Nucleophilic substitution reactions of aralphyl halides

Alan Queen

How to cite:

Queen, Alan (1961) Nucleophilic substitution reactions of aralphyl halides. Doctoral thesis, Durham University.

510

NUCLEOPHILIC SUBSTITUTION REACTIONS OF ARALPHYL HALIDES.

A THESIS SUBMITTED FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY
OF THE UNIVERSITY OF DURHAM

BY

ALAN QUEEN

HATFIELD COLLEGE
1961

ACKNOWLEDGMENTS

The author wishes to express his gratitude to his supervisor, Dr. G. Kohnstam, for his constant encouragement and advice throughout the course of these studies and to his father-in-law for the generous support which enabled the work to be undertaken.

Thanks are also reorded for the award of a Research Studentship by the Council of the Durham Colleges.

ABSTRACT.

The investigation is concerned with the effect of electrolytes on the rates of reaction of p-methoxybenzyl chloride and benzhydryl chloride in 70% acetone, where both compounds hydrolyse entirely by mechanism S_N1. The work was designed to test the possibility that better nucleophilic reagents than water could react with p-methoxybenzyl chloride by the concurrent operation of mechanisms S_N1 and S_N2. Since electrolytes had been previously demonstrated to have specific effects on the rates of ionisation of organic compounds[29,86,87], it was also necessary to measure their effect on an ionisation process before the quantitative treatment of the first problem was possible. Benzhydryl chloride, which is not susceptible to bimolecular attack,[61b] was chosen for this purpose because its rate of ionisation was known to have the same sensitivity as that of p-methoxybenzyl chloride to changes in the solvent composition and to additions of sodium perchlorate[29].

The studies have shown that the specific effects of electrolytes on the rate of reaction of benzhydryl chloride in the present solvent are consistent with the operation of two effects i) a non-specific acceleration of the rate of reaction due to ion-atmosphere stabilisation of the transition state for ionisation[80], ii) a specific change in the "effective" solvent

composition due to solvation of the electrolytes[87]. The effect is greater for p-methoxybenzyl chloride than for benzhydryl chloride by a constant small amount. The application of these principles to the effects of electrolytes on the rate of reaction of p-methoxybenzyl chloride, has confirmed that azide ions and chloride ions react with this compound by the simultaneous operation of the S_N1 and S_N2 processes. This is probably also the case for the substitutions by bromide, nitrate and fluoride ions. The non-electrolyte, pyridine, has also been shown to react with p-methoxybenzyl chloride by concurrent operation of the two S_N mechanisms, but no allowance for the medium effect could be made in this case, because other inert non-electrolytes were found to affect the rates of ionisation of benzhydryl chloride and p-methoxybenzyl chloride in different ways.

Additional evidence is provided for the validity of the criterion[61] of mechanism on which it was concluded[29] that p-methoxybenzyl chloride hydrolyses by mechanism S_N1 in 70% aqueous acetone. This mechanistic criterion requires that the value of the ratio $\Delta C^{*}/\Delta S^{*}$ should be independent of the nature of the substrate for S_N1 reactions. The value of this ratio for the hydrolysis of p-nitrobenzhydryl chloride in 50% aqueous acetone is shown to be the same as the corresponding values for the structurally different compounds <u>tert</u>-butyl chloride, benzylidene chloride, p-methylbenzylidene chloride and benzotrichloride in the same solvent[62], where the reactions all follow the S_N1 path.

INDEX

Page

CHAPTER I

MECHANISM OF SUBSTITUTION AT A SATURATED CARBON ATOM.

CHAPTER II

ACTIVATION PARAMETERS IN S_N SOLVOLYSIS.

CHAPTER III

THE EFFECT OF ELECTROLYTES ON THE RATES OF S_N REACTIONS

CHAPTER IV

THE EFFECTS OF ELECTROLYTES ON THE RATES OF REACTION OF BENZHYDRYL CHLORIDE AND P-METHOXYBENZYL CHLORIDE IN 70% AQUEOUS ACETONE.

CHAPTER V

CHAPTER VI

THE EFFECT OF UNREACTIVE NON-ELECTROLYTES ON THE RATES OF SOLVOLYSIS OF BENZHYDRYL CHLORIDE AND p-METHOXYBENZYL CHLORIDE.

CHAPTER VII

EXPERIMENTAL

APPENDIX A.

CHAPTER I

MECHANISMS OF SUBSTITUTION AT A SATURATED CARBON ATOM.

1. Types of substitution.[1]

Organic substitution reactions are essentially electrical phenomena. It is now recognised that chemical bonding involves interactions between the bonded centres and an associated pair of electrons. Formation or rupture of bonds must therefore be accompanied by modifications of the bonding electron pair. In substitutions such as

$$Y + R - X \longrightarrow Y - R + X$$

in which a single bond is exchanged, two main types of bond rupture are recognised.

In homolytic or symmetric fission,

$$Y. + R\,.\,.\,X \longrightarrow Y\,.\,.\,X + .X$$

(The dots represent electrons)

the departing group separates with one of the bonding electrons and a new bond is formed by the pairing of an electron on the reagent with that left on R. Such reactions, although common in the gas phase, are not the concern of the present studies and will not be given any further consideration.

In heterolytic or dissymmetric fission, which is frequently observed for reactions in solution, the departing group either leaves behind, or separates with the pair of "bonding" electrons. It is therefore necessary to subdivide heterolytic fissions into two classes.

(i) When the reagent is electron deficient and makes up a complete "octet" by utilising the discarded pair at the reaction centre, the process is termed <u>electrophilic</u> substitution (S_E).

$$Y + R : X \longrightarrow Y : R + X$$

(ii) When the deficiency of electrons arises at the reaction centre and the product is formed by co-ordination with a pair of electrons on the reagent, the process is termed a <u>nucleophilic</u> substitution (S_N).

$$Y{:} + R : X \longrightarrow Y : R + {:}X$$

It can be seen that such reactions are accompanied by a transfer of electrons from the substituting group Y to the substitution centre and from here to the expelled group X. In nucleophilic substitutions, therefore, Y becomes one unit more positive and X one unit more negative and provided that this condition is fulfilled the charged states of the species involved need not be restricted. The following examples, which cover a variety of charge distributions, will serve to illustrate this point[1,2].

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

$$R'_3N + RCl \longrightarrow R\overset{+}{N}R'_3 + Cl^-$$

$$H_2O + RBr \longrightarrow ROH + Br^-$$

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

Since the present studies are restricted to nucleophilic substitutions, a more detailed consideration of this class of reactions will now be given.

2. Mechanisms of nucleophilic substitution.

Two mechanisms are currently recognised for nucleophilic substitution reactions.

When the product is formed from the reagents in a single step, in which two molecules simultaneously undergo covalency change, the reaction is a bimolecular one and is designated S_N2. For an ionic reagent the reaction is

$$Y^{-} + RX \longrightarrow \underset{\text{transition state}}{\left[\overset{-}{Y}----R----\overset{-}{X}\right]} \longrightarrow YR + X^{-}$$

When the reagent is not ionic, the charge distributions are suitably modified. The hydrolysis of methyl bromide in aqueous ethanol follows this mechanism[3].

When the rate of reaction is determined by a preliminary slow ionisation of the compound RX, to give a highly reactive carbonium ion which then rapidly co-ordinates with the reagent, the mechanism is designated S_N1. Since only one molecule is undergoing covalency change in the rate determining step, the process is regarded as unimolecular[1,4].

$$RX \longrightarrow \underset{\text{transition state}}{\left[\overset{+}{R}------\overset{-}{X}\right]} \longrightarrow \overset{+}{R} + \overset{-}{X}$$

$$R^{+} + Y^{-} \longrightarrow RY$$

The magnitudes of the energies required for the ionisation step in the gas phase, are too large to give a reasonable rate of reaction by such a mechanism, a fact which has caused considerable opposition to the ionisation concept[4]. However it is now recognised that in condensed systems solvation of the polar transition state for ionisation can reduce the activation energies to more accessible values[3].

Tert-butyl chloride in aqueous acetone hydrolyses by this mechanism[5].

3. Recognition of mechanism.

The kinetic criterion is often used as a method of determining the mechanism of a reaction. Provided that both reacting species are in small and controllable concentration, the bimolecular process should lead to second-order kinetics while the unimolecular mechanism requires first-order kinetics. Thus,

$$\text{Rate} = k_2[RX][Y]. \qquad (S_N2)$$

$$\text{Rate} = k_1[RX] \qquad (S_N1)$$

However in solvolytic reactions, with which these investigations are concerned, the substituting reagent is a major constituent of the solvent and is therefore present in virtually constant excess. The rate equation hence reduces to a first order form, irrespective of mechanism. The kinetic criterion cannot therefore be used to determine the mechanism of solvolytic reactions. It must be stressed, at this point, that unimolecular reactions may exhibit small but characteristic deviations from first-order kinetics (see Chapter III).

Several criteria of mechanism are available for solvolytic reactions, each of which has a limited range of utility. It is the general rule to apply as many of them as possible to the solution of a particular problem. Hughes has reviewed the methods in some detail[6]. They are listed below, and those of most significance in these investigations will be discussed later in this chapter.

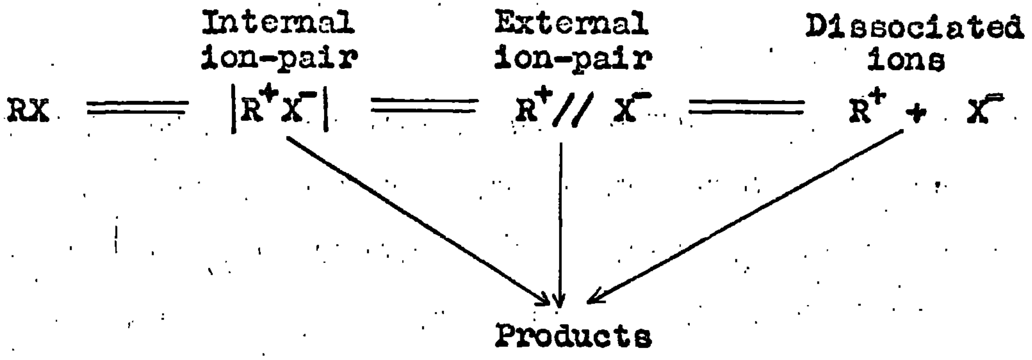
(i) The effect of structural changes in the compound substituted.
(ii) The effect of variation in the substituting reagent.
(iii) The effect of solvent changes on reaction rates and products.
(iv) The stereochemical course of the substitution.
(v) The kinetic form of the substitution reaction.
(vi) The effect of salt additions on rate and products.

4. Ion-pair intermediates in solvolysis.

Since the S_N1 mechanism leads to a planar carbonium ion, unimolecular substitution of an optically active compound should lead to a racemic product. Hughes, Ingold and their co-workers[7] have found it necessary to postulate shielding effects by the departing group, in order to account for the partial inversion of a-phenylethyl chloride during solvolysis by the S_N1 mechanism. Objections have been raised to this proposal[8]. Hammett[9] first suggested that an explanation may lie in the formation of an "ion-pair" intermediate, prior to the attainment of full ionisation of the substrate and that reaction of this entity with solvent would lead to inversion. The relative rates of reaction of the "ion-pair" and the carbonium ion, then control the ratio of inversion to racemisation.

In recent years Winstein and his co-workers have modified Hammett's original suggestion in order to explain the results of their solvolytic studies with optically active aryl sulphonates in acetic acid[10], where they believe the S_N1 mechanism to operate. Racemisation was found to be several times faster than acetolysis and for compounds with long-lived carbonium ions a two stage acceleration of the latter rate was induced by lithium perchlorate; i) an initial steep rise in the first-order rate coefficient for small concentrations of the salt ("special salt effect") ii) a subsequent gradual increase which was almost linear with salt concentration ("normal salt effect").

These workers proposed that ionisation occurs through two metastable intermediates, an "internal" ion-pair and an "external" ion-pair. The former, in which the partly seperated entities are surrounded by a common solvation shell, can return to the initial state (internal return) with accompanying racemisation. The solvent-seperated "external" ion-pair may either form the fully developed carbonium ion, return to the initial state through the "internal" form (external return) or react with nucleophilic reagents. The internal form is much less reactive but it is also susceptible to attack[10c]. The "special salt effect" was explained by postulating that the external ion-pair may be progressively stabilised by electrolytes, thus preserving it for acetolysis and reducing return to the initial state. The reaction steps may be represented thus,



Winstein and his co-workers[11] have recently demonstrated that the racemisation of p-chlorobenzhydryl chloride procedes more rapidly than substitution by radio-active chloride ions in acetone, and more rapidly than hydrolysis and chloride exchange in 80% aqueous acetone. Pocker[12] has reported similar results for the reactions of an unsymmetrical, deuterated benzhydryl chloride in 70% aqueous acetone. Since the substitutions of benzhydryl chlorides are considered to occur entirely by mechanism S_N1[61b], these results are consistent with "internal return" but they do not show that any of the substitutions involve attack on ion-pair intermediates. Indeed the only evidence indicating that such reactions may occur in aqueous organic solvents arises from a statement by Pocker (loc. cit.) that the rate of exchange between benzhydryl chloride and isotopic chloride ions is somewhat greater than that normally associated with a mass-law effect. No details were given but the effect appears to be small and to become progressively less important in more aqueous media. On the other hand, it has been concluded, from studies of the effects of mixed chlorides and bromides on the rate of hydrolysis of dichlorodiphenylmethane in aqueous acetone, that any ion-pairs formed in these systems do not react significantly compared to the fully formed carbonium ion.[13] If this is the general case for aqueous solvents, then ion-pair intermediates have no effect on the overall course of unimolecular nucleophilic substitution and it is therefore concluded that they may be neglected for the time being.

5. Factors affecting rate and mechanism.

(i) Variations in the substituting agent.

In reaction by mechanism S_N1, the rate is controlled by the ionisation of RX and the nucleophilic power of the reagent should therefore have no effect on the rate. In practice the nature of the reagent may influence the rate slightly by the operation of "medium" effects, which are however not related to the nucleophilic power. These medium effects are discussed in more detail in Chapters III and VI.

The bimolecular mechanism requires covalent attachment of the reagent in the rate determining step and its nucleophilic power is thus an important factor governing the rate of reaction by this mechanism. Tables of nucleophilicities have been compiled using the data from a number of sources[14].

It follows from these considerations that if the addition of a strong nucleophile does not alter the rate of reaction of RX, the original reaction must occur unimolecularly[6]. Tert-butyl chloride and benzhydryl chloride, are sterically hindered to bimolecular attack, and it has been demonstrated that the hydrolyses of these two compounds in aqueous ethanol are practically unaffected by the addition of hydroxide ions[16,17,20].

The converse of this criterion will clearly not apply since it is quite possible to visualise a compound reacting by mechanism S_N2 with powerful nucleophiles, but finding the S_N1 path energetically more favourable when only weak reagents are present. Indeed it has been demonstrated that chlorodimethyl ether, in ethanol and ether/ethanol mixtures, solvolyses by the unimolecular mechanism in the absence of ethoxide ions, but reacts predominantly by the bimolecular mechanism in the presence of this powerful reagent[18]. Similarly the rate of reaction of the trimethylsulphonium ion with various anions in ethanol[19], follows the sequence $OH^- > PhO^- > CO_3^= \approx Br^- \approx Cl^-$, and this has been interpreted as indicating a progressive decrease in S_N2 substitution as the nucleophilic power of the reagent falls. The mechanism was regarded as S_N1 for the last three anions, but Streitweiser[14c] has pointed out that the results are equally consistent with bimolecular attack by the solvent which, though a weaker nucleophile than these ions, is present in much larger amounts.

(ii) Structural variations in R.

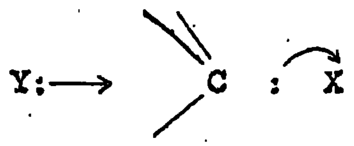
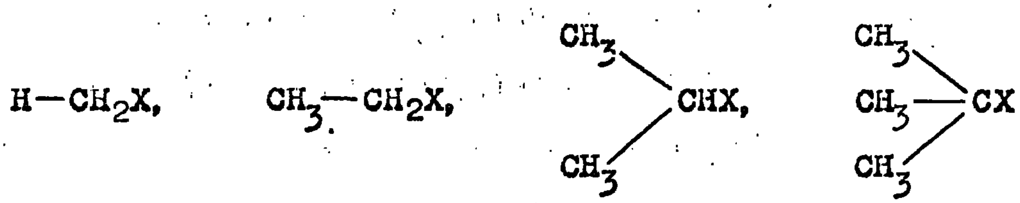


Figure I-1

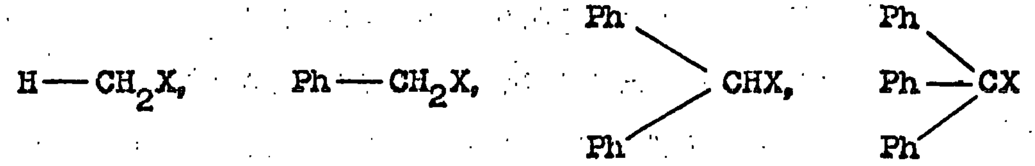
In nucleophilic substitutions the departing group carries the pair of bonding electrons away from the reaction centre and the resulting electron deficiency is made up by co-ordination with the reagent. These processes are indicated diagramatically in Figure I-1. The bond breaking process will be enhanced by an increase of electron release to the reaction centre by the groups attached to it. It follows that the tendency to react by the ionisation process (S_N1) will increase with increasing electron accession to the reaction centre. Therefore, since methyl groups can release electrons towards the reaction centre by the inductive effect, a transition from mechanism S_N2 to S_N1 is to be expected for the series



$H{-}CH_2X$, $CH_3{-}CH_2X$, $(CH_3)_2CHX$, $(CH_3)_3CX$

It has been observed for this series of bromides that the rate of solvolysis in aqueous ethanol is least for the isopropyl compound and that hydroxide ions have no effect on the rate of hydrolysis of the <u>tert</u>-butyl compound, although the corresponding rates for the others are affected in the order methyl > ethyl > iso-propyl[3,5,20]. <u>Tert</u>-butyl bromide must, therefore undergo S_N1 solvolysis, and methyl and ethyl bromides S_N2 solvolysis. Bimolecular substitution of <u>iso</u>-propyl bromide by water is not unambiguously indicated by the small accelerating effect of hydroxide ions (compare page 10). The region of minimum reaction rate, which approximately corresponds with iso-propyl bromide, marks the so-called "border-line region" where the mechanistic transition occurs. Border-line reactions will be discussed in more detail later in this chapter.

Whereas the inductive mode of electron release is the important one for alkyl compounds, phenyl groups can release electrons by the conjugative effect. Therefore the series



should also show an increasing tendency to react by the S_N1 mechanism. This series has been studied sufficiently to indicate a transition of mechanism approximately corresponding to the benzyl compound[19,21,22]. Consistent with these conclusions, hydroxide ions have been observed to increase the rates of hydrolysis of methyl halides in aqueous media[3,5,20] but to have little effect on the rates of hydrolysis of benzhydryl halides[17,23].

The solvolysis of benzyl chloride in aqueous solvents displays features of both the S_N1 and S_N2 processes. Thus the acceleration produced by hydroxide ions[24] argues in favour of mechanism S_N2 but does not preclude mechanism S_N1 (see page 10). The small retardation caused by chloride ions[25] indicates a mass-law retardation, the most common diagnostic feature of S_N1 reactions, but it has also been explained as a neutral salt effect on S_N2 substitution.[26] Bensley and Kohnstam[27] have concluded, from a consideration of the available evidence, that the mechanism is mainly, if not entirely, S_N2 in 50% aqueous acetone.

Variation of electron release to the reaction centre can also be realised by the introduction of polar substituents in the ring of aralphyl compounds. Experiments with such compounds have the advantage that steric effects, which may arise with substituents at the reaction centre, can be avoided. Thus the effects of meta- and para- substituents arise solely from polar influences. For example the para- substituents

NO_2; H; CH_3; p-$MeOC_6H_4$; PhO; MeO;

in an aralphyl halide, represent a series with increasing facility of electron release towards an electron-demanding reaction centre. It has been shown that, in aqueous acetone, only the last two substituents induce S_N1 solvolysis for para-substituted benzyl chlorides[28,29]. The <u>para</u>-methyl and <u>para</u>-anisyl compounds are regarded as border-line cases and the parent compound and its <u>para</u>-nitro derivative appear to undergo S_N2 solvolysis.

In reaction by the bimolecular mechanism, electron release towards the reaction centre will facilitate the fission of the R-X bond but will, at the same time, tend to inhibit the approach of the reagent by electrostatic interaction with its bond-forming electron pair, the effect being more pronounced for anionic reagents. Depending, therefore, on whether the bond-forming or bond-breaking tendency predominates in the activation process, electron release to the reaction centre can increase or decrease the rates of S_N2 substitutions. This has been demonstrated for the bimolecular exchange between para-substituted benzyl bromides and radio-active bromide ions in ethylene diacetate[30], and the Finkelstein reaction with benzyl chlorides in acetone[31], where the S_N2 mechanism also operates (see Table I-1).

TABLE I-1

Relative Rates of Substitution of Benzyl Halides in Ethylene Diacetate* and Acetone†.

Substituent Reaction	NO_2	CN	Cl	H	Me	t-Bu	OMe	Ref.
* $RBr + Br^-$	11.2	10.0	-	1.0	-	-	6.2	30
† $RCl + I^-$	6.19	-	2.12	1.00	1.17	1.35	-	31

It might be expected, with formally neutral reagents such as water, that electrostatic interactions would be less than with charged reagents. In consequence the main effect of a change in electron release to the centre of substitution would be on the bond breaking process, for such reactions. Thus an increase of electron accession to the reaction centre should be accompanied by an increase in the rate of reaction. This is substantiated by the progressive increase in the rates of solvolysis of <u>para</u>-NO_2, -H, and -Me benzyl chlorides in partly aqueous solvents[29,32]. On the other hand the rates of reaction of methyl, ethyl and <u>iso</u>-propyl bromides with ethanol exhibit a progressive decrease[33]. This has been attributed to increasing steric hindrance to bimolecular attack[34], and is supported by the similar effect observed for a variety of reactions with the alkyl series methyl, ethyl, <u>iso</u>-butyl and neopentyl[35]. The retardation observed for the neopentyl compounds, for which considerable steric hindrance has been theoretically demonstrated[35a], is particularly large. It is noteworthy that in formic acid, where reactions are usually conceded to be S_N1, the solvolysis rates for methyl and neopentyl p-toluenesulphonates differ by only a factor of two[35b].

6. <u>Mechanism in the border-line region.</u>

Up to this point, although considerable attention has been given to the extreme S_N1 and S_N2 mechanisms, the border-line region, where the actual transition from one to the other occurs, has only been briefly mentioned. The true nature of border-line reactions, which are almost, but not quite, S_N1, has been the subject of a great deal of controversy.

It is instructive to consider nucleophilic substitutions in terms of the valence bond concept[36]. The transition state of any such reaction can be regarded as a resonance hybrid of the canonical forms (I), (II) and (III).

Y: R—X	Y—R :X	Y: R :X
(I)	(II)	(III)

When structure (III) does not contribute to the transition state the operative mechanism is S_N2 and when only (I) and (III) do so it is S_N1. On the other hand, if all three canonical forms make contributions to the transition state, the mechanism must be regarded as bimolecular, since covalent participation by the reagent is still an essential feature of the activation process[37].

Two possibilities must be considered for reactions occuring in the mechanistic border-line region. Both have been proposed by a number of different authors[36b,38,39].

(i) It has been asserted that such reactions proceed through a single intermediate reaction path. The transition state has contributions from all three canonical forms and the mechanism must hence be bimolecular. The greater the contribution from (III) relative to (II), the more does the reaction tend to be S_N1 in character.

(ii) The second alternative postulates that the individual acts of substitution may occur through a 'continuous spectrum' of transition states. The contributions from the canonical forms vary for each and some may have none at all from (II).

The S_N1 and S_N2 mechanisms can, therefore, operate concurrently and independently. A variant of this view is that reaction involves separate operation of the extreme cases of S_N1 and S_N2.

At the begining of the present work, no unambiguous evidence in favour of the two general alternatives was available.

Winstein, Grunwald and Jones[36b] considered that a linear free energy relationship applied to the effect of solvent changes on the rates of solvolytic reactions and suggested that

$$\log k = \log k^{\circ} + mY \qquad \ldots\ldots\ I\text{-}1$$

where Y is a measure of the ionising power of the solvent, relative to a standard solvent (80% aqueous ethanol), to which k° refers, and m is a constant which is independent of the nature of the substrate but dependent on the reaction mechanism. Values of Y for various solvents were obtained by assuming that m was equal to unity for S_N1 reactions* and studying the solvolysis of tert-butyl chloride with various solvents, when

$$\log (k/k^{\circ})_{t\text{-BuCl}} = Y$$

---

* A different mechanistic classification was actually proposed by these workers but they showed that their two classes, Lim. and N, closely correspond to the S_N1 and S_N2 mechanisms.

Values of m for S_N2 reactions (m_2) were obtained from the application of equation I-1 to studies on n-alkyl halides. These were found to be appreciably less than unity,

If a mechanistically border-line solvolysis involves the concurrence of mechanisms S_N1 and S_N2, then

$$k = k_1 + k_2$$

Therefore, from equation I-1

$$k \text{ antilog}_{10} -m_2 Y = k_1^\circ \text{ antilog}_{10}(1-m_2)Y + k_2^\circ \quad . . \text{ I-2}$$

The solvolysis of iso-propyl bromide in aqueous ethanol was chosen as a possible border-line reaction and studied in a series of solvents which varied from pure ethanol to water. The results showed that k did not vary in the manner predicted by equation I-2 and much better agreement with their observations was obtained by using equation I-1 with a value for m intermediate between m_2 and unity. It was therefore concluded that this reaction involved a single reaction path intermediate between S_N1 and the extreme form of S_N2.

This approach, though not necessarily the conclusion about the nature of border-line reactions, has been severely criticised. Streitwieser[14b] has pointed out that m is not independent of the nature of the substrate for S_N1 reactions and Bird, Hughes and Ingold[39] have shown that log k, for the solvolysis of methyl of ethyl bromide, does not vary linearly with Y, as required by equation I-1. Winstein and his co-workers have accepted these criticisms[40] but their revised views of the effect of solvent changes on the rates of solvolytic reactions do not contribute to the interpretation of border-line reactions.

The reactions of m-chlorobenzhydryl chloride in liquid sulphur dioxide[39] with fluoride ions and also triethylamine and pyridine, have been studied. The substitutions by the amines showed "mass-law" retardations with added chloride ions, a feature usually associated with the unimolecular mechanism (see Chapter III, page 41). However the dependence of rate on the reagent and the variation of rate with reagent concentration were inconsistent with substitution by mechanism S_N1 or by the concurrent operation of the S_N1 and extreme S_N2 processes. It was suggested that the reactions occurred through transition states which were intermediate to various degrees between those for the two mechanistic extremes. The suggestion was only a qualitative one and, moreover, no allowance was made for medium effects (see Chapter VI). This work cannot therefore, be regarded as making a valid contribution to the border-line problem.

The solvolytic reactions of benzyl chloride in partially aqueous solvents have been discussed in terms of the two mechanistic alternatives for border-line reactions[27]. The kinetic data were consistent with either of the views already put forward (see page 15) but it was considered unlikely that the extreme S_N1 and S_N2 mechanisms were operating together.

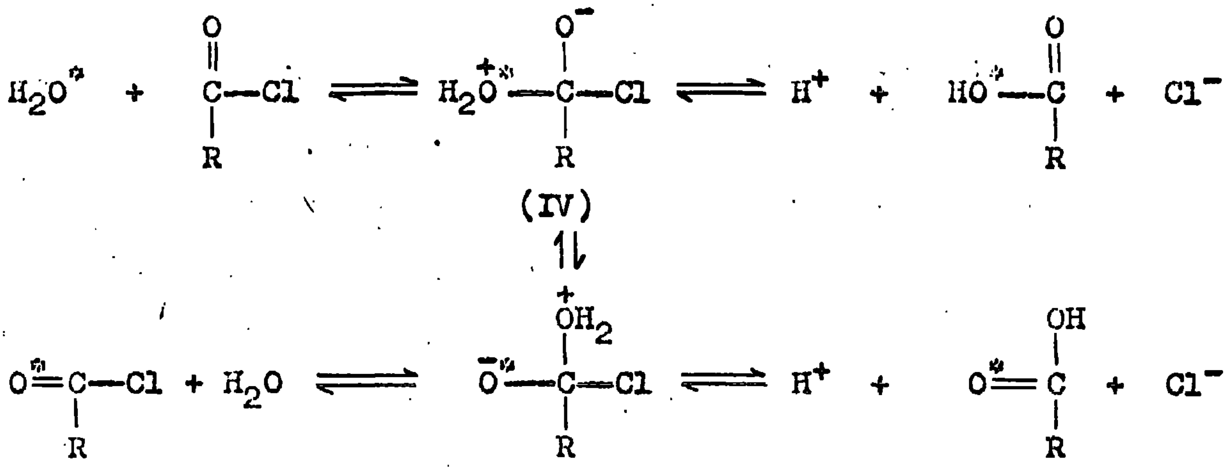
Nair[41] has studied the effect of cyanide ions on the reactions of benzyl chloride in 80% aqueous ethanol. The considerable increase in the rate, which depended on the concentration of the reagent, could not be explained as a salt-effect. However the constant first-order rates, obtained with a slight excess of the reagent, precluded the possibility of direct bimolecular substitution by cyanide ions. An unstable pentavalent state was postulated for carbon, analogous to similar suggestions made by Doering and Zeiss[42]. Gillespie[43] has also suggested that carbon may utilise its 3d orbitals in bond formation but Dewar[44] has shown that any such contributions from the 3d orbitals would leave the general configuration of carbon unchanged. Nair's assumption of S_N1 solvolysis for benzyl chloride in 80% aqueous ethanol is open to serious criticism, since Bensley and Kohnstam[27] found that the reaction was mainly S_N2 in 50% aqueous ethanol, a better ionising medium. It cannot therefore be maintained that this work makes a valuable contribution to the knowledge of "border-line" mechanisms and in the author's view an analysis of the products of reaction is required before Nair's postulates are seriously considered.

The exchange between radioactive bromide ion and <u>tert</u>-butyl bromide in anhydrous acetone has been interpreted as the concurrent operation of the S_N1 and S_N2 processes,[45] but later work by de la Mare has not confirmed the kinetic data[46]. The validity of the conclusions drawn by both sets of workers has been questioned recently by Winstein[47] who has shown that elimination is the predominating reaction occurring in the presence of lithium bromide or chloride. The results suggest that elimination and exchange involve the same rate determining stage, probably ionisation of tert-butyl chloride. bromide.

Several sets of workers have considered the hydrolysis of benzoyl chloride as a border-line nucleophilic substitution reaction and the results have been interpreted in terms of the concurrent operation of mechanisms S_N1 and S_N2.

Crunden and Hudson[48] assumed that the reactions of para-substituted benzoyl chlorides in anhydrous formic acid involved only mechanism S_N1 and that the rate was the same as for the S_N1 reaction in 65% aqueous acetone, a solvent of the same ionising power (see page 17). Any difference between the rate observed in this solvent and that calculated for the S_N1 reaction was assumed to arise from the incursion of mechanism S_N2. On this view the parent compound and its para-methyl derivative hydrolysed unimolecularly, the para-nitro compound bimolecularly and the para-bromo compound by both mechanisms. It must be stressed that this approach, even if valid, does not consider the possibility of a single reaction path intermediate between mechanism S_N1 and the extreme form of mechanism S_N2. The concurrence of the two mechanisms is therefore assumed at the outset. Similar objections apply to Kelly and Watson's[49] conclusion of simultaneous S_N1 and S_N2 hydrolysis of benzoyl chloride in aqueous acetone. These workers found that the observed rates were consistent with the assumption that the S_N1 rate was proportional to $[H_2O]^q$ and the S_N2 rate to $[H_2O]^{n+1}$, where n and q were independent of solvent composition. The proportionality constants were obtained by assuming only the S_N2 reaction to occur in solvents of low water content. It must be stressed, however, that there is no reason why an expression such as $k \propto [H_2O]^q$ should hold over a large range of solvent variation, even for the operation of a single mechanism.

Gold, Hilton and Jefferson[50] studied the intervention of aromatic amines in the reaction between benzoyl chloride and aqueous acetone, pointing out that the concurrence of the two mechanisms would result in a decrease in the rate of hydrolysis and an increase in the overall rate of decomposition of the chloride on addition of the base. They concluded that each mechanism was responsible for about half the observed rate in 50% acetone. Although these workers were not able to make an allowance for the medium effect caused by the addition of the amine (see Chapter VI), their conclusion of concurrent operation of the unimolecular and bimolecular mechanisms would be unassailable if the hydrolysis of benzoyl chloride involved only the S_N mechanisms. Recent work[51] has shown that the reaction of benzoyl chloride with water can, however, involve other paths. "Unreacted" chloride, isolated from experiments conducted in aqueous solvents containing H_2O^{18}, were found to contain isotopic oxygen. The interpretation of this observation is analogous to that previously proposed[52] for the hydrolysis of carboxylic esters by mechanism $B_{AC}2$. It is assumed that the first step in the reaction involves the addition of a water molecule to form the intermediate (IV), which is sufficiently stable to undergo rapid proton exchange before it decomposes to the initial state.



The original acid chloride may therefore contain O^{18}. It must be stressed that these results do not show that the hydrolysis of benzoyl chloride procedes exclusively by this mechanism, but they do show that the reaction does not only involve S_N processes. As a result, conclusions based on the study of acyl chlorides are not considered to provide information about the mechanism in the border-line region of nucleophilic substitution. It must be held, therefore, that there is no evidence favouring either of the alternative views of the nature of the operative mechanism (see page 15).

The present thesis describes an attempt to obtain evidence for, or against, the concurrent operation of the two S_N mechanisms in such reactions. After this work had been commenced, Pocker[53] reported reaction by simultaneous first- and second-order processes between benzhydryl bromide and bromide, chloride and azide ions as well as triethylamine, aniline and pyridine in solvent nitromethane. These results suggest the concurrent operation of mechanisms S_N1 and S_N2 but it must be stressed that reactions in this solvent have been considered to involve the participation of partially heterolysed species[54]. These may, or may not, be the ion-pairs postulated by Winstein and his collaborators as intermediates in reactions carried out in media of low dielectric constant (see page 5).

Information about the possible concurrence of the two mechanisms has now been sought by studying the intervention of added substances in the S_N1 hydrolysis of an organic halide (p-methoxybenzyl chloride) whose structure did not render it sterically unfavourable to bimolecular attack. Since carbonium ions must be formed in the present reacting system, reaction between these ions and the added material may occur; this corresponds to unimolecular substitution. If however the added substance is a better nucleophile than water, direct reaction with the unionised substrate is also possible, leading to bimolecular substitution.

Most of the organic halides which are recognised to undergo S_N1 solvolysis are also sterically hindered to substitution by the bimolecular mechanism and could not, therefore, be used in the present studies. Examples of such compounds are tert-butyl chloride[55] and benzhydryl chloride[7b]. p-Methoxybenzyl chloride does not suffer from this drawback but part of the evidence from which it was concluded that its hydrolysis occurs by mechanism S_N1 [29] depended on the value of the ratio $\Delta C^{\neq}/\Delta S^{\neq}$ for this reaction, where $\Delta C^{\neq}$ and $\Delta S^{\neq}$ are the heat capacity and entropy of activation, respectively. Bensley and Kohnstam[27] had previously proposed that this ratio should be independent of the substrate in S_N1 reactions but confirmatory evidence for this hypothesis was still required at the beginning of the present studies. The relevant experimental work which was carried out for this purpose, is discussed in Chapter II together with the hypothesis on which it is based.

It must also be stressed that the addition of substances to the reaction mixture will alter the rate of ionisation of organic halides. Parallel experiments were also carried out with benzhydryl chloride as the substrate in an attempt to measure the magnitude of the effects of added materials on the rate of an S_N1 reaction. It is generally accepted that this compound reacts entirely by this mechanism in aqueous solvents and preliminary experiments had shown that it behaved in a similar manner to p-methoxybenzyl chloride when the solvent composition was changed, or when weakly nucleophilic electrolytes were added. Most of the reagents employed in the present experiments were ionic and previous work on the effect of electrolytes on nucleophilic substitution reactions is discussed in Chapter III. The results now obtained are summarised and discussed in Chapters IV and V. It was also necessary to study the effects of unreactive non-electrolytes on the S_N1 solvolyses of benzhydryl chloride and p-methoxybenzyl chloride. Chapter VI deals with this aspect of the work. Full experimental details are given in Chapter VII.

/ Foot-note to page 25.
The evidence for this view has been recently summarised[28].

CHAPTER II

ACTIVATION PARAMETERS IN S_N SOLVOLYSIS.

The temperature dependence of the Arrhenius parameters.

The Arrhenius equation[56] defines the variation of reaction rate with temperature by the relationship

$$\ln k = B - \frac{E}{RT} \qquad \ldots\ldots \text{II-1}$$

where k is the rate constant, R the gas constant, T the absolute temperature, B a constant and E another constant with the dimensions of energy.

Experimental results usually indicate that E, the energy of activation, is independent of temperature but several workers have concluded on theoretical grounds that the activation energy should vary with temperature[57]. It is therefore better to define the activation energy by the differential form of equation II-1,

$$\frac{d \ln k}{dT} = \frac{E}{RT^2} \qquad \ldots\ldots \text{II-2}$$

Equation II-1 is then still valid if it is recognised that E and B may not be constant and that

$$\frac{dB}{dT} = \frac{1}{RT} \cdot \frac{dE}{dT} \qquad \ldots\ldots \text{II-3}$$

Eyring's absolute rate equation may be written in the form

$$\ln k = \ln \frac{\bar{k}T}{h} + \frac{\Delta S^{\ast}}{R} - \frac{\Delta H^{\ast}}{RT} \quad \ldots\ldots \text{II-4}$$

where $\bar{k}$ is the Boltzmann constant, h is Plank's constant,

R is the gas constant, T is the absolute temperature.

$\Delta S^{\ast}$ is the entropy of activation,

$\Delta H^{\ast}$ is the enthalpy of activation.

The energy of activation, E, can be expressed in terms of these parameters by differentiating equation II-4 with respect to temperature and remembering that

$$\frac{d\,\Delta H^{\ast}}{dT} \doteq T \cdot \frac{d\,\Delta S^{\ast}}{dT} = \Delta C^{\ast} \quad \ldots\ldots \text{II-5}$$

where $\Delta C^{\ast}$ is the heat capacity of activation. Therefore,

$$E = \Delta H^{\ast} + RT \quad \ldots\ldots \text{II-6}$$

Making this substitution for $\Delta H^{\ast}$ in equation II-4 and comparison with equation II-1 leads to

$$B = \ln \frac{\bar{k}T}{h} + \frac{\Delta S^{\ast}}{R} + 1$$

The Arrhenius parameters can therefore be expressed in terms of the entropy and enthalpy of activation.

It also follows from equations II-5 and II-6 that the temperature dependence of the activation energy is given by the relationship

$$\frac{dE}{dT} = \Delta C^{\ddagger} + R$$

so that any detectable variation in the value of E with temperature must be due to a difference in the heat capacities of the initial and transition states.

Temperature dependent activation energies for reactions in solution have been reported on a number of occaissions[27,59,63] and the earlier reports have been reviewed in a number of places[29,60,61]. Despite the considerable number of studies that have been made of the effect of temperature on reaction rates, many of the measurements were not accurate enough to reveal variations in E and this applies to some cases where temperature dependence has been reported[59g,64]. Nearly all the reliable results refer to solvolyses of organic halides, nitrates and arlysulphonates, for which the transition states are more polar than the initial states. In all cases the energy of activation decreased with temperature.

Possible causes for the finite heat capacities of activation will now be considered.

Causes for changes in heat capacity.

1. Electrostatic approach.

Reactions which involve a change in polarity on passage into the activated complex have often been discussed on a simple electrostatic basis, by assuming that the solvent merely acts as a continuous dielectric and that solvent changes alter the rate by changing the stabilities of dipoles in the dielectric.

Kirkwood's equation[65] gives the change in free energy, ΔG, for the transfer of a dipole from a continuous medium of unit dielectric constant to one of dielectric constant D; thus

$$\Delta G = -\frac{\mu^2}{r^3} \cdot \frac{(D-1)}{(2D+1)} \qquad \ldots\ldots\ \text{II-7}$$

where μ is the dipole moment, r the radius of the molecule containing the dipole and D the dielectric constant of the medium. Differentiation of this expression with respect to temperature gives the electrostatic contribution to the entropy of activation by the expression

$$-\frac{d\,\Delta G_D^{\ddagger}}{dT} = \Delta S_D^{\ddagger} = \left[\frac{\mu_t^2}{r_t^3} - \frac{\mu_i^2}{r_i^3}\right] \cdot \frac{3D}{(2D+1)^2} \cdot \frac{d\ \ln D}{dT} \qquad \ldots\ \text{II-8}$$

D always decreases with increasing temperature so that $\Delta S_D^{\ddagger}$ must be temperature dependent. If (d ln D)/dT is not temperature dependent, which is the case for aqueous ethanol and aqueous acetone solutions[66], the electrostatic contribution to the heat capacity of activation is obtained by differentiation of equation II-8 with respect to temperature and application of equation II-5.

Thus,

$$\Delta C_D^{*} = -\left[\frac{\mu_t^2}{r_t^3} - \frac{\mu_i^2}{r_i^3}\right] \cdot \frac{3DT(2D-1)}{(2D+1)^3} \cdot \left[\frac{d \ln D}{dT}\right]^2 \quad ..II-9$$

For the reactions under consideration, μ_t is greater than μ_i and the theory therefore predicts a negative value for the heat capacity of activation, in agreement with experiment.

The observed values of ΔC^{*} and ΔS^{*} for the ionisation of the C—Cl linkage, however, show serious discrepancies from those calculated using equations II-8 and II-9 [61a]. The theory predicts that the entropy and heat capacity of activation should be affected in the same manner by a change of solvent. For benzylidene chloride and benzotrichloride, the two compounds studied, an increase in ΔS^{*} was accompanied by an appreciable decrease in ΔC^{*} on changing from 50% acetone to 50% ethanol. The calculated values of the ratio $\Delta C_D^{*}/\Delta S_D^{*}$ were consistently lower than the observed ratio $\Delta C^{*}/\Delta S^{*}$. It must be concluded, therefore, that the electrostatic approach does not account for the values of the heat capacities of activation for reactions which involve a transition state which is more polar than the initial state.

Other objections have been raised to the general theory. Thus it has been reported that only part of the heat capacity of ionisation of weak acids can be accounted for by the electrostatic treatment[67] and that the constant isodielectric activation energies[†] predicted by the theory are not observed in practice.[59f,68] It has also been shown that the rates of ionisation of triphenylmethyl chlorides and <u>tert</u>-butyl chloride do not vary with D in the expected manner[69]. Caldin and Peacock[70] have compared experimental $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values for a number of bimolecular reactions involving an increase of polarity in the transition compared to the initial state. They have reported significant discrepancies between the two.

The simple electrostatic treatment is therefore inadequate to explain the variation of the Arrhenius parameters and an alternative approach is preferred in the present studies.

2. Solvation hypothesis.

Both S_N1 and S_N2 reactions involve the development of electric charges on passage into the transition state. It is now widely accepted that in polar solvents such charge development is facilitated by solvation forces which result from the electrostatic interaction between solvent molecules and the charged centres. The existence of these solvation forces is considered to reduce the large ionisation energy of carbon-halogen bonds to the accessible values of the activation energy which are observed for S_N1 reactions[71].

Since solvating molecules are less free to move than

[†] The solvent is varied in such a way that D remains constant as the temperature is changed.

normal molecules in the bulk of the solvent, they are less able to absorb energy and thus have a reduced heat capacity. Observations of negative partial molar heat capacities for electrolytes in solution[72] and negative changes in the heat capacity for the ionisation of weak acids[67,73] are consistent with this view.

Since both the S_N1 and S_N2 solvolyses of organic halides involve an increase in solvation on passage into the activated complex, it is to be expected that these reactions should also be associated with negative heat capacities of activation, as observed. On the simplest interpretation, the heat capacity of activation arises entirely from the increase in the number of solvent molecules attached to the activated complex, relative to the initial state[27,61].

3. Other views.

Robertson and his co-workers[75] have recently pointed out that the neutral substrates employed in solvolytic reactions usually have positive partial molar heat capacities in water. They have suggested that the observed negative heat capacities of activation in solvolysis arise from this factor and from the negative heat capacity of the highly polar complex, since

$$\Delta C^{\ddagger} = \overline{C}_t - \overline{C}_i$$

where $\overline{C}$ is the partial molar heat capacity and the subscripts i and t refer to the initial and transition state, respectively.

Moelwyn-Hughes[59d] had previously suggested that the activated complex represents a state of maximum enthalpy and that consequently the heat capacity of activation should equal $-C_i$, since $dH^{*}_{t}/dT = C_t = 0$. This interpretation is hardly tenable when it is realised that the heat capacity of the activated complex depends <u>inter alia</u> on vibrations in parts of the molecule not involved in the activation process. An earlier suggestion[76], based on the collision theory of reactions, is not considered to require serious comment now.

<u>Mechanistic interpretations.</u>

The simple solvation approach discussed on page 31 suggests that the heat capacity of activation in S_N1 solvolysis arises almost entirely from the increase in solvation on passage into the activated complex. Solvation results in an increase in the degree of order for the solvating molecules and should, therefore, cause a reduction in the entropy. It has been suggested[27,77] that this factor is mainly, if not entirely, responsible for the entropy of activation in S_N1 reactions, since the contribution from the partially heterolysed bond is likely to be small. This interpretation requires that, in unimolecular reactions, the same factor controls the magnitude of the heat capacity and entropy of activation. Therefore the ratio $\Delta C^{*}/\Delta S^{*}$ should be independent of the nature of the substrate[27]. S_N2 solvolysis is characterised by the partial covalent attachment of a single water molecule and it has been assumed[27] that the associated loss of heat capacity is approximately the same as for solvation. However the greater degree of ordering, which results from covalent binding, should result in a greater loss of entropy[69a, 74]. Thus, for negative values of ΔC^{*} and ΔS^{*}, a new criterion of solvolytic mechanism becomes available; the ratio $\Delta C^{*}/\Delta S^{*}$ should be independent of the substrate for S_N1 reactions and its value should be greater than for S_N2 solvolysis.

Measurements carried out in the laboratories at Durham have now confirmed these predictions for a variety of chlorides and bromides[28, 62]. p-Methoxybenzyl chloride was chosen as a suitable compound for the present studies of the possible concurrent operation of mechanisms S_N1 and S_N2 in substitutions by powerful nucleophiles (see Chapter I, page 23), partly on the basis of this criterion of mechanism. It was known that the value of the ratio $\Delta C^{*}/\Delta S^{*}$ for this compound in 70% aqueous acetone[29] was the same as that for benzhydryl chloride in the same medium[61b]. The latter compound was known to react entirely by the unimolecular mechanism[55b, 61b]. However at the beginning of the present work, the constancy of this ratio had still to be established for the S_N1 solvolysis of a number of structurally different halides. Results were available for the hydrolyses of tert-butyl chloride, benzylidene chloride p-methylbenzylidene chloride and benzotrichloride in 50%

aqueous acetone and the reaction of p-nitrobenzhydryl chloride with this solvent was therefore studied in an attempt to obtain further confirmation.

Robertson and his co-workers[75] have recently discussed the factors contributing to the magnitude of $\Delta C^{\ddagger}$ and $\Delta S^{\ddagger}$ for solvolysis in water. Their interpretation (see page 32) leads to the conclusion that $\Delta C^{\ddagger}$ and $\Delta S^{\ddagger}$ are affected in different ways by variations in the structure of the substrate, a conclusion which would invalidate the use of the ratio $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ as a criterion of mechanism. It may well be that the factors controlling the heat capacity and entropy of activation are not the same in pure water as in aqueous organic solvents where one of the components can "solvate" an organic substrate. Thus, for example, the entropy of activation for the hydrolysis of tert-butyl chloride in water decreases markedly on the addition of small amounts of acetone to the solvent although the change in the partial molar entropy of water is very small[59h, 62].

The hydrolysis of p-nitrobenzhydryl chloride in 50% aqueous acetone.

The hydrolysis of p-nitrobenzhydryl chloride in 50% aqueous acetone was studied at five temperatures in the range 20°-60°C. In order to permit comparison with the compounds previously investigated in this solvent, the solvent now employed was monitored by studying the rate of hydrolysis of benzotrichloride. The runs were followed by noting the development of acidity; details are given in the experimental section (page 129).

The rates and activation parameters are summarised in Table II-1, details of the individual runs are given in Appendix A, experiments 1-6, and the methods employed in the calculation of activation parameters and their errors in Appendix B.

TABLE II-1

Activation Parameters for the Reaction of p-Nitrobenzhydryl Chloride with 50% Aqueous Acetone.

Temp. °K.	10^6 k sec.$^{-1}$	Mean Temp. °K.	E kcal.		$-\Delta S^{\ddagger}$	
			obs.	calc.≠	obs.	calc.ø
293.76	5.320	298.29	22.430	22.479	8.14	8.15
302.81	16.81	307.64	22.187	22.187	9.17	9.15
312.47	52.55	317.51	21.889	21.879	10.19	10.21
322.55	158.1	328.06	21.539	21.550	11.34	11.34
333.57	479.9					

$$\frac{dE}{dT} = -31.2 \pm 0.4 \text{ (slope)}$$

$$= -31.2 \pm 2.4 \quad \sigma(E)$$

$$\Delta S^{\ddagger}_{50^\circ C.} = 10.81$$

$$E_{50^\circ C.} = 21.703$$

$$\frac{\Delta C^{\ddagger}}{\Delta S^{\ddagger}}\ 50^\circ C = 3.10$$

≠ From equation B-3 } Appendix B
ø From equation B-4 }

The results in Table II-1 show the expected decrease of activation energy with increasing temperature. Energies and entropies of activation, calculated on the assumption that $\Delta C^{\ddagger}$ is constant over the experimental temperature range, can be seen to be in good agreement with those observed.

A comparison of the present results with those previously obtained for S_N1 reactions is given in Table II-2 and it can be seen that, within the limits of experimental error, the ratio $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ for these reactions is clearly independent of the nature of the substrate. The value of this ratio is larger than for the S_N2 solvolysis of benzyl chloride[27] and its p-nitroderivative[29]. It therefore seemed likely that a valid mechanistic test could be based on the values of the ratio $\Delta C^{\ddagger}/\Delta S^{\ddagger}$.

TABLE II-2

Activation Parameters for S_N1 solvolysis in 50% Aqueous Acetone at 50°C [62].

Substrate	E	$-\Delta S^{\ddagger}$	$-\Delta C^{\ddagger}$	$\Delta C^{\ddagger}/\Delta S^{\ddagger}$
$PhCCl_3$ $\neq$	19.315	16.17	45.8	2.83 ± 0.28
$PhCHCl_2$ $\neq$	22.917	11.33	29.7	2.62 ± 0.32
$p\text{-}MeC_6H_4CHCl$ $\neq$	20.140	11.97	39.1	3.27 ± 0.31
$p\text{-}NO_2C_6H_4CHPhCl$	21.702	10.81	33.5	3.10 ± 0.22
<u>tert</u>-BuCl	19.917	10.28	27.0	2.63 ± 0.21

$\neq$ $\Delta S^{\ddagger}$ and $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ per replacable chlorine atom.

Mechanism in the hydrolysis of p-methoxybenzyl Chloride in 70% aqueous acetone.

Results already available at the commencement of the present studies had shown that $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ for the hydrolysis of p-methoxybenzyl chloride in 70% aqueous acetone had the same value as for the hydrolysis of benzhydryl chloride in the same solvent(see page 35). Mechanism S_N1 was therefore indicated for the hydrolysis of the substituted benzyl compound. Other evidence supported this view. The hydrolysis of both compounds showed almost the same sensitivity to changes in the solvent composition, and to additions of sodium perchlorate[78], and both reactions were significantly retarded by the addition of sodium chloride[29], a fact which provided clear evidence for the operation of the mass-law effect which is specific to S_N1 reactions.(compare Chapter III).

It was therefore concluded that the reaction of p-methoxybenzyl chloride with 70% aqueous acetone occurred entirely by the unimolecular mechanism (S_N1).

CHAPTER III

THE EFFECT OF ELECTROLYTES ON THE RATES OF S_N REACTIONS.

1. Qualitative discussion.

The hydrolysis of alkyl and aralphyl halides can occur either by the synchronous bimolecular mechanism (S_N2),

$$RCl + H_2O \rightleftharpoons \left[H_2\overset{+}{O}\text{---}R\text{---}\overset{-}{Cl}\right] \longrightarrow ROH + H^+ + Cl^-$$

or by the multistage unimolecular mechanism (S_N1),

$$RCl \rightleftharpoons \left[\overset{+}{R}\text{-----}\overset{-}{Cl}\right] \rightleftharpoons R^+ + Cl^-$$

$$R^+ + H_2O \longrightarrow ROH + H^+$$

Since the reagent is present in virtually constant excess in most aqueous solvents, both processes should lead to first-order kinetics, provided that in the latter the ionisation step is rate determining.

The transition states for both mechanisms are more polar than the initial states. It is therefore to be expected, by analogy with the situation for fully formed ions, that the activated complexes will be subject to ion atmosphere stabilisation in the presence of electrolytes, irrespective of their nature. This stabilisation, which leads to an acceleration of the rate of reaction, is called the "ionic-strength effect"[80]. It has much less effect on S_N2 reactions than on S_N1 reactions, due to the more diffuse disposition of charge in the bimolecular transition state.

Electrolytes containing the common anion, X^-, can cause a reversal of the ionisation of the organic halide, RX, and hence retard the rates of S_N1 reactions. This is called the "mass-law"effect"[80] and quite obviously cannot operate in S_N2 substitutions.

Clearly both effects will operate during the hydrolysis of an organic halide, even when no electrolyte is initially present, because acid is formed as the reaction procedes. Since the two effects act in opposite ways on the rate of reaction, the overall result will depend on their relative sizes. Thus constant first-order rates have been observed for the reaction of benzhydryl chloride with aqueous acetone[81], whereas the corresponding reaction of tert-butyl bromide[82] is progressively accelerated as the reaction procedes and that of dichlorodiphenylmethane[13a] is progressively retarded. However the effects are usually quite small in the dilute solutions which are normally employed in kinetic experiments and can generally be neglected.

2. Quantitative treatment.

The S_N1 hydrolysis of an organic halide, RX, procedes through the following steps.

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

$$R^+ \xrightarrow{3} ROH$$

Since stage 1 is slow (rate determining) and stages 2 and 3 are rapid, the concentration of the carbonium ion, R^+, must always be very small and it is therefore valid to apply the steady state principle to this species. It then follows that the rate coefficient, k_X, for the hydrolysis is given by ≠

$$k_X = -\frac{1}{RX} \cdot \frac{d\,RX}{dt} = \frac{k_1}{1 + \alpha X^-} \quad \ldots\ldots \text{III-1}$$

where α is called the mass-law constant and has the value k_2/k_3. The subscript numerals indicate the stage to which a given rate coefficient k refers.

Electrolytes accelerate the rates of unimolecular reactions by increasing the rates of ionisation and this is reflected in the rate coefficient k_1. The effect of electrolytes on stage 1 is given by the Bronsted equation[83] in the form

$$k_1 = k_1^\circ \frac{f_{RX}}{f_t} \quad \ldots\ldots \text{III-2}$$

≠ Throughout this thesis the normal square brackets denoting concentration are omitted. Thus for a species X, the more usual $[X^-]$ is replaced by X^- alone.

where f is the activity coefficient relative to unit value at zero ionic strength, to which k°, refers, and the subscripts RX and t indicate the initial and transition states, respectively.

Hughes, Ingold and their co-workers[80] have developed a simple electrostatic theory to account for the observed effects of uni-univalent electrolytes on S_N1 reactions.

In treating stage 1 they proposed that the effect of electrolytes on the transition state was so much more than their effect on the initial state that the latter could be neglected. A value of unity was therefore assumed for f_{RX}.

In order to calculate f_t, the transition state was regarded as a permanent dipole consisting of two point charges ($\pm$ ze) separated by a distance d. The Debye-Poisson equation for the potential ψ at a point, due to any central distribution of charge in a dilute atmosphere of univalent ions, was applied to this simple model to give the expression

$$-\log_{10} f_t = -B.(z^2d).c \qquad \ldots\ldots \text{III-3}$$

where c is the molar ionic-strength of the solution and B is a constant for a given solvent and temperature. It has the value

$$B = -\frac{1}{2.303}\cdot\frac{4\pi}{1000}\cdot\frac{Ne^4}{K^2}\cdot\frac{1}{(DT)^2} = -\frac{0.912 \times 10^6}{(DT)^2}$$

where N is Avogadro's number,

D is the dielectric constant of the medium,

$\bar{k}$ is Boltmann's constant,

T is the absolute temperature.

Equation III-3 contains one unknown parameter, $z^2d = \sigma$, which Hughes and Ingold termed the "ionic-strength" constant. It has the dimensions of length and is a measure of the ion-atmosphere stabilisation of the transition state for ionisation. It was pointed out that the expression is a limiting one, only strictly applicable to very dilute solutions. However, because of the relatively smaller variations in the density of the ion-atmospheres around dipoles, it was considered that it would apply over a greater range of concentrations than the corresponding limiting law for ions. It was also concluded that variations in molecular shape would be absorbed into the parameter σ.

Equations III-2 and III-3 were then combined and the appropriate substitution made for z^2d to give

$$k_1 = k_1^{\circ} \text{ antilog}_{10} - B\sigma c \qquad \ldots\ldots \text{ III-4}$$

The Bronsted equation was applied to stages 2 and 3 to give the effect of electrolytes on these processes; thus

$$k_2 = k_2^{\circ} \frac{f_+ \, f_-}{f_t} \; ; \qquad k_3 = k_3^{\circ} \frac{f_+}{f_{+aq}}$$

where f_+ and f_- are the activity coefficients of the carbonium ion and expelled ion X^-, respectively, relative to unit value at zero ionic strength. f_{+aq} is the activity coefficient of the transition state for the collapse of the solvation shell. Since this is associated with a very large spacial distribution of charge, it was concluded that f_{+aq} must approximate to unity. Therefore, since α is equal to k_2/k_3,

$$\alpha = \alpha^\circ \frac{f_-}{f_t} \qquad \ldots\ldots \text{III-5}$$

It was then assumed that the activity coefficient of the anion could be evaluated from Debye's limiting law.

$$-\log_{10} f_- = -Ac^{\frac{1}{2}} \qquad \ldots\ldots \text{III-6}$$

where,

$$A = \frac{1}{2.303} \cdot \sqrt{\frac{2}{1000}} \cdot \frac{N^{\frac{1}{2}} e^3}{k^{\frac{3}{2}}} \cdot \frac{1}{(DT)^{\frac{3}{2}}} = -\frac{1.815 \times 10^6}{(DT)^{\frac{3}{2}}}$$

Hence the effect of electrolytes on the mass-law constant was obtained from equations III-3, III-4 and III-6,

$$\alpha = \alpha^\circ \,\mathrm{antilog}_{10}(Ac^{\frac{1}{2}} - B\sigma c) \qquad \ldots\ldots \text{III-7}$$

Making the appropriate substitutions in equation III-1 then gave

$$k_X = -\frac{1}{RX} \cdot \frac{d\,RX}{dt} = \frac{k_1^\circ}{\mathrm{antilog}_{10} B\sigma c + \alpha^\circ / \mathrm{antilog}_{10} Ac^{\frac{1}{2}} \quad X^-/}$$

$$\ldots\ldots \text{III-8}$$

Equation III-8 predicts that the accelerating effect of added electrolytes is independent of their nature and depends only on the ionic strength. It has been applied with success to the S_N1 solvolyses of tert-butyl chloride, benzhydryl chloride, substituted benzhydryl chlorides[80,84] and dichlorodiphenylmethane[13a] in aqueous acetone. Consistent with the definition of the ionic-strength constant, viz. $\sigma = z^2 d$, this parameter was observed to have the largest values for those compounds for which the greatest charge separation in the transition state was to be expected. The mass-law constant, α°, was found to increase with increasing stability of the carbonium ion. This was considered reasonable since α° represents the rate of attack of the common anion on the carbonium ion, relative to the rate of collapse of the solvation shell around the carbonium ion.

Contrary to the predictions of this simple electrostatic theory, specific electrolyte effects have been reported on a number of occaissions. Most of these reports refer to experiments carried out in media of low dielectric constant, which may well account for some of the effects. Hughes and Ingold have pointed out[80] that their approach leads to a limiting expression, which is strictly only valid at increasingly lower concentrations of the electrolyte as the ionising power of the medium decreases. Deviations from this limiting law may well account for small effects in media of low water content.[85c]

Nash and Monk[86a] have pointed out that the effective ionic-strength could be altered by association of the ions of electrolytes to give ion-pairs. They investigated the effects of lithium, potassium and sodium bromides on the hydrolysis of <u>tert</u>-butyl bromide in aqueous acetone and concluded, after allowing for ion-pair association, that the agreement with Hughes and Ingold's theoretical expression was satisfactory. However, the validity of their conclusions is somewhat impaired by unsound mechanistic arguments. For instance, they compared their experimental integrated rates with the theoretical instantaneous values derived from equation III-4 and also neglected the mass-law effect. Never-the-less, ion-pair association may be an important factor in solvents of low dielectric constant, and could account for Speith and Olson's observation[86b] that the rates of hydrolysis of <u>tert</u>-butyl chloride and <u>tert</u>-butyl bromide were altered to different extents by lithium chloride, lithium bromide and lithium perchlorate and that the effect of each salt varied differently with changing solvent composition. Ion-pair association could also account for reports that tetra-butylammonium salts and lithium salts have different effects on the rates of racemisation, chloride exchange and solvolysis of p-chlorobenzhydryl chloride in acetone and 80% aqueous acetone[11]. This also applies to a recent report of specific electrolyte effects on the rate of solvolysis of benzhydryl chloride in 90%

aqueous bis (2-ethoxyethyl) ether.[84] However the method used to obtain the initial rates of reaction are open to criticism, and the results are not regarded as particularly important.

It is not proposed to discuss the observations of specific electrolyte effects in acetic acid which have caused Winstein and his collaborators[10] to postulate that the ionisation step in S_N1 reactions proceeds through meta-stable ion-pair intermediates (compare, however, Chapter I, page 6 for a discussion of Winstein's views). The solvent is a poor ionising medium and in fact Hughes, Ingold and their co-workers[94] have criticised Winstein's proposals on the ground that complete dissociation of the electrolytes is assumed. Moreover, it has been shown[13] that the S_N1 hydrolysis of dichlorodiphenylmethane in 70% and 75% aqueous acetone, in the presence of mixed chlorides and bromides, is consistent with the electrostatic treatment of Hughes and Ingold, a fact which argues against active participation of intermediate ion-pairs even if they are formed.

On the other hand the reports of specific electrolyte effects in good ionising solvents requires explanation. Lucas and Hammett[87] observed that the rate of S_N1 hydrolysis of tert-butyl nitrate in aqueous dioxane was affected by electrolytes in the order $ClO_4^- > NO_3^- > Cl^- > OH^-$, the latter indeed depressing the rate. The results were explained by assuming different degrees of solvation of the electrolytes by water. The resulting changes in the effective composition of binary solvent were regarded as causing the specific effects on the reaction rate, a plausible explanation since unimolecular reactions are highly sensitive to change in solvent composition. Hydroxide ions were postulated to abstract so much water as to more than cancel the accelerating effect of the increased ionic strength.

Baughmann, Grunwald and Kohnstam[88] have recently concluded, from investigations of the fugacities of the solvent components of aqueous dioxane solutions of electrolytes, that solvation of ions by both solvent components needs to be taken into account.

While admitting the plausibility of Lucas and Hammett's postulate, Benfey, Hughes and Ingold[89] have shown that differential solvation of ions could not account for the common anion retardations observed in many unimolecular solvolyses. It was shown that this was not consistent with the fact that bromide ions retard the rate of hydrolysis of benzhydryl bromide in aqueous solvents but increase the rate of hydrolysis of benzhydryl chloride. On the other hand it was observed that hydroxide ions caused a small decrease in the rate of reaction in aqueous dioxane, thus supporting Lucas and Hammett's observation with *tert*-butyl nitrate, and a similar effect was noted with ethoxide ions in ethanol. These were regarded, however, as forming a special case, only applicable to lyate ions, which were considered to distribute their charge over a large number of solvent molecules. It was proposed that the resulting proton deficiency in the solvent impaired the solvation of the polar transition state for ionisation, thus accounting for the retarding effect.

Pocker[85] has studied the effect of changing ionic-strength on the competition between water and azide ions for the triphenylmethyl cation in 75% and 50% aqueous dioxane. He found that ionised chlorides and perchlorates increased the proportion of hydrolysis for the sequence $NEt_4 > Li > Na$. The problem of the specific effects of these electrolytes was not studied by this worker, however.

More recently Duynstee, Grunwald and Kaplan[$\overset{9}{80}$] have observed specific electrolyte effects on the solvolysis of neophyl p-toluenesulphonate and on the racemisation of L-(+)-threo-3-phenyl-2-butyl p-toluenesulphonate in 50% aqueous dioxane. These reactions follow the unimolecular path and the measured rate represented the rate of ionisation. These authors developed a theory to account for their observations, which is based on an extension of Lucas and Hammett's original suggestion (see page 48). In particular, they proposed that the effect of electrolytes on both the initial and transition states must be taken into account.

Some earlier studies[91] of the solubilities of non-electrolytes in aqueous dioxane had shown that the effect of electrolytes on the activity coefficients of a non-electrolyte could be expressed by the equation

$$K_s = \frac{d \ln f_{RX}}{dc} = A_{RX} + B_{RX}\left(\frac{\partial \mu^\circ_{RX}}{\partial x_1}\right)_c \frac{d\mu^\circ_{\pm}}{dx_1} \qquad \text{. III-9}$$

where K_s is the Setschenow constant,

f_{RX} is the molar activity coefficient of the non-electrolyte, RX, relative to unit value at zero ionic-strength,

c is the molar concentration of the electrolyte,

x_1 is the mole fraction of water in the solvent,

μ°_{RX} is the standard chemical potential of the non-electrolyte,

$\mu^\circ_{\pm}$ is the mean standard ionic chemical potential of the electrolyte. The differentials represent their change with variation in solvent composition.

A_{RX} and B_{RX} are empirical constants.

A_{RX} is analogous to the electrostatic term employed by Long and McDevitt[92] in discussing salting-in and salting-out, and it can also be related to the electrostatic ionic strength term of the Hughes/Ingold treatment of electrolyte effects in S_N1 solvolysis. B_{RX} is rather insensitive totthe nature of the non-electrolyte.

S_N1 processes were treated by applying equation III-9 to the initial state, and assuming that a similar expression, with different constants, A_t and B_t, could also be applied to the transition state for ionisation. Differentiation of the Bronsted equation (III-2), in its logarithmic form, with respect to electrolyte concentration and comparison with the appropriate form of equation III-9 then gave

$$\frac{d\ \ln k_1}{dc} = (A_{RX} - A_t) + \left(B_{RX}\frac{d\mu^\circ_{RX}}{dx_1} - B_t\frac{d\mu^\circ_t}{dx_1}\right)\frac{d\mu^\circ_\pm}{dx_1}$$

. . . . . . III-10

where the subscripts RX and t refer to the initial and transition states, respectively, and k_1 is the rate coefficient for ionisation.

$(A_{RX} - A_t)$ was then combined in a single constant, C', and a quantity B' defined by the relationship

$$B' = \left(B_{RX}\frac{d\mu^\circ_{RX}}{dx_1} - B_t\frac{d\mu^\circ_t}{dx_1}\right)\Bigg/\left(\frac{d\mu^\circ_{RX}}{dx_1} - \frac{d\mu^\circ_t}{dx_1}\right)$$

These values were substituted in equation III-10 to give

$$\frac{d\ \ln k_1}{dc} = C' + B'\left(\frac{d\mu^\circ_{RX}}{dx_1} - \frac{d\mu^\circ_t}{dx_1}\right)\frac{d\mu^\circ_\pm}{dx_1}$$

. . . III-11

Since the Gibb's free energy of activation, ΔG^*, is given by

$$-\frac{\Delta G^*}{RT} = \ln k^\circ - \ln\frac{\bar{k}T}{h}$$

where $\bar{k}$, h and R are universal constants and T is the absolute temperature (compare pages 27 and 43) the term in the bracket on the right hand side of equation III-11 was modified in the following way.

$$\frac{d\mu^{\circ}_{RX}}{dx_1} - \frac{d\mu^{\circ}_{t}}{dx_1} = -\frac{d\,\Delta G^{\ddagger}}{dx_1} = RT\,\frac{d\ln k^{\circ}_1}{dx_1}$$

at constant temperature. This substitution was made in equation III-11 to give

$$\frac{d\ln k_1}{dc} = C' + D\left(\frac{d\ln k^{\circ}_1}{dx_1}\right)\frac{d\mu^{\circ}_{\pm}}{dx_1} \quad \ldots\ldots \text{III-12}$$

where $D = RT.B'$

It is considered necessary to emphasise, at this point, the factors governing the empirical constants C' and D. Both are governed by the solvent, the temperature and the nature of the substrate but are independent of the nature of the electrolyte. C' may be correlated with the Hughes/Ingold electrostatic ionic-strength term and then has the value $-2.303B\alpha$. (compare page 42).

Equation III-12 predicts specific electrolyte effects on S_N1 reactions if the value of $d\mu^{\circ}_{\pm}/dx_1$ depends on the nature of the electrolyte. Fugacity measurements on solutions of electrolytes in 50% aqueous dioxane have shown that this is indeed the case[86].

Duynstee, Grunwald and Kaplan were able to integrate equation III-12 by assuming that the parameters, C' and D', and the differentials were independent of the concentration of the electrolyte; hence they obtained the expression

$$S' = \frac{1}{c} \ln \frac{k_1}{k_1^{\circ}} = C' + D \left(\frac{d \ln k_1^{\circ}}{dx_1} \right) \frac{d\mu^{\circ}_{\pm}}{dx_1} \quad . . . . \text{III-13}$$

Equation III-13 predicts that for a given solvent, temperature and substrate, S' should vary in a linear fashion with $(d\mu^{\circ}_{\pm}/dx_1)$. This was confirmed with heophyl p-toluenesulphonate as the substrate and simple inorganic salts, but large discrepancies were noted for electrolytes having large organic ions. With L-(+)-threo-3-phenyl-2-butyl p-toluenesulphonate, although most of the plotted points lay on a straight line, it appeared that a second line could be drawn through the points for the sodium halides with that for the chloride common to both. Electrolytes with large organic ions did not correspond with either line. Short range interactions between the substrate and the electrolyte were therefore regarded as becoming significant for the exceptional cases and it was considered possible, but unlikely, that some degree of S_N2 attack was occuring with the halide ions and the phenylbutyl compound.

This approach is open to criticism since it is assumed that electrolytes affect the activities of non-electrolytes in saturated solutions in the same way as they affect their activities in solutions which are far from saturated. It is further assumed that the initial state and the polar state for ionisation are subject to similar effects. However, there is little doubt that electrolytes have specific effects on S_N1 reactions, and this approach represents the best theory available at the moment. It would appear that electrolytes may influence reactions on three ways;

(i) By ion-atmosphere stabilisation of the transition state. This electrostatic effect is independent of the nature of the electrolyte and is given by the parameter C'(equation III-13).

(ii) By an effect which depends on the solvation of the electrolyte and is defined by the second term on the right hand side of equation III-13.

(iii) By short-range interactions between the electrolytes and the substrate. These effects are not amenable to treatment, since nothing is known of their nature.

In the present work it was proposed to examine the effects of added electrolytes on the rate of reaction of p-methoxybenzyl chloride in aqueous acetone. Attack by both S_N mechanisms is feasible with this compound when the reagents are better nucleophiles than water, and any detailed analysis of the results obtained in the present systems clearly requires a knowledge of the effects of electrolytes on the rate of ionisation of the substrate. Shillaker[29] had previously observed specific electrolyte effects on the S_N1 reactions of benzhydryl chloride and p-methoxybenzyl chloride, and had also shown that both compounds were similarly affected by changes in the solvent composition and by additions of sodium perchlorate[79]. An attempt was therefore made to obtain a measure of the effect of electrolytes on an ionisation process by also studying the effect of electrolytes on the rate of reaction of benzhydryl chloride in the same solvent. It was assumed that this compound was not subject to S_N2 attack by the present reagents (compare Chapter I, page 25). It was hoped, incidently, that these experiments would supply additional evidence for the specific effects of electrolytes on S_N1 processes. The results are discussed in the next chapter.

CHAPTER IV

THE EFFECT OF ELECTROLYTES ON THE RATES OF REACTION OF BENZHYDRYL CHLORIDE AND p-METHOXYBENZYL CHLORIDE IN 70% AQUEOUS ACETONE.

1. Results.

The solvolyses of approximately 0.02 molar solutions of benzhydryl chloride and p-methoxybenzyl chloride in 70% aqueous acetone were studied at 20.08°C. The effects of added $NaClO_4$, $NaBF_4$, $PhSO_3Na$, $NaNO_3$, Me_4NF, HCl, NaCl, KBr and NaN_3 on the rates of disappearance of the halides (rate coefficient k_{Cl}) and on the rates of hydrolysis (rate coefficient k_H) were determined. Reactions were followed by noting the development of chloride ions and the development of acidity. The effects of ionised chlorides were also studied by working with the organic chlorides containing Cl^{36} and noting the appearance of radio-activity in the reaction products (rate coefficient k_E). Full details are given in Chapter VII and details of the kinetic runs in Appendix A, pages 173-217.

The integrated first-order rate coefficients (k_{Cl}, k_H and k_E) usually stayed constant throughout the course of the reaction but decreasing values of k_{Cl} were obtained when NaN_3 was present in small amounts, probably because of the reduction in the concentration of N_3^- resulting from the formation of RN_3 and undissociated HN_3. The values of k_E

also decreased slightly for the experiments with p-methoxybenzyl chloride and 0.1 molar sodium chloride, probably because the rapid rate of chloride exchange caused the concentration of active chloride ions to approach the equilibrium value.

Increasing values of k_H, which approached the constant values of k_{Cl}, were obtained for the reaction of the same substrate in the presence of KBr and $NaNO_3$. This probably arose from the formation of significant amounts of the organic bromide and nitrate, and for these reactions only the values of k_{Cl} (or the values of k_H referred to a "zero" reading taken after the reaction had proceeded for some time) will be considered in this chapter.

The effect of 0.05 molar concentrations of the electrolytes[ø] on the rates of reaction of the organic halide (rate coefficients $k_X = k_{Cl}$ or k_E)[≠] are summarised in Table IV-1.

[ø] It was assumed that the percentage change in the rate due to the addition of electrolyte varied in a linear fashion with the concentration of the electrolyte. While this was not strictly the case for the cases where a stable product was formed ($Y^- = N_3, F^-$), the errors arising from this assumption are not important in a qualitative discussion.

[≠] In some cases where $k_{Cl} = k_H$ (compare Chapter VII, page 138) the latter values are used, without comment, in the tables of results given in this chapter.

TABLE IV-1

The Effect of Electrolytes on the Rates of Reaction of Benzhydryl Chloride and p-Methoxybenzyl Chloride in 70% Aqueous Acetone at 20.08°C.

Added Electrolyte	% change in k_X on addition of 0.05M. electrolyte	
	$PhCH_2Cl$	$MeOC_6H_4CH_2Cl$
$NaClO_4$	+15.08[b]	+15.93
$NaBF_4$	+11.96	+13.13
$PhSO_3Na$	+ 5.70	+10.91
$NaNO_3$	+ 6.85	+14.24
Me_4NF	- 5.21	+ 1.96
NaCl	+ 2.38[†]	+16.30[†]
HCl	+ 7.02[†]	+21.62[†]
KBr	+ 9.15	+25.67
NaN_3	+11.20[‡]	-
‡ NaCl (0.1)	+ 1.90[†]	+13.39[†]
NaCl (0.025)	+ 2.95[†]	+17.67[†]
NaN_3 (0.02)	+ 8.41	+48.96
NaN_3 (0.03)	+ 8.94	+60.13
NaN_3 (0.04)	-	+62.69

ø From results obtained by Shillaker[29].

≠ Referred to an initial electrolyte concentration of 0.05 M. electrolyte.

‡ Calculated from experiments where the electrolyte concentration was not 0.05 M. by assuming that the percentage change in k_X varies linearly with electrolyte concentration. The initial concentration is indicated in the brackets.

Since only S_N1 substitution is possible with benzhydryl chloride, the values of k_X for this compound are usually very nearly the same as k_1, the rate coefficient for ionisation (see Appendix C). The figures in Table IV-1 thus represent the percentage change in the rate of ionisation due to the added electrolytes and hence are a measure of the ionic-strength effect. It is evident that each electrolyte has a different effect on the rate of ionisation, contrary to the requirements of the electrostatic theory of Hughes and Ingold. Ion-atmosphere stabilisation of the transition state for ionisation (ionic-strength effect) requires that all electrolytes should accelerate the rate of ionisation of organic compounds. It is impossible, therefore, to account for the observed retardation of the rate of reaction of benzhydryl chloride by added tetramethylammonium fluoride in terms of ion-pair association of the electrolyte or departures from the limiting-law.

p-Methoxybenzyl chloride hydrolyses entirely by mechanism S_N1 (see Chapter II, page 37) but, unlike benzhydryl chloride, it is not sterically unfavourable to S_N2 attack. The following interesting points emerge from a consideration of the results given in Table IV-1. $NaClO_4$ and $NaBF_4$, whose anions are such poor nucleophiles that they are unlikely to react with the substrate by either of the S_N mechanisms, have much the same effect on the rates of hydrolysis of benzhydryl chloride and p-methoxybenzyl chloride. Other electrolytes, however, accelerate the rate of reaction of the latter compound more than that of the former, and the difference between the effects produced by a given electrolyte increases in the order $NaClO_4 \approx NaBF_4 < PhSO_3Na < NaNO_3 \approx Me_4NF < NaCl \approx HCl < KBr < NaN_3$; that is in the order of increasing nucleophilic power of the anions[14]. This suggests that the differences arise from an increasing degree of S_N2 attack on p-methoxybenzyl chloride as the electrolyte is changed along this series. It is interesting to note that this arrangement of the electrolytes is in no way connected with their effects on the rate of ionisation of benzhydryl chloride.

Before it is possible to discuss the S_N2 substitutions of p-methoxybenzyl chloride, it is necessary to establish the effect of electrolytes on S_N1 ionisation. The quantitative treatment of this problem will, therefore, now be discussed.

2. The Effect of Electrolytes on the Rates of Ionisation of Organic Halides.

Duynstee, Grunwald and Kaplan[90] considered that electrolytes altered the rates of S_N1 reactions by affecting the activities of both the initial and transition states for ionisation. By assuming that the effects for both states could be expressed by equations of the same form, they derived a theoretical expression (III-12) for the effect of electrolytes on the rate of ionisation and were able to integrate it by assuming that the various parameters and differentials were independent of the concentration of the electrolyte. The approach has been discussed in detail in the preceding chapter. Their final expression (III-13) has the form

$$S = \frac{1}{c} \ln \frac{k_1}{k_1^0} = C + D \frac{d \ln k^0}{dx_1} \frac{d\mu_\pm^\circ}{dx_1}$$

where c is the molar concentration of the electrolyte,

k_1 is the rate coefficient for ionisation in the presence of electrolyte,

k_1^0 is the rate coefficient for ionisation at zero ionic strength,

x_1 is the molar fraction of water in the solvent,

$\mu_\pm^\circ$ is the mean ionic standard chemical potential of the electrolyte,

C and D are constants which depend on the solvent,

temperature and the nature of the substrate but
are independent of the nature of the electrolyte.

For the purposes of the present discussion, this equation may be related to the experimental data for 0.05 M. electrolytes when it may be conveniently written in the form

$$S = \frac{1}{0.05} \log \frac{k_1}{k_1^o} = C + D \frac{d \log k_1^o}{dx_1} \frac{d\mu_{\pm}^o}{dx_1} \quad \ldots\ldots \text{IV-1}$$

with the parameter C equal to $C'/2.303$.

In the present studies k_X is usually equal to k_1 to a very close approximation (see Appendix C) to that equation IV-1 can be modified to

$$S = \frac{1}{0.05} \log \frac{k_X}{k_X^o} = C + D \frac{d \log k_X^o}{dx_1} . \frac{d\mu_{\pm}^o}{dx_1} \quad \ldots\ldots \text{IV-2}$$

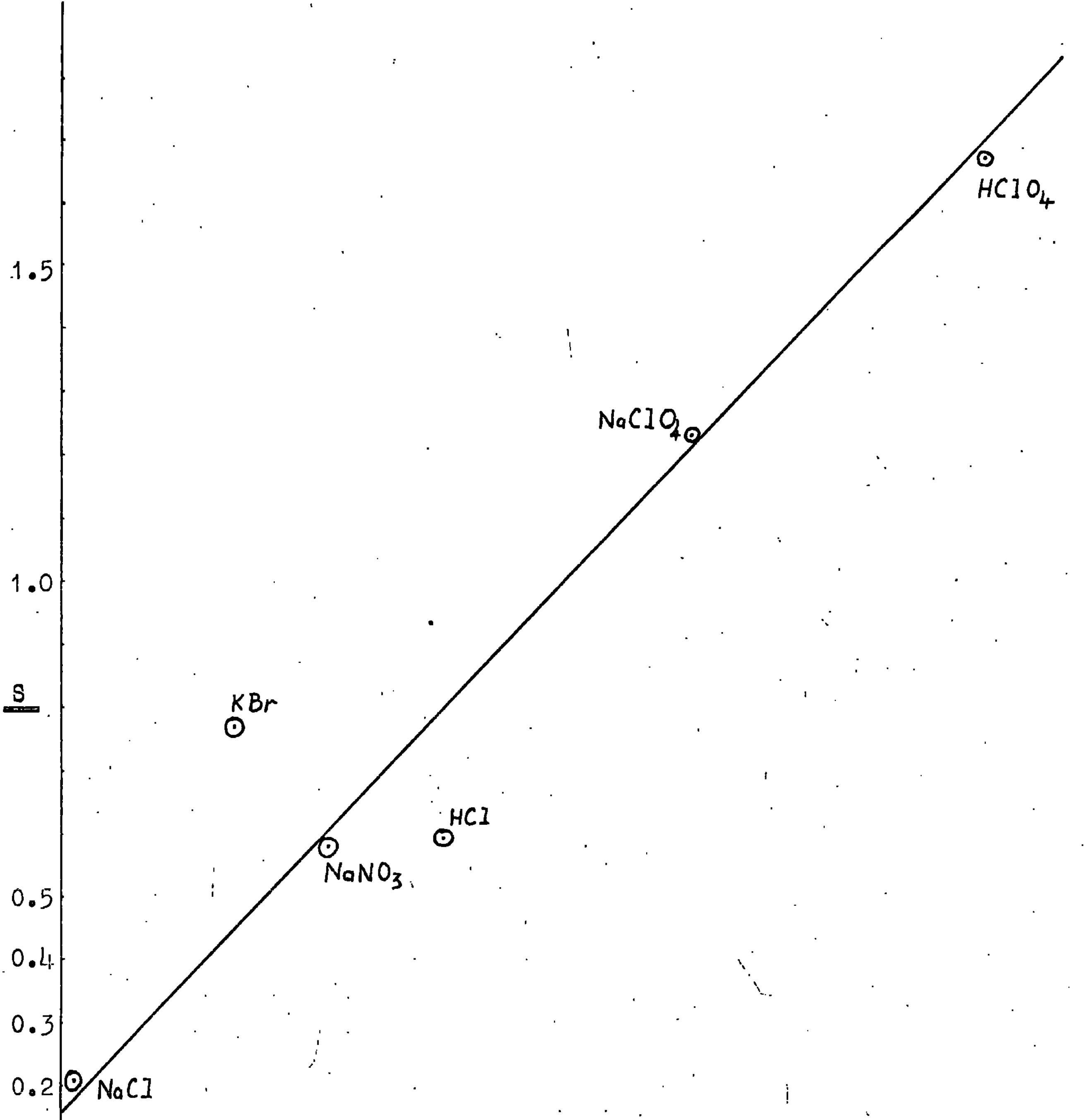
where k_X^o is the rate coefficient for the reaction in the absence of added electrolyte. Since its value was invariably determined by observing the development of acidity, $k_X^o = k_H^o$.

k_X is the rate coefficient for the overall reaction of the substrate in the presence of added electrolyte.

At constant temperature and with a given substrate, C, D and $(d \log k_X^o)/dx_1$ are constant, so that S should vary in a linear manner with $d\mu_{\pm}^o/dx_1$ (compare Chapter III, page 54).

Unfortunately no rigorous test of equation IV-2 is possible with the present results, since no values of $d\mu^\circ_\pm/dx_1$ are available for aqueous acetone solutions. However, it can be seen from Table IV-2 that the values for 50% aqueous dioxane[88] vary in much the same manner as the present values of S for the reactions of benzhydryl chloride in 70% aqueous acetone containing electrolytes. The only clear exception occurs with potassium bromide. In Figure IV-1 the values of S are plotted against the available values of $d\mu^\circ_\pm/dx_1$ for 50% aqueous dioxane. Most of the points lie on a straight line, but those for potassium bromide and hydrochloric acid are exceptions. It is probably incorrect to assume an exact correlation between the values of $d\mu^\circ_\pm/dx_1$ for aqueous acetone and aqueous dioxane solutions, which may account for these anomalous results. However, Duynstee, Grunwald and Kaplan have noted that potassium bromide has a similarly anomolous effect on the rate of ionisation of L - (+) - threo - 3 - phenyl - 2 - butyl p-toluene sulphonate in 50% aqueous dioxane. Since the bromide ion is a fairly powerful nucleophile, it is possible that bimolecular attack by this reagent on the phenyl-butyl compound in aqueous dioxane and on benzhydryl chloride in the present solvent needs to be considered. Steric factors make this form of substitution unlikely in the present studies[55b], and other evidence leads to the same conclusion[17, 61b, 89]. Moreover, sodium perchlorate and sodium borofluoride, whose weakly nucleophilic anions

FIGURE IV-1


HClO4
NaClO4
KBr
HCl
NaNO3
NaCl
1.5
1.0
S
0.5
0.4
0.3
0.2
0.0
-14
-12
-10
-8
-6
-4
-2
0
+2
$2\frac{d\mu_{\pm}^{\circ}}{dx_1}$

probably do not react with benzhydryl chloride by either of the S_N mechanisms, accelerate the rate of reaction of this compound much more than potassium bromide does. If S_N2 attack by bromide ions were appreciable, it would be expected that azide ions would be even more effective, since their nucleophilicity is greater. Table IV-1 shows, however, that the effect of sodium azide on the rate of reaction is less than that of sodium perchlorate. It must be held, therefore, that bimolecular attack by bromide ions on benzhydryl chloride is not indicated by the present results and the same must apply to azide ions.

TABLE IV-2

The effect of 0.05 M. Electrolyte on the Rate of Reaction of Benzhydryl Chloride in 70% Aqueous Acetone at 20.08°C.

Electrolyte	$\frac{k_X}{k_X^o}$	$2.\frac{d\mu^{\circ}}{dx_1}$ k cal.
$HClO_4$	1.2111 ≠	+ 0.6
$NaClO_4$	1.1507	- 4.0
$NaBF_4$	1.1196	-
NaN_3	1.1120	-
KBr	1.0919	-11.3
HCl	1.0702	- 7.9
$NaNO_3$	1.0685	- 9.8
$PhSO_3Na$	1.0570	-
NaCl	1.0237	-13.8
Me_4NF	0.9500	-

≠ From results obtained by Shillaker[29].

≠ Data for electrolytes in 50% aqueous dioxane[38].

In view of the qualitative agreement between the present values of S for benzhydryl chloride in 70% aqueous acetone and those of $d\mu_1^\circ/dx_1$ for 50% aqueous dioxane, it seems worth while comparing the results with other requirements of equation IV-2. It has been considered convenient, however, to employ a different approach[95] to that of Duynstee, Grunwald and Kaplan in order to obtain this equation. Lucas and Hammett[87] suggested that electrolytes, in addition to their electrostatic effects on reactions, alter reaction rates by changing the "effective" solvent composition. The final result is thus the sum of an effect depending only on the concentration of the elctrolyte at constant solvent composition and an effect due to a change in the solvent composition. Making the plausible assumption that, for the present dilute solutions, the dependence of rate on solvent composition is independent of the concentration of the electrolyte, the total effect on the rate of ionisation can be expressed in the form

$$\frac{d\ \ln k_1}{dc} = \left(\frac{\partial\ \ln k_1}{\partial c}\right)_{\chi} + \frac{d\chi}{dc}\left(\frac{\partial x_1}{\partial \chi}\right)_{c=0}\left(\frac{d\ \ln k_1^\circ}{dx_1}\right) \quad \ldots\ldots \text{IV-3}$$

where c is the concentration of the electrolyte,

x_1 is the mole fraction of water in the solvent

χ is a measure of the effective solvent composition.

The first term on the right hand side of equation IV-3 can be correlated with the electrostatic ionic-strength effect of Hughes and Ingold (see Chapter III, page 40), since it expresses the dependence of rate on the concentration of the electrolyte, independent of its nature. The second term represents the influence of changes in the effective solvent composition due to solvation of the electrolyte. It seems reasonable to assume a simple relation between χ and the activities of the solvent components. Grunwald and Bacarella[97] have shown that the activities of the solvent components, a_1 and a_2, are related to the mean standard ionic chemical potential of the electrolyte, $\mu^{\circ}_{\pm}$, by the expression

$$\frac{d \ln a_1/a_2}{dc} = \frac{2M_{12}}{1000RT} \frac{d\mu^{\circ}_{\pm}}{dx_1}$$

where R is the gas constant, T the absolute temperature and M_{12} the molar weight of the binary solvent; $d\chi/dc$ is therefore proportional to $d\mu^{\circ}_{\pm}/dx_1$. Hence making this substitution in equation IV-2 and integrating the resulting expression, with respect to electrolyte concentration, assuming that the parameters and differentials are independent of this variable, leads to

$$\frac{1}{c} \cdot \ln \frac{k_1}{k_1^{\circ}} = \left(\frac{\partial \ln k_1}{\partial c}\right)_{\chi} + P\left(\frac{\partial x_1}{\partial \chi}\right)_{c=0} \left(\frac{d \ln k_1^{\circ}}{dx_1}\right) \frac{d\mu^{\circ}_{\pm}}{dx_1}$$

where P is a proportionality constant relating $d\mu^{\circ}_{\pm}/dx_1$ to $d\chi/dc$.

For 0.05 M. electrolyte this becomes equation IV-2 with, however, the following difference. Since D involves only the constant P and the differential $(\partial x_1/\partial \chi)_{c=0}$, which depends only on the solvent and the temperature, this parameter is now independent of the nature of the substrate and the electrolyte. For a given substrate, RX, and a given electrolyte, MY, equation IV-2 can thus be conveniently written in the form

$$S_{RX.MY} = C_{RX} + D.\ E_{MY}\ F_{RX} \quad \ldots\ldots\ldots \quad \text{IV-4}$$

where D is a constant for a given solvent and temperature and is independent of the nature of the electrolyte or substrate.

E_{MY} is equal to $d\mu^{o}_{\pm}/dx_1$ and is independent of the nature of the substrate.

C_{RX} and F_{RX}, which is equal to $(d \log k^{o}_{1})/d x_1$, are independent of the nature of the electrolyte but depend on the nature of the substrate.

It is now possible to consider and test the requirements of equation IV-4 and thus attempt to establish the validity of the present approach. This will now be done.

The difference between the effects of a given electrolyte on two different substrates (RX and R'X), which react entirely by mechanism S_N1, is obtained by subtraction of the corresponding forms of equation IV-4; thus

$$S_{RX} - S_{R'X} = (C_{RX} - C_{R'X}) + D.\ E_{MY}\ (F_{RX} - F_{R'X})$$

Since F_{RX} and $F_{R'X}$ measure the sensitivity of the two compounds to changes in the composition of the solvent, this expression reduces to

$$S_{RX} - S_{R'X} = \frac{1}{0.05} \cdot \log \frac{\left(k_X/k_X^{o}\right)_{RX}}{\left(k_X/k_X^{o}\right)_{R'X}} = C_{RX} - C_{R'X} \quad . \; . \quad IV\text{-}5$$

for two substrates with the same values of $F = (d \log k^{o})/dx_1$. Under these conditions $(S_{RX} - S_{R'X})$ should therefore be independent of the nature of the electrolyte.

Benzhydryl chloride, p-methoxybenzyl chloride and p-phenoxybenzyl chloride all hydrolyse by mechanism S_N1 in aqueous acetone solutions[28] and it has been shown[29, 96] that the rate of each reaction is affected to very nearly the same extent by changes in the water content of the binary solvent. This is shown in Table IV-3. Since perchlorate and borofluoride ions are even less powerful nucleophiles than water, no S_N2 attack by these anions should occur with the present systems and hence equation IV-5 should be obeyed. The appropriate data are available from the present studies and those of Shillaker[29] and Kohnstam and Ribar[96], and it is shown in Table IV-4 that the ratio $\dfrac{(k_X/k_X^{o})_{RX}}{(k_X/k_X^{o})_{Ph_2CHCl}}$, with RX = p-$MeOC_6H_4CH_2Cl$ and p-$PhOC_6H_4CH_2Cl$, depends only on the nature of RCl as required by the present approach[≠].

≠ It is easily shown from the definition of S (see equations IV-1 and IV-2) that a constant value of $(S_{RX} - S_{R'X})$ is equivalent to a constant value of $\frac{(k_X/k_X^o)_{RX}}{(k_X/k_X^o)_{R'X}}$ when the k_X values refer to the same electrolyte concentrations.

TABLE IV-3

Solvent Effects in Unimolecular Solvolysis in Aqueous Acetone at 20.00°C.

	Substrates		
	Ph_2CHCl	$MeOC_6H_4CH_2Cl$	$PhOC_6H_4CH_2Cl$
$\log \frac{(k_X^o)_{50\%}}{(k_X^o)_{70\%}}$	-	1.4610‡	1.4041/
$\log \frac{(k_X^o)_{70\%}}{(k_X^o)_{80\%}}$	0.8577‡	0.8750‡	-

‡ From results obtained by Shillaker[29]

/ From results communicated by Kohnstam and Ribar.

TABLE IV-4

Values of the Ratio $\frac{(k_X/k_X^o)_{RX}}{(k_X/k_X^o)_{Ph_2CHCl}}$ for the effect of

0.05 M. Electrolytes on Unimolecular Solvolysis in 70% Aqueous Acetone at 20.08°C.

Electrolyte	Substrate	
	$MeOC_6H_4CH_2Cl$	‡$PhOC_6H_4CH_2Cl$
$HClO_4$	-	0.9742
$NaClO_4$	1.0074	0.9761
$NaBF_4$	1.0105	0.9812

‡ From results obtained by Kohnstam and Ribar[96].

Baughman, Grunwald and Kohnstam[88] have shown that the value of $d\mu_{\pm}^{o}/dx_1$, which is designated by E_{MY} in the present discussion, is largely controlled by the solvation of the individual ions in solution. It is therefore reasonable to assume, for a given electrolyte MY, that the ions independently and additively contribute to this factor; hence

$$E_{MY} = E_{M^+} + E_{Y^-}$$

A similar expression will apply to any other electrolyte and if this has the same anion, Y^-, but a different cation, M'^+, then for a given solvent, temperature and substrate

$$E_{MY} - E_{M'Y} = E_{M^+} - E_{M'^+} \quad \ldots\ldots \text{IV-6}$$

Subtraction of the appropriate forms of equation IV-4 for the effects of two electrolytes, with the same anion, on a given substrate, and comparison with equation IV-6, leads to the expression

$$S_{MY} - S_{M'Y} = \frac{1}{0.05} \log \frac{(k_X/k_X^o)_{RX.MY}}{(k_X/k_X^o)_{RX.M'Y}} = D.F_{RX} (E_{M^+} - E_{M'^+})$$

Thus $(S_{MY} - S_{M'Y})$ is independent of the nature of the anion and should, moreover, have the same value for all substrates which have the same value for F_{RX}. This latter requirement is met by benzhydryl, p-methoxybenzyl and p-phenoxybenzyl chlorides in aqueous acetone (compare page 70 and Table IV-3). Appropriate experimental data are available for these three compounds and the electrolyte pairs $HClO_4/NaClO_4$ and $HCl/NaCl$[≠] in 70% aqueous acetone. Table IV-5 gives values of the ratio $\frac{(k_X/k_X^o)_{HY}}{(k_X/k_X^o)_{NaY}}$ and it can be seen that the values are constant, in agreement with the predictions of the present approach.

[≠] When the added electrolyte is hydrochloric acid the concentration of this species increases throughout the course of the experiment due to hydrolysis of the substrate. The mean concentration for the kinetic run will thus be higher than the initial value. It must be emphasised that the rate data for the effect of acid and salt must refer to the same initial value of 0.05 M. electrolyte.

TABLE IV-5

Values of the Ratio $\frac{(k_X/k_X^o)_{HY}}{(k_X/k_X^o)_{NaY}}$ for the effects of 0.05 M. Electrolytes on Unimolecular Solvolysis in 70% Aqueous Acetone at 20.08°C.

Anion	Substrate		
	Ph_2CHCl	$MeOC_6H_4CH_2Cl$	‡$PhOC_6H_4CH_2Cl$
ClO_4^-	1.0524 ≁	-	1.0512
Cl^-	1.0543	1.0546	1.0483

‡ From results communicated by Kohnstam and Ribar.

≁ Data for $HClO_4$ were obtained by Shillaker[29].

It would therefore appear that the requirements of equation IV-4 are obeyed and that the treatment on which this equation is based can be accepted. As a result, the effect of electrolytes on the rate of ionisation of p-methoxybenzyl chloride can be obtained from their effect on the rate of ionisation of benzhydryl chloride by using equation IV-5, since the two compounds are equally sensitive to changes in the solvent; i.e. they have the same value for F_{RX} (compare page 70)

3. Calculation of the Effect of Electrolytes on Rates of Ionisation.

The present discussion has so far been based on the assumption that $k_1/k_1^o = k_X/k_X^o$ for S_N1 reactions. Strictly, this is not correct (though the error caused by this assumption is usually very small) since the overall rate (k_X) is affected by the operation of mass-law effects. In the quantitative treatment of the effect of electrolytes on the rates of ionisation of the present compounds it has been found to be more convenient to employ the Hughes/Ingold formulation

$$k_1 = k_1^o \ \text{antilog}_{10} - B\sigma^{MY}c^{MY} \quad \ldots\ldots \ \text{IV-6}$$

but it must be recognised that the "ionic-strength" parameter, σ^{MY}, now depends on the nature of the substrate <u>and</u> on the nature of the electrolyte. Comparison of equations IV-1, IV-4 and IV-6 shows that

$$-B\sigma^{MY} = C_{RX} + D.\,E_{MY}.\,F_{RX}$$

and, since F_{RX} has the same value for p-methoxybenzyl chloride and benzhydryl chloride, (compare page 70) it follows that for a given electrolyte

$$\sigma^{MY}_{RX} - \sigma^{MY}_{R'X} = -\frac{1}{B}\left(C_{RX} - C_{R'X}\right) = \text{Constant} \ .\ .\ \text{IV-7}$$

The value of $(\sigma_{RX}^{MY} - \sigma_{R'X}^{MY})$ is therefore independent of the nature of the electrolyte and values of σ for the reactions of p-methoxybenzyl chloride in the presence of electrolytes may thus be obtained from the corresponding values for benzhydryl chloride, provided that the constant in equation IV-7 can be determined. This should be possible from experiments with these two compounds in 70% aqueous acetone containing unreactive electrolytes.

In practice at least two electrolyte species are present in most experiments (the added electrolyte and the acid produced by hydrolysis) and equation IV-6 must therefore be written in the more general form

$$k_1 = k_1^o \text{ antilog}_{10} - B\sum\sigma_i c_i \qquad \text{. . . . . IV-8}$$

where $\sum\sigma_i c_i$ sums the effect of all the electrolytes present.

Before discussing the application of this expression to the determination of the σ parameters it is necessary to consider an experimental difficulty which now arises. The rate coefficients so far considered refer to instantaneous values, as do the theoretical rate equations derived in Chapter III. On the other hand, the experimental measurements are more conveniently, and more accurately, reported in the form of integrated rate coefficients. Admittedly, the theoretical expressions could be integrated but this procedure would have to be carried out graphically for each kinetic run, a very lengthy task.

Fortunately a shorter approach was available.

In the present studies the integrated first-order rate coefficients were generally constant throughout the course of the reactions, and where this was not the case[≠] the variations were only small. It seems reasonable, therefore, to assume that the integrated rate coefficient, $\bar{k}$, for the time interval 0 - t represents the instantaneous value at t/2. The concentrations of the various species, to which this instantaneous rate coefficient refers are also those at t/2. The mean of the integrated rates may then be equated to the instantaneous value at the stage when

$$Cl^- = Cl^-_\infty - RCl_0^{\frac{1}{2}}/n . \sum RCl_t^{\frac{1}{2}}$$

where n is the number of determinations of $\bar{k}$ and the subscript t refers to the experimental sampling time. Full details of the derivation and application of these expressions are given in the experimental section (pages 143-145). The validity of the assumption is examined and confirmed in Appendix E

When the anion of the added electrolyte reacts with the carbonium ion to give a product, RY, the reaction scheme outlined previously (Chapter III, page 42) must be extended to include the steps

$$R^+ + Y^- \underset{5}{\overset{4}{\rightleftharpoons}} RY$$

where k_5 may be negligibly small (e.g. $Y^- = N_3^-$). The

[≠] The exceptional cases have already been discussed on page 57.

substituting anion, Y^-, therefore competes with water for the carbonium ion in the same way that the common anion, X^-, does. A competition factor β may thus be defined by the ratio k_4/k_3 and is thus similar to the mass-law constant, $\alpha = k_2/k_3$.

The Parameters α, β and σ for the Reactions of Benzhydryl Chloride in 70% Aqueous Acetone containing Electrolytes.

The appropriate rate equations and methods of calculation used to obtain the parameters α, β and σ for the reactions of benzhydryl chloride in 70% acetone containing 0.05 M. electrolytes are fully described in Chapter VII (pages 146-156) and the values are given in Table IV-6.

TABLE IV-6

The Rates of Reaction of Benzhydryl Chloride with 70% Aqueous Acetone containing 0.05 M. Electrolytes.

Electrolyte	(k_X/k_X^0)	$10^8\sigma$	α	β
$NaClO_4$	1.1507	1.80	-	0
$NaBF_4$	1.1196	1.46	-	0
$PhSO_3Na$	1.0570	0.71	-	-
$NaNO_3$	1.0685	0.86	-	-
Me_4NF	0.9500	-0.68	-	0.54
NaCl	1.0237	0.30	2.35‡	-
HCl	1.0702	0.89	2.25‡	-
KBr	1.0915	1.13	-	-
NaN_3	1.1120	1.81	-	6.46

‡ These are experimental values. In calculating the values a mean value of 2.30 was assumed for α.

(i) The σ values.

It can be seen that the σ values closely follow the same sequence as the observed values of k_X/k^o_X for 0.05 M. electrolyte, as would be expected from the present treatment. It should be noticed that the retarding effect of tetramethylammonium fluoride is reflected in a negative value for σ. This is in accord with the usual assumption that the small fluoride ion is relatively highly hydrated in aqueous media, which would be expected to lead to an effectively "drier" solvent and hence to a decrease in the rate of ionisation. It should also be observed that ionic chlorides, which also retard the rate of reaction, have positive values of σ. This means that sodium chloride and hydrochloric acid are hydrated to a less extent than tetramethylammonium fluoride and that the mass-law effect is responsible for the retardation. The results for these two ionic chlorides, however, mean that sodium chloride results in an effectively "drier" solvent than hydrochloric acid. This would be surprising if solvation of the ions involved only water, since the proton is usually regarded as being highly hydrated in aqueous media. However Baughmann, Grunwald and Kohnstam[88] have shown that solvation of electrolytes by the organic component of the solvent is important in aqueous dioxane solutions. The results therefore suggest that the overall effect depends on the relative amounts of the solvation of the electrolytes by acetone and water.

The large value of σ for sodium perchlorate suggests a high degree of solvation by acetone and hence an effectively "wetter" solvent, which is in agreement with the observations made with this electrolyte in 50% aqueous dioxane[88] and is also consistent with its high solubility in pure acetone.

At first sight the values of σ and k_X/k_X^o for sodium azide appear to be in poor agreement. Despite the fact that this electrolyte is associated with a value of σ which is the same as that for sodium perchlorate, its accelerating effect is much less than that of the other salt. However, the concentration of azide ions progressively decreases throughout the course of the reaction due to formation of unreactive RN_3 and undissociated HN_3 (compare page 57), so that the value of k_X/k_X^o for this electrolyte refers to a mean sodium azide concentration which is less than 0.05 M. This fact has been allowed for in the calculation of σ but not in the qualitative values of k_X/k_X^o.

(ii) The values of α and β .

The values of the mass-law and intervention constants, α and β , require some comment. When the electrolytes were $PhSO_3Na$, $NaNO_3$ and KBr the products formed by reaction of the anions with the carbonium ion, ionised again much more rapidly than benzhydryl chloride[ø]. It may be readily shown that when

---

[ø] Baker and Heggs[226] have concluded that organic nitrates ionise almost as rapidly as bromides and Robertson[98] has shown that the this situation obtains, the overall effect is kinetically indistinguishable from an ionic-strength effect, and that although RY is formed it is not possible to calculate β (compare Chapter VII, page141). The values of α and β have been determined for the other reactive electrolytes ($Y^- = Cl^-, N_3^-, F^-$). Since these parameters measure the ability of the reagent to compete with water for the carbonium ion, it might be expected that their sizes would depend on the nucleophilic power of the anions. On the other hand the highly reactive carbonium ion will not be very discriminating with respect to this property[53,14b] which may also be subordinated to the ability of the anion to penetrate the solvation shell surrounding the carbonium ion, before the collapse of this shell leads to hydrolysis products. The small increases of the intervention constants with nucleophilic power are therefore in accord with expectations.

It can be seen that the values of α for 0.05 M. sodium chloride and hydrochloric acid are in good agreement, as they should be. The value quoted for the salt is a mean value of three independent determinations with different concentrations of sodium chloride, and it will be shown in Chapter VII that the experimental values all agree within the limits of the experimental

---

Footnote cont'd.

rates of solvolysis of organic substrates decrease for the sequence RSO_3Ph, RBr, RNO_3.

errors. A value of 2.30 was therefore assumed for the mass-law constant in order to calculate the values of σ. These points are fully discussed in the experimental section (pages 146–156).

The value of β for fluoride ions is subject to the possibility of large errors, due to uncertainties which arose in the determination of acidity in the presence of tetramethylammonium fluoride (see page 132). However, neglect of this parameter has been shown to have no effect on the value of β (compare Table VII-2) and it is difficult to decide whether or not fluoride ions do react with the carbonium ion in the present system. Bateman, Hughes and Ingold[101] have concluded that the chloride ion is twenty times as reactive as the fluoride ion towards the p:p -dimethylbenzhydryl carbonium ion in liquid sulphur dioxide. The value of β for the reaction of azide ions with the benzhydryl cation is also in agreement with previous conclusions that this reagent is more reactive than chloride ions towards carbonium ions[53, 80].

The Effect of Electrolytes on the Rate of Reaction of p-Methoxybenzyl Chloride in 70% Aqueous Acetone.

(i) The determination of the σ values.

Since the values of σ for the reactions of benzhydryl chloride in 70% aqueous acetone containing electrolytes are now available, it is possible to obtain the corresponding values for the effect of the same electrolytes on the rate of ionisation of p-methoxybenzyl chloride in the same solvent, via equation IV-7. The constant in this equation can be calculated from the present results with benzhydryl chloride and p-methoxybenzyl chloride in 70% aqueous acetone containing 0.05 M. sodium perchlorate and 0.05 M. sodium borofluoride. Since these two electrolytes have very weakly nucleophilic anions, no reaction occurs between them and either of the substrates and the σ values may thus be obtained for both compounds by similar methods. The appropriate equations and methods of calculation are given in Chapter VII (pages 156-162). Both electrolytes yielded values of σ which were 0.12×10^{-8} cms. greater for p-methoxybenzyl chloride than for benzhydryl chloride, and it was assumed that this difference applied to all electrolytes. The resulting values of σ for the effect of electrolytes on the rate of ionisation of p-methoxybenzyl chloride are given in Table IV-7.

(ii) The determination of bimolecular substitution.

The mass-law and intervention constants, α and β (see pages 42 and 78), must be first determined, using the calculated values of σ. The methods of calculation are fully described in the experimental section (Chapter VII, pages 156 - 162) and the values are discussed later in this chapter (page 93).

The values of α, β and σ may now be used to calculate the rate of substitution of p-methoxybenzyl chloride by mechanism S_N1. This leads to a rate coefficient, $(k_X)_{calc.}$, which may be compared with the experimental rate coefficient, $(k_X)_{obs.}$. Any difference between these two values must, on the present view, be due to bimolecular attack on p-methoxybenzyl chloride by the anion, Y^-. The difference is thus equal to k_6Y^-, since

$$(k_X)_{obs.} = \underbrace{\frac{k\,(1 + Y^-)}{1 + \alpha Cl^- + \beta Y^-}}_{S_N1} + \underbrace{k_6Y^-}_{S_N2} \quad \ldots\ldots\ldots \text{IV-8.}$$

(compare Chapter VII, page 141).

where k_6 is the rate coefficient for the direct substitution of the substrate by Y^-,

Y^- represents the concentration of the reagent.

The appropriate equations and methods of calculation are fully described in the experimental section (pages 156-162) and the results are summarised in Table IV-7.

TABLE IV-7

The Rates of Substitution of p-Methoxybenzyl Chloride in 70% Aqueous Acetone at 20.08°C.

Electrolyte	Initial Concentration	$10^8\sigma$	$10^4(k_X)_{calc.}$	$10^4(k_X)_{obs.}$	10^4k_6
$NaClO_4$	0.05015	1.92	(2.981)	2.975	0
$NaBF_4$	0.05001	1.58	(2.825)	2.835	0
$PhSO_3Na$	0.04997	0.83	2.475	2.574	1.981
$NaNO_3$	0.05021	0.98	2.586	2.750	3.253
Me_4NF	0.04677	0.56	2.396	2.554	4.234
NaCl	0.02484	0.42	2.400	2.577	7.692
NaCl	0.05154	0.42	2.390	2.711	6.610
NaCl	0.10070	0.42	2.500	2.995	5.222
HCl	0.05146	1.01	2.481	2.824	7.268
KBr	0.05041	1.25	2.629	3.026	7.898
NaN_3	0.01983	1.93	2.740	3.160	34.01
NaN_3	0.03104	1.93	2.822	3.634	35.89
NaN_3	0.03997	1.93	2.910	3.972	33.20

It can be seen that the values of k_6 increase in the sequence $NaClO_4 \approx NaBF_4 \approx 0 < PhSO_3Na < NaNO_3 < Me_4NF < NaCl \approx HCl < KBr < NaN_3$; that is, in the order of increasing power of the anion as a nucleophilic reagent. This should be compared with the differences between the values of (k_X/k_X^o) for 0.05 M. electrolyte for p-methoxybenzyl chloride and benzhydryl chloride, which also increase in the same sequence (see Table IV-2). These results are in accord with the correlation of k_6 as a rate coefficient for bimolecular attack on the substituted benzyl compound by Y^-, since its value must depend on the nucleophilic power of the reagent.

Comparable studies have been carried out recently using p-phenoxybenzyl chloride under the same conditions as those employed in the present studies[96]. This compound has been shown to undergo hydrolysis entirely by mechanism S_N1, but is also susceptible to S_N2 attack by reagents which are better nucleophiles than water. The values of k_6 for the two compounds are compared in Table IV-8 and it is gratifying to find that they both increase for the same electrolyte sequence. It is interesting to note that even such poor nucleophilic reagents as $PhSO_3^-$ and NO_3^- are capable of displacing the chlorine atom by the bimolecular mechanism.

TABLE IV-8

The Effect of Varying the Polar Substituent on the Rates of Bimolecular Substitution of para-Substituted Benzyl Chlorides by Anions in 70% Aqueous Acetone at 20.08°C.

Electrolyte	$(10^4 k_6)_{MeO}$ †	$(10^6 k_6)_{PhO}$ ‡ †	$\frac{(k_6)_{MeO}}{(k_6)_{PhO}}$
$NaClO_4$	0	0	-
$NaBF_4$	0	0	-
$PhSO_3Na$	1.98	1.77	112
$NaNO_3$	3.25	2.35	138
Me_4NF	4.23	5.15	82
NaCl	6.51	8.43	77
HCl	7.27	-	-
KBr	7.90	53.05	14.9
NaN_3	34.37	781.3	4.4

$$\frac{(k_X^o)_{MeO}}{(k_X^o)_{PhO}} = \frac{2.500 \times 10^{-4}}{1.856 \times 10^{-6}} = 134^{\ddagger}$$

---

‡ The data for p-phenoxybenzyl chloride were communicated by Kohnstam and Ribar.

† The subscripts MeO and PhO refer to p-methoxybenzyl chloride and p-phenoxybenzyl chloride, respectively.

There is one feature of the results with the two substituted benzyl compounds which demands an explanation. All previous evidence suggests that bimolecular substitution by a given negatively charged reagent should be much less sensitive to changes in the polar effects of substituents (compare page 14, Table I-1), than S_N1 reactions (see pages 10-14). Since the two compounds now under consideration differ only in the identity of the para-substituent, the ratio≠ $(k_6)_{MeO}/(k_6)_{PhO}$ is a measure of the sensitivity of a given bimolecular substitution to the polar effects of the substituents. In the same way, the ratio $(k_X^o)_{MeO}/(k_X^o)_{PhO}$, for the solvolyses of the two compounds in the absence of added electrolyte, is a measure of the sensitivity of the ionisation process to the polar effects of the substituents. These ratios are given in Table IV-8 and comparison of their values reveals the very interesting fact that the rates of bimolecular attack by the very weakest reagents ($PhSO_3^-$, NO_3^-) show almost the same sensitivities to polar effects as the rate of ionisation. More-over, the sensitivity decreases with increasing nucleophilic power of the anionic reagent, and the ratio $(k_6)_{MeO}/(k_6)_{PhO}$ for the attack by azide ions has a low value, in reasonable

---

≠ The subscripts MeO and PhO refer to p-methoxybenzyl chloride and p-phenoxybenzyl chloride, respectively.

agreement with the data given for other S_N2 substitutions in Table I-1. These results argue strongly against the operation of the extreme form of mechanism S_N2 for attack by the weak reagents, although they suggest that this process probably operates in the substitution by azide ions.

It is suggested that the processes, which have been identified as "bimolecular" in the present studies, represent attack by the reagent on a partially heterolysed species. As the nucleophilic power of the reagent increases, this attack can occur at progressively earlier stages in the ionisation process and bimolecular attack by azide ions most probably commences when little or no extension of the carbon-chlorine has occurred. On the other hand ionisation is probably almost complete before the benzenesulphonate ion participates in the reaction. Since covalent attachment of the reagent is still, however, a feature of the activation process, such reactions must still be regarded as bimolecular[37]. The energy-profile diagram (Figure IV-1) gives a qualitative representation of the nucleophilic substitution of a partially heterolysed substrate, the broken line indicating the modified energy requirements compared to the ionisation process (continuous line). It is not envisaged that attack by a given reagent occurs only at a single stage in the bond-breaking process, but rather that it may commence at some minimum stage, which will depend on the nucleophilic power of the reagent, and probably continue up to the stage when full ionisation is attained. It may well be that nearly all of the attack by very powerful reagents occurs with little preliminary bond-extension. The overall result will thus be an average of the attacks at a number of different stages in the ionisation process.

FIGURE IV-1

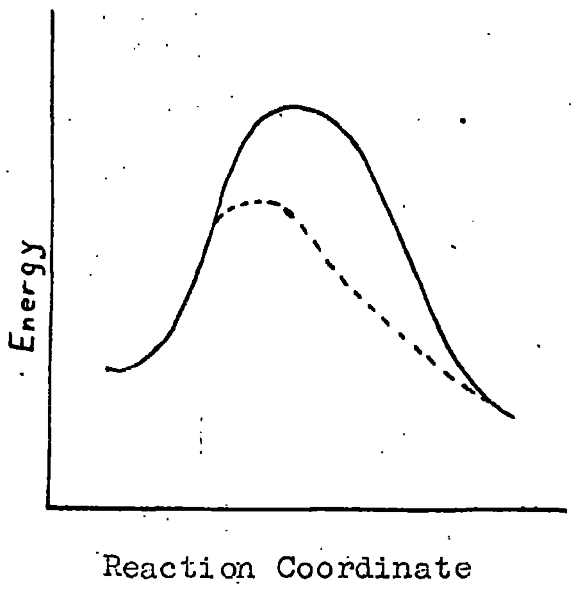
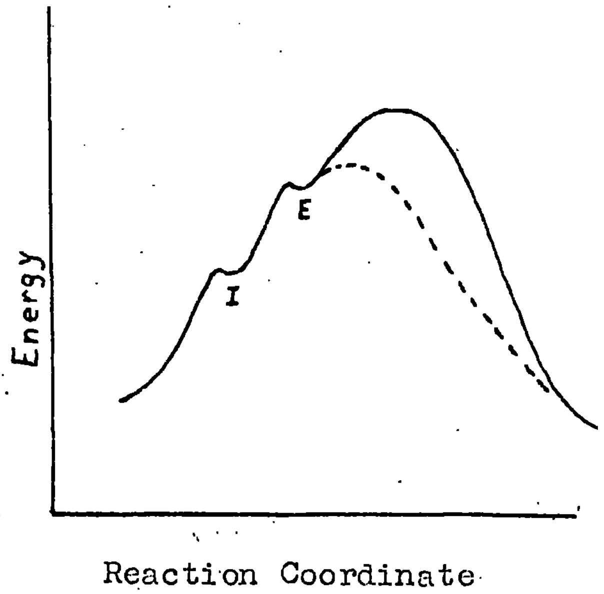


FIGURE IV-2



Energy profile diagrams for the reaction of a nucleophilic reagent with a partially heterolysed substrate (Fig. IV-1) and an ion-pair (Fig. IV-2).

It is of interest to consider whether or not the results might be better explained in terms of the meta-stable ion-pairs, which Winstein and his co-workers have proposed as intermediates in S_N1 processes (see Chapter I, page 6). The existence of such intermediates implies a degree of stabilisation for each variety, which should result in a number of 'troughs' in the energy-profile diagram. Hitherto Winstein has only found it necessary to invoke two forms of ion-pair, and the situation is indicated diagramatically in Figure IV-2, where I and E represent the "internal" and external ion-pair, respectively. Any attack by the reagent on either of these intermediates must be considered a unimolecular process, since the charges in both I and E are fully developed prior to the covalent attachment of the reagent, although in the absence of attack at this stage energy is still required to form the completely separated ions. However, the bond-breaking process is the same for the formation of ion-pairs and the carbonium ion, and it would therefore be expected that polar substituents would affect the reactivities of all these species in much the same way. This being so, it must be allowed that k_6 for the substitutions by azide ions measures predominantly, if not entirely, attack by mechanism S_N2. Even if it is maintained that the increasing sensitivity of k_6 to the polar effects of the para-substituents is due to ion-pair intervention, it must nevertheless be conceded that this rate coefficient for the substitutions by chloride and bromide ions (and probably by fluoride ions) also measures a considerable amount of attack by the extreme form of mechanism S_N2. It is therefore concluded that k_6 can be legitimately regarded as measuring some form of bimolecular attack, and in the author's view the present results are more convincingly explained in terms of attack by the reagents on a partially heterolysed substrate, than in terms of attack on ion-pair intermediates.

(iii) The determination of the rate of unimolecular formation of RY.

The total rate of reaction of p-methoxybenzyl chloride in aqueous acetone containing an anionic reagent, Y^-, is given by equation IV-8, which may be written in the form

$$(k_X)_{obs} = \frac{k_1}{1 + \alpha Cl^- + \beta Y^-} + \left(\frac{k_1 \beta}{1 + \alpha Cl^- + \beta Y} + k_6 \right) Y^-$$

for the purposes of the present discussion. The first-order rate coefficient for the formation of RY is given by the second term on the right hand side of this expression, and the unimolecular formation of RY thus is given by

$$\frac{k_1 \beta Y^-}{1 + \alpha Cl^- + \beta Y^-} = k_H Y^-$$

where k_H is the first-order rate coefficient for hydrolysis (compare Chapter VII, page 141).

Experimental values of α and β have been obtained only for the cases where the electrolytes were HCl, NaCl, NaN_3 and Me_4NF. The latter salt, however, gave a small negative value for β_F-and, while this probably arose from inaccuracies in the experimental determination of the acidity of the reaction mixture (compare Chapter VII, page 132), no estimate of S_N1 attack by fluoride ions was possible.

No values of β could be determined for the reactions of p-methoxybenzyl chloride with $PhSO_3^-$, NO_3^- and Br^-, since the product, RY, ionised again more rapidly than the chloride, and the effect on the rate of hydrolysis was indistinguishable from an ionic strength effect (compare Chapter VII, page 141). Since the carbonium ion reacts with chloride ions, it must also react with bromide and nitrate ions (and possibly with benzene sulphonate ions) and β values for these reactions had therefore to be assumed. Approximate[≠] experiments with p-methoxybenzyl bromide in 70% aqueous acetone at 0°C. indicated that this

---

[≠] The first-order rate coefficients decreased by about 12% throughout the course of the reactions. The small effect of added potassium bromide precluded the possibility of explaining this as a mass-law effect. Although the bromide was prepared by halogen exchange between bromide ion and p-methoxybenzyl chloride, it was considered unlikely that the product contained any unreacted chloride. It is possible that the acid formed in the hydrolysis reacted with the solvent, but there was no time to investigate this possibility.

compound reacts about ten times more quickly than the chloride and that β_{Br^-} is equal to α_{Cl^-}. It was therefore assumed that these parameters had the same values in the present systems. No experiments were carried out with the nitrate and no values of $\beta_{NO_3^-}$ have previously been determined, although p-methoxybenzyl nitrate has been investigated in aqueous ethanol solutions[22]. However, it has been concluded[99] that nitrate ions are less reactive than chloride ions towards the p:p -dimethybenzhydryl cation in aqueous acetone and similar conclusions have been drawn[100] from studies with p-toluene sulphonates in aqueous acetone. A value of $\frac{1}{2}\alpha$ was therefore assumed for $\beta_{NO_3^-}$ in the present reactions. These values are probably not seriously different from the true ones, since carbonium ions are generally not very discriminating with regard to the nucleophilic power of the reagent[53, 14b]. However the S_N1 contributions for these ions can only be regarded as rough estimates of the true values. No similar assumptions have been made for the reaction of the very weakly nucleophilic benzenesulphonate ion, but it is thought likely that any S_N1 attack by this reagent on the p-methoxybenzyl carbonium ion was very small.

The methods used to calculate the S_N1 rates are described in the experimental section (Chapter VII, page 156) and the values are given in Table IV-9 together with the values of the parameters α and β . It can be seen that, as the nucleophilic power of the reagent increases, the percentage of unimolecular attack by the anion decreases. This is considered reasonable, since the amount of bimolecular attack on the unionised substrate (or partially heterolysed substrate) depends directly on the nucleophilic power of the reagent and the carbonium ion is much less sensitive to this property[53, 14b].

TABLE IV-9

The Relative Amounts of Unimolecular and Bimolecular Substitution of p-Methoxybenzyl Chloride by Anions in 70% Aqueous Acetone at 20.08°C.

Electrolyte	Initial Concentration	Intervention Constant	$10^4k_HY^-$	$10^4k_6Y^-$	$\%S_N1$
$NaClO_4$	0.05015	-	-	-	-
$NaBF_4$	0.05001	-	-	-	-
$PhSO_3Na$	0.04997	-	-	0.099	-
$NaNO_3$	0.05021	2.0 #	0.253	0.164	60.7
Me_4NF	0.04677	(-0.54)$^{\neq}$	-	0.158	-
NaCl	0.02484	3.81	0.203	0.177	53.4
NaCl	0.05154	4.05	0.388	0.321	54.7
NaCl	0.10070	4.22	0.677	0.495	57.8
HCl	0.05146	3.73	0.398	0.343	53.7
KBr	0.05041	4.0$^{\angle}$	0.461	0.397	53.7
NaN_3	0.01983	8.68$^{\delta}$	0.243	0.420	36.7
NaN_3	0.03104	7.53$^{\delta}$	0.433	0.812	34.8
NaN_3	0.03997	7.68$^{\delta}$	0.594	1.062	35.9

(Footnote overleaf).

Footnote :

≠ β_{F^-} was neglected in the calculation of k_6. No S_N1 rate was determined because of possibly large errors in the value of β_{F^-}

A mean value of 4.0 was assumed for α in all these calculations.

It was assumed that $\beta_{NO_3^-} = \frac{1}{2}\alpha$

/ It was assumed that $\beta_{Br^-} = \alpha$

δ A mean value of 7.96 was assumed for $\beta_{N_3^-}$ in all these calculations.

The results are therefore considered to provide considerable evidence for the concurrent operation of first- and second-order processes, which may be identified with mechanisms S_N1 and S_N2, in the substitution of p-methoxybenzyl chloride by azide, bromide and chloride ions in 70% aqueous acetone. Both processes probably operate for the corresponding substitutions by nitrate and fluoride ions. In view of the theoretical importance of this conclusion, it is considered necessary to re-examine the evidence on which it is based. This will now be done.

The quantitative treatment of the ionisation process for p-methoxybenzyl chloride depends on the electrolyte solvation approach, which developed to account for the specific effects of electrolytes on the rate of reaction of benzhydryl chloride.

In developing this approach it was assumed that this compound reacts entirely by mechanism S_N1, even with such powerful reagents as azide ions. Kohnstam[61b] has recently summarised a considerable amount of evidence supporting this view which is also substantiated by previous studies of the rates and products of its reaction with sodium azide in aqueous acetone solvents[81]. In addition Winstein and his co-workers[11] have recently concluded that only a small fraction of the exchange reaction between p-chlorobenzhydryl chloride and isotopic chloride ions could possibly be bimolecular. On the other hand the same group of workers postulate that ion-pair intermediates react to a significant extent in this system and that even in 80% aqueous acetone the active participation of such species is not negligible[11b, 11c]. Pocker[12] has recently drawn similar conclusions from studies of the rates of racemisation and chloride exchange with an unsymmetrical, deuterium substituted, benzhydryl chloride in 80% aqueous acetone. However the effect is very small and diminishes very rapidly as the water content of the solvent is increased. Insufficient data were given to allow any conclusions to be drawn regarding the importance of ion-pair participation in the present systems. It is quite clear, however, that complete ionisation of benzhydryl chloride is the predominating rate-determining process. Thus even if the assumption that this compound reacts solely by mechanism S_N1 is not quite correct, this only means that the values of the σ parameters are slightly too large. This error will be carried over into the values for the reactions of p-methoxybenzyl chloride and will result in an over-estimate of the rate of ionisation and hence in an under-estimate of the bimolecular substitution by the reagent, Y^-. However the depression of the rate of hydrolysis of this substrate by chloride ions and azide ions confirms that some S_N1 attack by these reagents occurs. Moreover, the very large acceleration of the total rate of reaction by azide ions cannot possibly be explained as an ionic-strength effect, so that S_N2 attack by this reagent must also occur. Concurrent operation of the two S_N mechanisms must therefore be still conceded, even if objections are raised to the method of calculating the relative proportions of each.

The method used to calculate the bimolecular rates depends on the acceptance of the view that the ionisation processes for benzhydryl chloride and p-methoxybenzyl chloride are affected in the same way by electrolytes, although the sizes of the effects on the two compounds are slightly different. It is difficult to see why this should not be the case. However, on the unlikely view that p-methoxybenzyl chloride reacts entirely by mechanism S_N1, values of σ may be calculated for the reactions of this substrate in 70% aqueous acetone containing electrolytes. The equations and methods of calculation are the same as those employed in calculating the σ values for benzhydryl chloride (see pages 146-156) and the values are given in Table IV-10, where they are compared with those for benzhydryl chloride. It can be seen that whereas the values for benzhydryl chloride have no connection with the nucleophilic power of the reagent, those for p-methoxybenzyl chloride increase with this property. The values for this compound, moreover, are considerably larger than those for benzhydryl chloride, and the value for σ^{NaN_3} is so improbably large as to exclude the possibility that p-methoxybenzyl chloride reacts entirely by mechanism S_N1 in the presence of this reagent.

TABLE IV-10

Values of the σ Parameters assuming Mechanism S_N1 for the Decomposition of Benzhydryl Chloride and p-Methoxybenzyl Chloride in 70% Aqueous Acetone at 20.08°C.

Electrolyte	$10^3\sigma$	
	Ph_2CHCl	$MeOC_6H_4CH_2Cl$
$NaClO_4$	1.80	1.89
$NaBF_4$	1.46	1.65
$PhSO_3Na$	0.71	1.34
$NaNO_3$	0.86	2.19
Me_4NF	-0.68	0.21
NaCl	0.30	1.91
HCl	0.89	2.66
KBr	1.13	3.05
NaN_3	1.81	9.67

It is therefore concluded that although the values of k_6 and S_N1 percentages may be in error by an unknown amount, the concurrent operation of mechanisms S_N1 and S_N2 is firmly established for the reactions of p-methoxybenzyl chloride with azide and chloride ions, is extremely probable for its reaction with bromide ions and may possibly also apply to the corresponding reactions with fluoride and nitrate ions.

The Nature of the Mechanistic Transition.

It is considered legitimate to speculate about the nature of the mechanistic transition from the extreme form of S_N2 to S_N1.

It was concluded earlier in this chapter that as the nucleophilic power of the substituting anion increases, attack can occur at a progressively earlier stage in the bond-breaking process. It was also mentioned that, in agreement with the views of Bird, Hughes and Ingold[39], it was not envisaged that such attack could take place only at a single stage, but rather that it occurs at all stages after a necessary minimum amount of bond extension. This would depend on the nucleophilic power of the attacking group, and the overall effect is thus an average of the reactions at all of these stages. The fact that unimolecular attack is observed to occur together with S_N2 attack, suggests that a continuous spectrum of transition states is available for nucleophilic attack, some of which still involve covalent participation by the reagent. It has already been stressed (see pages 15 and 90) that such processes must be considered to be bimolecular. Those which do not involve covalent attachment of the reagent, before ionisation is complete, are unimolecular. Thus reactions occuring by mechanistically border-line processes are considered to involve the concurrent operation of the S_N1 and S_N2 processes, where the latter processes can involve varying degrees of bond-stretching prior to the covalent attachment of the reagent. Gold[38c] has previously propounded compelling arguments for the same view without, however, being able to call upon any supporting evidence.

CHAPTER V

THE EFFECT OF PYRIDINE ON THE RATES OF REACTION OF p-METHOXYBENZYL CHLORIDE AND BENZHYDRYL CHLORIDE WITH 70% AQUEOUS ACETONE.

The effect of pyridine on the rate of reaction and rate of hydrolysis of p-methoxybenzyl chloride in 70% aqueous acetone was studied as an extension of the investigations carried out with ionic reagents (compare Chapter IV). It was hoped that evidence would be obtained for the concurrent operation of mechanisms S_N1 and S_N2 in the substitution by this reagent. However preliminary work had shown the reaction to be slow compared to hydrolysis in 70% aqueous acetone. This necessitated the use of relatively large amounts of pyridine with consequently large changes in the ionising power of the medium. It was therefore necessary to obtain an independent estimate of the effect of pyridine on the rate of ionisation of p-methoxybenzyl chloride before it was possible to establish substitution by either mechanism.

Preliminary work by Shillaker[29] had shown that changes in the ionising power of aqueous acetone solvents, when caused by variation in the acetone content, affected the rates of hydrolysis of p-methoxybenzyl chloride and benzhydryl chloride to the same extent. Shillaker's work was therefore extended by studies of the effects of a number of inert non-electrolytes on the rates of hydrolysis of the same two compounds in 70% aqueous acetone, in the hope that the similarity would continue to hold. Had this proved to be the case it would have been reasonable to assume that the correlation could be extended to the corresponding effect of added pyridine. Unfortunately this hope was not fulfilled (see Chapter VI) and it has not been possible, therefore, to allow quantitatively for the effect of pyridine on the rate of ionisation of p-methoxybenzyl chloride. Nevertheless the effect of pyridine on the rate of ionisation of benzhydryl chloride may be used to give a qualitative estimate of its effect on the rate ionisation of the substituted benzyl compound.

<u>Results.</u>

Reactions were carried out with approximately 0.02 molar solutions of benzhydryl chloride and p-methoxybenzyl chloride in 70% aqueous acetone containing 0.25, 0.5 and 0.75 molar concentrations of pyridine. The total rates of reaction of the substrates were determined by observing the production of chloride ions. The rate of hydrolysis of p-methoxybenzyl chloride was also determined by observing the development of acidity. In all cases constant first-order integrated rate coefficients were obtained. The results are summarised in Table V-1 and also as a plot of $(1-k/k^{o})$[≠] against the concentration of pyridine (Figure V-1). Full experimental details and methods of calculation are given in Chapter VI.

[≠] k and k^{o} are the rate coefficients in the presence and absence of pyridine respectively. When k refers to the total rate of reaction of RCl it is called k_{Cl} and when it refers to the rate of hydrolysis it is called k_{H}.

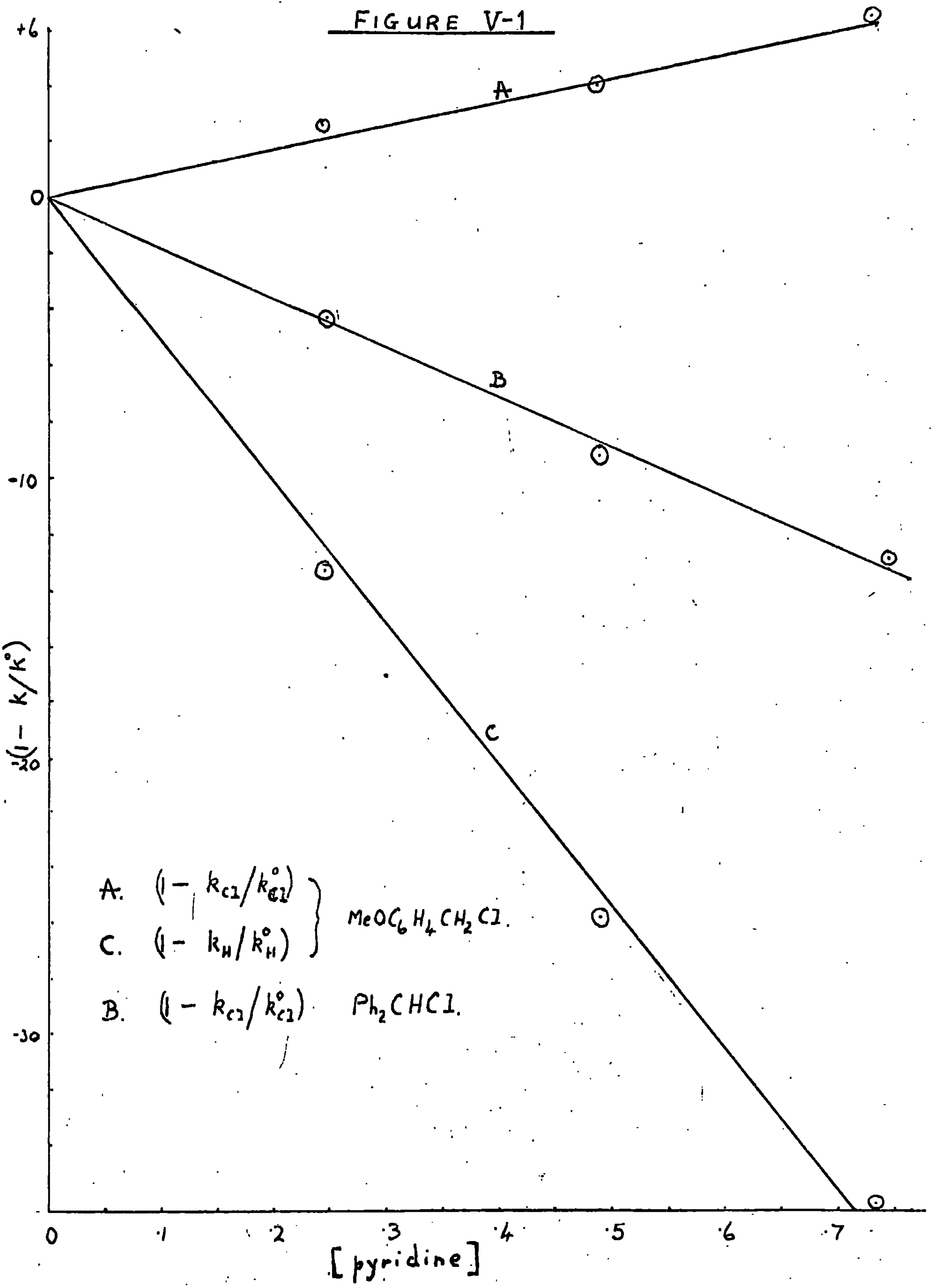
TABLE V-1

The Effect of Pyridine on the Rates of Reaction of Benzhydryl Chloride and p-Methoxybenzyl Chloride in 70% Aqueous Acetone at 20.49°C.

Substrate	Pyridine concentration	% change in the rate coefficients	
		k_{Cl}	k_H
Benzhydryl Chloride	0.2502	- 4.37	-
	0.4932	- 9.25	-
	0.7478	-12.85	-
p-Methoxy benzyl Chloride	0.2472	+ 2.63	- 13.36
	0.4942	+ 3.95	- 25.61
	0.7420	+ 6.10	- 35.73

Figure V-1 shows that the changes in the rates of total reaction and hydrolysis, for which the rate coefficients are k_{Cl} and k_H respectively, have a linear dependence on the concentration of the pyridine. It is reasonable to suppose that the ionising power of the medium would vary in such a simple fashion with the amount of pyridine, especially since the range of concentrations employed was small when considered in terms of solvent variation.

FIGURE V-1


+6
0
-10
-20
-30
$(1 - k/k^{\circ})$
0
·1
·2
·3
·4
·5
·6
·7
[pyridine]
A
B
C
A. $(1 - k_{Cl}/k^{\circ}_{Cl})$
C. $(1 - k_{H}/k^{\circ}_{H})$
$MeOC_6H_4CH_2Cl$.
B. $(1 - k_{Cl}/k^{\circ}_{Cl})$ Ph_2CHCl.

It does not seem likely that bimolecular substitution of benzhydryl chloride by pyridine could occur in the present systems especially since such powerful reagents as hydroxide ions and azide ions (compare Chapter IV) have been shown to be incapable of promoting this mode of attack. If this is so then k_{Cl} must correspond closely to k_1, the rate coefficient for ionisation (see Appendix C). It can be seen that the rate of reaction of benzhydryl chloride is retarded by added pyridine, a fact which suggests that the addition of this reagent lowers the ionising power of the medium.

The rate of reaction of p-methoxybenzyl chloride is accelerated by added pyridine. If it is accepted that the addition of pyridine to the aqueous acetone solvent results in a decrease in the ionising power of the medium, then this result is completely inconsistent with the view that the reagent either does not react at all or that any reaction which does occur follows the unimolecular path. Substitution by pyridine is, indeed, confirmed by the fact that the rate of hydrolysis of p-methoxybenzyl chloride in the presence of this reagent is less than its total rate of reaction. It is therefore clear that S_N2 attack must be taking place.

The status of S_N1 substitution by pyridine is not so certain. If the whole of the attack by this reagent occurs bimolecularly, then virtually all of the formed carbonium ion must react with water[≠] and the rate of hydrolysis must correspond

---

[≠] The small reversal of the ionisation can be neglected in a qualitative discussion.

closely to the rate of ionisation (see Appendix C). In order to preclude S_N1 attack by pyridine, therefore, it is necessary to postulate that the rate of ionisation of p-methoxybenzyl chloride is depressed 2.8 times as much as that of benzhydryl chloride by a decrease in the ionising power of the medium, due to the addition of the base. The results with inert non-electrolyte, however, show that a decrease in the ionising power of the solvent usually has a greater effect on the rate of ionisation of benzhydryl chloride than on the corresponding rate for p-methoxybenzyl chloride and, moreover, the largest factor observed was 1.8. It is difficult to see why pyridine should act in a diametrically opposite way to the other non-electrolytes, benzene, toluene, chlorobenzene, nitrobenzene and acetone. It must be held, therefore, that the rate of hydrolysis of p-methoxybenzyl chloride is less than the rate of ionisation, in the presence of pyridine, and hence that pyridine captures some of the carbonium ions. S_N1 attack is therefore strongly indicated by the present results and since S_N2 attack has already been concluded the concurrent operation of both mechanisms must be allowed.

Unfortunately there is not enough information available to justify the assumptions that would be necessary in order to obtain an estimate of the relative amounts of substitution by the two processes. If it is assumed, however, that the effect of pyridine on the rate of ionisation of p-methoxybenzyl chloride is the same as its effect on the rate of ionisation of benzhydryl chloride, then 52.6% of the substitution by this reagent follows the S_N1 path. Details of this calculation are given in Chapter VII (page 162).

CHAPTER VI

THE EFFECT OF UNREACTIVE NON-ELECTROLYTES ON THE RATES OF SOLVOLYSIS OF BENZHYDRYL CHLORIDE AND p-METHOXYBENZYL CHLORIDE.

1. Results.

Interest in the problem of the effects of inert non-electrolytes on the rates of solvolysis of benzhydryl chloride and p-methoxybenzyl chloride arose from the studies of the effects of pyridine on the rates of reaction of these two compounds (compare Chapter V). The substances used were acetone, benzene, toluene, nitrobenzene and chlorobenzene. The same quantities (5 ml.) were made up to exactly 100 ml. with 70% aqueous acetone and the rate of hydrolysis of the two organic chlorides examined at 20.49°C. Constant first-order rates were obtained in all cases. The experimental details and methods of calculation are given in the experimental section (Chapter VII) and the results summarised in Table VI-1.

Preliminary work by Shillaker[29] had already shown that variation of the acetone content of the aqueous acetone solvent had the same effect on the rates of hydrolysis of both compounds and it was hoped that this would be the case when other non-electrolytes were added.

Shillaker's results have been confirmed with added acetone but the other non-electrolytes had considerably different effects on the rates of reaction of benzhydryl chloride and p-methoxybenzyl chloride. Each of the added substances decreased the ionising power of the medium and this was accompanied by a retardation of the rate of hydrolysis. It can be seen from the results given in Table VI-1 that the effects were always greater for benzhydryl chloride. Moreover, the magnitudes of the retardations caused by the same volumes of different non-electrolytes were considerably different for this compound but almost the same for p-methoxybenzyl chloride.

TABLE VI-1

The Effect of Non-Electrolytes on the Hydrolyses of Benzhydryl Chloride and p-Methoxybenzyl Chloride in 70% Aqueous Acetone at 20.49°C.

Non-Electrolyte	Ph_2CHCl		p-MeOC$_6$H$_4$CH$_2$Cl	
	Concentration	% Retardation	Concentration	% Retardation
Acetone	1.0884	23.63	1.0890	23.98
Benzene	0.5606	36.40	0.5606	22.41
Toluene	0.6276	39.28	0.6271	24.39
Nitrobenzene	0.4908	28.54	0.4913	21.67
Chlorobenzene	0.4018	38.49	0.4024	22.18

2. Discussion.

Since the present studies were only concerned with the effects of added inert non-electrolytes on unimolecular (S_N1) solvolysis, the discussion will be restricted to this class of reactions.

Winstein, Grunwald and Jones[36] have attempted to correlate the rates of solvolytic reactions with the ionising power of the medium by means of a linear free-energy relationship,

$$\log k = \log k^o + m\mathcal{Y} \qquad \text{VI-1}$$

where k and k^o are the rate coefficients for reaction with the given solvent and standard solvent, respectively, is a measure of the ionising power of the solvent and m is a constant which is characteristic of the reaction mechanism. Reactions whose rates depend only on the ionising power of the solvent were classified as limiting and shown to correspond closely to the unimolecular (S_N1) class of Hughes and Ingold. A value of unity was assumed for the constant m for limiting reactions. These points and the methods used to obtain values of $\mathcal{Y}$ have been discussed in Chapter I (see page 16).

Winstein, Grunwald and their co-workers[36, 101] have reported linear correlations between log k and $\mathcal{Y}$ for a number of unimolecular solvolyses, in agreement with the requirements of equation VI-1. However the approach is of limited use when it is necessary to correlate solvolysis rates in a quantitative manner[101, 102]. It has been shown[101] that different substrates often require values of m which differ appreciably from unity and that, in some cases, a single substrate gave plots of log k against Y which showed marked dispersions into separate lines for different solvent systems. This latter tendency was particularly marked for benzhydryl chloride[101b] and it seems likely that the present results with this compound are examples of this dispersion.

Clearly the present results are not in accord with the requirements of the Grunwald/Winstein correlation and this fact, coupled with the other contradictory evidence, indicates that ionising power cannot be the only factor governing solvolysis by the unimolecular mechanism.

The rates of solvolytic reactions might be expected to depend on the dielectric constant of the medium (compare Chapter II, page 29). It has been shown[103] that the application of Kirkwood's equation[65] (see Chapter II, equation II-7) to the unimolecular process leads to

$$\ln k = \ln k^{\circ} - \frac{1}{\bar{k}T} \cdot \frac{(D-1)}{(2D+1)} \cdot \left(\frac{\mu_t^2}{r_t^3} - \frac{\mu_i^2}{r_i^3}\right) \quad \ldots\ldots \text{VI-2}$$

where k and k^{o} are the rate coefficients in the media of dielectric constant D and unity, respectively.

$\bar{K}$ is the Boltzmann constant.

μ and r are the dipole moment and molecular radius, respectively, and the subscripts i and t refer to the

In agreement with the predictions of equation VI-2, linear plots of $(D-1)/(2D+1)$ against log k have been reported for a number of solvolytic reactions[50, 59f, 103, 104]. In general, however, only a small range of solvents have been investigated and even so marked deviations from linearity have been observed. Fainberg and Winstein[105] plotted the values of log k and $(D-1)/(2D+1)$ for <u>tert</u>-butyl chloride using all the available data. Not only was there a considerable dispersion into separate lines for each solvent pair, but pronounced curvature of the lines was apparent. Linear plots were obtained only for media with high dielectric constants. This approach could be rationalised with a non-linear variation of log k with $(D-1)/(2D+1)$ if the value of $\left(\mu_t^2/r_t^3 - \mu_i^2/r_i^3\right)$ varied with the dielectric constant (compare equation VI-2). It is difficult to see, however, why there should be no correlation between the results for benzhydryl chloride and p-methoxybenzyl chloride when the ionisations of these two compounds proceed through similar transition states.

Laidler and Landskroener[106] have recently concluded that log k should vary linearly with $(1-D)/(1+D)$, or nearly so with $1/D$. Moelwyn-Hughes and Kilpi[107] have proposed similar relationships. However, for media of dielectric constant greater than 7 or 8, $(D-1)/(2D+1)$ is linear with $1/D$ to an excellent approximation. The relative merits of these alternatives cannot, therefore, be established. It follows that they all exhibit the same deviations from linear relationship to log k.

Bohme[108] and Fainberg and Winstein[105] have concluded that the best function of D, so far as linearity with log k is concerned, is log D. Conversely, Tommila and his collaborators[109] have shown that such plots for the solvolytic reaction of benzyl halides are decidedly non-linear, and in fact that a superior straight line often results from plotting log k against D. It is quite clear that the simple electrostatic approach is inadequate for the treatment of solvolytic reactions, and the importance of the water content of aqueous solvents, which overshadows any variation in dielectric constant, has been previously emphasised[69a, 110]. It can be seen that equations VI-1 and VI-2 are similar in form and yet there is no clear correlation between Y and functions of D. For instance solvolytic rates and Y values are very nearly the same for similarly aqueous acetone and dioxane solutions but the dielectric constants differ considerably.

The application of the Bronsted equation[33] (compare Chapter III, page 41) to the rates of unimolecular solvolytic reactions leads to the expression

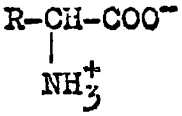
$$k = k^{o} \frac{f_i}{f_t}$$

where k and k^{o} are rate coefficients in the given solvent and standard solvent, respectively.

f_i and f_t are the activity coefficients of the initial and transition states, respectively, relative to unit value in the standard solvent. This may be conveniently defined as 70% aqueous acetone for the purpose of the present discussion.

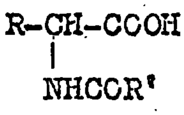
It has been assumed in the past that the activity coefficient of the transition state is so much greater than that of the initial state that the latter may be taken as unity[80]. Medium effects are thus usually considered in terms of effects on the transition state only. If this assumption is not valid, changes in the medium could give rise to specific effects on the rates of ionisation of different compounds if the ratio f_i/f_t does not vary in the same way for all unimolecular solvolyses. This possibility has been previously recognised[111] but so far there has been no systematic investigation of the problem. It has been concluded for reactions in aqueous ethanol, however, that this ratio is almost independent of the substrate[36a]. The analogous situation for reactions occuring in the presence of electrolytes has already been considered from this point of view (compare Chapter III).

The most relevant data for the effect of solvent variation on activity are those derived from studies of the solubilities of α-amino acids, which exist in solution as zwitter-ions (I), and their N-substituted derivatives (II), which cannot form zwitter-ions[112]. From the point of view of its function as a dipole, a zwitter-ion is formally similar to the S_N1 transition state, although differing somewhat in having fully developed charge separation. The derivatives, moreover, bear roughly the same relation to the zwitter-ion as the initial state of an S_N1 reaction does to the transition state. The analogy must not be taken too far, but can nevertheless prove a useful one.



$$\begin{array}{l} R\text{-}CH\text{-}COO^- \\ \quad\;| \\ \quad NH_3^+ \end{array}$$

(I)



$$\begin{array}{l} R\text{-}CH\text{-}COOH \\ \quad\;| \\ \quad NHCOR' \end{array}$$

(II)

For saturated solutions of substances of low solubility, it may be shown that

$$S/S^\circ = 1/f$$

where S and S° are the solubilities in the given solvent and standard solvent, respectively, and f is the activity coefficient of the dissolved substance, relative to unit value in the standard solvent. Hence, for two substances, which may be called (I) and (II) for the purposes of the present discussion,

$$(S/S^\circ)_{II}/(S/S^\circ)_I = f_I/f_{II}$$

The solubility data for the amino acids glycine (I; R=H) and α-aminobutyric acid (I; R=Et) and their N-formyl derivatives (II; R=H or Et; R' = Me) have been referred to ethanol as the standard solvent. Table VI-2 lists values of f_I/f_{II} for these substances, relative to the standard solvent. It can be seen that the values are dependent on the structure of the substances. It can be argued, by analogy, that the ratio f_t/f_i, for unimolecular reactions, might be expected to show a dependence on the nature of the substrate and hence that solvent changes may have specific effects on different S_N1 solvolyses.

TABLE VI-2

Values of f_I/f_{II} for α-Amino Acids (I) and their N-Formyl Derivatives (II) in Aqueous Ethanol Solutions, Relative to Ethanol as the Standard Solvent.

Parent acid	Aqueous ethanol solvents		
	60%	80%	90%
Glycine	81.2	19.9	5.91
α-aminobutyric acid	50.3	12.4	3.78

Unfortunately no comparable data are available for three component solvents. It does not seem likely, however, that such solvents will prove any less complicated than binary solvents. It is not possible, in the present state of knowledge, to formulate a quantitative approach to the problem of these medium effects, but it might prove a fruitful approach if sufficient data could be obtained.

3. A Possible Explanation of the Specific Effects of Non-Electrolytes on the Solvolyses of Benzhydryl Chloride and p-Methoxybenzyl Chloride in 70% Aqueous Acetone.

It is tentatively suggested that the specific effects of the non-electrolytes may arise from solvation of the initial and transition states by the non-electrolytes. If it is postulated that this solvation is associated with the aromatic rings of the aralphyl compounds, the effect should be larger for benzhydryl chloride than p-methoxybenzyl chloride. Steric factors in the former compound could, however, prevent the solvation being twice as much as for the substituted benzyl compound. On passage into the transition state, which tends to the planar configuration of the fully developed carbonium ion, steric hindrance would be reduced. Such considerations do not arise to any great extent for p-methoxybenzyl chloride. In consequence the transition state of ionisation for benzhydryl chloride could be more solvated, relative to the initial state, than the corresponding transition state for p-methoxybenzyl chloride, with a consequent greater retarding effect on the solvolysis of the former compound. It is likely that this effect with acetone is already at a maximum for the present solvents, so that changes in the acetone content of aqueous acetone solvents will make little or no difference, as observed.

CHAPTER VII

EXPERIMENTAL

Preparation and purification of materials.

p-Nitrobenzhydrol.

p-Nitrodiphenylmethane was prepared by Friedal-Crafts reaction between p-nitrobenzyl chloride and benzene[113] and the crude product purified by distillation under reduced pressure. It was converted into p-nitrobenzhydryl bromide by refluxing a solution in dry carbon tetrachloride with N-bromosuccinimide and a small quantity of benzoyl peroxide for 3 hours[114]. After filtration and evaporation of the solvent, the product was refluxed for 2 hours with 50% aqueous acetone, the acetone then removed and the alcohol extracted with ether. It was purified by recrystallisation from petroleum ether (40°/60°) and had m.p. 73—74°C. A sample was also prepared by Meerwein-Ponndorf reduction of p-nitrobenzophenone and had the same m.p. and mixed m.p.

p-Nitrobenzhydryl chloride.

A stream of dry hydrogen chloride gas was bubbled into a solution of p-nitrobenzhydrol in benzene/ether (8:1), in the presence of anhydrous zinc chloride for 8 hours. The solution was washed with water and 5% sodium bicarbonate solution, dried over anhydrous magnesium sulphate and the crude product obtained by evaporation of the solvent. It was purified by repeated recrystallisation from petroleum ether (40°/60°) and had m.p. 43.5—44.5°C. The hydrolysable chloride content was 100% of the theoretical amount.

Benzhydryl chloride.

Dry hydrogen chloride gas was passed through a solution of benzhydrol (BDH., 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 at the water pump and dry petroleum ether (40°/60°) (200 ml.) was added to the residue. After washing with water, 5% sodium bicarbonate solution and water, the solution was dried over potassium carbonate. The solvent was then removed on the water-bath and the residual oil purified by distillation under reduced pressure, the product being a colourless liquid, B.P. 104—105°C at 0.4 mm. The hydrolysable chloride content of a sample was never less than 99.2% of the theoretical amount.

Radioactive benzhydryl chloride.

This was prepared in small samples, as required, by the exchange between a pure inactive sample of benzhydryl chloride and a large excess of active tetramethylammonium chloride in liquid sulphur dioxide at -10°C. The solvent was prepared in the anhydrous state in the following way: The gas from a commercial cylinder was bubbled through concentrated sulphuric acid, then over molecular seives (Linde, type 4A) and finally over P_2O_5. It was condensed onto the dry salt by cooling the receiver in an ice/salt mixture at -20°C. and the benzhydryl chloride then introduced. After 2 hours the solvent was allowed to evaporate at room temperature and petroleum ether (40°/60°; 200ml) added. The precipitated salt was filtered off, the solution washed with ice-cold water and dried with anhydrous magnesium sulphate. The concentration and specific activity of the benzhydryl chloride in this solution were determined by hydrolysing a sample in aqueous acetone, after removal of the petroleum ether, and then making up to a known volume. A 10ml. sample was counted in a liquid counter and the acidity determined with standard sodium hydroxide solution. Inactive benzhydryl chloride was added to give the required specific activity (about 3.5×10^6 counts/mole/minute in the apparatus used in these studies). Samples were prepared for kinetic runs by evaporating the required volume of the petrol solution on a water bath at 70°C. and removing the last traces of solvent at 40°C. and 0.5mm. pressure.

<u>p-Methoxybenzyl chloride</u>.

This was prepared from anisyl alcohol by a method similar to that used for benzhydryl chloride. Distillation under reduced pressure yielded a colourless oil, B.P. 84-86°C/0.4mm. The hydrolysable chloride content was never less than 99.4% of the theoretical amount.

Radioactive p-methoxybenzyl chloride.

The preparation of this was exactly the same as for benzhydryl chloride except that the exchange was carried out for 4 days in dry acetone at room temperature, using active lithium chloride instead of the tetramethylammonium salt.

p-Methoxybenzyl bromide.

p-Methoxybenzyl chloride (4 gm.) was reacted for 8 days with a large excess of dry sodium bromide in boiling anhydrous acetone (25 ml.). The mixture was allowed to cool and the solution decanted from the crystals which formed. These were washed with a little dry acetone (5 ml.) and the solution refluxed with more sodium bromide for a further 18 hours. Petroleum ether (40°/60°; 200 ml.) was then added, the solution filtered and the solvent removed on a water bath at 80°C. The residue was dissolved in petrol (50 ml.), this solution washed with water, dried over anhydrous magnesium sulphate and worked up in the usual way. The crude yellow product was distilled under reduced pressure, to give a slightly yellow light-sensitive oil, B.P. 93°C/0.2mm. The hydrolysable bromide content was 99.9% of the theoretical amount. A sample was hydrolysed in 70% aqueous acetone and the solution tested for traces of chloride ion[115]. The test indicated that this ion was absent. However a trial run in 70% aqueous acetone at 0°C. gave first order rate coefficients which decreased as the reaction proceded. The product was therefore refluxed for a further 4 days with dry lithium bromide, in case the falling rates were due to small amounts of unreacted chloride. The product was worked up as before.

Anhydrous acetone was prepared for the exchange reactions by standing the purified Analar grade over molecular seives (Linde, type 4A) for several days.

Sodium perchlorate (B.D.H.) was recrystallised from aqueous dioxane and dried to constant weight in a pistol at 100°C. and a pressure of 0.5 mm.

Sodium borofluoride was recrystallised from water and dried in a pistol at 100°C. and a pressure of 0.5 mm. for 6 hours.

Sodium azide (Hopkin and Williams) was recrystallised from water and dried in the oven at 120°C. for 24 hours.

Potassium bromide (B.D.H.m Analar) was dried in the oven at 120°C. for 12 hours.

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

Sodium nitrate(Analar) was dried in the oven at 120°C. for 4 hours.

Sodium benzenesulphonate was recrystallised from ethanol (95%) and dried at 100°C. and 0.5mm. pressure for 6 hours.

Tetramethylammonium fluoride was prepared in the following way. Silver carbonate was prepared (in a darkened room) from a solution of silver nitrate (10%) and an equivalent amount of sodium hydroxide solution (10%), through which a slow stream of carbon dioxide had been passed for 12 hours. After filtering and washing with water, the silver carbonate was suspended in water and treated with an equivalent amount of 5% hydrofluoric acid.[116] The resulting solution was evaporated in a platinum dish to about 50 ml. and then treated with methanol (200 ml.) and ether (1 litre). The precipitated silver fluoride was isolated by decanting the liquid and washed several times with a mixture of methanol and ether (1:2). It was dissolved in water (250 ml.) and the solution filtered. The strength was determined in two ways, after diluting a 5.0 ml. sample to 500.0 ml.

(i) 5.0 ml. was treated with a measured excess of standard hydrochloric acid solution and the excess chloride-ions determined by potentiometric titration with silver nitrate solution.

(ii) 5.0 ml. was passed down a column containing a cationic exchange resin (Amberlite I.R.120) and titrating the liberated hydrofluoric acid with standard sodium hydroxide solution, using mixed methyl red/methylene blue as indicator.[117] Both methods gave the same result and the solution contained no free hydrofluoric acid.

The solution of silver fluoride was treated with an equivalent amount of tetramethylammonium bromide, the silver bromide precipitate filtered off and the solution saturated with hydrogen sulphide. No silver sulphide was formed. After filtration the solution was evaporated to a viscous oil, which gave crystals of tetramethylammonium fluoride on triturating with a little acetone. These were dried in a pistol for 12 hours at 150°C. and 0.5 mm. pressure. The fluoride ion content, determined by method (11), was 99% of the theoretical amount.

Hydrochloric acid was introduced into the 70% aqueous acetone by passing a slow stream of the dry gas, prepared by dropping concentrated sulphuric acid onto 'voltoids', into a small volume of the solvent at 0°C. and then adding sufficient 70% acetone to make the final strength 0.05 molar. Shillaker[29] has shown that this procedure does not cause any significant change in the proportions of the solvent components.

Radioactive lithium chloride was prepared from the sample of active hydrochloric acid (Radiochemical Centre, Amersham.) by treating it with an equivalent amount of lithium carbonate and evaporating the solution to dryness. The salt was dried at 100°C. and 0.5 mm. pressure.

Radioactive tetramethylammonium chloride was prepared by precipitating the active chlorine as silver chloride and shaking this with an equivalent amount of a 10% solution of tetramethylammonium bromide for 2 days. The solution, which contained no bromide ion, was evaporated down and the salt dried as for the lithium salt.

70% aqueous acetone was made up made up by mixing 70 volumes of acetone and 30 volumes of water and 50% aqueous acetone by mixing equal volumes. The acetone was the Analar grade solvent which had been refluxed with sodium hydroxide and potassium permanganate for four hours[118] and distilled, before being fractionated from hydroquinone. The water was distilled water which had been passed down a column containing mixed ion-exchange resin.

Solvents were standardised by determining the rate of hydrolysis of benzhydryl chloride or p-methoxybenzyl chloride at 20.08°C., in the absence of added electrolyte.

Titration acetone was prepared from the commercial grade solvent by refluxing with sodium hydroxide and potassiom permanganate for four hours and then distilling. When acidity was to be determined lacmoid indicator was added and the solution neutralised.

Benzene was the analar grade which was extracted several times with concentrated sulphuric acid, washed with water, 10% sodium bicarbonate solution and water, and dried over anhydrous potassium carbonate. It was then fractionated through a small column. The other inert non-electrolytes were Analar grade toluene, nitrobenzene and chlorobenzene, which were used without further treatment.

Pyridine was the analar grade reagent which was fractionated several times, after drying over Analar potassium hydroxide. It was stored over this compound and samples distilled prior to use.

Petroleum ether 40°/60° was the Analar grade which had been extracted several times with concentrated sulphuric acid, washed with water, 10% sodium bicarbonate solution and then pure water. It was dried over anhydrous magnesium sulphate and filtered.

Estimation of Added Electrolytes.

Sodium perchlorate, solium borofluoride, sodium azide, potassium bromide, sodium chloride, sodium nitrate and sodium benzenesulphonate were weighed into a standard grade A flask and made up to the required volume with 70% aqueous acetone, at the thermostat temperature. The concentration of sodium azide was also estimated by potentiometric titration of the azide ion with standard silver nitrate solution. Tetramethylammonium fluoride was estimated by rapidly adding about the required ammount of the salt to 70% aqueous acetone and determining the fluoride ion by the method described on page 125. Hydrochloric acid was determined by titration with standard sodium hydroxide solution.

Preparation of Solutions of Non-Electrolytes.

The non-electrolytes employed were pyridine, acetone, benzene, toluene, nitrobenzene and chlorobenzene. Samples were measured by means of a pipette, weighed and made up to 100 ml. in a standard flask with 70% aqueous acetone at the thermostat temperature.

Thermostats.

The thermostats were of conventional design and consisted of a large, well-lagged tank containing water, a large stirrer, a xylene/mercury regulator, a permanent heater varying in size for the different temperatures and a 60-100 watt intermittent electric lamp bulb heater. Temperatures were constant within ± 0.01°C.

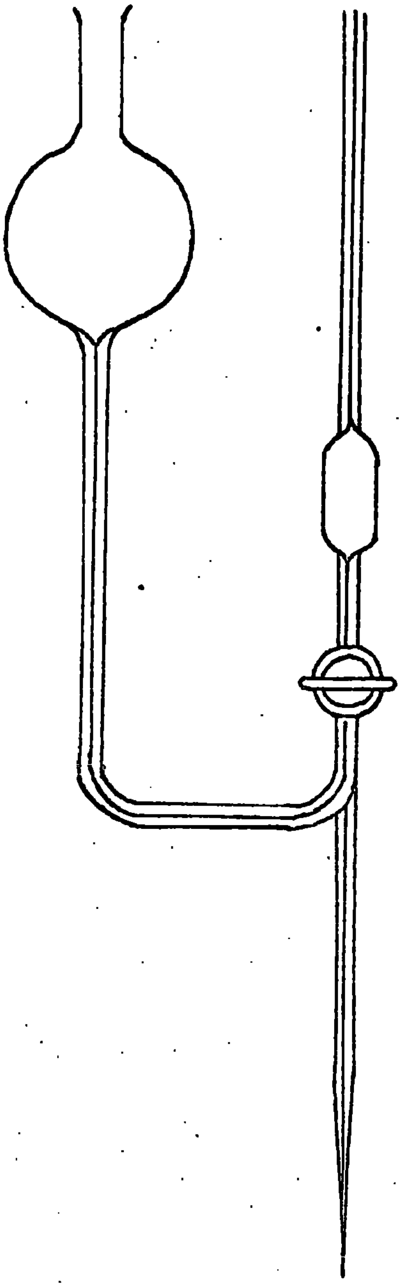
Rate Measurements

Kinetic runs were carried out in the thermostats described. The reactions were always allowed to procede for at least ten 'half-lives' in order to obtain 'infinity' values. Velocity constants were therefore calculated from a knowledge of the acidity after various time intervals and at 100% reaction without the necessity of using weighed amounts of the chlorides. Two methods were used for the kinetic runs.

(i) Tube runs.

This method was only used at temperatures aboce 30°C where there was a possibility of evaporation of the solvent during the course of the kinetic run. p-Nitrobenzhydryl chloride was added to about 150 ml. of the solvent and well shaken. The reaction mixture was run into tubes using the apparatus shown in figure VII-1. The tubes were sealed off, attached to sinkers and placed in the thermostat and well shaken for about two minutes. After suitable time intervals

FIGURE VII-1



TUBE FILLER.

tubes were withdrawn from the thermostat and plunged into a mixture of acetone and "dri-cold" in order to stop the reaction. They were then cleaned, broken under neutralised acetone and the acidity determined as detailed below.

(ii) Flask runs.

About 100 ml. of the solvent was brought to thermostat temperature, the organic chloride added and the flask thoroughly shaken. A zero sample of 5 ml. was removed as soon as possible, and other samples at convenient time intervals. The reaction was quenched by running the samples into about 150 ml. of cold acetone.

Runs containing $NaClO_4$, KBr, NaCl, $NaNO_3$, NaO_3SPh and HCl were followed by measuring the development of acidity in the solution. Runs containing $NaBF_4$[*], $NaNO_3$, NaN_3[†], and Me_4NF[†] were followed by determining the change in chloride ion concentration. The rate of reaction of azide ion was determined by potentiometric determination of azide ion plus chloride ion. This was

---

[*] It was found that the BF_4^- ion was slowly hydrolysed,[119] and that the resulting hydrofluoric acid caused a buffering effect at the end-point of the titration with sodium hydroxide solution.

[†] Azide ions reacted with the carbonium ion forming a product which did not ionise. The rate of formation of hydrogen ion was therefore less than the rate of reaction of the substrate. This also applied to fluoride ions.

necessary because the development of acidity (equivalent to the amount of ROH formed) could not be accurately determined. It has been reported[120] that a suitable indicator for this purpose in the presence of azide ion is bromothymol blue, but the end-points with the weak solutions used in present work were found to be fugative. In consequence of the adoption of the potentiometric method of determining RN_3, the large titres (approximately 35ml. for initially 0.05M sodium azide) could lead to large inaccuracies in the integrated rates of hydrolysis.

When Me_4NF was the electrolyte, development of acidity was also followed by quenching samples in ice-cold petroleum ether (40°/60°), extracting with carbon dioxide free water and titrating with standard sodium hydroxide solution using methyl red/methylene blue as indicator. It was confirmed that no hydrolysis occured during this extraction. However it was found that an acidic solution of Me_4NF in 70% aqueous acetone became less acid at a rate which depended on the acidity of the solution. The reason for this was not investigated but independent experiments (Appendix A, experiments 50 and 51) were carried out with 0.05 M. solutions of tetramethylammonium fluoride in 70% aqueous acetone containing hydrochloric acid. The rate of decrease of acidity was found to be almost proportional to the time and the concentration of the acid. A mean rate of loss of acidity, equivalent to 0.10 ml. of 0.01036 N.

sodium hydroxide solution per hour in the presence of an 0.01 M. concentration of acid, was estimated from these experiments. Hence,

$$\frac{d\,H^+}{dt} \equiv \frac{0.1 \times 0.01036}{36} \text{ ml. of N NaOH/5 ml. sample/sec.}$$

in a 1.0 M. solution of hydrochloric acid.

Therefore,

$$\Delta H^+ = 2.88 \times 10^{-5} \int_0^t H^+ \, dt$$

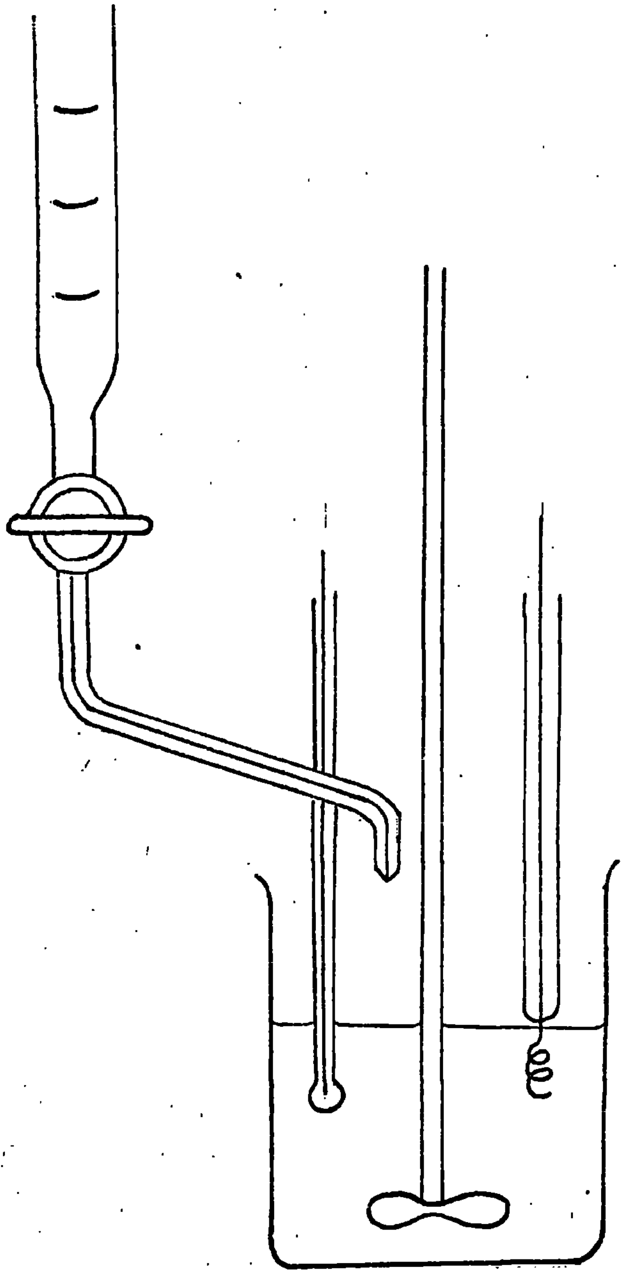
where ΔH^+ is in ml. of normal sodium hydroxide solution per 5 ml. sample of the reaction mixture and H^+ is the molar concentration of acid.

It was assumed that this correction could be applied to the kinetic experiments with benzhydryl chloride and p-methoxybenzyl chloride and the appropriate corrections in the acidity titrations accordingly made.

Potentiometric Determination of Chloride ion, Azide ion and Hydrogen ion Concentrations

The apparatus is shown diagramatically in Figure VII-2. The acetone containing the sample had a volume of about 300 ml. and was contained in a beaker standing in ice-cold water. The solution was well stirred. If only chloride ion was to be determined, a few drops of concentrated nitric acid were added,

FIGURE VII-2



and standard silver nitrate added from a burette until within 0.5ml. of the end-point. The e.m.f. between the glass electrode and the silver (or Ag/AgCl) electrode was determined using a Doran pH. meter (model). The procedure was repeated after each addition of 0.1ml. of silver nitrate solution until the equivalence point was passed. At the end-point the change of e.m.f. per unit titre, was a maximum.

When both chloride and azide ions were to be determined the procedure was modified as follows. A single drop of lacmoid indicator in acetone solution was added to the solution which was to be titrated. 0.1N nitric acid was added until it was slightly acid and chloride ion then determined as above. 2ml. of a saturated solution of sodium fluoride was then added from a pipette and the second equivalence point determined in a similar way. The changes of e.m.f. per unit titre ($\frac{\Delta E}{\Delta V}$) were very much smaller than for the chloride ion determination.

When hydrogen ion was determined, in the presence of pyridine, the procedure was exactly the same, except that sodium hydroxide solution was added instead of silver nitrate solution. If chloride ion was also to be determined this was carried out as detailed above, after the determination of the acidity.

Rate Measurements with Radioactive Compounds.

5ml. samples of the reaction mixture were withdrawn at suitable times and the reaction stopped by running them into petroleum ether (40°/60°; 25 ml.) and water (approximately 8 ml. accurately measured from a dispenser - see figure VII-1), cooled in an ice-salt mixture. After shaking for three minutes, most of the aqueous layer was separated and stored in a stoppered test-tube until ready for counting. A 10 ml. sample of the aqueous extract, after standing for a half hour in a thermostat at 20°C, was counted for one hour. A standard halogen-quenched liquid counter, a thermostated lead-lined "castle" and standard counting equipment were used. The background count was determined several times, for periods of a half hour. The procedures were standard ones and have been adequately described in several publications dealing with radio-chemical techniques[121]. The counted samples were then run into neutral acetone containing lacmoid indicator and the acidity determined with standard sodium hydroxide solution. Any slight hydrolysis of the substrate during extraction was shown to make no difference to the value of (k_E-k_H). This is shown in appendix D. In general, good first-order hydrolysis rates were obtained, indicating that hydrolysis during extraction was unimportant and this was confirmed by independent experiments.

Theoretical Rate Expressions.

The different processes which concern the present investigations are represented by the following steps.

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

$$R^+ \xrightarrow{3} ROH$$

$$R^+ + Y^- \underset{5}{\overset{4}{\rightleftharpoons}} RY$$

$$RCl + Y^- \underset{7}{\overset{6}{\rightleftharpoons}} RY + Cl^-$$

Since stages 1 and 5 are slow (rate determining) and stages 3 and 4 are very fast, the carbonium ion must always have a very small concentration, so that it is valid to apply the "steady-state" principle to this species. It is then possible to derive expressions for the rate of hydrolysis of the substrate (rate coefficient k_H) and for its total rate of disappearance (rate coefficient k_{Cl}). Thus[≠],

$$\frac{dR^+}{dt} = k_1RCl - k_2R^+Cl - k_3R^+ - k_4R^+Y + k_5RY = 0$$

therefore, $R^+ = \frac{1}{k_3} \cdot \frac{k_1RCl + k_5RY}{1 + \alpha Cl^- + \beta Y^-}$

[≠] Throughout this thesis the normal square brackets denoting concentration have been omitted, in order to avoid overcrowding the rate equations. Thus, for example, where-ever a term X^- appears it is equivalent to the more usual $[X^-]$.

and it follows that

$$\frac{d\ ROH}{dt} = \frac{k_1RCl + k_5RY}{1 + \alpha Cl^- + \beta Y^-}$$

and/ $$-\frac{d\ RCl}{dt} = \frac{k_1RCl(1 + \beta Y^-) - \alpha k_5Cl^-.RY}{1 + \alpha Cl^- + \beta Y^-} + k_6RCl.Y^- - k_7RY.Cl^-.$$

where, α is the mass-law constant, defined as k_2/k_3

β is similarly defined as k_4/k_3

Y^- is the anion of the electrolyte MY.

Therefore

$$k_H = \frac{1}{RCl + RY} \cdot \frac{d\ ROH}{dt} = \frac{k\,\frac{RCl}{RCl + RY} + k_5\frac{RY}{RCl + RY}}{1 + \alpha Cl^- + \beta Y^-} \quad . \text{VII-1}$$

and/ $$k_{Cl} = -\frac{1}{RCl} \cdot \frac{d\ RCl}{dt}$$

$$= \frac{k_1(1 + \beta Y^-) - \alpha k_5Cl^-\,\frac{RY}{RCl}}{1 + \alpha Cl^- + \beta Y^-} + k_6Y^- - k_7\frac{RY}{RCl}.Cl^- \quad \text{VII-2}$$

It is convenient to consider separately several distinct cases, which arise as a result of the differences in the nucleophilic power and identity of the anions of the added electrolytes. This will now be done.

(i) When the electrolyte is either an ionised chloride or the anion does not react with the substrate, steps 4, 5, 6 and 7 are not applicable, and the rate coefficients, k_H and k_{Cl}, become equal. They are given by the expression

$$k = \frac{k_1}{1 + \alpha Cl^-} \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{VII-3}$$

(ii) A special case arises when the substrate contains radio-active chlorine and the electrolyte is an inactive chloride. Y^- becomes Cl^{*-}, where the superscript star indicates a radio-active species, $k_1 = k_4^*$, $k_2 = k_5^*$ and $k_6 = k_7$. The rate of hydrolysis is still given by VII-3 but the rate of disappearance of RCl (rate coefficient k_E) involves k_6. The concentration of carbonium ion is given by

$$R^+ = \frac{k_1\,(RCl + RCl^*)}{1 + \alpha(Cl^- + Cl^{*-})} \approx \frac{k_1 RCl}{1 + \alpha Cl^-}$$

since the inactive species is always present in great excess. Therefore,

$$k_E = -\frac{1}{RCl^*} \cdot \frac{d\,RCl^*}{dt}$$

$$= k_1 - Cl^{*-} \cdot \frac{k_1}{1 + \alpha Cl^-} \cdot \frac{RCl}{RCl^*} + k_6 \cdot \frac{RCl^*Cl^- - RClCl^{*-}}{RCl^*}$$

$$= \frac{k_1}{1 + \alpha Cl^-} \cdot \left[1 + \frac{RCl^*Cl^- - RClCl^{*-}}{RCl^*}\left(\alpha + \frac{k_6}{k_1/(1 + \alpha Cl^-)}\right)\right]$$

In addition

$$Cl^- = Cl^-_o + RCl_o - RCl = Cl^-_\infty - RCl$$

and/ $Cl^{*-} = RCl^*_i - RCl^*$

where the subscript 'o' refers to the experimental zero of time and 'i' refers to initial values.

Therefore,

$$k_E = \frac{k_1}{1 + \alpha Cl^-}\left[1 + \left(\alpha + \frac{k_6}{k_1/(1 + \alpha Cl^-)}\right)\left(Cl^-_\infty - RCl^*_i . \frac{RCl}{RCl^*}\right)\right]$$

$$= \frac{k_1}{1 + \alpha Cl^-} + Cl^-_R . \left(\frac{\alpha k_1}{1 + \alpha Cl^-} + k_6\right) \ldots\ldots\ldots \text{VII-4}$$

where, $Cl^-_R = Cl^-_\infty - RCl^*_i . \frac{RCl}{RCl^*}$

(iii) When reaction between the anion and the substrate leads to a product (RY) which ionises again much more rapidly than the chloride (e.g. $Y^- = PhSO_3^-$, NO_3^- and Br^-), another special case arises. The concentration of RY must always be very small and the last term on the right hand side of equation VII-2 can therefore be neglected, since the amount chloride ion produced in the reaction is also small. Moreover, RY/RCl is much less than unity so that it is possible to write,

$$k_H = \frac{k_1 + k_5 \frac{RY}{RCl}}{1 + \alpha Cl + \beta Y}$$

and/ $$k_{Cl} = \frac{k_1(1 + \beta Y^-) - \alpha k_5 \frac{RY}{RCl} Cl^-}{1 + \alpha Cl^- + \beta Y^-} + k_6 Y^-$$

When k_H and k_{Cl} are equal

$$k_1 + k_5 \frac{RY}{RCl} = k_1(1 + \beta Y) - \alpha k_5 \frac{RY}{RCl} Cl^- + k_6 Y^-(1 + \alpha Cl^- + \beta Y^-)$$

or/ $$k_5 \frac{RY}{RCl} = \frac{1}{1 + \alpha Cl^-}\left[k_1 \beta Y^- + k_6 Y^-(1 + \alpha Cl^- + \beta Y^-)\right]$$

Therefore,

$$k_H = \frac{k_1 + k_6Y^-}{1 + \alpha Cl^-} \qquad \text{. . . . . VII-5}$$

This is identical with equation VII-3 when $k_6=0$, which is the case when benzhydryl chloride is the substrate. The overall effect on S_N1 substitution is therefore kinetically indistinguishable from an ionic-strength effect, and it is not possible to calculate β for the reactions of such anions with carbonium ions.

When k_H and k_{Cl} are not equal, it is necessary to make some assumptions about the size of β. It will be shown later in this chapter that this situation need only be considered for the reactions between p-methoxybenzyl chloride and nitrate and bromide ions.

(iv) The final case to be considered arises when the reaction yields a product (RY) which does not react significantly compared to the chloride ($Y^- = N_3^-$, F^-). The rate coefficients, k_H and k_{Cl}, are then not equal and are given by the equations

$$k_H = \frac{k_1}{1 + \alpha Cl^- + \beta Y^-} \qquad \text{. . . . . VII-6}$$

and/ $$k_{Cl} = \frac{k_1(1 + \beta Y^-)}{1 + \alpha Cl^- + \beta Y^-} + k_6Y^- \qquad \text{. . . . . VII-7}$$

Ionic-Strength Effects.

The theoretical treatment described in Chapter IV (pages 75 - 78) defines the effect of a single electrolyte on the rate of ionisation by the expression

$$k_1 = k_1^o \text{ antilog}_{10} - B\sigma c$$

where, k_1 is the rate of ionisation at the molar ionic strength, c.

k_1^o is the rate of ionisation at zero ionic strength.

σ is a parameter with the dimensions of length (cms), which is characteristic of the electrolyte for a given substrate.

B is a constant with the value given on page 43

In practice, at least two electrolyte species are present in most runs (the electrolyte and the acid produced by hydrolysis). A more general expression for the effect of electrolytes on the rate determining ionisation is therefore necessary; thus

$$k_1 = k_1^o \text{ antilog}_{10} - B\sum \sigma_i c_i \quad \ldots\ldots\ldots \text{VII-8}$$

in which $\sum \sigma_i c_i$ sums the effect of all the electrolytes present. This value of k_1, in the form appropriate to the conditions of the experiment, is substituted in the rate equations derived in the preceding pages.

Instantaneous and Integrated Rates.

The theoretical rate equations derived earlier in this chapter, refer to instantaneous rates, whereas the values determined in the present studies were all integrated ones. It was found to be more convenient to use these equations in their present form than to attempt the task of integrating them, a process which would have to be repeated for each experiment (compare Chapter IV, page 76). The integrated rate coefficients were therefore converted to instantaneous values in the following way.

The observed first-order integrated rate coefficients, apart from a few exceptional cases (compare Chapter IV, page 57), were constant throughout the course of the reactions. It was therefore assumed that the integrated rate coefficient, $\bar{k}_X$, for the time interval o - t, represented the instantaneous value at $^t/_2$. The concentration of chloride ions at this time is given by

$$
\begin{aligned}
Cl^-_{t/2} &= Cl^-_o + RCl_o - RCl_{t/2} \\
&= Cl^-_\infty - RCl_{t/2}
\end{aligned}
$$

Assuming that the reaction of the substrate follows first-order kinetics, the concentration of RCl at time $^t/_2$ is given by

$$
\begin{aligned}
RCl_{t/2} &= RCl_o . e^{-kt/2} \\
&= RCl_o^{\frac{1}{2}} . \left(RCl_o . e^{-kt}\right)^{\frac{1}{2}} \\
&= \left(RCl_o . RCl_t\right)^{\frac{1}{2}}
\end{aligned}
$$

The chloride ion concentration at $t/2$ is therefore

$$Cl^-_{t/2} = Cl^-_{\infty} - (RCl_o . RCl_t)^{\frac{1}{2}}$$

The mean of the integrated rate coefficients therefore corresponds to an instantaneous value at a mean chloride-ion concentration which has the value

$$Cl^- = \frac{1}{n}\sum Cl^-_{t/2} = Cl^-_{\infty} - \frac{RCl_o^{\frac{1}{2}}}{n} . \sum RCl_t^{\frac{1}{2}} \quad . \; . \; . \; . \; VII\text{-}9$$

where n is the number of determinations of $\overline{k}_X$ and the subscript t refers to the experimental times at which the individual values were determined.

The validity of this assumption is examined and confirmed in Appendix E , for an extreme case where constant first order rate coefficients were not observed.

A quantity Cl^-_R was defined earlier in this chapter (see page 140) for the experiments with substrates containing Cl^{36}. If the same assumptions regarding the relation between integrated and instantaneous rates is accepted for the coefficient k_E, the value of Cl^-_R, to which the mean of the integrated values of $\overline{k}_E$ refer, is given by

$$(Cl^-)_{t/2} = Cl^-_{\infty} - RCl^*_i . \left(\frac{RCl}{RCl^*}\right)_{t/2}$$

If the reaction of RCl follows first-order kinetics,

$$(RCl^*)_{t/2} = RCl^*_o \, e^{-k_E t/2} = (RCl^*_o \, RCl^*_t)^{\frac{1}{2}}$$

and therefore

$$Cl^-_R = Cl^-_\infty - \frac{RCl^*_i}{n} \cdot \left(\frac{RCl_o}{RCl^*_o}\right)^{\frac{1}{2}} \sum \left(\frac{RCl_t}{RCl^*_t}\right)^{\frac{1}{2}} \quad \ldots\ldots \text{VII-10}$$

More-over,

$$\left(\frac{RCl_o . RCl_t}{RCl^*_o . RCl^*_t}\right)^{\frac{1}{2}} = \frac{RCl_o}{RCl^*_o} \cdot e^{(k_E - k_H)t/2}$$

$$= \frac{RCl_o}{RCl^*_o}\left[1 + \tfrac{1}{2}(k_E - k_H)t + \ldots\ldots\right]$$

when $(k_E - k_H)$ is very much less than unity, only the first two terms of the expansion in the square bracket are significant. For such cases the value of Cl^-_R can be calculated from

$$Cl^-_R = Cl^-_\infty - RCl^*_i \cdot \frac{RCl_o}{RCl^*_o}\left[1 + \frac{(k_E - k_H)}{2n}\sum t\right] \quad \ldots \text{VII-11}$$

Ionic Strengths.

The ionic strengths to which these instantaneous rates refer, were calculated from the following equations;

For most electrolytes, the ionic strength, c, is given by

$$\left.\begin{aligned} c^{\mathrm{HCl}} &= c_{\infty}^{\mathrm{HCl}} - \mathrm{Cl}^{-} \\ \sum c &= c^{\mathrm{HCl}} + c_{i}^{\mathrm{MY}} \end{aligned}\right\} \quad \ldots\ldots\ \mathrm{VII\text{-}12}$$

When the electrolytes were $\mathrm{Me_4NF}$ and $\mathrm{NaN_3}$, the anions were removed from the solution by reaction with the substrate and also as undissociated hydrofluoric and hydrazoic acids. For these cases the ionic strengths are given by,

$$\left.\begin{aligned} c^{\mathrm{MCl}} &= \mathrm{Cl}^{-} \\ c^{\mathrm{MY}} &= c_{i}^{\mathrm{MY}} - \mathrm{Cl}^{-} \\ \sum c &= c^{\mathrm{MY}} + c^{\mathrm{MCl}} = c_{i}^{\mathrm{MY}} \end{aligned}\right\} \quad \ldots\ldots\ \mathrm{VII\text{-}13}$$

It can be seen that the ionic strengths, in the presence of these salts, stay constant throughout the course of the reactions.

The Determination of the Parameters α, β and σ for the Reactions of Benzhydryl Chloride in 70% Aqueous Acetone in the Presence of Electrolytes.

In this section, the following nomenclature will be used.

c is the molar ionic-strength of the solution for a given electrolyte, MY.

The subscript o refers to experiments carried out in the absence of added electrolyte.

k_H° is the rate coefficient for the hydrolysis of the substrate in the absence of added electrolyte.

k_1° is the rate coefficient for the ionisation of the substrate at zero ionic-strength.

$$k_{Cl} = -\frac{1}{RCl} \cdot \frac{d\ RCl}{dt}$$

$$k_E = -\frac{1}{RCl^*} \cdot \frac{d\ RCl^*}{dt}$$

$$k_H = +\frac{1}{RCl} \cdot \frac{d\ ROH}{dt}$$

where RCl* indicates a substrate containing Cl^{36} (Cl*). The rate coefficient k_6 is zero for the reactions of benzhydryl chloride.

(i) σ and a.

The calculation of the effects of electrolytes on the rate of ionisation requires a knowledge of the parameter σ (defined in equation IV-6). It was first necessary to calculate the mass-law constant, a, and this was done by using the data from experiments with benzhydryl chloride containing Cl^{36}, in the presence of ionised chlorides. Equations VII-3 and VII-4 were combined to give the expression

$$a = \frac{k_E - k_H}{k_H Cl_R^-}$$

Four estimates of a were obtained from the experiments with added HCl (0.05M) and NaCl (0.1, 0.05 and 0.025 M). The values are given in Table VII-1 and it can be seen that they do not vary with the ionic-strength. This point will be discussed after a description of the method used to calculate σ^{HCl}.

In the absence of added electrolyte equation VII-3 takes the form

$$k_H^\circ = \frac{k_1^\circ \text{ antilog}_{10} - B\sigma^{\mathrm{HCl}} c_o^{\mathrm{HCl}}}{1 + a_o\mathrm{Cl}_o^-} \quad \ldots\ldots \text{VII-14}$$

With added hydrochloric acid it becomes

$$k_H = \frac{k_1^\circ \text{ antilog}_{10} - B\sigma^{\mathrm{HCl}} c^{\mathrm{HCl}}}{1 + a\mathrm{Cl}^-} \quad \ldots\ldots \text{VII-15}$$

and with added sodium chloride

$$k_H = \frac{k_1^\circ \text{ antilog}_{10} - B(\sigma^{\mathrm{NaCl}} c^{\mathrm{NaCl}} + \sigma^{\mathrm{HCl}} c^{\mathrm{HCl}})}{1 + a\mathrm{Cl}^-}. \quad \text{VII-16}$$

It was assumed that a did not vary with ionic strength (compare page 149). Therefore for added HCl, equations VII-14 and VII-15 were combined to give

$$\frac{k_H}{k_H^\circ} = \frac{(1 + a\mathrm{Cl}_o^-)}{(1 + a\mathrm{Cl}^-)} \text{ antilog}_{10} - B\sigma^{\mathrm{HCl}}(c^{\mathrm{HCl}} - c_o^{\mathrm{HCl}}). \ldots \text{VII-17}$$

and for added sodium chloride equations VII-14 and VII-16 similarly gave

$$\frac{k_H}{k_H^o} = \frac{(1 + \alpha Cl_o^-)}{(1 + \alpha Cl^-)} \ \mathrm{antilog}_{10} - B\left[\sigma^{NaCl}c^{NaCl} + \sigma^{HCl}(c^{HCl} - c_o^{HCl})\right] \qquad \ldots\ldots \text{VII-18}$$

The mean value of α was inserted in these equations to give three estimates of σ^{NaCl} and one of σ^{HCl}. The values are given Table VII-1. It can be seen that the values of σ^{NaCl} decrease as the ionic strength increases, which is unexpected. This may be real, but it seems more likely that the variations are within the limits of the experimental errors and that the drift is artificial. This may be easily demonstrated. The σ values are sensitive to errors in $\frac{k_H}{k_H^o}$, particularly for small concentrations of electrolyte. If the experimental error in $\frac{k_H}{k_H^o}$ is x%, the error in σ is given by $\frac{\log(1 \pm x/100)}{-Bc^{NaCl}}$. (see Appendix F).

Table VII-1 gives the mean value of these errors, assuming a value of 0.05 for x. The discrepancies are serious for the addition of 0.025M electrolyte and significant at 0.05M.

The apparent constancy of α is more serious. The treatment developed by Hughes and Ingold, and adopted with variations in the present studies, relates the mass-law constant at a given ionic strength to its value at zero ionic strength by the expression

$$\alpha = \alpha^\circ \ \mathrm{antilog}_{10}(A\sum c_i^{\frac{1}{2}} - B\sum \sigma_i c_i)$$

TABLE VII-I

The Effect of Ionised Chlorides on the Reaction of Benzhydryl Chloride with 70% Aqueous Acetone at 20·08°C.

Electrolyte	$C^{MCl}_{initial}$	α	$10^8\sigma$	$\Delta\sigma$	$(10^4 k_H)_{obs.}$	A″		B″	
						α^o	$(10^4 k_H)_{calc.}^{*}$	α^o	$(10^4 k_H)_{calc.}^{\neq}$
HCl	0·05000	2·25	0·89	–	–	–	–	–	–
NaCl	0·02512	2·38	0·36	±0·12	2·449	4·1	2·449	3·5	2·435
NaCl	0·05134	2·35	0·31	±0·06	2·365	5·0	2·391	3·9	2·373
NaCl	0·10034	2·37	0·23	±0·03	2·127	6·2	2·280	4·2	2·197

* Calculated assuming $10^8\sigma = 0\cdot30.$, $\alpha^o = 5\cdot0$

≠ Calculated assuming $10^8\sigma = 0\cdot30.$, $\alpha^o = 4\cdot0$

A″. From $\alpha = \alpha^o \text{antilog}_{10}(Ac^{\frac{1}{2}} - B\Sigma\sigma c)$

B″. From $\alpha = \alpha^o \text{antilog}_{10}\left(\frac{Ac^{\frac{1}{2}}}{1+Cc^{\frac{1}{2}}} - B\Sigma\sigma c\right)$

(see Chapter III, page 45). The parameter a should therefore decrease with increasing ionic strength. Values of a°, calculated from the present data using a mean value of 0.30 for σ^{NaCl}, are included in Table VII-1. It can be seen that they are markedly different. Values of k_H are also calculated, assuming that $a^\circ = 5$ and $\sigma^{\mathrm{NaCl}} = 0.30$, and are very different from the experimental values.

Hughes and Ingold assumed that the activity coefficient of the anion, X^-, could be expressed by the Debye-Huckel limiting expression

$$-\ln f_- = \sqrt{\frac{2}{1000}} \cdot \frac{N^{\frac{1}{2}} e^3}{k^{\frac{3}{2}}} \cdot \frac{c^{\frac{1}{2}}}{(DT)^{\frac{3}{2}}}$$

Consideration of the more extended form of the Debye-Huckel equation,

$$-\ln f_- = \sqrt{\frac{2}{1000}} \cdot \frac{N^{\frac{1}{2}} e^3}{k^{\frac{3}{2}}} \cdot \frac{c^{\frac{1}{2}}}{(DT)^{\frac{3}{2}}} \left(1 + \frac{8\pi N e^2}{1000k} \cdot \frac{a c^{\frac{1}{2}}}{(DT)^{\frac{1}{2}}}\right)^{-1}$$

where 'a' is a measure of the distance of closest possible approach, shows that significant departures from the predictions of the limiting law should aride at the ionic strengths employed in the present work. From studies of activity coefficients of sodium chloride in water it appears that 'a' should be of the order of 4 — 4.8 Ångstrom units[122]. Accepting the lower figure as a mean value for the present situation, the appropriate modification of the Hughes/Ingold treatment leads to

$$a = a^{\circ}\ \text{antilog}_{10}\ \frac{A(\sum c_i)^{\frac{1}{2}}}{1 + C(\sum c_i)^{\frac{1}{2}}} - B\sum o_i c_i$$

where $C = \frac{8\pi Ne}{1000k} \cdot \frac{4}{(DT)^{\frac{1}{2}}} = 1.86$ for 70% aqueous acetone at 20°C.

The new values for a° and calculated k_H, assuming a value of 4.0 for a°, are also given in Table VII-1. The agreement is now acceptable, and it is probable that it could have been much improved either by using the value of 4.8 Å for 'a', or by employing one of the empirical activity coefficient relationships which have been proposed[123].

Since most of the remaining work was carried out with 0.05 molar solutions of the electrolytes, the constant values were accepted for a. The values are in any case very small and a considerable refinement of the present techniques would be required in order to eliminate the uncertainties due to experimental error.

A mean value of 2.3 was accepted for a, $0.\overset{89}{98} \times 10^{-8}$ cms. for o^{HCl} and 0.30×10^{-8} cms. for o^{NaCl}. It was now possible to treat the remaining electrolytes by analogous procedures.

When the anion of the added electrolyte was unreactive ($MY = NaClO_4$, $NaBF_4$), or when it reacted to give a product which ionised faster than benzhydryl chloride ($MY = PhSO_3Na$, $NaNO_3$

KBr) the procedure was exactly the same as that in section (i), because the rate equations were the same (see pages 137-140). Equation VII-18 was thus employed, with σ^{NaCl} and c^{NaCl} replaced by the corresponding values for the electrolyte, MY.$^{\neq}$

(ii) σ and β.

It was only possible to calculate values of the intervention constant, β, for the reactions of the benzhydryl cation with fluoride ions and azides ions. Equations VII-6 and VII-7 were combined to give

$$\beta = \frac{k_{Cl} - k_H}{k_H Y^-}$$

where $Y^- = F^-$ or N_3^-. The values of β, calculated from this expression, are given in Table VII-2 and they will be discussed after a description of the method used to obtain the σ-values.

The concentrations of the electrolytes were given by equations VII-13. Since Shillaker[29] had shown that Me_4NBr and NaBr accelerated the rate of reaction of benzhydryl chloride equally, it was assumed that Me_4NCl and NaCl were equivalent. Equation VII-7 thus took the form,

---

$^{\neq}$ Since k_{Cl} and not k_H was determined for the reaction in the presence of ~~this~~ added $NaBF_4$, the ratio is k_{Cl}/k_H° for this electrolyte.

$$k_{Cl} = \frac{(1 + \beta Y^-)}{1 + \alpha Cl^- + \beta Y^-} k_1 \text{ antilog}_{10} -B(\sigma^{MY}c^{MY} + \sigma^{NaCl}c^{NaCl})$$

where $MY = Me_4NF$ or NaN_3.

Combination of this equation and equation VII-14 then gave

$$\frac{k_{Cl}}{k_H^o} = \frac{(1 + \alpha Cl_o^-)(1 + \beta Y^-)}{1 + \alpha Cl^- + \beta Y^-} \text{antilog}_{10} -B(\sigma^{MY}c^{MY} + \sigma^{NaCl}c^{NaCl} - \sigma^{HCl}c_o^{HCl}) \quad \ldots\ldots \text{VII-19}$$

Values of σ^{MeNF} and σ^{NaN_3} were then calculated from this expression by inserting the other known values, and they are shown in Table VII-2.

TABLE VII-2

Values of β and σ for the Reactions of Benzhydryl Chloride with Sodium Azide and Tetramethylammonium Fluoride in 70% Aqueous Acetone at 20.08°C.

Electrolyte.	c^{MY}	β	$10^8\sigma$	Q∅	R⌿	$10^8\sigma$≠	$10^8\Delta\sigma$
Me_4NF	0.04530	0.54	−0.68	-	-	−0.68	-
NaN_3	0.01254	5.02	2.01	1.0003	0.9993	2.06	± 0.26
NaN_3	0.01965	5.07	2.01	0.9955	0.9934	2.08	± 0.16
NaN_3	0.04121	6.46	1.74	0.9999	0.9957	1.81	± 0.08

∅ $Q = \frac{(1 + \alpha Cl_o^-)(1 + \beta Y^-)}{1 + \alpha Cl^- + \beta Y^-}$. ⌿ $R = \frac{1 + \alpha Cl_o^-}{1 + \alpha Cl^-}$

≠ Values obtained by neglecting β.

It can be seen from Table VII-2 that the values of $\beta_{N_3^-}$ are much greater than β_{F^-}. Since fluoride ions are rather poor nucleophilic reagents, the small value of β_{F^-} is not unreasonable. However, the values of k_H from which it was determined were probably not very accurate (compare page 132) but it can be seen that neglect of β has no effect on the value of the σ parameter. Since this is determined from k_{Cl}, which is not subject to the same inaccuracies as k_H, the experimental value can be accepted without reserve. Azide ions are generally regarded as rather powerful nucleophiles and the values of $\beta_{N_3^-}$ are in agreement with previous conclusions that these ions are more reactive than chloride ions (compare Table IV-1) towards carbonium ions. Sodium azide was used at three different concentrations (0.02M, 0.03M and 0.05M) and therefore three estimates of $\beta_{N_3^-}$ were obtained (see Table VII-2). The value at the highest concentration is in poor agreement with those at the lower concentrations. This probably originated in the values of k_H which are open to the possibility of large errors (see page 132). However, it is obvious from the results given in Table VII-2 that

$$\frac{(1 + \alpha Cl_0^-)(1 + \beta N_3^-)}{1 + \alpha Cl^- + \beta N_3^-} \quad \text{and} \quad \frac{1 + \alpha Cl_0^-}{1 + \alpha Cl^-}$$

differ by less than the experimental error in $\frac{k_{Cl}}{k_H^o}$.

Comparison of values of σ^{NaN_3} calculated using the experimental values of β and those obtained by neglecting $\beta_{N_3^-}$ show that the differences are unimportant, and the second method avoids the uncertainty of errors in k_H. The differences in the σ-values may be attributed to the experimental errors in the rate coefficients, k_{Cl}. If the ratio k_{Cl}/k_H° is in error by x%, the error in β is given by $\frac{\log(1 + x/100)}{-Bc^{NaN_3}}$, (see Appendix F). Table VII-2 gives the values of these errors, assuming a value of 0.5 for x, and it can be seen that such a small error in the experimantal value of k_{Cl} could account for the observed differences in the σ-values. It was therefore decided that the best value of σ^{NaN_3} was that for initially 0.05M electrolyte, calculated on the assumption that β was zero. The value of 1.81 was therefore accepted.

The Determination of the Parameters α, β and σ for the Reactions of p-Methoxybenzyl Chloride in 70% Aqueous Acetone in the Presence of Electrolytes.

The nomenclature used in this section is the same as that employed in the preceding section (see page 146).

(i) σ and α.

Any calculation of the effects of electrolytes on the rate of ionisation (S_N1) of p-methoxybenzyl chloride requires a knowledge of the parameter σ (defined in equation IV-6). In general, this parameter cannot be determined directly from observed rates of reaction since added nucleophiles may react directly (S_N2) with the substrate. This objection does not, however, apply to reactions in the presence of the very weakly nucleophilic sodium perchlorate and sodium borofluoride. Values of σ were therefore obtained directly from experiments with these compounds and σ values for all electrolyte were obtained by utilising the relation

$$\sigma_{RX} - \sigma_{R'X} = \text{Constant} = \Delta \qquad \ldots\ldots \text{VII-20}$$

where RX and R'X refer to p-methoxybenzyl chloride and benzhydryl chloride, respectively (compare Chapter IV, page 75)

We thus have, by analogy with equation VII-18

$$\frac{k_H}{k_H^\circ} = \frac{1 + aCl_o^-}{1 + aCl^-} \text{antilog}_{10} - B\left[\sigma^{MY} c^{MY} + \sigma^{HCl}(c^{HCl} - c_o^{HCl})\right]$$

Whence in view of equation IV-20

$$\frac{k_H}{k_H^\circ} = \frac{1 + aCl_o^-}{1 + aCl^-} \text{antilog}_{10} - B\left[\sigma_1^{MY} c^{MY} + \sigma_1^{HCl}(c^{HCl} - c_o^{HCl})\right] \quad x$$

$$\text{antilog}_{10} - B\Delta(c^{MY} + c^{HCl} - c^{HCl}) \qquad \ldots\ldots \text{VII-21}\ ≰$$

where σ_1^{MY} refers to the effect of the electrolytes on the rate of ionisation of benzhydryl chloride. Equation VII-21 contains

---

≰ Since k_{Cl} and not k_H was determined for the reaction in the presence of $NaBF_4$, this ratio is k_{Cl}/k_H° for this electrolyte.

two unknown parameters, Δ and α, the mass-law constant for the p-methoxybenzyl cation. However, the appropriate chloride ion concentration is small in the runs with these electrolytes and moreover, not greatly different from the value Cl_o^- (see Appendix A, Tables A1 and A2). As a first approximation the terms involving α in equation VII-21 can be expected to cancel, so that we have

$$\frac{k_H}{k_H^o} = \text{antilog}_{10} - B\left[\sigma_1^{MY} c^{MY} + \sigma_1^{HCl}(c^{HCl} - c_o^{HCl})\right] \quad x$$

$$\text{antilog}_{10} - B\Delta(c^{MY} + c^{HCl} - c^{HCl}) \qquad \text{. . . . . VII-22}$$

Application of this equation to the results with 0.05 M. sodium perchlorate and 0.05 M. sodium borofluoride gave $10^8\Delta$ as 0.11 and 0.12, respectively. A value of 0.12×10^{-8} cms. was therefore accepted for Δ and σ for the other electrolytes were calculated from equation IV-20 on this basis.

It must be stressed that the neglect of the terms containing α causes no error. Values of α were calculated on the assumption that $10^8\Delta$ is equal to 0.12 (see next section) and their substitution in equation VII-B did not alter the value of Δ.

(ii) <u>The determination of α.</u>

The rates of hydrolysis of p-methoxybenzyl chloride in the presence of added hydrochloric acid or sodium chloride are given by equations VII-3. The ratios k_H/k_H^o are therefore given by equations VII-17 and VII-18, respectively. Once the values of σ are known, a can be calculated without difficulty. The values obtained are given in Table VII-3.

TABLE VII-3

Mass-law Constants for the Reaction of p-Methoxybenzyl Chloride in 70% Aqueous Acetone at 20.08°C.

Electrolyte	c^{MCl}	a
HCl	0.05146	3.73
NaCl	0.02484	3.81
NaCl	0.05154	4.05
NaCl	0.10070	4.22

It can be seen that the values of a are constant within the limits of experimental error. While a variation of this parameter with changing ionic-strength is to be expected (compare page 149), the present results are completely analogous to those obtained with benzhydryl chloride, and the constancy of the value of a for this compound has already been discussed (see page 151). It must be stressed that although the a values are now almost twice as large as those with benzhydryl chloride, they are still small and quite unsuitable for any detailed discussion of the effect of changing experimental conditions on the mass-law constant. A mean value of 4.00 was accepted for α, and assumed to be the same for all the other experiments.

(iii) The determination of β.

It is readily shown from equation VII-6 that the ratio k_H/k_H°, for the hydrolysis of p-methoxybenzyl chloride in the presence of sodium azide or tetramethylammonium fluoride, is given by

$$\frac{k_H}{k_H^\circ} = \frac{(1 + \alpha Cl_o)}{(1 + \alpha Cl^- + \beta Y^-)} \text{antilog}_{10} - B(\sigma^{MY} c^{MY} + \sigma^{MCl} c^{MCl} - \sigma^{HCl} c_o^{HCl}) \phi$$

where MY = Me_4NF or NaN_3. Since β is the only unknown parameter in this expression it may readily be determined, and the values obtained are listed in Table VII-4.

TABLE VII-4

Values of β for the Reaction of p-Methoxybenzyl Chloride with Sodium Azide and Tetramethylammonium Fluoride in 70% Aqueous Acetone at 20.08°C.

Electrolyte	c^{MY}	β	$\Delta\beta$
Me_4NF	0.03731	-0.54	-
NaN_3	0.01234	8.68	± 0.91
NaN_3	0.02263	7.53	± 0.54
NaN_3	0.03199	7.68	± 0.40

It can be seen that the β values for the azide ion only agree tolerably well with each other, but the agreement is within the limits of experimental error. A small error in the observed hydrolysis rate has the most serious effect on the value of β, particularly those determined from experiments with the most dilute solutions. It may easily be shown that an error of ±x% in the ratio k_H/k_H^o leads to an error of

$$\Delta\beta = \pm \frac{x}{100}\left(\beta + \frac{1 + c_{Cl^-}}{N_3^-}\right)$$

These errors are shown in Table VII-4 assuming a value of 7.96 for β and an error of 1% in k_H/k_H^o. They entirely account for the observed differences in the value of this parameter and the mean value of 7.96 was therefore accepted for β for the reaction between azide ions and the p-methoxybenzyl cation.

The results in Table VII-4 show a small negative value for β for the reaction in the presence of tetramethylammonium fluoride. It seems likely that this value arises from the experimental error in the determination of k_H, since an allowance had to be made for the disappearance of acid from the reaction mixture.

Foot-note to page 160.

ø It was assumed that Me_4Cl and NaCl were equivalent (compare page 153).

Calculated Values of k_x for the Reactions of p-Methoxybenzyl Chloride in the Presence of Electrolytes, Assuming only S_N1 Reaction.

The rates of decomposition of p-methoxybenzyl chloride (k_x), expected on the assumption that there was no S_N2 substitution of the substrate, were calculated by inserting the appropriate values of α, β and σ in the expressions for k_E, k_{Cl} and k_H which have already been derived for benzhydryl chloride.

The Calculation of the Relative Amounts of Unimolecular and Bimolecular Attack by Pyridine on p-Methoxybenzyl Chloride in 70% Aqueous Acetone at 20.49°C.

The rate of hydrolysis (S_N1) and rate of total reaction ($S_N1 + S_N2$) of p-methoxybenzyl chloride by water and pyridine are given by

$$k_H = \frac{k_1}{1 + \alpha Cl^- + \beta P}$$

and/

$$k_{Cl} = \frac{k_1(1 + \beta P)}{1 + \alpha Cl^- + \beta P} + k_6 P$$

$$= k_H(1 + \beta P) + k_6 P \qquad \text{. . . . . VII-23}$$

respectively, (compare equations VII-6 and VII-7), where P is the concentration of the reagent.

Thus attack by pyridine is given by

$$k_{Cl} - k_H = \underset{S_N1}{k_H \beta P} + \underset{S_N2}{k_6 P}$$

Assuming that the attack on this substrate followed only mechanism S_N1, a value $(k_{Cl})_{calk}$ could be determined from equation VII-23, omitting k_6; thus

$$(k_{Cl})_{calc.} = k_H(1 + \beta P)$$

Therefore

$$(k_{Cl})_{calc.} - k_H = \underset{S_N1.}{k_H\beta P} \qquad \ldots\ldots \text{VII-25}$$

The value of $(k_{Cl})_{calc}$ could not be determined directly, since the effect of pyridine on the rate of ionisation of p-methoxybenzyl chloride could not be determined (Compare Chapter V). It was assumed, however, that this effect was the same as the corresponding effect on the rate of ionisation of benzhydryl chloride. The effect of pyridine on the rate of reaction of benzhydryl chloride is given by the ratio $k_{Cl}/\bar{k}_H^o$, where $\bar{k}_H^o$ is the rate coefficient for the hydrolysis of this compound in the absence of pyridine.

Therefore,

$$\left(\frac{k_{Cl}}{\bar{k}_H^o}\right)_{PhCH_2Cl} = \frac{(k_{Cl})_{calc}}{k_H^o} = K$$

and comparison with equation VII-25 gives

$$Kk_H^o - k_H = \underset{S_N1}{k_H\beta P} \qquad \ldots\ldots \text{VII-26}$$

where k_H^o is the rate coefficient for the hydrolysis of p-methoxybenzyl chloride in the absence of pyridine. The percentage of the attack by pyridine on this compound which proceeds by mechanism S_N1 can be readily calculated from equations VII-24 and VII-26. The values obtained are given in TableVII-5 and can be seen to be constant within the limits of experimental error.

TABLE VII-5

The Reaction of Pyridine with p-Methoxybenzyl Chloride in 70% Aqueous Acetone at 20.39°C.

Pyridine Concentration	10^4k_{Cl}	10^4k_H	K	$10^4(k_{Cl})^{\neq}$ calc.	% S_N1
0.2472	2.573	2.172	0.9448	2.369	49.1
0.4942	2.606	1.865	0.9093	2.280	56.0
0.7420	2.660	1.611	0.8647	2.169	52.8

$\neq$ $10^4k^{\circ}_H$ = 2.507

Calculation of Results.

Mean rate coefficients, k_m, were obtained for each run. The standard deviation $\sigma(k)$ was obtained from the relation

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

where n is the number of seperate determinations of k.

First-order rate coefficients were obtained from the equations

$$k_{CL} = -\frac{1}{t}\int_{o}^{t}\frac{1}{RCl}\cdot dRCl$$

$$k_{H} = \frac{1}{t}\int_{o}^{t}\frac{1}{RCl}\cdot dROH$$

$$k_{E} = -\frac{1}{t}\int_{o}^{t}\frac{1}{RCl^{*}}\cdot dRCl^{*}$$

where the star indicates a radio-active species.

The kinetic runs are shown in detail in Appendix A at the end of this chapter and are summarised in Tables A1, A2 and A3 (pages 236—245).

CHAPTER VII. APPENDIX A.

1. HYDROLYSIS OF p-NITROBENZHYDRYL CHLORIDE IN 50% AQUEOUS ACETONE.

2. REACTIONS OF BENZHYDRYL CHLORIDE AND p-METHOXYBENZYL CHLORIDE IN 70% AQUEOUS ACETONE IN THE PRESENCE OF ELECTROLYTES. AND NON-ELECTROLYTES.

Details of kinetic runs .

Rate coefficients are all first-order values calculated by the equations given on page 165. In each case full details of one run is given and the mean rate coefficients k', k" etc. of the duplicate runs are quoted.

A list of solvents is given at the end of this section and also a summary of the mean values of the rate coefficients and the ionic-strengths of each experiment.

Expt.1. p-Nitrobenzhydryl Chloride in 50% aq.Acetone at 20.60°C

6 ml. titrated with 0.003273 N NaOH.

Time*	Titre	10^6 k
0	1.37	-
1119	4.55	5.340
1436	5.21	5.252
1765	5.95	5.375
3052	7.93	5.309
4270	9.21	5.305
0	0.20	-
363	1.47	5.265
2618	6.76	5.224
2921	7.35	5.374
3969	8.62	5.322
∞	11.92	

k = 5.307 (9 readings)

Duplicate Experiment. k' = 5.332 (10 readings)

Mean k = 5.320 ± 0.0124.

* Time in minutes.

Expt.2. p-Nitrobenzhydryl Chloride in 50% aq.Acetone at 29.56°C

6 ml. titrated with 0.003286 N NaOH.

Time*	Titre	10^5 k
0	0.21	-
700	6.46	1.680
842	7.30	1.696
1018	8.16	1.697
1200	8.90	1.697
1441	9.65	1.681
0	00.29	-
123	1.71	1.673
241	2.92	1.674
363	4.02	1.669
483	4.99	1.672
603	5.82	1.662
725	6.68	1.697
773	7.01	1.678
∞	12.53	

k = 1.681 ± 0.0013

(12 readings)

* Time in minutes.

Expt.3. p-Nitrobenzhydryl Chloride in 50% aq.Acetone at 39.31°C

6 ml. titrated with 0.003333 N NaOH.

Time*	Titre	10^5 k
0	0.25	-
32	1.50	5.228
61	2.51	5.192
102	3.80	5.184
124	4.52	5.323
157	5.33	5.251
202	6.33	5.174
262	7.57	5.235
322	8.61	5.295
402	9.68	5.316
483	10.50	5.311
563	11.13	5.310
∞	13.30	

k = 5.254 (11 readings)

Duplicate Experiment. k' = 5.256 (12 readings)

Mean k = 5.255 ± 0.0104

---

* Time in minutes.

Expt.4. p-Nitrobenzhydryl Chloride in 50% aq.Acetone at 49.39°C

6 ml. titrated with 0.003333 N NaOH.

Time	Titre	10^4 k
0	0.36	-
360	0.99	1.580
600	1.40	1.589
1140	2.22	1.557
1860	3.27	1.577
2580	4.19	1.579
3420	5.10	1.563
4380	6.10	1.590
5400	6.89	1.565
6480	7.70	1.582
7680	8.45	1.597
9000	9.04	1.577
10440	9.65	1.597
12240	10.19	1.598
∞	11.81	

k = 1.581 (13 readings)

Duplicate Experiment. k' = 1.582 (13 readings)

Mean k = 1.581 ± 0.0023

Expt.5. p-Nitrobenzhydryl Chloride in 50% aq.Acetone at 60.41°C

6 ml. titrated with 0.003333 N NaOH.

Time	Titre	10^4 k
0	0.80	-
240	2.01	4.760
630	3.71	4.780
2290	8.24	4.784
2890	9.21	4.828
3600	10.03	4.852
4425	10.65	4.811
0	1.10	-
400	2.99	4.773
710	4.21+	4.745
1105	5.58	4.804
1410	6.48	4.840
1845	7.48	4.787
∞	11.98	

k = 4.797 (11 readings)

Duplicate Experiment. k' = 4.801 (11 readings)

Mean k = 4.799 ± 0.0087

Expt. 6. Benzotrichloride in 50% aq.Acetone at 20.59°C

No added salts.

5 ml. titrated with 0.009259 N NaOH.

Time	Titre	10^4 k
0	0.10	-
1495	1.12	5.900
3120	2.13	5.889
4720	3.02	5.856
6480	3.90	5.818
8160	4.69	5.848
10080	5.45	5.792
11820	6.08	5.776
12990	6.51	5.808

k = 5.835 (8 readings)

Expt. 7. Benzhydryl Chloride in 70% aq.Acetone V at 20.08°C

No added salts.

5 ml. titrated with 0.007893 N NaOH.

Time	Titre	10^4 k
0	0.20	-
425	1.48	2.498
850	2.65	2.522
1350	3.88	2.540
1745	4.71	2.515
2345	5.88	2.533
2995	6.90	2.506
3650	7.81	2.510
4440	8.77	2.534
5255	9.52	2.523
6195	10.25	2.535
7230	10.83	2.515
∞	12.89	

k = 2.524 ± 0.0040 (11 readings)

k' = 2.530 ± 0.0064 (11 readings)

Expt.8. **Benzhydryl Chloride in 70% aq.Acetone I at 20.08°C**

Added HCl 0.04762 M.

5 ml. titrated with 0.02215 N NaOH.

Time	Titre	$10^4 k$
0	10.81	-
495	11.42	(2.433)
1055	12.07	2.537
1585	12.62	2.592
2060	12.99	2.528
2615	12.42	2.546
3255	13.86	2.578
4000	14.27	2.585
4745	12.58	2.552
5395	14.85	2.588
6390	15.13	2.554
7070	15.39	2.543
∞	16.18	

$k = 2.560 \pm 0.0070$ (10 readings)

Duplicate Experiment.

Added HCl 0.05086 M. $k' = 2.566 \pm 0.0105$ (9 readings)

Av. $k = 2.563$ $10^3\sigma/k = 2.42$

Expt.9. Benzhydryl Chloride in 70% aq.Acetone II at 20.08°C

Added NaCl 0.02519.

5 ml. titrated with 0.008726 N NaOH.

Time	Titre	10^4 k
0	0.20	-
435	1.40	2.435
865	2.49	2.462
1275	3.40	2.449
1735	4.30	2.427
2285	5.30	2.441
2890	6.24	2.442
3610	7.20	2.448
4435	8.10	2.447
5345	8.85	2.416
6395	9.60	2.425
7630	10.31	2.465
∞	12.13	

k = 2.441 ± 0.0043 (11 readings)

Duplicate Experiment.

Added NaCl 0.02503 M. k' = 2.457 ± 0.0056 (11 readings)

Av. k = 2·449 $10^3 \sigma/k$ = 1·59

Expt.10. Benzhydryl Chloride in 70% aq.Acetone III at 20.08°C

Added NaCl 0.05144 M.

5 ml. titrated with 0.008726 N NaOH.

Time	Titre	10^4 k
0	0.27	-
500	1.52	2.372
895	2.41	2.396
1385	3.38	2.368
2290	4.90	2.353
2865	5.71	2.345
3520	6.50	2.334
4260	7.29	2.342
5040	7.99	2.351
6025	8.69	2.350
7290	9.40	2.360

k = 2.358 ± 0.0 (10 readings)

Duplicate Experiments.

Added NaCl 0.05149 M. k' = 2.365 ± 0.0 (9 readings)

0.05092 M. k'' = 2.360 ± 0.0 (10 readings)

0.05138 M. k''' = 2.375 ± 0.0 (12 readings)

Av. k = 2.365 $10^3 \sigma/k$ = 1.61

Expt.11. <u>Benzhydryl Chloride in 70% aq.Acetone V at 20.08°C</u>

Added NaCl 0.1004 M.

5 ml. titrated with 0.007893 N NaOH.

Time	Titre	10^4 k
0	0.15	-
475	1.44	2.119
980	2.70	2.146
1505	3.82	2.112
1980	4.77	2.122
2665	5.95	2.113
3435	7.15	2.135
4280	8.30	2.171
5225	9.14	2.107
5940	9.81	2.127
6795	10.41	2.111
7855	11.10	2.133
∞	13.62	

- - - - - - - - - - - - - - - - - -

k = 2.127 ± 0.0054 (11 readings)

<u>Duplicate Experiments.</u>

Added NaCl 0.1003 M. k' = 2.140 ± 0.0056 (11 readings)

0.1003 M. k" = 2.115 ± 0.0039 (11 readings)

Av k in solvent II 2.160 $10^3\delta/k = 1.59$.

Expt.12. Benzhydryl Chloride in 70% aq.Acetone I at 20.08°C

Added HCl 0.05000 M.

10 ml. of aqueous extract counted for 1 hour and titrated with 0.02215 N NaOH.

Time	Count/min.	Titre	$10^4 k_E$	$10^4 k_H$
0	175	9.92	-	-
465	893	10.39	2.764	2.496
870	1454	10.76	2.793	2.509
1270	1954	11.11	2.813	2.566
1700	2449	11.44	2.846	2.582
2150	2863	11.70	2.809	2.501
2630	3316	12.04	2.868	2.600
3105	3664	12.28	2.859	2.582
3590	3946	12.50	2.814	2.573
4200	4285	12.73	2.813	2.545
4885	4623	12.95	2.834	2.520
5400	4818	13.10	2.830	2.516
6105	5059	13.30	2.842	2.555
∞	6105	14.20		

$k_E = 2.824$; $k_H = 2.545$.

$(k_E - k_H) = 0.279 \pm 0.0066$ (12 readings)

Duplicate Experiment.

Added HCl 0.05000 M. $(k_E' - k_H') = 0.277 \pm 0.0166$ (9 readings)

Expt.13. Benzhydryl Chloride in 70% aq.Acetone XXX at 20.08°C

Added NaCl 0.02513 M.

10 ml. of aqueous extract counted for 1 hour and titrated with 0.008726 N NaOH.

Time	Count/min.	Titre	$10^4 k_E$	$10^4 k_H$
0	231	0.20	-	-
455	1083	1.21	2.551	2.490
980	1965	2.20	2.592	2.432
1485	2697	3.05	2.585	2.418
1945	3277	3.84	2.572	2.507
2420	3815	4.57	2.569	2.489
2910	4300	5.01	2.563	2.449
3555	4873	5.62	2.574	2.401
4160	5302	6.22	2.559	2.441
4800	5726	6.71	2.577	2.438
5615	6139	7.19	2.565	2.402
6445	6497	7.67	2.571	2.432
7600	6872	8.20	2.567	2.475
∞	7973	9.64		

$k_E = 2.570$; $k_H = 2.448$.

$(k_E - k_H) = 0.122 \pm 0.0108$ (12 readings)

Duplicate Experiments

Added NaCl 0.02511 M. $(k_E' - k_H') = 0.163 \pm 0.0077$ (10 readings)

$k_H = 2.434$

Expt.14. Benzhydryl Chloride in 70% aq.Acetone IV at 20.08°C

Added NaCl 0.05150 M.

10 ml. of aqueous extract counted for 1 hour and titrated with 0.009560 N NaOH.

Time	Count/min.	Titre	$10^4 k_E$	$10^4 k_H$
0	290	0.23	-	-
755	1549	1.40	2.875	(2.709)
1210	2173	1.94	2.854	2.606
1585	2653	2.40	2.876	2.649
2065	3169	2.86	2.861	2.601
2545	3670	3.32	2.915	2.632
2980	4080	3.71	2.969	2.679
3610	4359	4.01	(2.757)	2.589
4140	4771	4.40	2.863	2.597
4690	5086	4.70	2.902	2.611
5655	5456	5.07	2.894	2.559
6655	5778	5.40	2.854	2.551
∞	6745	6.56		

$k_E = 2.881$; $k_H = 2.607$.

$(k_E - k_H) = 0.274 \pm 0.0092$ (10 readings)

Duplicate Experiment.

Added NaCl 0.05133 M. $(k_E' - k_H') = 0.286 \pm 0.0137$ (9 readings)

Expt.15. Benzhydryl Chloride in 70% aq.Acetone II at 20.08°C

Added NaCl 0.1005 M.

10 ml. of aqueous extract counted for 1 hour and titrated with 0.008726 N NaOH.

Time	Count/min.	Titre	$10^4\ k_E$	$10^4\ k_H$
0	269	0.26	-	-
455	1097	1.05	2.769	2.136
985	1910	1.92	2.717	2.191
1595	2699	2.78	2.680	2.190
2030	3205	3.31	2.683	2.171
2650	3804	3.97	2.661	2.147
3340	4390	4.69	2.667	2.186
4225	4958	5.14	2.630	(2.003)—why?
5060	5404	5.84	2.622	2.090
5945	5815	6.42	2.653	2.145
6885	6104	6.87	2.615	2.155
7750	6325	7.17	2.598	2.131
8760	6555	7.50	2.621	2.142
∞	7259	8.81		

Mean k_E = 2.660; k_H = 2.153.

$(k_E - k_H)$ = 0.505 ± 0.0135 (11 readings)

$\underline{\underline{.519}}$

From $k_{ROH} \propto k_E - k_H$

$k_E = 2.679$ $\quad 10^3\,\sigma/k = 5.29$

Expt.16. Benzhydryl Chloride in 70% aq.Acetone VI at 20.08°C

Added $NaBF_4$ 0.05082 M.

5 ml. titrated with 0.009560 N $AgNO_3$.

Time	Titre	10^4 k
0	0.19	-
300	1.18	3.101
605	2.09	3.091
925	2.97	3.102
1275	3.82	3.091
1705	4.74	3.077
2165	5.65	3.109
2705	6.56	3.132
3335	7.34	3.075
4160	8.23	3.070
5040	8.97	3.074
5335	9.23	3.121
6050	9.62	3.089
∞	11.34	

k = 3.094 ± 0.0054 (12 readings)

Duplicate Experiments.

Added $NaBF_4$ 0.05036 M. k' = 3.040 ± 0.0029 (9 readings)

0.05082 M. k" = 3.055 ± 0.0067 (11 readings)

Av k = 3.065 $10^5\sigma/k$ = 1.37

Expt.17. Benzhydryl Chloride in 70% aq.Acetone VII at 20.08°C

Added Me_4NF 0.03752 M.

(i) 5 ml. titrated with 0.009775 N $AgNO_3$

(ii)5 ml. titrated with 0.01036 N NaOH.

Time	Cl^-	$10^4 k_{Cl}$	Time*	(a-x)	H $H^+_{obs.}$	$H^+_{corr.}$	$10^4 k_H$
0	0.33	-	0	9.18	1.12	1.12	-
660	1.92	2.620	660	7.72	2.59	2.60	2.672
1265	3.13	2.592	1255	6.60	3.66	3.68	2.615
1905	4.25	2.606	1905	5.56	4.65	4.68	2.592
2575	5.21	2.593	2490	4.76	5.50	5.55	2.642
3255	6.08	2.621	3300	3.85	6.26	6.33	2.577
3990	6.86	2.644	3990	3.21	6.89	6.99	2.592
4645	7.43	2.656	4640	2.70	7.34	7.46	2.579
5315	7.93	2.674	5225	2.32	7.71	7.86	2.590
6010	8.35	2.682	5995	1.89	8.04	8.22	2.567
6690	8.73	(2.718)	6680	1.58	8.35	8.57	2.584
7290	8.92	2.672	7270	1.35	8.50	8.74	2.565
∞	10.35						

- -

k_{Cl} = 2.636 ± 0.0102 (10 readings)

k_H = 2.596 ± 0.0095 (11 readings)

Duplicate Experiment.

k_{Cl} = 2.570 ± 0.0055 (11 readings)

(Time* = Time + 115 seconds)

Expt.18. Benzhydryl Chloride in 70% aq.Acetone X at 20.08°C

Added $PhSO_3Na$. 0.04983 M.

5 ml. titrated with 0.009398 N NaOH.

Time	Titre	10^4 k
0	0.21	-
450	1.48	2.677
800	2.36	2.660
1200	3.26	2.637
1695	4.30	2.673
2195	5.19	2.671
2860	6.20	2.665
3590	7.11	2.655
4365	7.92	2.658
5200	8.63	2.665
6120	9.28	2.694
7220	9.82	2.682
∞	11.44	

$k = 2.667 \pm 0.0043$ (11 readings)

Duplicate Experiment.

Added $PhSO_3Na$. 0.05003 M.

$k' = 2.679 \pm 0.0034$ (11 readings)

Expt.19. Benzhydryl Chloride in 70% aq.Acetone IX at 20.08°C

Added $NaNO_3$ 0.05015 M.

5 ml. titrated with 0.01008 N NaOH.

Time	Titre	10^4 k
0	0.20	-
380	1.38	3.122
825	2.57	3.107
1300	3.70	3.120
1675	4.49	3.138
2115	5.28	3.127
2575	5.98	3.107
3115	6.78	3.164
3725	7.48	3.174
4530	8.22	3.186
5400	8.80	3.166
6560	9.36	3.139
∞	10.70	

k = 3.141 ± 0.0079 (11 readings)

Expt. 20. Benzhydryl Chloride in 70% aq. Acetone IX at 20.08°C

Added $NaNO_3$ 0.05032 M.

5 ml. titrated with 0.008170 N $AgNO_3$.

Time	Titre	10^4 k
0	0.47	-
370	1.87	3.062
840	3.44	3.150
1930	6.32	3.180
2400	7.24	3.155
2825	7.96	3.135
3550	9.05	3.148
4220	9.78	3.105
4845	10.44	3.144
5415	10.90	3.147
6325	11.38	3.065
∞	13.22	

k = 3.129 ± 0.0105 (10 readings)

Duplicate Experiment.

Added $NaNO_3$ 0.05025 M. k' = 3.147 ± 0.0082 (10 readings)

Expt.21. Benzhydryl Chloride in 70% aq.Acetone IX at 20.08°C

Added KBr 0.05008 M.

5 ml. titrated with 0.009560 N NaOH.

Time	Titre	10^4 k
0	0.21	-
470	1.78	3.151
830	2.89	3.224
1170	3.75	3.114
1530	4.62	3.191
1900	5.40	3.190
2355	6.28	3.221
2855	7.06	3.195
3395	7.80	3.220
4295	8.78	3.232
5040	9.40	3.241
5805	9.88	3.232
6500	10.23	3.229
∞	11.63	

k = 3.206 ± 0.0089 (12 readings)

Expt.22. Benzhydryl Chloride in 70% aq.Acetone IX at 20.08°C

Added KBr 0.05010 M.

10 ml. of aqueous extract counted for 1 hour and titrated with 0.009560 N NaOH.

Time	Count/min.	Titre	$10^4 k_E$	$10^4 k_H$
0	266	0.33	-	-
430	1113	1.56	3.069	3.112
830	1880	2.64	3.224	3.224
1220	2409	3.43	3.069	3.109
1525	2828	4.00	3.063	3.063
1995	3431	4.90	3.097	3.135
2430	3838	5.41	3.022	2.993
3045	4387	6.26	3.011	3.036
3705	4850	6.83	2.972	2.922
4565	5350	7.58	2.954	2.931
5470	5761	8.18	2.945	2.934
6485	6063	8.59	2.867	2.829
∞	7133	10.16		

- -

Expt.23. Benzhydryl Chloride in 70% aq.Acetone VIII at 20.10°C

Added NaN_3 0.02026 M. (0.2100)

5 ml. titrated with 0.009132 N $AgNO_3$

$Y_c \equiv 11.50$*

Time	Cl^-	$Cl^- + N_3^-$	N_3^-	$10^4 k_{Cl}$	$10^4 k_H$
0	0.39	11.89	11.50	-	-
825	2.84	14.12	11.28	2.677	2.457
1295	4.03	15.21	11.18	2.698	2.473
1670	4.85	16.05	11.20	2.682	2.524
2250	6.03	17.11	11.08	2.708	2.522
2815	6.86	17.87	11.01	2.634	2.446
3470	7.83	18.72	10.89	2.657	2.441
4210	8.64	19.67	11.03	2.615	2.516
4965	9.31	20.34	11.03	2.577	2.494
5950	10.10	21.05	10.95	2.589	2.480
6940	10.66	21.56	10.90	2.562	2.440
∞	12.75				

$a = .00845$

$k_{Cl} = 2.640 \pm 0.0163$ (10 readings)

$k_H = 2.479 \pm 0.0110$ (10 readings)

Duplicate Experiments.

Added NaN_3 0.01980 M.

$k'_{Cl} = 2.640 \pm 0.0154$ (10 readings)

$k'_H = 2.489 \pm 0.0109$ (7 readings)

* Not quite guided one

Expt.24. Benzhydryl Chloride in 70% aq.Acetone VIII at 20.10°C

Added NaN_3 0.02966 M.

5 ml. titrated with 0.009132 N $AgNO_3$

Time	Cl^-	$Cl^- + N^-$	$10^4\ k_{Cl}$	$10^4\ k_H$
0	1.72	18.17	-	-
410	2.85	19.20	2.691	2.454
825	3.93	20.15	2.766	2.481
1315	4.94	21.05	2.685	2.403
1850	6.03	21.99	2.744	2.432
2490	7.02	22.95	2.700	2.451
3120	7.84	23.74	2.670	2.454
3845	8.60	24.41	2.625	2.397
4615	9.36	24.98	2.649	-
5530	10.07	25.64	2.666	2.396
6480	10.66	26.21	2.695	2.455
∞	12.55			

- -

$\mu = 0.0433.$

k_{Cl} = 2.689 ± 0.0125 (10 readings)

k_H = 2.436 ± 0.0122 (9 readings)

Duplicate Experiments.

Added NaN_3 0.02983 M.

k'_{Cl} = 2.692 ± 0.0134 (9 readings)

k'_H = 2.456 ± 0.0225 (7 readings)

Expt. 25. Benzhydryl Chloride in 70% aq. Acetone I at 20.08°C

Added NaN_3 0.05018 M.

5 ml. titrated with 0.009461 N $AgNO_3$.

Time	Titre	10^4 k
0	0.34	-
420	1.91	(3.038)
720	2.86	2.965
1115	4.06	2.993
1715	5.61	3.001
2270	6.76	2.968
2685	7.53	2.966
3275	8.48	2.966
2995	9.38	2.933
4630	10.06	2.927
6275	11.37	2.941
∞	13.44	

$a = 00828$

$N_3 = 04190$

k = 2.962 ± 0.0083 (9 readings)

Duplicate Experiment.

Added NaN_3 0.05023 M. k' = 2.945 ± 0.0147 (11 readings)

Expt.26. Benzhydryl Chloride in 70% aq.Acetone I at 20.10°C

Added NaN_3 0.05017 M.

5 ml. titrated with 0.009461 N $AgNO_3$.

Time	Cl^-	$Cl^- + N_3^-$	$10^4 k_{Cl}$	$10^4 k_H$
0	0.27	26.97	-	-
425	1.66	-	2.996	-
815	2.83	28.85	3.049	2.289
1225	3.34	29.65	2.990	2.287
1715	4.88	(30.44)	2.941	-
2360	6.13	(31.36)	2.968	-
3045	7.16	32.22	2.944	2.331
3710	8.02	32.95	2.955	2.373
4390	8.73	33.52	2.956	2.377
5105	9.26	33.96	2.899	2.342
5865	9.77	34.37	2.889	2.334
6695	10.25	34.76	2.911	2.356
∞	11.91			

k_{Cl} = 2.954 ± 0.0134 (11 readings)

k_H = 2.336 ± 0.0111 (8 readings)

Duplicate Experiments.

Added NaN_3 0.05051 M.

k'_{Cl} = 2.936 ± 0.0226 (11 readings)

k'_H = 2.321 ± 0.0029 (8 readings)

Expt.27.p-Methoxybenzyl Chloride in 70% aq.Acetone XIII at 20.08°C

No added salts.

5 ml. titrated with 0.003881 N NaOH.

Time	Titre	10^4 k
0	0.19	-
355	1.23	2.297
725	2.28	2.354
1150	3.29	2.301
1640	4.40	2.321
2175	5.50	2.336
2850	6.60	2.302
3440	7.51	2.319
4070	8.30	2.306
4820	9.12	2.303
5635	9.90	2.317
6620	10.60	2.298
7415	11.10	2.306
∞	13.51	

k = 2.313 ± 0.0048 (12 readings)

k' = 2.315 ± 0.0054 (11 readings)

Expt.28. p-Methoxybenzyl Chloride in 70% aq. Acetone XIII at 20.08°C

Added HCl 0.05177 M.

5 ml. titrated with 0.02168 N NaOH.

Time	Titre	10^4 k
0	11.81	-
490	12.31	2.002
910	12.73	2.075
1330	13.10	2.076
1865	13.51	2.055
2465	13.94	2.064
3275	14.47	2.106
3840	14.75	2.083
4680	15.17	2.099
5525	15.49	2.115
6395	15.72	2.061
7300	16.00	2.104
∞	17.15	

k = 2.072 ± 0.0092 (11 readings)

Duplicate Experiment. = 2·084 ± 0064 (10, bm pt) ——— Accept

Added HCl 0.05133 M. k' = 2.059 ± 0.0141 (10 readings)

2·066 ± 0084

Expt.29.p-Methoxybenzyl Chloride in 70% aq.Acetone XIV at 20.08°C

Added NaCl 0.02477 M.

5 ml. titrated with 0.008013 N NaOH.

Time	Titre	10^4 k
0	0.21	-
480	1.58	2.269
930	2.72	2.253
1415	3.79	2.220
2060	5.08	2.211
2430	5.72	2.203
2940	6.56	2.208
3555	7.40	2.189
4260	8.29	2.196
5165	9.22	2.191
6250	10.14	2.197
7510	10.93	2.184
∞	13.51	

- - - - - - - - - - - - - - - - -

k = 2.211 ± 0.0075 (11 readings)

Allin zero 2.187 (bar 1st).

Duplicate Experiment.

Added NaCl 0.02512 M. k' = 2.212 ± 0.0044 (11 readings)

Av 2.211 ± 0043

Chang zero → av. 2.199 Accept & dup corrn 0043.

Expt.30.p-Methoxybenzyl Chloride in 70% aq.Acetone XV at 20.08°C

Added NaCl 0.05202 M.

5 ml. titrated with 0.009398 N NaOH.

Time	Titre	$10^4 k$
0	0.20	-
510	1.32	1.973
856	2.05	1.991
1320	2.90	1.992
1935	3.95	2.002
2595	4.92	1.995
3325	5.89	2.007
4065	6.70	2.001
4860	7.51	2.022
5995	8.35	1.996
6910	8.94	1.996
7910	9.50	2.012
∞	11.88	

$k = 1.999 \pm 0.0036$ (11 readings)

Duplicate Experiment.

Added NaCl 0.05140 M. $k' = 1.994 \pm 0.0065$ (11 readings)

1·996± 0038

Expt.31.p-Methoxybenzyl Chloride in 70% aq.Acetone XVI at 20.08°C

Added NaCl 0.1003 M.

5 ml. titrated with 0.008881 N NaOH.

Time	Titre	10^4 k
0	0.21	-
460	1.18	1.812
955	2.11	1.777
1460	3.02	1.801
2015	3.90	1.797
2700	4.88	1.796
3430	5.77	1.783
4235	6.63	1.774
5125	7.43	1.760
6120	8.27	1.780
7320	9.01	1.760
8815	9.83	1.780
∞	12.36	

k = 1.784 ± 0.0047 (11 readings)

Duplicate Experiment.

Added NaCl 0.1008 M. k' = 1.794 ± 0.0021 (11 readings)

1.789 ± 0028

Expt.32.p-Methoxybenzyl Chloride in 70% aq.Acetone XVII at 20.08°C

Added NaCl 0.1008 M.

5 ml. titrated with 0.008013 N NaOH.

Time	Titre	10^4 k
0	0.20	–
470	1.21	1.735
955	2.21	1.777
1515	3.25	1.783
2095	4.19	1.769
2765	5.20	1.774
3500	6.14	1.763
4340	7.10	1.764
5095	7.86	1.769
6120	8.70	1.758
7325	9.51	1.747
8680	10.31	1.764
∞	13.10	

k = 1.764 ± 0.0039 (11 readings)

Duplicate Experiment.

Added NaCl 0.1012 M. k' = 1.762 ± 0.0025 (11 readings)

1.763 ± 0023

Expt.33.p-Methoxybenzyl Chloride in 70% aq.Acetone XIII at 20.08°C

Added HCl 0.05142 M.

10 ml. of aqueous extract counted for 1 hour and titrated with 0.02168 N NaOH.

Time	Count/min.	Titre	$10^4\ k_E$	$10^4\ k_H$
0	340	10.21	-	-
975	2008	10.91	2.759	2.048
1395	2609	11.18	2.782	2.017
1810	3131	11.41	2.778	2.051
2395	3811	11.71	2.825	2.048
3100	4411	11.98	2.772	1.972
3785	4928	12.30	2.771	2.052
4435	5355	12.51	2.793	2.035
5140	5697	12.74	2.766	2.064
5870	5987	12.85	2.739	1.951
6585	6265	13.16	2.774	2.182
7460	6516	13.30	2.783	2.147
∞	7402	14.08		

$k_E = 2.777$; $k_H = 2.052$.

$(k_E - k_H) = 0.724 \pm 0.0186$ (11 readings)

Duplicate Experiment.

Added HCl 0.05133 M. $(k_E' - k_H') = 0.703 \pm 0.0180$ (11 readings)

Expt.34.p-Methoxybenzyl Chloride in 70% aq.Acetone XIV at 20.08°C

Added NaCl 0.02462 M.

10 ml. of aqueous extract counted for 1 hour and titrated with 0.008013 N NaOH.

Time	Count/min.	Titre	$10^4 k_E$	$10^4 k_H$
0	397	0.51	-	-
960	1687	2.38	2.538	2.233
1420	2272	3.16	2.655	2.248
1915	2757	3.88	2.623	2.234
2480	3269	4.65	2.646	2.250
3050	3689	5.30	2.627	2.240
3690	4033	5.83	2.545	2.162
4455	4431	6.50	2.528	2.165
5270	4910	7.29	2.675	2.287
6210	5172	7.80	2.590	2.253
7045	5356	8.10	2.520	2.176
7840	5547	8.38	2.531	2.148
∞	6368	10.19		

$k_E = 2.589$; $k_H = 2.218$.

$(k_E - k_H) = 0.371 \pm 0.0088$ (11 readings)

Duplicate Experiment.

Expt.35.p-Methoxybenzyl Chloride in 70% aq.Acetone XV at 20.08°C

Added NaCl 0.05128 M.

10 ml. of aqueous extract counted for 1 hour and titrated with 0.008881 N NaOH.

Time	Count/min.lu*		Titre		$10^4 k_E$	$10^4 k_H$
0	448	7206 6445	0.33	9.97	-	-
435	1371	6283	1.31	8.99	3.134	2.377
890	2114	5540	2.12	8.18	2.955	2.215
1335	2711	4943	2.80	7.50	2.824	2.130
1805	3312	4342	3.42	6.88	2.808	2.198
2375	3871	3783	4.16	6.14	2.714	2.042
3060	4473	3181	4.90	5.40	2.674	2.003
3775	5039	2615	5.48	4.82	2.686	1.925
4485	5484	2170	6.19	4.11	2.676	1.976
6000	6236	1418	7.13	3.17	2.710	1.910
6680	6416	1238	7.62	2.68	2.637	1.967
7370	6673	981	7.90	2.40	2.706	1.932
∞	7654		10.30			

$(k_E - k_H) = 0.714 \pm 0.0168$ (11 readings)

Duplicate Experiment.

Added NaCl 0.05145 M. $(k_E' - k_H') = 0.714 \pm 0.0223$ (10 readings)

Expt.36.p-Methoxybenzyl Chloride in 70% aq.Acetone XVI at 20.08°C

Added NaCl 0.1006 M.

10 ml. of aqueous extract counted for 1 hour and titrated with 0.008881 N NaOH.

Time	Count/min.	Titre	$10^4 k_E$	$10^4 k_H$
0	424	0.35	-	-
475	1500	1.22	3.147	1.775
1490	3244	2.79	3.040	1.747
2040	4059	3.69	3.106	1.845
2760	4795	4.51	3.011	1.795
3495	5460	5.39	3.005	1.836
4275	5990	6.09	2.965	1.812
5150	6419	6.70	2.887	1.761
6175	6900	7.42	2.928	1.766
7215	7188	8.02	2.856	1.766
8540	7504	8.68	2.872	1.785
∞	8171	11.00		

Mean k_E = 2.982; k_H = 1.789.

$(k_E - k_H)$ = 1.193 ± 0.0277 (10 readings)

Duplicate Experiment.

Added NaCl 0.1005 M. $(k'_E - k'_H)$ = 1.224 ± 0.0246 (9 readings)

Expt.37.p-Methoxybenzyl Chloride in 70% aq.Acetone XI at 20.08°C

Added $NaClO_4$ 0.05015 M.

5 ml. titrated with 0.01001 N NaOH.

Time	Titre	10^4 k
0	0.34	-
425	1.56	2.959
880	2.78	2.982
1350	3.86	2.999
1855	4.84	2.989
4285	5.89	2.995
3085	6.69	2.977
3805	7.51	2.981
4585	8.22	2.984
5576	8.89	2.968
6435	9.31	2.935
7410	9.73	2.959
∞	10.91	

k = 2.975 ± 0.0014 (11 readings)

Duplicate Experiment.

Added $NaClO_4$ 0.05015 M.

k' = 2.975 ± 0.0014 (11 readings)

Av. 2.975 ± 0038 $10^3 \sigma/k$ = 1.28

Expt.38.p-Methoxybenzyl Chloride in 70% aq.Acetone XVIII at 20.08°C

Added $NaBF_4$ 0.05127 M.

5 ml. titrated with 0.009560 N $AgNO_3$.

Time	Titre	10^4 k
0	0.32	-
565	2.09	2.817
885	2.99	2.839
1255	3.96	2.876
1675	4.87	2.841
2090	5.76	2.883
2600	6.65	2.877
3265	7.55	2.819
4070	8.48	2.791
5010	9.42	2.826
6230	10.35	2.821
∞	12.34	

k = 2.839 ± 0.0092 (10 readings)

Duplicate Experiment.

Added $NaBF_4$ 0.04875 M. k' = 2.831 ± 0.0076 (10 readings)

Av. 2.835 ± 0060 . $10^3\sigma/k$ = 2.12

Expt.39.p-Methoxybenzyl Chloride in 70% aq.Acetone XIX at 20.08°C

Added Me_4NF 0.04544 M.

5 ml. titrated with 0.01071 N $AgNO_3$

Time	Titre	10^4 k
0	0.43	-
360	1.72	2.613
710	2.83	2.637
1080	3.89	2.619
1500	4.97	2.601
1920	5.93	2.586
2430	7.01	2.600
3030	8.04	2.574
3755	9.13	2.571
4655	10.28	2.593
5735	11.25	2.564
6990	12.11	2.546
∞	14.48	

k = 2.591 ± 0.0076 (11 readings)

Duplicate Experiment.

Added Me_4NF 0.05089 M. k' = 2.607 ± 0.0080 (10 readings)

Expt.40.p-Methoxybenzyl Chloride in 70% aq.Acetone XX at 20.08°C

Added Me_4NF 0.04584 M.

(i) 5 ml. titrated with 0.009569 N $AgNO_3$.

(ii)5 ml. titrated with 0.01041 N NaOH.

Time/(secs)	Cl^-	$10^4 k_{Cl}$	Time*	(a-x)	$H^+_{obs.}$	$H^+_{corr.}$	$10^4 k_H$
0	0.57	-	0	9.51	1.40	1.40	-
715	2.27	2.577	720	7.91	3.05	-	-
1395	3.63	2.587	1390	6.67	4.08	4.10	2.429
2125	4.82	2.569	2115	5.54	5.05	5.09	2.375
2830	5.75	2.542	2815	4.63	5.97	6.03	2.424
3520	6.55	2.548	3485	3.91	6.69	6.77	2.450
4290	7.33	2.579	4275	3.19	7.39	7.50	2.466
5015	7.86	2.552	4980	2.67	7.82	7.96	2.451
5715	8.28	2.523	5670	2.23	8.23	8.40	2.457
6545	8.75	2.549	6510	1.80	8.60	8.81	2.489
7325	9.08	2.524	7295	1.47	8.89	9.14	2.494
∞	10.67		∞				

---

k_{Cl} = 2.555 ± 0.0067 (10 readings)

k_H = 2.448 ± 0.0113 (9 readings)

Duplicate Experiment.

Added Me NF 0.04584 M. k' = 2.548 ± 0.0120 (8 raedings)

k' = 2.439 ± 0.0090 (10 readings)

(Time* = Time - 95)

Expt.41.p-Methoxybenzyl Chloride in 70% aq.Acetone XV at 20.08°C

Added $PhSO_3Na$ 0.04978 M.

5 ml. titrated with 0.009398 N NaOH.

Time	Titre	10^4 k
0	0.22	-
380	1.31	2.582
765	2.32	2.601
1180	3.30	2.606
1660	4.30	2.601
2180	5.23	2.578
2810	6.20	2.560
3510	7.12	2.554
4320	8.01	2.553
5145	8.75	2.556
6055	9.39	2.550
7020	9.92	2.541
∞	11.88	

k = 2.571 ± 0.0067 (11 readings)

Duplicate Experiment.

Added $PhSO_3Na$ 0.05016 M. k' = 2.577 ± 0.0079 (11 readings)

Expt.42.p-Methoxybenzyl Chloride in 70% aq.Acetone XV at 20.00°C

Added NaNO$_3$ 0.05026 M.

5 ml. titrated with 0.009398 N NaOH.

Time	Titre	10^4 k
0	0.29	-
460	1.50	2.368
915	2.63	2.431
1250	3.40	2.473
1770	4.46	2.486
2160	5.19	2.509
2760	6.15	2.513
3560	7.23	2.522
4435	8.20	2.539
5270	8.90	2.522
6180	9.59	2.562
6755	9.90	2.545
∞	12.00	

Zero at 915 seconds. k = 2.557 ± 0.0039 (9 readings)

Duplicate Experiment.

Added NaNO$_3$ 0.05019 M. k' = 2.562 ± 0.0065 (9 readings)

Expt.43.p-Methoxybenzyl Chloride in 70% aq.Acetone XV at 20.08°C

Added $NaNO_3$ 0.05039 M.

5 ml. titrated with 0.009200 N $AgNO_3$.

Time	Titre	10^4 k
0	0.33	-
370	1.42	2.652
780	2.50	2.645
1285	3.74	2.695
1830	4.84	2.678
2500	5.97	2.649
3395	7.33	2.706
4135	8.15	2.691
5055	8.94	2.658
5800	9.54	2.696
6705	9.96	2.614
7475	10.37	2.648
∞	11.98	

k = 2.667 ± 0.0082 (11 readings)

Duplicate Experiment.

Added $NaNO_3$ 0.05015 M. k' = 2.664 ± 0.0082 (11 readings)

0.05034 M. k" = 2.643 ± 0.0166 (10 readings)

Expt.44.p-Methoxybenzyl Chloride in 70% aq.Acetone XXI at 20.08°C

Added $NaNO_3$ 0.05041 M.

5 ml. titrated with (i) 0.008772 N NaOH. (ii) 0.009050 N $AgNO_3$.

Time	H^+	Cl^-	$10^4 k_H$	$10^4 k_{Cl}$
0	0.32	0.36	-	-
355	1.28	1.15	2.485	(2.128)
760	2.31	2.44	2.530	2.791
1195	3.31	3.44	2.552	2.786
1670	4.31	4.39	2.587	2.776
2285	5.30	5.43	2.578	2.746
3000	6.50	6.45	2.612	2.735
3730	7.34	7.28	2.572	2.710
4570	8.20	8.16	2.581	2.762
5545	9.00	8.80	2.595	2.696
6645	9.70	9.43	2.617	2.694
7505	10.10	9.83	2.614	2.723
∞	11.70	11.24		

$k_{Cl} = 2.742 \pm 0.0109$ (10 readings)

Duplicate Experiment.

Added $NaNO_3$ 0.05038 M. $k'_{Cl} = 2.750 \pm 0.0109$ (10 readings)

Expt.45.p-Methoxybenzyl Chloride in 70% aq.Acetone XV at 20.08°C

Added KBr 0.05087 M.

5 ml. titrated with 0.009488 N NaOH.

Time	Titre	10^4 k
0	0.18	-
355	1.10	2.297
780	2.30	2.560
1165	3.31	2.671
1600	4.34	2.743
2020	5.23	2.779
2545	6.20	2.841
3250	7.25	2.853
3955	8.10	2.859
4735	8.86	2.861
5730	9.63	2.878
6735	10.21	2.891
∞	11.88	

- - - - - - - - - - - - - - - - - - -

Zero at 780 seconds, k = 2.931 ± 0.0052 (9 readings)

Duplicate Experiment.

Added KBr 0.05025 M. k' = 2.944 ± 0.0077 (7 readings)

Expt.46.p-Methoxybenzyl Chloride in 70% aq.Acetone XXI at 20.08°C

Added KBr 0.05028 M.

5 ml. titrated with (i) 0.008772 N NaOH. (ii) 0.01878 N $AgNO_3$.

Time	H^+	Br^-+Cl^-	$10^4\ k_H$	$10^4\ k_{Cl}$
0	1.24	14.33	-	-
850	3.60	15.43	2.882	3.050
1285	4.66	15.84	2.943	2.934
1785	5.70	16.35	2.963	3.051
2260	6.60	16.73	3.010	3.059
3000	7.60	17.16	2.938	2.942
3735	8.50	17.60	2.956	3.050
4485	9.26	17.93	2.990	3.077
5390	9.92	18.24	2.960	(3.110)
6555	10.55	18.55	2.972	(3.151)
∞	12.10	19.19		

- -

$k_{Cl} = 3.024 \pm 0.0215$ (7 readings)

Zero at 850 seconds.

$k_H = 3.011 \pm 0.0125$ (8 readings)

Duplicate Experiments.

Added KBr 0.05030 M. $k'_{Cl} = 3.010 \pm 0.0118$ (8 readings)

0.05033 M. $k''_{Cl} = 3.028 \pm 0.0244$ (8 readings)

Expt.47.p-Methoxybenzyl Chloride in 70% aq.Acetone XII at 20.08°C

Added NaN_3 0.01977 M.

5 ml. titrated with 0.008711 N $AgNO_3$.

Time	Cl^-	$Cl^- + N_3^-$	$10^4\ k_{Cl}$	$10^4\ k_H$
0	0.43	11.53	-	-
530	2.37	12.94	3.311	2.425
770	3.13	13.56	3.308	2.499
1070	3.97	14.20	3.259	2.471
1435	4.86	14.92	3.2021	2.468
1895	5.90	15.75	3.199	2.491
2440	6.87	16.58	3.141	2.498
3070	7.80	17.37	3.090	2.492
3830	8.64	18.15	2.995	2.482
4730	9.49	18.87	2.958	2.466
5815	10.27	19.58	2.930	2.490
∞	12.46	-		

- -

Mean k_{Cl} = 3.139 k_H = 2.478 (10 readings)

Duplicate Experiments.

Solvent.	Added NaN_3	k_{Cl}	k_H	Number of readings.
XII	0.01983 M.	3.138	2.465	10
XI	0.01990 M.	3.106	2.406	11

Expt.48.p-Methoxybenzyl Chloride in 70% aq.Acetone XI at 20.08°C

Added NaN_3 0.03131 M.

5 ml. titrated with 0.008711 N $AgNO_3$.

Time	Cl^-	$Cl^- + N_3^-$	$10^4\ k_{Cl}$	$10^4\ k_H$
0	0.64	18.45	-	-
285	2.02	19.26	4.040	2.382
555	3.10	19.88	3.888	2.267
850	4.12	20.56	3.782	2.307
1185	5.12	21.21	3.683	2.289
1560	6.20	21.92	3.708	2.337
2015	7.25	22.65	3.665	2.364
2550	8.14	23.33	3.521	2.360
3135	9.00	23.99	3.445	2.368
3785	9.79	24.56	3.390	2.351
4510	10.51	25.09	3.354	2.351
5415	11.13	25.56	3.258	2.314
∞	13.30			

Mean k_{Cl} = 3.612 k_H = 2.335   (11 readings)

Duplicate Experiments.

Solvent.	Added NaN_3.	k_{Cl}	k_H	Number of readings.
XI	0.03006 M.	3.382	2.336	10
XII	0.03176 M.	3.688	2.412	11

Expt.49.p-Methoxybenzyl Chloride in 70% aq.Acetone XII at 20.08°C

Added NaN_3 0.03929 M.

5 ml. titrated with 0.008711 N $AgNO_3$.

Time	Cl^-	$Cl^- + N_3^-$	$10^4\ k_{Cl}$	$10^4\ k_H$
0	0.78	22.89	-	-
300	2.27	23.75	4.076	2.350
563	3.42	23.42	4.033	2.346
905	4.67	25.19	3.939	2.338
1225	5.79	25.85	3.984	2.362
1550	6.68	26.37	3.911	2.314
1915	7.56	26.99	3.859	2.263
2302	8.33	27.50	3.788	2.348
2785	9.18	28.02	3.741	2.317
3355	10.00	28.52	3.694	2.284
4040	10.80	29.10	3.660	2.330
4895	11.61	29.59	3.674	2.325
∞	13.76			

Mean k_{Cl} = 3.851 k_H = 2.334 (11 readings)

Duplicate Experiments.

Solvent.	Added NaN_3	k_{Cl} =	k_H	Number of readings.
XII	0.04067 M.	4.034	2.340	10
XI	0.03993 M.	3.909	2.259	11

Expt.50. The Reaction of Hydrochloric Acid and Tetramethylammonium Fluoride with 70% aqueous acetone at 20.08°C

15 ml. of a stock solution of hydrochloric acid.

35 ml. of pure acid.

Me_4NF 0.2640 gram.

These were mixed at thermostat temperature to give a solution containing 0.05678 M.

5 ml. titrated with 0.01036 N NaOH using screened methyl red/methylene blue indicator in conjunction with a rapid stream of nitrogen.

Time	Titre	$H^+-H^+_0$
0	9.23	-
1465	9.23	0
2440	9.25	+02
3405	9.12	-11
4480	9.06	-17
5570	8.98	-25
6930	8.80	-43
11380	8.40	-83

-------- Mean titre = 9.01 ml.

$\frac{dH^+}{dt}$ = 0.24 ml. per hour. Mean HF = 0.01867

Expt.51. The Reaction of Hydrochloric Acid and Tetramethylammonium Fluoride with 70% aqueous acetone at 20.08°C

The stock solution used in experiments 50 was diluted to twice the volume of solvent and a solution made up as before using 0.2413 grams of Me_4NF.

Molarity of Me_4NF 0.05189.

5 ml. titrated with 0.01036 N NaOH.

Time	Titre	H^+-H_0
0	4.87	-
690	4.90	+03
1710	4.88	+01
2970	4.86	-01
4945	4.80	-07
6280	4.73	-14
7730	4.70	-17
9235	4.65	-22
6		

$\frac{dH^+}{dt}$ = 0.10 ml. per hour.

Mean titre = 4.80 ml.

HF = 0.009946

Expt.52. Benzhydryl Chloride in 70% aq.Acetone XXVII at 20.49°C

Added pyridine 0.2502 M.

5 ml. titrated with 0.009050 N $AgNO_3$.

Time	Titre	10^4 k
0	0.37	-
515	1.94	2.611
910	2.99	2.589
1300	3.95	2.601
1725	4.86	2.586
2190	5.86	2.647
2700	6.75	2.652
3330	7.64	2.624
4020	8.53	2.640
4915	9.46	2.653
6055	10.42	2.641
7495	11.14	2.653
∞	12.85	

k = 2.627 ± 0.0075 (11 readings)

Expt.53. Benzhydryl Chloride in 70% aq.Acetone XXVII at 20.49°C

Added pyridine 0.4922 M.

5 ml. titrated with 0.009050 N $AgNO_3$.

Time	Titre	10^4 k
0	0.34	-
485	1.82	2.522
920	2.97	2.494
1325	3.94	2.485
1745	4.84	2.476
2235	5.77	2.462
2790	6.76	2.487
3420	7.73	2.509
4085	8.48	2.463
4870	9.35	2.488
5725	10.07	2.481
6690	10.81	2.531
∞	13.17	

k = 2.491 ± 0.0064 (11 readings)

Duplicate Experiment.

Added pyridine 0.4942 M.

k' = 2.494 ± 0.0075 (10 readings)

Expt.54. Benzhydryl Chloride in 70% aq. Acetone XXVIII at 20.49°C

Added pyridine 0.7450 M.

5 ml. titrated with 0.009050 N $AgNO_3$.

Time	Titre	10^4 k
0	0.33	-
505	1.74	2.375
925	2.76	2.346
1395	3.83	2.363
1940	4.86	2.342
2545	5.94	2.352
3205	6.95	2.364
3980	7.95	2.376
4940	8.89	2.352
6095	9.83	2.358
7465	10.72	2.305
8800	11.29	2.306
∞	12.79	

k = 2.367 ± 0.0088 (11 readings)

Duplicate Experiment.

Added pyridine 0.7506 M.

k' = 2.381 ± 0.0048 (9 readings)

Expt.55.p-Methoxybenzyl Chloride in 70% aq.Acetone XXIX at 20.49°C

Added pyridine 0.2473 M.

5 ml. titrated with (i) 0.01010 N NaOH. (ii) 0.009050 N $AgNO_3$.

Time	H^+	Cl^-	$10^4 k_{Cl}$	$10^4 k_H$
0	0.27	0.35	-	-
520	1.43	1.88	2.599	2.203
940	2.20	2.95	2.570	2.132
1395	3.05	4.02	2.588	2.197
1880	3.81	5.02	2.590	2.201
2380	4.41	5.91	2.583	2.142
2985	5.14	6.86	2.584	2.160
3695	5.79	7.80	2.584	2.131
4590	6.56	8.77	2.589	2.170
5885	7.35	9.81	2.582	2.179
7255	7.96	10.58	2.568	2.193
8810	8.45	11.18	2.551	2.215
∞		12.46		

---

k_{Cl} = 2.581 ± 0.0038 (11 readings)

k_H = 2.175 ± 0.0086 (11 readings)

Duplicate Experiment.

Added pyridine 0.2470 M. k'_{Cl} = 2.565 ± 0.0070 (11 readings)

k'_H = 2.168 ± 0.0066 (10 readings)

Expt.56.p-Methoxybenzyl Chloride in 70% aq.Acetone XXIX at 20.49°C

Added pyridine 0.4943 M.

5 ml. titrated with (i) 0.01010 N NaOH. (ii) 0.009050 N $AgNO_3$

Time	H^+	Cl^-	$10^4 k_{Cl}$	$10^4 k_H$
0	0.22	0.38	-	-
513	1.22	1.95	2.631	1.867
933	-	3.08	2.621	--
1413	2.67	4.21	2.603	1.869
1903	3.33	5.26	2.615	1.870
2448	3.95	6.21	2.581	1.853
3053	4.63	7.23	2.617	1.896
3768	5.14	8.14	2.592	1.833
4668	5.79	9.06	2.620	1.848
5808	6.35	10.08	2.601	1.827
7163	6.91	10.85	2.567	1.857
8708	7.32	11.53	2.595	1.864
∞		12.83		

---

k_{Cl} = 2.604 ± 0.0055 (11 readings)

k_H = 1.860 ± 0.0060 (10 readings)

Duplicate Experiment.

Added pyridine 0.4941 M. k'_{Cl} = 2.607 ± 0.0056 (10 readings)

k'_H = 1.870 ± 0.0057 (10 readings)

Expt.57.p-Methoxybenzyl Chloride in 70% aq.Acetone XXIX at 20.49°C

Added pyridine 0.7422 M.

5 ml. titrated with (i) 0.01010 N NaOH. (ii) 0.009050 N $AgNO_3$.

Time	H^+	Cl^-	$10^4\ k_{Cl}$	$10^4\ k_H$
0	0.20	0.33	-	-
570	1.14	2.06	2.659	1.617
1055	1.83	3.36	2.677	1.610
1570	2.43	4.54	2.664	1.574
2115	3.04	5.64	2.667	1.582
2800	3.68	6.79	2.655	1.595
3510	4.26	7.83	2.674	1.621
4305	4.69	8.74	2.667	1.581
5260	5.20	9.60	2.655	1.608
6560	5.64	10.53	2.683	1.589
7640	5.96	11.04	2.665	1.621
∞		12.65		

k_{Cl} = 2.667 ± 0.0028 (10 readings)

k_H = 1.600 ± 0.0053 (10 readings)

Duplicate Experiment.

Added pyridine 0.7418 M. k'_{Cl} = 2.653 ± 0.0027 (11 readings)

k'_H = 1.622 ± 0.0088 (10 readings)

Expt.53. Benzhydryl Chloride in 70% aq.Acetone XXII at 20.49°C

Added acetone 1.0884 M.

5 ml. titrated with 0.01010 N NaOH.

Time	Titre	10^4 k
0	0.23	-
430	1.25	2.147
840	2.11	2.141
1285	2.99	2.165
1765	3.82	2.156
2310	4.71	2.180
2945	5.59	2.189
3690	6.49	2.185
4645	7.41	2.171
5905	8.42	2.185
7585	9.33	2.160
9885	10.16	2.140
∞	11.52	

---

k = 2.165 ± 0.0048 (11 readings)

Expt.59. Benzhydryl Chloride in 70% aq.Acetone XXII at 20.49°C

Added benzene 0.5592 M.

5 ml. titrated with 0.01010 N NaOH.

Time	Titre	10^4 k
0	0.20	-
420	1.01	1.799
840	1.78	1.821
1320	2.58	1.820
1860	3.40	1.819
2460	4.20	1.807
3145	5.05	1.817
3920	5.83	1.795
4885	6.71	1.796
5975	7.53	1.793
7335	8.40	1.813
9150	9.22	1.809
∞	11.35	

k = 1.808 ± 0.0031 (11 readings)

Duplicate Experiments.

Added benzene 0.5610 M.

k' = 1.810 ± 0.0038 (11 readings)

0.5615 M.

k" = 1.791 ± 0.0056 (11 readings)

Expt.60. Benzhydryl Chloride in 70% aq.Acetone XXIII at 20.49°C

Added toluene 0.6276 M.

5 ml. titrated with 0.009804 N NaOH.

Time	Titre	10^4 k
0	0.16	-
420	1.08	1.776
865	1.99	1.776
1315	2.81	1.760
1810	3.69	1.777
2345	4.50	1.760
2980	5.40	1.760
3750	6.34	1.751
4645	7.30	1.752
6065	4.42	1.759
7350	9.48	1.761
9020	10.39	1.767
∞	13.00	

$k = 1.764 \pm 0.0026$ (11 readings)

Expt.61. Benzhydryl Chloride in 70% aq.Acetone XXII at 20.49°C

Added nitrobenzene 0.4908 M.

5 ml. titrated with 0.01010 N NaOH.

Time	Titre	10^4 k
0	0.20	-
420	1.11	2.011
840	1.99	2.053
1280	2.79	2.035
1770	3.61	2.030
2295	4.40	2.025
2880	5.20	2.030
3675	6.13	2.024
4580	7.00	2.011
5655	7.93	2.038
7290	8.87	2.000
9035	9.70	2.033
∞	11.50	

k = 2.026 ± 0.0042 (11 readings)

Expt.62. Benzhydryl Chloride in 70% aq.Acetone XXIII at 20.49°C

Added chlorobenzene 0.4018 M.

5 ml..titrated with 0.009804 N NaOH.

Time	Titre	10^4 k
0	0.16	-
420	1.02	1.755
840	1.85	1.787
1290	2.67	1.799
1775	3.48	1.803
2315	4.29	1.801
2975	5.15	1.776
3720	6.04	1.780
4740	7.10	1.794
6745	8.69	1.804
7780	9.23	1.773
9855	10.20	1.788
∞	12.28	

k = 1.787 ± 0.0043 (11 readings)

Expt.63.p-Methoxybenzyl Chloride in 70% aq.Acetone XXV at 20.49°C

Added acetone 1.0890 M.

5 ml. titrated with 0.009804 N NaOH.

Time	Titre	10^4 k
0	0.20	-
415	1.35	2.037
875	2.51	2.037
1325	3.57	2.054
1805	4.53	2.025
2345	5.58	2.042
3000	6.65	2.031
3780	7.78	2.032
4740	8.91	2.018
5880	10.02	2.017
7020	10.86	1.997
8255	11.63	2.001
∞	14.34	

k = 2.026 ± 0.0049 (11 readings)

Expt.64.p-Methoxybenzyl Chloride in 70% aq.Acetone XXIV at 20.49°C

Added benzene 0.5612 M.

5 ml. titrated with 0.01010 N NaOH.

Time	Titre	10^4 k
0	0.49	-
420	1.39	1.980
845	2.23	1.984
1300	3.07	1.998
1780	3.82	1.965
2315	4.68	2.006
2945	5.47	1.979
3720	6.37	1.975
4625	7.24	1.972
5770	8.19	1.989
7270	9.13	1.998
9190	9.99	2.009
∞	11.77	

k = 1.987 ± 0.0041 (11 readings)

Duplicate Experiments.

Added benzene 0.5615 M. k' = 1.998 ± 0.0060 (11 readings)

0.5591 M. k" = 2.014 ± 0.0106 (11 readings)

0.5606 M. k'" = 1.991 ± 0.0050 (10 readings)

Expt.65.p-Methoxybenzyl Chloride in 70% aq.Acetone XXVI at 20.49°C

Added toluene 0.6271 M.

5 ml. titrated with 0.009804 N NaOH.

Time	Titre	10^4 k
0	0.20	-
420	1.21	2.007
830	2.19	2.036
1280	3.13	2.031
1755	4.00	2.008
2300	4.96	2.021
2935	5.90	2.007
3740	6.99	2.021
4705	8.01	2.002
5900	9.08	2.005
7280	10.01	1.997
8960	10.83	1.981
∞	13.00	

k = 2.015 ± 0.0047 (11 readings)

Expt.66.p-Methoxybenzyl Chloride in 70% aq.Acetone XXVI at 20.49°C

Added nitrobenzene 0.4912 M.

5 ml. titrated with 0.01010 N NaOH.

	Time	Titre	10^4 k
	0	0.50	-
	390	1.37	2.066
	810	2.25	2.089
	1255	3.09	2.088
	1735	3.92	2.092
	2280	4.76	2.090
	2905	5.60	2.082
	3700	6.50	2.063
	4595	7.35	2.046
	5740	8.25	2.038
+	7230	9.19	2.052
	9180	10.04	2.058
	∞	11.74	

k = 2.069 ± 0.0056 (11 readings)

Duplicate Experiment.

Added nitrobenzene 0.4913 M.

k' = 2.072 ± 0.0056 (11 readings)

Expt.67.p-Methoxybenzyl Chloride in 70% aq.Acetone XXVI at 20.49°C

Added chlorobenzene 0.4024 M.

5 ml. titrated with 0.009804 N NaOH.

Time	Titre	10^4 k
0	0.20	–
425	1.28	1.113
840	2.21	2.081
1290	3.17	2.096
1765	4.01	2.054
2310	5.00	2.090
2945	5.92	2.071
3720	6.92	2.065
5015	8.30	2.074
6195	9.23	2.058
7870	10.25	2.058
9905	11.10	2.059
∞	12.73	

---

k = 2.074 ± 0.0054 (11 readings)

Expt.68.p-Methoxybenzyl Bromide in 70% aq.Acetone XVII at 0°C

No added salts.

5 ml. titrated with 0.009709 N NaOH.

Time	Titre	10^4 k
0	0.41	-
365	1.25	1.981
845	2.27	1.979
1325	3.19	1.969
1865	4.04	1.915
2460	4.90	1.885
3180	5.83	1.868
4020	6.79	1.864
5035	7.70	1.833
6300	8.70	1.835
7685	9.50	1.811
9520	10.25	1.763
∞	12.51	

Mean k = 1.882 (11 readings)

Expt.69.p-Methoxybenzyl Bromide in 70% aq.Acetone XVII at 0°C

Added KBr 0.050110 M.

5 ml. titrated with 0.009709 N NaOH.

Time	Titre	10^4 k
0	0.31	-
490	1.30	1.739
980	2.23	1.767
1465	3.00	1.723
2030	3.83	1.699
2695	4.72	1.686
3480	5.64	1.676
4485	6.65	1.661
5615	7.58	1.642
7080	8.58	1.633
8750	9.45	1.618
11295	10.30	1.557
∞	12.38	

Mean k = 1.673 (11 readings)

TABLE A.1

LIST OF SOLVENTS

Benzhydryl Chloride in 70% Aqueous Acetone

No added salts.

Temp. °C.	Solvent	10^4k.sec.$^{-1}$	Cl$^-$
20.08	I	2.651	0.00704
	II	2.566	0.00806
	III	2.582	0.00684
	IV	2.892	0.00763
	V	2.527	0.00664
	VI	2.732	0.00658
	VII	2.734	0.00717
? 2.643 probably	VIII	563 2.343	0.00719
	IX	2.937	0.00717
	X	2.529	0.00714
	XXX	2.535	0.00723
20.49	XXII	2.835	-
	XXIII	2.905	-
	XXVII	2.747	-
	XXVIII	2.724	-

p-Methoxybenzyl Chloride in 70% Aqueous Acetone

No added salts.

Temp. °C.	Solvent	10^4k.sec.$^{-1}$	Cl^-
20.08	XI	2.565	0.00845
	XII	2.646	0.00795
	XIII	2.314	0.00718
	XIV	2.369	0.00684
	XV	2.321	0.00703
	XVI	2.359	0.00705
	XVII	2.343	0.00719
	XVIII	2.506	0.00658
	XIX	2.549	0.00719
	XX	2.508	0.00762
	XXI	2.404	0.00668
20.49	XXIV	2.575	-
	XXV	2.607	-
	XXVI	2.665	-
	XXIX	2.507	-

TABLE A-2. THE EFFECT OF ELECTROLYTES ON THE RATE OF REACTION OF BENZHYDRYL CHLORIDE IN 70% AQUEOUS ACETONE AT 20.08°C.

Expt.	Solvent	Added Electrolyte	Initial Concentration	Cl^-	Cl^-_R	10^4k_H	10^4k_{Cl}	$10^4(k_E - k_H)$
8	I	HCl	0.05030	0.05870	-	2.566	-	-
			0.04762	0.05670	-	2.560	-	-
12			0.05000	0.05524	0.04784	2.563	-	0.277
			0.05000	0.05666	0.04855	2.545	-	0.278
9	II	NaCl	0.02519	0.03200	-	2.441	-	-
			0.02503	0.03194	-	2.457	-	-
13			0.02511	0.03315	0.02460	2.464	- ✓	0.165
			0.02513	0.03169	0.02455	2.478 [illegible]	-	0.123
10	III	NaCl	0.05138	0.05905	-	2.375	-	-
			0.05092	0.05868	-	2.360	-	-
			0.05149	0.06030	-	2.365	-	-
			0.05144	0.05791	-	2.358	-	-
14			0.05150	0.05656	0.05070	-	-	0.286
			0.05133	0.05965	0.05030	-	-	0.274

Expt.	Solvent	Added Electrolyte	Initial Concentration	Cl^-	Cl^-_R	10^4k_H	10^4k_{Cl}	$10^4(k_E - k_H)$
16	VI	$NaBF_4$	0.05082	0.00719	-	-	3.094	-
			0.05036	0.00815	-	-	3.040	-
			0.05082	0.00755	-	-	3.055	-
17	VII	Me_4NF	0.03752	0.00915	-	2.596	2.636	-
			0.05307	0.00751	-	-	2.570	-
18	X	$PhSO_3Na$	0.05003	0.00726	-	2.679	-	-
			0.04983	0.00754	-	2.667	-	-
23	VIII	NaN_3	0.01980	0.00652	-	2.489	2.640	-
			0.02026	0.00846	-	2.479	2.640	-
24	VIII	NaN_3	0.02983	0.01118	-	2.456	2.692	-
			0.02966	0.00902	-	2.436	2.689	-
25	I	NaN_3	0.05023	0.00892	-	-	2.945	-
			0.05018	0.00917	-	-	2.962	-
26			0.05017	0.01006	-	2.336	2.954	-
			0.05015	0.00775	-	2.321	2.936	-

Expt.	Solvent	Added Electrolyte	Initial Concentration	Cl^-	Cl^-_R	10^4k_H	10^4k_{Cl}	$10^4(k_E - k_H)$
21	IX	KBr	0.05008	0.00816	-	3.206	-	-
19	IX	$NaNO_3$	0.05015	0.00759	-	3.141		-
			0.05025	0.00843	-	-	3.147	-
20			0.05032	0.00833	-	-	3.129	-

TABLE A-3 THE EFFECT OF ELECTROLYTES ON THE RATE OF REACTION OF p-METHOXYBENZYL CHLORIDE IN 70% AQUEOUS ACETONE AT 20.03°C.

Expt.	Solvent	Added Electrolyte	Initial Concentration	Cl^-	Cl^-_R	10^4k_H	10^4k_{Cl}	$10^4(k_E - k_H)$
28	XIII	HCl	0.05133	0.0539		2.113	-	-
			0.05177	0.06036		2.106	-	-
33			0.05133	0.05893	0.04480	2.066	-	0.703
			0.05142	0.06144	0.04653	2.052	-	0.724
29	XIV	NaCl	0.02477	0.03163		2.211	-	-
			0.02512	0.03131		2.188	-	-
34			0.02462	0.03158	0.02301	2.218	-	0.371
30	XV	NaCl	0.05140	0.05871		1.999	-	-
			0.05202	0.05897		1.994	-	-
35			0.05128	0.05748	0.04785	-	-	0.714
		?	0.05845	0.05845	0.04926	-	-	0.714
31	XVI	NaCl	0.10030	0.10656		1.784	-	-
			0.10080	0.10661		1.794	-	-

Expt.	Solvent	Added Electrolyte	Initial Concentration	Cl^-	Cl^-_R	10^4k_H	10^4k_{Cl}	$10^4(k_E - k_H)$
32	XVII	NaCl	0.10080	0.10676		1.776	-	-
			0.10120	0.10603		1.774	-	-
36			0.10060	0.10765	0.09498	1.789	-	1.193
			0.10050	0.10689	0.09459	1.800	-	1.224
37	XI	$NaClO_4$	0.05015	0.00853	-	2.975	-	-
			0.05015	0.00849	-	2.975	-	-
38	XVIII	$NaBF_4$	0.05127	0.00761	-	-	2.839	-
			.04875	0.00845	-	-	2.831	-
39	XX	Me_4NF	0.05089	0.00724	-	-	2.565	-
			0.04544	0.00972	-	-	2.549	-
40			0.04500	0.00957	-	2.448	2.555	-
			0.04584	0.01137	-	2.439	2.548	-
41	XV	$PhSO_3Na$	0.05016	0.00731	-	2.577	-	-
			0.04978	0.00722	-	2.571	-	-

Expt.	Solvent	Added Electrolyte	Initial Concentration	Cl^-	Cl^-_R	10^4k_H	10^4k_{Cl}	$10^4(k_E - k_H)$
47	XII	NaN_3	0.01977	0.00720	-	2.478	3.139	-
			0.01983	0.00718	-	2.465	3.138	-
			0.01990	0.00808	-	2.482	$3.\overset{1}{\cancel{2}}04$	-
48	XII	NaN_3	0.03131	0.00799	-	2.410	3.489	-
			0.03006	0.00955	-	2.409	3.726	-
			0.03176	0.00771	-	2.412	3.688	-
49	XII	NaN_3	0.03929	0.00845	-	2.334	3.851	-
			0.04067	0.00776	-	2.340	4.034	-
			0.03993	0.00771	-	2.330	4.032	-
45	XXI	KBr	0.05087	0.00998	-	3.036		-
			0.05025	0.01161	-	3.049		-
46			0.05028	0.01141	-	3.011	3.024	-
			0.05030	0.01011	-	-	3.010	-
			0.05033	0.00901	-	-	3.028	-

Expt.	Solvent	Added Electrolyte	Initial Concentration	Cl^-	Cl^-_R	$10^4 k_H$	$10^4 k_{Cl}$	$10^4 (k_E - k_H)$
42	XV	$NaNO_3$	0.05019	0.00938	-	(2.562)		
			0.05026	0.01002	-	(2.557)		
43			0.05051	0.00857	-	-	2.759	
			0.05039	0.00810	-	-	2.762	
			0.05034	0.00690	-	-	2.738	
44			0.05038	0.00848	-		2.750	
			0.05041	0.00806	-		2.742	

TABLE A-4

THE EFFECT OF NON-ELECTROLYTES ON THE RATES OF REACTION OF BENZHYDRYL CHLORIDE AND p-METHOXYBENZYL CHLORIDE IN 70% AQUEOUS ACETONE AT 20.49°C.

Non-Electrolyte	$Ph_2CH\,Cl$				p-MeOC$_6$H$_4$CH$_2$CHCl				
	Solvent	Expt.	Non-electrolyte concentration	10^4k_{Cl}	Solvent	Expt.	Non-electrolyte concentration	10^4k_{Cl}	10^4k_H
	XXVIII	54	0.7450	2.367	XXIX	57	0.7422	2.667	1.600
			0.7506	2.381			0.7418	2.653	1.622
Pyridine	XXVII	53	0.4922	2.491	XXIX	56	0.4941	2.607	1.870
			0.4942	2.494			0.4943	2.604	1.860
		52	0.2502	2.672	XXIX	55	0.2470	2.565	2.168
							0.2473	2.581	2.175
Acetone	XXII	58	1.0884	2.165	XXV	63	1.0890	-	2.026
Benzene	XXII	59	0.5592	1.808	XXIV	64	0.5612	-	1.987
			0.5610	1.810			0.5615	-	1.998
			0.5615	1.791			0.5591	-	2.014
							0.5606	-	1.991
Toluene	XXIII	60	0.6276	1.764	XXVI	65	0.6271	-	2.015
Nitrobenzene	XXII	61	0.4908	2.026	XXVI	66	0.4912	-	2.069
							0.4913	-	2.072
Chlorobenzene	XXIII	62	0.4018	1.787	XXVI	67	0.4024	-	2.074

APPENDIX B

1. Determination of the Activation Parameters.

Energies of activation were obtained from the rate coefficients at adjacent temperatures by the equation

$$E = \frac{RT\,T_2}{(T_2 - T)} \cdot \ln \frac{k_2}{k} \quad \ldots\ldots\ldots\ldots\ldots \text{B-1}$$

and ΔS^* from the expression

$$\Delta S^* = R \quad \ln k - \ln \frac{\bar{k}}{h} - 1 - \ln \frac{(T + T_2)}{2} + \frac{E}{RT} \quad \ldots \text{B-2}$$

where E has the value given by equation B-1.

It has already been shown[61a] that the values of E and ΔS^* obtained from these equations refer to the temperature $\frac{T + T_2}{2}$ if ΔC^* is constant over the experimental temperature range, a condition fulfilled by the present system (see page 38).

The heat capacity of activation was obtained from the equation

$$\frac{dE}{dT} = \Delta C^* + R$$

(see page 28). The value of dE/dT was obtained as the slope of the "best" straight line, E against T, by the method of least squares.

The energy and entropy of activation, E and ΔS^*, could then be calculated from the expressions

$$E = E_m + \frac{dE}{dT}\,(T - T_m) \quad . . . . B\text{-}3$$

$$\Delta S^* = \Delta S^*_m + \Delta C^*\left[\ln T - (\ln T)_m\right] \quad . . . . B\text{-}4$$

where E_m and ΔS^*_m are the means of the observed values of the energy and entropy of activation, respectively, and T_m and $(\ln T)_m$ the means of the values of T and ln T to which they refer.

2. Errors in dE/dT.

Two methods were used to calculate the standard deviation of dE/dT.

(i) From the "best" straight line, E against T.

The standard deviation of the slope of the best straight line, E against T, is given by

$$\sigma(dE/dT) = \left[\frac{\sum(E - E_{calc.})^2}{(n-2)\sum(T-T_m)^2}\right]^{\frac{1}{2}} \quad . . . . B\text{-}5$$

where n is the number of separate determinations of E and $E_{calc.}$ is given by equation B-3.

(ii) From the standard error of E.

If the rate coefficient k is subject to a standard error σ, it can easily be shown that the standard error in the value of E, calculated from equation B-1, is

$$\sigma(E) = \frac{R\,T_1 T_2}{(T_2 - T_1)} \left[\left(\frac{\sigma_1}{k_1}\right)^2 + \left(\frac{\sigma_2}{k_2}\right)^2\right]^{\frac{1}{2}} \quad \ldots\ldots \quad \text{B-6}$$

The slope of the "best" straight line, E against T, is given by

$$\frac{dE}{dT} = \frac{\sum(E-E_m)\times(T-T_m)}{\sum(T-T_m)^2}$$

and the standard error $\sigma(E)$ for each value of E therefore yields a standard deviation of dE/dT, given by

$$\sigma(dE/dT) = \frac{\left[\sum(E-E_m)^2(T-T_m)^2\right]^{\frac{1}{2}}}{\sum(T-T_m)^2} \quad \ldots\ldots \quad \text{B-7}$$

APPENDIX C.

Mass-law effects in the Rate of Reaction of Benzhydryl Chloride.

The overall rate of reaction of benzhydryl chloride with water and an anionic reagent, Y^-, is given by

$$k_x = \frac{k_1(1 + \beta Y^-)}{1 + \alpha X^- + \beta Y^-} \quad \ldots\ldots \text{C-1}$$

Compare Chapter VII, pages 137-141.

Where k_1 is the rate coefficient for ionisation,

α is the mass-law constant,

β is a similar intervention constant (see page 78).

For cases where $\beta = 0$,

$$k_x = \frac{k_1}{1 + \alpha X^-} \quad \ldots\ldots \text{C-2}$$

In the present studies α was 2.3 and typical concentrations of $X^- = Cl^-$ are 0.008 M. and k_x therefore approximates closely to k_1. The values of k_x/k_x° given in Chapter IV thus correspond closely to k_1/k_1°. Even for appreciable values of β (eg. 5-6) and 0.05 M. electrolyte, the ratio k_x/k_x° is still a very close approximation to k_1/k_1°.

APPENDIX D

The effect of hydrolysis of RCl during extraction on the rates coefficients, k_E and k_H.

In one or two of the experiments with benzhydryl chloride and p-methoxybenzyl chloride containing Cl^{36}, the values of the integrated first-order rate coefficients, k_E and k_H, were observed to decrease throughout the course of the reaction. Since in each of these cases an extraction procedure was employed, it seemed possible that hydrolysis of the substrate was occuring during the extraction. The amount of acid measured experimentally was thus greater than the amount produced during the kinetic run. If the observed and true amounts of acid are T^{obs} and T, respectively, then

$$T^{obs} = T + K(T_{\infty} - T) \qquad \ldots\ldots D\text{-}1$$

where K is not a constant but depends on the amount of RCl present, and decreases as $(T_{\infty} - T)$ decreases. This proviso is equivalent to proposing that it takes longer to extract large amounts of the substrate than small amounts.

Therefore

$$k_H^{obs} = \frac{1}{t} \ln \frac{T_{\infty}^{obs} - T_o^{obs}}{T_{\infty}^{obs} - T^{obs}}$$

$$= \frac{1}{t} \ln \frac{T_{\infty} - T_o}{T_{\infty} - T} \cdot \frac{1 - K_o}{1 - K}$$

$$k_H^{obs} = k_H + \frac{1}{t} \ln \frac{1 - K_o}{1 - K} \qquad \ldots\ldots \text{D-2}$$

For the rate of production of active chloride ions (Cl^{*-}), the extra Cl^{*-} produced must be the same fraction of the total RCl^* present as the fraction of RCl which yields H^+.

Therefore

$$C^{obs} = C + K(C_\infty - C)$$

where C is the concentration of Cl^{*-} produced.

It follows that

$$k_E^{obs} = k_E + \frac{1}{t} \ln \frac{1 - K_o}{1 - K} \qquad \ldots\ldots \text{D-3}$$

Since K_o is greater than K, the values of k_E^{obs} and k_H^{obs} must decrease throughout the course of the run and must be too small. Subtraction of equations D-2 and D-3 shows, however, that

$$(k_E - k_H)_{obs} = k_E - k_H$$

For runs where the rates were observed to decrease, the values of $(k_E - k_H)$ were therefore accepted.

APPENDIX E

In the present work it was assumed that the integrated rate coefficient for the interval o - t could be equated to the instantaneous value at t/2. This led to the conclusion that the mean instantaneous rate coefficient referred to the time when

$$Cl^- = Cl^-_\infty - \frac{RCl_o^{\frac{1}{2}}}{n} \sum RCl_t^{\frac{1}{2}} \qquad \ldots\ldots E\text{-}1$$

(see page 144). On the other hand, the integrated mean chloride ion concentration for the time interval 0—t is given by

$$(Cl^-)_{0-t} = \frac{1}{t}\int_0^t Cl^-.\, dt$$

$$= Cl^-_i + \frac{RCl_o}{t}\int_0^t (1 - e^{-kt})\, dt$$

$$= Cl^-_i + RCl_o + \frac{RCl_o}{kt}.\,(e^{-kt} - 1)$$

$$= Cl^-_\infty - (Cl^- - Cl^-_o)/kt$$

Therefore the mean of these values for the run is given by

$$Cl^- = Cl^-_\infty - \frac{1}{n}\sum \frac{(Cl^-_t - Cl^-_o)}{kt} \qquad \ldots\ldots E\text{-}2$$

The values of Cl^- given by equations E-1 and E-2 for experiment 23 (see page 189) are 8.43 ml. and 8.61 ml., respectively. The first order rate coefficients were not constant for this run, but the two estimates of Cl^- agree well enough for the purposes of the present investigations. It is concluded, therefore, that the assumptions that have been made concerning the relation between instantaneous and integrated rates are valid ones.

APPENDIX F

Errors in the values of σ for the reaction of benzhydryl chloride with chloride or azide ions in 70% aqueous acetone.

(i) When the electrolyte is sodium chloride the value of σ^{NaCL} may be obtained from

$$-B\sigma^{NaCl}c^{NaCl} = \log\frac{(1+\alpha Cl^{-})}{(1+\alpha Cl_{o}^{-})} + \log\frac{k_{Cl}}{k_{H}^{o}} + B(\sigma^{HCl}c^{HCl} - \sigma^{HCl}c_{o}^{HCl})$$

(compare equation VII-18)

If the error in k_{Cl}/k_{H} is $\pm x\%$, the true value of σ (σ_{T}^{NaCl}) is given by

$$-B\sigma_{T}^{NaCl}c^{NaCl} = \log\frac{(1+\alpha Cl^{-})}{(1+\alpha Cl_{o}^{-})} + \log\frac{k_{Cl}}{k_{H}^{o}}\left(1 \pm \frac{x}{100}\right) + B(\sigma^{HCl}c^{HCl} - \sigma^{HCl}c_{o}^{HCl})$$

Subtration of these two expressions gives

$$-Bc^{NaCl}(\sigma_{T}^{NaCl} - \sigma^{NaCl}) = -Bc^{NaCl}\Delta\sigma^{NaCl} = \log\left(1 \pm \frac{x}{100}\right)$$

(ii) When the electrolyte is sodium azide the value of σ^{NaN_3} may be obtained from

$$-B\sigma^{NaN_3}c^{NaN_3} = \log\frac{1+\alpha Cl^{-}+\beta N_3^{-}}{(1+\beta N_3^{-})(1+\alpha Cl_{o}^{-})} + \log\frac{k_{Cl}}{k_{H}^{o}} + B(\sigma^{NaCl}c^{NaCl} - \sigma^{HCl}c_{o}^{HCl})$$

(compare equation VII-19).

A similar treatment to that given in (i) may be easily shown to give the result

$$-Bc^{NaN_3}(o_T^{NaN_3} - o^{NaN_3}) = -Bc^{NaN_3}\Delta o^{NaN_3} = \log\left(1 \pm \frac{x}{100}\right)$$

APPENDIX G

Errors in the parameter β for the reaction of azide ions with p-methoxybenzyl chloride.

The observed value of β is given by

$$\beta = \frac{\text{Antilog}_{10} - B(\sigma^{NaCl}c^{NaCl} + \sigma^{NaN_3}c^{NaN_3} - \sigma^{HCl}c_o^{HCl})}{N_3^- \, k_H/k_H^\circ}(1 + \alpha Cl_o^-)$$

$$- \frac{1 + \alpha Cl^-}{N_3^-}$$

If the value of k_H/k_H° is in error by ±x%, the true value of β (β_T) is given by a similar expression with k_H/k_H° replaced by

$$\frac{k_H}{k_H^\circ}(1 \pm {}^x/100)$$

Therefore,

$$(\beta_T - \beta) = \Delta\beta = \frac{\text{Antilog}_{10} - B(\sigma^{NaCl}c^{NaCl} + \sigma^{NaN_3}c^{NaN_3} - \sigma^{HCl}c^{HCl})}{N_3^- \, k_H/k_H^\circ}$$

$$(1 + \alpha Cl_o^-)\left(\frac{1}{1 \pm \frac{x}{100}} - 1\right)$$

$$= \pm\left(\beta + \frac{1 + \alpha Cl^-}{N_3^-}\right)\frac{x}{100 \pm x}$$

for small values of x this reduces to

$$\Delta\beta = \pm\frac{x}{100}\left(\beta + \frac{1 + \alpha Cl^-}{N_3^-}\right)$$

REFERENCES

1. a) Hughes, Quart.Rev., 1951, 5, 245.

   b) Ingold, "Structure and Mechanism in Organic Chemistry", G.Bell and Sons, London, 1953, Chapters 5 and 7.

2. Hughes, Trans.Faraday Soc., 1941, 37, 603.

3. Hughes, and Ingold, J.Chem.Soc., 1935, 244.

4. a) Olson and Voge, J.Amer.Chem.Soc., 1934, 56, 1690

   b) Ogg, ibid., 1939, 61, 1946.

5. Hughes, J.Chem.Soc., 1935, 255.

6. Ref.2, p.607.

7. a) Cowdrey, Hughes, Ingold, Masterman and Scott, J.Chem.Soc., 1937, 1252.

   b) Bateman, Church, Hughes, Ingold and Taher, ibid., 1940, 925.

   c) Ingold, Trans.Faraday Soc., 1938, 34, 222.

8. Winstein, J.Amer.Chem.Soc., 1939, 61, 1635.

9. Hammett, Physical Organic Chemistry, McGraw-Hill Book Company, Inc., New York, 1940, p.172.

10. Winstein, Clippinger, Fainberg, Heck and Robinson, J.Amer.Chem.Soc., 1956, 78, 328; Winstein and Clippinger, ibid., 1956, 78, 2784; Fainberg and Winstein, ibid., 1956, 78, 2763, 2767, 2780; Fainberg, Robinson and Winstein, ibid., 1956, 78, 2777; Robinson and Winstein, ibid., 1958, 80, 169.

11. a) Winstein and Gall, *Tetrahedron Letters,* 1960, No.2, 31.
    b) Winstein, Hojo and Smith, ibid., 1960, No.22, 12.
    c) Winstein, Gall, Hojo and Smith, *J.Amer.Chem.Soc.*, 1960, *82,* 1010.

12. Pocker, *Proc.Chem.Soc.*, 1961, 140

13. a) Bensley and Kohnstam, *J.Chem.Soc.*, 1955, 3408.
    b) Kohnstam and Shillaker, *ibid.*, 1959, 1915.

14. a) Hine, "Physical Organic Chemistry", McGraw-Hill Book Company, Inc., New York, 1956, p.140.
    b) Streitweiser, *Chem.Reviews.*, 1956, *56,* 571.
    c) Swain and Scott, *J.Amer.Chem.Soc.*, 1953, *75,* 146.

15. Cooper and Hughes, *J.Chem.Soc.*, 1937, 1183.

16. Benfey, Hughes and Ingold, J.Chem.Soc., 1952, 2488.

17. Ward, *J.Chem.Soc.*, 1927, 2285.

18. Ballinger, de la Mare, Kohnstam, and Prestt, *J.Chem.Soc.*, 1955, 3641.

19. Gleave, Hughes and Ingold, *J.Chem.Soc.*, 1935, 236.

20. a) Hughes, Ingold and Shapiro, *J.Chem.Soc.*, 1936, 225.
    b) Bateman, Cooper, Hughes and Ingold, *ibid.*, 1940, 925.

21. Baker and Easty, *J.Chem.Soc.*, 1952, 1193, 1208.

22. a) Baker and Neale, *J.Chem.Soc.*, 1955, 608.
    b) Baker and Heggs, *ibid.*, 1955, 616.

23. Benfey, Hughes and Ingold, *J.Chem.Soc.*, 1952, 2494.

24. Olivier and Weber, *Rec.Trav.chim.*, 1934, *53,* 867.

25. McCleary and Hammett, *J.Amer.Chem.Soc.*, 1941, *63*, 2254.

26. Coburn, Grunwald and Marshall, *J.Amer.Chem.Soc.*, 1953, *75*, 5735.

27. Bensley and Kohnstam, *J.Chem.Soc.*, 1957, 4747.

28. Cowie, Fox, Fitches, Hooton, Hunt, Kohnstam and Shillaker, *Proc.Chem.Soc.*, 1961, 222.

29. Shillaker, *Ph.D.Thesis*, Durham, 1960.

30. Sugden and Willis, *J.Chem.Soc.*, 1951, 1360.

31. Bennett and Jones, *J.Chem.Soc.*, 1935, 1815.

32. Olivier, *Rec.Trav.Chim.*, 1937, *56*, 247.

33. Balfe, Kenyon and Wicks, *J.Chem.Soc.*, 1946, 807.

34. a) Evans, *Nature*, 1946, *157*, 438.
    b) Evans, Evans and Polanyi, *J.Chem.Soc.*, 1947, 558.
    c) Reeve, McCaffery and Kaiser, *J.Amer.Chem.Soc.*, 1954, *76*, 2280.

35. a) Dostrovsky, Hughes and Ingold, *J.Chem.Soc.*, 1946, 173.
    b) Winstein, and Marshall, *J.Amer.Chem.Soc.*, 1952, *74*, 1120.
    c) Calhoun and Barwell, *ibid.*, 1955, *77*, 6441.

36. a) Grunwald and Winstein, *J.Amer.Chem.Soc.*, 1948, *70*, 846.
    b) Winstein, Grunwald and Jones, *ibid.*, 1951, *73*, 2700.

37. Ref.1b., p.310.

38. a) Swain and Langsdorf, *J.Amer.Chem.Soc.*, 1951, *73*, 2813.
    b) Kornblum, Smiley, Blackwood and Iffland, *ibid.*, 1955, *77*, 6269.
    c) Gold, *J.Chem.Soc.*, 1956, 4633.

39. Bird, Hughes and Ingold, J.Chem.Soc., 1954, 634.

40. Winstein, Fainberg and Grunwald, J.Amer.Chem.Soc., 1957, 79, 4146.

41. Nair, Ph.D.Thesis, Arkansas, 1957.

42. Doering and Zeiss, J.Amer.Chem.Soc., 1953, 75, 4733.

43. Gillespie, J.Chem.Soc., 1952, 1002.

44. Dewar, J.Chem.Soc., 1953, 3180.

45. Le Roux and Swart, J.Chem.Soc., 1955, ~~3180.~~ 1475

46. de la Mare, J.Chem.Soc., 1955, 3180.

47. Winstein, Smith and Darwish, Tetrahedron Letters., 1959, No.16, 24.

48. Crunden and Hudson, J.Chem.Soc., 1956, 501.

49. Kelly and Watson, J.Phys.Chem., 1958, 62, 260

50. Gold, Hilton and Jefferson, J.Chem.Soc., 1954, 2756.

51. a) Bunton, Lewis and Llewellyn, Chem. and Ind., 1954, 1154.
    b) Bunton and Lewis, ibid., 1956, 180

52. Day and Ingold, Trans.Faraday Soc., 1941, 37, 686.

53. Pocker, J.Chem.Soc., 1959, 3939, 3944.

54. Pocker, Trans.Faraday Soc., 1959, 55, 1266.

55. a) de la Mare, Fowden, Hughes, Ingold and Mackie, J.Chem.Soc., 1955, 3200.
    b) Hughes and de la Mare, ibid., 1956, 845.

56. Arrhenius, Z.Phys.Chem., 1889, 4, 226.

57. a) Trautz, Z.Anorg.Chem., 1918, 102, 81.

57. b) Scheffer and Brandsma, Rec.Trav.Chim., 1926, 45, 522.

c) La Mer, J.Chem.Phys., 1933, 1, 289.

58. Glasstone, Laidler and Eyring, "The Theory of Rate Processes", McGraw-Hill Book Company, New York, 1941, p.199.

59. a) La Mer and Miller, J.Amer.Chem.Soc., 1935, 57, 2674.

b) Moelwyn-Hughes, Proc.Roy.Soc., 1938, A, 164, 295.

c) Glew and Moelwyn-Hughes, ibid., 1952, A, 211, 254.

d) Moelwyn-Hughes, ibid., 1953, A, 220, 386.

e) McKinly-McKee and Moelwyn-Hughes, Trans.Faraday Soc., 1952, 48, 247.

f) Gold, ibid., 1948, 44, 506.

g) Tommila, Paakkala, Virtanen, Erva and Varila, Ann.Acad. Sci.Fennicae, 1959, AII, NO.91.

h) Tommila, Tilikainen and Voipio, ibid., 1955, AII, No.65.

60. a) Bensley, Ph.D.Thesis, Durham, 1956., Kohnstam,

b) Kohnstam, Ph.D.Thesis, London, 1948.

61. a) Bensley and Kohnstam, J.Chem.Soc., 1956, 277.

b) Kohnstam, ibid., 1960, 2066.

62. Brittain, Kohnstam, Shillaker and Queen, J.Chem.Soc., 1961, 2045.

63. a) Robertson, Proc.Roy.Soc., 1959, A, 252, 273.

b) Hamilton and Robertson, Canad.J.Chem., 1959, 37, 966.

64. Semerano, Gazzetta, 1931, 61, 921.

65. Kirkwood, J.Chem.Phys., 1934, 2, 351.

66. Åkerlof, J.Amer.Chem.Soc., 1932, 54, 4125.

67. Everett and Wynne-Jones, Trans.Faraday Soc., 1939, 35, 1
1380.

68. a) Amis and Price, J.Phys.Chem., 1943, 47, 338.
 b) Amis and Holmes, J.Amer.Chem.Soc., 1941, 63, 2231.
 c) Amis and Cook, ibid., 1941, 63, 2621.
 d) Amis and Potts, ibid., 1941, 63, 2883.

69. a) Brown and Hudson, J.Chem.Soc., 1953, 3352,
 b) Evans, Price and Thomas, Trans.Faraday Soc., 1955, 51,481.

70. Caldin and Peacock, Trans.Faraday Soc., 1955, 51, 1217.

71. Ref.1b, p.312.

72. Randall and Rossini, J.Amer.Chem.Soc., 1929, 51, 323.

73. Everett and Coulson, Trans.Faraday Soc., 1940, 36, 633.

74. Gold and Jefferson, J.Chem.Soc., 1953, 1409.

75. a) Robertson, Heppolette and Scott, Canad.J.Chem., 1959,
37, 83.
 b) Robertson, Suomen Kem., 1960, 33, A, 44.

76. Moelwyn-Hughes, Proc.Roy.Soc., 1938, A, 164, 295.

77. a) Evans and Hamann, Trans.Faraday Soc., 1951, 47, 259.
 b) Buchanan and Hamann, ibid., 1953, 49, 1425,
 c) Burris and Laidler, ibid., 1955, 51, 1497.

78. Kohnstam, Shillaker and Queen, Proc.Chem.Soc., 1959,

79. Ref.1b, p.360.

80. Bateman, Church, Hughes, Ingold and Taher, J.Chem.Soc., 1940, 979.

81. Church, Hughes and Ingold, J.Chem.Soc., 1940, 966.

82. Bateman, Hughes and Ingold, J.Chem.Soc., 1940, 960.

83. Bronsted, Z.Phys.Chem., 1922, 102, 109, 1925, 115, 337.

84. Clements and McMichael, J.Org.Chem., 1961, 26, 620.

85. Pocker, Chem. and Ind., 1957, 1599.

86. a) Bronsted, Nash and Monk, J.Chem.Soc., 1955, 1899.
   b) Speith and Olson, J.Amer.Chem.Soc., 1955, 77, 1412.

87. Lucas and Hammett, J.Amer.Chem.Soc., 1942, 64, 1928.

88. Baughmann, Grunwald and Kohnstam, J.Amer.Chem.Soc., 1960, 82, 5801.

89. Benfey, Hughes and Ingold, J.Chem.Soc., 1952, 2488, 2494.

90. Duynstee, Grunwald and Kaplan, J.Amer.Chem.Soc., 1960, 82, 5654.

91. Butler and Grunwald, J.Amer.Chem.Soc., 1960, 82, 5647.

92. Long and McDevitt, Chem.Rev., 1952, 51, 119.

93. Ref.58, p.195.

94. Hughes, Ingold, Mok, Patai and Pocker, J.Chem.Soc., 1957, 1265.

95. Kohnstam, personal communication.

96. Kohnstam and Ribar, results personally communicated.

97. Grunwald and Bacarella, J.Amer.Chem.Soc., 1958, 80, 3840.

98. Robertson, *Canad.J.Chem.*, 1953, *31*, 589.

99. a) Bateman, Hughes and Ingold, *J.Chem.Soc.*, 1940, 974.

b) Bateman, Hughes and Ingold, *J.Chem.Soc.*, 1940, 1017.

100. Hammond, Peloquin, Fang and Kochi, *J.Amer.Chem.Soc.*, 1960, *82*, 443.

101.a) Fainberg and Winstein, *J.Amer.Chem.Soc.*, 1957, *79*, 1602, 1608.

b) Winstein, Fainberg and Grunwald, *ibid.*, 1957, *79*, 4146.

102.a) Speith, Ruebsamen and Olson, *J.Amer.Chem.Soc.*, 1954, *76*, 6253.

b) Wilputte-Steinert and Fierens, *Bull.Soc.Chim.Belges.*, 1955, *64*, 299.

103. Laidler and Eyring, *Ann.N.Y.Acad.Sci.*, 1940, *39*, 303.

104.a) Archer and Hudson, *J.Chem.Soc.*, 1950, 3259.

b) Kochi and Hammond, *J.Amer.Chem.Soc.*, 1953, *75*, 3445, 3452.

c) Hackett and Thomas, *ibid.*, 1950, *72*, 4962.

d) Salomaa, *Ann.Univ.Turkuensis*, 1953, *A14*.

105. Fainberg and Winstein, *J.Amer.Chem.Soc.*, 1956, *78*, 2770.

106. Laidler and Landskroener, *Trans.Faraday Soc.*, 1956, *52*, 200.

107. Kilpi, *Suomen Kem.*, 1953, 26B, No.2, 9.

108. Bohme and Schurhoff, *Chem.Ber.*, 1951, *84*, 28.

109. Tommila, Paqkhala, Virtanen, Erva and Varilla, *Ann. Acad.Sci.Fennicae*, 1959, AII, No.91.

110. Hudson and Saville, J.Chem.Soc., 1955, 4114.

111. Grunwald, J.Phys. and Colloid.Chem., 1951, 55, 881.

112.a) Cohn, McMeekin, Edsall and Weare, J.Amer.Chem.Soc., 1934, 56, 2271.

b) McMeekin, Cohn and Wease, ibid., 1935, 57, 626.

113. Baeyer and Villiger, Ber., 1904, 37, 605.

114. Dauben and Layton, J.Amer.Chem.Soc., 1959, 81, 5404.

115. McAlpine and Soule, "Qualitative Chemical Analysis", Chapman Hall Ltd., London, 1933, p.570.

116. Moissan, Bull. Soc. Chim., 1891, (3), 5, 456.

117. Banks, Cuthbertson and Musgrave, Anal.Chim.Acta., 1955, 13, 442.

118. Conant and Kirner, J.Amer.Chem.Soc., 1924, 46, 232.

119. Ryss, Compt.read.accad.Sei.US.S.R., 1946, 52, 417, cf., Chem.Abs., 1947, 41, 1534.

120. Hawdon, Hughes and Ingold, J.Chem.Soc., 1952, 2499.

121.a) Overman and Clark, "Radioisotope Techniques", McGraw Hill Book Company, N.Y., 1960.

b) Whitehouse and Putman, "Radio-active Isotopes", Oxford, 1953.

c) Friedlander and Kennedy, "Intwoduction to Radiochemistry", Chapman and Hall, London, 1949.

122. Robinson and Stokes, "Electrolyte Solutions", Butter-Worths Scientific Publications, London, 1959, p.236.

123.a) Guggenheim, Phil.Mag., 1935, 19, 558.

b) Davies, J.Chem.Soc., 1938, 2093.