Kinetic studies on the solvolyses of alkyl halides in the presence of added nucleophiles

Reid, Donald J.

How to cite:

Reid, Donald J. (1974) *Kinetic studies on the solvolyses of alkyl halides in the presence of added nucleophiles*, Durham theses, Durham University. Available at Durham E-Theses Online: http://etheses.dur.ac.uk/8362/

UNIVERSITY OF DURHAM

A THESIS

entitled

KINETIC STUDIES ON THE SOLVOLYSES OF ALKYL HALIDES IN THE PRESENCE OF ADDED NUCLEOPHILES

by

DONALD J. REID, B.Sc. (DUNELM)

(Grey College)

A candidate for the degree of Doctor of Philosophy

1974

ACKNOWLEDGEMENTS

The author would like to express his sincere thanks to Dr. G. Kohnstam for his continued help, advice and encouragement throughout the course of the work described here and also to Drs. M.R. Crampton, B.J. Gregory, M. Weston and D.L.H. Williams for help at various times. Thanks are also due to the Science Research Council for the award of a postgraduate studentship.

MEMORANDUM

I declare that the work described in this thesis has, except where indicated by references, been carried out by the author during the period of registration for the degree of Ph.D. at the University of Durham. No part of it has been submitted for any other degree.

SUMMARY

The aim of this study was to investigate the effect of added nucleophiles on the kinetics of the reactions of 4-nitrobenzyl compounds and 4-methoxybenzyl chloride under solvolytic conditions. Such reactions of the 4-nitro compounds are generally regarded as occurring via the bimolecular mechanism (S_N2) whereas 4-methoxybenzyl chloride is thought to undergo unimolecular (S_N1) hydrolysis in aqueous solvents, though there is evidence to suggest that its reaction with stronger nucleophiles (e.g. azide ions) occurs bimolecularly. Parallel studies on benzhydryl chloride, a substrate where nucleophilic bimolecular attack is subject to considerable steric hindrance, were carried out in order to estimate the magnitude of electrolyte effects on hydrolysis under these conditions.

Anions were found to accelerate the decomposition of the 4-nitro and 4-methoxy compounds in aqueous acetone, the acceleration increasing with increasing nucleophilicity of the anion and was more pronounced for the 4-nitro compounds than in the case of 4-methoxybenzyl chloride.

The results obtained were found to be fully consistent with an interpretation in terms of reactions by mechanisms S_N1 and S_N2, as long as it is assumed that the transition state for the bimolecular process (S_N2) can have varying degrees of carbonium character according to the ease of ionisation of the substrate relative to the ease of attack by the nucleophile.

The results were also considered in terms of schemes involving ion-pair intermediates prior to full ionisation to the fully developed carbonium ion, which is still necessarily required in any scheme where unambiguous common-ion retardation is observed for hydrolysis. Such ion-pair schemes, which

explicitly exclude direct attack by nucleophiles on the substrate (i.e. mechanism S_N2), lead to serious inconsistencies with the present results.

It is concluded that both classical mechanisms (S_N1 and S_N2) are required to explain the experimental evidence.

CONTENTS

CHAPTER 1

Introduction

1.1 Types of Reaction[1]

Chemical reactions are conveniently discussed in terms of the modifications of electron pairs involved in the rupture of existing bonds and the formation of new bonds. On this view three basic types of substitution reactions can be considered:

$$\begin{array}{lllllll}
Y: & + & R:X & \longrightarrow & Y:R & + & :X \qquad \text{Ia} \\
Y & + & R:X & \longrightarrow & Y:R & + & X \qquad \text{Ib} \\
Y\cdot & + & R:X & \longrightarrow & Y:R & + & \cdot X \qquad \text{II}
\end{array}$$

Reactions of type II involve homolytic or symmetric bond fission; the leaving group separates with one electron whilst the new bond is formed from the pairing of electrons from Y and R. These reactions are not the concern of the present study and will not be considered further.

Reactions of type I involve heterolytic bond fission, the bonding electrons either departing with the leaving group as in (Ia) or remaining with the reaction centre (Ib).

Reaction type (Ib), where an electron deficient reagent Y gains a share in paired electrons from the reaction site, is known as electrophilic substitution (S_E). When an electron deficiency arises at the reaction site which is satisfied by an electron donating reagent Y, as in (Ia), the reaction is a nucleophilic substitution (S_N).

The requirements for nucleophilic substitution are that the nucleophile Y should possess an unshared electron pair and that an overall transfer of electrons occurs from Y to the leaving group X. Thus the formal charge state of Y becomes a unit charge more positive, that of X one unit more negative as illustrated by the following typical examples.[2]

$$N_3^- + RCl \longrightarrow RN_3 + Cl^-$$

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

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

$$R'_3N + R_3S^+ \longrightarrow \overset{+}{R}NR'_3 + SR_2$$

This thesis is only concerned with nucleophilic substitution in neutral substrates and the subsequent discussion is therefore confined to these systems.

1.2 Classical Mechanisms of Nucleophilic Substitution

1.2.1 Duality of mechanism[1,2]

Originally, two distinct mechanisms were postulated for nucleophilic substitution reactions. Reaction by mechanism S_N2 is considered to occur via a single bimolecular step, involving a synchronous formation and destruction of chemical bonds. A necessary requirement of this mechanism is that both nucleophile and substrate are covalently involved in the rate determining transition state.

$$Y^- + RX \longrightarrow [Y^{\delta-} - - - R - - - X^{\delta-}] \longrightarrow YR + X^- \qquad (S_N2)$$

In reaction by mechanism S_N1, the essential feature is a slow, rate-determining ionisation of the substrate, RX, to form a carbonium ion, R^+. This species then reacts rapidly with the nucleophiles present.

$$\begin{array}{l} RX \longrightarrow \underset{\text{transition state}}{[R^{\delta+} - - - X^{\delta-}]} \longrightarrow R^+ + X^- \\ R^+ + Y^- \xrightarrow{\text{fast}} RY \end{array} \qquad (S_N1)$$

The S_N1 transition state involves a partially ionised bond of the substrate RX and, whilst solvation plays an enormously important role in facilitating the ionisation, there is no direct covalent attachment of the nucleophile in the transition state. The mechanism is, therefore, regarded as unimolecular.

Recently, it has been proposed[3] that these schemes, particularly the S_N1 reaction, require modification by the inclusion of intermediate ion-pairs in the reaction scheme. These ion-pairs and their relative importance in discussing nucleophilic substitution reactions, are the central theme of this thesis. They are discussed in section (1.3) but those earlier experimental results which can, however, be interpreted on the basis of classical S_N1 and S_N2 mechanisms, are discussed in these terms in the succeeding sub-sections, for the sake of simplicity.

1.2.2 Kinetic form of nucleophilic substitutions[1,2]

Reaction by the bimolecular mechanism (S_N2) is considered to occur via a single step and can therefore be expected to follow second-order kinetics, first-order with respect to both the substrate and the nucleophile. In solvolyses, however, the nucleophile (HS) is present in vast excess, being a major component of the solvent and first-order kinetics can therefore be expected.

For unimolecular (S_N1) solvolysis, application of the steady state approximation to the highly reactive carbonium ion intermediate leads to the rate law shown in equation (1.1). First-order kinetics will be observed in

$$RX \underset{-1}{\overset{1}{\rightleftharpoons}} R^+ + X^- \;;\; R^+ \xrightarrow[HS]{2} RS + H^+ \qquad (S_N1)$$

$$\frac{-d[RX]}{dt} = \frac{k_1[RX]}{1+\alpha[X^-]}\;^{\dagger} \qquad (1.1)$$

where $\alpha = k_{-1}/k_2$

---

† Throughout this thesis rate constants with arabic subscripts (e.g. k_1, k_2) refer to the rate constants for the individual steps in a reaction scheme.

S_N1 solvolysis if the value of the mass-law constant, α, is such that $\alpha[X^-] << 1$, even though X^- is produced as the reaction proceeds.

Under these conditions, both S_N1 and S_N2 solvolyses have the same kinetic order and cannot be distinguished on the basis of their kinetics. Other less direct methods must be employed to determine the mechanism. These methods are illustrated in the subsequent sub-sections and most of them have been extensively reviewed (for example see reference 4).

However, when α is large enough to ensure $\alpha[X^-]$ is not negligible compared with unity the instantaneous rate coefficient for decomposition of the substrate, can be expected to decrease as the reaction proceeds.

$$k_{RX}^{inst} = \frac{k_1}{1+\alpha[X^-]} \qquad \text{(see equation (1.1)}$$

Innumerable examples of such mass-law retardations are known (for example, see reference 5).

Similarly the addition of common anions, X^-, will significantly retard the S_N1 decomposition of RX under solvolytic conditions if $\alpha[X^-]$ is not negligibly small (for example, see reference 5). These common-ion effects are strong evidence in favour of reaction by mechanism S_N1 but are not necessarily observed in the majority of unimolecular solvolyses. Indeed, the effect is often masked by the simultaneous accelerating electrolyte effect (see sub-section 1.2.6).

1.2.3 Structural changes in the substrate[1,2]

The rate of reaction by mechanism S_N1 is controlled by the ionisation of the substrate. Associated with this is an increase in positive charge at the reaction site in the transition state for this process. Hence, electron release by substituents toward the reaction centre is expected to facilitate the ionisation through stabilisation of the polar transition state.

In bimolecular substitution, the electronic requirements in the transition state are ambiguous. The S_N2 mechanism is essentially a process of synchronous bond formation and dissociation. Therefore, electron release toward the reaction centre should aid the expulsion of the leaving group, whilst hindering approach by the nucleophile. The overall effect depends on an inequality of these two requirements and as such is expected to be much smaller than in unimolecular reactions.

Methyl groups are capable of stabilising a positive charge by inductive and hyperconjugative effects. In the series of alkyl bromides, RBr, the capacity for electron donation toward the central carbon atom increases in the order,

$$R: \quad Me < Et < {}^{i}Pr < {}^{t}Bu$$

but the rates of their solvolyses in aqueous ethanol follows the sequence,[6]

$$R: \quad Me > Et < {}^{i}Pr << {}^{t}Bu \qquad \text{(see Table 1.1)}$$

Table (1.1)

Relative rates of solvolysis of alkyl bromides RBr in 80% aqueous ethanol† at 55°C [6d]

R	Me	Et	^{i}Pr	^{t}Bu
Relative rates	2·5	1	1·7	7300

The large rate for the tertiary alkyl halide in this series, convincingly demonstrates the operation of mechanism S_N1 for this compound. This conclusion is confirmed by the lack of any acceleration by the more powerful nucleophile, hydroxide ion.[6d]

---

† Throughout this thesis an 'X%' solvent refers to (100-X) volumes of the first-named component mixed with X volumes of the second-named component of a mixed solvent.

A phenyl group directly attached to the reaction centre is capable of stabilising the developing positive charge for the S_N1 transition state, by resonance interaction with this charge.[2] The rate of solvolysis of benzhydryl chloride in 70% aqueous acetone at 50°C is greater by a factor of 1600 than the corresponding solvolysis of the primary halide, benzyl chloride.[7] Such sensitivity to structural change is, again, highly indicative of unimolecular solvolysis for the former compound. This conclusion is also supported by the absence of any acceleration on the addition of hydroxide ions[8] and the retardation of solvolysis by common anions.[5] Thus with phenylmethyl chlorides unimolecular solvolysis is observed for the secondary halide, benzhydryl chloride.

The solvolysis of benzhydryl halides and substituted benzhydryl halides has been widely studied in aqueous solvents and shown to be a model S_N1 reaction.[5,7] The steric requirements of the two phenyl groups are thought to inhibit the approach of the nucleophiles to the covalent substrate thus hindering mechanism S_N2 while, at the same time, the polar effects of these groups have a large stabilising influence on the partial positive charge at the reaction centre in the S_N1 transition state.

Steric complications arising from the introduction of substituents in the vicinity of the reaction centre can be avoided by studying 4-substituted benzyl halides ($4\text{-}ZC_6H_4CH_2X$) where the effect of the substituent on the rate arises mainly, if not entirely from their polar effects. Solvolysis in aqueous acetone occurs by mechanism S_N1 in the compounds capable of substantial electron donation to the reaction centre (Z = MeO, PhO) while the bimolecular reaction path is followed with less efficient electron releasing groups (Z = H, NO_2).[9] These compounds also demonstrate the ambiguity of the polar requirements for S_N2 reactions with anions. For bromide exchange in diethylene diacetate, the powerful electron donating and attracting groups

(Z = MeO, NO_2) lead to virtually the same rate while a rate minimum is observed with the parent compound.[10]

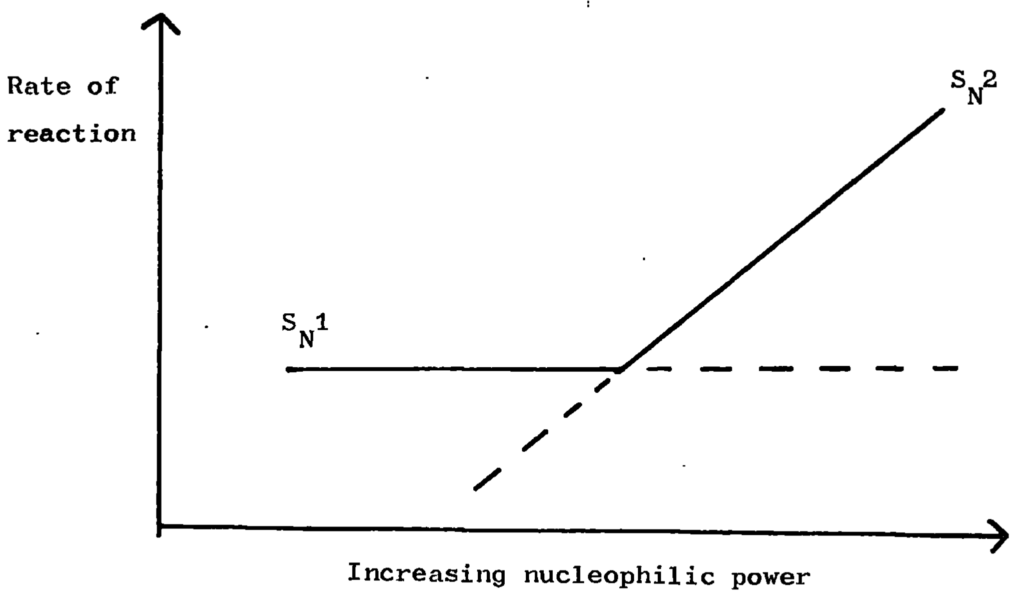
1.2.4 Variation of the nucleophile [1,2]

In S_N1 reactions the overall rate of decomposition of the substrate depends on its rate of ionisation and should therefore not be affected by the nature of any nucleophiles present as these only react with the carbonium ion intermediate formed in the rate-determining step. Added substances will however influence the rate of ionisation to a relatively small extent through medium effects (see sub-section 1.2.6) but it must be stressed that the magnitude of these effects rarely, if ever, follows the order of the nucleophilic power of the species under consideration.

The nature of the nucleophile is, however, an important factor in determining the rate of S_N2 reactions. Thus the solvolysis of methyl and ethyl bromide in aqueous ethanol is greatly accelerated by the addition of hydroxide ions,[6d] thus indicating bimolecular attack by these ions though not necessarily by the much more weakly nucleophilic solvent molecules.

It is therefore possible to envisage the situation illustrated in Figure (1.1) where S_N2 reaction becomes the energetically more favourable process if a sufficiently powerful nucleophile is present. This behaviour

Figure (1.1)



has been reported for the reactions of trimethyl sulphonium salts in ethanol[11] but the interpretation has been criticised on the grounds that the constant rate observed in the presence of the weaker nucleophiles could arise from bimolecular reaction with the solvent which is present in vast excess.[12] A less ambiguous demonstration is afforded by the reactions of 4-methoxy- and 4-phenoxy-benzyl chlorides in 70% aqueous acetone. The reaction centre of these compounds is not sterically unfavourable to S_N2 attack but solvolysis occurs unimolecularly[9] while the decomposition is accelerated by the addition of azide ions far beyond the limits to be expected from the operation of a medium effect.[13]

1.2.5 Solvent effects

The kinetic effect of solvent changes or other alterations in the medium is given by the well known Brönsted relation[14] which can be expressed in the form of equation (1.2) for the reaction between an organic halide (RX) and an anion (Y^-). In this expression

$$\frac{k_A}{k_B} = \frac{(f_{RX})_A (f_{Y^-})_A}{(f_{\ddagger})_A} \cdot \frac{(f_{\ddagger})_B}{(f_{RX})_B (f_{Y^-})_B} \qquad (1.2)$$

the subscripts A and B refer to the two media, the f's to the activity coefficients, and the subscript $\ddagger$ to the activated complex. Equation (1.2) also applies to solvolysis if the f_{Y^-} terms are omitted.

Earlier workers considered the kinetic effect of solvent changes in terms of the solvation requirements associated with the activation process.[6a] The creation of electric charges was considered to require increased solvation, and vice versa, while a proportionally smaller decrease in solvation was involved in the dispersal of a given charge. Solvents were classified in terms of their solvating (ionising) power which was affected by the water content of aqueous organic solvents and controlled the stabilisation of solute species in relation to their solvation requirements. The vast majority of the available results is fully consistent with this view. Thus the S_N2 reactions of organic halides with anions are slightly decelerated by making the solvent more aqueous (charge dispersal) while the same solvent change greatly accelerates S_N1 decomposition where charges are created in the activation process.[6b] Similarly the smaller degree of charge development and its greater dispersal in S_N2 solvolyses, relative to the S_N1 process, should render these reactions less sensitive to solvent changes, as observed for the S_N2 solvolysis of 4-nitrobenzyl chloride when compared with the S_N1 reaction of 4-nitro-4'-phenylbenzhydryl chloride.[8]

More recent observations however require a modification of this interpretation. Determinations of the activity coefficient of the substrate (f_{RX}) from solubility or partial vapour pressure measurements show that about one half of the effect of changes in the composition of aqueous ethanol on the rate of the S_N1 solvolysis of t-butyl chloride arises from changes in the stability of the substrate (i.e. f_{RX})[15] and that such initial state effects are almost entirely responsible for the kinetic effect of altering the water content of aqueous acetone on the rate of hydrolysis of 4-nitro-4'-phenylbenzhydryl chloride by the same mechanism.[8] Moreover, the transition state for the S_N2 solvolysis of 4-nitrobenzyl chloride is actually destabilised on increasing the solvating power, the observed rate increase arising from an even larger destabilisation of the initial state.[8]

No similar study of the relative importance of initial and transition state effects has been reported for the bimolecular attack by anions on neutral substrates. The rates are almost invariably reduced on increasing the ionising power of the solvent,[16] as predicted by the simple solvation approach and a few exceptions involve systems with an appreciable degree of charge development at the reaction centre in the transition state.[17]

Under these conditions 'S_N1-like' behaviour with respect to solvent changes is not unreasonable.

Similarly the simple solvation approach appears to predict the majority of the observations for solvolytic reactions if it is viewed slightly differently from the original proposal.[8]

1.2.6 The effect of added electrolytes

This thesis is mainly concerned with the effect of added anions (Y^-) on the decomposition of substrates (RX) and it is therefore convenient to limit the subsequent discussion to this area. In elementary terms the addition of Y^- will accelerate the overall decomposition and leave the rate of production of the solvolysis product unaltered if Y^- attacks the substrate bimolecularly. However, the anion competes with the solvent for the carbonium ion formed in the rate determining step if mechanism S_N1 is operating so that Y^- will leave the overall rate of decomposition unaltered under these conditions though the formation of the solvolysis product will be retarded.

Superimposed on these elementary considerations will be the medium effect arising from the changes in ionic strength caused by the addition of the electrolyte. This is conveniently discussed in terms of the Brönsted relation[14] (cf. equation 1.2) in the form,

$$k = k^o \frac{f_{RX}}{f_\ddagger} \qquad (1.3)$$

where the superscript 'o' refers to zero ionic strength and the f's now represent the activity coefficients relative to unity at zero ionic strength. Equation (1.3) is valid for S_N1 decomposition or S_N2 solvolysis but S_N2 reaction with an anion (Y^-) requires the relation,

$$k = k^o \frac{f_{RX} f_{Y^-}}{f_\ddagger} \qquad (1.4)$$

The kinetic effects of added electrolytes were originally rationalised in terms of a simple electrostatic model which assumes that polar species were stabilised by their surrounding ion-atmosphere by amounts which increased with increasing charge and decreased with the dispersal of a given charge; the effect on the stability of a formally neutral substrate (RX) was regarded as negligibly small.[18] On this view the rate coefficient of the S_N2 reaction with an anion should decrease with increasing ionic strength ($f_{\ddagger} > f_{Y^-}$), as generally observed.[19] Unimolecular decomposition and bimolecular solvolysis should be unambiguously accelerated by the addition of electrolytes and though this is usually found exceptions are known (for examples, see reference 20 and Table 1.2).

A quantitative development of the electrostatic approach for S_N1 reactions leads to the conclusion that the acceleration caused by electrolytes was independent of their nature and was solely controlled by the ionic strength and the nature of the substrate, at least in very dilute solutions.[18] Contrary to this requirement, specific electrolyte effects have been observed on many occasions (for examples see references 20 and 21). In addition the original assumption of negligibly small changes in the stability of neutral solutes on the addition of electrolytes is contradicted by the large amount of information on salting-in and -out, and this also applies to substrates which undergo nucleophilic substitution reactions.[20b,22]

Specific electrolyte effects in mixed aqueous solvents have been ascribed to the different degrees of solvation of different ions so that the 'effective' solvent composition depends on the nature of the added ions.[21] A quantitative development of these views[20a] combined with experimental information on the effect of electrolytes on the activities of the components of aqueous dioxan[23] showed that the observed influence of electrolytes on solvolytic rates was consistent with the operation of such a 'salt induced medium effect' and an electrostatic effect of the type originally envisaged, provided that both initial and transition state stabilities were taken into account.

Table (1.2)[20a]

Kinetic salt effects in the solvolysis of neophyl p-toluenesulphonate in 50% aqueous dioxan at 50°C

Salt	k_1/k_1^o	
	[Salt] = 0·1M	[Salt] = 0·2M
NaOH	0·86	0·73
NaCl	0·98	0·92
LiCl	1·00	1·01
NaBr	1·05	1·05
$NaNO_3$	1·06	1·08
NaI	1·06	1·12
$NaClO_4$	1·16	1·30
$2\text{-}C_{10}H_7SO_3Na$	1·03	1·10

1.2.7 Activation parameters for solvolytic reactions[7,24]

The conventional form of the absolute rate equation for reaction in solution[25]

$$\ln k = \ln \frac{\bar{k}T}{h} + 1 + \frac{\Delta S^{\ddagger}}{RT} - \frac{E}{RT} \qquad (1.5)$$

allows the calculation of energies and entropies of activation (E and $\Delta S^{\ddagger}$, respectively) provided it is recognised that the definition of these parameters requires them to vary with temperature according to the relations[26]

$$T\frac{\delta \Delta S^{\ddagger}}{\delta T} = \frac{\delta E}{\delta T} - R = \Delta C_p^{\ddagger}$$

where the heat capacity of activation, $\Delta C_p^{\ddagger}$, represents the difference between the standard heat capacities of the initial and transition states. Negative values for this quantity have been observed in numerous solvolytic reactions of neutral substrates in water[24] and aqueous organic solvents,[7] resulting in a significant temperature dependence of the energy and entropy of activation. Valid comparisons of these parameters for different systems must therefore refer to the same temperature and it is found that for solvolysis in a given medium, $\Delta S^{\ddagger}$ is considerably more negative for the S_N2 process than for the S_N1 reaction of a structurally similar compound,[7,24] in agreement with earlier suggestions.[27] Apparently a solvent molecule suffers a greater loss of entropy when it forms a partial covalent bond than when it merely participates in the solvation of a charged centre.

The ratio $\Delta C_p^{\ddagger}/\Delta S^{\ddagger}$ has been found to be larger for S_N1 than for S_N2 solvolysis in aqueous organic solvents and independent of the nature of the substrate when the unimolecular mechanism is operating. This property affords a sensitive test of solvolytic mechanism particularly in the vicinity of the mechanistic borderline region (see sub-section 1.2.8) where the other criteria do not always provide unambiguous answers and may arise from the fact that the changes in solvation accompanying the activation process are by far the most important factors controlling the magnitudes of both $\Delta C_p^{\ddagger}$ and $\Delta S^{\ddagger}$.[7,28] It must however be stressed that this criterion of mechanism will not apply to solvolysis in highly structured solvents like water. Here $\Delta C_p^{\ddagger}/\Delta S^{\ddagger}$ for S_N1 solvolysis is not independent of the nature of the substrate, possibly because changes in solvent-solvent interactions resulting from passage into the transition state contribute substantially to the magnitudes of these parameters.

1.2.8 The mechanistic borderline region

It has already been pointed out in previous sub-sections that the introduction of electron-donating groups, or alterations in the nature of the nucleophile or solvent can progressively favour reaction by mechanism S_N1 relative to mechanism S_N2 until ultimately the unimolecular process is the energetically more favourable. The mechanistic 'borderline' region is defined as the earlier stage when S_N1 and S_N2 reactions are about equally likely and is now considered since some of the reactions described in this thesis occur in or near this region.

It is convenient to base the discussion on the general formulations,

$$\left.\begin{array}{l} \overset{(1+\phi-\theta)-}{Y}\text{--------}\overset{\phi+}{R}\text{--------}\overset{\theta-}{X} \\[1em] \overset{(\theta-\phi)+}{HS}\text{-------}\overset{\phi+}{R}\text{--------}\overset{\theta-}{X} \end{array}\right\} \quad (0 \leqslant \phi \leqslant \theta \leqslant 1)$$

for the transition states of the reactions with anions (Y^-) and solvent (HS), respectively, instead of the alternative equivalent description in terms of resonances hybrids of appropriate canonical forms[13,29]: e.g.,

$$Y^- \; RX; \quad YR \; X^-; \quad Y^- \; R^+ \; X^-$$

On the present formulation the degree of covalent attachment by the nucleophile (Y^-,HS) increases with increasing difference between the magnitudes of the opposing charges created on the substrate and on the leaving group (X) in the transition state. When this difference is zero ($\phi = \theta$) no covalent participation by the nucleophile occurs in the activated complex and the reaction is therefore unimolecular. However, the mechanism must be regarded as bimolecular whenever $\phi < \theta$ since the nucleophile is now covalently involved in the activation process and it is therefore apparent that mechanism S_N2 can proceed via a wide spectrum of different transition states, subject only to the requirement $0 \leqslant \phi \leqslant \theta \leqslant 1$.

The precise nature of the reaction path in the mechanistic borderline region has aroused considerable interest. Some workers consider that all the individual molecular acts of substitution proceed via identical transition states such that ϕ tends progressively closer to θ as the mechanism approaches the limiting S_N1 form.[29,30] However, ϕ is less than θ until this stage is reached and this view therefore demands bimolecular reaction in the borderline region though the relative high degree of charge development in the substrate can be expected to lead to characteristics (e.g. kinetic solvent effects) closer to those for S_N1 reactions than to those for the more extreme forms of mechanism S_N2 where $\phi << \theta$. Alternatively, reaction may occur via a whole spectrum of transition states associated with varying values of ϕ, including $\phi = \theta$.[31] Such a process must be considered to involve the concurrent operation of mechanisms S_N1 and S_N2.

In principle it should be easy to distinguish between these two possibilities for non-solvolytic reactions since reaction via identical transition states with $\phi < \theta$ should result in second-order kinetics while mixed first- and second-order kinetics should be observed for reaction by concurrent S_N1 and S_N2 processes. Such mixed kinetics have been reported for the reactions of benzhydryl compounds in sulphur dioxide,[31a] nitromethane,[32] dimethylformamide,[33] and acetonitrile and acetone[34] and also for the bromide exchange of tert.butyl bromide in acetone[35] though this observation was not confirmed by subsequent studies.[36] These substrates are generally considered to be sterically unfavourable with respect to bimolecular attack by nucleophiles but this does not rule out such processes for strong nucleophiles and poor ionising conditions. For example, the decomposition of 4-nitrobenzhydryl chloride in 85% aqueous acetone is accelerated very substantially by the addition of small amounts of azide ions, presumably because of an energetically favourable S_N2 reaction.[37] Nevertheless, the observation of mixed kinetics in the reactions of these compounds does not unequivocally demand the concurrence of S_N1 and S_N2 processes in the absence of information about the medium effects resulting from the introduction of the nucleophiles.

Conclusions about the mechanism of solvolyses in the borderline region have been sought from the effect of solvent changes on the rate via the Grunwald-Winstein relation,[29a]

$$\log(k/k_o) = mY \qquad (1.6)$$

where the subscript 'o' refers to a reference solvent (80% aqueous ethanol), and Y to the ionising power of the solvent defined as $\log(k/k_o)$ for the solvolysis of tert.butyl chloride. The parameter 'm' was found to be unity for S_N1 solvolysis and very much smaller when the alternative mechanism was operating. The intermediate value of m (0·54) found for the solvolysis of isopropyl bromide was held to result from reaction via identical transition states for all the individual molecular decompositions[29b] but this conclusion has been criticised on the grounds that m depends on the nature of the substrate in S_N1 solvolysis[12] and that the linear relation between logk and Y, required by equation (1.6) does not always apply to S_N2 solvolysis.[31a]

Information has also been sought from the effect of added nucleophiles (N) on the rate coefficients for solvolysis (k_{RS}) and total decomposition (k_{RX}) of a substrate (RX). This approach was originally suggested by Gold who pointed out that S_N2 attack by N must inevitably lead to a larger k_{RX} in its presence without any effect on k_{RS}, while concurrent S_N1 and S_N2 reaction with N should increase k_{RX} and decrease k_{RS} if the solvolysis occurs wholly or partially by mechanism S_N1.[31b,d] Unfortunately the example studied (benzoyl chloride) probably does not undergo solvolysis by S_N mechanisms.[38]

This approach has been applied to the reactions of 4-methoxy- and 4-phenoxy-benzyl chloride in 70% aqueous acetone.[11,31e] These systems have the advantage that solvolysis is known to occur entirely by mechanism S_N1[7,9] so that carbonium ions are inevitably available for reaction with added nucleophiles. At the same time the reaction centre is not sterically unfavourable to bimolecular attack and the magnitude of medium effects can be estimated by analogy with the corresponding behaviour of benzhydryl chloride which does not undergo S_N2 reaction to any detectable extent in this solvent and shows remarkable similarities to the two benzyl chlorides with respect to solvent changes and the addition of non-nucleophilic anions. For both alkoxy-benzyl compounds the addition of azide or chloride ions increased k_{RX} well beyond the limits expected from the appropriate electrolyte effects and, at the same time, reduced k_{RS}. Concurrent S_N1 and S_N2 attack by these anions therefore appeared to be indicated.

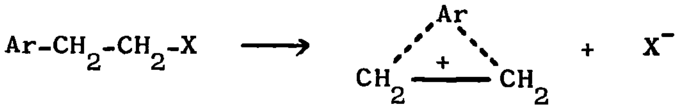
The mechanism for borderline solvolysis cannot yet be established unambiguously. It has already been pointed out (see sub-section 1.2.3) that the 4-substituted benzyl compounds ($4\text{-}ZC_6H_4CH_2X$) represent a series in which electron supply to the reaction centre can be altered by a suitable choice of the substituent, Z, leading to S_N1 solvolysis for good electron donors (Z = MeO,PhO) and S_N2 reaction for significantly less efficient donors (Z = H,NO_2). Substituents with a capacity for electron release intermediate between these extremes (Z = Me, $4\text{-}MeOC_6H_4$) led to entropies of activation intermediate between the values expected for S_N1 and S_N2 solvolysis, while the ratio $\Delta C_p^\ddagger/\Delta S^\ddagger$ (sub-section 1.2.7) suggested that the reaction did not occur entirely by mechanism S_N1.[7,28] This indication of borderline behaviour is strongly reinforced by the observation that $\Delta C_p^\ddagger \simeq 0$ for reaction with 50% aqueous acetone when Z = Me. Normally a significantly negative $\Delta C_p^\ddagger$ is expected for solvolysis[7,24] and this finding therefore requires an additional positive contribution which could arise from the concurrence of several different processes having different activation energies but could equally well result if only one reaction path is available provided the structure (ϕ/θ) of the transition state is temperature dependent in the sense of a positive temperature coefficient for its enthalpy.[7,28]

1.2.9 The stereochemistry of nucleophilic substitutions

The energetically most favourable path of bimolecular (S_N2) substitution involves attack by the nucleophile on the opposite side of the substrate to that of the group being displaced.[6a] For an asymmetrically substituted reaction centre such acts of substitution would be expected to give inverted products, as observed on innumerable occasions; for example, symmetrical halide exchange of organic halides in acetone where the rate of racemisation is twice the rate of exchange.[39]

In S_N1 reactions a planar configuration is to be expected for the carbonium ion if it has a sufficiently long lifetime and attack by nucleophiles should then lead to a totally racemic product from an initially optically active substrate. If the carbonium ions are short-lived some of their reactions with nucleophiles may occur while the departing group is still in the immediate vicinity thus providing some shielding against nucleophilic attack on that side of the ion; inversion should accompany racemisation under these conditions.[2] In agreement with these predictions the S_N1 solvolysis of 1-phenylethyl chloride in alcohols occurs with complete racemisation; hydrolysis in aqueous acetone showed a small amount of excess inversion, increasing with increasing water content, presumably because of the reduction of the half-life of the carbonium ion as the water content is raised.[40] Inversion accompanying racemisation during the hydrolysis of this compound has also been reported on many other occasions (cf. reference 41). On the other hand the hydrolysis of 1-phenylethyl bromide in water leads to a totally racemic product[40] although it is difficult to see how the departing group can alter the stability of a carbonium ion with respect to the collapse of the solvation shell.

Varying degrees of retention of optical configuration should accompany unimolecular reactions subject to anchimeric assistance by neighbouring groups; for example,



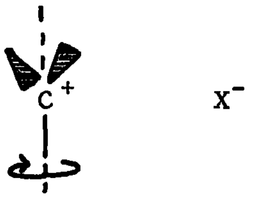
Under these conditions the side opposite to that of the departing group is shielded against nucleophilic attack but such systems represent a special case which is not relevant to the present study. They are, therefore, not considered further in this thesis; a review is available.[42]

1.3 Ion-Pair Intermediates in Nucleophilic Substutition Reactions

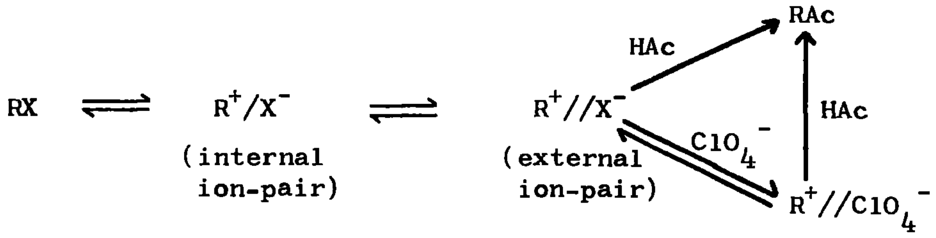
1.3.1 Evidence of ion-pair intermediates

The original explanation of racemisation and some inversion in the S_N1 reactions of some optically active compounds (see sub-section 1.2.9) was considered to suffer from the conceptual difficulty that it required an ionisation process, complete enough for the reaction to be regarded as unimolecular, but in which the intermediate carbonium ion was not sufficiently distinct from the leaving group to adopt its expected planar configuration.[43] This objection vanishes if the reactions proceeded via an intermediate ion-pair which could react with the solvent or other nucleophiles to form an inverted product.[44]

More compelling reasons for considering ionisation via these intermediates arose from observations that the unimolecular reactions of many optically active substrates in a variety of solvents were accompanied by an intramolecular racemisation of the initial reactant (for a summary see reference 45). Experimentally this was detected from the ratio of the first-order rate coefficients for the disappearance of optical activity and the formation of the product, and the effect was found to be significantly enhanced by using poorer ionising solvents; for example, their ratio is 2·6 and 38 for the solvolysis of 4-chlorobenzhydryl chloride in 80% aqueous acetone and acetic acid, respectively.[45,46] Reaction via a fully developed carbonium ion, as postulated in the original definition of S_N1 reaction, would require the same rate coefficients for solvolysis and racemisation. Similarly, the rate of chloride exchange of this compound in acetone was much less than the rate of racemisation under the same conditions.[45] These observations were interpreted in terms of ionisation via an intermediate ion-pair which could return to the initial state with either retention or inversion of configuration, presumably by rotation of the cationic moiety; e.g.

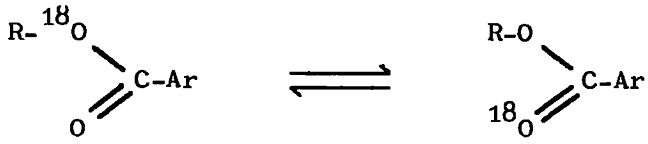


The existence of more than one intermediate ion-pair was deduced from the effect of lithium perchlorate on rates of solvolysis. Addition of the salt initially caused a very marked acceleration, the 'special salt effect', followed by a more gradual increase in rate, the 'normal salt effect' (see sub-section 1.2.6), as the ionic strength increased.[47] It was assumed that the special salt effect arose from the suppression of the return from an ion-pair resulting from its capture by the added salt and the rapid hydrolysis of the resulting species (see below). For threo-3-anisyl-2-butyl 4'-toluenesulphonate the rate of racemisation was found to be greater than the rate of solvolysis even when a special salt effect was operating, suggesting ionisation via an 'internal' and an 'external' ion-pair which were both regarded as capable of return with racemisation while only the external ion-pair could be captured by perchlorate ions.[48]

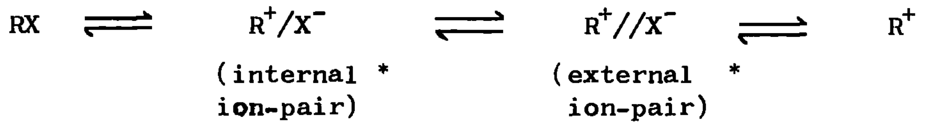


It has however, been pointed out that the observation of special and normal salt effects could simply be a consequence of a substantial ion-pair association constant for lithium perchlorate in acetic acid.[49]

Further indications of the existence of intermediate ion-pairs arose from studies on the solvolysis of 4-nitrobenzoates which are also believed to react by the ionisation mechanism, S_N1. Esters labelled with 18-oxygen were found to undergo equilibration in the 'unreacted' substrate during



solvolysis, the rate of equilibration being greater than the accompanying rate of racemisation of the substrate.[50] For a series of 4-substituted benzhydryl compounds an approximately 2500-fold increase in the solvolytic rate coefficient (k_t) was accompanied by similar changes in the first-order rate coefficients for oxygen equilibration (k_{eq}) and racemisation of the substrate (k_{rac}), as shown in Table (1.3).[51] The three processes were therefore considered to involve a common initial step in unimolecular solvolysis, with ionisation via two intermediate ion-pairs:



$$RX \rightleftharpoons \underset{\text{(internal ion-pair)*}}{R^+/X^-} \rightleftharpoons \underset{\text{(external ion-pair)*}}{R^+//X^-} \rightleftharpoons R^+$$

---

* The nomenclature 'internal' and 'external' has been retained for the sake of uniformity, and the fully developed carbonium ion has been included in the scheme

Table (1.3)[51]

Rate coefficients for the solvolysis of 4-Z-benzhydryl 4'-nitrobenzoates in 90% aqueous acetone

Z	k_t (relative)	k_{eq}/k_t	k_{rac}/k_{eq}
Cl	1	2·4 (99°C)	0·35 (99°C)
H	2	2·9 (99°C)	-
Me	22	2·9 (99°C,49°C)	0·60, 0·17 (99°C,49°C)
MeO	$>$ 2500	2·9 (49°C)	0·28 (49°C)

It was suggested that only $R^+//X^-$ could return to give an inverted substrate, while both R^+/X^- and $R^+//X^-$ could give the substrate with the oxygen label interchanged. The species undergoing reaction with the solvent received no explicit attention, but this process can obviously not be rate-determining when a unimolecular mechanism is operating.

Ingold[52], however, argued that excess racemisation and oxygen equilibration do not necessitate return from ion-pair intermediates. He suggested that, at all degrees of separation after the free energy maximum has been passed, there is a probability of the counter ions recombining. Thus, as the separation increases, the probability of the carbonium ion moiety reacting with solvent increases, whilst the still finite probability of return, decreases. Of the proportion of ions that recombine, there will also be a probability of the carbonium ion inverting, as long as the separation is greater than a certain critical distance. Similarly, there will be another, smaller, critical separation above which the anionic charge can spread to cause the oxygen atoms in the ester group to become equivalent and thus randomise on recombination. These processes would, therefore, share the same maximum in the free energy profile and be expected to respond to solvent and structural changes in a similar way. Strictly such a detailed description offends the requirements of the transition state theory which does not envisage any situation intermediate between an activated complex and the stable or metastable products of its decomposition, but there is no fundamental objection to considering several different probabilities for the decomposition of the activated complex to give the substrate unaltered, with an interchanged label and/or inversion of configuration, and the solvolysis products. There is now some agreement that details of the stereochemical course of unimolecular substitution are still uncertain[41] but it could be significant that the effects which have been interpreted in terms of ion-pair intermediates are most marked in poor ionising solvents where their influence is most likely to be appreciable.

Reaction of intermediate ion-pairs with external reagents is implicit in the proposed explanation of the special salt effect for reactions in acetic acid though an alternative interpretation has been offered (see page 21) and has also been suggested to account for the observation that the rate of decomposition of triphenylmethyl chloride in benzene depends on the nature but not the concentration of added nucleophiles.[49] Capture of reagents by intermediate ion-pairs in better ionising solvents like aqueous acetone and aqueous dioxan has also been proposed during the last few years. This aspect of the problem forms the basis of the present thesis and is therefore considered below in some detail.

Goering and his co-workers have examined the effect of the strongly nucleophilic azide ion on the rates of decomposition, racemisation and 18-oxygen equilibration of 4-nitrobenzoates in aqueous acetone.[50,51,53] The studies included a series of 4-substituted benzhydryl 4'-nitrobenzoates where steric factors are generally believed to render bimolecular (S_N2) attack by nucleophiles relatively difficult. Racemisation of the 4-chloro derivative was completely suppressed by the presence of 0·14M sodium azide while the rate of 18-oxygen equilibration was virtually the same as in the absence of the salt.[53] However, the 4-methyl compound showed a small deceleration of both racemisation and equilibration on the addition of similar amounts of azide.[51] These observations were considered to show that azide attack occurred mainly on the external ion-pair ($R^+//X^-$) which was regarded as capable of return to the substrate with inversion or exchange of the oxygen label, but unfortunately the additional confirmation which would have resulted from studies over a range of azide concentrations is not available.

However, the other conclusion to be drawn from these crucial results does not appear to have attracted any attention in the literature. The accelerating effect of the added azide ions is vastly greater than that expected from a normal electrolyte effect (see sub-section 1.2.6) on the rate of formation of an intermediate ion-pair so that two possibilities must be considered. If azide ions act solely by capturing intermediate ion-pairs the results require the rate determining decomposition of $R^+//X^-$ to give the azide and alcohol (see Figure 1.2), contrary to the conclusion reached on the basis of solvolytic studies (see page 21). Azide attack must be regarded as bimolecular though not entirely identical with the S_N2 reaction as

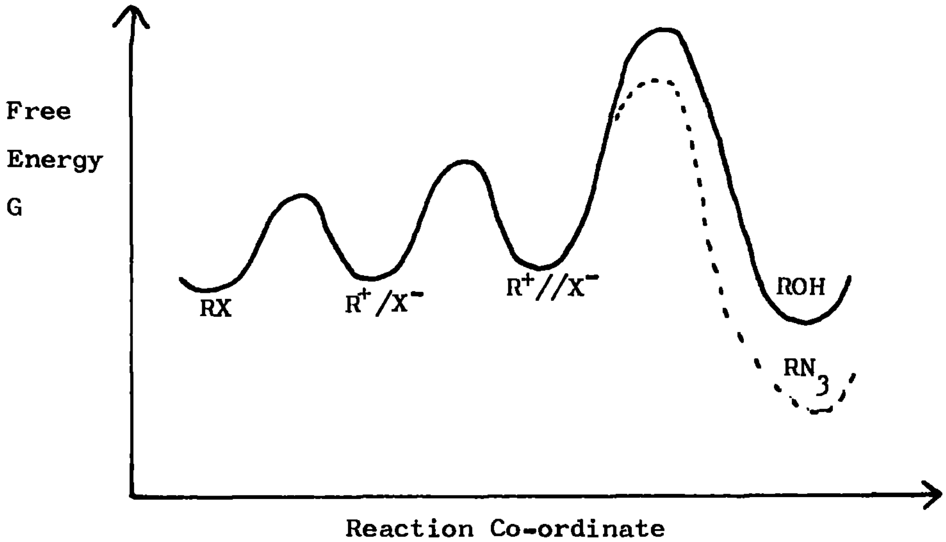


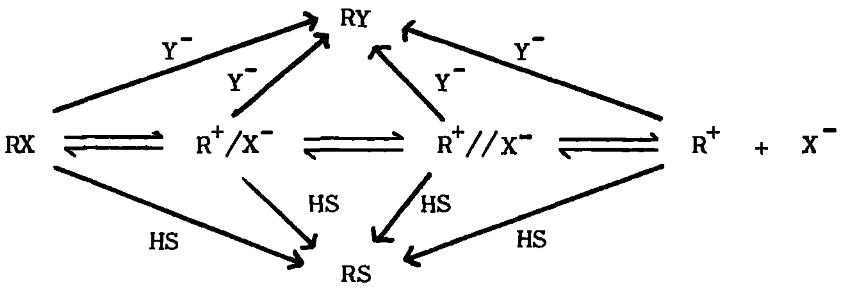
Figure (1.2)

originally defined (see sub-section 1.2.1). If on the other hand, the formation of R^+/X^- or $R^+//X^-$ is rate determining (cf. Figure 1.1) the vast majority of azide attack must proceed via an entirely different bimolecular reaction path, i.e. by mechanism S_N2.

Organic 4-nitrobenzoates ionise much less readily than the corresponding chlorides and, under relatively poor ionising conditions, it is conceivable that the steric factors opposing S_N2 attack by a linear azide ion are too small to reduce the rate below the rate of ionisation. This possibility receives support from the approximately 6- and 60-fold acceleration of the decomposition of 4-nitrobenzhydryl chloride by 0·05M sodium azide in 70% and 85% aqueous acetone, respectively,[37] while the parent compound which ionises 1000 times more rapidly decomposes at the rate expected from the operation of normal electrolyte effects (see sub-section 1.2.6). These observations suggest strongly that azide ions can attack benzhydryl compounds bimolecularly, even in aqueous organic solvents.

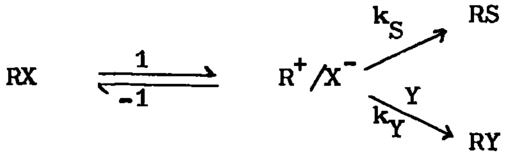
1.3.2 The unified mechanism

A general reaction scheme for nucleophilic substitution was proposed by Winstein and his co-workers[45] which includes attack by nucleophiles on covalent substrate (S_N2), a fully developed carbonium ion (S_N1) and on intermediate ion-pairs,



Such a general scheme was deemed necessary, in their opinion, on the grounds of the evidence in a number of systems concerning the special salt effect and the relative rates of racemisation, 18-oxygen equilibration and solvolysis (see sub-section 1.3.1). However, no evidence has yet been brought forward indicating that, in any one reaction studied, all these steps are necessarily significant and indeed the number of disposable parameters involved makes this extremely difficult to establish.

Sneen and his co-workers[3,54] have put forward a simpler view and have suggested that nucleophilic attack on the covalently bound substrate (RX) has yet to be demonstrated. In effect their conclusions are essentially based on the effect of added azide ions, under solvolytic conditions, on the proportions and optical configuration of organic azide (RN_3) and solvolysis product (RS) formed in the reaction. Their original scheme envisaged reaction entirely via a single intermediate ion-pair,



which was formed via a reversible ionisation of the substrate and destroyed by reaction with either the solvent (HS) or the added nucleophile (Y). The kinetic form of reactions proceeding via this 'unified scheme' will be governed by the magnitude of the ratio $x = k_{-1}/k_S$. First-order kinetics will be observed if formation of the ion-pair is rate determining ($x << 1$) and describes the reactions previously regarded as occurring via mechanism S_N1. On the other hand, classical bimolecular reactions (S_N2) are considered by these workers to occur via a rate-determining attack on the ion-pair ($x >> 1$), such reactions following second-order kinetics. Borderline reactions (see sub-section 1.2.8) following mixed kinetics are considered to occur when the free energies of the transition states for ion-pair formation and its subsequent reaction with nucleophiles are similar in magnitude (i.e. $x \approx 1$). The free energy profiles for these conditions are shown in Figure (1.3).

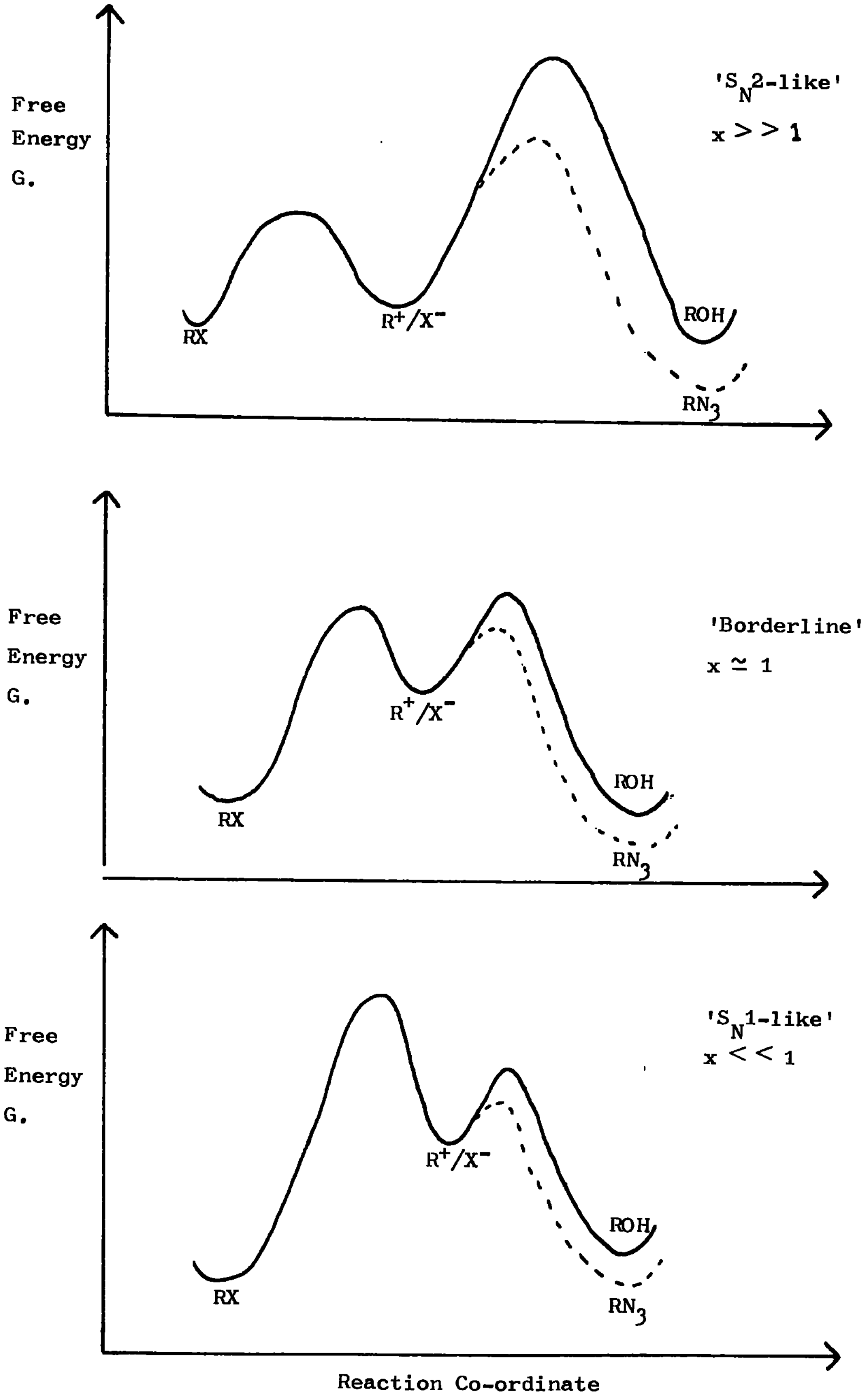


Figure (1.3)

Free energy profiles for the unified scheme

The basic conclusion reached by these workers has been widely criticised and indeed von Schleyer[55] and Kohnstam[56] have pointed out that the product ratio $[RN_3]/[ROH]$ variation with $[N_3^-]$ will be consistent with the unified scheme, to the exclusion of the classical S_N scheme, only if the electrolyte parameter (see Chapter 4) for azide ions has a particular value; the converse will apply if another value is assumed. Similarly, a substantial enhancement of the rate of decomposition of the substrate by added azide ions becomes difficult to envisage in an aqueous solvent where the solvolysis is believed to occur unimolecularly (i.e. via the rate-determining formation of the ion-pair in the unified scheme). Furthermore, for a substrate solvolysing bimolecularly ($x >> 1$ in unified scheme), where acceleration of the decomposition by added nucleophile, can be considered, there should be a limit reached after which an increase in nucleophilicity or concentration of the added nucleophile produces no further rate increase since the ion-pair formation has now become the rate-determining step (i.e. $k_Y[Y] > k_{-1}$ in the unified scheme). No such behaviour has yet been reported. The scheme has also been criticised on a number of other accounts[57] and in particular on the observation of common-ion retardation (see sub-section 1.2.2) which is difficult to explain in terms of Sneen's scheme.

At the very least one would therefore have to envisage the possibility of including a fully developed carbonium ion and possibly two intermediate ion-pairs as envisaged by Winstein[45] and Goering.[51,53] The question then arises as to whether an extension of Sneen's scheme which <u>does not</u> involve attack by nucleophiles on the covalently bound substrate (i.e. mechanism S_N2) can explain the existing body of information. The present work was carried out to establish this point.

1.4 The Present Study

The present study was aimed at obtaining mechanistic information from the effect of added nucleophiles on the rates of decomposition in aqueous solvents both for systems where hydrolysis was previously believed to be bimolecular and for those where earlier evidence had suggested unimolecular hydrolysis. Clearly, it was desirable to ensure that the reaction centres were not unfavourable to attack by nucleophiles and it was therefore decided to study reactions for substituted benzyl compounds.

All the available evidence suggested that 4-nitrobenzyl halides and 4'-toluenesulphonates undergo what was previously presumed to be bimolecular (S_N2) solvolysis and that reaction with more powerful nucleophiles was very much more rapid than reaction with water. This system was therefore chosen as typifying substrates likely to react bimolecularly in an attempt to see if the processes could be explained solely in terms of intermediate ion-pairs and a fully developed carbonium ion.

For alkoxybenzyl halides there is much evidence indicating that in aqueous solvents their solvolyses occur unimolecularly but that more powerful nucleophiles could react with these substrates by both classical mechanisms (i.e. S_N1 and S_N2). Some preliminary investigations were already available but it was decided to do more in an attempt to establish whether the results could be explained solely in terms of reactions via intermediate ion-pairs and a carbonium ion. Parallel experiments were also carried out with benzhydryl chloride, where nucleophilic attack on the reaction centre is subject to considerable steric hindrance, mainly to establish estimates of the magnitudes of electrolyte effects due to the presence of anionic nucleophiles.

CHAPTER 2

Nucleophilic Substitution On 4-Nitrobenzyl Chloride And 4'-Toluenesulphonate In Aqueous Acetone

2.1 Introduction

This chapter reports the effect of a number of salts (MY) on the rate of decomposition of 4-nitrobenzyl chloride and 4'-toluenesulphonate (RX) in aqueous acetone. Under these conditions the substrate will undergo hydrolysis,

$$RX + H_2O \xrightarrow{k_a} ROH + H^+ + X^- \qquad (A)$$

but may also react with nucleophilic anions,

$$RX + Y^- \xrightarrow{k_b} RY + X^- \qquad (B)$$

to give a product (RY) which may undergo further hydrolysis,

$$RY + H_2O \xrightarrow{k_c} ROH + H^+ + Y^- \qquad (C)$$

It is convenient to define a first-order rate coefficient for the decomposition of RX, k_{RX}, by

$$-\frac{1}{[RX]} \cdot \frac{d[RX]}{dt} = k_{RX}^{inst}$$

$$\text{where } k_{RX}^{inst} = k_a + k_b[Y^-].$$

It must be recognised, however, that k_{RX}^{inst} will not be a constant if reaction B contributes measurably to the rate of decomposition of RX and $[Y^-]$ varies significantly over the range of reaction studied. In practice instantaneous rate coefficients cannot be determined accurately and it was found more convenient to employ the integrated form of the rate equation which gave,

$$k_{RX} = \frac{1}{t}\int_{o}^{t} k_{RX}^{inst}.dt = \frac{1}{t}\ln\frac{[RX]_o}{[RX]_t} \qquad (2.1)$$

Most of the studies were carried out on the reactions at 20°C where only the rate in the presence of azide ions was large enough to permit study over 80-90% of the reaction in a reasonable time. Initial rates were measured for all the other systems. The relatively small effect of perchlorate ions was obtained from the solvolysis at 60°C in order to obtain a more reliable estimate of the effect of this salt than could be obtained from the much slower rate at 20°C. The reactions were followed via the production of acid or chloride ions or the disappearance of azide ions. The concentration of Y^- could be equated to $[Y^-]_i$ (the initial concentration of Y^-) to within a negligibly small error when initial rates were studied so that the integrated first-order rate coefficient (k_I)[†] was given by,

$$k_I = k_{RX} = k_a + k_b[Y^-]_i \qquad (2.2)$$

The vast acceleration on the addition of azide ions implied $k_b[Y^-] >> k_a$ and the expected second-order kinetics were indeed observed. The resulting integrated second-order rate coefficients (k_{II})[‡], were equated to k_b (i.e. $k_{II} \simeq k_b$) to within a negligibly small error. The integrated first-order rate coefficient for a system in which the concentration of the nucleophile is buffered, or for initial rates is then given by,

$$k_{RX} = k_{II}[Y^-]$$

[†] Throughout this thesis k_I and k_{II} represent the first- and second-order rate coefficients for the decomposition of the substrate as measured by the appearance of products.

The interpretation of the rate measurements in the presence of bromide ions was complicated by the hydrolysis of any 4-nitrobenzyl bromide produced. Although this compound undergoes hydrolysis about 60 times more rapidly than the corresponding chloride, the steady state approximation could not be employed since the reaction was only followed over its initial early stages. For this system k_b and hence k_{RX}^{inst} was obtained from the development of acidity and from similar experiments on the decomposition of the organic bromide in the presence of chloride ions. Full details are given in Appendix B and the experimental procedures explained in Chapter 6.

2.2 Results

The decomposition of the organic chloride in 70% aqueous acetone and in the presence of azide ions was studied over a range of initial electrolyte concentrations. The resulting second-order rate coefficients, summarised in Table (2.1), decrease with increasing initial azide ion concentration according to equation (2.3)

$$10^4\ k_{II} = 2{\cdot}581(1-1{\cdot}8[N_3^-]_i) \qquad (2.3)$$

consistent with a negative salt effect for bimolecular reaction between this nucleophile and substrate (see section 1.2.6). Strictly the values of k_{II} in Table (2.1) include changes due to hydrolysis of the substrate but the vast acceleration of decomposition by added azide ions (see Table 2.2) shows that hydrolysis only accounts for a negligibly small fraction of the total reaction.

The principal results are summarised in Table (2.2) which shows the first-order rate coefficient, $(k_{RX})_{0{\cdot}05}$, at an electrolyte concentration of $0{\cdot}05\underline{M}$. These values were obtained by direct measurements, interpolation or extrapolation (see section 2.1). For example the reactions of the 4-toluenesulphonate in the presence of $0{\cdot}03\underline{M}$ azide ions were extrapolated $[N_3^-]_i = 0{\cdot}05\underline{M}$,

Table (2.1)

Second-order rate coefficients (k_{II}) for the decomposition of 4-nitrobenzyl chloride in 70% aqueous acetone in the presence of azide ions at 20^{o}C

$[N_3^-]_i$ mole.l^{-1}	$10^4(k_{II})_{obs}$ l.mole^{-1}sec^{-1}	$10^4(k_{II})_{calc}$ † l.mole^{-1}sec^{-1}
0·03082	2·494	2·438
0·02982	2·421	2·442
0·04814	2·339	2·357
0·04800	2·344	2·358
0·07349	2·275	2·240
0·07315	2·197	2·241
0·09369	2·141	2·146
0·1014	2·125	2·110

† From equation (2.3)

allowing for a similar negative salt effect as observed for the organic chloride reactions with azide ions (see equation 2.3).

It can be seen that sodium perchlorate slightly decelerates the hydrolysis of RCl, indicative of a small, negative salt effect for this electrolyte. The other more nucleophilic anions accelerate the decomposition of both the substrates by factors which qualitatively follow their nucleophilic power.[13,58]

Table (2.2)

The effect of 0·05M electrolytes on the rates of decomposition of 4-nitrobenzyl chloride (RCl) and 4'-toluenesulphonate (ROTS) in aqueous acetone at 20°C

Substrate	% Acetone	Electrolyte	$(k_{RX})_{0 \cdot 05}$ sec^{-1}	$(k_{RX})_{0 \cdot 05}/(k_{RX})_0$
RCl	70	-	$2 \cdot 1 \times 10^{-9}$	-
	70	$NaClO_4$	-	(·979) †
	70	$NaNO_3$	$3 \cdot 4 \times 10^{-9}$	1·6
	70	KOPNB	$5 \cdot 66 \times 10^{-8}$	27
	70	NaBr	$5 \cdot 0 \times 10^{-7}$	248
	70	NaN_3	$1 \cdot 17 \times 10^{-5}$	5600
	85	-	$5 \cdot 4 \times 10^{-10}$	-
	85	$NaClO_4$	-	(·977) †
	85	NaN_3	$1 \cdot 96 \times 10^{-5}$	36000
ROTS	70	-	$1 \cdot 214 \times 10^{-6}$	-
	70	NaCl	$8 \cdot 4 \times 10^{-6}$	6·9
	70	NaN_3	$5 \cdot 70 \times 10^{-4}$	450
	85	-	$3 \cdot 287 \times 10^{-7}$	-
	85	NaCl	$1 \cdot 23 \times 10^{-5}$	37
	85	NaN_3	$9 \cdot 0 \times 10^{-4}$	2630

† At 60°C

2.3 Discussion

2.3.1 Mechanism of solvolysis

There is much evidence to suggest that in the solvents of interest to the present study, 4-nitrobenzyl chloride and 4'-toluenesulphonate solvolyse by mechanism S_N2. Table (2.3)[7] shows that the value of the ratio of the heat capacity to the entropy of activation ($\Delta C_p^{\ddagger}/\Delta S^{\ddagger}$) for the chloride is much smaller than that for S_N1 reactions in 50% aqueous acetone. Similar considerations apply to the 4-toluenesulphonate in 70% aqueous acetone, strongly suggesting hydrolysis by mechanism S_N2 in both these cases (see section 1.2.7). Furthermore it is virtually inconceivable that the alternative ionisation mechanism S_N1 should apply in the less aqueous and therefore less powerfully ionising solvents employed for some of the present reactions.

The values of the entropy of activation ($\Delta S^{\ddagger}$) for the 4-substituted benzyl compounds confirm this conclusion (see Table 2.3), being more negative for the 4-NO_2 compound than for the parent compound which is in turn more negative than for the 4-PhO and 4-MeO compounds. Solvolysis of the 4-PhO and 4-MeO compounds gives a value of the ratio $\Delta C_p^{\ddagger}/\Delta S^{\ddagger}$ in agreement with the S_N1 value and the more negative value of $\Delta S^{\ddagger}$ for the parent and 4-NO_2 compounds is therefore fully consistent with reaction of structurally similar compounds by different mechanisms (see section 1.2.7). The activation parameters of Table (2.3) also provide good evidence that the 4-phenoxy- and 4-methoxy-benzyl chlorides hydrolyse by mechanism S_N1, a conclusion relevant to the discussion in Chapters 3, 4 and 5.

Further confirmation of these conclusions arises from the sensitivities of the rates of solvolysis of the 4-NO_2 and 4-MeO compounds to solvent variation or the nature of the departing group. This is illustrated in Table (2.4) where figures for the 4-nitrobenzhydryl system (believed to undergo

Table (2.3)[7]

Activation parameters for the hydrolysis of benzyl compounds in aqueous acetone at 50°C

Substrate	X	% Acetone	$-\Delta S^{\ddagger}$ cal.deg^{-1}	$\Delta C_p^{\ddagger}/\Delta S^{\ddagger}$
$4\text{-}XC_6H_4CH_2Cl$	NO_2	50	23·49	0·84
	H	50	22·41	0·95
	PhO	50	11·12	2·54
	H	70	23·96	0·91
	PhO	70	11·98	3·60
	MeO	70	11·99	3·83
$4\text{-}XC_6H_4CH_2OT_s$	NO_2	70	19·62	1·55
	H	70	16·64	1·68
	H	85	19·62	1·35
	PhO	85	10·47	2·81
	MeO	85	10·29	2·88
S_N1 reactions		50	-	2·9 ± 0·3 *
		70	-	3·7 ± 0·4 *
		85	-	2·8 ± 0·2 *

* Mean values for reactions known to occur by mechanism S_N1

Table (2.4)

Solvolytic rates in aqueous acetone at 20^{o}C

Substrate	X	% Acetone	k_{RX} sec^{-1}	$\frac{k_{RX}\ (85\%)}{k_{RX}\ (70\%)}$	$\frac{k_{ROT_s}}{k_{RCl}}$
4-$XC_6H_4CH_2Cl$	NO_2	70	2·1 x 10^{-9}	0·26	
		85	5·4 x 10^{-10}		
	MeO	70	2·0 x 10^{-4} *	0·043	
		85	8·6 x 10^{-6}		
4-$XC_6H_4CH_2OT_s$	NO_2	70	1·21 x 10^{-6}	0·27	576
		85	3·29 x 10^{-7}		609
	MeO	85 †	3·24 x 10^{-1}		37700
4-$XC_6H_4CHPhCl$	NO_2 ††	70	2·13 x 10^{-7}	0·059	
		85	1·27 x 10^{-8}		
4-$XC_6H_4CHPhOT_s$	NO_2	85 †	6·53 x 10^{-4}		51400

* From reference 37.

† Calculated from reference 7

†† Fox and Kohnstam - unpublished results.

S_N1 solvolysis - see reference 7) have been included for comparison. It can be seen that the hydrolysis of the 4-methoxybenzyl and 4-nitrobenzhydryl compounds show similar rate retardations on changing the solvent from 70% to 85% aqueous acetone and similar rates of hydrolysis of the 4-toluenesulphonate relative to the chloride. Both these ratios (solvent and departing group variation) have substantially different values for the 4-nitrobenzyl system. This is fully consistent with the operation of mechanism S_N2 and S_N1 for the 4-nitro- and 4-methoxy-benzyl compounds respectively (see section 1.2.5 and reference 59).

2.3.2 Reaction in the presence of nucleophiles

Arguments have been advanced in the previous section strongly suggesting that the 4-nitrobenzyl compounds react with water by mechanism S_N2 in aqueous acetone. Any reaction with more powerful nucleophiles than water is, therefore, by the same mechanism. This proposal is fully consistent with the substantial acceleration with added anions which increases with their nucleophilicity (Table 2.2) and with the observation of second-order kinetics for the reaction with azide ions (Table 2.1).

Comparison of the rate ratios in Table (2.5) with those in Table (2.4) shows that, unlike the hydrolysis, the reaction with azide ions is accelerated by reducing the water content of the solvent and that the

Table (2.5)

Rates of reaction of 4-nitrobenzyl chloride and 4'-toluenesulphonate with azide ions in aqueous acetone at 20°C

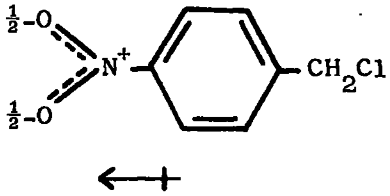
$\frac{k\ (85\%)}{k\ (70\%)}$	$\frac{k_{ROT_s}}{k_{RCl}}$
1·66 (RCl)	48·5 (70% aqueous acetone)
1·58 (ROT_s)	46·0 (85% aqueous acetone)

k_{ROT_s}/k_{RCl} ratio is even smaller than for hydrolysis, as expected for the operation of mechanism S_N2 (see section 1.2.5 and reference 59).

2.3.3 Electrolyte effects

The negative electrolyte effect observed for the reaction of 4-nitrobenzyl chloride with azide ions (see equation 2.3) is also fully consistent with the operation of mechanism S_N2 (see section 1.2.6). On the other hand, the small retardation of hydrolysis by sodium perchlorate (see Table 2.2) is surprising. Even in S_N2 hydrolyses passage into the transition state involves a creation of electric charges and, therefore, according to the electrostatic effect proposed by Ingold (see section 1.2.6) an accelerating electrolyte effect would be expected. The salt induced medium effect exerted by the perchlorate anion in aqueous organic solvents is in the direction of increasing the activity of the water component[23] and should, therefore, also enhance the solvolytic rate.

It is suggested, that, in this instance, a specific electrolyte-substrate interaction or complex formation is being observed. The 4-nitro group will tend to give rise to a dipole moment in the covalent substrate,



which is, therefore, quite capable of complexing with the polarisable perchlorate anion and stabilising the initial state in the hydrolytic process. In the S_N2 transition state, electron donation by the nucleophile toward the reaction centre would be expected to reduce the dipole moment and, therefore, the tendency for complex formation, resulting in a net negative electrolyte effect. The opposite tendency would be expected if the S_N1 mechanism were operative since development of a positive charge at the reaction centre would enhance the dipole moment and complex formation relative to the initial state, accelerating the hydrolysis. Having established that the hydrolysis is via mechanism S_N2 (see section 2.3.1), this somewhat tentative explanation of the anomalous perchlorate effect is fully consistent with the operation of that mechanism.

2.4 Conclusion

All the evidence present in this chapter is fully consistent with the operation of mechanism S_N2 for the reactions of 4-nitrobenzyl chloride and 4'-toluenesulphonate with water and nucleophilic anions. The alternative explanation of these reactions via intermediate ion-pairs with no direct attack by the nucleophile on covalently bound substrate is considered in Chapter 5.

CHAPTER 3

The Effect Of Added Electrolytes On The Decomposition Of 4-Methoxybenzyl And Benzhydryl Chlorides In Aqueous Acetone

3.1 Introduction

This chapter presents the results for the effect of added nucleophiles on the rate of decomposition of 4-methoxybenzyl chloride in 85% aqueous acetone. Parallel experiments were also carried out with benzhydryl chloride as the substrate since it is a widely held view that this compound is sterically unfavourable to bimolecular attack, unlike 4-methoxybenzyl chloride. The results of a study of these systems in 70% aqueous acetone by other workers[37,60] in these laboratories are included in the discussion in an attempt to obtain a more complete interpretation.

It has been pointed out in the previous chapter that all the observations of the hydrolysis of 4-methoxybenzyl chloride in aqueous acetone are fully consistent with the operation of mechanism S_N1, but strictly the evidence merely suggests that attack by water occurs on an intermediate (or several intermediates) whose formation is rate determining. This intermediate could be a fully developed carbonium ion (mechanism S_N1) or one or more ion pair intermediates as recently postulated.[54]

In view of the vast amount of evidence consistent with reaction via S_N mechanisms it is proposed to discuss the results qualitatively on this basis in the present chapter. The various possibilities are considered in detail in Chapters 4 and 5.

Values of $(k_{RX})_{0{\cdot}05}$, the integrated first-order rate coefficient for the disappearance of substrate in the presence of 0·05M electrolyte, were obtained by direct measurement, extrapolation or interpolation of the rate coefficients obtained from determinations of the development of acidity or production of chloride ions. Rates of decomposition of the organic chlorides in the presence of chloride ions were obtained from measuring the release of $^{36}Cl^-$ ions from substrates containing 36-chlorine. The principle results are shown in Table (3.1). Details of the experimental procedures are given in Chapter 6.

3.2 Discussion

The electrolytes listed in Table (3.1) are arranged in the order of increasing nucleophilicity of the anions. It can be seen that this order is in no way related to the magnitude of their effect on the decomposition of benzhydryl chloride where steric factors are considered to oppose bimolecular attack by nucleophiles. As a first approximation therefore, the values of $(k_{RX})_{0.05}/(k_{RX})_0$ for this compound can be taken as a measure of the magnitude of the electrolyte effect in the rate-determining ionisation of the S_N1 reaction i.e.,

$$Ph_2CHCl \longrightarrow Ph_2CH^+ + Cl^-$$

Although the reaction centre of the 4-alkoxybenzyl halides is not sterically unfavourable to bimolecular attack, no such reaction of these compounds can be envisaged with the very weakly nucleophilic perchlorate and tetrafluoroborate anions. The effect of these anions on the rates of decomposition therefore also reflects the magnitude of electrolyte effects on the rate-determining ionisation and it can be seen that relative to benzhydryl chloride, the effects are about 1% larger for 4-methoxybenzyl chloride in 70% aqueous acetone (~ 3% in 85% aqueous acetone) and about 2% less for the 4-phenoxy compound. Since all three compounds show virtually the same sensitivity to changes in the solvent composition these differences probably arise from some non-specific electrostatic interaction (see sub-section 1.2.6).

Table (3.1)

Values of $(k_{RX})_{0\cdot05}/(k_{RX})_0$ for the decomposition in aqueous acetone of 4-$ROC_6H_4CH_2Cl$ and Ph_2CHCl at 20°C

	70% aqueous acetone*			85% aqueous acetone	
	$ROC_6H_4CH_2Cl$		Ph_2CHCl	$MeOC_6H_4CH_2Cl$	Ph_2CHCl
	RO=MeO	RO=PhO			
$HClO_4$	-	1·178	1·210	-	-
$NaClO_4$	1·159	1·128	1·151	1·320	1·274
$NaBF_4$	1·131	1·110	1·120	-	-
$NaSO_3Ph$	1·109	1·073	1·057	-	-
$NaNO_3$	1·144	1·109	1·070	-	1·212
Me_4NF	1·025	1·059	0·935	-	-
HCl	1·210	-	1·068	-	-
NaCl	1·162	1·217	1·015	1·609	1·154
KBr	1·255	2·496	1·091	-	-
NaN_3	1·793	19·82	1·136	9·506 (4·464)†	1·365 (1·047)†

* Results from reference 60

† $$\frac{k_{RX}\ (0\cdot05\underline{M}\ NaN_3 + 0\cdot15\underline{M}\ NaClO_4)}{k_{RX}\ (0\cdot2\underline{M}\ NaClO_4)}$$

$$\frac{(k_{RX})0\cdot2\underline{M}\ NaClO_4}{(k_{RX})_0} = 2\cdot15 \text{ for 4-}MeOC_6H_4CH_2Cl \text{ in 85\% aqueous acetone}$$

The accelerating effect of electrolytes on the decomposition of benzhydryl chloride is about 13% larger in the less aqueous solvent suggesting that this difference too arises from electrostatic effects which depend on the dielectric constant of the medium.[18] The somewhat larger difference found in the presence of azide ions is anomalous but may arise from some bimolecular attack which could conceivably occur in the less powerfully ionising 85% solvent. It is consdered that bimolecular attack on benzhydryl systems is feasible in the light of recent studies (see sub-section 1.3.1, page 25).

Apart from the perchlorates and tetrafluoroborates all the other electrolytes examined show a larger accelerating effect on the decomposition of the alkoxybenzyl chlorides than is to be expected on the basis of the observations of the effect of weakly nucleophilic anions. This difference increases with increasing nucleophilic power of the anion and is greater for the 4-phenoxy compound than for the 4-methoxy compound. The very substantial acceleration by azide ions, the most powerful nucleophile employed is particularly striking.

Qualitatively these results are clearly consistent with bimolecular (S_N2) attack by these nucleophiles accompanying the hydrolysis of the alkoxybenzyl compounds, the larger effect for the 4-phenoxy compound arising from the poorer capacity of the PhO group for electron release which can be expected to effect the rate of S_N1 hydrolysis to a greater extent than the rate of S_N2 attack by nucleophiles.[13] Similarly, the much larger accelerating effect of the azide ions on the 4-methoxy compound in the less aqueous solvent is fully consistent with the prediction and many previous observations[61] that the rate of S_N2 attack by anions is much less sensitive to solvent changes than the rate of ionisation of a C-Cl linkage.

A full quantitative discussion of these results requires a consideration of the reactions of the carbonium ions produced in the S_N1 solvolysis with the anions present in the reaction mixture since an estimate of the rate coefficients for bimolecular (S_N2) attack is only possible when this information is available. The determination of these required intervention constants is considered in the following chapter.

CHAPTER 4

Electrolyte Parameters And Intervention Constants For The Solvolysis Of 4-Methoxybenzyl And Benzhydryl Chlorides In Aqueous Acetone

4.1 The Mechanism of Solvolysis

4.1.1 The need for a carbonium ion intermediate

It has already been pointed out (see section 2.3.1) that the activation parameters for the hydrolysis of 4-methoxybenzyl and benzhydryl chlorides demand the rapid attack of water on an intermediate formed in the rate-determining step. Mechanism S_N1 assumes this intermediate to be the fully developed carbonium ion whose formation is reversible,

$$\mathrm{RCl} \underset{-3}{\overset{1}{\rightleftharpoons}} \mathrm{R^+} + \mathrm{Cl^-}$$

so that its stationary concentration is affected by the concentration of the common chloride ions which are produced as the reaction proceeds. Assuming a rapid reaction of the carbonium ion with water,

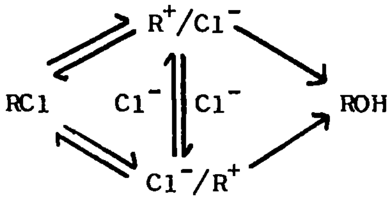
$$\mathrm{R^+} + \mathrm{H_2O} \xrightarrow{6} \mathrm{ROH} + \mathrm{H^+}$$

the observed rate coefficient for hydrolysis

$$k_{\mathrm{ROH}}^{\mathrm{inst}} = \frac{k_6[\mathrm{R^+}]}{[\mathrm{RCl}]} = \frac{k_1}{1+\alpha[\mathrm{Cl^-}]}$$

$$(\alpha = k_{-3}/k_6)$$

can be expected to decrease as the reaction proceeds if $\alpha[\mathrm{Cl^-}]$ is not negligibly small compared with unity and to be reduced by the addition of chloride ions. This common-ion effect (mass-law retardation) is diagnostic of reaction by this mechanism and cannot arise in hydrolysis via the attack of water on intermediate ion-pairs since the principle of microscopic reversibility[62] requires that any reaction of an anion with such an ion-pair will form a similar ion-pair without affecting the rate of hydrolysis.



In practice added chloride ions retarded the hydrolysis of the present compounds (see Table 4.1)* suggesting reaction via an intermediate carbonium ion (i.e. mechanism S_N1). If hydrolysis occurs via the attack of water on an intermediate ion-pair the present observations could only arise from a negative electrolyte effect on the addition of sodium chloride but such an assumption is fraught with difficulties. Evidence presented in the previous chapter demands that under these conditions $(k_{ROH})_{0\cdot05}/(k_{ROH})_0$ should be about 1% greater for 4-methoxybenzyl chloride than for benzhydryl chloride in the 70% solvent and about 3% greater in 85% aqueous acetone. In fact these ratios now have the smaller value for the methoxy compound. However, the change in $(k_{ROH})_{0\cdot05}/(k_{ROH})_0$ on altering the solvent from 70% to 85% aqueous acetone is much less than that found using sodium perchlorate† (see Table 3.1) suggesting that these ratios do not arise solely from a negative

---

* Integrated first-order rate coefficients for hydrolysis are reported in Table (4.1) as these coefficients were constant over the course of any given run and can therefore be expected to differ only minimally from k_{ROH}^{inst}.

† In the presence of $NaClO_4$,

$$k_{RX} = k_{ROH}$$

Table (4.1)

The effect of 0·05M chloride ions on the rate of hydrolysis and of overall decomposition of 4-methoxybenzyl and benzhydryl chlorides in aqueous acetone at 20°C

% Acetone	Substrate	$(k_{RX})_{0\cdot05}/(k_{RX})_0$	$(k_{ROH})_{0\cdot05}/(k_{ROH})_0$
70*	$4\text{-MeOC}_6H_4CH_2Cl$	1·162	0·865
	Ph_2CHCl	1·014	0·914
85	$4\text{-MeOC}_6H_4CH_2Cl$	1·609	0·935
	Ph_2CHCl	1·212	0·960

* From reference 60

electrolyte effect. Furthermore, the fact that chloride ions have a larger effect on the total rate of decomposition of benzhydryl chloride than on its rate of hydrolysis ($k_{RX} > k_{ROH}$ for [NaCl] > 0) would then require attack of chloride ions either on covalently bound substrate or on an ion-pair, contrary to widely held views. In any case the effect of a solvent change on $(k_{RX})_{0\cdot05}/(k_{RX})_0$ for the decomposition of this compound in the presence of chloride ions is virtually the same as when the electrolyte is sodium perchlorate while any attack of chloride ions on the covalent substrate or on ion-pairs derived from it should give a proportionally larger value for this ratio in the less aqueous solvent (cf. the effect of N_3^- and Cl^- ions on the decomposition of $4\text{-MeOC}_6H_4CH_2Cl$ - see Table (3.1)).

It would therefore, appear that the reactions of 4-methoxybenzyl and benzhydryl chlorides certainly occur via an intermediate carbonium ion and this species must therefore be included in any reaction scheme. The question of whether hydrolysis can also occur via attack by water on intermediate ion-pairs now needs discussion.

4.1.2 The possibility of ion-pair hydrolysis

It has already been pointed out that a consideration of the activation parameters have provided a delicate criterion of solvolytic mechanisms (see sub-sections 1.2.7 and 2.3.1) considered at the time in terms of classical S_N1 and S_N2 reactions. On this view benzhydryl and 4-methoxybenzyl chlorides react via the unimolecular (S_N1) mechanism whereas 4-nitrobenzyl chloride undergoes bimolecular (S_N2) solvolysis. If this bimolecular solvolysis actually involves the rate-determining attack by water on one or more intermediate ion-pairs as postulated by Sneen,[54] then the exclusion of any significant 'S_N2' hydrolysis in the reactions of 4-methoxybenzyl and benzhydryl chlorides also excludes the reaction paths postulated by Sneen i.e. hydrolysis would occur almost completely if not entirely via the fully developed carbonium ion.

On the other hand the hydrolysis of the methoxy compound and benzhydryl chloride could conceivably involve reactions between water and ion-pairs which do not contribute to the 4-nitrobenzyl chloride solvolysis e.g. if this reaction occurs via the classical S_N2 route. Qualitatively, the substantial acceleration of decomposition of 4-methoxybenzyl chloride by azide ions (see Table 3.1) demands the rate-determining attack of this nucleophile on the substrate (S_N2) or on an intermediate ion-pair such that the free energy of the transition state for its formation is considerably less than the free energy of the transition state for formation of the fully developed carbonium ion. It can then be shown[63] that any significant hydrolysis of such an ion-pair in addition to the hydrolysis of the carbonium ion would be inconsistent with the observation that the ratio $\Delta C_p^{\ddagger}/\Delta S^{\ddagger}$ is independent of the nature of the substrate for hydrolyses generally regarded as S_N1 and that certainly no more than 10% of the hydrolysis of the present compounds can conceivably occur by attack of water on intermediate ion-pairs.

It therefore seems safe to assume that S_N1 hydrolysis of 4-methoxybenzyl and benzhydryl chlorides occurs entirely via the fully developed carbonium ion, a conclusion which greatly facilitates the calculation of electrolyte parameters and intervention constants and also strongly supports mechanism S_N1 as previously postulated for unimolecular hydrolysis. At present, however, this conclusion does not preclude the attack of nucleophilic anions on any intermediate ion-pairs.

4.2 Estimation of the Anion Intervention Constants

4.2.1 The mass-law constant (α) for benzhydryl chloride solvolysis

It has been shown previously that the decomposition of $Ph_2CH^{36}Cl$ in the presence of chloride ions is fully consistent with the added chloride ions only accelerating the rate of decomposition by the amount expected for an electrolyte effect (see section 3.2). Only the fully developed carbonium ions formed in the rate-determining step react with chloride ions. As both k_{RX} and k_{ROH} can be measured for a system containing added sodium chloride it is convenient to define a parameter,

$$\alpha_{obs} = \frac{k_{RX}-k_{ROH}}{k_{ROH}Cl_R^-}^{\dagger} \qquad (4.1)$$

$$\text{where } Cl_R^- = \frac{1}{t}\int \left([Cl^-]-[RCl]\,\frac{[^{36}Cl^-]}{[R^{36}Cl]}\right) dt$$

[†] k_{RX} and k_{ROH} measured at the same time t

It is shown in Appendix E that if reaction occurs by mechanism S_N1

$$RX \underset{-3}{\overset{1}{\rightleftharpoons}} R^+ + X^- ; \qquad R^+ \xrightarrow[H_2O]{6} ROH$$

then α_{obs} is identical with α defined as,

$$\alpha = k_{-3}/k_6$$

If on the other hand ionisation occurs via intermediate ion-pairs,

$$RX \underset{-1}{\overset{1}{\rightleftharpoons}} R^+/X^- \underset{-2}{\overset{2}{\rightleftharpoons}} R^+//X^- \underset{-3}{\overset{3}{\rightleftharpoons}} R^+ + X^-$$

$$R^+ \xrightarrow{6} ROH$$

then,

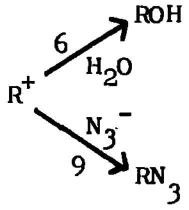
$$\alpha_{obs} = \frac{\alpha}{1+x+xy}$$

where $\alpha = k_{-3}/k_6$; $\quad x = k_3/k_{-2}$; $\quad y = k_2/k_{-1}$

Values of α_{obs} obtained from equation (4.1) for benzhydryl chloride in 85% aqueous acetone are shown in Table (4.2).

4.2.2 Azide ion intervention in the solvolysis of benzhydryl chloride

The reactions of all the other anions studied, except azide ions, form products which hydrolyse rapidly and do not therefore retard the solvolysis reaction. In principle it is possible to obtain the intervention constant for azide ions ($\beta_{N_3^-}$),



$$\beta_{N_3^-} = k_9/k_6$$

Table (4.2)

The parameter α_{obs} for the decomposition of $Ph_2CH^{36}Cl$ in 85% aqueous acetone at 20°C

[NaCl] mole.l^{-1}	10^5 $(k_{RX})_{mean}$ sec^{-1}	10^5 $(k_{ROH})_{mean}$ sec^{-1}	$[Cl_R^-]_{mean}$ mole l^{-1}	α_{obs} mole^{-1} l †
0·05106	1·310	1·095	0·0483	4·06 ± 0·08
0·05058	1·301	1·076	0·0480	4·33 ± 0·11
0·09997	1·401	1·022	0·0949	3·92 ± 0·08
0·09914	1·389	1·021	0·0940	3·84 ± 0·11

† The error quoted is the standard error of the mean

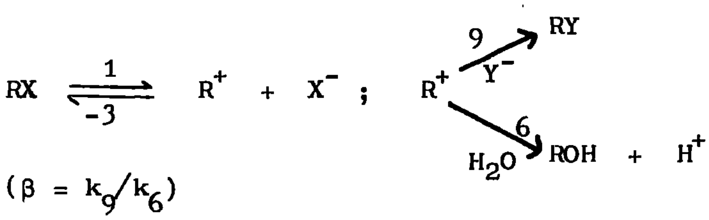
by measuring k_{RX} and k_{ROH} (as for Cl^- intervention constant α) provided that no azide ions attack the covalent substrate or any intermediate ion-pairs. However the ratio $(k_{RX})_{0\cdot05}/(k_{RX})_0$ for the decomposition of benzhydryl chloride in the presence of NaN_3 increases more in changing the solvent from 70% to 85% aqueous acetone than it does in the presence of weakly nucleophilic anions suggesting that there may be a small but significant rate-determining attack by azide ions (see Chapter 3, section 3.2. and Table 3.1). It is therefore necessary to employ indirect methods for estimating $\beta_{N_3^-}$ in the 85% solvent.

Carbonium ions are notoriously unselective reagents[12,32] though there is much evidence that the selectivity of such species increases with their increasing stability under solvolytic conditions.[18,64] Consequently, the ratio $\beta_{N_3^-}/\alpha_{Cl^-}$ for a highly stabilised carbonium ion could be taken as an upper limit for this ratio for the present compounds. The 4-methoxybenzhydryl system was chosen for these experiments since the approximately 1000-fold acceleration of the solvolysis on introducing the 4-MeO group will be accompanied by a very much smaller acceleration of any rate-determining reaction with anions so that it seemed likely that all the decomposition occurred via the fully developed carbonium ion.

4.2.3 The 4-methoxybenzhydryl system - a model for anion interventions on a carbonium ion

It has already been pointed out (see previous section) that the reactions of 4-methoxybenzhydryl compounds (RX) under solvolytic conditions should occur entirely via the fully developed carbonium ion (R^+). If this assumption is correct any intervention of anions which combine with R^+ to form a product stable under the prevailing conditions should be independent of the nature of the leaving group (X).

The decomposition of the organic chloride (RCl) and 4-nitrobenzoate (ROPNB) was studied in 85% aqueous acetone; the chloride (RCl) in the presence of added azide ions (N_3^-) and 4-nitrobenzoate ions ($OPNB^-$), the 4-nitrobenzoate (ROPNB) only in the presence of azide ions. Under these conditions the product (RY) of any attack by the anion (Y^-) on the carbonium ion (R^+) undergoes no significant solvolysis during the life-time of the substrate (RX). For reaction solely by mechanism S_N1,



$(\beta = k_9/k_6)$

it is shown in Appendix D that

$$[ROH]_x = \frac{1}{\beta} \ln \frac{1+\beta[Y^-]_i}{1+\beta([Y^-]_i - [RX]_i)}$$

where the subscript 'i' refers to initial concentration (t=0) and 'x' to the time ($t = t_x$) when decomposition of the substrate (RX) is complete. The intervention constant (β) was obtained graphically from the observed $[ROH]_x([ROH]_x = [H^+]_x + [HY]_x)$. The values thus obtained are quoted in Table (4.3) and it can be seen that the nature of leaving group (X) does not influence the value of the intervention constant (β) in this system supporting the view that all reactions occur via the fully developed carbonium ion, under these conditions, as envisaged above. Full experimental details are given in Chapter 6.

Table (4.3)

Intervention constants (β) for various anions (Y^-) on the 4-methoxybenzhydryl cation (R^+) in 85% aqueous acetone

Y^- ††	RX ††	Temp. °C	β $mole^{-1}l$
N_3^-	ROPNB	50·51	1270 ± 48 †
N_3^-	ROPNB	71·18	1236 ± 50 †
N_3^-	RCl	-0·21	1334 ± 40 †
Cl^-	RCl	0	700 *
$OPNB^-$	ROPNB	71·33	100 *
$OPNB^-$	RCl	-0·21	73·8 ± 2·6 †

* Results from reference 65

† Error calculated for 1% error in $[RX]_i$

†† R = 4-MeOC_6H_4CHPh- ; OPNB = $4\text{-NO}_2C_6H_4CO_2-$

Previous evidence[66] indicated a small positive temperature effect for intervention constants, however no such effect was observed for the azide ion intervention constant in the present system (Table 4.3) but a small temperature dependence of β_{OPNB^-} was observed. It is suggested that in this system the attack by azide ions (very powerful nucleophiles) on the carbonium ion (R^+) requires little extra activation energy than collapse of the solvation sphere around R^+ to form the alcohol (ROH). In the case of 4-nitrobenzoate anions additional activation over the hydrolytic process may well reflect the very poor nucleophilic power of this anion in agreement with the $\beta_{N_3^-}/\beta_{OPNB^-}$ ratio of 13-15 (see Table 4.3).

The value of $\beta_{N_3^-}/\beta_{Cl^-} \simeq 2$ which in the case of RCl is identical with the ratio β/α. is similar to that for the $\beta_{N_3^-}/\alpha$ ratio for the carbonium ion derived from benzhydryl chloride in 70% aqueous acetone.[60] It therefore seems reasonable to consider $\beta_{N_3^-}/\alpha$ ratios between 1·5 and 2 for the carbonium ions derived from 4-methoxybenzyl and benzhydryl chlorides in 70% and 85% aqueous acetone since these carbonium ions are regarded as less stable and therefore less selective than their 4-methoxybenzhydryl counterpart. Such values are employed in the quantitative analysis of the kinetic data in Chapter 5.

4.3 Electrolyte Parameters for 4-Methoxybenzyl and Benzhydryl Chloride

It was argued earlier (see section 4.1) on the basis of the activation parameters, that hydrolysis of alkoxybenzyl and benzhydryl chlorides in aqueous acetone can be assumed to occur entirely via the fully developed carbonium ion (R^+) which can either be formed directly from the covalent substrate,

$$RCl \underset{-3}{\overset{1}{\rightleftharpoons}} R^+ + Cl^- \qquad (S_N1)$$

or via one or two intermediate ion-pairs,

$$\mathrm{RCl} \underset{-2}{\overset{1}{\rightleftharpoons}} \mathrm{R^+/Cl^-} \underset{-3}{\overset{3}{\rightleftharpoons}} \mathrm{R^+} + \mathrm{Cl^-}$$

$$\mathrm{RCl} \underset{-1}{\overset{1}{\rightleftharpoons}} \mathrm{R^+/Cl^-} \underset{-2}{\overset{2}{\rightleftharpoons}} \mathrm{R^+//Cl^-} \underset{-3}{\overset{3}{\rightleftharpoons}} \mathrm{R^+} + \mathrm{Cl^-}$$

A knowledge of the magnitude of the electrolyte effects (see section 1.2.6) on each individual step of these solvolysis schemes is obviously desirable in the detailed discussion of the possible reaction mechanisms but this knowledge is not available. It has therefore been assumed that the electrolyte effect on k_1 in all the schemes is by far the most significant since it is here that the electric charges are created. The following determination of the electrolyte parameters for solvolysis of these compounds is therefore considered to apply equally well to k_1 for all schemes.

The effect of an electrolyte on k_1 can be considered in terms of the Brönsted relation[14] (see sub-section 1.2.6 and equation 1.3). Strictly this would require a knowledge of the electrolyte effect on the activity coefficients of both the substrate (f_{RX}) and the transition state ($f_{\ddagger}$), but in line with previous workers the effect on their ratio need only be considered. All the available theories concerning kinetic electrolyte effects lead to limiting laws in very dilute solutions in the form,

$$\ln \frac{k_1}{k_1^o} = 1 + B_{MY}[MY] \qquad (4.2)$$

where B_{MY} is a constant for a given salt, MY. However, many workers[67] have claimed that a linear relation between k_1 and the electrolyte concentration,

$$k_1 = k_1^o\,(1 + b_{MY}[MY]) \qquad (4.3)$$

gives a better fit with experimental results. There is no significant difference between the two approaches for small values of the ionic strength when electrolyte effects are small and it may well be that equation (4.3) is to be preferred at ionic strengths up to approximately 0·1$\underline{M}$ since this formulation partly cancels the effect of higher order terms in equation (4.2). In the present work, calculations were greatly simplified by the use of equation (4.3) which has therefore been employed throughout.

It is shown in Appendix E that provided no reaction occurs with the substrate (RX) or the intermediate ion-pairs (R^+/X^-, $R^+//X^-$), then both classical (S_N) and ion-pair schemes give rise to:

†

$$\frac{k_{RX}}{(k_{RX})_0} = \frac{1 + b_{HCl}[HCl] + b_{MY}[MY]}{1 + b_{HCl}[HCl]_0} \cdot \frac{1 + \alpha[HCl]_0}{1 + \alpha[HCl]} \qquad (4.4)$$

in the absence of added chloride ions. In the presence of added Cl^- ions,

†

$$\frac{k_{ROH}}{(k_{ROH})_0} = \frac{1 + b_{HCl}[HCl] + b_{NaCl}[NaCl]}{1 + b_{HCl}[HCl]_0} \cdot \frac{1 + \alpha[HCl]_0}{1 + \alpha[Cl^-]} \qquad (4.5)$$

However, all the above expressions apply to instantaneous rates whereas in practice integrated rate equations were used and the mean integrated rate coefficient for a given run calculated. This difficulty can be overcome by integrating equations (4.2) and (4.3) but the 'square-root approximation' (see appendix A) by which the mean integrated rate coefficient can be equated to an instantaneous rate coefficient at a particular ionic strength, is perfectly satisfactory and was employed in the calculation of the electrolyte parameters.

---

† Subscript '0' refers to solvolysis in the pure solvent (i.e. no added salts).

4.3.1 Electrolyte parameters for the solvolysis of benzhydryl chloride

Values of $b_{MY}^{Ph_2CHCl}$ were obtained for reaction in 70% aqueous acetone from the results of Queen[60] and Shillaker[68], and were calculated by a similar method to that employed by Queen except that the linear relation (equation (4.3)) was assumed.

The value of the chloride ion intervention constant, α, determined from hydrolysis and radio-chlorine exchange experiments, did not require any knowledge of the electrolyte parameters (see section 4.2). Hydrolysis in the pure solvent and in the presence of added HCl then gave b_{HCl} from equation (4.5). The electrolyte parameters for NaCl and $NaClO_4$ can then be obtained from experiments in the presence of these salts via equations (4.5) and (4.4) respectively.

Azide ions, the only other nucleophile of interest in the present work, provide some addition problems since HN_3 will not be dissociated to any significant extent in the solvents now employed. As a result the electrolyte produced by hydrolysis in the presence of NaN_3 is, in effect, NaCl so that,

$$\frac{k_{RX}}{(k_{RX})_0} = \frac{1+b_{NaCl}[Cl^-]+b_{NaN_3}[N_3^-]}{1+b_{HCl}[HCl]_0} \cdot \frac{(1+\beta[N_3^-])(1+\alpha[Cl^-]_0)}{1+\alpha[Cl^-]+\beta[N_3^-]} \qquad (4.6)$$

$$\text{where } [Cl^-] = [RCl]_{initial} - [RCl]$$

$$[N_3^-] = [N_3^-]_{initial} - [Cl^-]$$

and β, the intervention constant for azide ions, could be determined independently without any knowledge of the electrolyte parameters.

The virtually constant difference between the accelerating effect of 0·05<u>M</u> electrolytes on the decomposition of benzhydryl chloride in aqueous acetone (see Table 3.1 section 3.2) suggests that

$$b^{Ph_2CHCl}(85\%) = b^{Ph_2CHCl}(70\%) + 2{\cdot}6 \qquad (4.7)$$

Table (4.4) shows the values of these parameters and it is noteworthy that $b_{NaCl}^{PH_2CHCl}$ (85%) and $b_{NaClO_4}^{Ph_2CHCl}$ (85%) obtained from equations (4.4) and (4.5) and a knowledge of α in this solvent ($\alpha = 4{\cdot}0$, see section 4.2) agree well with those obtained from equation (4.7).

No direct evaluation of the intervention constant for azide ions, β, was possible since the results in this solvent indicated additional attack on species other than the carbonium ion (see section 3.2).

4.3.2 Electrolyte parameters for the solvolysis of 4-methoxybenzyl chloride

An extensive study[60] of the reactions of benzhydryl chloride (I) and 4-methoxybenzyl chloride (II) in 70% aqueous acetone showed that a constant difference existed between the accelerating effects of weakly nucleophilic anions (ClO_4^-, BF_4^-) on the rates of decomposition of the two substrates (I and II), irrespective of the nature of the cation. Some of the results of this study[60] are quoted in Table (4.4). It therefore seems reasonable to write,

$$b_{II}\ (70\%) = b_I\ (70\%) + 0{\cdot}2 \qquad (4.8)$$

where the subscripts I and II indicate the substrate to which the electrolyte parameter (b) refers. The present study on the reactions of these substrates in 85% aqueous acetone in the presence of sodium perchlorate suggests that,

$$b_{II}\ (85\%) = b_I\ (85\%) + 0{\cdot}8 \qquad (4.9)$$

The resulting values of the electrolyte parameters are summarised in Table (4.4). As expected, they indicate effects which are specific to the electrolyte but the methods by which they were calculated ensures the absence of any features not already mentioned (see section 1.2.6) and rationalised previously by Queen.[60] No further discussion of the electrolyte effects therefore seems necessary.

Table (4.4)

Electrolyte parameters (b) for S_N1 reaction in aqueous acetone at 20°C

	70% aqueous acetone*		85% aqueous acetone	
MY	Ph_2CHCl	$MeOC_6H_4CH_2Cl$ †	Ph_2CHCl ‡	$MeOC_6H_4CH_2Cl$ ††
$NaClO_4$	3·01	3·21	5·61 (5·62)ϕ	6·4
NaCl	0·36	0·56	2·97 (3·01)ϕ	3·8
HCl	1·51	1·71	4·1	4·9
NaN_3	3·00	3·20	5·6	6·4
α_{obs} (mole^{-1} l)	2·2	4·0	4·0	5·5
$\beta_{N_3^-}$ (mole^{-1} l)		7·0‡‡	7·0‡‡	9·6‡‡

* Calculated from the data of Queen[60] and Shillaker[68]

† Calculated from equation (4.8)

‡ Calculated from equation (4.7)

ϕ Values in parentheses from equation (4.4) and (4.5)

†† Calculated from equation (4.9)

‡‡ Assuming $\beta = 1{\cdot}75\ \alpha_{obs}$ (see sub-section 4.2.3)

Intervention constants, α, for the competition between chloride ions and water for the carbonium ion derived from 4-methoxybenzyl chloride were obtained via equation (4.5), once b_{NaCl} and b_{HCl} had been obtained. The values and the results on which they are based are shown in Table (4.5(a)) from which it can be seen that the mean value of α in 85% aqueous acetone (5·52 mole^{-1} l) is greater than that in the 70% solvent (4·00 mole^{-1} l).^{60}

Table (4.5(b)) shows the values of α in solutions of constant ionic strength ($[NaClO_4] + [NaCl] = 0{\cdot}2\underline{M}$) derived from the expression,

$$\frac{k_{ROH}}{(k_{ROH})_{0\cdot2\ NaClO_4}} = \frac{1+b_{NaCl}[NaCl]+b_{HCl}[HCl]+b_{NaClO_4}[NaClO_4]}{1+0\cdot2 \times b_{NaClO_4}+b_{HCl}[HCl]_{0\cdot2}} \cdot \frac{1+\alpha[Cl^-]_0}{1+\alpha[Cl^-]}$$

The resulting values of α are indistinguishable from those in Table (4.5(a)), within the limits of experimental error, thus confirming that electrolyte effects on intervention constants can be neglected and justifying this assumption in the subsequent calculations.

4.4 Conclusion

A knowledge of the electrolyte parameters and intervention constants for the various added anions makes it possible to calculate the rate of S_N1 reaction of the alkoxybenzyl compounds in the presence of these electrolytes and hence, by comparison with the observed rates of decomposition, k_{RX}, to estimate the bimolecular (S_N2) contribution to the overall rate of reaction. However, if there is any attack by these anions on intermediate ion-pairs, the corresponding analysis becomes rather different. As it is possible to derive a general rate equation covering all the possibilities, the discussion of these possibilities is deferred until the next chapter.

Table (4.5)

Intervention constants for chloride ions (α) in the S_N1 hydrolysis of $4\text{-}MeOC_6H_4CH_2Cl$ in 85% aqueous acetone at 20^oC

(a)

[NaCl]	[HCl] *	$[HCl]_0$*	$\frac{k_{ROH}}{(k_{ROH})_0}$		α $mole^{-1}$ l.
0·05036	0·00596	0·00477	0·931		5·60
0·04945	0·00481	0·00477	0·930		5·66
0·05037	0·00719	0·00725	0·939		5·45
0·05037	0·00821	0·00725	0·940		5·38
				Av.	5·52

(b) At constant ionic strength; $[NaClO_4]$ + [NaCl] = 0·2M

[NaCl]	[HCl]*	$[HCl]_0$*	$\frac{k_{ROH}}{(k_{ROH})_{0\cdot2\ NaClO_4}}$		$\alpha^{\dagger}$ $mole^{-1}$ l.	$\alpha^{\ddagger}$ $mole^{-1}$ l.
0·02000	0·00746	0·00839	0·8834		5·82	5·65
0·01973	0·00745	0·00839	0·8865		5·68	5·54
0·05097	0·00742	0·00839	0·7496		5·39	5·23
0·04944	0·00801	0·00839	0·7559		5·35	5·19
				Av.	5·56	5·40

* Effective concentrations from the 'square root' approximation (see Appendix A)

† Salt parameters from Table (4.4) for 0·05M salts

‡ All salt parameters in Table (4.4) reduced by 0·7 to allow for use of 0·2M salts (see sub-section 5.4.1. page 80)

CHAPTER 5

Interpretation Of The Present Results According To The 'S_N' And Ion-Pair Schemes

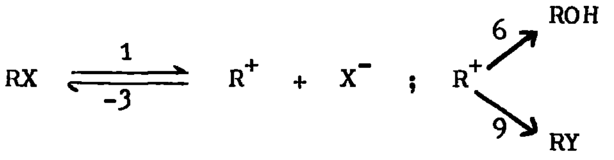
5.1 Introduction

This chapter considers the possibility of the present reactions proceeding by way of the 'S_N' or the ion-pair mechanisms. Two ion-pair schemes are considered but it is assumed that neither involves direct attack on the covalent substrate, RX (i.e. mechanism S_N2).

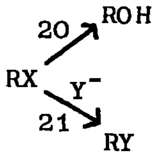
5.2 Reaction Schemes and Rate Equations

The three general schemes which are considered are illustrated below,

S_N:

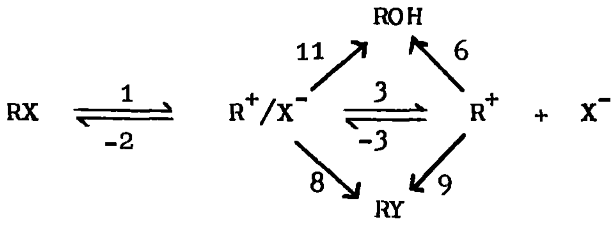


(S_N1)

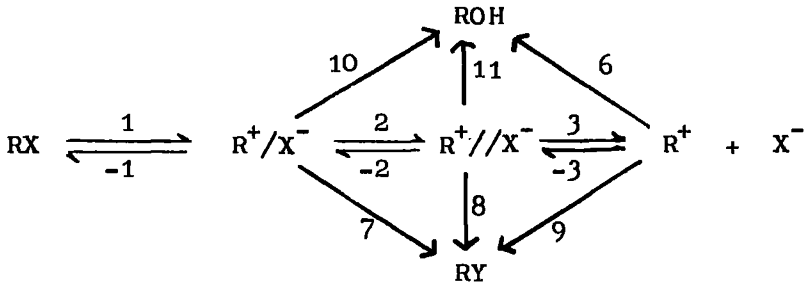


(S_N2)

I.P.1:



I.P.2:



In practice it is possible to obtain a rate coefficient for the overall decomposition of the substrate,

$$k_{RX}^{inst} = -\frac{1}{[RX]}\frac{d[RX]}{dt}$$

by measuring the rate of production of X^- ions. If the anion (Y^-) is such that RY is stable under the experimental conditions then it is also possible to evaluate a rate coefficient for hydrolysis,

$$k_{ROH}^{inst} = \frac{1}{[RX]}\frac{d[ROH]}{dt}$$

Application of the stationary state approximation to the reactive intermediates then gives general expressions for k_{RX}^{inst} and k_{ROH}^{inst} appropriate to each scheme (see appendix E) but for the ion-pair schemes these expressions are rather complicated. Fortunately, simplifications are possible for the two types of systems considered. For the 4-nitrobenzyl compounds, previously regarded as solvolysing via mechanism S_N2, the fully developed carbonium ion can be neglected, i.e.

$$k_3,\ k_6,\ k_9 = 0$$

For 4-alkoxybenzyl and benzhydryl chlorides it has been shown previously (see section 4.1) that their hydrolysis in aqueous acetone proceeds entirely (or nearly entirely) via the fully developed carbonium ion, R^+, so that,

$$k_{20},\ k_{21},\ k_{10},\ k_{11} = 0$$

The modified general rate equations then become (see appendix E),

$$k_{RX}^{inst} = k_1 f \frac{1+Q[Y^-]\left(\frac{\alpha[X^-]}{1+\beta[Y^-]}+1\right)}{1 + R[Y^-]} \qquad (5.1)$$

$$k^{inst}_{ROH} = k_1 f \frac{1}{(1+\beta[Y^-])(1+R[Y^-])} \qquad (5.2)$$

where $\alpha = k_{-3}/k_6$, $\beta = k_9/k_6$ and the parameters f, Q and R are functions of the rate coefficients of the individual steps in the reaction scheme (see Table 5.1).

In practice, results were calculated from the integrated forms of equations (5.1) and (5.2) but the details are more conveniently discussed separately in conjunction with the two systems studied.

5.3 The 4-Nitrobenzyl Systems

5.3.1 Azide ions as nucleophiles

The decomposition of 4-nitrobenzyl chloride in 70% and 85% aqueous acetone is substantially accelerated by azide ions; even for the smallest electrolyte concentrations employed ($[Y^-]_i \simeq 0{\cdot}03\underline{M}$) the first order rate of decomposition (k_T) is more than 1000 times greater than the rate in the pure solvent $[(k_T)_0 = (k_1f)_0]$ so that Q (see Table 5.1, equation 5.1) is sufficiently large to ensure that

$$Q[Y^-] >> 1 \qquad (5.3)$$

Hydrazoic acid is a weak acid in aqueous acetone (in water $pK_a = 4{\cdot}7$)[69] so that,

$$[Y^-] = [Y^-]_i - [X^-] = [Y^-]_i - [RX]_i + [RX] \qquad (5.4)$$

where the subscript i refers to the initial concentrations. Assuming linear salt effects (see section 4.3), substitution from equations (5.4) and (5.3) in (5.1) and rearrangement then gives, for reaction in the presence of sodium azide,

$$-\left(\frac{1}{[RX][Y^-]} + R.\frac{1}{[RX]}\right)\frac{d[RX]}{dt} = (k_1f)_0(1+b_{NaY}[Y^-]_i)(1-b[X^-])Q$$

Table (5.1)

Expressions for f, Q and R

Substrates	Scheme	f	Q	R
$4\text{-}NO_2C_6H_4CH_2X$ $(X = Cl, OT_s)$	S_N	$\frac{k_{20}}{k_1}$	$\frac{k_{21}}{k_{20}}$	0
	I.P.1	$\frac{\mu}{1+\mu}$	$\frac{\epsilon}{\mu}$	$\frac{\epsilon}{1+\mu}$
	I.P.2	$\frac{\lambda(1+\mu)+\mu y}{1+\lambda(1+\mu)+\mu(1+y)}$	$\frac{\delta(1+\mu+\epsilon[Y^-])+\epsilon(\lambda+y)}{\lambda(1+\mu)+\mu y}$	$\frac{\delta(1+\mu+\epsilon[Y^-])+\epsilon(1+y+\lambda)}{1+\lambda(1+\mu)+\mu(1+y)}$
$4\text{-}MeOC_6H_4CH_2Cl$ and Ph_2CHCl	S_N	$\frac{1+\beta[Y^-]}{1+\alpha[X^-]+\beta[Y^-]}$	$\frac{k_{21}}{k_1}$	0
	I.P.1	$\frac{1+\beta[Y^-]}{1+\alpha[X^-]+\beta[Y^-]} \cdot \frac{x}{1+x}$	$\frac{\epsilon}{x}$	$\frac{\epsilon}{1+x}$
	I.P.2	$\frac{1+\beta[Y^-]}{1+\alpha[X^-]+\beta[Y^-]} \cdot \frac{xy}{1+x+xy}$	$\frac{\delta(1+x+\epsilon[Y^-])+\epsilon y}{xy}$	$\frac{\delta(1+x+\epsilon[Y])+\epsilon(1+y)}{1+x+xy}$

† $y = k_2/k_{-1}$; $\lambda = k_{10}/k_{-1}$; $\delta = k_7/k_{-1}$

$x = k_3/k_{-2}$; $\mu = k_{11}/k_{-2}$; $\epsilon = k_8/k_{-2}$

where $b = \dfrac{b_{NaY}-b_{NaX}}{1+b_{NaY}[Y]_i}$. Integration then gives,

$$\frac{k_{II}}{S} = Q - R.\frac{k_I}{S} \qquad (5.5)$$

where k_I and k_{II} are the observed integrated first- and second-order rate coefficients for the decomposition* and

$$S = (k_1 f)_0(1+b_{NaY}[Y_i])(1-\frac{b}{t}\int_0^t [X^-]dt)$$

In principle, Q and R can be obtained as the slope of the straight line required by equation (5.5) but in practice this requires a significant change of k_I as reaction proceeds, a requirement which is only met when the initial concentrations of azide ions and the substrate do not differ too greatly from each other. The greatest opportunity for obtaining meaningful values of R therefore arises from experiments 1 and 13 (see appendix J) where k_I decreases by approximately 40% over the course of the reaction ($[Y^-]_i \simeq 0{\cdot}03\underline{M}$, $[RX]_i \simeq 0{\cdot}02\underline{M}$).

The results of the calculations are shown in Table (5.2) on the assumption that the electrolyte effects are either zero (as for $NaClO_4$, see section 2.2) or similar to those found for 4-methoxybenzyl chloride which are regarded as an upper limit. It can be seen that the 'best' (least squares) values of R increase with increasing electrolyte effects but do not exceed R = 1•5; in the statistical sense these parameters do not differ significantly from zero since $\sigma(R) \simeq 1$. Qualitative confirmation that R is small arises from the requirement that substantial values of R require an increase in k_{II} as the reaction proceeds; this is not observed (see

---

*

$$k_I = \frac{1}{t}\ln\frac{[RX]_0}{[RX]}$$

$$k_{II} = \frac{1}{t([Y^-]_i-[RX]_i)}\ln\frac{[RX]_0}{[RX]}\cdot\frac{[Y^-]}{[Y^-]_0}$$

experiments 1-4, 13, 14, appendix J).

Table (5.2)

Values of Q and R for the reaction of $4\text{-}NO_2C_6H_4CH_2Cl$ with N_3^- in aqueous acetone at 20·41°C

% Acetone	Expt.	$[Y^-]_i$	b_{NaY}	b_{NaX}	10^{-5} Q	R
70	1b	0·03082	0	0	1·1624	0·34
		0·03082	3·0	0·6	1·1269	1·30
85	13b	0·02924	0	0	7·575	-0·35
		0·02924	6·5	4·1	6·756	1·54

Alternatively, the means of the experimental variables in any one run, $(k_I)_m$, $(k_{II})_m$ and S_m, can be introduced into equation (5.5) which then gives, on rearrangement

$$Q = \frac{(k_{II})_m}{S_m} + R\frac{(k_I)_m}{S_m} \qquad (5.6)$$

so that Q can be calculated for various arbitrarily chosen values of R subject to the restriction $R \leqslant 2$. For S_N2 attack by Y^-, $k_{21} = (k_{II})_m$.

The results are summarised in Tables (5.3) and (5.4) for reaction in 70% and 85% aqueous acetone, respectively. It can be seen that $(k_I)_m/S_m$ decreases with decreasing $[Y^-]_i$ and it can easily be shown that this parameter becomes extremely small when $[Y^-]_i = 0$. As a result, the value of Q at zero ionic strength, Q^o, is virtually independent of R and can therefore be obtained directly from Q(R=0), assuming a linear salt effect; i.e.

$$Q(R=0) = Q^o(1+b_Q[Y^-]_i)$$

and similarly

$$k_{21} = k_{21}^o(1+b_{21}[Y^-]_i)$$

Table (5.3) †

$4\text{-}NO_2C_6H_4CH_2Cl + NaN_3$ in 70% aqueous acetone at 20·41°C

Experiment	1a	1b	2a	2b	3a	3b	4a	4b
$[Y^-]_i$ mole l^{-1}	·02982	·03082	·04814	·04800	·07315	·07349	·09369	·10140
$10^6(k_I)_m$ sec^{-1}	5·753	6·289	9·828	9·633	14·823	14·963	18·748	20·239
$10^4(k_{II})_m$ mole^{-1} l.sec^{-1}	2·421	2·494	2·339	2·344	2·197	2·275	2·141	2·125
$(\frac{1}{t}\int[X^-]dt)_m$ mole l^{-1}	·00608	·00558	·00617	·00687	·00577	·00771	·00619	·00626
$10^{-5}Q(R=0)^{‡}$ mole^{-1}l.	1·1533	1·1859	1·1148	1·1149	1·0475	1·0830	1·0202	1·0129
$10^{-5}(k_I)_m/S_m^{‡}$	·0284	·0308	·0474	·0464	·0710	·0717	·0896	·0967
$10^{-5}Q(R=0)^*$ mole^{-1} l.	1·0678	1·0955	·9787	·9828	·8581	·8915	·7942	·7735
$10^{-5}(k_I)_m/S_m^*$	·0254	·0276	·0411	·0404	·0579	·0586	·0695	·0737
10^4k_{21} mole^{-1} l.sec^{-1}	2·422	2·490	2·341	2·341	2·200	2·274	2·142	2·127

† $[RX]_i \simeq 0{\cdot}02\underline{M}$; $(k_I)_0 = (k_{20})_0 = 2{\cdot}1 \times 10^{-9}$ sec^{-1}.

‡ $b_{NaY} = b_{NaX} = 0$

* $b_{NaY} = 3{\cdot}2$; $b_{NaX} = 0{\cdot}6$

Table (5.4)†

$4\text{-}NO_2C_6H_4CH_2Cl + NaN_3$ in 85% aqueous acetone at 20·41°C

Experiment	13a	13b	14a	14b
$[Y^-]_i$ mole l^{-1}	·02925	·02924	·04960	·05014
$10^6(k_I)_m$ sec^{-1}	9·590	9·532	15·015	16·949
$10^4(k_{II})_m$ mole^{-1} l.sec^{-1}	4·186	4·137	3·905	3·915
$(\frac{1}{t}\int[X^-]dt)_m$ mole l^{-1}	·00630	·00618	·01121	·00684
$10^{-5}Q(R=0)^{‡}$ mole^{-1} l	7·738	7·655	7·243	7·249
$10^{-5}(k_I)_m/S_m^{‡}$	·185	·184	·289	·318
$10^{-5}Q(R=0)^{*}$ mole^{-1} l	6·621	6·542	5·613	5·563
$10^{-5}(k_I)_m/S_m^{*}$	·152	·151	·216	·241
10^4k_{21} mole^{-1}l.sec^{-1}	4·178	4·134	3·911	3·915

† $[RX]_i \simeq 0{\cdot}01\underline{M}$; $(k_I)_0 = (k_{20})_0 = 5{\cdot}4 \times 10^{-10}$ sec^{-1}

‡ $b_{NaY} = b_{NaX} = 0$

* $b_{NaY} = 6{\cdot}4$; $b_{NaX} = 3{\cdot}8$

Table (5.5)

Kinetic parameters for the attack of azide ions on 4-nitrobenzyl chloride in aqueous acetone at 20·41°C

% Acetone	b_{NaY}	b_{NaX}	$10^{-5}Q^o$ mole^{-1} l	b_Q mole^{-1} l	$10^4\ k^o_{21}$ mole^{-1} l.sec^{-1}	b_{21} mole^{-1} l
70	0	0	1·2294	-1·80	2·582	-1·80
	3·0	0·6	1·2021	-3·63	2·582	-1·80
85	0	0	8·272	-3·04	4·467	-3·04
	6·5	4·1	7·991	-6·03	4·467	-3·04

Values of Q^o and k^o_{21}, together with the appropriate electrolyte parameters, are summarised in Table (5.5) and require little comment beyond noting the increase of Q^o and k^o_{21} as the solvent becomes less aqueous and the negative electrolyte effects, as expected.

It has already been pointed out that the results which allow the calculation of R permit zero value for this parameter, within the limits of the experimental error. Reaction via the S_N scheme, i.e. S_N2 attack by azide ions on the covalently bound substrate, is therefore fully consistent with the observations. On the other hand, the operation of scheme I.P.1 and I.P.2 cannot be immediately excluded at this stage provided it is recognised that R is small ($\leqslant 2$).

The expressions for f, Q and R in Table (5.1) show that,

$$f^o = \frac{\mu}{1+\mu} = \frac{R}{Q^o} \qquad \text{(I.P.1)}$$

$$= \frac{\lambda(1+\mu)+\mu y}{1+\lambda(1+\mu)+\mu(1+y)} = \frac{R}{Q^o} \cdot \frac{\epsilon(y+\lambda)+\delta(1+\mu)}{\epsilon(1+y+\lambda)+\delta(1+\mu)} \qquad \text{(I.P.2)}$$

Since $R \leqslant 2$ and $Q^o > 10^5$ (see Table 5.5), $f^o << 1$

so that

$$\left.\begin{array}{ll} \mu << 1 & \text{(I.P.1)} \\ \lambda,\ \mu,\ \mu y << 1 & \text{(I.P.2)} \end{array}\right. \qquad (5.7a)$$

or $$\mu >> 1;\quad \lambda,\ y << 1 \quad \text{(I.P.2)} \qquad (5.7b)$$

Substitution of equation (5.7b) into the expression for R leads to,

$$R = \delta + {}^{\epsilon}/_{\mu} \qquad \text{(I.P.2)}$$

so that for $[Y^-] \leqslant 0{\cdot}1$

$$\epsilon[Y^-] < \mu \quad (\text{since } R \leqslant 2)$$

However from the definition of ϵ and μ (see Table 5.1) this would mean that any second ion-pairs formed would react more rapidly with water than with azide ions. Under these conditions any RY formed would be derived from an attack by azide ions on the first formed ion-pair; any other subsequent reaction of that ion-pair would yield the alcohol, ROH, either by direct reaction with water or via another ion-pair, R//X. However in these systems hydrolysis only represents a minute fraction of the reaction so that at best only a very small fraction of the overall decomposition can occur via the ion pair, R//X. This is equivalent to considering the one ion-pair scheme (I.P.1) so that $\mu >> 1$ in scheme I.P.2 requires no further consideration.

The inequalities of equation (5.7a) lead to the following expressions for R,

$$R = \epsilon \qquad \text{(I.P.1)}$$

$$= \epsilon(1+y+\lambda)+\delta(1+\mu) = \epsilon(1+y)+\delta \qquad \text{(I.P.2)}$$

so that for $[Y^-] \leqslant 0{\cdot}1$

$$\epsilon[Y^-],\ \delta[Y^-] < 1 \quad (\text{since } R \leqslant 2)$$

Thus ion-pair schemes require rate-determining attack by Y^- and H_2O on intermediate ion-pairs, as illustrated qualitatively in the free energy schemes (Figure 5.1).

5.3.2 Other anions as nucleophiles

The effect of other nucleophiles on the decomposition of 4-nitrobenzyl chloride was studied less extensively than the reaction in the presence of azide ions. The results (see Table 2.2) show that for all anions ($Y^- \neq N_3^-$) now examined, the acceleration is less than one tenth of the acceleration caused by the same concentration of azide ions and it can therefore be concluded that,

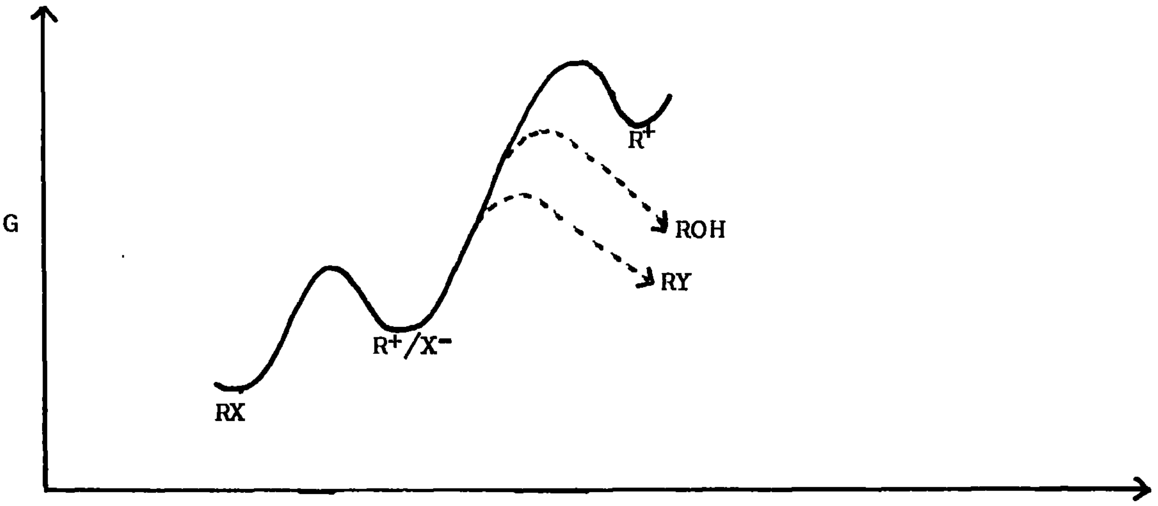
$$R(Y^- \neq N_3^-) < 0{\cdot}1\ R(Y^- = N_3^-)^*$$

---

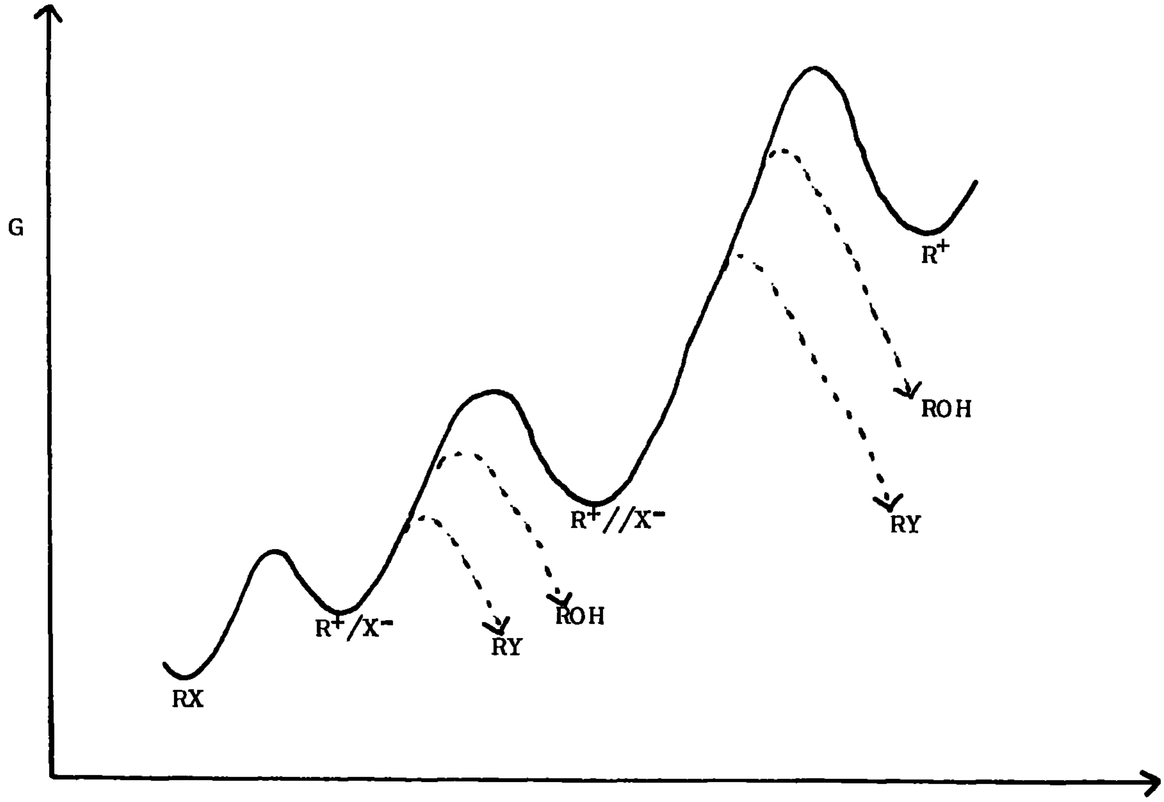
[*] In the ion-pair schemes, different accelerations by difference nucleophiles (Y^-) arise solely from the different ϵ and δ parameters. Only these parameters control R for a given substrate.

FIGURE (5.1)

Free energy reaction profiles for azide ion (Y^-) attack on 4-nitrobenzyl chloride (RX) in aqueous acetone according to the ion-pair schemes



Scheme (I.P.1)



Scheme (I.P.2)

but since $R(Y^- = N_3^-) \leqslant 2$,

$$R(Y^- \neq N_3^-)[Y^-] << 1 \text{ for } [Y^-] \leqslant 0{\cdot}1$$

so that the initial integrated first-order rate coefficient for the decomposition of the substrate (k_{RX}) can be expressed in the form,

$$k_{RX} = (k_{RX})_0(1+Q[Y^-]_i) \tag{5.8}$$

Equation (5.8) is obtained from equation (5.1) and the limitations of the system under consideration (k_3, α, $\beta = 0$; see section 5.2) and also implies zero electrolyte effects but the resulting error is not serious for any comparison of the Q's of different anions.

Table (5.6) summarises the Q's obtained from equation (5.8) and the results summarised in Table (5.3) and (5.4). Values for the reaction of 4-nitrobenzyl-4'-toluenesulphonate in the presence of azide ions and chloride ions have been included, though the basic assumption of equations (5.8) (i.e. $R[Y^-] << 1$) has not been established for these systems. Analogy with the chlorides, however, suggests that the effective assumption ($R=0$) produces only a negligibly small error in Q.

Detailed consideration of the Q's and R's for the different anions is deferred until section (5.5). It is. however. worth noting that the nature of the anion has a very marked effect on the value of Q in nitrobenzyl systems.

5.4 The 4-Methoxybenzyl and Benzhydryl Systems

5.4.1 Decomposition in the presence of azide ions

From the expression for f (see Table 5.1), equation (5.1) for the reactions of 4-methoxybenzyl and benzhydryl chlorides can be written in the form,

$$\frac{-1}{[RX]}\frac{d[RX]}{dt} = k_1 g \frac{1+\beta[Y^-]}{1+\alpha[X^-]+\beta[Y^-]} \cdot \frac{1+Q[Y^-](1+\frac{\alpha[X^-]}{1+\beta[Y^-]})}{1+R[Y^-]}$$

Table (5.6)

Values of Q and k_{21} for the reactions of $4\text{-}NO_2C_6H_4CH_2X$ with anions in aqueous acetone at 20·41°C

% Acetone	X	Electrolyte*	Q	k_{21}
70	Cl	$NaNO_3$	12·4	$2{\cdot}6 \times 10^{-8}$
		KOPNB †	520	$1{\cdot}1 \times 10^{-6}$
		NaBr	4960	$1{\cdot}0 \times 10^{-5}$
		NaN_3 ††	$1{\cdot}16 \times 10^{5}$ ‡	$2{\cdot}44 \times 10^{-4}$
	OT_s	NaCl	120	$1{\cdot}45 \times 10^{-4}$
		NaN_3 ††	9340	$1{\cdot}13 \times 10^{-2}$
85	Cl	NaN_3 ††	$7{\cdot}52 \times 10^{5}$ ‡	$4{\cdot}06 \times 10^{-4}$
	OT_s	NaCl	720	$2{\cdot}38 \times 10^{-4}$
		NaN_3 ††	$5{\cdot}52 \times 10^{4}$	$1{\cdot}82 \times 10^{-2}$

* At 0·05M; †† At 0·03M; † -OPNB = $4\text{-}NO_2C_6H_4CO_2\text{-}$

‡ From Table (5.5) with $b_{NaY} = b_{NaX} = 0$

$$\text{where} \quad g = \frac{1+\alpha[X^-]+\beta[Y^-]}{1+\beta[Y^-]} \cdot f$$

Substitution from equation (5.4) and the assumption of linear electrolyte effects (see section 4.3) then gives,

$$\frac{-1}{[RX]}\frac{d[RX]}{dt}\left\{1+R([Y^-]_i-[RX]_i+[RX])\right\} =$$

$$(k_1g)_0(1+b_{NaY}[Y^-]_i)(1-b[X^-])\left\{Q([Y^-]_i-[x^-])+1-\frac{\alpha[X^-]}{1+\beta[Y^-]_i}\left(1+\frac{\alpha[X^-]}{1+\beta[Y^-]_i}\right)\right\} \qquad (5.9)$$

where $b = \frac{b_{NaY}-b_{NaX}}{1+b_{NaY}[Y^-]_i}$ and it has been assumed that,

$$\frac{\alpha[X^-]}{1+\alpha[X-]+\beta[Y^-]} = \frac{\alpha[X^-]}{1+\beta[Y^-]_i}\left(1+\frac{\alpha[X^-]}{1+\beta[Y^-]_i}\right) \qquad (5.10)$$

It can be shown that the use of equation (5.10) introduces only a negligibly small error.

Integration of equation (5.9) between the usual limits (t = 0 and t = t) then gives,

$$\frac{\frac{k_I}{k_b}-M}{M_Q} = Q - R \cdot \frac{M_R}{M_Qk_b} \qquad (5.11)$$

$$\text{where } k_I = \frac{1}{t}\ln\frac{[RX]_0}{[RX]}$$

$$k_b = (k_1g)_0(1+b_{NaY}[Y^-]_i) = (k_I)_0(1+b_{NaY}[Y^-]_i)$$

$$M_Q = [Y^-]_i-(1+b[Y^-]_i)I_1+bI_2$$

$M = 1-(b+\frac{\alpha}{1+\beta[Y^-]_i})I_1$ + negligible terms in I_2, I_3

$$M_R = ([Y^-]_i - [RX]_i)k_I + \frac{[X^-]-[X^-]_0}{t}$$

$$\text{with } I_n = \frac{1}{t}\int_0^t [X^-]^n dt$$

In principle, Q and R can then be obtained from the intercept and slope of the straight line required by equation (5.11) but in practice this procedure suffers from the difficulties already mentioned in connection with the similar calculation of Q and R for the reactions of 4-nitrobenzyl chloride (see section 5.3). The resulting values of R (not shown) vary between 0 and 2·6 but are not statistically significantly different from zero since their standard errors are generally about 1·7.

Values of Q for arbitrarily chosen R's were therefore obtained from the means of the variables in equation (5.11) by writing,

$$Q = Q(R{=}0) + R.\Delta Q(R{=}1) \qquad (5.12)$$

where,

$$Q(R{=}0) = \frac{\dfrac{(k_I)_M}{k_b} - (M)_m}{(M_Q)_m}$$

$$\Delta Q(R{=}1) = (M_R)_m/(M_Q)_m k_b$$

and the subscript m refers to the mean value over the experimental range. The estimation of Q(R=0) and ΔQ(R=1) from equation (5.12) requires a knowledge of the intervention constants $\beta(=k_q/k_6)$ and $\alpha(=k_{-3}/k_6)$ for the competition between water and either azide or chloride ions for the fully developed carbonium ions. In the present calculations α was identified with the observed mass-law constant, α_{obs},† as evaluated in sections (4.2) and (4.3) and it was assumed that $\beta = 2\alpha_{obs}$. This procedure is not necessarily valid, especially if reaction occurs via ion-pair schemes. However, the results for hydrolysis allow upper and lower limits to be assigned to α and β

---

† Strictly $\alpha = \alpha_{obs}\,(1+x+xy)$ for I.P.2

$= \alpha_{obs}\,(1+x)$ for I.P.1

but it can be shown that x or (x+xy) are never greater than about 0·25 (Appendix F). Only negligible errors are introduced by this assumption.

(see section 5.4.2) and it was found that variations within these limits had only a negligibly small effect on the parameters obtained from equation (5.12).

The main results for the decomposition of benzhydryl chloride in 85% aqueous acetone and in the presence of azide ions are summarised in Table (5.7) where it can be seen that the values of Q and k_{21} are relatively small. It can easily be shown from these figures that only about 10% of the reaction in the presence of $0{\cdot}05\underline{M}$ N_3^- occurs via either S_N2 attack of azide ions on the substrate or combination of the anion with ion-pairs but it must be stressed that this conclusion arises from choosing the electrolyte parameters (b_{NaY}) for sodium azide as identical with that for sodium perchlorate. This procedure is supported by results[60] for the reaction in 70% aqueous acetone (see also section 3.2) but it is noteworthy that all the results for reaction in 85% aqueous acetone would be consistent with reaction solely via the benzhydryl carbonium ion (mechanism S_N1) if,

$$b_{NaY} = b_{NaClO_4} + 2{\cdot}0$$

in this solvent. However, this difference is larger than might have been expected (see section 4.3) and it is therefore considered likely that some of the reaction with azide ions in 85% aqueous acetone occurs either via intermediate ion-pairs or by S_N2 attack on the substrate. Unfortunately, the relevant parameters (Q or k_{21}) arise as small differences between much larger quantities* and are therefore not accurate enough to allow definite conclusions.

---

* From equation (5.12),

$$Q(R=0) = \frac{\dfrac{(k_I)_m}{k_b} - (M)_m}{M_Q}$$

with $(k_I)_m \simeq k_b$ and $(M)_m \simeq 0{\cdot}95$.

Table (5.7)†

Ph$_2$CHCl + NaN$_3$ in 85% aqueous acetone at 20·41°C

Experiment	32‡	33‡	34‡	35‡	37*	38*	39*	40*	41*	42*
$[Y^-]_i$ mole l^{-1}	·04945	·04897	·04899	·05047	·03026	·04121	·04986	·05016	·10020	·09983
$[RX]_i$ mole l^{-1}	·02128	·02164	·02207	·02130	·01891	·02218	·01975	·01921	·02154	·02007
$10^5(k_I)_m$ sec^{-1}	1·597	1·566	1·600	1·584	2·415	2·430	2·445	2·493	2·540	2·644
$10^3(I_1)_m$ mole l^{-1}	6·67	6·11	6·44	6·62	6·72	7·44	6·23	5·55	6·65	5·73
Q(R=0) mole^{-1} l	2·655	2·136	2·731	2·260	2·010	1·617	1·281	1·662	0·994	1·437
ΔQ(R=1)	1·10	1·08	1·10	1·08	1·03	1·03	1·04	1·06	1·08	1·12
10^5k_{21} mole^{-1}l.sec^{-1}	3·881	3·118	3·985	3·319	4·736	3·811	3·018	3·916	2·342	3·386

† $\alpha = 4$, $\beta = 8$; $10^5(k_I)_0 = 1{\cdot}159$; $b_{NaY} - b_{NaX} = 2{\cdot}6$;

‡ $[NaClO_4] = 0$; $b_{NaY} = 5{\cdot}6$; calculations via equation (5.12);

* $[NaClO_4] = 0{\cdot}2\underline{M} - [Y^-]_i$; $10^5(k_I)_{0\cdot2\ NaClO_4} = 2{\cdot}356$; see Appendix G for calculations.

Results for the reaction of 4-methoxybenzyl chloride with azide ions $[Y^-]$ in 85% aqueous acetone are summarised in Table (5.8); data for the corresponding reactions in 70% aqueous acetone shown in Table (5.9), were calculated from the measurements of Gregory.[37] For the reactions carried out in the absence of $NaClO_4$ (i.e. not at constant ionic strength), Q(R=0) and k_{21} decrease while $\Delta Q(R=1)$ increases with increasing ionic strength, as in the reactions of the 4-nitrobenzyl system (see section 5.3). Similarly, $\Delta Q(R=1)$ becomes very small when $[Y^-]_i = 0$ so that Q^o, the value at zero ionic strength is virtually independent of the value of R* and can be identified with Q(R=0) under these conditions. Assuming a linear salt effect

$$Q(R=0) = Q^o(1+b_Q[Y^-])$$

$$k_{21} = k_{21}^o(1+b_{21}[Y^-])$$

for the experiments without added $NaClO_4$. The relevant values are shown in Table (5.10) and require little comment beyond noting the unexpected variation of the salt parameters, b_Q and b_{21} as the composition of the solvent is altered. This could well arise from errors in the parameters for the 70% solvent where the majority of the reaction occurs via the carbonium ion so that Q and k_{21} are in effect obtained from a relatively small difference between two large quantities and are therefore subject to larger errors than the parameters for the 85% solvent where this disadvantage does not apply.

The values of Q(R=0) and k_{21} calculated for reaction in 85% aqueous acetone at constant ionic strength ($[NaClO_4] + [Y^-]_i = 0{\cdot}2\underline{M}$) are larger than those predicted from the parameters given in Table (5.10) but this is

---

* It is shown later in this chapter (section 5.4.2) that $R \lesssim 1{\cdot}5$.

Table (5.8)[†]

$4\text{-MeOC}_6H_4CH_2Cl$ + NaN_3 in 85% aqueous acetone at 20·41°C

Experiment	48[‡]	49[‡]	50[‡]	51[‡]	53[*±]	55[*±]	57[*±]	54[*∅]	56[*∅]	58[*∅]
$[Y^-]_i$ mole l^{-1}	·03132	·03067	·05023	·05025	·03109	·05161	·1017	·03026	·05076	·10090
$[RX]_i$ mole l^{-1}	·02173	·03020	·01940	·02117	·02261	·02253	·02303	·02297	·02220	·02279
$10^5(k_I)_m$ sec^{-1}	4·530	4·018	7·002	7·200	4·312	6·687	11·750	4·215	6·707	11·859
$10^3(I_1)_m$ mole l^{-1}	6·27	8·91	6·39	5·62	7·37	6·34	7·45	7·78	6·34	7·47
Q(R=0) mole^{-1} l	141·5	141·6	122·4	124·0	57·99	58·73	57·38	60·89	61·66	59·83
ΔQ(R=1)	4·64	4·23	6·41	6·57	2·38	3·66	6·40	2·40	3·82	6·70
10^3k_{21} mole^{-1} l.sec^{-1}	1·419	1·408	1·352	1·371	1·067	1·080	1·055	1·097	1·113	1·078

[†] $b_{NaY}-b_{NaX} = 2·6$, $\beta = 11$

[‡] $[NaClO_4] = 0$; $b_{NaY} = 6·4$, $b_{NaX} = 3·8$, $\alpha = 5·75$, $10^5(k_I)_O = 0·8454$; calculations via equation (5.12)

[*] $[NaClO_4] = 0·2\underline{M} - [Y^-]_i$; $\alpha = 5·5$; for calculations see Appendix G

[±] $10^5(k_I)_O = 0·8454$, $10^5(k_I)_{0·2\ NaClO_4} = 1·8394$

[∅] $10^5(k_I)_O = 0·8292$, $10^5(k_I)_{0·2\ NaClO_4} = 1·8043$

Table (5.9)†

$4\text{-}MeOC_6H_4CH_2Cl$ + NaN_3 in 70% aqueous acetone at 20°C

$[Y^-]_i$ mole l^{-1}	·02971	·02973	·04002	·05483
$10^4(k_I)_m$ sec^{-1}	3·4533	3·4539	3·7889	4·2983
$10^3(I_1)_m$ mole l^{-1}	6·39	6·82	7·88	7·83
$10^5(I_2)_m$ mole^2l^{-2}	6·66	6·41	8·34	8·26
$10^4(M_R)_m$ mole l^{-1}sec^{-1}	·0786	·0811	·1225	·2017
Q(R=0) mole^{-1} l	10·65	11·09	10·03	9·17
ΔQ(R=1)	1·22	1·24	1·30	1·41
10^3k_{21} mole^{-1} l.sec^{-1}	3·022	3·149	2·932	2·801

† From the results of Gregory and Kohnstam.[37]

Using $\alpha = 4$, $\beta = 8$, $b_{NaY} = 3{\cdot}2$, $b_{NaX} = 0{\cdot}6$, $10^4(k_I)_0 = 2{\cdot}620$

Calculations via equation (5.12)

Table (5.10)

Kinetic parameters for the attack of azide ions on 4-methoxybenzyl chloride in aqueous acetone at 20°C

Solvent	70% aqueous acetone	85% aqueous acetone
Q^o	12·85	171·1
b_Q	-5·29	-5·57
$10^3k^o_{21}$	3·418	1·497
b_{21}	-3·35	-1·80

hardly surprising since the assumption of linear electrolyte effects is generally only valid at low ionic strengths (see for example reference 67b). The increase of $\Delta Q(R=1)$ with increasing $[y^-]_i$ under these conditions (see Table 5.8) is an inevitable consequence of the definition of this parameter (see equation 5.12 and Appendix G) but the accompanying constancy of $Q(R=0)$, within the limits of the experimental error, demands $R \leqslant 0{\cdot}5$.* This conclusion depends on the value assigned to the electrolyte parameters (i.e. $b_{NaY} = b_{NaClO_4}$ as elsewhere in this thesis) but the assumption

$$b_{NaY} = b_{NaClO_4} + 1$$

only raises the upper limit of R to 0·8.

Slightly larger upper limits for R are obtained from the results for the hydrolyses of the 4-methoxy compound in the presence of NaN_3 (see section 5.4.2) but even here $R \leqslant 1{\cdot}5$. For reaction via intermediate ion-pairs,

$$x,\ x + xy \leqslant 0{\cdot}25 \quad \text{(see Appendix F)}$$

so that $$\epsilon \leqslant 1{\cdot}25\ R;\quad \delta < 1{\cdot}25\ R \quad \text{(see Table 5.1)}$$

Hence

$$\epsilon[Y^-],\ \delta[Y^-] \leqslant 0{\cdot}2 \quad (\text{for } [Y^-]_i < 0{\cdot}1\underline{M})$$

so that any attack of Y^- on ion-pairs must be rate-determining. The appropriate free energy profiles are illustrated in Figure (5.2).

5.4.2 Hydrolysis in the presence of azide ions

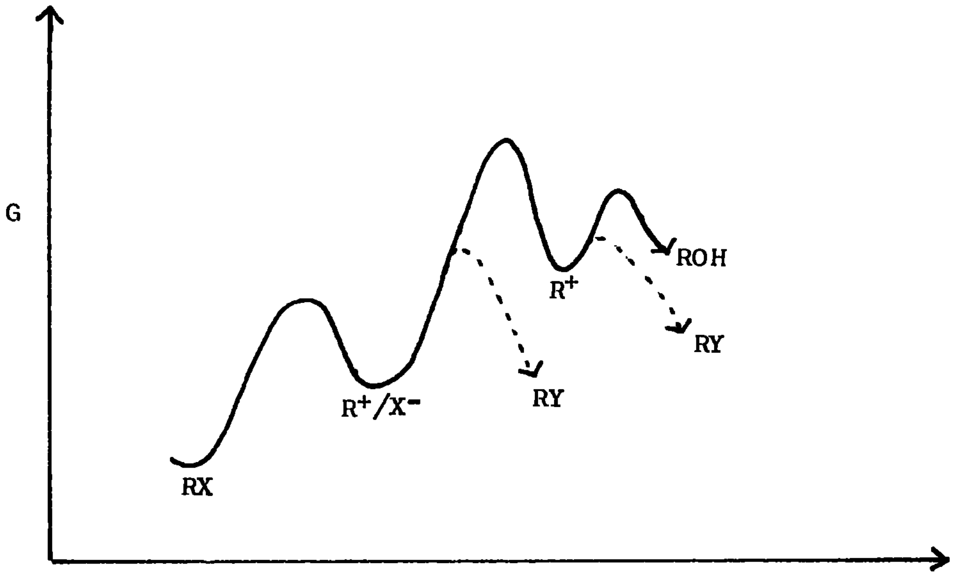
The rate of hydrolysis of 4-methoxybenzyl chloride in 70% aqueous acetone in the presence of azide ions $[Y^-]$ was measured by Gregory.[37]

---

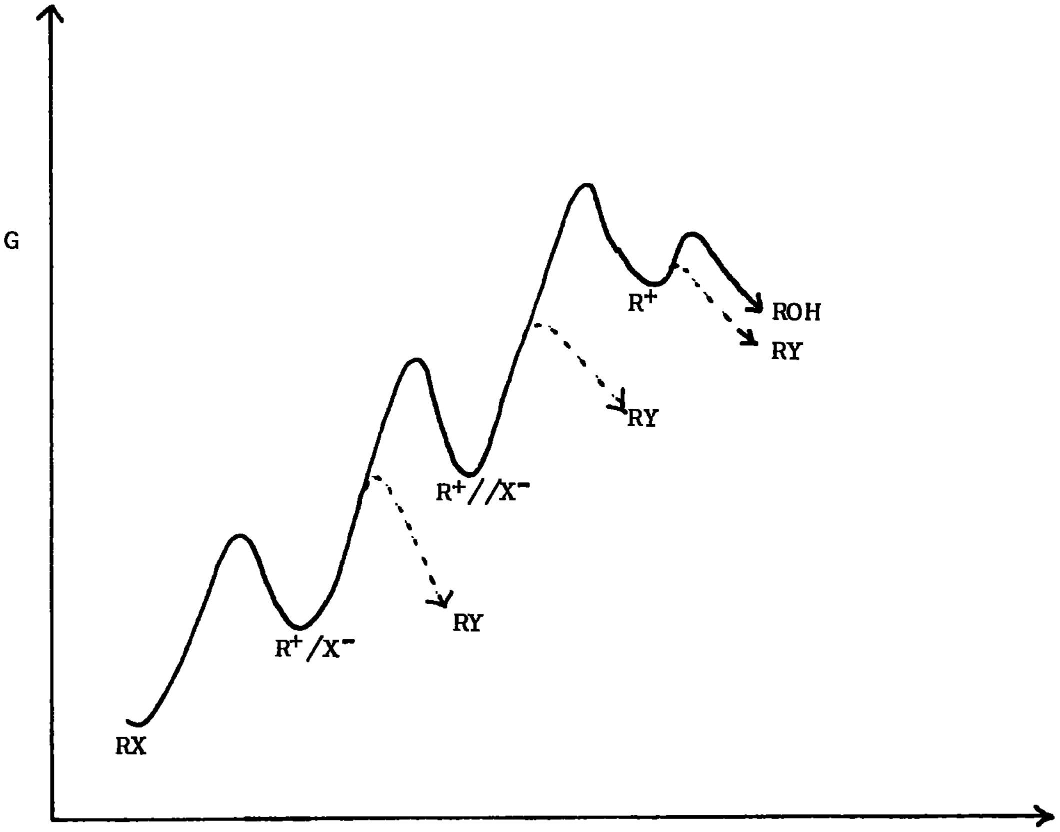
* A larger value for R would require an increase of Q with increasing $[Y^-]_i$. Such an increase can be envisaged in principle for reaction by scheme I.P.2 (see Table 5.1) but a check shows that it would be quantitatively insignificant.

FIGURE (5.2)

Free energy reaction profiles for the attack of azide ions (Y^-) on 4-methoxybenzyl chloride (RX) in 85% aqueous acetone according to the ion-pair schemes



Scheme (I.P.1)



Scheme (I.P.2)

Assuming linear electrolyte effects, substitution from equation (5.4) in equation (5.2) then gives,

$$k_{ROH}^{inst} = \frac{k_I^o(1+b_{NaY}[Y^-]_i)(1-b[X^-])}{(1+\alpha[X^-]+\beta[Y^-])(1+R[Y^-])}$$

where $\quad b = \dfrac{b_{NaY}-b_{NaX}}{1+b_{NaY}[Y^-]_i}$

and $\quad k_I^o = \dfrac{(k_1f)^o(1+\alpha[X^-]+\beta[Y^-])}{1+\beta[Y^-]}$

with the superscript 'o' referring to zero ionic strength. Further substitution from equation (5.4) and the relation $(1+x)^{-1} = 1-x+....$ give the expression for k_{ROH}^{inst} as

$$k_{ROH}^{inst} = \frac{k_I^o(1+b_{NaY}[Y^-]_i)}{(1+\beta[Y^-]_i)(1+R[Y^-]_i)}\left\{1+[X^-]\left(\frac{\beta-\alpha}{1+\beta[Y^-]_i} - + \frac{R}{1+R[Y^-]_i} - b\right)\right\}$$

where the neglect of terms involving higher powers of $[X^-]$ causes a negligibly small error. Thus the mean integrated rate coefficient for hydrolysis can be expressed in the form,

$$k_{ROH} = \left(\frac{1}{t}\int_o^t k_{ROH}^{inst}.dt\right)_m = \left(\frac{1}{t}\int_o^t \frac{d[ROH]}{[RX]}\right)_m \qquad (5.13)$$

$$= \frac{k_I^o(1+b_{NaY}[Y^-]_i)}{(1+\beta[Y^-]_i)(1+R[Y^-]_i)}\left(1 + I_1\left\{\frac{\beta-\alpha}{1+\beta[Y^-]_i} + \frac{R}{1+R[Y^-]_i} - b\right\}\right) \qquad (5.14)$$

where $I_1 = \left(\frac{1}{t}\int_o^t [X^-]dt\right)_m$ and the subscript 'm' refers to the mean of the experimental points. As $I_1 \simeq 0{\cdot}007$, for the present experiments on solutions in 70% aqueous acetone, (see Table 5.11) the value of k_{ROH} calculated from equation (5.14) is not significantly affected by the choice of α and agreement with $(k_{ROH})_{obs}$ (obtained from equation 5.13) depends on the values of β and R.

The values which can be legitimately assigned to β require some discussion. Experiments with 4-methoxy-benzhydryl compounds (see section 4.2.3) showed the reactions of the resulting carbonium ions in aqueous acetone required,

$$\beta = k_9/k_6 = 2\alpha = 2k_{-3}/k_6$$

and it therefore seemed reasonable to assume that β lies in the range $1{\cdot}5\alpha$ to 2α for the reactions of the less stable carbonium ion derived from 4-methoxybenzyl chloride. Values of the intervention constant, α_{obs}, for this carbonium ion were discussed in section (4.3) where they were in effect obtained via equation E.2 (Appendix E) from experiments without added non-common ions (i.e. $Y^- = 0$). Comparison with equations (E.4) and (E.6) shows that,

$$\alpha = \alpha_{obs}(1+x+xy)$$

where xy = 0 for the operation of scheme I.P.1 and both x and xy are zero for reaction by scheme S_N. Thus β can at best only vary between

$$\beta_{max} = 2\alpha_{obs}(1+x+xy)_{max} \text{ and } \beta_{min} = 1{\cdot}5\ \alpha obs.$$

Table (5.11) shows sets of β and R, consistent with this restriction, which give good agreement between $(k_{ROH})_{obs}$ and $(k_{ROH})_{calc}$ obtained from equations (5.13) and (5.14) respectively; the sensitivity of $(k_{ROH})_{calc}$ to changes in β or R is also given. It can be seen that the results are fully consistent with the requirements of scheme S_N (R=0) since the appropriate value of β (=8) is not more than twice α_{obs} (=4). Good agreement is however also obtained for R values in the range $0 \leqslant R \leqslant 1{\cdot}5$ so that schemes I.P.1 and I.P.2 are equally possible on the basis of these results. Larger values of R would require $\beta < 1{\cdot}5\ \alpha_{obs}$ and cannot therefore

Table (5.11)

The hydrolysis$^{\phi}$ of 4-$MeOC_6H_4CH_2Cl$ in the presence of N_3^- in 70% aqueous acetone at 20°C

$[N_3^-]_i$ mole l^{-1}	·05483	·04002	·02973	·02971
I_1 mole l^{-1}	·00783	·00788	·00682	·00639
$10^4(k_{ROH})_{obs}$* sec^{-1}	2·166	2·265	2·384	2·347
$10^4(k_{ROH})_{calc}$† sec^{-1}				
R = 0, β = 8	2·168	2·265	2·341	2·341
R = 0·1, β = 7·9	2·164	2·263	2·343	2·343
R = 0·25, β = 7·7	2·164	2·264	2·343	2·343
R = 0·5, β = 7·35	2·166	2·267	2·344	2·344
R = 1·0, β = 6·75	2·162	2·266	2·345	2·345
R = 1·5, β = 6·0	2·172	2·276	2·354	2·354
$10^4\ \partial k_{ROH}/\partial\beta$	-·075	-·059	-·045	-·045
$10^4\ \partial k_{ROH}/\partial R$	-·099	-·072	-·052	-·052

* From equation (5.13)

† From equation (5.14) using $10^4 k_I^o = 2{\cdot}62$, $b_{NaY} = 3{\cdot}4$, $b_{NaCl} = 0{\cdot}6$, $\alpha = 4$

ø From the results of Gregory and Kohnstam[37] be envisaged for the reactions of $4\text{-MeOC}_6H_4CH_2Cl$ in 70% aqueous acetone.

The small amount of hydrolysis for this system in the 85% solvent makes it impossible to obtain meaningful values of k_{ROH} but the amount of alcohol produced at the completion of reaction, $[ROH]_\infty$, allowed permissible limits to be calculated for β and R.

From equation (5.1) and (5.2),

$$\frac{k_{ROH}^{inst}}{k_{RX}^{inst}} = -\frac{d[ROH]}{d[RX]}$$

$$= \frac{1}{(1+\beta[Y^-])\left\{1+Q[Y^-](1+\frac{\alpha[X^-]}{1+\beta[Y^-]})\right\}}$$

Noting that

$$d[RX] = -d[X^-] = d[Y^-]$$

and $[X^-] = [Y^-]_i - [Y^-]$

this expression can be written in the form,

$$d[ROH] = \frac{d[X^-]}{a+b[X^-]+c[X^-]^2}$$

where $a = (1+\beta[Y^-]_i)(1+Q[Y^-]_i)$

$b = -\left\{\beta+(1+\beta[Y^-]_i)Q+Q[Y^-]_i(\beta-\alpha)\right\}$

$c = Q(\beta-\alpha)$

Integration between the limits $[ROH] = 0$, $[X^-] = 0$ and $[ROH] = [ROH]_\infty$, $[X^-] = [X^-]_\infty$ gives

$$[ROH]_\infty = \frac{1}{z^{\frac{1}{2}}} \ln \frac{1+\frac{2c[X^-]_\infty}{b-z^{\frac{1}{2}}}}{1+\frac{2c[X^-]_\infty}{b+z^{\frac{1}{2}}}} \qquad (5.15)$$

where $z = b^2-4ac.$

The experimental values of $[ROH]_\infty$ for the hydrolysis of 4-methoxybenzyl chloride in the presence of azide ions in 85% aqueous acetone are compared with those calculated from equation (5.15) in Table (5.12). Bearing in mind the experimental error of $([ROH]_\infty)_{obs}$ - ca. 0·0002M - good agreement is obtained for scheme S_N (R=0) with $\beta = 1{\cdot}75\ \alpha_{obs}$ and for the ion-pair schemes with $0 \leqslant R \leqslant 1$; larger values of R require $\beta < 1{\cdot}5\ \alpha_{obs}$ and cannot therefore be considered.

Similar data are available for the corresponding reactions of benzhydryl chloride under the same conditions but $([ROH]_\infty)_{calc}$ is now relatively insensitive to significant variations in the adjustable parameters (β and R) so that no clear conclusions are possible. The results are therefore not summarised in this section but can be obtained from the details of the relevant experiments in appendix J.

5.4.3 Reactions with other anions

This section considers the reactions of anions other than N_3^- with alkoxybenzyl chloride in aqueous acetone in terms of the three possible reaction schemes. Most of the results were obtained by other workers in these laboratories (Queen[60], Gregory[37], Ribar[70]) but the effect of chloride ions on the decomposition of 4-methoxybenzyl 36-chloride in 85% aqueous acetone has not been studied before. All these anions accelerate decomposition less than azide ions at the same concentration (see Table 3.1) so that $R(Y^- \neq N_3^-) < R(Y^- = N_3^-)$. Since $R(Y^- = N_3^-) < 1{\cdot}5$ (sections 5.4.1, 5.4.2) no significant error results from the neglect of the $R[Y^-]$ term in equation (5.1) for $[Y^-] \leqslant 0{\cdot}05$M. Moreover, for all experiments without added chloride ions, $\alpha[X^-] = \alpha[Cl^-] << 1^*$ so that equation (5.1) can be written in the form,

---

* The mean value of $[X^-]$ over the course of a kinetic run, $(\frac{1}{t}\int[X^-]dt)_m$, is about 0·006M for $[RX]_i \simeq 0{\cdot}02$M (see for example, Table 5.8).

Table (5.12)

Reaction products for decomposition of 4-MeO$C_6H_4CH_2Cl$ in 85% aqueous acetone in the presence of N_3^- ions at 20·41°C

Experiment	53*	55*	57*	54*	56*	58*	62a†	62b†
$[N_3^-]_i$ mole l^{-1}	·03109	·05161	·1017	·03026	·05076	·1009	·04865	·04856
$[Cl^-]_\infty$ mole l^{-1}	·02261	·02253	·02303	·02297	·02220	·02279	·02209	·02129
$([ROH]_\infty)_{obs}$ mole l^{-1}	·00877	·00470	·00214	·00896	·00486	·00194	·00298	·00281
$([ROH]_\infty)_{calc}$ mole l^{-1}								
R = 0, $\beta = 1{\cdot}75\ \alpha_{obs}$	·00889	·00472	·00190	·00940	·00472	·00190	·00281	·00271
R = 0·5, $\beta = 1{\cdot}62\ \alpha_{obs}$	·00883	·00471	·00189	·00934	·00475	·00190	·00279	·00269
R = 1·0, $\beta = 1{\cdot}5\ \alpha_{obs}$	·00875	·00469	·00179	·00927	·00470	·00192	·00277	·00274
$\partial[ROH]_\infty/\partial\beta$	-·00013	-·00013	-·00009	-·00013	-·00013	-·00009	-·00007	-·00008
$\partial[ROH]_\infty/\partial R$	-·00031	-·00021	-·00012	-·00032	-·00022	-·00010	-·00014	-·00011

* Ionic strength 0·2M : $Q = 59{\cdot}4 + 4{\cdot}2R$, $\alpha_{obs} = 5{\cdot}5$

† Ionic strength 0·5M : $Q = 123{\cdot}2 + 6{\cdot}5R$, $\alpha_{obs} = 5{\cdot}75$

$$k_{RX}^{inst} = k_I^o(1+b_{MY}[Y^-]_i + b_{HCl}[HCl])(1+Q[Y^-]_i) \qquad (5.16)$$

where k_I^o is the rate of reaction at zero ionic strength, given by,

$$(k_I)_o = k_I^o\left\{1+b_{HCl}\left(\frac{1}{t}\int_o^t [HCl]_o dt\right)_m\right\}$$

where the subscript 'o' refers to reaction in the pure solvent. Equation (5.16) assumes that the conjugate acid (HY) of the anion $[Y^-]$ is fully ionised and that any RY formed undergoes hydrolysis much more rapidly than RCl. Integration of equation (5.16) thus gives the mean integrated first-order rate coefficient for decomposition,

$$(k_I)_m = k_I^o(1+b_{MY}[Y^-]_i)(1+Q[Y^-]_i)\left\{1+\left(\frac{b}{t}\int_o^t [HCl]dt\right)_m\right\} \qquad (5.17)$$

where $b = \dfrac{b_{HCl}}{1+b_{MY}[Y^-]_i}$ and the effect on Q of changes in ionic strength during the reaction is neglected. For reaction by scheme S_N, the rate coefficient for bimolecular (S_N2) attack by Y^- then becomes,

$$k_{21} = \frac{Q}{k_I^o(1+b_{MY}[Y^-]_i)\left\{1+\left(\frac{b}{t}\int_o^t [HCl]dt\right)_m\right\}}$$

Chloride ion exchange ($Y^- = Cl^-$) was followed by the production of $^{36}Cl^-$ using $R^{36}Cl$ as the substrate and by the simultaneous production of H^+ ions (ROH). The resulting rate equations can then be expressed in the form,

$$\frac{k_{RX} - k_{ROH}}{k_{ROH}(Cl_R^-)_m} - \alpha_{obs} = \frac{k_{21}}{k_{ROH}} \qquad (S_N)$$

$$(5.18)$$

$$= Q(1+\alpha_{obs}[Cl^-]_m) \qquad (I.P.1,\ I.P.2)$$

where $k_{RX} = \left(\frac{1}{t}\ln\frac{[R^{36}Cl]_o}{[R^{36}Cl]}\right)_m = \left(\frac{1}{t}\int\frac{-d[R^{36}Cl]}{[R^{36}Cl]}\right)_m$

$$k_{ROH} = \left(\frac{1}{t}\int\frac{d[ROH]}{[RX]}\right)_m = \left(\frac{1}{t}\int k_{ROH}^{inst} \cdot dt\right)_m$$

$$(Cl_R^-)_m = \left(\frac{1}{t}\int\left([Cl^-] - \frac{[R^{36}Cl]}{[^{36}Cl^-]} \cdot [RCl]\right) \cdot dt\right)_m$$

$$[Cl^-]_m = \left(\frac{1}{t}\int[Cl^-]dt\right)_m$$

Details of the derivation of the expressions and of the approximations employed are given in Appendix E.

Values of $\frac{k_{RX} - k_{ROH}}{k_{ROH} \cdot Cl_R^-}$ for the hydrolysis and chloride ion exchange of $Ph_2CH^{36}Cl$ in 85% aqueous acetone have already been reported in section (4.2) when it was shown that the assumption of all chloride exchange via the carbonium ion (mechanism S_N1) for the benzhydryl compound (i.e. k_{21}, $Q = 0$) gave a value of α_{obs} which in turn required the expected electrolyte parameter, b_{NaCl}, to give agreement with the observed rate of hydrolysis.

The results observed using $4\text{-}MeOC_6H_4CH_2{}^{36}Cl$ are summarised in Table (5.13) and require no comment at this stage, beyond noting that Q and k_{21} are considerably smaller than for attack by azide ions.

Table (5.14) summarises k_{21} and Q from equations (5.16) and (5.18) for various anions reacting with 4-methoxy and 4-phenoxybenzyl chlorides, though it must be stressed that the approximations made in these calculations can only be assumed for the 4-PhO compound as the substrate since insufficient experimental evidence is available. It can be seen that k_{21} and Q decrease in the generally accepted order of decreasing nucleophilicity though the variation is less than that found for the similar sequence of k_{21} and Q in the reaction of $4\text{-}NO_2C_6H_4CH_2Cl$ (see Table 5.6).

5.5 Discussion

5.5.1 S_N Mechanisms

The discussion of the present results in earlier chapters showed that

Table (5.13)

Chloride exchange of 4-MeO$C_6H_4CH_2{}^{36}Cl$ in 85% aqueous acetone at 20·31°C

Experiment	46	47
[NaCl] mole l^{-1}	·05040	·09986
$[Cl^-]_m$ mole l^{-1}	·05749	·10643
$10^6 k_{ROH}$ sec^{-1}	8·496	8·291
$\frac{k_{RX} - k_{ROH}}{k_{ROH} \cdot Cl_R^-}$ mole^{-1} l	16·12 ± 0·50	15·63 ± 0·44
$Q^{\dagger}$ mole^{-1} l	7·75	6·13
$10^5 k_{21}{}^{\dagger}$ mole^{-1} l.sec^{-1}	8·81	8·19

$\dagger$ From equation (5.18), $\alpha_{obs} = 5·75$

all the observations were fully consistent with the S_N scheme. In particular, the reactions of the 4-nitrobenzyl compounds can be quantitatively explained in terms of S_N2 attack by all nucleophiles while 4-methoxybenzyl chloride undergoes entirely S_N1 reaction with water though more powerful nucleophiles can be envisaged to attack the carbonium ion and the substrate, thus requiring the concurrence of mechanisms S_N1 and S_N2.

The nature of the bimolecular (S_N2) process in the reactions between anions and alkoxybenzyl chlorides has already been discussed by Kohnstam, Queen and Ribar,[13] in effect on the basis of the values of k_{21} in 70% aqueous acetone (see Table 5.14). In terms of the model previously mentioned (see section 1.2.8) for the S_N2 transition state,

$$\begin{array}{ccc} (1+\phi-\theta)e- & \phi e+ & \theta e- \\ Y\text{-----------} & R & \text{-----------}X \end{array}$$

Table (5.14)

Values of Q and k_{21} for the reactions of 4-PhO and 4-$MeOC_6H_4CH_2Cl$ with anions in aqueous acetone at 20°C

	4-$PhOC_6H_4CH_2Cl$*	4-$MeOC_6H_4CH_2Cl$	
	70% aq. acetone	70% aq. acetone†	85% aq. acetone
Q : 0·05M $NaSO_3Ph$	0·79	0·92	-
0·05M $NaNO_3$	1·34	1·67	-
0·05M NaCl	4·45	2·80	8·00
0·05M KBr	33·34	4·26	-
0·03M NaN_3	352·4	10·07 ø	140·0
10^5k_{21} : 0·05M $NaSO_3Ph$	0·139	23·3	-
0·05M $NaNO_3$	0·249	44·5	-
0·05M NaCl	0·778	70·5	9·23
0·05M KBr	6·29	113·9	-
0·03M NaN_3	63·86	308·5	141·3

* Ribar and Kohnstam [70]

† Queen [60]

ø Gregory and Kohnstam [37]

they concluded that the precise structure of the transition state depended on the nucleophilic power of the anion (Y^-) and the ease of ionisation of the substrate in the sense that ϕ/θ increased with decreasing nucleophilicity and increasing ease of ionisation. The present results provide some additional confirmation for this interpretation.

4-Nitrobenzyl chloride and 4'-toluenesulphonate have generally been considered to react by a relatively extreme form of mechanism S_N2, with little positive charge development at the reaction centre in the transition state (i.e. $\phi/\theta \simeq 0$). On this view the rate coefficient for bimolecular (S_N2) attack by anions should be increased slightly on changing to a poorer ionising solvent but this increase should be virtually independent of the anion as it arises essentially from electrostatic considerations. A more substantial contribution from the bond fission process ($\phi/\theta > 0$) has been postulated for the bimolecular reactions of 4-methoxybenzyl chloride and should result in a reduced sensitivity of the rate coefficient (k_{21}) to the nature of the nucleophile and a tendency for k_{21} to decrease on changing to a poorer ionising solvent; this tendency becoming progressively greater with decreasing nucleophilic power of the reagent.

It is shown in Table (5.15) that all these requirements are met by the present results. The remainder of this chapter, therefore, considers whether the observations are also consistent with the ion-pair schemes (I.P.1 and I.P.2) which do not involve direct S_N2 attack on the substrate.

5.5.2 R Values

The relatively small upper limits allowed by the present results for the parameter R ($\leqslant 2$) imply that any attack of the anions (Y^-) on intermediate ion-pairs must be rate-determining (see sections 5.3.1 and 5.4.1) and therefore only accounts for a small fraction of the conversion of these ion-pairs into other species. To all intents and purposes, the formation

Table (5.15)

Values of k_{21} (mole^{-1} l.sec^{-1}) for the attack of anions on benzyl compounds in aqueous acetone at 20^{o}C

		$4\text{-}NO_2C_6H_4CH_2X^*$		$4\text{-}ROC_6H_4CH_2Cl^\dagger$	
		X = Cl	X = OT_s	RO = PhO	RO = MeO
$\frac{k_{21}(N_3^-\ 85\%)}{k_{21}(N_3^-\ 70\%)}$		1·66	1·61	-	0·458
$\frac{k_{21}(Cl^-\ 85\%)}{k_{21}(Cl^-\ 70\%)}$		-	1·64	-	0·131
$\frac{k_{21}(N_3^-)}{k_{21}(Cl^-)}$	70%	-	77·9	82·1	4·38
	85%	-	76·5	-	15·3
$\frac{k_{21}(N_3^-)}{k_{21}(Br^-)}$	70%	24·4	-	10·1	2·71

---

* From results quoted in Table (5.6)

† From results quoted in Table (5.14)

of the product (RY) does not therefore modify the rates of the other reactions of the ion-pairs so that it becomes difficult to draw a clear distinction between attack by Y^- on the covalent substrate (S_N2) and on ion-pairs.

The substantial acceleration of the decomposition of 4-NO_2 and 4-$MeOC_6H_4CH_2Cl$ by added azide ions show that in reaction via schemes I.P.1 or I.P.2 the initial ionisation,

$$RX \xrightarrow{1} R^+/X^-$$

must occur relatively rapidly and certainly much more rapidly than hydrolysis, since the attack by Y^- is itself rate-determining for the formation of RY. Unfortunately no values for the rate coefficient of the initial ionisation (k_1) can be calculated in the absence of a knowledge of the parameter R. However, other considerations provide a clearer indication of the reaction mechanisms.

5.5.3 Solvent Effects

The expression for Q in the present reactions for 4-nitrobenzyl chloride and 4'-toluenesulphonate (see Table 5.1) show that for a change from 70% to 85% aqueous acetone,

$$\frac{Q^{85}}{Q^{70}} = \frac{\mu^{70}}{\mu^{85}} \cdot \frac{\epsilon^{85}}{\epsilon^{70}} \qquad \text{(I.P.1)}$$

$$\qquad\qquad (5.19)$$

$$= \frac{A_1^{\,70}}{A_1^{\,85}} \cdot \frac{\epsilon^{85}}{\epsilon^{70}} \cdot \frac{[\frac{\delta}{\epsilon}(1+\mu)+y+\lambda]^{85}}{[\frac{\delta}{\epsilon}(1+\mu)+y+\lambda]^{70}} \qquad \text{(I.P.2)*}$$

where $A_1 = \lambda(1+\mu)+\mu y$ and the superscripts refer to the solvent. From the

---

* This expression assumes $\epsilon[Y^-] << 1$, an assumption which is justified when $[Y^-]$ is small since $\epsilon < R \leqslant 2$

definitions of δ and ϵ it follows that,

$$\delta/\epsilon = \frac{k_7}{k_8} \cdot \frac{k_{-2}}{k_{-1}}$$

where k_{-2} and k_{-1} depend only on the substrate and solvent while k_7 and k_8 refer to the attack of an anion on an ion-pair and should therefore undergo similar changes on altering the solvent or the nature of the anion. As a result, k_7/k_8 can be assumed constant and equations (5.19) can therefore be written in the form,

$$\frac{Q^{85}}{Q^{70}} = \frac{A^{70}}{A^{85}} \cdot \frac{k_8^{\,85}}{k_8^{\,70}} \tag{5.20}$$

where A depends only on the substrate and solvent. It can easily be shown from Table (5.1) that equation (5.20) also applies to the present reactions of 4-methoxybenzyl chloride via schemes I.P.1 and I.P.2 though A is now given by different expressions.

The effect of solvent changes on the rate coefficient, k_8, for the attack of a singly charged anion on an ion-pair should be independent of the nature of the anion so that equation (5.20) predicts Q^{85}/Q^{70} constant for a given substrate, irrespective of the anion considered. Table (5.16) shows that this requirement is met by the reactions of the 4-nitrobenzyl compounds but not when 4-methoxybenzyl chloride is employed as the substrate, suggesting strongly that the reaction of this compound with added anions does not occur exclusively via intermediate ion-pairs. It must however be stressed that Q^{85}/Q^{70} for both sets of compounds is fully consistent with S_N2 attack by the anions if the charge development in the transition state of this process is independent of the nature of the anion and solvent in the reactions of the 4-nitrobenzyl compounds and varies in the manner outlined in section (5.5.1) for 4-methoxybenzyl chloride.

Table (5.16)

The effect of solvent change on kinetic parameters

		$4\text{-}NO_2C_6H_4CH_2X$		$4\text{-}MeOC_6H_4CH_2Cl$
		X = Cl	X = OT_s	
$(k_I)_o^{70}/(k_I)_o^{85}$		3·89	3·67	29·1
Q^{85}/Q^{70}	$(Y^- = N_3^-)$	6·69*	5·91†	13·8*
	$(Y^- = Cl^-)$	-	6·00‡	2·86*
Z^{ϕ}	$(Y^- = N_3^-)$	0·58*	0·62†	2·19*
	$(Y^- = Cl^-)$	-	0·61‡	10·2 *

φ $$Z = \frac{(k_I)_o^{70}/(k_I)_o^{85}}{Q^{85}/Q^{70}}$$

* $[Y^-] = 0$; † $[Y^-] = 0{\cdot}03\underline{M}$; ‡ $[Y^-] = 0{\cdot}05\underline{M}$

It has already been pointed out that,

$$\lambda,\ \mu,\ \mu y << 1$$

for the present reactions of 4-nitrobenzyl chloride (see section 5.3.1) and similar arguments can be employed to show that this must also apply to the decomposition of the toluenesulphonate. Equation (5.1) and the expressions in Table (5.1) then give the relation,

$$\left.\begin{aligned} Z &= \frac{(k_I)_0^{70}/(k_I)_0^{85}}{Q^{85}/Q^{70}} = \frac{k_1^{70}/k_1^{85}}{\epsilon^{85}/\epsilon^{70}} && \text{(I.P.1)} \\ &= \frac{k_1^{70}/k_1^{85}}{\epsilon^{85}/\epsilon^{70}} \cdot \frac{(\frac{\delta}{\epsilon}+y+\lambda)^{70}}{(\frac{\delta}{\epsilon}+y+\lambda)^{85}} && \text{(I.P.2)} \end{aligned}\right\} \quad (5.21)$$

The parameter ϵ ($= k_8/k_{-2}$) represents a ratio of rate coefficients for processes which are accelerated (though not excessively) by changing to a less aqueous solvent and should therefore, at best, be only slightly larger in 85% aqueous acetone than in the 70% solvent. The rate coefficient (k_1) for the initial ionisation,

$$RX \longrightarrow R^+/X^-$$

should however decrease substantially for such a solvent change so that the parameter Z (equation 5.21) should be greater than unity for reaction by scheme I.P.1. The same conclusion applies even more forcibly if scheme I.P.2 is operating since δ/ϵ should be independent of the nature of the present solvents while y ($= k_2/k_{-1}$) and λ ($= k_{10}/k_{-1}$) are ratios of rate coefficients which vary in opposite directions as the solvent is altered, the overall effect being in the direction of larger values in the more aqueous solvent.

Contrary to these requirements, $Z \simeq 0{\cdot}6$ for the reactions of the 4-nitrobenzyl compounds (see Table 5.16) and it must therefore be concluded that the acceleration of the decomposition of these compounds by added anions, excluding electrolyte effects, cannot arise exclusively from attack on intermediate ion-pairs. On the other hand, no inconsistencies arise if this acceleration results from S_N2 attack. Under these conditions Z simply represents the ratio of the rate coefficients for the bimolecular process (k_{21}^{70}/k_{21}^{85}) which is less than unity unless the transition state involves substantial development of positive charge at the reaction centre (see for example reference 17).

5.5.4 Q Values

Table (5.1) shows that Q for reaction by ion-pair mechanisms can be written in the form,

$$Q = \epsilon A(\frac{\delta}{\epsilon} + B) \qquad (5.22)$$

where δ is zero for reaction via scheme I.P.1 and A and B are independent of the anion under consideration. If, as seems likely, δ/ϵ also depends only on the substrate and solvent (see section 5.5.3) the definition of ϵ (see Table 5.1) gives equation (5.22) in the form,

$$Q = A_s k_8 \qquad (5.23)$$

where A_s is independent of the nature of the anion and k_8 represents the rate coefficient for its reaction with the carbonium ion moiety of the ion-pair. As a first approximation, this rate coefficient should be as sensitive to variations in the attacking anion as the rate coefficient (k_9) for reaction with a fully developed carbonium ion, given by the intervention constant,

$$\beta = k_9/k_6 \qquad (5.24)^*$$

where k_6 is also independent of the nature of the anion.

Intervention constant of some of the anions under consideration are available for reaction with the relatively stable 4-methoxybenzhydryl carbonium ion (see section 4.2) so that a relative scale of k_9 values for these systems can be obtained. It is generally agreed that the sensitivity

---

* This formulation includes attack by Cl^- for which the intervention constant is usually given the symbol α and the rate coefficient the symbol k_{-3}.

of the rate of attack on a carbonium ion centre to variations in the nature of the nucleophile (i.e. the selectivity of the centre) decreases with its decreasing stability with respect to hydrolysis[55] so that this sensitivity could be expected to be least for k_8 (4-nitrobenzyl systems), intermediate for k_8 (4-alkoxybenxyl systems) and greatest for k_9 (4-methoxybenzhydryl systems).

In practice, the converse of this prediction is found to apply (see Table 5.17) and it must therefore be concluded that the dependence of Q on the nature of the anion also argues against the view that attack on intermediate ion-pairs is entirely responsible for the additional acceleration of the decomposition of 4-nitro and 4-methoxybenzyl compounds by added anions.

5.5.5 Conclusions

The present results show quite clearly that reactions previously regarded as bimolecular cannot occur exclusively via intermediate ion-pairs with no attack on the covalently bound substrate (i.e. mechanism S_N2). This applies not only to the reactions of 4-nitrobenzyl chloride and 4'-toluenesulphonate (typical bimolecular reactions) but also to the acceleration of the decomposition of 4-methoxybenzyl chloride (previously regarded as mechanistically borderline) by added anions after allowing for the electrolyte effects on the ionisation. Indeed the vast majority of the 'bimolecular component' must involve the operation of mechanism S_N2 though the possibility that a small fraction involves the rate-determining attack of nucleophiles on one or more ion-pairs cannot be completely excluded, or established. However, the fact that the small fraction of the reactions which could occur via intermediate ion-pairs demands the rate-determining attack of the nucleophile could equally well be regarded as a special case of a more general scheme in which a whole series of reaction paths, varying in the

Table (5.17)

Relative values of k_8 and k_9 for reaction in aqueous acetone at 20°C

Substrate	% Acetone	SO_3Ph^-	NO_3^-	$OPNB^-$	Cl^-	Br^-	N_3^-
$4\text{-}NO_2C_6H_4CH_2Cl$*	70	-	0·11	4·5	-	41·0	1000
$4\text{-}NO_2C_6H_4CH_2OT_s$*	70	-	-	-	12·85	-	1000
	85	-	-	-	13·0	-	1000
$4\text{-}PhOC_6H_4CH_2Cl$*	70	2·2	3·8	-	12·6	94·6	1000
$4\text{-}MeOC_6H_4CH_2Cl$*	70	86	156	-	262	398	1000
	85	-	-	-	57·1	-	1000
$4\text{-}MeOC_6H_4CHPhCl$†	85	-	-	62·5	500	~ 500 ϕ	1000

* $(k_8)_{rel}$ calculated from dated in Table (5.14)

† $(k_9)_{rel}$ at 0°C from data in Table (4.3)

ϕ Calculated from observations that Br^- and Cl^- ions compete equally efficiently for a fully developed carbonium ion (see reference 60).

degree of separation of the leaving group in the transition state, is available for the bimolecular route, a suggestion which has been made on several occasions in the past. Under these conditions it is attractive to consider that all the present results for reaction with external nucleophiles are most satisfactorily explained in terms of the classical S_N scheme as originally proposed by Hughes and Ingold.

On this view, the formidable evidence supporting ionisation via intermediate ion-pairs (racemisation of the substrate and 18-oxygen equilibration in the 4-nitrobenzoates - see for example reference 50) must either mean that the ion-pairs do not react with external reagents or that the postulate of their existence as discrete metastable entities represents a gross oversimplification, with the true picture closer to that envisaged by Ingold[52] (a definite probability of return to RX with racemisation after passing through the free energy maximum for ionisation to R^+ - see section 1.3). Such a conclusion is diametrically opposed to that reached by several different sets of authors but in many cases this has been based on an ab initio assumption of ion-pair mechanisms although the results can be shown to be equally consistent with S_N reactions.

For example, the conclusions to be reached from the relation between product proportions and the rate coefficient on changing the azide ion concentration (often employed by Sneen and his co-workers[54]), depends on the magnitude assumed for the electrolyte parameters.[55,56] Similarly, the substantial acceleration of the decomposition of benzhydryl 4-nitrobenzoates by azide ions[51] could equally well result from S_N2 attack, a process already considered feasible for benzhydryl compounds which ionise slowly (see section 1.3.1, page 25). Unfortunately the reports do not contain sufficient information to allow any distinction between the possible reaction schemes.

Two reports of the complete suppression of the racemisation of the substrate on the addition of azide ions[51,71] cannot be interpreted in terms of S_N2 attack on the substrate but the proposed explanation in terms of overwhelming attack on the ion-pair responsible for racemisation appears to be oversimplified. Rate equations obtained by applying the stationary state approximation to the intermediates show that these observations at one particular concentration of N_3^- could arise from a fortuitous cancellation of terms but results at other N_3^- concentrations (which would give a different result) would be needed for confirmation; these additional results are not available. Moreover, other similar systems[51] do not show a large decrease of the rate coefficient for racemisation on the addition of relatively small amounts of N_3^- though such a decrease would be expected if azide attack on an ion-pair is energetically much more favourable than racemisation at $[N_3^-] \simeq 0{\cdot}1\underline{M}$. Further work on this problem is clearly necessary.

A recent report[72] casts doubt on the interpretation of reactions of benzhydryl 4-nitrobenzoates in terms of ion-pair schemes by claiming that the reaction of the parent compound with the solvent (and therefore presumably also with nucleophilic anions) occurs at least partly by mechanism S_N2. An examination of the paper, however, shows that it is only justifiable to conclude that the solvolysis products in the reaction between diphenyl diazomethane and nitrobenzoic acid are not formed by the same route as the solvolysis products of benzhydryl nitrobenzoate in the same solvent. Moreover, the activation parameters for the reaction of thenitrobenzoate with a more aqueous solvent suggest entirely S_N1 solvolysis.[65]

CHAPTER 6

Experimental

6.1 Preparation and Purification of Materials

4-Nitrobenzyl Chloride

The commercial product (B.D.H. Chemicals Ltd.) was recrystallised twice from ethanol. The hydrolysable chloride content was 99•5% of the theoretical amount. M.p. 73°C (lit. 71°C).[73]

4-Nitrobenzyl Bromide

The commercial product (Emanuel Ltd.) was purified by reduced pressure sublimation (100°C. 1 mm. Hg). The hydrolysable chloride content was 97% of the theoretical amount. Account was taken of the purity in calculating the initial organic bromide content for the hydrolysis and added chloride experiments. M.p. 98°C (lit. 99-100°C).[74]

4-Nitrobenzyl 4'-toluenesulphonate[75]

4-Toluenesulphonyl chloride (9•2 gm.) was dissolved in dry pyridine (36 ml.) and cooled to -15°C. Nitrobenzyl alcohol (6•2 gm.) was added whilst maintaining the temperature, when after about 45 minutes fine crystals began to appear. After a further 30 minutes, pre-cooled sulphuric acid (100 ml., 6N) was carefully added, whilst keeping the temperature below 20°C. The solution was allowed to stand for an hour as the crude product crystallised.

The product was filtered off and dissolved in benzene, washed with dilute sulphuric acid, water, sodium bicarbonate solution and water, then dried over anhydrous magnesium sulphate. After filtration and removal of the solvent on a water bath, the product was recrystallised from a petrol (100°/60°) and benzene mixture. Hydrolysis yielded 99% of the theoretical amount of acid. M.p. 103°C (lit. 103-104°C).[75]

4-Methoxybenzyl Chloride[60]

Dry hydrogen chloride gas was passed through a solution of anisyl alcohol (25 gm.) in dry ether (200 ml.), in the presence of granular calcium chloride, for 10 hours at 0°C. The excess HCl and most of the ether were removed from the filtered solution using a rotary evaporator and petroleum ether (40°/60°) (200 ml.) was added to the residue. The crude product was not allowed to stand in the concentrated ether solution, at the end of the evaporation, for too long to avoid its polymerisation in the presence of HCl. The petrol solution was washed with water, 5% sodium bicarbonate, water and finally dried over anhydrous potassium carbonate. The solvent was removed, after filtration, on a rotary evaporator and the residual product distilled under reduced pressure (60°C, 0·3 mm. Hg). Hydrolysis yielded 99·3% of the theoretical amount of acid.

4-Methoxybenzyl-36-chloride[60]

Pure 4-methoxybenzyl chloride was allowed to exchange with lithium-36-chloride in dry acetone for four days. After this time, the solvent was removed on a rotary evaporator and petroleum ether (40°/60°) was added. The precipitated salt was removed by filtration and the solution washed with water and dried over anhydrous magnesium sulphate. The concentration and specific activity of the 4-methoxybenzyl chloride in this solution were determined by hydrolysing a small sample, after removal of the petrol, in aqueous acetone and making up to a known volume. A 10 ml. sample was then counted in a liquid counter and the acid produced titrated with standard sodium hydroxide.

Samples were prepared for the kinetic runs by evaporating the required volume of the petrol stock solution on a water bath at 70°C and removing the last traces of solvent at 40°C and 0·5 mm. Hg pressure.

Benzhydryl Chloride

The commercial product (Koch-Light) was dissolved in petroleum ether ($40^o/60^o$), washed with water, 5% sodium bicarbonate and water, and then dried over anhydrous potassium carbonate. The solvent was removed from the filtered solution and the oil distilled at reduced pressure (108^o, 0·7 mm. Hg). The acid produced on hydrolysis was 99·3% of the theoretical amount.

Benzhydryl-36-chloride

A more highly active sample of lithium 36-chloride was employed in this preparation than in that of 4-methoxybenzyl-36-chloride. A sample of an aqueous solution of the lithium-36-chloride was evaporated and dried at 100^oC at reduced pressure and then dissolved in 100 ml. of dry dimethyl sulphoxide. Pure benzhydryl chloride (3·6 ml.) was then added and allowed to exchange for 12 hours. The active benzhydryl chloride was then extracted with benzene (100 ml.), thoroughly washed with water and finally dried over anhydrous magnesium sulphate. The concentration and specific activity of the benzhydryl chloride in this benzene solution were determined by hydrolysis and samples for the kinetic runs prepared in a similar manner to that employed for the 4-methoxybenzyl-36-chloride stock solution.

4-Methoxybenzhydrol[76]

A solution of bromobenzene (90 gm.) in dry ether (300 ml.) was slowly added to a well stirred mixture of magnesium (14·4 gm.) in dry ether (150 ml.) under an atmosphere of nitrogen. After completion of reaction, the mixture was refluxed for 15 minutes. Anisaldehyde (52 gm.) in dry ether (50 ml.) was then slowly added to the cooled Grignard reagent and after completion the mixture was reheated for about 15 minutes.

The bromomagnesium salt was hydrolysed by the slow addition of dilute sulphuric acid (700 ml., 2N) and allowed to stand until the reaction was complete. The ether layer was separated, washed with water, sodium bicarbonate, water and then dried over anhydrous magnesium sulphate. After filtration and removal of the solvent, the crude carbinol was recrystallised from a petroleum ether (80°/100°) and benzene mixture. M.p. 67°C (lit. 68°C)[76].

4-Methoxybenzhydryl Chloride[76]

Dry hydrogen chloride gas was bubbled through a solution of p-methoxybenzhydrol in dry petroleum ether (80°/100°) over phosphorus pentoxide, for about 6 hours. The product was allowed to crystallise from the filtered solution at -20°C. The product was purified by recrystallisation from dry petroleum ether (80°/100°). Hydrolysis in aqueous acetone yielded 99% of the theoretical amount of acid. M.p. 63°C (lit. 64°C)[76].

4-Methoxybenzhydryl 4'-nitrobenzoate[65]

4-Methoxybenzhydrol (10 gm.), 4-nitrobenzoyl chloride (8·7 gm.) and pyridine (7·4 gm.) were refluxed together in dry benzene as solvent for about 2 hours. The excess pyridine was removed by passing dry hydrogen chloride through the solution and filtering. The filtrate was washed with water and dried over anhydrous magnesium sulphate. After removal of the solvent, the crude product was recrystallised from petroleum ether (80°/100°). Hydrolysis in aqueous acetone yielded 99·5% of the theoretical amount of acid.
M.p. 80°C (lit. 79°-82°C)[77].

Dry Acetone was prepared for the exchange reactions from 'Analar' grade acetone by refluxing with sodium hydroxide and potassium permanganate for 2 hours[78] before distillation. The acetone was then fractionated from hydroquinone and then dried by standing over molecular sieves (Linde, type 4A) for several days.

Dry DMSO, also for the exchange reaction, was the commercial product (Koch-Light, puriss) which had been dried over calcium hydride for 4 days before being distilled from calcium hydride under reduced pressure. The distillate was collected and stored over molecular sieves (Linde, type 4A).

Sodium Chloride (Fisons) was dried in the oven at 120°C for 12 hours.

Sodium Bromide (B.D.H. Analar) was dried in the oven at 120°C for 12 hours.

Sodium Perchlorate (B.D.H. Analar) was dried at 100°C and a pressure of 0•5 mm. Hg for 12 hours.

Sodium Nitrate (Hopkins and Williams) was dried in the oven at 120°C for 6 hours.

Sodium Azide (Fisons): 50 gms. were dissolved in 150 ml. of hot water and filtered into 250 ml. of hot ethanol. A further 500 ml. of warm ethanol were added and the product allowed to crystallise. The recrystallisation was repeated and the filtered product washed with ethanol and then with a little pure, dry acetone before drying in the oven at 120° for 12 hours.

Potassium 4-Nitrobenzoate was prepared by adding a slight excess of 4-nitrobenzoic acid to a weighed amount of potassium hydroxide in water. The mixture was shaken for 12 hours before filtering off the excess acid and washing the filtrate with ether. The water was removed at reduced pressure and the salt recrystallised from aqueous ethanol before drying over phosphorus pentoxide. The purity was determined by passing a 5 ml. sample of an aqueous acetone stock solution of the salt down a cation exchange column (Amberlite 120 H) previously washed with water then acetone. The sample was eluted with 70 ml. of acetone (neutral) and titrating the acid against standard sodium hydroxide potentiometrically using a calomel/glass dual electrode. The purity thus determined was 99•9%.

Lithium 36-Chloride was prepared from a sample of active hydrochloric acid (Radiochemical Centre, Amersham) by treatment with an equivalent of lithium hydroxide, determined potentiometrically. The required volume of this stock solution was then evaporated down and dried at 100°C and 0•5 mm. Hg pressure in the reaction flask to be used for the exchange reaction.

Trans-4,4'-dinitrostilbene[79] was prepared by shaking 4-nitrobenzyl chloride (1 gm.) with a mixture of sodium hydroxide (20 ml., 2N) and ethanol (80 ml.) for about 2 hours. Fine yellow crystals were formed which were recrystallised from glacial acetic acid. M.p. 278°-283°C (lit. 286°-288°C)[80]

Solvents

The acetone used was 'Analar' grade which had been refluxed with sodium hydroxide and potassium permanganate for 2 hours[78] and distilled, before being fractionated from hydroquinone. 70% aqueous acetone was made up by mixing the acetone and distilled water in the volume ratio 7:3, 85% aqueous acetone being made analagously.

Titration acetone was prepared from the commercial grade solvent by refluxing with sodium hydroxide and potassium permanganate for 2 hours before distillation. The first 500 ml. of a batch being discarded before collection of the titration acetone. The solvent was neutralised before acidity determinations to the lacmoid indicator end-point.

Added Electrolytes

Normally, the concentration was determined by making up standard solutions at the thermostat temperature required. In the case of sets of experiments at various sodium azide concentrations made to constant ionic strength with sodium perchlorate, the following procedure was adopted. Stock solutions of accurately 0·2M sodium perchlorate and 0·2M sodium azide were made up with the aqueous acetone solvent. These were then mixed in approximately the right amounts to give the desired sodium azide concentration in the resulting solutions. The precise sodium azide concentration was then determined by potentiometric titration with standard silver nitrate solution.

Thermostats

These consisted of a well-lagged tank containing water or oil with a large stirrer. Intermittant heating by light bulbs was controlled by a contact thermometer and relay. Permanent heating by a suitable light bulb or cooling by a water cooling coil was used when necessary, depending on the thermostat temperature required and the ambient room temperature. Temperature control was within ±0·01°C of the quoted temperature.

6.2 Rate Measurements

The initial substrate concentration was either obtained from the 'infinity' value at complete reaction after at least 10 half-lives or from accurately weighing the substrate of known purity and making up to a known volume with the solvent. Infinity values were determined by allowing the 10 half-lives to proceed either under the experimental conditions employed in the kinetic run or by increasing the rate by raising the temperature or increasing the water content of the solvent. Thus a 5 ml. sample was either sealed into a clean dry tube and immersed in a higher temperature thermostat or about 4 ml. of distilled water was added to the sample taken from the reaction vessel. For some of the product runs and slow kinetic experiments the 'sealed ampoule technique' was also employed.

For the flask runs, the solvent or electrolyte solution was brought to thermostat temperature before the substrate was added. In the case of 4-nitrobenzyl chloride with sodium azide, both were weighed out accurately into a volumetric flask and made up to the mark with solvent at thermostat temperature. In all cases the reaction mixture was well shaken and if necessary transferred from the volumetric flask to the reaction vessel which had a double sealed stopper to minimise solvent evaporation. A sample was removed as soon as possible, the time being taken as zero time and further samples removed at convenient time intervals, the samples being quenched in cold acetone.

Kinetic runs with added NaCl, NaBr, $NaClO_4$ and no salt additions, were followed by measuring the production of acid, by titration with standard sodium hydroxide using lacmoid as an indicator. Those with added $NaNO_3$, NaN_3 and $KO_2CC_6H_4NO_2$ were followed by monitoring the production of chloride ions. The experiments on 4-nitrobenzyl tosylate with added sodium azide were followed by determining the azide ion concentration at various time intervals.

Chloride ions were determined by quenching the sample in ice cold acetone and then titrating potentiometrically against silver nitrate. Nitric acid 0•5 ml., 50%) was added to prevent the precipitation of silver azide. The e.m.f. between a glass electrode and silver electrode was determined at each addition of 0•1 ml. of the silver nitrate solution around the end-point using a pH meter. At the end-point the change of e.m.f. per unit titre was at a maximum.

For the azide ion determination in the reaction with 4-nitrobenzyl chloride, the procedure was the same as that for chloride ions except that no nitric acid was added.

Exchange Experiments

5 Ml. samples of the reaction mixture were removed at suitable time intervals and quenched by running into benzene ('Analar', 25 ml.). The acid was extracted using water (approximately 10 ml. accurately delivered as two quantities from a 5 ml. tube filler), shaken for 3 minutes before separating the aqueous layer. A 10 ml. sample of the aqueous layer was then counted for 1 hour using a standard halogen-quenched liquid counter, a lead-lined castle and standard counting equipment. The background count was determined at several times for periods of half an hour. The counted samples were then run into neutral acetone containing lacmoid indicator and titrated with standard sodium hydroxide to determine the acidity. The extraction process was found to yield 85% of the amount of acid in the original 5 ml. sample. Thus, in calculating k_{ROH}, the observed titres can be used in the general first-order rate equation (Appendix A). However in calculating Cl^-_R (see section 4.2) the recovery factor is of importance in estimating the mean

chloride ion concentration. The count rates, after the background and dead-time correction had been made were used to calculate k_{RX}.

Product Data

The proportion of alcohol produced during solvolysis of an alkyl halide in the presence of salts was determined by titration of the acid produced after at least ten half-lives. In the presence of azide ions or 4-nitrobenzoate ions any hydrogen ions produced would form hydrazoic or 4-nitrobenzoic acid, both weak acids. There determination was therefore carried out by potentiometric titration with standard sodium hydroxide solution using a dual glass-calomel electrode. A sample was run into, or in the case of a tube sample, broken under, 100 ml. of 'equilibrium' water* and 20 ml. of carbon tetrachloride. The mixture was shaken to separate the organic material into the carbon tetrachloride phase and the sample titrated while a constant stream of nitrogen was passed through the solution to remove the last traces of CO_2. Blank determinations on the carbon tetrachloride and 'equilibrium' water were also made in a similar way. The initial concentration of substrate was determined by titrating the produced chloride ions in the usual manner.

All the substrates thus determined were shown to be initially free from acid except for 4-methoxybenzhydryl 4'-nitrobenzoate. For this substrate a small correction had to be made for the initial acid concentration corresponding to a level of about 2% in the substrate. As hydrolysis of this substrate produced the theoretical yield of acid, it was assumed that the initial acid corresponded to smaller equimolar quantities of unreacted p-nitrobenzoic acid and p-methoxybenzhydrol; corrections to the initial substrate and final alcohol concentration were based on this assumption.

---

* Distilled water through which air had been bubbled to reduce the carbon dioxide level to that in equilibrium with the air.

Product experiments on 4-methoxybenzhydryl chloride had to be carried out at 0°C due to the rapid solvolysis of this compound. The procedure used was to prepare a stock solution of the salt in the appropriate solvent and bring to the thermostat temperature in the reaction vessel. This was fitted with a paddle stirrer which rapidly stirred the solution prior to and during the addition of the substrate, which was achieved by dissolving the substrate in 1 ml. of dry acetone and rapidly injecting into the salt solution. 0·17 Ml. water were previously added to the solution so that the solvent composition would be maintained on addition of the substrate.

The rate of decomposition of 4-nitrobenzyl 4'-toluenesulphonate in the presence of chloride ions was calculated from a determination of the acidity after ten half-lives for solvolysis of this compound in the pure solvent. Any RCl formed after this time can be regarded as not having undergone any significant hydrolysis since it solvolyses some 600 times slower than ROT_s. The method of calculation is shown in Appendix C.

APPENDICES

APPENDIX A

Integrated And Instantaneous Rate Coefficients

Almost all the reactions discussed in this thesis were followed by titration of a product (H^+, Cl^-) in samples removed from the reaction mixture at various times. Integrated first-order rate coefficients were then obtained from,

$$(k_I)_{OBS} = \frac{1}{t} \ln \left(\frac{T_\infty - T_o}{T_\infty - T}\right)$$

where T_t represents the titre at time t = t.

However, the instantaneous rate equations predict a change of $(k_I)_{OBS}$ as the reaction proceeds for almost all the present systems. The special integrated rate equations required when this change is substantial have been given in the text as they were required, but $(k_I)_{OBS}$ was found to be constant or almost constant (within the limits of experimental error) over the range examined (15-85% completion of reaction) for many of the present systems.

Under these conditions only a negligible error results from assuming that the integrated rate coefficient $(k_I)_{OBS}$, calculated for the time interval t = 0 to t = t, is identical with the instantaneous rate coefficient (k_I^{inst}) at the time t = $^t/2$ and calculating the concentrations of the various species at that time by assuming accurately first-order kinetics (rate coefficient $(k_I)_{OBS}$) over the time interval t = 0 to t = t.[64] Thus,

$$[RX]_{t/2} = [RX]_0 e^{-(k_I)_{OBS} t/2}$$

$$= [RX]_0^{\frac{1}{2}} \left\{ [RX]_0 e^{-(k_I)_{OBS} t} \right\}^{\frac{1}{2}}$$

$$= [RX]_0^{\frac{1}{2}} [RX]_t^{\frac{1}{2}} \qquad \text{(A.1)}$$

where $[RX]_t$ is the observed concentration of RX at time t ($\alpha T_\infty - T$). Hence

$$[X^-]_{t/2} = [X^-]_0 + [RX]_0 - [RX]_0^{\frac{1}{2}}[RX]_t^{\frac{1}{2}}$$

and the mean of the values of $(k_I)_{OBS}$ refers to the instantaneous rate coefficient at

$$[X^-] = ([X^-]_{t/2})_m$$

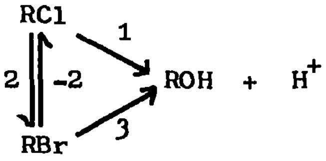
Rate coefficients and other relevant information given in the earlier chapters were obtained via this 'square root' approximation whenever no statment to the contrary appears.

APPENDIX B

Determination Of The Rates Of Halide Exchange In 4-Nitrobenzyl Chloride

B.1 The Processes Involved

The effect of bromide ions on the decomposition of 4-nitrobenzyl chloride (RCl) in 70% aqueous acetone was followed via the development of acidity over the early stages of reaction. Parallel experiments were carried out with the bromide (RBr) in solutions containing chloride ions. The processes occurring in both systems can be represented in the form,



so that,

$$[H^+]_t - [H^+]_0 = [ROH]_t - [ROH]_0 = k_1 \int_0^t [RCl]dt + k_3 \int_0^t [RBr]dt \qquad (B.1)$$

In the early stages of reaction,

$$[ROH] << [RCl] + [RBr] \qquad (B.2)$$

so that equation (B.1) may be written,

$$[H^+]_t - [H^+]_0 = k_3([RBr]_0 + [RCl]_0)t - (k_3-k_1) \int_0^t [RCl]dt \qquad (B.3)$$

The rate coefficients k_3 and k_1 for the hydrolysis of RBr and RCl were determined independently (Experiments 6 and 7, Appendix J) and the unknown rate coefficients for halide ion exchange (k_2 and k_{-2}) are contained in the integral which needs to be determined before equation (B.3) can be used with the present results.

B.2 Evaluation Of The Integral

For the above reaction scheme,

$$[\mathrm{ROH}] = [\mathrm{RBr}]_0 - [\mathrm{RBr}] + [\mathrm{RCl}]_0 - [\mathrm{RCl}]$$

$$[\mathrm{Cl}^-] = [\mathrm{Cl}^-]_0 + [\mathrm{RCl}]_0 - [\mathrm{RCl}]$$

$$[\mathrm{RBr}] = [\mathrm{RBr}]_0 + [\mathrm{RCl}]_0 - [\mathrm{RCl}] - [\mathrm{ROH}]$$

$$[\mathrm{Br}^-] = [\mathrm{Br}^-]_0 - [\mathrm{RCl}]_0 + [\mathrm{RCl}] + [\mathrm{ROH}]$$

Hence,

$$\begin{aligned}\frac{d[\mathrm{RCl}]}{dt} &= k_{-2}[\mathrm{RBr}][\mathrm{Cl}^-] - k_1[\mathrm{RCl}] - k_2[\mathrm{RCl}][\mathrm{Br}^-] \\ &= k_{-2}[a - [\mathrm{ROH}]([\mathrm{Cl}^-]_0 + [\mathrm{RCl}]_0) \\ &\quad + [\mathrm{RCl}]\left\{b' + c([\mathrm{Br}^-]_0 - [\mathrm{RCl}]_0) + c[\mathrm{ROH}]\right\} \\ &\quad + c[\mathrm{RCl}]^2] \end{aligned} \qquad (\mathrm{B}.4)$$

where,

$$a = ([\mathrm{RBr}]_0 + [\mathrm{RCl}]_0)([\mathrm{RCl}]_0 + [\mathrm{Cl}^-]_0)$$

$$b' = -([\mathrm{RBr}]_0 + [\mathrm{Br}^-]_0 + [\mathrm{Cl}^-]_0 + [\mathrm{RCl}]_0)$$

$$c = 1 - \frac{k_2}{k_{-2}}$$

Table (B.1) shows that the terms involving [ROH] represent only a very small fraction of the coefficients with which they are associated and the neglect of these terms gives equation (B.4) in the form,

$$\frac{d[\mathrm{RCl}]}{dt} = k_{-2}(a + b[\mathrm{RCl}] + c[\mathrm{RCl}]^2)$$

where $b = b' + c([\mathrm{Br}^-]_0 + [\mathrm{RCl}]_0)$.

Integration between the limits $t = 0$ and $t = t$ then gives

$$k_{-2}t = \frac{1}{q}\ln\frac{1 - \dfrac{2c([\mathrm{RCl}]_0 - [\mathrm{RCl}])}{b - q + 2c[\mathrm{RCl}]_0}}{1 - \dfrac{2c([\mathrm{RCl}]_0 - [\mathrm{RCl}])}{b + q + 2c[\mathrm{RCl}]_0}}$$

where $q = (b^2 - 4ac)^{\frac{1}{2}}$

Rearrangement gives,

$$[RCl] = -\frac{b+q}{2c} - \frac{q}{c}\,\frac{Ze^{-qk_{-2}t}}{1 - Ze^{-qk_{-2}t}}$$

where

$$Z = \frac{b + q + 2c[RCl]_0}{b - q + 2c[RCl]_0}$$

and integration between the limits t = 0 and t = t gives

$$\int_0^t [RCl]dt = \frac{-(b+q)}{2c}\,t + \frac{1}{ck_{-2}}\ln\left(\frac{1 - Z}{1 - Ze^{-qk_{-2}t}}\right) \qquad (B.5)$$

B.3 Determination Of The Unknown Rate Coefficients

In practice, the acidity was found to vary linearly with time once the initial stages of hydrolysis had been completed (see Experiments 8 and 9, Appendix J) and comparison of the resulting experimental rate equation,

$$[H^+]_t - [H^+]_0 = A + Bt \qquad (B.6)$$

with equations (B.3) and (B.5) suggests that after the expiring of this initial period ($t = t_{min}$),

$$e^{-qk_{-2}t} << 1 \qquad (t > t_{min})^*$$

so that,

$$A = \frac{-(k_3-k_1)}{ck_{-2}}\ln(1-Z) \qquad (B.7)$$

$$B = k_3([RBr]_0 + [RCl]_0) + \frac{(k_3-k_1)(b+q)}{2c} \qquad (B.8)$$

---

* This assumption is easily justified *a posteriori*. Thus:

	$10^{-5}t_{min}$	10^4k_{-2} (eqn. B.7)	q	$e^{-qk_{-2}t_{min}}$
Experiment 8(a)	3·562 secs	1·78	·04585	·0546
Experiment 9(a)	6·743 secs	1·31	·02602	·0302

Equation (B.8) contains only one unkown parameter (c) which can therefore be calculated from the experimentally observed B as

$$c = \frac{\beta b' - a}{\beta(\beta - [Br^-]_0 + [RCl]_0)}$$

where

$$\beta = \frac{B - k_3([RBr]_0 + [RCl]_0)}{k_3 - k_1}$$

and $$b' = -([RBr]_0 + [Br^-]_0 + [RCl]_0 + [Cl^-]_0)$$

Substitution for c in equation (B.7) then gives k_{-2} and hence $k_2 = (1-c)k_{-2}$.

The results are summarised in Table (B.2). It can be seen that experiments 8(a), 8(b) and 9(a) give the same value of k_2 (though experiment 9(b) appears to be anomalous). The k_{-2} calculated from experiments on solutions of RCl differs by about 40% from the value obtained with RBr as the substrate, possibly because of the neglect of terms in [ROH] (see above) which could have a more serious effect on results obtained from experiments 9(a), 9(b) which involve up to about 7% hydrolysis over the range examined (see Appendix J). On the other hand, these discrepancies are not very serious since A and B calculated from equations (B.7) and (B.8) are not very sensitive to the values chosen for k_2 and k_{-2}. This is illustrated in Table (B.3) where it can be seen that A and B can be calculated to agree within about 10% with the observations (for experiments 8(a), 8(b) and 9(a)) by taking $10^5 k_2 = 1$ mole^{-1} l.sec^{-1} and $10^4 k_{-2} = 1{\cdot}5$ mole^{-1} l.sec^{-1}; the effect of small changes in k_2 and k_{-2} on the calculated values of A and B are also shown.

TABLE (B.1)

Maximum values of [ROH] terms in equation B.4

Experiment	8(a)	9(a)
$[ROH]_{max}$	0·00280	0·00316
a	0·03849	0·002247
$([Cl^-]_0 + [RCl]_0)[ROH]_{max}$	0·00055	0·000146
$b' + c([Br^-]_0 - [RCl]_0)^*$	-0·3924	-0·09485
$c[ROH]_{max}^*$	0·0028	0·00316

* Calculated assuming c = 1

TABLE (B.2)†

Kinetic parameters for halide exchange in 4-nitrobenzyl halides in 70% aqueous acetone at 20·41°C

Experiment	8(a)	8(b)	9(a)	9(b)
$[RCl]_0$ (mole l^{-1})	0·1962	0·1991	-	-
$[RBr]_0$ (mole l^{-1})	-	-	0·04871	0·04792
$[Br^-]_0$ (mole l^{-1})	0·04962	0·05051	-	-
$[Cl^-]_0$ (mole l^{-1})	-	-	0·04614	0·05035
$10^4 A_{OBS}$ (mole l^{-1})	-3·41	-3·21	8·98	7·23
$10^9 B_{OBS}$ (mole $l^{-1}sec^{-1}$)	2·664	2·681	1·589	1·558
$10^5 k_2$ (l.mole^{-1}sec^{-1})	0·933	1·008	0·972	1·58
$10^4 k_{-2}$ (l.mole^{-1}sec^{-1})	1·78	1·96	1·310	1·362

† $10^9 k_1 = 2·1$ sec^{-1}; $10^7 k_3 = 1·31$ sec^{-1}

TABLE (B.3)†

Comparison of calculated and observed kinetic parameters for halide exchange in 4-nitrobenzyl halides in 70% aqueous acetone at 20·41°C

Experiment		8(a)	8(b)	9(a)	9(b)
10^4A (mole l^{-1})	OBS	-3·41	-3·21	8·98	7·23
	CALC	-3·86	-3·86	8·15	8·17
10^9B (mole $l^{-1}sec^{-1}$)	OBS	2·664	2·684	1·589	1·558
	CALC	2·864	2·917	1·534	1·250
$10^4\Delta A_{CALC}$					
	($10^5\Delta k_2 = 0·05$)	0·05	0·05	-0·23	-0·17
	($10^5\Delta k_{-2} = 0·1$)	0·22	0·21	-0·36	-0·36
$10^9\Delta B_{CALC}$					
	($10^5\Delta k_2 = 0·05$)	0·044	0·045	0·025	0·026
	($10^4\Delta k_{-2} = 0·1$)	-0·073	-0·070	-0·034	-0·036

† Calculations based on,

$$10^9k_1 = 2·1 \ sec^{-1}$$

$$10^7k_3 = 1·31 \ sec^{-1}$$

$$10^5k_2 = 1·0 \ mole^{-1} \ l.sec^{-1}$$

$$10^4k_{-2} = 1·5 \ mole^{-1} \ l.sec^{-1}$$

APPENDIX C

The rate of decomposition of 4-nitrobenzyl 4'-toluenesulphonate in aqueous acetone in the presence of chloride ions

The decomposition of 4-nitrobenzyl 4'-toluenesulphonate (ROT_s) in aqueous acetone containing chloride ions can be represented by the processes,

$$ROT_s + Cl^- \xrightarrow{2} RCl + OT_s^-$$

$$ROT_s \xrightarrow{1} ROH + H^+$$

The approximately 600-fold difference between the rates of hydrolysis of RCl and ROT_s (see Table 2.4) allows the determination of acidity after the complete decomposition of ROT_s but before any significant hydrolysis of RCl has occurred.* Using the subscript x to indicate this stage, the stoichiometry of the processes involved requires that,

$$[Cl^-]_x = [Cl^-]_o + [H^+]_x - [ROT_s]_o$$

so that Cl^-_x can be obtained from a knowledge of the initial concentrations and the acidity at time t_x.

From the rate equations for the two processes,

$$-\frac{1}{[Cl^-]} \cdot \frac{d[Cl^-]}{dt} = \frac{k_2}{k_1}\frac{d[H^+]}{dt}$$

and hence on integration between t = 0 and t = t_x,

$$\ln\frac{[Cl^-]_o}{[Cl^-]_x} = \frac{k_2}{k_1}([H^+]_x - [H^+]_o)$$

---

* This is readily verified from the times of these determinations (see Experiments 18 and 21) and the rate coefficients for the hydrolysis of RCl (see Table 2.4).

Thus k_2 was obtained from a knowledge of the initial concentrations, $[H^+]_x$ and k_1; k_1 being obtained from independent experiments (e.g. Experiments 16 and 19).

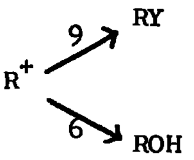
APPENDIX D

Calculation of intervention constant (β) for the 4-methoxybenzhydryl cation

Intervention constants for the competition between anions and water for the 4-methoxybenzhydryl carbonium ion (R^+) were obtained from the acidities after the complete decomposition of the substrate (RX; $X^- = Cl^-$, $OPNB^-$)* in 85% aqueous acetone containing anions [$Y^- = N_3^-$ or $OPNB^-$ (for RX = RCl only)]; the large differences between the reactivities of RX and RY ensured that at this time ($t = t_x$) no significant hydrolysis of RY had occurred.

Assuming that all reactions occur via the carbonium ion (S_N1 reaction),

$$RX \underset{-3}{\overset{1}{\rightleftharpoons}} R^+ + X^-$$



the rate equations for the disappearance of RX and the formation of ROH give, on combination,

$$\frac{d[H^+]}{dt} = \frac{d[ROH]}{dt} = \frac{-1}{1+\beta[Y^-]} \frac{d[RX]}{dt} \qquad (D.1)$$

where the intervention constant, $\beta = k_9/k_6$. Both anions (Y^-) are such that their conjugate acids (HY) are virtually undissociated in aqueous acetone, so that,

$$[Y^-] = [Y^-]_i - [RX]_i + [RX]^{\dagger}$$

Substituion in equation (D.1) and integration between the limits t = 0 and $t = t_x$ then gives,

$$[ROH]_x = \frac{1}{\beta} \ln \frac{1 + \beta[Y^-]_i}{1 + \beta([Y^-]_i - [RX]_i)} \quad \dagger$$

and hence the values of β required by this identity.

---

* $OPNB^- = 4\text{-}NO_2C_6H_4CO_2^-$

† The subscript 'i' refers to concentrations at t = 0

APPENDIX E

Derivation Of The Rate Equations For The S_N And Ion-Pair Schemes

E.1 Introduction

The overall decomposition of the substrate (RX) was followed via the development of the anions, X^-, so that the fate of the product (RY) of reaction with added anions (Y^-) has no effect on the experimental rate coefficient,

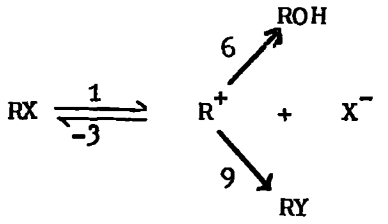
$$k_{RX}^{inst} = \frac{-1}{[RX]} \cdot \frac{d[RX]}{dt}$$

When RY undergoes no further reactions, the study of the production of acidity gives the rate coefficient for hydrolysis,

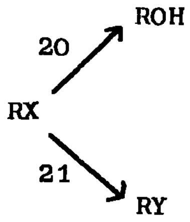
$$k_{ROH}^{inst} = \frac{1}{[RX]} \cdot \frac{d[ROH]}{dt}$$

E.2 Added Non Common Anions

E.2.1 S_N Mechanisms



(S_N1)



(S_N2)

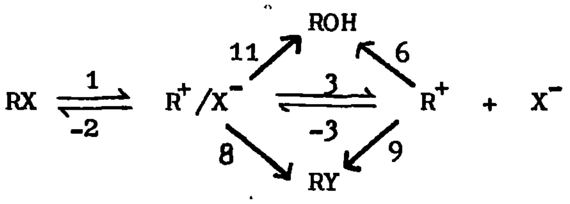
The stationary state approximation for the carbonium ion (R^+ then gives,

$$k_{RX} = k_1 \cdot \frac{1 + \beta[Y^-]}{1 + \alpha[X^-] + \beta[Y^-]} + k_{20} + k_{21}[Y^-] \qquad (E.1)$$

$$k_{ROH} = k_1 \cdot \frac{1}{1 + \alpha[X^-] + \beta[Y^-]} + k_{20} \qquad (E.2)$$

where $\alpha = k_{-3}/k_6$ and $\beta = k_9/k_6$

E.2.2 Reaction via R^+ and one ion-pair



Application of the stationary state approximation to the reactive intermediates gives,

$$k_{RX}^{inst} = k_1 \cdot \frac{x+\mu}{1+x+\mu} \cdot \frac{1+\beta[Y^-]}{1+\alpha[X^-]+\beta[Y^-]} \cdot \frac{A_{IP1}}{B_{IP1}} \qquad (E.3)$$

$$k_{ROH}^{inst} = k_1 \cdot \frac{x+\mu}{1+x+\mu} \cdot \frac{1}{1+\alpha[X^-]+\beta[Y^-]} \cdot \frac{A'_{IP1}}{B_{IP1}} \qquad (E.4)$$

where

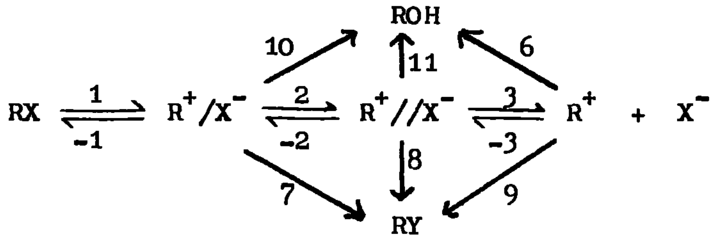
$$A_{IP1} = 1 + \frac{\epsilon[Y^-]}{x+\mu}\left(1 + \frac{\alpha[X^-]}{1+\beta[Y^-]}\right) + \frac{\mu}{x+\mu} \cdot \frac{\alpha[X^-]}{1+\beta[Y^-]}$$

$$B_{IP1} = 1 + \frac{\epsilon[Y^-]}{1+x+\mu} - \frac{x}{1+x+\mu} \cdot \frac{\alpha[X^-]}{1+\alpha[X^-]+\beta[Y^-]}$$

$$A'_{IP1} = 1 + \frac{\mu}{x+\mu}(\alpha[Y^-] + \beta[Y^-])$$

with $x = k_3/k_{-2}$, $\mu = k_{11}/k_{-2}$, $\epsilon = k_8/k_{-2}$

E.2.3 Reaction via R^+ and two ion-pairs



Application of the stationary state approximation to R^+/X^-, $R^+//X^-$ and R^+ gives,

$$k^{inst}_{RX} = k_1 \frac{xy+\lambda(1+x+\mu)+\mu y}{1+x+xy+\lambda(1+x+\mu)+\mu(1+y)} \cdot \frac{A_{IP2}}{B_{IP2}} \qquad (E.5)$$

$$k^{inst}_{ROH} = k_1 \frac{xy+\lambda(1+x+\mu)+\mu y}{1+x+xy+\lambda(1+x+\mu)+\mu(1+y)} \cdot \frac{1}{1+\beta[Y^-]} \cdot \frac{A'_{IP2}}{B_{IP2}} \qquad (E.6)$$

where

$$A_{IP2} = 1 + \frac{\delta[Y^-](1+x+\mu+\epsilon[Y^-])+\epsilon[Y^-](y+\lambda)}{xy+\lambda(1+x+\mu)+\mu y}$$

$$+ \frac{\alpha[X^-]}{1+\beta[Y^-]} \left\{\frac{\lambda(1+\mu)+\mu y+\delta[Y^-](1+\mu+\epsilon[Y^-])+\epsilon[Y^-](y+\lambda)}{xy+\lambda(1+x+\mu)+\mu y}\right\}$$

$$B_{IP2} = 1 + \frac{\delta[Y^-](1+x+\mu+\epsilon[Y^-])+\epsilon[Y^-](1+y+\lambda)}{1+x+xy+\lambda(1+x+\mu)+\mu(1+y)}$$

$$+ \frac{\alpha[X^-]}{1+\beta[Y^-]} \left\{\frac{1+\lambda(1+\mu)+\mu(1+y)+\delta[Y^-](1+\mu+\epsilon[Y^-])+\epsilon[Y^-](1+y+\lambda)}{1+x+xy+\lambda(1+x+\mu)+\mu(1+y)}\right\}$$

$$A'_{IP2} = 1 + \frac{\alpha[X^-]\{\mu y+\lambda(1+\mu+\epsilon[Y^-])\}+\lambda\epsilon[Y^-](1+\beta[Y^-])+\beta[Y^-]\{\mu y+\lambda(1+x+\mu)}{xy+\lambda(1+x+\mu)+\mu y}$$

with $y = k_2/k_{-1}$, $\lambda = k_{10}/k_{-1}$, $\delta = k_7/k_{-1}$

E.2.4 4-Nitrobenzyl chloride and 4'-toluenesulphonate

All the available evidence suggests that no part of the hydrolyses of 4-nitrobenzyl chloride and 4'-toluenesulphonate proceed via the carbonium ion R^+ and it seems reasonable to assume that this also applies to reaction with more powerful nucleophiles, Y^-. Equations (E.1) to (E.6) can therefore be greatly simplified since;

(i) $k_3 = 0$; i.e. $x = 0$

(ii) $\alpha = \beta = 0$ since no carbonium ions are involved in the reaction scheme.

Hence,

$$A'_{IP1} = 1$$

and

$$A'_{IP2} = 1 + \frac{\lambda\epsilon[Y^-]}{\lambda(1+\mu)+\mu y} \simeq 1$$

since $\epsilon[Y^-] << (1+\mu)$ (see Section 5.3).

The resulting modified forms of equations (E.1) to (E.6) can be written as equations (5.1) and (5.2) with the values of Q and R given in Table (5.1).

E.2.5 4-Methoxybenzyl and benzhydryl chlorides

It has already been pointed out that the hydrolyses of 4-methoxybenzyl and benzhydryl chlorides occur entirely (or almost entirely) via the fully developed carbonium ion, R^+ (see section 4.1). As a result k_{20}, λ and μ are all zero so that $A'_{IP1} = A'_{IP2} = 1$. Equations (E.1) and (E.2) can now be expressed in the form of equations (5.1) and (5.2) with the values of Q and R given in Table (5.1).

In equations (E.3) to (E.6),

$$B_{IP1} = 1 + \frac{\epsilon[Y^-]}{1+x} - \frac{x}{1+x}\,\frac{\alpha[X^-]}{1+\alpha[X^-]+\beta[Y^-]}$$

$$A_{IP2} = 1 + \frac{\delta[Y^-](1+x+\epsilon[Y^-])+\epsilon[Y^-]y}{xy}\left(1 + \frac{\alpha[X^-]}{1+\beta[Y^-]}\right) - \frac{x\delta[Y^-]}{xy}\,\frac{\alpha[X^-]}{1+\beta[Y^-]}$$

$$B_{IP2} = \left\{1 + \frac{\delta[Y^-](1+x+\epsilon[Y^-])+\epsilon[Y^-](1+y)}{1+x+xy}\right\}\left(1 + \frac{\alpha[X^-]}{1+\beta[Y^-]}\right)$$

$$- \frac{x+xy+x\delta[Y^-]}{1+x+xy} \cdot \frac{\alpha[X^-]}{1+\beta[Y^-]}$$

It is shown below that the negative terms can be neglected without error so that equations (E.3) to (E.6) can be expressed in the form of equations (5.1) and (5.2) with the values of Q and R given in Table (5.1).

The neglect of the negative terms requires that,

(i) $\frac{x}{1+x} \cdot \alpha[X^-] << 1$ in B_{IP1}

(ii) $x.\alpha[X^-] << 1 + \alpha[X^-]$ in A_{IP2} and B_{IP2}

(iii) $\frac{x+xy}{1+x+xy} \cdot \alpha[X^-] << 1$ in B_{IP2}

where $[X^-]$ is taken as the 'effective' concentration of these anions; $\left(\frac{1}{t}\int_{o}^{t} [X^-]dt\right)_m \simeq 0{\cdot}007\underline{M}$ for initially $0{\cdot}02\underline{M}$ substrates. The upper limit for x and x+xy can be obtained from the figures in Table F.1) and hence $\alpha_{MAX} = \alpha_{OBS}(1+x)$ for I.P.1 or $\alpha_{OBS}(1+x+xy)$ for I.P.2. The relevant figures given below show that in all cases the required inequalities hold true for the reactions of 4-methoxybenzyl chloride,

		70%	85%
I.P.1 :	x_{MAX}	0·077	0·0028
	α_{MAX}	4·31	5·76
	$\frac{x}{1+x} \cdot [X^-]$	$2{\cdot}1 \times 10^{-3}$	$1{\cdot}1 \times 10^{-4}$
I.P.2 :	$x_{MAX} = (x+xy)_{MAX}$	0·261	0·0315
	α_{MAX}	5·04	5·93
	$x.\alpha[X^-]$	$9{\cdot}2 \times 10^{-3}$	$1{\cdot}31 \times 10^{-3}$
	$\frac{x+xy}{1+x+xy} \cdot \alpha[X^-]$	$7{\cdot}3 \times 10^{-3}$	$1{\cdot}26 \times 10^{-3}$

E.3 Added Common Ions

The effect of common ions (X^-) on the decomposition of the substrate (RX) was studied by following the hydrolysis and the loss of radioactivity from the labelled substrate (RX^*); in all experiments, X = Cl and $X^* = {}^{36}Cl$.

The three possible reaction schemes can be represented as follows for substrates undergoing entirely S_N1 hydrolysis:

$$RX \underset{-3}{\overset{1}{\rightleftharpoons}} R^+ + X^-$$

$$R^+ \xrightarrow{6} ROH \qquad (S_N1)$$

$$RX^* \underset{-3}{\overset{1}{\rightleftharpoons}} R^+ + X^{*-} \qquad (S_N)$$

$$RX^* + X^- \underset{21}{\overset{21}{\rightleftharpoons}} RX + X^{*-} \qquad (S_N2)$$

$$\begin{tikzcd}
RX \arrow[r, shift left, "1"] & R^+/X^- \arrow[l, shift left, "-2"] \arrow[dd, shift left, "8"] \arrow[dr, shift left, "3"] & & \\
& & R^+ \arrow[ul, shift left, "-3"] \arrow[dl, shift left, "-3"] \arrow[r, "6"] & ROH \\
RX^* \arrow[r, shift left, "1"] & R^+/X^{*-} \arrow[l, shift left, "-2"] \arrow[uu, shift left, "8"] \arrow[ur, shift left, "3"] & &
\end{tikzcd}$$

(I.P.1)

$$\begin{tikzcd}
RX \arrow[r, shift left, "1"] & R^+/X^- \arrow[l, shift left, "-1"] \arrow[r, shift left, "2"] \arrow[dd, shift left, "7"] & R^+//X^- \arrow[l, shift left, "-2"] \arrow[dd, shift left, "8"] \arrow[dr, shift left, "3"] & & \\
& & & R^+ \arrow[ul, shift left, "-3"] \arrow[dl, shift left, "-3"] \arrow[r, "6"] & ROH \\
RX^* \arrow[r, shift left, "1"] & R^+/X^{*-} \arrow[l, shift left, "-1"] \arrow[r, shift left, "2"] \arrow[uu, shift left, "7"] & R^+//X^{*-} \arrow[l, shift left, "-2"] \arrow[uu, shift left, "8"] \arrow[ur, shift left, "3"] & &
\end{tikzcd}$$

(I.P.2)

For these systems, the rate of destruction of the substrate is represented by the rate of destruction of RX^*, so that,

$$k_{RX}^{inst} = \frac{-1}{[RX^*]} \cdot \frac{d[RX^*]}{dt}$$

Expressions for k_{ROH}^{inst} are readily obtained from equations E.1 to E.6 with $[Y^-] = 0$, noting that $\lambda, \mu = 0$ for the present substrates. Application of the stationary state approximation to the reactive intermediates then gives the general rate equation,

$$k_{RX}^{inst} = k_{ROH}^{inst} \left\{ 1 + \left([X^-] + \frac{[RX]}{[R\overset{*}{X}]}[\overset{*}{X}^-]\right)(\alpha_{OBS} - T)\right\}$$

where

$$T = k_{21}/k_{ROH}^{inst} \qquad (S_N)$$

$$\doteq \frac{Q\left\{1 + \alpha([X^-] + [\overset{*}{X}^-])\right\}}{(1+x)\left\{1 + R([X^-] + [\overset{*}{X}^-])\right\}} \qquad (I.P.1)$$

$$= \frac{Q\left\{1 + \alpha([X^-] + [\overset{*}{X}^-])\right\}}{(1+x+xy)\left\{1 + R([X^-] + [\overset{*}{X}^-])\right\}} \qquad (I.P.2)$$

where Q and R are the quantities defined in Table (5.1) except that they now contain no term $\delta\epsilon[Y^-]$.

Making the reasonable approximations

$$[\overset{*}{X}^-] << [X^-]$$

$$R[X^-] << 1 \qquad \text{(see section 5.4.3)}$$

$$1+x+xy \simeq 1 + x \simeq 1 \qquad \text{(see Appendix F)}$$

integration then gives equation (5.18).

E.4 Electrolyte Effects on Solvolyses Occurring Entirely Via a Carbonium Ion

Consider the following reaction steps,

$$RX \underset{-1}{\overset{1}{\rightleftharpoons}} R^+/X^- \underset{-2}{\overset{2}{\rightleftharpoons}} R^+//X^- \underset{-3}{\overset{3}{\rightleftharpoons}} R^+ + X^-$$

$$R^+ + N_3^- \xrightarrow{9} RN_3$$

$$R^+ \xrightarrow{6} ROH$$

$$R^+ + Y^- \xrightarrow{10} RY \xrightarrow{11} ROH \qquad (Y^- \neq N_3^-)$$

Steps 10 and 11 are equivalent to considering,

$$R^+ \xrightarrow{11} ROH$$

Application of the steady state approximation to the reactive intermediate gives,

$$k_{RX} = \frac{k_1 \cdot xy}{1+x+xy + \dfrac{\alpha[X^-]}{1+\beta[N_3^-]+k_{11}/k_6}}$$

and now $k_{11}/k_6 = \beta'[Y^-]$ where β' is the intervention constant of $Y^- \ddagger N_3^-$. Since azide ions are never present with any ion other than Cl^- then in general,

$$k_{RX} = \frac{k_1 xy}{1+x+xy} \cdot \frac{1}{1 + \dfrac{\alpha[X^-]}{1+\beta[Y^-]} \cdot \dfrac{1}{1+x+xy}}$$

for any Y^- presently under consideration. This gives the result $\alpha_{OBS} = \alpha/(1+x+xy)$ needed earlier. Hence,

$$k_{RX} = \frac{k^0_{RX}(1+\Sigma b_{MY}[MY])}{1 + \dfrac{\alpha_{OBS}[X^-]}{1+\beta[Y^-]}}$$

where b_{MY} is the electrolyte parameter for the salt MY and k^0_{RX}, the hydrolysis rate coefficient at zero ionic strength is given by

$$k^0_{RX} = \frac{k^0_1 xy}{1+x+xy}$$

In practice in estimating b_{MY}, X^- is present in only small amounts and therefore $\alpha[X^-] << 1$. Hence approximate values of $\beta < \beta_{N_3^-}$ will suffice. For calculations of the electrolyte parameters, k_{RX} and $(k_{RX})_0$ are compared, and

$$(k_{RX})_0 = \frac{k^0_{RX}(1+b_{HCl}[HCl]_0)}{1+\alpha_{OBS}[HCl]_0}$$

where subscript '0' refers to solvolysis in the pure solvent (no added salts. For runs over the same sort of concentration range,

$$1 + \alpha_{OBS}[HCl]_0 \simeq 1 + \frac{\alpha_{OBS}[X^-]}{1+\beta[Y^-]}$$

on the square root approximation (see Appendix A) provided no chloride ions are added. In the presence of added chloride ions,

$$\frac{k_{ROH}}{(k_{ROH})_0} = \frac{1+b_{HCl}[HCl]+b_{NaCl}[NaCl]}{1+b_{HCl}[HCl]_0} \cdot \frac{1+\alpha_{OBS}[HCl]_0}{1+\alpha_{OBS}[Cl^-]}$$

and therefore b_{HCl} may be calculated if α is known from experiments with added HCl and then b_{NaCl} from added NaCl runs. The electrolyte parameters for other salts can then be calculated from,

$$\frac{k_{RX}}{(k_{RX})_0} = \frac{1+b_{HCl}[HCl]+b_{MY}[MY]}{1+b_{HCl}[HCl]_0} \cdot \frac{1+\alpha[HCl]_0}{1+\alpha[HCl]}$$

provided no reaction occurs with the substrate or intermediate ion-pairs and it is realised that in the presence of azide ions, NaCl will be produced instead of HCl.

APPENDIX F

Maxima For x And x+xy In Reaction Via Ion-Pair Schemes

Two entirely different criteria limit the values of x and x+xy which can be envisaged for the reactions of 4-methoxybenzyl chloride via schemes I.P.1 or I.P.2. Clearly, the lower of the two limits thus obtained represents that maximum value which can be considered.

Studies of the hydrolysis in the presence of N_3^- ions give an upper limit for the parameter R and values of β appropriate to this range of allowed R's (see section 5.4.2). A knowledge of β allows the calculation of an upper limit for α and hence for x and x+xy from,

$$\begin{aligned} \alpha_{MAX} &= \frac{\beta}{1\cdot5} = \alpha_{OBS}[1 + x_{MAX}] && \text{(I.P.1)} \\ &= \alpha_{OBS}[1 + (x+xy)_{MAX}] && \text{(I.P.2)} \end{aligned} \qquad \text{(F.1)}$$

Strictly, the upper limits given by equation (F.1) refer to the ionic strength of the experiment but as β appears to be constant over the range of ionic strengths studied (see section 5.4.2) no error should be caused by assuming that these values also apply at zero ionic strength.

Alternatively, the expressions for Q and R (see Table 5.1) show that,

$$\frac{R}{Q^o} = \frac{x}{1+x} \qquad \text{(I.P.1)} \qquad \text{(F.2)}$$

$$= \frac{xy}{1+x+xy}\left[1 + \frac{\epsilon}{\epsilon y+\delta(1+x)}\right] \qquad \text{(I.P.2)} \qquad \text{(F.3)}$$

A value for x, appropriate to the chosen R, can be obtained directly from equation (F.2) but a more complex situation occurs in reaction by scheme I.P.2. However, there is no point in considering this scheme as opposed to scheme I.P.1, unless attack by Y^- ions on one of the ion-pairs occurs less than (say)

10 times as frequently as on the other, formally represented by writing,

$$F = \frac{\delta(1+x)}{\epsilon y} \qquad (0\cdot1 \leqslant F \leqslant 10) \qquad (F.4)$$

as an additional requirement for scheme I.P.2. Substitution from equation (F.4) in equation (F.3) and rearrangement then gives,

$$x+xy = \frac{1}{\frac{Q^o}{R} - 1 - \frac{Q^o}{R} \cdot \frac{F}{1+F} \cdot \frac{1}{1+y}} \qquad (F.5)$$

which shows that the upper limit of (x+xy) arises from maximum F (= 10) and minimum y ($\simeq$ 0).

Upper limits for x and x+xy obtained from equation (F.1) are compared with those from equations (F.2) and (F.5), for the range of R values consistent with other observations (see sections 5.4.1, 5.4.2), in Table (F.1). It can be seen that these maximum values are never large and it must be stressed again that the smaller of the maxima obtained by the two methods are the values to be considered in any calculations.

TABLE (F.1)

Upper limits for x and x+xy in the decomposition of 4-methoxybenzyl chloride

				I.P.1		I.P.2	
% Acetone	R	Q^o	α_{MAX}	x_{MAX} ‡	x §	$(x+xy)_{MAX}$ ‡	$(x+xy)_{MAX}$ ϕ
70%*	0	13·05	5·33	0·332	0	0·332	0
	0·1	13·15	5·27	0·317	0·008	0·317	0·091
	0·25	13·30	5·13	0·282	0·019	0·282	0·261
	0·5	13·55	4·90	0·225	0·038	0·225	0·683
	1·0	14·05	4·50	0·102	0·077	0·102	3·61
	1·5	14·55	4·00	0	0·115	0	-
85%†	0	177	6·71	0·167	0	0·167	0
	0·5	180	6·23	0·084	0·003	0·084	0·0315
	1·0	183	5·75	0	0·0055	0	0·0640

* α_{OBS} = 4; § From equation (F.2); † α_{OBS} = 5·75; ϕ From Equation (F.5)

‡ From α_{MAX}, equation (F.1)

APPENDIX G

Equation (5.12) For Systems At Constant Ionic Strength

Systems in which the ionic strength is kept constant by the addition of sodium perchlorate require a slight modification to equations (5.11) and (5.12). In these expressions the term $(1 + b_{NaY}[Y^-]_i)$ in k_b and b, reflect the effect of the electrolyte present initially on the first ionisation step; i.e. on k_1. When sodium perchlorate is also present this term becomes $(1 + b_{NaClO_4}[ClO_4^-] + b_{NaY}[Y^-]_i)$. It is assumed that

$$b_{NaClO_4} = b_{NaY} \qquad \text{for } Y^- = N_3^-$$

so that for the reactions at ionic strength 0·2,

$$k_b = (k_I)_{0\cdot 2\underline{M}\ NaClO_4}$$

and

$$b = \frac{(k_I)_0(b_{NaY} - b_{NaX})}{(k_I)_{0\cdot 2\underline{M}\ NaClO_4}}$$

APPENDIX H

Product Of Reaction Of 4-Nitrobenzyl Chloride With Azide Ions In Aqueous Acetone

It has been demonstrated[79] that hydroxide ions in aqueous acetone or dioxane promote the formation of 4,4'-dinitrostilbene from 4-nitrobenzyl chloride by the removal of the elements of HCl. Since azide ions are also basic in aqueous acetone it was felt necessary to establish to what extent, if any, the stilbene could be detected in the reaction products.

A stock solution of 4,4'-dinitrostilbene in aqueous acetone was used as a standard. The acetone was removed from a known sample of this solution at reduced pressure and extracted with 5 x 10 ml. portions of chloroform. The chloroform extracts were thoroughly washed with water, sodium bisulphite solution and finally water. After drying over alumina, the filtered solution was made up to 100 ml. with chloroform. The 4,4'-dinitrostilbene was estimated from its absorbance in the u.v. (330-345 mμ) as a rather flat peak.

A similar extraction was performed on the products of a reaction in 70% aqueous acetone between 4-nitrobenzyl chloride (0·02M) and sodium azide (0·1M). In the region of 325-350 mμ, there was observed a shoulder on the side of a much larger peak at 268 mμ. The peak at 268 mμ was presumed to be due to the organic azide.

Comparison of the absorbancies of both samples in the 325 - 350 mμ region indicates that at most 5% of the reaction produces the stilbene product. Indeed, the shoulder produced in the u.v. spectrum was masked by the large peak at 268 mμ such that the amount of stilbene produced, if any, is probably much less than 5%.

APPENDIX J

Details Of Individual Kinetic Experiments

The following pages list details of the individual kinetic runs. Times of sampling (t) are expressed in seconds and titres in millilitres. The rate coefficients are integrated first-order (k_I) or second-order (k_{II}) observed values, in units of sec^{-1} and $mole^{-1}\ l.sec^{-1}$ respectively, from the relationships,

$$K_I = \frac{1}{t} \ln \frac{[A]_0}{[A]}$$

and

$$K_{II} = \frac{1}{t([A]_0-[B]_0)} \ln \frac{[A].[B]_0}{[B].[A]_0}$$

for reaction between species A and B. Also quoted are the mean values of k_I and k_{II} together with the standard error of the mean (expressed as an error).

EXPERIMENT 1

4-Nitrobenzyl chloride in 70% acetone I at 20•41°C

Added NaN_3 0•03082M

5 Ml. titrated with 0•01001M $AgNO_3$

Time (secs.)	Titre	10^4 k_{II}
0	0•03	-
9700	0•70	2•521
21300	1•41	2•528
31785	1•96	2•503
45980	2•60	2•468
59295	3•13	2•453
83290	4•00	2•494
108240	4•68	2•473
129600	5•18	2•470
171870	5•99	2•483
200400	6•41	2•477
257090	7•09	2•495
282660	7•39	2•560
344280	7•79	2•497
∞	9•48	-

10^4 k_{II} = 2•494 ± 0•0080 (13 readings)

Duplicate Experiment

Added NaN_3 0•02982M

10^4 k'_{II} = 2•421 ± 0•0105 (11 readings)

EXPERIMENT 2

4-Nitrobenzyl chloride in 70% acetone I at 20•41°C

Added NaN_3 0•04814M

5 Ml. titrated with 0•01001M $AgNO_3$

Time (secs.)	Titre	$10^4\ k_{II}$
0	0•09	-
6320	0•75	2•343
14610	1•59	2•461
14765	2•40	2•397
39965	3•41	2•347
54095	4•19	2•323
77700	5•22	2•286
93600	5•80	2•283
126500	6•80	2•321
163610	7•58	2•330
178890	7•85	2•348
251555	8•63	2•292
∞	9•85	-

$10^4\ k_{II} = 2{\cdot}339 \pm 0{\cdot}0157$ (11 readings)

Duplicate Experiment

Added NaN_3 0•04800M

$10^4\ k'_{II} = 2{\cdot}344 \pm 0{\cdot}0171$ (10 readings)

EXPERIMENT 3

4-Nitrobenzyl chloride in 70% acetone I at 20•41°C

Added NaN_3 0•07349M

5 Ml. titrated with 0•01001M $AgNO_3$

Time (secs.)	Titre	10^4 k_{II}
0	0•05	-
7265	1•42	2•352
13825	2•43	2•290
21340	3•43	2•258
30860	4•56	2•271
37290	5•19	2•258
52870	6•50	2•259
82060	8•19	2•238
93080	8•70	2•254
104425	9•19	2•296
115560	9•48	2•255
135000	10•05	2•301
∞	11•89	-

10^4 k_{II} = 2•275 ± 0•0097 (11 readings)

Duplicate Experiment

Added NaN_3 0•07315M

10^4 k'_{II} = 2•197 ± 0•0190

EXPERIMENT 4

4-Nitrobenzyl chloride in 70% acetone I at 20•41°C

Added NaN_3 0•09369M

5 Ml. titrated with 0•01001M $AgNO_3$

Time (secs.)	Titre	10^4 k_{II}
0	0•10	-
5660	1•06	2•129
9065	1•61	2•177
15900	2•53	2•149
23800	3•50	2•189
27375	3•85	2•172
45790	5•45	2•219
87095	7•30	2•133
96090	7•57	2•137
113145	7•94	2•106
139965	8•29	2•003
∞	9•20	-

10^4 k_{II} = 2•141 ± 0•0191 (10 readings)

Duplicate Experiment

Added NaN_3 0•1014

10^4 k'_{II} = 2•125 ± 0•0202 (10 readings)

EXPERIMENT 5

4-Nitrobenzyl chloride in 70% acetone II at 20·41°C

Added $NaNO_3$ 0·06605M

5 Ml. titrated with 0·01003M $AgNO_3$

Time (secs.)	Titre	$10^9\ k_I$
0	0·00	-
670260	0·26	3·924
947160	0·37	3·952
1100640	0·41	3·768
1271820	0·48	3·818
1531800	0·60	3·963
1704420	0·65	3·858
1897560	0·71	3·785
2163960	0·81	3·787
2334480	0·89	3·857
2508180	0·96	3·872
2741520	1·00	3·690
2913720	1·12	3·889
∞	98·85	-

$10^9\ k_I = 3·847 \pm 0·0235$ (12 readings)

Duplicate Experiment

Added $NaNO_3$ 0·04914M

$10^9\ k_I = 3·352 \pm 0·150$ (4 readings)

70% Acetone I

EXPERIMENT 6

4-Nitrobenzyl chloride in 70% acetone II at 20•41°C

No added salt

5 Ml. titrated with 0•01003M $AgNO_3$

Time (secs.)	Titre	10^9 k_I
0	0•00	-
336310	0•06	1•804
677090	0•11	1•641
954430	0•20	2•118
1158200	0•24	2•096
1279400	0•27	2•134
1539000	0•29	1•906
1711700	0•35	2•069
1901800	0•40	2•129
2171600	0•49	2•285
2341200	0•52	2•249
2516700	0•53	2•133
2820900	0•61	2•191
2921300	0•71	2•463
∞	99•01	-

10^9 k_I = 2•094 ± 0•0587 (13 readings)

Duplicate Experiment

10^9 k_I = 2•106 ± 0•026 (5 readings)

70% Acetone I

EXPERIMENT 7

4-Nitrobenzyl bromide in 70% acetone II at 20·41°C

No added salt

5 Ml. titrated with 0·01001M NaOH

Time (secs.)	Titre	10^7 k_I
0	0·02	-
167760	0·55	1·327
255600	0·81	1·306
344040	1·09	1·322
444360	1·39	1·319
514740	1·58	1·302
600300	1·89	1·347
685800	2·10	1·318
773100	2·29	1·281
858000	2·62	1·332
964440	2·89	1·317
1037460	3·15	1·343
∞	24·09	-

10^7 k_I = 1·319 ± 0·0057 (11 readings)

Duplicate Experiment

10^7 k_I' = 1·302 ± 0·0097 (12 readings)

EXPERIMENT 8

4-Nitrobenzyl chloride in 70% acetone II at 20·41°C

Added NaBr 0·04962M

5 Ml. titrated with 0·01000M NaOH

$[RCl]_0$ = 0·1962M

Time (secs.)	Titre	10^4 $([H^+]-[H^+]_0)$ gm ions l^{-1}
0	0·00	-
86160	0·02	0·4
177900	0·10	2·0
252840	0·20	4·0
356220	0·30	6·0
425400	0·40	8·0
511140	0·51	10·2
597240	0·61	12·2
716400	0·79	15·8
794340	0·88	17·6
857640	0·97	19·4
942600	1·11	22·2
1028100	1·22	24·4
1116960	1·31	26·2
1203300	1·41	28·2

'Best straight line' from t = 356220:-

$[H^+]-[H^+]_0 = 2{\cdot}664 \times 10^{-9} \times t - 3{\cdot}41 \times 10^{-4}$ (11 readings)

Duplicate Experiment

Added NaBr 0·05051M

$[RCl]_0$ 0·1991M

'Best straight line' :-

$[H^+]-[H^+]_0 = 2{\cdot}684 \times 10^{-9} \times t - 3{\cdot}21 \times 10^{-4}$ (9 readings)

EXPERIMENT 9

4-Nitrobenzyl bromide in 70% acetone II at 20·41°C

Added NaCl 0·04614M

5 Ml. titrated with 0·01000M NaOH

$[RBr]_0$ = 0·04871M

Time (secs.)	Titre	10^4 $([H^+]-[H^+]_0)$ gm ions l^{-1}
0	0·00	-
70980	0·19	3·8
157380	0·33	6·6
271560	0·50	10·0
363360	0·62	12·4
423120	0·69	13·8
502920	0·78	15·6
595800	0·81	16·2
674340	0·98	19·6
762060	1·06	21·2
866160	1·11	22·2
951480	1·19	23·8
1026900	1·28	25·6
1107900	1·37	27·4
1193160	1·41	28·2
1278540	1·47	29·4
1366080	1·53	30·6
1454940	1·58	31·6

'Best straight line' from t = 674340:-

$$[H^+]-[H^+]_0 = 1{\cdot}589 \times 10^{-9} \times t + 8{\cdot}98 \times 10^{-4}$$

Duplicate Experiment

Added NaCl 0·05035M

$[RBr]_0$ 0·04792M

'Best straight line' :-

$$[H^+]-[H^+]_0 = 1{\cdot}558 \times 10^{-9} \times t + 7{\cdot}23 \times 10^{-4}$$

EXPERIMENT 10

4-Nitrobenzyl chloride in 70% acetone II at 20•41°C

Added p-$NO_2C_6H_4CO_2K$ 0•05274M

5 Ml. titrated with 0•009823M $AgNO_3$

Time (secs.)	Titre	10^8 k_I
0	0•00	-
363840	0•20	5•621
465420	0•28	6•177
599940	0•31	5•314
686220	0•44	6•639
789000	0•49	6•447
1119720	0•59	5•499
1568400	0•82	5•524
1728240	0•87	5•334
1989300	1•03	5•534
∞	9•88	-

10^8 k_I = 5•788 ± 0•166 (9 readings)

Duplicate Experiment

Added p-$NO_2C_6H_4CO_2K$ 0•04877M

10^8 k_I' = 5•542 ± 0•236 (10 readings)

EXPERIMENT 11

4-Nitrobenzyl chloride in 70% acetone III at 59•87°C

Added $NaClO_4$ 0•09969

4•925 Ml. samples titrated with 0•010147M NaOH

Time (secs.)	Titre	10^7 k_I
0	0•01	-
55740	0•95	1•751
143820	2•35	1•702
261900	4•30	1•731
433380	7•06	1•745
488820	7•91	1•742
572220	9•11	1•726
† ∞	96•79	-

10^7 k_I = 1•733 ± 0•0194 (6 readings)

Duplicate Experiment

Added $NaClO_4$ 0•09794 10^7 k_I' = 1•749 ± 0•0218 (6 readings)

† No added salts : 10^7 k_I = 1•811 ± 0•0179 (4 readings)

10^7 k_I' = 1•824 ± 0•0135 (4 readings)

† Infinity values calculated for weighed stock solution of organic chloride. The same solution was used for pairs of runs, with and without added perchlorate.

$$\frac{k_I \text{ (salt)}}{k_I \text{ (no salt)}} = \begin{matrix} 0{\cdot}959 \\ 0{\cdot}956 \end{matrix}$$

10^7 k_I' = 1•824
10^7 k_I = 1•811 no salt

EXPERIMENT 12

4-Nitrobenzyl chloride in 85% acetone II at 20•41°C

No added salts

5 Ml. titrated with 0•010004M NaOH

Time (secs.)	Titre	10^{10} k_I
0	0•00	-
1900200	0•09	4•641
2512500	0•13	5•071
3017400	0•16	5•198
3630300	0•21	5•672
4324800	0•24	5•442
4828500	0•28	5•687
∞	102•1	-

10^{10} k_I = 5•285 ± 0•164 (6 readings)

Duplicate Experiment

10^{10} k_I' = 5•483 ± 0•156 (5 readings)

EXPERIMENT 13

4-Nitrobenzyl chloride in 85% acetone II at 20•41°C

Added NaN_3 0•02924M

5 Ml. titrated with 0•009896M $AgNO_3$

Time (secs.)	Titre	$10^4 k_{II}$
0	0•06	-
8220	0•97	4•099
16200	1•76	4•187
24660	2•43	4•105
36960	3•32	4•158
52320	4•23	4•204
74820	5•17	4•112
93720	5•81	4•092
119760	6•58	4•177
162300	7•40	4•146
202980	7•95	4•116
268620	8•58	4•116
∞	10•10	-

$10^4 k_{II} = 4{\cdot}137 \pm 0{\cdot}0117$ (11 readings)

Duplicate Experiment

Added NaN_3 0•02925M

$10^4 k'_{II} = 4{\cdot}186 \pm 0{\cdot}0163$ (11 readings)

EXPERIMENT 14

4-Nitrobenzyl chloride in 85% acetone II at 20·41°C

Added NaN_3 0·04960M

5 Ml. titrated with 0·009896M $AgNO_3$

Time (secs.)	Titre	10^4 k_{II}
0	0·24	-
4200	1·49	(4·356)
9420	2·63	3·976
17340	4·30	4·094
25140	5·45	3·940
32700	6·47	3·929
43800	7·68	3·897
55920	8·73	3·865
75840	10·09	3·846
97140	11·07	3·793
123240	12·04	3·815
165780	13·11	3·869
205260	13·74	3·908
∞	15·15	-

10^4 k_{II} = 3·903 ± 0·0251 (11 readings)

Duplicate Experiment

Added NaN_3 0·05014M

10^4 k'_{II} = 3·915 ± 0·0181 (11 readings)

EXPERIMENT 15

4-Nitrobenzyl chloride in 85% acetone VIII at 59•87°C

Added $NaClO_4$ 0•10005M

4•925 Ml. samples titrated with 0•010147M NaOH

Time (secs.)	Titre	$10^8 . k_I$
0	0•02	-
143460	0•51	3•537
242640	0•90	3•764
433020	1•59	3•775
488280	1•77	3•735
572580	2•03	3•664
† ∞	96•85	-

$10^8\ k_I = 3{\cdot}695 \pm 0{\cdot}044$ (5 readings)

Duplicate Experiment

Added $NaClO_4$ 0•09835 $10^8\ k_I' = 3{\cdot}781 \pm 0{\cdot}085$ (5 readings)

† No added salts : $10^8\ k_I = 3{\cdot}884 \pm 0{\cdot}093$ (4 readings)

$10^8\ k_I' = 3{\cdot}945 \pm 0{\cdot}127$ (5 readings)

† Infinity values calculated for weighed stock solution of organic chloride. The same solution was used for pairs of runs, with and without added perchlorate.

$$\frac{k_I\ (\text{salt})}{k_I\ (\text{no salt})} = \begin{matrix}0{\cdot}951\\0{\cdot}958\end{matrix}$$

$10^8\ k_I = 3{\cdot}884$

$10^8\ k_I' = 3{\cdot}945$ no salt

EXPERIMENT 16

4-Nitrobenzyl 4'-toluenesulphonate in 70% acetone II at 20•41°C

No added salts

5 Ml. titrated with 0•01033M NaOH

Time (secs.)	Titre	10^6 k_I
0	0•01	-
64770	0•78	1•218
116760	1•37	1•232
179460	2•07	1•264
257460	2•77	1•233
333900	3•41	1•222
427320	4•12	1•215
515340	4•75	1•221
669360	5•52	1•169
785460	6•21	1•202
946860	6•95	1•216
1121340	7•58	1•222
∞	10•16	-

10^6 k_I = 1•219 ± 0•0069 (11 readings)

Duplicate Experiments

10^6 k'_I = 1•215 ± 0•0071 (8 readings)

10^6 k''_I = 1•208 ± 0•0099 (10 readings)

EXPERIMENT 17

4-Nitrobenzyl 4'-toluenesulphonate in 70% acetone II at 20·41°C

Added NaN_3 0·02973M

5 Ml. titrated with 0·009823M $AgNO_3$

Time (secs.)	Titre	10^2 k_{II}
0	13·50	-
825	12·05	1·134
1720	11·00	1·089
2415	10·18	1·182
3025	9·72	1·173
3830	9·23	1·162
4780	8·75	1·165
5875	8·32	1·169
8115	7·72	1·171
12565	7·13	1·141
∞	6·56	-

10^2 k_{II} = 1·154 ± 0·0096

Duplicate Experiment

Added NaN_3 0·03014M

10^2 k'_{II} = 1·127 ± 0·010

EXPERIMENT 18

4-Nitrobenzyl 4'-toluenesulphonate in 70% acetone II at 20·41°C

Added NaCl 0·05246M

5 Ml. titrated with 0·009434 NaOH

$[\text{ROT}_s]_0$ = 0·01836M

Time (secs.)	Titre
0	0·00
942600	1·53
1197000	1·55
1353600	1·56
1528200	1·57

T_∞ = 1·56 ml. ≡ 2·94 x 10^{-3} g. ions H^+/l = $[H^+]_x$

$[\text{ROT}_s]_0$	0·01836
$[\text{Cl}^-]_0$	0·05246
$[H^+]_x$	0·00294
$[\text{Cl}^-]_x$	0·03704
k_2/k_1	1·184 x 10^2 mole^{-1}l. (see Appendix C)

Duplicate Experiment

$[\text{ROT}_s]_0$	0·01892
$[\text{Cl}^-]_0$	0·04842
$[H^+]_x$	0·00328
$[\text{Cl}^-]_x$	0·03278
k_2/k_1	1·189 x 10^2 mole^{-1}l.

EXPERIMENT 19

4-Nitrobenzyl 4'-toluenesulphonate in 85% acetone I at 20•41°C

No added salts

5 Ml. titrated with 0•009434M NaOH

Time (secs.)	Titre	$10^7 k_I$
0	0•00	-
158700	0•54	3•333
371520	1•20	3•273
518880	1•63	3•258
690960	2•12	3•271
849840	2•51	3•222
1100280	3•28	3•412
1380180	3•80	3•263
1717740	4•51	3•276
1968240	5•07	3•359
2149380	5•39	3•360
∞	10•48	-

$10^7 k_I = 3{\cdot}303 \pm 0{\cdot}0188$ (10 readings)

Duplicate Experiment

$10^7 k_I' = 3{\cdot}271 \pm 0{\cdot}141$ (9 readings)

EXPERIMENT 20

4-Nitrobenzyl 4'-toluenesulphonate in 85% acetone I at 20•41°C

Added NaN_3 0•02934M

5 Ml. titrated with 0•009823M $AgNO_3$

Time (secs.)	Titre	$10^2\ k_{II}$
0	13•67	-
544	11•80	1•784
1014	10•62	1•846
1450	9•74	1•862
2002	9•00	1•812
2403	8•56	1•791
2960	7•99	1•819
3675	7•44	1•832
4460	6•99	1•834
5412	6•58	1•834
7084	6•08	1•837
10042	5•59	1•831
∞	5•01	-

$10^2\ k_{II}$ = 1•826 ± 0•0076

Duplicate Experiment

Added NaN_3 0•02934M

$10^2\ k'_{II}$ = 1•787 ± 0•0265

EXPERIMENT 21

4-Nitrobenzyl 4'-toluenesulphonate in 85% acetone I at 20·41°C

Added NaCl 0·05126M

5 Ml. titrated with 0·009434M NaOH

$[\mathrm{ROT_s}]_0$ = 0·02130M

Time (secs.)	Titre
0	0·00
267600	0·32
1230660	0·37
1479960	0·37
1636560	0·36
1820160	0·37

T_∞ = 0·37 ≡ 6·98 x 10^{-4} g.ions H^+/l. = $[H^+]_x$

$[\mathrm{ROT_s}]_0$ 0·02130

$[Cl^-]_0$ 0·05126

$[H^+]_x$ 6·98 x 10^{-4}

$[Cl^-]_x$ 0·03064

k_2/k_1 = 7·581 x 10^2 $\mathrm{mole^{-1}l.}$ (see Appendix C)

Duplicate Experiment

$[\mathrm{ROT_s}]_0$ 0·02376

$[Cl^-]_0$ 0·05321

$[H^+]_x$ 8·11 x 10^{-4}

$[Cl^-]_x$ 0·03026

k_2/k_1 = 6·96 x 10^2 $\mathrm{mole^{-1}l.}$

EXPERIMENT 22

4-Methoxybenzhydryl 4'-nitrobenzoate in 85% acetone I at 50·51°C

Added NaN_3 0·021503M

4·9247 Ml. titrated potentiometrically with 0·009885M NaOH

$[ROPNB]_0$ = 0·01955M

Time (secs.)	Titre	β
0	0·22	
∞	1·03	1290
	1·09	1192
	1·10	1175
	1·06	1240
	1·06	1240
	1·01	1330
	1·11	1160
	1·06	1240

Mean β = 1233 ± 21M^{-1}

Duplicate Experiment

Added NaN_3 0·021503M $[ROPNB]_0$ 0·01952M

Mean β = 1306 ± 33M^{-1}

EXPERIMENT 23

4-Methoxybenzhydryl 4'-bitrobenzoate in 85% acetone I at 71·18°C

Added NaN_3 0·021503M

4·9247 Ml. titrated potentiometrically with 0·009885M NaOH

$[ROPNB]_0$ 0·01955M

Time (secs.)	Titre	β
0	0·22	
∞	1·02	1312
	1·03	1293
	1·07	1223
	1·06	1240
	1·13	1132
	1·08	1208

Mean β = 1235 ± 27M^{-1}

Duplicate Experiment

Added NaN_3 0·021503M

$[ROPNB]_0$ 0·01952M

Mean β = 1237 ± 29M^{-1}

EXPERIMENT 24

4-Methoxybenzhydryl chloride in 85% acetone I at -0·21°C

Added NaN_3 0·021195M

5 Ml. samples titrated with 0·01004M NaOH

5 Ml. sample also titrated with 0·009823M $AgNO_3$ to give initial RCl.

$[N_3^-]_0$ = 0·020950M

$[RCl]_0$ = 0·016247M

$[H^+]$ Titre	β
(0·45)	(1588)
0·54	1307
0·53	1335
(0·48)	(1485)
0·52	1360
0·52	1360

Mean β = 1340 ± 44M^{-1}

Duplicate Experiment

Added NaN_3 0·020950M

$[RCl]_0$ 0·17956

Mean β = 1329 ± 40M^{-1}

EXPERIMENT 25

4-Methoxybenzhydryl chloride in 85% acetone I at -0•21°C

Added 4-$NO_2C_6H_4COOK$ 0•021152M

5 Ml. titrated with 0•010004M NaOH potentiometrically

5 Ml. titrated with 0•009823M $AgNO_3$ for initial RCl

$[KOPNB]_0$ 0•020907

$[RCl]_0$ 0•018231

$[H^+]$ Titre	β
5•10	73•8
5•09	74•2
5•10	73•8

Mean β = 73•9 ± 2•6M^{-1}

Duplicate Experiment

$[KOPNB]_0$ 0•020907

$[RCl]_0$ 0•018172

Mean β = 73•6 ± 2•6M^{-1}

EXPERIMENT 26

Benzhydryl chloride in 85% acetone IV at 20•41°C

No added salts

5 Ml. titrated with 0•01004M NaOH

Time (secs.)	Titre	$10^5 k_I$
0	0•10	-
7380	0•86	1•170
15120	1•58	1•161
21780	2•13	1•146
28440	2•68	1•159
40860	3•58	1•165
49860	4•19	1•181
70020	5•22	1•163
86281	5•93	1•166
105000	6•56	1•156
122640	7•11	1•173
170400	8•07	1•185
∞	9•29	-

$10^5 k_I$ = 1•166 ± 0•0034 (11 readings)

Duplicate Experiments

$10^5 k_I'$ = 1•165 ± 0•0020 (11 readings)

Solvent 85% V:

$10^5 k_I$ = 1•160 ± 0•0074 (10 readings)

$10^5 k_I'$ = 1•158 ± 0•0044 (10 readings)

$10^5 k_I''$ = 1•159 ± 0•0082 (10 readings)

EXPERIMENT 27

Benzhydryl chloride in 85% acetone IV at 20•41°C

Added $NaClO_4$ 0•05164M

5 Ml. titrated with 0•01004M NaOH

Time (secs.)	Titre	$10^5\ k_I$
0	0•12	-
7260	1•09	1•502
15120	2•00	1•478
21660	2•70	1•483
28380	3•36	1•491
40560	4•39	1•495
49800	5•05	1•495
69660	6•19	1•493
86220	6•88	1•476
104760	7•51	1•476
122580	8•00	1•491
∞	9•51	-

$10^5\ k_I$ = 1•488 ± 0•0027 (10 readings)

Duplicate Experiment

Added $NaClO_4$ 0•05078M

$10^5\ k_I'$ = 1•496 ± 0•0032 (11 readings)

EXPERIMENT 28

Benzhydryl chloride in 85% acetone IV at 20•41°C

Added NaCl 0•04792M

5 Ml. titrated with 0•01004M NaOH

Time (secs.)	Titre	$10^5\ k_I$
0	0•08	-
15000	1•49	1•101
21600	2•09	1•133
28260	2•61	1•129
40380	3•48	1•133
49860	4•06	1•127
69720	5•09	1•117
86160	5•79	1•113
104640	6•50	1•130
122640	7•00	1•122
170580	7•97	1•120
∞	9•34	-

$10^5\ k_I$ = 1•122 ± 0•0032 (10 readings)

Duplicate Experiment

Added NaCl 0•04931M

$10^5\ k_I'$ = 1•117 ± 0•0037 (10 readings)

EXPERIMENT 29

Benzhydryl 36-chloride in 85% acetone IV at 20·31°C

Added NaCl 0·05106M

10 Ml. of aqueous extract counted for 1 hour and titrated with 0·010417M NaOH

Time (secs.)	c.p.m.	Titre	$10^5\ k_{RX}^{*}$	$10^5\ k_{ROH}^{*}$	$\dfrac{k_{RX}-k_{ROH}}{Cl^{-}_{R}.k_{ROH}}^{*}$
0	91	0·07	-	-	-
7800	751	1·06	1·173	1·063	(2·03)
15780	1505	2·03	1·314	1·087	4·16
24060	2151	2·97	1·324	1·103	4·00
32520	2700	3·79	1·303	1·093	3·87
43380	3348	4·80	1·301	1·103	3·63
53340	3912	5·61	1·322	1·105	4·01
72240	4734	6·88	1·321	1·098	4·21
90420	5343	7·86	1·315	1·088	4·39
104760	5711	8·53	1·301	1·088	4·16
125100	6147	9·37	1·294	1·101	3·76
163200	6744	10·41	1·304	1·090	4·38
∞	7643	12·51	-	-	-

$$\left(\frac{k_{RX}-k_{ROH}}{Cl^{-}_{R}.k_{ROH}}\right)_{mean} = 4{\cdot}06 \pm 0{\cdot}078 \text{ mole}^{-1}\text{l.} \quad \text{(10 readings)}$$

Duplicate Experiment

Added NaCl 0·05058M

$$\left(\frac{k_{RX}-k_{ROH}}{Cl^{-}_{R}.k_{ROH}}\right)_{mean} = 4{\cdot}33 \pm 0{\cdot}114 \text{ mole}^{-1}\text{l.} \quad \text{(11 readings)}$$

* See section (5.4.3)

EXPERIMENT 30

Benzhydryl 36-Chloride in 85% acetone IV at 20•31°C

Added NaCl 0•09997M

10 Ml. of aqueous extract counted for 1 hour and titrated with 0•10417M NaOH

Time (secs.)	c.p.m.	Titre	$10^5\ k_{RX}$ *	$10^5\ k_{ROH}$ *	$\frac{k_{RX}-k_{ROH}}{Cl^-_R.k_{ROH}}$ *
0	115	0•10	-	-	-
13020	1355	1•62	1•395	1•017	3•76
21060	2056	2•45	1•430	1•010	4•22
30420	2690	3•38	1•390	1•024	3•66
41400	3424	4•38	1•414	1•037	3•74
50880	3861	5•09	1•369	1•027	3•44
73740	4961	6•59	1•420	1•022	4•11
89400	5493	7•46	1•425	1•026	4•16
106980	5898	8•25	1•393	1•022	3•92
130140	6382	9•11	1•405	1•020	4•17
170820	6860	10•19	1•368	1•014	3•97
∞	7581	12•36	-	-	-

$$\left(\frac{k_{RX}-k_{ROH}}{Cl^-_R.k_{ROH}}\right)_{mean} = 3{\cdot}92 \pm 0{\cdot}080\ \text{mole}^{-1}\text{l.}\quad \text{(10 readings)}$$

Duplicate Experiment

Added NaCl 0•09914M

$$\left(\frac{k_{RX}-k_{ROH}}{Cl^-_R.k_{ROH}}\right)_{mean} = 3{\cdot}84 \pm 0{\cdot}106\ \text{mole}^{-1}\text{l.}\quad \text{(12 readings)}$$

EXPERIMENT 31

Benzhydryl chloride in 85% acetone V at 20•41°C

Added $NaNO_3$ 0•05042M

5 Ml. titrated with 0•01062M $AgNO_3$

Time (secs.)	Titre	10^5 k_I
0	0•17	-
11520	1•65	1•410
18300	2•47	1•450
25380	3•16	1•422
32700	3•85	1•427
40380	4•43	1•399
48780	5•07	1•407
68160	6•16	1•370
86940	7•07	1•381
100440	7•57	1•379
124380	8•28	1•386
∞	10•04	-

10^5 k_I = 1•403 ± 0•0079 (10 readings)

Duplicate Experiment

Added $NaNO_3$ 0•05041M

10^5 k_I' = 1•406 ± 0•0087 (10 readings)

EXPERIMENT 32

Benzhydryl chloride in 85% acetone V at 20•41°C

Added NaN_3 0•04954

5 Ml. titrated with 0•01062M $AgNO_3$

Time (secs.)	Titre	10^5 k_I
0	0•11	-
11520	1•84	1•665
18240	2•69	1•653
25440	3•50	1•646
32580	4•17	1•618
40320	4•84	1•609
48900	5•45	1•583
67680	6•50	1•529
86820	7•45	1•556
98460	7•90	1•566
124500	8•58	1•549
∞	10•02	-

10^5 k_I (mean) = 1•597

EXPERIMENT 33

Benzhydryl chloride in 85% acetone V at 20•41°C

Added NaN_3 0•04897M

5 Ml. titrated with 0•04897M $AgNO_3$

Time (secs.)	Titre	10^5 k_I
0	0•13	-
7200	1•25	1•639
14220	2•20	1•620
20040	2•97	1•655
26400	3•58	1•591
39480	4•52	1•452
45060	5•27	1•587
54300	5•86	1•553
65100	6•50	1•541
94500	7•69	1•473
118020	8•59	1•547
∞	10•19	-

10^5 k_I (mean) = 1•566

EXPERIMENT 34

Benzhydryl chloride in 85% acetone V at 20•41°C

Added NaN_3 0•04899M

5 Ml. titrated with 0•01062M $AgNO_3$

Time (secs.)	Titre	10^5 k_I
0	0•25	-
7020	1•38	1•683
13920	2•33	1•649
19740	3•05	1•637
25920	3•70	1•605
35640	4•65	1•597
44340	5•24	1•528
53880	6•10	1•596
64680	6•72	1•571
94320	8•07	1•564
117900	8•79	1•566
∞	10•39	-

10^5 k_I (mean) = 1•600

EXPERIMENT 35

Benzhydryl chloride in 85% acetone V at 20•41°C

Added NaN_3 0•05047M

5 Ml. titrated with 0•01062M $AgNO_3$

Time (secs.)	Titre	10^5 k_I
0	0•04	-
11340	1•76	1•666
18300	2•64	1•647
25380	3•44	1•639
32460	4•09	1•602
40140	4•75	1•589
48900	5•44	1•590
67440	6•43	1•513
86520	7•37	1•529
98340	7•85	1•548
124320	8•51	1•515
∞	10•03	-

10^5 k_I (mean) = 1•584

EXPERIMENT 36

Benzhydryl chloride in 85% acetone VII at 20•41°C

0•2<u>M</u> Ionic strenght maintained with $NaClO_4$

No added salts

5 Ml. titrated with 0•01043 NaOH

Time (secs.)	Titre	10^5 k_I
0	0•06	-
6720	1•31	2•272
11460	2•11	2•305
15240	2•74	2•373
19020	3•28	2•385
22740	3•72	2•354
27660	4•31	2•373
33900	4•90	2•343
40440	5•51	2•375
54840	6•42	2•323
81720	7•55	2•307
∞	8•89	-

10^5 k_I (mean) = 2•341 ± 0•0128 (10 readings)

Duplicate Experiment

10^5 k_I' (mean) = 2•371 ± 0•0154

EXPERIMENT 37

Benzhydryl chloride in 85% acetone VII at 20•41°C

0•2M Ionic strength with $NaClO_4$

Added NaN_3 0•03026M

5 Ml. titrated with 0•009953M $AgNO_3$

Time (secs.)	Titre	$10^5\ k_I$
0	1•40	-
4800	2•28	2•396
8460	2•89	2•403
12300	3•49	2•426
16080	4•07	2•487
21000	4•63	2•423
27240	5•30	2•411
33840	5•92	2•413
48360	6•95	2•390
75060	8•15	2•387
∞	9•50	-

$10^5\ k_I$ (mean) = 2•415

EXPERIMENT 38

Benzhydryl chloride in 85% acetone VII at 20•41°C

0•2M Ionic strength maintained with $NaClO_4$

Added NaN_3 0•04121M

5 Ml. titrated with 0•009953M $AgNO_3$

Time (secs.)	Titre	10^5 k_I
0	0•59	-
7560	2•39	2•475
12000	3•34	2•517
14940	3•82	2•447
19380	4•56	2•436
23340	5•15	2•425
27660	5•77	2•441
32580	6•36	2•430
39960	7•11	2•408
48600	7•87	2•410
73020	9•35	2•429
86040	9•70	2•315
∞	11•14	-

10^5 k_I (mean) = 2•430

EXPERIMENT 39

Benzhydryl chloride in 85% acetone VII at 20•41°C

0•2M Ionic strength maintained with $NaClO_4$

Added NaN_3 0•04986M

5 Ml. titrated with 0•009953M $AgNO_3$

Time (secs.)	Titre	10^5 k_I
0	0•32	-
7440	1•95	2•501
10920	2•59	2•471
15720	3•40	2•461
19560	4•02	2•489
24000	4•63	2•483
28740	5•16	2•441
36180	5•95	2•441
46200	6•78	2•419
69180	8•06	2•372
82200	8•55	2•369
∞	9•92	-

10^5 k_I (mean) = 2•445

EXPERIMENT 40

Benzhydryl chloride in 85% acetone VII at 20•41°C

0•2M Ionic strength maintained with $NaClO_4$

Added NaN_3 0•05016M

5 Ml. titrated with 0•009953M $AgNO_3$

Time (secs.)	Titre	10^5 k_I
0	0•39	-
4980	1•47	2•490
8280	2•12	2•498
12000	2•78	2•488
15840	3•45	2•533
19920	4•05	2•525
24540	4•67	2•528
30900	5•38	2•505
38040	6•05	2•484
54480	7•13	2•389
78660	8•34	2•486
∞	9•65	-

10^5 k_I (mean) = 2•493

EXPERIMENT 41

Benzhydryl chloride in 85% acetone VII at 20•41°C

0•2M Ionic strength maintained with $NaClO_4$

Added NaN_3 0•1002M

5 Ml. titrated with 0•009953M $AgNO_3$

Time (secs.)	Titre	10^5 k_I
0	0•47	-
5520	1•87	2•633
7860	2•38	2•595
12600	3•34	2•577
16380	3•97	2•520
20760	4•75	2•570
25620	5•40	2•525
33060	6•29	2•499
44340	7•45	2•531
65820	8•81	2•490
78960	9•33	2•455
∞	10•82	-

10^5 k_I (mean) = 2•540

EXPERIMENT 42

Benzhydryl chloride in 85% acetone VII at 20·41°C

0·2M Ionic strength maintained with $NaClO_4$

Added NaN_3 0·09983M

5 Ml. titrated with 0·009953M $AgNO_3$

Time (secs.)	Titre	10^5 k_I
0	0·31	-
3900	1·29	2·710
7080	2·00	2·683
20920	2·75	2·631
14700	3·48	2·668
19380	4·24	2·655
25560	5·10	2·636
30600	5·74	2·652
36780	6·37	2·633
51000	7·49	2·603
77640	8·75	2·568
∞	10·08	-

10^5 k_I (mean) = 2·644

EXPERIMENT 43

4-Methoxybenzyl chloride in 85% acetone II at 20•41°C

No added salts

5 Ml. titrated with 0•010178M NaOH

Time (secs.)	Titre	10^6 k_I
0	0•03	-
8220	0•73	8•385
17760	1•50	8•484
26220	2•09	8•320
38760	2•91	8•262
55020	3•95	8•484
74280	4•90	8•380
90720	5•68	8•502
111780	6•42	8•378
135240	7•23	8•543
170340	8•09	8•549
197940	8•59	8•510
∞	10•54	-

10^6 k_I = 8•436 ± 0•0288 (11 readings)

Duplicate Experiments

10^6 k'_I = 8•481 ± 0•0165 (7 readings)

Solvent 85% III - 10^6 k_I = 9•340 ± 0•0087 (10 readings) at 20•31°C

Solvent 85% V - 10^6 k_I = 8•709 ± 0•0279 (10 readings)

10^6 k'_I = 8•659 ± 0•0272 (10 readings

Solvent 85% VIII - 10^6 k_I = 8•030 ± 0•0254 (11 readings) at 20•05°C

10^6 k'_I = 8•050 ± 0•0203 (11 readings) at 20•05°C

EXPERIMENT 44

4-Methoxybenxyl chloride in 85% acetone II at 20•41°C

Added $NaClO_4$ 0•04975M

5 Ml. titrated with 0•01004M NaOH

Time (secs.)	Titre	$10^5\ k_I$
0	0•09	-
7260	0•91	1•140
18060	1•95	1•100
25560	2•60	1•090
36960	3•57	1•113
49500	4•48	1•119
61200	5•16	1•104
82380	6•28	1•112
98640	7•00	1•123
114420	7•54	1•119
137820	8•15	1•102
179520	9•00	1•109
∞	10•41	-

$10^5\ k_I$ = 1•112 ± 0•0038 (11 readings)

Duplicate Experiments

Added $NaClO_4$ 0•05035M

$10^5\ k_I'$ = 1•116 ± 0•0068 (10 readings)

Solvent 85% III : Added $NaClO_4$ 0•04961M

$10^5\ k_I$ = 1•236 ± 0•0029 at 20•31°C (10 readings)

EXPERIMENT 45

4-Methoxybenzyl chloride in 85% acetone II at 20•41°C

Added NaCl 0•05036M

5 Ml. titrated with 0•01004M NaOH

Time (secs.)	Titre	10^6 k_I
0	0•05	-
14160	1•11	7•701
25680	1•91	7•789
37800	2•70	7•905
48300	3•29	7•857
71340	4•48	7•923
87660	5•20	7•952
102600	5•79	7•990
126000	6•50	7•862
166860	7•59	7•956
257280	8•93	7•798
∞	10•31	-

10^6 k_I = 7•873 ± 0•0269 (10 readings)

Duplicate Experiments

Added NaCl 0•04945M

10^6 k_I' = 7•866 ± 0•0434 (10 readings)

Solvent 85% III

Added NaCl 0•05037M

10^6 k_I = 8•771 ± 0•0254 (10 readings) at 20•31°C

Added NaCl 0•05037M

10^6 k_I' = 8•781 ± 0•0270 (11 readings) at 20•31°C

EXPERIMENT 46

4-Methoxybenzyl 36-chloride in 85% acetone III at 20•31°C

Added NaCl 0•05040M

10 Ml. of aqueous extract counted for 1 hour and titrated with 0•010178M NaOH

Time (secs.)	c.p.m.	Titre	10^5 k_{RX}*	10^6 k_{ROH}*	$\frac{k_{RX}-k_{ROH}}{Cl^-_R . k_{ROH}}$ *
0	98	0•23	-	-	-
10800	798	1•58	1•622	10•095	(12•33)
19800	1262	2•35	1•570	8•938	15•75
31140	1684	3•17	1•454	8•183	16•56
42540	2139	4•17	1•486	8•433	16•76
52860	2428	4•90	1•448	8•363	16•44
67860	2807	5•94	1•433	8•462	16•14
82140	3037	6•72	1•367	8•355	15•09
107280	3514	8•12	1•429	8•627	17•17
128760	3730	8•98	1•394	8•598	17•12
164220	3976	10•07	1•346	8•512	17•63
∞	4454	13•30	-	-	-

$$\left(\frac{k_{RX}-k_{ROH}}{Cl^-_R . k_{ROH}}\right)_{mean} = 16•52 \pm 0•24 \text{ mole}^{-1}\text{l.}$$ (9 readings)

Duplicate Experiment

Added NaCl 0•05040M

$$\left(\frac{k_{RX}-k_{ROH}}{Cl^-_R . k_{ROH}}\right)_{mean} = 15•73 \pm 0•71 \text{ mole}^{-1}\text{l.}$$ (9 readings

* See section (5.4.3)

EXPERIMENT 47

4-Methoxybenzyl 36-chloride in 85% acetone III at 20·31°C

Added NaCl 0·1009M

10 Ml. of aqueous extracted counted for 1 hour and titrated with 0·00998M NaOH

Time (secs.)	c.p.m.	Titre	$10^5\ k_{RX}$	$10^6\ k_{ROH}$	$\frac{k_{RX}-k_{ROH}}{Cl^-_R . k_{ROH}}$
0	136	0·27	-	-	-
7260	782	1·21	2·130	9·475	12·59
12240	1118	1·68	2·007	8·582	13·64
17820	1470	2·23	1·968	8·373	13·94
26040	2064	2·99	2·143	8·204	17·15
33540	2331	3·89	1·989	8·817	13·45
44820	2765	4·69	1·952	8·363	14·75
59820	3210	5·69	1·914	8·081	15·85
73680	3485	6·60	1·843	8·057	15·42
86100	3713	7·39	1·831	8·133	15·62
104700	3986	8·48	1·837	8·300	16·35
140700	4229	9·95	1·694	8·201	15·77
171480	4387	10·88	1·668	8·093	18·68
∞	4645	14·41	-	-	-

$\left(\frac{k_{RX}-k_{ROH}}{Cl^-_R . k_{ROH}}\right)_{mean}$ = 15·27 ± 0·49 mole^{-1}l. (12 readings)

Duplicate Experiment

Added NaCl 0·09881M

$\left(\frac{k_{RX}-k_{ROH}}{Cl^-_R . k_{ROH}}\right)_{mean}$ = 16·06 ± 0·26 mole^{-1}l. (10 readings)

EXPERIMENT 48

4-Methoxybenzyl chloride in 85% acetone II at 20•41°C

Added NaN_3 0•03067M

5 Ml. titrated with 0•009896M $AgNO_3$

Time (secs.)	Titre	10^5 k_I	10^3 k_{II}
0	1•17	-	-
1320	2•06	4•943	1•800
2400	2•68	4•723	1•762
4200	3•67	4•651	1•808
6000	4•48	4•463	1•800
7920	5•22	4•279	1•790
11400	6•07	4•190	1•836
13320	6•97	3•982	1•842
16800	7•83	3•809	1•868
21540	8•85	3•656	1•943
26760	9•71	3•482	2•003
35240	10•62	3•143	1•999
47340	11•68	2•894	2•136
∞	15•62	-	-

10^5 k_I (mean) = 4•018

10^3 k_{II} (mean) = 1•882

EXPERIMENT 49

4-Methoxybenzyl chloride in 85% acetone II at 20•41°C

Added NaN_3 0•03132M

5 Ml. titrated with 0•01007M $AgNO_3$

Time (secs.)	Titre	10^5 k_I	10^3 k_{II}
0	0•12	-	-
1080	0•70	5•175	1•698
2700	1•53	5•249	1•773
4800	2•41	5•033	1•759
7320	3•34	4•907	1•783
10680	4•38	4•771	1•821
14460	5•26	4•545	1•818
18360	6•02	4•385	1•836
23040	6•75	4•215	1•854
28860	7•46	4•035	1•875
37020	8•24	3•866	1•928
47640	8•91	3•644	1•955
∞	10•79	-	-

10^5 k_I (mean) = 4•530

10^3 k_{II} (mean) = 1•827

EXPERIMENT 50

4-Methoxybenzyl chloride in 85% acetone II at 20•41°C

Added NaN_3 0•05023M

5 Ml. titrated with 0•01007M $AgNO_3$

Time (secs.)	Titre	10^5 k_I	10^3 k_{II}
0	0•01	-	-
1860	1•45	8•038	1•650
2700	1•95	7•671	1•593
3840	2•63	7•584	1•600
6300	3•77	7•148	1•553
7500	4•32	7•163	1•580
9360	4•97	6•952	1•562
13020	6•16	6•905	1•613
16560	6•91	6•611	1•587
20400	7•62	6•489	1•604
25740	8•35	6•336	1•621
33660	9•06	6•124	1•631
∞	10•38	-	-

10^5 k_I (mean) = 7•002

10^3 k_{II} (mean) = 1•599

EXPERIMENT 51

4-Methoxybenzyl chloride in 85% acetone II at 20•41°C

Added NaN_3 0•05025M

5 Ml. titrated with 0•01007M $AgNO_3$

Time (secs.)	Titre	10^5 k_I	10^3 k_{II}
0	0•02	-	-
720	0•62	8•180	1•649
1440	1•13	7•767	1•583
2595	1•97	7•925	1•646
3960	2•74	7•580	1•603
5700	3•50	7•072	1•525
8340	4•76	7•209	1•609
11100	5•66	6•950	1•595
14100	6•57	6•945	1•645
17880	7•32	6•658	1•623
22200	8•06	6•551	1•650
27420	8•68	6•368	1•655
∞	10•51	-	-

10^5 k_I (mean) = 7•200

10^3 k_{II} (mean) = 1•617

EXPERIMENT 52

4-Methoxybenzyl chloride in 85% acetone VI at 20•41°C

0•2M Ionic strenght maintained with $NaClO_4$

No added salts

5 Ml. titrated with 0•01043M NaOH

Time (secs.)	Titre	$10^5\ k_I$
0	0•03	-
14220	2•19	1•861
22440	3•17	1•838
29340	3•91	1•843
34560	4•40	1•839
41760	5•01	1•839
52500	5•76	1•827
63720	6•43	1•833
84000	7•33	1•835
∞	9•32	-

$10^5\ k_I$ = 1•839

Duplicate Experiments

85% VIII at 20•41°C - $10^5\ k_I'$ = 1•804

85% VIII at 20•05°C - $10^5\ k_I$ = 1•722

85% VIII at 20•05°C - $10^5\ k_I'$ = 1•730

EXPERIMENT 53

4-Methoxybenzyl chloride in 85% acetone VI at 20•41°C

0•2M Ionic strength maintained with $NaClO_4$

Added NaN_3 0•03109M

5 Ml. titrated with 0•01012M $AgNO_3$

Time (secs.)	Titre	10^5 k_I	10^3 k_{II}
0	1•14	-	-
1500	1•82	4•680	1•667
3120	2•49	4•633	1•693
5460	3•36	4•582	1•737
8220	4•25	4•515	1•784
12180	5•28	4•370	1•822
16920	6•29	4•258	1•887
24300	7•46	4•093	1•974
31680	8•27	3•917	2•028
39840	8•93	3•763	2•088
∞	11•17	-	-

10^5 k_I (mean) = 4•312

10^3 k_{II} (mean) = 1•853

EXPERIMENT 54

4-Methoxybenzyl chloride in 85% acetone VIII at 20·41°C

0·2M Ionic strength maintained with $NaClO_4$

Added NaN_3 0·03026M

5 Ml. titrated with 0·009953M $AgNO_3$

Time (secs.)	Titre	10^5 k_I	10^3 k_{II}
0	2·15	-	-
1560	2·78	4·452	1·757
3720	3·56	4·374	1·784
6000	4·34	4·426	1·872
9480	5·28	4·277	1·900
13260	6·14	4·172	1·949
16920	6·80	4·040	1·971
25620	7·96	3·764	2·009
37320	11·54	-	-

10^5 k_I (mean) = 4·215

10^3 k_{II} (mean) = 1·892

EXPERIMENT 55

4-Methoxybenzyl chloride in 85% acetone VI at 20·41°C

0·2M Ionic strength maintained with $NaClO_4$

Added NaN_3 0·05161M

5 Ml. titrated with 0·01012M $AgNO_3$

Time (secs.)	Titre	$10^5\ k_I$	$10^3\ k_{II}$
0	0·26	-	-
1650	1·48	7·215	1·448
3180	2·45	7·075	1·451
5220	3·55	6·906	1·455
6900	4·32	6·777	1·456
9420	5·45	6·890	1·529
11520	5·97	6·468	1·458
15180	7·02	6·407	1·497
18060	7·65	6·307	1·509
24000	8·64	6·141	1·534
∞	11·13	-	-

$10^5\ k_I$ (mean) = 6·687

$10^3\ k_{II}$ (mean) = 1·482

EXPERIMENT 56

4-Methoxybenzyl chloride in 85% acetone VIII at 20•41°C

0•2M Ionic strength maintained with $NaClO_4$

Added NaN_3 0•05076M

5 Ml. titrated with 0•009953M $AgNO_3$

Time (secs.)	Titre	10^5 k_I	10^3 k_{II}
0	0•27	-	-
1800	1•64	7•477	1•532
2760	2•22	7•156	1•485
4800	3•42	7•121	1•520
6540	4•20	6•853	1•493
8700	5•06	6•670	1•488
12900	6•41	6•441	1•498
15960	7•21	6•364	1•522
20400	8•05	6•155	1•522
23820	8•62	6•124	1•553
∞	11•15	-	-

10^5 k_I (mean) = 6•707

10^3 k_{II} (mean) = 1•513

EXPERIMENT 57

4-Methoxybenzyl chloride in 85% acetone VI at 20•41°C

0•2M Ionic strength maintained with $NaClO_4$

Added NaN_3 0•1017M

5 Ml. titrated with 0•01012M $AgNO_3$

Time (secs.)	Titre	10^4 k_I	10^3 k_{II}
0	0•51	-	-
930	1•69	1•236	1•243
2250	3•16	1•242	1•269
3360	4•10	1•193	1•233
5100	5•37	1•162	1•221
6240	6•14	1•169	1•242
7800	6•99	1•162	1•250
9900	7•87	1•142	1•246
12120	8•63	1•134	1•256
14160	9•20	1•135	1•270
∞	11•38	-	-

10^4 k_I (mean) = 1•175

10^3 k_{II} (mean) = 1•248

EXPERIMENT 58

4-Methoxybenzyl chloride in 85% acetone VIII at 20•41°C

0•2M Ionic strength maintained with $NaClO_4$

Added NaN_3 0•1009M

5 Ml. titrated with 0•009953M $AgNO_3$

Time (secs.)	Titre	10^4 k_I	10^3 k_{II}
0	0•55	-	-
2160	3•16	1•267	1•305
3360	4•19	1•209	1•261
4980	5•46	1•202	1•274
6360	6•29	1•176	1•260
7980	7•16	1•169	1•269
9660	7•85	1•147	1•259
11460	8•47	1•132	1•256
∞	11•45	-	-

10^4 k_I (mean) = 1•186

10^3 k_{II} (mean) = 1•269

EXPERIMENT 59

4-Methoxybenzyl chloride in 85% acetone VIII at 20•05°C

0•2M Iomic strength maintained with $NaClO_4$

Added NaCl 0•02000M

5 Ml. titrated with 0•01015M NaOH

Time (secs.)	Titre	$10^5 k_I$
0	0•18	-
7200	1•49	1•549
12360	2•35	1•550
19440	3•38	1•534
27300	4•40	1•522
35340	5•39	1•541
44940	6•32	1•519
54480	7•19	1•527
74280	8•53	1•504
87660	9•25	1•497
105840	10•05	1•499
∞	12•59	-

$10^5 k_I$ = 1•525 ± 0•0064 (10 readings)

Duplicate Experiment

Added NaCl 0•01973M

$10^5 k_I'$ = 1•530 ± 0•0053 (10 readings)

EXPERIMENT 60

4-Methoxybenzyl chloride in 85% acetone VIII at 20•05°C

0•2M Ionic strength maintained with $NaClO_4$

Added NaCl 0•05097M

5 Ml. titrated with 0•01015M NaOH

Time (secs.)	Titre	$10^5\ k_I$
0	0•23	-
7320	1•39	1•333
12480	2•10	1•301
19620	3•04	1•300
27420	3•97	1•299
35520	4•82	1•291
45240	5•78	1•300
54660	6•56	1•295
74520	7•91	1•282
88020	8•68	1•284
106140	9•49	1•276
125940	10•18	1•267
∞	12•71	-

$10^5\ k_I$ = 1•294 ± 0•0052 (11 readings)

Duplicate Experiment

Added NaCl 0•04944M

$10^5\ k'_I$ = 1•305 ± 0•0037 (10 readings)

EXPERIMENT 61

Benzhydryl chloride in 85% acetone V at 20•41°C

Added NaN_3 0•04857M

4•925 Ml. titrated with 0•01062M $AgNO_3$

4•925 Ml. titrated with 0•010309M NaOH

$([H^+]_\infty - [H^+]_0)_{OBS}$ = 0•01415M

$[Cl^-]_\infty$ = 0•02055M

Duplicate Experiment

$[NaN_3]_0$ = 0•04982M

$[Cl^-]_\infty$ = 0•02146M

$([H^+]_\infty - [H^+]_0)_{OBS}$ = 0•01463

EXPERIMENT 62

4-Methoxybenzyl chloride in 85% acetone V at 20•41°C

Added NaN_3 0•04865M

5 Ml. titrated with 0•009986M $AgNO_3$

5 Ml. titrated with 0•01042M NaOH

$[Cl^-]_\infty$ = 0•02209M

$([H^+]_\infty - [H^+]_0)_{OBS}$ = 0•00298M

Duplicate Experiment

$[NaN_3]_0$ = 0•04856M

$[Cl^-]_\infty$ = 0•02129M

$([H^+]_\infty - [H^+]_0)_{OBS}$ = 0•00281M

REFERENCES

1. E.D. Hughes, *Quart. Rev.*, 1951, *5*, 245.
2. C.K. Ingold, '*Structure and Mechanism in Organic Chemistry*', 2nd Edn. G. Bell and Sons Ltd., London, 1969.
3. See for example; R.A. Sneen, *Accounts Chem. Res.*, 1973, *6*, 46.
4. E.D Hughes, *Trans. Faraday Soc.*, 1941, *37*, 603.
5. L.C. Bateman, E.D. Hughes and C.K. Ingold, *J. Chem. Soc.*, 1940, 974.
6. (a) E.D. Hughes and C.K. Ingold, *J. Chem. Soc.*, 1935, 244;
   (b) E.D. Hughes, *J. Chem. Soc.*, 1935, 255;
   (c) E.D. Hughes, C.K. Ingold and U.G. Shapiro, *J. Chem. Soc.*, 1936, 225;
   (d) L.C. Bateman, K.A. Cooper, E.D. Hughes and C.K. Ingold, *J. Chem. Soc.*, 1940, 925.
7. G. Kohnstam, *Adv. Phys. Org. Chem.*, 1967, *5*, 121.
8. W. Featherstone, E. Jackson and G. Kohnstam, *Proc. Chem. Soc.*, 1963, 175.
9. G.R. Cowie, J.R. Fox, M.J.H. Fitches, K.A. Hooton, D.M. Hunt, G. Kohnstam and B. Shillaker, *Proc. Chem. Soc.*, 1961, 222; see also reference 7, page 152.
10. S. Sugden and J.B. Willis, *J. Chem. Soc.*, 1951, 1360.
11. J.L. Gleave, E.D. Hughes and C.K. Ingold, *J. Chem. Soc.*, 1935, 236.
12. A. Streitweiser, *Chem. Rev.*, 1956, *56*, 571.
13. G. Kohnstam, A. Queen and T. Ribar, *Chem. Ind.*, 1962, 1287.
14. J.N. Brönsted, *Z. Physik. Chem.*, 1922, *102*, 169.
15. S. Winstein and A.H. Fainberg, *J. Amer. Chem. Soc.*, 1957, *79*, 5937.
16. A.J. Parker, *Adv. Phys. Org. Chem.*, 1967, *5*, 173.
17. P.B.D. de la Mare and C.A. Vernon, *J. Chem. Soc.*, 1954, 3679.
18. L.C. Bateman, M.G. Church, E.D. Hughes, C.K. Ingold and N.A. Taher, *J. Chem. Soc.*, 1940, 979.

19. C.A. Bunton and L. Robinson, J. Amer. Chem. Soc., 1968, 90, 5965.

20. (a) E.F.J. Duynstee, E. Grunwald and M.L. Kaplan, J. Amer. Chem. Soc., 1960, 82, 5654;

(b) E. Jackson and G. Kohnstam, Chem. Comm., 1965, 979.

21. G.R. Lucas and L.P. Hammett, J. Amer. Chem. Soc., 1942, 64, 1928.

22. G. A. Clarke and R.W. Taft, J. Amer. Chem. Soc., 1962, 84, 2295.

23. G. Baughmann, E. Grunwald and G. Kohnstam, J. Amer. Chem. Soc., 1960, 82, 5801.

24. R.E. Robertson, Progress Phys. Org. Chem., 1967, 4, 213.

25. S. Glasstone, K.J. Laidler and H. Eyring, 'The Theory of Rate Processes', McGraw-Hill, New York and London, 1941, p.199.

26. See reference 7, page 126.

27. V. Gold and E.G. Jefferson, J. Chem. Soc., 1953, 1409; L.L. Schaleger and F.A. Long, Adv. Phys. Org. Chem., 1963, 1, 1.

28. G. Kohnstam, Chem. Soc. Special Publication No. 16, 1962.

29. (a) E. Grunwald and S. Winstein, J. Amer. Chem. Soc., 1948, 70, 846;

(b) S. Winstein, E. Grunwald and H.W. Jones, J. Amer. Chem. Soc., 1951, 73, 2700.

30. (a) C.G. Swain and W.P. Langsdorf, J. Amer. Chem. Soc., 1951, 73, 2813;

(b) N. Kornblum, R.A Smiley, R.K. Blackwood and D.C. Iffland, J. Amer. Chem. Soc., 1955, 77, 6269.

31. (a) M.L. Bird, E.D. Hughes and C.K. Ingold, J. Chem. Soc., 1954, 634;

(b) V. Gold, J. Hilton and E.G. Jefferson, J. Chem. Soc., 1954, 2756;

(c) E.W. Crunden and R.F. Hudson, J. Chem. Soc., 1956, 501;

(d) V. Gold, J. Chem. Soc., 1956, 4633;

(e) G. Kohnstam, A. Queen and B. Shillaker, Proc. Chem. Soc., 1959, 157.

32. Y. Pocker, J. Chem. Soc., 1959, 3939.

33. P. Casapieri and E.R. Swart, J. Chem. Soc., 1961, 4342.

34. (a) A. Fava, A. Illiceto and A. Ceccon, Tetrahedron Lett., 1963, 685;

(b) A. Ceccon, I. Papa and A. Fava, J. Amer. Chem. Soc., 1966, 88, 4643.

35. L.J. LeRoux and E.R. Swart, J. Chem. Soc., 1955, 1475.

36. P.B.D. de la Mare, J. Chem. Soc., 1955, 3180.

37. B.J. Gregory and G. Kohnstam, private communication.

38. C.A. Bunton, T.A. Lewis and D.R. Llewellyn, Chem. Ind., 1954, 1154;

C.A. Bunton and T.A. Lewis, Chem. Ind., 1958, 180.

39. (a) E.D. Hughes, F. Juliusberger, S. Mastermann, B. Topley and J. Weiss, J. Chem. Soc., 1935, 1525;

(b) E.D. Hughes, F. Juliusberger, A.D. Scott, B. Topley and J. Weiss, J. Chem. Soc., 1936, 1173;

(c) W.A. Cowdrey, E.D. Hughes, T.P. Nevell and C.L. Wilson, J. Chem. Soc., 1938, 209.

40. (a) E.D Hughes, C.K. Ingold and S. Mastermann, J. Chem. Soc., 1937, 1196, 1236;

(b) E.D. Hughes, C.K. Ingold and A.D. Scott, J. Chem. Soc., 1937, 1201.

41. P.B.D. de la Mare, D.M. Hall and E. Manger, Rec. Trav. Chim., 1968, 87, 1394.

42. B. Capon, Quart. Rev., 1964, 18, 45.

43. S. Winstein, J. Amer. Chem. Soc., 1939, 61, 1635.

44. L.P. Hammett, 'Physical Organic Chemistry', McGraw-Hill, New York, 1940.

45. S. Winstein, B. Appel, R. Baker and A. Diaz, Chem. Soc. Special Publication No.19, 1965.

46. S. Winstein, J.S. Gall, M. Hojo and S. Smith, J. Amer. Chem. Soc., 1960, 82, 1010.

47. S. Winstein, E. Clippinger, A.H. Fainberg, R. Heck and G.C. Robinson, J. Amer. Chem. Soc., 1954, 76, 2597.

48. S. Winstein and K.C. Schreiber, J. Amer. Chem. Soc., 1952, 74, 2165.

49. E.D Hughes, C.K. Ingold, S.F. Mok, S. Patai and Y. Pocker, J. Chem. Soc., 1957, 1265.

50. (a) H.L. Goering and M.M. Pombo, J. Amer. Chem. Soc., 1960, 82, 2515;
    (b) H.L. Goering and J.T. Doi, J. Amer. Chem. Soc., 1960, 82, 5850;
    (c) H.L. Goering and J.F. Levy, J. Amer. Chem. Soc., 1962, 84, 3853.

51. H.L. Goering and H.H. Hopf, J. Amer. Chem. Soc., 1971, 93, 1224.

52. See reference 2, page 527.

53. (a) H.L. Goering and J.F. Levy, J. Amer. Chem. Soc., 1964, 86, 120;
    (b) H.L. Goering, R.G. Briody and G. Sandrock, J. Amer. Chem. Soc., 1970, 92, 7401.

54. R.A. Sneen and J.W. Larsen, J. Amer. Chem. Soc., 1969, 91, 362, 6031.

55. D.J. Raber, J.M. Harris, R.E. Hall and P. von R. Schleyer, J. Amer. Chem. Soc., 1971, 93, 4821.

56. B.J. Gregory, G. Kohnstam, M. Paddon-Row and A. Queen, J. Chem. Soc. (D), Chem. Comm., 1970, 1032.

57. (a) M.H. Abraham, J. Chem. Soc. Chem. Comm., 1973, 51;
    (b) J.L. Kurz and J.C. Harris, J. Amer. Chem. Soc., 1970, 92, 4117;
    (c) D.J. McLennan, J. Chem. Soc., Perkin II, 1972, 1577;
    (d) V.J. Shiner, M.W. Rapp and H.R. Pinnick, J. Amer. Chem. Soc., 1970, 92, 232.

58. J.O. Edwards and R.G. Pearson, J. Amer. Chem. Soc., 1962, 84, 16.

59. M.H.R. Hoffmann, J. Chem. Soc., 1965, 6253, 6762.

60. A. Queen, Ph.D. Thesis, University of Durham, 1961.

61. See reference 2, page 457.

62. See reference 2, page 250.

63. G. Kohnstam, private communication.

64. J.H. Bailey, J.R. Fox, E. Jackson, G. Kohnstam and A. Queen, J. Chem. Soc. Chem. Comm., 1966, 122.

65. J.R Fox and G. Kohnstam, J. Chem. Soc., 1963, 1593.

66. (a) A.R. Hawdon, E.D. Hughes and C.K. Ingold, J. Chem. Soc., 1952, 2499;
(b) B. Bensley and G. Kohnstam, J. Chem. Soc., 1955, 3408.

67. See for example; (a) A.H. Fainberg and S. Winstein, J. Amer. Chem. Soc., 1956, 78, 2763;
(b) B. Shillaker, Ph.D. Thesis, University of Durham, 1960.

69. D. Bunn, F.S. Dainton and S. Duckworth, Trans. Faraday Soc., 1961, 57, 1131.

70. G. Kohnstam and T. Ribar, unpublished results.

71. H. Weiner and R.A. Sneen, Tetrahedron Lett., 1963, 1309;
H. Weiner and R.A. Sneen, J. Amer. Chem. Soc., 1965, 87, 287, 292.

72. D.J. McLennan and P.L. Martin, Tetrahedron Lett., 1973, 43, 4215.

73. J.F Norris and H.B. Taylor, J. Amer. Chem. Soc., 1924, 46, 753.

74. Wachendorff, Analen., 1877, 185, 266.

75. J.K. Kochi and G.S. Hammond, J. Amer. Chem. Soc., 1953, 75, 3443.

76. J.R. Fox, Ph.D. Thesis, University of Durham, 1962.

77. M.S. Silver, J. Amer. Chem. Soc., 1961, 83, 404.

78. J.B. Conant and W.R. Kirner, J. Amer. Chem. Soc., 1924, 46, 232.

79. S.B. Hanna, Y. Iskander and Y. Riad, J. Chem. Soc., 1961, 217.

80. P. Ruggli and F. Lang, Helv. Chim. Acta, 1938, 21, 50.