground and transition states of the organic substrate.

A different approach was adopted by Winstein and his coworkers[32,43] who attempted to correlate the change in rate with a parameter Y, characteristic of a particular solvent and defined by

$$Y = \log_{10}k_x/k_x^o \qquad \text{-------} \qquad 1.3.$$

where k_x is the rate of solvolysis of tert.-butyl chloride (or diphenylmethyl chloride) in a given solvent and k_x^o the rate of solvolysis in 80% aquous ethanol at the same temperature. This parameter was taken to represent a measure of the ionising power of the solvent so that the rates of solvolysis of other compounds were given by

$$\log_{10}k_1/k_1^o = mY \qquad \text{-------} \qquad 1.4.$$

where k_1 is the first-order rate constant for the reaction of the compound under investigation and the superscript, o, refers to the reference solvent, 80% aqueous ethanol. The constant, m, was found to be unity for S_N1 solvolysis and ca. 0.3 when mechanism S_N2 was operating. Equation 1.4., has been shown to be successful in a number of cases,[32,43.] although it is not of general application.[37,42.] However, this is not surprising if one considers that Y reflects the solvation changes occurring on passage from the initial state to the transition state of tert.-butyl chloride (or diphenylmethyl chloride) in a given solvent and in 80% aqueous ethanol; there is no guarantee that the solvation changes in these solvents will be the same for different compounds. The observation that, for aqueous acetone, it was necessary to use two sets of Y values,[32] one based on tert.-butyl bromide and the other based on diphenylmethyl chloride, also represents a limitation to equation 1.4. A more complicated classification was attempted by Winstein and his coworkers[32b,] but this only tended to make the application of equation 1.4., more difficult.

Swain and his coworkers[33f,] attempted a correlation using a four parameter equation in which two of the parameters depended on the nature of the substrate while the other two parameters were related to the nature of the solvent. However, this approach did not allow any mechanistic distinctions.

The failure of correlations involving the dielectric constant and the Winstein Y values to account for experimental observations in the solvolysis of dimethyl-tert.-butyl sulphonium iodide[42] in various aqueous organic solvents led Hyne and his coworkers to attempt a correlation involving the parameter Z, originally proposed by Kosower.[44] Values of this parameter reflect the importance of specific solvent-substrate interactions in the activation process since Z is a measure of the specific effect of the solvent components on a charge delocalisation process in passing from pyridine-1-oxide to the charge transfer complex. This process has formal similarity to the activation process in the solvolysis of a sulphonium salt. The existence of specific solvent-substrate interactions has also been invoked to explain deviations from the simple continuous dielectric model in other systems.[45] For most of the binary solvent mixtures studied, Hyne and his coworkers[42] observed a linear relationship between $\log_{10}k$ and experimental Z values and concluded that specific solvent-solute interactions must be of importance in the activation process.

While this conclusion is probably justified, it provides no information about the relative importance of these interactions in the initial and transition states in solvolysis. However, the use of the Z parameter in rate correlations is a major improvement on the earlier attempts[32,33f,36-41] since it takes into account the individual properties of the solvent components. Recent work has attempted to establish at what stage in the activation process the solvent-solute interactions are important, but a discussion of these investigations is deferred. (see section I. 11).

I. 7. The Effect of Electrolytes on the Rate of Solvolysis.

I. 7.1. The Mass-Law effect.

In the S_N1 solvolysis of an organic chloride, the rate-determining ionisation is reversible:

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

$$R^+ + H_2O \xrightarrow{3} ROH + H^+ \qquad \text{(fast)}$$

Application of the stationary-state principle to the highly reactive carbonium ion and comparison with equation I. 1. gives;

$$k_1^{obs.} = k_1/(1 + \alpha\left[Cl^-\right]) \text{ ------- } \qquad 1.5$$

where $\alpha = k_2/k_3$ and is called the mass-law constant.

Since chloride ions are produced as the reaction proceeds, the first order rate constant ($k_1^{obs.}$) will decrease under these conditions. This effect is illustrated in table II.

TABLE II

The Mass-Law effect in the hydrolysis of 4,4', dimethyl-diphenylmethyl chloride in 90% aqueous acetone at 0°C.[1b.]

Time (mins.)	16.0	35.4	68.8	103.9	152.7	212.2	286.8	340.3
10^5k_1 (secs.$^{-1}$)	8.68	8.30	7.83	7.53	7.33	7.05	6.87	6.77

This retardation of solvolysis by common anions is called the mass-law effect and can, of course, also be observed by comparing the rates of solvolysis in the presence and absence of added common-ion salts.

No similar retardation should be observed in S_N2 solvolysis, but it must be stressed that a small reduction in rate on addition of a common-ion salt does not necessarily prove the operation of mechanism S_N1. The mass-law effect is not the only effect invoked on the addition of electrolytes and general salt effects will alter the rates of both S_N1 and S_N2 solvolysis. These effects are discussed in more detail in sections I. 7.2. and I. 7.3. It is noteworthy that the hydrolysis of benzyl chloride is retarded on the addition of sodium chloride,[46] although all other evidence suggests that reaction occurs mainly, if not entirely, by mechanism S_N2.[47]

I. 7.2. The Ionic-Strength effect.

Hughes, Ingold and their coworkers[1] originally pointed out that the highly dipolar transition state of solvolysis by both mechanism S_N1 and S_N2 should be subject to ion-atmosphere stabilisation when electrolytes are present, in the same way as fully-developed ions are stabilised under these conditions. This ionic-strength effect should be shown by all electrolytes and would tend to accelerate solvolysis irrespective of the mechanism; the effect of electrolytes on the initial state was neglected.

These workers proposed a quantitative treatment for the resulting effect of electrolytes on the rate determining step of S_N1 reactions i.e., the ionisation.

Their approach is outlined below. According to the transition state theory, the rate of ionisation of the substrate in the presence of an electrolyte (k_1) is given by;

$$\frac{k_1}{k_1^o} = \frac{\gamma_{RX}}{\gamma_{RX}^o} \cdot \frac{\gamma_{\ddagger}^{o}}{\gamma_{\ddagger}} \quad \text{-------} \quad 1.6$$

where γ_{RX} and $\gamma_{\ddagger}$ are the activity coefficients of the substrate (RX) and the activated complex respectively, and the superscript o, refers to the value in the absence of added electrolyte.

Hughes, Ingold and their coworkers[48] assumed that the reacting molecule is unaffected by the presence of electrolytes i.e., $\gamma_{RX}/\gamma_{RX}^o = 1$, so that equation I.6. becomes

$$k_1 = k_1^o \, (\gamma_{\ddagger}/ \gamma_{\ddagger}^{o})^{-1} \quad \text{-------} \quad 1.7$$

Using the model of a permanent dipole with two point charges ± Ze, separated by a fixed distance d, surrounded by an ion-atmosphere, an expression for $\gamma_{\ddagger} / \gamma_{\ddagger}^{o}$ was obtained, which on substituting in equation 1.7 gave, for uni-univalent electrolytes.

$$k_1/k_1^o = \text{antilog}_{10} \, (-B\mu\sigma) \text{-------} \quad 1.8$$

where the ionic-strength constant σ, is equal to Z^2d, μ is the ionic strength of the solutions and B is a constant for a given solvent and temperature, which increases with decreasing ionic strength.

This equation predicts that the effects of uni-univalent electrolytes on S_N1 reactions should be independent of the nature of the electrolyte, but it was pointed out that equation 1.8 represented a limiting case and could only be expected to be valid in very dilute solutions of electrolytes.

In practice common-ions are produced as the reaction proceeds and the mass-law effect must therefore be taken into account in any discussion of the effect of added electrolytes on the observed rate of solvolysis (k_h). If the Debye limiting law predicts the activity coefficients of fully-developed ions with sufficient accuracy, the rate of hydrolysis is given by

$$k_h/k_h^o = \left\{(\text{antilog}_{10} B\mu\sigma) + (\alpha^o [X^-] \text{antilog}_{10} A\mu^{\frac{1}{2}})\right\}^{-1} \qquad 1.9$$

where A is the Debye limiting slope and $\alpha^o = k_2^o/k_3^o$ the mass-law constant at zero ionic strength.

Equation 1.9 has been applied successfully to the S_N1 solvolysis of <u>tert</u>.-butyl chloride, diphenylmethyl chloride, substituted diphenylmethyl chlorides,[48] and dichlorodiphenyl methane[16b], in aqueous acetone. However, it should be stressed that in some cases[48] the comparison between observed and calculated rate constants was carried out using experimental integrated rate constants as distinct from the instantaneous values derived from equation 1.9. Thus the validity of any conclusions is somewhat impaired by an unsound kinetic procedure in these cases.[48]

Contrary to the predictions of this simple electrostatic theory (equation 1.8), specific electrolyte effects have been reported on a number of occasions <u>i.e.</u>, the magnitude of the effect of added electrolytes on k_1/k_1^o was found to depend on the nature of the electrolyte. These observations are discussed in the next subsection, but it must be stressed now that small differences between the accelerating effects of different electrolytes do not offend the requirements of an ionic-strength effect, since equation 1.8 may not strictly be valid at the experimental concentrations of electrolytes, particularly in solvents of low water content.

I. 7.3. Specific Electrolyte Effects in S_N1 Reactions

Nash and Monk[49a], pointed out that the effective ionic strength in the solvents employed in this type of work could be depressed well below the expected value by ion-pairing of the added electrolyte. They investigated the effects of lithium, potassium and sodium bromides on the S_N1 solvolysis of _tert_.-butyl bromide in aqueous acetone and obtained good agreement with equation 1.8 provided that ion-pairing of the added electrolyte was taken into account. However, some doubt must be cast on their conclusions since they compared experimental integrated rates with predicted instantaneous values and also neglected the mass-law effect. Nevertheless, ion-pair association may be an important factor in solvents of low dielectric constant. This could account for the observations of Speith and Olson[49b], that the rates of hydrolysis of _tert_.-butyl chloride and bromide were altered to different extents by lithium chloride, bromide and perchlorate and that the relative effect of each salt varied with changing solvent composition. Similarly, ion-pair association may be responsible for the specific electrolyte effects in the solvolysis of diphenylmethyl chloride in 90% aqueous bis (2-ethoxyethyl) ether[49c], at relatively large ionic strengths, but the method used to obtain the rates of reaction is open to criticism.

On the other hand, highly specific electrolyte effects have been reported in good ionising solvents[50,51] and their magnitude and direction are such that they cannot possibly be accounted for by a simple failure of the limiting law or by ion-pair association under the experimental conditions. Thus tetra-n-butylammonium salts have been found to accelerate solvolysis to a much smaller extent than lithium salts in two different systems;[51] indeed, sometimes the tetra-alkylammonium salts even retarded solvolysis. Lucas and Hammett[50a.] found that the rate of S_N1 hydrolysis of tert.-butyl nitrate in aqueous dioxan was accelerated by anions in the order $ClO_4^- > NO_3^- > Cl^- > OH^-$; hydroxide (or lyate) ions were found to depress the rate, and perchlorate ions accelerated the reaction. Similar orders for anion effects have been found in other systems.[29,50]

Lucas and Hammett[50a.] noted that anions which increased the water activity in the solvent medium showed the greatest accelerating effect on solvolysis and vice versa. On the basis of this observation, the results were explained by assuming that the different degrees of solvation of the electrolytes by water, altered the "effective" solvent composition of the binary solvent to different extents. This explanation of the specific effects of different electrolytes on the reaction rate appeared to be reasonable since unimolecular reactions are highly sensitive to changes in the solvent composition. The lyate ion was thought to abstract so much water as to more than cancel the accelerating effect of the ionic strength. Similar arguments can be put forward for other anions which were found to produce retardations e.g., the chloride ion in the solvolysis of benzyl chloride.[46]

While admitting the plausibility of Lucas and Hammett's postulate, Benfey, Hughes and Ingold[52.] pointed out that it could not account for the retardation of S_N1 reactions by common-ions to the exclusion of the mass-law effect. They did however confirm the retarding effect of the lyate ion, but suggested that this ion was a special case, being inferior to chloride or azide ion in penetrating the solvation shell of the carbonium ion. This was considered to be due to the spreading of the ionic charge over a number of solvent molecules.

More recently other examples of highly specific electrolyte effects, contrary to the requirements of equation 1.8., have been reported on a number of occasions.[50,51] Work on diphenylmethyl halides in aqueous acetone[50f,g,h,51c.] has shown that the accelerating effect of anions on the rate of solvolysis follows the sequence;

$ClO_4^- > Br^- > BF_4^- > NO_3^- > SO_3Ph^- > OH^- > Cl^- > F^-$

and for cations the sequence appears to be;

$H^+ > Na^+, K^+, Li^+, Rb^+, Me_4N^+ > Et_4N^+ > n\text{-}Pr_4N^+ > n\text{-}Bu_4N^+$.

Some of the ions at the ends of both these series actually retard solvolysis. Much of the anion sequence is also confirmed by work on the solvolysis of two different sulphonates in aqueous dioxan.[50e] The workers[50e] were able to explain their results in terms of the different effects of the different electrolytes on the effective composition of the solvent. Their explanation differed from that of Lucas and Hammett[50a] in that they allowed for solvation of the ions by both water and the organic solvent component and an independent study[53] had already given the necessary relative solvation numbers. On the basis of this argument the greater "drying action" of chloride relative to perchlorate ions is consistent with the smaller acceleration of solvolysis shown by chloride ions.[50e] It seems likely that the highly hydrated fluoride ion would give rise to an even "drier" solvent than chloride ions, consistent with the order $Cl^- > F^-$ for the accelerating power of these ions.

Grunwald[50e,58] developed a quantitative treatment in which the presence of electrolytes alters the rate by invoking;

(i) an electrostatic effect, which is independent of the nature of the electrolyte and can be identified with the ionic-strength effect. (see section I. 7.2.)

(ii) a salt-induced medium effect which can be qualitatively considered to arise from changes in the effective solvent composition caused by solvation of the electrolyte, as discussed in the preceeding paragraph.

(iii) specific short-range interactions between the substrate and the electrolyte (in some cases).

An attempt at a quantitative discussion of the magnitude of the combined ionic-strength and salt-induced medium effects on the rate of ionisation[50e] involved the consideration of the separate effects on the stabilities of the initial and transition states. Although, it is widely recognised that the effect of changes in the reaction conditions results from the effects on the stabilities of both these states, many early discussions have concentrated exclusively on transition state effects. The effect of such changes on the stability of the initial state in chemical reactions has only rarely been studied[50b-i, 55]. but a large amount of independent information about the stability of organic compounds in solution is available. It is therefore necessary to consider this information before proceeding with the discussion of the main topic of this thesis i.e., the effect of changes in the reaction conditions on the rates of ionisation.

I. 8. The Determination of the Effect of Changes in the Medium on the Stability of Solutes.

Changes in the reaction medium, VIZ., the effect of added inert substances or changes in the solvent composition, should modify the rate coefficient for the ionisation (k_1^o) according to the Brønsted equation

$$k_1 = k_1^{o} \frac{\gamma_{RX}}{\gamma^{o}_{RX}} \frac{\gamma^{o}_{\ddagger}}{\gamma_{\ddagger}} \quad \text{-------} \quad 1.6.$$

If $\gamma_{RX}/\gamma^{o}_{RX} < 1$, the change in the reaction medium can be said to have stabilised the substrate and the rate coefficient for the reaction will be decreased. If, however, $\gamma_{\ddagger}/\gamma_{\ddagger}^{o} < 1$, the activated complex will have been stabilised and the reaction should be accelerated. The actual magnitude and direction of the change in the rate of reaction (k_1) will depend on the effect which predominates. Hence any detailed discussion concerning the effect of changes in the reaction medium on the rate is complicated by the fact that the experimental observations result from the combination of two separate factors. It has already been pointed out (see section I. 7.2.) that changes in the reaction medium have often been discussed on the assumption that $\gamma_{RX}/\gamma^{o}_{RX} = 1$. Much of the available independent information argues strongly against such an assumption, as do the few experiments already carried out in which both $\gamma_{RX}/\gamma^{o}_{RX}$ and $\gamma_{\ddagger}/\gamma_{\ddagger}^{o}$ have been determined.[50b,c,d,g,h,i,55.] Thus it would appear essential that effects of changes in the medium on $\gamma_{RX}/\gamma^{o}_{RX}$ should also be brought into any discussion of the effects of such changes on the rates of nucleophilic substitution reactions. In principle, the experimental determination of the ratio $\gamma_{RX}/\gamma^{o}_{RX}$ for neutral, inert substances presents no difficulties. Some of the common methods used, and their merits, are discussed briefly below.

I. 8.1. Methods used in the measurement of the ratio $\gamma_{RX}/\gamma^{o}_{RX}$

(i) Solubility Measurements: Since the chemical potential of a species is the same in all solutions in equilibrium with the pure solid, its activity is constant. The solubilities under a given set of conditions (S) and in an arbitrary reference state (S_o) are therefore related by

$$S^o/S = \gamma_{RX}/\gamma^o_{RX} \qquad \text{-------} \qquad 1.10.$$

The most obvious advantages of this method are its experimental simplicity and precision, but it requires the use of a solid substrate; in the mixed solvents now employed a liquid phase in equilibrium with the saturated solution usually contains one of the solvent components and its activity cannot be therefore regarded as independent of the solvent composition. This method forms the basis of the very large amount of work which has been done on the salting-in and salting-out of non-electrolytes (see section I.10) but it does not seem to have been used for substrates which have also been the subject of kinetic studies.

(ii) Vapour pressure measurements: If the substrate is so volatile that its partial vapour pressure over the solution (p_{RX}) can be measured, then its activity in the solution is given by

$$p_{RX}/p^{\dagger}_{RX} = a_{RX} \equiv \gamma_{RX}m_{RX} \qquad \text{----} \qquad 1.11.$$

where $p^{\dagger}_{RX}$ is the vapour pressure of pure substrate (RX) and m_{RX} its molality in the solution. Consequently, the comparision of a given system with the system in an arbitrary reference state (superscript o) gives

$$\frac{p}{p^o} = \frac{\gamma_{RX}m_{RX}}{\gamma^o_{RX}m^o_{RX}} \qquad \text{-------} \qquad 1.12.$$

If the solutions are kept so dilute that Henry's Law applies, the ratio $\gamma_{RX}/\gamma^{o}_{RX}$ in equation 1.12., represents the effect of changes in the reaction conditions on the activity coefficient of the ideal solute and has the same significance as $\gamma_{RX}/\gamma^{o}_{RX}$ in equation 1.10. This method suffers from the disadvantage that it is often necessary to study relatively concentrated solutions in order to obtain vapour pressures of reasonable accuracy; under these conditions Henry's Law may not be valid. The vapour pressure method has been used by various workers in investigations of the effect of solvent changes and salt additions on the rate of solvolysis of <u>tert</u>.-butyl chloride (see refs., 50b,55a,b,d,e,f.), the only reliable previous work in which attempts were made to measure $\gamma_{RX}/\gamma^{o}_{RX}$ and $\gamma_{\ddagger}/\gamma_{\ddagger}^{o}$

(iii) Distribution: If the solvent employed is not miscible with a third solvent in which the substrate is soluble, measurements of the distribution coefficients yield:

$$\frac{\gamma_{RX}}{\gamma^{o}_{RX}} = \frac{m^{o}_{RX}}{m_3} \; \frac{m^{o}_{3}}{m_{RX}} \qquad \text{-------} \qquad 1.13.$$

where m_{RX} is the molality of the substrate in the solvent under consideration in equilibrium with its solution of molality m_3 in a third solvent. Again it is necessary to study dilute solutions of the substrate in order that $\gamma_{RX}/\gamma^{o}_{RX}$ will reflect the effect of changes in the medium on the behaviour of an ideal substrate. This method has been used to determine $\gamma_{RX}/\gamma^{o}_{RX}$ for acetic anhydride[50i] in solutions of aqueous electrolytes. Although, this method has many advantages, there are considerable difficulties in determining $\gamma_{RX}/\gamma^{o}_{RX}$ in the mixed solvents with which the present work is concerned, since it is difficult to find a third solvent in which both water and another organic solvent are virtually insoluble.

Methods (i) - (iii) can be used to determine $\gamma_{RX}/\gamma^{o}_{RX}$ for a neutral substrate both for the addition of electrolytes and changes in the solvent composition. Additional methods are available for substrates which are ionised in the solvent; e.g., freezing point and E.M.F., measurements can be used in some cases. If the substrate reacts with the solvent, as in the systems with which this thesis is concerned, it is of course necessary that the various equilibria should be attained very rapidly compared with the rate of reaction.

I. 9. The Effect of Changes in the Medium on Transition States in Solvolysis.

The ratio $\gamma_{\ddagger}/\gamma_{\ddagger}^{o}$, which represents the effect of changes in the medium on the stability of the transition state has rarely been determined.[50h,54,55.] In general, this ratio is obtained from the values of $\gamma_{RX}/\gamma^{o}_{RX}$ (see section I. 8.1.) and from the accompanying changes in the rate coefficients (k_1/k_1^o). However, a direct **determination** of $\gamma_{\ddagger}/\gamma_{\ddagger}^{o}$ is possible if the activity of the substrate is kept constant and independent of the solvent composition or the presence of other added substances. For any given set of experimental conditions γ_{RX} is constant, so that the concentration of RX is constant if its activity remains constant. Hence

$$v = -\frac{d\,[RX]}{dt} = k_1\,[RX] = k_o \quad \text{---} \quad 1.14.$$

i.e., zeroth-order kinetics will be observed.
From the Brønsted equation (1.6.) and from the fact that $a_{RX} = [RX]\,\gamma_{RX}$ and is independent of reaction conditions

equation 1.14., becomes

$$k_o/k_o^o = \gamma_{\ddagger}^{o}/\gamma_{\ddagger} \qquad \text{-------} \qquad 1.15.$$

where the superscript, o, again refers to an arbitrary reference state.

For a sparingly soluble substrate, $\gamma_{\ddagger}/\gamma_{\ddagger}^{o}$ can be obtained by measuring the rate of reaction in a solution permanently saturated with respect to the substrate.[50h,54.]

Similarly, a volatile substrate at constant pressure in equilibrium with its solution would also allow the determination of $\gamma_{\ddagger}/\gamma_{\ddagger}^{o}$. Alternatively, it can easily be shown that the first-order rates of the decrease of the partial pressure of a volatile substrate in a closed system also give $\gamma_{\ddagger}/\gamma_{\ddagger}^{o}$.[50b,55a.]

I. 10. The Effect of Added Electrolytes on the Solubility of Non-Electrolytes in Aqueous and Aqueous Organic Solvents.

In the determination of the ratio $\gamma_{RX}/\gamma_{RX}^{o}$ by far the largest amount of work has been aimed at obtaining the value of this ratio from solubility measurements, usually in water. This work has been the subject of an excellent review[56] and the following discussion is only intended to illustrate some of the important features which have become apparent from investigations of the effects of added electrolytes on the solubility. The results of these investigations are often reported in the form of an ion-non electrolyte parameter, k_s., which is related to the solubility by

$$\log \gamma_{RX}/\gamma_{RX}^{o} = \log S^{o}/S = k_s C_s + k_i\,(S-S^{o}) \quad \text{---}1.16.$$

where γ_{RX}^{o} and γ_{RX} are the activity coefficients in the pure solvent and in the solvent with added electrolyte, respectively, S^o and S are the corresponding solubilities, C_s is the molar concentration of the added electrolyte, and k_i is a parameter which takes into account the interaction of the non-electrolyte with itself. (self-interaction parameter). If S and S^o are small the latter term can be neglected and equation 1.16., becomes,

$$\log \gamma_{RX}/\gamma^{o}_{RX} = \log S^o/S = k_s C_s \quad \text{-------} \; 1.17.$$

which is a form of the well-known Setschenow equation.[57] However, even if S and S^o are large, equation 1.17., can still be applied by replacing k_s by another constant k, but it must be remembered that although k may be described as the Setschenow constant it is not now identical with the ion-non-electrolyte interaction parameter (k_s).

If the addition of electrolyte decreases the solubility, salting-out of the non-electrolyte is said to occur ($k_s > 0$), while an increase in the solubility (salting-in) requires a negative value of k_s. Some typical results are illustrated in table III.

Thus for benzoic acid in water[56] values of k_s follow the sequence $NaCl > NaBr > NaNO_3 > NaClO_4$ while for 1-naphthoic acid in 50%(w/w) aqueous dioxan[58] the sequence is exactly reversed. The results for 4-nitrodiphenylmethyl chloride[50g] follow a similar pattern to those obtained for 1-naphthoic acid[58] with the exception that sodium perchlorate shows a much greater salting-in effect in acetone-water mixtures. A possible reason for this apparent anomoly will be suggested later (see Chapter III., page 93). It is significant that although benzoic acid and 1-naphthoic acid are structurally similar, a complete reversal of the salting-out order is observed. However for two compounds which are structurally different, but were studied in similar solvents <u>e.g.</u>, 1-naphthoic acid in 50%(w/w) aqueous

TABLE III

The effect of 0.05M electrolytes on S, γ_{RX} and k_s for water, and aqueous organic solvents.

Electrolyte (0.05M)	Benzoic Acid in water (ref.56)			1-Naphthoic Acid in 50%(w/w) aqueous dioxan (ref.58)			4-Nitrodiphenymethyl chloride in 50%(v/v) aqueous acetone (ref.50g).		
	S/S^o	$\gamma_{RX}/\gamma^o_{RX}$	k_s	S/S^o	$\gamma_{RX}/\gamma^o_{RX}$	k_s	S/S^o	$\gamma_{RX}/\gamma^o_{RX}$	k_s
NaCl	0.978	1.023	0.182	1.006	0.994	-0.048	1.031	0.970	-0.264
NaBr	0.987	1.013	0.109	1.001	0.999	-0.003	1.014	0.985	-0.124
$NaNO_3$	0.991	1.009	0.075	——	——	——	1.013	0.987	-0.114
$NaClO_4$	0.994	1.006	0.052	0.964	1.038	+0.320	1.085	0.922	-0.706

dioxan and 4-nitrodiphenylmethyl chloride in 50% (v/v) aqueous acetone, the order of effects on k_s is identical, with the exception of the result for the perchlorate ion. The magnitude of k_s then clearly seems to depend on the nature of the electrolyte and the solvent, although the structure of the substrate appears to be of importance in some cases. In general, k_s usually follows the sequence $Cl^- > Br^- > NO_3^- > ClO_4^-$ in water but this sequence is reversed on passing from aqueous to aqueous organic solvents. Values of k_s have been interpreted in a variety of ways, which are conveniently considered under three headings.

I. 10.1. The Electrostatic Approach.

In the original approach the solvent is considered to act as a continuous dielectric. The only departures from ideality, which are taken into account arise from electrostatic interaction involving ionic charges; the most widely known theories are those of Debye and McAulay[59] and Debye.[60] The former related electrolyte effects to the influence of the solute on the dielectric constant of the solvent and predicted a linear relationship between log γ_{RX} and the added electrolyte concentration: VIZ.,

$$\log \gamma_{RX} = \frac{\delta_i \epsilon^2}{2kTD_o} \sum C_j Z_j^2 / b_j \qquad 1.18.$$

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

The later more exact theory of Debye[60] took into account the heterogeneity of the solution and required a linear dependence of γ_{RX}^{-1} on the electrolyte concentration <u>i.e.</u>,

$$\frac{1}{\gamma_{RX}} = 1 - \frac{4\pi N}{1000} \sum_{j} J_j C_j \qquad \text{-----} \quad 1.19.$$

where $J_j = b_j \int^{\infty} (1 - e^{-(R_j)^4/r4})\, r^2 dr$, r is the separation between an ion and a molecule of solute, and R is defined by,

$$R^4 = \frac{\epsilon^2 z_j^2 \quad 1000\ \delta_i}{8\pi RTD_o}$$

Similar approaches have been proposed by Altshuller and Everson,[61] Butler[62] and Belton,[63] while Kirkwood[64] has predicted a linear relationship between log γ_{RX} and the concentration of the added electrolyte.

Equations 1.18., and 1.19., have often been applied successfully to studies of the effect of added electrolytes on the solubility of non-electrolytes in water (see ref.65). The fact that salting-out is observed experimentally suggests that non-electrolytes decrease the dielectric constant of the solution, as expected. On the other hand, the addition of phenylthiourea to ethanol increases the dielectric constant[66] and hence salting-in is predicted, as found in practice. However, contrary to the requirements of these equations γ-butyrolactone[50j] is salted-in by some electrolytes but salted-out by others in the same solvent, possibly because of the existence of other types of interaction (e.g., non-electrostatic) not allowed for in the original treatment.

(see refs. 59,60). Nevertheless, this treatment has been very successful in many discussions of solubilities in water, particularly when very dilute solutions were employed,[65] although it cannot explain the reversal of salt order on changing the solvent from water to an aqueous organic solvent. (see Table III). It is also noteworthy that equations 1.18., and 1.19., predict that different electrolytes should show, at least, very similar values of k_s unless the ions concerned have greatly different radii. Contrary to this requirement surprising variations of k_s with the nature of the electrolyte have been reported on a number of occasions; e.g., in the aniline-water[67] and diacetone alcohol-water[68] systems, and it must also be stressed that equations 1.18., and 1.19., cannot possibly predict a change from salting-out to salting-in in the same system.[50j]

I. 10.2. Short-Range Interactions.

McDevit and Long[56] attempted to explain the deviations from equations 1.18., and 1.19., by taking into account short-range interactions between ions and the solute, following an earlier suggestion by Kortüm.[69] This new approach led to equation 1.20.

$$\log \gamma_{RX} = A \sum Z^2_j C_j - B \sum \alpha_j C_j \quad \text{----} \; 1.20.$$

A and B are parameters which depend on the nature of the solute. γ_{RX} may vary a little with the nature of the electrolyte since α_j represents the polarisability of the ion j. The first term in equation 1.20., allows for electrostatic interactions while the second takes into account any short-range interactions. Equation 1.20., represents a major step forward since electrolyte effects were examined in terms of the nature of both the electrolyte and the solute. Bockris and his coworkers[70] later modified this equation but the two approaches were similar in that they can accommodate the change from salting-out to salting-in in the same system, particularly the many observations of salting-in by large anions or cations[71] when salting-out would have been predicted by the electrostatic approach. Nevertheless, equation 1.20., fails to predict the anomolous low salting-out effect of small cations *e.g.*, Li^+ (see ref. 72) and H^+ (see ref. 73).

Sergeeva and his coworkers[75] have recently provided direct evidence for the existence of stabilising short-range interactions between some ionised benzoates and benzoic acid, although they also found anomolous effects on the solubility in the presence of electrolytes where such interactions were not indicated. It must, however, be stressed that in addition to the objections already mentioned, the treatments based on short-range electrolyte-non-electrolyte interactions cannot explain the reversal of the salt order on passing from water to aqueous organic solvents.

I. 10.3. Salt-Induced Medium Effects.

Various authors have suggested that interactions between the added electrolyte and the solvent could also affect the stability of the dissolved non-electrolyte. One of the earliest attempts[76] to account for the salting-out which was usually observed in aqueous solution involved the assumption that solvation of the added electrolyte removed some of the water molecules which would otherwise have been available for dissolving the non-electrolyte. However, improbably large solvation numbers had to be assumed in order to account satisfactorily for the relatively large salting-out effect shown by some electrolytes. While this approach was soon discarded, it is noteworthy that the solvation of the electrolyte, or, at least, solvent-electrolyte interactions are now considered to play an important role in determining the activity coefficient of an unionised solute. (see page 38).

Other views have been expressed regarding the effect of added organic solutes or electrolytes on the properties of the solvent. McDevit and Long[71] have suggested that the effect of the solute was simply one of occupying volume. A limiting law was derived which related the magnitude of k_s to the volume change produced when the electrolyte and water are mixed. Such an effect creates variations in the internal pressure and the resulting limiting law can accommodate both salting-out and salting-in. This approach was able to explain the small salting-out effects observed with lithium and hydrogen ions in the benzene-water system,[71c,d,77] the abnormal salting-out effects caused by large ions,[71] and also the normal effects usually observed with simple sodium or potassium salts. Similar results were obtained[71e] in the study of the solubilities of naphthalene and diphenyl in aqueous electrolyte solutions, and it is also interesting to note that the magnitude of the salt effect increased along the series benzene $<$ naphthalene $<$ diphenyl, apparently paralleling the increase in molal volume of the solute. A modification[78] of McDevit and Long's original approach takes into account the dielectric decrement of the electrolyte and the solute, and has been shown to give better agreement with experiment. Deno[79] has also related, with some success, the magnitude of k_s in aqueous electrolytes to the change in the internal pressure of the solvent and the molal volume of the solute. On the whole, theories of this type seem to account quite well for the experimental results, when the solvent is water, but discrepancies occur for results in aqueous organic solvents.

Lucas and Hammett,[50a] however, suggested that changes in the composition of a binary aqueous solvent could be brought about by preferential attraction of the water to the added electrolyte. This would, in effect, increase the effective mole fraction of the organic component in the solvent and would therefore result in the salting-in of an organic solute. This conclusion is borne out by the work of Grunwald,[80] and Egan[81] had previously shown the inapplicability of the earlier theories to the salting-out of benzoic acid in methanol-water, ethanol-water and dioxan water mixtures by sodium chloride. Both sets of workers observed that although the addition of sodium chloride caused salting-out in water, salting-in occured in aqueous organic solvents, and they concluded that a qualitative account of this phenomena could only be given on the basis of preferential solvation of the sodium chloride by water. This work again illustrated the marked difference in properties between aqueous and aqueous organic solvents and it is noteworthy that the Setschenow equation (1.17.) appears to break down at much lower electrolyte concentrations in aqueous organic media than in water. However, it has often been pointed out that the local solvent structure of aqueous[82] and partially aqueous[42,45,50,53,81,83] systems plays an important role in determining the magnitude of the salt effect on the stability of the solute. Presumably such effects on the structure would be more apparent in water than in aqueous organic solvents.

Grunwald and Butler[58] attempted to place the qualitative theory of preferential solvation of the electrolyte on a quantitative basis. A quantitative measure of the "wetting" and"drying" effects of added electrolytes was obtained by measurements of the vapour pressure of the two solvent components.[53] This effect can be conveniently expressed as the rate of change of the mean ionic standard chemical potential of the added electrolyte with the solvent composition (dG^o_{4m}/dZ_1). Values of this parameter were obtained for 50% (w/w) aqueous dioxan.[53] As the stability of the solute (or G^o_{3m}) is also affected by changes in the solvent composition, the presence of added electrolytes will result in a contribution from the product (dG^o_{3m}/dZ_1) (dG^o_{4m}/dZ_1) which can be considered to be proportional to the magnitude of the salt-induced medium effect. In their semi-quantitative treatment, Grunwald and his coworkers[53,58] invoked two electrolyte effects *i.e.*, the normal electrostatic effect and a contribution due to the operation of a salt induced medium effect, and obtained equation 1.21.,

$$k_{3,4} = A_i + B_i \frac{dG^o_{4m}}{dZ_1} \frac{dG^o_{3m}}{dZ_1} \qquad \text{------} \quad 1.21.$$

where $k_{3.4}$ the electrolyte-non-electrolyte interaction parameter is related to γ_{RX} by,

$$k_{3.4} = \frac{1}{m_4} \log \gamma_{RX} \qquad \text{------} \quad 1.22.$$

Subscripts 1, 3 and 4 refer to water, the solute, and the electrolyte, respectively and the parameters A_i and B_i are constants characteristic of the solvent, the temperature and the solute. It is, in fact, the last term in this equation which is capable of accounting for the observed specific electrolyte effects since dG^o_{4m}/dZ_1 depends on the nature of the added electrolyte. The results from a study of the effects of added electrolytes on the solubilities of naphthalene and 1-naphthoic acid in 50% (w/w) aqueous dioxan[58] gave the required linear relation between $k_{3.4}$ and dG^{o}_{4m}/dZ_{1}[53] for most of the added electrolytes(see fig.I.I). The anomolous behaviour shown in the presence of large ions (which are not all shown in the figure) was explained in terms of short-range interactions between the electrolyte and the solute, since such interactions had been neglected in the derivation of equation 1.21.

More recently, Sergeeva and his coworkers[74] have investigated the effect of sodium and lithium salts on the solubility of benzoic acid in methanol-water mixtures and found that the change in k_s for a given electrolyte as the solvent is made less aqueous could be correlated with accompanying changes in the alteration of the partial vapour pressures of the solvent components on the addition of salts. Such findings strongly support the ideas of Grunwald.[53,58]

A survey of some of the existing information in terms of k_s, which is related to $k_{3.4}$ by equation 1.23., is given in tables III and IV.

$$k_{3.4} = k_s (1 + 2.303\, k_{3.3}\, S^{o}) \quad \text{------} \quad 1.23.$$

where $k_{3.3}$ is the self-interaction coefficient of the non-electrolyte.

The most important feature of the results is seen to be the change in direction of the electrolyte effect when the solvent is changed from water to an aqueous organic medium. However, there is evidently not a complete reversal of the effects on passing from water to aqueous organic media as was at first thought[58,80] and although there is a greater tendency towards salting-out in pure water, this trend does not apply universally.[75] It should be stressed however that these anomolies may be due to the falure of the Setschenow equation at the high electrolyte concentrations

FIG. I. 1. The variation of $k_{3.4}$ with dG^o_{4m} / dz_1 in 50 % (w/w) aqueous dioxan for (A) Naphthalene and (B) 1 - Naphthoic Acid.

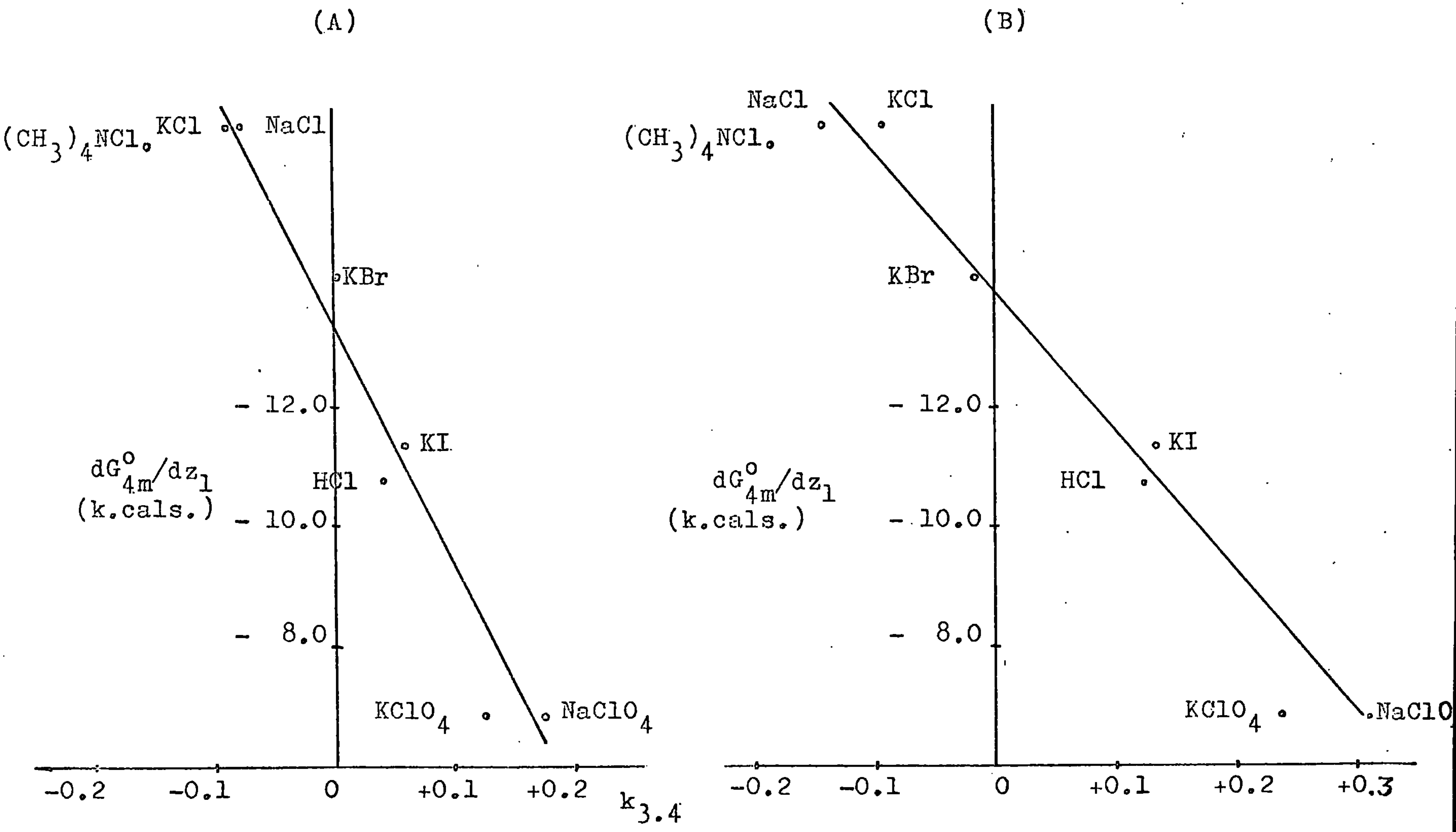


TABLE IV

k_s values for organic compounds in aqueous organic solvents.

System \ Electrolyte[†]	$NaClO_4$	KI	HCl	KBr	NaCl	$(CH_3)_4NCl$
Naphthalene in 50% aqueous dioxan (ref.58)	+0.190	+0.072	+0.053	+0.011	0.062	-0.086
1-Naphthoic Acid in 50% aqueous dioxan[a] (ref.58)	+0.320	+0.158	+0.139	-0.003	-0.048	-0.119
Exo-norbornyl bromide in 85% aqueous dioxan[b] (ref.50c)	-0.044	——	——	-0.177[*]	-0.266[*]	——
Benzoic acid in equimolar methanol-water[c] (ref.75)	+0.136	+0.157[ϕ]	——	+0.122[ϕ]	+0.087	——
Tert.-butyl chloride in water[d] (ref.50b)	+0.24	+0.25[ϕ]	+0.04	+0.19	+0.35	+0.02[‡]
Ethylene Sulphite in water[e] (ref.84)	-0.207	-0.047	——	+0.033[ϕ]	+0.089	-0.062[$]

[†] Electrolyte additions made at a) 0-1.0M, b) 0.1M, c) 0.5M, d) 0-1.0M and e) 1.0M.

[*] For the addition of the corresponding lithium salts.
[ϕ] For the addition of the corresponding sodium salts,
[‡] For the addition of tetramethylammonium bromide.
[$] For the addition of tetraethylammonium chloride.

employed in the relevant experiments[58,75,84] and no further test of Grunwald's approach can be carried out at the present time due to lack of values of dG^o_{4m}/dZ_1 for aqueous organic solvents other than 50% (w/w) aqueous dioxan. Even the assumption that dG^o_{4m}/dZ_1 follows the same sequence in aqueous methanol and aqueous acetone as in aqueous dioxan does not account for all the anomolies in tables III and IV. Short-range interactions may provide the answer in some cases but do not seem able to explain all the deviations (see fig. I.1), particularly the anomolous effects of sodium and potassium perchlorates. The solvation hypothesis on which equation 1.21., is based has been challenged by Feakins and his coworkers,[83a,b,c] who proposed that the values of dG^o_{4m}/dZ_1[53] could arise from modifications in the acidic and basic properties of the solvent molecules. However, both these approaches arrive at the same conclusion VIZ., that changes in the stability of solutes in binary solvents can be caused by electrolytes bringing about changes in the properties of the solvent and the same anomolies are bound to arise in both treatments.

At present no theory can account for all the observed changes in the stability of solutes on the addition of electrolytes. It is, however, clear from the solubility studies that the nature of an added electrolyte may well be an important factor in determining its effect on the stability of the initial state in nucleophilic substitution reactions, since there is no reason to believe that the salt-induced medium effect will not operate under these conditions. However, similar considerations may apply to the transition state since the activated complex can be regarded as almost a normal chemical species. If a salt induced medium effect is indeed responsible for the appearance of specific salt effects in these reactions, at least qualitatively similar changes in the rate should be observed on changing the solvent composition. It is therefore necessary to discuss the experimental information available for the effect of changes in the solvent composition in solvolysis, particularly those investigations where the separate initial and transition state effects have been determined. A similar conclusion was also reached in the discussion of the use of the Kosower[44] Z parameter to correlate changes in rate with solvent properties. (see section 1.6.).

I. 11. The Effect of Changes in the Solvent Composition on the Initial and the Transition States in Solvolysis.

Very few workers have carried out investigations designed to obtain the separate initial and transition state effects of a change in the solvent composition on the rate of reaction for the same compound. Previous work in this field appears to have been carried out on volatile alkyl halides,[55] usually *tert*.-butyl chloride. The effect of solvent changes on the stability of the initial state, as expressed by $\gamma_{RX}/\gamma^{o}_{RX}$, was always obtained by measurement of Henry's Law constants (see section 1.8.1.(ii)) and the corresponding transition state effects ($\gamma_{\ddagger} / \gamma_{\ddagger}{}^{o}$) were usually calculated from the first-order rates *via*., the Brønsted equation. (1.6.-). Winstein has twice[32a,55b] examined the effect of solvent changes on the rate of solvolysis of *tert*.-butyl chloride in aqueous ethanol. Originally,[32a] Olson's[55d] values of the Henry's Law constants led to the conclusion that, in good ionising solvents, changes in the rate resulted from changes in the stability of the initial state, while, in poor ionising solvents, rate changes were due to effects on the stability of the transition state. When further values of the Henry's Law constants were available[55b,d,e] the kinetic measurements[55b] showed that initial and transition state effects contributed about equally to the total solvent effect for reaction with aqueous alcohols.

On the other hand, Taft[55a] has shown that the addition of small amounts of dioxan to water alters the rate of solvolysis of <u>tert</u>.-butyl chloride predominantly by increased stabilisation of the transition state; this was also seen to apply for a change from light to heavy water.

Studies of the effects of solvent changes on the rates of solvolysis of alkyl halides in aqueous ethanol[55c] led to ambiguous results since similar results would have been expected for the ethyl and n-butyl compounds. A change in the solvent composition from 1% (w/w) to 24.1% (w/w) water was found to alter the rate of ethyl bromide by exerting approximately equal influences on the stabilities of the initial and transition states, whilst the change in rate for n-butyl bromide, caused by the same change in solvent composition, was seen to result mainly from effects on the stability of the initial state. However, it should be pointed out that in this study[55c] the rates of reaction of n-butyl bromide were interpolated from results of earlier experiments[31] and the calculation of the initial state effects for both these compounds involved the use of Henry's Law constants. The difficulties in obtaining accurate values of these constants when the substrate reacts to a significant extent with the solvent during the time required for the vapour pressure measurements have already been stressed.[55b] These disadvantages would lead to serious errors in the results.

More recently,[50g] a decrease in the water content of the solvent has been found to alter the rate of the S_N2 solvolysis of 4-nitrobenzyl chloride, in aqueous acetone, by an increased stabilisation of the initial state; transition state effects made a smaller contribution, and actually opposed the observed change in rate. However, in the S_N1 solvolysis of 4-nitrodiphenyl methyl chloride in the same system,[50g] a decrease in the water content of the solvent was found to retard the reaction by increasing the stability of the substrate; transition state effects being negligibly small.

Moreover the enthalpy of activation ($\Delta H^{\ddagger}$) for the solvolysis of tert.-butyl chloride in aqueous ethanol is known to pass through a minimum on changing the solvent composition.[55b] Measurements of the partial molar heats of solution of tert.-butyl chloride in aqueous alcohol solutions have shown that at least 95% of the variation in $\Delta H^{\ddagger}$ in the region of the minimum can be accounted for by changes in the initial state solvation.[55g,85]

It can be seen from the above survey of the existing experimental data that no general conclusions can be drawn regarding the effects of solvent changes on the stabilities of the initial and transition states in solvolysis. Nevertheless, it is evident that initial state effects cannot be neglected in any discussion of the effects of such changes on the rates of solvolysis. It was therefore decided to obtain further information about both the initial and transition state contributions to the effect of solvent changes in the rate for the S_N1 solvolyses of 4-nitrodiphenylmethyl and 4-phenyl:4'-nitrodiphenylmethyl chlorides in aqueous acetone. A similar study was also carried out of the S_N2 solvolysis of 4-nitrobenzyl chloride in aqueous acetone. (see Chapter II).

It was also hoped that a study of the effect of solvent changes on the rates of these reactions would provide a useful basis for the understanding of specific electrolyte effects in terms of the operation of a salt-induced medium effect. (see page 49).

I. 12. The Effect of Added Electrolytes on the Stabilities of the Initial and Transition states in Solvolysis.

Evidence from various independent sources (see section 1.8.) has suggested that added electrolytes should produce specific effects on the stability of the initial state in solvolysis, but there seems to be no reason why the observed specific effects on the rate could not also result from changes in the stability of the transition states of these reactions, or indeed from both.

Taft and Clarke[50b] have determined the effect of added electrolytes on the first order rate of solvolysis of tert.-butyl chloride in water in terms of the separate effects on the stabilities of the initial ($\gamma_{RX}/\gamma^{\circ}_{RX}$) and transition ($\gamma_{\ddagger}/\gamma_{\ddagger}^{\circ}$) states. They found that, for many of the electrolytes used, both $\gamma_{RX}/\gamma^{\circ}_{RX}$ and $\gamma_{\ddagger}/\gamma_{\ddagger}^{\circ}$ depended on the nature of the added electrolyte; possibly due to the operation of a salt-induced medium effect in these two states. However, many of these salts were observed to have the same effect on the rate of solvolysis. Apart from the possible inaccuracies in the values of $\gamma_{RX}/\gamma^{\circ}_{RX}$ (which were in fact determined from Henry's Law constants), it is difficult to see why opposing salt-induced medium effects of the same magnitude should operate in the initial state and the transition state of solvolysis. There is also no guarantee that such cancellation will occur in aqueous organic solvents.

Thus the large specific salt effects observed on the rate of solvolysis of exo-norbornyl bromide in 85% (w/w) aqueous dioxan[50c] have been reported to arise almost exclusively from changes in the stability of the transition state. However, it should be stressed that this work was carried out at relatively large electrolyte concentrations; a factor which may be responsible for some of the observations.

Bunton and his coworkers[50d] concluded from a study of electrolyte effects on the rates of hydrolysis of alkyl sulphites in water that although specific effects were evident they could not be correlated solely with the effects on the stability of the initial state, as shown by solubility studies,[84] or with effects on the stability of the transition state. Specific effects were apparent in both the initial and transition states in some cases.

However, a study of the effect of added electrolytes on the hydrolysis of acid anhydrides in water,[50i,k,l,m] and on their distribution between carbon tetrachloride and water, has shown that the specific electrolyte effects observed on the rates of hydrolysis did not arise solely from effects on the initial or transition states. It would therefore appear that the cancellation, apparent in the work of Taft,[50b] does not always occur in water. The retarding effect of salts on the hydrolysis of acetic anhydride in water[50i] arose from both initial and transition state contributions; the stability of the transition state being the more sensitive to the nature of the salt. It was pointed out that in these reactions classical ionic-strength effects are only of secondary importance and the predominant feature of the activation process is the hydrogen bonding of water molecules to the activated complex. The ions of the electrolyte were considered to destabilise the transition state by competing with it for the water molecules and the ionic-strength effect was regarded as small since the charges on the transition state are diffused by hydrogen bonding. It was also suggested that the observed effects may be due, in part, to the effects of the added electrolytes on the activity of the water, an effect ignored in their treatment. On the other hand, Long and his coworkers[50j] have shown that the effect of added electrolytes on the acid-catalysed hydrolysis of γ-butyrolactone in water was determined to a large extent by their effect on the activity of the lactone.

The results of a study of the effect of added electrolytes on the rate of solvolysis of neophyl-p-toluene sulphonate in 50% (w/w) aqueous dioxan[50e] revealed that the specific effects of electrolytes on the rate were exactly paralleled by their effects on the activity coefficients of other neutral substrates in the same solvent,[58] which could be quantitatively explained by equation 1.21. (see section I. 10.3.). This expression can be written in the form;

$$\frac{1}{m_4} \log \gamma_{RX} = A_i + B_i \frac{dG^o_{4m}}{dZ_1} \frac{dG^o_{3m}}{dZ_1} \quad \text{-------} \quad 1.24.$$

Grunwald and his coworkers[50e] assumed that equation 1.24., applied to all neutral substrates, at least in 50% (w/w) aqueous dioxan, and that an analogous expression also described the effects of electrolytes on the activity coefficient of the transition state in S_N1 solvolysis, whence

$$\frac{1}{m_4} \log \frac{k_1}{k^o_1} = A + BRT \frac{d\ln k^o_1}{dZ_1} \frac{dG^o_{4m}}{dZ_1} \quad \text{-------} \quad 1.25.$$

$$\text{where} \quad \bar{A} = A_i - A_{\ddagger}$$

$$\text{and} \quad B = \left(B_i \frac{dG^o_{RX}}{dZ_1} - B_{\ddagger} \frac{dG^o_{\ddagger}}{dZ_1}\right) / \left(\frac{dG^o_{RX}}{dZ_1} - \frac{dG^o_{\ddagger}}{dZ_1}\right)$$

The parameters A and B are therefore characteristic of the substrate, transition state, and the solvent, and independent of the nature of the added electrolyte. Since log k_1/k^o_1 is seen to depend on dG^o_{4m}/dZ_1, equation 1.25., predicts specific electrolyte effects on the rate. Results from the solvolysis of neophyl-p-toluene sulphonate[50e] gave the required linear relationship with independently determined values[53] of dG°_{4m}/dZ_1 for the effects of simple inorganic salts (see Fig., I.2.) while the results from the racemisation of α - (+) - threo - 3 - phenyl - 2-butyl p - toluenesulphonate[50e] were not in such good agreement with equation 1.25., (see Fig., I.3). Large ions produced anomolous results which were considered to be due to the existence of short-range interactions between the electrolyte and the substrate in its initial and transition states, since such interactions had been neglected in the derivation of equation 1.25.

Quantitative agreement with equation 1.25.., has been reported for solvolysis in aqueous acetone[17b,50f,g] but these results will be discussed with those obtained from the present investigation. (see Chapter III).

Grunwald's theory of salt-induced medium effects, as represented by equation 1.25., therefore seems to be reasonably successful in predicting the effects of added electrolytes on the rates of S_N1 reactions in 50% (w/w) aqueous dioxan, but it still cannot accommodate all the observed results. Nearly all previous work on the separation of electrolyte effects into initial and transition state contributions has involved solvolysis in water. It was therefore considered desirable to obtain similar information from work in aqueous organic solvents, since the success of equation 1.25., in accounting for solvolysis in 50% (w/w) aqueous dioxan could arise from the fact that equation 1.24., (on which equation 1.25., is based) applies only to the initial state; if $\gamma_{\ddagger} / \gamma_{\ddagger}^{o}$ is independent of the nature of the added electrolyte. Thus it was decided to obtain the required information concerning the separate initial and transition state contributions to the total electrolyte effect on the rate for the S_N1 solvolysis of

FIG. I. 2. The variation of ($\log_{10}k_1/k_1^o$)/m_4 with dG_{4m}/dz_1 for the solvolysis of neophyl-4-toluenesulphonate in 50%(w/w) aqueous dioxan at 50°C

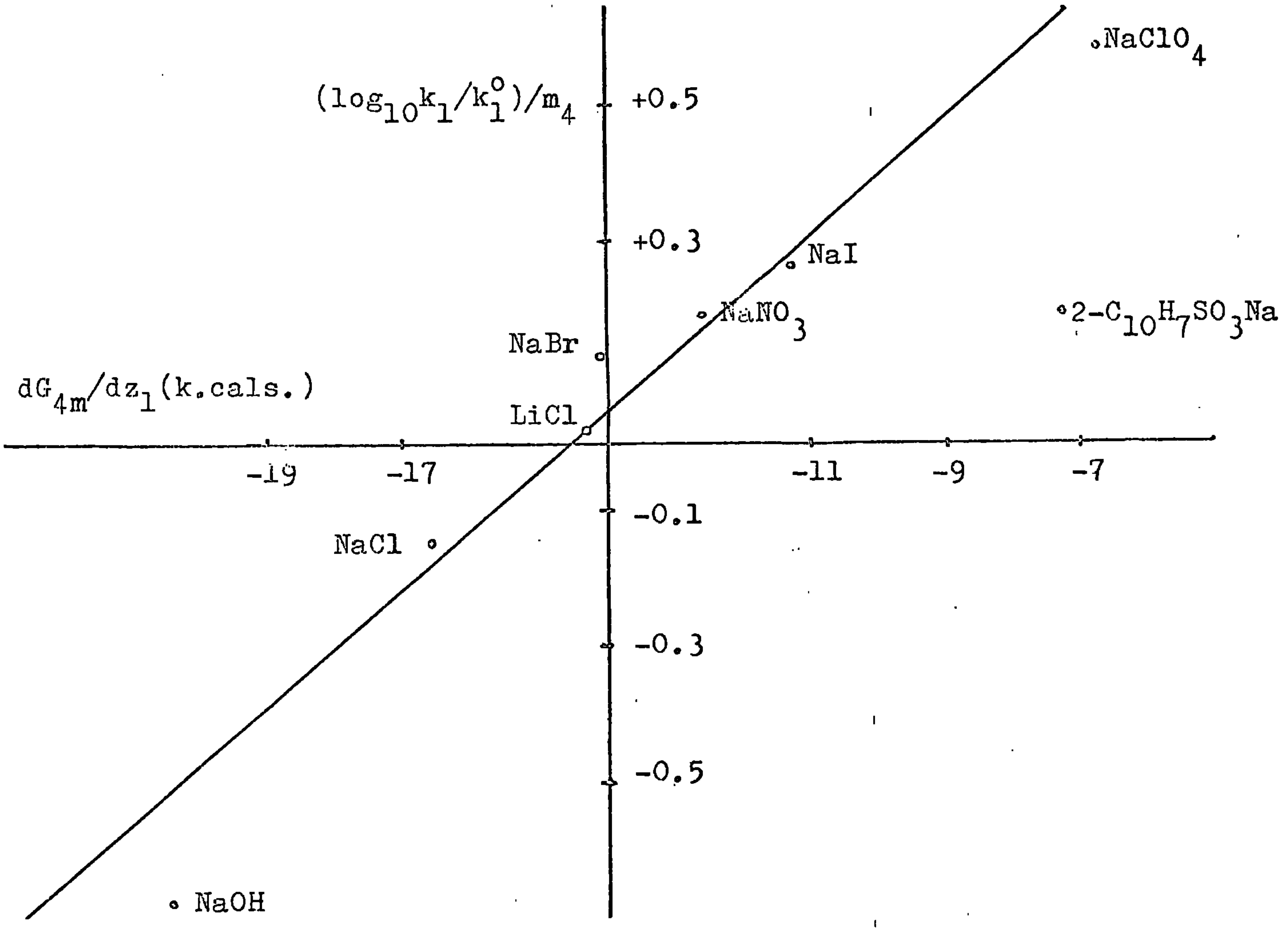
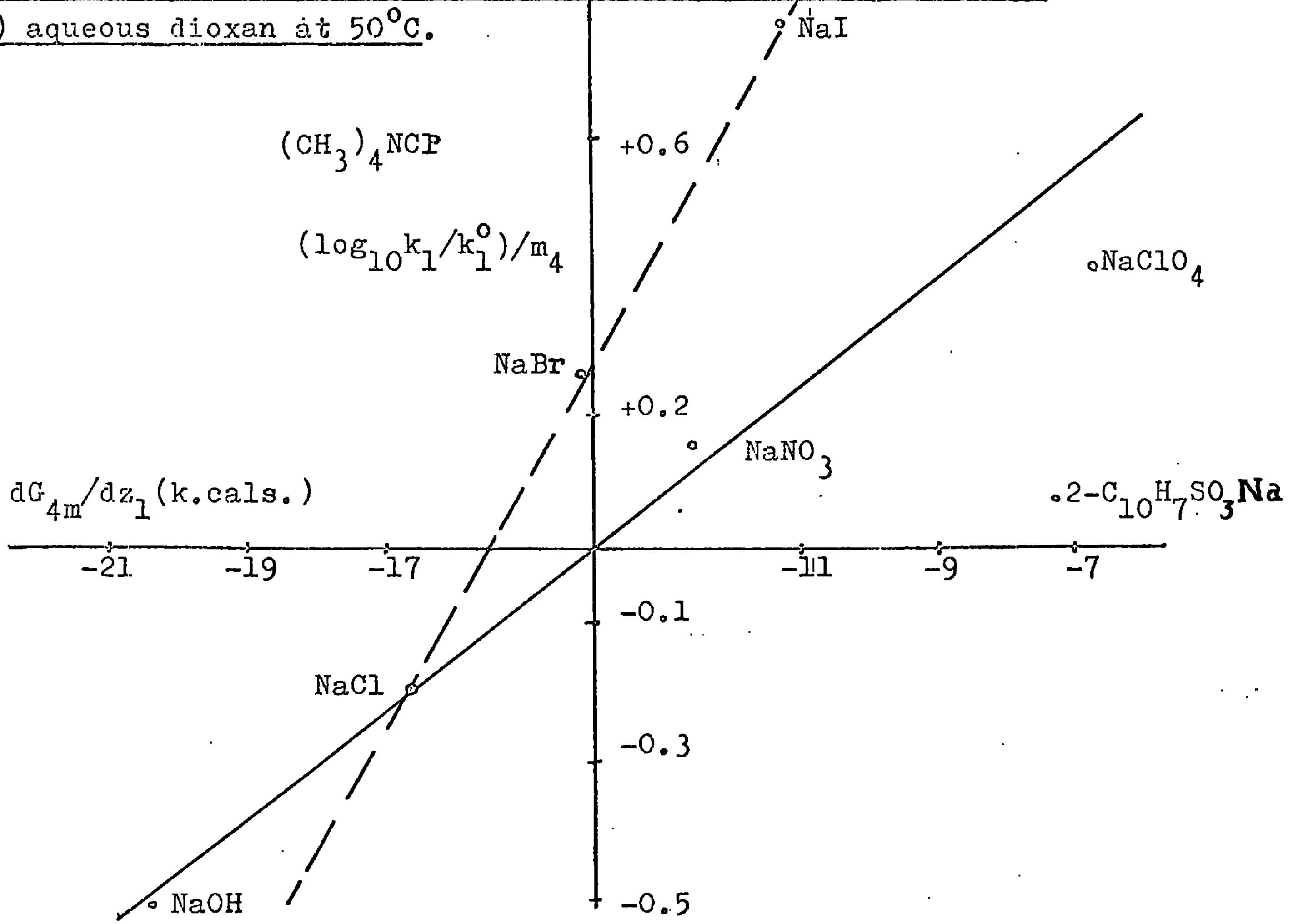


FIG. I. 3. The variation of $(\log_{10}k_1/k_1^o)/m_4$ with dG_{4m}/dz_1 for the racemisation of α-(+)-threo-3-phenyl-2-butyl-4-toluenesulphonate in 50%(w/w) aqueous dioxan at 50°C.



4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone. It has already been pointed out that this system is highly suitable for such a study, since the substrate hydrolyses at a reasonably slow rate and is sparingly soluble in 70% (v/v) aqueous acetone. (see page 29). The results of this study are discussed in Chapter III.

CHAPTER II

The Effects of Changes in the Solvent Composition in Solvolysis; Results and Discussion.

A variety of acetone-water mixtures were employed to investigate the effects of changes in the solvent composition on the rates, and on the stabilities of the initial and transition states in the solvolysis of 4-phenyl: 4'-nitrodiphenylmethyl (I), 4-nitrodiphenylmethyl (II), and 4-nitrobenzyl (III) chlorides. Compounds I and II have been shown to react by mechansim S_N1 in aqueous acetone, whilst it is widely recognised that compound III undergoes reaction by mechanism S_N2.[17,86] Most of the work involved the use of compound I, but a less extensive investigation was made with compounds II and III, mainly to extend earlier studies carried out in these laboratories.[50g]

The effects of solvent changes on the first-order rates of hydrolysis of compound I in dilute solution, and on the zeroth-order rate of solvolysis of permanently saturated solutions of this compound were studied. It has already been pointed out (see sections I.8. and I.9) that the relevant information concerning the effects of changes in the solvent composition on the stabilities of the initial and transition states (represented by the ratios $\gamma_{RX}/\gamma^{o}_{RX}$ and $\gamma_{\ddagger}/\gamma_{\ddagger}^{o}$ respectively) can be obtained from these rate measurements <u>via</u>., equations I.6. and I.15. However, it it should be stressed that the experimental rate coefficients refer to the hydrolysis while those in equations I.6. and I.15. refer to the rate-determining ionisations. However, mass-law and other electrolyte effects were extremely small in the dilute solutions employed in the present experiments and constant values were observed for the first and zeroth-order rate coefficients.[†] Under these conditions no error is caused by identifying the rate coefficient for the hydrolysis with that for the ionisation. Solubilities were also measured for this compound, but their accuracy did not justify their use to calculate $\gamma_{RX}/\gamma^{o}_{RX}$, and they were only employed to check the internal consistancy of equations I.6., I.10. and I.15. (see page 116).

The effects of solvent changes on the rate of hydrolysis of compound II, in terms of the separate effects on the stabilities of the initial and transition states, were calculated from solubility measurements (equation I.10.), and the zeroth-order rate coefficients, (equation I.15.),

In the solvolysis of compound III, the required information was more conveniently obtained from solubility measurements and first-order rate coefficients (equations I.10. and I.6., respectively). Experimental details are given in Chapter IV and the individual results are listed in appendices C, D and E.

Compounds I - III were particularly suitable for study in the present solvents since their solubilities were small enough to permit the assumption that the solutions are ideal at all concentrations up to saturation. Moreover, solubility equilibrium was attained relatively rapidly.

[†] As the reaction proceeds, the solubility could be altered by the chloride ions produced. This, in turn, effects the value of k_o. Moreover, the production of chloride ion may retard the reaction by operation of the mass-law effect. It is however shown for the present systems (see section IV 10) that the maximum possible error that these effects could cause in k_o and k_1 are 0.16% and 0.07% respectively.

Even the most reactive substrate (compound I) was found to saturate the solutions in less than one hour and only fifteen minutes were required to reach 95% saturation, (see appendix C). In 50% (v/v) aqueous acetone at 20.18°C less than 5% of this compound is hydrolysed in one hour and it therefore seemed reasonable to assume that the reaction did not disturb the equilibrium between the solvent and the dissolved substrate. Under all other conditions, reaction was even less rapid while the time required for saturation remained approximately constant.

II. 1. The Effects of Changes in the Solvent Composition on the First-Order Rate of Solvolysis.

The first-order rate coefficients for the solvolysis of compounds I - III in the different media are summarised in Table V. Compounds II and III were not studied in the less aqueous solvents since their solubilities were then too large to assume that the saturated solutions would behave ideally.

The results show that the reactions occurring by mechanism S_N1 are more sensitive to changes in the solvent composition than the S_N2 reaction of compound III, in agreement with the qualitative predictions of Ingold and his coworkers.[1]

The present data can be employed to test the various quantitative relationships which have been proposed to account for the effects of changes in the solvent composition on the rates of reactions which proceed <u>via</u>., an ionisation mechanism. The information required to carry out such a test is given in Table VI and the results are shown graphically in figures II.1., II.2., and II.3.

TABLE V

The Effect of Changes in the Solvent Composition on k_1

Solvent Acetone % (v/v)	Mechanism S_N1		Mechanism S_N2
	Compound (I) (20.18°C) 10^7k_1 (secs^{-1})	Compound (II) (1.62°C) (10^7k_1 (secs^{-1})	Compound (III) (1.67°C) $10^{10}k_1$ (secs^{-1})
40	—	22.91†	16.79*
50	676.4ϕ	3.552*	8.118*
60	—	—	4.615*
65	101.1	—	—
70	40.26	—	—
75	18.23	—	—
85	2.620*	—	—

ϕ Calculated from data for similar compounds (see section IV.12).

† Calculated from solubility and zeroth-order rate coefficient data at 1.62°C.

* Interpolated from rate data at higher temperatures.

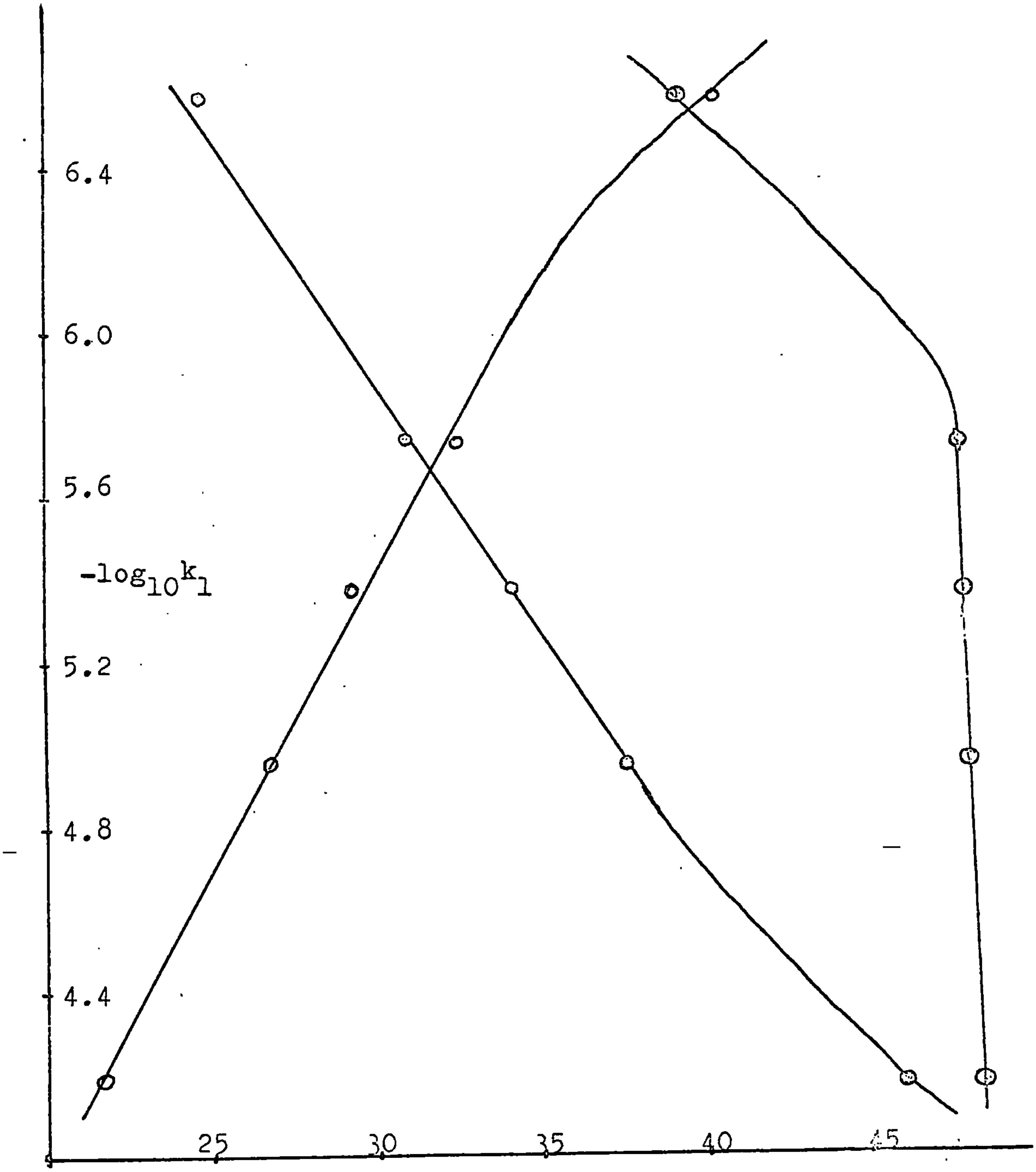
TABLE VI

Values of $\log_{10}k_1$ and solvent properties.

Solvent Acetone %(v/v)	$-\log_{10}k_1$	D^a	Y^b		Z^c k cals/mole
			tert.-butyl bromide	Diphenylmethyl chloride	
50	4.170$^+$	46.0	+1.54	+0.497	——
65	4.958	37.6	+0.504	-0.550	84.3
70	5.395	34.2	+0.205	-0.946	83.2
75	5.739	30.8	-0.100	-1.28	82.1
85	6.582*	24.8	-1.000	-2.38	78.7

a. see reference 35.
b. see reference 32.
c. see reference 44.
+. Calculated value (see section IV.12).
*. Interpolated from rate data at higher temperatures.

FIG.II.1. The variation of $\log_{10}k_1$ with D, D^{-1} and $(D-1)/(2D+1)$.



D represented by ○

$(10^3)\ D^{-1}$ represented by ○

$(10^2)\ (D-1)/(2D+1)$ represented by ⦶

FIG.II.2. The variation of $\log_{10}k_1$ with Y values.

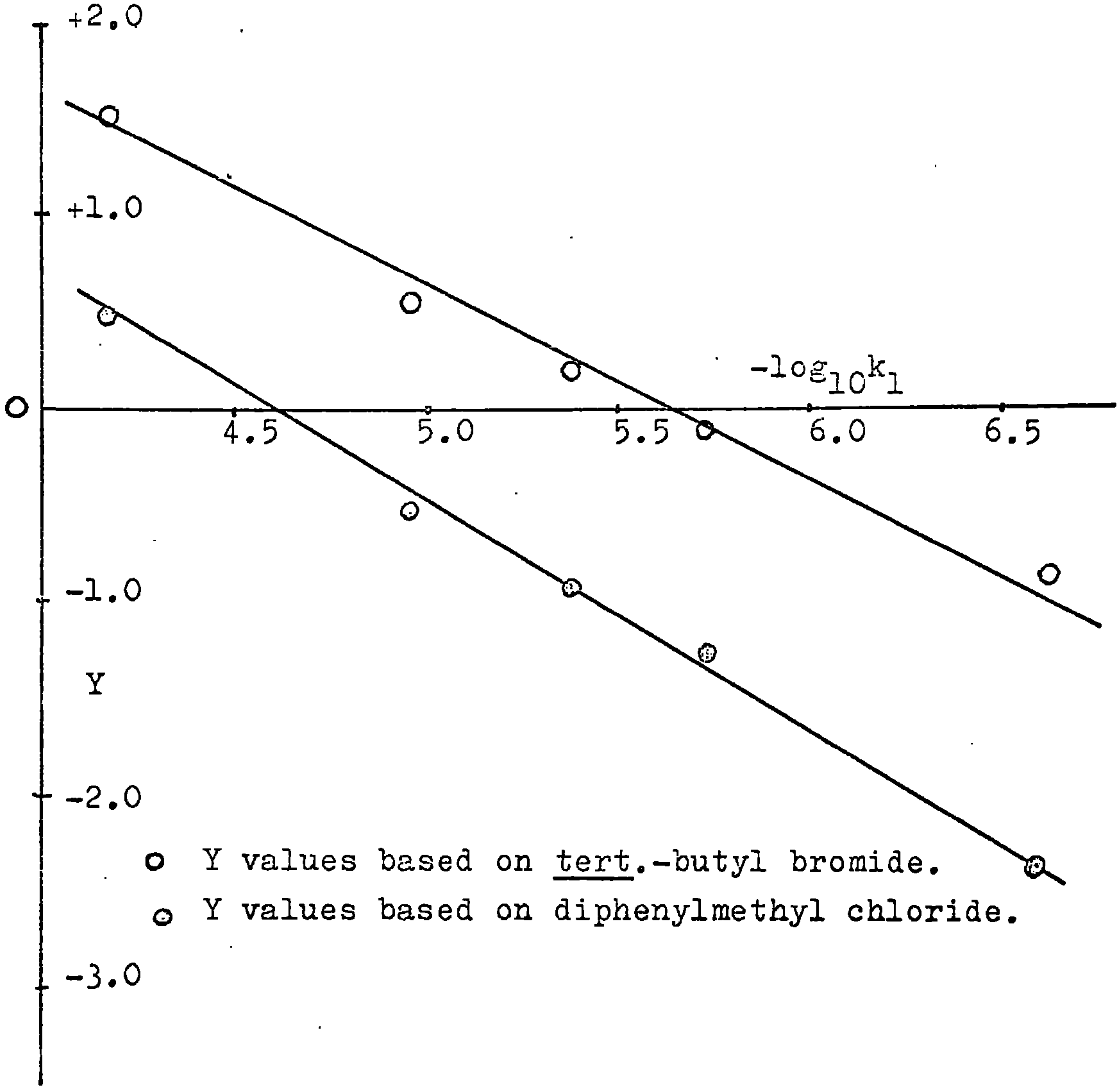
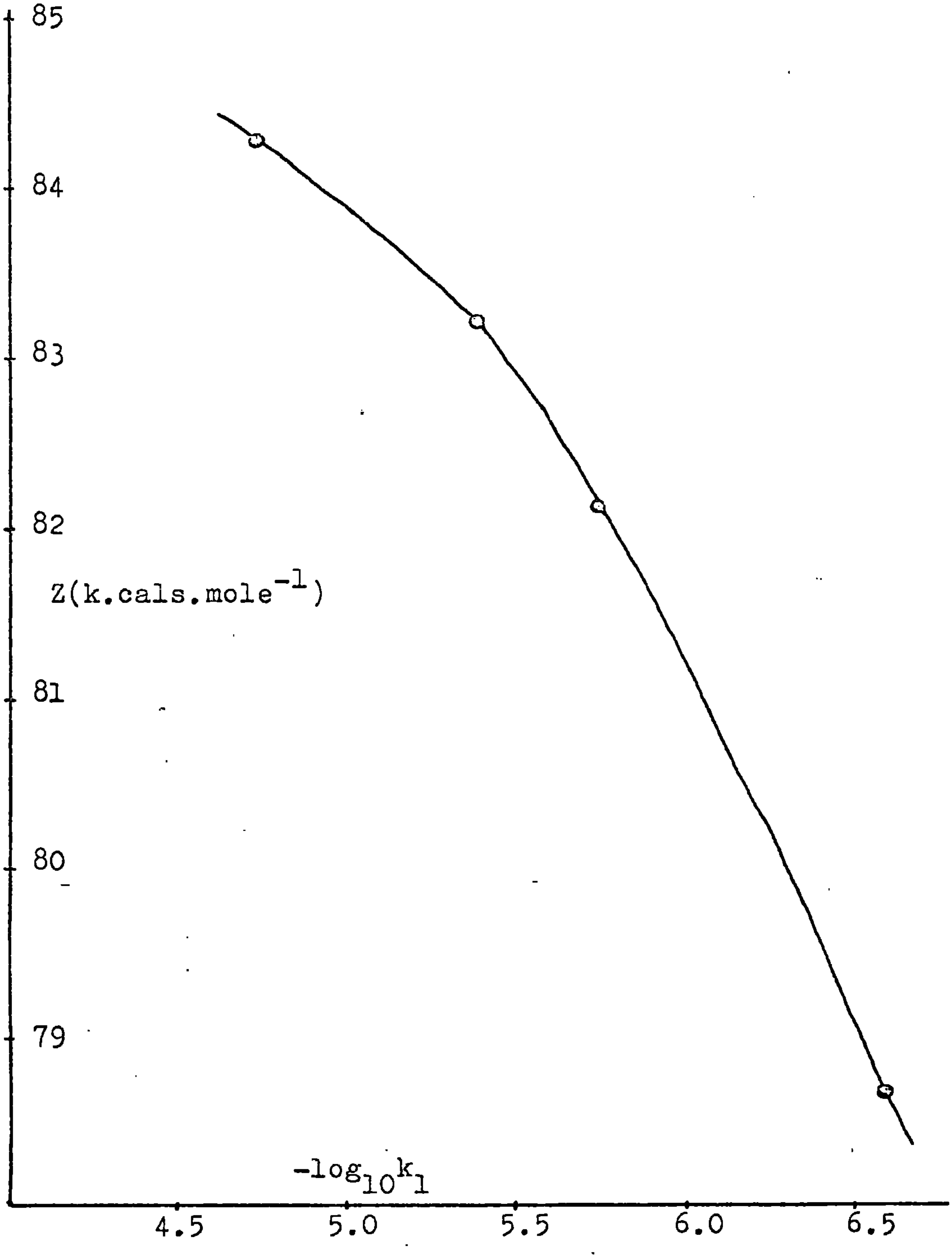


FIG.II.3. The variation of $\log_{10}k_1$ with Z values.



A good linear relation was obtained between $\log_{10}k_1$ and Winstein's Y values[32] (fig. II.2.) and the plots of $\log_{10}k_1$ against D,[39] 1/D,[40] (D-1)/(2D+1)[41] (fig. II.1) or Z[44] (fig. II.3.) also gave a reasonably good, though not perfect, straight lines. It is noteworthy that all these relationships would have given a better fit if the point for 85% (v/v) aqueous acetone had been discarded. The good agreement with the Winstein mY relation[32] is hardly surprising since the Y values derived from studies on diphenylmethyl chloride vary in much the same way with changes in the solvent composition as those obtained from the solvolysis of tert.- butyl bromide; the same conclusion could therefore have been reached by noting that the solvolysis of compound I is similar to diphenylmethyl chloride in its response to a change in the solvent composition. It is difficult to draw any conclusions from the reasonable linearity of the other plots. This could well result from the fact that the various parameters reflect in a similar way the changes in those factors which are responsible for the changes in the rate of solvolysis. Values of $\log_{10}k_1$ also vary almost linearly with the mole fraction of water in the media (see fig. II.4.) and even with the molar concentration of the water.

II. 2. The Effect of Changes in the Solvent Composition on the Relative Stabilities of the Initial and Transition States in Solvolysis.

The effects of solvent changes on the relative activity coefficients of the initial and transition states are summarised in table VII for the solvolysis of compound I (at 20.18°C), compound II (at 1.62°C) and compound III

FIG.II.4. The variation of $\log_{10}k_1$ with the mole fraction of water in the solvent(z_1).

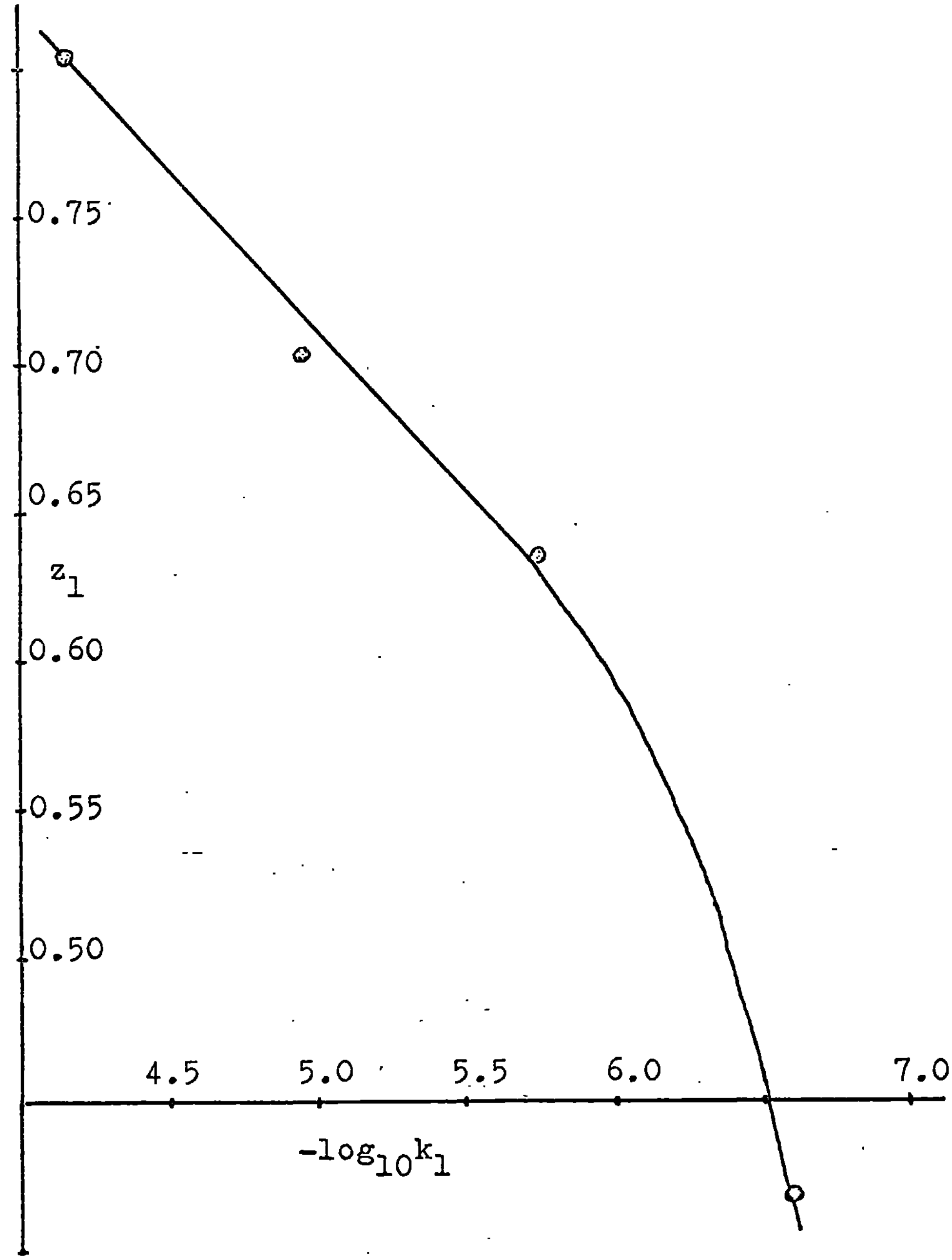


TABLE VII

Relative Rates and Activity Coefficients for Solvolysis in Aqueous Acetone (All values are relative to those obtained in 50% (v/v) aqueous acetone).

Solvent % (v/v) Acetone	Mechanism S_N1						Mechanism S_N2		
	Compound I at 20.18°C			Compound II at 1.62°C			Compound III at 1.67°C		
	$\log \frac{\gamma_{RX}}{\gamma^{o}_{RX}}$	$-\log \frac{\gamma_{\ddagger}}{\gamma^{o}_{\ddagger}}$	$\log \frac{k_1}{k^{o}_1}$	$\log \frac{\gamma_{RX}}{\gamma^{o}_{RX}}$	$-\log \frac{\gamma_{\ddagger}}{\gamma^{o}_{\ddagger}}$	$\log \frac{k_1}{k^{o}_1}$	$\log \frac{\gamma_{RX}}{\gamma^{o}_{RX}}$	$-\log \frac{\gamma_{\ddagger}}{\gamma^{o}_{\ddagger}}$	$\log \frac{k_1}{k^{o}_1}$
40	——	——	——	+0.798	+0.024	+0.810†	+0.555	−0.139	+0.316*
50	0	0	0	0	0	0	0	0	0
60	——	——	——	——	——	——	−0.357	−0.112	−0.245*
65	−0.914	+0.136	−0.778	——	——	——	——	——	——
70	−1.328	+0.102	−1.226	——	——	——	——	——	——
75	−1.634	+0.065	−1.569	——	——	——	——	——	——
85	−2.198	−0.211	−2.409*	——	——	——	——	——	——

† Calculated from results of solubility and zeroth-order rate measurements.

* Interpolated from rate data at higher temperatures.

FIG.II.5. The effect of solvent changes on $\log_{10}k_1/k_1^o$ $\log_{10}\gamma_{RX}/\gamma_{RX}^o$ and $\log_{10}\gamma_{\ddagger}/\gamma_{\ddagger}^o$ in the S_N1 solvolysis of 4-phenyl:4'-nitrodiphenylmethyl chloride in aqueous acetone at 20.18°C.

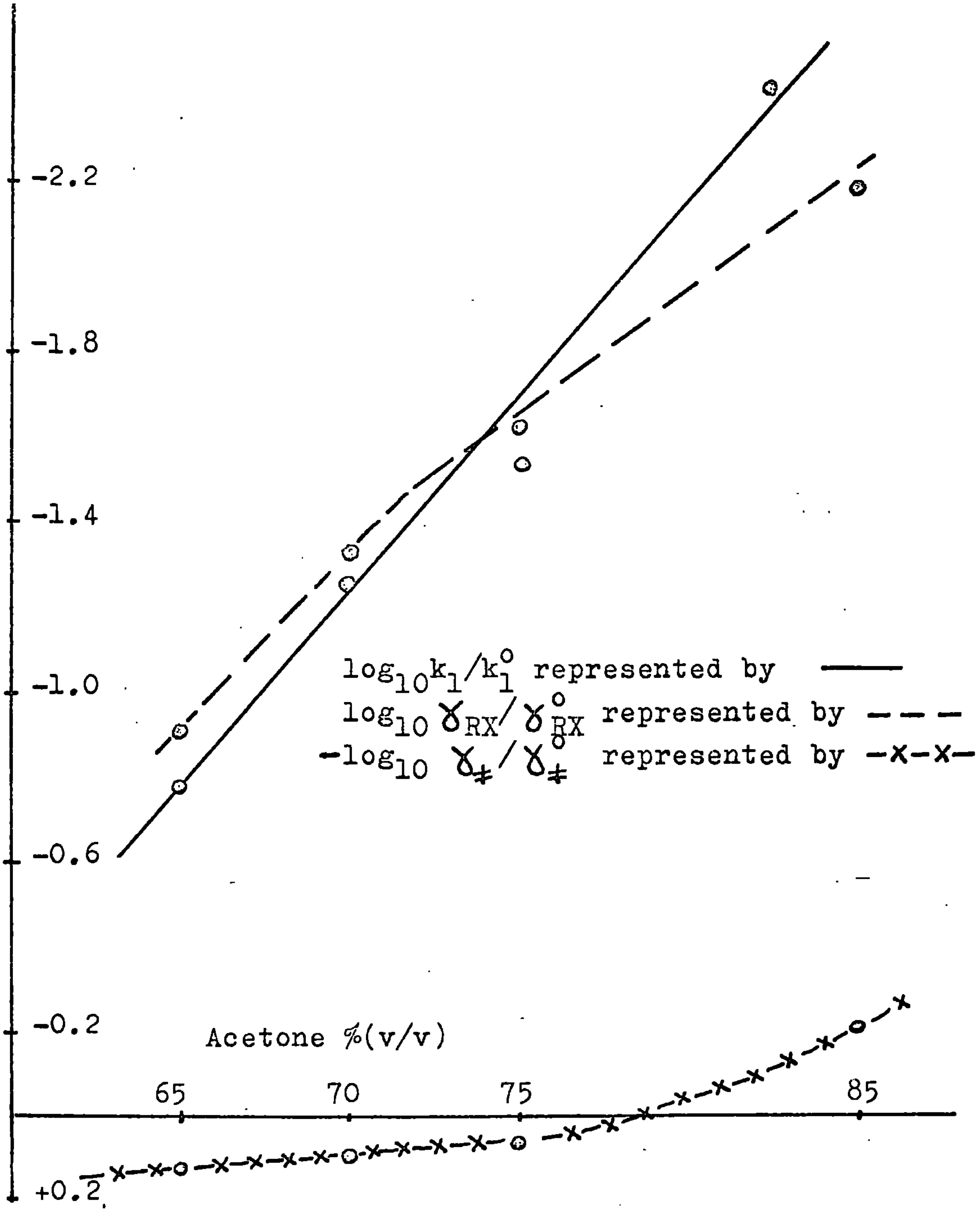
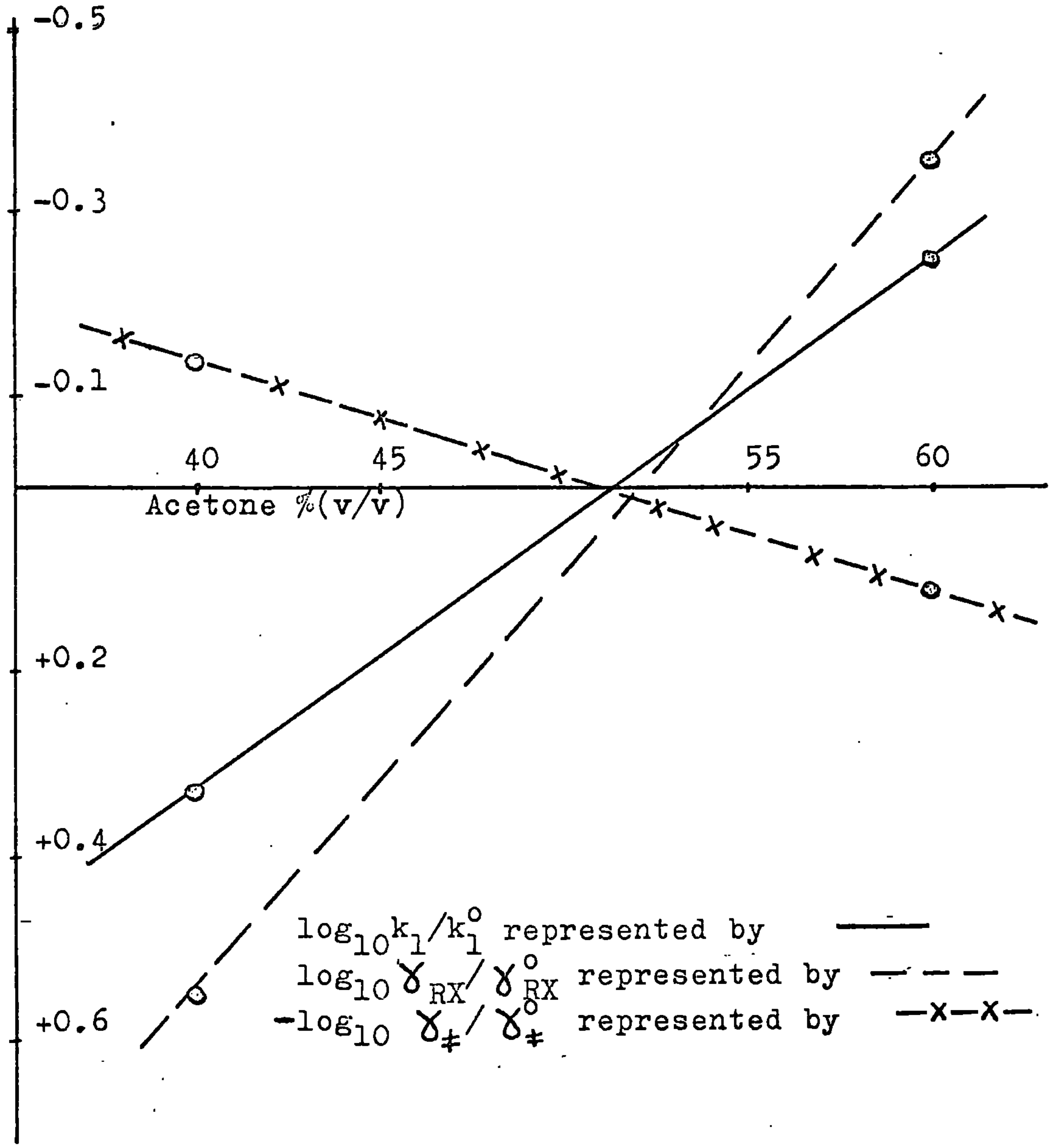


FIG.II.6. The effect of solvent changes on $\log_{10}k_1/k_1^o$ $\log_{10}\gamma_{RX}/\gamma_{RX}^o$ and $-\log_{10}\gamma_{\ddagger}/\gamma_{\ddagger}^o$ in the S_N2 solvolysis of 4-nitrobenzyl chloride in aqueous acetone at 20.18°C.



(at 1.67^{o}C) in aqueous acetone. All the figures are on a scale relative to unit value for the activity coefficients in 50% (v/v) aqueous acetone. Some of the results are also presented in graphical form in figures II.5. and II.6.

The most striking feature of these results is that the stability of the transition state in S_N1 reactions ($-\log \gamma_{\ddagger}/\gamma_{\ddagger}^{o}$) is remarkably insensitive to solvent variations so that the decrease in rate as the solvent is made less aqueous arises almost entirely from the accompanying increase in the stability of the initial state. In the S_N2 reaction of compound III, however, the increase in the stability of the initial state is accompanied by a similar, but smaller, increase in the stability of the transition state. This is partly responsible for the difference in the sensitivity of S_N1 and S_N2 reactions to changes in the solvent composition. These observations are contrary to earlier views,[1] and it is noteworthy that other workers have also observed considerably smaller initial state contributions to log k_1/k_1^{o} in different aqueous organic media.(see ref. 55.)

The present observation that the total kinetic effect of changes in the solvent composition on the rate of solvolysis is controlled mainly by changes in the stability of the initial state is diametrically opposed to the earlier predictions of Hughes and Ingold.[1b] However, it is not really surprising that the stability of the initial state increases with an increase in the acetone content of the solvent, since such a change is merely a consequence of its increased solubility, and it seems reasonable to assume that this arises from the greater facility for the operation of attractive forces between acetone and the substrate (<u>i.e.</u> "solvation" by acetone). While it also seems likely that the polar component of the solvent (water) is responsible for solvation of the charged transition state at those points where the charges are located,[†] it must be remembered that parts of the substrate will retain their non-polar character in the transition state and will therefore also be solvated by acetone.

On this view, the near-constancy of $-\log \gamma_{\ddagger}/\gamma_{\ddagger}^{o}$ in S_N1 reactions on making the solvent less aqueous is consistent with a balance between the increased ease of solvation of the transition state by acetone and the decrease in the ease of solvation by water. The decrease in rate on decreasing the mole fraction of water in the solvent can then be regarded as almost entirely a consequence of the greater ease of solvation of the initial state by acetone. In reaction by mechanism S_N2, the decrease of $-\log \gamma_{\ddagger}/\gamma_{\ddagger}^{o}$ as the acetone content of the solvent is increased then suggests that the transition state requires proportionally less solvation by water; in agreement with earlier views[34] and with conclusions based on the heat capacities of activation.[35] Specific interactions between the solvent and the substrate have, of course, been invoked on a number of occasions[45c,55g,75,83e,85,87] to explain deviations from the simple electrostatic approach.

[†] On the basis of measurements of the heat capacity and entropy of activation for the solvolysis of organic halides in aqueous organic solvents,[35] it has been suggested that the additional solvation requirements for passage from the initial to the transition state are met by solvation of the charged transition state by water molecules.

Featherstone's results (see Table VIII) also confirm the present findings. Although he used solubilities measured at 0°C. and first-order rate coefficients obtained at 39.75°C. to calculate the transition state contributions to the total effect of solvent changes on the rate, the results in Table IX show that these factors are unlikely to cause serious errors, since the values of the relative activity coefficients in the present system are virtually independent of the temperature.

However, it must be realised that the present results do not necessarily invalidate the views of earlier workers[1b]: the rate of solvolysis of S_N2 reactions is shown to be less sensitive to changes in the water content of the solvent than when mechanism S_N1 is in operation, and this difference arises essentially from a greater degree of stabilisation (or a smaller degree of destabilisation) of the transition state in S_N1 reactions. Nevertheless, it is abundantly clear that effects on the stability of the initial state cannot be neglected. However, it should be stressed that initial state solvation effects may not always play such an important role in determining the effects of solvent changes on the rate of solvolysis as the present discussion has been limited to investigations in acetone-water mixtures using very similar compounds. It has indeed been shown that the relative contributions of both the initial and transition states to the total solvent effect in the solvolysis of <u>tert.</u>-butyl chloride in aqueous alcohols[31,55b] depend markedly on the ionising power of the solvent (see Table X).

It seems extremely likely that the magnitude of the initial state contribution will depend to a large extent on the nature of both the solvent and the substrate. It is

TABLE VIII

Relative Rates and Activity Coefficients in the Solvolysis of 4-nitrodiphenyl methyl chloride and 4-nitrobenzyl chloride in aqueous acetone (see ref. 50g). (All values are relative to those obtained in 50% (v/v) aqueous acetone).

Solvent % (v/v)	Mechanism S_N2			Mechanism S_N1		
	4-nitrodiphenylmethyl chloride			4-nitrobenzyl chloride		
Acetone	†$\log \frac{\gamma_{RX}}{\gamma^{o}_{RX}}$	$-\log \frac{\gamma_{\ddagger}}{\gamma_{\ddagger}^{o}}$	*$\log \frac{k_1}{k_1^{o}}$	†$\log \frac{\gamma_{RX}}{\gamma^{o}_{RX}}$	$-\log \frac{\gamma_{\ddagger}}{\gamma_{\ddagger}^{o}}$	*$\log \frac{k_1}{k_1^{o}}$
45	+0.476	-0.146	+0.330	+0.338	-0.184	+0.154
50	0	0	0	0	0	0
55	-0.290	-0.024	-0.314	-0.202	+0.080	-0.122

† Calculated from solubilities measured at 0°C.

* First-order rate coefficients at 39.75°C.

TABLE IX

The variation of the relative activity coefficients with temperature for the S_N1 solvolysis of 4-phenyl:4'-nitro diphenyl methyl chloride in aqueous acetone.
(All values are relative to those obtained in 50% (v/v) aqueous acetone).

Solvent % (v/v)	Temp. °C.	$\log \frac{\gamma_{RX}}{\gamma^{o}_{RX}}$	$-\log \frac{\gamma_{\ddagger}}{\gamma^{o}_{\ddagger}}$	$\log \frac{k_1}{k^{o}_1}$
50	20.18	0	0	0
	9.46	0	0	0
	1.71	0	0	0
70	20.18	-1.328	+0.102	-1.226
	9.46	-1.443	+0.162	-1.281*
	1.71	-1.497	+0.169	-1.328*
85	20.18	-2.198	-0.211	-2.409*
	9.46	-2.364	-0.096	-2.470*
	1.71	-2.469	-0.069	-2.538*

* Interpolated from rate data at higher temperatures.

TABLE X

The solvolysis of <u>tert</u>.-butyl chloride in aqueous alcohols (see ref. 55b).

(The figures quoted refer to the variation in the standard free energy with changes in the solvent composition).

Solvent Change.	Total Solvent Effect (k.cals.mole^{-1})	Initial State Effect (k.cals.mole^{-1})	Transition State Effect (k.cals.mole^{-1})
100%MeOH-70.5%MeOH	-2.80	-1.21	-1.59
100%EtOH-70%EtOH	-2.30	-1.06	-1.24
100%MeOH-100%H_2O	-6.25	-4.09	-2.16
100%EtOH-100%H_2O	-3.85	-3.03	-0.82

certainly not surprising, on the basis of the present hypothesis, that solvation effects are different in aqueous alcohol and aqueous acetone; alcohols, being considerably more polar than acetone, are less likely to participate in the solvation of non-polar groups.

II. 3. Thermodynamic Parameters derived from Solubilities and from the First-order and Zeroth-order Rates of Solvolysis of 4-phenyl:4'-nitrodiphenylmethyl chloride in Aqueous Acetone.

The measured or calculated values of the solubility and zeroth-order rate coefficients were originally obtained in concentration units. In order to deduce the appropriate thermodynamic parameters from data at different temperatures it is more convenient to employ molality units as the standard state is then independent of the temperature. The densities of the solvents employed in the present investigation were therefore used to convert the experimental values to the required molality units, on the assumption that the density of the saturated solutions was the same as that of the solvent. These determinations were only carried out with compound I which is only sparingly soluble and this assumption therefore is likely to be valid to a good degree of approximation.

The resulting solubilities, zeroth-order and first-order rate coefficients then provide the changes in the thermodynamic parameters for the hypothetical processes;

A) $RCl_s \longrightarrow$ Activated Complex (ideal, $m = 1$)
B) RCl(ideal, $m = 1$) $\longrightarrow$ Activated Complex (ideal, $m = 1$)
C) $RCl_s \longrightarrow RCl$ (ideal, $m = 1$)

Solubilities and rate measurements at the three experimental temperatures, namely 20.18°C, 9.46°C and 1.71°C, are given in Table XI and values of the appropriate thermodynamic parameters at two temperatures are shown in Table XII; their values at the mean experimental temperature 10.20°C are given in Table XIII.

The enthalpy of activation for process A is large (ca. 33 k.cals.) and the zeroth-order reactions could therefore only be conveniently studied over about twenty degrees. This restricted the rate measurements to three temperatures and the reliability of the values of the heat capacities of activation (ΔC^{o}) may be worse than indicated by the figures in Table XII. However, the striking difference between the values in 70% and 85% aqueous acetone is probably genuine.

The free energy of activation for process A (ΔG^{o}) is very much less sensitive to changes in the solvent composition than the standard free energy changes of the other two processes (see Table XIII), but this observation merely states in a different manner the earlier conclusion that the stability of the activated complex depends only to a slight extent on the nature of the present solvents. However, the virtually constant values of ΔG^{o} for process A arise from the cancellation of the relatively large effect of alterations in the nature of the solvent on the corresponding standard enthalpy and entropy changes. As the solvent is made less aqueous, the enthalpy change tends to make the process more favourable while entropy changes have an equivalent opposing effect.

Similar considerations apply to the solution process C, although now the unfavourable effect of decreasing the water content on ΔS^{o} is not sufficient to balance the accompanying favourable effect on ΔH^{o} (see Table XIII).

TABLE XI

Solubilities and Rates for the Solvolysis of 4-phenyl:4'-nitrodiphenylmethyl chloride in Aqueous Acetone.

Solvent % (v/v) Acetone	Temperature °C	† Solubility (10^4) (moles.1000gms.$^{-1}$)	k_1 (10^8) (secs.$^{-1}$)	k_o (10^{10}) (moles. 1000gms.$^{-1}$ secs.$^{-1}$)
50	20.18	3.674	6764*	248.5 ± 0.496
	9.46	1.752	1667*	29.20 ± 0.107
	1.71	0.960	563.2*	5.406 ± 0.0214
70	20.18	81.93	402.6	329.8 ± 0.419
	9.46	48.66	87.21*	42.42 ± 0.102
	1.71	31.50	26.45*	8.332 ± 0.0221
85	20.18	645.4	26.20	169.1 ± 0.356
	9.46	414.3	5.654*	23.42 ± 0.061
	1.71	315.1	1.606*	5.059 ± 0.0207

† Calculated via. equations I.6., I.10 and I.15.

* Calculated values. For details see experimental section (page 123).

TABLE XII

Values of ΔH^o, ΔG^o, ΔS^o and ΔC^o for processes A, B and C in the solvolysis of 4-phenyl: 4'-nitrodiphenylmethyl chloride in Aqueous Acetone.

Parameter		50% (v/v) Acetone		70% (v/v) Acetone		85% (v/v) Acetone	
		14.82°C	5.58°C	14.82°C	5.58°C	14.82°C	5.58°C
ΔH^o (k.Cals.)	A	33.483±0.069	34.151±0.144	32.092±0.058	32.977±0.079	30.956±0.059	31.078±0.082
	B	21.821	22.162	24.058	24.320	23.965	24.337
	C	11.662	11.989	8.034	8.657	6.991	6.741
ΔG^o (k.cals.)	A	28.515±0.244	28.646±0.425	28.417±0.208	28.512±0.291	28.779±0.208	28.815±0.301
	B	23.762	23.770	25.532	25.452	27.092	26.957
	C	4.753	4.876	2.885	3.060	1.687	1.858
ΔS^o (cals.)	A	17.25±0.24	19.75±0.40	12.76±0.20	16.02±0.28	7.56±0.20	8.12±0.29
	B	-6.74	-5.77	-5.12	-4.06	-10.86	-9.40
	C	23.99	25.52	17.88	20.08	18.42	17.52
ΔC^o (cals.)	A	-76.4 ± 14.4		-97.9 ± 10.6		-15.3 ± 10.9	
	B	-30		-32.5		-45.1	
	C	-46.4		-65.4		+29.7	

TABLE XIII

Thermodynamic Parameters at 10.20°C.

Parameter	Process	50% (v/v) Acetone	70% (v/v) Acetone	85% (v/v) Acetone
ΔH^{o} (k.cals)	A	33.819	32.536	31.028
	B	22.044	24.188	24.161
	C	11.775	8.348	6.867
ΔG^{o} (k.cals)	A	28.575	28.458	28.806
	B	23.821	25.492	27.026
	C	4.754	2.966	1.780
ΔS^{o} (cals.)	A	18.50	14.39	7.84
	B	-6.27	-4.60	-10.11
	C	24.77	18.99	17.95

Positive standard entropy changes are associated with both processes A and C, although ΔS^o has the smaller values for process A. In qualitative terms this could be interpreted as a consequence of the solvation of the activated complex by water and the same conclusion can be reached on the basis of the negative values of ΔS^o in process B.

Although the effect of solvent changes on ΔG^o for process A can be interpreted in terms of a simple solvation model,[88] this model is quite inadequate for explaining the other results shown in Table XIII. Changes in the structure of the solvent may make a substantial contribution to the standard partial molar entropies and enthalpies of solutes although these contributions may well cancel to a greater or smaller extent in the chemical potential (μ^o). At present the experimental information available is not sufficient to allow such a hypothesis to be developed further.

A similar analysis of the effect of solvent changes on the partial molar properties of initial and transition states has recently been reported for the solvolysis of *tert*.-butyl chloride in ethanol-water mixtures;[85] the data being collected from various sources. The results are strikingly different, in some respects, from those now reported and are summarised schematically in Table XIV. However, both studies show quite clearly that the effect of solvent changes on the properties of the initial state is an extremely important factor in determining the effect of such changes on the rates of solvolysis and certainly cannot be neglected.

TABLE XIV

The Effect of Solvent Changes on the partial molar properties of Initial and Transition States in Solvolysis.

		tert.-BuCl* in Ethanol-Water	$NO_2.C_6H_4.CHCl.C_oH_4.C_6H_5$ in Acetone-Water
Initial state	μ^o	increase	increase
	H^o	small increase	large increase
	S^o	little change	increase
Transition state	$\mu^{\ddagger}$	decrease	little change
	$H^{\ddagger}$	decrease	increase
	$S^{\ddagger}$	small increase	increase

* See reference 85.

CHAPTER III

Electrolyte Effects in Solvolysis; Results and Discussion.

A series of uni-univalent electrolytes were employed to investigate the effects of added electrolytes on the rates, and on the stabilities of the initial and transition states in the S_N1 solvolysis of 4-phenyl:4'-nitrodiphenyl methyl chloride in 70% (v/v) aqueous acetone at 20.18°C. The required information concerning the effects of added electrolytes on the stabilities of the initial and transition states (as represented by the ratios $\gamma_{RX}/\gamma^{o}_{RX}$ and $\gamma_{\ddagger}/\gamma_{\ddagger}^{o}$ respectively) was obtained from measurements of the first-order rates of solvolysis in dilute solutions and of the zeroth-order rates in permanently saturated solutions via. equations 1.6 and 1.15. The relevant rate coefficients were determined by noting the development of acidity or chloride ions in the solutions. Experimental details are given in Chapter IV and the results are listed in full in appendix A. Solubility determinations were also carried out in a limited number of cases, but their accuracy was not sufficient to allow the calculation of $\gamma_{RX}/\gamma^{o}_{RX}$, and they were only used to check the internal consistency of equations 1.6., 1.10. and 1.15. (see page 116)

III. 1. The Effects of Electrolytes on the Rates of Hydrolysis.

The present study was aimed at obtaining information about the effects of added electrolytes on the initial and transition states in the ionisation of organic halides. Although, the experimental measurements gave this information for hydrolysis, it is shown below that the required data for the ionisation can be readily obtained from the observations.

It is assumed that the rate of ionisation (k_1) of an organic halide in the presence of an electrolyte (MX) is given by

$$\ln k_1 = A_{MX}\,\mu_{MX} + \ln k_1^o \qquad \text{------} \qquad 3.1.$$

where μ_{MX} is the ionic strength of the solution, A_{MX} a parameter dependent on the nature of the electrolyte (MX), and the superscript, o, refers to zero ionic strength. This expression allows for the observation of specific electrolyte effects (see section I. 7.3.) and is of the form required by theoretical arguments. (see page 85). However, hydrochloric acid is produced as the present reactions proceed and equation 3.1., must therefore be modified in order to ensure that it applies at all stages of the reaction; <u>viz</u>.,

$$\ln k_1 = A_{MX}\,\mu_{MX} + A_{HCl}\,\mu_{HCl} + \ln k_1^o \text{ --- } 3.2.$$

The rate of ionisation can then be related to the rate of hydrolysis by means of equation I.5:

$$\ln k_h = A_{MX}\,\mu_{MX} + A_{HCl}\,\mu_{HCl} + \ln k_1^o - \ln(1-\alpha[\overline{Cl^-}]) \qquad \text{------} \quad 3.3.$$

The mass-law constant, α, should, of course, depend on the ionic strength of the chloride ion,[1b] but Queen[50f] has shown that no error is caused by assuming α to be constant for solutions containing up to 0.1M added chloride ions. In the absence of added electrolytes (superscript $\dagger$), the rate of hydrolysis is therefore given by

$$\ln k_h^{\dagger} = A_{HCl}\,\mu_{HCl}^{\dagger} + \ln k_1^{o} - \ln(1 + \alpha[Cl^-]^{\dagger}) \text{ ---- } 3.4.$$

Hence.

$$\ln \frac{k_h}{k_h^{\dagger}} = A_{MX}\,\mu_{MX} + A_{HCl}(\mu_{HCl} - \mu_{HCl}^{\dagger}) - \ln \frac{(1-\alpha[Cl^-])}{(1-\alpha[Cl^-]^{\dagger})} \text{ -------- } 3.5.$$

It should be stressed that equations 3.3 - 3.5 refer to instantaneous rate coefficients, while integrated rate coefficients are determined in practice. However, the observed integrated rate coefficients did not vary in any systematic manner during the course of the experiments and it has been shown that under these conditions, the integrated rate coefficient for the time interval 0 - t can be identified with the instantaneous rate coefficient at the concentration prevailing at the time t/2.[50f] The mean integrated rate coefficients reported in this chapter can therefore be regarded as indentical with the mean instantaneous rate coefficients at the means of these concentrations, since all the experiments were carried out with solutions containing initially the same amount of organic halide, and since the stages at which readings were taken did not differ greatly from one experiment to another. Under these conditions, $\mu_{HCl} = \mu_{HCl}^{\dagger}$ within an extremely small error, since these terms refer to the mean of the hydrochloric acid concentrations at the various times of t/2. Similarly, $[Cl^-] = [Cl^-]^{\dagger} + [Cl^-]_{added}$ so that equation 3.5 can be written in the form

$$\ln \frac{k_1}{k_1^{o}} = A_{MX}\,\mu_{MX} = \ln \frac{k_h}{k_h^{\dagger}} + \ln(1-\alpha[Cl^-]_{added}) \text{ --- } 3.6.$$

When no ionised chloride has been added the last term in this equation vanishes.

Queen[89] found by the use of a radioactive labelling technique[50f] that α had the value of I.8., litres, moles^{-1} for 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone at 20°C. This value has been accepted for the present work.

Equations 3.1. - 3.6., are equally valid when applied to measurements of permanently saturated solutions (zeroth-order rates, electrolyte parameter A^*_{MX}), and to conventional experiments involving unsaturated solutions (first-order rates, electrolyte parameter A_{MX}).

III. 2. Electrolyte Effects in Solvolysis.

III. 2.1. The Effect of Added Electrolytes on First-order Rates of Solvolysis.

The results summarised in Table XV show the percentage increase in the first-order rate of ionisation caused by the addition of electrolytes. A negative value indicates that the added electrolyte retarded the reaction.

The present results clearly show that the nature of the added electrolyte is an important factor in determining its effect on the rate. This observation is discussed in more detail on page 90. It is noteworthy that doubling the concentration of the added electrolyte usually doubles the percentage increase in rate, within the limits of experimental error. The most obvious discrepancies arise with those electrolytes which show large accelerating effects possibly because the error is more easily recognised under these conditions. The effect of changes in the salt

TABLE XV

Electrolyte Effects on the First-order Rate of Ionisation of 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) Aqueous Acetone at 20.18°C.

Electrolyte	100 (k_1/k_1^o-1)	
	0.05M	0.10M
$(CH_3)_4NF$[*]	-11.64 ± 0.57[ø]	-24.87 ± 0.67[ø]
NaCl	2.70 ± 0.36	3.66 ± 0.40
$NaSO_3Ph$	6.71 ± 0.41	12.49 ± 0.35
$NaNO_3$	8.77 ± 0.41	16.83 ± 0.86
$NaBF_4$[*]	11.55 ± 0.49	20.46 ± 0.40
$NaBr_4$	14.04 ± 0.33	27.46 ± 0.38
HNO_3[*]	15.28 ± 0.39	31.05 ± 0.66
$NaClO_4$	17.13 ± 0.59	32.83 ± 0.49
$HClO_4$[*]	22.47 ± 0.52[ø]	41.84 ± 0.47[ø]
NaN_3[*]	61.44 ± 1.74	99.99 ± 1.20

[*] Followed by noting the development of chloride ions.

[ø] Interpolated from results at different added electrolyte concentrations.

concentration on k_1 is further illustrated in Table XVI for sodium perchlorate.

TABLE XVI

The Effect of Added Sodium Perchlorate on $100\ (k_1/k_1^o-1)$ in 70% (v/v) Aqueous Acetone at 20.18°C.

Salt Concentration	$100\ (k_1/k_1^o-1)$
0.025M	8.62 ± 0.60
0.050M	17.13 ± 0.51
0.075M	22.93 ± 0.50
0.10M	32.83 ± 0.49

Winstein and his coworkers[5a] have shown that a linear relation of k_1 with the salt concentration is to be prefered to a linear relation involving $\log_{10}k_1$.[1b] However, a distinction between these two proposals is not possible when k_1/k_1^o is close to unity. Larger differences between k_1 and k_1^o unfortunately involve the use of relatively large salt concentrations when the departure of the system from ideal behaviour is likely to obscure the nature of the relation between k_1 and the ionic strength at high dilutions. All the theoretical expressions for the effect of added electrolytes on the rates of reactions, or on activity coefficients (e.g. the Setschenow equation: see page 31) require the logarithmic relation, which has therefore been accepted in the present discussion even though it is not supported by all the results in Table XV. The deviations now observed may well be a consequence of working with 0.1M electrolytes.

The present results are compared in Table XVII with those obtained in a similar study[17b,50f.] of diphenylmethyl chloride. On the whole, both reactions show the same response to the addition of a particular electrolyte, except the fluoride, bromide and azide. The increase in rate now observed on addition of sodium azide is considered too large to arise from a simple salt effect in an S_N1 reaction and it therefore seems very likely that at least a part of this increase is a consequence of bimolecular (S_N2) attack of these ions on the substrate. The present compound undergoes solvolysis ca. forty times more slowly than diphenylmethyl chloride because of its poor capacity for electron-release towards a positive centre, but S_N2 reactions with anions are notoriously insensitive to the polar situation at the reaction centre. It is therefore quite conceivable that S_N2 attack by the powerfully nucleophilic azide ion should make a significant contribution to the rate of disappearance of 4-phenyl:4'-nitrodiphenylmethyl chloride, but not to the much more rapid decomposition of diphenylmethyl chloride. The greater accelerating effect of bromide ion in the present system may well arise from similar considerations. Rate enhancement by added bromide is much less than for the azide, consistent with the greater nucleophilic power of the azide ion. The other anions are much weaker nucleophiles and do not show any abnormal effects.

No explanation can be advanced at this stage for the discrepancy of the results for tetramethylammonium fluoride but Queen's[50f] value is based on a single determination

TABLE XVII

Electrolyte Effects on the First-order Rates of Ionisation in 70% (v/v) aqueous acetone, at 20°C.
(The figures reported refer to the percentage change in rate caused by the addition of 0.05M electrolyte).

Electrolyte	Diphenylmethyl chloride	4-phenyl:4'-nitro diphenylmethyl chloride
$(CH_3)_4NF$	-5.65	-11.64
NaCl	1.82	2.70
$NaSO_3Ph$	5.70	6.71
$NaNO_3$	6.85	8.77
NaBr	8.60	14.04
$NaBF_4$	11.96	11.55
$NaClO_4$	15.07	17.13
$HClO_4$	21.06	22.47
NaN_3	11.20	61.44

which may be erroneous.

Apart from the anomalous effects of bromide and azide ions, which probably arise from the special considerations already discussed, the present results not only confirm the appearance of specific electrolyte effects in S_N1 solvolysis but also that the effects of anions follow the sequence; $ClO_4^- > BF_4^- \cong N_3^- > Br^- > NO_3^- > SO_3Ph^- > Cl^- > F^-$ while the cation order is $H^+ > Na^+$. Similar orders have been observed in other S_N1 reactions in aqueous organic solvents.[50c,e,f,g.]

III. 2.2. The Effect of Added Electrolytes on Zeroth-order Rates of Solvolysis.

Good zeroth-order kinetics were observed for solvolysis in permanently saturated solutions in the presence of all the added electrolytes, except sodium azide. The results are summarised in Table XVIII, and refer to the percentage change in rate caused by the addition of electrolyte. The figure quoted for the effect of 0.05M sodium azide was calculated from initial readings obtained in duplicate experiments, as k_0 was found to decrease as the reaction proceeded when this electrolyte was present. This behaviour is an inevitable consequence of the very large accelerating effect shown by azide ions, since they are removed from the system in the form of RN_3 or HN_3 as the reaction proceeds.

It is noteworthy that all the electrolytes accelerate the zeroth-order ionisation and that this acceleration depends less strongly on the nature of the salt (see Table XVIII) than in the first-order ionisation (see Table XVII). Indeed several different salts show almost the same effect on k_0. Doubling the concentration of added electrolyte doubles the effect on k_0, probably because

TABLE XVIII

Electrolyte Effects on the Zeroth-order rate of Ionisation (permanently saturated solutions) of 4-phenyl:4'-nitrodiphenyl methyl chloride in 70% (v/v) aqueous acetone at 20.18°C.

Electrolye	$100\ (k_o/k_o^o-1)$	
	0.05M	0.10M
$(CH_3)_4NF$[*]	1.39 ± 0.68	2.78 ± 0.66[ø]
$NaCl$	5.42 ± 0.33	10.48 ± 0.31
$NaSO_3Ph$	9.25 ± 0.31	19.04 ± 0.37
$NaNO_3$	7.39 ± 0.19	14.67 ± 0.38
$NaBF_4$[*]	8.43 ± 0.28	16.85 ± 0.49
$NaBr$	11.22 ± 0.39	22.97 ± 0.49
HNO_3[*]	9.71 ± 0.32	17.52 ± 0.29
$NaClO_4$	14.71 ± 0.20	29.14 ± 0.36
$HClO_4$[*]	14.55 ± 0.42[ø]	28.67 ± 0.76[ø]
NaN_3[*]	49.7	————————

[*] Followed by noting the development of chloride ion.

[ø] Interpolated from results at a different electrolyte concentration.

the magnitude of the electrolyte effect is never large.

III. 3. The Effect of Added Electrolytes on the Stabilities of the Initial and Transition States in the S_N1 Solvolysis of 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) Aqueous Acetone at 20.18°C.

Table XIX shows the total kinetic salt effects and the contributions from accompanying changes in the stabilities of the initial and transition states. This information was obtained from the present results using the methods previously discussed (see section I.9.) and the data are reported in such a way that a positive value indicates acceleration by the electrolyte (stabilisation of the transition state, destabilisation of the initial state). The results for added sodium azide are not now considered since some bimolecular attack appears to take place in its presence.

Apart from the two perchlorates, which appear to be anomolous and will be discussed later, the specific effects of all the other electrolytes on the rate (k_1) arises largely from a specific effect on the stability of the initial state; on passing down the series from tetramethyl ammonium fluoride to nitric acid, $\log_{10} \gamma_{RX}/\gamma^{o}_{RX}$ changes by 0.184 while $-\log_{10} \gamma_{\ddagger}/\gamma_{\ddagger}^{o}$ changes only by 0.058. It is noteworthy that electrolytes have also been found to produce marked specific effects on various physical properties of non-electrolytes in aqueous organic media,[45c,58,71f,74,75,81,82g] and the present results confirm and extend the salt-order previously reported for the salting-in and salting-out of naphthalene and 1-naphthoic acid in 50% (w/w) aqueous dioxan.[58]

TABLE XIV

Relative Rates and Activity Coefficients for Solvolysis in Electrolyte Solutions

Electrolyte	$\log_{10} k_1/k_1^o$ **		$\log_{10} \gamma_{RX}/\gamma_{RX}^o$ *		$-\log_{10} \gamma_{\ddagger}/\gamma_{\ddagger}^o$ †	
Concentration	0.05M	0.10M	0.05M	0.10M	0.05M	0.10M
$(CH_3)_4NF$	−0.053ø	−0.124ø	−0.059	−0.136	+0.006	+0.012ø
NaCl	+0.012	+0.016	−0.011	−0.027	+0.023	+0.043
$NaSO_3Ph$	+0.028	+0.051	−0.011	−0.025	+0.039	+0.076
$NaNO_3$	+0.037	+0.067	+0.006	+0.007	+0.031	+0.060
$NaBF_4$	+0.048	+0.081	+0.013	+0.013	+0.035	+0.068
NaBr	+0.057	+0.106	+0.011	+0.016	+0.046	+0.090
HNO_3	+0.062	+0.118	+0.022	+0.048	+0.040	+0.070
$NaClO_4$	+0.069	+0.123	+0.009	+0.012	+0.060	+0.111
$HClO_4$	+0.088	+0.152ø	+0.029	+0.042	+0.059ø	+0.110ø

** Error in $\log k_1/k_1^o \leqslant 0.004$

* Error in $\log_{10} \gamma_{RX}/\gamma_{RX}^o \leqslant 0.006$

† Error in $\log_{10} \gamma_{\ddagger}/\gamma_{\ddagger}^o \leqslant 0.004$

ø Interpolated from results at different salt concentrations.

With the exception of added tetramethylammonium fluoride, the electrolytes affect the stability of the transition state more than that of the initial state, and the resulting stabilisation of the transition state does not vary greatly with different electrolytes. This observation partly supports the original suggestion[1b] of an accelerating ionic-strength effect, which is independent of the nature of the electrolyte. It must be stressed, however, that sodium chloride, and particularly tetramethylammonium fluoride stabilise the transition state less than the other salts now considered.

It has previously been suggested[50e] that specific electrolyte effects on the rates of S_N1 reactions can be explained by the combination of the ionic-strength effect and a salt-induced medium effect, which depends on the nature of the added electrolyte. The latter effect was considered to operate by the electrolyte rendering the solvent effectively "wetter" or "drier" by preferential attraction of one of the solvent components. The magnitude of any such salt-induced medium effect depends, of course, on the sensitivity of the rate to changes in the solvent composition. The present work (see chapter II) showed that the stability of the initial state ($\log_{10} \gamma_{RX}/\gamma^{o}_{RX}$) was much more sensitive to solvent changes than the stability of the transition state ($-\log_{10} \gamma_{\ddagger}/\gamma^{o}_{\ddagger}$) and one might therefore conclude that $\log_{10} \gamma_{RX}/\gamma^{o}_{RX}$ will be more sensitive to the nature of the added electrolyte than $-\log_{10} \gamma_{\ddagger}/\gamma^{o}_{\ddagger}$, as observed in the present system. On this view, chloride and fluoride ions which would be expected to be more heavily solvated by water than nitrate and perchlorate ions should render the solvent effectively "drier" and hence $\log_{10}k_1/k^{o}_1$ should have a smaller value for the halide ions. This has now been observed.

Sodium perchlorate and perchloric acid can be regarded as reasonably good "wetting" agents in these solvents, since it seems very likely that the perchlorate ion is relatively well solvated by the organic component.[53] The fact that sodium perchlorate is extremely soluble in acetone tends to support this conclusion. However, these compounds stabilise both the initial and transition states considerably more than would have been expected from the behaviour of the other electrolytes. Anomolous results have previously been discussed[50e,90] in terms of specific attractive short-range interactions between the substrate and the electrolyte. It seems likely that the presence of the nitrophenyl group facilitates such interactions with perchlorate ions since sodium perchlorate has a much greater salting-in effect on 4-nitrobenzyl chloride in aqueous acetone than other electrolytes[17c] while the converse applies to solutions of naphthalene and 1-naphthoic acid in aqueous dioxan.[58] Qualitatively, however, the solvating properties of the perchlorates explain their effects on the rate, so that the short-range interactions now postulated apparently stabilise the initial and transition states to approximately the same extent.

Bromide ions increase the stability of the transition state a little more than might be expected for a "normal" electrolyte, but since this ion is a relatively powerful nucleophile the possibility of bimolecular attack on the substrate cannot be excluded (see page 86). Although diphenylmethyl halides are usually considered sterically unfavourable to the operation of mechanism S_N2,[24] reaction by this mechanism has been reported.[26]

The present results are compared in Table XX with those obtained from the S_N1 solvolysis of 4-nitrodiphenyl methyl chloride in 50% aqueous acetone;[50g] it has already been pointed out (see page 69) that the present data are

TABLE XX

Electrolyte Effects in S_N1 reactions.

Electrolyte (0.10M)	4-Nitrodiphenyl methyl chloride in 50% (v/v) aqueous acetone			4-phenyl:4'-nitrodiphenyl methyl chloride in 70% (v/v) aqueous acetone at 20.18°C		
	$\log_{10}\frac{k_1}{k_1^o}$ †	$\log_{10}\frac{\gamma_{RX}}{\gamma_{RX}^o}$ *	$-\log_{10}\frac{\gamma_\ddagger}{\gamma_\ddagger^o}$	$\log_{10}\frac{k_1}{k_1^o}$	$\log_{10}\frac{\gamma_{RX}}{\gamma_{RX}^o}$	$-\log_{10}\frac{\gamma_\ddagger}{\gamma_\ddagger^o}$
NaCl	+0.031	−0.020	+0.051	+0.016	−0.027	+0.043
$NaSO_3Ph$	+0.009	−0.031	+0.040	+0.051	−0.025	+0.076
$NaNO_3$	+0.032	−0.006	+0.038	+0.067	+0.007	+0.060
NaBr	+0.036	−0.019	+0.055	+0.106	+0.016	+0.090
HNO_3	+0.079	+0.027	+0.052	+0.118	+0.048	+0.070
$NaClO_4$	+0.036	−0.057	+0.093	+0.123	+0.012	+0.111
$HClO_4$	+0.088	−0.024	+0.112	+0.152	+0.042	+0.110

* Calculated from solubilities measured at 0°C.

† Rate coefficients measured at 39.75°C.

probably the more reliable. With the exception of the result for sodium perchlorate, the earlier results[50g] parallel those now observed, although the effects of salts on the rates of ionisation are smaller in the 50% (v/v) solvent. Qualitatively, this consistent with the reduction of the magnitude of the ionic-strength effect as the dielectric constant increases.[1b] As a first approximation, a large part of the acceleration of the first order rate of ionisation arises essentially from a non specific stabilisation of the transition state; (see page 19) these effects can be identified with the ionic strength effect, as originally postulated.[1b] It is also noteworthy that the earlier results show a very much greater acceleration by acids than their corresponding sodium salts.

III. 4. The Semi-Quantitative Theory of Electrolyte Effects.

If an attempt is made to put the simple solvation model, discussed in the previous section on a quanitative basis, some of the added electrolytes (*e.g.*, tetramethyl ammonium fluoride) require incredibly large solvation numbers to explain the observations. A more useful semi quantitative treatment has been proposed by Grunwald and his coworkers (see sections I. 10.3. and I. 12.). The present results can be used to test this approach which leads to equation I. 25. (see section I. 12.) *viz.*

$$\frac{\log_{10} k_1/k_1^o}{m_4} = A + BRT \frac{dG^o_{4m}}{dZ_1} \frac{d\ln k_1^o}{dZ_1}$$

Values of dG^o_{4m}/dZ_1 are only available for 50% (w/w) aqueous dioxan as the solvent but it seems likely that the values of this parameter will follow the same sequence for the reaction medium now employed. If this assumption is valid, equation I.25., requires a linear relation between $(\log_{10} k_1/k_1^o)/m_4$ and dG^o_{4m}/dZ_1 and figure III. 1. shows that this requirement is met by most of the electrolytes studied. It is noteworthy that sodium perchlorate and perchloric acid,which showed anomolous effects on the separate stabilities of the initial and transition states, behave in accordance with equation I.25., suggesting again that short-range interactions stabilise both these states to the same extent. (see page 93). The point for sodium bromide lies well off the best straight line, possibly because of incursion of reaction by mechanism S_N2. (see page 86).

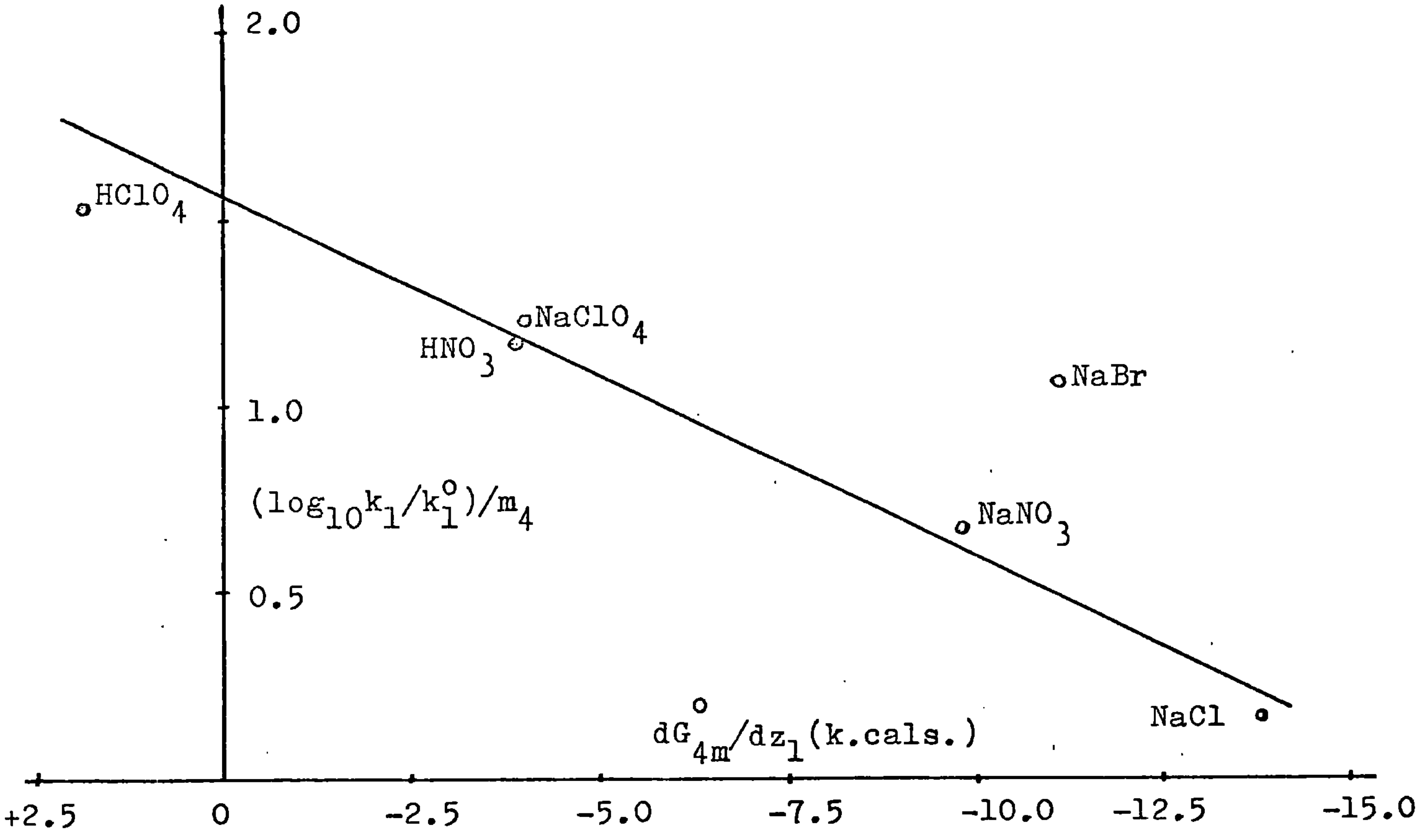
Figure III.1. strongly supports the assumption that the specific acceleration of S_N1 reactions by different electrolytes arises from the operation of the salt-induced medium effect,[50e] but no examination of all the present data is possible since values of dG^o_{4m}/dZ_1 for all the present electrolytes are not even available for 50% (w/w) aqueous dioxan.

A more complete test can be carried out by combining equations I.24. and I.25., whence

$$\frac{\log_{10} k_1/k_1^o}{m_4} = A' + \frac{1}{m_4}\left(\frac{B}{B_i}\,\frac{d\ln k_1^o/dZ_1}{d\ln S^o/dZ_1}\right)\left(-\log_{10} \gamma_{RX}/\gamma^o_{RX}\right) \quad\text{--3.7.}$$

where $A' = A_i + A\left(\frac{B}{B_i}\,\frac{d\ln k_1^o/dZ_1}{d\ln S^o/dZ_1}\right)$

FIG.III.1. The variation of$(\log_{10}k_1/k_1^o)/m_4$ with dG^o_{4m}/dz_1 for the addition of 0.1M electrolytes.



A plot of $(\log_{10} k_1/k_1^o)/m_4$ against $-\log_{10} \gamma_{RX}/\gamma^{o}_{RX}$ is shown in figure III.2., and it can be seen that most of the salts lie on the straight line required by equation 3.7. The anomolous behaviour of the two perchlorates and sodium bromide (see pages 93, 96) can again be recognised, but it is noteworthy that the point for sodium benzenesulphonate is also divergent, possibly because the anion can also undergo short-range attractive interactions with the substrate. Values of $d\ln k_1^o/dZ_1$ and $d\ln S^o/dZ_1$ can be obtained from the results in figures III.3. and III.4. respectively and hence the straight line in figure III.2. shows that the ratio B/B_i has the value 1.05, compared with the value of 1.04 obtained for the solvolysis of 4-nitrodiphenylmethyl chloride in 50% (v/v) aqueous acetone.[50g] This result is in excellent agreement with the suggestion[50e,5] that the value of B/B_i should be close to unity and therefore supports the Grunwald approach.

It would therefore appear that the semi-quantitative treatment of Grunwald and his coworkers accommodates most of the experimental data for the effects of simple salts on S_N1 reactions, whilst purely electrostatic theories cannot predict the specific electrolyte effects which are observed. Thus it may be assumed with reasonable certainty that added electrolytes change the rate of S_N1 solvolytic reactions by a combination of a purely electrostatic effect and a salt-induced medium effect. However, the Grunwald treatment is somewhat empirical and does not really give a quantitative insight into the true nature of the salt-induced medium effect. Indeed, it has already been pointed out (see page 95) that the present results do not permit the interpretation of a salt-induced medium effect in terms of a simple solvation model since this requires the assumption

FIG.III.2. The variation of $(\log_{10}k_1/k_1^o)/m_4$ with $\log_{10}\gamma_{RX}/\gamma_{RX}^o$ for 0.1M electrolyte additions

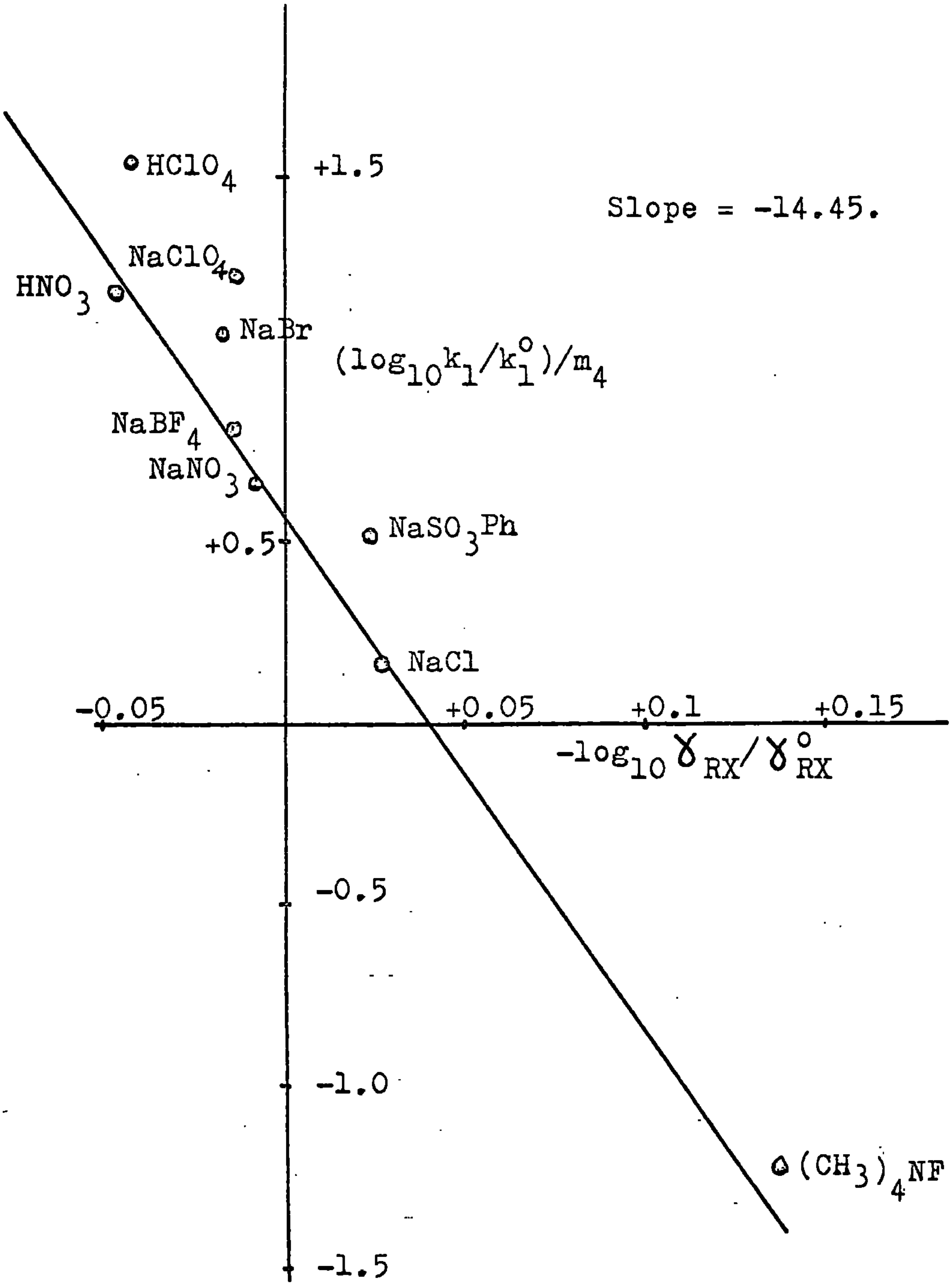


FIG.III.3. The variation of $\ln k_1^o$ with the mole fraction of water in the solvent (z_1).

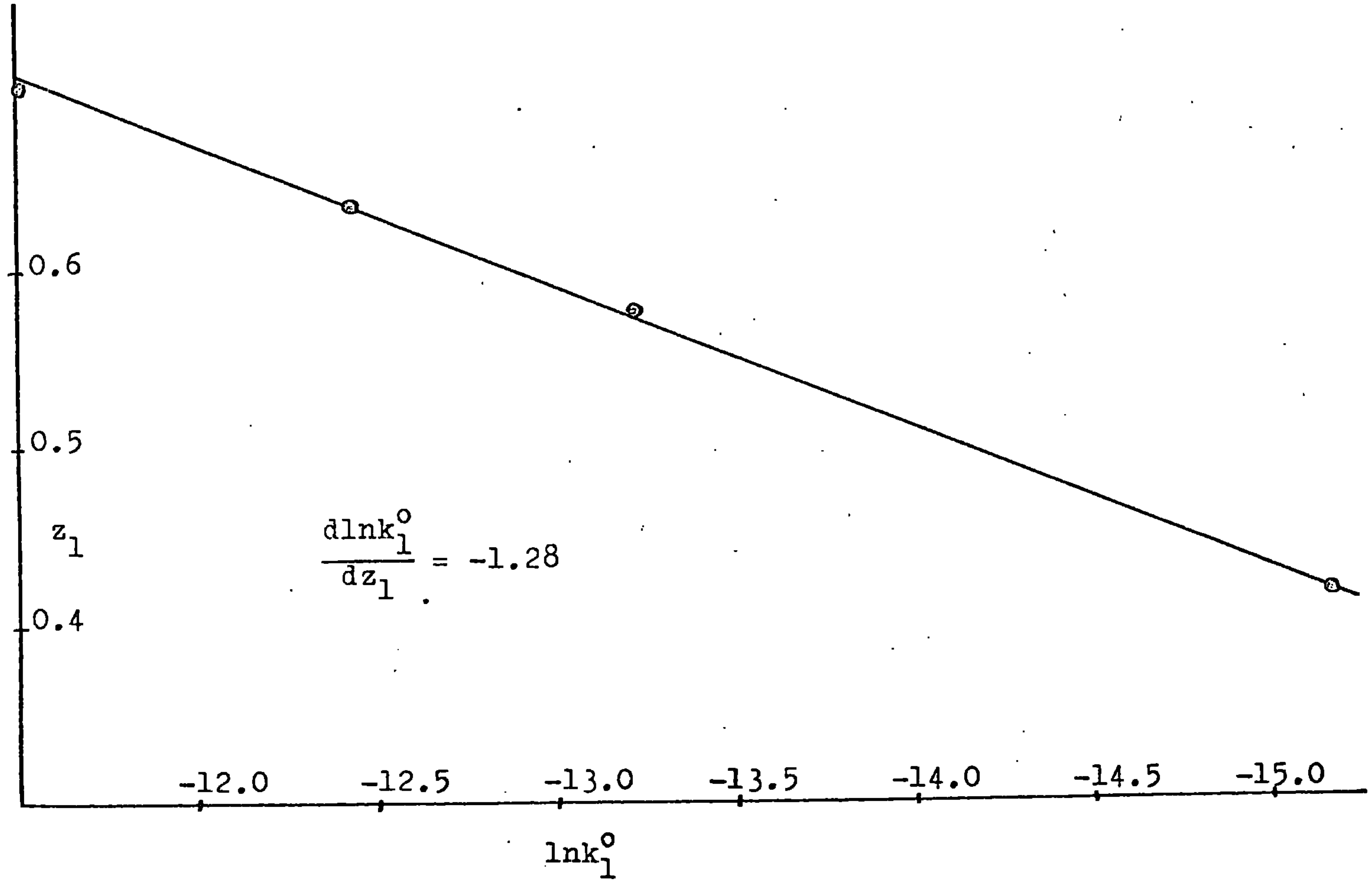
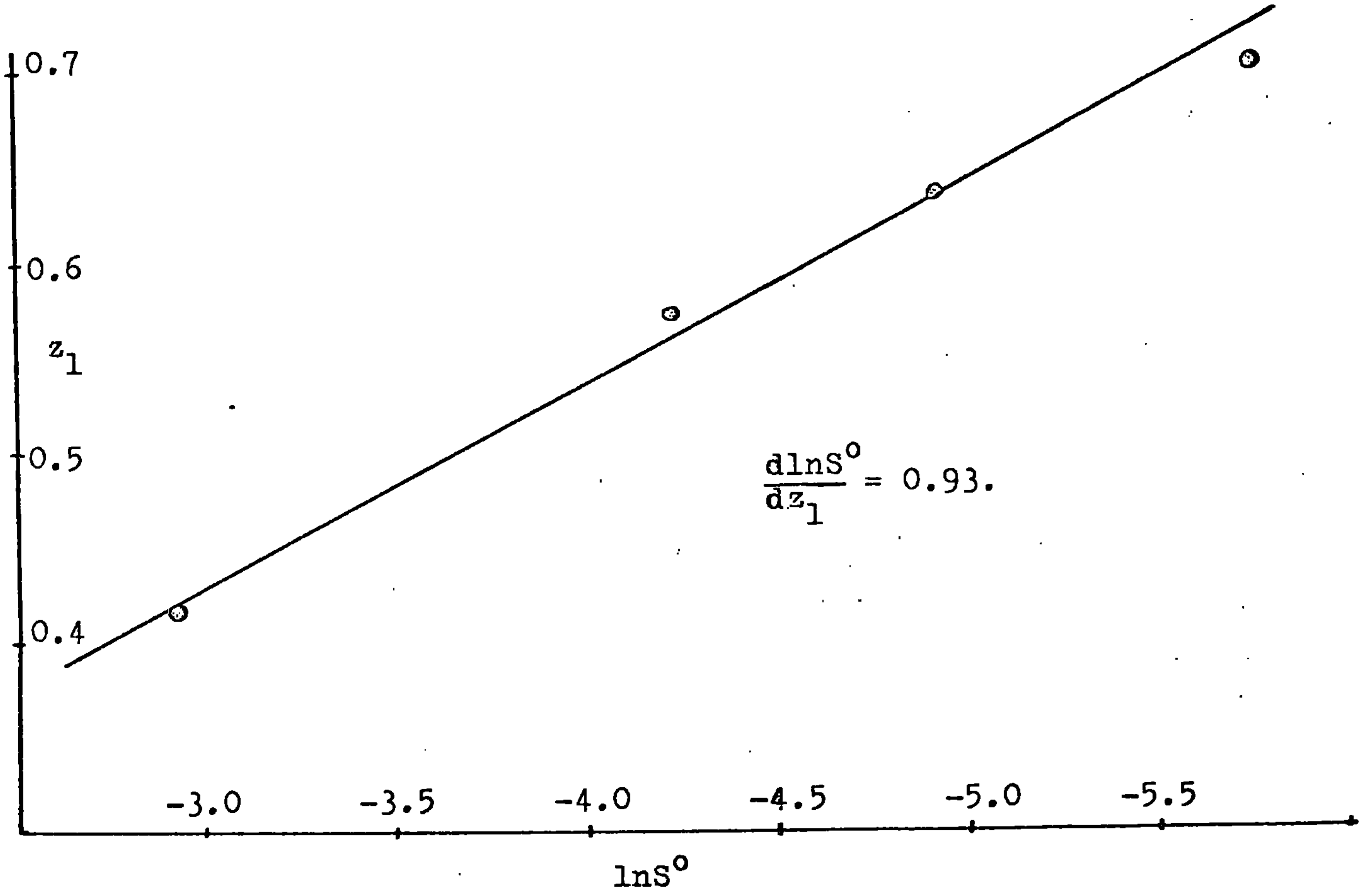


FIG.III.4. The variation of $\ln S^{o}$ with the mole fraction of water in the solvent. (z_1)



of improbably large solvation numbers to give agreement with the experimental observations. Thus it would appear that other alterations in the nature of the solvent, *e.g.*, structural changes, must also make a contribution to the salt-induced medium effect. Indeed, the effect of electrolytes dissolved in water on the properties of the solvent has often been discussed in terms of structural hypotheses.[82b,c,d.]

Naim and his coworkers[82f,g,83e] have gone one stage further and suggested that two types of molecule exist in equilibrium in liquid water, *i.e.*, monomeric water molecules not linked by hydrogen bonds to other molecules and clusters of water molecules linked by hydrogen bonds. Electrolytes were considered to disturb the position of this equilibrium and it was found that this model could be used satisfactorily to explain the anomalous enthalpy and entropy effects in water which are not satisfactorily explained by the Frank model.[82,a,b,c,d.] They found that the effects of added non-electrolytes,[83e] and electrolytes[82g] on the solubility of argon in aqueous solution could be accounted for in terms of changes in the "degree of crystallinity" of the hydrogen-bonded portion of the solvent. It would, therefore, appear that structural changes can be important in aqueous solution and such changes would probably be even more complicated in aqueous organic solvents A different, but equally plausible explanation has been proposed by Feakins and his coworkers[83a,b,c] based on the results of investigations of the free energies of transfer of simple electrolytes from water to aqueous organic solvents. They found that they could satisfactorily account for their experimental results by considering that added electrolytes modified the acidic or basic properties of the solvent molecules.

Hence, although the theory of salt-induced medium effects as proposed by Grunwald and his coworkers goes a long way towards explaining the observed specificity of electrolyte effects, the theory appears to be too simple to accommodate all the observations and it is very likely that structural changes in the solvent should also be taken into account. However, before the semi-quantitative approach of Grunwald[50e,58] can be improved, much more fundamental information is required about the exact nature of electrolytic solutions.

Although no complete explanation can yet be advanced for the effects of all electrolytes on the rates of S_N1 reactions in mixed solvents, the assumption of the operation of an ionic-strength effect and a salt-induced medium effect accounts for many of the present results. The fact that the stability of the transition state is only slightly altered by solvent changes (see Chapter II) and is relatively insensitive to the nature of added electrolytes argues strongly in favour of the view that the specific electrolyte effects, now observed, arise mainly from the operation of a salt-induced medium effect in the initial state of reaction.

CHAPTER IV. EXPERIMENTAL

IV. I. The Purification and Preparation of Solvents.

Solvent Acetone.

A.R. grade acetone was refluxed over sodium hydroxide and potassium permanganate for two hours and then distilled, the distillate being fractionated from hydroquinone. Generous head and tail fractions were discarded.

Titration Acetone.

Commercial acetone was refluxed for two hours over sodium hydroxide and potassium permanganate and then distilled.

Aqueous Acetone Mixtures.

Solvents were made up by volume. X mls. of solvent acetone were added to (100 - X) mls. of demineralised water in order to prepare an X % solvent.

The Measurement of Solvent Densities.

The densities of the whole range of aqueous acetone mixtures employed in the present investigation were measured at 20.18°C and 9.46°C using the standard pycnometer technique for volatile liquids.[91] The experimental values are listed in appendix. I.

IV. 2. The Purification of Electrolytes and the Preparation of Electrolyte Solutions.

With the exception of tetramethylammonium fluoride (see below), all the electrolytes employed were commercially available and A.R. grade materials were used wherever possible. The electrolytes were usually dried in air or *in vacuo* at elevated temperatures. Sodium perchlorate was recrystallised from aqueous dioxan and dried *in vacuo* at 100°C to constant weight. Sodium benzenesulphonate was recrystallised from ethanol and dried similarly.

Tetramethylammonium fluoride was prepared by the direct neutralisation of tetramethylammonium hydroxide (2N) with hydrofluoric acid (2N). Mixed methyl red/methylene blue was used as an internal indicator and was later removed with Norrit charcoal. During the preparation precautions were taken to avoid the entrance of carbon dioxide into the apparatus. The bulk of the water was removed by static distillation, while the last traces were pumped off at 40 - 50°C and 0.007 mms. pressure. The purity of the white, extremely hygroscopic solid obtained was determined by ion exchange and subsequent titration of the liberated hydrofluoric acid with standard sodium hydroxide and was always greater than 95% of the theoretical value, but never 100%. It was found that this discrepancy arose from the presence of some tetramethylammonium chloride in the original tetramethylammonium hydroxide solution. All the results from experiments with added tetramethylammonium fluoride were therefore corrected for the presence of chloride ion by assuming that the tetramethylammonium cation had the same effect on the rate as the sodium ion. (see ref. 17b.).

When the added electrolyte was a solid, solutions were made up by weight. Solutions of acids were prepared by adding a calculated amount of the acid of known strength to a known volume of 70% (v/v) aqueous acetone. A volume of pure acetone was then added so that the final solution corresponded to the required concentration of the anhydrous acid in 70% (v/v) aqueous acetone. Values of the density and strength of the samples of A.R. perchloric and nitric acids used are listed in appendix H.

IV. 3. The Potentiometric Determination of Chloride Ion.

The chloride ion content of a given solution was determined by the following technique. (see ref. 50f.). In the titration, 300 - 400 mls. of titration acetone were used as the solvent, a silver wire was employed as the indicator electrode, while a glass electrode served as the reference. The end-point was indicated by a large change in the E.M.F. produced for small additions (0.1 ml.)of *ca.* 0.005M silver nitrate. This method has always been found to give good results in dilute chloride solutions.

IV. 4. Preparation of the Organic Halides.

IV. 4.1. 4-nitrobenzyl chloride.

Commercial grade material was recrystallised from ethanol and dried. The hydrolysable chloride content of a sample was 99.7% of the theoretical amount.

IV. 4.2. 4-nitrodiphenylmethyl chloride.

The following reaction scheme was used.

$$\begin{tikzcd}
4\text{-}NO_2.C_6H_4.CH_2Cl \arrow[r, "I"] & 4\text{-}NO_2.C_6H_4.CH_2.C_6H_5. \arrow[d, "II"] \\
4\text{-}NO_2.C_6H_4.CHOH.C_6H_5 \arrow[d, "IV"] & 4\text{-}NO_2.C_6H_4.CHBr.C_6H_5 \arrow[l, "III"'] \\
4\text{-}NO_2.C_6H_4.CHCl.C_6H_5. &
\end{tikzcd}$$

Stage I

4-nitrodiphenylmethane was prepared by the Friedel Crafts reaction between 4-nitrobenzyl chloride and benzene in the presence of anhydrous aluminium chloride.[92]
The product obtained from this reaction, after distillation under reduced pressure, was a pale yellow solid. m.pt. 30°C (uncorrected); literature value 31°C.[92]

Stage II

The hydrocarbon, obtained from Stage I, was brominated with N-bromosuccinimide in carbon tetrachloride,[93] yielding a yellow oil.

Stage III

4-nitrodiphenylmethyl alcohol was obtained by refluxing the bromide with 50% (v/v) aqueous acetone for 2 - 3 hours. The solution was neutralised, evapourated, extracted with ether, and the ethereal extract washed and dried. After removal of the ether, the pure alcohol was obtained by recrystallisation from 40 - 60° petroleum ether as a white crystalline solid. m.pt. 73°C (uncorrected); literature value 73 - 74°C.[50f]

Stage IV

The chloride was obtained from the alcohol by a standard chlorination technique, which is adequately described elsewhere.[50f] After repeated recrystallisation of the product from 40 - 60° petroleum ether, a white crystalline solid was obtained. m.pt. 43°C (uncorrected); literature value 43.5 - 44.5°C.[50f] The hydrolysable chloride content was 99.7% of the theoretical amount.

IV. 4.3. 4-phenyl:4'-nitrodiphenylmethyl chloride.

This compound was prepared via. the following reactions;

$$\begin{tikzcd}
\mathrm{4\text{-}NO_2.C_6H_4COCl} \arrow[r, "\mathrm{I}"] & \mathrm{4\text{-}NO_2.C_6H_4CO.C_6H_4.C_6H_5\text{-}4'} \arrow[d, "\mathrm{II}"] \\
\mathrm{4\text{-}NO_2C_6H_4CHClC_6H_4C_6H_5\text{-}4'} & \mathrm{4\text{-}NO_2.C_6H_4CHOHC_6H_4C_6H_5\text{-}4'} \arrow[l, "\mathrm{III}"']
\end{tikzcd}$$

Stage I

4-phenyl:4'-nitrobenzophenone was prepared by the Friedel-Crafts reaction between 4-Nitrobenzoyl chloride and diphenyl in carbon disulphide.[17c] After repeated recrystallisation of the product from 50:50 chloroform: benzene, a pale-yellow solid was obtained. m.pt. 170°C (uncorrected); literature value 170°C.[17c]

Stage II

4-phenyl:4'nitrodiphenylmethyl alcohol was obtained from the ketone by reduction with aluminium iso-propoxide in anhydrous iso-propanol.[94] This reaction yielded, after recrystallisation of the product from 100 - 120° petroleum ether, a white crystalline solid. m.pt. 140°C (uncorrected); literature value 140°C.[17c]

Stage III

The chlorination was carried out in a manner analogous to that described previously (see page 108); the product being obtained as a white micro-crystalline solid by recrystallisation of the crude material from 80 - 100° petroleum ether. m.pt. 115°C (uncorrected); literature value 115°C.[17c] The hydrolysable chloride contents of different samples of this compound, prepared by the above method, were never less than 99.8% of the theoretical amount.

IV. 5. Thermostats.

The thermostats used were of conventional design. and the temperature was controlled to $< \pm 0.01^{\circ}C$ by contact thermometers and relays. Electric light bulbs were used as heaters. In addition, for measurements at room temperature, a water cooler had to be incorporated, while for temperatures below this a T.K.I. refrigeration unit had to be used to maintain the temperature equilibrium.

The temperatures quoted throughout this thesis were measured with thermometers, which had previously been standardised by the National Physical Laboratory.

IV. 6. Methods of Rate Measurement.[†]

IV. 6.I. The Measurement of First-order Rates.

The reactions of the compounds studied always went to completion and were followed by noting the concentration of acid or chloride ion present in the reaction mixture at various times. The techniques used for carrying out such experiments are fully described elsewhere. (see ref. 50f.).

First-order integrated rate coefficients were calculated from equation 4.I.

$$k_1 = \frac{2.303}{t} \log_{10} \frac{T_{\infty} - T_0}{T_{\infty} - T_t} \qquad \text{-----} \quad 4.1$$

where t is the time in seconds, and T_{∞}, T_t and T_0 are the titres at times of t = infinity, t = t and t = 0 respectively.

[†] Although the methods described in this section yield values of rate coefficients for the hydrolysis (k_h), it has previously been pointed out that in the present work, rates of hydrolysis can be identified with rates of ionisation

(k_1) within the limits of experimental error (see page 80). For convenience, the symbol k_1 will therefore be used to refer to experimental rate coefficients in the following discussion, even though the symbol k_h should strictly be used for this purpose.

The values of k_1 quoted in this thesis are mean values of usually about ten separate rate determinations and all experiments were carried out in duplicate.

The standard error (σ) in the mean rate coefficient (k_m) was obtained from equation 4.2.

$$\sigma(k_1) = \frac{\left[\sum(k_1-k_m)^2\right]^{\frac{1}{2}}}{n} \qquad \text{-----} \qquad 4.2$$

where n was the number of separate determinations of k_1. If any individual values of k_1 differed from the mean by more than $2\frac{1}{2}\,\sigma$(each), where $\sigma(\text{each}) = n^{\frac{1}{2}}\,\sigma(k_1)$, these values were rejected and a new mean rate coefficient and $\sigma(k_1)$ were determined. This process was repeated until all the individual values of k_1 were within $2\frac{1}{2}\,\sigma$(each) of the mean value (k_m). The standard error on the overall mean $(k)_m$ (i.e., the mean of the duplicate experiments) was calculated using equation 4.2. by treating the two experiments as one.

IV. 6.2. The Measurement of Zeroth-order Rates.

Rates of hydrolysis of permanently saturated solutions of organic halides (leading to zeroth-order rate coefficients) were determined by noting the development of acidity or chloride ions in solutions containing a two or three-fold excess of the organic chloride. The mixtures were contained in doubly-sealed vessels attached to a vertical wheel which was rotated at 30 - 40 r.p.m. The double-seal ensured that no water entered the reaction mixture either during its immersion in the thermostat or when samples were taken. The method employed for following the reactions had the advantage that solid particles of the organic halide did not affect the determinations. Check experiments (see page 56) showed that the time required for the attainment of solubility equilibrium and "zero time" for the kinetic experiments was always <u>ca</u>. twenty minutes. No readings were therefore taken until this period of time had elapsed. Samples were then taken at various time intervals until the solution was approximately 0.01M in hydrochloric acid or chloride ion.

Zeroth-order rate coefficients (k_o) were calculated from equation 4.3.

$$k_o = \frac{x\,(T_t - T_o)}{v\,(t - t_o)} \qquad \text{-----} \qquad 4.3.$$

where T_t and T_o are the titres in mls. at times of t and t_o (zero time) respectively, v is the volume of the sample taken, and x the normality of the standard alkali or silver nitrate employed in the titration.

The values of k_o quoted in this thesis are the mean values of at least ten separate rate determinations and the standard errors were obtained by a procedure analogous to that used for the first-order rate coefficients (see page 111).

IV. 7. Measurement of the Solubility.

Solubilities were measured using the apparatus described in the previous section. Samples of the saturated solution, free from suspended solid, were removed from the reaction vessels and stored at the same temperature. 5 ml. aliquots of this solution were hydrolysed completely at 100°C in sealed ampoules, also containing 1 ml. of water, and the total amount of product (T_∞) determined by titration with standard alkali or silver nitrate.
The extent of reaction (T_t) at the time of withdrawal of the sample (t) was also determined (see section IV. 6.2.), so that the solubility (S) was given by,

$$S = \frac{x}{v}(T_\infty - T_t) \qquad \text{------} \qquad 4.4.$$

The standard error $\sigma(S)$ quoted for the mean solubility (S_m) was obtained from,

$$\sigma(S) = \frac{\left[\sum(S - S_m)^2\right]^{\frac{1}{2}}}{n} \qquad \text{------} \qquad 4.5.$$

where S_m is the mean of n individual solubility determinations.

IV. 8. The Ratios k_1/k_1^o, k_o/k_o^o and S^o/S.

In experiments with added electrolytes, or experiments involving changes in the solvent composition, an experiment in the reference system (superscript, o; see sections I.8., and I.9.), was always carried out at the same time to avoid the appearance of errors in the ratios k_1/k_1^o, k_o/k_o^o and

S^o/S due to solvent deterioration on standing.

The standard errors in these ratios were calculated from equation 4.6.

$$\sigma\left(\frac{X_1}{X_2}\right) = \frac{X_1}{X_2}\left[\left(\frac{\sigma X_1}{X_1}\right)^2 + \left(\frac{\sigma X_2}{X_2}\right)^2\right]^{\frac{1}{2}} \quad \text{---- 4.6.}$$

where X refers to the mean value of the measured quantity (k_1, k_o or S) and the subscripts 1 and 2 refer to the experimental conditions and the reference system, respectively, σX_1 and σX_2 are the corresponding standard errors in X_1 and X_2.

When determining the standard error in the ratio S^o/S, the symbols, obviously, have the reverse meaning <u>i.e.</u>, subscripts 1 and 2 then refer to the reference system and the experimental conditions, respectively.

The overall mean values of k_1/k_1^o and k_o/k_o^o quoted were calculated from the mean values of these ratios, and their standard errors were obtained from equation 4.7.

$$\sigma\left(\frac{X_1}{X_2}\right)_m = \frac{1}{n}\left[\sum\left\{\frac{X_1}{X_2} - \left(\frac{X_1}{X_2}\right)_m\right\}^2 + \left\{\sigma\left(\frac{X_1}{X_2}\right)\right\}^2\right]^{\frac{1}{2}} \quad \text{---- 4.7.}$$

where $\sigma\left(\frac{X_1}{X_2}\right)_m$ is the standard error in the overall mean $\left(\frac{X_1}{X_2}\right)_m$ of n individual determinations of $\frac{X_1}{X_2}$ having standard errors of $\sigma\left(\frac{X_1}{X_2}\right)$

IV. 9. Relative Activity Coefficients.

It has already been pointed out that the ratios $\gamma_{RX}/\gamma^{o}_{RX}$ and $\gamma_{\ddagger}/\gamma_{\ddagger}^{o}$ can be obtained from the experimental observations via. equations I.6., I.10. and I.15. (see sections I.8. and I.9.).

When values of $\gamma_{RX}/\gamma^{o}_{RX}$ were calculated from solubility measurements via. equation I.10., the standard error, $\sigma(\gamma_{RX}/\gamma^{o}_{RX})$, was given by,

$$\sigma(\gamma_{RX}/\gamma^{o}_{RX}) = \frac{S^{o}}{S}\left[\left(\frac{\sigma_{S^{o}}}{S^{o}}\right)^{2} + \left(\frac{\sigma_{S}}{S}\right)^{2}\right]^{\frac{1}{2}} \qquad \text{---} 4.8.$$

where σ_{S^o} and σ_{S} are the standard errors in S^{o} and S, respectively.

However, when this ratio was calculated from first-and zeroth-order rate measurements via. equations I.6. and I.15., the standard error was obtained from equation 4.6. by putting X_1 and X_2 equal to $(k_1/k_1^{o})_m$ and $(k_o/k_o^{o})_m$, respectively. It should be stressed that values of the relative activity coefficients were always calculated from overall mean values of the rate ratios viz. $(k_1/k_1^{o})_m$ and $(k_o/k_o^{o})_m$.

Equation 4.9. allows the calculation of the standard error in the ratio, $\gamma_{\ddagger}/\gamma_{\ddagger}^{o}$, which was always obtained from the ratio $(k_o/k_o^{o})_m$ via. equation I.15.

$$\sigma(\gamma_{\ddagger}/\gamma_{\ddagger}^{o}) = \frac{\sigma(k_o/k_o^{o})_m}{(k_o/k_o^{o})_m^{2}} \qquad \text{-----} \qquad 4.9.$$

where $\sigma(k_o/k_o^{o})_m$ is the standard error in the overall mean $(k_o/k_o^{o})_m$.

Equations I.6., I.10. and I.15., can be expected to be valid only if the solutions behave ideally at all concentrations up to saturation. As the compounds used in the present investigations were sparingly soluble in all the solvents used, it seems reasonably safe to make this assumption. Nevertheless, the consistency of the above equations can be examined by comparing experimental values of k_1 ($k_1^{obs.}$) with those obtained from experimental determinations of solubility and zeroth-order rate coefficients (k_1^{calc}) <u>via</u>. equation 4.10.

$$k_1 = k_o/S \qquad \text{-----} \qquad 4.10.$$

Table XXI shows the results of a comparison of $k_1^{calc.}$ and $k_1^{obs.}$ for the S_N1 solvolysis of 4-phenyl:4'-nitro diphenylmethyl chloride in aqueous acetone at 20.18°C. No values are included for work in 50% (v/v) aqueous acetone since no direct determination of k_1 was possible in this solvent (see page 127).

In view of the accuracy with which the solubilities could be measured, the agreement between $k_1^{obs.}$ and $k_1^{calc.}$ is reasonable. Incomplete removal of the organic halide from the supernatent liquid was considered to be responsible for the inaccuracies in the solubility determinations and this was also the reason why most of the work done with this compound involved the measurement of first-and zeroth-order rate coefficients.

The agreement between $k_1^{obs.}$ and $k_1^{calc.}$ in 85% (v/v) aqueous acetone is rather poor. This is probably because the solubility quoted was the mean of only three individual determinations (see appendix B) and $k_1^{obs.}$ was interpolated from results at higher temperatures; both quantities are therefore subject to rather large errors.

TABLE XXI

Calculated and observed first-order rate coefficients for the hydrolysis of 4-phenyl: 4'-nitrodiphenylmethyl chloride in aqueous acetone at 20.18°C.

System	$(10^8)\ k_o$	$(10^4)\ S$	$(10^7)\ k_1^{obs.}$	$(10^7)\ k_1^{calc.}$
70% (v/v) Aqueous Acetone (No added salt)	2.929 ± 0.004	75.51 ± 0.24	40.00 ± 0.21	38.79 ± 0.14
85% (v/v) Aqueous Acetone (No added salt)	1.424 ± 0.003	466.2 ± 3.6	2.620 ± 0.05†	3.054 ± 0.025
70% (v/v) Aqueous Acetone (0.05M $NaSO_3Ph$ added)	3.266 ± 0.005	76.97 ± 0.09	42.68 ± 0.10*	42.42 ± 0.08
70% (v/v) Aqueous Acetone (0.05M $NaNO_3$ added)	3.230 ± 0.005	75.66 ± 0.19	43.51 ± 0.10*	42.70 ± 0.13
70% (v/v) Aqueous Acetone (0.05M $NaClO_4$ added)	3.455 ± 0.005	77.43 ± 0.23	46.85 ± 0.10*	45.92 ± 0.15

* Based on experimental values of k_1/k_1^o

† Interpolated from results at higher temperatures

However, the results in Table XXI show that the equations used in the present calculations can be assumed valid under the experimental conditions for the S_N1 solvolysis of 4-phenyl:4'-nitrodiphenylmethyl chloride in aqueous acetone. Since 4-nitrodiphenylmethyl and 4-nitrobenzyl chlorides are about as soluble as 4-phenyl:4'-nitrodiphenylmethyl chloride and react very much more slowly in the solvents now employed, equations I.6., I.10. and I.15., are also likely to be equally valid when applied to these systems.

IV. 10. The Effect of the Chloride Ion Produced during the Hydrolysis on the First-and Zeroth-Order Rate Coefficients and on the Solubility.

Although the effects of added hydrochloric acid were not studied in the present systems, the effects, which would have been produced by the addition of this electrolyte, can be readily obtained from the experimental observations for the effects of sodium chloride, sodium nitrate and nitric acid. (see Tables XV and XVIII).

Since the final concentration of hydrochloric acid produced in the first-order reactions was usually ca. 0.005M, the maximum accelerating effect from this cause is of the order of 0.1% for the solvolysis of 4-phenyl:4'-nitro diphenylmethyl chloride in 70% (v/v) aqueous acetone at 20.18°C. In view of the accuracy of the results, this effect can be neglected.

Similarly, it can be seen that the maximum accelerating effect of the hydrochloric acid produced during the zeroth order solvolysis of 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone at 20.18°C is about 0.2%. Thus it again seems reasonable to assume that the effect of the hydrochloric acid produced during reaction can be neglected. Similar arguments can be shown to apply to effects on the other substrates studied.

The above considerations apply to the electrolyte effect of the hydrochloric acid, but the production of chloride ion will also tend to retard the reaction by the operation of the mass-law effect (see page 18). However, as the mass-law constant for 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone at 20°C is 1.8 litres. moles.$^{-1}$ (see ref. 89), the resulting retardation will be less than 1% in the present reactions. In any case, cancellation of effects due to mass-law retardation will occur in the ratios k_1/k_1^o and k_o/k_o^o.

The effect of the hydrochloric acid produced on the solubility of the substrate can also be expected to be negligible in the present systems, since the solubility is related to the first-and zeroth-order rate coefficients by equation 4.10.

IV. 11. Activation Parameters from First-Order and Zeroth Order Rate Measurements.

The Energy of Activation

The activation energy, E, was calculated from values of the rate coefficients (k) at adjacent temperatures and refers to the mean temperature, $(T_a + T_b)/2$:

$$E = \frac{2.303RT_aT_b}{T_b - T_a} \log_{10} \frac{k_a}{k_b} \qquad \text{------} \qquad 4.11.$$

where k_a and k_b are the values of k at the absolute temperatures T_a and T_b.

The standard error in E was obtained from equation 4.12.

$$\sigma(E) = \frac{RT_aT_b}{T_b - T_a}\left[\left(\frac{\sigma a}{k_a}\right)^2 + \left(\frac{\sigma b}{k_b}\right)^2\right]^{\frac{1}{2}} \qquad \text{-----} \quad 4.12.$$

where σ_a and σ_b are the standard errors in k_a and k_b respectively.

The Enthalpy of Activation

The enthalpy of activation was calculated from experimental values of the energy of activation by,

$$\Delta H^{\ddagger} = E + RT \qquad \text{-----} \quad 4.13.$$

The Free Energy of Activation

The free energy of activation, $\Delta G^{\ddagger}$, was obtained from $\Delta S^{\ddagger}$ and E *via*.,

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \qquad \text{-----} \quad 4.14.$$

When $\Delta G^{\ddagger}$ is calculated from equation 4.14., its standard error, $\sigma(\Delta G^{\ddagger})$, is given by,

$$\sigma(\Delta G^{\ddagger}) = \left[\left\{\sigma(E)^{2}\right\} + \left\{T\sigma(\Delta S^{\ddagger})\right\}^{2}\right]^{\frac{1}{2}} \text{--}4.15.$$

where $\sigma(E)$ and $\sigma(\Delta S^{\ddagger})$ are the standard errors in E and $\Delta S^{\ddagger}$, respectively.

The Entropy of Activation

The entropy of activation ($\Delta S^{\ddagger}$) at the temperature $(T_a + T_b)/2$ was calculated from equation 4.16.,

$$\frac{\Delta S^{\ddagger}}{2.303R} = \log_{10}k_a - 10.7531 - \log_{10}\left(\frac{T_a + T_b}{2}\right) - \frac{E}{2.303RT_a} \qquad \text{------} \quad 4.16.$$

where k_a refers to the temperature T_a, and E to $(T_a + T_b)/2$.

The standard error in $\Delta S^{\ddagger}$, $\sigma(\Delta S^{\ddagger})$, was obtained from the approximation,

$$\sigma(\Delta S^{\ddagger}) \cong \frac{\sigma(E)}{(T_a + T_b)/2}$$

The Heat Capacity of Activation

The heat capacity of activation, $\Delta C^{\ddagger}$, is given by equation 4.17.,

$$\Delta C^{\ddagger} = dE/dT - R \qquad \text{------} \quad 4.17.$$

For compounds studied at three temperatures, dE/dT was obtained from,

$$E_T = E_o + (T - T_o)\ dE/dT \qquad \text{------} \quad 4.18.$$

This procedure assumes dE/dT to be independent of temperature, but this has been found to be true within the limits of experimental error.[86]

The error in dE/dT was obtained from,

$$\sigma\left(\frac{dE}{dT}\right) = \frac{\left[(\sigma E_T)^2 + (\sigma E_{To})^2\right]^{\frac{1}{2}}}{(T - T_o)} \quad \text{-----} \quad 4.19.$$

As the required values of the zeroth-order rate coefficients were measured at three temperatures, equation 4.18., could be used to calculate dE/dT for these reactions. However, first-order rate coefficients were never determined at more than two experimental temperatures and no direct measurement of dE/dT was therefore possible for these reactions. Nevertheless, a knowledge of dE/dT is essential in order to calculate values of the activation parameters at non-experimental temperatures <u>via</u>. equations 4.20., 4.21. and 4.22.

$$E_T = E_m + (\Delta C^{\ddagger} + R)(T - T_m) \quad \text{-----} \quad 4.20.$$

$$\Delta H_T^{\ddagger} = \Delta H_m^{\ddagger} + (\Delta C^{\ddagger} + R)(T - T_m) \quad \text{-----} \quad 4.21.$$

$$\Delta S_T^{\ddagger} = \Delta S_m^{\ddagger} (2.303\ \Delta C^{\ddagger})(\log_{10} T/T_m) \quad \text{-----} \quad 4.22.$$

where T refers to the non-experimental temperature and T_m is the mean of the experimental temperatures <u>i.e</u>. $(T_a+T_b)/2$.

It has, however, been pointed out[35] that, for compounds which react by mechanism S_N1, the ratio $\Delta C^{\ddagger} / \Delta S^{\ddagger}$ is approximately constant for a given solvent and temperature and appears to be independent of the nature of the substrate. Since the variation of $\Delta C^{\ddagger} / \Delta S^{\ddagger}$ with temperature can be represented by equation 4.23., a knowledge of $\Delta S^{\ddagger}$ at any temperature enables $\Delta C^{\ddagger}$ to be calculated; the variation of $\Delta S^{\ddagger}$ with temperature being given by equation 4.22.

$$\frac{\Delta S_T^{\ddagger}}{\Delta C^{\ddagger}} = \frac{\Delta S_{T_o}^{\ddagger}}{\Delta C^{\ddagger}} + 2.303 \log_{10} \frac{T}{T_o} \qquad \text{-----} \; 4.23.$$

where T again refers to the non-experimental temperature and T_o is any temperature at which an experimental value of $\Delta C^{\ddagger} / \Delta S^{\ddagger}$ is available.

Values of $\Delta C^{\ddagger}$ were obtained in this manner for the S_N1 solvolysis of 4-nitrodiphenylmethyl chloride in 50% (v/v) aqueous acetone and 4-phenyl:4'-nitrodiphenylmethyl chloride in 85% (v/v) aqueous acetone.

For the S_N2 solvolysis of 4-nitrobenzyl chloride, where the rates were only measured at two temperatures in 40, 50 and 60% (v/v) aqueous acetone, no values of $\Delta C^{\ddagger}$ could be calculated. A value of $\Delta C^{\ddagger}$ for this compound was however available[17b] in 50% (v/v) aqueous acetone, and as the present value for E agreed well with Shillaker's[17b] value, (see Table XXII), it was decided to accept his value of $\Delta C^{\ddagger}$ for this solvent. The best available approximation for $\Delta C^{\ddagger}$ in the 40% (v/v) and 60% (v/v) solvents seemed to be to assume that $\Delta C^{\ddagger}$ had the same value in all three solvents. The error caused by such an assumption can be shown to be small.

Activation parameters obtained from the zeroth-order rates of solvolysis of 4-phenyl:4'-nitrodiphenylmethyl chloride in aqueous acetone have already been listed (see pages 76 and 77). Values obtained by the methods discussed here, or from other sources, are listed in Tables XXII, XXIII and XXIV for all the first-order solvolyses, with the exception of those for the hydrolysis

TABLE XXII

Activation parameters in the S_N2 solvolysis of 4-nitrobenzyl chloride in aqueous acetone.

Solvent (v/v %)	$10^6 k_1$ (secs.$^{-1}$)	Temp. ($^\circ$K)	Mean Temp. ($^\circ$K)	E (k cals)	$-\Delta S^{\ddagger}$ (cals)
40 (A)	4.475 ± 0.0151 37.06 ± 0.0996	344.58 370.82	357.70	20.459 ± 0.042	26.00 ± 0.12
50 (C)	2.402 ± 0.0087 20.48 ± 0.0393	344.58 370.82	357.70	20.740 ± 0.039[†]	26.42 ± 0.11
60 (A)	1.235 ± 0.0039 10.24 ± 0.0209	344.58 370.82	357.70	20.470 ± 0.036	28.52 ± 0.10

[†] Shillaker's[17b] value for E = 20.896 k.cals. at 357.70°K

$\Delta C^{\ddagger}$ valued used in calculations = -19.83[17b] cals./deg.C.

TABLE XXIII

Activation parameters for the S_N1 solvolysis of 4-nitrodiphenylmethyl chloride in 50% (C) aqueous acetone.

$10^6 k_1$ (secs^{-1})	Temp. (°K)	Mean Temp. (°K)	E (k cals.)	$- \Delta S^{\ddagger}$ (cals.)	$- \Delta C^{\ddagger}$[*] (cals.)
5.765	293.34	303.31	22.218 ± 0.038[†]	8.76 ± 0.12	33.2
65.21	313.28				

[*] See ref. 50f.

[†] Queen's value for E = 22.322 k.cals. at 303.31°K. (see ref. 50f.).

TABLE XXIV

Activation parameters for the S_N1 solvolysis of 4-phenyl: 4'-nitrodiphenylmethyl chloride in 85% (C) aqueous acetone.

$10^5 k_1$ ($secs^{-1}$)	Temp. (^oK)	Mean Temp. (^oK)	E (k cals.)	$- \Delta S^{\ddagger}$ (cals.)	$- \Delta C^{\ddagger}$ * (cals.)
7.203 ± 0.0181	344.29	354.22	20.544 ± 0.045	20.16 ± 0.13	45.1
37.04 ± 0.096	364.15				

* Based on the $\Delta C^{\ddagger} / \Delta S^{\ddagger}$ ratio.[35]

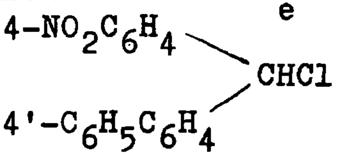
of 4-phenyl:4'-nitrodiphenylmethyl chloride in 50% (v/v) and 70% (v/v) aqueous acetone. For the latter solvent, the values obtained by Fox[17c] were used. No experimental values of E, $\Delta S^{\ddagger}$ and $\Delta C^{\ddagger}$ could be obtained due to the low solubility and rapid rate of reaction of the substrate in 50% (v/v) aqueous acetone. However, as it was essential to have values of these parameters for work in 50% (v/v) aqueous acetone, they were calculated by the method described in the next section.

IV. 12. Activation Parameters for the S_N1 Solvolysis of 4-phenyl:4'-nitrodiphenylmethyl Chloride in 50% (v/v) Aqueous Acetone.

Activation parameters for the S_N1 solvolysis of 4-phenyl:4'-nitrodiphenylmethyl chloride in 50% (v/v) aqueous acetone were calculated from an examination of the effects of changes in the solvent composition on these parameters for the S_N1 reactions of similar compounds at 10.20°C. (see Table XXV.). The results for the first two compounds listed in Table XXV show that a change in the solvent composition from 85% (v/v) to 70% (v/v) aqueous acetone caused changes in the energy and entropy of activation of approximately the same order of magnitude as those now observed. (see Table XXVI.). It therefore seemed safe to assume that the corresponding changes in E, $\Delta S^{\ddagger}$ and $\Delta C^{\ddagger}$ on passing from 70% (v/v) to 50% (v/v) aqueous acetone would be approximately the same for all the compounds listed in Table XXVI. Activation parameters for the S_N1 solvolysis of 4-phenyl:4'-nitrodiphenylmethyl chloride in 50% (v/v) aqueous acetone at 10.20°C were then calculated from the results in Tables XXV and XXVI on

TABLE XXV

Activation parameters at 10.20°C for the first-order rates of solvolysis of some organic halides in aqueous acetone.

Compound	Solvent (v/v %)	E (k cals)	$-\Delta S^{\ddagger}$ (cals)	$-\Delta C^{\ddagger}$ (cals)
$C_6H_5CHClC_6H_5$ [a]	85	21.476	9.64	46.5
	70	20.941	5.31	37.6
$4\text{-}NO_2C_6H_4CHClC_6H_5$ [b]	85	25.448	9.72	42.7
	70	25.276	4.73	39.8
	50	22.955	6.40	33.5
$4\text{-}PhOC_6H_4CH_2Cl$ [c]	70	23.540	6.30	43.1
	50	21.375	7.61	28.5
t-BuCl [d]	70	22.913	5.89	38.0
	50	20.966	6.73	27.0
 $\begin{matrix}4\text{-}NO_2C_6H_4 \\ 4'\text{-}C_6H_5C_6H_4\end{matrix} > CHCl$ [e]	85	23.598	10.11	45.1
	70	23.625	4.60	32.5

a) See ref. 88.
b) See refs. 50f, 88, 17c.
c) See refs. 29, 17c.
d) See ref. 95.
e) Present work.

TABLE XXVI

The effect of changes in the solvent composition on the activation parameters for the S_N1 reactions of some organic halides in aqueous acetone at 10.20°C.

Compound	ΔE E − E 70% 50% k cals.	$\Delta\Delta S^{\ddagger}$ $\Delta S^{\ddagger} - \Delta S^{\ddagger}$ 70% 50% cals.	ΔE E − E 85% 70% k cals.	$\Delta\Delta S^{\ddagger}$ $\Delta S^{\ddagger} - \Delta S^{\ddagger}$ 85% 70% cals.
$C_6H_5CHClC_6H_5$ [a]	———	———	+0.535	-4.33
$4\text{-}NO_2C_6H_4CHClC_6H_5$ [b]	+2.321	+1.67	+0.172	-4.99
$4\text{-}PhOC_6H_4CH_2Cl$ [c]	+2.165	+1.31	———	———
t-BuCl [d]	+1.947	+0.84	———	———
$4\text{-}NO_2C_6H_4$ CHCl [e] $4'\text{-}C_6H_5C_6H_4$	———	———	-0.027	-5.51

a) See ref. 88.
b) See refs. 50f, 88, 17c.
c) See refs. 29, 17c.
d) See ref. 95.
e) Present work.

the basis of this assumption; the values of E, $\Delta S^{\ddagger}$ and $\Delta C^{\ddagger}$ so obtained being 21.481 k cals., -6.27 cals. and -30 cals. respectively.

IV. 13. The Calculation of Rate Coefficients at Temperatures other than the Experimental Temperature.

The rate coefficient (k_A) at any temperature (T_A) can be calculated from that at the nearest experimental temperature (T) by,

$$\log_{10}\left(\frac{k}{k_A}\right) = \frac{E \quad (T - T_A)}{2.303.\ R.T.T_A} \qquad \text{-----} \qquad 4.24.$$

where k is the rate coefficient at the temperature T and E is the energy of activation at the mean temperature of $(T_A + T)/2$; the variation of the energy of activation with temperature being given by equation 4.20.

APPENDICES A - J

DETAILS OF INDIVIDUAL EXPERIMENTS

The letters in parenthesis refer to the particular batch of solvent used in the experiment described.

APPENDIX A

The effects of added electrolytes on the solvolysis of 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone at 20.18°C.

APPENDIX A.1.

Details of individual kinetic experiments carried out to investigate the effects of added electrolytes on the first-order rates of solvolysis.

EXPT. I. 0.004048M 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (E').

0.05008M NaBr added.

10 ml. samples titrated with 0.004153M sodium hydroxide.

Time (hrs)	Titre (mls)	k_1 (10^6) ($secs^{-1}$)
0	0.11	———
16.950	3.02	5.884
21.033	3.59	5.916
24.033	3.98	5.936
28.416	4.44	5.828
41.449	5.79	5.962
44.882	6.02	5.877
48.198	6.27	5.873
52.081	6.50	5.800
65.241	7.33	5.888
69.280	7.44	(5.729)
72.230	7.78	(6.107)
89.896	8.28	5.812
∞	9.75	———

Mean k_1 = $5.878 \pm 0.0152 \times 10^{-6}$ $secs^{-1}$.

Additional Experiments

Solvent	Added NaBr	Mean k_1(10^6) ($secs^{-1}$)
(D)	0.04968M	6.220 ± 0.0187
(H)	0.05005M	4.666 ± 0.0250

EXPT. 2. 0.002952M 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (N).

0.09988M NaBr added.

10 ml. samples titrated with 0.004864M sodium hydroxide.

Time (hrs)	Titre (mls)	k_1 (10^6) (secs^{-1})
0	0.09	——
21.833	2.25	5.699
26.233	2.58	5.699
28.916	2.78	5.743
45.733	3.72	5.675
50.200	3.94	5.714
52.717	4.00	5.592
69.750	4.67	5.783
74.400	4.77	5.699
77.467	4.88	5.790
93.917	5.26	(5.915)
100.284	5.32	5.752
∞	6.07	——

Mean k_1 = $5.715 \pm 0.0173 \times 10^{-6}$ secs^{-1}.

Additional Experiment.

Solvent	Added NaBr	Mean $k_1(10^6)$ (secs^{-1})
(N)	0.1001M	5.723 ± 0.0105

EXPT. 3. 0.003949M 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (E).

0.04992M $NaNO_3$ added.

10 ml. samples titrated with 0.004153M sodium hydroxide.

Time (hrs)	Titre (mls)	k_1 (10^6) $(secs^{-1})$
0	0.25	———
7.100	1.51	5.730
20.116	3.44	5.836
23.566	3.83	5.760
26.882	4.20	5.747
30.848	4.61	5.734
43.881	5.72	5.655
47.964	6.11	5.805
50.880	6.30	5.786
54.330	6.50	5.746
68.596	7.38	(5.952)
70.812	7.43	5.859
74.778	7.55	5.769
∞	9.51	———

Mean k_1 = $5.766 \pm 0.0160 \times 10^{-6}$ $secs^{-1}$.

Additional Experiments.

Solvent	Added $NaNO_3$	Mean $k_1 (10^6)$ $(secs^{-1})$
(F)	0.04966M	4.347 ± 0.0160
(G)	0.05017M	4.402 ± 0.0121
(H)	0.05001M	4.510 ± 0.0157
(R)	0.05014M	4.697 ± 0.0171

EXPT. 4. 0.003775M 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (R).

0.1001M $NaNO_3$ added.

10 ml. samples titrated with 0.004431M silver nitrate.

Time (hrs)	Titre (mls)	k_1 (10^6) $(secs^{-1})$
0	0.46	——
18.550	2.63	(4.695)
23.483	3.31	(5.165)
26.050	3.51	5.072
42.867	4.77	4.959
47.067	5.05	4.974
49.917	5.23	4.986
67.167	6.01	4.967
73.467	6.37	4.998
90.617	6.94	4.996
96.700	7.13	5.050
∞	8.52	——

Mean k_1 = $5.000 \pm 0.0115 \times 10^{-6}$ $secs^{-1}$.

Additional Experiments.

Solvent	Added $NaNO_3$	Mean $k_1 (10^6)(secs^{-1})$
* (J)	0.09994M	4.863 ± 0.0363
* (L)	0.09994M	5.286 ± 0.0430

* Followed by noting development of the acidity.

EXPT. 5. 0.002707M 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (H).

0.04991M $NaSO_3Ph$ added.

10 ml. samples titrated with 0.005435M sodium hydroxide.

Time (hrs)	Titre (mls)	k_1 (10^6) $(secs^{-1})$
0	0.12	——
5.683	0.58	(4.874)
18.367	1.39	(4.584)
22.217	1.57	4.429
29.184	1.90	4.342
42.167	2.48	4.380
46.217	2.63	4.369
53.734	2.87	4.313
66.000	3.22	4.276
69.068	3.34	4.369
75.735	3.53	4.437
91.785	3.87	4.470
95.918	3.91	4.384
100.285	3.97	4.352
∞	4.98	——

Mean k_1 = $4.375 \pm 0.0161 \times 10^{-6}$ $secs^{-1}$.

Additional Experiments.

Solvent	Added $NaSO_3Ph$	Mean $k_1 (10^6)(secs^{-1})$
(D)	0.04966M	5.766 ± 0.00945
(D)	0.05019M	5.867 ± 0.0156
(F)	0.05025M	4.242 ± 0.0216
(G)	0.04977M	4.392 ± 0.0175
(H)	0.04991M	4.338 ± 0.0147
(H)	0.04999M	4.339 ± 0.0197

EXPT. 6. 0.003526M 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (O).

0.09965M $NaSO_3Ph$ added.

10 ml. samples titrated with 0.005916M sodium hydroxide.

Time (hrs)	Titre (mls)	k_1 (10^6) ($secs^{-1}$)
0	0.20	——
18.150	1.78	4.910
21.900	2.03	4.855
25.200	2.22	4.760
42.000	3.20	4.868
46.000	3.40	4.898
49.083	3.45	4.702
65.783	4.15	4.889
69.816	4.30	4.951
72.733	4.30	4.752
89.416	4.72	4.772
95.416	4.90	4.923
∞	5.96	——

Mean k_1 = $4.844 \pm 0.0240 \times 10^{-6}$ $secs^{-1}$.

Additional Experiments.

Solvent	Added $NaSO_3Ph$	Mean k_1(10^6)($secs^{-1}$)
(J)	0.09963M	4.661 ± 0.0087
(O)	0.09948M	4.806 ± 0.0126

EXPT. 7. 0.002412M 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (G).

0.05002M $NaBF_4$ added.

10 ml. samples titrated with 0.003768M silver nitrate.

Time (hrs)	Titre (mls)	k_1 (10^6) ($secs^{-1}$)
0	0.26	———
4.033	0.63	(4.283)
17.966	1.84	4.593
22.633	2.16	4.545
28.916	2.57	4.533
41.533	3.26	4.484
48.800	3.58	4.430
66.617	4.30	4.475
71.534	4.50	4.570
76.734	4.67	4.586
∞	6.40	———

Mean k_1 = $4.527 \pm 0.0194 \times 10^{-6}$ $secs^{-1}$.

Additional Experiments.

Solvent	Added $NaBF_4$	Mean k_1(10^6)($secs^{-1}$)
(G)	0.05002M	4.498 ± 0.0216
(S')	0.05003M	4.568 ± 0.0355

EXPT. 8. 0.003219M 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (N).

0.1001M $NaBF_4$ added.

10 ml. samples titrated with 0.005030M silver nitrate.

Time (hrs)	Titre (mls)	k_1 (10^6) ($secs^{-1}$)
0	0.42	——
18.483	2.22	5.401
23.100	2.57	5.356
26.100	2.81	5.434
42.583	3.79	5.408
47.000	3.97	5.323
50.000	4.17	5.461
66.400	4.75	5.387
70.667	4.89	5.411
73.967	4.97	5.374
90.817	5.39	5.441
97.184	5.50	5.414
∞	6.40	——

Mean k_1 = 5.401 ± 0.0114 x 10^{-6} $secs^{-1}$.

Additional Experiments.

Solvent	Added $NaBF_4$	Mean k_1(10^6)($secs^{-1}$)
(N)	0.1002M	5.409 ± 0.0223

EXPT. 9. 0.002611M 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (G).

0.05001M HNO_3 added.

10 ml. samples titrated with 0.003768M silver nitrate.

Time (hrs)	Titre (mls)	k_1 (10^6) ($secs^{-1}$)
0	0.22	———
18.000	1.96	4.631
22.700	2.31	4.565
28.917	2.79	4.641
41.567	3.56	4.603
48.800	3.93	4.584
66.667	4.74	4.666
71.534	4.89	4.624
76.701	5.09	4.687
89.768	5.42	4.617
97.068	5.63	4.700
101.168	5.75	4.773
∞	6.93	———

Mean k_1 = 4.645 ± 0.0170 x 10^{-6} $secs^{-1}$.

Additional Experiments.

Solvent	Added HNO_3	Mean k_1(10^6)($secs^{-1}$)
(G)	0.05026M	4.680 ± 0.0184
(H)	0.05131M	4.696 ± 0.0172
(S')	0.04990M	4.734 ± 0.0176

EXPT. 10. 0.002789M 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (N).

0.09845M HNO_3 added.

10 ml. samples titrated with 0.004413M silver nitrate.

Time (hrs)	Titre (mls)	k_1 (10^6) ($secs^{-1}$)
0	0.30	———
17.200	2.15	5.936
21.633	2.55	6.015
25.833	2.87	5.985
41.135	3.79	5.854
45.716	4.05	5.926
48.099	4.15	5.893
65.132	4.82	5.926
69.782	4.92	5.808
72.849	5.01	5.816
89.316	5.41	5.877
95.649	5.54	5.936
∞	6.32	———

Mean k_1 = $5.906 \pm 0.0187 \times 10^{-6}$ $secs^{-1}$.

Additional Experiments.

Solvent	Added HNO_3	Mean k_1(10^6)($secs^{-1}$)
(N)	0.09767M	5.907 ± 0.0181
(R)	0.09981M	5.642 ± 0.0461

<u>EXPT. 11</u>. 0.003420M 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (N).

0.02469M $NaClO_4$ added.

10 ml. samples titrated with 0.005097N sodium hydroxide.

Time (hrs)	Titre (mls)	$k_1(10^6)$ $(secs^{-1})$
0	0.10	——
18.283	1.92	4.895
23.166	2.31	4.879
25.866	2.50	4.845
42.466	3.59	4.912
47.833	3.80	4.764
50.616	3.91	4.715
67.133	4.69	4.906
71.816	4.80	4.803
74.999	4.97	4.944
91.349	5.40	4.922
95.999	5.50	4.914
98.432	5.58	4.986
∞	6.71	——

Mean k_1 = $4.874 \pm 0.0217 \times 10^{-6}$ $secs^{-1}$.

EXPT. 12. 0.003605M 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (E').

0.04996M $NaClO_4$ added.

10 ml. samples titrated with 0.004149M sodium hydroxide.

Time (hrs)	Titre (mls)	k_1 (10^6) $(secs^{-1})$
0	0.08	——
16.883	2.74	6.085
20.283	3.13	5.996
24.383	3.61	6.013
40.299	4.95	5.748
44.482	5.40	6.007
47.482	5.67	6.130
51.565	5.90	6.073
64.581	6.55	5.988
67.997	6.73	6.047
71.330	6.88	6.074
75.313	7.02	6.050
∞	8.69	——

Mean k_1 = $6.046 \pm 0.0138 \times 10^{-6}$ $secs^{-1}$.

Additional Experiments.

Solvent	Added $NaClO_4$	Mean $k_1 (10^6)(secs^{-1})$
(D')	0.05001M	6.517 ± 0.0096
(S)	0.04994M	4.679 ± 0.0146

EXPT. 13. 0.002988M 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (N).

0.07493M $NaClO_4$ added.

10 ml. samples titrated with 0.005097N sodium hydroxide.

Time (hrs)	Titre (mls)	k_1 (10^6) $(secs^{-1})$
0	0.16	———
16.950	1.72	(5.246)
21.817	2.17	5.539
24.534	2.30	(5.330)
41.134	3.33	5.487
45.484	3.57	5.571
48.301	3.69	5.558
64.801	4.28	5.502
69.468	4.40	5.447
72.668	4.49	5.451
89.018	4.89	5.526
93.668	4.99	5.575
96.085	5.01	5.503
∞	5.86	———

Mean k_1 = $5.516 \pm 0.0138 \times 10^{-6}$ $secs^{-1}$.

EXPT. 14. 0.003857M 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (O).

0.1000M $NaClO_4$ added.

10 ml. samples titrated with 0.005916M sodium hydroxide.

Time (hrs)	Titre (mls)	k_1 (10^6) $(secs^{-1})$
0	0.23	———
18.917	2.25	5.688
23.334	2.62	5.692
26.451	3.00	(6.097)
43.301	3.94	5.718
47.184	4.17	5.797
50.817	4.33	5.768
67.301	4.92	5.651
71.484	5.06	5.677
74.267	5.15	5.702
91.134	5.54	5.668
96.217	5.64	5.679
∞	6.52	———

Mean k_1 = $5.704 \pm 0.0137 \times 10^{-6}$ $secs^{-1}$.

Additional Experiments.

Solvent	Added $NaClO_4$	Mean $k_1(10^6)(secs^{-1})$
(O)	0.1000M	5.716 ± 0.0319
(S)	0.1002M	5.334 ± 0.0218

EXPT. 15. 0.002589M 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (G).

0.05037M $HClO_4$ added.

10 ml. samples titrated with 0.003768M silver nitrate.

Time (hrs)	Titre (mls)	k_1 (10^6) ($secs^{-1}$)
0	0.14	———
19.750	2.13	4.933
25.700	2.61	4.946
38.350	3.45	4.906
41.700	3.63	4.871
45.567	3.99	(5.176)
63.500	4.71	4.973
68.317	4.89	4.976
73.460	5.03	4.905
86.943	5.42	4.905
93.843	5.66	5.067
97.860	5.75	5.091
∞	6.87	———

Mean k_1 = 4.957 ± 0.0216 x 10^{-6} $secs^{-1}$.

Additional Experiments.

Solvent	Added $HClO_4$	Mean k_1(10^6)($secs^{-1}$)
(G)	0.05052M	4.955 ± 0.0438
(S')	0.05024M	5.012 ± 0.0148

EXPT. 16. 0.003026M 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (O).

0.09370M $HClO_4$ added.

10 ml. samples titrated with 0.004437M silver nitrate.

Time (hrs)	Titre (mls)	k_1 (10^6) (secs^{-1})
0	0.21	———
5.717	0.98	6.031
22.317	2.68	5.831
26.217	3.02	5.861
29.267	3.31	6.009
45.550	4.33	5.955
49.900	4.56	5.975
52.883	4.69	5.949
69.850	5.34	5.952
77.483	5.58	6.000
95.833	5.97	5.946
100.916	6.10	6.103
∞	6.82	———

Mean k_1 = $5.965 \pm 0.0216 \times 10^{-6}$ secs^{-1}.

Additional Experiments.

Solvent	Added $HClO_4$	Mean k_1(10^6)(secs^{-1})
(O)	0.09547M	5.999 ± 0.0256
(S')	0.09900M	5.827 ± 0.0182
(U)	0.09638M	5.949 ± 0.0309
(U)	0.09671M	5.964 ± 0.0240

EXPT. 17. 0.002623M 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (H).

0.05017M NaCl added.

10 ml. samples titrated with 0.004710M sodium hydroxide.

Time (hrs)	Titre (mls)	k_1 (10^6) ($secs^{-1}$)
0	0.11	——
6.900	0.60	3.811
19.100	1.39	3.879
23.817	1.61	3.750
30.334	1.96	3.789
42.917	2.52	3.770
50.017	2.83	3.832
55.567	3.02	3.806
67.217	3.40	3.814
76.417	3.65	3.800
92.784	4.03	3.789
100.934	4.21	3.826
115.334	4.49	3.904
∞	5.57	——

Mean k_1 = $3.814 \pm 0.0119 \times 10^{-6}$ $secs^{-1}$.

Additional Experiments.

Solvent	Added NaCl	Mean k_1(10^6)($secs^{-1}$)
(H)	0.05011M	3.838 ± 0.0165

EXPT. 18. 0.004277M 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (S).

0.09996M NaCl added.

10 ml. samples titrated with 0.004985M sodium hydroxide.

Time (hrs)	Titre (mls)	k_1 (10^6) (secs^{-1})
0	0.11	———
16.483	1.68	3.462
20.950	2.08	3.508
24.050	2.37	3.586
40.283	3.41	3.403
44.500	3.70	3.443
47.750	3.87	3.415
64.033	4.76	3.455
68.783	4.97	3.444
72.750	5.06	3.353
89.333	5.78	3.442
94.100	5.95	3.453
113.967	6.49	3.412
∞	8.58	———

Mean k_1 = $3.448 \pm 0.0159 \times 10^{-6}$ secs^{-1}.

Additional Experiments.

Solvent	Added NaCl	Mean $k_1(10^6)(\text{secs}^{-1})$
(S)	0.1000M	3.451 ± 0.0167

EXPT. 19. 0.002555M 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (G).

0.05018M NaN_3 added.

10 ml. samples titrated with 0.003589M silver nitrate.

Time (hrs)	Titre (mls)	k_1 (10^6) ($secs^{-1}$)
0	0.51	———
6.033	1.37	6.436
19.533	2.89	6.350
25.900	3.54	6.575
43.167	4.70	6.467
49.467	5.00	6.388
54.484	5.32	6.633
67.484	5.77	6.539
73.917	5.94	6.477
78.034	6.02	6.385
90.917	6.30	6.378
96.717	6.40	6.368
∞	7.12	———

Mean k_1 = $6.454 \pm 0.0277 \times 10^{-6}$ $secs^{-1}$.

Additional Experiments.

Solvent	Added NaN_3	Mean k_1(10^6)($secs^{-1}$)
(G)	0.04994	6.696 ± 0.0255
(H)	0.04991	6.411 ± 0.0201
(H)	0.04993	6.705 ± 0.0255

<u>EXPT. 20</u>. 0.003280M 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (N).

0.1000M NaN_3 added.

10 ml. samples titrated with 0.005015N silver nitrate.

Time (hrs)	Titre (mls)	k_1 (10^6) ($secs^{-1}$)
0	0.39	———
16.017	2.86	8.907
20.884	3.44	9.116
23.617	3.65	8.882
40.217	4.83	8.841
44.550	5.07	8.926
47.383	5.19	8.892
64.166	5.76	8.941
68.533	5.86	8.928
71.833	5.93	8.935
88.116	6.16	8.777
∞	6.54	———

Mean k_1 = 8.915 ± 0.0261 x 10^{-6} $secs^{-1}$.

<u>Additional Experiments</u>.

Solvent	Added NaN_3	Mean k_1(10^6)($secs^{-1}$)
(N)	0.09995M	9.032 ± 0.0498

EXPT. 21. 0.004274M 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (S").
0.03168M $(CH_3)_4NF$ (containing 0.00132M $(CH_3)_4NCl$) added.
10 ml. samples titrated with 0.005076M silver nitrate.

Time (hrs)	Titre (mls)	k_1 (10^6) ($secs^{-1}$)
0	3.01	———
18.417	4.98	4.012
23.267	5.45	4.083
26.200	5.71	4.100
42.733	6.91	4.045
49.550	7.29	3.980
66.667	8.18	3.968
71.317	8.45	4.047
74.184	8.55	4.019
90.951	9.12	3.951
95.318	9.34	4.062
∞	11.43	———

Mean k_1 = $4.027 \pm 0.0149 \times 10^{-6}$ $secs^{-1}$.

Additional Experiments.

Solvent	Added $(CH_3)_4NF$	Mean k_1(10^6)($secs^{-1}$)
(S")	0.02804M (containing 0.00117M $(CH_3)_4NCl$)	4.053 ± 0.0294
(T)	0.05023M (containing 0.0008M $(CH_3)_4NCl$)	3.809 ± 0.0109

APPENDIX A.2.

Details of individual kinetic experiments carried out in the investigation of the effects of added electrolytes on the zeroth-order rates of solvolysis.

EXPT. 22. 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (D).

0.05062M NaBr added.

5 ml. samples titrated with 0.003451M sodium hydroxide.

Time (hrs)	Titre (mls)	$k_o(10^8)$(moles. litres.$^{-1}$secs.$^{-1}$)
0.483	0.08	———
13.850	2.42	(3.361)
15.133	2.61	3.313
16.716	2.89	3.301
20.499	3.55	3.328
36.965	6.41	3.328
39.031	6.78	3.332
41.531	7.15	3.303
45.164	7.79	3.307
48.647	8.37	3.301
61.180	10.56	3.309
63.013	10.86	3.306
65.729	11.24	3.304
68.529	11.75	3.288
72.459	12.46	3.296

Mean k_o = 3.309 ± 0.0035 x 10^{-8} moles. litres.$^{-1}$secs^{-1}.

Additional Experiments.

Solvent	Added NaBr	Mean $k_o(10^8)$(moles. litres.$^{-1}$secs.$^{-1}$)
(A)	0.05017M	3.318 ± 0.0046
(E)	0.05004M	3.390 ± 0.0071
(E)	0.05006M	3.391 ± 0.0040

EXPT. 23. 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (I).

0.1000M NaBr added.

5 ml. samples titrated with 0.004936M sodium hydroxide.

Time (hrs)	Titre (mls)	$k_o(10^8)$(moles.litres.$^{-1}$secs.$^{-1}$)
0	0	——
5.817	0.77	(3.631)
11.184	1.46	3.579
23.801	3.08	3.548
31.101	4.03	3.554
48.234	6.27	3.565
54.017	6.97	3.537
59.434	7.64	3.523
72.901	9.54	3.589
77.834	10.05	3.540
83.684	10.85	3.557
95.751	12.36	3.540
101.751	13.19	3.554

Mean k_o = $3.553 \pm 0.0055 \times 10^{-8}$ moles.litres.$^{-1}$secs^{-1}.

Additional Experiments.

Solvent	Added NaBr	Mean $k_o(10^8)$(moles.litres.$^{-1}$secs.$^{-1}$)
(I)	0.1000M	3.506 ± 0.0117
(L)	0.1003M	3.758 ± 0.0179

EXPT. 24. 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (A).

0.04991M $NaNO_3$ added.

5 ml. samples titrated with 0.004549M sodium hydroxide.

Time (hrs)	Titre (mls)	$k_o(10^8)$(moles. litres.$^{-1}$secs.$^{-1}$)
0	0.11	———
11.770	1.60	3.200
18.836	2.50	3.207
24.457	3.24	3.234
36.464	4.80	3.251
39.928	5.20	3.222
43.721	5.73	3.249
47.769	6.25	3.248
60.562	7.85	3.230
64.172	8.34	3.241
67.271	8.64	3.204
71.672	9.31	3.244
84.698	10.88	3.213

Mean k_o = $3.229 \pm 0.0052 \times 10^{-8}$ moles.litres.$^{-1}$secs^{-1}.

Additional Experiments.

Solvent	Added $NaNO_3$	Mean $k_o(10^8)$(moles.litres.$^{-1}$secs.$^{-1}$)
(A)	0.04998M	3.229 ± 0.0076
(E)	0.04927M	3.281 ± 0.0082

EXPT. 25. 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (I).

0.1000M $NaNO_3$ added.

5 ml. samples titrated with 0.004936M sodium hydroxide.

Time (hrs)	Titre (mls)	$k_o(10^8)$(moles.litres.$^{-1}$secs.$^{-1}$)
0	0	———
5.817	0.70	3.299
11.200	1.38	(3.378)
23.817	2.88	3.315
31.117	3.74	3.296
48.234	5.86	3.332
54.034	6.54	3.318
59.467	7.15	3.296
72.917	8.83	3.321
77.834	9.44	3.325
83.701	10.13	3.318
95.701	11.59	3.321
101.768	12.29	3.313

Mean k_o = $3.314 \pm 0.0035 \times 10^{-8}$ moles.litres.$^{-1}$secs.$^{-1}$

Additional Experiments.

Solvent	Added $NaNO_3$	Mean $k_o(10^8)$(moles.litres.$^{-1}$secs.$^{-1}$)
(I)	0.1000M	3.281 ± 0.0116
(L)	0.1000M	3.491 ± 0.0136

EXPT. 26. 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (A).

0.04997M $NaSO_3Ph$ added.

5 ml. samples titrated with 0.004549M sodium hydroxide.

Time (hrs)	Titre (mls)	$k_o(10^8)$(moles.litres.$^{-1}$secs.$^{-1}$)
0	0.04	———
12.391	1.63	3.242
19.371	2.54	3.258
24.827	3.28	3.295
36.950	4.85	3.287
40.324	5.15	(3.202)
44.184	5.75	3.266
48.144	6.28	3.275
60.961	7.92	3.266
64.696	8.44	3.281
67.823	8.83	3.275
72.123	9.32	3.252
85.056	11.00	3.256

Mean k_o = 3.268 ± 0.0046 x 10^{-8} moles.litres.$^{-1}$secs.$^{-1}$)

Additional Experiments.

Solvent	Added $NaSO_3Ph$	Mean $k_o(10^8)$(moles.litres.$^{-1}$secs.$^{-1}$)
(A)	0.04952M	3.292 ± 0.0075
(E)	0.04999M	3.346 ± 0.0018

EXPT. 27. 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (P).

0.09944M $NaSO_3Ph$ added.

5 ml. samples titrated with 0.004826M sodium hydroxide.

Time (hrs)	Titre (mls)	$k_o(10^8)$(moles.litres^{-1}secs^{-1})
0	0.11	———
16.850	2.32	3.517
21.650	2.92	3.481
24.467	3.26	3.451
40.834	5.41	3.480
45.401	5.99	3.472
47.984	6.31	3.464
64.817	8.45	3.451
69.517	9.11	3.472
72.550	9.50	3.469
88.767	11.73	3.509
95.300	12.69	3.539

Mean k_o = $3.482 \pm 0.0080 \times 10^{-8}$ moles.litres^{-1}secs^{-1}

Additional Experiment.

Solvent	Added $NaSO_3Ph$	Mean $k_o(10^8)$(moles.litres^{-1}secs^{-1})
(P)	0.09936M	3.503 ± 0.0085

EXPT. 28. 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (E).

0.05003M $NaBF_4$ added.

5 ml. samples titrated with 0.003546M silver nitrate.

Time (hrs)	Titre (mls)	$k_o(10^8)$(moles.litres.$^{-1}$secs.$^{-1}$)
0.350	0.12	——
12.983	2.25	3.321
16.533	2.87	3.347
19.949	3.45	3.347
37.199	6.27	3.288
40.765	6.91	3.310
43.898	7.45	3.316
48.514	8.23	3.318
61.164	10.31	3.302
64.647	10.88	3.296
68.013	11.45	3.298
71.029	11.94	3.290
84.845	14.24	3.292

Mean k_o = 3.310 ± 0.0056 x 10^{-8} moles.litres.$^{-1}$secs.$^{-1}$

Additional Experiment.

Solvent	Added $NaBF_4$	Mean $k_o(10^8)$(moles.litres.$^{-1}$secs.$^{-1}$)
(R)	0.05005M	3.263 ± 0.0057

<u>EXPT. 29</u>. 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (P').

0.1000M $NaBF_4$ added.

5 ml. samples titrated with 0.004386M silver nitrate.

Time (hrs)	Titre (mls)	$k_o(10^8)$(moles.litres^{-1}secs^{-1})
0	0.12	———
16.950	2.48	3.392
20.767	2.97	3.343
23.750	3.63	(3.601)
40.683	5.76	3.377
45.366	6.42	3.385
48.399	6.85	3.389
64.516	9.10	3.392
68.766	9.69	3.392
71.249	10.05	3.396
88.649	12.42	3.380
95.032	13.25	3.367

Mean k_o = 3.381 ± 0.0048 x 10^{-8} moles.litres^{-1}secs^{-1})

<u>Additional Experiment</u>.

Solvent	Added $NaBF_4$	Mean $k_o(10^8)$(moles.litres^{-1}secs^{-1})
(P')	0.1002M	3.415 ± 0.0076

EXPT. 30. 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (E).

0.05185M HNO_3 added.

5 ml. samples titrated with 0.003546M silver nitrate.

Time (hrs)	Titre (mls)	$k_o(10^8)$(moles.litres.$^{-1}$secs.$^{-1}$)
0.650	0.14	———
13.200	2.28	3.333
16.983	2.92	3.353
20.033	3.48	3.394
37.433	6.46	3.384
40.949	7.01	3.359
44.065	7.52	3.349
48.615	8.31	3.356
61.165	10.46	3.359
64.815	11.07	3.356
67.498	11.64	3.367
72.231	12.38	3.368
84.331	14.46	3.367

Mean k_o = 3.362 ± 0.0044 x 10^{-8} moles.litres.$^{-1}$secs.$^{-1}$

Additional Experiments.

Solvent	Added HNO_3	Mean $k_o(10^8)$(moles.litres.$^{-1}$secs.$^{-1}$)
(E)	0.05093M	3.360 ± 0.0049
(F)	0.05068M	3.354 ± 0.0108
(R)	0.05033M	3.294 ± 0.0085

EXPT. 31. 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (P')

0.09940M HNO_3 added.

5 ml. samples titrated with 0.004496M silver nitrate.

Time (hrs)	Titre (mls)	$k_o(10^8)$(moles.litres.$^{-1}$secs.$^{-1}$)
0	0.15	———
16.183	2.37	3.427
20.966	3.00	3.394
23.933	3.53	(3.527)
40.366	5.73	3.452
44.849	6.34	3.447
47.866	6.72	3.429
64.366	8.92	3.404
68.816	9.53	3.404
71.933	9.95	3.402
88.183	12.30	3.442
94.566	13.21	3.449

Mean k_o = 3.425 ± 0.0067 x 10^{-8} moles.litres.$^{-1}$secs.$^{-1}$

Additional Experiments.

Solvent	Added HNO_3	Mean $k_o(10^8)$(moles.litres.$^{-1}$secs.$^{-1}$)
(P')	0.09913M	3.422 ± 0.0081
(R)	0.09944M	3.527 ± 0.0159

EXPT. 32. 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (A).

0.04987M $NaClO_4$ added.

5 ml. samples titrated with 0.004612M sodium hydroxide.

Time (hrs)	Titre (mls)	$k_o(10^8)$(moles.litres.$^{-1}$secs.$^{-1}$)
0	0.12	—
12.893	1.88	3.498
16.406	2.36	3.499
19.415	2.76	3.484
22.736	3.19	3.467
36.673	5.07	3.457
40.944	5.61	3.436
43.703	5.95	3.422
49.179	6.69	3.422
60.988	8.22	3.402
62.769	8.58	3.453
64.586	8.75	3.424
68.047	9.24	3.436
71.864	9.78	3.443

Mean k_o = $3.449 \pm 0.0082 \times 10^{-8}$ moles.litres.$^{-1}$secs.$^{-1}$

Additional Experiment.

Solvent	Added $NaClO_4$	Mean $k_o(10^8)$(moles.litres.$^{-1}$secs.$^{-1}$)
(A)	0.04987M	3.454 ± 0.0049

EXPT. 33. 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (P).

0.1003M $NaClO_4$ added.

5 ml. samples titrated with 0.004845M silver nitrate.

Time (hrs)	Titre (mls)	$k_o(10^8)$(moles.litres.$^{-1}$secs.$^{-1}$)
0	0.06	——
16.950	2.44	3.779
20.767	2.99	3.798
23.734	3.39	3.776
40.667	5.79	3.792
45.367	6.48	3.809
48.400	6.82	3.760
64.667	9.13	3.776
68.917	9.78	3.795
71.384	10.11	3.790
88.801	12.51	3.773
95.201	13.32	3.749

Mean k_o = $3.782 \pm 0.0050 \times 10^{-8}$ moles.litres.$^{-1}$secs.$^{-1}$

Additional Experiment.

Solvent	Added $NaClO_4$	Mean $k_o(10^8)$(moles.litres.$^{-1}$secs.$^{-1}$)
(P)	0.1001M	3.796 ± 0.0137

<u>EXPT. 34</u>. 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (E).

0.05130M $HClO_4$ added.

5 ml. samples titrated with 0.003546M silver nitrate.

Time (hrs)	Titre (mls)	$k_o(10^8)$(moles.litres.$^{-1}$secs.$^{-1}$)
0.55	0.19	———
13.516	2.48	3.479
17.161	3.18	(3.547)
20.294	3.68	3.483
37.410	6.72	3.491
41.293	7.42	3.497
44.226	7.97	3.508
48.676	8.77	3.516
61.409	10.93	3.477
64.992	11.61	3.491
68.375	12.23	3.497
71.358	12.71	3.483
85.374	15.13	3.469

Mean k_o = $3.490 \pm 0.0039 \times 10^{-8}$ moles.litres.$^{-1}$secs.$^{-1}$)

<u>Additional Experiment</u>.

Solvent	Added $HClO_4$	Mean $k_o(10^8)$(moles.litres.$^{-1}$secs.$^{-1}$)
(E)	0.05145M	3.522 ± 0.0056

EXPT. 35. 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (P).

0.09735M $HClO_4$ added.

5 ml. samples titrated with 0.004378M silver nitrate.

Time (hrs)	Titre (mls)	$k_o(10^8)$(moles.litres.$^{-1}$secs.$^{-1}$)
0	0.21	——
17.350	2.91	3.784
20.483	3.38	3.765
23.433	3.83	3.758
41.283	6.55	3.736
44.500	7.03	3.729
47.350	7.44	3.714
63.833	9.94	3.707
68.566	10.64	3.699
71.249	11.03	3.695
87.749	13.57	3.704
92.949	14.45	3.726

Mean k_o = $3.729 \pm 0.0084 \times 10^{-8}$ moles.litres.$^{-1}$secs.$^{-1}$

Additional Experiments.

Solvent	Added $HClO_4$	Mean $k_o(10^8)$(moles.litres.$^{-1}$secs.$^{-1}$)
(P')	0.09438M	3.762 ± 0.0091
(P)	0.09761M	3.745 ± 0.0102
(R)	0.09771M	3.819 ± 0.0087

EXPT. 36. 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (H).

0.05005M NaCl added.

5 ml. samples titrated with 0.005000M sodium hydroxide.

Time (hrs)	Titre (mls)	$k_o(10^8)$(moles.litres.$^{-1}$secs.$^{-1}$)
0	0	———
8.316	0.82	2.739
12.233	1.23	2.792
24.366	2.45	2.792
28.183	2.85	2.808
32.183	3.26	2.814
48.450	4.85	2.781
54.283	5.40	2.763
60.016	6.00	2.777
71.966	7.17	2.768
79.316	7.92	2.774
83.416	8.28	2.757
96.249	9.20	(2.655)

Mean k_o = 2.779 ± 0.0064 x 10^{-8} moles.litres.$^{-1}$secs.$^{-1}$

Additional Experiment.

Solvent	Added NaCl	Mean $k_o(10^8)$(moles.litres.$^{-1}$secs.$^{-1}$)
(H)	0.05007M	2.794 ± 0.0112

<u>EXPT. 37</u>. 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (H).

0.09993M NaCl added.

5 ml. samples titrated with 0.005000M sodium hydroxide.

Time (hrs)	Titre (mls)	$k_o(10^8)$(moles.litres^{-1}secs^{-1})
0	0.07	———
13.200	1.36	2.715
21.533	2.16	2.696
25.466	2.57	2.727
37.583	3.69	2.676
41.416	4.07	2.683
45.416	4.47	2.691
61.666	5.99	2.667
67.499	6.55	2.667
73.249	7.05	2.647
85.182	8.18	2.645
92.515	8.86	2.639
96.665	9.19	2.621
109.448	10.11	2.639

Mean k_o = 2.670 ± 0.0084 x 10^{-8} moles.litres^{-1}secs^{-1}

<u>Additional Experiment</u>.

Solvent	Added NaCl	Mean $k_o(10^8)$(moles.litres^{-1}secs^{-1})
(U)	0.1000M	2.868 ± 0.0121

EXPT. 38. 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (E).

0.05000M NaN_3 added.

5 ml. samples titrated with 0.003546M silver nitrate.

Time (hrs)	Titre (mls)	$k_o(10^8)$(moles.litres.$^{-1}$secs.$^{-1}$)
0.383	0.10	——
12.866	3.08	4.703
16.649	4.04	4.771
19.749	4.73	4.711
37.049	8.71	4.625
40.665	9.58	4.635
43.798	10.35	4.651
48.214	11.28	4.604
60.814	14.16	4.584
64.697	15.12	4.600
67.697	15.76	4.582
72.463	16.84	4.574
84.513	19.42	4.523

Additional Experiment.

See Experiment 39.

EXPT. 39. 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (E).

0.05022M NaN_3 added.

5 ml. samples titrated with 0.003546M silver nitrate.

Time (hrs)	Titre (mls)	$k_o(10^8)$(moles.litres.$^{-1}$secs.$^{-1}$)
0.350	0.11	———
13.016	3.16	4.744
16.649	4.04	4.750
19.682	4.80	4.779
36.848	8.57	4.567
40.798	9.56	4.602
43.598	10.21	4.600
48.214	11.24	4.580
60.814	14.08	4.551
64.330	14.85	4.539
67.680	15.56	4.521
71.030	16.31	4.515
85.030	19.17	4.435

Additional Experiment.

See Experiment 38.

EXPT. 40. 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (T).

0.05023M $(CH_3)_4NF$ (containing 0.0008M $(CH_3)_4NCl$) added.

5 ml. samples titrated with 0.004625M silver nitrate.

Time (hrs)	Titre (mls)	$k_o(10^8)$(moles.litres.$^{-1}$secs.$^{-1}$)
0	0.88	——
6.567	1.59	2.778
23.050	3.49	2.908
27.817	3.99	2.873
30.600	4.24	2.821
47.517	6.10	2.824
53.684	6.83	2.847
71.167	8.74	2.837
75.817	9.34	2.868
78.767	9.61	2.847
95.117	11.42	2.847

Mean k_o = 2.845 ± 0.0104 x 10^{-8} moles.litres.$^{-1}$secs.$^{-1}$)

Additional Experiments.

Solvent		Mean $k_o(10^8)$(moles.litres.$^{-1}$ secs.$^{-1}$)
(T)	0.1004M $(CH_3)_4NF$ (containing 0.0016M $(CH_3)_4$ NCl)	2.883 ± 0.0244
(S")	0.08975M $(CH_3)_4NF$ (containing 0.00373M $(CH_3)_4$ NCl)	3.272 ± 0.0219

APPENDIX A.3.

A summary of first-and-zeroth-order rates of solvolysis of 4-phenyl:4'-nitrodiphenylmethyl chloride in different batches of 70% (v/v) aqueous acetone at 20.18°C.

(No electrolytes added).

Solvent	k_1^o (10^6) * (secs.$^{-1}$)	k_o^o (10^8) † (moles.litres.$^{-1}$secs.$^{-1}$)
(A)	———	3.009 ± 0.0041
(D)	5.465 ± 0.0216	2.947 ± 0.0080
(D')	5.526 ± 0.0232	———
(E)	5.343 ± 0.0163	3.050 ± 0.0080
(E')	5.155 ± 0.0086	———
(F)	4.000 ± 0.0209	3.075 ± 0.0075
(G)	4.052 ± 0.0095	———
(H)	4.083 ± 0.0091	2.890 ± 0.0070
(I)	———	2.873 ± 0.0067
(J)	4.136 ± 0.0096	———
(L)	4.487 ± 0.0228	3.050 ± 0.0048
(N)	4.487 ± 0.0146	———
(O)	4.293 ± 0.0107	———
(P)	———	2.934 ± 0.0063
(P')	———	2.908 ± 0.0077
(R)	4.344 ± 0.0064	3.012 ± 0.0106
(S)	4.027 ± 0.0182	———
(S')	4.082 ± 0.0242	———
(S")	4.362 ± 0.0232	3.204 ± 0.0153
(T)	4.311 ± 0.0301	2.812 ± 0.0159
(U)	4.255 ± 0.0157	3.098 ± 0.0098

* The initial concentration of substrate was approximately 4 x 10^{-3}M, and 10 ml. samples were titrated with <u>ca</u>. 5 x 10^{-3}M sodium hydroxide.

† 5 ml. samples were titrated with approximately 5 x 10^{-3}M sodium hydroxide.

APPENDIX A.4.

A summary of electrolyte effects on first-and zeroth-order rates of solvolysis of 4-phenyl: 4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone at 20.18°C.

First-order rates of solvolysis

Electrolyte	Solvent	k_1 (10^6) (secs.$^{-1}$)	k_1^o (10^6) (secs.$^{-1}$)	k_1/k_1^o
0.03168M $(CH_3)_4NF$ containing 0.00132M $(CH_3)_4NCl$ *	(S")	4.031 ± 0.0149*†	4.326 ± 0.0232	0.9241 ± 0.0060
0.02804M $(CH_3)_4NF$ containing 0.00117M $(CH_3)_4NCl$	(S")	4.053 ± 0.0294*†	4.326 ± 0.0232	0.9292 ± 0.0084
0.05023M $(CH_3)_4NF$ containing 0.00080M $(CH_3)_4NCl$	(T)	3.809 ± 0.0109*†	4.311 ± 0.0301	0.8836 ± 0.0067
0.05018M NaN_3	(G)	6.454 ± 0.0277*	4.052 ± 0.0095	1.5928 ± 0.0078
0.04994M NaN_3	(G)	6.696 ± 0.0255*	4.052 ± 0.0095	1.6525 ± 0.0074
0.04993M NaN_3	(H)	6.705 ± 0.0255*	4.083 ± 0.0091	1.6422 ± 0.0072
0.04993M NaN_3	(H)	6.411 ± 0.0201*	4.083 ± 0.0091	1.5702 ± 0.0060
0.1000 M NaN_3	(N)	8.915 ± 0.0261*	4.487 ± 0.0146	1.9869 ± 0.0087
0.09995M NaN_3	(N)	9.032 ± 0.0498*	4.487 ± 0.0146	2.0129 ± 0.0129
0.05017M NaCl	(H)	3.814 ± 0.0119	4.083 ± 0.0091	0.9341 ± 0.0036

First-order rates of solvolysis (continued)

Electrolyte	Solvent	k_1 (10^6) (secs.$^{-1}$)	k_1^o (10^6) (secs.$^{-1}$)	k_1/k_1^o
0.05011M NaCl	(H)	3.838 ± 0.0165	4.083 ± 0.0091	0.9400 ± 0.0046
0.09996M NaCl	(S)	3.448 ± 0.0159	4.027 ± 0.0182	0.8562 ± 0.0055
0.1000 M NaCl	(S)	3.451 ± 0.0167	4.027 ± 0.0182	0.8570 ± 0.0057
0.04991M $NaSO_3Ph$	(H)	4.375 ± 0.0161	4.083 ± 0.0091	1.0715 ± 0.0046
0.04966M $NaSO_3Ph$	(D)	5.766 ± 0.0094	5.465 ± 0.0216	1.0552 ± 0.0045
0.05019M $NaSO_3Ph$	(D)	5.867 ± 0.0156	5.465 ± 0.0216	1.0736 ± 0.0051
0.05025M $NaSO_3Ph$	(F)	4.242 ± 0.0216	4.000 ± 0.0209	1.0605 ± 0.0071
0.04977M $NaSO_3Ph$	(G)	4.392 ± 0.0175	4.052 ± 0.0095	1.0836 ± 0.0050
0.04991M $NaSO_3Ph$	(H)	4.338 ± 0.0147	4.083 ± 0.0091	1.0625 ± 0.0043
0.04991M $NaSO_3Ph$	(H)	4.339 ± 0.0197	4.083 ± 0.0091	1.0627 ± 0.0051
0.09965M $NaSO_3Ph$	(O)	4.844 ± 0.0240	4.293 ± 0.0107	1.1283 ± 0.0062
0.09963M $NaSO_3Ph$	(J)	4.661 ± 0.0087	4.136 ± 0.0096	1.1269 ± 0.0033

First-order rates of solvolysis (continued)

Electrolyte	Solvent	k_1 (10^6) (secs.$^{-1}$)	k_1^o (10^6) (secs.$^{-1}$)	k_1/k_1^o
0.09948M $NaSO_3Ph$	(O)	4.806 ± 0.0126	4.293 ± 0.0107	1.1195 ± 0.0041
0.04992M $NaNO_3$	(E)	5.766 ± 0.0160	5.343 ± 0.0163	1.0792 ± 0.0044
0.04966M $NaNO_3$	(F)	4.347 ± 0.0160	4.000 ± 0.0209	1.0868 ± 0.0069
0.05017M $NaNO_3$	(G)	4.402 ± 0.0121	4.052 ± 0.0095	1.0864 ± 0.0039
0.05001M $NaNO_3$	(H)	4.510 ± 0.0157	4.083 ± 0.0091	1.1046 ± 0.0046
0.05014M $NaNO_3$	(R)	4.697 ± 0.0171	4.344 ± 0.0064	1.0813 ± 0.0043
0.1001M $NaNO_3$	(R)	5.000 ± 0.0115*	4.344 ± 0.0064	1.1510 ± 0.0031
0.09994M $NaNO_3$	(J)	4.863 ± 0.0363	4.136 ± 0.0096	1.1758 ± 0.0092
0.09994M $NaNO_3$	(L)	5.286 ± 0.0430	4.487 ± 0.0228	1.1781 ± 0.0113
0.05002M $NaBF_4$	(G)	4.527 ± 0.0194*	4.052 ± 0.0095	1.1172 ± 0.0055
0.05002M $NaBF_4$	(G)	4.498 ± 0.0216	4.052 ± 0.0095	1.1101 ± 0.0059
0.05003M $NaBF_4$	(S')	4.568 ± 0.0355*	4.082 ± 0.0242	1.1191 ± 0.0109
0.1001M $NaBF_4$	(N)	5.401 ± 0.0114*	4.487 ± 0.0146	1.2055 ± 0.0063
0.1002M $NaBF_4$	(N)	5.409 ± 0.0223*	4.487 ± 0.0146	1.2037 ± 0.0047

First-order rates of solvolysis (continued)

Electrolyte	Solvent	k_1 (10^6) (secs.$^{-1}$)	k_1^o (10^6) (secs.$^{-1}$)	k_1/k_1^o
0.05008M NaBr	(E')	5.878 ± 0.0152	5.155 ± 0.0086	1.1403 ± 0.0035
0.04968M NaBr	(D)	6.220 ± 0.0187	5.465 ± 0.0216	1.1382 ± 0.0057
0.05005M NaBr	(H)	4.666 ± 0.0250	4.083 ± 0.0091	1.1428 ± 0.0066
0.09988M NaBr	(N)	5.715 ± 0.0173	4.487 ± 0.0146	1.2737 ± 0.0057
0.1001M NaBr	(N)	5.723 ± 0.0105	4.487 ± 0.0146	1.2755 ± 0.0048
0.05021M HNO_3	(G)	4.645 ± 0.0170*	4.052 ± 0.0095	1.1463 ± 0.0050
0.05026M HNO_3	(G)	4.680 ± 0.0184*	4.052 ± 0.0095	1.1550 ± 0.0053
0.05131M HNO_3	(H)	4.696 ± 0.0172*	4.083 ± 0.0092	1.1501 ± 0.0049
0.04990M HNO_3	(S')	4.734 ± 0.0176*	4.082 ± 0.0242	1.1597 ± 0.0081
0.09845M HNO_3	(N)	5.906 ± 0.0187*	4.487 ± 0.0146	1.3162 ± 0.0060
0.09767M HNO_3	(N)	5.907 ± 0.0181*	4.487 ± 0.0147	1.3165 ± 0.0059
0.09981M HNO_3	(R)	5.642 ± 0.0461*	4.344 ± 0.0064	1.2989 ± 0.0108
0.04996M $NaClO_4$	(E')	6.046 ± 0.0138	5.155 ± 0.0086	1.1728 ± 0.0033
0.05001M $NaClO_4$	(D')	6.517 ± 0.0096	5.526 ± 0.0232	1.1793 ± 0.0052

First-order rates of solvolysis (continued)

Electrolyte	Solvent	k_1 (10^6) (secs.$^{-1}$)	k_1^o (10^6) (secs.$^{-1}$)	k_1/k_1^o
0.04994M $NaClO_4$	(S)	4.679 ± 0.0146	4.027 ± 0.0182	1.1619 ± 0.0064
0.1000M $NaClO_4$	(O)	5.704 ± 0.0137	4.293 ± 0.0107	1.3287 ± 0.0046
0.1000M $NaClO_4$	(O)	5.716 ± 0.0319	4.293 ± 0.0107	1.3315 ± 0.0104
0.1002M $NaClO_4$	(S)	5.334 ± 0.0218	4.027 ± 0.0182	1.3246 ± 0.0081
0.02469M $NaClO_4$	(N)	4.874 ± 0.0217	4.487 ± 0.0146	1.0862 ± 0.0060
0.07493M $NaClO_4$	(N)	5.516 ± 0.0138	4.487 ± 0.0146	1.2293 ± 0.0051
0.05037M $HClO_4$	(G)	4.957 ± 0.0216*	4.052 ± 0.0095	1.2233 ± 0.0061
0.05052M $HClO_4$	(G)	4.955 ± 0.0438*	4.052 ± 0.0095	1.2229 ± 0.0112
0.05024M $HClO_4$	(S')	5.012 ± 0.0148*	4.082 ± 0.0242	1.2278 ± 0.0081
0.09370M $HClO_4$	(O)	5.965 ± 0.0216*	4.293 ± 0.0107	1.3895 ± 0.0061
0.09547M $HClO_4$	(O)	5.999 ± 0.0256*	4.293 ± 0.0107	1.3974 ± 0.0069
0.09900M $HClO_4$	(S')	5.827 ± 0.0182*	4.082 ± 0.0242	1.4275 ± 0.0096
0.09638M $HClO_4$	(U)	5.949 ± 0.0309*	4.255 ± 0.0157	1.3981 ± 0.0089
0.09671M $HClO_4$	(U)	5.964 ± 0.0240*	4.255 ± 0.0157	1.4016 ± 0.0077

* Followed by noting the development of chloride ion.

† Corrected for the retardation produced by the chloride ion present

Zeroth-Order Rates

Electrolyte	Solvent	$k_o(10^8)$(moles. litres.$^{-1}$secs.$^{-1}$)	$k_o^o(10^8)$(moles. litres.$^{-1}$secs.$^{-1}$)	k_o/k_o^o
0.05023M $(CH_3)_4NF$ containing 0.00080M $(CH_3)_4NCl$	(T)	2.851 ± 0.0104*†	2.812 ± 0.0159	1.0139 ± 0.0068
0.08975M $(CH_3)_4NF$ containing 0.00373M $(CH_3)_4NCl$	(S")	3.284 ± 0.0219*†	3.204 ± 0.0153	1.0250 ± 0.0084
0.1004M $(CH_3)_4NF$ containing 0.0016M $(CH_3)_4NCl$	(T)	2.890 ± 0.0244*†	2.812 ± 0.0159	1.0277 ± 0.0102
0.05005M NaCl	(H)	2.779 ± 0.0064	2.890 ± 0.0070	0.9616 ± 0.0032
0.05007M NaCl	(H)	2.794 ± 0.0112	2.890 ± 0.0070	0.9668 ± 0.0045
0.09994M NaCl	(H)	2.670 ± 0.0084	2.890 ± 0.0070	0.9238 ± 0.0037
0.1000M NaCl	(U)	2.868 ± 0.0121	3.098 ± 0.0088	0.9258 ± 0.0047
0.04997M $NaSO_3Ph$	(A)	3.268 ± 0.0046	3.009 ± 0.0041	1.0861 ± 0.0021
0.04952M $NaSO_3Ph$	(A)	3.293 ± 0.0075	3.009 ± 0.0041	1.0944 ± 0.0029
0.04999M $NaSO_3Ph$	(E)	3.346 ± 0.0018	3.050 ± 0.0080	1.0970 ± 0.0029
0.09944M $NaSO_3Ph$	(P)	3.482 ± 0.0080	2.934 ± 0.0062	1.1868 ± 0.0037
0.09936M $NaSO_3Ph$	(P)	3.503 ± 0.0085	2.934 ± 0.0062	1.1939 ± 0.0038

Zeroth-Order Rates (continued)

Electrolyte	Solvent	$k_o(10^8)$(moles. litres.$^{-1}$secs.$^{-1}$)	$k_o^o(10^8)$(moles. litres.$^{-1}$secs.$^{-1}$)	k_o/k_o^o
0.04991M $NaNO_3$	(A)	3.229 ± 0.0052	3.009 ± 0.0041	1.0731 ± 0.0023
0.04998M $NaNO_3$	(A)	3.229 ± 0.0076	3.009 ± 0.0041	1.0731 ± 0.0029
0.04927M $NaNO_3$	(E)	3.281 ± 0.0082	3.050 ± 0.0080	1.0756 ± 0.0039
0.1000M $NaNO_3$	(I)	3.314 ± 0.0035	2.873 ± 0.0067	1.1535 ± 0.0029
0.1000M $NaNO_3$	(I)	3.281 ± 0.0116	2.873 ± 0.0067	1.1420 ± 0.0048
0.1000M $NaNO_3$	(L)	3.491 ± 0.0136	3.050 ± 0.0038	1.1446 ± 0.0047
0.05003M $NaBF_4$	(E)	$3.310 \pm 0.0056^*$	3.050 ± 0.0080	1.0852 ± 0.0034
0.05005M $NaBF_4$	(R)	$3.263 \pm 0.0057^*$	3.012 ± 0.0106	1.0833 ± 0.0042
0.1000M $NaBF_4$	(P')	$3.381 \pm 0.0048^*$	2.908 ± 0.0076	1.1627 ± 0.0035
0.1002M $NaBF_4$	(P')	$3.415 \pm 0.0076^*$	2.908 ± 0.0076	1.1743 ± 0.0041
0.05062M NaBr	(D)	3.309 ± 0.0035	2.947 ± 0.0079	1.1228 ± 0.0033
0.05017M NaBr	(A)	3.318 ± 0.0046	3.009 ± 0.0041	1.1027 ± 0.0021
0.05004M NaBr	(E)	3.390 ± 0.0071	3.050 ± 0.0080	1.1118 ± 0.0032
0.05006M NaBr	(E)	3.391 ± 0.0040	3.050 ± 0.0080	1.1115 ± 0.0037

Zeroth-Order Rates (continued)

Electrolyte	Solvent	$k_o(10^8)$(moles. litres.$^{-1}$secs.$^{-1}$)	$k_o^o(10^8)$(moles. litres.$^{-1}$secs.$^{-1}$)	k_o/k_o^o
0.1000M NaBr	(I)	3.553 ± 0.0055	2.873 ± 0.0067	1.2367 ± 0.0035
0.1000M NaBr	(I)	3.506 ± 0.0117	2.873 ± 0.0067	1.2203 ± 0.0050
0.1003M NaBr	(L)	3.758 ± 0.0179	3.050 ± 0.0038	1.2321 ± 0.0061
0.05185M HNO_3	(E)	3.362 ± 0.0044*	3.050 ± 0.0080	1.1023 ± 0.0032
0.05093M HNO_3	(E)	3.360 ± 0.0049*	3.050 ± 0.0080	1.1016 ± 0.0033
0.05068M HNO_3	(F)	3.354 ± 0.0108*	3.075 ± 0.0075	1.0907 ± 0.0044
0.05033M HNO_3	(R)	3.294 ± 0.0085*	3.012 ± 0.0106	1.0936 ± 0.0048
0.09940M HNO_3	(P')	3.425 ± 0.0067*	2.908 ± 0.0076	1.1778 ± 0.0039
0.09913M HNO_3	(P')	3.422 ± 0.0081*	2.908 ± 0.0076	1.1768 ± 0.0042
0.09944M HNO_3	(R)	3.527 ± 0.0159*	3.012 ± 0.0106	1.1710 ± 0.0042
0.04987M $NaClO_4$	(A)	3.454 ± 0.0049	3.009 ± 0.0041	1.1479 ± 0.0023
0.04987M $NaClO_4$	(A)	3.449 ± 0.0082	3.009 ± 0.0041	1.1462 ± 0.0031
0.1003M $NaClO_4$	(P)	3.782 ± 0.0050	2.934 ± 0.0063	1.2890 ± 0.0033
0.1001M $NaClO_4$	(P)	3.796 ± 0.0137	2.934 ± 0.0063	1.2938 ± 0.0054

Zeroth-Order Rates (continued)

Electrolyte	Solvent	$k_o(10^8)$(moles. litres.$^{-1}$secs.$^{-1}$)	$k_o^o(10^8)$(moles. litres.$^{-1}$secs.$^{-1}$)	k_o/k_o^o
0.05130M $HClO_4$	(E)	3.490 ± 0.0039*	3.050 ± 0.0080	1.1443 ± 0.0033
0.05145M $HClO_4$	(E)	3.522 ± 0.0057*	3.050 ± 0.0080	1.1548 ± 0.0035
0.09735M $HClO_4$	(P)	3.729 ± 0.0084*	2.934 ± 0.0063	1.2710 ± 0.0040
0.09438M $HClO_4$	(P')	3.762 ± 0.0091*	2.908 ± 0.0077	1.2937 ± 0.0046
0.09761M $HClO_4$	(P)	3.745 ± 0.0102*	2.934 ± 0.0063	1.2764 ± 0.0045
0.09771M $HClO_4$	(R)	3.819 ± 0.0087*	3.012 ± 0.0106	1.2679 ± 0.0053

* Followed by noting the development of chloride ion.

† Corrected for the retardation produced by the chloride ion present.

APPENDIX B

Details of individual experiments carried out to determine the effects of added electrolytes on the solubility of 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone at 20.18°C.

<u>EXPT. 41</u>. 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone. (A).

0.04991M $NaNO_3$ added.

5 ml. samples titrated with 0.004549N sodium hydroxide.

Time (hrs)	T_t (mls)	T_∞ (mls)	Solubility (10^3) (moles.litres.$^{-1}$)
16.678	2.12	10.49	7.615
16.678	2.12	10.46	7.590
42.854	5.48	13.75	7.525
66.680	8.54	16.82	7.533

Mean Solubility = 7.566 ± 0.019 x 10^{-3} moles.litres.$^{-1}$

EXPT. 42. 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (A).

0.04997M $NaSO_3Ph$ added.

5 ml. samples titrated with 0.004549N sodium hydroxide.

Time (hrs)	T_t (mls)	T_∞ (mls)	Solubility (10^3) $(\text{moles.litres.}^{-1})$
16.827	2.13	10.59	7.698
16.842	2.13	10.57	7.678
43.088	5.52	14.00	7.715

Mean Solubility = $7.697 \pm 0.009 \times 10^{-3}$ moles.litres.$^{-1}$

EXPT. 43. 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (A).

0.04987M $NaClO_4$ added.

5 ml. samples titrated with 0.004562N sodium hydroxide.

Time (hrs)	T_t (mls)	T_∞ (mls)	Solubility (10^3) (moles.litres.$^{-1}$)
40.661	5.50	13.90	7.692
84.952	11.50	19.95	7.787
84.938	11.50	19.91	7.750

Mean Solubility = 7.743 ± 0.023 x 10^{-3} moles. litres.$^{-1}$

APPENDIX C

Details of individual experiments carried out to determine the effects of solvent changes on the solubilities of organic chlorides in aqueous acetone mixtures.

<u>EXPT. 44</u>. 4-nitrodiphenylmethyl chloride in 40% (v/v) aqueous acetone (A) at 1.62°C.

5 ml. samples titrated with 0.004878N sodium hydroxide.

Time (hrs)	T_t (mls)	T_∞ (mls)	Solubility (10^4) (moles.litres.$^{-1}$)
24.000	——	1.11	8.976
24.417	——	1.11	8.976
24.567	0.19	1.11	8.976
*27.784	——	2.37	9.756
*27.984	——	2.32	9.365
28.134	0.20	1.15	9.286

* 10 ml. samples.

Mean Solubility = 9.223 ± 0.116 x 10^{-4} moles.litres.$^{-1}$

EXPT. 45. 4-nitrodiphenylmethyl chloride in 50% (v/v) aqueous acetone (C) at 1.62°C.

10 ml. samples titrated with 0.004878N sodium hydroxide.

Time (hrs)	T_t (mls)	T_∞ (mls)	Solubility (10^3) (moles.litres^{-1})
24.867	——	6.04	5.707
24.900	——	6.02	5.688
25.050	——	6.03	5.698
28.350	——	6.31	5.961
28.383	——	6.19	5.844
28.433	0.20	6.22	5.873
47.667	——	6.82	6.293
47.700	——	6.90	6.371
47.833	0.37	——	——
96.733*	——	6.82	5.978
96.766	0.72	——	——

* Sample titrated with 0.004900N sodium hydroxide.

Mean solubility = 5.935 ± 0.078 x 10^{-3} moles.litres^{-1}

EXPT. 46. 4-nitrobenzyl chloride in 40% (v/v) aqueous acetone (A) at 1.67°C.

5 ml. samples titrated with 0.004892N sodium hydroxide.

The amount of substrate hydrolysed during the measurement was undetectable.

Time (hrs)	T_∞ (mls)	Solubility (10^3) (moles. litres^{-1})
*23.667	2.92	6.6692
*28.900	2.92	6.6692
23.685	6.96	6.8096
23.817	6.97	6.8194
23.833	6.94	6.7900
24.067	6.93	6.7804
28.933	6.91	6.7608
29.233	6.95	6.7998
29.267	6.95	6.7998
29.350	6.96	6.8096

* Samples titrated with 0.01142N sodium hydroxide.

Mean solubility = $6.7708 \pm 0.0168 \times 10^{-3}$ moles.litres^{-1}

EXPT. 47. 4-nitrobenzyl chloride in 50% (v/v) aqueous acetone (C) at 1.67°C.

5 ml. samples titrated with 0.004902N sodium hydroxide.

The amount of substrate hydrolysed during measurement was undetectable.

Time (hrs)	T_∞ (mls)	Solubility (10^2) (moles.litres.$^{-1}$)
41.950	24.99	2.4500
41.983	25.00	2.4510
42.300	24.81	2.4324
42.350	24.93	2.4442
65.566	24.96	2.4470
65.600	24.88	2.4392
66.033	24.81	2.4324
66.083	24.95	2.4460
66.800	24.97	2.4480
*72.050	10.45	2.3804
†72.066	10.51	2.4004
†72.233	10.50	2.3982

* Sample titrated with 0.01139N sodium hydroxide.

† Samples titrated with 0.01142N sodium hydroxide.

Mean solubility = 2.4308 ± 0.0067 x 10^{-2} moles.litres.$^{-1}$

EXPT. 48. 4-nitrobenzyl chloride in 60% (v/v) aqueous acetone (A) at 1.67°C.

5 ml. samples titrated with 0.02112N silver nitrate.

The amount of substrate hydrolysed during measurement was undetectable.

Time (hrs)	T_∞ (mls)	Solubility (10^2) (moles.litres.$^{-1}$)
41.800	13.02	5.4996
41.916	12.96	5.4744
42.266	13.05	5.5125
42.300	13.16	5.5588
42.866	13.04	5.5080
65.466	13.08	5.2501
65.483	13.06	5.5166
65.933	13.02	5.4996
66.783	13.03	5.5038
*70.799	24.54	5.6050
*70.833	24.51	5.5980

* 5 ml. samples titrated with 0.01142N sodium hydroxide.

Mean solubility = 5.5274 ± 0.0121 x 10^{-2} moles. litres.$^{-1}$

EXPT. 49. 4-phenyl:4'-nitrodiphenylmethyl chloride in 50% (v/v) aqueous acetone (A) at 20.18°C.

5 ml. samples titrated with 0.005203N sodium hydroxide.

Time (hrs)	T_t (mls)	T_∞ (mls)	Solubility (10^4) (moles.litres.$^{-1}$)
0.166	0.01	0.21	2.186
0.450	0.04	0.28	2.496
0.550	0.05	0.30	2.498
2.266	0.19	0.38	1.978
24.250	1.99	2.18	1.978

Mean solubility = 2.227×10^{-4} moles. litres.$^{-1}$

<u>EXPT. 50</u>. 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (A) at 20.18°C.

5 ml. samples titrated with 0.003679N sodium hydroxide.

Time (hrs)	T_t (mls)	T_∞ (mls)	Solubility (10^3) (moles.litres^{-1})
0.148	0.01	10.23	7.519
0.151	0.02	10.01	7.323
0.558	0.09	10.41	7.548
0.581	0.09	10.51	7.671
1.251	0.18	10.60	7.670
1.629	0.24	10.44	7.460
3.792	0.57	10.94	7.631
6.171	0.90	11.28	7.640
25.093	3.64	13.94	7.578
25.561	3.51	13.79	7.518
27.539	4.04	14.34	7.582
28.881	4.20	14.51	7.590
29.555	4.31	14.60	7.569
72.107	10.68	20.90	7.471

Mean solubility = 7.551 ± 0.024 x 10^{-3} moles. litres^{-1}

<u>EXPT. 51</u>. 4-phenyl:4'-nitrodiphenylmethyl chloride in 85% (v/v) aqueous acetone (A) at 20.18°C.

5 ml. samples titrated with 0.005203N sodium hydroxide.

Time (hrs)	T_t (mls)	T_∞ (mls)	Solubility (10^2) (moles.litres.$^{-1}$)
0.216	0.01	37.67	(3.919)
0.466	0.02	40.30	(4.192)
0.733	0.03	44.03	4.579
2.333	0.11	45.53	4.726
24.316	1.18	46.17	4.682

Mean solubility = $4.662 \pm 0.036 \times 10^{-2}$ moles. litres.$^{-1}$

APPENDIX D

Details of individual experiments carried out to investigate the effects of solvent changes on the first-order rates of solvolysis of organic chlorides in aqueous acetone mixtures.

EXPT. 52. 0.005593M 4-nitrodiphenylmethyl chloride in 50% (v/v) aqueous acetone at 20.18°C.

10 ml. samples titrated with 0.004840N sodium hydroxide.

Time (hrs)	Titre (mls)	10^6 k_1 (secs.^{-1})
0	0.10	———
7.500	1.71	5.723
23.950	4.49	5.737
27.183	4.94	5.747
31.183	5.39	5.664
48.033	7.10	5.630
51.233	7.44	5.731
55.233	7.77	5.759
58.966	8.06	5.791
74.066	8.97	5.826
∞	11.35	———

Mean k_1 = 5.734 ± 0.0187 x 10^{-6} secs.^{-1}

Duplicate Experiment.

Mean k_1 = 5.797 ± 0.0266 x 10^{-6} secs.^{-1}

Overall Mean

$(k_1)_m$ = 5.766 ± 0.0176 x 10^{-6} secs.^{-1}

EXPT. 53. 0.004319M 4-nitrodiphenylmethyl chloride in 50% (v/v) aqueous acetone (C) at 40.12°C.

6.2 ml. samples titrated with 0.005236N sodium hydroxide.

Time (hrs)	Titre (mls)	10^5 k_1 (secs.$^{-1}$)
0	0	———
0.450	0.49	6.440
1.367	1.38	(6.748)
1.967	1.80	6.381
2.700	2.35	6.627
3.300	2.79	(6.983)
3.883	2.96	6.519
4.516	3.20	6.420
4.966	3.40	6.497
5.399	3.56	6.535
5.982	3.72	6.466
7.199	4.02	6.452
∞	4.95	———

Mean k_1 = 6.495 ± 0.0216 x 10^{-5} secs.$^{-1}$

Duplicate Experiment.

Mean k_1 = 6.546 ± 0.0178 x 10^{-5} secs.$^{-1}$

Overall Mean.

$(k_1)_m$ = 6.517 ± 0.0160 x 10^{-5} secs.$^{-1}$

<u>EXPT. 54</u>. 0.005371M 4-nitrobenzyl chloride in 40% (v/v) aqueous acetone (A) at 71.42°C.

6.2 ml. samples titrated with 0.004897N sodium hydroxide.

Time (hrs)	Titre (mls)	k_1 $(10^6)(\text{secs}^{-1})$
0	0	——
13.667	1.24	(4.096)
17.850	1.66	4.358
24.217	1.97	(3.926)
37.667	3.08	4.450
41.667	3.29	4.409
50.317	3.77	4.462
61.500	4.28	4.484
73.783	4.72	4.460
85.916	5.15	4.579
98.449	5.46	4.583
110.416	5.64	4.450
121.899	5.63	(4.011)
∞	6.80	——

Mean $k_1 = 4.471 \pm 0.0224 \times 10^{-6} \text{secs.}^{-1}$

<u>Duplicate Experiment</u>.

Mean $k_1 = 4.480 \pm 0.0186 \times 10^{-6}$ secs.$^{-1}$

<u>Overall Mean</u>.

$(k_1)_m = 4.475 \pm 0.0151 \times 10^{-6}$ secs.$^{-1}$

<u>EXPT. 55</u>. 0.004960N 4-nitrobenzyl chloride in 40% (v/v) aqueous acetone (A) at 97.66°C.

6.2 ml. samples titrated with 0.004897M sodium hydroxide.

Time (hrs)	Titre (mls)	k_1 $(10^5)(\mathrm{secs.}^{-1})$
0	0	———
0.950	0.70	3.711
1.700	1.22	(3.530)
2.733	1.84	(3.520)
3.800	2.47	3.653
4.717	2.96	3.755
5.700	3.31	3.649
7.150	3.86	3.706
9.567	4.56	3.761
10.317	4.69	3.699
10.950	4.81	3.684
∞	6.28	———
0	0	———
15.016	5.15	3.661
16.133	5.42	3.657
∞	6.28	———

Mean k_1 = 3.694 ± 0.0121 x 10^{-5} $\mathrm{secs.}^{-1}$

<u>Duplicate Experiment</u>.

Mean k_1 = 3.720 ± 0.0137 x 10^{-5} $\mathrm{secs.}^{-1}$

<u>Overall Mean</u>.

$(k_1)_m$ = 3.706 ± 0.00996 x 10^{-5} $\mathrm{secs.}^{-1}$

EXPT. 56. 0.01752N 4-nitrobenzyl chloride in 50% (v/v) aqueous acetone (C) at 71.42°C.

6.2 ml. samples titrated with 0.01072M sodium hydroxide.

Time (hrs)	Titre (mls)	k_1 (10^6)(secs.$^{-1}$)
0	0.12	———
9.000	0.89	2.459
24.167	1.99	2.380
45.434	3.36	2.394
55.467	3.92	2.391
71.617	4.71	2.380
97.834	5.76	2.354
116.967	6.48	2.396
128.100	6.78	2.374
143.850	7.29	2.433
166.467	7.80	2.433
196.067	8.34	2.439
222.917	8.66	2.391
∞	10.13	———

Mean $k_1 = 2.402 \pm 0.00871 \times 10^{-6}$ secs.$^{-1}$

EXPT. 57. 0.01713M 4-nitrobenzyl chloride in 50% (v/v) aqueous acetone (C) at 97.66°C.

6.2 ml. samples titrated with 0.01058M sodium hydroxide.

Time (hrs)	Titre (mls)	k_1 $(10^5)(\text{secs.}^{-1})$
0	0.09	—
13.500	6.38	2.058
18.000	7.41	2.054
21.350	8.01	2.068
25.000	8.50	2.073
∞	10.04	—
0	0.10	—
4.016	2.64	2.040
5.717	3.48	2.019
7.783	4.42	2.036
11.417	5.76	2.050
24.367	8.37	2.034
27.950	8.79	2.010
31.583	9.11	2.084
34.750	9.30	2.077
∞	10.04	—

Mean $k_1 = 2.050 \pm 0.00642 \times 10^{-5}$ secs.^{-1}

Duplicate Experiment.

Mean $k_1 = 2.046 \pm 0.00314 \times 10^{-5}$ secs.^{-1}

Overall Mean.

$(k_1)_m = 2.048 \pm 0.00393 \times 10^{-5}$ secs.^{-1}

EXPT. 58. 0.01262M 4-nitrobenzyl chloride in 60% (v/v) aqueous acetone (A) at 71.42°C.

6.2 ml. samples titrated with 0.01149M sodium hydroxide.

Time (hrs)	Titre (mls)	k_1 $(10^6)(\text{secs.}^{-1})$
0	0	——
42.650	1.18	1.242
78.050	1.99	1.230
119.116	2.77	1.219
167.333	3.59	1.244
190.400	3.89	1.236
214.400	4.16	1.223
246.216	4.58	1.260
292.883	4.94	1.226
336.666	5.30	1.243
381.016	5.52	1.213
403.516	5.71	1.255
∞	6.81	——

Mean $k_1 = 1.236 \pm 0.00427 \times 10^{-6}$ secs.$^{-1}$

Duplicate Experiment.

Mean $k_1 = 1.234 \pm 0.00683 \times 10^{-6}$ secs.$^{-1}$

Overall Mean.

$(k_1)_m = 1.235 \pm 0.00390 \times 10^{-6}$ secs.$^{-1}$

<u>EXPT. 59</u>. 0.01837M 4-nitrobenzyl chloride in 60% (v/v) aqueous acetone (A) at 97.66°C.

6.2 ml. samples titrated with 0.01154M sodium hydroxide.

Time (hrs)	Titre (mls)	k_1 (10^5)(secs.$^{-1}$)
0	0	——
3.983	1.37	1.043
6.450	2.06	1.010
11.017	3.27	1.014
27.383	6.24	1.015
30.566	6.38	(0.945)
36.166	7.25	1.019
∞	9.87	——
0	0	——
15.000	4.18	1.017
19.767	5.11	1.025
23.515	5.71	1.021
36.467	7.26	1.013
42.500	7.80	1.021
62.245	8.85	1.018
∞	9.87	——

Mean k_1 = 1.020 ± 0.00254 x 10^{-5} secs.$^{-1}$

<u>Duplicate Experiment</u>.

Mean k_1 = 1.030 ± 0.00300 x 10^{-5} secs.$^{-1}$

<u>Overall Mean</u>.

$(k_1)_m$ = 1.024 ± 0.00229 x 10^{-5} secs.$^{-1}$

EXPT. 60. 0.002074M 4-phenyl:4'-nitrodiphenylmethyl chloride in 65% (v/v) aqueous acetone (A) at 20.18°C. 20 ml. samples titrated with 0.005325M sodium hydroxide.

Time (hrs)	Titre (mls)	k_1 $(10^5)(\text{secs.}^{-1})$
0	0.28	——
4.650	1.39	0.953
8.850	2.38	1.030
21.417	4.37	1.020
27.984	4.91	0.952
33.201	5.46	0.979
50.068	6.52	0.986
52.735	6.60	0.971
∞	7.79	——
0	0.40	——
11.800	1.69	1.027
18.533	2.19	1.010
37.433	3.20	1.081
43.233	3.40	1.109
∞	4.05	——

Mean $k_1 = 1.011 \pm 0.0144 \times 10^{-5}$ secs.$^{-1}$

<u>EXPT. 61</u>. 0.003760M 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (F) at 20.18°C. 10 ml. samples titrated with 0.005208M sodium hydroxide.

Time (hrs)	Titre (mls)	k_1 $(10^6)(\text{secs.}^{-1})$
0	0.15	——
16.600	1.66	4.027
20.350	1.95	4.014
23.750	2.21	4.029
27.783	2.49	4.020
40.466	3.25	3.963
44.132	3.44	3.940
47.998	3.62	3.907
52.298	3.83	3.907
64.598	4.42	3.984
68.098	4.61	4.126
77.398	4.83	3.893
89.881	5.31	4.045
118.414	6.01	4.141
∞	7.22	

Mean $k_1 = 4.000 \pm 0.0209 \times 10^{-6}$ secs.$^{-1}$

EXPT. 62. 0.002990M 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (G) at 20.18°C. 10 ml. samples titrated with 0.005274M sodium hydroxide.

Time (hrs)	Titre (mls)	k_1 $(10^6)(\text{secs.}^{-1})$
0	0.09	———
16.433	1.28	4.052
20.000	1.46	(3.909)
27.967	1.98	4.108
40.867	2.62	4.109
46.484	2.81	3.994
52.267	3.02	3.958
64.700	3.49	4.036
93.417	4.24	4.049
98.350	4.34	4.050
112.717	4.60	4.070
123.500	4.77	4.104
136.767	4.90	4.023
∞	5.67	———

Mean $k_1 = 4.050 \pm 0.0137 \times 10^{-6} \text{secs.}^{-1}$

Duplicate Experiment.

Mean $k_1 = 4.055 \pm 0.0124 \times 10^{-6} \text{secs.}^{-1}$

Overall Mean.

$(k_1)_m = 4.052 \pm 0.0095 \times 10^{-6} \text{secs.}^{-1}$

EXPT. 63. 0.005151M 4-phenyl:4'-nitrodiphenylmethyl chloride in 75% (v/v) aqueous acetone (A) at 20.18°C. 8.28 ml. samples titrated with 0.005325M sodium hydroxide.

Time (hrs)	Titre (mls)	k_1 $(10^6)(\text{secs.}^{-1})$
0	0.20	———
21.050	1.18	1.808
42.833	2.02	1.721
64.933	2.90	1.813
93.700	3.80	1.832
115.300	4.37	1.840
139.250	4.98	1.890
160.133	5.20	1.773
186.766	5.72	1.825
213.116	6.09	1.829
239.033	6.47	1.887
263.783	6.69	1.872
∞	8.01	———

Mean $k_1 = 1.826 \pm 0.0142 \times 10^{-6}$ secs.^{-1}

Duplicate Experiment.

Mean $k_1 = 1.820 \pm 0.0098 \times 10^{-6}$ secs.^{-1}

Overall Mean.

$(k_1)_m = 1.823 \pm 0.0088 \times 10^{-6}$ secs.^{-1}

EXPT. 64. 0.006298M 4-phenyl:4'-nitrodiphenylmethyl chloride in 85% (v/v) aqueous acetone (C) at 71.13°C. 6.2 ml. samples titrated with 0.005388M sodium hydroxide.

Time (mins)	Titre (mls)	$k_1(10^5)(\text{secs.}^{-1})$
0	0.06	———
30.000	0.93	7.178
60.000	1.71	7.254
90.000	2.38	7.212
120.000	2.96	7.174
150.000	3.49	7.201
180.000	3.92	7.126
212.000	4.38	7.220
240.000	4.72	7.254
270.000	4.97	7.092
300.000	5.24	7.082
341.000	5.62	7.255
390.000	5.92	7.213
450.000	6.20	7.127
∞	7.25	———

Mean $k_1 = 7.184 \pm 0.0169 \times 10^{-5}$ secs.$^{-1}$

Duplicate Experiment.

Mean $k_1 = 7.233 \pm 0.0315 \times 10^{-5}$ secs.$^{-1}$

Overall Mean.

$(k_1)_m = 7.209 \pm 0.0180 \times 10^{-5}$ secs.$^{-1}$

EXPT. 65. 0.006083M 4-phenyl:4'-nitrodiphenylmethyl chloride in 85% (v/v) aqueous acetone (C) at 90.99°C. 6.2 ml. samples titrated with 0.05388M sodium hydroxide.

Time (mins)	Titre (mls)	k_1 (10^4)(secs.^{-1})
0	0.14	——
6.000	0.93	(3.397)
12.000	1.76	3.736
18.000	2.40	3.700
24.000	2.95	3.662
30.000	3.46	3.677
36.000	3.95	3.752
42.000	4.23	(3.599)
48.000	4.61	3.661
54.000	4.91	3.669
64.000	5.33	3.680
74.000	5.61	(3.596)
84.000	5.93	3.688
∞	7.00	——

Mean k_1 = 3.692 ± 0.0102 x 10^{-4} secs.^{-1}

Duplicate Experiment.

Mean k_1 = 3.716 ± 0.0139 x 10^{-4} secs.^{-1}

Overall Mean.

$(k_1)_m$ = 3.706 ± 0.0096 x 10^{-4} secs.^{-1}

APPENDIX E

Details of individual experiments carried out to determine the effects of changes in the solvent composition on the zeroth-order rates of solvolysis of organic chlorides in aqueous acetone mixtures.

EXPT. 66. 4-nitrodiphenylmethyl chloride in 40% (v/v) aqueous acetone at 1.62°C.

5 ml. samples titrated with sodium hydroxide.

Time (hrs)	Titre (mls)	Normality of NaOH. (10^3)	k_o (10^9)(moles. litres.$^{-1}$secs.$^{-1}$)
0	0	——	——
435.834	3.07	5.280	2.066
461.734	3.28	5.269	2.080
606.417	4.44	5.274	2.146
773.950	5.52	5.308	2.090
942.750	6.86	5.297	2.141
1110.517	8.61	5.000	2.154

Mean k_o = 2.113 ± 0.0143 x 10^{-9} moles.litres.$^{-1}$secs.$^{-1}$

<u>EXPT. 67</u>. 4-nitrodiphenylmethyl chloride in 50% (v/v) aqueous acetone (C) at 1.62°C.

5 ml. samples titrated with sodium hydroxide.

Time (hrs)	Titre (mls)	Normality of NaOH. (10^3)	k_o (10^9)(moles. litres.$^{-1}$secs.$^{-1}$)
0	0.19	——	——
40.967	0.44	5.277	(1.789)
141.950	1.05	5.280	(1.775)
477.000	3.53	5.280	2.054
502.583	3.81	5.269	2.109
647.366	4.84	5.274	2.105
815.033	6.11	5.308	2.143
983.816	7.30	5.297	2.126
1151.416	9.04	5.000	2.135
1340.466	10.49	5.000	2.134
1509.733	11.65	5.000	2.109
1679.511	12.63	5.000	2.058

Mean k_o = 2.108 ± 0.0102 x 10^{-9} moles.litres.$^{-1}$secs.$^{-1}$

EXPT. 68. 4-phenyl:4'-nitrodiphenylmethyl chloride in 50% (v/v) aqueous acetone (C) at 20.18°C.

5 ml. samples titrated with 0.004883M sodium hydroxide.

Time (hrs)	Titre (mls)	k_o (10^8)(moles.litres.$^{-1}$secs.$^{-1}$)
0	0.03	——
4.783	0.44	2.325
16.766	1.45	2.298
21.767	1.89	2.328
28.360	2.43	2.296
40.860	3.49	2.297
46.660	3.97	2.291
51.610	4.41	2.302
64.860	5.57	2.316
70.010	5.97	2.302
89.627	7.64	2.301
93.860	8.02	2.309

Mean k_o = 2.306 ± 0.0035 x 10^{-8} moles.litres.$^{-1}$secs.$^{-1}$

Additional Experiments.

Mean k_o = 2.300 ± 0.0048 x 10^{-8} moles.litres.$^{-1}$secs.$^{-1}$

Mean k_o = 2.345 ± 0.0084 x 10^{-8} moles.litres.$^{-1}$secs.$^{-1}$

Overall Mean.

$(k_o)_m$ = 2.318 ± 0.0050 x 10^{-8} moles.litres.$^{-1}$secs.$^{-1}$

EXPT. 69. 4-phenyl:4'-nitrodiphenylmethyl chloride in 65% (v/v) aqueous acetone (A) at 20.18°C.

5 ml. samples titrated with 0.005313M sodium hydroxide.

Time (hrs)	Titre (mls)	k_o (10^8)(moles.litres.$^{-1}$secs.$^{-1}$)
0	0.09	——
16.167	1.83	3.176
20.450	2.31	3.206
23.483	2.68	3.256
40.050	4.57	3.303
44.800	4.84	3.129
48.017	5.20	3.141
63.934	6.90	3.143
68.833	7.41	3.138
72.033	7.78	3.152
87.966	9.45	3.141

Mean k_o = 3.179 ± 0.0177 x 10^{-8} moles.litres.$^{-1}$secs.$^{-1}$

Additional Experiments.

Mean k_o = 3.195 ± 0.0089 x 10^{-8} moles. litres.$^{-1}$secs.$^{-1}$

Mean k_o = 3.143 ± 0.0063 x 10^{-8} moles. litres.$^{-1}$secs.$^{-1}$

Overall Mean.

$(k_o)_m$ = 3.173 ± 0.0077 x 10^{-8} moles.litres.$^{-1}$secs.$^{-1}$

<u>EXPT. 70</u>. 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (F) at 20.18°C.

5 ml. samples titrated with 0.005203M sodium hydroxide.

Time (hrs)	Titre (mls)	k_o (10^8)(moles.litres^{-1}secs^{-1})
0.366	0.07	———
13.183	1.45	3.114
16.283	1.79	3.126
20.633	2.26	3.126
23.649	2.56	3.091
37.515	4.00	3.059
40.448	4.31	3.059
44.031	4.71	3.074
61.014	6.54	3.086
65.114	6.93	3.062
68.180	7.24	3.057
72.380	7.67	3.054
85.746	9.10	3.060
89.029	9.37	3.034
95.612	10.13	3.054

Mean $k_o = 3.075 \pm 0.0075 \times 10^{-8}$ moles.litres^{-1}secs^{-1}

EXPT. 71. 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (G) at 20.18°C.

5 ml. samples titrated with 0.005000M sodium hydroxide.

Time (hrs)	Titre (mls)	k_o (10^8)(moles.litres^{-1}secs^{-1})
0	0.09	——
9.567	1.06	(2.817)
21.850	2.45	3.000
25.667	2.84	2.975
34.384	3.71	2.925
46.451	5.06	2.972
51.501	5.59	2.967
57.318	6.20	2.961
70.968	7.63	2.950
81.185	8.71	2.950
96.102	10.28	2.944
105.902	11.32	2.944
118.985	12.72	2.947

Mean k_o = 2.958 ± 0.0058 x 10^{-8} moles.litres^{-1}secs^{-1}

Duplicate Experiment.

Mean k_o = 2.947 ± 0.0108 x 10^{-8} moles.litres^{-1}secs^{-1}

Overall Mean.

$(k_o)_m$ = 2.952 ± 0.0064 x 10^{-8} moles.litres^{-1}secs^{-1}

<u>EXPT. 72</u>. 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (I') at 20.18°C.

5 ml. samples titrated with 0.004883M sodium hydroxide.

Time (hrs)	Titre (mls)	k_o (10^8)(moles.litres.$^{-1}$secs.$^{-1}$)
0	0.12	——
16.800	1.93	2.922
21.700	2.50	(2.976)
28.550	3.18	2.908
41.083	4.53	2.911
46.866	5.17	2.924
51.733	5.70	2.927
65.016	7.10	2.913
70.183	7.62	2.900
74.533	8.11	2.908
89.783	9.78	2.919
94.016	10.18	2.902
98.949	10.72	2.905

Mean k_o = 2.913 ± 0.0026 x 10^{-8} moles.litres.$^{-1}$secs.$^{-1}$

<u>Additional Experiments</u>.

Mean k_o = 2.916 ± 0.0029 x 10^{-8} moles.litres.$^{-1}$secs.$^{-1}$
Mean k_o = 2.904 ± 0.0060 x 10^{-8} moles.litres.$^{-1}$secs.$^{-1}$

<u>Overall Mean</u>.

$(k_o)_m$ = 2.911 ± 0.0025 x 10^{-8} moles.litres.$^{-1}$secs.$^{-1}$

EXPT. 73. 4-phenyl:4'-nitrodiphenylmethyl chloride in 75% (v/v) aqueous acetone (A) at 20.18°C.

5 ml. samples titrated with 0.00531M sodium hydroxide.

Time (hrs)	Titre (mls)	k_o (10^8)(moles.litres.$^{-1}$secs.$^{-1}$)
0	0.06	——
16.150	1.53	2.687
20.437	1.92	2.686
23.454	2.21	2.706
40.037	3.71	2.691
44.737	4.16	2.705
48.037	4.42	2.679
63.937	5.83	2.664
68.820	6.25	2.655
72.020	6.58	2.672
87.970	8.19	2.728

Mean k_o = 2.687 ± 0.0065 x 10^{-8} moles.litres.$^{-1}$secs.$^{-1}$

Additional Experiments.

Mean k_o = 2.687 ± 0.0069 x 10^{-8} moles.litres.$^{-1}$secs.$^{-1}$
Mean k_o = 2.705 ± 0.0123 x 10^{-8} moles.litres.$^{-1}$secs.$^{-1}$

Overall Mean.

$(k_o)_m$ = 2.693 ± 0.0055 x 10^{-8} moles.litres.$^{-1}$secs.$^{-1}$

EXPT. 74. 4-phenyl:4'-nitrodiphenylmethyl chloride in 85% (v/v) aqueous acetone (C) at 20.18°C.

5 ml. samples titrated with 0.005000M sodium hydroxide.

Time (hrs)	Titre (mls)	k_o (10^8)(moles.litres.$^{-1}$secs.$^{-1}$)
0	0.10	———
21.866	1.28	(1.499)
25.633	1.43	1.441
34.316	1.90	1.457
46.316	2.49	1.433
51.399	2.78	1.448
57.182	3.03	1.423
70.949	3.76	1.433
81.099	4.24	1.418
95.966	4.98	1.413
105.799	5.48	1.413
118.949	6.17	1.418

Mean k_o = 1.430 ± 0.0046 x 10^{-8} moles.litres.$^{-1}$secs.$^{-1}$

Additional Experiments.

Mean k_o = 1.432 ± 0.0073 x 10^{-8} moles.litres.$^{-1}$secs.$^{-1}$
Mean k_o = 1.410 ± 0.0031 x 10^{-8} moles.litres.$^{-1}$secs.$^{-1}$

Overall Mean.

$(k_o)_m$ = 1.424 ± 0.0034 x 10^{-8} moles.litres.$^{-1}$secs.$^{-1}$

EXPT. 75. 4-phenyl:4'-nitrodiphenylmethyl chloride in 50% (v/v) aqueous acetone (C) at 9.46°C.

5 ml. samples titrated with sodium hydroxide.

Time (hrs)	Titre (mls)	Normality of NaOH (10^3)	k_o(10^9)(moles. litres.$^{-1}$secs.$^{-1}$)
0	0.02	4.955	———
48.000	0.54	4.955	(2.981)
120.000	1.22	4.955	2.753
168.000	1.72	4.975	2.797
216.000	2.20	4.975	2.789
288.000	2.80	5.071	2.660
336.000	3.28	5.094	2.746
384.100	3.75	5.094	2.749
480.100	4.68	5.094	2.747
528.100	5.15	5.094	2.750
576.100	5.62	5.094	2.752

Mean k_o = 2.749 ± 0.0121 x 10^{-9} moles.litres.$^{-1}$secs.$^{-1}$

Duplicate Experiment.

Mean k_o = 2.735 ± 0.0167 x 10^{-9} moles.litres.$^{-1}$secs.$^{-1}$

Overall Mean.

$(k_o)_m$ = 2.742 ± 0.0107 x 10^{-9} moles.litres.$^{-1}$secs.$^{-1}$

EXPT. 76. 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (I') at 9.46°C.

5 ml. samples titrated with sodium hydroxide.

Time (hrs)	Titre (mls)	Normality of NaOH (10^3)	$k_o(10^9)$(moles. litres.$^{-1}$secs.$^{-1}$)
0	0.07	4.955	———
48.000	0.74	4.955	3.843
120.000	1.70	4.955	3.739
168.000	2.38	4.975	3.800
216.000	3.00	4.975	3.748
288.000	3.92	5.071	3.766
336.000	4.52	5.094	3.749
384.117	5.18	5.094	3.764
480.117	6.56	5.094	3.827
528.117	7.21	5.094	3.827
576.117	7.85	5.094	3.821

Mean k_o = 3.788 ± 0.0113 x 10^{-9} moles.litres.$^{-1}$secs.$^{-1}$

Duplicate Experiment.

Mean k_o = 3.812 ± 0.0159 x 10^{-9} moles.litres.$^{-1}$secs.$^{-1}$

Overall Mean.

$(k_o)_m$ = 3.800 ± 0.0102 x 10^{-9} moles.litres.$^{-1}$secs.$^{-1}$

EXPT. 77. 4-phenyl:4'-nitrodiphenylmethyl chloride in 85% (v/v) aqueous acetone (C) at 9.46°C.

5 ml samples titrated with sodium hydroxide.

Time (hrs)	Titre (mls)	Normality of NaOH (10^3)	$k_o(10^9)$(moles. litres^{-1} secs^{-1})
0	0.07	4.955	——
48.000	0.42	4.955	2.008
120.000	0.95	4.955	2.019
168.000	1.30	4.975	2.023
216.000	1.64	4.975	2.009
288.000	2.11	5.071	1.995
336.000	2.45	5.094	2.005
384.117	2.77	5.094	1.990
480.117	3.44	5.094	1.987
528.117	3.77	5.094	1.983
576.117	4.09	5.094	1.973

Mean $k_o = 1.999 \pm 0.0048 \times 10^{-9}$ moles.litres^{-1}secs^{-1}

Duplicate Experiment.

Mean $k_o = 1.996 \pm 0.0118 \times 10^{-9}$ moles. litres^{-1} secs^{-1}

Overall Mean.

$(k_o)_m = 1.997 \pm 0.0102 \times 10^{-9}$ moles. litres^{-1} secs^{-1}

EXPT. 78. 4-phenyl:4'-nitrodiphenylmethyl chloride in 50% (v/v) aqueous acetone (C) at 1.71°C.

5 ml. samples titrated with sodium hydroxide.

Time (hrs)	Titre (mls)	Normality of NaOH (10^3)	$k_o(10^{10})$(moles. litres^{-1}secs^{-1})
0	0.00	4.883	——
642.617	1.24	4.776	5.293
959.934	1.82	4.950	5.214
1319.934	2.48	4.955	5.172
1703.934	3.10	5.107	5.159
2182.101	3.90	5.133	5.098
2634.468	4.81	5.082	5.155
3023.851	5.44	5.082	5.077
3551.851	6.63	4.970	5.157
4007.851	7.60	4.864	5.129
4343.851	8.34	4.820	5.141
4679.851	9.02	4.826	5.168
5013.951	9.53	4.845	5.049
5326.684	9.96	4.941	5.133

Mean k_o = 5.154 ± 0.0161 x 10^{-10} moles.litres^{-1}secs^{-1}

Duplicate Experiment.

Mean k_o = 5.078 ± 0.0374 x 10^{-10} moles.litres^{-1}secs^{-1}

Overall Mean.

$(k_o)_m$ = 5.114 ± 0.0214 x 10^{-10} moles.litres^{-1}secs^{-1}

<u>EXPT. 79</u>. 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone (I') at 1.71°C.

5 ml. samples titrated with sodium hydroxide.

Time (hrs)	Titre (mls)	Normality of NaOH (10^3)	$k_o(10^{10})$(moles. litres.$^{-1}$secs.$^{-1}$)
0	0.01	4.883	———
642.617	1.92	4.776	(7.886)
959.767	2.65	4.950	7.565
1319.767	3.63	4.955	7.550
1703.767	4.58	5.107	7.606
2182.067	6.00	5.133	(7.831)
2634.450	7.39	5.082	(7.905)
3023.850	7.87	5.082	7.335
3551.850	9.67	4.970	7.510
4007.850	10.94	4.864	7.377
4343.850	12.18	4.820	7.503
4679.850	13.28	4.826	7.604
5013.900	14.54	4.845	(7.800)
5326.250	14.70	4.941	7.571
5685.983	14.68	5.313	7.618

Mean k_o = 7.524 ± 0.0291 x 10^{-10} moles.litres.$^{-1}$secs.$^{-1}$

<u>Duplicate Experiment</u>.

Mean k_o = 7.565 ± 0.0307 x 10^{-10} moles.litres.$^{-1}$secs.$^{-1}$

<u>Overall Mean</u>.

$(k_o)_m$ = 7.548 ± 0.0221 x 10^{-10} moles.litres.$^{-1}$secs.$^{-1}$

EXPT. 80. 4-phenyl:4'nitrodiphenylmethyl chloride in 85% (v/v) aqueous acetone (C) at 1.71°C.

5 ml. samples titrated with sodium hydroxide.

Time (hrs)	Titre (mls)	Normality of NaOH (10^3)	$k_o(10^{10})$(moles. litres.$^{-1}$secs.$^{-1}$)
0	0.02	4.883	——
357.800	0.64	4.771	4.598
642.600	1.03	4.776	4.323
959.983	1.61	4.950	4.544
1319.983	2.13	4.955	4.358
1703.983	2.85	5.107	(4.711)
2182.033	4.03	5.133	(5.243)
2638.433	4.35	5.082	4.634
3027.850	4.56	5.082	4.231
3555.850	5.88	4.970	4.553
4011.850	6.49	4.864	4.362
4341.850	7.16	4.820	4.397
4683.850	7.72	4.826	4.408
5017.883	8.24	4.845	4.408
5330.416	8.35	4.941	4.290
5692.983	8.48	5.313	4.388

Mean k_o = 4.423 ± 0.0327 x 10^{-10} moles.litres.$^{-1}$secs.$^{-1}$

Duplicate Experiment.

Mean k_o = 4.425 ± 0.0322 x 10^{-10} moles.litres.$^{-1}$secs.$^{-1}$

Overall Mean.

$(k_o)_m$ = 4.424 ± 0.0230 x 10^{-10} moles.litres.$^{-1}$secs.$^{-1}$

EXPT. 81. 4-phenyl:4'-nitrodiphenylmethyl chloride in 85% (v/v) aqueous acetone (C) at 1.62°C.

5 ml. samples titrated with sodium hydroxide.

Time (hrs)	Titre (mls)	Normality of NaOH (10^3)	$k_o(10^{10})$(moles. litres.$^{-1}$secs.$^{-1}$)
0	0.10	5.000	———
498.467	0.87	5.000	4.292
648.334	1.17	4.721	4.327
817.301	1.41	4.721	4.205
1005.301	1.63	4.757	4.023
1170.418	1.92	4.735	4.090
1513.085	2.15	5.400	4.071
1846.335	2.58	5.435	4.056
2201.885	3.57	4.902	4.292

Mean $k_o = 4.170 \pm 0.0478 \times 10^{-10}$ moles.litres.$^{-1}$secs.$^{-1}$

Duplicate Experiment.

Mean $k_o = 4.256 \pm 0.0128 \times 10^{-10}$ moles.litres.$^{-1}$secs.$^{-1}$

Overall Mean.

$(k_o)_m = 4.213 \pm 0.0205 \times 10^{-10}$ moles.litres.$^{-1}$secs.$^{-1}$

APPENDIX F.

The results obtained from a study of the effect of added hydrochloric acid on 70% (V/V) aqueous acetone at 20.18°C.

In this investigation, 5 mls. of 0.1M hydrochloric acid were added to 100 mls. of 70% (V/V) aqueous acetone (E) at 20.18°C, and 10 ml. samples of the mixture were titrated with 0.004587N sodium hydroxide at various times.

EXPT. 82. A check on the reaction between hydrochloric acid and 70% (v/v) aqueous acetone at 20.18°C.

Time (hrs)	Change in titre (mls)
0	0
24.050	-0.03
47.366	-0.01
71.566	-0.01
119.499	+0.03
144.149	-0.04

As there was no appreciable change in the titre with time, it can be assumed that there was no significant reaction between the hydrochloric acid and the acetone-water mixtures used in the present investigations.

APPENDIX G.

The results of an experiment carried out to determine the amount of hydrochloric acid absorbed by solid 4-phenyl:4'-nitrodiphenylmethyl chloride during the measurement of zeroth-order rates and solubilities.

The procedure used was similar to that employed for the measurement of zeroth-order rates except that hydrogen chloride gas was first bubbled through the solvent until the solution was 0.008654N in hydrochloric acid.

EXPT. 83. 4-phenyl:4'-nitrodiphenylmethyl chloride in 70% (v/v) aqueous acetone at 20.18°C.

5 ml. samples titrated with 0.004778N sodium hydroxide.

Time (hrs)	Change in the titre (mls)†
0	0
0.131	+0.04
0.324	-0.03
0.487	+0.14
0.855	-0.02
1.083	+0.03
1.419	+0.01

† Titres were corrected for the hydrochloric acid produced by hydrolysis.

The above results show that the amount of acid absorbed by the solid organic halide during the measurement of zeroth-order rates or solubilities is likely to be negligibly small.

APPENDIX H.

The density and strength of samples of A.R. perchloric and nitric acids used in the study of electrolyte effects.

EXPT. 84. The determination of the strengths and densities of A.R. Perchloric and A.R. Nitric acids at 21.4°C.

	A.R. Perchloric Acid	A.R. Nitric Acid
†Weight of 25 ml. of water (gms)	24.8785	24.8785
†Weight of 25 mls. of acid (gms)	32.0062	35.2139
Density gms/ml.	1.2838	1.4125
Normality of acid	4.92	15.99

†Mean of 4 separate weighings.

APPENDIX I.

Experimental values of the densities of various acetone-water mixtures at 20.18°C and 9.49°C.

DENSITIES OF ACETONE-WATER MIXTURES AT 20.18°C.

Density of water at 20.18°C = 0.99802 gms/ml.

(see International Critical Tables. Vol II)

Solvent (vol %)	Wt. of Solvent* (gms)	Volume of picnometer.* (mls)	Corrected Weight of Solvent. gms.	Density gms/mls.
water	8.9379 ± 0.00018	8.9652 ± 0.00018	8.9474 ± 0.00018	0.99802
40% (A)	8.5011 ± 0.00003	8.9652 ± 0.00018	8.5106 ± 0.00003	0.94929 ± 0.00004
50% (C)	8.3530 ± 0.00010	8.9652 ± 0.00018	8.3626 ± 0.00010	0.93278 ± 0.00004
60% (A)	8.1499 ± 0.00012	8.9652 ± 0.00018	8.1595 ± 0.00012	0.91013 ± 0.00005
65% (A)	8.0481 ± 0.00010	8.9652 ± 0.00018	8.0577 ± 0.00010	0.89878 ± 0.00004
70% (H)	7.9524 ± 0.00024	8.9652 ± 0.00018	7.9620 ± 0.00024	0.88810 ± 0.00008
75% (A)	7.8142 ± 0.00013	8.9652 ± 0.00018	7.8238 ± 0.00013	0.87269 ± 0.00004
85% (C)	7.5402 ± 0.00015	8.9652 ± 0.00018	7.5498 ± 0.00015	0.84212 ± 0.00004

* Mean of at least three separate determinations.

DENSITIES OF ACETONE-WATER MIXTURES AT 9.49°C.

Density of water at 9.49°C = 0.99976 gms/ml.

(see International Critical Tables. Vol II)

Solvent (vol %)	Wt. of Solvent.* (gms)	Volume of picnometer.* (mls)	Corrected Weight of Solvent. gms.	Density gms/mls.
water	8.9440 ± 0.00049	8.9555 ± 0.00049	8.9534 ± 0.00049	0.99976
40 %(A)	8.5769 ± 0.00015	8.9555 ± 0.00049	8.5864 ± 0.00015	0.95878 ± 0.00007
50% (C)	8.4510 ± 0.00013	8.9555 ± 0.00049	8.4605 ± 0.00013	0.94472 ± 0.00006
60% (A)	8.2332 ± 0.00058	8.9555 ± 0.00049	8.2427 ± 0.00058	0.92041 ± 0.00010
70% (I)	7.9699 ± 0.00015	8.9555 ± 0.00049	7.9795 ± 0.00015	0.89102 ± 0.00006
85% (C)	7.6365 ± 0.00012	8.9555 ± 0.00049	7.6461 ± 0.00012	0.85377 ± 0.00007

* Mean of at least three separate determinations.

APPENDIX J.

Calculated densities for acetone-water mixtures at 20.18°C, 9.46°C and 1.71°C and details of the method used in their calculation.

Densities were calculated via., equation J.1., using the data given in International Critical Tables Vol. II.

$$\text{Density} = d = d_w + Ap_s + Bp_s^2 + Cp_s^3 \qquad \text{-----} \qquad \text{J.1.}$$

where d_w is the density of water at the required temperature and p_s the weight percentage acetone in the solvent. A, B and C are parameters dependent on the nature of the solvent and the temperature.

Table XXVII lists the values of d_w, A, B and C. (see International Critical Tables, Vol. II.)

Values of the densities calculated from equation J.1., are given in Table XXVIII.

TABLE XXVII

Values of d_w, A, B and C for aqueous acetone.

Temp. (°C)	d_w (gm/ml)	A	B	C
0	0.999867	$-0.0_{3}856$	$-0.0_{5}449$	$-0.0_{7}588$
4	1.000000	$-0.0_{3}765$	$-0.0_{4}1193$	$-0.0_{8}272$
15	0.999126	$-0.0_{2}1009$	$-0.0_{5}9682$	$-0.0_{8}624$
20	0.998023	$-0.0_{2}1233$	$-0.0_{5}3529$	$-0.0_{7}533$
25	0.997007	$-0.0_{2}1171$	$-0.0_{5}904$	$-0.0_{8}560$

TABLE XXVIII

Calculated densities for acetone-water mixtures.

Solvent (v/v %)	Density (gm/ml)		
Acetone	20.18°C	9.46°C	1.71°C
40	0.94891	0.95608	0.96155
50	0.93219	0.93855	0.94629
60	0.91206	0.91871	0.92789
65	0.89960	0.90668	0.91801
70	0.88849	0.89582	0.90582
75	0.87561	0.88160	0.89362
85	0.84421	0.85279	0.86361

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