Solvolytic studies of benzyl halides

Shillaker, Brian

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SOLVOLYTIC STUDIES OF BENZYL HALIDES

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BRIAN SHILLAKER

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ABSTRACT

The investigation concerns the solvolytic study of p-substituted benzyl halides in aqueous acetone. By a suitable choice of substituents it is possible to obtain a finely graded sequence of mechanisms, by which hydrolysis occurs, ranging from extreme S_N2 to S_N1 and the work aimed at obtaining information about the mechanistic border-line region, a region where the mechanism is almost, but not quite, S_N1. For this a new approach was necessary since criteria which are well established for the investigation of the extreme forms of mechanism could not be used in this region. This approach involved the verification of the hypothesis that the ratio of the heat capacity of activation to the entropy of activation for the S_N1 hydrolysis of an alkyl chloride in a given solvent at a given temperature has a constant value. Extension of the earlier work carried out by Bensley and Kohnstam[1] shows that this hypothesis is essentially correct and that the ratio of the heat capacity of activation to the entropy of activation has a lower value for S_N2 reactions than for S_N1 reactions. Application of these ideas to the present experiments shows that p-methoxybenzyl chloride in 50% aq.acetone reacts by mechanism S_N1, p-methylbenzyl chloride is border-line and the unsubstituted

compound and p-nitrobenzyl chloride react by a mechanism which progressively approaches the more extreme form of S_N2.

An additional problem investigated concerns the effect of electrolyte additions on the hydrolysis rate of benzhydryl chloride, a compound which reacts by mechanism S_N1. The specific electrolyte effects found are interpreted as arising from changes in the solvent composition caused by the solvation of the electrolyte. This effect would be superimposed upon the ionic-strength effect of Hughes and Ingold[2].

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1. Bensley and Kohnstam, J.Chem.Soc., 1957, 4747.
2. Bateman, Church, Hughes, Ingold and Taher, J.Chem.Soc., 1940, 979.

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CHAPTER I

MECHANISM OF SUBSTITUTION AT A SATURATED CARBON ATOM[1,2]

Types of Substitution.

In a substitution of the form

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

in which only one bond is exchanged, there are two main types of bond fission.

(A) Homolytic or symmetric fission.

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

(The dots represent electrons)

This type of rupture is common in gas-phase reactions,

e.g. $H + H - H \longrightarrow H - H + H$

(B) Heterolytic or dissymmetric fission.

This form of fission is common for reactions in solution. It is necessary to distinguish between two types of heterolytic substitution.

(1) Electrophilic (labelled S_E).

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

In this type the substituting agent uses its electrons to attack the nucleus of R or uses its nucleus to combine with the electrons of R.

e.g. $D^{+} + R - H \longrightarrow D - R + H^{+}$

(2) Nucleophilic (labelled S_N).

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

In this type the expelled group separates with its electrons

e.g. $I^{-} + R - Cl \longrightarrow I - R + Cl^{-}$

In nucleophilic substitution there is an electron transfer from the substituting agent Y to the centre of substitution in R, and from this centre to the expelled group X; so that, in consequence of the substitution, Y becomes formally one electronic unit more positive, and X one unit more negative. Subject to this, there need be no restriction on the states of electrification of the species involved. The present investigation is concerned with reactions of this type.

Mechanisms of Nucleophilic Substitution.

Two mechanisms are recognised for nucleophilic substitution.

The first is a one stage process, in which two molecules simultaneously undergo covalency change in the rate-determining step; it is therefore called bimolecular and labelled S_N2. In this mechanism we have synchronous bond making and breaking.

$$Y^- + R - X \rightleftharpoons \left[\overset{\delta-}{Y}\text{---}R\text{---}\overset{\delta-}{X}\right] \rightleftharpoons Y - R + X^- \qquad (S_N2)$$

The solvolysis of methyl bromide in aqueous ethanol occurs by this mechanism[3].

The second mechanism involves two stages, a slow ionisation of the compound substituted is followed by a rapid co-ordination between the formed carbonium ion and the substituting agent. The rate-determining stage is the first, and since in that stage only one molecule is undergoing covalency change, the mechanism is called unimolecular and labelled S_N1.

$$R - X \rightleftharpoons \left[\overset{\delta+}{R}\text{----}\overset{\delta-}{X}\right] \rightleftharpoons R^+ + X^- \text{ (slow)} \qquad (S_N1)$$

$$R^+ + Y^- \longrightarrow R - Y \qquad \text{(fast)}$$

At one time it was thought that organic compounds did not ionise in this way in view of the large activation energy which would be required[4,5]. It is now postulated however that ionisation does occur due to the activation energy being reduced to accessible values by the solvation of the polar transition state in the ionisation process[3].

This mechanism operates in the solvolysis of <u>tert</u>.-butyl chloride in aqueous acetone[6].

Formation of Ion-pairs.

An extension of the S_N1 mechanism has been proposed by Winstein and co-workers to explain "special salt effects" in the acetolysis of some toluenesulphonates and benzenesulphonates in acetic acid[7,8]. These authors hold the view that two types of ion-pair may be concerned in these heterolyses; the first, an "internal" ion-pair, in which the partly separated particles are surrounded by a common solvation shell; the second, an "external" or "solvent-separated" ion-pair.

$$RX \rightleftharpoons \underset{\substack{\text{Internal}\\ \text{ion-pair}}}{\left[R^+\ X^-\right]} \rightleftharpoons \underset{\substack{\text{External}\\ \text{ion-pair}}}{\left[R^+//\ X^-\right]} \rightleftharpoons \underset{\substack{\text{Dissociated}\\ \text{ions}}}{R^+ \ + \ X^-}$$

These ion-pairs, which exist as metastable intermediates, are capable of reacting directly with the solvent and anions.

Although the evidence for ion-pair formation cited by Winstein appears to be satisfactory for acetolysis, the intervention of ion-pairs in hydrolysis has yet to be established. For example, it has been shown[9,10] that even if the S_N1 heterolysis of the C-Cl linkage involves intermediate ion-pairs, these need not react significantly relative to the fully developed carbonium ion with water and with anions. This has been demonstrated for the hydrolysis of dichlorodiphenylmethane in aqueous acetone.

Determination of Mechanism.

The present investigation is essentially concerned with the mechanism operating in solvolysis. Several methods are available for the recognition of mechanism and these will now be discussed.

I. The kinetic criterion. Provided both reacting species are in small and controllable concentration, the bimolecular mechanism of substitution should lead to second order kinetics, as expressed in the equation,

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

When however, as in the present case, the substituting agent is a main constituent of the solvent and therefore present in constant excess, the bimolecular mechanism leads to first order kinetics. The unimolecular mechanism also gives first order kinetics, with an overall rate equal to the heterolysis rate, provided that the rate of reversal of the heterolysis is much smaller than the rate of co-ordination of the carbonium ion with the substituting agent. Thus in solvolytic reactions the kinetic order of a reaction cannot be used as a criterion of mechanism.

II. The effect of structural changes in the compound substituted on reaction rate. This will be discussed fully in the following pages.

III. The effect of systematic changes in the substituting agent on reaction rate.

IV. The effect of solvent changes on reaction rate and on the products. The effect on rate will be discussed in connection with the work of Winstein, Grunwald and Jones[11] (see page 11).

V. The stereochemical course of the substitution.

VI. The kinetic form of the substitution reaction.

VII. The effect of salt additions on rate and products.

Full details of the above methods are given in a review by Hughes[12].

Effect of Substituents on Mechanism and Rate.

Bimolecular nucleophilic substitutions involve simultaneous electron transfers from the substituting agent to the reaction centre and from the latter to the expelled group. In general, these transfers will not be exactly balanced in the transition state of the reaction, so that a polar effect on the rate is to be expected. When the nucleophilic reagent is negative, this effect is only small. When the reagent is neutral however (e.g. water) the effect may be quite large, as is observed when the rate of hydrolysis of p-nitrobenzyl chloride is compared with that of the parent compound (see

Table IV 3). It should be emphasised that even in this latter category the effect on the rate is not so large as for S_N1 reactions.

The rate-determining stage of unimolecular nucleophilic substitutions involves an electron transfer from the reaction centre to the displaced group, without any compensating gain of electrons by the reaction centre. A large kinetic polar effect, of certain direction, is therefore expected. Electron release to the reaction centre must facilitate such substitutions by stabilising the transition state.

As a general rule, the inductive mechanism of electron release is the important one. Since the inductive effect for the methyl group is greater than for hydrogen, it follows that electron release to the reaction centre should increase along the following series of alkyl halides.

Me < Et < <u>i</u>-Pr < <u>tert</u>.-Bu

As already stated, electron release facilitates S_N1 substitutions, and this series must therefore have an increasing tendency to react by mechanism S_N1 on going from left to right. This may be demonstrated by examining the alkaline hydrolysis of methyl, ethyl, <u>iso</u>-propyl and <u>tert</u>.-butyl bromides[13,3,6]. For this series it is possible to determine the molecularity of the reaction from the kinetic order. For methyl, ethyl and *iso*-propyl bromides second order kinetics were found showing that the reaction was bimolecular. *tert*.-Butyl bromide exhibited first order kinetics and was therefore unimolecular. For the solvolysis of these bromides the kinetic criterion of molecularity no longer holds (see p. 5). Although the methyl and ethyl compounds still react by mechanism S_N2 and the *tert*.-butyl compound by mechanism S_N1 the position regarding *iso*-propyl bromide is not so certain. While the reaction with hydroxide ion may be S_N2, this does not necessarily hold for the reaction with water since an hydroxide ion is a better nucleophile than water, a factor which increases the tendency to react by mechanism S_N2. The mechanism for the solvolysis of *iso*-propyl bromide is however probably S_N2 rather than S_N1. This type of effect has already been demonstrated on a previous occasion. Ballinger, de la Mare, Kohnstam and Prestt[14] examined the reaction of chlorodimethyl ether in ethanol and in mixtures of ethanol and diethyl ether in both the presence and absence of ethoxide ions. Whilst the solvolysis was shown to be unimolecular, reactions in the presence of ethoxide ion, a better nucleophile than ethanol, were found to be substantially bimolecular.

In aralphyl compounds containing *α*-phenyl substituents, the more powerful mechanism of conjugative electron displacements is available to assist the separation of the displaced group and a formed carbonium ion is stabilised by conjugative mesomerism. It is found, in accordance with prediction, that $\underline{\alpha}$-phenyl substituents in aralphyl groups exert a strong facilitating polar effect on mechanism S_N1 and a weaker one on mechanism S_N2. One $\underline{\alpha}$-phenyl group is roughly about as effective as two $\underline{\alpha}$-methyl substituents for the purpose of determining the relative importance of the two mechanisms.

In the solvolysis of the following series of chlorides in aqueous solvents,

CH_3Cl $PhCH_2Cl$ Ph_2CHCl Ph_3CCl

methyl chloride is S_N2, whilst benzhydryl chloride and triphenylmethyl chloride are S_N1. There has been much controversy concerning the mechanism by which benzyl chloride reacts. An examination of the available evidence led Bensley and Kohnstam[15] to conclude that the mechanism was mainly, if not entirely, S_N2 in 50% aqueous acetone.

A detailed picture of the manner in which a change from mechanism S_N1 to mechbanism S_N2 occurs is of interest.

Mechanism in the "border-line" region.

Several views have been put forward about the mechanistic "border-line" region, which marks the transition from one mechanism to the other. It is convenient to regard the transition state of nucleophilic substitution reactions as the resonance hybrid of the following three canonical structures[11]

$$\begin{array}{ccc} Y \quad R - Cl & \overset{+}{Y} - R \quad \overset{-}{Cl} & Y \quad \overset{+}{R} \quad \overset{-}{Cl} \\ \mathrm{I} & \mathrm{II} & \mathrm{III} \end{array}$$

If the reaction is extreme S_N2 there is no contribution from structure III whereas if the reaction goes entirely by mechanism S_N1, structure II does not contribute to the transition state structure. If structures I, II and III all contribute to the structure of the transition state, the reaction must be regarded as bimolocular since covalent participation by the reagent Y is still an essential feature of the activation process[16].

There are two possibilities for a reaction occurring by the "border-line" mechanism.

(i) The reaction proceeds via a single intermediate transition state with contributions from I, II and III and which is therefore bimolecular. The more the reaction conditions favour mechanism S_N1, the greater is the contribution from III relative to II.

(ii) The individual molecular acts occur via any one of a continuous spectrum of transition states each with varying contributions from II and III and some having no contributions from II i.e. concurrent S_N1 and S_N2. A variant on this view is that the reaction occurs via one S_N1 and one S_N2 process.

In order to obtain further information concerning the "borderline" mechanism, Winstein, Grunwald and Jones[11] studied the dependence of solvolysis rate on solvent on the basis that the relevant solvent properties which affect the rate, nucleophilic character and ionising power, vary independently. Nucleophilic solvolyses were divided into two categories - the limiting class, (Lim), rate constant k_1, whose rates depend on the ionising power of the solvent, and the nucleophilic class (N), rate constant k_v, whose rates depend on both the ionising power and the nucleophilic character. These classes correspond roughly to S_N1 and S_N2 respectively. The variation of solvolysis rate with solvent was represented by the following linear free energy relationship which applies to both Lim and N classes

$$\log k = \log k^o + mY \qquad \text{..........I-1}$$

where k and k^o are the rate constants in a solvent and in the standard solvent respectively, Y a measure of the solvent ionising power, and m is a constant independent of the substrate with one value for Lim reactions and another for N reactions.

The solvolysis of iso-propyl bromide, a reaction expected to be border-line, was studied for the entire solvent range from ethanol to pure water. Assuming two simultaneous processes for the solvolysis

$$k = k_1 + k_x \qquad \text{..........I-2}$$

Applying equation I-1 for each process

$$\log k_1 = m_1Y + \log k_1^o \qquad \text{..........I-3}$$

$$\text{and} \quad \log k_x = m_xY + \log k_x^o \qquad \text{..........I-4}$$

Substituting for k_1 and k_x in equation I-2 gives

$$(10^{-m_xY})\,k = (10^{m_1Y - m_xY})\,k_1^o + k_x^o \qquad \text{....I-5}$$

m_1 was assumed to be the same as for tert.-butyl bromide (which reacts by the limiting mechanism) and m_x, for ethyl bromide (which reacts by the nucleophilic mechanism). Substituting for m in equation I-5 gave values of k_1^o and k_x^o which were then used to calculate k_1, k_x and thus k. The agreement with the observed values of k was poor, a single m value between m_1 and m_x giving a better fit to the experimental data.

The authors therefore hold the view that solvolysis in the border-line region should be regarded as a single process and not as two simultaneously occurring processes.

Bird, Hughes and Ingold[17], while agreeing with the above conclusion, have pointed out that it was ensured by the procedure used. In addition they emphasised that the free energy relation used is non-linear for methyl and ethyl bromides (compounds solvolysing by the N mechanism). In a later paper Winstein, Fainberg and Grunwald[18] showed that there are definite structural limitations to the use of the free energy relationship for the quantitative interpretation of solvolysis rates. In conclusion it should be noted that even if this relationship is valid it only shows the general trend in the mechanistic change between S_N1 and S_N2 and not the point of mechanistic change.

Bird, Hughes and Ingold[17] have studied substitution in m-chlorobenzhydryl chloride by fluoride ion, pyridine and triethylamine using sulphur dioxide as solvent. If the substitutions are unimolecular the initial rates of the different reactions should be equal to one another and independent of reagent concentrations. If however some of the substitutions are bimolecular, then the initial rates, although varying for the different substitutions following this mechanism, should each converge on zero as the reagent concentration is diminished. If unimolecular and bimolecular reactions run concurrently, then the rates should converge on a finite value as the initial concentration of the reagent is diminished.

The authors found that substitution by the amines showed common-ion retardations, the most diagnostic kinetic feature of mechanism S_N1, but deviated from the requirements of that mechanism in at least two important respects. The rates were sensitive firstly to the nature of the substituting agent, and secondly to the concentrations of the reagents although in each respect not nearly to the extent appropriate to bimolecular reactions. In addition it was found for the reactions of pyridine and triethylamine that an equation derived assuming the operation of mechanism S_N1 reproduced the observed course of the reaction more accurately than one obtained by assuming a bimolecular process, though not as perfectly as for the fluoride ion reaction. A suggested explanation was that the mechanism has some degree of bimolecular character. Concurrent S_N1 and S_N2 processes were not envisaged since the rates did not converge when the concentration of the reagent was low. The results obtained thus favoured the view that reaction occurs via transition states intermediate between the two mechanistic extremes.

It has often been assumed that the solvolysis of benzoyl chloride occurs by a border-line mechanism. This reaction has been studied by several sets of workers and their conclusions will now be discussed.

Gold, Hilton and Jefferson[19] examined the hydrolysis of benzoyl chloride and acetic anhydride in aqueous acetone in the presence of different amounts of an aromatic amine, which can compete with the solvent for the acylating agent. The relative contributions of unimolecular and bimolecular mechanisms to the acylation of the amine and to the acylation of water were determined by examining the influence of the amine on the rate and final product composition. The authors concluded from their results that acetic anhydride in 50% acetone and benzoyl chloride in 80% acetone react by the bimolecular mechanism, but only half of the total reaction of benzoyl chloride with 50% acetone proceeds by this mechanism. The border-line mechanism was regarded as the concurrence of an S_N1 and an S_N2 process.

Crunden and Hudson[20] studied the effect of added formate ions and solvent variation on the rate of solvolysis of p-methyl-, p-bromo- and p-nitrobenzoyl chloride and the parent compound in aqueous formic acid. The authors concluded from their results that the p-nitro compound reacts by mechanism S_N2 and the p-methyl and parent compounds react by mechanism S_N1. The reaction rates were found to be less in formic acid than in 65% aqueous acetone, a solvent with the same solvating power (denoted by Y by Grunwald and Winstein[21]); the greater the ease of electron release to the reaction centre, the closer were the two corresponding rate constants.

The authors assumed that concurrent unimolecular and bimolecular mechanisms operate and that the rate of the S_N1 process is equal in the two solvents, the excess rate in the aqueous acetone being due to reaction by mechanism S_N2. Values for the percentage of S_N1 reaction in the aqueous acetone were obtained.

Kelly and Watson[22] have studied the effect of solvent composition on the solvolysis rate of benzoyl chloride in aqueous acetone. They proposed that when hydrolysis occurs by the unimolecular mechanism the observed rate constant can be represented by

$$k'_{obs.} = k_1 \left[H_2O\right]^q \qquad \text{..........I-6}$$

where k_1 and q are constants, independent of solvent composition, and that when the bimolecular mechanism operates, the observed rate constant k''_{obs} is given by

$$k''_{obs.} = k_2 \left[H_2O\right]^n\left[H_2O\right] \qquad \text{.........I-7}$$

where k_2 and n are constants, independent of solvent composition.

Assuming concurrent unimolecular and bimolecular processes, the observed rate constant is then given by the expression

$$k_{obs} = k_2 \left[H_2O\right]^n\left[H_2O\right] + k_1\left[H_2O\right]^q$$

and therefore

$$\frac{k_{obs}}{[H_2O]} = k_2 [H_2O]^n + k_1 [H_2O]^{q-1}$$

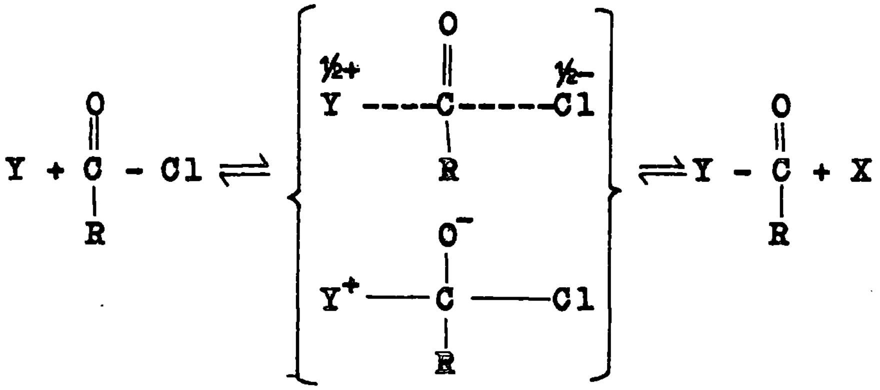
At low water concentration $k_1 [H_2O]^{q-1}$ was assumed to be negligible, i.e. no unimolecular contribution, and a linear relationship between $\log(k_{obs}/[H_2O])$ and $\log [H_2O]$ was therefore expected in this region. The experimental results verified this prediction. At higher water concentrations however this curve showed departures from linearity, thereby indicating a mechanistic change. Analysis of this curve gave values for the relative contributions from the unimolecular and bimolecular mechanisms to the total reaction.

An equation of the type

$$k_{obs} = k [H_2O]^m$$

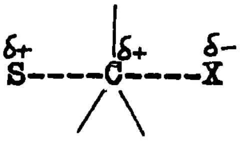
where k and m are constants, independent of solvent composition, is however unlikely to hold over the whole solvent composition range for mechanism S_N1 or mechanism S_N2.

Bunton, Lewis and Llewellyn[23], by studying O^{18} exchange between some benzoyl chlorides and water during hydrolysis, showed that intermediates are formed, of finite life, which contain a water molecule. Further work[24] led them to conclude that these reactions should be regarded not in terms of the S_N mechanisms but as two stage processes in which the reagent adds to the carbonyl carbon atom to give an intermediate, which breaks down with loss of halide ion, or reagent. This mechanism, analogous to acyl-oxygen fission for carboxyl ester hydrolysis can be represented by two limiting representations of the reaction path[25],

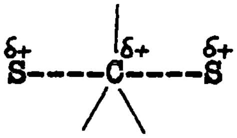


Since at least part of the solvolysis of benzoyl chlorides goes by this mechanism, conclusions reached concerning the border-line mechanism in nucleophilic substitution using this reaction are therefore rendered doubtful.

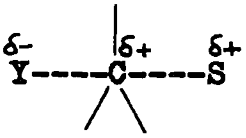
Nair[26] has studied the reaction between 0.04M benzyl chloride and potassium cyanide in 80% ethanol kinetically and using isotopes. The rate of formation of chloride ions produced from the reaction with potassium cyanide and the concurrent solvolysis of benzyl chloride for a cyanide concentration of 0.05M showed good first order kinetics, thus excluding the possibility of a straight bimolecular displacement of halogen by cyanide ion. For smaller concentrations of potassium cyanide however the first order rate constants decreased with time. The initial first order rates showed a dependence on the concentration of cyanide ions which could not be attributed to a salt effect, showing that at least part of the reaction which produces the nitrile does not take place by mechanism S_N1. The author postulates the existence of intermediates with "pentacovalent carbon atoms" having structures like IV, V and VI, a postulate made by Doering and co-workers to account for stereochemical results[27].



IV



V



VI

Attack by a solvent molecule S results in the partially ionised intermediate IV, from which a lateral displacement of solvent could femove X, the displaced halogen, to give V, described as a covalently solvated carbonium ion. X can also be displaced by Y^-, the negatively charged cyamdde ion to give VI, which is also formed by the attack of Y^- on V. If the degradation of intermediate V is the rate-determining step for solvolysis and if the formation of VI from IV is the rate-determining step for nitrile formation the expression obtained for the formation of chloride ions explains the data. The intermediate character of the mechanism is also reflected in the isotope effects obtained. The Cl^{35}- Cl^{37} isotope effect showed the reaction to be nearly half way between the two mechanistic types while a significant amount of bond formation before bond rupture is complete was indicated by the C^{12}- C^{14} isotope effect for the benzyl carbon atom. An approximate value obtained for the C^{12}- C^{14} effect at the cyanide carbon atom was consistent with the other isotope effects.

A similar view on bonding has been proposed by Gillespie[28] who suggests that carbon can utilise one or more of its 3d orbitals for bond formation. For example, the transition state of a bimolecular substitution reaction is described as an unstable compound of quinquevalent carbon, where the carbon atom is using five orbitals for bond formation, one 2S, three 2p and one 3d.

It has however been shown by Dewar[29] that any contributions from 3d orbitals to the valency states of carbon leaves the general configuration of the valency electrons unchanged, a demonstration which is inconsistent with the mechanistic picture proposed by Nair.

Le Roux and Swart[30] have interpreted kinetic data which they obtained for the isotope-exchange reaction between radioactive bromine and <u>tert</u>.-butyl bromide in anhydrous acetone in terms of concurrent unimolecular and bimolecular processes. Their experimental evidence was not however confirmed by later work[31].

Hyne and Robertson[32] have interpreted activation energies for the solvolyses of benzenesulphonic esters on the basis of a continuous spectrum of mechanisms intermediate between S_N1 and extreme S_N2 and have presented a semi-empirical equation relating the activation energies to physical properties of the solvolysing medium. This correlation is not thought to be particularly relevant to the border-line question[33].

Bensley and Kohnstam[15] using an approach similar to that which will be used for the solvolysis of p-methylbenzyl chloride in the present investigation (see Chapter IV), examined the solvolysis of benzyl chloride in 50% aqueous acetone and showed that both general mechanistic alternatives were consistent with the data obtained. The concurrence of mechanism S_N1 with extreme S_N2 is however not supported by the evidence.

Kohnstam, Queen and Shillaker[34] have shown that S_N1 and S_N2 processes operate simultaneously in the attack of azide ions on p-methoxybenzyl chloride. The reaction was carried out in 70% aqueous acetone where hydrolysis occurs exclusively by mechanism S_N1 (see p. 61).

For the investigation of mechanism in the border-line region the criteria of mechanism already outlined (p. 5) are insufficient. A reaction in the border-line region may have a transition state with a large contribution from structure III but also some contribution from II. The stability of the transition state will thus be largely controlled by factors affecting III. An S_N2 reaction could thus behave more like S_N1 than S_N2 with both solvent variation and changes in substituents and mechanistic tests based on the sensitivity to solvent changes and the effect of substituent groups would therefore not give an unambiguous indication of mechanism.

Stereochemical evidence is equally unsatisfactory since S_N1 reactions show inversion of configuration when the carbonium ion is unstable (i.e. has a very short lifetime) as there is then considerable shielding by the leaving group[35].

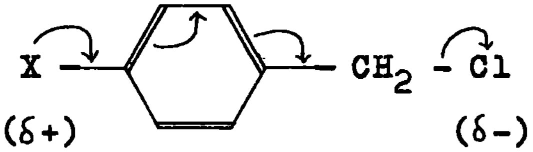
The mass-law effect (discussed in detail in Part II) does not always show up in S_N1 reactions where there is an unstable carbonium ion, since the solvation shell collapses with the formation of the alcohol before the carbonium ion has completely freed itself from the bound anion. Since the carbonium ion would be destroyed too rapidly to participate in the equilibrium between any added common-ions, the effect of these ions would not be observed. Thus, although the observation of mass-law retardation is diagnostic of mechanism S_N1, the absence of this effect could mean that the mechanism is either S_N2 or S_N1 with a highly unstable carbonium ion.

A further test of mechanism has recently been proposed by Bensley and Kohnstam[15]. For S_N1 solvolysis it has been found that the activation energy decreases with increasing temperature, an observation which will be discussed in Chapter II. Eyring's absolute rate equation shows that this decrease in activation energy, related to a decrease in enthalpy, is due to a negative heat capacity of activation. It is an essential feature of an S_N1 solvolysis that the activation energy is reduced to accessible values by the solvation of the transition state, involving a definite orientation of solvent molecules around the ions. These molecules are less free to move than those in the bulk of the solvent and are therefore expected to have a lower heat capacity. This solvation of the transition state relative to the initial state is also the most important factor controlling the magnitude of the entropy of activation. It is therefore reasonable to expect that the ratio $\Delta C^*/\Delta S^*$, where ΔC^* and ΔS^* are the heat capacity and entropy of activation respectively, for the S_N1 solvolysis of organic chlorides depends only on the solvent and the temperature. ΔS^* would be expected to be more negative for S_N2 solvolyses since the transition state of the rate-determining step involves some covalent attachment of a solvent molecule, requiring a less random arrangement of this solvent molecule than when it solvates. When the change in heat capacity for an S_N2 process is considered, the considerations used to determine the effect on ΔS^* are no longer applicable. In fact, the loss in heat capacity on solvation by a water molecule is equivalent to the loss involved in forming a partial covalent bond. The ratio $\triangle C^{*}/\triangle S^{*}$ for an S_N2 reaction should therefore have a lower value than for an S_N1 reaction under the same conditions.

The ratio $\triangle C^{*}/\triangle S^{*}$ appeared to have a constant value for S_N1 reactions investigated prior to the commencement of the present work. These predictions however still required confirmation and it was therefore necessary to investigate further the value of this ratio. Once the predictions had been confirmed, it was intended to use this mechanistic test for a detailed investigation of the border-line region.

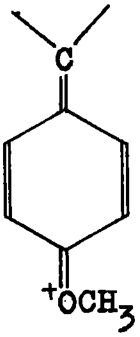
The compounds chosen for this study were a series of <u>para</u>-substituted benzyl chlorides and by a suitable choice of substituents the electron supply to the reaction centre can be varied and a finely graded sequence of reaction mechanism obtained. Moreover, any change in mechanism along this series is due to polar effects and not to steric effects. The following substituents were used:- nitro, methyl and methoxy. The kinetics of the unsubstituted compound had already been studied in sufficient detail[15].

When an electropositive group is attached to an unsaturated residue e.g. benzyl, the conjugative mechanism of electron displacement always operates in such a way as to decrease the electron content at X, and increase that of the unsaturated residue. The halide atom thus becomes more negative in the substituted benzyl chloride



In the transition state of S_N1 substitution reactions the stretching of the C-Cl bond requires an increased amount of electrons which is met by the increased supply available by the electromeric release of X. It is possible by successively making the group X more electropositive to cause a reaction which proceeds by mechanism S_N2 to have an increased S_N1 character. If the electron releasing ability is large enough the reaction will be entirely S_N1.

Electron releasing groups, such as p-methyl and p-methoxy, show a marked increase in solvolysis rate[36], the effect of the p-methoxy group being particularly large. This is due to the oxygen atom being able to accept a considerable fraction of the positive charge via resonance structures such as



Olivier[37] and Bennett and Jones[38] had previously studied the solvolysis of several p-substituted benzyl chlorides in 50% aqueous acetone and Fierens and co-workers[39] had studied the solvolysis of p-methoxy- and p-methylbenzyl chlorides in 50% and 80% aqueous dioxan. Unfortunately these investigations fail to provide sufficient data for the determination of $\Delta C^{*}/\Delta S^{*}$ ratios since Olivier and Bennett measured rates for each compound at only two temperatures, whilst although Fierens measured the rates at several temperatures, the data obtained were too inaccurate (see Chapter III). From the variation of rate with solvent however, Fierens concluded that the solvolyses of p-methyl- and p-methoxybenzyl chlorides were, if not S_N1, not far from this limit.

CHAPTER II

TEMPERATURE DEPENDENCE OF THE ARRHENIUS PARAMETERS

The Arrhenius equation, which describes the variation of the rate of a reaction with temperature[40], defines the activation energy E in terms of the differential equation

$$E = RT^2 \frac{d \ln k}{dT} \qquad \ldots\ldots\ldots\ldots\ldots\ldots \text{II-1}$$

The activation energy has usually been assumed to be constant and Eqn.II-1 may therefore be integrated to give

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

The non-exponential term B can be identified with the frequency factor ln(PZ) of the collision theory, which predicts $k = PZ^{-E/RT}$, where Z is the collision number and P the steric factor. B thus represents the probability of attaining the transition state.

As the Arrhenius equation is empirical, a theoretical rate equation is accepted in order to interpret the significance of the Arrhenius parameters. The most satisfactory equation of this type is due to Eyring[41],

$$\ln k = \ln\left(\frac{k\,T}{h}\right) + \frac{\Delta S^*}{R} - \frac{\Delta U^*}{RT} \qquad \ldots\ldots\ldots\ldots \text{II-3}$$

where k is in concentration units.

ΔS^* and ΔU^* refer to the standard changes of S, the entropy and U, the internal energy, on going from the initial reactants to the transition state

$\bar{k}$ is the Boltzmann constant

R is the gas constant

h is the Planck constant

T is the absolute temperature.

Differentiation of Eqn.II-3 with respect to T leads to

$$\frac{d \ln k}{d T} = \frac{1}{T} + \frac{\Delta U^*}{R T^2}$$

which on comparison with Eqn.II-1 gives Eqn.II-4

$$E = RT + \Delta U^* \qquad \ldots\ldots\ldots\ldots \text{II-4}$$

Since for reactions in solution, $\Delta U^* = \Delta H^*$, where ΔH^* is the enthalpy or heat of activation, then

$$E = RT + \Delta H^* \qquad \ldots\ldots\ldots\ldots \text{II-5}$$

Differentiation of Eqn.II-5 and application of Kirchoff's law gives

$$\frac{dE}{dT} = R + \Delta C^* \qquad \ldots\ldots\ldots\ldots \text{II-6}$$

where ΔC^* is the heat capacity of activation and represents the difference in heat capacity between the initial and transition states. Thus, the temperature dependence of E arises from a difference in heat capacity.

Several workers[42,43,44] have previously pointed out on theoretical grounds that if the heat capacity of the activated complex differs appreciably from that of the initial state, the activation energy is expected to vary with temperature.

Observed Variation of Activation Energy.

The temperature dependence of activation energy for reactions in solution has been reported on several occasions[45, 46,47,48,49] and these observations have been reviewed in detail[50,51,52]. Many early observations of reaction rates at several different temperatures are not sufficiently accurate to establish whether the activation energy varies with temperature, and this also applies to a few of the reactions for which such a variation has been claimed[53,44]. Recently, however, accurate data have been reported for solvolytic reactions, where the transition state is more polar than the initial state, which show that the activation energy decreases with increasing temperature. These data are summarised in Table II-1.

Causes for Changes in Heat Capacity.

Solvation of the Transition State[58]

Differences in the heat capacities of the initial and

TABLE II-1

OBSERVED VARIATION OF ACTIVATION ENERGY WITH TEMPERATURE

(dE/dT in cal.deg.$^{-1}$)

Reaction	$-dE/dT$	Reference
Methyl benzenesulphonate in water	31	54
Ethyl benzenesulphonate in water	32	54
iso-Propyl benzenesulphonate in water	39	54
n-Propyl benzenesulphonate in water	29	54
Methyl *p*-methylbenzenesulphonate in water	31	55
Methyl *p*-nitrobenzenesulphonate in ethanol	19	56
tert.-Butyl chloride in 50% acetone	25	57
Benzyl chloride in 50% acetone	19	15
Benzylidene chloride in 50% acetone	27	15
Benzotrichloride in 50% acetone	44	15
Benzyl chloride in 50% ethanol	29	15
Benzylidene chloride in 50% ethanol	57	15
Benzotrichloride in 50% ethanol	71	15
Ethyl bromide in 50% acetone	33	52
n-Propyl bromide in 50% acetone	21	52
n-Butyl bromide in 50% acetone	31	52
p-Methylbenzyl chloride in aqueous acetone	53*	59
p-Nitrobenzyl chloride in aqueous acetone	24*	59

* These values are probably subject to considerable errors (see page 57).

transition states in the S_N solvolyses of organic halides are usually considered as being due to an increase in solvation as the reactants pass into the more polar transition state (see Chapter I). This "freezing out" of solvent molecules in the immediate neighbourhood of charged particles has been stated to account for the negative partial molar heat capacities of electrolytes[60] and the negative values obtained for the change in heat capacity in the ionisation of weak acids[61].

As well as applying to fully developed ions in solution, these considerations should also apply to reactions involving an increase of electric charge in solution and these should therefore show negative ΔC^* values. Negative ΔC^* values have in fact been observed for several reactions, where the transition state is more polar than the initial reactants (see p. 29). These have been summarised by Bensley and Kohnstam[58].

Dielectric Constant Theory

The prediction that an increase of electric charge on passing over into the transition state reduces the heat capacity, also arises out of the electrostatic approach which does not take solvation into account and regards the mixed solvent as a continuous dielectric.

Kirkwood's equation[62] gives the change in free energy for the transfer of a dipole from a continuous medium of dielectric constant unity to a similar medium of dielectric constant D,

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

where μ is the dipole moment and r is the radius of the molecule containing the dipole.

For a unimolecular reaction*, one then obtains[63] (from the transition state theory)

$$\ln k = \ln k_o - \frac{1}{\bar{k}\, T} \cdot \frac{D - 1}{2D + 1} \left[\frac{\mu_i^2}{r_i^3} - \frac{\mu_t^2}{r_t^3} \right] \qquad \text{...II-8}$$

where k is the rate constant in a medium of dielectric constant D

k_o is the rate constant in a medium of dielectric constant unity

$\bar{k}$ is the Boltzmann constant

T is the absolute temperature

μ and r are the dipole moment and molecular radius respectively and the subscripts i and t refer to the initial state and transition state respectively.

---

* For a bimolecular reaction

$$\ln k = \ln k_o - \frac{1}{\bar{k}\, T} \cdot \frac{D - 1}{2D + 1} \left[\frac{\mu_A^2}{r_A^3} + \frac{\mu_B^2}{\mu_B^3} - \frac{\mu_t^2}{r_t^3} \right]$$

where the subscripts A and B refer to the initial state.

The dipole moment of the transition state is much greater than the dipole moment of the initial state in an ionisation reaction and therefore k exceeds k_o.

It is apparent that if this approach is valid a linear relation between log k and (D - 1)/(2D + 1) is expected. Plots of log k against (D - 1)/(2D + 1) have been made for the solvolyses of acetic anhydride[64,19], benzoyl chloride[19,65] and benzyl[66] and substituted benzyl[67] *p*-toluenesulphonates in aqueous acetone; for *tert*.-butyl chloride[63] and ethylene bromo- and iodohydrins[68] in aqueous ethanol; for *p*-nitrobenzyl bromide[69] in aqueous dioxan; and for methyl chloromethyl ether[70] in mixtures of ethanol with dioxan, benzene and carbon tetrachloride, and of *n*-butanol with benzene. In most cases the solvent range in which the dielectric constant was investigated was not large, so that linearity of the plot was tested over only limited portions of the possible ranges. Even so, definite departures from linearity are observable in a number of the plots, and in some, the curvature is considerable. Fainberg and Winstein[71] plotted log k *vs*.(D-1)/(2D+1) for *tert*.-butyl chloride for all the data in the solvent mixtures for which dielectric constants are available. These solvent pairs included 0-90% aqueous dioxan (D=78-6)[72], 0-95% aqueous acetone (D=78-22)[73], 0-100% aqueous ethanol (D=78-24)[74] and 0-100% aqueous methanol (D=78-33)[75]. The resulting graph showed a large dispersion of the plot into separate lines for each solvent pair and a pronounced curvature of the separate lines. The linear portions of the plots extended only over the ranges of solvent composition of dielectric constant greater than about 53. These regions included 0-30% aqueous dioxan and 0-50% aqueous acetone, ethanol and methanol.

Laidler and Landskroener[76] in a recent paper concluded that log k should vary linearly with (1-D)/(1+D) or approximately so with 1/D. It is however impossible to decide between the functions 1/D and (D-1)/(2D+1) on the basis of linearity of log k plots for dielectric constants greater than about 8[71]. This is readily seen by dividing (D-1) by (2D+1).

$$\frac{D-1}{2D+1} = \frac{1}{2} + \frac{3}{4D} + \frac{3}{8D^2} - \frac{3}{16D^3} + ----$$

For D=8, the error involved in neglecting terms in D^2 and higher powers is less than one per cent. Therefore, (D-1)/(2D+1) is linear in 1/D to an excellent approximation. This is true in all solvent mixtures of water with acetone, ethanol and methanol. This approximation would become inexact only for such solvent mixtures as aqueous dioxan containing less than 10% water. Plots of log k vs. 1/D must therefore show a similar curvature to the plots of log k vs. (D-1)/(2D+1).

The evidence discussed above shows that there are serious discrepancies between the predictions of the electrostatic theory and experimental observations.

The electrostatic contribution to the entropy and heat capacity of activation will now be examined.

The electrostatic contribution to ΔS^* is obtained from Kirkwood's equation[77] using the relationship

$d(\Delta G)/dT = -\Delta S,$

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

Using $\Delta H = \Delta G + T\Delta S$ the electrostatic contribution to ΔH^*, the enthalpy of activation and thus to E, the activation energy is readily obtained

$$\Delta H_D = E_D = -\left[\frac{\mu_i^2}{r_i^3} - \frac{\mu_t^2}{r_t^3}\right]\left[\frac{D-1}{2D+1} - \frac{3DT}{(2D+1)^2} \cdot \frac{d \ln D}{dT}\right] \qquad \text{..II-10}$$

For all known solvents D decreases with increasing temperature, so that E_D and hence E can be expected to be temperature dependent.

If (d ln D / dT) is independent of temperature, the electrostatic contribution to ΔC^* is obtained using

$d(\Delta S^*)/dT = \Delta C^*/T$ [58]

$$\Delta C_D = -\left[\frac{\mu_i^2}{r_i^3} - \frac{\mu_t^2}{r_t^3}\right]\frac{3DT(2D-1)}{(2D+1)^3}\left[\frac{d \ln D}{dT}\right]^2 \qquad \text{.....II-11}$$

Bensley and Kohnstam[58] compared the experimental values for $\triangle S^*$ and $\triangle C^*$ with those calculated for $\triangle S_D$ and $\triangle C_D$ for the ionisation of the C-Cl linkage in aqueous acetone and aqueous ethanol, solvents for which $d \ln D / dT$ is independent of T[78], and found serious discrepancies. A change of solvent should affect $\triangle S^*$ and $\triangle C^*$ in the same manner. It was found however that the two compounds studied, benzylidene chloride and benzotrichloride, both showed an increase in $\triangle S^*$ and an appreciable decrease in $\triangle C^*$ on going from 50% acetone to 50% ethanol. Gold[64] and Amis[79,80] have found that temperature-dependent E values are not in accordance with constant isodielectric activation energies[≠] as required by the theory. In addition Caldin and Peacock[81] have compared enthalpies and entropies of activation derived from Kirkwood's equation with the experimental values for a number of bimolecular reactions which involve an increase in polarity on passage into the transition state and found that the simple electrostatic theory is inadequate when the range of solvents is considerable.

In view of the above exceptions, the dielectric constant effect cannot be regarded as a satisfactory explanation for the variation of activation energy with temperature.

[≠] Isodielectric activation energies are determined by varying the solvent composition in such a way that D is independent of the temperature.

Extension of the Collision Theory.

Moelwyn-Hughes[48] accounts for the negative value of ΔC^* by assuming that H^*, the partial molar enthalpy of the activated complex, is constant with temperature and has the maximum value which the molecules can possess in solution. The transition state is thus regarded as having zero heat capacity, ΔC^* being equal to $-C^o$ of the initial state. If H is the partial molar heat content of the initial state, then $E = H^* - H$ and therefore $dE/dT = -dH/dT$. The variation of E with T is explained as being due to the variation of H with T.

Serious objections to this explanation have however been raised[52]. It is difficult to justify the assumption that H^* is constant. It would be reasonable to assume that the energy contained in the breaking bond is at its limiting value, but as the temperature rises, the energy distributed amongst the various degrees of freedom in the rest of the molecule must increase. Another objection to this approach is that it contradicts the assumptions of the transition state theory which treats the activated complex as a normal molecule with one degree of vibrational freedom missing. In addition, it is very difficult to visualise why the heat capacity of such a molecule should differ greatly from a molecule in the initial state as this approach does not take into account solvation, an essential feature of the activation process. Furthermore it is difficult to understand why the heat capacity of activation should rise, maximise and then fall as is observed, since there is little reason to expect such behaviour for the partial molar heat capacity of the initial state.

It may be concluded therefore that the heat capacity of activation can best be explained as due to changes in the degree of solvation on passage into the transition state. This explanation only applies if the transition state structure is independent of temperature, a point which will be considered further when the solvolysis of p-methylbenzyl chloride in 50% aqueous acetone is discussed.

CHAPTER II. APPENDIX

Experimental Determination of the Arrhenius Parameters.[51,52]

(i) Activation Energy

The experimental activation energy, E_{obs}, for the temperature range T_1 - T_2 was calculated from Eqn.II-12

$$E_{obs} = \frac{R\,T_1\,T_2}{T_1 - T_2} \cdot \ln\left(\frac{k_1}{k_2}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{II-12}$$

where k_1 and k_2 are the rate constants at the absolute temperatures T_1 and T_2 respectively.

The true Arrhenius activation energy, E_A, at the Temperature T is given by Eqn. II-13

$$\frac{d(\ln k)}{dT} = \frac{E_{A(T)}}{RT^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{II-13}$$

Assuming E_A varies linearly with temperature over the range T_1 - T_2, then

$$E_{A(T)} = E_{A(T_1)} + c(T - T_1) \quad \ldots\ldots\ldots\ldots \text{II-14}$$

where c is a constant and T lies between T_1 and T_2.

Therefore

$$\frac{E_{A(T)}}{RT^2} = \frac{E_{A(T_1)}}{RT^2} + \frac{c}{RT} - \frac{cT_1}{RT^2} = \frac{d(\ln k)}{dT}$$

Integration between the limits T_1, k_1, and T_2, k_2 gives

$$\ln\frac{k_2}{k_1} = E_{A(T_1)}\frac{\Delta T}{RT_1T_2} + \frac{c}{R}\ln\frac{T_2}{T_1} - \frac{cT_1\Delta T}{RT_1T_2} = E_{obs}\frac{\Delta T}{RT_1T_2}$$

where $\Delta T = T_2 - T_1$

$$\therefore E_{obs} = E_{A(T_1)} - cT_1 + c.\ln(T_2/T_1).\frac{T_1T_2}{\Delta T}$$

From Eqn. II-14

$$E_{A(\frac{T_1+T_2}{2})} = E_{A(T_1)} + c(\frac{T_2-T_1}{2})$$

$$\therefore E_{obs} = E_{A(\frac{T_1+T_2}{2})} + c\ln(T_2/T_1)\frac{T_1T_2}{\Delta T} - c(\frac{T_1+T_2}{2})$$

Writing $\ln(T_2/T_1)$ in the form $\ln(1 + \frac{\Delta T}{T_1})$ it can be expanded as a power series,

$$\ln(1 + \frac{\Delta T}{T_1}) = \frac{\Delta T}{T_1} - \frac{(\Delta T)^2}{2T_1^2} + \frac{(\Delta T)^3}{3T_1^3} ---- \text{ if } -1 < \frac{\Delta T}{T_1} < 1$$

Typical values of ΔT and T are 10 and 300 respectively. These give the first three terms of the series the values, 0.0333, -0.00056, and +0.00001; only the first two terms need therefore be considered

$$\therefore E_{obs} = E_{A(\frac{T_1+T_2}{2})} - \frac{c(\Delta T)^2}{2T_1}$$

A typical value of c is 50 cals/mole.deg.; $c.\frac{(\Delta T)^2}{2T_1}$ is thus of the order of 10 cals. and, therefore, is negligible with respect to activation energies of the order of 20,000 cals.

$$\therefore E_{obs} = E_{A(\frac{T_1 + T_2}{2})}$$

If E determined in this way varies linearly with temperature over the experimental range then the initial assumption that

E varies linearly with temperature between T_1 and T_2 is justified. Within the limits of experimental error, this is always found to be the case in the present work and E_{obs} is thus identified with the true Arrhenius activation energy at the mean temperature of the interval for which it was calculated.

(ii) B Factor

The true Arrhenius B factor at temperature T is defined by the equation

$$\ln k_{(T)} = B - \frac{E_{A(T)}}{RT} \qquad \ldots\ldots\ldots\ldots \text{II-15}$$

Differentiation with respect to T gives

$$\frac{dB}{dT} = \frac{dE_A}{dT} (RT)^{-1} \qquad \ldots\ldots\ldots\ldots \text{II-16}$$

Since E_A is not constant. This means that B is also temperature dependent.

The experimental B factor in the temperature range $T_1 - T_2$ is given by

$$B_{obs} = \ln k_{(T_1)} + \frac{E_{obs}}{RT_1} \qquad \ldots\ldots\ldots \text{II-17}$$

and the temperature coefficient of B when E varies linearly with temperature is c/RT (from Eqn. II-16).

It follows that

$$B_{\frac{T_1+T_2}{2}} - B_{(T_1)} = \frac{c}{R} \cdot \ln\left[\frac{T_1 + T_2}{2T_1}\right] \quad \text{.......II-18}$$

Since it has been shown that $E_{obs} = E_{A(\frac{T_1+T_2}{2})}$ it follows that

$$B_{obs} = \ln k_{(T_1)} + E_{A(\frac{T_1+T_2}{2})} \cdot \frac{1}{RT_1}$$

$$= \ln k_{(T_1)} + \frac{E_{A(T_1)}}{RT_1} + \frac{c}{RT_1} \cdot \left[\frac{T_2 - T_1}{2}\right]$$

$$= B(T_1) + \frac{c}{RT_1} \cdot \left[\frac{T_2 - T_1}{2}\right]$$

From Eqn.II-18

$$B_{obs} = B_{\frac{T_1+T_2}{2}} + \frac{c}{RT_1}\left[\frac{T_2-T_1}{2}\right] - \frac{c}{R} \cdot \ln\left[\frac{T_1+T_2}{2T_1}\right]$$

$$= B_{\frac{T_1+T_2}{2}} + \frac{c}{R}\left\{\left[\frac{T_2-T_1}{2T_1}\right] - \ln\left[1 + \frac{T_2-T_1}{2T_1}\right]\right\}$$

which on expanding and taking the first two terms, leads to

$$B_{obs} = B_{\frac{T_1+T_2}{2}} + \frac{c}{R} \cdot \frac{\Delta T^2}{8T_1^{\,2}}$$

A typical value of B is 25 and if c, ΔT and T have values as before,

$$\frac{c}{R} \cdot \frac{(\Delta T)^2}{8T_1^{\,2}} = 0.0035$$

and is therefore negligible.

Thus, B_{obs} may be identified with $B_{\left(\frac{T_1+T_2}{2}\right)}$ i.e. the experimentally determined B factor is equal to the true Arrhenius B factor at the mean temperature of the interval for which it was calculated.

(iii) Entropy of Activation

On consideration of the equations

$$\ln k_{(T)} = \ln\left(\frac{\bar{k}\,T}{h}\right) + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT}$$

and

$$E_{A(T)} = \Delta H^* + RT$$

it follows that

$$\ln k_{(T)} = \ln\left(\frac{\bar{k}\,T}{h}\right) + 1 + \frac{\Delta S^*}{R} - \frac{E_{A(T)}}{RT}$$

which on comparison with Eqn.II-15 shows that

$$B = 1 + \ln\left(\frac{\bar{k}\,T}{h}\right) + \frac{\Delta S^*}{R}$$

where B and ΔS^* refer to the temperature T and therefore ΔS^* may be calculated from a knowledge of B.

Since Eqn.II-17 leads to the identification of B_{obs} with B at temperature $\frac{T_1+T_2}{2}$, as ΔS^* is calculated from B_{obs}, it too must correspond to $\frac{T_1+T_2}{2}$ i.e. ΔS^* at $\frac{T_1+T_2}{2}$ is given by

$$B_{obs} = 1 + \ln\left(\frac{\bar{k}}{h}\right)\frac{T_1+T_2}{2} + \Delta S^*$$

CHAPTER III

RESULTS

The solvolysis of p-methoxy-, p-methyl-, and p-nitrobenzyl chlorides was investigated mainly in 50% aqueous acetone though some of the compounds were also studied in the corresponding 70% and 80% solvents. The reaction of p-methylbenzylidene chloride with 50% aqueous acetone was also examined as the data for this compound were required for a discussion of the extent of simultaneous S_N1 and S_N2 reactions in p-methylbenzyl chloride (see page 69).

The results are summarised in Tables III-1 to III-8, details of the experimental procedures and methods employed in the calculation of the results being given in Chapter VI. Throughout the Tables k represents the first order rate coefficient (in $sec.^{-1}$), σ the standard error in k, E the activation energy (in kcal./mole), ΔS^* the entropy (in cal./mole/deg.) and ΔC^* the heat capacity of activation (in cal./mole/deg.). The units of temperature are degrees centigrade and dE/dT values are in cal./mole/deg. σ (dE/dT), the standard error in dE/dT, was obtained in two ways

(i) From the deviations of experimental values of E from the 'best' straight line, E vs. T

(ii) From the standard deviations of E (σ (E)).

Full details are given in Chapter VI.

TABLE III - 1

HYDROLYSIS OF p-NITROBENZYL CHLORIDE IN 50% AQUEOUS ACETONE

Experimental Values						'Least Squares' Values	
Temp.	k	$\frac{\sigma}{k}$	Mean Temp.	E	$-\Delta S^*$	E	$-\Delta S^*$
108.84	4.671×10^{-5}	0.0036	104.22	20.78 ± 0.133	26.4	20.74	26.6
99.60	2.370×10^{-5}	0.0024	94.60	20.84 ± 0.077	26.2	20.91	26.1
89.61	1.092×10^{-5}	0.0016	85.04	21.09 ± 0.088	25.5	21.08	25.5
80.47	5.128×10^{-6}	0.0027	75.24	21.27 ± 0.103	24.9	21.26	25.0
70.02	2.040×10^{-6}	0.0035					

$\frac{dE}{dT} = -17.83 \pm 2.71$ (slope)

or ± 5.48 (σ (E))

$\Delta S^*(50^\circ) = -23.46 \pm 0.34$

$\Delta C^* = -20.03$ (from ΔS^* plot)

$E(50^\circ) = 21.71$

$\frac{\Delta C^*}{\Delta S^*}(50^\circ) = 0.85$ (using $\Delta C^* = -19.8$)

TABLE III - 2

HYDROLYSIS OF p-METHYLBENZYL CHLORIDE IN 50% AQUEOUS ACETONE

(SET A)

Experimental Values						$-\Delta S^*$ calculated for $dE/dT = 0$
Temp.	k	$\frac{\sigma}{k}$	Mean Temp.	E	$-\Delta S^*$	
69.99	1.742×10^{-4}	0.0017	65.05	21.11 ± 0.023	16.46	16.20
60.12	6.963×10^{-5}	0.0015	55.10	21.20 ± 0.058	16.13	16.14
50.09	2.578×10^{-5}	0.0023	45.03	21.42 ± 0.069	15.40	16.08
39.98	8.782×10^{-6}	0.0026	34.76	21.07 ± 0.062	16.45	16.02
29.55	2.735×10^{-6}	0.0022				

Mean E = 21.20 ± 0.066 $\Delta C^* = -1.99$ (for $dE/dT = 0$)

$\Delta S^*(50^\circ) = -16.11$

NOTE The observation that $dE/dT = 0$ was unexpected (see p. 53). Confirmation of this was obtained by carrying out a completely separate series of experiments in another batch of solvent (see Table III-3).

TABLE III - 3

HYDROLYSIS OF p-METHYLBENZYL CHLORIDE IN 50% AQUEOUS ACETONE

(SET B)

Experimental Values						$-\Delta S^*$ calculated for dE/dT = 0
Temp.	k	$\frac{\sigma}{k}$	Mean Temp.	E	$-\Delta S^*$	
80.04	4.233×10^{-4}	0.0027	74.97	21.28 ± 0.076	16.02	15.85
69.91	1.730×10^{-4}	0.0017	64.75	21.24 ± 0.048	16.09	15.79
59.60	6.588×10^{-5}	0.0014	54.60	21.39 ± 0.050	15.58	15.73
49.60	2.419×10^{-5}	0.0019	44.69	21.40 ± 0.044	15.49	15.67
39.79	8.500×10^{-6}	0.0011	34.84	21.38 ± 0.038	15.49	15.61
29.89	2.767×10^{-6}	0.0016				

Mean E = 21.34 ± 0.046

$\Delta C^* = -1.99$ (for dE/dT = 0)

$\Delta S^*(50^\circ) \simeq -15.70$

TABLE III - 4

HYDROLYSIS OF p-METHOXYBENZYL CHLORIDE IN 50% AQUEOUS ACETONE

Experimental Values					
Temp.	k	$\frac{\sigma}{k}$	Mean Temp.	E	$-\Delta S^*$
9.97	2.143×10^{-3}	0.0019	4.98	19.68 ± 0.060	3.08
0.00	5.980×10^{-4}	0.0033	-5.03	19.71 ± 0.055	2.94
-10.07	1.495×10^{-4}	0.0020			

$\frac{dE}{dT} = -15.0^{\neq}$ $\qquad$ $\Delta C^* = -17.0^{\neq}$

$\Delta S^*\ (50^\circ) = -5.84^{\neq}$ $\qquad$ $E(50^\circ) = 18.94^{\neq}$

$\neq$ Values calculated from other data (see Chapter VI).

TABLE III - 5

HYDROLYSIS OF p-METHYLBENZYLIDENE CHLORIDE IN 50% AQUEOUS ACETONE

Experimental Values						Least Squares' Values	
Temp.	k	$\frac{\sigma}{k}$	Mean Temp.	E	$-\Delta S^*$	E	$-\Delta S^*$
39.77	8.008×10^{-4}	0.0024	34.83	20.75 ± 0.053	9.88	20.68	10.10
29.90	2.702×10^{-4}	0.0013	24.68	20.98 ± 0.040	9.06	21.07	8.73
19.46	7.799×10^{-5}	0.0019	14.75	21.46 ± 0.054	7.32	21.46	7.36
10.05	2.287×10^{-5}	0.0024	5.02	21.86 ± 0.047	5.86	21.83	5.95
0.00	5.475×10^{-6}	0.0019					

$\frac{dE}{dT} = -38.6 \pm 3.8$ (slope)

or ± 1.1 (σ (E))

$\Delta S^*(50^\circ) = -12.05 \pm 0.38$

$\Delta C^* = -40.6$ (from ΔS^* plot)

$E(50^\circ) = 20.07$

$\frac{\Delta C^*}{\Delta S^*}(50^\circ) = 3.37$ (using $\Delta C^* = -40.6$)

TABLE III - 6

HYDROLYSIS OF p-METHYLBENZYL CHLORIDE IN 70% AQUEOUS ACETONE

Experimental Values						'Least Squares' Values	
Temp.	k	$\frac{\sigma}{k}$	Mean Temp.	E	$-\Delta S^*$	E	$-\Delta S^*$
98.80	1.772×10^{-4}	0.0026	93.80	21.68 ± 0.089	19.83	21.62	20.03
88.79	7.876×10^{-5}	0.0030	84.01	21.59 ± 0.093	20.03	21.77	19.54
79.24	3.492×10^{-5}	0.0019	74.20	22.05 ± 0.104	18.65	21.91	19.04
69.17	1.383×10^{-5}	0.0039	64.65	22.03 ± 0.120	18.65	22.06	18.55
60.12	5.743×10^{-6}	0.0027					

$\frac{dE}{dT} = -15.27 \pm 7.68$ (from slope)

or ± 4.26 (σ (E))

$\Delta S^*(50^\circ) = -17.77 \pm 0.71$

$\Delta C^* = -17.77$ (from ΔS^* plot)

$E(50^\circ) = 22.28$

$\frac{\Delta C^*}{\Delta S^*}(50^\circ) = 0.97$ (using $\Delta C^* = -17.3$)

TABLE III - 7

HYDROLYSIS OF p-METHOXYBENZYL CHLORIDE IN 70% AQUEOUS ACETONE

Experimental Values						'Least Squares'Value	
Temp.	k	$\frac{\sigma}{k}$	Mean Temp.	E	$-\Delta S^*$	E	$-\Delta S^*$
39.40	1.941×10^{-3}	0.0036	34.67	19.68 ± 0.084	10.30	19.65	10.04
29.94	7.218×10^{-4}	0.0021	25.16	19.96 ± 0.056	9.29	20.07	8.65
20.38	2.452×10^{-4}	0.0022	15.16	20.68 ± 0.045	6.54	20.51	7.15
9.93	6.625×10^{-5}	0.0018	4.97	20.90 ± 0.011	5.17	20.96	5.51
0.00	1.717×10^{-5}	0.0015					

$\frac{dE}{dT} = -43.77 \pm 6.80$ (from slope)

or ± 2.81 (σ (E))

$\Delta S^*(50^\circ) = -12.32 \pm 0.63$

$\Delta C^* = -45.65$ (from ΔS^* plot)

$E(50^\circ) = 18.99$

$\frac{\Delta C^*}{\Delta S^*}(50^\circ) = 3.72$ (using $\Delta C^* = -45.8$)

TABLE III - 8

HYDROLYSIS OF p-METHOXYBENZYL CHLORIDE IN 80% AQUEOUS ACETONE

Experimental Values						'Least Squares' Values	
Temp.	k	$\frac{\sigma}{k}$	Mean Temp.	E	$-\Delta S^*$	E	$-\Delta S^*$
39.68	2.806×10^{-4}	0.0017	34.81	20.10 ± 0.048	12.59	20.15	12.43
29.94	9.928×10^{-5}	0.0018	25.17	20.56 ± 0.046	11.02	20.48	11.27
20.39	3.270×10^{-5}	0.0017	15.59	20.78 ± 0.036	10.18	20.80	10.11
10.78	9.788×10^{-6}	0.0012	5.39	21.14 ± 0.019	8.86	21.15	8.81
0.00	2.232×10^{-6}	0.0005					

$\frac{dE}{dT} = -34.02 \pm 2.56$ (from slope)

or ± 1.68 (σ (E))

$\Delta S^*(50^\circ) = -14.61 \pm 0.26$

$\Delta C^* = -35.97$ (from ΔS^* plot)

$E(50^\circ) = 19.63$

$\frac{\Delta C^*}{\Delta S^*}(50^\circ) = 2.46$ (using $\Delta C^* = -36.0$)

For the solvolysis of p-methoxybenzyl and p-methylbenzylidene chlorides, both S_N1 reactions (see Chapter IV), the rates were found to be affected by changes in the concentration of the organic chloride. It was necessary to establish whether this concentration effect, which is greatest for S_N1 reactions, arises out of competing ionic-strength and mass-law effects. Experiments carried out in the presence of 0.02 N. HCl, the same concentration as the organic chloride used, suggest that part of the concentration effect is due to these factors but since ionic-strength effects are independent of temperature (see Part II) and the differences in the magnitude of mass-law effects over the experimental temperature range are relatively small, the results are not affected apart from a very small effect on ΔS^*. Full details are given in Chapter VI.

The results are discussed in detail in Chapters IV and V. Since a negative value for dE/dT for the solvolysis of p-methyl- and p-methoxybenzyl chlorides is expected, due to the transition state being more polar than the initial state, it is therefore noteworthy that the observed dE/dT is virtually zero for both these compounds in 50% aqueous acetone. It must be emphasised however that the zero dE/dT for p-methoxybenzyl chloride was obtained from mean rate constants at only three temperatures since the reaction was too fast to measure accurately at 20° (time of half change is two minutes) and ice was precipitated from the solvent at -20°. The probable error in the activation energies is such that dE/dT could be equal to -15 cal.deg.$^{-1}$ (see p. 107). The zero dE/dT for p-methylbenzyl chloride was obtained using two separate series and must therefore be regarded as genuine (see Tables III-2 and III-3). It is considered that this observation is connected with the reaction mechanism (see Chapter IV). It is also noteworthy that on changing to 70% aqueous acetone the expected negative dE/dT was obtained for both the above compounds.

It is useful to compare the present results with those obtained by previous workers.

Comparison with Previous Results.

The solvolysis of p-substituted benzyl chlorides in aqueous acetone has previously been investigated by Olivier[37], Bennett and Jones[38] and Tommila and co-workers(59). Table III-9 compares the results obtained.

The rates are not expected to be precisely the same for solvents made up by volume, a 20% difference being easily permitted. Slight changes in solvent composition should have no effect on E and a 20% change in rate leads to only a 0.4 cal. change in ΔS^*.

<u>TABLE III - 9</u>

VALUES OF k, E, $\triangle S^*$, AND dE/dT FOR HYDROLYSIS OF p-Me.$C_6H_4.CH_2Cl$ AND p-$NO_2.C_6H_4.CH_2Cl$ (k in $sec.^{-1}$, E in kcal., $\triangle S^*$ and dE/dT in $cal.deg.^{-1}$).

Reaction		Present Results	Olivier[37]	Present Results	Bennett and Jones[38]	Present Results	Tommila[59]
p-Methylbenzyl Chloride in 50% aqueous acetone.	10^5k	6.851 (60°)	6.666 (60°)	4.078 (54.8°)	4.130 (54.8°)	2.521 (50°)	2.14 (50°)
	E	21.27 (45°)	21.44 (45°)	21.27 (62.3°)	21.1 (62.3°)	21.27 (50°)	20.68 (50°)
	$-\triangle S^*$	15.9 (45°)	15.4 (45°)	16.0 (62.3°)	16.4 (62.3°)	15.9 (50°)	18.1 (50°)
	dE/dT	-	-	-	-	0	-53.3$^{\neq}$
p-Nitrobenzyl Chloride in 50% aqueous acetone.	10^7k	7.966 (60°)	7.667 (60°)	19.98 (69.8°)	19.61 (69.8°)	2.843 (50°)	2.57 (50°)
	E	21.80 (45°)	21.51 (45°)	21.23 (77.15°)	20.6 (77.15°)	21.61 (55.83°)	21.09 (55.83°)
	$-\triangle S^*$	23.4 (45°)	24.1 (45°)	25.1 (77.15°)	31.5 (77.15°)	23.5 (50°)	25.6 (50°)
	dE/dT	-	-	-	-	-17.8	-23.5$^{\neq}$
p-Methylbenzyl Chloride in 70% aq.acetone	10^6k	-	-	-	-	2.019 (50°)	2.14 (50°)
	E	-	-	-	-	22.28 (50°)	21.06 (50°)
	$-\triangle S^*$	-	-	-	-	17.80 (50°)	21.4 (50°)

≠ Mean values in acetone-water mixtures containing 0-60% acetone.

Rates on the whole correspond quite well throughout. Olivier and Bennett obtained their data from rates at only two temperatures and the values they obtained for E and ΔS^* must therefore refer to the mean temperature. The present values obtained for E and ΔS^* have been corrected to this mean temperature in order that comparisons can be made. The values for E and ΔS^* obtained in the present investigation for p-methylbenzyl chloride in 50% acetone are in good agreement with the values obtained by Olivier and Bennett. The value obtained by Tommila for E however appears to be rather low and the value for ΔS^* too negative. The same criticism can be made of his results for p-methylbenzyl chloride in 70% aqueous acetone. For p-nitrobenzyl chloride in 50% aqueous acetone the present values for E and ΔS^* show the closest agreement with those obtained by Olivier. The ΔS^* value obtained by Bennett is much too negative whilst the values obtained by Tommila for this compound show similar discrepancies to those for the p-methyl compound.

The present values for $\delta E/dT$ can only be compared with those obtained by Tommila, who quotes an average for several solvents. For p-methylbenzyl chloride, a compound for which the present results were obtained in duplicate, there is serious disagreement, although the values for p-nitrobenzyl are comparable. The value quoted by Tommila for benzyl chloride is roughly twice that obtained by Bensley and Kohnstam[15]. A detailed examination of Tommila's paper does not reveal how the values for dE/dT were obtained. Using his mean rate coefficients and the method of calculation employed in the present investigation showed that dE/dT is solvent dependent (though not in any regular manner) and that it is subject to such large errors that it is difficult to attach much value to the quoted figures. This is illustrated in Table III-10 for p-methyl- and p-nitrobenzyl chlorides. It is noteworthy that a recalculation of Tommila's data shows p-nitrobenzyl chloride to have a positive dE/dT whereas Tommila quotes a negative value for this compound. The values quoted by Tommila are regarded as too inaccurate to merit serious consideration and the results obtained in the present investigation are therefore preferred.

TABLE III - 10

VALUES FOR dE/dT

(dE/dT in cal.deg.^{-1})

Compound	Solvent		
	40% acetone	50% acetone	60% acetone
p-Methylbenzyl Chloride	-89.6± 29.5	-51.8± 23.8	+23.5±125.7
p-Nitrobenzyl Chloride	+ 7.8± 3.9	+36.7± 4.4	+18.2±100.9

Fierens and co-workers[39] have investigated the solvolysis of *p*-methoxy- and *p*-methylbenzyl chlorides in aqueous dioxan at several temperatures. Some of the data, recalculated in Table III-11, show that there is no regular variation of activation energy with temperature and thus no value for dE/dT can be obtained.

TABLE III - 11

p-Me.C_6H_4.CH_2Cl AND *p*-MeO.C_6H_4.CH_2Cl IN AQUEOUS DIOXAN

(E in kcal.)

p-Me.C_6H_4.CH_2Cl				*p*-MeO.C_6H_4.CH_2Cl	
50% aq. dioxan		80% aq. dioxan		50% aq. dioxan	
Temp.	E	Temp.	E	Temp.	E
94.9	21.44	71.4	20.92	12.5	18.71
85.5	20.60	52.5	20.42	5.0	20.35
75.5	21.30				

CHAPTER IV

MECHANISM OF SOLVOLYSIS

Validity of $\Delta C^*/\Delta S^*$ Criterion.

Bensley and Kohnstam[15] originally proposed that the ratio $\Delta C^*/\Delta S^*$ could be used as a criterion of mechanism (see page 22) and further data are now available which support the validity of this.

In 50% aqueous acetone the ratio $\Delta C^*/\Delta S^*$ for four compounds, which go by mechanism S_N1[≠] is constant (see Table IV-1) the greatest error in ΔC^* being ± 4 cal.deg.$^{-1}$ (for benzotrichloride). It should be taken into account that ΔC^* values are subject to a 10% error and probably further inaccuracies, due to extrapolation of data outside the experimental temperature range. In 70% and 85% aqueous acetone, the ratio $\Delta C^*/\Delta S^*$ for S_N1 solvolyses is also constant. In addition, two S_N1 reactions which have been investigated in 50% aqueous ethanol[15] have the same value for this ratio. It therefore seems reasonable to accept the criterion that S_N1

[≠] Independent evidence shows that the hydrolysis of benzylidene chloride, benzotrichloride and *tert*-butyl chloride in 50% aqueous acetone react by mechanism S_N1 (12,82) while both the unsubstituted and substituted benzhydryl chlorides are sterically hindered with respect to mechanism S_N2 and must therefore also be S_N1.

TABLE IV - 1.

$\Delta C^{*}/\Delta S^{*}$ RATIOS FOR S_N1 REACTIONS AT 50°C.

(ΔC^{*} and ΔS^{*} in cal.deg.$^{-1}$)

Compound	Solvent	$-\Delta C^{*}$	$-\Delta S^{*}$	$\Delta C^{*}/\Delta S^{*}$
$Ph.CHCl_2$[15]	50% acetone	29 ± 3	11.4$^{\neq}$	2.5$^{\neq}$
$Ph.CCl_3$[15]	"	46 ± 4	16.2$^{\neq}$	2.9$^{\neq}$
t.-BuCl[57]	"	26.7	10.8	2.6
p-Mo.$C_6H_4.CHCl_2$	"	40.6 ± 3.8	12.1$^{\neq}$	3.37$^{\neq}$
$Ph_2.CHCl$[50]	70% acetone	37.6 ± 2.7	10.3	3.66
p-$NO_2.C_6H_4.CHCl.Ph$[50]	"	41.4 ± 1.6	10.0	4.14
p-$Cl.C_6H_4.CHCl.Ph$[50]	"	32.9 ± 2.8	10.1	3.26
p-$Br.C_6H_4.CHCl.Ph$[50]	"	40.6 ± 3.4	10.4	3.90
p-I. $C_6H_4.CHCl.Ph$[50]	"	37.9 ± 1.9	10.3	3.68
p-$MeO.C_6H_4.CH_2Cl$	"	45.8 ± 6.8	12.3	3.72
$Ph_2.CHCl$[50]	80% acetone	38.9	12.9	3.01
p-$MeO.C_6H_4.CH_2Cl$	"	36.0 ± 2.6	14.6	2.47
$Ph_2.CHCl$[50]	85% acetone	46.5 ± 4.1	12.0	3.88
p-$Me.C_6H_4.CHCl.Ph$[50]	"	43.0 ± 6.1	12.8	3.35
p-$Ph.C_6H_4.CHCl.Ph$[50]	"	36.7 ± 9.7	11.2	3.27

$\neq$ Per replaceable chlorine atom.

reactions have the same $\Delta C^{*} / \Delta S^{*}$ ratio.

The ratio $\Delta C^{*} / \Delta S^{*}$ for p-methoxybenzyl chloride in 70% and 80% aqueous acetone agrees with the S_N1 value showing that it goes by the unimolecular mechanism in these solvents. This compound must therefore react by mechanism S_N1 in 50% aqueous acetone, since a higher percentage of water favours this mechanism.

It is noteworthy that p-methoxybenzyl chloride has a similar rate constant to benzhydryl chloride and shows similar changes with solvent variation (see Table IV-3).

While the ratio $\Delta C^{*} / \Delta S^{*}$ is found to be constant for S_N1 reactions, as predicted, the mechanistic test proposed by Bensley and Kohnstam requires that this ratio should be less for S_N2 reactions (see page 24). Unfortunately few results are available for this latter class but it has been found[52] that the ratio for primary alkyl bromides in 50% aqueous acetone is considerably less than the ratio for chlorides reacting by mechanism S_N1 (see Table IV-2). An even lower value for chlorides reacting by mechanism S_N2 is expected since ΔS^{*} is generally less negative for an alkyl bromide than for the corresponding chloride. For p-nitrobenzyl chloride and the parent compound, the ratio is found to be less than for S_N1 reactions in the same solvent. The results for the parent compound have already been analysed by Bensley and Kohnstam[15] who concluded that the mechanism by which it reacts in 50% aqueous acetone is mainly, if not entirely, S_N2. The p-nitro-compound is even less likely to go by mechanism S_N1 than the parent compound. The ratio $\Delta C^* / \Delta S^*$ can therefore be accepted as a criterion of mechanism, with $\Delta C^* / \Delta S^* = 2.9$ for S_N1 reactions of chlorides in 50% acetone at 50°C. Lower values indicate reaction by mechanism S_N2 and therefore the parent compound and the p-nitro compound (where the ratio is much less) belong to that class.

TABLE IV - 2

$\Delta C^* / \Delta S^*$ RATIOS FOR S_N2 REACTIONS AT 50°C.
(ΔC^* and ΔS^* in cal.deg.$^{-1}$)

Compound	Solvent	$-\Delta C^*$	$-\Delta S^*$	$\Delta C^*/\Delta S^*$
p-Me.C_6H_4.CH_2Cl	50% acetone	0	15.90	-
Ph.CH_2Cl[15]	"	21 ± 2.5	22.8	0.9
p-NO_2.C_6H_4.CH_2Cl	"	19.8 ± 5.5	23.46	0.85
Et Br[52]	"	34.8 ± 11.4	18.13	1.92
n-Pr Br[52]	"	23.4 ± 6.2	20.79	1.13
n-Bu Br[52]	"	33.4 ± 6.1	20.60	1.62
p-Me.C_6H_4.CH_2Cl	70% acetone	17.3 ± 7.7	17.77	0.97

p-Methylbenzyl Chloride

For the solvolysis of p-methylbenzyl chloride in 70% acetone, $\Delta C^* / \Delta S^* = 0.97$ at 50°C (Table IV-2) and although this value is subject to considerable errors, it is much less than the value of 3.7 which is observed for S_N1 reactions under the same conditions (Table IV-1). It can therefore be concluded that the solvolysis of p-methylbenzyl chloride in 70% acetone does not occur entirely by mechanism S_N1.

The zero dE/dT for this compound in 50% acetone can be interpreted in two ways.

(i) The hydrolysis proceeds via several reaction paths, the frequency with which the reaction occurs by any particular path varying with temperature and being greater at higher temperatures for paths with a higher activation energy.

(ii) The hydrolysis proceeds via a single transition state, the structure of which is not independent of temperature but changes in the direction of increased C-Cl ionisation (i.e. increased S_N1 character and therefore having a higher activation energy) with increasing temperature.

Both explanations allow for the expected decrease of activation energy with increasing temperature to be balanced. The first interpretation will be discussed in detail. No quantitative treatment of the second is possible however.

Mechanism in the benzyl series.

Table IV-3 contains data showing the variation of rate, activation energy and entropy of activation with changing para-substituents in the benzyl series. Values for p-methoxybenzyl chloride in 50% aqueous acetone have been calculated from data at $0^{o}C$. (see Chapter VI). The $\Delta C^{*}/\Delta S^{*}$ ratio criterion has already suggested that the p-methoxy compound is S_N1 and that the p-methyl compound is certainly not completely S_N1. Data in Table IV-3 support this view. It has been found on several occasions[50,83,84] that para-substituents in S_N1 reactions always affect the rate mainly through changes in the activation energy. On replacing the p-methyl substituent by a methoxy group in the present series however, by far the greater part of the rate increase results from an increase in entropy rather than from a decrease in the activation energy.

It is also noteworthy that the rates of solvolysis for the substituted benzyl chlorides become increasingly solvent dependent in the order $p\text{-}NO_2 < H < p\text{-}Me < p\text{-}MeO$ (Table IV-3). Since S_N1 reactions are affected by increasing water content of the solvent to a greater extent than S_N2 reactions, this demonstrates the progressive increase in S_N1 character in this series of compounds on going from p-nitro- to p-methoxybenzyl chloride.

TABLE IV - 3

VARIATION OF k, E AND ΔS^* WITH CHANGE IN SOLVENT COMPOSITION
(Values at 50°C, unless otherwise stated; k in sec^{-1}, E in kcal., ΔS^* in $cal.deg^{-1}$.)

Compound	50% aqueous acetone			70% aqueous acetone			80% aqueous acetone			Ref.
	k	E	$-\Delta S^*$	k	E	$-\Delta S^*$	k	E	$-\Delta S^*$	
p-$NO_2.C_6H_4.CH_2Cl$	2.84×10^{-7} ⌿	21.71⌿	23.5⌿	-	-	-	-	-	-	
	2.57×10^{-7}	21.09 (55.83°)	25.6	7.22×10^{-8}	20.76 (61.25°)	29.0	3.06×10^{-8}	20.85 (61.25°)	30.5	59
$C_6H_5.CH_2Cl$	3.10×10^{-6}	20.60	22.8	-	-	-	-	-	-	15
	2.61×10^{-6}	20.52 (51.25°)	22.8	3.74×10^{-7}	20.99 (55.83°)	25.2	1.25×10^{-7}	20.82 (55.83°)	27.9	59
p-$Me.C_6H_4.CH_2Cl$	2.52×10^{-5}	21.28	15.9	2.04×10^{-6}⌿	22.28⌿	17.8⌿	-	-	-	
	2.14×10^{-5}	20.68	18.1	2.14×10^{-6}	21.06	21.4	6.04×10^{-7}	-	-	59
p-$MeO.C_6H_4.CH_2Cl$	1.45×10^{-1}⌿	18.94⌿	5.8⌿	5.28×10^{-3}⌿	18.99⌿	12.3⌿	7.87×10^{-4}⌿	19.63⌿	14.6⌿	
Ph_2CHCl	-	-		6.70×10^{-3}⌿	19.52⌿	10.3⌿	9.80×10^{-4}⌿	19.85⌿	12.9⌿	50

⌿ Calculated from data obtained at other temperatures.

Benzyl chloride undergoes solvolysis in 50% aqueous acetone mainly, if not entirely, by mechanism S_N2[15] and it therefore seems reasonable to assume that this mechanism is involved when electron-attracting substituents are introduced into the benzene ring, para to the reaction centre. It is noteworthy that the hydrolysis of the p-nitro compound has almost the same ΔS^* as the hydrolysis of the parent compound (see Table IV-3), in agreement with the observations of Olivier[37]. Olivier's results show that similar considerations apply to the introduction of other electron-attracting substituents which appear to alter the rate of hydrolysis almost entirely by changing the activation energy (see Table IV-4). This conclusion has not been reached before for S_N2 reactions, but it is to be expected if the covalent attachment of water in the transition state of hydrolysis is associated with the same loss of entropy, no matter how strong or weak this attachment.

When the transition state for hydrolysis is regarded in terms of contributions from the following valence bond structures (see page 10), the plausibility of this view is apparent. S represents a molecule of the nucleophilic reagent, i.e. water

$$\underset{\text{I}}{\overset{+}{S} - R \quad \overset{-}{Cl}} \qquad\qquad \underset{\text{II}}{S \quad \overset{+}{R} \quad \overset{-}{Cl}}$$

TABLE IV - 4

EFFECT OF META- ANDY PARA- SUBSTITUTION ON ARRHENIUS PARAMETERS.

(Using Olivier's data[37])

(k in sec^{-1}. E in kcal. ΔS^* in cal.deg.$^{-1}$)

Substituent	$10^7k(60^\circ)$	$E(45^\circ)$	$-\Delta S^*(45^\circ)$	$E(55^\circ)$	$-\Delta S^*(55^\circ)$
p-NO_2	7.667	21.51	24.09	-	-
m-NO_2	8.500	21.68	22.91	-	-
p-CN	9.667	-	-	21.45	23.87
m-CN	10.33	-	-	20.69	26.01
p-COOH	14.33	21.10	24.08	-	-
m-COOH	22.00	21.70	21.41	-	-
p-$CONH_2$	24.33	-	-	21.00	23.39
m-$CONH_2$	33.83	-	-	20.85	23.17
m-Cl	15.50	21.50	22.71	-	-
p-Cl	44.67	20.87	22.51	-	-
H	76.67	20.60	22.25	$20.41^{\neq}$	$22.90^{\neq}$
m-CH_3	91.67	20.38	22.54	-	-
p-CH_3	666.7	21.44	15.43	-	-

$\neq$ Calculated from data at 45°C. using $\Delta C^* = -21$[15]

A solvolytic study of benzyl chloride in 50% acetone has shown that valence bond structures I and II both make an appreciable contribution to the structure of the transition state[15]. In S_N1 reactions (where structure II is important) the p-nitro group is found to have a very large effect on the rate[≠] thus showing that the stability of II is greatly reduced by the presence of this group. For the solvolysis of p-nitrobenzyl chloride, where structure I makes a greater contribution to the transition state structure than II (i.e. more covalent attachment), the p-nitro group has a much smaller effect on the rate (viz. the rate is reduced by a factor of 10) and therefore a smaller effect on the stability of I. This demonstrates that even where there are different degrees of solvent attachment in the transition state (i.e. varying contributions from I) the loss of entropy associated with this attachment should in each case be similar.

If this view is correct, it follows that the entropy of activation for the hydrolysis of substituted benzyl chlorides should depend only on the reaction mechanism (for a given solvent and temperature), irrespective of the nature

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[≠] Brown and Okamoto[85], studying the solvolysis of p-substituted phenyldimethylcarbinyl chlorides in 90% acetone, found that the presence of the p-nitro group reduced the rate of the parent compound by a factor of 3900.

of the substituent. This assumes the same degree of solvation for reaction by a given mechanism, a fairly reasonable assumption. The hydrolysis of the p-methyl compound in 50% and 70% acetone is however associated with an entropy of activation which is intermediate between that for p-methoxybenzyl chloride (S_N1) and the parent compound (S_N2) . This argues strongly against reaction via a single transition state, irrespective of whether water is considered to participate covalently (S_N2) or not (S_N1), and it therefore appears that the hydrolysis of p-methylbenzyl chloride in 50% aqueous acetone involves the concurrence of reactions operating by mechanisms S_N1 and S_N2. Such concurrence has already been demonstrated for the reaction of azide ions with p-methoxybenzyl chloride in aqueous acetone[34]. It has not been established before for solvolysis and it must be stressed that the present conclusion can only be regarded as provisional since the constant entropy loss on covalent attachment requires a complete demonstration.

Calculation of the Fraction of S_N1 Solvolysis.

It is of interest to establish what proportion of the solvolysis of p-methylbenzyl chloride in 50% aqueous acetone goes by mechanism S_N1 and what proportion by mechanism S_N2. The approach used is essentially that of Bensley and

Kohnstam[15]. A continuous range of transition states is considered available to the reacting system. The activation energy E must have a minimum value E_m before the reaction will occur but can take up values to infinity. If each possible transition state is defined by the value of E associated with it, the rate coefficient can be expressed in the form

$$k = \frac{1}{Nh} \int_{E_m}^{\infty} e^{-\Delta G^{*}/RT} \, dE$$

where the free energy of activation, $\Delta G^{*} = E - RT - T \Delta S^{*}$, and ΔS^{*} must initially be regarded as a function of the transition state structure and thus a function of E. This equation reduces to Eyring's rate equation if ΔS^{*} is constant and independent of E. It is convenient to consider that mechanism S_N1 operates when E is greater than some value E_1.

The experimental evidence discussed above strongly suggests that all S_N2 processes are associated with the same entropy of activation and this also appears to hold true for S_N1 processes (see page 64).

Making these assumptions for the entropies of the S_N1 and S_N2 processes it can be shown (see Appendix A) that even if a continuous spectrum of transition states is available to the reacting system, the solvolysis can be treated as though it involved a simultaneous concurrence of one S_N2 process of activation energy E_2 (of value E_m), entropy of activation ΔS_2^*, and heat capacity of activation ΔC_2^* and one S_N1 process of activation energy E_1, entropy of activation ΔS_1^*, and heat capacity of activation ΔC_1^*. The mathematical treatment is thus considerably simplified. Since $k = k_1 + k_2$,

$$E = RT^2 \frac{d \ln k}{dT} = \frac{E_1k_1 + E_2k_2}{k} \qquad \text{..........IV-1}$$

From this expression, equation IV-2 can be derived (see Appendix B).

$$\Delta C^* = \frac{dE}{dT} - R = \frac{(E_1-E_2)^2 k_1k_2}{RT^2k^2} + \frac{(k_1 \Delta C_1^* + k_2 \Delta C_2^*)}{k} \qquad \text{..IV-2}$$

It is now necessary to consider the maximum values of k_1/k which are consistent with equation IV-2 and the observed value of ΔC^*.

ΔC_1^* was taken to be equal to ΔC^* for the ionisation of p-methylbenzylidene chloride, ΔC_2^* was taken to be the same as for p-nitrobenzyl chloride and the unsubstituted compound since S_N2 reactions appear to have similar values for ΔC^*, and E_1 was obtained by assuming that α-chlorination on p-methylbenzyl chloride reduces the S_N1 activation energy by the same amount as α-chlorination in benzylidene chloride. Data necessary for the calculation of E_1 are given in Table IV-5. Values of E_1 are shown in Table IV-6, $\Delta C_1^* = -40$,

TABLE IV-5

VALUES OF E AND dE/dT FOR THE SOLVOLYSIS OF α-CHLORODERIVATIVES OF BENZYL AND p-METHYLBENZYL CHLORIDES AT 50°C.

(E in kcal. dE/dT in cal.deg.$^{-1}$)

Compound	E	-dE/dT
$PhCHCl_2$ (15)	22.91	27
$PhCCl_3$ (15)	19.31	44
p-Me.$C_6H_4.CH_2Cl$	21.27	0
p-Me.$C_6H_4CHCl_2$	20.07	38

$\Delta C_2^{*} = -20$ and $\Delta C^{*} = -2.0$ (assuming constant activation energy for p-methylbenzyl chloride).

A number of values of k_1/k at 50°C were arbitrarily chosen. Using Eqn.IV-1 and assuming $dE_2/dT = -18$, corresponding values of E_2 were obtained at temperatures at 10° intervals over the experimental temperature range. From these, values of k_1/k at other temperatures were obtained. Eqn.IV-2 was considered to be satisfied when the mean of the right hand terms over the experimental range was equal to ΔC^{*}. Table IV-6 shows the results obtained for three values of k_1/k; the values obtained using E_2 (50°) = 18.86 give the closest agreement.

TABLE IV - 6

CALCULATION OF THE FRACTION OF S_N1 SOLVOLYSIS FOR p-METHYLBENZYL CHLORIDE IN 50% AQUEOUS ACETONE

(E in kcal.)

Temp.	E_1	E_2	k_1/k	E_2	k_1/k	E_2	k_1/k
70°	22.91	18.95	0.586	18.50	0.628	17.97	0.668
60°	23.29	19.13	0.514	18.68	0.562	18.15	0.607
50°	23.67	19.31	0.450	18.86	0.500	18.33	0.550
40°	24.05	19.49	0.390	19.04	0.445	18.51	0.498
30°	24.43	19.67	0.336	19.22	0.393	18.69	0.449
		$\Delta C^*_{(calc)} = -6.7$		$\Delta C^*_{(calc)} = -2.4$		$\Delta C^*_{(calc)} = +2.8$	

$$\Delta C^*_{(obs.)} = -2.0$$

If therefore the solvolysis of p-methylbenzyl chloride in 50% aqueous acetone occurs by a continuous spectrum of transition states, the following values represent the upper limit for the fraction of the total solvolysis which may proceed by unimolecular mechanisms.

Temp.	70°	50°	30°
$\frac{100\ k_1}{k}$	63	50	39

The assumptions made may be subject to the following errors[15]. α-Chlorination decreases ΔC^* for the ionisation of the C-Cl linkage and ΔC_1^* may therefore be less negative than ΔC^* (p-Me.C_6H_4.$CHCl_2$). Any steric inhibition of solvation would be greater in benzotrichloride than in benzylidene chloride; this would partially obscure the effect of α-chlorination in the S_N1 activation energy, leading to too small a value for E_1. Both these errors overestimate k_1/k.

Unfortunately a similar calculation cannot be carried out for the solvolysis of p-methylbenzyl chloride in 70% aqueous acetone since there are insufficient data available to enable a value for E_1, the S_N1 activation energy in this solvent, to be obtained. Certain qualitative conclusions can however be drawn.

(i) The ratio $\Delta C^*/\Delta S^*$=0.97, which is considerably less than 3.7, the value for the S_N1 reactions of aralphyl chlorides in 70% acetone. (See Table IV-1). It is therefore clear that the reaction does not occur by mechanism S_N1.

(ii) ΔS^*(at 50°) for p-methylbenzyl chloride is less than for the S_N1 solvolysis of p-methoxybenzyl chloride and is greater than for the S_N2 solvolysis of benzyl halides in the 50% solvent (see Table IV-7). Since the entropy of activation must decrease on passing to the 70% solvent it can be seen that ΔS^* for the p-methyl compound lies between the values expected for the S_N1 and S_N2 reactions.

It is suggested that in this solvent also, S_N1 and S_N2 solvolysis may occur concurrently.

TABLE IV - 7

ΔS^* VALUES AT 50°C

(ΔS^* in cal.deg.$^{-1}$)

Compound	Solvent	Mechanism	$-\Delta S^*$
p-MeO.$C_6H_4.CH_2Cl$	70 % acetone	S_N1	12.32
p-Me.$C_6H_4.CH_2Cl$	70 % acetone	-	17.77
p-$NO_2.C_6H_4.CH_2Cl$	50 % acetone	S_N2	23.46
Ph.CH_2Cl	50 % acetone	S_N2	22.8

CHAPTER IV , APPENDIX A

The rate coefficient for the reaction may be expressed in the form

$$k = \frac{1}{N\,h} \int_{E_m}^{\infty} e^{-\Delta G^*/RT} \, . \, dE$$

Since mechanism S_N1 operates when $E > E_1$,

$$k_1 = \frac{1}{N\,h} \int_{E_1}^{\infty} e^{-\Delta G^*/RT} \, . \, dE$$

and

$$k_2 = \frac{1}{N\,h} \int_{E_m}^{E_1} e^{-\Delta G^*/RT} \, . \, dE$$

where the rate coefficients, with subscripts 1 and 2, refer to unimolecular and bimolecular processes respectively. ΔS^* is assumed to have a constant value, ΔS_2^* , for all S_N2 processes and a constant value, ΔS_1^* , for all S_N1 processes. Then, using the expression $\Delta G^* = E - RT - T\,\Delta S^*$, integration gives

$$k_1 = \frac{\bar{k}\,T}{h} \, e \; e^{\Delta S_1^*/R} \; e^{-E_1/RT}$$

and

$$k_2 = \frac{\bar{k}\,T}{h} \, e \; e^{\Delta S_2^*/R} \left[e^{-E_m/RT} - e^{-E_1/RT} \right]$$

$$\therefore\ k_1 + k_2 = \frac{\bar{k}\,T}{h}\, e\, e^{\Delta S_2^*/R}\, e^{-E_m/RT}$$

$$+ \frac{\bar{k}\,T}{h}\, e\, e^{-E_1/RT}\left[e^{\Delta S_1^*/R} - e^{\Delta S_2^*/R}\right]$$

Assuming $\Delta S_1^* = -10$ and $\Delta S_2^* = -20$, $e^{\Delta S_2^*/R}$ is negligible compared with $e^{\Delta S_1^*/R}$.

$$\therefore\ k_1 + k_2 = \frac{\bar{k}\,T}{h}\, e\left[e^{\Delta S_2^*/R}\, e^{-E_m/RT} + e^{\Delta S_1^*/R}\, e^{-E_1/RT}\right]$$

The system can thus be treated as the sum of only two processes.

CHAPTER IV. APPENDIX B

If solvolysis occurs by one unimolecular and one bimolecular path, the overall rate $k = k_1 + k_2$

Then

$$E = RT^2 \frac{d \ln k}{dT} = RT^2 \frac{d \ln (k_1 + k_2)}{dT}$$

$$= \frac{RT^2}{k_1 + k_2} \left(\frac{dk_1}{dT} + \frac{dk_2}{dT}\right)$$

$$= \frac{RT^2}{k_1 + k_2} \left(\frac{E_1 k_1}{RT^2} + \frac{E_2 k_2}{RT^2}\right) = \frac{E_1 k_1 + E_2 k_2}{k_1 + k_2}$$

$$\therefore \quad \Delta C^* = dE/dT - R = \frac{E_1 k_1 + E_2 k_2}{(k_1 + k_2)^2} \left(\frac{dk_1}{dT} + \frac{dk_2}{dT}\right)$$

$$+ \frac{E_1 (dk_1/dT) + E_2 (dk_2/dT)}{k_1 + k_2}$$

$$+ \frac{k_1 (dE_1/dT) + k_2 (dE_2/dT)}{k_1 + k_2} - R$$

$$= \frac{(E_1 - E_2)^2 k_1 k_2}{RT^2 k^2} + \frac{k_1 \Delta C_1^* + k_2 \Delta C_2^*}{k}$$

CHAPTER V

SUBSTITUENT EFFECTS

Effect of p-Substituents on the Arrhenius Parameters

The results of Olivier[37], Bennett[38], and Tommila[59], for the solvolysis of para-substituted benzyl chlorides in aqueous acetone show that not only electron-attracting but also electron-repelling substituents increase the activation energy (see Tables IV-3 and IV-4) although, as has already been observed (see page 56), Tommila's data cannot be regarded as reliable. The results obtained in the present investigation, with the exception of those for p-methoxybenzyl chloride, confirm this picture. p-Methoxybenzyl chloride, a compound not studied by Olivier, Bennett or Tommila, was found to have a lower activation energy than the parent compound, an observation confirmed by Fierens and co-workers[39] who investigated the solvolysis of the p-methoxy compound in 50% aqueous dioxan.

It has already been noted (page 66) that the present results and those of Olivier show that p-nitrobenzyl chloride and the unsubstituted compound in 50% aqueous acetone have similar entropies of activation. Although Tommila's results for p-nitrobenzyl chloride[59] in 50%, 70% and 80% aqueous acetone show an appreciable difference in the entropy of activation from the unsubstituted compound, his results in

40% and 60% aqueous acetone confirm the present observations. The results for p-methylbenzyl chloride are unsatisfactory for supporting Tommila's conclusion that "substituents exert their main influence through the activation entropy and not through the activation enthalpy term" since, as has already been shown, the mechanism for this compound is border-line and a less negative entropy is expected due to the reaction proceeding partly by an ionisation process.

Effect of Solvent Variation on the Arrhenius Parameters.

The present results (see Tables IV-3 and V-1) show that for S_N1 solvolyses the activation energy is fairly constant for solvent changes in the range 50% - 80% aqueous acetone, the observed decrease in rate being due to the entropy of activation becoming more negative as the acetone content is increased. This is in agreement with the observations of Hughes[6], who studied the solvolysis of tert-butyl chloride in aqueous acetone (an S_N1 reaction) and Winstein and Fainberg[86] who investigated the same compound in both aqueous acetone and aqueous dioxan. Both Hughes and Winstein found that the activation energy changed little with solvent composition. The change in ΔS^* at 50°C for p-methoxybenzyl chloride is very pronounced on going from 50% to 70% aqueous acetone. The actual difference may not be as large as that shown however since data were extrapolated from lower temperatures, the extrapolation being particularly large for 50% acetone (see page 107). A comparison of values of ΔS^* at 0°C for these solvents (Table V-1) reveals a similar trend although the change in ΔS^* is not so pronounced.

TABLE V - 1.

VARIATION OF k, E AND ΔS^* WITH SOLVENT COMPOSITION IN THE SOLVOLYSIS OF p-METHOXYBENZYL CHLORIDE

(k in sec.^{-1}, E in kcal., ΔS^* in cal.deg.^{-1})

Solvent	0°C			50°C		
	k	E	$-\Delta S^*$	k	E	$-\Delta S^*$
50% acetone	5.98×10^{-4}	19.70	3.0	1.45×10^{-1}	18.94	5.8
70% acetone	1.72×10^{-5}	21.18	4.6	5.28×10^{-3}	18.99	12.3
80% acetone	2.23×10^{-6}	21.32	8.1	7.87×10^{-4}	19.63	14.6

The Hammett Equation

The Hammett equation, Eqn.V-1[87], has often been used to predict the effects of *meta*- and *para*-substituents on the rates of chemical reactions.

$$\log \frac{k_X}{k_H} = \sigma\rho \qquad \text{.......V-1}$$

The σ value represents the effect of the substituent on the electron density at the reaction centre and depends only on the substituent; the quantity ρ represents the sensitivity of the reaction to such electron shifts and depends only on the reaction. k_X is the rate constant when the reactant contains a substituent and k_H is the corresponding rate constant for the unsubstituted compound.

The σ values were determined from the ionisation constants of *meta*- and *para*-substituted benzoic acids by assuming $\rho = 1$ for this reaction.

On several occasions it has been observed that reactions facilitated by electron supply fail to give satisfactory plots for the Hammett relation.[87,88,89]

Swain and Langsdorf[89] have interpreted curved σ *vs.* $\log (k_X/k_H)$ plots in terms of the operation of only one mechanism for most reactions of organic halides. The existence of a delicate balance between bond-making and bond-breaking in the transition state was envisaged and the polar effects of the substituents on rates over wide ranges of polarity were therefore not expected to be linearly related to σ values.

Kochi and Hammond[66] have studied the rates of solvolysis of m- and p- substituted benzyl tosylates in aqueous acetone. Although the p-nitro and meta-substituents gave an adequate fit to the Hammett equation, the σ values which these authors obtained for the p-methyl and p-methoxy substituents were more negative than the standard σ values, the divergence being greater for the p-methoxy group. They suggested that the deviation of the p-methyl and p-methoxy groups showed that in addition to the large increase in ionic character in, and the normal resonance stabilisation of, the transition state of benzyl tosylates, there is possibly an additional amount of ionic character and certainly an exceptional increase in resonance stabilisation when these two substituents are present due to the interaction of these groups with the electron deficient aromatic ring. A similar explanation to account for divergencies from Hammett plots has been put forward by de la Mare[90] who emphasised that the standard σ values reflect to a greater extent the inductive rather than the tautomeric effect of substituents.

Numerous attempts have been made to take into account these conjugative effects of substituents, not allowed for in the original σ values.

Brown and co-workers[84,85,91,92] investigated the solvolysis rates of m- and p-substituted phenyldimethylcarbinyl chlorides in aqueous acetone, a reaction believed to proceed via the formation of the phenyldimethylcarbonium ion in the transition state. Meta-substituents were assumed to have little, if any, conjugative effect and in fact a plot of the rate constants against the standard σ values revealed a good linear relationship[†]. The reaction constant ρ was thus determined. Using this value for ρ and the rate data for the p-substituted compounds, a new set of substituents constants σ^+ were calculated for the para-substituents from the modified Hammett equation,

$$\log k_X/k_H = \rho\sigma^+ \qquad \text{.........V-2.}$$

These σ^+ values allow for resonance interactions between the para-substituents and the electron-deficient centre in the transition state and thus represent inductive effects (represented by the standard σ values) together with these conjugative effects.

Brown[93] applied these σ^+ values to the solvolysis

[†] For the m-nitro and m-methoxy groups the use of the standard σ values caused large deviations from the Hammett plot. New σ values for these groups were therefore calculated.

of substituted triphenylcarbinyl chlorides in 40% ethanol - 60% ethyl ether[94], and substituted benzhydryl chlorides in ethanol[95,96] and *iso*-propyl alcohol[97]. Good correlations were obtained.

Taft[98], using an approach analogous to that employed by Hammett, developed a procedure for quantitatively evaluating inductive effects. A polar substituent constant, σ^*, for a group R relative to the CH_3 group was defined by the equation,

$$\sigma^* = \frac{1}{2.48}\left[\log(k/k_o)_B - \log(k/k_o)_A\right]$$

The symbol k refers to the rate constant for the normal hydrolysis of an ethyl ester of the formula $R\,CO_2C_2H_5$; k_o is the rate constant for ethyl acetate. The subscripts B and A refer to the alkaline saponification and the acid-catalysed hydrolysis reactions, respectively, under otherwise identical conditions of solvent and temperature. The factor 1/2.48 is a constant introduced in an attempt to put the polar effects obtained in this manner on about the same scale as for the Hammett σ values.

The σ^* values have been found to correlate in a quantitative manner the effects of structure on a variety of reaction rates and equilibria of the general type

$$R - Y + Z \rightleftharpoons P$$

(where R is the substituent, Y the functional group, Z the reagent, and P the reaction transition state or the reaction products) given relative to that for the CH_3-Y molecule[99]. The correlation equation is

$$\log\ (k/k_0) = \sigma^* \rho^* \qquad ....V-3$$

where ρ^* is the reaction susceptibility constant analogous to the ρ of the Hammett equation.

It should be stressed that Eqn.V-3 is implied to fail for those reaction series within which there are substantial resonance effects on the rate constants. The series of substituted benzyl chlorides at present being investigated cannot therefore be discussed in terms of this equation.

Brown's treatment,which allows for conjugative in addition to inductive effects, is however highly relevant and the present results will now be discussed using this approach.

Rate constants at 50°C, calculated from data published by Olivier[37], Bennett and Jones[38], Simonetta and Favini[100] and Bensley and Kohnstam[15] have been used to supplement data obtained in the present investigation. Table V-2 summarises the data for the solvolysis of <u>meta</u>-substituted benzyl chlorides in 50% aqueous acetone. It has already been pointed out (page 84) that the σ values for the <u>m</u>-nitro and <u>m</u>-methoxy groups obtained by Brown differed significantly from the Hammett standard σ values and ρ has therefore been calculated using both. In all other cases only the standard

σ values, from the compilation by Jaffé[88], have been used. In order to minimise the effect of solvent variation on the rates, where Olivier's rate constants have been used, his data for the unsubstituted compound were used also; similarly for the results of Bennett and Jones. Simonetta and Favini publish no data for the unsubstituted compound and the data of Bensley and Kohnstam were therefore used in connection with the *m*-methoxy substituent. The results of Bennett and Jones for *m*-nitro-, *m*-iodo-, *m*-bromo- and *m*-chlorobenzyl chlorides lead to similar ρ values as those shown in Table V-2.

TABLE V - 2

SOLVOLYSIS OF META-SUBSTITUTED BENZYL CHLORIDES IN 50% AQUEOUS ACETONE AT 50°C.
(k in $sec.^{-1}$)

Substituent	σ	10^7 k	ρ	Refer.
(H)	-	31.03	-	15
NO_2	0.662[a] or 0.710[b]	3.087	-1.476[a] or -1.376[b]	37
CN	0.678	3.930	-1.286	37
I	0.352	5.495	-2.064	37
Br	0.391	5.637	-1.830	37
Cl	0.373	5.676	-1.910	37
F	0.337	6.936	-1.867	38
COOH	0.355	7.982	-1.590	37
$CONH_2$	0.280	12.77	-1.287	37
CH_3O	0.0465[a] or 0.115[b]	23.33	-2.662[a] or -1.076[b]	100
CH_3	-0.069	35.38	-1.191	37

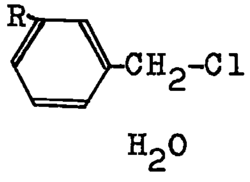
[a] Using Brown's σ [b] Using standard σ (Jaffé)

It is noteworthy that the meta-substituents do not lead to a constant value for ρ. The "true" value of σ for m-methoxybenzyl chloride appears to lie between the two values quoted.

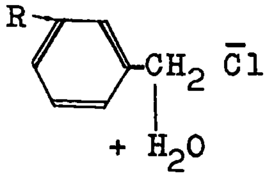
The basic requirement of the Hammett equation is that the substituent donates the same number of electrons in all reactions. This condition is however unlikely to be obeyed since the degree of charge development at the reaction centre in the transition state is not always the same i.e. there is differing electron demand. However, this factor can be allowed for in the ρ values and the relation would then hold provided (i) there is the same electron demand at the reaction centre in a given reaction and (ii) the response of substituents to electron demand is proportional to that demand in all cases.

The second of these conditions is obeyed for meta-substituents, where electron movements occur essentially by the inductive mechanism. There is however no guarantee that the degree of charge development at the reaction centre is always the same in the series of meta-substituted benzyl chlorides, at present under consideration.

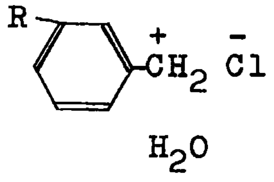
The transition state structure may be regarded as the resonance hybrid of the following three canonical structures (see page 10), where R is the <u>meta</u>-substituent.



I



II



III

As the electron attracting power of R decreases the transition state structure will change in the direction of increased S_N1 character i.e. an increased contribution from structure III. This increase in charge development in the transition state causes an increase in the electron demand at the reaction centre and thus the first of the above conditions, viz. the same electron demand at the reaction centre, is not obeyed. If this view is correct a steady decrease in the value of ρ as the rate constant increases would be expected. This is however not observed (Table V-2). The likely explanation is that a second order relay of conjugative effects occurs in the molecule. This effect must be greater for the methoxy group than for the methyl in the present case relative to the ionisation of the corresponding benzoic acids.

Nevertheless, despite the large deviations found in calculating ρ from <u>meta</u>- σ values, a mean value will be accepted in discussing the effect of <u>para</u>-substituents. Rate constants for the solvolysis of <u>para</u>-substituted benzyl chlorides in aqueous acetone were predicted using Brown's σ^+ values, with $\rho = -1.918$, the mean of the values obtained for the <u>meta</u>-iodo, bromo, chloro, and fluoro compounds. Table V-3 compares these rate constants with the observed values.

<u>TABLE V - 3</u>

SOLVOLYSIS OF PARA-SUBSTITUTED BENZYL CHLORIDES IN 50% AQUEOUS ACETONE AT 50°C.

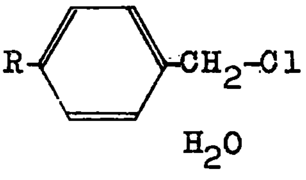
Substituent	σ^+	$(k/k_H)_{calc.}$	$(k/k_H)_{obs.}$	Ref.
NO_2	0.777	0.03243	0.0887	37
I	0.132	0.5582	0.460	37
Br	0.148	0.5201	0.502	37
Cl	0.112	0.6098	0.575	37
F	-0.0714	1.371	1.776	38
Me	-0.306	3.863	8.35	37
MeO	-0.764	29.17	4.677×10^4	-

Agreement is satisfactory for the <u>p</u>-halogen compounds while for the <u>p</u>-nitro and <u>p</u>-methyl compounds the Eqn.V-2 predicts rate constants within a factor of three. With the <u>p</u>-methoxy compound however serious discrepancies occur, the observed rate being greater than the calculated rate by a factor of about 10^3. Brown's σ^+ values are clearly not applicable to the benzyl system though it should be noted that Brown has never claimed that they would apply to this system.

An approach similar to that used in discussing the effects of meta-substituents may be employed in order to account for these observations.

When para-substitution in the benzene ring is considered, conjugative effects (which operate to only a slight extent for meta-substituents) now play a prominent role. Brown's σ^+ values allow for conjugative electron release from the substituent to the reaction centre in the transition state. For σ^+ values to be of general application the substituent must donate the same number of electrons in all reactions where conjugation is possible. This condition is unlikely to be realised since the charge development at the reaction centre in the transition state is not always the same thus causing differing electron demand at the reaction centre. This difference in electron donation can be allowed for in the ρ values and Brown's modification of the Hammett equation would therefore hold provided firstly there is the same electron demand at the reaction centre in a given reaction and secondly the response of substituents to the electron demand is proportional to that demand in all cases. The two conditions will be considered by reference to the transition state structure for three para-substituted benzyl chlorides reacting by widely different mechanisms.

The transition state for the hydrolysis of a para-substituted benzyl chloride can be regarded as the resonance hybrid of the following three canonical structures, where R is the substituent.



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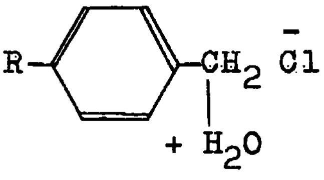
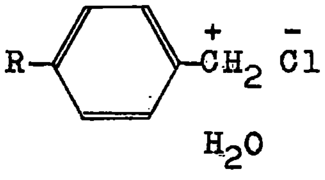


II



III

It has already been shown that in 50% acetone p-methoxybenzyl chloride reacts by mechanism S_N1, p-methylbenzyl chloride is border-line and p-nitrobenzyl chloride goes by mechanism S_N2. In the transition state structure for the three cases there are thus varying contributions from structure III relative to structure II, the greatest contribution from III being for the p-methoxy compound and the least for the p-nitro compound. Each transition state thus has a different degree of charge development and consequently a varying electron demand. The first of the conditions necessary for a Hammett-type correlation using Brown's σ^+ values is therefore not satisfied.

The electron demand will be satisfied by conjugation since groups in the *para*-position can conjugate with the reaction centre. The extent to which conjugation can occur in order to satisfy this demand depends on the relative contribution from structure III.

The *p*-methoxy group can conjugate particularly effectively with the reaction centre due to the presence of unshared p-electrons. It is evident that the second condition, viz. the response of substituents to the electron demand being proportional to the demand, is unlikely to be obeyed.

It is noteworthy that the observed rate of solvolysis of *p*-methoxybenzyl chloride exceeds the predicted rate by a factor of 1,600 whereas the corresponding factor for the *p*-methyl compound is 2. This emphasises the extensive conjugation of the *p*-methoxy group in the transition state.

Mechanistic Change.

Okamoto and Brown[93] found that when the σ^+ constants were applied to the results obtained by Hammond[66] for the solvolysis of *meta*- and *para*-substituted benzyl tosylates in aqueous acetone, a simple linear relationship was not obtained. Electron-supplying substituents (*p*-methyl, *p*-methoxy) appeared to lie on a different line to electron-withdrawing substituents. They explained this in terms of a duality of mechanism. Benzyl tosylates containing electron-supplying substituents were envisaged as reacting by mechanism S_N1, thereby following the σ^+ constants. With electron-withdrawing substituents, this path was regarded as being less favourable than a bimolecular displacement by the solvent (S_N2) and the reaction rates would then follow the standard σ values.

In a recent paper, Hammond and co-workers[101] applied Brown's σ^+ values to the solvolysis of benzyl tosylates and found a lack of correlation between the rates and the σ^+ values, the p-methoxy compound deviating considerably from the linear plot. These authors maintained that if two distinctly different mechanisms are involved, the two reaction types would be expected to show different responses to solvent changes i.e. the ionisation rates would be expected to slow down much more than the rates of a direct displacement if the water content of the solvents were reduced. This was not observed and these workers concluded that changes in the reaction type must be more subtle and continuous than is implied by the "two mechanisms" analysis.

Conclusion

The consideration of the transition state structure in the preceding pages, together with the examination of the experimental results, leads to the conclusion that a single set of σ^+ values cannot be used to accommodate the effects of para-substituents and it is therefore preferable to use Ingold's approach[2] and discuss reactions of this type in terms of polarisation and polarisability effects, and the reaction mechanism.

CHAPTER VI

EXPERIMENTAL

Preparation and Purification of Materials

p-Methylbenzyl Chloride.

p-Methylbenzyl chloride was prepared from p-toluic acid via the following reactions.

$$RCOOH \longrightarrow RCOOC_2H_5 \longrightarrow RCH_2OH \longrightarrow RCH_2Cl$$

The ethyl ester of p-toluic acid was prepared by refluxing recrystallised p-toluic acid (56 gm.) (melting point 179°-180°C) with absolute alcohol (120 gm.) in the presence of conc. H_2SO_4 (12 gm.) for 3 hours. The greater part of the alcohol was then distilled off, and the product was poured into about five times its volume of distilled water and neutralised with solid sodium carbonate. The ester was extracted with ether and this ethereal solution dried over anhydrous potassium carbonate. After the ether had been distilled off, the ester was purified by distillation under reduced pressure. Refractive index of ester $n_D^{22^\circ} = 1.5084$

This ester was then reduced to p-methylbenzyl alcohol in the following way. The ester (52 gm.) dissolved in dry ether (600 ml.) was added from a dropping funnel to lithium aluminium hydride (12 gm.) suspended in dry ether (1 litre), the rate of addition being adjusted to maintain a gentle reflux. A steady flow of nitrogen was passed through the apparatus during this operation. After the excess lithium aluminium hydride had been destroyed by the addition of an ethereal solution of ethyl acetate, 10% H_2SO_4(600 ml.) was cautiously added. The ethereal layer was separated, washed in succession with water, sodium carbonate solution and water, and finally dried over anhydrous potassium carbonate. The ether was removed by distillation and the alcohol purified by recrystallisation from petroleum ether (40°-60°). Melting point of p-methylbenzyl alcohol = 61°C.

p-Methylbenzyl chloride was prepared by passing hydrogen chloride gas through an ethereal solution (100 ml.) of the alcohol (15 gm.), containing granular calcium chloride, for 12 hours at 0°C. After the excess HCl and most of the ether had been removed by distillation, dry ether was added to the residue. This ethereal solution was washed successively with water, sodium bicarbonate solution and water and finally dried over potassium carbonate. The chloride was then frozen out and purified by distillation under reduced pressure. The hydrolysable chloride content of the sample was identical with the theoretical amount.

p-Methoxybenzyl Chloride.

p-Methoxybenzyl chloride was prepared by passing hydrogen chloride gas through a solution of anisyl alcohol (50 gm.) in dry ether (250 ml.), containing 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°) was added to the residue. This solution was washed with water, sodium bicarbonate solution, and water, in that order and then dried over potassium carbonate. The chloride was frozen out and purified by distillation under reduced pressure. The hydrolysable chloride content of the sample was 99.1% of the theoretical amount.

p-Methylbenzylidene Chloride.

p-Methylbenzylidene chloride was prepared by treating p-tolualdehyde (10 gm.) dissolved in petroleum ether (40°-60°) (60 ml.) with phosphorus pentachloride until the latter ceased to dissolve[102]. The petroleum ether, the oxychloride and the p-methylbenzylidene chloride were then successively distilled off, the latter two compounds under reduced pressure. The chloride was purified by recrystallising it twice from ethanol and twice from petroleum ether (40°-60°). The hydrolysable chloride content of the sample was identical with the theoretical amount; melting point of chloride = 47.5°C.

p-Nitrobenzyl Chloride.

p-Nitrobenzyl chloride (Light's) was recrystallised twice from ethanol. The hydrolysable chloride content of the sample was 99.3% of the theoretical amount; melting point of chloride = 70°C.

Solvents.

"50%" aqueous acetone was made up by mixing 500 volumes acetone and 500 volumes water. The acetone was the Analar product which had been refluxed with sodium hydroxide and potassium permanganate for two hours[103] before being fractionated from hydroquinone and the water was distilled water which had been passed down a column containing mixed ion exchange resin. The "70%" and "80%" solvents were made up in an analogous manner.

When more than one batch of solvent was used every batch was monitored by examining the rate of hydrolysis of the same compound at the same temperature in them.

Titration acetone.

The acetone used for titrations was the commercial product which was distilled after being refluxed with sodium hydroxide and potassium permanganate for two hours. The indicator lacmoid was added and the solution neutralised before use.

Methods of Rate Measurement

Kinetic runs were carried out at temperatures ranging from -20° to 120°C. The thermostat for the range 100°- 120°C consisted of a well-lagged 20 litre beaker containing well-stirred paraffin oil, a xylene-mercury regulator, a permanent heating coil and a 100 w. intermittent electric lamp bulb heater. The 0° thermostat consisted of a bath of well-stirred melting ice. The thermostat for temperatures below 0° consisted of a well-stirred ethanol-water mixture in a large Dewar vessel. Cooling was effected by filling the inner of two concentric glass tubes with solid carbon dioxide, and the outer with sufficient acetone to keep the temperature of the bath just below the desired temperature in the absence of heating. A 5 w. intermittent heater was included to maintain a constant temperature. The other thermostats were of conventional design. The 10° thermostat contained, in addition, a coil of copper tubing through which cooled water circulated. At temperatures below 100° the temperature was constant to within ± 0.01°; at 100° and above, ± 0.02°. Thermometers standardised to ± 0.02°C by the National Physical Laboratory were used for temperature measurement.

The hydrolysis of the chlorides always went to completion and velocity constants could therefore be calculated from a knowledge of the acidity after various time intervals and at 100% reaction without the necessity of using weighed amounts of chlorides.

Two methods were used for following kinetic runs.

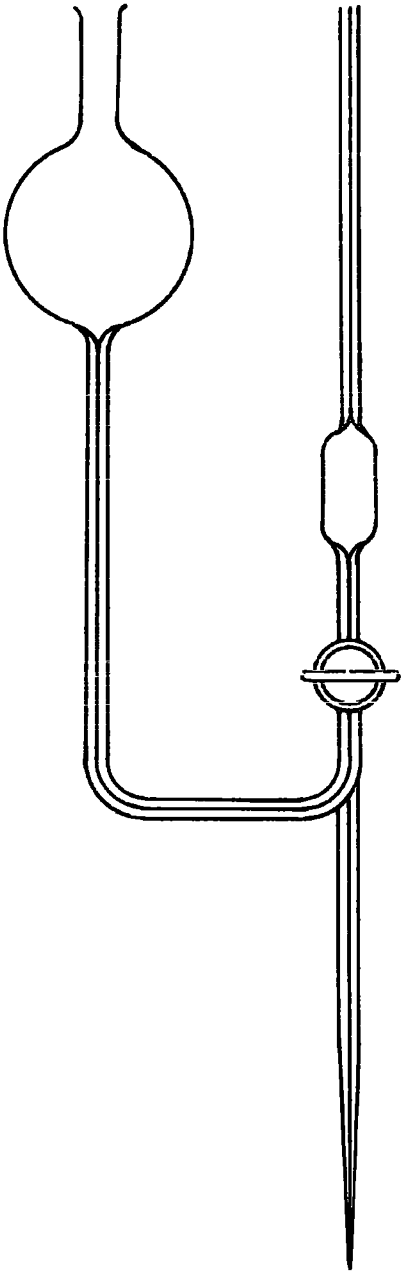
Flask Runs.

In general this method was used at temperatures of 30° and under although it was used at 40° for a fast reaction. The chloride was added to about 100 ml. of the solvent in a stoppered flask at the thermostat temperature and the flask thoroughly shaken. After suitable time intervals 5 ml. samples were removed by means of a pipette and run into about 200 ml. of neutralised acetone to stop the reaction. The acidity of this solution was determined by titration with standard sodium hydroxide, lacmoid being used as the indicator.

Tube Runs.

This method was used at temperatures above 30° where the possibility of evaporation of solvent from the reaction flask during extraction made the use of the previous method undesirable. The chloride was added to about 100 ml. of solvent and well shaken. The reaction mixture was pipetted into tubes using the apparatus shown in Fig.VI-1. The tubes were sealed off, attached to shakers and placed in the

FIGURE VI 1



TUBE FILLER

thermostat in batches of about seven. Each batch was shaken vigorously for about two minutes. After suitable time intervals, tubes were removed from the thermostat and plunged into a carbon dioxide - acetone bath to stop the reaction. They were then cleaned, broken under neutralised acetone and the acidity determined as before.

Calculation of the Results

Rate Constants.

First order rate constants were calculated from the equation

$$k = 2.303 / t.\log(a/a-x)$$

where t is the time in seconds and "a" and "a-x" are the concentrations of the alkyl halide at $t = 0$ and $t = t$ respectively. The time of the first reading was taken as zero, "a" being the difference between the first reading and the reading when the reaction had gone to completion (10 times the half life period). Details of individual runs are given in the Appendix to this Chapter.

When more than one batch of solvent was used for carrying out the experiments in a particular series, the results in one solvent were made comparable with those in another by monitoring each solvent, i.e., comparing the rate constants for the same chloride at the same temperature in each.

The mean rate coefficients, k_m, were obtained by statistical treatment of at least two runs at any one temperature, the runs being considered as one for statistical purposes. The standard deviation of the final mean rate coefficient, $\sigma(k)$, was obtained from Eqn.VI-1

$$\sigma(k) = \frac{\left[\Sigma(k - k_m)^2\right]^{1/2}}{n} \qquad \text{..............VI-1}$$

where n was the number of separate determinations of k. Individual rate constants differing from the mean by more than 2½ σ_{each}, where $\sigma_{each} = n^{1/2}\sigma$, were rejected and a new $\sigma(k)$ found.

Activation Parameters.

The activation energy, E, at the temperature $(T_1 + T_2)/2$ (see page 39) was calculated from the mean rate coefficients at adjacent temperature intervals using Eqn.VI-2.

$$E = \frac{2.303\ RT_1T_2}{T_2 - T_1}\log\frac{k_2}{k_1} \qquad \text{...........VI-2}$$

where k_1 and k_2 are the mean rate coefficients at the absolute temperatures T_1 and T_2 respectively.

The standard deviations of E, σ (E), was obtained from Eqn.VI-3[104].

$$\sigma\,(E) = \frac{RT_1T_2}{T_2 - T_1}\left[\left(\frac{\sigma_1}{k_1}\right)^2 + \left(\frac{\sigma_2}{k_2}\right)^2\right]^{1/2} \qquad \text{........VI-3}$$

where σ_1 and σ_2 are the standard deviations of the mean rate coefficients, k_1 and k_2. It should be noted that this standard deviation, σ (E), is not the maximum possible error.

The temperature coefficient of activation energy, dE/dT, was calculated from the 'best' straight line E vs. T by a least squares method on the assumption that E is linearly dependent on temperature.

$$\text{Then} \qquad E = E_o + \frac{dE}{dT}\,.\,T \qquad \text{........VI-4}$$

whence the least squares value of dE/dT is given by Eqn.VI-5

$$\frac{dE}{dT} = \frac{\Sigma(E - E_m)(T - T_m)}{\Sigma(T - T_m)^2} \qquad \text{.........VI-5}$$

where E_m is the mean of the experimental activation energies and T_m is the mean of the temperatures. E can be calculated at any temperature from

$$E = E_m + \frac{dE}{dT}(T - T_m)$$

The standard deviation of dE/dT was obtained in two ways:-

(i) From the 'best' straight line E vs. T using Eqn.VI-6

$$\sigma\left(\frac{dE}{dT}\right) = \left[\frac{\Sigma(E_{obs.} - E_{calc.})^2}{(n - 2)\ \Sigma(T - T_m)^2}\right]^{1/2} \qquad \ldots\ldots\ldots VI\text{-}6$$

where n is the number of determinations of E.

(ii) From σ(E) using Eqn.VI-7

$$\sigma\left(\frac{dE}{dT}\right) = \frac{\left[\Sigma(\sigma(E))(T - T_m)^2\right]^{1/2}}{\Sigma(T - T_m)^2} \qquad \ldots\ldots\ldots VI\text{-}7$$

Both values are quoted in Tables III-1 to III-8 though Tables IV-1 and IV-2 contain only the larger of the two values.

The entropy of activation, ΔS^*, at the temperature $(T_1 + T_2)/2$ was calculated from Eqn.VI-8 (see page 43)

$$\ln k_1 = \ln\left(\frac{\bar{k}}{h}\right) + \ln\frac{(T_1 + T_2)}{2} + 1 + \frac{\Delta S^*}{R} - \frac{E}{RT_1} \quad \ldots VI\text{-}8$$

where k_1 refers to the temperature T_1, and E to $(T_1 + T_2)/2$

A value for the heat capacity of activation, ΔC^*, was obtained from the 'best' straight line ΔS^* vs. log T.

$$\text{Since} \quad \frac{d(\Delta S^*)}{dT} = \frac{(\Delta C^*)}{T} \qquad \ldots\ldots\ldots\ldots VI\text{-}9$$

Then, by integration

$$\Delta S^* = \Delta S^*_0 + 2.303\ \Delta C^* \log T \quad \ldots VI\text{-}10$$

Therefore

$$\Delta C^* = \frac{1}{2.303} \; \frac{\Sigma(\Delta S^* - \Delta S^*_m)(\log T - \log T_m)}{\Sigma(\log T - \log T_m)^2} \qquad \ldots\ldots VI\text{-}11$$

where ΔS^*_m is the mean of the experimental entropies of activation, and T_m the mean of the experimental temperatures. ΔC^*, calculated in this way, was always in good agreement with ΔC^*, obtained from dE/dT using the relation

$$dE/dT = R + \Delta C^*$$

where R is the gas constant.

ΔS^* could be calculated at any temperature by means of Eqn.VI-12

$$\Delta S^* = \Delta S^*_m + 2.303\, \Delta C^*(\log T - \log T_m) \qquad \ldots\ldots VI\text{-}12$$

The standard deviation of ΔS^*, $\sigma(\Delta S^*)$, can be obtained from Eqn.VI-13[104].

$$\sigma(\Delta S^*) = \frac{R}{T_2 - T_1} \sqrt{\left(T_1 \cdot \frac{\sigma_1}{k_1}\right)^2 + \left(T_2 \cdot \frac{\sigma_2}{k_2}\right)^2} \qquad \ldots\ldots VI\text{-}13$$

It can be shown however that Eqn.VI-14 holds true approximately and this has been used here,

$$\sigma(\Delta S^*) \simeq \frac{\sigma(E)}{T} \qquad \ldots\ldots\ldots\ldots\ldots\ldots VI\text{-}14$$

Since $\sigma(E_{calc.}) = (T - T_m)\,\sigma\left(\frac{dE}{dT}\right)$

then $\sigma(\Delta S^*_{calc.}) = \left(\frac{T - T_m}{T}\right)\sigma\left(\frac{dE}{dT}\right) \qquad \ldots\ldots\ldots\ldots VI\text{-}15$

Activation Parameters for the reaction of p-Methoxybenzyl Chloride in 50% aqueous acetone.

Values for k (50°), E (50°) and $\Delta S^*(50^\circ)$ for p-methoxybenzyl chloride in 50% aqueous acetone, an S_N1 reaction (see page 61) were obtained by the following procedure.

Using the expression

$$\Delta S^*_{T_1} = \Delta S^*_{T_2} + 2.303\,\Delta C^* \log(T_1/T_2),$$

values for $\Delta C^*/\Delta S^*$ at 0° were calculated for tert.-BuCl, $PhCHCl_2$, $PhCCl_3$ and p-$Me.C_6H_4.CHCl_2$, all S_N1 compounds, from values at 50°. The mean value for $\Delta C^*/\Delta S^*$ at 0° was 5.64. Since for p-$MeO.C_6H_4.CH_2Cl$, $\Delta S^*(0^\circ) = -3.01$, then $\Delta C^* = -17.0$ giving $dE/dT = -15.0$. The following values are then obtained:-

$k(50^\circ) = 1.455\text{x}10^{-1}\text{sec}^{-1}$ $E(50^\circ) = 18.94$ $\Delta S^*(50^\circ) = -5.84$

Since the standard errors in the two values of E, separated by a temperature interval of 10°, are ± 0.06 kcal. (see Table III-4), the value $dE/dT = -15.0$ is not inconsistent with the experimental results.

Concentration Effects.

The rates of solvolysis of p-methoxybenzyl and p-methylbenzylidene chloride in 50% aqueous acetone were found to be affected by changes in the concentration of the organic chloride in the following manner.

p-Methoxybenzyl Chloride at 0.00°C.

Concn. of Chloride	10^4k(sec.$^{-1}$)	Change in Rate
0.0169 M	5.764	1.8 %
0.0113 M	5.873	

p-Methylbenzylidene Chloride at 19.46°C.

Concn. of Chloride	10^5k(sec.$^{-1}$)	Change in Rate
0.0103 M	7.799	2.0 %
0.00570 M	7.954	

All experiments using p-methoxybenzyl chloride were therefore carried out at the same concentration. For the solvolysis of p-methylbenzylidene chloride it was necessary to use the chloride at a higher concentration in the upper temperature range and at a lower concentration at lower temperatures due to the suspected incomplete solubility of the compound at 0°C. Two series of runs at 19.46°C (quoted above) were carried out and used to obtain rate constants relating to the same concentration over the complete temperature range.

Effect of Added HCl

As already pointed out in Chapter III, experiments were carried out in the presence of approximately 0.02 N HCl to establish whether this concentration effect arises out of competing ionic-strength and mass-law effects.

Solvolysis of p-methoxybenzyl chloride in 70% aqueous acetone at 29.88°C in the presence of HCl.

Added HCl	10^4k(sec.$^{-1}$)	Change in Rate	Change for 0.02 N HCl
-	7.048	-	-
0.02250 N	6.788	-3.7 %	-3.0 %
0.01777 N	6.884	-2.3 %	

Solvolysis of p-methylbenzylidene chloride in 50% aqueous acetone at 24.76°C in the presence of HCl.

Added HCl	10^4k(sec.$^{-1}$)	Change in Rate	Change for 0.02 N HCl
-	1.391	-	-
0.01545 N	1.365	-1.9 %	-1.7 %
0.01697 N	1.380	-0.8 %	

CHAPTER VI, APPENDIX

Solvolysis of p-Methylbenzyl Chloride, p-Methoxybenzyl Chloride, p-Nitrobenzyl Chloride and p-Methylbenzylidene Chloride in Aqueous Acetone.

Details of Individual Runs.

First order rate constants were calculated from the equation,

$$k = 2.303 / t.\log (a/a-x)$$

where k is the rate constant in $\sec.^{-1}$,

t is the time in seconds,

a is the concentration of alkyl chloride at t = 0,

a-x is the concentration of alkyl chloride at t = t.

Titres are expressed in ml. of NaOH per sample.

In each case details of one run are given and the mean rate coefficients k', k'', etc. of duplicate runs are also quoted.

In the solvolysis of p-methylbenzylidene chloride it was assumed that after the first chlorine atom had been hydrolysed off, the second one instantly followed it.

Expt.1. p-Methylbenzyl Chloride in 50% aq.Acetone I at 29.55°C

5.315 ml. titrated with 0.009931 N NaOH

Time	Titre	10^6 k
0	0.03	-
61800	1.53	2.684
92280	2.20	2.706
149400	3.31	2.720
186780	3.96	2.739
233880	4.71	2.770
264060	5.03	2.695
320460	5.74	2.715
326760	5.80	2.762
495780	7.36	2.770
520320	7.54	2.782
586200	7.93	2.783
689460	8.38	2.755
755760	8.63	2.758
∞	9.85	-
- - - - -	- - - - -	- - - - -
470500	0.02	-
433500	6.86	2.745
458820	7.04	2.725
∞	9.85	-

k = = 2.740 (15 readings)

k' = 2.768 (13 readings)

k'' = 2.723 (9 readings)

k''' = 2.703 (14 readings)

Mean k = 2.735 ± 0.00607

Expt.2. p-Methylbenzyl Chloride in 50% aq.Acetone I at 39.98°C

5.315 ml. titrated with 0.01085 N NaOH

Time	Titre	10^6 k
0	0.05	-
41880	3.33	(8.458)
51840	4.07	8.775
68640	5.03	8.782
127260	7.46	8.802
137640	7.44	(8.095)
156480	8.29	8.840
223680	9.55	8.912
241620	9.80	9.002
∞	11.05	-

Time	Titre	10^6 k
0	0.06	-
11620	1.09	8.537
28740	2.50	8.735
87180	5.91	8.717
97740	6.42	8.847
116100	7.10	8.837
183480	8.88	8.845
219540	9.00	8.863
∞	11.05	-

k = 8.807 (13 readings)

k' = 8.757 (13 readings)

Mean k = 8.782 ± 0.0228

Expt.3. p-Methylbenzyl Chloride in 50% aq.Acetone I at 50.09°C

5.315 ml. titrated with 0.009931 N NaOH

Time	Titre	10^5k
0	0.06	-
55680	8.88	2.602
60960	9.22	2.595
66900	9.57	2.605
76020	10.00	2.605
86760	10.40	2.617
∞	11.59	-
0	1.05	-
3720	2.00	2.538
7200	2.83	2.568
11700	3.80	2.585
14880	4.39	2.567
18900	5.13	2.590
22620	5.71	2.580
26940	6.28	2.545
33960	7.14	2.540
39260	7.89	2.602
∞	11.59	-

k = 2.581 (14 readings)

k' = 2.575 (9 readings)

Mean k = 2.578 ± 0.00592

Expt.4 p-Methylbenzyl Chloride in 50% aq.Acetone I at 60.12°C

5.301 ml. titrated with 0.009951 N NaOH

Time	Titre	10^5 k
0	1.40	-
1860	2.69	6.908
5340	4.73	6.987
7140	5.58	6.945
8880	6.34	6.982
10080	6.80	6.978
27240	10.50	6.983
∞	12.09	-
0	3.65	-
9060	7.62	7.015
10800	8.11	6.960
12420	8.51	6.905
14264	9.01	7.062
16110	9.98	(8.607)
∞	12.09	-

k = 6.973 (10 readings)

k' = 6.957 (11 readings)

Mean k = 6.963 ± 0.0103

Expt.5. p-Methylbenzyl Chloride in 50% aq.Acetone I at 69.99°C

5.315 ml. titrated with 0.009931 N NaOH

Time	Titre	10^4 k
0	0.18	-
600	1.33	(1.639)
800	3.45	1.720
3000	5.26	1.780
4320	6.70	1.753
5940	8.09	1.740
8280	9.60	1.758
∞	12.46	-
0	0.13	-
1260	2.53	1.720
2460	4.41	1.733
3900	6.23	1.752
4860	7.21	1.753
7140	8.93	1.753
9780	10.27	1.767
∞	12.46	-

k = 1.748 (11 readings)
k' = 1.738 (8 readings)
k'' = 1.740 (12 readings)
Mean k = 1.742 ± 0.00305

Expt.6 p-Methylbenzyl Chloride in 50% aq.Acetone IV at 29.89°C

4.330 ml. titrated with 0.007676 N NaOH

Time	Titre	10^6 k
0	0.03	-
58410	1.76	2.734
87420	2.47	(2.672)
145620	3.89	2.741
172080	4.44	2.741
231540	5.54	2.741
258120	6.03	2.776
317520	6.92	2.789
345360	7.20	2.739
∞	11.76	-

0	0.12	-
27480	0.98	2.741
34554	1.28	2.764
517740	9.00	2.781
546480	9.22	2.787
603480	9.56	2.762
631320	9.69	2.739
690060	10.03	2.764
778680	10.38	2.739
∞	11.76	-

k = 2.756 (15 readings)
k' = 2.782 (14 readings)
k'' = 2.766 (10 readings)

Corrected to Solvent I Mean k = 2.767 ± 0.00455

Expt.7. p-Methylbenzyl Chloride in 50% aq.Acetone IV at 39.79°C

4.330 ml. titrated with 0.008702 N NaOH

Time	Titre	10^6 k
0	0.17	-
43380	3.44	8.523
58560	4.34	8.558
70740	4.97	8.548
129300	7.19	8.428
150660	7.95	8.490
216180	9.07	8.513
∞	10.75	-
0	0.24	-
14400	1.42	(8.272)
27360	2.41	8.452
86040	5.69	8.500
101460	6.29	8.450
113700	6.73	8.455
172860	8.36	8.468
186240	8.60	8.522
∞	10.75	-

k = 8.492 (12 readings)
k' = 8.500 (13 readings)

Corrected to Solvent I Mean k = 8.500 ± 0.00932

Expt.8 p-Methylbenzyl Chloride in 50% aq.Acetone IV at 49.60°C

4.330 ml. titrated with 0.007676 N NaOH

Time	Titre	10^5 k
0	0.24	-
48720	8.95	2.384
55320	9.54	2.390
63480	10.19	2.420
72600	10.79	2.457
85260	11.34	2.444
∞	12.92	-
0	1.09	-
3780	2.12	2.412
7320	3.00	2.404
12540	4.17	2.407
14940	4.66	2.405
18300	5.32	2.419
21660	5.95	2.444
25200	6.50	2.425
28920	7.10	2.454
36600	8.00	2.397
∞	12.92	-

k = 2.419 (14 readings)

k' = 2.419 (10 readings)

Corrected to Solvent I Mean k = 2.419 ± 0.00448

Expt.9 p-Methylbenzyl Chloride in 50% aq.Acetone IV at 59.60°C

5.330 ml. titrated with 0.008702 N NaOH

Time	Titre	$10^5 k$
0	1.51	-
1980	2.64	6.596
3840	3.55	6.501
5520	4.32	6.573
16320	7.61	6.615
18120	7.98	6.651
21660	8.54	6.623
24960	8.98	6.623
∞	10.75	-

Time	Titre	$10^5 k$
0	1.73	-
7680	5.30	6.565
9000	5.74	6.538
10620	6.29	6.635
12420	6.80	6.651
14640	7.30	6.568
∞	10.75	-

k = 6.595 (12 readings)
k' = 6.583 (12 readings)

Corrected to Solvent I Mean k = 6.588 ± 0.00918

Expt.10 p-Methylbenzyl Chloride in 50% aq.Acetone IV at 69.91°C

4.330 ml. titrated with 0.007676 N NaOH

Time	Titre	10^4 k
0	1.30	-
660	2.49	1.762
1200	3.32	1.719
1800	4.28	(1.789)
3000	5.70	1.737
3840	6.58	1.740
4200	6.88	1.725
4800	7.41	1.735
∞	12.13	-
0	0.31	-
2940	4.98	1.710
6000	7.96	1.737
6480	8.29	1.735
7140	8.70	1.734
8460	9.43	1.745
9540	9.87	1.735
10680	10.29	1.742
∞	12.13	-

k = 1.735 (13 readings)
k' = 1.725 (11 readings)

Corrected to Solvent I   Mean k = 1.730 ± 0.00292

Expt.11 p-Methylbenzyl Chloride in 50% aq.Acetone IV at 80.04°C

4.330 ml. titrated with 0.008702 N NaOH

Time	Titre	10^4 k
0	1.71	-
420	3.21	4.321
1260	5.46	4.254
2340	7.35	4.178
∞	10.75	-
0	2.30	-
360	3.50	4.263
1320	5.90	4.213
2520	7.84	4.233
∞	10.75	-
0	0.97	-
900	4.00	4.121
1920	6.38	4.198
∞	10.75	
0	2.29	-
780	4.70	4.299
1800	6.81	4.248
2880	8.27	4.263
∞	10.75	-

k = 4.236 (11 readings)

k' = 4.233 (13 readings)

Corrected to Solvent I Mean k = 4.233 ± 0.0115

Expt.12 p-Methoxybenzyl Chloride in 50% aq.Acetone III at -10.07°C

5 ml. titrated with 0.005328 N NaOH

Time	Titre	10^4 k
0	0.75	-
521	1.60	(1.556)
1116	2.41	1.480
1697	3.20	1.498
2331	3.98	1.505
2914	4.55	1.469
3546	5.23	1.491
4652	6.10	1.449
5949	7.06	1.452
7020	7.77	1.470
8346	8.44	1.462
9266	8.86	1.468
10655	9.40	1.479
∞	11.66	-

k = 1.475 (11 readings)

k' = 1.470 (10 readings)

Corrected to Solvent I Mean k = 1.495 ± 0.00299

Expt.13 p-Methoxybenzyl Chloride in 50% aq.Acetone III at 0.00°C

5 ml. titrated with 0.005328 N NaOH

Time	Titre	10^4 k
0	1.23	-
159	2.16	6.068
350	3.11	5.876
533	3.99	5.977
704	4.70	5.967
889	5.36	5.900
1092	6.04	5.909
1409	6.90	5.832
1724	7.68	5.886
2068	8.35	5.880
2386	8.87	5.892
2823	9.43	5.888
3183	9.75	5.797
∞	11.35	-

k = 5.906 (12 readings)

k' = 5.908 (10 readings)

Corrected to Solvent I Mean k = 5.980 ± 0.0198

Expt.14 p-Methoxybenzyl Chloride in 50% aq.Acetone II at 9.97°C

5 ml. titrated with 0.005328 N NaOH

Time	Titre	10^3 k
0	1.71	-
75	2.92	(2.008)
139	3.89	2.089
243	5.18	2.110
321	5.93	2.084
394	6.62	2.128
469	7.15	2.115
589	7.87	2.114
690	8.36	2.123
761	8.61	(2.191)
832	8.83	2.083
897	9.04	2.083
∞	10.36	-

k = 2.103 (9 readings)

k' = 2.114 (9 readings)

Corrected to Solvent I Mean k = 2.143 ± 0.00407

Expt.15 p-Methoxybenzyl Chloride in 50% aq.Acetone III at 19.54°C

5 ml. titrated with 0.004666 N NaOH

Time	Titre	10^3 k
0	4.18	-
16	5.06	6.103
40	6.33	6.454
59.5	7.17	6.401
78.5	7.85	6.263
103	8.69	6.299
122	9.26	6.322
141	9.78	6.368
173	10.39	6.189
197	10.88	6.267
222	11.28	6.267
270	11.90	6.290
313	12.30	6.266
∞	13.63	-

k = 6.291 (12 readings)
k' = 6.281 (10 readings)

Corrected to Solvent I   Mean k = 6.361 ± 0.0250

Expt.16 p-Nitrobenzyl Chloride in 50% aq.Acetone IX at 70.02°C

4.370 ml. titrated with 0.008026 N NaOH

Time	Titre	10^6 k
0	0.05	-
60600	1.16	2.010
82920	1.56	2.047
147840	2.50	1.979
172740	2.82	1.954
235200	3.67	1.994
254040	3.91	2.005
317940	4.69	2.055
∞	9.72	-

Time	Titre	10^6 k
0	0.09	-
60720	1.11	(1.844)
318000	4.62	1.999
489840	6.27	2.097
531180	6.40	2.005
591840	6.83	2.034
678780	7.32	2.047
754620	7.58	1.994
∞	9.72	-

k = 2.017 (13 readings)

k' = 2.004 (14 readings)

Corrected to Solvent I Mean k = 2.040 ± 0.00718

Expt.17 p-Nitrobenzyl Chloride in 50% aq.Acetone IX at 80.47°C

4.370 ml. titrated with 0.008026 N NaOH

Time	Titre	10^6 k
0	0.09	-
44172	1.92	(4.819)
69060	2.90	5.053
130800	4.64	4.956
153960	5.26	5.073
217920	6.50	5.116
252360	6.96	5.059
303840	7.48	4.906
475200	8.79	5.114
∞	9.63	-

0	0.12	-
21276	1.08	5.001
85340	3.39	5.058
106260	4.10	5.104
170160	5.61	5.064
204300	6.25	5.066
256680	6.92	4.894
427200	8.56	5.116
∞	9.63	-

k = 5.041 (14 readings)

k' = 5.068 (11 readings)

Corrected to Solvent I   Mean k = 5.128 ± 0.0137

Expt.18 p-Nitrobenzyl Chloride in 50% aq.Acetone IX at 89.61°C

4.370 ml. titrated with 0.007219 N NaOH

Time	Titre	10^5 k
0	0.03	-
7608	0.85	(1.033)
14640	1.62	1.084
22758	2.39	1.079
28368	2.89	1.080
85680	6.60	1.088
100680	7.22	1.081
108840	7.50	1.074
114720	7.69	1.070
∞	10.87	-

0	0.13	-
49560	4.51	1.057
54120	4.89	1.082
58140	5.10	1.069
72780	5.98	1.081
136440	8.29	(1.046)
151620	8.74	1.070
161280	9.00	1.084
∞	10.87	-

k = 1.077 (13 readings)
k' = 1.076 (9 readings)

Corrected to Solvent I   Mean k = 1.092 ± 0.00173

Expt.19 p-Nitrobenzyl Chloride in 50% aq.Acetone IX at 99.60°C

4.370 ml. titrated with 0.007219 N NaOH

Time	Titre	10^5 k
0	0.30	-
47772	7.39	2.342
62280	8.39	2.349
69780	8.83	2.382
77340	9.20	2.412
83700	9.42	2.402
∞	10.83	-
0	0.20	-
3561	1.00	(2.192)
7020	1.78	2.294
18636	3.91	2.304
34140	6.07	2.354
38820	6.55	2.344
∞	10.83	-
0	0.30	-
10536	2.68	2.430
15552	3.57	2.392
22476	4.57	2.314
25098	4.99	2.349
∞	10.83	-

k = = 2.359 (13 readings)
k' = 2.315 (10 readings)
k'' = 2.314 (12 readings)
k''' = 2.327 (13 readings)
k'''' = 2.350 (15 readings)

Corrected to Solvent I Mean k = 2.370 ± 0.00560

Expt.20 p-Nitrobenzyl Chloride in 50% aq.Acetone IX at 108.84°C

4.370 ml. titrated with 0.007219 N NaOH

Time	Titre	10^5 k
0	0.30	-
1511	1.00	(4.314)
3252	1.88	4.733
5075	2.60	4.584
29240	8.59	4.694
31150	8.79	4.666
∞	11.38	-
0	0.60	-
9330	4.32	4.539
11952	5.10	4.521
16332	6.29	4.596
24672	7.99	4.691
∞	11.38	-
0	0.30	-
7080	3.36	4.564
10860	4.60	4.524
14910	5.76	4.554
19236	6.87	4.674
21792	7.35	4.644
∞	11.38	-

k = 4.614 (13 readings)

k' = 4.586 (10 readings)

Corrected to Solvent I Mean k = 4.671 ± 0.0167

Expt.21 p-Methylbenzylidene Chloride in 50% aq.Acetone VIII at

0.00°C

5 ml. titrated with 0.005037 N NaOH

Time	Titre	10^6 k
0	0.11	-
41541	2.32	5.518
49725	2.68	5.473
57552	3.04	5.508
70620	3.57	5.476
125940	5.43	5.396
137820	5.78	5.409
155340	6.28	5.463
212820	7.58	5.541
223440	7.68	5.414
240480	8.06	5.553
300540	8.79	5.433
∞	10.90	-

k = 5.471 (11 readings)

k' = 5.481 (9 readings)

k'' = 5.436 (11 readings)

Corrected to Solvent I Mean k = 5.587 ± 0.00916

Expt.22 p-Methylbenzylidene Chloride in 50% aq.Acetone VIII at 10.05°C

5 ml. titrated with 0.005037 N NaOH

Time	Titre	10^5 k
0	2.05	-
4263	2.96	(2.367)
9378	3.86	2.259
14154	4.70	2.318
22396	5.80	2.248
26499	6.36	2.289
31119	6.85	2.269
35432	7.30	2.278
42608	7.98	2.305
46350	8.25	2.289
53606	8.69	2.249
∞	11.53	-

k = 2.278 (9 readings)

k' = 2.284 (9 readings)

Corrected to Solvent I   Mean k = 2.333 ± 0.00551

Expt.23 p-Methylbenzylidene Chloride in 50% aq.Acetone VIII at 19.46°C.

5 ml. titrated with 0.005037 N NaOH

Time	Titre	10^5 k
0	0.90	-
1113	1.74	(7.595)
2280	2.58	7.749
3490	3.39	7.859
4965	4.21	7.738
6553	5.01	7.696
7907	5.66	7.791
9953	6.53	7.856
11452	7.02	7.778
13339	7.59	7.754
15030	8.07	7.809
18348	8.84	7.893
∞	11.28	-

k = 7.792 (10 readings)

k' = 7.757 (9 readings)

Corrected to Solvent I Mean k = 7.954 ± 0.0151

Expt.24 p-Methylbenzylidene Chloride in 50% aq.Acetone VII

at 19.46°C

5 ml. titrated with 0.008292 N NaOH

Time	Titre	10^5 k
0	0.30	-
1202	1.33	7.645
2417	2.30	7.739
3721	3.22	7.695
4787	3.90	7.661
5710	4.42	7.578
6339	4.78	7.593
11235	7.01	7.551
11952	7.31	7.621
14017	8.01	7.642
17480	8.98	7.709
20912	9.65	7.630
∞	12.03	-

k = 7.642 (11 readings)

k' = 7.600 (8 readings)

Corrected to Solvent I Mean k = 7.799 ± 0.0120

Expt.25 p-Methylbenzylidene Chloride in 50% aq.Acetone VII at 29.90°C

5 ml. titrated with 0.008292 N NaOH

Time	Titre	10^4 k
0	0.59	-
231	1.29	2.662
530	2.10	(2.589)
935	3.18	2.661
1502	4.41	2.612
1792	5.02	2.636
2385	6.08	2.634
2624	6.44	2.619
3242	7.39	2.661
4050	8.30	2.628
5290	9.45	2.642
∞	12.36	-

k = 2.639 (9 readings)

k' = 2.643 (9 readings)

Corrected to Solvent I   Mean k = 2.702 ± 0.00348

Expt.26 p-Methylbenzylidene Chloride in 50% aq.Acetone VII at 39.77°C

5 ml. titrated with 0.008292 N NaOH

Time	Titre	10^4 k
0	2.01	-
113.5	2.79	7.811
341	4.15	7.778
473	4.87	7.893
635	5.50	(7.534)
732	6.01	7.820
887	6.60	7.816
1082	7.30	7.936
1272	7.78	7.785
1373	8.03	7.767
1561	8.48	7.818
∞	11.19	-

k = 7.825 (9 readings)

k' = 7.831 (11 readings)

Corrected to Solvent I   Mean k = 8.008 ± 0.0180

Expt.27 p-Methylbenzyl Chloride in 70% aq.Acetone I at 60.12°C

4.378 ml. titrated with 0.08778 NaOH

Time	Titre	10^6 k
0	0.12	-
16590	1.06	5.651
24275	1.49	5.759
83220	4.10	5.723
92220	4.40	5.671
112560	5.11	5.724
169680	6.55	5.579
255300	8.24	5.803
∞	10.63	-

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0	0.12	-
59530	3.19	5.803
69060	3.53	5.683
145920	6.10	5.785
173160	6.78	5.801
231660	7.84	5.729
∞	10.62	-

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k = 5.726 (12 readings)

k' = 5.766 (10 readings)

Mean k = 5.743 ± 0.0157

Expt.28 p-Methylbenzyl Chloride in 70% aq.Acetone I at 69.17°C.

4.738 ml. titrated with 0.008778 N NaOH

Time	Titre	10^5 k
0	0.28	-
11060	1.53	(1.311)
14825	2.01	1.336
22300	2.78	1.347
33190	3.80	1.371
78900	6.60	1.354
86100	7.06	1.415
99360	7.51	1.399
107160	7.72	1.382
∞	9.91	-

0	0.14	-
44610	4.61	1.371
47730	4.80	1.358
50820	5.13	1.407
55465	5.40	1.394
63600	5.95	1.420
66540	6.10	1.416
∞	9.91	-

k = 1.382 (13 readings)

k' = 1.385 (11 readings)

Mean k = 1.383 ± 0.00546

Expt.29 p-Methylbenzyl Chloride in 70% aq.Acetone I at 79.24°C

4.378 ml. titrated with 0.008778 N NaOH

Time	Titre	10^5 k
0	0.12	-
36510	7.17	3.469
50670	7.86	3.514
59010	8.27	3.529
∞	9.43	-
0	0.39	-
3420	1.40	3.469
6988	2.30	3.456
8278	2.65	3.472
14383	3.93	3.456
16258	4.30	3.486
19582	4.85	3.474
23623	5.47	3.496
26723	5.90	3.517
∞	9.43	-

k = 3.485 (11 readings)

k' = 3.499 (11 readings)

Mean k = 3.492 ± 0.00655

Expt.30 p-Methylbenzyl Chloride in 70% aq.Acetone I at 88.79°C

4.738 ml. titrated with 0.008778 N NaOH

Time	Titre	10^5 k
0	1.23	-
1204	2.34	8.015
7615	6.70	7.936
9470	7.52	7.784
10409	7.91	7.754
18125	10.46	7.997
20959	11.05	8.036
∞	13.29	-
0	1.00	-
2312	3.01	7.731
3651	4.00	7.670
5470	5.22	7.693
12490	8.60	7.714
14380	9.40	8.002
16415	9.89	7.827
∞	13.29	-

k = 7.846 (12 readings)

k' = 7.903 (13 readings)

Mean k = 7.876 ± 0.0234

Expt.31 p-Methylbenzyl Chloride in 70% aq.Acetone I at 98.80°C

4.378 ml. titrated with 0.007787 N NaOH

Time	Titre	10^4 k
0	2.69	-
1931	5.39	1.800
2818	6.32	1.782
9061	9.99	1.742
∞	11.89	-
0	0.71	-
1361	3.07	1.742
3613	5.95	1.750
4736	7.03	1.760
5416	7.59	1.764
6293	8.22	1.769
∞	11.89	-
0	1.07	-
1678	3.89	1.799
3635	6.30	1.818
5043	7.45	1.766
5493	7.83	1.784
7420	8.93	1.747
∞	11.89	-

k = 1.771 (13 readings)

k' = 1.773 (11 readings)

Mean k = 1.772 ± 0.00463

Expt.32 p-Methoxybenzyl Chloride in 70% aq.Acetone II at 0.00°C

5 ml. titrated with 0.008000 N NaOH

Time	Titre	10^5 k
0	0.21	-
3410	0.99	(1.865)
6311	1.51	1.712
8940	2.04	1.745
14810	3.07	1.725
19115	3.75	1.714
22830	4.34	1.725
25644	4.72	1.712
28830	5.17	1.720
35400	5.97	1.710
37005	6.19	1.724
38930	6.31	1.684
42277	6.70	1.694
∞	12.90	-

k = 1.715 (11 readings)

k' = 1.710 (10 readings)

k'' = 1.709 (9 readings)

Corrected to Solvent I Mean k = 1.717 ± 0.00252

Expt.33 p-Methoxybenzyl Chloride in 70% aq.Acetone II at 9.93°C

5 ml. titrated with 0.008273 N NaOH

Time	Titre	10^5 k
0	0.90	-
1501	1.99	6.720
2813	2.81	6.540
4900	4.01	6.519
6196	4.70	6.560
7388	5.30	6.616
9052	6.04	6.640
11101	6.88	6.717
13013	7.50	6.671
14855	8.01	6.600
16654	8.50	6.621
19346	9.14	6.656
21463	9.54	6.637
∞	12.28	-

k = 6.625 (12 readings)

k' = 6.583 (11 readings)

Corrected to Solvent I Mean k = 6.625 ± 0.0122

Expt.34 p-Methoxybenzyl Chloride in 70% aq.Acetone II at 20.38°C

5 ml. titrated with 0.008273 N NaOH

Time	Titre	10^4 k
0	1.00	-
310	1.90	2.429
559	2.65	(2.559)
922	3.54	2.491
1305	4.40	2.461
1630	5.07	2.445
2019	5.81	2.436
2538	6.70	2.431
3210	7.73	2.444
3985	8.69	2.436
5132	9.81	2.423
6075	10.53	2.425
7260	11.21	2.399
oo	13.38	-

k = 2.438 (11 readings)

k' = 2.453 (10 readings)

Corrected to Solvent I Mean k = 2.452 ± 0.00529

Expt.35 p-Methoxybenzyl Chloride in 70% aq.Acetone II at 29.94°C

5 ml. titrated with 0.008000 N NaOH

Time	Titre	10^4k
0	2.57	-
107	3.31	7.081
240	4.20	7.333
457	5.41	7.202
577	6.00	7.164
702	6.59	7.204
1002	7.78	7.204
1255	8.61	7.230
1522	9.35	7.271
1758	9.80	7.117
2052	10.41	7.247
2261	10.70	7.178
∞	12.70	-

k = 7.201 (11 readings)

k' = 7.191 (9 readings)

Corrected to Solvent I Mean k = 7.218 ± 0.0151

Expt.36 p-Methoxybenzyl Chloride in 70% aq.Acetone II at 39.40°C

5 ml. titrated with 0.008273 N NaOH

Time	Titre	10^3 k
0	1.39	-
43	2.31	1.997
93	3.21	1.914
141	4.09	1.963
197	4.83	1.870
257	5.77	1.939
311	6.42	1.926
376	7.18	1.945
450	7.80	1.898
512	8.21	1.845
572	8.81	1.911
633	8.95	(1.787)
695	9.65	1.939
∞	12.55	-

k = 1.922 (11 readings)

k' = 1.938 (12 readings)

Corrected to Solvent I Mean k = 1.941 ± 0.00706

Expt.37 p-Methoxybenzyl Chloride in 80% aq.Acetone at 0.00°C

5 ml. titrated with 0.008273 N NaOH

Time	Titre	10^6 k
0	0.00	-
43107	1.41	2.217
84240	2.64	2.217
131700	3.89	2.197
173160	4.99	2.249
218040	5.95	2.225
252240	6.73	2.262
301440	7.59	2.244
330660	8.24	(2.299)
388440	8.99	2.239
413280	9.37	2.250
473820	10.10	2.232
∞	15.48	-

k = 2.233 (10 readings)

k' = 2.230 (10 readings)

Mean k = 2.232 ± 0.00112

Expt.38 p-Methoxybenzyl Chloride in 80% aq.Acetone at 10.78°C

5 ml. titrated with 0.008273 N NaOH

Time	Titre	10^6 k
0	0.08	-
14350	2.14	9.649
21448	3.10	9.844
28375	3.90	9.704
33070	4.45	9.757
86100	9.05	9.687
91020	9.48	9.867
101100	10.05	9.800
105300	10.27	9.772
109260	10.49	9.777
113700	10.76	9.850
115980	10.83	9.772
∞	15.94	-

k = 9.771 (11 readings)

k' = 9.750 (9 readings)

k'' = 9.854 (9 readings)

Mean k = 9.788 ± 0.0121

Expt.39 p-Methoxybenzyl Chloride in 80% aq.Acetone at 20.39°C

5 ml. titrated with 0.008273 N NaOH

Time	Titre	10^5 k
0	0.19	-
3510	1.85	3.222
7065	3.44	3.329
12223	5.30	3.372
13800	5.80	3.257
17907	7.05	3.267
21270	8.00	3.299
25027	8.86	3.277
27890	9.50	3.296
35632	10.82	3.254
39760	11.48	3.282
41715	11.75	3.287
∞	15.68	-

k = 3.276 (11 readings)

k' = 3.264 (11 readings)

Mean k = 3.270 ± 0.00558

Expt.40 p-Methoxybenzyl Chloride in 80% aq.Acetone at 29.94°C

5 ml. titrated with 0.008273 N NaOH

Time	Titre	10^5 k
0	0.68	-
1237	2.32	9.906
2117	3.38	9.942
3185	4.51	9.847
4162	5.49	9.910
5772	6.81	9.761
6672	7.58	9.947
7947	8.47	9.979
9342	9.26	9.891
10617	9.90	9.833
11642	10.40	9.872
12659	10.89	9.986
14452	11.48	9.847
∞	14.91	-

k = 9.893 (12 readings)

k' = 9.964 (11 readings)

Mean k = 9.928 ± 0.0181

Expt.41 p-Methoxybenzyl Chloride in 80% aq.Acetone at 39.68°C

5 ml. titrated with 0.008273 N NaOH

Time	Titre	10^4 k
0	1.21	-
595	3.46	2.818
1211	5.41	2.807
1530	6.29	2.799
1961	7.37	2.799
2440	8.38	2.778
2811	9.15	2.798
3714	10.66	2.809
4006	11.00	2.776
4438	11.52	2.765
4690	11.93	2.830
∞	15.80	-

k = 2.799 (10 readings)

k' = 2.814 (10 readings)

Mean k = 2.806 ± 0.00473

Expt.42. p-Methoxybenzyl Chloride in 50% aq.Acetone II at 0.00°C

5 ml. titrated with 0.008533 N NaOH

Time	Titre	10^4 k
0	1.99	-
165	2.65	5.820
415	3.51	5.706
585	4.05	5.751
760	4.58	5.859
1305	5.79	5.738
1818	6.69	5.805
2386	7.38	5.771
2614	7.61	5.784
2875	7.82	5.750
3223	8.09	5.806
∞	9.20	-

k = 5.779 (10 readings)

k' = 5.754 (12 readings)

Mean k = 5.764 ± 0.0099

Expt.43 p-Methoxybenzyl Chloride in 50% aq.Acetone II at 0.00°C

5 ml. titrated with 0.005328 N NaOH

Time	Titre	10^4k
0	2.17	-
183	3.03	5.989
380	3.82	5.848
560	4.50	5.900
753	5.10	5.799
935	5.70	5.943
1173	6.28	5.849
1543	7.03	5.731
1863	7.69	5.879
2211	8.19	5.873
2600	8.65	5.870
3025	9.04	5.855
∞	10.45	-

k = 5.867 (11 readings)

k' = 5.878 (11 readings)

Mean k = 5.872 ± 0.0113

Expt.44 p-Methoxybenzyl Chloride in 70% aq.Acetone III at 29.88°C

5 ml. titrated with 0.007657 N NaOH

No added salts.

Time	Titre	10^4 k
0	1.09	-
145	2.30	6.972
290	3.40	6.997
441	4.49	7.134
598	5.40	7.001
738	6.18	7.013
895	6.90	6.908
1285	8.57	7.009
1425	9.13	7.134
1654	9.75	7.030
2122	10.86	7.041
2565	11.65	7.099
2843	12.00	7.066
∞	13.69	-

k = 7.034 ± 0.0184 (12 readings)

k' = 7.062 ± 0.0124 (10 readings)

Mean k = 7.046 ± 0.0150

Expt.45 p-Methoxybenzyl Chloride in 70% aq.Acetone III at 29.85°C

5 ml. titrated with 0.007314 N NaOH

Added HCl 0.01777 N

Time	Titre	10^4 k
0	12.15	-
127	13.20	6.908
273	14.30	6.916
420	15.30	6.921
580	16.30	6.956
685	16.80	6.798
792	17.41	6.902
1172	18.99	6.769
1428	19.87	6.745
1730	20.66	(6.612)
1947	21.31	6.790
2097	21.68	6.866
∞	24.64	-

k = 6.857 ± 0.0224 (10 readings)

Duplicate Experiment

Added HCl 0.02250 N k' = 6.756 ± 0.0234 (9 readings)

Expt.46 p-Methylbenzylidene Chloride in 50% aq.Acetone VIII at 24.76°C

5 ml. titrated with 0.007314 N NaOH

No added salts.

Time	Titre	10^4 k
0	0.60	-
526	1.62	1.419
1176	2.75	1.398
1690	3.60	1.405
2514	4.77	1.385
3531	6.14	1.401
3771	6.34	1.375
4641	7.39	1.402
5585	8.20	1.372
6611	9.14	1.392
7506	9.80	1.393
8609	10.50	1.388
∞	14.80	-

k = 1.394 ± 0.0039 (11 readings)

k' = 1.387 ± 0.0033 (9 readings)

Mean k_1 = 1.391 ± 0.00272

Expt.47 p-Methylbenzylidene Chloride in 50% aq.Acetone VIII at 24.76°C

5 ml. titrated with 0.007314 N NaOH

Added HCl 0.01545 N

Time	Titre	10^4 k
0	10.56	-
682	11.99	1.344
1633	13.84	1.375
2121	14.61	1.345
2867	15.85	1.366
3518	16.78	1.363
4058	17.50	1.363
5266	19.00	1.380
6466	20.18	1.375
7684	21.15	1.359
8253	21.55	1.353
9396	22.41	1.375
10218	22.90	1.377
∞	26.90	-

k = 1.365 ± 0.0034 (12 readings)

Duplicate Experiment

Added HCl 0.01697 k' = 1.380 ± 0.0041 (10 readings)

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PART II

ELECTROLYTE EFFECTS IN UNIMOLECULAR NUCLEOPHILIC SUBSTITUTION REACTIONS

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CHAPTER I

ELECTROLYTE EFFECTS IN NUCLEOPHILIC ALIPHATIC SUBSTITUTION[1]

The hydrolysis of alkyl and aralphyl halides can occur either by the single stage mechanism, S_N2,

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

or by the multi-stage mechanism, S_N1,

$$RCl \rightleftharpoons \left[\overset{\delta+}{R}\text{-----}\overset{\delta-}{Cl}\right] \rightleftharpoons R^+ + Cl^- \qquad \text{(slow)}$$

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

Since the nucleophilic reagent, water, is present in vast excess, both reactions can be expected to show first-order kinetics, provided that the ionisation of RCl is the rate-determining step in the S_N1 process. Hughes, Ingold and co-workers have however pointed out that two opposing effects can cause deviations from first-order kinetics in S_N1 solvolysis.[1]

The first of these, the mass-law effect, arises from the reversal of the rate-determining ionisation by the chloride ions produced (step 2). This results in a progressive retardation of hydrolysis, as the reaction proceeds, corresponding to decreasing first-order rate coefficients. The addition of chloride ions will enhance this effect and, similarly, "common-anions" will retard the S_N1 reactions of other compounds. "Non-common-ion" electrolytes cannot show this effect.

The second effect, the ionic-strength effect, arises from the stabilisation of the charged transition state in the rate-determining ionisation by electric charges, an effect analogous to the ion-atmosphere stabilisation of ions in solution. Since the hydrolysis is accompanied by the production of ions, this effect should enhance the rate of ionisation of RCl and, hence, its rate of hydrolysis. Added electrolytes will cause further acceleration of hydrolysis by this effect irrespective of whether they contain common-ions, or not.

In the unimolecular mechanism one therefore expects a progressive increase in the calculated first-order rate coefficient, due to the ionic-strength effect, superimposed on a progressive decrease in the rate constant, due to the mass-law effect. It is therefore evident that in a solvolysis occurring by this mechanism there are three possibilities,

(i) Calculated first-order rate coefficients rise as the reaction proceeds. This is due to the ionic-strength effect outweighing the mass-law effect, e.g. in the hydrolysis of <u>tert</u>-butyl bromide in aqueous acetone[2].

(ii) Rate coefficients remain constant due to a cancellation of the two effects, e.g. in the hydrolysis of benzhydryl chloride in 80% aqueous acetone[3].

(iii) Rate coefficients fall due to the mass-law effect outweighing the ionic-strength effect, e.g. in the hydrolysis of pp'-dimethylbenzhydryl chloride and p-methylbenzhydryl chloride in aqueous acetone[4,5].

The predicted effects of the products of hydrolysis and of added electrolytes are summarised in Table I-1.

In S_N2 hydrolysis,

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

the transition state is also subject to ion-atmosphere stabilisation and reaction by this mechanism should therefore also show the ionic-strength effect. The magnitude of this effect will however be much smaller than in S_N1 hydrolysis since the electric charges in the transition state are now much more diffuse. No mass-law effect is possible in S_N2 hydrolysis.

The present investigation is only concerned with the effect of added electrolytes on S_N1 hydrolysis, and the discussion is now restricted to reaction by this mechanism.

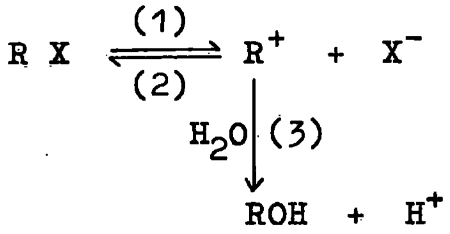
TABLE I - 1

PREDICTED MASS-LAW AND IONIC-STRENGTH EFFECTS IN THE UNIMOLECULAR SOLVOLYSIS OF AN ALKYL HALIDE[1]

	Mass-Law	+	Ionic-Strength
Formed Ions	(Progressive fall in specific rate)	+	(Progressive rise in specific rate)
"Common-ion" electrolyte	Retardation	+	Acceleration
"Non-common-ion" electrolyte	No effect	+	Acceleration

Quantitative Approach.

Hughes, Ingold and co-workers[1] have developed a simple electrostatic theory to account quantitatively for the operation of mass-law and ionic-strength effects in S_N1 reactions.



$$\begin{tikzcd} RX \arrow[r, shift left, "(1)"] & R^+ \arrow[l, shift left, "(2)"] \arrow[d, "H_2O"', "(3)"] + X^- \\ & ROH + H^+ \end{tikzcd}$$

If v_1, v_2 and v_3 are the instantaneous rates of stages

(1), (2) and (3) respectively, then

$$v_1 = k_1[RX] \;, \quad v_2 = k_2[R^+][X^-] \,, \quad v_3 = k_3[R^+]$$

The carbonium ion R^+ was assumed to be in the stationary state since it reacts by either stage (2) or stage (3) almost as soon as it is formed.

$$\therefore \quad v_1 = v_2 + v_3$$

The measured rate,

$$\frac{dx}{dt} = v_3 = \frac{v_1 v_3}{v_2 + v_3} \qquad \text{.........I-1}$$

Using the formalism of Polanyi, Evans and Eyring[6] it was shown that

$$v_1 = \frac{k_1^o (a - x)}{f_T} \qquad \text{.........I - 2}$$

where f_T is the activity coefficient of the transition state and k_1^o is the first-order rate constant for zero ionic-strength. The approximation was made that f_T differs from unity by so much more than does the activity coefficient of RX that the latter may be set equal to unity.

The activity coefficient, f_T , for the transition state of ionisation was then calculated. The transition state was treated as a dipole. The surrounding ions reduce the magnitude of the electrical potential of each of the dipole charges thus stabilising the system.

The transition state was regarded as two point charges ± ze separated by a fixed distance d and surrounded by a dilute atmosphere of point-ions of charges ± e. Using the Debye-Poisson equation for the potential ψ at a point due to any central electrical distribution in a dilute atmosphere of univalent ions, it was found that

$$- \ln f_T = \frac{4\pi}{1000} \cdot \frac{Ne^4}{\bar{k}^2} \cdot z^2 d \cdot \frac{\mu}{(DT)^2} \qquad \text{......I-3}$$

where N is Avagadro's number

μ is the ionic strength of the solution

D is the dielectric constant of the medium

$\bar{k}$ is Boltzmann's constant

T is the absolute temperature.

Eqn.I-3 contains one unknown constant, $\sigma = z^2 d$. σ was termed the ionic-strength constant and is a measure of the ion atmosphere stabilisation of the transition state in the rate-determining process.

Eqns.I-2 and I-3 were combined and the values of the universal constants inserted giving

$$v_1 = k_1^o(a-x)\ \text{antilog}_{10}(0.912 \times 10^{16} \sigma\ \mu/D^2T^2) \qquad \text{....I-4}$$

The effect of ionic strength on stage (2) was calculated on the basis that this stage is unimolecular with respect to each of the participating ions. The Brönsted activity correction, $f_+ f_- / f_T$, was introduced into the right hand side of Eqn.I-5

$$v_2 = k_2[R^+][X^-] = \frac{f_+ f_-}{f_T} k_2^o[R^+][X^-] \qquad \text{...........I-5}$$

where k_2^o is the value of k_2 at zero ionic strength. f_T, the activity coefficient of the transition state, is given by Eqn.I-3. Debye's limiting law,

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

was used to evaluate f_+ and f_-. These expressions were substituted into Eqn.I-5 and the values of the universal constants inserted giving

$$v_2 = k_2^o[R^+][X^-] \text{ antilog}_{10}\left\{\left(0.912 \times \frac{10^{16}\sigma\mu}{D^2T^2}\right) - \left(3.63 \times \frac{10^6\mu^{1/2}}{D^{3/2}T^{3/2}}\right)\right\}$$

Stage (3) is unimolecular with respect to the ion R^+ and it was found by trial to be multimolecular with respect to water.

There is a very large spatial distribution of the positive charge in the transition state for the collapse of the shell. Its activity coefficient could not therefore be calculated by means of Debye's limiting law. As the spatial distribution is increased the extra factor which enters into the Debye-Hückel law causes $-\ln f_{+aq.}$ to approach zero. The Brönsted correction factor becomes $f_+ / f_{+aq.} = f_+$. The rate equation is therefore

$$v_3 = \frac{k_3^o \left[R^+\right]}{\text{antilog}_{10}(1.815 \times 10^6 / u^{\frac{1}{2}} / D^{3/2} T^{3/2})}$$

On substituting in Eqn. I-1 for v_1, v_2 and v_3 and defining α^o , the mass-law constant equal to k_2^o / k_3^o , the following equation was obtained,

$$\frac{dx}{dt} =$$

$$\frac{k_1^o \, (a - x)}{\alpha^o \left[X^-\right] \text{antilog}_{10} \left(-1.815 \times \frac{10^6 / u^{\frac{1}{2}}}{D^{3/2} \, T^{3/2}} \right) + \text{antilog}_{10} \left(-0.912 \times \frac{10^{16} \sigma / u}{D^2 \, T^2} \right)}$$

Putting $A = -1.815 \times 10^5 (DT)^{-3/2}$ and $B = -0.912 \times 10^{16} (DT)^{-2}$

$$\frac{dx}{dt} = \frac{k_1^o \, (a - x)}{\alpha^o \left[X^-\right] \text{antilog}_{10}(A / u^{\frac{1}{2}}) + \text{antilog}_{10}(B\sigma / u)} \qquad \text{......I-6}$$

which, on integration, gives

$$k_1^o t = \alpha^o \int_0^x \frac{\left[X^-\right]}{(a-x)} \text{antilog}_{10} A / u^{\frac{1}{2}} . dx \; + \; \int_0^x \frac{\text{antilog}_{10} B\sigma / u}{(a-x)} . \, dx$$

.......I-7

Combination of Eqn. 1-7 with the observed first-order rate coefficients gave very reasonable values for the parameters σ and α^o for the S_N1 hydrolysis of a number of alkyl and aralphyl halides in aqueous acetone. The requirements of Eqn.I-6 were obeyed and the parameters σ and α^o found to be independent of the nature of the added electrolyte, within the limits of experimental error.

Consistent with the definition of the ionic-strength constant, viz. $\sigma = z^2d$, this parameter was found to increase on passing to compounds in which a greater separation of charges in the transition state of ionisation was to be expected, and the mass-law constant, α^o, was found to increase with increasing stability of the carbonium ion, R^+. Hughes, Ingold and co-workers considered this reasonable since α^o represents the rate of attack of common-anions on R^+ relative to the rate of collapse of its solvation shell; the greater the stability of R^+, the greater the chance that a common-anion can penetrate this solvation shell before it collapses.

The simple electrostatic treatment of Hughes and Ingold requires that the magnitude of the ionic-strength effect is independent of the nature of the electrolyte and depends only on the ionic strength of the solution. Contrary to this requirement, specific electrolyte effects have been reported on a number of occasions[7,8,9,10].

Hughes and Ingold themselves have pointed out that this approach is strictly only applicable to very dilute solutions, analogous to Debye's limiting law for the activity coefficients of ions. This approximation only holds true at increasingly lower concentrations as the ionising power of the solvent decreases, and this may account for some of the reports of specific electrolyte effects.

Nash and Monk[7] have drawn attention to the association of electrolytes in solution to give ion-pairs which may affect the ionic strength of the solution in a manner depending on the association constant of the electrolyte in question. Such considerations could account for Spieth and Olson's observation that lithium chloride, lithium bromide and lithium perchlorate have different effects on the rate of hydrolysis of <u>tert</u>.-butyl bromide and <u>tert</u>.-butyl chloride in aqueous acetone and that the effect of each salt does not vary in the same manner with changing solvent composition[9]. The quantitative arguments of Nash and Monk are however subject to errors and their conclusion that the effect of lithium, potassium and hydrogen bromides on the rate of hydrolysis of <u>tert</u>.-butyl bromide is equally well predicted by the simple electrostatic treatment of Hughes and Ingold and by Moelwyn-Hughes' expression[11] for the reaction between an ion (R^+) and a dipole (H_2O) cannot be maintained, for the following reasons,

(i) The treatment used by Nash and Monk does not take into account the mass-law effect of either the formed ions or the added ions.

(ii) Integrated rate coefficients were compared with Moelwyn-Hughes' theoretical expression, which involves instantaneous rate coefficients.

(iii) In order to apply Moelwyn-Hughes' equation, the rate-determining stage was assumed to be the reaction of the carbonium ion with a water molecule. If this is the case, the observed first-order rate coefficient for hydrolysis is not the same as the rate coefficient of the rate-determining step, due to bromide ions reacting with the carbonium ions, and the hydrolysis rate would be inversely proportional to the bromide ion concentration. This is however contrary to observation.

Fainberg and Winstein[10] investigated the effects of several electrolytes, including lithium and diphenylguanidinium acetates, lithium and diphenylguanidinium perchlorates, lithium *p*-toluenesulphonate and *p*-toluenesulphonic acid, on the rates of acetolysis of neophyl and *p*-methoxyneophyl halides and arylsulphonates. Although each salt increased the rate, a marked specificity in the electrolyte effects was found. This behaviour was also observed when the effect of electrolytes on the rates of acetolysis of a series of secondary arylsulphonates was studied[12]. Since both addition of electrolyte to a solvent and gross variation of solvent are medium changes, a parallelism between the responses of various structures to electrolyte and solvent composition was expected. It was in fact found that changing R in the solvolysing material RX from neophyl to p-methoxyneophyl reduced both the magnitude of the electrolyte effects and the sensitivity to gross solvent variation. This parallelism was not observed however when the leaving group X of RX was changed.

The effect of lithium perchlorate was investigated over a range of salt concentrations and a linear relationship, Eqn.I-8, was found between the solvolysis rate constant, k, and the molar concentration of lithium perchlorate up to a concentration of 0.06 M. lithium perchlorate. This was designated a "normal" salt effect.

$$k = k^{o} (1 + bx) \qquad \text{.........I-8}$$

where k^{o} is the solvolysis rate constant at zero salt concentration

b is a constant, equal to the percentage increase in rate constant over k^{o} per 0.01 M. increment of $LiClO_4$

x is the concentration of $LiClO_4$.

The expression used by Hughes, Ingold and co-workers[1] for electrolyte effects in solvolysis in media of considerably higher dielectric constant than that of acetic acid, Eqn.I-9, predicts a linear dependence of log k on the molar concentration of the added electrolyte.

$$\log k = \log k^{o} + \frac{0.912 \times 10^{16} \sigma \mu}{D^{2} T^{2}} \quad \ldots\ldots\ldots \text{I-9}$$

where D is the dielectric constant of the solvent

T is the absolute temperature

μ is the ionic strength, or molar concentration for uni-univalent electrolytes

σ is the ionic-strength constant.

It was found by Fainberg and Winstein that this expression was inferior to Eqn.I-8 for predicting the effect of lithium perchlorate in acetolysis.

As a result of their experiments on acetolysis, Winstein and co-workers proposed an elaboration of the S_N1 mechanism[13]. These authors considered that in a heterolysis of this type, two types of ion-pairs are concerned as metastable intermediates prior to the formation of the fully developed carbonium ion; the first an "internal" ion-pair in which no solvent molecules are interposed between the ions; the second an "external" ion-pair, where a small number of solvent molecules are interposed between the ions.

$$\begin{tikzcd}
\text{I} & \text{II} & \text{III} & \text{IV} \\
 & \text{Internal ion-pair} & \text{External ion-pair} & \text{Dissociated ions.} \\
RX \arrow[r, shift left] & R^{+}X^{-} \arrow[l, shift left] \arrow[r, shift left] \arrow[dr] & R^{+}//\,X^{-} \arrow[l, shift left] \arrow[r, shift left] \arrow[d] & R^{+} + X^{-} \arrow[l, shift left] \arrow[dl] \\
 & & ROS &
\end{tikzcd}$$

In general, all three varieties of carbonium ion II, III and IV may lead to the solvolysis product ROS. The return to the covalent RX, accompanying acetolysis, may be from any of the ionic stages, II, III or IV.

Fainberg and Winstein[14] found that the addition of lithium perchlorate in the acetolysis of 2-anisylethyl p-toluenesulphonates gave rise to a two-stage acceleration of rate: (i) an initial very steep rise in the first-order solvolysis rate constant at low concentrations of lithium perchlorate ("special" salt effect); (ii) a subsequent small increase in the rate constant virtually linear with salt concentration at somewhat higher lithium perchlorate concentrations ("normal" salt effect). Special salt effects, which are found to occur only with systems giving rise to the longer-lived carbonium ion species, e.g. chlolesteryl and 2-(2,4-dimethoxyphenyl)-ethyl arylsulphonates[15], were regarded as being due to the elimination of a substantial ion-pair return by the salt. The lack of specificity in the magnitude of the special salt effect produced by different salts showed that the same fraction of ion-pair return is eliminated in the special salt effect by all salts.

Special salt effects in the acetolysis of threo-3-p-anisyl-2-butyl benzenesulphonates were studied in order to determine whether all or only part of ion-pair return was eliminated in this system[16]. The fraction of ion-pair return being eliminated in the special salt effect was obtained by observing the effect of lithium perchlorate on the gap between the rates of ionisation and solvolysis. It was found that the special salt effect only partly closes the gap and therefore ion-pair return is only partly eliminated by this effect. This was interpreted on the basis that the special salt effect eliminates external ion-pair return (from the external ion-pair III) due to a trapping of $R^+//X^-$ as a quadruple with $Li^+ClO_4^-$, thereby preserving it for reaction with the solvent. Internal return (from the internal ion-pair II) is however still permitted.

Special salt effects observed in the acetolysis of 2-p-anisyl-1-propyl p-toluenesulphonate were interpreted in a similar way.[17]

Hughes, Ingold and co-workers[18] have criticised Winstein's scheme as it assumes the complete dissociation of an electrolyte in a poorly ionising solvent and Bensley and Kohnstam[19] and Kohnstam and Shillaker[20] have shown that the effect of mixed chlorides and bromides in the S_N1 hydrolysis of dichlorodiphenylmethane is consistent with the electrostatic treatment of Hughes and Ingold and argues strongly against the intervention of internal or external ion-pairs for reaction with 70% or 75% aqueous acetone.

Lucas and Hammett[8] found specific salt effects in the S_N1 hydrolysis of <u>tert</u>.-butyl nitrate in aqueous dioxan. Anions affected the rate in the order $ClO_4^- > NO_3^- > Cl^- > OH^-$, the latter actually causing a depression of the rate. They interpreted their results by assuming differing degrees of solvation of these ions by the water in the solvent. The solvent composition was considered to change as a result of this solvation, and it was of course well known that S_N1 reactions are highly sensitive to changes in the solvent composition. Thus OH^- ions, which were regarded as the most strongly solvated, 'dry' the solvent to such an extent that the resulting decrease in rate is more than enough to counterbalance the increase in rate to be expected from the ionic-strength effect. The freezing points of electrolytes in aqueous dioxan and analyses of the solid phases, gave qualitative support to their views. Recent work on the activities of the solvent components of water-dioxan mixtures in the presence of electrolytes has confirmed Lucas and Hammett's view of a differential solvation of ions though it now appears that solvation of both solvent components must be taken into account[21].

Benfey, Hughes and Ingold, while acknowledging the plausibility of Lucas and Hammett's views, showed that differential solvation of ions could not account for the "common-ion" effect in S_N1 solvolysis to the exclusion of the mass-law effect[22]; chloride ions retard the hydrolysis of benzhydryl chloride while bromide ions accelerate it but retard the hydrolysis of benzhydryl bromide. These authors confirmed Lucas and Hammett's observations on the effect of OH^- ions but regarded this as a special case, applicable to lyate ions only[23]. The OH^- ions were considered to distribute their charge by proton shifts over a number of solvent molecules. The distributed proton defect in the solvent then impairs the solvation of the forming halide ion more than it aids the solvation of the developing carbonium ion. This would be likely to reduce the reaction rate.

Interest in this problem arose from the work described in Part I. The rate of hydrolysis of p-methoxybenzyl chloride was found to depend to some extent on the concentration of the halide. It was thought that this could have arisen from a combination of mass-law and ionic-strength effects, as had already been demonstrated for similar observations in the hydrolysis of dichlorodiphenylmethane[19]. Experiments with added sodium chloride (a common-ion salt) and sodium perchlorate[≠] (a non-common-ion salt) led to values for the mass-law and ionic-strength constants which predicted that the integrated first-order rate coefficients in the reaction with the pure solvent should decrease as the reaction proceeds. Constant rate coefficients were however observed under these conditions and it was therefore decided to investigate the effects of a variety of electrolytes in S_N1 hydrolysis in more detail. Preliminary work was carried out using p-methoxybenzyl chloride but most of the measurements were carried out using benzhydryl chloride since this compound is sterically unfavourable to bimolecular attack[24] and therefore permitted the use of a wider range of electrolytes. All the work was carried out in 70% aqueous acetone, where ion-pair association is negligibly small for most strong electrolytes[25,7].

[≠] Sodium bromide could not be used because of the danger of bimolecular attack by the bromide ions.

CHAPTER II

ELECTROLYTE EFFECTS IN S_N1 HYDROLYSIS

p-Methoxybenzyl Chloride in 70% acetone.

The solvolysis of p-methoxybenzyl chloride in 70% acetone was studied at 29.88°C in the presence of 0.05 M. $NaClO_4$, 0.05 M. NaCl and in the absence of added electrolytes. The data obtained are shown in Table II-1. The first-order integrated rate coefficients in the absence of added electrolytes were found to remain constant as the reaction proceeded. This means that, even though in the absence of added electrolytes mass-law and ionic-strength effects both operate, due to the formed ions, these effects must balance. Verification of this was sought by studying the reaction in the presence of $NaClO_4$, which led to σ , the ionic-strength constant, and also in the presence of NaCl, which gave α^o, the mass-law constant. This procedure assumes that the value of σ is independent of the nature of the added electrolyte. The methods by which σ and α^o were obtained are given in Chapter IV; for these calculations mean quantities throughout a run were used. The values obtained were $\sigma = 2 \times 10^{-8}$, $\alpha^o = 16$. Substitution of these values into Eqn.I-7 however showed that the integrated first-order rate coefficients should decrease by more than 7% over the course of a kinetic run in

TABLE II - 1

ELECTROLYTE EFFECTS IN THE HYDROLYSIS OF p-METHOXYBENZYL CHLORIDE IN 70% AQUEOUS ACETONE AT 29.88°C.

Added Electrolyte	Electrolyte Concn.	$10^4 k(\text{sec}^{-1})$	% change in rate for 0.05 M. electrolyte
-	-	7.046	-
$NaClO_4$	0.04984	8.212	+16.6 ± 0.46
NaCl	0.05008	6.013	-14.6 ± 0.23
			% change in rate for 0.02 M. electrolyte
NaCl	0.02039	6.594	- 6.4 ± 0.48
HCl	0.02013	6.829	- 3.1 ± 0.29

TABLE II - 2

ELECTROLYTE EFFECTS IN THE HYDROLYSIS OF p-METHOXYBENZYL CHLORIDE IN 70% AQUEOUS ACETONE AT 0.00°C.

Added Electrolyte	Electrolyte Concn.	$10^5 k(\text{sec}^{-1})$	% change in rate for 0.05 M. electrolyte
-	-	1.690	-
$NaClO_4$	0.05005	1.970	+16.6 ± 0.25
NaCl	0.05010	1.511	-10.6 ± 0.21

the absence of added electrolyte. This is illustrated in Table II-3 where it can be seen that such a variation is outside the limits of experimental error. It must therefore be concluded that the electrolyte effects noted in this investigation cannot be accounted for entirely using the Hughes-Ingold approach, which assumes that the ionic-strength effect is independent of the nature of the electrolyte. Confirmation of this conclusion also arises from the fact that for a given electrolyte concentration, HCl and NaCl do not have the same effect on the rate (Table II-1).

A possible method of accounting for the present observations involves assuming that the magnitude of the ionic-strength effect depends on the nature of the electrolyte. The reasons for this will be discussed later. If this view is correct, Eqn.I-7 will still hold provided σ is allowed to vary with the salt added. On this view the observation that the accelerating effect of $NaClO_4$ is virtually independent of temperature (see Tables II-1 and II-2) is fully in accordance with the Hughes-Ingold approach since it can readily be shown from Eqn.I-7 that the magnitude of the ionic-strength effect, in the present solvent, changes little with temperature. Similarly the decrease in the retarding effect of NaCl with decreasing temperature is fully in accordance with previous observations that α^0 has a positive temperature coefficient[19,20,26].

TABLE II - 3.

OBSERVED AND CALCULATED INTEGRATED FIRST-ORDER COEFFICIENTS FOR HYDROLYSIS OF p-METHOXYBENZYL CHLORIDE IN 70% ACETONE IN ABSENCE OF ADDED ELECTROLYTES

Time (sec.)	$\frac{a}{a - x}$	$10^4 k$ obs. (sec.$^{-1}$)	$10^4 k$ calc. (sec.$^{-1}$)
145	1.106	6.972	7.301
290	1.224	6.997	7.237
441	1.369	7.134	7.168
598	1.520	7.001	7.138
738	1.678	7.013	7.099
895	1.856	6.908	7.124
1285	2.461	7.009	6.960
1425	2.763	7.134	6.968
1654	3.198	7.030	6.944
2122	4.452	7.041	6.873
2565	6.176	7.099	6.797
2843	7.456	7.066	6.779

Although there is a slight retarding effect by the HCl, the temperature-dependence of this effect is so small that it has little influence on the values of the activation energies and hence on the dE/dT values, which were of such importance in Part I.

Benzhydryl Chloride in 70% acetone.

Electrolyte effects in the solvolysis of benzhydryl chloride in 70% acetone were investigated, for reasons already discussed in Chapter I. The results obtained using approximately 0.05 M. electrolytes, with the exception of HCl, NaCl and LiCl, where the concentration was approximately 0.02 M. , are given in Table II-4. Full details of the methods of calculation used are given in Chapter IV. For experiments with $HClO_4$, HNO_3, NaN_3, $NaNO_3$ and $(CH_3)_4NF$ the rate of formation of chloride ion was followed; for runs with $NaClO_4$, $LiClO_4$, CsBr, $(CH_3)_4NBr$, NaBr, LiBr, HCl, NaCl and LiCl, the development of acidity in the solution was noted (see Chapter IV). When the added electrolyte is a chloride, the mass-law effect operates and these results are therefore considered separately.

It can be seen in Table II-4 that different electrolytes have different effects on the rates; $HClO_4$ being the most strongly accelerating and $(CH_3)_4NF$ actually retarding

TABLE II - 4.

ELECTROLYTE EFFECTS IN THE HYDROLYSIS OF BENZHYDRYL CHLORIDE IN 70% AQUEOUS ACETONE AT 24.80°C

Added Electrolyte	Electrolyte Concn.	$10^4k(\text{sec}^{-1})$	% change in rate for 0.05 M. electrolyte
-	-	4.386	-
$HClO_4$	0.04886	5.291	+21.1 ± 1.06
HNO_3	0.04952	5.225	+19.3 ± 0.71
NaN_3	0.05021	5.170	+17.8 ± 0.55
$NaNO_3$	0.05137	5.078	+15.3 ± 0.87
$NaClO_4$	0.05019	5.050	+15.1 ± 0.21
$LiClO_4$	0.04610	4.975	+14.5 ± 0.19
CsBr	0.04997	4.793	+ 9.3 ± 0.27
$(CH_3)_4NBr$	0.04695	4.767	+ 9.3 ± 0.23
NaBr	0.05020	4.765	+ 8.6 ± 0.24
LiBr	0.05010	4.685	+ 6.7 ± 0.29
$(CH_3)_4NF$	0.04293	4.211	- 4.7 ± 0.60
HCl	0.02131	4.326	- 3.2[†] ± 0.51
NaCl	0.01937	4.255	- 7.7[†] ± 0.30
LiCl	0.01703	4.273	- 7.7[†] ± 0.31

[†] Calculated on the assumption that the effect of 'Common-ion' electrolytes on the reaction rate obeys a linear relationship (see Table II-1).

the rate-determining ionisation.

Examination of the results shows that the effects of the various anions and cations are additive. This is illustrated in Table II-5, where it can be seen that within the limits of experimental error, the difference between the effect of an electrolyte and its corresponding sodium salt is always the same irrespective of the nature of the anion and that similar considerations apply to differences between chlorides and other anions irrespective of the nature of the cation.

It may be observed that of all the cationic species examined, H^+ ions have the greatest accelerating effect on the rate while the others (i.e. alkali metals and $(CH_3)_4N^+$) behave in a similar manner. It is also noteworthy that azide, nitrate and perchlorate ions increase the rate of ionisation greatly while fluoride and chloride ions exert retarding effects, although in the latter case this is most probably due to the operation of the mass-law effect. Some doubt must be expressed regarding the validity of results obtained for the bromides since it is possible that the bromide ions react with the formed carbonium ions. This point is discussed more fully in Chapter IV.

The differences between the effects of $NaClO_4$ and NaCl and also between the effects of HCl and NaCl are found to be greater for p-methoxybenzyl chloride than for benzhydryl

TABLE II - 5

SPECIFIC EFFECTS OF CATIONS AND ANIONS

(Cations are compared with Na^+; anions are compared with Cl^-, except for F^- which is compared with Br^- [†])

	CATIONS			
	$(H^+) - (Na^+)$	$(Cs^+) - (Na^+)$	$(MeN_4^+) - (Na^+)$	$(Li^+) - (Na^+)$
ClO_4^-	+6.0 ± 1.1	-	-	-0.6 ± 0.3
NO_3^-	+4.0 ± 1.1	-	-	-
Cl^-	+4.5 ± 0.6	-	-	0.0 ± 0.4
Br^-	-	+0.7 ± 0.4	+0.7 ± 0.3	-1.9 ± 0.4

	ANIONS				
	$(N_3^-) - (Cl^-)$	$(ClO_4^-) - (Cl^-)$	$(NO_3^-) - (Cl^-)$	$(Br^-) - (Cl^-)$	$(F^-) - (Br^-)$
Na^+	+25.5 ± 0.6	+22.8 ± 0.4	+23.0 ± 0.9	+16.3 ± 0.4	-
$(CH_3)_4N^+$	-	-	-	-	-14.0 ± 0.6
H^+	-	+24.3 ± 1.2	+22.5 ± 0.9	-	-
Li^+	-	+22.2 ± 0.4	-	+14.4 ± 0.4	-

[†] Differences refer to percentage change in rate due to addition of 0.05 M. electrolyte

chloride (see Table II-6). A plausible explanation for the former observation is that the p-methoxy compound has larger values than benzhydryl chloride for the ionic-strength and mass-law constants. The latter observation indicates that the specificity of the added electrolyte is more pronounced in the case of the p-methoxy compound.

TABLE II - 6.

COMPARISON OF DIFFERENCES IN ELECTROLYTE EFFECTS IN HYDROLYSIS OF BENZHYDRYL CHLORIDE AND p-METHOXYBENZYL CHLORIDE IN 70% ACETONE

(Differences refer to percentage change in rate due to addition of 0.05 M. electrolyte)

Compound	Temp.	($NaClO_4$) - ($NaCl$)	(HCl) - ($NaCl$)
Benzhydryl chloride	24.80	+22.8 ± 0.4	+4.5 ± 0.6
p-Methoxybenzyl chloride	29.88	+31.2 ± 0.5	+8.2 ± 0.6

CHAPTER III

DISCUSSION

Possible explanations to account for the specific electrolyte effects observed in the S_N1 hydrolysis of p-methoxybenzyl and benzhydryl chlorides, reactions where ionic-strength effects operate, will now be discussed.

Association between the electrolyte ions seems unlikely to be responsible for two reasons; firstly, the observed additivity of the effects of ions would not be expected and secondly, the negative effect of the fluoride ion could not be accounted for on this basis.

The suggestion of Lucas and Hammett (see Chapter I) that the specificity of salt effects is due to a varying affinity of the different ions for water, thus giving a decreased activity on the part of the water[8], is a distinct possibility and an adaptation of this approach will now be used in an attempt to explain the effects observed in the present investigation.

Qualitative Approach.

When the problem is considered in a qualitative manner, small ions are expected to be more highly solvated than large ions by water and the former should therefore exert the greatest retarding effect. Data for the anion series support this prediction (see Table III-1); the largest acceleration is observed for the largest ions, viz. perchlorate, nitrate and azide, while for the fluoride ion, the smallest ion, a retardation actually occurs. The large effect of the anions is perhaps rather surprising since in water anions are regarded as less strongly solvated than cations. When the cations are considered, the size of the ion seems to have little effect; on going from the lithium to the tetramethylammonium ion, little change in rate is found. The hydrogen ion, which is usually regarded as being fairly strongly solvated and which should therefore be strongly retarding, is however found to be the best accelerating ion.

Recent work by Baughman, Grunwald and Kohnstam[21] suggests that in addition to solvation of the ions by water, solvation by the organic component should also be taken into account and it is possible that the behaviour of cations, noted above, can be accounted for in this way.

Quantitative Treatment.

The approach outlined above will now be discussed in a quantitative manner.

If the electrolyte is solvated, the true composition of the solvent (mole fraction of water, x_1') is not the same as the formal composition (formal mole fraction of water, x_1) which does not take this solvation into account. The effect of an electrolyte, concentration c, on the first-order rate of solvolysis, k, can therefore be considered to result from an effect at constant solvent composition, x_1', and a contribution from the change in x_1' caused by the solvation of the added electrolyte.

Hence, for reactions with a given solvent

$$\frac{d\ \ln k}{dc} = \left(\frac{\partial \ln k}{\partial c}\right)_{x_1'} + \left(\frac{\partial \ln k}{\partial x_1'}\right)_c \cdot \frac{dx_1'}{dc} \quad \ldots\ldots\ldots\ldots \text{III-1}$$

The first term on the right hand side of this equation is assumed to be given by the electrostatic theory of Hughes, Ingold and co-workers[1] and represents the ionic-strength effect proposed by these workers; hence

$$\left(\frac{\partial \ln k}{\partial c}\right)_{x_1'} = A\,\sigma \quad \text{, with } A = 2.10 \times 10^{16}/D^2T^2$$

where σ is the ionic-strength constant, D the dielectric constant of the solvent and T the absolute temperature.

As a first approximation it is assumed that the effect of a change in the solvent composition on the rate is the same in the presence of electrolytes as in their absence. Hence

$$\left(\frac{\partial \ln k}{\partial x_1'}\right)_c = \left(\frac{\partial \ln k}{\partial x_1'}\right)_{c=0} = \left(\frac{d\ \ln k}{dx_1}\right)_{c=0}$$

since $x_1 = x_1'$ at zero electrolyte concentration.

If the solvation of the electrolyte is independent of its concentration, a reasonable assumption for dilute solutions

$$\frac{dx_1'}{dc} = \left(\frac{dx_1'}{dc}\right)_{c=o}$$

$$= \left(\frac{d \ln a_1/a_2}{dm}\right)_{c=o} \cdot \frac{dm}{dc} \cdot \left(\frac{dx_1}{d \ln a_1/a_2}\right)_{c=o}$$

since $x_1' = x_1$ when $c = 0$; a_1 and a_2 are the activities of the water and the organic component of the solvent respectively and m is the molality of the electrolyte.

Application of these considerations to Eqn.III-1 yields

$$\frac{d \ln k}{dc} = A\sigma + \left(\frac{d \ln k}{dx_1}\right)_{c=o} \cdot \frac{dm}{dc} \cdot \left(\frac{dx_1}{d \ln a_1/a_2}\right)_{c=o} \cdot \left(\frac{d \ln a_1/a_2}{dm}\right)_{c=o}$$

$$= A\sigma + B'\left(\frac{d \ln a_1/a_2}{dm}\right)_{c=o} \qquad \text{..............III-2}$$

where the constant B' represents the first three factors of the last term and is independent of the nature or concentration of the electrolyte.

Grunwald and Bacarella[27] have shown that the term $\left(\frac{d \ln a_1/a_2}{dm}\right)_{c=o}$ can be obtained from experimental measurements and that it is related to the mean ionic standard chemical potential, $\mu_\pm^0$, of the electrolyte by the expression

$$\left(\frac{d\ \ln a_1/a_2}{dm}\right)_{c=0} = \frac{2\ M_{12}}{1000R\ T} \cdot \frac{d\mu_\pm^0}{dx_1}$$

where $M_{12} = x_1M_1 + x_2M_2$; the molar weight of the binary solvent.

Substitution in Eqn.III-2 yields

$$\frac{d\ \ln k}{dc} = A\sigma + B \cdot \frac{d\mu_\pm^0}{dx_1} \qquad \text{........III-3}$$

where $B = \frac{2\ M_{12}}{1000\ R\ T} B'$

On this view specific salt effects are to be expected if the value of $d\mu_\pm^0/dx_1$ depends on the nature of the electrolyte, and it has been shown that this is indeed the case for solutions in 50% aqueous dioxan[21].

Unfortunately, no rigorous test of Eqn.III-3 is possible since values of $d\mu_\pm^0/dx_1$ are only available for 50% dioxan. These values are compared in Table III-1 with d ln k/dc[†] for 70% acetone; ionised chlorides are listed

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[†] Since for ionic-strength effects, a linear relationship holds between ln k and c[1,28], then, to a first approximation

$$\frac{d\ \ln k}{dc} = \frac{\ln k(0.05) - \ln k_0}{0.05}$$

where k(0.05) is the rate constant in the presence of 0.05 M electrolyte and k_0 is the rate constant in the absence of added electrolyte.

TABLE III - 1

CORRELATION OF KINETIC DATA FOR HYDROLYSIS OF BENZHYDRYL CHLORIDE IN 70% ACETONE WITH VALUES OF $d\mu_{\pm}^{o}/dx_1$[21] AND LOG f[30].

Added Electrolyte	Percentage Change in Rate Produced by 0.05 M Electrolyte	$\frac{d \ln k}{dc}$	$2.\frac{d\mu_{\pm}^{o}}{dx_1}$ (kcal) 50%dioxan 25°C	log f
$HClO_4$	21.1	3.84	+ 0.6	-0.041
HNO_3	19.3	3.53	- 4.6*	<-0.048†
NaN_3	17.8	3.27	-	-
$NaNO_3$	15.3	2.85	- 9.8	0.119
$NaClO_4$	15.1	2.81	- 4.0	0.103
$LiClO_4$	14.5	2.73	- 2.4*	-
CsBr	9.3	1.77	-10.0*	-
$(CH_3)_4NBr$	9.3	1.77	-11.0*	-0.24
NaBr	8.6	1.65	-11.3*	0.155
KBr	-	-	-11.3	-
LiBr	6.7	1.32	- 9.0*	-
$(CH_3)_4NF$	-4.7	-0.95	-	0.255**
HCl	-3.2	-0.65	- 7.9	-0.048
RbCl	-	-	-13.2	-
CsCl	-6.0*	-1.27*	-12.5	
$(CH_3)_4NCl$	-6.0*	-1.27*	-13.5	-
LiCl	-7.7	-1.54	-11.5	0.145
NaCl	-7.7	-1.57	-13.8	0.195
KCl	-	-	-13.8	-

† , * , ** ; - For footnotes see page 196.

separately in this table since their presence results in the operation of retarding mass-law effects which are not taken into account by Eqn.III-3. It can be seen that qualitatively d ln k / dc decreases with decreasing $d\mu_{\pm}^{o}/dx_1$ and it may well be that much better agreement would have been obtained if the values of the two parameters had been available for the same solvent. It is however noteworthy that the large change in d ln k / dc on replacing a salt by the corresponding acid, the similar effect of the other monovalent cations, and the accelerating effect of replacing a halide by the perchlorate are also reflected in $d\mu_{\pm}^{o}/dx_1$.

Footnotes for Table III-1.

[†] Unfortunately no data for the effect of HNO_3 is available for benzene. Studies for hydrogen, oxygen and carbon dioxide show that HNO_3 has a lower value than HCl for log f (see Table III-2). Assuming HNO_3 occupies a similar position in the series of electrolytes in benzene, the value for log f would be less than -0.048.

[*] Calculated from experimental data for other electrolytes using additivity relations, which have been established for d ln k / dc values (see page 187) and which also hold for 2 . $d\mu_{\pm}^{o}/dx_1$ values.

[**] Value obtained for NaF.

The approach which has been discussed above is similar, though it differs in detail, to one which has already been used by Duynstee[29] to account for salt effects in the racemisation of L-(+)-threo-3-phenyl-2-butyl-p-toluenesulphonate in 50% aqueous dioxan. This approach was found to be applicable for NaOH, NaCl, $NaNO_3$ and $NaClO_4$ but NaI, NaBr, and salts with organic ions were found to deviate considerably from the requirements of Eqn.III-3. Of this latter group of salts only NaBr has been investigated in the present work but here it appears to satisfy the theory outlined above. Duynstee postulated that in the anomalous cases, the reaction rate was affected by short-range interactions between the ions and the molecules of the reagent and transition state.

In conclusion it can be stated that the approach used above is consistent with the specific electrolyte effects obtained in the present investigation.

Salting-in and Salting-out.

The Hughes-Ingold treatment (see Chapter I) assumes that the effect of electrolytes on the activity of the initial state is so much less than their effect on the transition state that the former may be ignored. Salting-in and salting-out data however show that this effect is by no means negligible[30]. The question thus arises as to whether specific electrolyte effects arise from specific effects on the activity of the initial state of the organic chloride. Unfortunately this has not been investigated in practice. Data are however available for the effect of electrolytes on organic substrates in saturated solution, though even then the solvent is usually water. The only available data for the effect of electrolytes on the solubility of non-electrolytes in mixed solvents are due to Butler and Grunwald[31] who studied the effect of HCl, KI, NaCl and KCl on the solubility of α-naphthoic acid and of NaCl and KCl on the solubility of naphthalene, 50% dioxan being the solvent in both cases.

Electrolytes have been found to affect the solubility of different non-electrolytes in water in a similar manner. This is illustrated in Table III-2 using data for benzene, succinic acid, oxygen and carbon dioxide from the compilation of Long and McDevit[30].

If the specific electrolyte effects now found arise solely from the alteration in the activity coefficient of benzhydryl chloride, the activity coefficient of saturated solutions of non-electrolytes in water in the presence of electrolytes should parallel the effects of these electrolytes on the rates of ionisation in the present reaction. The appropriate data for benzene in water have therefore been included in Table III-1, where log f (f is the molar activity

TABLE III - 2

ELECTROLYTE EFFECTS FOR BENZENE, SUCCINIC ACID, OXYGEN AND SULPHUR DIOXIDE

Values of log f, the molar activity coefficient of the solute in the electrolyte solution, from solubility data[30]

Electrolyte	Benzene	Succinic Acid	Oxygen	Carbon Dioxide
$(CH_3)_4NBr$	-0.24	-	-	-
$HClO_4$	-0.041	-	-	-
HNO_3	-	-	0.019	-0.014
HCl	0.048	-	0.031	0.019
CsCl	0.088	-0.026	-	0.048
$NaClO_4$	0.106	-	-	-
KNO_3	-	-	0.100	0.044
$NaNO_3$	-	-	-	0.078
KBr	0.119	0.002	-	0.063
RbCl	0.141	-0.005	-	0.063
LiCl	0.141	0.154	0.100	-
NaBr	0.155	-	0.110	-
KCl	0.166	0.018	0.132	0.073
NaCl	0.195	0.088	0.141	0.101
NaF	0.255	-	-	-

coefficient of benzene) is compared with dlnk/dc. It can be seen that, with the exception of tetramethylammonium bromide, values of dlnk/dc and log f parallel each other.

There are however three objections to such a comparison,

(i) The effect of electrolytes on the activity of the solute in a saturated solution is assumed to be the same as the effect on the activity in a dilute one.

(ii) The effect of electrolytes on the activity of the solute in water is assumed to parallel its activity in aqueous organic solvents. The data of Butler and Grunwald[31] suggest that this is not the case.

(iii) The discussion assumes that these electrolytes have different effects on the activities of the initial state and either no effect or alternatively the same effect on the activity of the transition state in the S_N1 ionisation.

Duynstee[29] attempted to overcome this last objection in the following way.

The salting-in and salting-out of naphthalene and naphthoic acid were studied and from this work it was concluded that the Setschenow constant[32], **K** , which is equal to $d\ln f_3/dc$, (where f_3 is the molar activity coefficient and c the molar concentration of the non-electrolyte in the electrolyte solution) is given by an expression similar to Eqn.III-3, namely,

$$K = \frac{d \ln f_3}{dc} = A' + B' \frac{d\mu_\pm^{\circ}}{dx_1} \left(\frac{\partial \mu_3^{\circ}}{\partial x_1}\right)_c \quad \text{....III-4}$$

where A' is an empirical constant analogous to the ionic-strength term and also to the electrostatic term employed by Long and McDevit in discussing salting-in and salting-out[30].

B' is an empirical constant which is rather insensitive to the nature of the non-electrolyte.

$(\partial\mu_3^{\circ}/\partial x_1)_c$ represents the change in standard chemical potential of non-electrolyte solute with variation in solvent composition at constant electrolyte concentration.

$d\mu_\pm^{\circ}/dx_1$ represents the change in the mean ionic standard chemical potential of the electrolyte with variation in solvent composition.

Duynstee assumed that Eqn.III-4 applied to both the initial and transition states of ionisation. Thus,

$$\frac{d \ln f_3^{*}}{dc} = A'^{*} + B'^{*} \frac{d\mu_\pm^{\circ}}{dx_1} \left(\frac{\partial \mu_3^{*}}{\partial x_1}\right)_c \quad \text{.....III-5}$$

where the superscript * refers to the transition state.

The effect of electrolytes on the rate constant is given by the following equation due to Brønsted[33]

$$k = k_o . \frac{f_3}{f_3^{*}}$$

where f_3 and f_3^* are the molar activity coefficients of the reactant in the initial and transition states respectively and k_o is the rate constant at infinite dilution, when the activity coefficients are unity.

Therefore,

$$\frac{d\ \ln k}{dc} = \frac{d\ \ln f_3}{dc} - \frac{d\ \ln f_3^*}{dc} \qquad \text{.........III-6}$$

On substituting in Eqn. III-6 for $d\ln f_3/dc$ and $d\ln f_3^*/dc$ and assuming $B' = B'^*$, one obtains

$$\frac{d\ \ln k}{dc} = (A' - A'^*) + B' \frac{d u_{\pm}^{\circ}}{dx_1} \left[\frac{\partial u_3^{\circ}}{\partial x_1} - \frac{\partial u_3^*}{\partial x_1} \right] \qquad \text{....III-7}$$

But

$$\frac{\partial u_3^{\circ}}{\partial x_1} - \frac{\partial u_3^*}{\partial x_1} = - \frac{\partial(\Delta G^*)}{\partial x_1} \qquad \text{.............III-8}$$

where ΔG^* is the Gibb's free energy of the activation process and

$$\ln k = \ln \frac{\bar{k}T}{h} - \frac{\Delta G^*}{RT} \qquad \text{(Ref. 34)}$$

where $\bar{k}$ is Boltzmann's constant, h Planck's constant, R the gas constant and T the absolute temperature.

On substituting for ΔG^* in Eqn.III-8 one obtains

$$\frac{\partial \mu_3^{o}}{\partial x_1} - \frac{\partial \mu_3^{*}}{\partial x_1} = RT \left(\frac{d \ln k}{dx_1}\right)_{c=o}$$

$(d\ln k/dx_1)_{c=o}$ is a constant for a given solvent and hence, on substituting for $(\partial \mu_3^{o}/\partial x_1 - \partial \mu_3^{o}/\partial x_1)$ in Eqn.III-7, Eqn.III-9 is obtained.

$$\frac{d \ln k}{dc} = (A' - A'^{*}) + B \, . \, \frac{d \mu_{\pm}^{o}}{dx_1} \qquad \text{......III-9}$$

where B is a constant, equal to $B'RT(d\ln k/dx_1)_{c=o}$.

It is readily seen that Eqn.III-9 has the same form as Eqn.III-3. In the equation used by Duynstee, $A' - A'^{*}$ was in fact found to be of the order of magnitude to be expected for the ionic-strength term. The two approaches are thus equivalent.

The first approach (where the solvation of the electrolyte is considered), although it is more direct, does however involve the acceptance of a limiting expression of the Hughes-Ingold form for the ion-atmosphere stabilisation of the transition state. Using this approach, the specific effects of the electrolytes are interpreted as arising from their effects on the activities of the solvent components (which can be interpreted in terms of differential solvation of ions by both components) which change the ionising power of the solvent and hence the rate in a specific manner.

Duynstee's approach suffers from the disadvantage that the effect of electrolytes on the activity of saturated solutes is assumed to be the same as their effect on the activity of solutions which are very far from being saturated i.e. 0.02 M benzhydryl chloride in 70% acetone. The original views of Lucas and Hammett[8], viz. that the electrolyte causes a change in in the effective solvent composition, are also implicit in Duynstee's approach and in effect there is little distinction between his approach and the solvation one used in the present work.

The use of the solvation approach to account for specific electrolyte effects appears hopeful. It must however be stressed that this explanation can only be advanced provisionally at present since it depends on a comparison of kinetic electrolyte effects observed in aqueous acetone with the effect of electrolytes on the activities of the solvent components in 50% aqueous dioxan.

There are however some indications which suggest that this approach may be justified. For example, it has already been pointed out that $d\mu_{\pm}^{o}/dx_1$ values can be interpreted in terms of the solvation of the electrolytes by the two solvent components. Baughman, Grunwald and Kohnstam[21] have shown that solvation by dioxan increases relative to solvation by water as $d\mu_{\pm}^{o}/dx_1$ becomes increasingly more positive, the values for sodium perchlorate and perchloric acid (see Table III-1) thus corresponding to a relatively high degree of solvation by the organic component, dioxan. The abnormally high solubility of sodium perchlorate in anhydrous acetone, as compared with that of sodium chloride or bromide, suggests that powerful interactions may also occur between the perchlorate ion and acetone and it is therefore not unreasonable to expect a fairly high degree of solvation of perchlorate ions by acetone even in aqueous acetone mixtures. The comparison of the present kinetic data for acetone with the measurements of $d\mu_{\pm}^{0}/dx_1$ in dioxan assumes that ions which are strongly solvated by dioxan in dioxan-water mixtures are also strongly solvated by acetone in acetone-water mixtures; further work is necessary before it can be concluded that this assumption is of general validity.

CHAPTER IV

EXPERIMENTAL

Preparation and Purification of Materials

Benzhydryl chloride was prepared from benzhydrol (B.D.H.) by a method analogous to that for p-methoxybenzyl chloride (Part I) and purified by distillation under reduced pressure. The hydrolysable chloride content of the sample was identical with the theoretical amount.

p-Methoxybenzyl chloride was prepared as described in Part I.

Sodium chloride (Analar) was dried by keeping in the oven at 120°C for 2 hours.

Sodium bromide (Hopkin and Williams) was dried by keeping in the oven at 120°C for 4 hours.

Sodium nitrate (Analar) was dried by keeping in the oven at 120°C for 24 hours.

Sodium perchlorate (B.D.H.) was purified by recrystallisation from aqueous dioxan and dried by heating in a pistol at 100°C at 0.5 mm. pressure for 3 hours.

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

Lithium chloride (Hopkin and Williams) was dried by roughly the required amount being placed in a pistol which was heated at 100°C at 0.5 mm. pressure. The salt was then quickly transferred to the solvent and the exact concentration determined by potentiometric titration with standard silver nitrate solution.

Lithium bromide (Hopkin and Williams) was dried and made up into a standard solution by a method analogous to that for lithium chloride.

Lithium perchlorate (Hopkin and Williams) was dried by heating roughly the required amount in a pistol at 150°C at 5 mm. pressure for 3 hours. The salt was then quickly transferred to the solvent, the exact concentration being determined by passing a sample of the solution down a cationic exchange column and titrating with standard sodium hydroxide.

Caesium bromide (B.D.H. laboratory reagent) was dried by heating in a pistol at 100°C at 0.5 mm. pressure for 3 hours.

Tetramethyl ammonium bromide was prepared by adding trimethylamine (12.5 gm.) to methyl bromide (20 gm.) dissolved in dry ether. The product was filtered off, washed with water and purified by heating in a pistol at 100°C at 0.5 mm. pressure for 4 hours. The sample obtained was 100% pure.

Tetramethyl ammonium fluoride was prepared by the addition of the appropriate amount of an aqueous solution of tetramethyl ammonium bromide to a solution of silver fluoride. The silver bromide precipitated was filtered off and hydrogen sulphide passed through the warm solution to remove traces of silver. The solution was evaporated down and the fluoride dried by pumping for 20 hours at 150°C at 0.5 mm. pressure. The fluoride content of the sample was 98% of the theoretical amount. The salt was quickly added to the solvent, the exact concentration being determined in a manner analogous to that for lithium perchlorate.

The silver fluoride was prepared by the action of a solution of 40% hydrofluoric acid (Analar) on silver carbonate[35].

Perchloric acid was the B.D.H. Analar product containing 72% $HClO_4$. The appropriate amount of the acid was added to the solvent together with sufficient purified acetone to ensure that the solvent composition remained unchanged. The exact concentration of $HClO_4$ in the solvent was determined by titration with standard sodium hydroxide solution.

Nitric acid was Hopkin and Williams' Analar product containing 70% HNO_3. It was added to the solvent and the exact concentration determined by methods analogous to those used for perchloric acid.

Hydrochloric acid. In Expt.5, HCl was introduced into the solvent by passing sufficient HCl gas (generated by the action of sulphuric acid on voltoids) through the solvent, which was cooled in ice. Since there is the possibility that evaporation of the solvent occurs using this technique, for Expt.28 a method similar to that used for adding perchloric acid was employed, the acid in the present case being the B.D.H.Analar product containing 35.4% HCl. The exact concentration of HCl in the solvent was determined by titration with standard sodium hydroxide solution.

The solvent ("70%" aqueous acetone) was made up by the method described in Part I.

Estimation of Added Electrolytes

Sodium chloride, sodium bromide, sodium nitrate, sodium perchlorate, sodium azide, caesium bromide and tetramethylammonium bromide were weighed into a known volume of solvent. In other cases the concentration of the added electrolyte was obtained by methods already described.

Rate Measurement

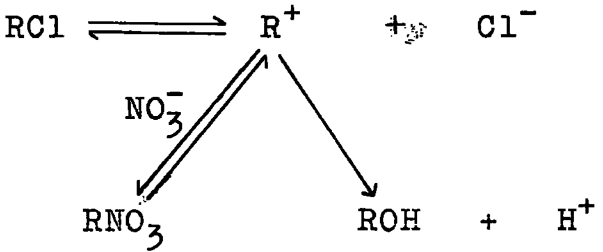
Kinetic runs were carried out at 24.80°C (for benzhydryl chloride) and 0.00°C and 29.88°C (for p-methoxybenzyl chloride), the thermostats being as described in Part I. All runs were flask runs. About 100 ml. of solvent in a stoppered flask were allowed to come to the thermostat temperature. The reactant was added and the flask thoroughly shaken. Samples were removed after suitable intervals of time using a 5 ml. pipette and the reaction stopped by running these samples into about 150 ml. of ice-cold acetone.

Runs containing HCl, NaCl, LiCl, $LiClO_4$, $NaClO_4$, NaBr, LiBr, CsBr, Me_4NBr were followed by measuring the change in acidity of the solution. For runs containing $HClO_4$, HNO_3, NaN_3, $NaNO_3$ and Me_4NF the change in chloride ion concentration was followed, using the apparatus described in the next section. This was necessary for the following reasons,

(i) If samples containing 0.05 N acid had been titrated with alkali large inaccuracies in the titres obtained would have been expected.

(ii) Sodium azide reacts with a carbonium ion forming a stable organic azide which does not ionise. The reaction rate followed by measuring the increase in acidity would thus be less than the true ionisation rate.

(iii) For runs carried out in the presence of $NaNO_3$ a percentage increase in rate of 19.3% was observed when the rate of chloride formation was followed but the value for the increase was only 7.1% when the rate of production of hydrogen ions was utilized. This is probably due to the reaction of nitrate ions with the formed carbonium ions according to the following system,



Even though the ionisation of nitrates is approximately forty times that of chlorides[†], on this basis it is possible for the rate of production of chloride ions to be greater than that of hydrogen ions.

It is possible that the results for bromides are also low since bromides ionise at a similar rate to nitrates[†]. Unfortunately no accurate method exists for following the rate of production of chloride ions in the presence of a relatively large concentration of bromide ions and the present results for bromides are therefore accepted.

Details of individual runs are given in Appendix A, at the end of this chapter.

[†] For the solvolysis of tert.-butyl nitrate in 60% aqueous ethanol at 0°C, $10^5k(\text{sec.}^{-1}) = 12.5$[36]; for tert.-butyl bromide under similar conditions, $10^5k(\text{sec.}^{-1}) = 13.3$[37].

For the solvolysis of tert.-butyl bromide in 80% aqueous ethanol at 25°C, $10^4k(\text{sec.}^{-1}) = 3.74$; for tert.-butyl chloride under similar conditions, $10^6k(\text{sec.}^{-1}) = 9.14$[38].

Potentiometric Determination of Chloride-ion Concentration

The apparatus used is shown diagrammatically in Fig.IV-1.

The acetone containing the chloride ion, the concentration of which was to be determined, was contained in a beaker which was well stirred. Standard silver nitrate solution was added from the burette and after each addition the e.m.f. between the glass electrode and the Ag/AgCl electrode was determined using a pH meter. At the equivalence point, the change of e.m.f. per unit titre was at a maximum.

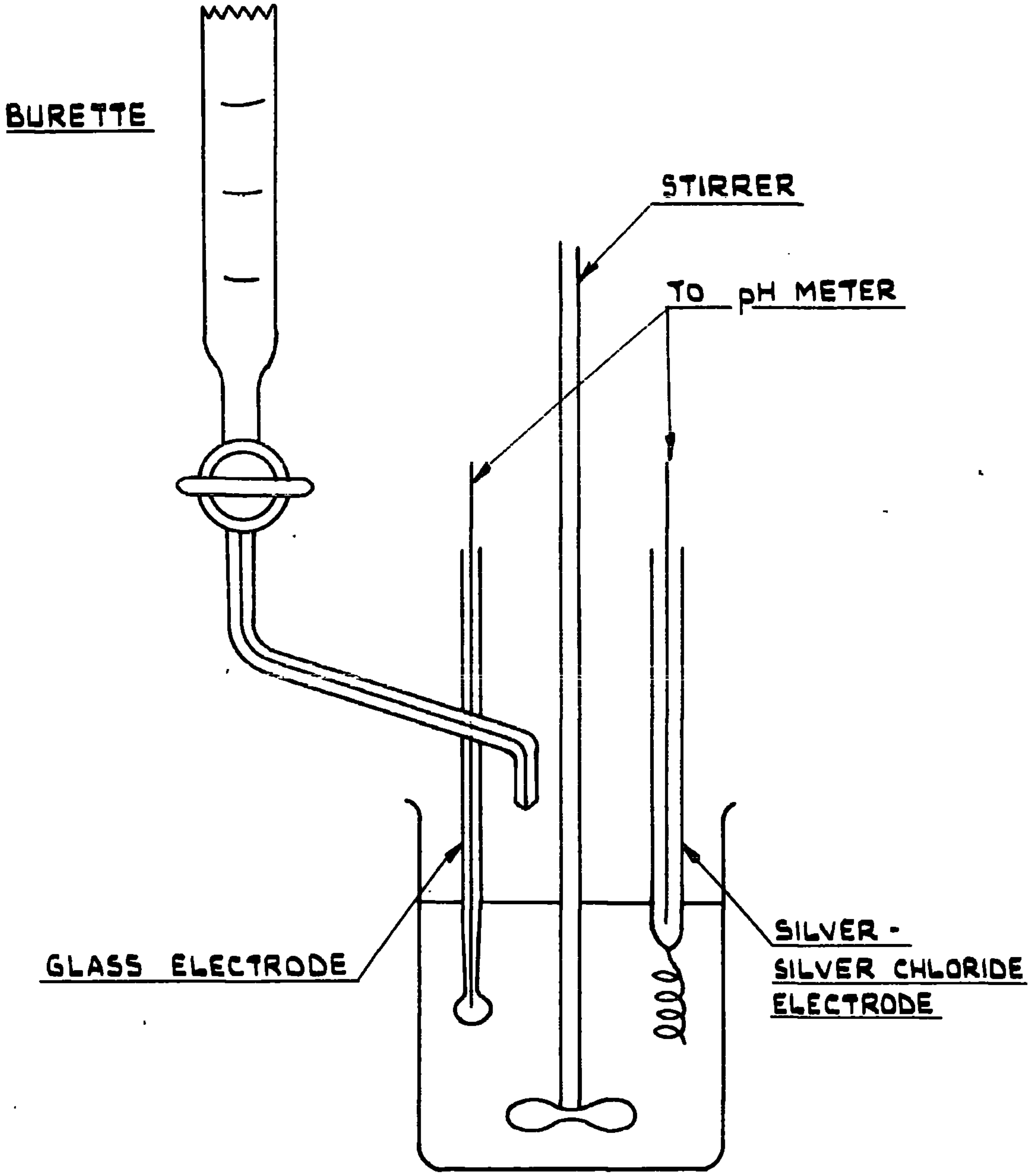
Determination of σ, the ionic-strength constant and α^{o}, the mass-law constant in the hydrolysis of p-methoxybenzyl chloride in 70% aq. acetone at 29.88°C

The ionic-strength and mass-law effects affect the measured reaction rate in accordance with Eqn.I-7 (see page 170).

$$k_1^{o}t = \alpha^{o}\int_{o}^{x}\frac{[X^-]}{(a-x)}\,\text{antilog}_{10}A\,/\mu^{\frac{1}{2}}.dx + \int_{o}^{x}\frac{\text{antilog}_{10}B\sigma\ /u}{(a-x)}\,.\,dx \qquad \text{....I-7}$$

where the symbols have the same significance as in Chapter I. Let c represent the concentration of added common-ion

FIGURE IV I



POTENTIOMETRIC DETERMINATION OF CHLORIDE - ION CONCENTRATION.

electrolyte and b the concentration of non-common-ion electrolyte. Writing $[X^-] = c + x$ and $\mu = b + c + x$ one obtains,

$$\frac{I}{t} = k_1^{\circ} - \alpha^{\circ}\left(\frac{J}{t}\right) \qquad \text{...........IV-1}$$

where

$$I = \int_0^x \frac{\text{antilog}_{10} B\sigma\, (b + c + x)}{(a - x)} \,.\, dx$$

and

$$J = \int_0^x \frac{(c+x)\ \text{antilog}_{10} A\, (b + c + x)^{1/2}}{(a - x)} \,.\, dx$$

A and B were evaluated from Åkerlöf's data for the dielectric constants of acetone-water mixtures[39] and are given for 70% acetone at 30°C in Table IV-1. The integral I was obtained from the expression

$$I = (k_1 t - 2.303\, B\sigma\, x)\ \text{antilog}_{10} B\sigma\, (b + c + a)$$

(see Appendix C, this chapter)

J was obtained graphically.

The ionic-strength constant, σ , was obtained from the effect of 0.04984 M $NaClO_4$ on the rate constant. For the operation of the ionic-strength effect only, the reaction rate is affected in accordance with Eqn.IV-2, the integrated form of Eqn.I-4.

$$k = k_1^{\circ} \text{ antilog}_{10} B \sigma \mu \quad \ldots\ldots \text{IV-2}$$

It was assumed, to a first approximation, that the ionic-strength and mass-law effects due to the chloride ions produced during hydrolysis are similar in the presence and absence of $NaClO_4$. The ratio k/k_1° (for $\mu = 0.04984$) is then equal to the ratio of the mean integrated rate coefficients in the presence and absence of 0.04984 N $NaClO_4$ (see Table II-1). σ was found to be equal to 1.9×10^{-8}. There is little point in using a value for σ more precise than 2×10^{-8} in view of the assumption made in the establishment of k_1/k_1° and this value was therefore used in the determination of α°, the mass-law constant. I and J integrals were obtained for experiments in the absence of added electrolytes (shown in Table IV-1) and in the presence of 0.05000 M NaCl. Using mean values for I/t and J/t, the two simultaneous equations obtained by applying Eqn.IV-1 to each experiment gave, on solution, $k_1^{\circ} = 7.469 \times 10^{-4}$, $\alpha^{\circ} = 16$.

Calculation of Results

Mean rate coefficients, k_m, were obtained for each run. The standard deviation σ (k) was obtained from

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

where n is the number of separate determinations of k.

TABLE IV - 1

I AND J INTEGRALS FOR REACTION OF p-METHOXYBENZYL CHLORIDE WITH 70% AQ.ACETONE AT 29.88°C. NO ADDED ELECTROLYTES (EXPT. 1)

(5 ml. samples titrated with 0.007657 N NaOH; D = 37.8,
A = -1.481, B = -0.6944×10^{8}, $\sigma = 2 \times 10^{-8}$)

Time (sec.)	Titre (ml.)	10^4 k (sec.$^{-1}$)	10^4 I/t (sec.$^{-1}$)	10^6 J/t (mole l.$^{-1}$ sec.$^{-1}$)
0	1.09	-	-	-
145	2.30	6.972	6.914	1.568
290	3.40	6.997	6.918	2.054
441	4.49	7.134	7.028	2.535
598	5.40	7.001	6.885	2.854
738	6.18	7.013	6.877	3.176
895	6.90	6.908	6.760	3.132
1285	8.57	7.009	6.827	4.301
1425	9.13	7.134	6.934	4.308
1654	9.75	7.030	6.818	4.565
2122	10.86	7.041	6.810	5.170
2565	11.65	7.099	6.827	5.750
2843	12.00	7.066	6.787	5.941
∞	13.69	-	-	-

Values for the percentage change in rate produced by each added electrolyte were obtained using the value for the mean rate constant for experiments with no electrolyte addition in the same solvent. The standard error for the percentage change in rate, $\sigma(x)$, was obtained from

$$\sigma(x) = \left[\left(\frac{\sigma(k)}{k}\right)^2 + \left(\frac{\sigma_1(k_1)}{k_1}\right)^2\right]^{1/2}$$

where $\sigma(k)$ and k refer to no electrolyte addition and $\sigma_1(k_1)$ and k_1 to the addition of the electrolyte.

Assuming that for small variations in the concentration of added electrolyte, the change in rate varies linearly with concentration, the percentages were corrected to a value corresponding to the addition of 0.05000 N electrolyte (or, in the case of NaCl, LiCl and HCl, 0.02000 N electrolyte) and an average value obtained for the percentage change in rate produced by each electrolyte added.

The standard deviation for this final percentage is given by,

$$\sigma = \left[\frac{n_1^2\sigma(x_1)^2 + n_2^2\sigma(x_2)^2 + n_1(x_1-y)^2 + n_2(x_2-y)^2}{(n_1 + n_2)^2}\right]^{1/2}$$

where $\sigma(x_1)$, x_1, and n_1 refer respectively to the standard error in the percentage change in rate, the percentage change and the number of separate determinations of the rate constant in an experiment; $\sigma(x_2)$, x_2 and n_2 are similar quantities in a duplicate experiment; y is the weighted mean of x_1 and x_2.

These calculations are shown in detail in Appendix B at the end of this chapter.

CHAPTER IV. APPENDIX A

HYDROLYSIS OF BENZHYDRYL CHLORIDE AND p-METHOXYBENZYL CHLORIDE IN 70% AQUEOUS ACETONE.

Details of Individual Runs.

First order rate constants were calculated from the equation,

$$k = 2.303/t. \log(a/a - x)$$

where k is the rate constant in sec.$^{-1}$,

t is the time in seconds,

a is the concentration of alkyl chloride at t = 0,

a-x is the concentration of alkyl chloride at t = t.

Titres are expressed in ml. of NaOH or $AgNO_3$ per sample.

In each case details of one run are given and the mean rate coefficients k', k'', etc. of duplicate runs are also quoted.

Expt.1 p-Methoxybenzyl Chloride in 70% aq.Acetone III at 29.88°C

5 ml. titrated with 0.007657 N NaOH

No added salts

Time	Titre	10^4 k
0	1.09	-
145	2.30	6.972
290	3.40	6.997
441	4.49	7.134
598	5.40	7.001
738	6.18	7.013
895	6.90	6.908
1285	8.57	7.009
1425	9.13	7.134
1654	9.75	7.030
2122	10.86	7.041
2565	11.65	7.099
2843	12.00	7.066
∞	13.69	-

k = 7.033 ± 0.0181 (12 readings)

k' = 7.062 ± 0.0237 (10 readings)

Mean k = 7.046 ± 0.0150

Expt.2 p-Methoxybenzyl Chloride in 70% aq.Acetone III at 29.88°C

5 ml. titrated with 0.007657 N NaOH

Added NaCl 0.05000 N.

Time	Titre	10^4 k
0	0.80	-
151	1.90	6.039
303	2.97	(6.226)
452	3.81	6.024
603	4.70	6.084
746	5.40	6.067
900	6.11	6.057
1241	7.49	6.074
1533	8.46	6.078
1768	9.13	6.087
2119	9.91	6.036
2528	10.70	6.049
2773	11.02	5.962
∞	13.44	-

k = 6.051 ± 0.0104 (11 readings)

Duplicate Experiment.

Added NaCl 0.05015 N k' = 5.971 ± 0.0117 (10 readings)

Mean k = 6.013

Expt.3 p-Methoxybenzyl Chloride in 70% aq.Acetone III at 29.88°C

5 ml. titrated with 0.007657 N NaOH

Added $NaClO_4$ 0.04984 N

Time	Titre	10^4 k
0	1.79	-
145	3.12	8.354
290	4.26	8.202
559	6.03	8.079
710	7.00	8.322
859	7.70	8.222
1292	9.40	8.175
1815	10.87	8.294
2075	11.33	8.198
2347	11.70	8.061
∞	13.46	-

k = 8.212 ± 0.0340 (9 readings)

Expt.4 p-Methoxybenzyl Chloride in 70% aq.Acetone III at 29.85°C

5 ml. titrated with 0.007314 N NaOH

Added NaCl 0.01979 N

Time	Titre	10^4 k
0	1.98	-
149	3.20	6.739
303	4.31	6.643
438	5.21	6.646
587	6.10	6.628
735	6.93	6.661
1115	8.66	6.628
1602	10.21	(6.440)
1778	10.87	6.680
1896	11.20	6.732
2086	11.60	6.688
2210	11.80	6.609
∞	14.77	-

k = 6.665 ± 0.0135 (10 readings)

Duplicate Experiment

Added NaCl 0.02100 N   k' = 6.482 ± 0.0494 (10 readings)

Mean k = 6.573

Expt.5 p-Methoxybenzyl Chloride in 70% aq.Acetone III at 29.85°C

5 ml. titrated with 0.007314 N NaOH

Added HCl 0.01777 N

Time	Titre	10^4 k
0	12.15	-
127	13.20	6.908
273	14.30	6.916
420	15.30	6.921
580	16.30	6.956
685	16.80	6.798
792	17.41	6.902
1172	18.99	6.769
1428	19.87	6.745
1730	20.66	(6.612)
1947	21.31	6.790
2097	21.68	6.866
∞	24.64	-

k = 6.857 ± 0.0224 (10 readings)

Duplicate Experiment

Added HCl 0.02250 N k' = 6.756 ± 0.0211 (9 readings)

Mean k = 6.829

Expt.6 p-Methoxybenzyl Chloride in 70% aq.Acetone III at 0.00°C

5 ml. titrated with 0.007657 N NaOH

No added salts

Time	Titre	10^5 k
0	1.48	-
5395	2.58	1.669
8805	3.21	1.656
12150	3.82	1.671
16315	4.59	1.711
19095	5.00	1.691
20796	5.29	1.707
26700	6.10	1.685
28170	6.36	1.710
30260	6.60	1.695
33625	7.00	1.685
∞	14.24	-

k = 1.688 ± 0.00539 (10 readings)

k' = 1.692 ± 0.00460 (10 readings)

Mean k = 1.690 ± 0.00355

Expt.7 p-Methoxybenzyl Chloride in 70% aq.Acetone III at 0.00°C

5 ml. titrated with 0.007657 N NaOH

Added NaCl 0.05000 N

Time	Titre	10^5 k
0	0.06	-
5886	1.23	(1.464)
11346	2.30	1.518
14659	2.88	1.518
18024	3.44	1.516
22108	4.09	1.519
24666	4.46	1.513
26606	4.71	1.500
32706	5.60	1.522
33971	5.73	1.510
36036	5.95	1.496
∞	14.19	-

k = 1.512 ± 0.00281 (9 readings)

Duplicate Experiment

Added NaCl 0.05020 N k' = 1.511 ± 0.00362 (10 readings)

Mean k = 1.511

Expt.8 p-Methoxybenzyl Chloride in 70% aq.Acetone III at 0.00°C

5 ml. titrated with 0.007657 N NaOH

Added $NaClO_4$ 0.05002 N

Time	Titre	10^5 k
0	0.06	-
4116	1.16	1.949
9269	2.41	1.937
12474	3.18	1.979
15865	3.92	1.987
19200	4.51	1.944
21667	5.01	1.964
29502	6.39	1.985
30842	6.55	1.964
33662	6.95	1.955
36217	7.32	1.960
∞	14.35	-

k = 1.962 ± 0.00674 (10 readings)

Duplicate Experiment

Added $NaClO_4$ 0.05007 N

k' = 1.977 ± 0.00412 (10 readings)

Mean k = 1.970

Expt.9 Benzhydryl Chloride in 70% aq.Acetone IV at 24.80°C

5 ml. titrated with 0.01099 N NaOH

No added salts

Time	Titre	10^4 k
0	0.53	-
230	1.50	(4.256)
425	2.29	4.384
667	3.19	4.454
925	4.00	4.412
1160	4.64	4.365
1375	5.20	4.365
1875	6.30	4.349
2233	6.99	4.384
2765	7.80	4.383
3090	8.21	4.385
3390	8.59	4.450
∞	10.88	-

k = 4.393 ± 0.0106 (10 readings)

k' = 4.376 ± 0.0109 (11 readings)

k''= 4.392 ± 0.0168 (9 readings)

Mean k = 4.386 ± 0.0073

Expt.10 Benzhydryl Chloride in 70% aq.Acetone IV at 24.80°C

5 ml. titrated with 0.01099 N NaOH

Added NaCl 0.01957 N

Time	Titre	10^4k
0	1.19	-
242	2.11	4.359
465	2.81	4.165
810	3.87	4.263
1045	4.53	4.329
1308	5.14	4.302
1860	6.20	4.243
2070	6.50	4.173
2483	7.15	4.220
2780	7.59	4.298
3375	8.19	4.261
∞	10.37	-

k = 4.261 ± 0.0190 (10 readings)

Duplicate Experiment

Added NaCl 0.01918 k' = 4.250 ± 0.0127 (11 readings)

Mean k = 4.255

Expt.11 Benzhydryl Chloride in 70% aq.Acetone IV at 24.80°C

5 ml. titrated with 0.01099 N NaOH

Added LiCl 0.01653 N

Time	Titre	10^4 k
0	0.40	-
237	1.35	4.218
453	2.12	4.169
668	2.87	4.247
1049	4.00	4.256
1302	4.70	4.319
1507	5.15	4.277
1972	6.10	4.281
2147	6.40	4.269
2577	7.09	4.291
2997	7.70	4.369
3382	8.10	4.346
∞	10.40	-

k = 4.277 ± 0.0162 (11 readings)

Duplicate Experiment

Added LiCl 0.01753 N k' = 4.267 ± 0.0114 (9 readings)

Mean k = 4.273

Expt.12 Benzhydryl Chloride in 70% aq.Acetone IV at 24.80°C

5 ml. titrated with 0.01099 N NaOH

Added $NaClO_4$ 0.05023 N

Time	Titre	10^4 k
0	0.60	-
196	1.56	5.041
366	2.33	5.071
531	3.00	5.044
786	3.96	5.077
1044	4.79	5.060
1303	5.56	5.098
1716	6.51	5.040
2063	7.20	5.041
2538	8.00	5.084
2890	8.46	5.083
3208	8.83	5.114
∞	10.81	-

k = 5.068 ± 0.0073 (11 readings)

Duplicate Experiment

Added $NaClO_4$ 0.05015 N

k' = 5.031 ± 0.0081 (10 readings)

Mean k = 5.050

Expt.13 Benzhydryl Chloride in 70% aq.Acetone IV at 24.80°C

5 ml. titrated with 0.01099 N NaOH

Added NaBr. 0.04988 N

Time	Titre	10^4 k
0	0.50	-
185	1.38	4.817
366	2.12	4.676
560	2.90	4.739
873	4.00	4.756
1103	4.70	4.751
1318	5.30	4.760
1796	6.40	4.735
2126	7.05	4.754
2593	7.85	4.822
2911	8.27	4.823
3263	8.61	4.746
∞	10.80	-

k = 4.762 ± 0.0127 (11 readings)

Duplicate Experiment

Added NaBr 0.05051 N   k' = 4.767 ± 0.0163 (11 readings)

Mean k = 4.765

Expt.14 Benzhydryl Chloride in 70% aq.Acetone IV at 24.80°C

5 ml. titrated with 0.01099 N NaOH

Added $NaNO_3$ 0.04965 N

Time	Titre	10^4 k
0	0.50	-
212	1.45	4.661
470	2.46	4.593
746	3.49	4.704
961	4.20	4.747
1209	4.90	4.734
1481	5.59	4.735
2141	6.90	4.691
2366	7.20	4.602
2773	7.82	4.652
3088	8.26	4.737
3313	8.48	4.688
∞	10.60	-

k = 4.686 ± 0.0145 (11 readings)

Duplicate Experiment

Added $NaNO_3$ 0.04993 N　　k' = 4.728 ± 0.0071 (9 readings)

Mean k = 4.705

Expt.15 Benzhydryl Chloride in 70% aq.Acetone IV at 24.80°C

5 ml. titrated with 0.009225 N NaOH

Added NaN_3 0.05049 N

Time	Titre	10^4 k
0	0.86	-
295	2.44	5.083
540	3.56	5.032
770	4.57	5.140
985	5.53	5.381
1257	6.44	5.384
1597	7.26	5.196
2037	8.33	5.271
3048	9.79	5.070
3210	10.06	5.186
∞	12.21	-

k = 5.194 ± 0.0377 (9 readings)

Expt.16 Benzhydryl Chloride in 70% aq.Acetone V at 24.80°C

5 ml. titrated with 0.01020 N NaOH.

No added salts.

Time	Titre	10^4 k
0	0.60	-
230	1.70	4.296
403	2.45	4.269
738	3.76	4.259
1033	4.82	4.324
1271	5.55	4.316
1468	6.10	4.316
1906	7.20	4.347
2311	7.96	4.281
2793	8.80	4.308
3068	9.20	4.315
3270	9.50	4.359
∞	12.32	-

k = 4.308 ± 0.0088 (11 readings)
k' = 4.325 ± 0.0195 (10 readings)
k'' = 4.342 ± 0.0178 (11 readings)

Mean k = 4.325 ± 0.0089

Expt.17 Benzhydryl Chloride in 70% aq.Acetone V at 24.80°C

5 ml. titrated with 0.01020 N NaOH

Added LiBr 0.05290 N

Time	Titre	10^4 k
0	0.51	-
261	1.70	(4.306)
522	2.80	(4.389)
752	3.79	4.617
967	4.50	4.567
1204	5.30	4.650
1454	5.99	4.637
1964	7.20	4.650
2265	7.80	4.668
2623	8.40	4.671
3047	8.79	4.647
3277	9.28	4.693
3546	9.52	4.633
∞	11.68	-

k = 4.643 ± 0.0103 (10 readings)

Duplicate Experiment

Added LiBr 0.04730 N k' = 4.586 ± 0.0216 (7 readings)

Corrected to Solvent IV Mean k = 4.685

Expt.18. Benzhydryl Chloride in 70% aq.Acetone V at 24.80°C

5 ml. titrated with 0.01056 N NaOH

Added CsBr 0.05015 N

Time	Titre	10^4 k
0	0.49	-
246	1.66	4.597
482	2.73	4.744
685	3.51	4.704
930	4.40	4.740
1167	5.14	4.729
1389	5.76	4.714
1954	7.18	4.820
2255	7.72	4.773
2631	8.30	4.732
3096	8.90	4.701
3548	9.42	4.742
∞	11.46	-

k = 4.727 ± 0.0164 (11 readings)

Duplicate Experiment

Added CsBr 0.04978 N k' = 4.728 ± 0.0111 (10 readings)

Corrected to Solvent IV Mean k = 4.793

Expt.19 Benzhydryl Chloride in 70% aq.Acetone V at 24.80°C

5 ml. titrated with 0.01056 N NaOH

Added Me_4NBr 0.04695 N

Time	Titre	10^4 k
0	0.45	-
248	1.51	(4.586)
613	2.89	4.643
876	3.87	4.713
1119	4.46	4.673
1281	4.90	4.692
1467	5.35	4.690
1955	6.39	4.726
2144	6.70	4.693
2578	7.37	4.703
2979	7.90	4.741
3395	8.30	4.697
∞	10.30	-

k = 4.697 ± 0.0081 (10 readings)

Duplicate Experiment

Added Me_4NBr 0.04695 N k' = 4.705 ± 0.0128 (11 readings)

Corrected to Solvent IV Mean k = 4.767

Expt.20 Benzhydryl Chloride in 70% aq.Acetone V at 24.80°C

5 ml. titrated with 0.01056 N NaOH

Added $LiClO_4$ 0.04996 N

Time	Titre	10^4 k
0	0.68	-
207	1.78	(5.229)
450	2.79	4.872
709	3.80	4.854
931	4.67	5.002
1181	5.45	4.985
1681	6.72	4.932
1948	7.36	5.009
2379	8.10	4.953
2650	8.50	4.934
2967	8.93	4.948
3414	9.49	5.054
∞	11.40	-

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k = 4.954 ± 0.0184 (10 readings)

Duplicate Experiment

Added $LiClO_4$ 0.04224 N k' = 4.852 ± 0.0084 (9 readings)

Corrected to Solvent IV Mean k = 4.975

Expt.21 Benzhydryl Chloride in 70% aq.Acetone V at 24.80°C

5 ml. titrated with 0.009225 N NaOH

Added NaN_3 0.04980 N

Time	Titre	10^4 k
0	2.06	-
217	3.21	5.125
473	4.49	5.316
690	5.25	5.003
895	6.25	5.401
1147	7.05	5.316
1590	8.05	4.996
1785	8.47	4.949
2150	9.20	4.928
2447	9.76	4.983
2657	10.05	4.944
2964	10.46	4.938
3214	10.55	(4.667)
∞	12.99	-

k = 5.082 ± 0.0520 (11 readings)

Duplicate Experiment

Added NaN_3 0.05045 N k'= 5.095 ± 0.0489 (8 readings)

Corrected to Solvent IV Mean k = 5.158

Expt.22 Benzhydryl Chloride in 70% aq.Acetone VI at 24.80°C

5 ml. titrated with 0.01056 N NaOH

No added salts.

Time	Titre	10^4 k
0	0.50	-
264	1.69	4.292
509	2.70	4.330
776	3.70	4.384
983	4.40	4.394
1311	5.29	4.308
1765	6.43	4.318
2117	7.18	4.338
2400	7.75	4.399
2652	8.14	4.381
2915	8.45	4.306
3157	8.80	4.347
∞	11.62	-

k = 4.352 ± 0.0113 (11 readings)

k' = 4.320 ± 0.0106 (11 readings)

Mean k = 4.336 ± 0.0078

Expt.23 Benzhydryl Chloride in 70% aq.Acetone VI at 24.80°C

5 ml titrated with 0.008857 N $AgNO_3$

Added $HClO_4$ 0.05028 N

Time	Titre	10^4 k
0	1.89	-
270	3.29	5.297
458	4.12	5.208
680	5.00	5.160
1155	6.75	5.376
1477	7.64	5.364
2217	8.90	4.961
2535	9.45	5.013
2701	10.00	5.469
∞	12.40	-

k = 5.231 ± 0.0594 (8 readings)

Duplicate Experiment

Added $HClO_4$ 0.04744 N k' = 5.226 ± 0.0589 (9 readings)

Corrected to Solvent IV Mean k = 5.291

Expt.24 Benzhydryl Chloride in 70% aq.Acetone VI at 24.80°C

5 ml. titrated with 0.008857N $AgNO_3$

Added $NaNO_3$ 0.05304 N

Time	Titre	10^4 k
0	0.87	-
448	3.37	4.894
638	4.27	4.884
852	5.36	5.124
1089	6.25	5.049
1436	7.56	5.211
1711	8.28	5.119
2184	9.55	5.265
2653	10.09	4.881
3306	10.96	4.787
3465	11.26	4.919
∞	13.57	-

k = 5.013 ± 0.0477 (10 readings)

Duplicate Experiments

Added $NaNO_3$ 0.05046 N k' = 5.032 ± 0.0823 (8 readings)

Added $NaNO_3$ 0.05062 N k'' = 5.011 ± 0.0664 (9 readings)

Corrected to Solvent IV Mean k = 5.078

Expt.25 Benzhydryl Chloride in 70% aq.Acetone VI at 24.80°C

5 ml. titrated with 0.008857 N $AgNO_3$

Added HNO_3 0.04892 N

Time	Titre	10^4 k
0	0.69	-
389	2.73	5.098
870	4.82	5.208
1432	6.70	5.273
1835	7.70	5.247
2220	8.47	5.220
2537	9.01	5.217
3387	10.07	5.184
3529	10.14	5.079
∞	12.03	-

k = 5.191 ± 0.0227 (8 readings)

Duplicate Experiment

Added HNO_3 0.05012 N k' = 5.134 ± 0.0567 (8 readings)

Corrected to Solvent IV Mean k = 5.225

Expt.26 Benzhydryl Chloride in 70% aq.Acetone VII at 24.80°C

5 ml. titrated with 0.009523 N NaOH

No added salts

Time	Titre	10^4 k
0	0.70	-
246	1.90	4.578
480	2.89	4.491
705	3.75	4.472
1045	4.95	4.519
1445	6.10	4.502
1732	6.80	4.486
2146	7.69	4.498
2425	8.20	4.523
2685	8.69	4.581
3365	9.50	4.493
3601	9.78	4.529
∞	11.99	-

k = 4.516 ± 0.0103 (11 readings)

k' = 4.551 ± 0.0343 (11 readings)

Mean k = 4.534 ± 0.0179

Expt.27 **Benzhydryl Chloride in 70% aq.Acetone VII at 24.80°C**

5 ml. titrated with 0.009497 N $AgNO_3$

Added Me_4NF 0.03314 N

Time	Titre	10^4 k
0	1.34	-
240	2.17	4.591
480	3.25	4.467
733	4.05	4.365
1033	4.88	4.284
1310	5.65	4.364
1651	6.40	4.335
2080	7.10	4.192
2543	7.95	4.333
2770	8.35	4.433
3005	8.74	4.581
∞	11.24	[illegible]

k = 4.395 ± 0.0378 (10 readings)

Duplicate Experiment

Added Me_4NF 0.05272 N k' = 4.301 ± 0.0268 (8 readings)

Corrected to Solvent IV Mean k = 4.211

Expt.28 Benzhydryl Chloride in 70% aq.Acetone VII at 24.80°C

5 ml. titrated with 0.009523 N NaOH

Added HCl 0.02192 N

Time	Titre	10^4 k
0	12.07	-
242	13.20	4.273
485	14.40	4.544
768	15.51	4.457
1040	16.45	4.410
1367	17.50	4.438
1677	18.29	4.379
2030	19.20	4.461
2315	19.70	4.379
2757	20.65	4.563
3047	20.91	4.387
3337	21.40	4.510
∞	24.08	-

k = 4.436 ± 0.0241 (11 readings)

Duplicate Experiment

Added HCl 0.02070 k' = 4.512 ± 0.0291 (10 readings)

Corrected to Solvent IV Mean k = 4.326

CHAPTER IV, APPENDIX B

HYDROLYSIS OF p-METHOXYBENZYL CHLORIDE IN 70% AQUEOUS ACETONE III

Expt.	Temp.	Added Electrolyte	Electrolyte Concn.	Percentage Change in Rate	Percentage Change for 0.05000 N electrolyte	Mean Percentage Change
2	29.88°	NaCl	0.05000	-14.12 ± 0.27	-14.12 ± 0.27	-14.6 ± 0.23
		NaCl	0.05015	-15.26 ± 0.29	-15.21 ± 0.29	
3	29.88°	$NaClO_4$	0.04984	+16.55 ± 0.46	+16.60 ± 0.46	+ 16.6± 0.46
4	29.88°	NaCl	0.01979	- 5.41 ± 0.29	-5.47* ± 0.27	-6.4* ± 0.48
		NaCl	0.02100	- 8.00 ± 0.79	-7.62* ± 0.79	-
5	29.88°	HCl	0.01777	- 2.68 ± 0.39	-3.02* ± 0.39	-3.1* ± 0.29
		HCl	0.02250	- 4.12 ± 0.44	-3.66* ± 0.44	
7	0.00°	NaCl	0.05000	-10.60 ± 0.28	-10.60 ± 0.28	-10.6 ± 0.21
			0.05020	-10.60 ± 0.32	410.60 ± 0.32	
8	0.00°	$NaClO_4$	0.05002	+16.09 ± 0.40	+16.09 ± 0.40	+16.6 ± 0.25
			0.05007	+16.98 ± 0.30	+16.98 ± 0.30	

* Percentage change for 0.02000 N electrolyte

HYDROLYSIS OF BENZHYDRYL CHLORIDE IN 70% AQUEOUS ACETONE IV AT 24.80°C

Expt.	Added Electrolyte	Electrolyte Concn.	Percentage Change in Rate	Percentage Change for 0.05000 N electrolyte	Mean Percentage Change
10	NaCl	0.01957	- 2.90 ± 0.34	- 2.96* ± 0.34	- 3.1* ± 0.30
	NaCl	0.01918	- 3.10 ± 0.48	- 3.23* ± 0.48	
11	LiCl	0.01653	- 2.49 ± 0.41	- 3.01* ± 0.41	- 3.1* ± 0.31
	LiCl	0.01753	- 2.71 ± 0.48	- 3.09* ± 0.48	
12	$NaClO_4$	0.05023	+15.55 ± 0.22	+15.48 ± 0.22	+15.1 ± 0.21
	$NaClO_4$	0.05015	+14.71 ± 0.23	+14.67 ± 0.23	
13	NaBr	0.04988	+ 8.57 ± 0.32	+ 8.59 ± 0.32	+ 8.6 ± 0.24
	NaBr	0.05051	+ 8.69 ± 0.38	+ 8.60 ± 0.38	
14	$NaNO_3$	0.04965	+ 6.84 ± 0.36	+ 6.89 ± 0.36	+ 7.3 ± 0.24
	$NaNO_3$	0.04993	+ 7.80 ± 0.22	+ 7.81 ± 0.22	
15	NaN_3	0.05049	+18.42 ± 0.75	+18.24 ± 0.75	-

* Percentage change for 0.02000 N salt.

HYDROLYSIS OF BENZHYDRYL CHLORIDE IN 70% AQUEOUS ACETONE V AT 24.80°C

Expt.	Added Salt	Concn. of salt	Percentage Change in Rate	Percentage Change for 0.05000 N salt	Mean Percentage Change
17	LiBr	0.04730	+ 6.03 ± 0.54	+ 6.37 ± 0.54	+ 6.7 ± 0.29
	LiBr	0.05290	+ 7.35 ± 0.29	+ 6.95 ± 0.29	
18	CsBr	0.05015	+ 9.29 ± 0.44	+ 9.26 ± 0.44	+ 9.3 ± 0.27
	CsBr	0.04978	+ 9.32 ± 0.34	+ 9.36 ± 0.34	
19	Me_4NBr	0.04695	+ 8.60 ± 0.29	+ 9.16 ± 0.29	+ 9.3 ± 0.23
	Me_4NBr	0.04694	+ 8.79 ± 0.37	+ 9.36 ± 0.37	
20	$LiClO_4$	0.04224	+12.18 ± 0.30	+14.42 ± 0.30	+14.5 ± 0.19
	$LiClO_4$	0.04996	+14.54 ± 0.24	+14.55 ± 0.21	
21	NaN_3	0.04980	+17.50 ± 1.04	+17.57 ± 1.04	+17.8* ± 0.55
	NaN_3	0.05045	+17.80 ± 0.98	+17.64 ± 0.98	

* Includes experiment carried out in Solvent IV

HYDROLYSIS OF BENZHYDRYL CHLORIDE IN 70% AQUEOUS ACETONE VI AT 24.80°C

Expt.	Added Electrolyte	Electrolyte Concn.	Percentage Change in Rate	Percentage Change for 0.05000 N electrolyte	Mean Percentage Change
23	$HClO_4$	0.05028	+20.64 ± 1.38	+20.52 ± 1.38	+21.1 ± 1.06
	$HClO_4$	0.04744	+20.53 ± 1.38	+21.64 ± 1.38	
24	$NaNO_3$	0.05046	+16.05 ± 1.65	+15.91 ± 1.91	+15.3 ± 0.87
	$NaNO_3$	0.05062	+15.57 ± 1.34	+15.38 ± 1.55	
	$NaNO_3$	0.05304	+15.61 ± 0.96	+14.72 ± 1.11	
25	HNO_3	0.05012	+18.40 ± 1.11	+18.36 ± 1.31	+19.3 ± 0.71
	HNO_3	0.04892	+19.72 ± 0.47	+20.15 ± 0.56	

HYDROLYSIS OF BENZHYDRYL CHLORIDE IN 70% AQUEOUS ACETONE VII AT 24.80°C

Expt.	Added Electrolyte	Electrolyte Concn.	Percentage Change in Rate	Percentage Change for 0.05000 N electrolyte	Mean Percentage Change
27	Me_4NF	0.03314	-3.07 ± 0.89	-4.63 ± 0.89	-4.7 ± 0.60
	Me_4NF	0.05272	-5.13 ± 0.74	-4.87 ± 0.70	
28	HCl	0.02192	-2.16 ± 0.66	-1.97* ± 0.65	-1.3* ± 0.51
	HCl	0.02070	-0.49 ± 0.75	-0.47* ± 0.75	

* Percentage change for 0.02000 N acid

CHAPTER IV, APPENDIX C

EVALUATION OF INTEGRAL

$$I = \int_0^x \frac{\text{antilog}_{10} \; B\sigma\,(b + c + x)}{a - x} \,.\, dx$$

$$= e^{2.303 \; B\sigma \; (b+c)} \int_0^x \frac{e^{2.303 \; B\sigma \; x}}{a - x} \;.\; dx$$

Let $Y = a - x$

$$\therefore \; dY = -dx$$

$$\therefore \; I = e^{2.303 \; B\sigma \; (b+c)} \int_0^{a-Y} - \frac{e^{\,2.303 \; B\sigma(a-Y)}}{Y} \,.\, dY$$

$$= e^{2.303 \; B\sigma \; (b+c+a)} \int_0^{a-Y} - \frac{e^{-2.303 \; B\sigma \, Y}}{Y} \;.\; dY$$

$$= e^{2.303 \; B\sigma \; (b+c+a)} \int_0^{a-Y} \left(- \frac{1}{Y} + 2.303 \; B\sigma \;\; \ldots .\right) dY$$

Only the first two terms of the series were taken, further terms being negligible

$$= e^{\,2.303 \; B\sigma \; (b+c+a)} \int_0^x \frac{1}{(a-x)} \; - \; 2.303 \; B\sigma \;\; dx$$

$$= e^{2.303\ B\sigma\ (b+c+a)} \left[\log \frac{a}{a - x} - 2.303\ B\sigma\ x \right]$$

$$\therefore \quad I = (\bar{k}_1\ t - 2.303\ B\sigma\ x)\ \text{antilog}_{10}\ B\sigma\ (b + c + a)$$

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