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THE SOLVOLYSIS OF SOME PRIMARY ALKYL BROMIDES

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By

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ABSTRACT

Recent evidence suggests that the solvolysis of organic halides is associated with Arrhenius activation energies which have negative temperature coefficients. It is considered that this is most probably due to the increased solvation of the transition state of the reaction relative to the initial state of the reactants. Bensley and Kohnstam have suggested that the heat capacity of activation ($\Delta Cp^{*} = dE/dT - R$) is a measure of this increase in solvation and also that in S_N1 reactions, the entropy of activation, ΔS^{*}, is a measure of the same phenomenon; whereas in S_N2 reactions an additional negative contribution to ΔS^{*} due to the covalent binding of the nucleophilic reagent must be considered. The solvolysis of R-Hal in a given solvent and at a given temperature should, therefore, have a constant value for the $\Delta Cp^{*}/\Delta S^{*}$ ratio for S_N1 reactions, independent of the nature of the group R and the ratio should have a lower value for S_N2 reactions (since ΔCp^{*} and ΔS^{*} are both negative in the type of reaction being considered).

At the commencement of this study these tentative suggestions required experimental verification. A parallel study has shown the constancy of $\Delta Cp^{*}/\Delta S^{*}$ for S_N1 reactions and this thesis describes the determination

of this ratio for the solvolysis of some n-alkyl bromides in 50% aq.acetone when the extreme form of the S_N2 mechanism is operative. These compounds all showed negative temperature coefficients of activation energy and the $\Delta Cp^{*}/\Delta S^{*}$ ratio was always lower than for S_N1 reactions, in agreement with the earlier predictions.

It can be concluded that the determination of this ratio provides an additional test of solvolytic mechanism which seems likely to be applicable to border-line reactions in which there is a transition from mechanism S_N2 to mechanism S_N1. Here, the 'classical' mechanistic tests do not always yield unambiguous results.

CHAPTER I

INTRODUCTION

Electronic Theory of Reactions (1)

Organic substitution reactions are essentially electrical phenomena and reagents react by a constitutional affinity either for electrons (electrophilic reagents) or for atomic nuclei (nucleophilic reagents). Thus, providing there is at some point in a molecule a sufficiently high electron density, then will an electrophilic reagent attack that point. Conversely, a nucleophilic reagent will attack a molecule provided that there is at some point a sufficiently low electron density. The development of the critical electron density at the reaction centre is an essential feature of the activation energy for the process. The replacement of one group by another at some point in the molecule, other than the reaction centre, will affect the facility of reaction depending on the effect each has on the electron density at the reaction centre.

Mechanisms of Electron Displacement (1)

All such mechanisms are based on the electronic theory of the atom and of valency. The electronic theory requires that electron displacements will maintain as completely as is possible, the pairing of electrons, and the octets or other stable electronic configurations in the atoms.

Two mechanisms have been proposed whereby substituents can transfer electrons towards, or away from, another part of the molecule without violating the principle of octet stability.

(i) Inductive Effect

Lewis (2), first proposed the inductive effect which arises from the electrical dissymmetry of the unequal sharing of the bonding electrons between two linked atoms which causes displacement of the electron pairs along the molecule by a process analogous to electrostatic induction. The mechanism is represented thus:

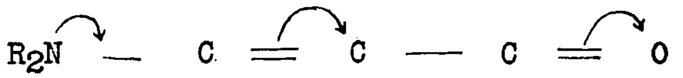
$$Cl \longleftarrow CH_2 \longleftarrow CH_2 \longleftarrow CH_3$$

the arrows pointing in the direction of electron concentration. In this case, the effect is caused by the electron dissymmetry of the C-Cl bond due to the electronegativity of the chlorine atom.

However, the electron displacements are not equal, as the further a group is from the C-Cl dipole, so will the induced dipole be progressively reduced.

(ii) Conjugative Mechanism (3)

The second method of electron displacement which preserves duplets and octets is characterised by the substitution of one duplet for another in the same electron octet, and is known as the conjugative mechanism. This type of displacement was assumed by Lowry(4), who showed how the entrance into an octet of an unshared duplet possessed by a neighbouring atom could cause the ejection of another duplet which would then either become unshared or initiate a similar change further along the molecule. This effect is represented by a curved arrow pointing from the duplet to the point towards which the displacement is assumed to occur. The effect can be propagated along a conjugated chain thus:



$R_2N - C = C - C = O$ Structure I

If such a duplet displacement carried on to completion the following structure would result -

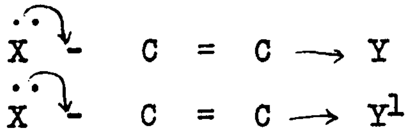
$R_2\overset{+}{N} = C - C = C - O^-$ Structure II

In actual fact the true picture is considered to be the resonance hybrid of the above two canonical forms. The greater the conjugative release of the group R_2N, the greater will be the contribution of structure II to the structure of the molecule. It is obvious that maximum transmission of this effect will be achieved when the releasing group is connected to a conjugated system. When the conjugative mechanism applies to the normal states of molecules it is called the Mesomeric Effect.

These effects are by far the most important in the kinetics of the alkyl halides, except in certain specially constituted systems, and so other electronic effects will not be considered here.

Dependence of Polar Effects on Environment.

It should be noted that polar effects of groups are not constant but vary with their environment. For example, if in the two molecules:-



$$\ddot{X} - C = C \rightarrow Y$$
$$\ddot{X} - C = C \rightarrow Y^1$$

X is capable of electron release by the mesomeric effect; Y and Y^1 are capable of electron attraction by the inductive effect, where Y^1 has the larger electron attracting power, then interaction polarisation between the groups X and Y (or Y^1) will cause each effect to be enhanced. Thus, the enhancement of the mesomeric effect of X will be greater in the second case, due to the extra electron attraction of Y^1 compared with Y.

Electron repulsions and attractions are usually considered on a relative basis, and by convention, the standard of reference is hydrogen. A group is said to be electropositive, or to repel electrons, if it does so more than hydrogen would in the same molecular situation. A group described as electronegative or electron attracting, attracts electrons more than would hydrogen if in the same molecular situation.

Mechanisms of Nucleophilic Substitution at a Saturated Carbon Atom. (1), (3), (4), (5).

It has previously been stated that the replacement of one group by another in a molecule will affect the ease of reaction according to the effect each has on the electron density at the reaction centre. In order to decide exactly what effect a particular change of substituent will have on the ease of reaction, it is necessary to consider the electrical requirements of the reaction in question. These electrical requirements are dependent upon the reaction mechanism, since this determines the electrical demands of the transition state. The various mechanisms of the substitution will, therefore, be considered below.

Reaction Types

In a simple substitution reaction of the form

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

in which only one bond is exchanged, it is necessary to distinguish between two main types of bond fission, defined as follows:

$$R\,\cdot\,\big|\,\cdot\,X \qquad \text{(homolytic fission)}$$

$$R\,\cdot\,\cdot\,\big|\,X \qquad \text{(heterolytic fission)}$$

where the dots represent electrons(6).

Processes involving the first type of rupture are common in gas phase reactions and produce or consume atoms or neutral particles.

e.g. $H + H\text{-}H \longrightarrow H\text{-}H + H$

The second form of fission is characteristic of a large proportion of substitution reactions in solution, which generally involve ions or entities which readily form ions. The reactions considered in this investigation are of this type. Within this category it is further necessary to distinguish between two types,

Nucleophilic Substitution,

$\overset{-}{Y}: + R/:X \longrightarrow Y:R + :\overset{-}{X}$ (Represented by S_N)

Electrophilic Substitution,

$\overset{+}{Y} + R:/X \longrightarrow Y:R + \overset{+}{X}$ (Represented by S_E)

In the S_N reaction, the expelled group carries the bonding electrons away with it and the deficit on R is made up by electrons from the attacking nucleophilic group Y

e.g. the Finkelstein reaction,

$I^- + R\text{-}Cl \longrightarrow I - R + Cl^-$

In an S_E reaction, the expelled group leaves the bonding electrons behind. The attacking electrophilic reagent has a deficit of electrons which is made up by the excess on R.

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

Only the S_N type is the concern of the present investigation.

The reactions to be considered are of the general type:

$\overset{-}{Y} + \text{Alk} \mid : X \longrightarrow Y\text{-Alk} + X^-$

where the new bond is formed by co-ordination and the old bond broken by heterolysis. There is an electron transfer from the substituting agent Y to the centre of substitution in Alk, and from this centre to the expelled group X. As a 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

e.g. Y may be neutral as in the hydrolysis of an alkyl halide

$$R\text{-}Br + H_2O \longrightarrow R\text{-}OH + HBr$$

or Y may be negative as in the Finkelstein reaction

$$I^- + R\text{-}Cl \longrightarrow R\text{-}I + Cl^-$$

Mechanisms of Nucleophilic Substitution

Two mechanisms, for which there is excellent evidence, have been proposed for nucleophilic substitution.

The first is a bimolecular process (7) which occurs in a single stage and involves the direct attack of Y on RX, the two molecules undergoing a simultaneous change in covalency. The mechanism is labelled S_N2 and may be represented thus:

$$\bar{Y}\!: + R\text{-}X \rightarrow \left[\begin{array}{c} \overset{\delta-}{Y}\text{----}R\text{----}\overset{\delta-}{X} \\ \text{transition state} \end{array}\right] \rightarrow Y - R + :\bar{X} \quad (S_N2)$$

The attacking nucleophile Y combines with the carbon atom at the side opposite to that at which the nucleophilic group is being displaced, thus inverting its steric configuration, as shown in the following equation (8)

$\bar{Y}\!: \quad +$

In the case where Y is neutral, the charge distribution in the transition state will be appropriately different. This type of process had been suggested by Le Bel (9) restated in an electronic form by Lewis (10) and applied by London (11) to give a physical interpretation of the reaction $H + H_2 \longrightarrow H_2 + H$, which although not a heterolytic reaction, involves an analogous synchronous bond forming and breaking process.

The second method of nucleophilic substitution involves two stages; a slow rate determining heterolysis of the compound to be substituted is followed by a rapid co-ordination between the formed carbonium ion and the substituting agent. Since only one molecule is undergoing covalency change in the rate determining stage, the mechanism is called unimolecular and labelled S_N1 (7).

It may be represented thus, where Y is negative.

$$\left.\begin{array}{llll} R - X \longrightarrow [\overset{\delta+}{R}----\overset{\delta-}{X}] \longrightarrow & R^{+} + \bar{X} & \text{Slow} \\ \qquad R^{+} + \bar{Y} \longrightarrow & R - Y & \text{Fast} \end{array}\right) (S_N1)$$

The rate controlling ionisation is slow because it must pass through an energy maximum for a certain critical extension of the bond and a certain critical degree of charge transfer. The very large energy values required for the formation of gaseous ions accounts for the fact that thermal ionisation does not occur at ordinary temperatures. However, in the case of an S_N1 reaction, which occurs in solution, the energy maximum is reduced to accessible values by solvation forces which increase as the charge transfer increases.

DETERMINATION OF S_N MECHANISM

I. Kinetic Criterion of Mechanism (12)

The simplest test of reaction mechanism is to determine whether the observed kinetics are of first or second order as found by substitution of the experimental data in the appropriate rate equation. Provided that both reacting species are in small and controllable concentrations, the bimolecular mechanism should lead to second order kinetics as expressed by the equation:-

$$\text{Rate} = K_2 \cdot [X] \cdot [RX]$$

On the other hand the unimolecular mechanism will lead to first order kinetics, with an overall rate equal to the rate of heterolysis, providing 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. If this condition does not apply, the S_N1 substitution will then show a complex kinetic form.

The present work is concerned with solvolytic reactions in which the nucleophilic substituting reagent, viz. the solvent, is present in large excess and its concentration may, therefore, be regarded as constant. In this case first order kinetics will be observed, the rate being equal to:-

$$\text{Rate} = K_1 \cdot [RX]$$

Thus in solvolytic reactions the kinetic criterion of mechanism does not apply. Various supplementary methods have been reviewed by Hughes (21) in an attempt to try to resolve this difficulty. These methods will be briefly discussed below.

II. Variation of Solvent Composition

It has already been indicated that most of the transition states and some of the reactants involved in S_N reactions possess formal electrical charges. In solution such species will, therefore, be solvated to a certain extent. Thus, when an ion or a polar molecule is surrounded by a solvent which is itself of a polar nature, it orientates and attracts some of the polar solvent molecules. This involves doing electrostatic work, in which case the system will lose energy and become more stable. This solvation energy of an ion can be very large in a polar solvent, often of the order of the strength of a covalent bond (13). Consequently a change from a less polar to a more polar solvent will increase or decrease the heat of activation (usually taken as the Arrhenius Activation Energy), depending on whether the transition state is more or less polar than the initial state of the reactants. There may also be a counteracting change in the entropy of activation, which the qualitative theory assumes, plays only a minor part compared with the activation energy in controlling the rate.

Three main assumptions have to be made as to the degree of solvation to be expected in the presence of electric charges - (14).

(i) Solvation will increase with the magnitude of the charge.

(ii) Solvation will decrease with increasing dispersal of a given charge.

(iii) The decrease in solvation due to the dispersal of charge will be less than that due to its destruction.

As for the solvents themselves, it has been assumed (15) that polarity or power to solvate charges will:-

(i) Increase with the molecular dipole moment of the solvent.

(ii) Decrease with increased shielding of the dipolar charges, e.g. in the series water, ethanol, acetone and benzene there is a gradual diminution in polarity.

The rates for S_N1 reactions are much more critically dependent on the ionising power of the solvent than are the rates for S_N2 reactions because there is a greater concentration of charge in the S_N1 transition state. The S_N1 transition state will therefore be solvated to a larger extent than would the S_N2 transition state, with the result that S_N1 reactions are accelerated (16) more than S_N2 reactions by increasing the ionising power of the solvent. It should be noted that before any quantitative or theoretical conclusions can be drawn from a study of S_N1 and S_N2 reactions, it is necessary to use only those solvent systems which lead to a 'pure' mechanism, because of the sensitivity of reaction mechanism to the ionising power of the solvent.

III. Variation in the Substituting Agent.

The rates of bimolecular reactions are dependent on the nucleophilic activity or nucleophilicity of the substituting agent. On the other hand unimolecular reactions are independent of the nucleophilicity (17) because it is the initial ionisation of the R - X bond which is the rate determining factor in S_N1 reactions, and not the rate of co-ordination of the nucleophile as in S_N2 reactions.

Thus in the S_N reactions of alkyl halides or alkyl sulphonium ions with a series of nucleophilic reagents arranged in order of decreasing nucleophilicity it is found that as we pass along the series the bimolecular rate falls. At some stage the rate falls below the rate of heterolysis of the molecule being substituted, in which case the reaction assumes a unimolecular character and is then independent of the substituting agent. This phenomena has been demonstrated for the substitution of the trimethylsulphonium salts in ethyl alcohol (18) using the series of nucleophiles (arranged in order of decreasing nucleophilicity) OH^-, OPh^-, HCO_3^-, OAC^- and Cl^- and also for a number of other reactions (17). It should be noted that the ethoxide ion is an even stronger nucleophile than the hydroxyl group.

IV. Structural Changes

The effect of structural changes in the reacting molecule on the mechanism of S_N reactions is dependent on the magnitude of the inductive effect, which is the most important mechanism of electron release, except in certain specially constituted systems. S_N2 reactions involve simultaneous electron transfers from the substituting agent to the alkyl group 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 rate is to be expected; this should only be small since it depends only on a lack of exact balance. The effect of electron releasing groups is thus ambiguous, because, whilst increasing electron release facilitates the breaking of the R - X bond, it hinders the approach of the nucleophilic reagent. Therefore, the polar effect of structural changes should only be small, causing only a slight increase or decrease in rate, depending on the relative effects on the breaking bond and the attacking nucleophile.

On the other hand, in the rate determining stage of a S_N1 reaction there is an electron transfer from the alkyl group to the displaced group, without any compensating gain of electrons by the alkyl group. Hence a large kinetic polar effect is to be expected and its direction is unambiguous; electron release must accelerate such substitutions.

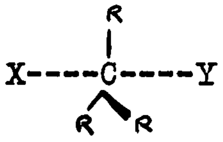
Thus the polar effect of structural changes in general has a much greater effect on S_N1 than on S_N2 reactions.

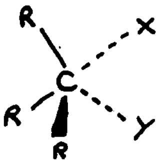
In alkyl compounds the separation of a group with its shared electrons is assisted by the inductive effect and any carbonium ion formed is stabilised at best by hyperconjugative mesomerism, whereas in aralphyl compounds containing an α-phenyl substituent, the more powerful mechanism of conjugative electron displacements is available to assist the separation of the displaced group and the carbonium ion formed is stabilised by conjugative mesomerism. It would thus be expected that the phenyl substituent would exert a facilitating polar effect on both S_N1 and S_N2 reactions, especially so for S_N1 reactions.

The sharp contrast in the magnitude of the kinetic effect on passing from any bimolecular substitution to a strongly electron-demanding unimolecular type of substitution illustrates not only the different electrical situations created in the two mechanisms, but also the importance of the electromeric aspect of the polar effect of alkyl and phenyl substituent groups.

V. Stereochemical Considerations

It has long been known that bimolecular reactions always produce inversion of configuration (19). This has been explained by asserting that the transition state (I) leading to inversion must have much less internal energy than the state corresponding to retention of configuration, structure II. The reason for this is





that in structure I, the partial bond binding X and Y will have an approximately planar surface of zero electronic density (exactly planar if X = Y) in which the three bonds CR_3 can lie. This arrangement ensures that the positive exchange energy between the altered and the preserved bonds is a minimum. Structure II, on the other hand, admits of no such stable arrangement.

The steric course of S_N1 reactions is less specific as there can be either racemisation or sometimes inversion and at other times retention of configuration if there is a configuration-holding group, such as the α-carboxylate-ion group present (20). Whilst these other stereochemical configurations do occur, the general rule for S_N1 reactions is the production of a racemised product as a result of the free carbonium ion formed in the rate determining step, when the attacking nucleophile can attack from any angle with the resulting formation of a racemic mixture.

However, as indicated, these general rules are not always obeyed. For instance, when the life of the carbonium ion is very short then the expelled anion will still be quite close to the carbonium ion and so exerts some influence on the direction of attack of the nucleophile, leading to inversion of configuration.

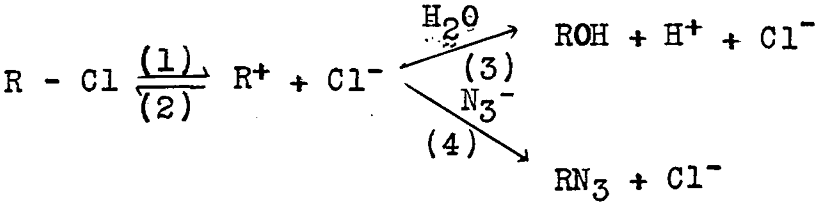
Great care, allied with other mechanistic information, must therefore be taken in assigning mechanistic categories based on stereochemical effects.

VI. Effect of Salt Additions on Kinetic Form

The unimolecular mechanism has a typically somewhat complex kinetic form which does not necessarily reduce to first order kinetics even for solvolytic reactions. The reason for this is the reversibility of the initial heterolysis in S_N1 reactions as:-

$$RC \underset{(2)}{\overset{(1)}{\rightleftharpoons}} \overset{+}{R} + Cl^- \xrightarrow[(3)]{H_2O} ROH + H^+ + Cl^-$$

As larger chloride ion concentrations are built up by reaction (3) so reaction (2) gains in importance with the result that the rate determining ionisation becomes progressively retarded by its reversibility, though without necessitating any reversal of the overall reaction. The rate then simply falls further and further behind the first order rate as the reaction proceeds. An analogous retardation effect is observed, if any common-ion salts (i.e. salts having an identical anion with that of the alkyl compound) are added at the start of the reaction. On the addition of a non-common ion salt such as sodium azide, there is a similar retardation of the hydrolysis, but the overall rate of destruction of the reacting molecule is not diminished because of the extra mode of attack on the carbonium ion by the azide ion.



In accordance with the Law of Mass-Action these salts can therefore have no effect on the initial rate of destruction of the solvolysing molecule. Superimposed on these mass-law effects there is always an accelerative electrostatic effect on the rate connected with the ionic strength of the solution, the theory of which is qualitatively analogous to that of solvent effects. This ionic strength effect (which is shown by all electrolytes) arises as a result of the stabilisation of the ion-atmosphere of a polar species such as the transition state due to ion electrostatic interactions.

S_N2 reactions involve quite a different set of circumstances because in the irreversible reactions by this mechanism mass action can confer no kinetic effect on either the produced chloride ion or on any added common-ions.

$$H_2O + R\text{-}Cl \longrightarrow ROH + H^+ + Cl^-$$

The addition of non-common ions can, however, sometimes cause an acceleration of rate due to the fact that an additional mode of attack on the molecule is provided (20). As is the case in S_N1 solvolysis, the ionic strength effect again causes some acceleration of rate in S_N2 reactions. The addition of a common-ion salt is thus the only effect which serves to distinguish between the S_N1 and S_N2 mechanisms. Even so, this is not always a good test of mechanism since as a result of the mass-law and the ionic-strength effects working in opposite directions for S_N1 reactions, the net effect is often ambiguous.

Methods reviewed here have all been well established for a large number of S_N1 and extreme S_N2 solvolytic reactions for which they are satisfactory methods. Full details may be found in extensive reviews by Hughes (21) and Ingold (22).

TRANSITION BETWEEN THE S_N1 AND S_N2 MECHANISMS

It is apparent from the previous discussion on the effect of structural changes on mechanism that electron donor substituents facilitate S_N1 reactions. Therefore, if we consider the S_N2 reaction of a given compound then by altering the substituents so as to give increased electron donation to the reaction centre, it would be expected that S_N1 reactions would be promoted.

This is well demonstrated by the alkaline hydrolysis of a series of alkyl bromides in which there is gradually increased α-methyl substitution (23), i.e. a series of increased capacity for electron release to the reaction centre. It is found that the primary alkyl bromides undergo S_N2 solvolysis, the rate for ethyl being less than that for methyl. But as we pass along the series to i-PrBr and t-BuBr so strong is the kinetic effect of electron release on the S_N mechanism that it causes a change in mechanism to S_N1 substitution. From this region of mechanistic change there is a considerable increase in the rate when first order kinetics are observed; the specific rate for t-butyl bromide being some 50 times the specific rate of the first member of the series, MeBr.

In a series of arylalkyl compounds where a phenyl substituent progressively replaces a hydrogen atom on the alkyl group, e.g. MeCl, $PhCH_2Cl$, Ph_2CHCl, Ph_3CCl a similar change of mechanism is observed (24) in the ethanolysis of these compounds. MeCl reacts by mechanism S_N2 and benzyl chloride mainly by S_N2, but from this region onwards there is a change in mechanism to S_N1 for chlorodiphenyl methane and chloro-triphenyl methane. As a result of the greater effect of conjugative electron release on the stability of the carbonium ion, the phenyl substituent causes the onset of the change in mechanism at an earlier stage than in the case of the substituted alkyl series previously mentioned.

The change in mechanism due to the effect of increasing electron release has further been demonstrated in the solvolysis in aqueous acetone of the p-substituted benzyl chlorides, p-NO_2, p-H, p-Me and p-MeO (25). From left to right this is a series of increasing electron release towards the reaction centre. It was found that the p-MeO compound solvolysed by mechanism S_N1, whereas the behaviour of the other compounds became increasingly like extreme S_N2 reactions as the electron-releasing power decreased. These results are thus in accord with the postulate that increasing electron accession to the reaction centre facilitates the S_N1 mechanism.

It is generally accepted that there are the two distinct mechanisms, S_N1 and S_N2, except for Swain (13) who believes there is only one mechanism. This alternative mechanism is, according to Swain, a termolecular "push-pull" mechanism in which one reagent pushes off the substituent ion by cationic solvation of, or nucleophilic attack on, the carbon atom and another reagent molecule pulls it off by solvating it. This hypothesis is not supported by the vast amount of evidence which substantiates the S_N1, S_N2 concept; whose kinetics and characteristics have been extensively studied and conditions for the operation of each of the mechanisms to the exclusion of the other have been obtained.

There is, however, less agreement on how the transition from mechanism S_N2 to mechanism S_N1 occurs. Several different views have been expressed about the nature of the reaction path in border-line reactions, i.e. in reactions which are almost, but not quite, S_N1 in character. The different views will be discussed in the following section.

Mechanisms of Border-Line Reactions

In accordance with the scheme of Winstein, Grunwald and Jones (26) it is convenient to regard the transition state of S_N reactions as the resonance hybrid of the three canonical structures:-

$$\overset{-}{Y}\ \ \underset{I}{R} - Cl \qquad Y-\underset{II}{R}\ \overset{-}{Cl} \qquad \overset{-}{Y}\ \ \underset{III}{\overset{+}{R}}\ \ \overset{-}{Cl}$$

Thus, if the extreme form of the S_N2 mechanism is in operation, only structures I and II will make an appreciable contribution to the transition state structure; whilst in the S_N1 mechanism only structures I and III will make any appreciable contribution. If I, II, and III all contribute to the structure of the transition state, the reaction must be regarded as bimolecular, by definition (27) since covalent participation by the reagent Y is still an essential feature of the activation process.

Winstein, Grunwald and Jones (26) have suggested that S_N reactions must always proceed via a single reaction path as a consequence of the considerable resonance energy represented by these three canonical structures. They consider that the importance of III relative to II increases as the experimental conditions (such as the structure of R or solvent composition) increasingly favour reaction by the S_N1 mechanism. A border-line reaction, therefore, occurs by mechanism S_N2 in view of their postulate of a single intermediate mechanism. These authors have also concluded that a border-line reaction does not occur by the concurrent operation of a S_N1 process and a process involving the extreme form of mechanism S_N2 (i.e. there is no contribution from III). Bird, Hughes and Ingold (37), while essentially agreeing with this conclusion, have criticised the method by which it was derived. Bensley and Kohnstam (28) have reported that the reaction of benzyl chloride with 50% aq. acetone cannot be explained in terms of a concurrence of S_N1 and extreme S_N2 mechanisms.

Other authors have suggested that a variety of reaction paths may be available in the border-line region. Bird, Hughes and Ingold (37) have suggested that there is no sharp line of demarcation between the S_N1 and S_N2 mechanisms; and that "there must be degrees of collaboration by the reagent in the process of expelling the substituent that is to be replaced." That is, the two mechanisms are regarded as the extremes of a graded range where many molecules may react along paths which cannot be clearly classified as belonging to either mechanism. In terms of canonical structures they thus favour an intermediate mechanism involving various transition states oscillating about some mean state and composed of structures I, II and III in different proportions. Crunden and Hudson (29) also accept this view of a 'continuous spectrum' of transition states, but on the basis of experiments on the hydrolysis of acyl chlorides they suggest that the 'spectrum' may be sufficiently 'broad' to allow simultaneous reaction by mechanism S_N2 (i.e. some contribution from structure II) and mechanism S_N1. Gold (30) considers that the 'broad spectrum' should be extended even further to include the whole range of transition states from the extreme form of the S_N2 mechanims to the S_N1 mechanism. On this basis, Gold, Hilton and Jefferson (31) have reported that the hydrolysis of benzoyl chloride can be explained in terms of concurrent S_N1 and S_N2 processes.

So far, there is no unambiguous evidence that S_N reactions can occur by simultaneous S_N1 and S_N2 processes. Results indicating this type of behaviour in bromine exchange with t-butyl bromide (32) are not confirmed by more recent work (33) and the interpretation of the simultaneous hydrolysis and ammonolysis of benzoyl chloride in such terms (31) appears to require further examination as it has been shown that at least part of the reaction does not involve an S_N mechanism (34).

While various mechanisms for the border-line region have been proposed, none have been identified with any certainty as the actual recognition of mechanism is extremely difficult in the border-line region. The 'classical' tests of solvolytic mechanism (discussed in the previous section) distinguish quite satisfactorily between S_N1 and extreme S_N2 reactions, but in the border-line region these methods are quite insufficient. For instance if one considers a reaction in the border-line region involving a single transition state intermediate between the extremes there will be a large contribution by canonical structure III, but also some contribution by II. The stability of the transition state will, therefore, be largely controlled by factors affecting structure III and so it is then feasible that an S_N2 reaction will behave more like an S_N1 reaction with, for instance, variation in solvent composition, than an extreme S_N2 reaction.

The question thus poses itself, how does one determine mechanism in the border-line region? Winstein, Grunwald and Jones (26) have tried to distinguish between intermediate mechanisms and concurrent S_N1 and S_N2 mechanisms by making a systematic study of the solvent effect on reactivity. They suggested that it was possible to arrange solvents on a scale of reactivity for S_N1 and extreme S_N2 mechanisms and to give a quantitative index to the reactivity for each solvent for each of the two mechanisms. They showed that for many alkyl halides there was a linear relation between the free energy of activation ΔG^* of R-Hal and ΔG^* for t-butyl chloride in the same solvent.

$$\Delta G^*_{R\text{-}Hal} = m.\Delta G^*_{t.BuCl} + \text{constant}$$

They further defined two mechanistic categories LIM and N, roughly corresponding to S_N1 and S_N2, and considered that when R-Hal solvolysed by the LIM mechanism, $m \doteq 1$, and when by mechanism N, $m \doteq 0.3$. As a result they showed that the rate of a reaction expected to be a border-line case, did not correspond to the rate predicted from solvent reactivities if the reaction were the sum of two concurrent mechanisms and therefore concluded that the reactions must proceed by an intermediate mechanism. Their conclusions have since been thrown into some doubt as Bird, Hughes and Ingold (37) have criticised their experimental technique and because the validity of the free energy relationship does not always hold as the plot is not linear for compounds solvolysing by the N mechanism. Additional limitations on the validity of the linear free energy relationship for the quantitative interpretation of solvolysis rates have been recently discussed by Winstein, Fainberg and Grunwald (35). However, even if such a relationship were valid, it would not serve to fix the point of mechanistic change between S_N1 and S_N2 as the relationship would merely show the general trend in the mechanistic change.

The other mechanistic tests for interpreting the border-line reactions are all open to objections. These will now be briefly discussed. The objections to the use of changing substituents as a test are the same as in the case of solvent compositional changes, in that the stability of structure III is largely controlled by these factors, as it is in S_N1 reactions. The stereochemical evidence is not always unambiguous as some S_N1 reactions show inversion of configuration; which they always do when the carbonium ion has a very short lifetime (i.e. unstable) as there is then shielding by the leaving group. This point was discussed more fully on p. 16. Finally, the mass-law effect does not always show up in S_N1 reactions where there is an unstable carbonium ion, for then the solvation shell collapses with the formation of the alcohol before the carbonium ion has completely freed itself from its bound anion. Thus the effect of any added common-ions would not be observed because the carbonium ion is being destroyed too rapidly to participate in the equilibrium between these ions. So, whilst no mass-law effect would be observed, which is characteristic of S_N2 reactions, the reaction would in fact still be S_N1 if there were no covalent bonding of the attacking nucleophile in the activated complex.

Mechanistic test based on the temperature dependence of the Arrhenius parameters

A new test of mechanism based on the temperature dependence of the Arrhenius parameters has been tentatively proposed by Bensley and Kohnstam (28). Eyring's absolute rate equation leads to the conclusion that the temperature coefficient of activation energy dE/dT is related to the heat capacity of activation ΔCp^*, which represents the difference in the heat capacities of the initial and final activated states. It is assumed that this difference arises from an increase in solvation as the reacting system passes into the more polar transition state. Full details will be given in Chapter II. ΔCp^* can, therefore, be taken as a measure of the solvation of the transition state relative to the initial state. The entropy of activation ΔS^* is also mainly controlled by this increase in solvation in S_N1 reactions. There is, however, a positive contribution to ΔS^* as a result of bond stretching in the alkyl halide. This contribution is likely to be very small and, therefore, is negligible compared with the negative contribution to ΔS^* as a result of solvation; a conclusion which has already been suggested by Evans and Haman (36). Thus to a first approximation, ΔS^* for S_N1 reactions can be taken as a measure of the solvation of the transition state relative to the initial state. It would, therefore, seem that ΔS^* and ΔCp^* in the S_N1 solvolysis of alkyl chlorides are measuring the same phenomenon. Consequently, $\Delta C_p^*/\Delta S^*$ ought to be a constant, independent of substrate and only dependent on temperature and solvent composition. It is reasonable to suppose that the change in heat capacity of a solvent molecule is very much the same when it forms a partial covalent bond in S_N2 reactions as when it helps to solvate an incipient ion. On the other hand, the increased order brought about by the formation of this covalent bond is likely to lower the entropy of a solvent molecule more than when it acts merely as a solvating agent. There will thus be an additional negative contribution to ΔS^* in S_N2 solvolysis, whereas there is no such contribution in S_N1 reactions. Assuming, therefore, that there is very little change in ΔCp^*, the ratio $\Delta Cp^*/\Delta S^*$ for S_N2 solvolysis could reasonably be expected to have a lower value than would an S_N1 reaction in the same solvent and at the same temperature.

At the commencement of this study the constancy of the $\Delta C_p^*/\Delta S^*$ ratio for S_N1 reactions had not been fully established, but as a result of a parallel investigation (25) the hypothesis of constant $\Delta C_p^*/\Delta S^*$ ratio seems to be quite justified. The present study was concerned with determining the $\Delta C_p^*/\Delta S^*$ ratio for a series of recognised S_N2 reactions proceeding by the extreme form of this mechanism. The compounds chosen were the primary alkyl bromides; ethyl, propyl and butyl bromides, and the solvent chosen was 50% aqueous acetone as this was the solvent used for the S_N1 reactions already studied from this point of view. It should be noted that strictly for purposes of comparison with the $\Delta C_p^{\#}/\Delta S^{\#}$ ratios for the S_N1 chlorides this work should be carried out on S_N2 chlorides. The primary alkyl chlorides are unfortunately all extremely volatile and, therefore, difficult to study under constant conditions, not very soluble in 50% aqueous acetone and furthermore their reaction rates in this solvent would be very slow. Consequently any rate data derived from these compounds would probably be insufficiently accurate for the determination of the Arrhenius parameters and hence the $\Delta C_p^{\#}/\Delta S^{\#}$ ratio.

Before discussing the results it is necessary to consider the reasons which led to the identification of $\Delta Cp^{\#}$ as a measure of the increase in solvation on passing from the initial to the transition state of the reaction and also to discuss methods by which this parameter can be derived from the experimental results. These points will be fully discussed in the following chapter.

CHAPTER II

The Temperature Dependence of the Arrhenius Parameters.

The refinement of the rate-temperature relation for kinetic data is essential for the long term development of a quantitative theory of reaction mechanism. A more immediate gain would be to provide a parameter which could be interpreted in a thermodynamic sense and could provide the means for obtaining a quantitative measure of the factors involved in solvation processes for reactions in solution; as opposed to the doubtful empirical method of using mixed solvent systems.

Derivation of the temperature dependent parameters.

The purely empirical Arrhenius equation which describes the variation of the rate of a reaction with temperature (38) defines the activation energy, E, in terms of the differential equation.

$$E = R\,T^2 \frac{d \ln k}{dT} \qquad \ldots\ldots\ldots\ldots\ldots(1)$$

This relationship was firmly established when the collision theory of reactions was found to lead to the same result. The activation energy has usually been assumed to be constant and, therefore, the above equation is more often used in its integrated form.

$$k = B - E/_{RT} \qquad \ldots\ldots\ldots\ldots\ldots(2)$$

E is defined as the energy requird to raise one mole of the reacting species into the activated state. The parameter B which arises as a constant of integration (the non-exponential term) can be identified with the frequency factor ln(PZ) of the collision theory which predicts $k = PZe^{-E/RT}$ (39) where Z is the collision number and P the steric factor. B can thus be considered to represent the probability of attaining the transition state. Most chemical reactions investigated have been found to obey the Arrhenius relationship, though in the past Trautz (40), La Mer (41), Scheffer and Brandsma (42) have stressed on theoretical grounds that E should vary with temperature.

The same conclusion arises from Eyring's absolute rate equation (43); a theoretical rate equation which is now universally accepted. This equation was derived assuming the reactants to be in equilibrium with the activated complex and then treating this equation by normal thermodynamic methods on the further assumption that the activated complex be treated as a normal molecule, except that translational motion along the reaction coordinates would lead to decomposition. As a result the following equation was derived:

$$\ln k = \ln\left(\frac{\bar{k}\,T}{h}\right) + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT} \quad \ldots\ldots\ldots\ldots(3)$$

ΔS^* is the entropy of activation, and throughout this study refers to the quantity calculated from the observed first order constants. This corresponds to defining the standard state of the reactant as its state in the solvent under consideration. ΔH^{*} is the enthalpy or heat of activation.

For reactions in condensed systems,

$$\Delta H^{*} = \Delta U^{*}$$

where ΔU^{*} is the increase in internal energy for the activation process.

Hence on differentiation of (3) with respect to T

$$\frac{d(\ln k)}{dT} = \frac{\Delta H^{*} + RT}{RT^2}$$

which on comparison with the Arrhenius equation (1) shows that

$$E = \Delta H^{*} + RT \qquad \text{..............(4)}$$

Since ΔH^{*} is a normal enthalpy change Kirchoff's Law applies then $\frac{d(E)}{dT} = \Delta Cp^{*} + R$ ....(5)

where ΔCp^{*} 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 and E will vary with temperature unless ΔCp^{*} is zero.

Observation of dE/dT

In general, the initial and activated states are unlikely to have the same heat capacity and, therefore, it would be expected that E should vary with temperature. However, E is more often than not reported as being constant. There are two main reasons for the lack of observation of dE/dT

(i) The activation energies of most solvolytic reactions lie in the range 10 - 30 K cals and so it becomes rather difficult to observe dE/dT values which are very much smaller than E itself. The value of dE/dT is generally in the range 10 - 70 cals/°, while values of E have often been quoted as being only reliable to 0.5 K cal. Considerable accuracy in the rate measurements is required to produce reliable values of E, such that the experimental errors are small enough to allow a variation of E to be detected. For example, standard deviations of 0.441% and 0.287% in the final mean rate coefficients of n-PrBr (Table II, Ch.III) at 80°C and 90°C respectively, lead to a standard deviation in E(21.07 K cals.) of ± 135 cals. as calculated by the method of Purlee, Taft and de Fazio (44). Errors of this order of magnitude in the measured rate constants over a 40° temperature range thus lead to an error in dE/dT (-21.4 cals/°) of ± 6 cals/°. It should be noted that such experiments should be carried out over as wide a temperature range as possible in order to observe dE/dT values of the above order of magnitude. In view of the accuracy required, it is hardly surprising that this effect has been missed when rate coefficients have been variously quoted as being from only 1 to 3% reliable.

(ii) Another reason why the non-observation of dE/dT is so common is that very often activation energies have been determined by plotting a graph of log k against $1/T$; the slope of which gives E according to equation (2). Such plots have usually been regarded as perfectly linear, when in fact there could be a slight curvature (see fig. 1). As the deviations from linearity are so small they may either not have been observed or not have been considered significant in view of experimental inaccuracies.

Temperature dependent values of E have been reported from time to time but many of these claims do not stand up to detailed analysis. However, unambiguous evidence observed in the last decade is now available. This confirms that E does in fact decrease with increasing temperature for solvolytic reactions in which the transition state is more polar than the initial state.

The first genuine observation of a negative temperature coefficient of E for solvolytic reactions was observed in 1938 by Moelwyn-Hughes (45) in the hydrolysis of the methyl halides when a value for dE/dT of -64 cals/° was reported. Whilst there is no doubt that his observation of dE/dT is correct, it would seem that his value for dE/dT is rather high. This probably arises from the experimental inaccuracy and the calculation of activation energies outside his experimental range by means of a rather dubious extrapolation. In the last decade more accurate data have been reported. In the substituted aryl sulphonates Robertson and co-workers (46) have found that dE/dT is of the order -25 to -35 cals/°. Tommila, Tiilikainen and Voipio (47) have reported an average dE/dT of -60 cals/° for t-butyl chloride in various acetone-water mixtures and predicted that dE/dT for ethyl bromide should be about -18 cals/° which is less than their experimental error. Bensley and Kohnstam (48) have also observed negative dE/dT values in the solvolyses of benzyl chloride and substituted benzyl chlorides when dE/dT varies between -19 and -44 cals/° in 50% aq.acetone and between -29 and -71 cals/° in 50% aq.ethanol.

It should be noted in passing that positive dE/dT values have been reported in reactions where reactants with opposite electrical charges yield a less polar transition state. Most of the studies showing this phenomenon are concerned with reactions between ammonium and cyanate ions (49) and it is now thought highly likely that the rate-determining step involves a molecular rather than an ionic mechanism (50). The net result of this is that the activation energy of the process is a composite quantity which involves the temperature dependent parameter ΔH^{o} for reactions such as:-

$$NH_4^+ + NCO^- \longrightarrow NH_3 + HNCO$$

Further critical details of the phenomenon can be obtained from the literature, e.g. Kemp and Kohnstam (50) and Frost and Pearson (51).

Heat capactites of initial and activated states.

It has been shown that if we accept the assumptions made in Eyring's Rate Equation, then the variation in E with T is related to the difference in heat capacities of the initial and activated states. It is, therefore, necessary to consider the reasons for this difference in heat capacity.

The well authenticated cases of temperature dependent activation energies (see previous section) all involve the creation of partial electrical charges on passage of the reactants into the transition state. As has already been mentioned (Ch. I, p. 9) the essential feature of reactions of this type is that solvation of the polar species reduces the activation energy to accessible values. It is, therefore, reasonable to postulate that there will be an increase in solvation as the reactants pass into the transition state.

Solvation of the transition state.

There are two kinds of solvation, primary and secondary (47). In primary solvation the forces involved are essentially chemical forces binding the solvent molecules firmly to the solute. In secondary solvation the binding of the solvent molecules is due to electrostatic interaction between charges. As a result of the pseudodipoles formed the effect tends to orientate solvent molecules successively from the seat of substitution into the bulk of the solvent though with rapidly diminishing effect.

Thus, when a solvent molecule solvates a charged body, the binding forces cause loss of rotational degrees of freedom; the orientated molecules will then be less free to move than those in the bulk of the solvent. These orientated molecules are, therefore, less able to absorb heat and so their heat capacity and entropy will decrease, e.g. ΔCp for the conversion of water to ice is -9 cal/°. 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 (52) and the negative heat capacity of ionisation of weak acids (53), (54). Whilst these considerations apply to fully developed ions in solution, it is quite reasonable to expect similar considerations to apply to the formation of partial ions or charges in solution. On this view, the transition state of an S_N reaction is, therefore, expected to have a lower heat capacity than the initial state due to the extra solvation of the partial charges created in the transition state, i.e. ΔCp^{*} should be negative.

Negative ΔCp^{*} values have been observed for a number of reactions in which the transition state is more polar than the initial reactants. In the hydrolysis of acetic anhydride in water and aqueous acetone, ΔCp^{*} varies between -85 and -55 cal, depending on the solvent composition (55); its value for the solvolysis of 1-methallyl chloride in 50% aq. ethanol is about -60 (56), about -40 for the hydrolysis of diphenylchloromethane in aqueous acetone (57), -45 for the hydrolysis of methyl nitrate in water (58) and about -66 for the hydrolysis of the methyl halides also in water (4), though in a later investigation over the same temperature range, ΔCp^{*} was found to increase with increasing temperature, finally attaining positive values (13). Values of ΔCp^{*} for the solvolysis of the α-chloro substituted benzyl chlorides and benzyl chloride itself were found to lie in the range -21 to -46 cals, in 50% aq. acetone, and between -31 and -73 cals in 50% aq. ethanol (59). Robertson and co-workers (60) (61) have quoted a large number of values for ΔCp^{*} in an extensive investigation on the hydrolysis of aryl sulphonic esters.

The postulate that negative ΔCp^{*} values arise from solvation of the transition state relatively to the initial state of the reactants is given support by other evidence:-

(i) Salts in aqueous solution are known to have negative partial molar heat capacities (52) due to solvation of the ionic species and

(ii) the heats of electrolytic dissociation of weak acids have negative temperature coefficients (53), (54), again due to the existence of charged bodies in the final but not in the initial state of the system. The common factor in these studies and in S_N reactions, is the existence of charged species in solution and hence the conclusions reached by Everett and Wynne-Jones (53), Everett and Coulson (54) and Randall and Rossini (52) should be applicable to S_N reactions with respect to solvation of the transition state.

Thus, it seems fully justified, that the concept of greater solvation of the transition state relatively to the initial state is the cause of negative ΔCp^* values. This explanation has been postulated on a number of occasions. Robertson (60) is of the opinion that solvation of the transition state is the principal factor controlling ΔCp^*, because the change in activation energy of -13 cal/^{o} for ionogenic reactions due to the temperature dependence of dielectric constant will not account for the large values of ΔCp^* (see following section for fuller discussion) nor will it account for the differences in ΔCp^* for different compounds. In view of the large differences in ΔCp^*

for different sulphonic esters and other compounds, he postulates that it seems probable that specific solvation of the anionic part of molecules may be very important in determining the value of ΔCp^{*}. Robertson accounts for these differences by assuming that ΔCp^{*} will be relatively smaller for those compounds in which the dipole-dipole interactions in the initial states are only slightly weaker than the interactions in the transition states. Thus, the sulphonic acid group is expected to have a relatively small value of ΔCp^{*} because of the intense solvent interaction in the initial state due to the great solubility of this group in water. The change in heat capacity will, therefore, be smaller on passing to the transition state as compared with, for example, the methyl halides in which solvent interaction in the initial state is relatively small. This would also account for the lower value of ΔCp^{*} for the hydrolysis of methyl nitrate than for the methyl halides reported by McKinley-McKee and Moelwyn-Hughes (58).

The values of ΔCp^{*} for the methyl halides are all the same in spite of very different bond strengths. This led Glew and Moelwyn-Hughes (62) to conclude that ΔCp^{*} is related to specific differences in the solvation of the reacting molecule. They accounted for the ΔCp^{*} values being the same because they calculated that six water molecules were 'frozen' to the transition state. Tommila, Tiilikainen and Voipio (47), Caldin, Long and Trowse (63) and Bensley and Kohnstam (48) have all explained $\Delta Cp^{\neq}$ in terms of the greater solvation of the transition state compared with the solvation in the initial state.

It is worth noting that the relative difference in solvation between the initial and transition state over a sixty degree range of temperature remains very much the same for a series of compounds. This is concluded from the observed constancy of the k_{H_2O}/k_{D_2O} ratio for a series of substituted benzene sulphonates and substituted benzyl bromides (61).

Dielectric Constant Theory

An alternative theory developed by Amis and La Mer (64) and Warner and co-workers (65) to account for the temperature coefficient of activation energy is based on the fact that the forces between charged bodies in solution depend on the dielectric constant of the medium. This electrostatic approach based on the Born relation, treats the solvent as a continuous dielectric having the macroscopic dielectric constant D and that there is a contribution E_D to E due to electrostatic effects in such a system. For all known solvents D decreases with increasing temperature, so that E_D and hence E, can be expected to be temperature-dependent, i.e. dE/dT does not equal zero. Details of the mathematical derivation of dE/dT by this approach have been given by Amis and La Mer (64) and Warner (55) assuming Kirkwood's (66) equation.

However, it seems most unlikely that a bulk property such as the dielectric constant of a mixed solvent should control the very short range forces which act between partial charges in the transition state. The distances over which these forces act are so small as to preclude the entrance of any one molecule, let alone several, between the charged particles. It is, therefore, extremely probable that the dielectric constant in this region is very small and independent of the components which constitute the activated complex. For example, Eyring and Ri (67) assumed D = 1 in the region between the partial charges for the nitration of substituted benzenes in polar solvents and obtained good results. Even if this is not the case, the composition of the activated complex and the solvent in its immediate vicinity will be different from the composition of the bulk of the solvent and hence the dielectric constant will not be the same. The work of Hasted, Ritson and Collie (68) is in agreement with this. These workers observed a decrease in the dielectric constant of ionic solutions with increasing salt concentration and found their results consistent with the assumption of negative dielectric constants in the immediate vicinity of the ions. A further compelling objection to this approach is that the predictions are inconsistent with the experimental evidence, e.g. in a study of the ionisation of triphenylmethyl chlorides (69) and the rate of ionisation of tertiary-butyl chloride (70) in widely differing solvents the behaviour of these compounds did not vary with D in the predicted manner. Enthalpies and entropies of activation derived from Kirkwood's equation have been compared by Caldin and Peacock (71) with the experimental values for a number of bimolecular reactions which involve an increase in polarity on passage into the transition state. Here too the predictions of the theory are not confirmed by the experimental evidence. Furthermore, this approach is insufficient to account for the negative partial molar heat capacities of electrolytes (53).

In view of these objections it is considered most unlikely that the dielectric constant effect is responsible for the relatively large values of the temperature coefficient of activation energy in S_N reactions.

Extension of the Collision Theory

Moelwyn-Hughes (45) has assumed that in reactions in solution the partial molar enthalpy of the activated complex ΔH^{*} is a constant, independent of temperature and having the maximum value which molecules can possess in solution. Consequently, he regarded the transition state as having zero heat capacity and, therefore ΔCp^{*} is equal to $-Cp^{o}$ of the initial state. If H is the partial molar heat content of the initial state, then,

$$E_A = \Delta H^{*} - H$$

and, therefore, $$\frac{d(E_A)}{dT} = -\frac{dH}{dT}$$

He therefore accounts for a negative dE/dT as being due to a variation of H with temperature. There seems to be no justification in his assumption that ΔH^{*} is constant. It would be reasonable to suppose 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 surely increase. Another objection to this approach is that it is in contradiction to the assumptions of Transition State Theory which treats the activated complex as a normal molecule with one degree of vibrational freedom missing. Furthermore, 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. A final objection to this approach is that it is hard to conceive why the partial molar enthalpy of the methyl halides in water should rise, maximise and then fall as he has observed. An even more remarkable fact is that the partial molar enthalpies of all the methyl halides examined maximised at about the same temperature, though this might be due to faulty data.

In conclusion it may be stated that it is more reasonable to assume that ΔCp^* arises from the additional solvation of the transition state (as previously mentioned p.39) than the other factors discussed. It should be mentioned that this explanation only applies if the transition state structure is independent of temperature which, to a first approximation, is quite a reasonable assumption.

Experimental Determination of the Arrhenius Parameters (72)

(i) Activation Energy

Experimental activation energies E_{obs} for the temperature range $T_1 - T_2$ are usually calculated on the basis of equation (2) which assumes E to be constant. Hence from a knowledge of the rate constants k_1 and k_2, at the absolute temperatures T_1 and T_2, E_{obs} is given by:-

$$E_{obs} = \frac{R\ T_1 T_2}{T_2 - T_1} \cdot \ln\left(\frac{k_1}{k_2}\right) \qquad \ldots\ldots\ldots(6)$$

It is now necessary to establish the temperature to which E_{obs} calculated from equation (6) refers.

It is assumed that E_{obs} varies linearly with temperature, which is reasonable since the experimental accuracy does not allow a better relation between E and T. Then over the temperature range $T_1 - T_2$ we can write:-

$$E_{(T)} = E_{(T_1)} + C(T - T_1) \qquad \ldots\ldots\ldots\ldots\ldots \quad (7)$$

where C is a constant and T lies between T_1 and T_2. Therefore,

$$\frac{E_{(T)}}{RT^2} = \frac{E_{(T_1)}}{RT^2} + \frac{C}{RT} - \frac{CT_1}{RT^2} = \frac{d(\ln k)}{dT}$$

which on integration between the limits T_1, k_1 and T_2, k_2 gives:

$$\frac{E_{(T_1)}}{R} \cdot \frac{\Delta T}{T_1 \cdot T_2} + \frac{C}{R} \cdot \ln\left(\frac{T_2}{T_1}\right) - \frac{C.T_1.\Delta T}{R.\ T_1.T_2} = \ln\left(\frac{k_2}{k_1}\right)$$

$$= E_{obs} \cdot \frac{\Delta T}{R.T_1.T_2}$$

therefore, $E_{obs} = E_{(T_1)} - C.T_1 + C.\ \ln\left(\frac{T_2}{T_1}\right) \cdot \frac{T_1 \cdot T_2}{T}$

From equation (7)

$$E_{\left(\frac{T_1 + T_2}{2}\right)} = E_{(T_1)} + C.\left[\frac{T_2 - T_1}{2}\right]$$

(N.B. $E_{\left(\frac{T_1 + T_2}{2}\right)}$ means E at the temperature $\frac{T_1 + T_2}{2}$)

Therefore,

$$E_{obs} = E._{\left(\frac{T_1 + T_2}{2}\right)} + C.\ \ln\left(\frac{T_2}{T_1}\right) \cdot \frac{T_1 \cdot T_2}{\Delta T} - C.\ \frac{T_1 + T_2}{2}$$

which on writing $\ln\left(\frac{T_2}{T_1}\right)$ in the form $\ln\left[1 + \frac{\Delta T}{T_1}\right]$ can be expanded as a power series if $-1 < \frac{\Delta T}{T_1} \leqslant 1$

$$\ln\left[1 + \frac{\Delta T}{T_1}\right] = \frac{\Delta T}{T_1} - \frac{(\Delta T)^2}{2T_1^2} + \frac{(\Delta T)^2}{3T_1^3} \text{ etc.}$$

Typical values of ΔT and T_1 are 10 and 300°K respectively. Hence the first three terms of the above series are 0.0333, -0.00056, and +0.00001; it is, therefore, only necessary to consider the first two terms. It follows that

$$E_{obs} = E_{\left(\frac{T_1 + T_2}{2}\right)} - C.\frac{(\Delta T)^2}{2T_1}$$

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

Thus $$E_{obs} = E_{\left(\frac{T_1 + T_2}{2}\right)}$$

E determined in this way varies linearly with temperature over the experimental range within the limits of experimental error, so that the initial assumption that E varies linearly with temperature between T_1 and T_2 was justified. E_{obs} can thus be identified with the true Arrhenius activation energy at the mean temperature of the interval for which it was calculated.

The activation energies in this study were, therefore, obtained by performing experiments at different temperatures and E was determined as a function of temperature by using the rates at adjacent 10° intervals. dE/dT was obtained from the "best" straight line E against T; hence ΔCp^* from the equation

$$\Delta Cp^* = dE/dT - R$$

(ii) B Factor

The true Arrhenius B factor is defined by the equation

$$\ln k = B - \frac{E}{R.T} \qquad \ldots\ldots\ldots\ldots (2)$$

where E refers to the temperature T.

Differentiation of this equation leads to

$$\frac{dB}{dT} = \frac{dE}{dT}\,(RT)^{-1} \qquad \ldots\ldots\ldots\ldots (8)$$

since $E = RT^2 \dfrac{d\ln k}{dt}$ .... (1)

which means that B is also temperature dependent.

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

$$B_{obs} = \ln k_{(T)} + \frac{E_{obs}}{RT_1} \qquad \ldots\ldots\ldots\ldots (9)$$

and the temperature coefficient of B when E varies linearly with temperature is $\frac{C}{R.T}$ from equation (8). It is again necessary to establish the temperature to which B_{obs} calculated from equation (9) refers. It follows that

$$B_{\left(\frac{T_1 + T_2}{2}\right)} - B_{(T_1)} = \frac{C}{R} \cdot \ln\left[\frac{T_1 + T_2}{2}\right] \quad \ldots\ldots\ldots\ldots (10)$$

Since it has been shown that $E_{obs} = E_{\left\{\frac{T_1 + T_2}{2}\right\}}$

it follows that $B_{obs} = \ln k_1 + E_{\left\{\frac{T_1 + T_2}{2}\right\}} \cdot \frac{1}{RT}$

$$= \ln k_1 + \frac{E_{(T_1)}}{R.T_1} + \frac{C}{R.T_1} \cdot \left[\frac{T_2 - T_1}{2}\right]$$

$$= B_{(T_1)} + \frac{C}{R.T} \cdot \frac{T_2 - T_1}{2}$$

From equation (10) it follows that

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

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

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

$$B_{obs} = B_{\left\{\frac{T_1 + T_2}{2}\right\}} + \frac{C}{R} \frac{\Delta T^2}{8T_1^2}$$

A typical value of B is 25 and if C, ΔT, and T are taken 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

$$\ln k_{(T)} = \ln\left(\frac{\bar{k}T}{h}\right) + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT} \quad \dots\dots\dots\dots (3)$$

and

$$E = \Delta H^* + RT \quad \dots\dots\dots\dots (4)$$

it follows that:-

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

which on comparison with equation (2) shows that

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

where B and ΔS^* refer to temperature T, and, therefore, ΔS^* may be calculated from a knowledge of B. It is, however, more convenient to have ΔS^*_{obs} at the same temperature as E_{obs}. Since equation (9) leads to the identification of B_{obs} with B at temperature $\frac{T_1 + T_2}{2}$, it follows that as ΔS^* is calculated from B_{obs}, it, too must correspond to the mean temperature of the interval.

i.e. ΔS^* at $\frac{T_1 + T_2}{2}$ is given by:-

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

The experimental determination of the rate coefficients at various temperatures, therefore, enables the Arrhenius parameters to be calculated. These parameters all refer to the mean temperature of the interval for which they were calculated.

CHAPTER III

The Solvolysis of Primary Alkyl Bromides

Results and Discussion

I. Procedure

The rates of reaction of EtBr, n - PrBr and n-BuBr with 50% aqueous acetone were each studied at five different temperatures using the sealed ampoule technique. The reactions were followed by observing the development of acidity in the solutions and all runs were carried out in duplicate. First-order rate coefficients, energies, entropies and heat capacities are given in Tables I, II and III, where the standard errors in these parameters are also reported. Full details of the experimental procedures and methods employed in the calculation of the results are given in the experimental section (Ch. IV).

Before the results can be discussed, it is necessary to establish that the measured rate coefficients refer to the rate of hydrolysis of the alkyl bromides since the compounds investigated could also yield olefines under the experimental conditions used. If this were the case, the observed first order rate constants would represent the combined rates of hydrolysis and olefine formation. It is unlikely that these two processes will have the same activation energy and the concurrent hydrolysis and olefine formation will, therefore, not yield the activation parameters for the hydrolysis. Moreover, there would be a positive contribution to dE_{obs}/dT * which would, therefore, invalidate any arguments based on the observed value of this parameter.

Olefine formation is usually small when an alkyl halide reacts with water in the absence of any alkali (73). A determination of the olefine formed in the hydrolysis of n-propyl and n-butyl bromide under the conditions of this investigation showed that the reaction was 100% hydrolysis within the limits of experimental error. Vapour phase chromatographic analysis of the reaction products from a much more concentrated solution of n -,PrBr than employed in the kinetic runs also failed to detect any propylene. (Details are given on p.74). Other experiments showed that the hydrolysis went to completion

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* If the observed rate coefficient, k, results from the concurrent operation of two separate processes having k_1 and k_2 and activation energies E_1 and E_2 respectively,

then $$k = k_1 + k_2$$

and $$E_{obs} = RT^2 \frac{d\ln k}{dt} = \frac{k_1E_1 + k_2E_2}{k_1 + k_2}$$

Hence $$dE_{obs}/dT = \frac{(E_1 - E_2)^2 . k_1k_2}{(k_1 + k_2)^2 \quad RT^2}$$ when E_1 and E_2 are assumed to be independent of temperature.

as there was no detectable reaction between HBr and EtOH, PrOH or BuOH over periods of time considerably longer than used for the rate measurements (see p.77). It can, therefore, be concluded that the observed first order rate constants refer to the hydrolysis of the alkyl bromides and, therefore, the observed activation energy is the activation energy of the hydrolysis.

Results

(i) EtBr in 50% aq.acetone

T^oC	$k \times 10^4(min^{-1})$	$\bar{E}_{obs}$(Kcal) $\pm\sigma(E)$(cal)	E_{calc}*	$-\Delta S^*$(cal/deg)
50.05	1.118			
54.98		22.07 ± 144	22.07	18.65
59.91	3.091			
64.98		21.76 ± 103	21.74	19.64
70.06	8.171			
75.03		21.42 ± 268	21.42	20.70
80.00	19.78			
85.00		21.09 ± 388	21.09	21.69
90.00	45.24			

$$\frac{dE}{dT} = -32.8 \pm 0.64(i) \quad \text{or} \pm \overset{*}{11.4}(ii)$$

$$\Delta S^*(50^o) = -18.13$$

$$\Delta C_p^* = -34.8 \pm 0.64 \text{ or } \pm 11.4$$

$$\frac{\Delta C_p^*}{\Delta S^*} \text{ at } 50^o = 1.92$$

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* E_{calc} was obtained from the 'best' straight line, Eobs against T. $\sigma(dE/dT)$ was obtained by two methods, (i) 'slope' method and (ii) from $\sigma(E)$; see p. 74 for details.

(ii) n - PrBr in 50% aq.acetone

T°C	k x 10^4(min^{-1})	Eobs(Kcal) ±σ(E)(cal)	Ecalc	-ΔS*(cal/deg)
50.02	0.5374			
54.82		21.76 ± 146	21.74	21.11
59.63	1.429			
64.73		21.48 ± 129	21.53	22.01
69.89	3.758			
74.95		21.39 ± 146	21.31	22.30
80.06	9.318			
85.03		21.07 ± 135	21.10	23.27
90.00	21.18			

$$\frac{dE}{dT} = -21.4 \pm 3.0 \text{ or } \pm 6.2$$

$$\Delta S^*(50^\circ) = -20.79$$

$$\Delta C_p^* = -23.4 \pm 3.0 \text{ or } \pm 6.2$$

$$\frac{\Delta C_p^*}{\Delta S^*}(50^\circ) = 1.13$$

(iii)

T°C	k x 10^4(min^{-1})	Eobs(Kcal) ±σ(E)(cal)	Ecalc	-ΔS*(cal/deg)
50.02	0.4625			
54.82		21.87 ± 115	21.85	21.02
59.63	1.236			
64.73		21.47 ± 119	21.54	22.29
69.89	3.249			
74.95		21.30 ± 142	21.22	22.85
80.06	8.022			
85.03		20.87 ± 156	20.90	24.13
90.00	18.10			

(iii) continued.

$$\frac{dE}{dT} = -31.4 \pm 3.62 \text{ or } \pm 6.05$$

$$\Delta S^*(50^\circ) = -20.60$$

$$\Delta C_p^* = -33.4 \pm 3.62 \text{ or } \pm 6.05$$

$$\frac{\Delta C_p^*}{\Delta S^*} = 1.62$$

II. Discussion of Results

(i) Accuracy

The least accurate results in this investigation are those of EtBr; in all probability due to its relatively high volatility. It would be instructive to consider what effect the volatility of a compound such as MeBr or EtBr has on the accuracy of rate measurements.

The observed rate constant is given by the equation

$$k_1 = \frac{1}{t} \cdot \ln\left[\frac{a}{a - x}\right]$$

where 'a' is the initial concentration of the halide determined from infinity readings and x is the concentration of acid produced at time t. In the early stages of the reaction $x \ll a$ and this equation can then be expressed in the form

$$k_1 = \frac{1}{t} \cdot \frac{x}{a}$$

If the halide is volatile some of it will be in the vapour phase at the beginning of the reaction and the true initial concentration will, therefore, be a^1, $<$ a, where a is determined from the infinity titres when all of the halide will have gone back into solution. The true initial rate constant will then be given by the equation

$$k_1^{1} = \frac{1}{t} \cdot \frac{x}{a^1}$$

It should be noted that this equation is only applicable to the early stages of the reaction though the underlying principle applies throughout the reaction. The observed rate constant k_1 will thus be smaller than the true value k_1^{1}, the relation between them being given by

$$k_1 = k_1^{1}(a^1/a)$$

The larger the fraction Air Space/Liquid Volume, the smaller will be the ratio a^1/a, which means that the observed rate constant will decrease with increasing air space. Furthermore, even if the air space is kept constant the observed rates will be slightly smaller than the true rate and this discrepancy will become more pronounced the higher the temperature, i.e. there will be an extra negative increment to dE/dT. Consequently, even if the reaction (i.e. the k_1^{1} values) obeys the Arrhenius equation the observed results (k_1) will indicate an apparent decrease of E with increasing temperature.

In this investigation of the solvolysis of EtBr the air space was kept as small as possible (see p.70 to try to minimise such an effect. Even so, the air space could not be maintained absolutely constant and, therefore, the amount of EtBr in the vapour phase could vary. This effect would increase with increasing temperature and would be expected to be reflected in the accuracy of the rate constants and the magnitude of dE/dT. This decrease in accuracy with temperature was in fact observed and could account for the high value of $\Delta Cp^{*}/\Delta S^{*}$ for this compound as a result of a slightly spurious dE/dT value. It should be noted that the experimental values of E are very close to the calculated values from the 'best' straight line. This must be regarded as purely fortuitous in view of the large experimental errors in the individual activation energies.

In the case of the relatively involatile propyl and butyl bromides the effect of the free space above the solution should have negligible effect on the rates and, therefore, no special precautions were taken to ensure a constant Air Space/Liquid Volume ratio. This assumption would seem to be borne out by the accuracy of the observed rate coefficients.

(ii) Comparison with Previous Work in 50% Aq.Acetone

It is only possible to compare the ethyl bromide results with those of Tommila, Tiilikainen and Voipio (47) who investigated the effect of solvent changes on the rate and related parameters of ethyl bromide in a range of solvent mixtures from 100% acetone to 100% water.

Table IV

	This Investigation	Tommila (47)[x]
$k \times 10^6 (sec.^{-1})$	1.863 (50.05°C.)	1.48 (50°C.)
$k \times 10^6 (sec.^{-1})$	5.152 (59.91°C.)	3.91 (60°C.)
E. (Kcal)	22.07 (55°C.)	20.80 (55°C.)

The large differences between these results are most probably due to the unreliability of Tommila's rate data, which for some solvent compositions in the 50% aq.acetone region actually lead to a positive dE/dT value. This effect is not considered to be 'real' as the experimental error of their dE/dT values is very much larger than the dE/dT values calculated from their rate data. A further source of discrepancy is the fact that in this investigation the solvent was made up by volume, whereas Tommila et al. made their solvents up by weight. It is generally found that solvents made up by volume by different workers vary in composition to quite a significant extent. Therefore, what is nominally a 50% v/v solvent may actually depart from its nominal composition by a large amount, in which case, the comparison made here may not be strictly valid. This would help to account for the differences in the quoted table.

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[x] Calculated by interpolation as these authors used solvent systems made up by weight.

(iii) Variation of Rate in the Alkyl Series

		Et	n-Pr	n-Bu
$k \times 10^5 (\mathrm{min}^{-1})$	at 50°C	11.18	5.374	4.625
	at 90°C	452.4	211.8	181.0
E.(Kcals)	at 55°C	22.07±.144	21.76± 146	21.87±.115
$-\Delta S^*$ (50°C)		18.13	20.79	20.60

As can be seen there is a decrease in rate with increasing alkyl chain length, the differences becoming less pronounced up the series. This decrease is in accordance with the predictions of Hughes (21) and other work on increasingly substituted alkyl systems. The cause of the decrease is in part due to the smaller inductive effect which influences the Arrhenius parameters and partly to steric hindrance. In the present investigation it appears at first sight that there is a decrease in E from Et Br to BuBr; the values for PrBr and BuBr being effectively the same within experimental error. In view of the relative inaccuracy of the EtBr results it is considered that the apparent trend is not real and that the activation energies are essentially the same for all three compounds if the experimental errors are taken into consideration. Similar conclusions apply to ΔS^*. It would, therefore, seem that as both E and ΔS^* for the three compounds are very much the same, the rate is controlled by both parameters, neither of which could be said to exert a predominating influence.

(iv) $\Delta Cp^{*}/\Delta S^{*}$ Ratios

$\Delta Cp^{*}/\Delta S^{*}$ ratios in 50% aq.acetone at 50°C

Table VI

Compound		Mechanism	$-\Delta Cp^{*}$	$-\Delta S^{*}$	$\Delta Cp^{*}/\Delta S^{*}$
$PhCHCl_2$	(59)	S_N1	29.0 ± 3	11.4	2.5
$PhCCl_3$	(59)	S_N1	46.0 ± 4	16.2	2.9
t - BuCl	(74)	S_N1	26.7	0.8	2.6
EtBr		S_N2	34.8 ± 11.4	18.13	1.92
n-PrBr		S_N2	23.4 ± 6.2	20.79	1.13
n-BuBr		S_N2	33.4 ± 6.1	20.60	1.62
$p\text{-}NO_2PhCH_2Cl$	(75)	S_N2	20.13	23.4	0.86
$PhCH_2Cl$	(59)	S_N2	21.0 ± 2.5	22.8	0.9

(a) Constancy of $\Delta Cp^{*}/\Delta S^{*}$ in S_N1 Reactions

At the commencement of this investigation the constancy of the $\Delta Cp^{*}/\Delta S^{*}$ ratio had not been fully established for S_N1 reactions. As a result of parallel investigations, the following compounds which undergo S_N1 hydrolysis, are now known to yield $\Delta Cp^{*}/\Delta S^{*}$ ratios which depend only on the solvent and temperature.

(i) in 50% aq. acetone, $PhCHCl_2$, $PhCCl_3$ (59), $p\text{-}MeC_6H_4CH_2Cl$ (75), t-BuCl (74).

(ii) in 70% aq. acetone, Ph_2CHCl, and its $p\text{-}NO_2$, p-Cl, p-Br and p-I derivatives (76) and $p\text{-}MeOC_6H_4CH_2Cl$ (75).

(iii) in 80% aq. acetone, Ph_2CHCl (76) and
p-$MeOC_6H_4CH_2Cl$ (75).

(iv) in 85% aq. acetone, Ph_2CHCl (76) and its
p-Me derivative (75).

(v) in 50% aq. ethanol, $PhCH_2Cl$ and $PhCCl_3$ (59).

The constancy of $\Delta Cp^{*}/\Delta S^{*}$ for S_N1 reactions can therefore be regarded as constant.

(b) $\Delta C_p^{*}/\Delta S^{*}$ for S_N2 reactions

It can be seen that the $\Delta C_p^{*}/\Delta S^{*}$ ratios for S_N2 reactions are rather lower than the ratios for S_N1 reactions and also it is worth noting that the ratios are higher for the alkyl bromides now studied than for the two benzyl chlorides quoted in Table IV. The ratio is largest for EtBr where ΔC_p^{*} is also subject to the largest error and it seems most probable in view of the experimental errors that it errs in the direction of being too high. The most probable value for $\Delta C_p^{*}/\Delta S^{*}$ for the alkyl bromides would seem to be in the region of 1.3, which is appreciably less than the quoted ratios for the S_N1 reactions of the various chlorides. The ratio $\Delta C_p^{*}/\Delta S^{*}$ therefore appears to be a valid test for S_N mechanism.

It must be pointed out that the ratios being compared are not strictly comparable unless certain reservations are made because on the one hand are quoted $\Delta C_p^{*}/\Delta S^{*}$ data for S_N1 <u>chlorides</u> whilst this investigation leads to data for S_N2 <u>bromides</u>. Alkyl bromides were chosen for the present work as the corresponding chlorides hydrolyse much more slowly and therefore would have necessitated higher temperatures when the accurate control of thermostats becomes more difficult. Furthermore, complications would have arisen due to the greater volatility of the alkyl chlorides.

It is considered that $\Delta C_p^{\ddagger}/\Delta S^{\ddagger}$ for primary alkyl chlorides would have been less than the ratio for the corresponding bromides for the following reason.

It is a general rule that $\Delta S^{\ddagger}$ is less negative for bromides than for chlorides in both S_N1 and S_N2 reactions, e.g.

Table VII

Compound		$-\Delta S^{\ddagger}$	Mechanism	Temperature ^{o}C
$PhCH_2Cl$	(77)	21.86	S_N2	37.5
$PhCH_2Br$	(77)	15.42	S_N2	37.5
$PhCHCl_2$	(77)	8.64	S_N1	37.5
$PhCHBr_2$	(77)	2.164	S_N1	37.5
$PhCCl_3$	(77)	10.01	S_N1	25.0
$PhCBr_3$	(77)	6.90	S_N1	25.0
MeCl	(62)	10.96	S_N2	62.4
MeBr	(62)	9.12	S_N2	62.4

This is in agreement with the lower solvation enthalpy of the bromide ion (78)

The results in Table VIII show that whilst the heat capacities of chlorides and bromides are very much the same those for the bromides are perhaps slightly more negative.

Table VIII

$-\Delta Cp^*$ in 50% Acetone

$PhCHCl_2$	(59)	29
$PhCH_2Cl$	(59)	21
$PhCCl_3$	(59)	46
EtBr, PrBr, BuBr		30
$p\text{-}NO_2C_6H_4CH_2Cl$	(75)	20

Hence the less negative entropy of bromides relative to chlorides would be expected to lead to a higher value of $\Delta Cp^*/\Delta S^*$ for bromides than for chlorides.

ΔCp^* would have to be very much more negative for chlorides than bromides if the ratios of $\Delta Cp^*/\Delta S^*$ were to be the same. Since the $\Delta Cp^*/\Delta S^*$ for S_N2 bromides is less than the ratio for S_N1 chlorides (Table VI) an even lower value is expected for S_N2 chlorides. This is consistent with the predicted view that the $\Delta Cp^*/\Delta S^*$ ratio for S_N2 reactions should be less than the ratio for S_N1 reactions. Additional evidence for this conclusion arises from the work on benzyl chloride (59) and its p-nitro derivative (the data for the latter compound were not available when the present study was started) which undergo hydrolysis essentially by the S_N2 mechanism and which show much lower values of the ratio than the S_N1 chlorides and also lower values than the S_N2 bromides of this investigation, in agreement with the considerations outlined above. Although no reliable data for S_N1 bromides are available at the present time, it seems reasonable to predict that their $\Delta Cp^*/\Delta S^*$ ratio will be considerably larger than the ratio for S_N2 bromides. The reasons for this are that the change of mechanism, from S_N2 to S_N1 leads to a less negative entropy (Table VI) for S_N1 reactions and the results in Table VIII indicate that ΔCp^* is possibly more negative for S_N1, than S_N2 reactions and therefore the ratio should be quite a lot larger than the S_N2 ratio. In conclusion it can be stated that the observed $\Delta Cp^*/\Delta S^*$ values have established the constancy of the ratio for the primary alkyl bromides within experimental error and moreover the values of the ratios are in agreement with the predictions of Bensley and Kohnstam (59).

CHAPTER IV

Experimental

Purification of Materials

1. Ethyl Bromide

Ethyl bromide (Light's) was shaken with concentrated sulphuric acid, separated, washed twice with distilled water, followed by further washings with potassium carbonate solution and then dried over phosphorus pentoxide. After decanting, the solution was fractionated and collected at 37.9 - 38.1°C (759 mm) (79).

2. n-Propyl Bromide

n-Propyl bromide (Light's) was dried over anhydrous potassium carbonate and calcium chloride, decanted and distilled. The fraction boiling at 70.4 - 70.6°C (751 mm) was collected (80).

3. n-Butyl Bromide

n-Butyl bromide (B.D.H.) was dried over anhydrous potassium carbonate and calcium chloride, decanted and distilled. The fraction boiling at 101.3°C (760 mm) was collected. (80).

4. Ethanol

Pure ethanol was obtained by refluxing absolute alcohol with magnesium, when magnesium ethylate was formed and then distilling from 10% silver nitrate. (81).

5. Hydrobromic Acid

"Constant boiling" commercial hydrobromic acid was decolourised by shaking with clean mercury.

6. Acetone

A.R. grade acetone was refluxed over potassium permanganate and caustic soda pellets for two hours, distilled from hydroquinone and then re-fractionated carefully, generous head and tail fractions being discarded (82).

The solvent as actually used in the solvolyses consisted of 50 volumes of acetone and 50 volumes of distilled water. Such a solvent composition is referred to as '50% aq. acetone.'

The acetone in which the titrations were carried out was ordinary acetone which had been refluxed with potassium permanganate and caustic soda pellets and distilled once. The indicator lacmoid was added and the solution neutralised before use.

Purity of Halides

The purities of the halides were determined by standard vapour phase chromatographic techniques, which indicated that all the halides were 99.5 - 100% pure.

Experimental Details

Rate Measurements

n-PrBr and n-BuBr

Kinetic runs were carried out over the temperature range 50°C to 90°C in thermostats of the conventional mercury-toluene regulated type with electric lamp bulb heaters. A layer of heavy white oil was necessary to prevent excessive loss of water by evaporation from the bath. The temperatures, which were constant to ± 0.01°C, were measured with thermometers standardised by the National Physical Laboratory to ± 0.02°C.

The solvolysis of the alkyl bromides in 50% aq.acetone goes to completion and the rate constants can, therefore, be calculated from a knowledge of the acid produced at various time intervals and the acidity produced at 100% reaction, without the necessity of using weighed amounts.

Approximately 0.02 M solutions of the halides were made up by dissolving the appropriate amount of halide in about 150 mls. of 50% aq.acetone at room temperature or at 0°C for the more volatile ethyl bromide. Aliquots were run into test tubes, partially drawn out in the middle, from a tube-filler (fig. IIa); the volume delivered being 6.213 mls. at 20°C. The ampoules were then sealed off, attached to holders and introduced into the thermostat in batches of about seven, accompanied by vigorous shaking. Tubes were not removed until the thermostat had regained its nominal value; normally this took from two to three minutes.

At suitable time intervals, tubes were removed from the thermostats and the reaction stopped by cooling in an ice-salt mixture. After cleaning, the tubes were broken under about 200 mls. of neutral acetone and the acidity determined by titration against standard caustic soda (ca. 0.01M) with lacmoid as indicator. The initial concentration of halide was determined by the acidity produced at 100% reaction, after heating the tubes in a boiling-water bath for 10-15 x the half-life period. The time of the first reading was taken as zero. Several batches of the solvent were used for the rate measurements. This necessitated monitoring each solvent by examining the rate of solvolysis of a reactant which had already been studied in a previous batch. The necessary correction factor was applied to the results to bring all the rate coefficients to a common batch of solvent.

Ethyl Bromide

Because of the volatility of ethyl bromide a different type of ampoule was necessary as it was known that reaction rates of volatile compounds are sensitive to the amount of free air space above the liquid. In an attempt to keep the air space/liquid volume ratio to a minimum, the reaction tubes consisted of glass bulbs joined to thin glass stems (fig. IIb), the volume of the bulb being such that the reaction solution completely filled the bulb and part of the stem. The air space was thus kept as small as possible by sealing off the stem at a distance above the liquid level such that as the liquid expanded on being introduced to the thermostat it completely filled the tube. In addition the tube-filler was kept at 0°C by circulating ice-water around it, otherwise the experimental procedure was the same as for the other halides.

Calculation of the Results

Since the solvent was present in large excess, the bimolecular solvolysis was kinetically of the first order. The rate constants were, therefore, calculated from the normal first order integrated rate equation

$$k_1 = \frac{1}{t} \, 2.303 \log \frac{a}{a-x}$$

where t is the time

a is the concentration of halide at time t = 0

a-x is the concentration of halide at time t = t

The time of the first reading was taken as zero and "a" calculated from this and the value of the acidity produced when the reaction had gone to completion. The rate constants determined in this way have already been summarised, more detailed records of individual runs are given at the end of this chapter.

The activation energies E, were obtained from the mean rate coefficients at adjacent temperature intervals:-

$$E = 2.303.R.\frac{T_1 \cdot T_2}{T_2 - T_1} \cdot \log \frac{k_{(T_2)}}{k_{(T_1)}} \qquad (2)$$

where T_1 and T_2 are the absolute temperatures, and E refers to the temperature $\frac{T_1 + T_2}{2}$ (Ch. II, p. 47).

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

Then $E = E^{o} + \frac{dE}{dT} . T$

whence the least squares value of dE/dt is given by:-

$$\frac{dE}{dT} = \frac{\Sigma(E-E_m)(T-T_m)}{\Sigma(T-T_m)^2} \qquad (3)$$

where E_m is the mean of the experimental activation energies and T_m is the mean temperature of the appropriate temperature range. Thus, on calculating dE/dt, E can be calculated at any temperature from:-

$$E = E_m + \frac{dE}{dT}(T-T_m) \qquad (4)$$

The 'best' values of E calculated from this equation are reported in the Tables (I, II, III) as E_{calc}.

The heat capacities of activation ΔCp^{*} were obtained from:-

$$\Delta Cp^{*} = \frac{dE}{dt} - R \qquad (5)$$

as shown in Ch. II, p. 32.

ΔCp^{*} could also be obtained from the 'best' straight line ΔS^{*} - T as follows.

Since $\frac{d}{dt} . \Delta S_o^{*} = \frac{\Delta Cp^{*}}{T}$

then $\Delta S^{*} = \Delta S_o^{*} + 2.303 \; \Delta Cp^{*} \log T \qquad (6)$

Therefore $\Delta Cp^{*} = \frac{1}{2.303} \; \frac{(\Delta S^{*}-\Delta S_m^{*})(\log T-\log T_m)}{(\log T - \log T_m)^2} \qquad (7)$

ΔCp^{*} calculated in this way was always in good agreement with ΔCp^{*} obtained from equation (5).

The entropy of activation, ΔS^*, at temperature $\frac{T_1 + T_2}{2}$ was calculated from:-

$$\Delta S^* = B_{obs} - 1 - \ln \bar{k} \frac{(T_1 + T_2)}{h \cdot 2} \qquad (8)$$

as shown in Ch. II, p. 31.

ΔS^*could be calculated at any temperature by means of the equation:-

$$\Delta S^* = \Delta S_m^* + 2.303 \Delta Cp^* (\log T - \log T_m)$$

The ΔS^* values at 50°C quoted in the Tables (I, II and III) were obtained from this equation.

Statistical Analysis

In a kinetic investigation of this type it is essential to carry out a statistical analysis of the results in order to estimate with some degree of certainty the value of dE/dt because its value is not large compared with E and so very often is less than the experimental errors of some investigators who have claimed to have observed 'real' values of dE/dt.

The mean rate coefficients, k_m, in this investigation were obtained by statistical treatment of two runs at any one temperature by considering the runs as one for statistical purposes. The standard deviation of the final mean rate coefficient, $\sigma(k)$, was obtained from:-

$$\sigma(k) = \frac{\left[\sum(k - k_m)^2\right]^{\frac{1}{2}}}{n} \qquad (9)$$

where n was the number of separate determinations of k.

According to Purlee, Taft and de Fazio (44) the standard deviation of E, $\sigma(E)$ is given by:-

$$\sigma(E) = \frac{R \cdot T_1T_2}{T_2-T_1}\left[\left(\frac{\sigma_1}{k_1}\right)^2 + \left(\frac{\sigma_2}{K_2}\right)^2\right]^{\frac{1}{2}} \qquad (10)$$

where σ_1 and σ_2 are the standard deviations of the mean rate coefficients, k_1 and k_2.

To give some idea of the accuracy required in k_m let us consider the temperature range 25 - 35°C. Then $\frac{R \cdot T_1T_2}{T_2-T_1}$ has the value 18,260 cals. and thus a standard deviation of 1% in k_1 and k_2 leads to a standard deviation in E of ± 256 cals, irrespective of the values of k. It should be noted that this standard deviation is not the maximum possible error.

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

(i) 'Best' straight line method

$$\sigma\left(\frac{dE}{dT}\right) = \left[\frac{\sum(E - E_{calc.})^2}{(n-2)\sum(T - T_m)^2}\right]^{\frac{1}{2}}$$

where n is the number of determinations of E.

(ii) From $\sigma(E)$,

$$\sigma\left(\frac{dE}{dT}\right) = \frac{\left[\sum(E-E_m)(T-T_m)^2\right]^{\frac{1}{2}}}{\sum(T-T_m)^2}$$

Method (ii) usually predicts the greater error as can be seen in Tables (I, II, III).

Olefine Determination

A number of experiments were performed in order to determine how much propylene or butylene (if any) was produced under the experimental conditions used for the solvolyses. The experiments were carried out in thermostats regulated at 60°C and 90°C. The concentration of halide used was about 0.04 - 0.06 M; at higher concentrations these halides were only partly soluble.

The extraction technique of Hughes, Ingold (83) was found to be unsuitable, due to its inherent inaccuracy for the low concentrations of olefine likely to be formed and to the interference of acetone in the titrations in carbon tetrachloride-bromine solution. The solutions were, therefore, analysed for olefine by an aspiration method based on the method of Hughes, Ingold and co-workers (84). The tubes were filled as in a normal kinetic run, heated for 10 - 15 x the half-life period at 60°C and 90°C, analysed by breaking the cleaned ampoule in a three-necked flask containing distilled water (100 ml), attached to which was a reflux condenser surmounted by a 'cold-finger' at -80°C, which led to two or three traps containing a standard bromine solution in carbon tetrachloride cooled to -15°C. Nitrogen was bubbled through the flask and apparatus to act as a carrier. The flask and contents were then heated to not more than 50°C for about an hour, when any olefine produced would have been driven from the flask and absorbed in the bromine solution. The excess bromine remaining in the traps was determined by titrating against standard sodium thiosulphate. Exactly the same procedure was carried out on an ampoule which had not been heated to obtain the titration blank.

The accuracy of the method was found by condensing some propylene into a weighed ampoule, sealed off, re-weighed and the aspiration procedure carried out. The method gave readings which were 5% too low, though this is quite adequate for the estimation as the absolute value of such an error is very small in the amounts of olefine expected to be formed.

Efficiency of Olefine Determination

Experiment 19

Weight propylene present = 0.01209 g.

Weight propylene found = 0.01150 g.

error = -5%

Olefine Determination from propyl bromide at 90.00°C

Run 3

Amount PrBr present determined from the infinity readings = 0.05610 g.

Theoretical yield of olefine if 100% conversion = 0.01914 g.

Average blank titre of bromine solution in traps = 2.891 ml 0.01009 M thiosulphate

Titre after absorption of propylene = 2.792 ml 0.01009 M thiosulphate

Weight propylene = 4.531×10^{-5} g.

olefine formation = 0.24%

This was a typical result for the amount of olefine formed and is, therefore, negligible with respect to the hydrolysis.

Products of Hydrolysis

To further verify whether or not there was any olefine formation an approximately molar solution of propyl bromide was made up in 100 ml. of 50% aq.acetone. At this concentration most of the halide formed a lower insoluble layer at room temperature. The reaction mixture was sealed off in a large ampoule and heated at 100°C for eight days, by which time the reaction should have gone to completion. The solution turned brown, with the formation of an upper dark brown layer. Water (200 ml) was added, the solution neutralised with ammonia followed by extraction with two 5 ml. portions of ether. The ether extract was dried over anhydrous magnesium sulphate. Two drops of the red-brown extract were analysed by vapour phase chromatography and a chromatogram obtained (fig. 3). The peaks were identified by putting known mixtures or single components through the column under the same conditions (fig. 4). The chromatograms (figs. 3 and 4) thus identify the constituents of the ether extract as:- ether, acetone, propanol and unreacted propyl bromide (due to the high concentration of halide used in the experiment). There was no evidence for the formation of any propylene.

Reversibility of Reactions

It was thought that there might be a back reaction of the products of the solvolyses, viz, hydrobromic acid reacting with the alcohol produced. Solutions (0.02M) of hydrobromic acid and the appropriate alcohol were made up in 50% aq.acetone. This concentration was used to give a solution of comparable strength to that of the actual solutions used in the rate measurements in the latter stages of their reaction. Ampoules were filled in the normal way, heated at 100°C for four days and the acidity determined. The initial acidity of the freshly prepared solution was also determined. Thus, if there were any reaction of hydrobromic acid with the alcohol, there would be a reduction in titre of the heated solutions. At the concentrations used, such a reversible reaction was not observed for any of the alkyl bromides.

e.g. Expt. 7.

0.02 M HBr and 0.02 M Et OH in 50% aq.acetone at 100°C

time (hrs.)	titre (mls. 0.01013 M NaOH)
0	16.86
12.5	16.88
17.00	16.87
19.00	16.87
37.0	16.80
51.0	16.83

A further series of experiments were performed as an additional source of information as to whether there was an equilibrium set up if the reactions did not go to 100% completion. If this were so the position of equilibrium would be temperature dependent. Solutions were made up in the usual manner and batches of three or four ampoules were placed in each of three thermostats at 70°C, 90°C and 100°C respectively, heated for 10-15 x the half-life period and the acidity determined. If there were a position of equilibrium then the titres would be different. In actual fact the titres were found to be all the same within experimental error, indicating the absence of an equilibrium and thus no reversibility of the reactions products.

e.g. <u>Expt. 16</u>. <u>Butyl Bromide</u>

Average titre (mls NaOH)	Temp. °C
17.69 ± 0.02	100
17.67 ± 0.03	90
17.70 ± 0.02	70

APPENDIX

Details of Kinetic Runs

First order rate constants, k_1', were calculated from the integrated rate equation:-

$$k_1' = \frac{1}{t} \; 2.303 \quad \log \left[\frac{a}{a-x} \right]$$

where the symbols have the usual meaning. In each case details of one run are given and the mean rate coefficient k_1'' of the duplicate run is also quoted.

n-Butyl Bromide at 50.02°C. Solvent III. Run XIV.

Initial Concentration = 0.02516 M

6.213 ml. titrated with 0.01039 M NaOH

t	a-x	$k \times 10^{-5}$
0	15.00	---
838	14.43	4.672
3755	12.63	4.581
5162	11.77	4.698
6780	11.04	4.525
8495	10.14	4.618
10936	8.98	4.689
13885	7.95	4.571
16446	6.85	4.766
19336	6.04	4.704
23715	4.82	4.788
∞	0.00	---

$k_1' = 4.661$

$k_1'' = 4.697$

mean k referred to solvent II = $\underline{4.624 \times 10^{-5}}$

n-Butyl Bromide at 59.63°C. Solvent II. Run IV

Initial Conentration = 0.021120 M
6.213 ml. titrated with 0.01205 M NaOH

t	a-x	k x 10^{-4}
0	10.88	---
161	10.65	(1.330)
890	9.75	1.234
1499	9.04	1.237
2352	8.19	1.208
3025	7.44	1.257
3769	6.80	1.247
4125	6.53	1.241
5234	5.68	1.243
8153	4.04	1.215
8797	3.70	1.227
9554	3.33	1.240
10995	2.78	1.241
12427	2.34	1.237
∞	0.00	---

$k_1' =$ 1.236
$k_1'' =$ 1.236

n-Butyl Bromide at 69.84°C. Solvent I. Run XII.

Initial concentration = 0.02028 M
6.213 ml. titrated with 0.01190 M NaOH

t	a-x	$k \times 10^{-4}$
0	10.46	---
234	9.69	3.268
505	8.88	3.243
854	8.05	3.066
1151	7.31	3.113
1425	6.69	3.137
1593	6.29	3.192
2007	5.39	3.305
2334	4.91	3.241
2702	4.23	3.352
2932	4.01	3.271
3230	3.73	3.193
3864	2.99	3.241
4162	2.67	3.282
∞	0.00	---

$k_1' = 3.225$

$k_1'' = 3.194$

mean k referred to solvent II = 3.248

n-Butyl Bromide at 80.06°C. Solvent III. Run XVII

Initial concentration = 0.01418 M
6.213 ml titrated with 0.01039 M NaOH

t	a-x	k x 10^{-4}
0	8.43	---
50	8.10	7.968
169	7.38	7.863
258	6.88	7.874
462	5.80	8.097
792	4.40	8.210
921	4.00	8.093
1033	3.58	8.292
1279	2.93	8.264
1586	2.35	8.052
1898	1.82	8.076
2469	1.05	8.439
∞	0.00	—

$k_1' = 8.111$

$k_1'' = 8.124$

mean k referred to solvent II = 8.022 x 10^{-4}

n-Butyl Bromide at 90.00°C. Solvent II. Run X.

Initial Concentration = 0.01818 M
6.213 ml. Titrated with 0.01190 M NaOh

t	a-x	k x 10^{-3}
0	8.49	---
30	8.06	1.735
65	7.51	1.845
95	7.16	1.794
122	6.79	1.831
142	6.54	1.838
208	5.82	1.816
270	5.21	1.809
322	4.70	1.837
361	4.34	1.859
0	9.35	---
498	3.80	1.808
572	3.37	1.784
633	2.97	1.811
715	2.55	1.818
∞	0.00	---

$k_1' = 1.821$

$k_1'' = 1.799$

n-Propyl Bromide at 50.02°C. Solvent III. Run XVI

Initial Concentration 0.01635 M
6.213 ml. titrated with 0.01039 M NaOH

t	a-x	$k \times 10^{-5}$
0	9.66	---
656	9.35	(4.985)
2103	8.62	4.421
5020	7.30	5.582
6427	6.83	5.396
7845	6.31	5.425
9760	5.68	5.444
12201	4.89	5.581
15150	4.20	5.499
17711	3.75	5.344
20592	3.15	5.443
24972	2.42	5.546
∞	0.00	---

$k_1' = 5.468$

$k_1'' = 5.410$

mean k referred to solvent II = 5.374×10^{-5}

n-Propyl Bromide at 59.63°C. Solvent II. Run IX

Initial concentration = 0.02160 M
6.213 ml titrated with 0.01205 M NaOH

k	a-x	k x 10^{-4}
0	11.01	---
660	10.04	1.399
1392	9.06	1.402
2063	8.25	1.398
2822	7.35	1.432
3568	6.62	1.430
5296	5.15	1.435
5946	4.61	1.468
6486	4.44	1.401
7151	3.97	1.427
7844	3.82	(1.350)
8591	3.38	1.375
9286	2.84	1.460
9973	2.53	1.475
10712	2.33	1.451
∞	0.00	---

$k_1' = 1.427$

$k_1'' = 1.431$

n-Propyl Bromide at 69.84°C. Solvent I. Run XII

Initial concentration = 0.02013 M
6.213 ml titrated with 0.01190 M NaOH

k	a-x	k x 10^{-4}
0	10.23	---
272	9.24	3.734
482	8.55	3.718
844	7.53	3.629
1149	6.77	3.592
1472	5.91	3.727
1778	5.23	3.772
2071	4.82	3.634
2333	4.59	(3.435)
2627	3.80	3.770
2852	3.68	3.586
2987	3.42	3.668
3273	3.04	3.708
3727	2.49	3.792
4084	2.24	3.719
∞	0.00	---

$k_1' = 3.689$

$k_1'' = 3.739$

mean k referred to solvent II = 3.758 x 10^{-4}

n-Propyl Bromide at 80.06°C. Solvent III. Run XVIII

Initial concentration = 0.02143 M
6.215 ml. titrated with 0.01039 M NaOH

t	a-x	$k \times 10^{-4}$
0	12.68	---
161	10.93	(8.428)
242	10.04	9.614
455	8.26	9.426
770	6.23	9.228
890	5.47	9.450
1011	5.11	(8.995)
1248	3.93	9.391
1570	2.83	9.557
1882	2.28	9.120
2182	1.65	9.346
2447	1.21	9.506
2669	0.92	(9.826)
∞	0.00	---

$k_1' = 9.404$

$k_1'' = 9.455$

mean k referred to solvent II = 9.318×10^{-4}

n-Propyl Bromide at 90.00°C. Solvent II. Run V

Initial concentration = 0.01632 M
6.213 ml. titrated with 0.01047 M NaOH

t	a-x	$k \times 10^{-3}$
0	9.30	---
37	8.60	2.116
68	8.03	2.161
99	7.55	2.108
126	7.11	2.131
156	6.74	2.067
217	5.84	2.145
277	5.13	2.149
336	4.58	2.109
400	4.02	2.097
455	3.55	2.117
0	9.26	---
518	3.12	2.100
576	2.88	2.028
638	2.34	2.157
698	2.14	2.105
∞	0.00	---

$k_1' = 2.113$
$k_1'' = 2.123$

Run 3. Ethyl Bromide at 50.05°C in 50% aq.acetone. Solvent A

Initial Concentration = 0.03204 M
4.667 ml. titrated with 0.009434 M NaOH

t	a-x	k x 10^{-5}
0	15.85	---
137	15.60	(9.919)
809	14.47	10.96
1358	13.59	11.16
2257	12.25	11.31
3740	10.34	11.36
5148	8.75	11.49
6577	8.45	(9.528)
∞	0.00	—

$k_1' = 1.126$

$k_1'' = 1.110$

Run 4. Ethyl Bromide at 59.91°C in 50% aq.acetone. Solvent A.

Initial Concentration = 0.03089 M
4.667 ml. titrated with 0.009434 M NaOH

t	a-x	k x 10^{-4}
0	15.21	---
116	14.77	(2.522)
780	11.93	3.116
943	11.35	3.103
1064	11.01	3.036
1243	10.11	(3.288)
2223	7.69	3.068
2348	7.39	3.075
2682	6.66	3.080
3709	4.74	3.145
∞	0.00	---

$k' = 3.094$

$k_1'' = 3.088$

Run 6. Ethyl Bromide at 70.06°C in 50% aq.acetone. Solvent A.

Initial Concentration = 0.03934 M
4.667 ml. titrated with 0.009434 M NaOH

t	a-x	$k \times 10^{-4}$
0	17.21	---
36	16.71	8.125
119	15.61	8.187
249	14.21	(7.686)
362	12.82	8.132
473	11.63	8.279
590	11.14	(7.374)
701	9.72	8.149
831	8.89	7.949
976	7.79	8.125
1079	7.50	(7.695)
1301	5.81	8.349
1330	5.75	8.241
1576	4.62	8.345
1930	3.47	8.296
∞	0.00	-

$k_1' = 8.198$

$k_1'' = 8.143$

Run 29. Ethyl Bromide at 80.00°C in 50% aq.acetone. Solvent D.

Initial concentration = 0.02263 M
4.667 ml. titrated with 0.008796 M NaOH

t	a-x	k x 10^{-4}
0	11.83	-
23	11.36	(1.762)
82	10.10	1.930
133	9.11	1.965
211	7.77	1.993
271	6.96	1.957
340	5.90	2.046
452	4.74	2.024
654	3.01	2.093
717	3.04	1.895
777	2.81	1.850
841	1.97	2.132
912	1.71	2.121
1010	1.69	1.928
1128	1.06	2.140
∞	0.00	–

$k_1' = 2.006$

$k_1'' = 2.024$

mean k relative to Solvent A = 1.978

Run 27. Ethyl Bromide at 90.00°C in 50% aq. acetone. Solvent D.

Initial Concentration = 0.02601 M
4.667 ml. titrated with 0.008796 M NaOH

t	a - x	k x 10^{-3}
0	13.55	-
15	12.65	4.575
36	11.39	4.823
64	10.01	4.732
86	8.98	4.783
115	8.18	4.387
138	7.08	4.704
152	6.63	4.704
200	5.74	(4.298)
236	4.83	4.375
264	3.87	4.751
286	3.77	4.478
315	3.39	4.402
338	2.76	4.712
∞	0.00	-

$k_2' = 4.618$

$k_1'' = 4.598$

mean k relative to Solvent A = (4.524)

Run 30. Ethyl Bromide at 60.02°C in 50% aq. acetone.

Solvent D

Initial concentration = 0.02144 M
4.667 ml. titrated with 0.008796 M NaOH

t	a - x	$k \times 10^{-4}$
0	10.89	-
170	10.38	(2.845)
352	9.75	3.147
957	8.43	(2.678)
1097	7.75	3.094
1922	5.91	3.181
1961	5.90	3.126
2269	5.38	3.109
2422	5.01	3.207
2695	4.48	3.297
3202	3.78	3.306
4537	3.45	(2.534)
∞	0.00	—

$k_1' = 3.183$

k_1' at 59.91°C = 3.149

Factor for solvent D: solvent A $= \dfrac{3.149}{3.091} = 1.019$

BIBLIOGRAPHY

(1) Ingold, *Chem. Rev.*, 15, 225, (1934).

(2) Lewis, The Valence and the Structure of Atoms and Molcules, New York, p. 139, (1923).

(3) Ingold, Structure and Mechanism in Organic Chemistry, London, p. 62, (1953).

(4) Lowry, *Nature*, *114*, 376, (1925).

(4') Hughes, *Quart. Rev.*, *5*, 245, (1951).

(5) Streitweiser, Jr., *Chem. Rev.*, *56*, pp. 571, (1956).

(6) Ingold, *Trans. Far. Soc.*, *34*, 227 (1938).

(7) Gleave, Hughes and Ingold, *J.C.S.*, 236 (1935).

(8) Hine, Physical Organic Chemistry, McGraw-Hill, p. 93, (1956).

(9) Le Bel, *J. Chim. Phys.*, *9*, 323 (1911).

(10) Lewis, see ref. (2), p. 113.

(11) London, *Z. Elektrochem.*, *35*, 552 (1929).

(12) Ingold, see ref. (3), p. 313.

(13) Swain and Eddey, *J.A.C.S.*, *70*, 2989, (1948).

(14) Hughes and Ingold, *Trans. Far. Soc.*, *37*, 665, (1941).

(15) Ingold, see ref. (3), p. 317

(16) Bateman, Cooper, Hughes and Ingold, *J.C.S.*, 945, (1940

(17) Ingold, see ref. (3), p. 335.

(18) Gleave, Hughes and Ingold, *J.C.S.*, 236, (1935).

(19) Cowdrey, Hughes, Ingold, Masterman & Scott, *J.C.S.*, 1252, (1937).

(20) Cowdrey, Hughes and Ingold, *J.C.S.*, 1208, (1937).

(21) Hughes, Trans. Far. Soc., *37*, 611, (1941).

(22) Ingold, see ref. (3), Ch. VII.

(23) Bateman, Cooper, Hughes & Ingold, J.C.S., 925, (1940).

(24) Bateman, Hughes and Ingold, J.A.C.S., 60, 3080, (1938).

(25) Shillaker, Private Communication.

(26) Winstein, Grunwald and Jones, J.A.C.S., 73, 2700, (1951).

(27) Ingold, see ref. (3), p. 310.

(28) Bensley and Kohnstam, J.C.S., 4747, (1957).

(29) Crunden and Hudson, J.C.S., 503, (1956).

(30) Gold, J.C.S., 4633, (1956).

(31) Gold, Hilton and Jefferson, J.C.S., 2756, (1954).

(32) Le Roux and Swart, J.C.S., 1475, (1955).

(33) de la Mare, J.C.S., 3180, (1955).

(34) Bunton, Lewis and Llewellyn, Chem. and Ind., 1154, (1954).

Bunton and Lewis, ibid., 180, (1956).

(35) Winstein, Fainberg & Grunwald, J.A.C.S., 79, 4146, (1957).

(36) Evans and Hamann, Trans. Far. Soc., 47, 25, (1951).

(37) Bird, Hughes and Ingold, J.C.S., 634, (1954).

(38) Arrhenius, Z. Phys. Chem., 4, 226, (1889).

(39) Hinshelwood, The Kinetics of Chemical Change in Gaseous Systems. Clarendon Press, Oxford, 1945.

(40) Trautz, Z. Anorg. Allg. Chem., 81, 102, (1918).

(41) La Mer, J. Chem. Phys., 1, 289, (1933).

(42) Brandsma and Scheffer, Rec. Trav. Chim., 45, 522, (1926).

(43) Glasstone, Laidler and Eyring, The Theory of Rate Processes, New York, 199, (1941).

(44) Purlee, Taft and de Fazio, J.A.C.S., 77, 837, (1955).

(45) Moelwyn-Hughes, *Proc. Roy. Soc.*, *A. 164*, 295, (1938).

(46) Robertson, *Canad. J. Chem.*, *33*, 1536, (1955).

(47) Tommila, Tiilikainen and Voipio, *Ann. Acad. Sci. Fennicae*, No. 2, A, (1955).

(48) Bensley and Kohnstam, *J.C.S.*, 292, (1956).

(49) Warner and Stutt, *J.A.C.S.*, 55, 4807, (1933).

(50) Kemp and Kohnstam, *J.C.S.*, 900, (1956).

(51) Frost and Pearson, Kinetics and Mechanism, Chapman & Hall, London, 257 et. seq., (1953).

(52) Randall and Rossini, *J.A.C.S.*, *51*, 323, (1928).

(53) Everett & Wynne-Jones, *Trans. Far. Soc.*, *35*, 1380, (1939).

(54) Coulson and Everett, *Trans. Far. Soc.*, *36*, 633, (1940).

(55) Gold, *Trans. Far. Soc.*, *44*, 506, (1948).

(56) Vernon, Private Communication.

(57) Kohnstam, Ph.D. Thesis, London, (1948).

(58) McKinley-McKee & Moelwyn-Hughes, *Trans. Far. Soc.*, *48*, 246 (1952).

(59) Bensley and Kohnstam, *J.C.S.*, 4750, (1947).

(60) Robertson, *Canad. J. Chem.*, *33*, 1536, (1955).

(61) Hyne & Robertson, *Canad. J. Chem.*, *34*, (I et seq.), 1714, (1956).

(62) Glew and Moelwyn-Hughes, *Proc. Roy. Soc.*, *211*, 254, (1952).

(63) Caldin, Long & Trowse, *Nature*, 171, 1124, (1953).

(64) Amis & La Mer, *J.A.C.S.*, *61*, 905, (1939).

(65) Warner & Stutt, *J.A.C.S.*, *55*, 4807, (1933).

Warner & Warrick, *ibid.*, 57, 1491, (1935).

(66) Kirkwood, *J. Chem. Phys.*, *2*, 251, (1934).

(67) Eyring & Ri, *J. Phys. Chem.*, *8*, 433, (1940).

(68) Hasted, Ritson and Collie, *J. Chem. Phys.*, *16*, 1, (1948).

(69) Brown & Hudson, *J.C.S.*, 3352, (1953).

(70) Evans, Price & Thomas, *Trans. Far. Soc.*, *51*, 481, (1955).

(71) Caldin & Peacock, *Trans. Far. Soc.*, *51*, 1217, (1955).

(72) Bensley, Ph.D. Thesis, (1954).

(73) Cooper, Hughes, Ingold and McNulty, *J.C.S.*, 2038, (1948).

(74) Brittain and Kohnstam, Unpublished work.

(75) Shillaker, Private Communication.

(76) Kohnstam, Private Communication.

(77) Hine & Lee, *J.A.C.S.*, *73*, 22, (1951).

(78) Benjamin and Gold, *Trans. Far. Soc.*, *50*, 797, (1954).

(79) Timmermans and Martin, *J. Chem. Phys.*, *23*, 733, (1926).

(80) Dostrovsky, Hughes and Ingold, *J.C.S.*, 2055, (1948).

(81) Weissberger and Proskauer, Organic Solvents, p. 117.

(82) Conant & Kirner, *J.A.C.S.*, *46*, 232, (1924).

(83) Hughes, Ingold, Masterman and McNulty, *J.C.S.*, 910, (1940).

(84) Hughes, Ingold and Shapiro, *J.C.S.*, 230, (1936).

(85) Cropper, Spieth and Olson, *J.A.C.S.*, *76*, 6248, (1954).