Solvolytic studies of organic sulphonates

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How to cite:

Tidy, D (1964) *Solvolytic studies of organic sulphonates*, Durham theses, Durham University. Available at Durham E-Theses Online: http://etheses.dur.ac.uk/9321/

SOLVOLYTIC STUDIES OF ORGANIC SULPHONATES.

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

BY
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HATFIELD COLLEGE
1964

ACKNOWLEDGEMENTS.

The author wishes to thank Dr. G. Kohnstam for his advice and encouragement.

Thanks are also due to the D.S.I.R. for the award of a Research Studentship.

ABSTRACT.

This thesis describes a kinetic study of the hydrolysis of alkyl and aralkyl esters of toluenesulphonic acid in aqueous acetone. The information available at the beginning of the present work suggested that these reactions can be regarded as nucleophilic substitution reactions but there was no certainty about the unimolecular mechanism, S_N1.

The determination of the activation parameters for the hydrolysis of compounds which can be expected to react either by mechanism S_N1 or by mechanism S_N2 showed that mechanistic tests based on the ratio of the heat capacity of activation to the entropy of activation (Bensley and Kohnstam, J.C.S. 1957, 4747.) could be applied to sulphonates as well as to halides. The application of this test to the hydrolysis of p-substituted benzyl toluenesulphonates showed that only p-substituents which were better electron-doners than the methyl group gave reaction entirely by mechanism S_N1. Anions which are more powerful nucleophiles than water gave some bimolecular reaction with the substrate even when hydrolysis occurred unimolecularly and bimolecular reaction was observed between hydroxide ions and benzyl toluenesulphonate, in contradiction to some earlier reports.

Changes in the composition of the solvent only have small effect on the reaction mechanism, though the hydrolysis of i-propyl toluenesulphonate was found to occur entirely by mechanism S_N1 in "50%" aqueous acetone, but not in the "85%" solvent.

Comparison of the activation parameters for the hydrolysis of toluenesulphonates and the corresponding halides shows that a significant part of the greater reactivity of the sulphonates results from the more favourable entropy of activation. It is considered that this arises from the fact that sulphonates require less additional solvation by water on activation than the halides.

CONTENTS

SECTION. PAGE.

CHAPTER I.

INTRODUCTION

I.1. Nucleophilic Substitution (S_N)[1]

Heterolytic processes in which a deficiency of electrons at the reaction centre is satisfied by co-ordination with the reactant, are termed nucleophilic substitution reactions (S_N).

$$\mathrm{Y:} \quad + \quad \mathrm{R..X} \quad \longrightarrow \quad \mathrm{Y:R} \quad + \quad \mathrm{:X} \qquad (S_N)$$

In these reactions the electrons binding the group to be displaced (X) to the reaction centre are retained by X. The new bond is formed from a lone pair of electrons from the group Y.
Y thus becomes one unit of charge more positive and X one unit more negative. This type of reaction, which is observed among halides, and sulphonium and ammonium compounds, is not restricted by the initial charges on Y and RX. It will be demonstrated later (see Sect. I. 6.) that the solvolytic reactions of sulphonates also fall into the S_N category.

I.1.i. Mechanisms of S_N Reactions

Two mechanisms are recognised for nucleophilic substitution reaction[1].

(a) The products are formed in a single, rate determining step in which the substrate, RX, and the reagent, Y, undergo simultaneous covalency change. The reaction is bimolecular and is labelled S_N2.

$$Y + RX \rightleftharpoons \underset{\text{Transition State}}{\left[Y^{\sim\frac{1}{2}+} -- R -- X^{\sim\frac{1}{2}-} \right]} \rightleftharpoons YR^{+} + X^{-} \quad (S_N2)$$

The hydrolysis of methyl bromide in aqueous ethanol is an example of this mechanism[2].

(b) The rate of reaction is determined by a preliminary slow ionisation of the substrate, RX, to give a highly reactive carbonium ion which then rapidly co-ordinates with the reagent, Y. Since only one molecule undergoes covalency change in the rate determining step, the process is unimolecular and is labelled S_N1.[1, 2]

$$RX \rightleftharpoons \underset{\text{Transition State}}{\left[\overset{\delta+}{R} \text{-------} \overset{\delta-}{X} \right]} \rightleftharpoons \overset{+}{R} + \overset{-}{X} \qquad \text{(slow)}$$

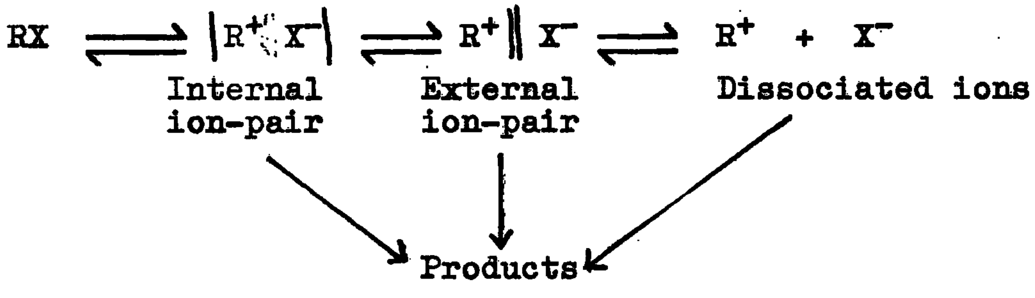
$$R^{+} + Y \longrightarrow RY^{+} \qquad \text{(fast)} \qquad (S_N1)$$

The large activation energy required for the ionisation of the C - X bond in the gaseous phase is reduced to an accessible value in solution by the solvation of the polar transition state.[2] Tert. - butyl chloride in aqueous acetone is hydrolysed by this mechanism.[3]

I.2. Ion - Pair Intermediates in Solvolysis

The nature of the S_N1 mechanism has been subjected to detailed scrutiny. Since the ionisation step leads to a planar carbonium ion, an optically active substrate should give a racemic substitution product. Shielding of the carbonium ion by the leaving group was suggested to account for the partial inversion accompanying the S_N1 solvolysis of α-phenylethyl chloride.[4] Winstein, however, held the view that if ionisation was complete enough to justify being labelled S_N1, then the ion, R^+, should be free from shielding.[5] As an alternative Hammett first suggested the formation of an ion-pair intermediate prior to the formation of the fully separated ions.[6] The reaction of this intermediate with the solvent would lead to inversion of configuration and the relative rates of reaction of the ion-pair and the carbonium ion would then control the extent to which such inversion occurred.

The original ion-pair postulate has since been modified by Winstein and his co-workers[7] to explain the behaviour of some optically active sulphonates in acetic acid where mechanism S_N1 was thought to operate. They found that solvolysis occurred much more slowly than racemisation and proposed the ion-pair mechanism shown below.



The reactivity of the first, the internal ion pair was much less than the external ion-pair or the fully developed ions; racemisation occurred in both ion-pairs. Two types of ion-pairs were required to account for the observed salt effects.

The evidence for ion-pair formation seems to be satisfactory for acetolysis and racemisation has been seen to occur more rapidly than hydrolysis in aqueous systems.[8] However, since the reactions of ion-pairs with nucleophiles in the latter solvents has not been unambiguously demonstrated, the simpler, S_N1 reaction scheme will be accepted in the present discussion. This simplification appears to be justified since it has been concluded that in the reactions of dichlorodiphenylmethane with mixed chlorides and bromides in aqueous acetone, the reactions of ion-pairs are not significant compared to the reactions of the fully developed carbonium ions.[9]

I.3 Recognition of Mechanism

The kinetic criterion can be used as a method of determining reaction mechanism as long as all reacting species are in small and controllable concentrations. Under these conditions the bimolecular process leads to second-order kinetics and the unimolecular process in its simplest form (see Section I, 3.i.b) requires first-order kinetics.

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

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

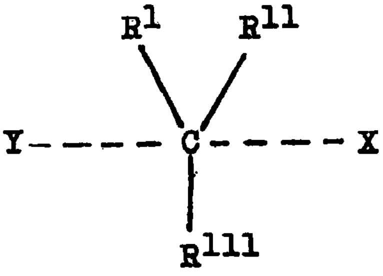
I.3.1. Recognition of the Mechanism of Solvolysis

In solvolytic reactions, with which the present investigations are mainly concerned, the substituting agent is a major component of the solvent and is, therefore, in virtually constant excess. The rate equation then reduces to the first-order irrespective of mechanism and the kinetic criterion cannot be used.

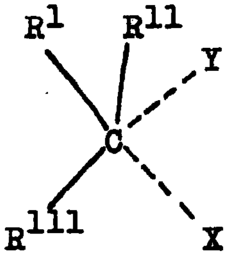
Several further criteria were reviewed in detail by Hughes.[10] Each has a limited range of utility and it is a general rule to apply them in conjunction with each other in the solution of a particular problem. Some of these criteria are discussed below and others will be discussed in their context as they arise.

(a) Optical Method[11]

The transition state, I, of a bimolecular reaction will have a lower energy than the transition state, II, since the repulsive interaction between X and Y is least when Y - C - X is linear.



I



II

Substitution via this symmetrical transition state will lead to optical inversion at the central carbon atom. Unimolecular substitution occurs via a carbonium ion intermediate which has a plane of symmetry and is, therefore, expected to give a racemic product. If the intermediate is very short-lived, the carbonium ion may not become completely free from the shielding of the leaving group, and then racemisation may be accompanied by inversion. (See, however, section I.2 for alternative explanation.)

(b) Electrolyte Effects.[4b]

The transition states of S_N2 and S_N1

$$\overbrace{S\text{-------}R}^{\sim\frac{1}{2}+}\text{------}\overset{\sim\frac{1}{2}-}{X}\quad S_N2;\quad \overset{\sim\frac{1}{2}+}{R}\text{------}\overset{\sim\frac{1}{2}-}{X}\quad S_N1$$

solvolyses are more polar than the uncharged initial states. By analogy with ion-atmosphere stabilisation of fully developed ions, it is expected that these charged transition states will be stabilised by the addition of electrolytes. On this view[4b]. an increase in rate with increasing ionic strength is to be expected but this increase will be greater in S_N1 than S_N2 processes since charge density is greater in the transition states of the former process. The ionic strength effect, however, is not highly diagnostic of mechanism.

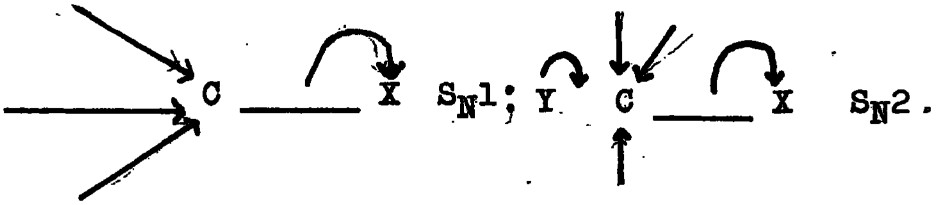
A further diagnostic salt effect occurs in S_N1 processes. The slow ionisation of RX may be reversed by the anions produced in the course of solvolysis or by added common ions, X^-. The reversal of the rate controlling step, known as the mass law effect, may result in a depression of the rate of destruction of RX.[4b] The mass law effect, which is specific to S_N1 processes, and the ionic strength effect are discussed more fully in Appendix VII. 2 and Section VI 1.

(c) Effect of Solvent Changes.

The charged transition states of S_N solvolyses (see P.6) are stabilised by solvation by the polar solvent. Any change of solvent which facilitates solvation will increase the solvent stabilisation of the transition state with respect to the initial state and give rise to an increase of reaction rate. As charge density in S_N2 transition states is less than in S_N1, changes in solvating power of the medium will be less effective in the former reactions.[12.]

More recent work[13] has confirmed the earlier view regarding the effect of changes of solvating power on the stability of the transition states of S_N1 and S_N2 processes. It has also shown that the stability of the initial state makes a significant contribution to changes in the rate arising from changes of solvent.

(d) Changes in the structure of R



In S_N reactions X carries the pair of bonding electrons away from the reaction centre, C. The resulting electron deficiency is made up by co-ordination with Y simultaneously (S_N2) or at a later stage (S_N1).

If the nature of R is varied to allow an increased degree of electron release to the reaction centre, the bond breaking process will be facilitated with consequent unambiguous acceleration of S_N1 reactions. Electron release to the reaction centre in S_N2 processes facilitates bond fission but may simultaneously inhibit the approach of the nucleophilic group Y. The effect of varying R in bimolecular processes will be less than in S_N1 processes and depending on whether bond formation or bond fission predominates, the rate may be decreased or increased. A negative charge on Y will accentuate the importance of the inhibition to bond formation. (See P.10)

It follows that increasing electron release to the central carbon atom of R will give increasing facility for reaction by mechanism S_N1. The expected transition from mechanism S_N2 to S_N1 has been observed in the series of alkyl halides[2, 3, 14].

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

where increasing electron release is by an inductive process. The rates of solvolysis of the bromides in aqueous ethanol are in the order Me > Et > i-Pr < t-Bu. The rate sequence of the first three compounds may be due to the polar effects in S_N2 reactions already discussed. Since such effects are likely to be small for attack by neutral reagents, a more probable explanation may lie in the steric requirements of S_N2 reactions. Increasing steric hindrance to S_N2 reaction, with increasing complexity of R, has been demonstrated frequently.[14c] The high rate of solvolysis of the tertiary halide clearly demonstrates that mechanism S_N1 occurs here. Added hydroxide ions yield an additional second order reaction whose rate decreases in the order Me > Et > i-Pr while the solvolysis of t-butyl bromide is not accelerated. It appears that mechanism S_N1 occurs for the latter compound even in the presence of base while the others react bimolecularly with the hydroxide ions. Bimolecular attack by hydroxide ions on the i-propyl bromide does not mean that the mechanism of solvolysis, <u>i.e.</u> reaction with the weaker nucleophile, water, is also bimolecular[15] and no definite conclusions about the mechanism of solvolysis of this compound can be made. It is, however, likely that the hydrolysis occurs in the borderline region which marks the transition from mechanism S_N2 to S_N1 (see Section I.4).

/10...

Similarly the corresponding phenyl substituted series,

CH_3X, $PhCH_2X$, Ph_2CHX, Ph_3CX,

where electron release is by a conjugative process, again represents a series with increasing electron release to the reaction centre and hence a series with increasing facility to react by mechanism S_N1. Rates in this series increase throughout and it is believed that mechanism S_N1 occurs in the solvolysis of the secondary and tertiary halides.[16, 17, 18.] The mechanism of solvolysis of benzyl halides is not so clearly defined. The acceleration produced by hydroxide[19] ions indicates an S_N2 reaction with base but does not exclude S_N1 hydrolysis. On the other hand, the small retardation by chloride ions[20] is suggestive of a mass law effect (see P.8) diagnostic of mechanism S_N1. The retardation may, however, be due to a negative salt effect on an S_N2 substitution.[21] It has been concluded from consideration of the available information that the mechanism of hydrolysis of benzyl chloride in 50% aqueous acetone is S_N2 in the main.[22]

Variation of electron release to the reaction centre of aralkyl compounds can be realised by the introduction of polar substituents into the aromatic ring. Meta and para substituents in phenylmethyl compounds will alter the reaction rate by virtue of these polar effects without additional steric complications which could result from substitution at or near the reaction centre. A series of para substituents

NO_2, H, Me, p-$MeOC_6H_4$, PhO, MeO,

represents a graded series with increasing facility for electron release towards the reaction centre and hence increasing tendency to react by mechanism S_N1. It has been shown that only the p-phenoxy[23] and p-methoxy[24] substituents induce mechanism S_N1 among the p-substituted benzyl chlorides in aqueous acetone while the solvolyses of the others do not occur completely by this mechanism.[24, 25].

In bimolecular processes the effect of such substitution is ambiguous (see P.6). If the nucleophilic reagent carries no formal charge, one would expect the effect of, say an electron-donating substituent in R on the bond forming process to be of minor importance. The effect of such a substituent would be mainly in the ease of C - X fission and one would, therefore expect an increase in the rate of reaction, as in S_N1 processes but to a smaller extent since the influence of bond forming is not entirely negligible and is in the opposite direction (TABLE I.1.).

/12...

TABLE I. 1.

Substituent Effects, k_X/k_H, for p-X-Benzyl Chloride and p-X-Benzhydryl Chloride

X =	NO_2	H	Me	Mechanism
	k_X/k_H			
p-X-$C_6H_4CH_2Cl^a$	9.16×10^{-2}	1	8.13	S_N2
p-X-$C_6H_4CHCl.Ph^b$	1.25×10^{-4}	1	21.2	S_N1

a At 50°C in 50% aqueous acetone ref 24

b At 25°C in 70% aqueous acetone ref 23

When Y carries a negative charge, the effect of polar substituents on the bond forming process is important, as is observed in the bimolecular reactions of radio-bromide ions with p-substituted benzyl bromides in ethylene diacetate[26] and in the Finkelstein reaction of benzyl chlorides[27] (TABLE I.2) It is noteworthy that the rates have a minimum value for the parent compound. Electron attracting substituents presumably increase

TABLE I. 2.

Substituent Effects k_X/k_H of p-X-Benzyl Halides (RX) in Ethylene Diacetate (A)[26] and Acetone (B)[27]

X =	NO_2	CN	Cl	H	Me	t-Bu	OMe
A. $RBr+Br^-$	11.2	10.0	-	1	-	-	6.2
B. $RCl+I^-$	6.19	-	2.12	1	1.17	1.35	-

the rate because they facilitate the approach of the negatively charged, Y^-, to the reaction centre. Electron releasing groups also accelerate the reaction, presumably because of the greater ease of bond fission.

I.4. Mechanism in the Borderline Region

A great deal of interest has centred on the mechanism of S_N reactions in the region which marks the transition from mechanism S_N2 to S_N1, the mechanistic borderline region. It is helpful to regard the transition state of an S_N reaction as a resonance hybrid of the three canonical forms:-[28]

$$\underset{\text{I}}{Y \quad R-X} \qquad \underset{\text{II}}{\overset{+}{Y}-R \quad \overset{-}{X}} \qquad \underset{\text{III}}{Y \quad \overset{+}{R} \quad \overset{-}{X}}$$

The transition state for S_N1 reactions will have no covalent attachment of Y and therefore no contribution from structure II.

If structure II contributes to a transition state, then the mechanism must be regarded as S_N2 since covalent participation of Y is an essential feature of the activation process.[29]

On this basis, mechanism in the borderline region may be regarded in one of two ways:-[28b, 30, 31].

All individual steps may proceed via the same transition state which can be regarded as a resonance hybrid of structures I, II and III. The more the conditions favour S_N1 reaction, the greater will be the contributions from III and the smaller the contribution from II. It must be emphasised that this mechanism must be regarded as S_N2 in this region since covalent attachment of Y is a feature of the transition state.

Alternatively, individual molecular acts may occur via any one of a number of transition states. If structures I, II and III contribute to the transition state the mechanism is essentially bimolecular, while if there are contributions from I and III only, the mechanism is unimolecular. Thus concurrence of S_N1 and S_N2 processes is postulated. Reaction by one S_N1 and one S_N2 process is a simplification of this scheme.

The problem of whether reaction occurs via a single transition state of whether concurrence of mechanisms S_N1 and S_N2 best describes S_N processes in the borderline region has aroused considerable interest. Winstein, Grunwald and Jones[28b] studied the relationship between solvolytic rates and solvent composition on the basis that the relevant solvent properties,

/15...

ie. nucleophilic power and ionising power, vary independently. They suggested that the rate ofsolvolysis, k, can be compared to the rate in a standard solvent, k^o, by the linear free energy relationship

$$\log(k/k^o) = m\, Y \qquad \text{------I.1.}$$

where Y is a measure of the ionising power of the solvent and m is a constant, independent of the substrate, with one value for S_N1 and one for S_N2 reactions. They concluded that the solvolysis of i-propyl bromide in aqueous alcohol was consistent with reaction via a single transition state rather than a concurrence of mechanisms. Bird, Hughes and Ingold,[30] however, pointed out that the requirements of Eqn.I.1 were not obeyed by the reaction from which the value of m for S_N2 solvolysis was obtained. Gold[32a] suggested that the value of m for S_N2 processes must vary with changes in the relative contributions of structures II and III to the transition state. Other limitations of Eqn.I.1 have also been discussed.[31]

Cruden and Hudson[33] assumed that the solvolysis of benzoyl chloride in formic acid occurred by mechanism S_N1 and concluded that the greater rate of reaction in aqueous organic solvents of the same Y value as formic acid arose from concurrence of S_N1 and S_N2 hydrolysis. The results of isotopic studies on the hydrolysis of acid chlorides, however, make it

/16...

appear doubtful if these reactions occur purely by S_N mechanisms.[34]

The kinetics of the reactions of m-chlorobenzhydryl halides with various reactants in sulphur dioxide[30] are not consistent with S_N1, S_N2 or concurrent mechanisms. The discrepancy may be due to medium effects (see Section VI.1) which were ignored or to the formation of ion-pairs in this solvent. Recently Pocker[35] studied the reactions of bromide, chloride and azide ions and triethylamine, aniline and pyridine with benzhydryl bromide in nitromethane. The results suggest concurrence of mechanisms S_N1 and S_N2 but since the rates of racemisation of aralphyl halides in nitromethane are greater than the rates of substitution and elimination, an intermediate state of heterolysis has been suggested.[36] This may be the ion-pair intermediate of Winstein (see P.3) which was also postulated for reactions in a medium of low dielectric constant. Direct attack on this intermediate by the reagent may account for the second order reaction.

Concurrence of S_N1 and S_N2 processes was thought to occur in the isotopic exchange between bromide ions and t-butyl bromide in acetone[37] but later work does not support this conclusion.[38] Recently evidence has been produced of the concurrence of mechanisms in the reactions of benzhydryl chloride and chloride ions in dimethyl formamide.[39].

/17...

Kohnstam and his co-workers[40] have shown that concurrent S_N1 and S_N2 reactions occur between azide, chloride, bromide and nitrate ions and p-phenoxy- and p-methoxy-benzyl chlorides in 70% aqueous acetone, where hydrolysis is unimolecular. The relative bimolecular rates of the two organic chlorides with the various ions and the relative rates of S_N1 hydrolysis led the authors to suggest that some heterolysis of the C-Cl bond occurs prior to nucleophilic attack. This was most noticeable in the cases of the weaker nucleophiles. Not all the results could be explained assuming that the reaction occurred via ion-pair and carbonium ion intermediates only.

The hydrolysis of 2-octyl p-bromobenzenesulphonate in 75% aqueous dioxan gave the alcohol with 77% inversion of configuration whereas hydrolysis in the presence of azide ions gave complete inversion.[41] Concurrence of S_N2 displacement with a reaction via an intermediate was proposed, the intermediate, in turn, giving a product with racemisation or retention of configuration. The azide ions, in reacting preferentially with the intermediate, were thought to prevent its conversion to the alcohol, which was thus all produced by mechanism S_N2. This result is rather unexpected since azide ions generally show a greater tendency to compete with water for the uncharged substrate (S_N2) than for a charged intermediate, be it an ion-pair or a fully developed carbonium ion.

Analysis of the activation parameters for the hydrolysis of benzyl[22] and p-methylbenzyl chloride[24] in aqueous acetone suggests that the results are consistent with a single mechanism or with concurrence of S_N1 and S_N2 processes. The authors favour concurrence of mechanisms but the operation of mechanism S_N1 in conjunction with the extreme form of the S_N2 process seems unlikely.

It would appear that S_N reactions in the borderline region probably occur by concurrence of mechanisms S_N1 and S_N2. The evidence does not discriminate between one reaction path for each process or a larger number of reaction paths for each process. It does seem, however, that concurrence of mechanism S_N1 with the extreme forms of mechanism S_N2 is unlikely.

I.5. Recognition of Mechanism in the Borderline Region

The criteria of mechanism listed earlier (Section I.3.) are of limited value in the borderline region. The charge density in the group R of RX in S_N2 transition states in this region may well be large and these reactions may then acquire appreciable S_N1 character with respect to solvent changes, ionic strength effects and substituent effects, since these properties are dependent on the charge density in R in the transition state (I.3.i.b.c. and d.). Furthermore S_N1 solvolysis close to the borderline region may not necessarily show an appreciable mass

/19...

law effect since the carbonium ion may be destroyed rapidly by the collapse of the solvation shell. Partial inversion of configuration in S_N1 reactions, which produce unstable carbonium ions, is likely to occur since shielding by the leaving group or ion-pair formation is more likely under these conditions. This makes stereochemical evidence unsatisfactory (see P.5).

Bensley and Kohnstam[22] proposed a further test of mechanism based on the observation that $\Delta C^{*}/\Delta S^{*}$ (where ΔC^{*} and ΔS^{*} are the increases in heat capacity and entropy respectively associated with the activation process) was independent of the substrate in S_N1 processes and that the value of this ratio was less if the mechanism was not S_N1. This test, which shows greater sensitivity to changes of mechanism than the classical tests, will be discussed in CHAPTER II.

I.6. Mechanism of Reactions of Toluenesulphonic Esters

The present thesis is concerned with the reactions of p-toluenesulphonic esters, mainly with their hydrolyses. These reactions can be considered to occur in one of two general ways:-

either via carbon - oxygen (C - O) fission

$$R \vdots O - SO_2R^1 + Y^- \longrightarrow RY + \overset{-}{O}SO_2R^1$$

$$R \vdots O - SO_2R^1 + H_2O \longrightarrow ROH + \overset{-}{O}SO_2R^1 + H^+$$

analogous to B_{AL} solvolysis of carboxylic esters,[42] or via sulphur - oxygen (S-O) fission

$$R - O \vdots SO_2R^1 + Y^- \longrightarrow RO^- + R^1SO_2Y$$
$$R - O \vdots SO_2R^1 + H_2O \longrightarrow ROH + \bar{O}SO_2R^1 + H^+$$

analogous to B_{AC} solvolysis of carboxylic esters[42].

I.6.i. Bond Fission in the Reactions of Sulphonic Esters

All the available evidence suggests that C - O fission occurs in the reactions of alkyl and aralphyl sulphonates and that S - O fission occurs more generally with aromatic sulphonates. The basis of this view will be considered under three headings.

(a) Chemical Evidence

Fern and Lapworth[43] pointed out that alkyl sulphonates, in contrast to carboxylic esters, are alkylating agents for alcohols, amines, acids and Grignard reagents.

$$\begin{array}{llcll}
ArSO_2OR & + R^1O^- & \longrightarrow & ArSO_2O^- & + R^1OR \\
ArSO_2OR & + R^1NH_2 & \longrightarrow & ArSO_2OH & + R^1NHR \\
ArSO_2OR & + R^1COO^- & \longrightarrow & ArSO_2O^- & + R^1COOR \\
ArSO_2OR & + R^1MgX & \longrightarrow & ArSO_2O^- & + MgX^+ + RR^1
\end{array}$$

Aromatic sulphonates are less reactive but give amides with amines and sulphones with Grignard compounds.

$$ArSO_2OAr^1 + RNH_2 \longrightarrow ArSO_2NHR + Ar^1OH$$

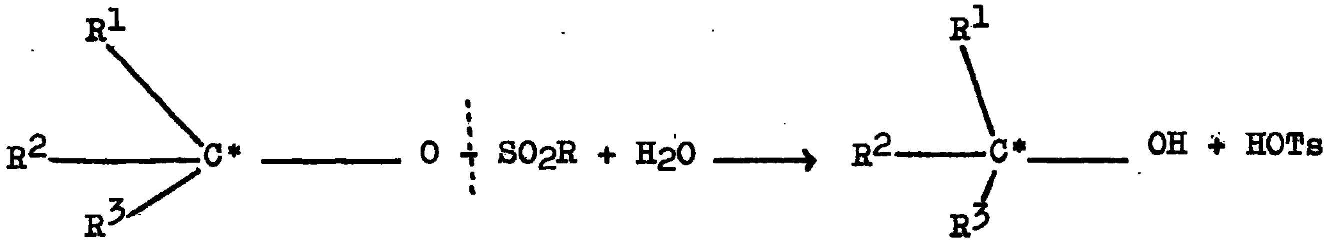
$$ArSO_2OAr^1 + Ar^{11}MgX \longrightarrow ArSO_2Ar^{11} + Ar^1O\ MgX$$

This suggests that aliphatic esters react with C - O fission and aromatic esters with S - O fission. Similar conclusions arise from the observation that lithium aluminium hydride reduces alkyl sulphonates to give hudrocarbons while the phenol is obtained from the aromatic esters.[44] Raney nickel, however gives the alkyl alcohol or the aromatic hydrocarbon.[45] The contrast between the two reductions is thought to be due to different reducing species. Raney nickel operates via a hydrogen radical, $H^{\bullet}$, while lithium aluminium hydride is regarded as a source of hydride ions, H^-, <u>i.e.</u>, a nucleophilic reagent.

The production of alkyl chlorides during the solvolysis of methyl[46] and ethyl toluenesulphonates[20] in the presence of chloride ions suggests C - O fission for attack by chloride ions. Although it has been inferred from this that C - O fission also occurs in hydrolysis,[53] this cannot be taken as conclusive evidence. Formation of olefin,[47] which accompanies the solvolysis of some sulphonic esters requires that C - O fission occurs at least in these reactions.

(b) Optical Evidence

Reactions of optically active sulphonates by



S - O fission must give the product with retention of configuration since the optically active centre (C*) is undisturbed. As was seen earlier (Section I.3.i.a.) for S_N processes bond fission at the optically active centre (C - O fission) may give inversion of configuration (S_N2) or racemisation, with or without accompanying inversion (S_N1). Retention of configuration only occurs in specialised cases.[48]

Optically active α -phenylethyl toluenesulphonate undergoes inversion of configuration accompanied by some racemisation in acetolysis and ethanolysis.[49] Further studies[50] of a number of optically active sec. - alkyl toluenesulphonates in ethanol and in ethanol containing lithium chloride or potassium acetate showed inversion of configuration in conjunction with some racemisation in the ether, chloride or acetate products. The absence of retention of configuration in the products suggests that C - O fission is predominant. The concurrence of C - O and S - O fission, which could give the observed optical results, cannot, however, be excluded. The proposed S_N1 mechanism for the solvolysis of α - phenylethyl chloride via a comparatively unstable carbonium ion, is consistent with the observed optical results.[51]

Solvolysis of optically active α - deuterobenzyl toluenesulphonate in ethanol and 80% aqueous ethanol gives, within experimental error, complete inversion of configuration in the ether and alcohol produced.[52] Complete C - O fission is indicated in this case.

(c) Evidence From Tracer Experiments

Hydrolysis of sulphonates, by a mechanism involving S - O fission, in water enriched in O^{18} will give the alcohol whose O^{18} content is normal.

$$\mathrm{R - O} \vdots \mathrm{SO_2R^1} + \mathrm{H_2O^{18}} \longrightarrow \mathrm{ROH} + \mathrm{HO^{18}\,SO_2R^1}$$

If C - O fission occurs the O^{18} content of the alcohol produced is expected to be the same as in the enriched water.

$$\mathrm{R} \vdots \mathrm{O - SO_2R^1} + \mathrm{H_2O^{18}} \longrightarrow \mathrm{RO^{18}H} + \mathrm{H\text{-}O\text{-}SO_2R^1}$$

The hydrolysis of methyl methanesulphonate in water enriched with O^{18} in alkaline and initially neutral conditions gave the amount of label in the methanol produced, that was consistent with C - O fission.[53]

Since the beginning of the present study further evidence of C - O fission of sulphonates from tracer studies has been reported.[54] Recovered substrate, from the formolysis of α- phenylethyl toluenesulphonate in the presence of sulphonate ions labelled with S^{35}, contained some of the label. This is consistent with reaction between the labelled sulphonate ions and the carbonium ions or ion-pairs resulting from the ionisation of the substrate.

Nucleophilic attack on sulphur, corresponding to S-O fission is, however, observed in alkaline hydrolysis of phenyl toluenesulphonate.[55] The rate of bimolecular attack of hydroxide ions on benzyl toluenesulphonate can be seen (TABLE I.3.) to be much larger than on phenyl toluenesulphonate where tracer evidence indicates S - O fission. Assuming that

TABLE I.3.

The Rates of Bimolecular Attack (k_2) of Hydroxide Ions on Sulphur and Carbon Atoms of Sulphonates at 20°C.

k_2 in $(m/l)^{-1}$ sec^{-1}

Substrate	$10^6 k_2$	Bond Fission
$C_6H_5CH_2OSO_2C_6H_4CH_3$ [a]	479.1	C - O
$C_6H_5OSO_2C_6H_4CH_3$ [b]	0.3673	S - O

a In 70% aqueous acetone from present work.

b In 70% aqueous dioxan ref. 55

the rates of nucleophic attack on the sulphur atoms, which are rather remote from the region of structural difference in the two substrates are of the same order in the benzyl and phenyl compounds, no S - O fission is to be expected in the alkaline hydrolysis of the former. In neutral solution no solvolysis of phenyl toluenesulphonate was observed alter 3 weeks at 120°C. It would, therefore, appear that S - O fission is negligible in the solvolysis of benzyl toluenesulphonate in alkaline and neutral conditions.

The solvolyses of alkyl and aralpyl sulphonates, must on the bulk of the evidence, be accepted as occurring by C - O fission. C - O fission of sulphonates

$$Y + R \vdots O - SO_2R^1 \longrightarrow YR^+ + \bar{O} - SO_2R^1$$

closely resembles the S_N reaction scheme (see P.1)

$$Y + RX \longrightarrow YR+ + X^-$$

where X^- now corresponds to $\bar{O}\text{-}SO_2R^1$, the stable sulphonate ion. The electrons of the breaking bond are retained by the sulphonate ion and the reagent Y supplies the electrons of the new bond. The reactions of sulphonates considered in this thesis, will, therefore, be discussed in terms of the S_N reaction mechanisms.

/26...

I.7. Effect of the Leaving Group, X, on Rate and Mechanism

Replacing halogen by sulphonate as the leaving group, X, in substitution reactions, results in a considerable increase in the reaction rates of S_N1 and S_N2 solvolysis in aqueous organic solvents.

TABLE I. 4.

The Relative Rates of ROTs and RCl at 50°C

R.	kROTs/kRCl	Mechanism
C_2H_5 [a]	1.1×10^2	S_N2
$p\text{-}NO_2C_6H_4CH_2$ [b]	4.8×10^2	S_N2
$p\text{-}NO_2C_6H_4CH.Ph$ [c]	3.0×10^4	S_N1
$p\text{-}MeOC_6H_4CH_2$ [c]	1.6×10^4	S_N1

a. Aqueous Dioxan ref. 20

b. 50% Acetone. Chloride result ref.24

c. 85% Acetone. $p\text{-}NO_2C_6H_4CHCl.Ph$[23], $p\text{-}MeOC_6H_4CH_2Cl$[24].

It is of interest to see whether this increased reactivity arises mainly from changes in E or $\Delta S^{\ddagger}$ or from both for S_N1 and S_N2 processes. Unfortunately the rate data have not always been of sufficient accuracy to allow much reliance being put on activation parameters.

Also these parameters were often obtained at different temperatures because of the widely different reactivities of

/27...

the various compounds, and since it has now been recognised that activation parameters for reactions which produce a polar transition state can be expected to be temperature dependent (details in CHAPTERII), strict comparison of these quantities often cannot be made. Although activation parameters and their temperature coefficients are now known for a number of halides, the corresponding information for sulphonates was not available. One of the aims of the present work was to obtain such information.

I.7.i. Mechanism of Solvolysis of Sulphonates

The greater ease of ionisation of the sulphonate leaving group has usually been expected to facilitate mechanism S_N1, resulting in this mechanism occurring at an earlier stage in a series of electron-releasing compounds.[56] Little difference of mechanism is observed between the reactions of chlorides and bromides[57] but this may be due to the importance of bond breaking in mechanisms S_N1 and S_N2 for halides.

Solvolytic studies of alkyl sulphonates in aqueous and anhydrous methanol indicated that a transition of mechanism occurred in the region of the primary and secondary compounds, the secondary sulphonate reacting by mechanism S_N1.[58] The evidence of the effect of added hydroxide ions supported this view.[59, 60] Other workers have suggested that the secondary sulphonates react by mechanism S_N1 generally but acquired bimolecular character in solvents of low aqueous content.[61]

The unimolecular character of the solvolysis of secondary sulphonates is in contrast to the corresponding chlorides where mechanism S_N1 first occurs with the tertiary compounds. Mechanism S_N1 has, however, been proposed for the hydrolysis of methyl methanesulphonate in water on the evidence of an apparent mass law effect.[53] Apart from this latter conclusion most workers agree that the mechanism of solvolysis of alkyl sulphonates in aqueous organic solvents seems to be generally established. Mechanism S_N1 is observed for the solvolysis of secondary compounds, at least in the more aqueous solvents. Thus compared with halides (see P.9) mechanism S_N1 appears to occur somewhat more easily for sulphonates.

The picture, with regard to the solvolysis of substituted benzyl sulphonates, is not as clear. Brown[62a,b] suggested a change of mechanism in the region of the m - or p - methyl derivative. His arguments are based on the linear free energy relationship (see Section IV.1).

$$\log(kX/kH) = \rho\sigma^{+}$$

where kX and kH are the rate coefficents of the substituted and unsubstituted compounds, ρ is a measure of the sensitivity of the reaction to substitution and σ^{+} is a substituent constant obtained from other systems where mechanism S_N1 operates. This relation accounts reasonably successfully for kX/kH in a number of S_N1 reactions.[62] When applied to the benzyl toluenesulphonates, it was claimed that the plot defined two

/29...

distinct lines of different slopes suggesting the change of mechanism mentioned. A detailed inspection of the $\log k_X - \sigma^+$ plot by Hammond[63e] showed that the data was best fitted to a smooth curve and he concluded that all the benzyl sulphonates react by mechanism S_N1 but that most or all of them may not be limiting in the Winstein sense. Substituent effects of p-X-benzyl toluenesulphonates are re-examined in Chapter IV.

The lack of catalysis of the hydrolysis of benzyl sulphonates by hydroxide ions,[63b] suggests mechanism S_N1 for reaction with this ion and, by inference, with the weaker nucleophile, water. Hammond[63b,g.] studied the hydrolysis of benzyl and m-halogenobenzyl toluenesulphonate, ROTs, in aqueous acetone in the presence of added ions, Y-, which could form a stable product, RY. If the reaction of Y^- with ROTs is unimolecular, then the reaction scheme is:-

$$\begin{array}{rcll}
\mathrm{ROTs} & \xrightarrow{k_1} & \mathrm{R^+ + \bar{O}Ts} & 1. \\
\mathrm{R^+ + H_2O} & \xrightarrow{k_{ROH}} & \mathrm{ROH + H^+} & 2. \\
\mathrm{R^+ + Y^-} & \xrightarrow{k_{RY}} & \mathrm{RY} & 3.
\end{array}$$

If bimolecular attack of Y^- on ROTs is also possible then reaction 4 must be included.

$$\mathrm{ROTs + Y^-} \xrightarrow{k_2} \mathrm{RY + OTs} \qquad 4.$$

If reaction of Y^- with ROTs is unimolecular, the rate of destruction of ROTs (k_{ROTs}) depends solely on the rate of

/30...

ionisation of ROTs (k_1). Thus k_{ROTs} will be uneffected by Y^-, except through medium effects, but k_{ROH} will be reduced by the competition from reaction 3. If bimolecular reaction between Y^- and ROTs occurs, then k_{ROTs} will be increased ($=k_1 + k_2[Y^-]$) while k_{ROH} will be unaltered. Hammond, in fact found that the added anions, $Y^- = NO_3^-$ or Cl^-, reduced k_{ROH} but did not alter k_{ROTs}, consistent with an S_N1reaction in the presence of these ions. Other aspects of this work were, however, inconsistent with the mechanistic interpretations and these will be discussed in CHAPTER VI where the effects of electrolyte additions are examined.

On the other hand the solvolysis of optically active α- deuterobenzyl toluenesulphonate in ethanol and80% aqueous ethanol occurs with complete inversion of configuration with respect to ethanolysis and hydrolysis.[52] Completely bimolecular reaction is, therefore, strongly indicated. (see Section I.3.i.a.)

I.8. The Present Study

Because of the widely differing views regarding the mechanism of solvolysis of benzyl sulphonates, it was decided to investigate the problem further. As some of the reactions can be expected to occur in the mechanistic borderline region where the classical tests of mechanism are unsatisfactory (see section I.5), the $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ test (see P19&Section II.1) was employed. In order to determine the mechanism of solvolysis of sulphonates using this test, it was first essential to establish that it could be used for these compounds. Once this was done (Sections III.1.i. and ii.), the test was applied to a series a p-X-benzyl toluenesulphonates and the mechanism throughout the series established (Section III.i.iv.). Since activation parameters and their temperature dependence became available from the present work, a comparison of rates and these parameters for chlorides and sulphonates can be made at the same temperature, in order to understand more fully the effect of changing the leaving group on the rate and mechanism (CHAPTER V). The results did not support Hammond's conclusions (see P.30) and additional experiments on the effect of added anions on the solvolysis of benzyl sulphonates were, therefore, carried out to resolve the discrepancies (CHAPTER VI).

CHAPTER II

THE TEMPERATURE DEPENDENCE OF ACTIVATION PARAMETERS.

The rates of chemical reactions are often expressed by the empirical Arrhenius equation:-[64]

$$\ln k = B - E/RT \qquad \text{II.1}$$

where E is the activation energy and B the non-exponential term. Alternatively, transition state theory yields the rate equation in the form:-[65]

$$\ln k = \ln(\bar{K}T/h) + \Delta S^{*}/R - \Delta H^{*}/RT \qquad \text{II.2}$$

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

h is the Plank constant

ΔS^{*} and ΔH^{*} are the entropy and enthalpy of activation and represent the increases in these quantities in the activation process. Activation parameters are of interest since rate data at any temperature and information about the transition state can be obtained from them.

Strictly E is defined by

$$E = RT^2.d(\ln k)/dT \qquad \text{II.3}$$

Eqn. II.1 is obtained from II.3, assuming that E is independent of temperature.

If this assumption is not made Eqns.II.2 and II.3 yield

$$E = \Delta H^{\ddagger} + RT \qquad \text{II.4}$$

whence $$dE/dT = \Delta C^{\ddagger} + R \qquad \text{II.5}$$

without this assumption, where $\Delta C^{\ddagger}$ is the difference of heat capacity between the initial (C_i) and transition (C_t) states,

$$\Delta C^{\ddagger} = C_t - C_i .$$

Combination of II.2 and II.4 gives the conventional form (II.6) of the absolute rate equation for reactions in solution.

$$\ln k = \ln(\bar{k}T/h) + 1 + \Delta S^{\ddagger}/R - E/RT \qquad \text{II.6}$$

This equation will be used in this thesis to obtain values of E, $\Delta S^{\ddagger}$ and k.

Although many previous authors have pointed out that, on purely theoretical grounds,[66] activation parameters can be expected to be temperature dependent (i.e. $\Delta C^{\ddagger} \neq 0$, see Eqn.II.5.), most workers have assumed these parameters to be constant and have cited experimental evidence (e.g. good linear Arrhenius plots) in support of the assumption . It does, however, seem likely that these observations arise, at least partly, from the use of rate data which were not sufficiently accurate to allow the variation of E and $\Delta S^{\ddagger}$ with temperature to be observed. In the last few years, however, temperature dependent activation parameters have been reported,[67] usually for solvolytic reactions. In these systems an increase in polarity of the substrate occurs in the activation process and in all cases $\Delta C^{\ddagger}$ has been negative, generally in the range - 10 to - 100 cals. and constant over the experimental range. Values of $\Delta C^{\ddagger}$ for various reactions have been reviewed on a number of occasions.[68, 71, 79]

II. 1 Causes of Change in Heat Capacity

For the S_N1 solvolysis of a number of structurally different organic halides[25] and one non-halide[69] in aqueous acetone, the value of the ratio $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ is found to depend only on the solvent composition and the temperature, and to be independent of the nature of the substrate. For S_N2 processes under the same conditions the value of this ratio is always lower than the S_N1 value.[70] These observations have been used to form the basis of a mechanistic test (see P.19) which has been used to elucidate the mechanism of solvolysis of substituted benzyl chlorides.[71] It appears, then, that the factors which control $\Delta C^{\ddagger}$ in S_N1 solvolysis, also control $\Delta S^{\ddagger}$ and any explanation of the negative $\Delta C^{\ddagger}$ values must take into account the constancy of the $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ ratio. Possible explanations are discussed below.

II.1.i. Electrostatic Approach

If the solvent is regarded as a continuous dielectric, there will be electrostatic contributions to the free energies of a dipolar initial state and of the more polar transition state. These contributions will depend on the dielectric constant, D, of the solvent and can be obtained from the Kirkwood equation.[72] The usual differentiation of this equation[70] with respect to temperature yields the electrostatic contributions, $\Delta C_D^{\ddagger}$ and

and $\Delta S_D^{\ddagger}$, to $\Delta C^{\ddagger}$ and $\Delta S^{\ddagger}$

$$\Delta S_D^{\ddagger} = \left\{\frac{\mu_t^2}{r_t^3} - \frac{\mu_i^2}{r_i^3}\right\} \frac{3D}{(2D+1)^2} \frac{d \ln D}{dT} \qquad \text{II.7.}$$

$$-\Delta C_D^{\ddagger} = \left\{\frac{\mu_t^2}{r_t^3} - \frac{\mu_i^2}{r_i^3}\right\} \frac{3DT(2D-1)}{(2D+1)^3} \left(\frac{d \ln D}{dT}\right)^2$$

where μ is the dipole moment, r, the radius of the molecule containing the dipole, and the subscripts t and i refer to the transition and initial states respectively. This approach predicts negative values of both $\Delta C_D^{\ddagger}$ and $\Delta S_D^{\ddagger}$ (d lnD/dT is negative) and a $\Delta C_D^{\ddagger}/\Delta S_D^{\ddagger}$ ratio which is independent of μ and r and therefore independent of the substrate. The calculated values of $\Delta C_D^{\ddagger}$ & $\Delta S_D^{\ddagger}$ from this simple electrostatic model are often considerably different from the observed figures but it must be pointed out that the calculation of $\Delta S_D^{\ddagger}$ and $\Delta C_D^{\ddagger}$ depend on assumed values of transition state radii and dipoles which may change with solvent variations. These quantities should, however, be affected similarly irrespective of the value of the $\frac{\mu_t^2}{r_t^3} - \frac{\mu_i^2}{r_i^3}$ term.

In fact increases of $\Delta S^{\ddagger}$ are accompanied by decreases of $\Delta C^{\ddagger}$ for the solvolyses of benzilidene chloride and benzo-trichloride when the solvent is changed from 50% acetone to 50% ethanol[70] (solvents of the same dielectric constant).

A comparison[71] of the observed and calculated values of $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ is given below (TABLE II.1).

TABLE II.1

Electrostatic and observed values of $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ for S_N1 solvolysis at 50°C.

Aqueous Solvent	D	$\Delta C^{\ddagger}/\Delta S^{\ddagger}$ calc.	$\Delta C^{\ddagger}/\Delta S^{\ddagger}$ obs.
50% EtOH	46.2	1.71	6.42
50% Acetone	46.0	1.56	2.89
70% Acetone	34.2	1.55	3.68
80% Acetone	28.0	1.54	2.75
80% EtOH	27.8	1.90	3.86
85% Acetone	24.3	1.53	2.77
EtOH	20.3	2.37	5.45

This comparison is more reliable than one based on $\Delta C^{\ddagger}$ or $\Delta S^{\ddagger}$ separately, since in this case no assumptions regarding the structure of the transition state are necessary. It does show that the approach is quantitatively inadequate. Observed values are invariably much larger than those calculated and widely different values are observed for different solvents of similar dielectric constant. It must, therefore, be concluded that electrostatic contributions do not account for the values of $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ and at most represent a small contribution to this ratio. The failure of the electrostatic approach has been noted before for S_N reactions in which an increase in polarity occurs on activation.[73] It is accepted that polar species in solution are solvated and the Born charging process, implicit in the Kirkwood equation, must apply to the solvated species. The results suggest that, under these conditions, electrostatic contributions to $\Delta C^{\ddagger}$ and $\Delta S^{\ddagger}$ may well be negligibly small.[71]

II.1.ii The solvation Model

S_N1 and S_N2 reactions involve an increase in polarity in the passage to the transition state (see P6). It is an essential feature of the S_N1 mechanism that the activation energy of ionisation is reduced to an accessible value by solvation of the transition state;[74] solvation of the less polar transition state of an S_N2 process is also expected to occur. It is accepted that solvation requires a definite orientation of solvent molecules round the incipient ions and that the smaller charge density in S_N2 reactions would be associated with less "freezing out" of solvent molecules in the neighbourhood of the developing dipole than in the S_N1 reaction. These orientated molecules are less free to move than those in the bulk of the solvent but still retain some lateral translational and librational freedom. They can, therefore, be expected to have a reduced capacity for taking up heat, i.e. $\Delta C^{\ddagger}$ will be negative. At the same time the entropy of the system will also be reduced. Solvation has been stated to account for the negative partial molar heat capacities of electrolytes[75] and negative heat capacities of ionisation of weak acids.[76]

a. S_N1 Reactions [22, 71]

In S_N1 reactions the small degree of bond stretching in the transition state is unlikely to make a significant contribution to $\Delta C^{\ddagger}$ and $\Delta S^{\ddagger}$ and the electrostatic contribution arising from Born charging of the solvated transition state will probably also be small. It, therefore, seems reasonable to assume that, as a close approximation, the magnitude of $\Delta C^{\ddagger}$ and $\Delta S^{\ddagger}$ are governed by the differences of the solvent - initial state and the solvent - transition state interactions resulting from increased solvation of the activated complex by the polar component of the solvent, in this case by water. If this applies then

$$\begin{aligned} \Delta S^{\ddagger} &= n\left[(S_s - S_1^{\circ}) - (S_1 - S_1^{\circ})\right] \\ \Delta C^{\ddagger} &= n\left[(C_s - C_1^{\circ}) - (C_1 - C_1^{\circ})\right] \end{aligned} \qquad \text{II 8}$$

where n is the effective increase in solvation number associated with the activation process, S_s and C_s are the molar contributions of a solvating water molecule to the entropy and heatcapacity of the activated complex, S_1 and C_1, the partial molar entropy and heat capacity of water in the solvent and the superscript, o, refers to pure water.

TABLE II.2

Observed and Calculated Values of $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ of S_N1 Solvolysis at 25°C

% Acetone		50	70	80	85
$C_1 - C_1^{\circ}$		1.75	3.31	3.53	3.32
$S_1 - S_1^{\circ}$		-0.34	-0.68	-0.28	-0.13
$\Delta C^{\ddagger}/\Delta S^{\ddagger}$	obs	3.77	5.24	3.53	3.58
	calc.[a]	3.03	5.37	4.09	3.62

[a] From Eqn.II8 with $C_s - C_1^{\circ} = -2.65$ cals.°K^{-1} moles^{-1}
and $S_s - S_1^{\circ} = -1.79$ cals °K^{-1} moles^{-1}

Equation II.8 predicts values of $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ independent of n and hence independent of the nature of the substrate, as observed. Also, the observed and calculated values of $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ in the various aqueous acetone mixtures agree reasonably well with each other if $S_s - S_1^{\circ} = -1.79$ cals. and $C_s - C_1^{\circ} = -2.65$ cals. (see TABLE II.2). The values of $S_s - S_1^{\circ}$ and $C_s - C_1^{\circ}$ employed are approximately one third of the value for the change

$$H_2O\ (\text{liquid}) \longrightarrow H_2O\ (\text{ice})$$

This seems reasonable since the loss of freedom by water in solvating the transition state is not expected to be as great as in the freezing of water. It appears that the solvation model is applicable to aqueous organic systems.

The simple solvation model and the use of Equation II.8 assume that the increase of solvation associated with the activation process involves only the more polar component of the solvent. It has been shown, however, that in aqueous organic solvents, solvation of electrolytes by both components occurs.[76] Solvation of the transition state by acetone to the same extent as in the initial state[13a] will not invalidate the simple solvation model. Since this model describes the behaviour of S_N reactions in aqueous organic solvents reasonably well, it will be accepted in the present discussion.

b. S_N2 Reactions [22, 71].

The ratio of $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ for S_N2 reactions is less than the corresponding S_N1 figure under the same conditions. This lower value may be explained tentatively in terms of the partial covalent attachment of one water molecule in the transition state. Such covalent attachment requires a less random arrangement of this water molecule and hence a greater loss of entropy and heat capacity. $\Delta C^{\ddagger}$ is, however, less negative in S_N2 reactions. This presumably arises because these processes are associated with a smaller increase in solvation in the activation step, which at the same time should lead to a more positive $\Delta S^{\ddagger}$. In fact

/41...

S_N2 reactions are associated with less negative $\Delta C^{\ddagger}$ and more negative $\Delta S^{\ddagger}$ than S_N1 reactions, suggesting that a water molecule loses a greater proportion of its entropy than of its heat capacity when it becomes covalently attached in the transition state. This argument agrees qualitatively with the predictions of $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ and may arise from the fact that the loss of librational heat capacity is, perhaps, partly compensated by contributions from new modes of vibration in the activated complex. Quantitative interpretation, however, leads to inconsistencies and further work on this problem is needed. It must, however, be stressed that, empirically the ratio $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ has provided a delicate test of mechanism for the solvents and compounds which have been studied.

The mechanistic test based on the ratio $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ has been criticised on the grounds that, as the temperature is reduced, $\Delta S^{\ddagger}$ increases and may become positive.[78] Hence $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ will be a discontinuous function with either a positive or negative value. It has been pointed out[57] that this is not a valid criticism provided $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ for S_N1 reactions is independent of the nature of the substrate at a given temperature, irrespective of whether $\Delta S^{\ddagger}$ is positive or negative. If $\Delta S^{\ddagger}$ is negative the original form of the mechanistic test[22]

$$\Delta C^{\ddagger}/\Delta S^{\ddagger}\ (S_N1) > \Delta C^{\ddagger}/\Delta S^{\ddagger}\ (S_N2)$$

is applicable. In any other case the value of $\Delta S^{\ddagger}$ for an S_N2

/42...

process will be more negative than the value calculated from the observed ΔC^{*} and $\Delta C^{*}/\Delta S^{*}$ (S_N1), this ratio having been obtained from compounds known to undergo S_N1 reaction under the experimental conditions. The experimental results lead to the equation

$$\Delta S^{*} = A + \Delta C^{*} \ln T$$

where A is a constant, strictly applicable only over the experimental range since it is only in this range that the constancy of ΔC^{*} has been demonstrated. ΔS^{*} changes sign at Ta such that

$$\ln Ta = - A/\Delta C^{*}$$

But for systems where $\Delta C^{*}/\Delta S^{*}$ for S_N1 hydrolysis is independent of the nature of the substrate, the calculated value of Ta is well outside the experimental range. There is no reason to assume that ΔC^{*} is independent of temperature over such wide temperature ranges, and, therefore, even the change of sign of ΔS^{*} in these reactions is still to be established.

II.1.iii. S_N Reactions in Water[79, 80, 71]

It must be stressed at this stage that this test of mechanism does not appear to be applicable to hydrolysis in water, although the relevent data are only available for a limited number of S_N1 reactions in this solvent (TABLE II.3.)

/43...

TABLE II.3.

$\Delta C^{*}/\Delta S^{*}$ [b] of S_N1 Hydrolyses in Water at 50°C

Substrate	$\Delta C^{*}/\Delta S^{*}$
$i\text{-}BuO_3SPh$	4.54[a]
$i\text{-}PrO_3SPh$	10.7
$i\text{-}PrO_3SMe$	7.72
$t\text{-}BuCH_2O_3SPh$	10.7
$t\text{-}BuCH_2O_3SMe$	6.77
$t\text{-}BuCH_2Br$	-5.26[a]
$t\text{-}BuCl$	-5.44[a]

a. Using estimated value of ΔC^{*}

b. Data from Ref. 79

The positive value of ΔS^{*} for the hydrolysis of t-butyl chloride in water[80, 81, 82] suggests that the simple solvation model (see Section II.1.ii.) does not apply in this solvent.

Strictly ΔS^{*} and ΔC^{*} are given by

$$\Delta S^{*} = S_t - S_i$$

$$\text{and} \quad \Delta C^{*} = C_t - C_i$$

Where the subscripts t and i refer to the transition and initial states respectively. Robertson[79, 80.] considered that S and C in water

/44...

were dependent on contributions from solvent - solvent and solute-solvent interactions induced by the presence of the substrate. A neutral molecule was thought to increase solvent - solvent interactions in its vicinity resulting in a negative Si and a positive Ci (the interaction is less at higher temperatures). This effect will be larger for large solute molecules. The transition state was discussed by analogy with ions. With increasing size C_t becomes more negative and S_t more positive. Since Si gives rise to a positive contribution to ΔS^*, with increasing size one might expect a value of St ($S_t > -S_i$) that would give rise to a positive ΔS^*. Thus ΔS^* is expected to increase and ΔC^* to decrease with increasing size of the substrate, making $\Delta C^*/\Delta S^*$ dependent on the structure of RX. The work of Robertson is open to the criticism that the distinction between mechanisms S_N1 and S_N2, which may cause considerable variations of ΔC^* and ΔS^* for structurally similar compounds (see Section III.2), has been largely ignored. Qualitatative agreement with this approach is, however, obtained in the positive ΔS^* and highly negative ΔC^* for the hydrolysis of t-butyl chloride.[80, 81, 82, 13b] For a quantitative treatment on these lines, allowance for solvent - solvent interaction, characteristic of the initial state, persisting to some extent in the transition state may be necessary.

Both the simple solvation model and the Robertson approach may well be applicable in the systems for which they were developed.

In water, for example reactants with polar or polarisable groups, or groups which can form hydrogen-bonds with water will increase solute-solvent and decrease solvent - solvent interactions in the initial state giving rise to a more negative ΔS^{*}. Thus in water, ΔS^{*} for benzyl chlorides is more negative than for n-alkyl halides[77, 79] and also more negative for sulphonates that for the corresponding halides.[79, 13b.] This is in contrast to aqueous organic solvents where ΔS^{*} is virtually the same for the hydrolysis of benzyl and n-alkyl halides and reactions of sulphonates have a more positive ΔS^{*} than those of halides. This type of presolvation has also been proposed to account for the increase of ΔS^{*} in S_N1 hydrolysis of alkyl halides on introduction of an α- carboxylate - ion substituent.[83]

It has been suggested that the difference between hydrolysis in water and in a aqueous organic solvent may be due to the solvation of the substrate in the initial state by the organic species, with a reduction of those solvent - solvent interactions induced by the substrate.[71] The sharp fall of ΔS^{*} for the hydrolysis of t-butyl chloride on addition of small amounts of acetone or dioxane to the solvent, water,[82] suggests that this might be the case. The solvent - solvent interactions in the initial state may be so reduced by the presence of the organic component that they are not further reduced by the increased solvation associated with the activation process.[71] The simple solvation model would then be valid.

Confirmation of the difference between water and aqueous organic solvents seems to be afforded by the ionisation of water and formic, acetic, propionic and butyric acids in aqueous dioxan solvents.[84] The ionisation equilibria of these acids

$$HA \longrightarrow H^+ + A^-$$

may be regarded as analogous to the activation process in S_N1 reactions since both involve the creation of electric charges.[80] The value of $\Delta C^\circ/\Delta S^\circ$ at 25°C depends only on the nature of the solvent in 45%, 70% and 82% solvent. This is no longer true in 20% dioxan and pure water.

In the solvents employed in the present work (i.e. 50%, 70% and 85% aqueous acetone), the solvation model appears to be satisfactory. It will, therefore, be employed in the further discussions of solvolytic reactions in these solvents.

CHAPTER III.

Activation Parameters and Mechanism of Solvolysis of p-Toluenesulphonic Esters

The main part of this thesis is concerned with the mechanistic conculsions that can be drawn from the activation parameters in the solvolysis of p-toluenesulphonic esters. These results will be discussed mainly in this chapter.

In the present work activation parameters have been obtained for the compounds given below.

p-Nitrobenzhydryl Toluenesulphonate

As the corresponding halides[57] are solvolysed by mechanism S_N1 and sulphonates are more likely to be hydrolysed by mechanism S_N1 than chlorides[56] (I.7.i.), it seemed certain that this sulphonate would follow this mechanism. Furthermore benzhydryl compounds are sterically unfavourable to reaction by mechanism S_N2.

i-Propyl Toluenesulphonate

The corresponding chloride hydrolyses by a mechanism in the borderline region (see P. 9) and it was hoped that the results from the hydrolysis of the sulphonate would give useful information about the effect of the leaving group on the mechanism.

n-Propyl Toluenesulphonate

Previous evidence suggests that primary sulphonates hydrolyse by mechanism S_N2. This compound was studied to demonstrate that $\Delta C^{*}/\Delta S^{*}$ for the S_N2 solvolysis of sulphonates is less than the $\Delta C^{*}/\Delta S^{*}$ value in S_N1 processes.

/48...

Benzyl Toluenesulphonate and its p-nitro, p-phenyl, p-methyl, p-anisyl, p-phenoxy and p-methoxy derivatives represent a graded series with increasing electron release from the substituents and hence an increasing facility to react by mechanism S_N1 (see P. 10). The study of this series was expected to yield information about the change of mechanism in the series.

The solvolysis of these compounds were carried out in 50%, 70% and 85% aqueous acetone. All compounds, however, were not studied in all three solvent mixtures. Some of the compounds have been investigated previously, in similar solvents. The present results can be seen to agree fairly well with these earlier results (Appendix V.II.1.).

In this chapter the conclusions based on activation parameters are given. The differences between halides and sulphonates as leaving groups are discussed in CHAPTERV; relative rates of the substituted benzyl compounds are considered in CHAPTER IV. Only the main results are used in the text but details of individual runs can be found in Appendix VII.4 and derived values of k, E, ΔS^{*} and ΔC^{*} in Appendix VII.3.

III.1. The $\Delta C^{*}/\Delta S^{*}$ Ratio

It was first necessary to establish that the $\Delta C^{*}/\Delta S^{*}$ ratio (see P. 19) can be used as a test of mechanism in the solvolysis of sulphonates.

III.1.i. Mechanism S_N1

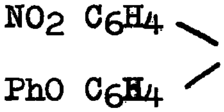
Mechanism S_N1 is expected to be facilitated by the change of leaving group from halide to sulphonate.[56] p-Nitrobenzhydryl[57] and p-phenoxy-[23] and p-methoxy - benzyl[24] chlorides are hydrolysed by mechanism S_N1. The corresponding sulphonates are, therefore, also expected to follow this mechanism.

TABLE III.1

$\Delta C^*/\Delta S^*$ for the S_N1 Solvolysis of ROTs in 85% Acetone at 50°C

R	$\Delta C^*/\Delta S^*$
$pPhOC_6H_4CH_2$	2.81 ± 0.30
$pMeOC_6H_4CH_2$	2.88 ± 0.28
$pNO_2C_6H_4CH.Ph$	3.03 ± 0.29
Mean S_N1 Value[a]	2.77

a. Mean S_N1 $\Delta C^*/\Delta S^*$ values in 85% Acetone. $p-XC_6H_4CHPhCl$ (X = H,[84] Ph[84], t-Bu[84], Me[84]) and



$\begin{matrix} NO_2\,C_6H_4 \\ PhO\,C_6H_4 \end{matrix} \Big\rangle CHCl$ [23]

Quite clearly the value of $\Delta C^*/\Delta S^*$ for the S_N1 hydrolysis of toluenesulphonates is the same as the accepted mean value obtained from the S_N1 hydrolysis of a number of halides (TABLE III.1).

III.1.ii. Mechanism S_N2

Previous work has indicated that n-propyl toluenesulphonate hydrolyses by mechanism S_N2. This compound was studied in 50% acetone because of its rather unreative nature. In this solvent the $\Delta C^*/\Delta S^*$ ratio for S_N1 reactions had been obtained for only a limited number of structurally different compounds. For this reason the S_N1 hydrolysis of p-phenoxybenzyl chloride[23] was now studied in this solvent.

	$\Delta C^{*}/\Delta S^{*}$ in 50% acetone at 50° C
$pPhOC_6H_4CH_2Cl$	2.54 ± 0.41
nPrOTs	2.06 ± 0.27
Mean S_N1 Value[a]	2.89

Clearly the S_N1 value of $\Delta C^{*}/\Delta S^{*}$ in 50% acetone is confirmed. The value of $\Delta C^{*}/\Delta S^{*}$ for the solvolysis of n-propyl toluenesulphonate is, equally, clearly, lower than the mean S_N1 figure and hence it may be concluded that the solvolyses of toluenesulphonates by mechanism S_N2 yield values of $\Delta C^{*}/\Delta S^{*}$ which are lower than the ratio for mechanism S_N1. Thus the mechanistic test based on this ratio is applicable to sulphonates. The value of $\Delta C^{*}/\Delta S^{*}$ is larger for the n-propyl toluensulphonate than the values obtained for the benzyl and p-nitrobenzyl compounds. This may arise from the fact that this ratio is not necessarily constant for S_N2 processes, in contrast to S_N1. Since this mechanistic test applies in the solvolysis of sulphonates, it will now be employed in cases where the mechanism is in doubt.

---

[a] Mean $\Delta C^{*}/\Delta S^{*}$ value from $PhCCl_3$,[70] $CH_3C_6H_4CHCl_2$,[86] $C_6H_5CHCl_2$,[70] $pNO_2C_6H_4CH.PhCl$[86] and t-BuCl[88] in 50% acetone

III.1.iii i-Propyl Toluenesulphonate

In 85% acetone the $\Delta C^{*}/\Delta S^{*}$ ratio suggests that this compound hydrolyses by a mechanism which is not completely S_N1. In

TABLE III. 2.

$\Delta C^{*}/\Delta S^{*}$ for the Hydrolysis of iPrOTs in X% Acetone at 50°C.

X =	50	85
iPrOTs	3.21 ± 0.27	2.17 ± 0.27
Mean S_N1 Value	2.89[a]	2.77[b]

a. See footnote P.50.

b. See Table III.1

50% aqueous acetone, a solvent which is more favourable to the ionisation process (see P.7), complete S_N1 hydrolysis is indicated (TABLE III.2). Previous conclusions that the hydrolysis of this compound occurs by a mechanism close to the point of mechanistic change, are confirmed by the present results.

III.1.iv. Benzyl Toluenesulphonates

The values of $\Delta C^{*}/\Delta S^{*}$ for the solvolysis of benzyl sulphonates are reported in TABLE III.3.

/52...

TABLE III.3

$\Delta C^{\ddagger}/\Delta S^{\ddagger}$ for the Hydrolysis of p-X-Benzyl Toluenesulphonate in x% Aqueous Acetone at 50°C.

X	x =	50	70	85
NO_2		0.97±0.20	1.55±0.14	--
H		1.45±0.16	1.68±0.17	1.35±0.15
Ph		--	2.53±0.28	--
Me		--	2.40±0.50	--
An		--	--	2.70±0.25
PhO		--	--	2.81±0.30
MeO		--	--	2.88±0.28
Mean S_N1 Value		2.89[a]	3.68[b]	2.77[c]

a. See footnote P. 50

b. Mean $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ value from t-BuBr[88], $pNO_2C_6H_4CH.BrPh$ [88] t-BuCl,[88] $p\text{-}XC_6H_4CH.ClPh$ (X = H[87], Cl[87], Br[87], I[87], NO_2[85]) and $pX\text{-}C_6H_4CH_2Cl$ (X = PhO[23], MeO[24]) in 70% Acetone

c. See Table III.1

The $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ ratio indicates that the three most reactive p-substituted benzyl sulphonates hydrolyse by mechanism S_N1. Since the p-methoxy - and p-phenoxy - benzyl chlorides undergo S_N1 reaction in aqueous acetone, it is not surprising to find that the hydrolysis of the corresponding sulphonates

/53...

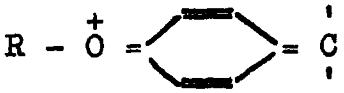
follow the same mechanism. The p-anisyl derivative is hydrolysed by mechanism S_N1 in contrast to the chloride which did not react completely by this mechanism. It, therefore, appears that a sulphonate as leaving group favours the operation of mechanism S_N1 more than a chloride. The change of mechanism due to this change of leaving group (discussed more fully in CHAPTER V) is not as pronounced as was formerly suggested (see Section I.7.i.). For example, the $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ values show quite clearly that p-methylbenzyl toluenesulphonate and less reactive compounds do not undergo S_N1 hydrolysis. This is contrary to the conclusions of Hammond and Brown whose views are discussed in more detail later (see Section IV.1 and CHAPTER VI).

III.2. $\Delta S^{\ddagger}$

The variation of $\Delta S^{\ddagger}$ at the same temperature, among a series of structurally similar compounds can lead to useful mechanistic conclusions.

The simple solvation model (see P.37) would suggest that in S_N1 reactions of structurally similar compounds, constant values of $\Delta S^{\ddagger}$ are expected if charge development, and hence solvation, in the transition states of all reactions is the same. If mechanism S_N2 is operating then a more negative value of $\Delta S^{\ddagger}$ is to be expected as a result of the covalent attachment of water molecules. In a series of structurally similar compounds, a comparison of $\Delta S^{\ddagger}$ values may, therefore, yield mechanistic conclusions. For example, a change of mechanism has been proposed for the acid catalysed ring opening of epoxides[89] and cyclic imines[90] on the basis of ΔS^{*} values. The generalisation[91] that bimolecular and unimolecular processes can be distinguished from one another by the magnitude of ΔS^{*}, irrespective of the structure of the substrate, is, however, of limited utility.

In TABLE III.4. are recorded the variations of ΔS^{*} for four series of compounds and it is important to note that structural changes are common to all series. The values of ΔS^{*} for the two benzhydryl series, where mechanism S_N1 operates throughout, are virtually constant except for the two alkoxy substituents where ΔS^{*} is more negative by about 4 - 5 eu. This property of the p-alkoxy substituent cannot be related in any way to the reaction rate since the rates of hydrolysis of Ph_2CHCl and $p\text{-}PhO\text{-}C_6H_4CHCl.C_6H_4\text{-}_pNO_2$ are much the same. The more negative value of ΔS^{*} associated with the p-RO - group has been explained in terms of the contribution from the structure



to the transition state.

Solvation of the alkoxy group is expected to result in greater overall solvation and hence in more negative values of ΔS^{*} for the compounds.

/55...

Entropies of the Hydrolysis of p-Substituted Aralkyl Sulphonates and Chlorides in x% Aqueous Acetone at 50°C.

(Values of $\Delta S_X^{*} - \Delta S_H^{*}$ are reported, where X is the p-substituent.)

		$\left.\begin{matrix} p\text{-X-}C_6H_4 \\ p\text{-NO}_2\text{-}C_6H_4 \end{matrix}\right\rangle CHCl$ [a]		$\left.\begin{matrix} p\text{-X-}C_6H_4 \\ C_6H_5 \end{matrix}\right\rangle CHCl$	$p\text{-X-}C_6H_4\text{-}CH_2OTs$		$p\text{-X-}C_6H_4\text{-}CH_2Cl$
Mechanism		S_N1		S_N1	?		?
X	x =	70	85	85	70	85	70
NO_2		-0.17	-	+0.31 [a]	-3.23	-	-
Ph		+1.09	-	+1.66 [b]	+4.73	-	-
Me		+0.06	-	-0.68 [b]	+4.69	-	+5.47 [c]
An		-	-0.11	+1.14 [a]	-	+8.33	+11.14 [a]
PhO		(-7.36)	-3.60	-4.00 [a]	-	+9.16	+11.98 [a]
MeO		-	-5.52	-1.86 [a]	-	+9.33	+11.97 [c]

a. Ref. 23 b. Ref. 85 c. Ref. 24

III.2.i. Variations of $\Delta S^{\ddagger}$ in the Benzyl Series

Values of $\Delta S^{\ddagger}$ for the hydrolysis of benzyl chlorides and sulphonates and two series of benzhydryl chlorides are recorded in TABLE III.5. The variation of $\Delta S^{\ddagger}$ for the hydrolysis of benzyl chlorides and sulphonates are quite different from the variation observed when the mechanism is S_N1 throughout. $\Delta S^{\ddagger}$ increases with increasing reactivity, giving a constant value for the p-phenoxy - and p-methoxy - derivatives. The value of $\Delta S^{\ddagger}$ for the latter two derivatives is approximately 12 eu. more positive than for the p-nitro compounds. The change of $\Delta S^{\ddagger}$ is clearly much larger and in the opposite direction to the variation of $\Delta S^{\ddagger}$ for the S_N1 hydrolysis of benzhydryl chlorides. These results suggest a change of mechanism from S_N2 to S_N1 with increasing electron release to the reaction centre in the hydrolysis of substituted benzyl chlorides and sulphonates. The similar values of $\Delta S^{\ddagger}$ for the hydrolysis of the p-phenoxy and p-methoxy compounds suggest that these compounds react by mechanism S_N1 while the less reactive compounds do not. Similar conclusions were reached from consideration of the ratio of $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ for the hydrolysis of these chlorides[23,24] and sulphonates (see P. 49).

$\Delta S^{\ddagger}$ for the hydrolysis of the p-anisyl compounds is only slightly more negative than the S_N1 values and it is suggested that the change of mechanism occurs in this region in the series. This conclusion is consistent with the values $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ for the hydrolysis of these compounds. Since the

/57...

TABLE III. 5.

$-\Delta S^{\ddagger}$ for the Hydrolysis for the Series of p-X-Benzyl Chloride (A), p-X-Benzyl Toluenesulphonate (B), p-X-Benzyhydryl Chloride (C), and p-X p'-NO_2- Benzhydryl Chloride (D) in x% Acetone at 50°C.

Series	Mechanism	x	X =	NO_2	H	Ph	Me	An	PhO	MeO
A	?	50		23.49^{a}	22.41^{b}	-	15.68^{a}	-	-	-
		70		-	23.96^{c}	-	17.49^{a}	12.82^{d}	11.98^{d}	11.99^{a}
B	?	70		19.87	16.64	11.81	11.95	-	-	-
		85		-	19.62	-	-	11.29	10.46	10.29
C	S_N1	85		15.41^{d}	15.75^{e}	14.09^{e}	16.43^{e}	14.51^{d}	19.75^{d}	17.62^{d}
D^{d}	S_N1	85		15.58^{f}	15.41	14.32^{f}	15.35^{f}	15.55	19.01	20.93

a. Ref 24, b. Ref. 22, c. Ref. 88, d. Ref.23, e. Ref. 85.

f. Extrapolated to 85% acetone from results in 70% acetone.

/58...

mechanistic test based on $\Delta C^{*}/\Delta S^{*}$ suggests that p-anisylbenzyl toluenesulphonate hydrolyses by mechanism S_N1, while the chloride does not react completely by this mechanism, it is concluded the ratio of $\Delta C^{*}/\Delta S^{*}$ forms a more sensitive test of mechanism in the borderline region than the variation of ΔS^{*}. ΔS^{*} for the hydrolysis of the parent sulphonate is less negative than that of the p-nitro derivative, suggesting that the parent compound may be closer to the borderline region of mechanism than the corresponding chloride, which has a similar value of ΔS^{*} to its p-nitro derivative.

The mechanism of hydrolysis of p-X-benzyl toluenesulphonates and the slight shift of mechanism on replacing chloride by sulphonate as leaving group was demonstrated by the $\Delta C^{*}/\Delta S^{*}$ ratio. It is now confirmed by the variations of the values of ΔS^{*} of these compounds but it would seem that $\Delta C^{*}/\Delta S^{*}$ is a more sensitive test of mechanism than the variations of ΔS^{*}.

Hammond[63e,f.] found a similar variation of ΔS^{*} in substituted benzyl toluenesulphonates (Appendix VII.1), although his results are not expected to be as accurate as those from the present work. He suggested that the high negative entropy of the p-nitro derivative was due to strong ordering of the relatively few water molecules associated with the hydrolysis of this compound. While this is to be expected for reactions by mechanism S_N2, the gradual change of $\Delta S^{\ddagger}$ through the series showed no division into two groups. He, therefore, concluded that only one mechanism was operating throughout, i.e. mechanism S_N1. If, however, mechanism S_N1 operated throughout the series of benzyl sulphonates, it would be difficult to explain why the value of $\Delta S^{\ddagger}$ for the hydrolysis of the p-nitro compound was so much more negative than the value for S_N1 reaction of other p-nitro compounds.

III.3. The Mechanistic Transition

In the series of p-substituted benzyl sulphonates the mechanism changes from S_N2 to S_N1. It is of interest to see if the present results help to elucidate the nature of reactions close to the point of transition between these two mechanisms.

The mechanistic borderline region has been described (see Section I.4.) as either a region in which reaction occurs via a single bimolecular transition state which requires some covalent participation by the nucleophilic reagent or as a region in which mechanisms S_N1 and S_N2 operate concurrently. If a concurrence of mechanisms S_N1 and S_N2 occurs, the rates of both types of reaction must be comparable. But it has, however, been shown earlier (see P. 53) that $\Delta S^{\ddagger}$ of S_N2 reactions will be different from that observed in $S_N1$processes. The activation energies of the two separate processes must, therefore, also differ by roughly equivalent amounts. The fact that E is obtained experimentally from single rate coefficients representating two concurrent processes having different activation energies will give rise to a positive contribution to ΔC^{*} which will be superimposed on the negative ΔC^{*} of the individual processes.[22] The maximum value of ΔC^{*} of p-X-benzyl chlorides (TABLE III.6.) at the

TABLE III. 6.

- ΔC^{*} for p-X-Benzyl Chloride and Toluenesulphonate in x% Aqueous Acetone at 50°C

	RCl		ROTS	
X x =	50	70	70	85
NO_2	20.0[a]	-	30.72	-
H	-	21.7[c]	27.98	26.55
Ph	-	-	29.90	-
Me	2.0[a]	20.8[a]	28.68	-
An	-	29.6[b]	-	30.51
PhO	28.2	43.1[b]	-	29.40
MeO	-	45.9[a]	-	29.62

a. Ref. 24, b. Ref. 23, c. Ref. 88.

p-methyl derivative in 50% acetone strongly suggests a concurrence of mechanisms for this compound. No such maximum was observed in the corresponding series of toluenesulphonates (see TABLE III.<u>6</u>)

This would be consistent with the view that this system undergoes hydrolysis by a single mechanism in the borderline region but it seems very unlikely, however, that a change of leaving group would affect the mechanism in this region drastically. Two possible explanations may be advanced to account for the differences in the two series. Firstly the substituents and reaction conditions examined in the sulphonate series may not have given the right proportion of S_N1 and S_N2 processes for the effect to be observable; it is noteworthy that the maximum of $\Delta C^{\ddagger}$ of the benzyl chlorides is practically absent in 70% acetone. A second explanation of the difference may be that the positive contribution to $\Delta C^{\ddagger}$ for the hydrolysis of p-methylbenzyl chloride arises from reaction by a single mechanism with a temperature dependent transition state.

A further anomaly is apparent in the activation parameters for the solvolysis of sulphonates. The solvation model, which has been accepted for these reactions (see P. 40) predicts that $\Delta C^{\ddagger}$ for S_N1 processes should be more negative than for S_N2. It has been noted that the variation of $\Delta C^{\ddagger}$ of organic chlorides is consistent with this model, as are the variations of $\Delta S^{\ddagger}$ for chlorides and sulphonates. The values of $\Delta C^{\ddagger}$ for the hydrolysis of p-X-benzyl toluenesulphonates (TABLE III.6.), however show very little variation although a mechanistic change is proposed. There are a number of alternatives that might give rise to this anomaly.

/62...

a. The solvolysis of the less reactive sulphonates occurs by a mechanism which does not parallel the reactions of halides, i.e. is not an S_N process. The most attractive alternative would be a reaction with S - O fission but this seems unlikely on the bulk of the earlier evidence (see Section I.6.).

b. It will be seen later (V.2.) that the sulphonate results are consistent with initial state solvation by water (hydrogen bonding to the oxygen atoms of the sulphonate group). The geometry of the S_N2 transition state is such that a water molecule, hydrogen bonded to the sulphonate, could act as the nucleophilic reagent (FIG.IV.1.)

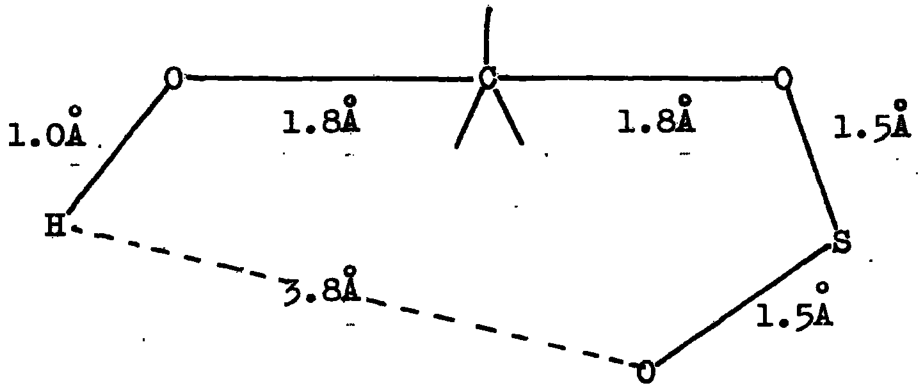


FIGURE IV.1.

Water in such a transition state would not be able to librate at all and will lose a great deal more heat capacity than if hydrogen bonding were absent as in transition states of halides.

$$H_2O \text{ -- } R \text{ -- } Cl$$

/63...

This view is only tentatively proposed, but it might account for the constant values of ΔC^{*} of the benzyl sulphonates. This cyclisation of structure might be expected to make a negative contribution to ΔS^{*}, but the change of ΔS^{*} between chlorides and sulphonates is approximately the same in S_N1 and S_N2 processes (see TABLE V.4.). Thus any contribution to ΔS^{*} from the cyclic structure would have to be small. It is difficult to see why this should be so, but if it were the case, then the abnormally high values of ΔC^{*} for S_N2 processes would lead to higher values of $\Delta C^{*}/\Delta S^{*}$ for S_N2 solvolysis of sulphonates than of chlorides, as is in fact observed.

c. The extensive solvation of the incipient sulphonate ion in S_N1 transition states may inhibit the solvation of the incipient carbonium ion. Restriction of solvation of the developing positive charge in S_N2 transition states would be less pronounced as the charge will be partially situated on the covalently attached water molecule which is further removed from the solvation shell of the sulphonate entity. On this view, ΔC^{*} and ΔS^{*} values of S_N1 processes which are less negative than expected, is proposed to explain the invariant nature of ΔC^{*}. The proposal suffers from the same weakness as alternative b.

It must be concluded that the interpretation of the present data to obtain information about the nature of mechanism

/64...

in the borderline region is not possible. More work on the problems of solvolysis in this region is required. It is worth noting that evidence of concurrent unimolecular and bimolecular nucleophilic substitution has been obtained for other substrates and it would also seem reasonable to expect concurrence of mechanisms with sulphonates.

As far as interpretation of mechanism in the series of p- substituted benzyl sulphonates is concerned, the information obtained from $\Delta S^{\ddagger}$ is consistent with that from $\Delta C^{\ddagger}/\Delta S^{\ddagger}$. These compounds which represent a series with increasing facility to react by mechanism S_N1 with increasing electron release from the p- substituents, follow the S_N1 reaction path when X=anisyl, phenoxy and methoxy. The less reactive compounds react by a mechanism which is not entirely S_N1.

/65...

Substituent Effects on the Solvolysis of Benzyl Toluenesulphonate

In this chapter the mechanistic information that can be obtained from the effects of substituents in the aromatic ring on side chain reactivity of sulphonates, is considered. The introduction of electron releasing substituents will facilitate the rupture of the R - X bond. The effect of such substituents on the reaction rate can be explained in terms of the polar properties of the substituents and a number of attempts at a quantitative correlation have been published.

IV.1. Quantitative Treatment

Hammett,[92] in effect, assumed that electron demand at the reaction centre was constant in the reactions of a series of structurally similar compounds and that the response of substituents depended on their intrinsic capacity for electron release and the electron demand. If the response of substituents is directly proportional to the electron demand, one obtains the Hammett equation IV.1.

$$\log (k_X/k_H) = \sigma \rho \qquad \text{IV.1.}$$

where k_X and k_H are the rate coefficients of the substituted and unsubstituted compounds respectively, σ is a substituent constant independent of the nature of the reaction and ρ is the reaction constant depending on the reaction and reaction

/66...

conditions. Values of σ were arbitarily obtained by assuming that $\rho = 1$ for a standard reaction; Hammett chose the equilibrium constants of the ionisation of benzoic acids. This ionisation process is not very sensitive to substituent effects and Equation IV.1 was found to be very useful in predicting the rates of reactions which were also rather insensitive to the polar effects of substituents. Despite the success in reactions where polar effects were mainly inductive, Equation IV.1. was often found to give poor results in reactions in which electron demand at the reaction centre was large. This was especially true when the system favoured conjugative electron release from the substituent.

Brown proposed a new scale of substituent constants, σ^+, which could apply to strongly electron-demanding reactions in which the substituent was conjugated to the reaction centre.

$$\log (k_X / k_H) = \sigma^+ . \rho \qquad \text{IV.2.}$$

Values of σ^+ were obtained from the results of the S_N1 solvolysis of α,α-dimethylbenzyl chlorides by assuming that the Hammett σ value applied to the m-substituents, which were not expected to donate electrons conjugatively to the reaction centre. The value of ρ could thus be obtained from the results for the m-substituted derivatives and hence a scale

/67...

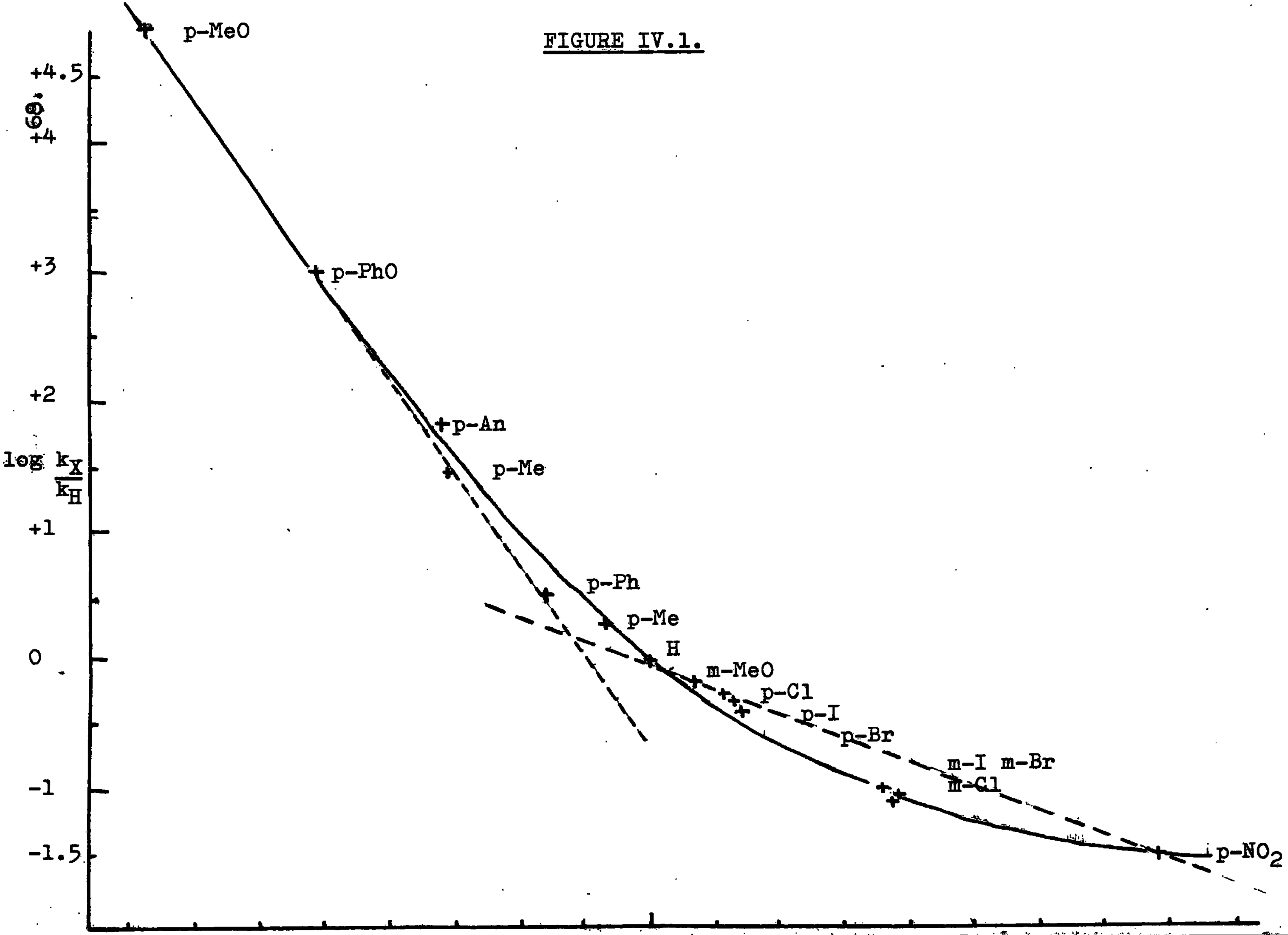
of σ^+ values for the p-substituents could be set up using Eqn.IV.2.

IV.1.i. Mechanistic Interpretations of Linear Free Energy Equations

Eqn. IV. 2. requires a linear relation between log (k_X / k_H) and σ^+ but the present results yield a distinctly curved plot (see FIG.IV.1.), similar to that obtained by Hammond.[63e] A curved plot was also obtained by Swain[93], using σ values, for the hydrolysis of substituted benzyl chlorides, an observation which has been confirmed by later results.[24]

The σ^+ plot might conceivably be resolved into two lines (representated by dotted lines in FIG. IV.1.) and it could be argued that such a division indicates a change from mechanism S_N2 for the less reactive compounds to S_N1 for the more reactive members. The different slopes of the two sections (different ρ) would arise from the difference of electron demand at the reaction centre in the two processes. This is in fact the way in which Brown interpreted the data, but even if the σ^+ values apply to the S_N1 reactions of benzyl sulphonates, there is little reason to assume that they apply to S_N2 reaction where the interpretation of kinetic effects of polar substituents may be ambiguous (see P. 11) and where conjugative effects are probably not important. If σ^+ values can be applied to S_N2 and S_N1 reactions, with different ρ values for the two processes, it is difficult to see how to choose between the use of σ and σ^+ for S_N2 reactions.

FIGURE IV.1.


+4.5
+4
+3
+2
+1
0
-1
-1.5
log $\frac{k_X}{k_H}$
p-MeO
p-PhO
p-An
p-Me
p-Ph
p-Me
H
m-MeO
p-Cl
p-I
p-Br
m-I m-Br
m-Cl
p-NO_2

Other works[94] have considered that a curved log k - σ^+ plot does not necessarily imply a mechanistic change and Hammond has suggested implicity that Eqn. IV.2. does not apply to the solvolysis of benzyl sulphonates.

IV.1.ii. Criticism of the σ or σ^+ Relationship

Eqn. IV.2. is quite inadequate in describing the behaviour of benzyl sulphonates and although the plots obtained from the results for the solvolysis of benzhydryl chlorides are more successful, they are still not completely adequate.[23] These linear free energy relationships, in effect, assume that the response of substituents is constant independent of the electron demand. But it appears reasonable to expect that an easily polarised group will respond more readily to moderate electron demand at the reaction centre than one less easily polarised. When the electron demand is much more powerful their relative responses may be quite different. This would, of course invalidate Eqns IV.1 and IV.2 and evidence that this does occur has been obtained in practice.[23]

The ambiguous nature of these equations has been recognised by others[95] who tried, by the introduction of additional disposable parameters, to allow for the overall electron release by conjugative and inductive mechanisms. These additional equations will not be discussed since it is difficult to see how mechanistic information can be obtained

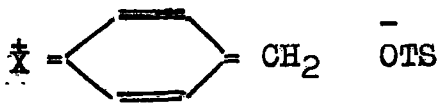
/70...

from them. Discussion of their validity in S_N1 solvolysis is also outside the scope of this thesis. It is noteworthy that Wepster[96] suggested that only a sliding scale of σ values, depending on the electron demand at the reaction centre, will be valid. This is, in fact, an alternative way of expressing the non-linear response to electron demand considered earlier in this section.

IV. 2. Qualitative Treatment

In view of the unsatisfactory nature of the quantitative correlations of kinetic substituent effects, it is believed that more useful mechanistic information can be obtained from qualitative considerations in terms of conjugative and inductive release by substituents.[97] Substitution alters the rates of chemical reactions by affecting the stabilities of the transition and initial states differently. It is reasonable to assume that the stability of the highly polar transition state will be much more sensitive to the presence of electron attracting or releasing substituents than the initial state.

Electromeric electron release, which probably gives rise to the larger substituent effects in the compounds studied can be represented[98] in valence bond terms by a contribution from the canonical structure, (A).



(A)

A is expected to have a much higher energy than the ground state (B) but may well be of comparable energy to the main canonical structure of the transition state (C), and will, therefore, have a

$$X - C_6H_4CH_2 - OTS \text{ (B)}, \quad X - C_6H_4-\overset{+}{C}H_2 \quad \overset{-}{O}Ts \text{ (C)}$$

greater stabilising effect in the latter. Electromeric electron release is probably a main cause of the accelerating effects of p-Ph, p-Anisyl, p-PhO and p-MeO substituents. Partial conjugation of the electrons constituting the C - H bonds of the p-methyl group with the aromatic system probably accounts for the electron releasing facility of this group. Electron withdrawal by a p-nitro group is thought to occur by two process; a strong inductive attraction of electrons by the dipolar substituent operates in conjunction with a weaker conjugative removal of electrons from the phenyl ring.

As mentioned above, the response of substituents will be qualitatively larger when the charge development in the group R in the transition state is larger. Since a greater concentration of charge is found at the reaction centre of S_N1 than S_N2 processes, comparison of substituent effects in the present system with the effects in systems of known mechanism can yield useful mechanistic information.

The effect of para-substitution on the rates for benzyl toluenesulphonates are greater than for the corresponding hydrolysis of chlorides (see TABLE IV.1.). This suggests a greater tendency to react by mechanism S_N1 or, at least, that charge development is greater, i.e. that bond-breaking is more important in the former reactions. Substituent effects in the hydrolysis of benzhydryl chlorides, where the mechanism is S_N1 throughout, are generally similar to the corresponding figures of benzyl sulphonates (TABLE IV.1.), except for the p-PhO and p-MeO substituents when the relative sulphonate figures are larger. Electron demand at the reaction centre in benzyl compounds is only

TABLE IV. 1

k_X/k_H for p-X-Benzyl Toluenesulphonate (A), p-X-Benzyl Chloride (B) and p-X-Benzhydryl Chloride (C) at 25° C

X	Series A	Series B	Series C
NO_2	3.633×10^{-2} [b]	1.11×10^{-1} [a,b.]	1.247×10^{-3} [c,d.]
H	1	1	1
Ph	3.012 [b]	-	6.99 [c, f.]
Me	29.27 [b]	4.50 [b, e.]	21.2 [c, f.]
An	68.29 [c]	12.8 [b, a.]	59.0 [c, d.]
PhO	963.3 [c]	144.9 [b, d.]	362.5 [c, d.]
MeO	2.33×10^4 [c]	1.70×10^4 [b,e.]	1.435×10^4 [c, d.]

a. 50% Acetone
b. 70% Acetone
c. 85% Acetone
d. Ref. 23
e. Ref. 24
f. Ref. 85

met from the substituted aromatic systems, whereas in the benzhydryl chlorides it is partially satisfied by the unsubstituted aromatic ring. The larger substituent effect of the p-methoxy and p-phenoxy groups in the benzyl compounds is, therefore, expected if these compounds undergo S_N1 hydrolysis, in agreement with the conclusions reached from consideration of the activation parameters (see Sections III.1.iv. and III.2.i.). The k_X/k_H ratio for the p-nitro derivative is considerably less in the benzyl sulphonates than in the benzhydryl chlorides, consistent with the operation of the more extreme form of mechanism S_N2 in the hydrolysis of the sulphonate. However comparison of the rates with those of the parent compound are of limited utility if the hydrolysis of the parent benzyl sulphonate occurs predominantly by mechanism S_N2. This would lead to a lower value of k_X/k_H than would be obtained for this ratio if the mechanism was S_N1 throughout since

$$k_H = k_H\ (S_N2) + k_H\ (S_N1) > k_H\ (S_N1)$$

More reliable information about mechanism can be obtained by comparing the relative rates of neighbouring pairs of p-X-benzyl sulphonates in the series X = NO_2, H, Me, An, PhO, MeO with corresponding relative rates of other systems. The similar change of rate produced by replacing a p-phenoxy by a p-methoxy group in benzyl chloride and benzyl toluenesulphonate suggests the same mechanism of hydrolysis (i.e. S_N1) for the four compounds. Examples have been cited to demonstrate that changes in rate caused by changes in R are fairly insensitive to changes of the leaving group.[99]

It is also of interest to compare the relative rates of neighbouring pairs with the corresponding values for the p-substituted benzhydryl chlorides and p-substituted p'-nitro- and p'-methoxy-benzhydryl chlorides (see TABLE IV. 2.). Although mechanism S_N1 operates in all the hydrolyses in these three benzhydryl systems, variation of the p'-substituent results in the electron demand on the p-substituent decreasing in the order p' = NO_2, H, MeO. Substitution in the benzyl sulphonates resembles the p' nitrobenzhydryl chlorides for the most reactive compounds. Intermediate compounds in the series have relative rates which are rather similar to those in the p'-H-benzhydryl system. The effect p-nitro substitution is of the same magnitude as is found in the p'-methoxy-benzhydryl chlorides, where electron demand on the substituent is at its lowest. This variation suggests that electron demand at the reaction centre in the solvolysis of p-X-benzyl toluenesulphonates changes considerably. Such a change is presumably due to a change of mechanism, in qualitative confirmation of the more precise mechanistic interpretation based on the values of $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ and $\Delta S^{\ddagger}$.

TABLE IV. 2.

Relative Rates of Neighbouring Pairs for the Series of Substituents p-NO_2, H, p-Me, p-An, p-PhO, p-MeO in 85% Acetone at 25°C.

	$PhCH_2OTS$	p-$NO_2C_6H_4CHClPh$[e]	Ph_2CHCl[d]	p-$MeOC_6H_4CHClPh$[c]
k_H/k_{NO_2}	27.5	5460[a]	802	75.9
k_{Me}/k_H	29.3	58.7[a]	21.2	5.9
k_{An}/k_{Me}	2.8[a]	6.52[b]	2.8	1.41
k_{PhO}/k_{An}	14	6.55	6.2	1.68
k_{MeO}/k_{PhO}	77	71.2	40	7.55

a. 70% Acetone

b. Assuing k_{Me}/k_H (70%) /k_{Me}/k_H (85%) = 1.18

c. Ref. 23

d. Refs. 23 and 85

e. Ref. 23

CHAPTER V.

The Effect of Changing the Leaving Group

This chapter deals with the effect of changing the leaving group, X, from halide to sulphonate in S_N solvolysis. It has been suggested that the operation of mechanism S_N1 is facilitated by a change of X, that will facilitate the ionisation of the R - X bond.[56] On the other hand, it has been observed that a change of X may alter the rates of S_N1 and S_N2 solvolysis to similar extents.[100] A survey of some of the available data (TABLE 1.) suggests that a change of X in theseries Cl', Br' and I'

TABLE V.1.

The relative Rates of S_N Reactions of RCl, RBr and RI

R	k_{RBr}/k_{RCl}	k_{RI}/k_{RBr}	Mechanism
Alkyl[a]	25 - 60	1.5 - 4.5	S_N1
Alkyl[b]	30 - 40	2 - 2.5	S_N2
$C_6H_5CH_2$[c]	28	-	S_N2
$4NO_2C_6H_4CH.Ph$[d]	20	-	S_N1

a. Refs. 102

b. Refs. 101 and 102

c. Mean of results in 50% and 70% aqueous acetone Refs. 57

d. 70% aqueous acetone Refs. 57

will not cause a large change in the reaction mechanism. Similarly mechanistic studies of the hydrolysis of benzyl chloride and bromide reveal little difference of mechanism.[57, 22]

These observations are, perhaps, not entirely unexpected as the heterolysis of the R - X bond is important in determining the rates of both S_N1 and S_N2 processes. On the other hand R - X fission is not compensated by any bond formation in S_N1 processes and the rate of reaction by this mechanism might be expected to be more strongly dependent on the nature of X than S_N2 hydrolysis. Bromide is not a much better leaving group than chloride and a clearer picture might be obtained of the effect of leaving group on mechanism by using a much better leaving group. Toluenesulphonate fulfills this requirement. Relative rates of the ethyl compounds in aqueous dioxan[103] are EtOTS: EtI: EtBr : EtCl = 5.5 : 1.o: 0.96: 0.048; benzyl toluenesulphonate reacts approximately 10^3 times as fast as the chloride and the p-methoxybenzyl figure is of the order of 10^4.

V. 1. Relative Reactivity of Chlorides, Bromides and Sulphonates

The effect of changing from chloride to sulphonate on the rate and the energy and entropy of activation is given in TABLE V. 2. The relevant information for changing from bromide to sulphonate is given in TABLE V.3.

/78...

TABLE V. 2.

Differences Between Rates and Activation Parameters in the Hydrolysis of ROTS and RCl^{d} at 50° C by Mechanism S_N1 (A), S_N2 (B) and Doubtful Mechanism (C).

$\Delta \log k = \log (k_{ROTS}/k_{RCl})$; $\Delta E = E_{ROTS} - E_{RCl}$;

$\Delta\Delta S^{+} = \Delta S^{+}_{ROTS} - \Delta S^{+}_{RCl}$.

	R	Δlog k	$-\Delta E/2.303RT$	$\Delta\Delta S^{+}/2.303R$
A.	$pNO_2C_6H_4CH.Ph$ [a]	4.4805	2.8062	1.6761
	$pMeOC_6H_4CH_2$ [a]	4.2004	2.5947	1.6062
	$pPhOC_6H_4CH_2$ [a]	4.3727	2.7543	1.6149
	$pAnC_6H_4CH_2$ [a]	4.2952	2.6731	1.6215
B.	$PhCH_2$ [b]	3.0707	1.4715	1.5996
	$PhCH_2$ [c]	3.1762	1.6824	1.5537
	$pNO_2C_6H_4CH_2$ [c]	2.6829	1.6973	0.9856
C.	$pMeC_6H_4CH_2$ [b]	3.8236	2.6150	1.2106

a. 85% aqueous acetone.

b. 70% aqueous acetone.

c. 50% aqueous acetone

d. RCl = $pNO_2C_6H_4CHClPh$[23] $p\text{-}X\text{-}C_6H_4CH_2Cl$ (X = NO_2[24], H,[22,88] Me[24], An,[23] PhO,[23], MeO[24])

/79...

TABLE V. 3

Difference Between Rates and Activation Parameters in the Hydrolysis of RBr^{d} and ROTS at 50°C by Mechanism S_N1 (A) and S_N2 (B)

$$\Delta \log k = \log (k_{ROTS}/k_{RBr}); \quad \Delta E = E_{ROTS} - E_{RBr}$$

$$\Delta\Delta S^{*} = \Delta S^{*}_{ROTS} - \Delta S^{*}_{RBr}$$

	R	$\Delta \log k$	$-\Delta E/2.303RT$	$\Delta\Delta S^{*}/2.303R$
A.	$pNO_2C_6H_4CH.Ph^{a}$	3.1821	1.8562	1.3265
B.	$PhCH_2$ [b]	1.5395	-0.0128	1.5370
	$PhCH_2$ [c]	1.8308	0.6148	1.2128
	nPr [c]	1.0315	-0.0290	1.0642

a. 85% aqueous acetone

b. 70% aqueous acetone

c. 50% aqueous acetone

d. RBr = $pNO_2C_6H_4CHBr.Ph$ [88], $PhCH_2Br$ [88], nPrBr[88]

It can be seen that a change from halide to sulphonate accelerates solvolysis considerably though this acceleration is greater in S_N1 hydrolysis ($k_{ROTS}/k_{RBr} \sim 10^3$, $k_{ROTS}/k_{RCl} \sim 10^4$) than when mechanism S_N2 operates ($k_{ROTS}/k_{RBr} \sim 10^2$, $k_{ROTS}/k_{RCl} \sim 10^3$), in contrast to the observation[57] that k_{RBr}/k_{RCl} is virtually independent of the mechanism of solvolysis. The mean relative contribution of changes in E to the observed rate changes are summarised below. It can be seen, that increased rates arise to a considerable extent from changes in ΔS^{*}. The

/80...

Change of X^-		$\Delta\log k$	% Change due to ΔE
$Br^- \longrightarrow OTS^-$	S_N1	3.1821	58.3
	S_N2	1.5339	12.4
$Cl^- \longrightarrow OTS^-$	S_N1	4.3372	62.9
	S_N2	2.9767	54.3

significance of this observation is discussed in the next section. For solvolysis by mechanism S_N1 it may be assumed that the values of E reflect the ease of C - X fission and the present results show that $E_{ROTS} - E_{RBr}$ and $E_{ROTS} - E_{RCl}$ are quite large. It may be inferred that the greater rate of solvolysis of sulphonates by mechanism S_N1, therefore arises partially from the greater ease of bond fission, i.e. from the reduced energy of the reaction $C - X \longrightarrow C^+ + X^-$. Bond fission is still important in S_N2 hydrolysis but there is some compensation from covalent participation by the nucleophile. The fact that $E_{ROTS} - E_{RBr} \ll E_{ROTS} - E_{RCl}$ suggests, that in bimolecular solvolysis once X is such that C - X fission is reasonably easy, any further increase in the facility of C - X fission has little effect on the rate. This point appears to be reached in RBr.

V.2. Entropy Difference in the Solvolysis of Chlorides and Sulphonates

It has been noted that the entropy differences are an important factor in determining the greater reactivity of sulphonates and these differences will now be discussed. The variation of ΔS^* for the change $RCl \longrightarrow ROTS$ are shown in TABLE V.4. The striking feature is that $\Delta\Delta S^*$ is almost always the same irrespective of mechanism. The solvation model suggests that the negative values of ΔC^* and ΔS^* in S_N1 processes arise mainly out of the increased solvation of the polar transition state by water. The more positive ΔS^* values observed for

TABLE V. 4.

Entropy Difference in the Hydrolysis of RCl[b] and ROTS at 50°C

$$\Delta\Delta S^{\ddagger} = \Delta S^{\ddagger}\text{ ROTS} - \Delta S^{\ddagger}_{RCl}$$

R	Mechanism	Vol.% Acetone	$\Delta\Delta S^{\ddagger}$
$pNO_2C_6H_4CH.Ph$	S_N1	85	7.36[a]
$pMeOC_6H_4CH_2$	S_N1	"	7.19[a]
$pPhOC_6H_4CH_2$	S_N1	"	7.00[a]
$pAnC_6H_4CH_2$	S_N1	"	7.01[a]
$pMeC_6H_4CH_2$	?	70	5.54
$PhCH_2$	S_N2	"	7.32
$PhCH_2$	S_N2	50	7.11
$pNO_2C_6H_4CH_2$	S_N2	"	4.58

a. Assumes $\Delta S^{\ddagger}_{RCl}$ (70%) $-\Delta S^{\ddagger}_{RCl}$ (85%) = 5.49 cals °A.m^{-1}. The figure is based on Ph_2CHCl.[87,85].

b. Source of chloride results :- RCl = $pNO_2C_6H_4CHCl.Ph$[23]
$p\text{-}X\text{-}C_6H_4CH_2Cl$ (X = NO_2,[24] H,[22, 88] Me,[24] An,[23] PhO[23]
MeO,[24])

sulphonate substrates then indicate that passage to the transition state for these compounds involves increased solvation by a smaller number of water molecules than the hydrolysis of chlorides.

It is believed that the smaller increase of solvation in the hydrolysis of sulphonates is due to solvation of the initial state. The sulphonate molecule will have water molecules hydrogen - bonded to the sulphonate - oxygen atoms in the initial state and these molecules will be correctly orientated to solvate the incipient negative charge in the transition state. Increased solvation in this region of the substrate in the activation process will not occur to any great extent and the overall increase of solvation on activation will be less for sulphonates than halides, giving rise to more positive values of ΔS^{*} for the former compounds. These considerations apply to the $\Delta\Delta S^{*}$ values observed in solvolysis by both mechanisms S_N1 and S_N2 and this illustrates the importance of the solvation of the leaving group irrespective of the mechanism which is operating.

ΔS^{*} for the hydrolysis of sulphonates in water is, however, more negative than for chlorides,[79] in contrast to the results in aqueous acetone. Robertson's proposals (see P43) concerning the factors controlling ΔC^{*} and ΔS^{*} in water, require that a substrate which interacts strongly with the solvent will have a more negative ΔS^{*} than one of the same size in which such initial state interactions are absent. The hydrogen bonding that occurs in the initial state of hydrolysis of sulphonates is expected, in this view, to give rise to the observed results in water. In aqueous organic solvents, the solvation model predicts the observed results. The fact that the same explanation, pre-solvation, accounts for the different observed results in the two different solvent systems represents a part of the evidence for the belief that different factors control the solvolytic process in water and in aqueous acetone.

The solvation number, **n**, associated with the passage to the polar transition states of halides and sulphonates can be estimated from the magnitude of ΔS^{*} using Eqn.II.8. The differences of n for chlorides and sulphonates δn, gives an indication of the number of water molecules associated with the initial states of the sulphonates. It appears that approximately three water molecules are hydrogen bonded in the

TABLE V. 5.

Solvation Number, n, for RCl and ROTS in 85% Acetone at 50°C

$\delta n = n(RCl) - n(ROTS)$

R	n(RCl)	n(ROTS)	δn
$pAnC_6H_4CH_2$	8.3	5.1	3.2
$pPhOC_6H_4CH_2$	7.9	4.7	3.2
$pMeOC_6H_4CH_2$	7.9	4.6	3.3
$pNO_2C_6H_4CH.Ph$	6.9	3.6	3.3

initial states of sulphonates. It is tempting to associate these water molecules with the three oxygen atoms in the sulphonate molecule but, as all water molecules may not be solvating equally strongly, δn only represents an effective solvation number.

V.3. Mechanistic Changes Due to Changing X

The present mechanistic conclusions can be compared to the similar conclusions for the hydrolysis of halides in similar solvents.

Mechanism S_N1 is thought to be facilitated by the better leaving group, sulphonate, and this view is supported by work with alkyl compounds. Secondary halides react by a mechanism

/84...

which is not entirely S_N1 (see P. 9) while secondary sulphonates react by mechanism S_N1 in all but the least aqueous solvents (see Section I.7.i.). Activation parameters suggest that mechanism S_N1 is slightly more favoured by replacing halide by sulphonate (see P.52) in benzyl derivatives, but that the effect is not as large as had been thought previously.

As previously noted (see P. 80) differences of $\Delta S^{\ddagger}$ for the hydrolysis of chlorides and sulphonates are practically the same by mechanisms S_N1 and S_N2. Hence the greater dependence of S_N1 processes on X arises mainly out of differences of E and mechanistic changes which result from the fact that sulphonates favour mechanism S_N1 more than chlorides may be discussed in terms of ΔE or the relative rates k_{ROTS}/k_{RCl} for S_N1 and S_N2 reactions. The latter will be employed here. Assuming that solvolysis in the borderline region can be described as a concurrence of mechanisms S_N1 and S_N2 (see Section I. 4.) and knowing the percentage S_N1 hydrolysis of chlorides in this region [22,71] it ought to be possible to calculate the percentage contribution of mechanism S_N1 to the total reaction of corresponding sulphonates. Assuming the ratio k_{ROTS}/k_{RCl} for the S_N2 component to have the same value as for the p-nitro compounds and the S_N1 component the same as for the p-phenoxy compounds,

$$S_N2 \quad k_{ROTS}/k_{RCl} = \frac{k(pNO_2C_6H_4CH_2OTS)}{k(pNO_2C_6H_4CH_2Cl)} = 1.83 \times 10^2$$

$$S_N1 \quad k_{ROTS}/k_{RCl} = \frac{k(pPhOC_6H_4CH_2OTS)}{k(pPhOC_6H_4CH_2Cl)} = 2.36 \times 10^4$$

the percentage contribution of the S_N1 process to the total reaction of sulphonates has been estimated and is given below.

% S_N1 (RCl)	1	10	20	40	75
% S_N1 (ROTS)	57	94	97	99	100

The figures for % S_N1 (RCl) of 1, 40 and 75 approximate to the parent,[22] p-methyl[71] and p-anisyl[71] compounds respectively. The changes of mechanism predicted for the change RCl to ROTS are quite considerable; on the basis of these calculations p-methylbenzyl toluenesulphonate should undergo almost complete S_N1 hydrolysis, contrary to the conclusions given earlier. It might be thought that this argues against the concurrence of mechanism, but the present calculations are based on a figure for k_{ROTS}/k_{RCl} in an S_N2 reaction (the hydrolysis of the p-nitro derivative) which is likely to occur by the extreme form of that mechanism. However, if the two mechanisms operate concurrently in the borderline region even the S_N2 process can be expected to have an appreciable S_N1 character, i.e. a large part of the positive charge in the transition state will be situated in the group R. Under these conditions too small a value may have been employed for k_{ROTS}/k_{RCl} in the S_N2 component, thus overestimating the proportion of the solvolysis of the sulphonate which occurs by mechanism S_N1. It is, therefore, not possible to draw any definite conclusions about the mechanism in the borderline region from the present results.

/87...

CHAPTER VI.

The Effect of Added Nucleophiles

The values of the activation parameters of the solvolysis of p-X-benzyl toluenesulphonates suggest that they react by mechanism S_N1 only slightly more readily than the corresponding chlorides. This conclusion is contradicted by the electrolyte effects published by Hammond and his co-workers.[63,b.g.] These workers found that the results of the solvolyses of benzyl and m-halogenobenzyl toluenesulphonates in the presence of chloride or nitrate ions, were consistent with entirely S_N1 solvolysis by both compounds (see P. 29).

There are two basic objections to assigning mechanism S_N1 to these reactions. Firstly, the substrate is not sterically hindered to S_N2 attack, and bimolecular reaction between benzyl chlorides and nucleophiles has been observed even when S_N1 hydrolysis occurs.[40] Secondly, if mechanism S_N1 is operating the intervention constant k_{RY}/k_{ROH} (see App. VII.2) which represents the competition between Y^- and water for the carbonium ion, R^+, can be expected to increase with increasing stability of R^+. This arises from the greater chance the more stable carbonium ions have of reacting with Y^- before their solvation shells collapse to give the alcohol (ROH).[4b] Hammond's figures at 25°C in aqueous acetone require that k_{RY}/k_{ROH} is larger for the benzyl carbonium ion than for the more stable benzhydryl and p-methoxybenzyl carbonium ions. Moreover k_{RY}/k_{ROH} is slightly larger again for the less stable m-bromobenzyl

k_{RY}/k_{ROH}	$m\text{-}BrC_6H_4CH_2OTS$[63] at 25°C	$PhCH_2OTS$[63] at 25°C	Ph_2CHCl[104] at 20°C	$pMeOC_6H_4CH_2Cl$[104] at 20°C
Cl^-	-	10.2(73%A)	4.0(70%A)	2.30(70%A)
NO_3^-	0.79 (56%A)	0.67(56%A)	-	-

carbonium ion. As these results appear to be inconsistent with Hammonds's mechanistic conclusions, it was decided to study the effect of some anions on the solvolysis of benzyl sulphonates. Since the addition of anions will effect the rate of ionisation of solvolytic reactions, electrolyte effects in S_N processes will be discussed in more detail.

VI.1. Effect of Electrolytes in S_N Reactions [4b]

Solvolytic nucleophilic substitutions occur by two mechanisms:-

$$RX + H_2O \rightleftharpoons \overbrace{H_2O \text{ --- } R}^{\delta+} \text{ --- } \overset{\delta-}{X} \rightleftharpoons ROH + H^+ + X^-$$

the single stage S_N2 process and

$$RX \rightleftharpoons \overset{\delta+}{R} \text{ ---- } \overset{\delta-}{X} \rightleftharpoons R^+ + X^- \qquad \text{(slow)}$$

$$R^+ + H2O \longrightarrow ROH + H^+ \qquad \text{(fast)}$$

the two stage S_N1 process.

Under the present conditions, first-order kinetics will be observed in both cases if the rate-determining stage in the S_N1

process is the ionisation step. The reactions proceed with an increase in polarity in the rate-determining step and the presence of electrolytes is expected to stabilise the transition state with respect to the initial state. This, the ionic strength effect, is analogous to ion-atmosphere stabilisation of ions in solution. Since charge density is greater in S_N1 than S_N2 transition states greater stabilisation, and hence a greater rate enhancement, is found in the former reactions.

VI.1.i. S_N1 Reactions

Hughes, Ingold and their co-workers proposed a simple electrostatic treatment to account quantitatively for the effect of electrolytes on the rates of S_N1 reactions. Strictly this approach was a limiting one that could only be applied to very dilute solutions. Under these conditions the accelerating effect of an electrolyte could be expected to be independent of its nature but contrary to this specific electrolyte effects have been observed[105, 7c]

a. Specific Electrolyte Effects

Specific electrolyte effects may be divided into two classes.

The first group, in which specificity is generally small in aqueous solvents, may be attributed to ion-pair formation by the electrolyte. The specific salt effects reported by Spieth and Olsen[105c] and Monk[105a] may be attributed to this. The latter results, however, are of somewhat doubtful value as mass-law constants were overlooked and as instantaneous rates calculated from theoretical expressions were compared with observed integrated rates. The formation of ion-pairs from added electrolytes has been inferred from kinetic data in 90% aqueous dioxan[106] but in aqueous acetone their formation is probably unimportant[9a,109,105a] in very dilute solution.

Specific salt effects in the second group are generally larger and have been observed on a number of occasions. Hammett[105b] suggested that the preferential solvation of ions can change the effective solvent composition of binary solvents. Grunwald[77] demonstrated that solvation of electrolytes by both solvent species in aqueous organic mixtures must be considered but this does not invalidate the Hammett proposal. The solvation of various electrolytes in aqueous dioxan was qualitatively consistent with the kinetic data of other workers.[110]

The effect of a number of salts on the rate of ionisation of benzhydryl chloride are clearly dependent on the nature of the electrolyte(see TABLE VI.1.). The accelerating effects of anions decrease in the order $ClO_4^- > N_3^- > NO_3^- > Cl^- > OH^-$, and it is particularly noteworthy that F^- and OH^- actually retard the rate.

TABLE VI. 1

The Effect of Electrolytes on the Rate of Ionisation of Benzhydryl Chloride in 70% Acetone at 20°C [a]

Salt Addition (0.05m)	% Increase in Rate
$NaClO_4$	+15.08
$NaBF_4$	+11.96
NaN_3 [b]	+11.20
KBr	+ 9.15
$NaNO_3$	+ 6.85
NaCl	+ 2.38
Me_4NF [b]	- 5.21
NaOH [b, c.]	-13.0

a. Ref. 102 except where stated

b. Initially 0.05 M

c. Present work (from TABLE VI.5)

VL.1.ii. S_N2 Reactions

Salt effects in S_N1 reactions arise from the specific solvent effects and the stabilisation of the polar transition state by a process analogous to ion-atmosphere stabilisation of fully developed ions. The S_N2 process also has a polar transition state, which can be expected to be subject to similar stabilisation, and the bimolecular mechanism is also dependent on solvent composition. Added anions should, therefore, affect S_N2 hydrolysis in much the same way although these effects will probably be smaller. However anions can also act as nucleophilic reagents and direct reaction between Y^- and RX can therefore be expected to accompany bimolecular solvolysis. Under these conditions the effect of added electrolyte en the overall rate of destruction of the substrate will depend on the nucleophilic power of the added anions. Attempts have been made to treat nucleophilic power quantitatively[111] but this quantity can vary with reaction conditions and the reaction under consideration. Nevertheless, in aqueous organic solvents and for the reagents now employed, nucleophilic power usually decreases along the series $N_3^- > OH^- > Cl^- > NO_3^- > H_2O > ClO_4^-$ which is quite different from the order of specific salt effects observed for S_N1 hydrolysis (see P. 90).

In view of Hammond's results (see P.29), the effects of added electrolytes on the rate of destruction of benzyl and m-chlorobenzyl toluenesulphonate were re-examined.

VI. 2. Salt Effects in the Solvolyses of Sulphonates

The interpretation of the effect of perchlorate, nitrate and chloride ions on the decomposition of benzyl and m-chlorobenzyl toluenesulphonates (TABLE VI.2,) obtained in the present work are quite unambiguous.

The accelerating effect of anions decreases in the order $Cl^- > NO_3^- > ClO_4^-$ which is the order of nucleophilic power (see P. 92) and the converse of the accelerating effects expected for S_N1 reactions (see P. 90). The accelerating effect of chloride ions on the destruction of the parent compound is approximately 50% for 0.05 m electrolyte, which is much greater than the 2-3% acceleration expected from a medium effect on an S_N1 process. The effect of nitrate ions on the destruction of the m-chloro compound is also too large to be due to a medium effect in an S_N1 reaction. These results are fully consistent with bimolecular attack by NO_3^- and Cl^- on both substrates. Hammond and his co-workers[63 b, g.] concluded that the intervention of NO_3^- and Cl^- in the hydrolysis of benzyl and m-Br-benzyl toluenesulphonate occurred with the fully developed carbonium ion; i.e. by mechanism S_N1.

TABLE VI. 2

The Rate of Decomposition (k_{ROTS}) of $X\text{-}C_6H_4CH_2OTS$ in the Presence of Electrolytes in 70% Acetone

X	Electrolyte	10^5k_{ROTS}	% Change in Rate[c] (0.05M salt)
H[a]	-	3.393	-
	0.1MKCl	6.753	+49.5
	0.1MKNO$_3$	3.985	+ 8.7
	0.26MKNO$_3$	4.847	+ 8.2
	0.1MNaClO$_4$	3.553	+ 2.4
	0.26MNaClO$_4$	3.852	+ 2.6

X	Electrolyte	10^5k_{ROTS}	% Change in Rate[c] (0.05M salt)
m-Cl[b]	-	34.65	-
	$0.1MKNO_3$	58.43	+ 34.3
	$0.26MKNO_3$	81.33	+ 25.9
	$0.1MNaClO_4$	42.31	+ 11.0
	$0.26MNaClO_4$	48.28	+ 7.6

a. At 20.04°C

b. At 69.86°C

c. These figures are calculated assuming that the acceleration varies linearly with concentration of electrolyte.

Their conclusions were based on the observation that

a) the addition of electrolytes did not increase k_{ROTS} by an amount greater than that expected for the operation of a medium effect and

b) that the rate of production of alcohol, k_{ROH}, was greatly reduced by the addition of electrolytes. Contrary to Hammond's observations, the results in TABLE VI.2 show that the increase in k_{ROTS} is very much greater than that expected from a medium effect. Moreover, the results on which the figures in TABLE VI.2 are based show indisputably that k_{ROH} is not reduced by the addition of electrolytes.

Substrate	Electrolyte	$10^5 k_{ROH}$
$C_6H_5CH_2OTS$ at 20°C	-	3.393
"	0.1 KCl	3.307
"	0.1 KNO_3	3.433
"	0.26 KNO_3	3.546
m-Cl-$C_6H_4CH_2OTS$ at 70°C	-	34.65
"	0.1 KNO_3	44.23
"	0.26 KNO_3	46.76

If the reaction with the anions occurs by mechanism S_N2, k_{ROH} remains virtually unaltered (see App.VII2).

Professor Hammond has now found errors of calculation of some of his results and the corrected figures in these cases are in agreement with the data now reported. He did not, however, find errors in the other results which form the basis of his mechanistic conclusions and it was therefore decided to obtain further information on the effect of added chloride ions on the solvolysis of a series of p-X-benzyl toluenesulphonates.

If the reaction of RX with Cl^- and water occurs entirely by mechanism S_N1, both processes proceed via the fully developed carbonium ion. The organic chloride and alcohol will then be formed in the same proportion irrespective of the nature of the leaving group. It can be shown (see AppVII2) that under these conditions the ratio, A, $= \frac{1}{[Cl^-]} \frac{[RCl]}{[ROH]} = \alpha_{Cl}$, where the

/96...

mass law constant, α_{Cl} , represents the competion between the Cl^- and water for the fully developed carbonium ion, R^+. On this view one would expect that A, for the reaction of sulphonates in the presence of Cl^-, should decrease with decreasing stability of R^+. Moreover, in some of the compounds now examined independent estimates of α_{Cl} were available from experiments with the corresponding organic chlorides, thus providing a further check on the interpretation of the results.

If however, attack of Cl^- on the sulphonates occurs by mechanism S_N2, $A > \alpha_{Cl}$ and A will not increase with increasing stability of R^+. The relevant results are shown in TABLE VI.3

TABLE VI.3.

The decomposition of ROTS in 70% Acetone at 25°C in the Presence of Chloride Ions.

R	$A = \frac{1}{[Cl']} \frac{RCl}{ROTS}$ [a]	$\alpha_{Cl'}$ [b]
$C_6H_5CH_2$	10.8[c]	-
iPr	4.1	-
$pMeC_6H_4CH_2$	3.0	-
$pNO_2C_6H_4CH.Ph$	0.6	0.5
$pPhOC_6H_4CH_2$	1.3	0.6
$pMeOC_6H_4CH_2$	2.7[c.d.]	4.0

a. From Sulphonates

b. From Chlorides

c. At 20°C

d. Anomolous result, but this ester is very unstable and the result may be due to some decomposition of the substrate prior to the experiment.

where the compounds have been arranged in order of increasing stability of R^+. It can be seen that the requirements of S_N1 reaction are not met. For the first four compounds listed, A decreases on going down the table and its value is greater than that of α_{Cl} when R is p-$PhOC_6C_4CH_2$. For p-nitrobenzhydryl compounds, however, which are sterically unfavourable to bimolecular attack by nucleophiles, $A = \alpha_{Cl}$ as expected for the operation of mechanism S_N1.

These results confirm the earlier conclusions (see P. 93) that nucleophiles react bimolecularly with toluenesulphonates. It is noteworthy that bimolecular reaction also occurs between anions and p-phenoxy- and p-methoxy- benzyl chlorides which undergo S_N1 hydrolysis. It must be stressed that bimolecular reaction between nucleophilic anions and the present sulphonates does not necessarily suggest that hydrolysis is by mechanism S_N2.[15,40] It does, however, remove the previous obstacle (see Section I.7.i.) to the mechanistic conclusions based on $\Delta C^{*}/\Delta S^{*}$ and ΔS^{*}.

The rates of bimolecular attack of chloride ions on benzyl toluenesulphonate is greater in 50% acetone (6.45×10^{-4} $(m/l)^{-1}$ sec^{-1}) than in 70% acetone (3.20×10^{-4} $(m/l)^{-1}$ sec^{-1}). This is contrary to what is expected for a simple S_N2 ion-dipole reaction where charge concentration is greater in the initial than the transition state.[113] This would suggest that the transition state for this ion-dipole reaction, although still essentially an S_N2 process, has an appreciable contribution from structure III (see P. 13). This would then give rise to an increase of charge in the activation process and to the observed solvent effect.[114]

VI.3. Solvolysis in the Presence of Base

As bimolecular attack of chloride and nitrate ions on benzyl sulphonates has been demonstrated, it is reasonable to expect that this mechanism would also apply for reaction with the stronger nucleophile, hydroxide ions. It has been reported, however, that the solvolysis of benzyl sulphonate is not catalysed by this base.[63b] A possible explanation was proposed by Tommila.[61] The high solvation of the initial state of the sulphonate substrate may shield the reaction centre from the large, hydrated, hydroxide ions. Bimolecular reaction with the smaller halide ions and with water from the solvation shell might still occur.

Work on the effect of added hydroxide ions in S_N1 hydrolysis in aqueous acetone had been started in this department but was discontinued when anomolous results were obtained.[110] It was, therefore, necessary to study the unusual behaviour of alkaline aqueous acetone and establish a method of obtaining reliable kinetic data. The details of this preliminary study are given in Section VII.8.

The rates of solvolysis of benzyl toluenesulphonate in alkaline aqueous acetone (TABLE VI.4) demonstrate quite clearly that a second-order process (rate co-efficent, k_2) which represents the bimolecular attack of the base on the substrate, occurs simultaneously with the first-order reaction with solvent (rate co-efficient, k_1). The first-order rate is probably depressed slightly, as expected, but the rather large errors in k_1 and k_2 make a detailed analysis impossible.

The relative rates of bimolecular attack by hydroxide, chloride and nitrate ions on benzyl toluenesulphonate are given below.

Anion	$10^4 k_2$ ($m/l^{-1} sec^{-1}$)
OH^-	4.79
Cl^-	3.36
NO_3^-	0.592

The differences between the rate co-efficients is less than that which would be expected from the nucleophilic powers of the anions[111a] and it may well be that this reduced sensitivity of benzyl toluenesulphonate to nucleophilic attack is due to some heterolysis of the substrate prior to bimolecular attack by lyate ions.

VI.4 Hydroxide Ions in the S_N1 Solvolysis of Chlorides

Although the retarding effect of hydroxide ions has been reported on a number of occasions, the effect had not been demonstrated in aqueous acetone. In order to ensure that the second order process does not arise from an accelerating salt

/100...

TABLE VI.4

The Hydrolysis of Benzyl Toluenesulphonate in 70% Acetone at 20.19°C in the Presence of Hydroxide Ions.

k_1 and k_1° in $\sec^{-1}$

k_2 in $\sec^{-1}$ $(m/l)^{-1}$

Electrolyte	10^5k_1	$k_1/k_1^{\circ b}$	10^4k_2
-	2.582	-	-
0.02062N NaOTS	2.590	1.0031	-
-	3.352^a	-	-
0.01877N NaOTS	3.362	1.0028^a	-
0.01877N NaOH	3.288±0.114	0.981±0.035	5.029±0.876
-	3.088^a	-	-
0.01922N NaOTS	3.017	1.0029^a	-
0.01922N NaOH	2.997±0.036	0.996±0.014	4.553±0.295

a. Calculated from the rate of solvolysis in the presence of NaOTS resulting from the neutralisation of the base with the appropriate acid,

b. k_1° is the first order rate in the absence of electrolyte.

effect, which diminishes as the base is used up, the effect of hydroxide ions on the rate of S_N1 hydrolysis of chlorides was studied.

Two organic chlorides were studied, benzhydryl and p-methoxybenzyl chlorides. The latter chloride is likely to react bimolecularly with hydroxide ions, since S_N2 reaction with other anions had been demonstrated,[40] but steric requirements make this unlikely in the former case.

These two halides have been studied extensively in the presence and absence of electrolytes.[104, 24.] Both compounds are hydrolysed by mechanism S_N1 and show a striking resemblance to each other with respect to reaction rates, solvent effects and salt effects. It was, therefore, felt that the effect of hydroxide ions on the rate of ionisation of benzhydryl chloride could be used to compute the similar effect for p-methoxybenzyl chloride.

The rate of hydrolysis of benzhydryl chloride is depressed appreciably by hydroxide ions whereas virtually no change of rate is observed with p-methoxybenzyl chloride (TABLE VI.5.).

TABLE VI.5.

The Hydrolyses of Ph_2CHCl and $pMeOC_6H_4CH_2Cl$ in 70% Acetone at 20.19°C in the Presence of Hydroxide Ions.

Substrate	OH' [b]	10^4k_1
Ph_2CHCl	-	3.715[a]
	0.01758	3.545
$pMeOC_6H_4CH_2Cl$	-	2.974[a]
	0.02147	2.980

a. Calculated (See TABLE VI.4.).

b. Initial concentrations.

The depression of the rate of benzhydryl chloride is consistent with an effective solvent change as a result of preferential solvation of the base by water in the binary solvent (see P. 90). An effect of similar magnitude is expected for the S_N1 hydrolysis of the p-methoxy compound. In fact the observed first order rate is not depressed, suggesting that bimolecular attack by the base is occurring. The rate of this attack is so much less than for the benzyl tolunesulphonate (see TABLE VI.4.) that the second - order rate constant could not be estimated with any degree of precision.

It can be concluded that hydroxide ions give a negative salt effect in S_N1 hydrolysis in aqueous acetone. The bimolecular component of the solvolysis of benzyl toluenesulphonate in the presence of the base must, therefore, be due to S_N2 attack on the substrate. Bimolecular attack of hydroxide ions on p-methoxybenzyl chloride also occurs although reaction with the solvent is unimolecular.

VI.5. Theoretical Treatment of Specific Salt Effects

The retarding effect of hydroxide ions in the S_N1 hydrolysis of benzhydryl chloride in aqueous acetone can be combined with the results of hydrolysis in the presence of other salts[104] to obtain information about specific salt effects.

It has been suggested that specific salt effects are due to changes of effective solvent composition as a result of differential solvation of the added ions.[105b] Grunwald[77] deduced, from the effect of solvent changes on the standard partial molar free energies of electrolytes in aqueous dioxan, that solvation by both solvent species was important. It was suggested that small cations were solvated appreciably by the organic species while small anions were predominently hydrated though solvation of perchlorate by dioxan was not ruled out. The predicted degrees of solvation of the various salts treated agreed qualitatively with their effects on the rates of solvolysis.

The kinetic effect of changing electrolyte concentration is twofold.[110] In the presence of electrolyte at concentration, c, the effective solvent composition, represented by $\mathcal{X}$, will be different from the formal value, x,. Very small changes of c, dc, will alter the rate due to changes of ionic strength at constant solvent composition, $\mathcal{X}$, and to changes of $\mathcal{X}$ as a result of the solvation of the electrolyte.

$$\frac{d\ln k}{dc} = \left(\frac{\partial \ln k}{\partial c}\right)_{\mathcal{X}} + \left(\frac{\partial \ln k}{\partial \mathcal{X}}\right)_{c} \frac{d\mathcal{X}}{dc} \qquad \text{VI.1.}$$

The first term on the right-hand side of Eqn. VI.1 can be identified with the ionic-strength term of the Hughes - Ingold approach.[4b]

/104...

$$\left(\frac{\partial \ln k}{\partial c}\right)_{\mathcal{X}} = A\sigma \qquad \text{where } A = 2.10 \times 10^{6} / D^{2}T^{2}$$

If the change in rate due to solvent changes is the same in the presence or absence of electrolytes

$$\left(\frac{\partial \ln k}{\partial \mathcal{X}}\right)_{c} = \left(\frac{\partial \ln k}{\partial \mathcal{X}}\right)_{c\,=\,0} = \left(\frac{\partial \ln k}{\partial x'}\right)_{c\,=\,0} \cdot \frac{dx'}{d\mathcal{X}} \qquad \text{VI.2}$$

Hence

$$\frac{d\ln k}{dc} = \left(\frac{\partial \ln k}{\partial c}\right)_{\mathcal{X}} + \left(\frac{\partial \ln k}{\partial x'}\right)_{c\,=\,0} \cdot \frac{d\mathcal{X}}{dc} \frac{dx'}{d\mathcal{X}} \qquad \text{VI.3}$$

$$= \left(\frac{\partial \ln k}{\partial c}\right)_{\mathcal{X}} + \left(\frac{\partial \ln k}{\partial x'}\right)_{c\,=\,0} \frac{d\ln^{a'/a_2}}{dc} \frac{d\mathcal{X}}{d\ln a'/a_2} \cdot \frac{dx'}{d\mathcal{X}}$$

$$= A + B' \frac{d\ln a'/a_2}{dc} \qquad \text{VI.4}$$

where a' and a_2 are activity co-efficients of the two solvent species. Only $d\ln(a'/a_2)/dc$ depends on the nature of the electrolyte and for small concentrations of electrolyte it seems reasonable to assume that $d\ln(a'/a_2)/dc = \left[\ln(a'/a_2)/dc\right]_{c\,=\,0}$ and thermodynamic arguments [115] have shown that

$$\frac{1000}{M_{12}} \left(\frac{d\ln a/a_2}{dc}\right)_{c=0} = \frac{2}{RT} \frac{d\mu^{\circ}+\pm}{dx_1} \qquad \text{VI.5}$$

where $M_{12} = x_1 M_1 + x_2 M_2$, the molar weight of the binary solvent. $\mu^{\circ}\pm$ is the mean ionic standard chemical potential of the electrolyte. Value of $d\mu^{\circ}\pm/dx_1$ have been evaluted for a number of electrolytes in 50% aqueous dioxan. They have been interpreted in terms of solvation by dioxan and water in the sense that increasing values of $-d\mu^{\circ}\pm/dx_1$ represent increased solvation by the water.

Combining Eqns. VI.4 and VI.5

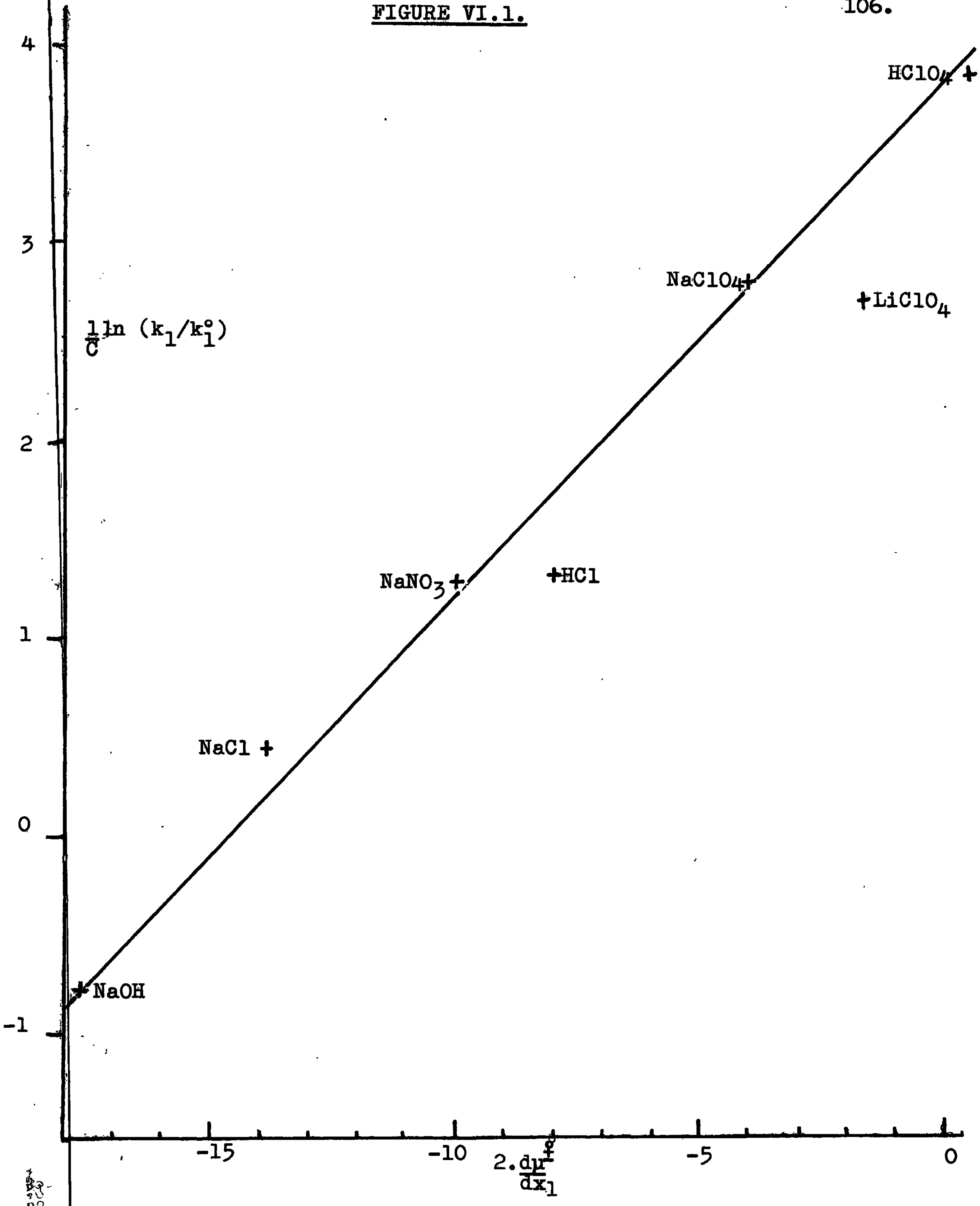
$$d\ln k/dc = A + B.\ d\mu^{\circ}\pm/dx_1 \qquad \text{VI.6}$$

Assuming lnk varies linearly with c over the experimental range, dlnk/dc can be equated with the macroscopic value $\frac{1}{c}.\ln(k_1/k^{\circ}_1)$ where k_1 and k°_1 refer to the rates of ionisation when c = 0.05M and zero respectively. A check of the validity of Eqn.VI.6 suffers from the disadvantage that the rate data in 70% acetone must be compared by values of $d\mu^{\circ}\pm/dx_1$ which refer to aqueous dioxan. On the other hand dioxan can be expected to parallel acetone in its capacity for solvating fully developed ions. FIG.VI.1 shows the linear relation between $1/c.\ln(k_1/k^{\circ}_1)$ and $d\mu^{\circ}\pm/dx_1$ which is predicted by Eqn.VI.6

This treatment assumes that $d\mu^{\circ}\pm/dx_1$ follows the same sequence in aqueous acetone and aqueous dioxan and there is

/106...

FIGURE VI.1.



4
3
2
1
0
-1
$\frac{1}{C}\ln (k_1/k_1^\circ)$
HClO$_4$
NaClO$_4$
LiClO$_4$
NaNO$_3$
HCl
NaCl
NaOH
-15
-10
-5
0
$2.\frac{d\mu_f^\circ}{dx_1}$

further qualitative support for this view and for the present interpretation of kinetic salt effects. Perchlorate ions are comparatively highly solvated by dioxan and the solubility of sodium perchlorate in acetone suggests that here too, solvation by the organic species is appreciable. The large acceleration of the rate of ionisation by this anion is in qualitative agreement with this view.

H_3O^+ ions are relatively more heavily solvated by the organic species than the alkali metal ions in dioxan. It is reasonable to expect the same effect in acetone as H_3O^+ does not differ greatly from H_2O and the latter interacts strongly with acetone. The greater acceleration of S_N1 hydrolysis by acids than by the corresponding alkali salts, is predicts by this interpretation. The fluoride ion is expected to be heavily hydrated in aqueous solvents and therefore, to have a negative $\frac{d\mu^{\ddagger}}{dx_1}$. Its effect on the rate of ionisation in aqueous acetone (see TABLE VI.1) lead to the same conclusion. Hydroxide ions spread their charge over a number of water molecules, i.e. they are heavily hydrated. Little effect from the organic species is to be expected, be it acetone or dioxan; this is reflected in the highly negative value of $d\mu^{\ddagger}/dx_1$. The rate depression which is observed also leads to this conclusion.

/108...

The specific salt effects observed for S_N1 reactions in mixed solvents are, thus, completely consistent with the suggestion of Hammett that specificity arises from the preferential solvation of the added ions. The present work with hydroxide ions in S_N1 hydrolysis further confirms this original postulate.

/109...

CHAPTER VII

EXPERIMENTAL

VII.1. Identification and Estimation of Purities of Halides and Sulphonates

Infra red spectra of the majority of the sulphonates were obtained and compared with the known spectra of the alcohols or halides from which they were obtained. The $-SO_2-$ group was identified by two strong bands at approximately 1360 cm^{-1} and 1180 cm^{-1}. Tipson[132] observed these bands for a variety of compounds of general formula $ROSO_2R^1$ and Robinson[133] also regarded them as characteristic of the $-SO_2-$ group. Materials were also identified by examination of their physical properties when these were known.

Purities of hydrolysable materials were estimated by determination of the acid produced by complete hydrolysis of weighed samples. Purities of 99% or better were normally obtained and samples of the same ester from separate preparations hydrolysed at the same rate. Sulphonates obtained from halides were shown to be free from halogen. The purity of p-methoxybenzyl toluenesulphonate could not be determined with any accuracy since the solid was found to decompose above -35°C. However, a number of separate preparations gave good first-order rates of hydrolysis, consistent among themselves; they contained no halide.

The pure alkyl sulphonates and the p-nitro- and m-chlorobenzyl compounds were stable at room temperature. All the other sulphonates were not stable at this temperature and decomposed to give coloured products. The rate of decomposition in the pure state appeared to parallel the rate of hydrolysis; e.g. p-methoxybenzyl toluenesulphonate quickly formed a bright crimson mass even at -30°C. The presence or absence of light, oxygen and nitrogen appeared to have no effect on the rate of decomposition. These unstable sulphonates were, therefore, stored in dry ether at -20°C (p-methoxybenzyl sulphonate in dry acetone at -70°C), the solvent being removed under reduced pressure immediately before use.

VII.2. Preparation and Purification of Materials

Three methods were employed for the preparation of organic sulphonates:-

i. Reaction of the appropriate sodium alcoholate with toluenesulphonyl chloride in ether[63a] (Method A).

ii. Reaction of the organic bromide with silver toluenesulphonate in acetonitrile[129] (Method B).

iii. Reaction of the appropriate alcohol with toluenesulphonyl chloride in the presence of pyridine.[116] (Method C).

The preparation of one compound by each of these methods is described in detail below. The experimental conditions employed in all the preparations are summarised in TABLES VII.1 and VII.2.

/112...

Method A Benzyl Toluenesulphonate[63a]

Benzyl alcohol (22 gms) in dry ether (200 mls.) were added slowly to sodium hydride (4.8 gms.); sodium hydride protected by oil was employed as it was found that the oil had no adverse effect. The mixture was refluxed with stirring for 12 hrs. (-20°C) and toluenesulphonyl chloride (38 gms.) in dry ether (200 mls.) added over a period of half an hour. After stirring for 2 hrs. at -10°C and for 1 hr. at room temperature, benzyl toluenesulphonate was obtained as white needles from the filtered ethereal extract at -20°C. The compound was purified by re-crystallisation from petrol (b.pt. 40-60°C.)

The more unstable sulphonates were re-crystallised from cold petrol.

TABLE VII.1

Method A - RONa + $R'SO_2Cl \longrightarrow ROSO_2R'$ + Na Cl

		p-X-$C_6H_4CH_2OH$		
Alcohol	X =	H	Me	PhO
Reaction with sodium hydride (hrs.)		12	12	12
Reaction with $R'SO_2Cl$	mixing	½hr. - 20°C	½hr. - 30°C	½hr. - 30°C
	reaction	2hrs.- 10°C	2hrs.-20°C	3hrs.-25°C
Product	m.pt.°C	58	58	40 (decomp.)
	m.pt.(lit.)	59[63a]	58[63a]	-
	Purity %	99.8	99.7	99.3
	Yield %	85	45	60

/114...

Attempts to prepare t-butyl and p-anisylbenzyl esters by this method were unsuccessful. Previous attempts[61, 130] to prepare the t-butyl compound had also failed, probably because elimination occurs. The failure to obtain the p-anisyl compound may have resulted from the low solubility of the alcohol in ether; the reaction in benzene was also not successful, probably for the same reason.

Method B p-Anisylbenzyl Toluenesulphonate[116]

A solution of p-anisylbenzyl bromide in acetonitrile was added to a solution of excess silver toluenesulphonate in the same solvent. The mixture was left in the dark for a day and filtered. The solvent was removed under reduced pressure at 0°C and the residue extracted with ether. The product was isolated and purified by the techniques described in Method A.

Acetone, ether, dioxan, nitromethane and liquid sulphurdioxide were investigated as solvents for this reaction, but without success.

Method C p-Nitrobenzyl Toluenesulphonate[116]

p-Nitrobenzyl alcohol (10 gms.) in dry pyridine (100 mls.) were cooled to - 5°C. Toluenesulphonyl chloride (1.1 equivalents) were added in one portion and the stoppered flask swirled till all the chloride had dissolved. The reaction mixture was maintained at 0°C for 2 hours before 10 mls (in 1,1,1,2 and 5 mls.

/115...

TABLE VII. 2

Method B - $RBr + R'SO_2OAg \longrightarrow R'SO_2OR + AgBr$

(figures in parenthesis refer to the values in the literature)

R.	Reaction Conditions	Temperature for Removal of MeCN	Product m.pt/n_D^{20}		Purity (%)
$C_6H_5CH_2$	20°C 7 days	20°C	58	(59^{63a})	99.7
i-Pr	20°C 14 "	20°C	1.5025	(1.5028^{129})	99.1
m-$ClC_6H_4CH_2$	20°C 14 "	20°C	82	(82^{63d})	99.0
p-$MeC_6H_4CH_2$	20°C 1 day	0°C	58	(58^{63a})	100.1
p-$PhOC_6H_4CH_2$	20°C ½ hr.	0°C	40 (decomp)	-	99.6
p-$AnC_6H_4CH_2$	20°C 1 day	0°C	45 "	-	98.5
p-$PhC_6H_4CH_2$	20°C 1 day	20°C	110 "	(114 decomp$)^{63f}$	98.9
p-$NO_2C_6H_4CH.Ph$	20°C ½ hr.	0°C	42 "	-	99.3
p-$MeOC_6H_4CH_2$	-40°C 1 day	-35°C	decomp	-	- *
n-Pr	20°C 1 month	20°C	1.5001	(1.4998^{131})	99.0

* See P.110

/116...

portions at 5 minute intervals) were added, maintaining the temperature below +5°C. Cold 5N H_2SO_4(100 mls) was added and the sulphonate crystallised out. The crystals were filtered off, washed free of pyridine and dried. The crude product was recrystallised from petrol.

m.pt. 104°C (lit[63a] 103 - 104°C) Yield 50% Purity 99.4%

The attempted sulphonation of p-nitrobenzhydrol by this method produced pale yellow crystals (m.pt. 136°C). The 1.R spectrum of this material showed no indication of the sulphonate group (See Sect.VII.1) but peaks corresponding to the nitro group were present. A further peak at 1150 cm^{-1} suggested the possible presence of an ether. Carbon - hydrogen analysis agreed with the formula

$(p\text{-}NO_2C_6H_4CH.Ph)_2O$ Found C = 70.5%, H = 4.6%

Calculated C = 70.9%, H = 4.5%. An ether was produced in the similar reaction of benzhydrol.[118.]

VII.3. Starting Materials

Benzyl Chloride. B.D.H. material was dried ($CaCl_2$) and distilled at reduced pressure, b.pt. 65°C at 15 mm.

Benzyl Alcohol was distilled at reduced pressure; b.pt. 81°C at 3mm.

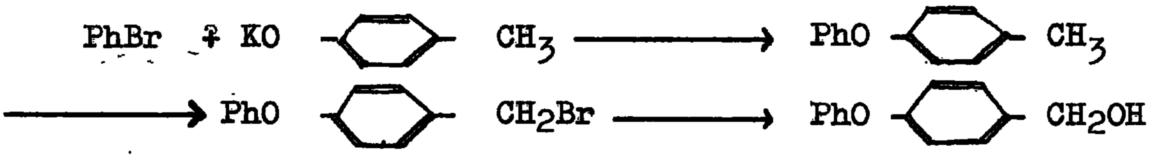
/117...

p-Nitrobenzyl Alcohol. p-Nitrobenzyl bromide was converted to the formate (m.pt. 78°C) by reaction with potassium formate.[117] The formate was hydrolysed in acid to give the alcohol which was re-crystallised from petrol; m.pt. 93°C.

m-Chlorobenzyl Bromide was distilled at reduced pressure; b.pt 76°C at o.5 mm.

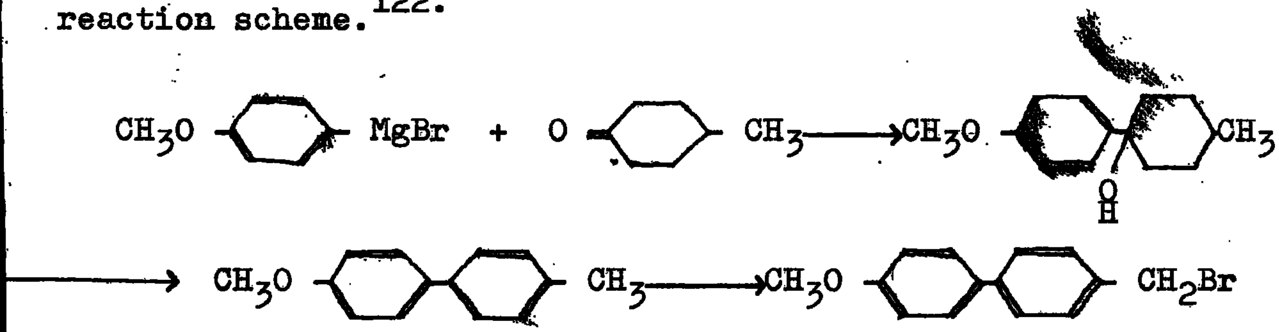
i-Propyl Bromide (Light's) was distilled at 60°C.

p-Phenoxybenzyl Alcohol and Bromide were prepared according to the reaction scheme.[119, 120, 121]

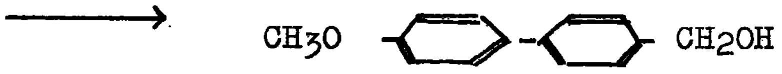


p-Phenoxybenzyl bromide was obtained as a colourless oil on decolourising with alumina (purity 99.0%). Hydrolysis of the bromide in aqueous acetone and re-crystallisation from petrol (b.pt. 40 - 60°C) gave white plates (m.pt. 52°C) of the alcohol.

p-Anisyl Alcohol and Bromide were prepared according to the reaction scheme.[122]



/118...

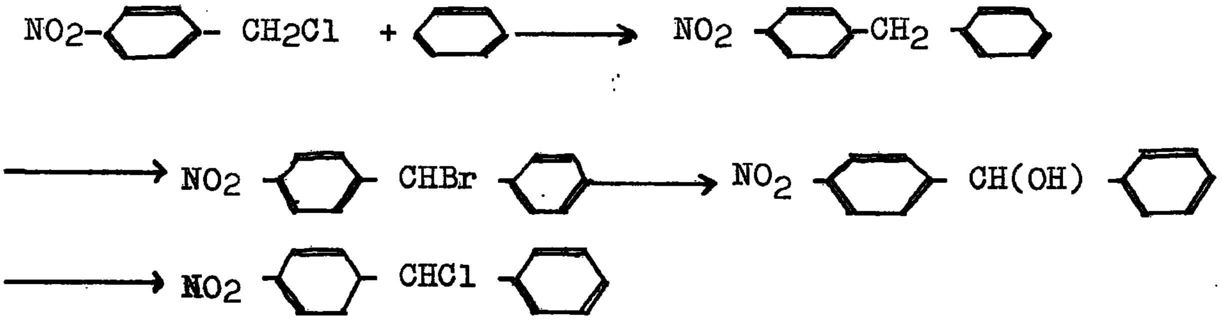


p-Anisylbenzyl bromide m.pt.114°C (lit[123] 114°C) with a purity of 100% was hydrolysed to the alcohol which was re-crystallised from ethanol m.pt. 164°C (lit[23] 164°C).

<u>p-Methoxybenzyl Chloride</u> was prepared by chlorinating anisyl alcohol[24, 104, 124]. The chloride was purified by distilling under reduced pressure. b.pt. 93°C at 1mm; N_D^{22} 1.5486, purity 99.3%.

<u>n-Propyl Bromide</u> (Light's) was distilled at 71°C.

<u>p-Nitrobenzhydrol and p-Nitrobenzhydryl Bromide and Chloride</u> were prepared according to the reaction scheme[125, 121].



The bromide was obtained as a pale yellow solid, m.pt 31-32°C (lit 32°C), which on hydrolysis gave the alcohol m.pt 73°C (lit[86] 73 - 74°C). The chloride had a melting point of 44°C (lit[86] 43.5 - 44.5°C).

<u>p-Phenylbenzyl Bromide</u> was prepared in a similar way to p-anisylbenzyl bromide, starting with cyclohexanone and the Grignard reagent of p-bromotoluene.

m.pt. 85°C (lit[125] 85°C) Purity 99.7%

<u>p-Methylbenzyl Alcohol</u> was obtained by reducing ethyl p-toluate (N_D^{20} 1.5123) with lithium aluminium hydride; m.pt. 61.5°C (lit[24] 61°C).

<u>Sodium Perchlorate</u> (Analar B.D.H.) was re-crystallised from aqueous dioxan and dried to constant weight in a pistol at 100°C and 0.5 mm pressure.

<u>Potassium Nitrate</u> (Analar B.D.H.) was dried at 120°C for 8 hours.

<u>Potassium Chloride</u> (Analar B.D.H.) was dried at 120°C for 1 day.

<u>Sodium Hydroxide</u> (Analar B.D.H.) material was used.

<u>Sodium Toluenesulphonate</u> was prepared from the Analar acid, and dried at 100°C and 0.5 mm.

VII.4. <u>Solvents</u>

Acetone employed in the solvent for kinetic runs was obtained from analar material by refluxing with sodium hydroxide and potassium permanganate for 2 hours, and distilling.[17] It was subsequently fractionated from hydroquinone.

Mixed aqueous solvents of "x%" acetone were prepared by mixing "x" volumes of acetone with "100-x" volumes of distilled water which had been passed through a mixed resin ion - exchange column. As the solvents were made up by volume, different batches of the same solvent (<u>e.g.</u> 70% acetone) did not have precisely the same composition. Each batch was, therefore, monitored by noting its rate of reaction with some reference compound (e.g. benzhydryl chloride) and applying the necessary correction factor to ensure that all rate co-efficients for any stated solvent composition referred to the same batch.

Acetone employed for quenching the reaction and for titrations was prepared by refluxing the commercial material with sodium hydroxide and potassium permanganate for 2 hours and then distilling it. Before use the indicator, lammoid, was added and the solution neutralised.

VII.5. Thermostats

The thermostats employed were of conventional design. Temperatures below 0°C were obtained by using a refrigeration unit to cool the bath (containing ethylene glycol/water) to just below the required temperature. The 10°C thermostat was cooled by circulating ice-cold water through a copper coil immersed in the bath. Temperature control of ± 0.01°C was obtained using contact thermometers or toluene - mercury regulators. The 0°C thermostat was a well stirred ice-water mixture; no temperature variation was observed. Temperatures were measured with thermometers, standardised by the National Physical Laboratory to ± 0.02°C for temperatures above - 10°C and to ± 0.1°C below that temperature.

VII.6. Methods of Rate Measurement

The hydrolysis of halides and sulphonates was usually studied in initially 0.01 M solution and followed by noting the development of acidity; the most rapid reaction (the hydrolysis of p-methoxybenzyl toluenesulphonate) was carried out in initially 0.002 M solution and followed by noting the conductance. Readings after completion of the reaction (i.e. after more than ten "half-lives" had elapsed) gave the initial concentration of the substrate.

Kinetic runs at moderate temperature were carried out in stoppered flasks, the substrate being added after the solvent had attained the temperature of the thermostat. Five or ten mls. samples were removed from time to time, quenched by running into cold, neutral (lacmoid) acetone, and titrated with standard sodium hydroxide. The first determination was taken to refer to "zero time".

For runs above 40°C a sealed ampoule technique was employed, the ampoules being allowed to reach the temperature of the thermostat before the first reading was taken. Tubes were removed at various times, rapidly cooled to - 70°C to stop reaction, cleaned, broken under neutral acetone and titrated.

The relatively rapid hydrolysis of p-methoxybenzyl toluenesulphonate was studied in a conductance cell which consisted of a 200 ml. flask with baffled sides to assist the stirring provided by a 1200 r.p.m. motor. The electrodes were bright platinum sheet, 0.5 m.m. thick, 1 sq. cm. area and 0.5 m.m. apart. They were supported by stout platinum wire sealed into glass. About 150 ml. of solvent were allowed

/122...

to attain the temperature of the thermostat and the sulphonate, dissolved in 0.4 ml. dry acetone, was added as rapidly as possible, with stirring. The appropriate quantity of water had previously been added to ensure that the composition of the solvent remained constant. Check experiments showed that complete mixing occurred in less than two seconds under these conditions.

The use of a Pye conductance bridge (Type 11700) allowed the determination of the time required for the resistance of the reaction mixture to attain the value of an external resistance. The use of a series of external resistances, each of which could be switched into the circuit rapidly, allowed 15 - 17 determinations to be carried out in each kinetic run. The time required for each resistance to be reached was determined by using a cine - camera to record simultaneously the oscilloscope trace and a mechanical counter which was operated by a synchronous motor and indicated times to 0.1 sec. Concentrations of p-toluenesulphonic acid, corresponding to the various resistance values, were obtained by determining the resistances of known concentrations of this acid. Reproducable calibration curves were obtained providing a small quantity of the acid was present initially, (ca. 10^{-4} M). p-Methoxybenzyl alcohol, the other reaction product, had no effect on the resistance of the solutions.

VII. Methods of Calculation and Errors

First-order rate co-efficients were calculated from the integrated rate equation

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

where t is the time in seconds and a and a - x are the concentrations of organic ester at times t = 0 and t = t respectively. First order rate co-efficents were obtained in most runs over 75 - 85% reaction. Experiments were duplicated or triplicated and the standard error $\sigma(k)$ of the final mean rate co-efficient, km, was obtained from

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

where n is the total number of determinations of k, treating the two or three runs together. Individual values of k differing from km by more than $2\frac{1}{2}\sigma_e$, where

$$\sigma_e = n^{\frac{1}{2}} \sigma(k)$$

were rejected and the new values of k_m and $\sigma(k)$ found.

The activation energy, E, was calculated from the values of k at adjacent temperatures and refers to the mean of the two temperatures, <u>i.e.</u> $(T_a + T_b) / 2$

$$E = \frac{2.303 \ R \ T_a \ T_b}{T_a - T_b} \log \frac{k_a}{k_b}$$

where k_a and k_b are the first order rate co-efficients at the absolute temperatures T_a and T_b.

The standard error of E, $\sigma(E)$ is given by[128]

$$\sigma(E) = \frac{R\, T_a T_b}{T_a - T_b} \left[\left(\frac{\sigma_a}{k_a} \right)^2 + \left(\frac{\sigma_b}{k_b} \right)^2 \right]^{\frac{1}{2}}$$

The entropy of activation, $\Delta S^{\ddagger}$, at $(T_a + T_b)/2$ was obtained from

$$\ln k_a = \ln\left(\frac{\bar{K}}{h} \right) + \ln \frac{T_a + T_b}{2} + \frac{\Delta S^{\ddagger}}{R} - \frac{E}{RT_a} \qquad \text{VII.1}$$

where E refers to $(T_a + T_b)/2$

The standard error in $\Delta S^{\ddagger}$, $\sigma(\Delta S^{\ddagger})$, is approximately given by

$$\sigma(\Delta S^{\ddagger}) = \frac{\sigma(E)}{T}$$

The heat capacity of activation was obtained from

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

and dE/dT was obtained from

$$E = E_o + T.\ dE/dT \qquad \text{VII.2.}$$

by the method of least squares. Equation VII.2 assumes that dE/dT, and hence $\Delta C^{\ddagger}$ are independent of temperature. This assumption appears to be true, within the limits of experimental range.[86] The error in dE/dT, $\sigma(dE/dT)$, was obtained in two ways:-

/125...

i. from the standard error in the slope of the best straight line of E against T using

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

where n is the number of values of E

ii. From $\sigma(E)$ using

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

In all cases the larger value of $\sigma(dE/dT)$ was accepted.

E at any temperature ,T, can be calculated from

$$E = E_m + dE/dT\ (T - T_m)$$

where E_m is the mean of the activation energies and T_m the mean of the temperatures to which the values of E refer

$\Delta S^{\ddagger}$ at any temperature can be obtained from

$$\Delta S^{\ddagger} = \Delta S^{\ddagger}_m + 2.303\ \Delta C^{\ddagger}\ (\log T - \log T_m)$$

where $\log T_m$ is the mean of the values of $\log (T_a + T_b)/2$ and $\Delta S^{\ddagger}_m$ is the entropy of activation at this temperature, T_m.

The rate at any temperature, T, can be calculated from E and $\Delta S^{\ddagger}$ at this temperature using equation VII.1 with $T_a = T_b = T$

The Standard error in $\Delta C^{\ddagger}/\Delta S^{\ddagger}$, $\sigma(\Delta C^{\ddagger}/\Delta S^{\ddagger})$, was obtained from

$$\sigma\left(\frac{\Delta C^{\ddagger}}{\Delta S^{\ddagger}}\right) = \frac{\Delta C^{\ddagger}}{\Delta S^{\ddagger}}\left\{\left[\frac{\sigma(\Delta C^{\ddagger})}{\Delta C^{\ddagger}}\right]^2 + \left[\frac{\sigma(\Delta S^{\ddagger})}{\Delta S^{\ddagger}}\right]^2\right\}^{\frac{1}{2}}$$

where $\sigma(\Delta C^{\ddagger}) = \sigma(dE/dT)$

/126...

VII.8 Hydrolysis in the Presence of Hydroxide Ions

The rate of hydrolysis in the presence of hydroxide ions was examined in order to determine whether these ions underwent bimolecular reaction with benzyl toluenesulphonates. The parent compound was examined, and the hydrolyses of diphenylmethyl chloride and p-methoxybenzyl chloride were also studied in order to determine the effect of these ions on the rate of S_N1 hydrolysis (diphenylmethyl chloride is sterically unfavourable to bimolecular attack by reagents but p-methoxybenzyl chloride is not). The alkaline solutions were prepared by adding sodium hydroxide, or the metal, to aqueous acetone. Samples of the reaction mixtures were quenched in acetone containing excess acid and back-titrated with standard sodium hydroxide with lacmoid as indicator.

VII.8.i. Diphenylmethyl Chloride

The initial results obtained with diphenylmethyl chloride are shown in TABLE VII.3. It can be seen that hydrolysis is accelerated by hydroxide ions, contrary to many earlier reports that lyate ions retard S_N1 reaction.[19,107,136,137].

However the results show several anomolous features. The acceleration caused by hydroxide ions could conceivably arise from a positive salt effect or from the incursion of bimolecular (S_N2) reaction but both these possibilities demand a decrease in the observed first-order rate co-efficient (k) as reaction proceeds (since hydroxide ions are removed under these conditions) and a roughly linear relation between k and

/127...

TABLE VII.3

The Hydrolysis of Benzhydryl Chloride in Alkaline 70% Aqueous Acetone at 20°C.

Run	Salt Addn.	10^4k	% Change in Rate
1.	-	2.529[a]	-
2.	0.0092N NaOH	3.125[a]	+ 23.57
3.	0.22N NaOH	3.078[a]	+ 21.71
4.	0.030N NaOH	2.965[a]	+ 17.24
5.	0.0099N Na_2CO_3	2.677[a, b.]	-
6.	0.0214N NaOH	2.798[c, d.]	+ 10.6
7.	0.0292N NaOH	3.020[c, e.]	+ 19.4

a. Solvent freed from CO_2 by refluxing under N_2

b. Falling rates

c. Solvent distilled from NaOH and composition adjusted to 70% by addition of water

d. Run commenced 15 minutes after addition of NaOH to solvent

e. Same as d. but 16 hours.

the concentration of hydroxide ions. Neither of these requirements are met. Individual k's usually had the same value in any one kinetic run and there was no apparent relation between k and $[OH^-]$. Anomolous results for hydrolysis in aqueous acetone had previously been reported.[19, 110].

/128...

Acetone usually contains relatively large amounts of carbon dioxide but the possibility of interference by sodium carbonate (formed by reaction with the hydroxide) must be rejected. The anomalies persisted in solvents from which carbon dioxide had been removed by distillation under nitrogen before use, and the addition of the carbonate to the neutral solvent had only a small effect on the rate.

Similarly the results cannot be explained by assuming the presence in the solvent of an impurity which reacts with the hydroxide ions to form a species capable of rapid reaction with the organic halide. Distillation of the solvent over sodium hydroxide and adjusting the composition back to 70% by the addition of water did not remove the anomoly.

It seems likely that the present results arise from the condensation of acetone to form diacetone alcohol. This condensation is catalysed by base[134] and the initial condensation product may undergo dehydration to form mesityl oxide and water, or by further condensation and de-hydration, form iso-phorone. These processes would, in effect, increase the water content of the solvent, yielding increased rates of hydrolysis, as observed. Moreover the equilibrium between acetone and its dimer and the subsequent de-hydration is independent of the base concentration. Confirmation of this interpretation arises from the observation that the addition of sodium hydroxide to the solvent first causes a relatively rapid change of volume (probably corresponding to the dimerisation) followed by a slow change which probably

/129...

corresponds to further condensation and dehydration. Alkaline solutions which have been kept for several weeks became yellow and the isolated coloured material showed the C = O frequency of iso-phorone.[135]

As the dilatometric measurements had suggested that the solvent composition changes only very slowly after several hours standing, kinetic runs were carried out in solvents which had been made alkaline 36 hours before use. As this solvent no longer had the composition of "70%" acetone, a portion of it was neutralised with aqueous hydrochloric acid, after addition of the amount of acetone required to ensure that the total added liquid corresponded in composition to "70%" acetone. The volume of this added liquid was small and was unlikely to affect the composition of the solvent significantly. The effect of hydroxide ions on the rate of hydrolysis was then obtained by comparison with the rate in the neutralised solvent _via,_ the known effect of sodium chloride on the rate .[104] The results showed the deceleration in the presence of hydroxide ions. First-order rate co-efficients were constant over the course of any one run (see Experiment 96 Appendix V.II.1.) within the limits of experimental error. This probably arises from the partial cancellation of the reduction of the retarding effect of hydroxide ions by the increased mass-law retardation by chloride ions as the reaction proceeds.

VII. 8.ii. p-Methoxybenzyl Chloride

Methods analogous to those described in Section VII.8.i.

were employed to study the effect of hydroxide ions on the rate of hydrolysis of p-methoxybenzyl chloride. Good first-order rate co-efficients were again observed (see Experiment 103). Previous work[24, 104] had shown that the salt effect of electrolytes was virtually the same as in the hydrolysis of diphenylmethyl chloride. The retarding effect of hydroxide ions is however significantly less when the substrate is the benzyl compound, suggesting that now some of the overall reaction involves bimolecular attack by the base. The constancy of the first-order rate co-efficients in any one run could arise from the cancellation of the retardation of ionisation and the enhancement of the bimolecular reaction by hydroxide ions.

VII.8.iii <u>Benzyl Toluenesulphonate</u>

The effect of hydroxide ions on the rate of hydrolysis of benzyl toluenesulphonate was studied by methods analogous to those described in Section VII.8.i., except that p-toluenesulphonic acid was employed to neutralise the solvent.

The reaction showed mixed first - and second - order kinetics and yielded an experimental first-order rate co-efficient

$$k_{expt} = \frac{1}{t} \ln \frac{a}{a-x} = k_1 + \frac{k_2}{t} \int_0^t (b - x)\, dt$$

where k_1 and k_2 are the "true" first - and second - order rate co-efficients, a and b are the concentrations of benzyl sulphonate and hydroxide ions at "zero" time, and x, the concentration of product formed at time t. The integral was

/131...

determined graphically, and k_1 and k_2 were obtained as the slope and intercept of the "best" straight line of k_{expt} against $\frac{1}{t}\int_{0}^{t}(b-x).\,dt$ by the method of least squares. Check experiments in "70%" acetone showed that toluenesulphonate ions at the experimental concentrations had only a negligibly small effect on the rate of hydrolysis (see Experiments 98) and the value of k_1 obtained from experiments with added hydroxide ions had almost the same value as the rate co-efficients for hydrolysis in the alkaline solvent which had been neutralised before use.

APPENDIX VII.1

Comparison with Previous Results

Alkyl Toluenesulphonates

The hydrolysis of n-propyl and i-propyl toluenesulphonate does not appear to have been studied in aqueous acetone. Data is, however, available for the benzenesulphonates[61] and the results for the ethyl compounds suggest[130] that

$$E_{ROBs} - E_{ROTs} = 0.24 \text{ Kcals.},$$
$$\Delta S^{*}_{ROBs} - \Delta S^{*}_{ROTs} = 0.29 \text{ cals.}$$

It has been assumed that these differences apply to all alkyl toluenesulphonates and the resulting values for n-propyl and i-propyl are compared in TABLE VII.4 with the present results. All data refers to 50°C and it has been assumed that $dE/dT = 25$ cals./degree irrespective of the compound or the composition of the solvent (see TABLE III.6.)

Considering the assumptions made, and possible inaccuracies in the earlier determinations of activation parameters, the present results are consistent with those previously obtained in different solvents.

/133...

TABLE VII.4

Values of k_1 E and ΔS^{*} for ROTs in Aqueous Acetone at 50°C

R	% Acetone	$10^{6}k(sec^{-1})$	E(Kcal)	$-\Delta S^{*}$(cals)
iPr	42[a]	252.4	22.65	7.05
	50	134.7	21.19	9.76
	61.7[a]	53.03	23.21	8.43
	83.3[a]	5.074	22.72	14.61
	85	3.840	22.30	13.36
n-Pr	56[a]	3.595	21.71	18.42
	50	9.158	21.92	15.92

a. Ref. 130

Benzyl Toluenesulphonates

The rate of reaction of some p-substituted benzyl toluenesulphonates with aqueous acetone was studied by Hammond and his co-workers at 25° and 45° C. The resulting rate co-efficients and activation parameters at 35°C are compared with those from the present work in TABLE VII.5.

Reasonable agreement between rate co-efficients in Hammonds and the present work is obtained. The fairly constant value of E and regular change in ΔS^{*} in the series pNO_2, H, pMe, is common to both sets of results and has been commented on in an earlier part of this thesis (See P. 58). The value of ΔS^{*} obtained by Hammond for the p-phenyl compound appears to be anomalous.

/134...

TABLE VII. 5.

Values of k_1 E and ΔS^{*} for the Hydrolysis of p-X-$C_6H_4CH_2OTs$ in Aqueous Acetone at 35°C

X	% Acetone	$10^6k(sec^{-1})$	E(Kcal.)	$-\Delta S^{*}$(cal)
NO_2	83.3 [63d]	1.507	19.97	22.43
	70	4.333	20.56	18.42
H	85 [63d]	19.68	19.70	18.44
	83.3	27.27	20.40	15.28
	56.6 [63c]	522.6	18.36	15.57
	50	929.2	18.47	14.08
Ph	83.3 [63f]	257.5	22.07	5.40
	70	895.4	19.77	10.39
Me	83.3 [63d]	586.6	20.61	8.50
	70	307.6	18.92	10.68

APPENDIX V.II.2.

The Intervention of Chloride Ions in the S_N1 Hydrolysis of a Toluenesulphonate.

Consider the S_N1 hydrolysis of a toluenesulphonate (ROTs) in the presence of chloride ions. These ions may react directly with the fully developed carbonium ions which will be present (S_N1 reaction) or they may attack substrate molecules before they have undergone hydrolysis (S_N2 reaction). Neglecting reaction between carbonium ions and toluenesulphonate ions, and the hydrolysis or ionisation of any RCl formed, the following processes then occur:-

$$\mathrm{ROTs} \xrightarrow{k_I} \mathrm{R^+ + OTs^-}$$
$$\mathrm{R^+ + H_2O} \xrightarrow{k_{ROH}} \mathrm{ROH + H^+}$$
$$\mathrm{R^+ + Cl^-} \xrightarrow{k_{RCl}} \mathrm{RCl}$$
$$\mathrm{ROTs + Cl^-} \xrightarrow{k_{II}} \mathrm{RCl + OTs^-}$$

Application of the stationary state principle to the highly reactive ion, R^+, yields

$$\frac{d\,[\mathrm{ROH}]}{dt} = [\mathrm{ROTs}]\,\frac{k_I}{1+\alpha_{Cl^-}[\mathrm{Cl^-}]}$$

and

$$\frac{d\,[\mathrm{RCl}]}{dt} = [\mathrm{ROTs}]\,[\mathrm{Cl^-}]\left\{\frac{k_I\,\alpha_{Cl^-}}{1+\alpha_{Cl^-}[\mathrm{Cl^-}]} + k_{II}\right\} \qquad \text{VII.3.}$$

where the mass-law constant, α_{Cl^-}, represents the ratio of the reactivities of chlorides ions and water for the carbonium ion, R^+. In the presence of a large excess of chloride ions, $[\mathrm{Cl^-}]$

remains virtually constant throughout the reaction. Hence

$$\frac{[\mathrm{RCl}]_{\infty}}{[\mathrm{ROH}]_{\infty}} = \frac{d[\mathrm{RCl}]}{d[\mathrm{ROH}]} = [\mathrm{Cl}^-]\left\{\alpha_{\mathrm{Cl}^-} + \frac{k_{II}}{k_I}\left(1 + \alpha_{\mathrm{Cl}^-}[\mathrm{Cl}^-]\right)\right\}$$

from Eqn. VII.3.

<u>i.e.</u> $$A = \frac{1}{[\mathrm{Cl}^-]}\;\frac{[\mathrm{RCl}]_{\infty}}{[\mathrm{ROH}]_{\infty}} = \alpha_{\mathrm{Cl}^-} + \frac{k_{II}}{k_I}\left(1 + \alpha_{\mathrm{Cl}^-}[\mathrm{Cl}^-]\right) \qquad \mathrm{VII.4}$$

The mass-law constant, α_{Cl^-}, is independent of the nature of the leaving group. In some cases, its value was available from previous work on organic chlorides, in others an upper limit could be placed on its value from the expected stability of the carbonium ion, R^+. It was, therefore, possible to employ Eqn. VII.4 to conclude whether any of the formation of RCl occurred bimolecularly. For bimolecular reaction between Cl^- and ROTs, $k_{II} > 0$ and hence $A > \alpha_{\mathrm{Cl}^-}$. If all RCl is formed unimolecularly $k_{II} = 0$ and hence $A = \alpha_{\mathrm{Cl}^-}$.

If reaction between Cl^- and ROTs occurs only by mechanism S_N2 then $\alpha_{\mathrm{Cl}^-} = 0$ and Eqn. VII.3 demonstrates that k_{ROH} is virtually unaltered by the addition of chloride ions (see P.95).

APPENDIX VII 3

Rates, E, $\Delta S^{\ddagger}$, $\Delta C^{\ddagger}$ and $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ for the Solvolyses of Sulphonates

The methods of calculating rate coefficients and activation parameters and their errors are given in VII. 8.

First order rate coefficients, k, are in sec^{-1}

E is in Kcals. $moles^{-1}$.

$\Delta S^{\ddagger}$, $\Delta C^{\ddagger}$ and dE/dT are in cals. $moles^{-1}$. $^{o}K^{-1}$.

/138...

TABLE VII. 6.

The Hydrolysis of Benzyl Toluenesulphonate in 70% Aqueous Acetone

Temp.	$10^{6}k$	10^{3}[illegible]	E(obs)	E(calc.)	$-\Delta S^{*}$
o	1.7111	0.7275			
			20.169 ± .027	20.163	12.98 ± .095
20.59	23.14	3.389			
			19.807 ± .076	19.773	14.32 ± .256
30.06	66.77	2.244			
			19.433 ± .069	19.519	15.62 ± .224
40.08	187.3	2.874			
			19.304 ± .081	19.257	16.09 ± .256
50.26	497.1	2.906			

$\frac{dE}{dT} = -25.98 \pm 2.86$ $\qquad \Delta S^{*}(50°C) = -16.64 \pm .19 \qquad \frac{\Delta C^{*}}{\Delta S^{*}} = 1.68 \pm .17$

$\Delta C^{*} = -27.98 \pm 2.86$ $\qquad E(50°C) = 19.131 \qquad 10^{4}k(50°C) = 4.899$

/139...

TABLE VII. 7.

The Hydrolysis of p-Nitrobenzyl Toluenesulphonate in 70% Aqueous Acetone

Temp.	$10^6 k$	$10^3 \frac{\sigma}{k}$	E(obs)	E(calc.)	$-\Delta S^*$
50.64	21.39	3.50			
			19.973± .09	19.976	20.41± .26
60.15	51.85	1.39			
			19.706± .12	19.699	21.27± .35
69.90	120.8	5.06			
			19.408± .14	19.415	22.19± .40
79.91	270.7	2.72			
			19.333± .08	19.131	23.03± .22
89.70	564.9	1.33			

$\frac{dE}{dT} = -28.72 \pm 2.68$

$\Delta S^*(50°C) = -19.87 \pm .16$

$\frac{\Delta C^*}{\Delta S^*} = 1.55 \pm .14$

$\Delta C^* = -30.72 \pm 2.68$

$E\ (50°C) = 20.31$

$10^6 k(50°C) = 20.28$

/140...

TABLE VII. 6.

The Hydrolysis of p-Methylbenzyl Toluenesulphonate in 70% Aqueous Acetone

Temp.	10^6k	$10^3\frac{\sigma}{k}$	E(obs)	E(calc.)	$-\Delta S^{\ddagger}$
-19.99	2.946	12.5			
			20.243±.18	20.261	5.60± .69
-10.23	13.12	3.24			
			20.022±.06	19.995	6.51± .22
o	55.10	2.61			
			19.722±.05	19.723	7.68± .16
10.13	202.0	1.31			
			19.440±.04	19.49	8.75± .15
20.57	689.1	2.36			

$\frac{dE}{dT} = -26.68 \pm 5.40$ $\Delta S^{\ddagger}(50°C) = -11.95 \pm .91$ $\frac{\Delta C^{\ddagger}}{\Delta S^{\ddagger}} = 2.40 \pm .50$

$\Delta C^{\ddagger} = -28.68 \pm 5.40$ $E(50°C) = 18.534$ $10^4k = 133.3$

/141...

TABLE VII. 9.

The Hydrolysis of p-Phenoxybenzyl Toluenesulphonate in 85% Aqueous Acetone

Temp.	10^6k	$10^3\frac{\sigma}{k}$	E(obs)	E(calc.)	$-\Delta S^{\ddagger}$
-30.15	3.985	4.18			
			20.010 ± .065	19.973	2.56 ± .26
-20.14	20.53	3.30			
			19.649 ± .050	19.699	4.07 ± .19
-10.20	89.93	1.72			
			19.409 ± .047	19.424	5.06 ± .17
0	359.9	2.84			
			19.170 ± .060	19.145	6.0. ± .22
10.14	1274.0	2.75			

$\frac{dE}{dT} = -27.40 \pm 2.74$ $\Delta S^{\ddagger}(50°C) = -10.46 \pm .56$ $\frac{\Delta C^{\ddagger}}{\Delta S^{\ddagger}}(50°C) = 2.81 \pm .30$

$\Delta C^{\ddagger} = -29.40 \pm 2.74$ $\bar{E}\,(50°C) = 17.914$ $10^4k(50°C) = 727.6$

/142...

TABLE VII. 10.

The Hydrolysis of p-Anisylbenzyl Toluenesulphonate in 85% Aqueous Acetone

Temp.	10^6k	$10^3\frac{\sigma}{k}$	E(obs)	E(calc.)	$-\Delta S^{\ddagger}$
-10.02	4.762	3.00			
			20.786±.065	20.802	5.69±.23
0	20.46	3.36			
			20.505±.074	20.515	6.78±.27
10.13	78.99	3.47			
			20.290±.063	20.221	7.62±.22
20.57	284.4	1.86			
			19.892±.055	19.934	8.94±.19
30.27	845.3	2.38			

$\frac{dE}{dT} = -28.51 \pm 2.69$ $\qquad \Delta S^{\ddagger}(50°C) = -11.29 \pm .35$ $\qquad \frac{\Delta C^{\ddagger}}{\Delta S^{\ddagger}}(50°C) = 2.70 \pm .25$

$\Delta C^{\ddagger} = -30.51 \pm 2.69$ $\qquad E\ (50°C) = 19.234$ $\qquad 10^4k(50°C) = 61.57$

/143...

TABLE VII. 12.

The Hydrelysis of p-Nitrobenzylhydryl Toluenesulphonate in 85% Aqueous Acetone

Temp.	10^6k	$10^3\sigma$	E(obs)	E(calc.)	$-\Delta S^{\ddagger}$
-19.94	2.340	3.30			
			21.119 ± .054	21.117	2.61 ± .21
-9.82	11.73	2.44			
			20.890 ± .054	20.893	3.55 ± .19
0	49.28	2.55			
			20.668 ± .044	20.664	4.44 ± .16
10.38	198.6	1.75			
			20.432 ± .041	20.432	5.35 ± .14
20.57	698.7	1.77			

$\frac{dE}{dT} = -22.56 \pm 2.11$

$\Delta S^{\ddagger}(50°C) = -8.10 \pm .35$

$\frac{\Delta C^{\ddagger}}{\Delta S^{\ddagger}}(50°C) = 3.03 \pm .29$

$\Delta C^{\ddagger} = -24.56 \pm 2.11$

$E(50°C) = 19.654$

$10^4k(50°C) = 159.2$

/144...

TABLE VII. 12

The Hydrolysis of Benzyl Toluenesulphonate in 85% Aqueous Acetone

Temp.	10^6k	$10^3\sigma/k$	E(obs)	E(calc.)	$-\Delta S^{\ddagger}$
34.16	17.93	2.28			
			19.531±.054	19.53	18.80±.17
44.09	48.77	1.51			
			19.279±.055	19.28	19.65±.17
54.29	126.4	2.26			
			19.032±.073	19.03	20.46±.22
64.15	297.2	2.34			
			18.799±.076	18.79	21.25±.22
74.55	687.8	2.46			

$\frac{dE}{dT} = -\ 24.55 \pm\ 2.93$ $\qquad \Delta S^{\ddagger}(50°C) = -19.62 \pm .047$ $\qquad \frac{\Delta C^{\ddagger}}{\Delta S^{\ddagger}}(50°C) = 1.35 \pm\ .149$

$\Delta C^{\ddagger} = -\ 26.55 \pm\ 2.93$ $\qquad E\ (50°C) = 19.263$ $\qquad 10^6k(50°C) = 85.88$

/145...

TABLE VII. 13.

The Hydrolysis of iso-Propyl Toluenesulphonate in 85% Aqueous Acetone

Temp.	$10^{6}k$	$10^{3}k$	E(obs)	E(calc.)	$-\Delta S^{\ddagger}$
60.39	11.70	2.30			
			22.830±.073	22.888	14.73±.215
70.49	32.19	2.32			
			22.707±.087	22.629	15.55 ±.250
79.60	75.94	2.39			
			22.385±.075	22.369	16.33±.210
89.73	185.2	1.77			
			22.060±.083	22.096	17.14±.226
99.85	424.6	2.55			

$\frac{dE}{dT} = -26.99 \pm 3.58$ $\Delta S^{\ddagger}(50°C) = -13.36 \pm .318$ $\frac{\Delta C^{\ddagger}}{\Delta S^{\ddagger}}(50°C) = 2.17 \pm .267$

$\Delta C^{\ddagger} = -28.99 \pm 3.58$ $E(50°C) = 23.304$ $10^{6}k(50°C) = 3.840$

/146...

TABLE VII.14.

The Hydrolysis of iso-Propyl Toluenesulphonate in 50% Aqueous Acetone

Temp.	$10^6 k$	$10^3 \sigma_k$	E(obs)	E(calc.)	$-\Delta S^{\ddagger}$
20.18	3.715	1.44			
			22.891±.045	22.92	7.24±.152
29.91	13.10	2.02			
			22.688±.044	22.63	8.26±.143
39.86	43.41	1.13			
			22.310±.031	22.34	9.26±.097
50.13	135.6	1.09			
			22.042±.072	22.04	10.24±.218
59.97	373.7	3.09			

$\frac{dE}{dT} = -29.30 \pm 2.60$ $\Delta S^{\ddagger}$ (50°C) $= -9.76 \pm .084$ $\frac{\Delta C^{\ddagger}}{\Delta S^{\ddagger}}$ (50°C) $= 3.21 \pm .268$

$\Delta C^{\ddagger} = -31.30 \pm 2.60$ E(50°C) $= 22.19$ $10^6 k$ (50°C) $= 134.7$

/147...

TABLE VII. 15.

The Hydrolysis of p-Phenylbenzyl Toluenesulphonate in 70% Aqueous Acetone

Temp.	$10^6 k$	$10^3 \frac{\sigma}{k}$	E(obs)	E(calc.)	$-\Delta S^{\ddagger}$
-9.83	3.029	3.03			
			20.875 ±.073	20.885	6.30±.271
0	12.73	3.94			
			20.633±.073	20.605	7.26±.262
10.22	50.12	2.78			
			20.298±.062	20.324	8.51±.214
20.20	170.8	2.46			
			20.054±.066	20.045	9.41±.221
30.13	526.8	2.74			

$\frac{dE}{dT} = -27.90 \pm 3.09$

$\Delta C^{\ddagger} = -29.90 \pm 3.09$

$\Delta S^{\ddagger}(50°C) = -11.81 \pm .406$

$E\ (50°C) = 19.353$

$\frac{\Delta C^{\ddagger}}{\Delta S^{\ddagger}} = 2.53 \pm .275$

$10^4 k = 39.43$

/148...

TABLE VII. 16.

The Hydrolysis of p-Methoxybenzyl Toluenesulphonate in 85% Aqueous Acetone

Temp.	10^4k	$10^3\sigma_k$	E(obs)	$-\Delta S^{\ddagger}$
-32.42	5.594	1.46		
			$17.508 \pm .017$	$2.31 \pm .067$
-20.44	31.71	o.707		
			$17.207 \pm .020$	$3.59 \pm .077$
-10.63	114.1	1.29		

$\frac{dE}{dT} = -27.62 \pm 2.37$ $\Delta S^{\ddagger}(50°C) = -10.29 \pm .599$ $\frac{\Delta C^{\ddagger}}{\Delta S^{\ddagger}}(50°C) = 2.88 \pm .283$

$\Delta C^{\ddagger} = -29.62 \pm 2.37$ $E(50°C) = 15.398$ $10^2k\ (50°C) = 398.9$

/149...

TABLE VII. 17.

The Hydrolysis of Benzyl Toluenesulphonate in 50% Aqueous Acetone

Temp.	10^4k	$10^3/T$	E(obs)	$-\Delta S^{\ddagger}$
0	0.2221	3.106		
			$18.921 \pm .030$	$12.39 \pm .11$
20.19	2.446	2.238		
			$18.522 \pm .038$	$13.89 \pm .12$
39.51	17.58	3.286		

$\frac{dE}{dT} = -20.141 \pm 2.44$ $\Delta S^{\ddagger}(50°C) = -15.30 \pm .24$ $\frac{\Delta C^{\ddagger}}{\Delta S^{\ddagger}}(50°C) = 1.45 \pm .16$

$\Delta C^{\ddagger} = -22.141 \pm 2.44$ $E\ (50°C) = 18.118$ $10^6k\ (50°C) = 46.52$

/150...

TABLE VII. 18.

The Hydrolysis of p-Phenoxybenzyl Chloride in 50% Aqueous Acetone

Temp.	$10^6 k$	$10^5 k$	E(obs)	E(calc.)	$-\Delta S^{\ddagger}$
9.99	11.71	1.40			
			$21.172 \pm .039$	21.241	$8.26 \pm .135$
20.20	43.38	1.96			
			$21.063 \pm .047$	20.978	$8.70 \pm .158$
30.02	139.8	1.69			
			$20.757 \pm .055$	20.717	$9.61 \pm .179$
40.16	426.3	2.40			
			$20.402 \pm .085$	20.456	$10.97 \pm .267$
49.93	114.8	3.32			

$\frac{dE}{dT} = -26.20 \pm 4.54$

$\Delta C^{\ddagger} = -28.20 \pm 4.54$

$\Delta S^{\ddagger}(50°C) = -11.12 \pm .289$

$\bar{E}\ (50°C) = 20.326$

$\frac{\Delta C^{\ddagger}}{\Delta S^{\ddagger}}(50°C) = 2.54 \pm .407$

$10^4 k(50°C) = 12.21$

/151...

TABLE VII. 19.

The Hydrolysis of n-Propyl Toluenesulphonate in 50% Aqueous Acetone

Temp.	$10^{6}k$	$10^{3}\frac{\sigma}{k}$	E(obs)	E(calc.)	$-\Delta S^{\ddagger}$
60.34	16.47	2.213			
			21.789 ± .083	21.767	17.34 ± .25
69.78	40.71	2.633			
			21.486 ± .086	21.473	18.20 ± .25
79.88	100.4	2.433			
			21.057 ± .075	21.155	19.63 ± .21
90.89	248.7	2.104			
			20.949 ± .107	20.885	19.90 ± .29
97.85	428.2	1.769			

$\frac{dE}{dT} = -30.11 \pm 4.26$ $\Delta S^{\ddagger}(50°C) = -15.92 \pm 0.38$ $\frac{\Delta C^{\ddagger}}{\Delta S^{\ddagger}}(50°C) = 2.06 \pm .27$

$\Delta C^{\ddagger} = -32.11 \pm 4.26$ $E(50°C) = 21.919$ $10^{6}k(50°C) = 9.158$

/152...

TABLE VII. 20.

The Hydrolysis of p-Nitrobenzyl Toluenesulphonate in 50% Aqueous Acetone

Temp.	$10^{5}k$	$10^{3}k$	E(obs)	$-\Delta S^{\ddagger}$
26.00	.9142	4.133		
			19.435 ± .046	18.13 ± .15
45.32	6.642	2.232		
			19.158 ± .045	19.11 ± .14
59.92	25.03	2.187		

$\frac{dE}{dT} = -16.33 \pm 3.82$ $\Delta S^{\ddagger}(50°C) = -18.95 \pm .07$ $\frac{\Delta C^{\ddagger}}{\Delta S^{\ddagger}}(50°C) = 0.97 \pm .20$

$\Delta C^{\ddagger} = -18.33 \pm 3.82$ $E(50°C) = 19.201$ $10^{4}k(50°C) = 1.370$

/153...

APPENDIX VII. 4.

Details of Individual Runs

First order rate coefficients were calculated from the equation

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

where k is the integrated rate constant in sec $^{-1}$

t is the time in seconds

a is the concentration of substrate at t = o

a - x is the concentration of substrate at t = t

Titres are expressed in mls. of NaOH

Concentration units (Experiments 67 - 69) are in moles l^{-1}.

In each case details of one run are given and the mean rate coefficients, k^{1}, h^{11}, etc., of duplicating runs are quoted.

Expt. 1 <u>Benzyl Toluenesulphonate 70% Acetone (3) at 0° C</u>

5.00 mls titrated with 0.02205N NaOH

Time	Titre	10^6k
0	0.11	-
59,100	5.17	2.549
83,225	6.98	2.530
144,180	11.20	2.539
231,420	16.18	2.534
317,700	20.12	2.535
346,260	21.30	2.547
∞	36.28	-
0	2.52	-
23,600	3.86	2.541
84,660	6.97	2.537
109,320	8.09	2.534
171,660	10.67	2.548
197,280	11.60	2.543
258,090	13.55	2.530
286,800	14.33	2.537
∞	25.53	-

10^6k = 2.539 (13 readings)
10^6k^1 = 2.547 (12 readings)
Mean k = $(2.543 \pm 0.00184) \times 10^6$
Corrected to 70% Acetone k = $(1.708 \pm 0.00;24) \times 10^6$

/155...

Expt. 2 Benzyl Toluenesulphomate in 70% Acetone (3) at 20.59°C

5.00 mls titrated with 0.02205 NaOH

Time	Titre	10^6k
0	1.48	-
57,600	15.79	3.446
61,200	16.04	3.433
64,860	16.42	3.558
0	2.01	-
3,600	3.88	3.430
7,200	5.53	3.436
10,800	6.95	3.404
14,400	8.30	3.450
18,000	9.43	3.444
21,700	10.50	3.462
25,200	11.34	3.451
∞	18.07	-

10^5k = 3.440 (10 readings)
10^5k^1 = 3.436 (8 readings)
Mean k = $(3.438 \pm 0.0125) \times 10^5$
Corrected to 70% Acetone k = $(2.309 \pm 0.00840) \times 10^5$

/156...

Exp. 3 **Benzyl Toluenesulphonate in 70% Acetone (2) at 30.06°C**

5.00 mls titrated with 0.02205N NaOH

Time	Titre	10^4k
0	1.43	-
1,200	3.87	1.055
2,400	6.10	1.076
3,600	7.92	1.066
5,400	10.26	1.042
7,260	12.54	1.075
9,000	14.06	1.063
10,860	15.51	1.069
12,600	16.61	1.070
13,980	17.36	1.073
16,200	18.33	1.073
∞	21.94	-

10^4k = 1.066 (10 readings)

10^4k^1 = 1.065 (8 readings)

Mean k = $(1.066 \pm 0.00239) \times 10^4$

Corrected to 70% Acetone k = $(0.6677 \pm 0.00150)\ 10^4$

/157...

Exp. 4 Benzyl Toluenesulphonate in 70% Acetone (2) at 40.08°C

6.220 mls titrated with 0.02205 N NaOH

Time	Titre	10^4k
0	1.64	-
360	2.90	2.943
720	4.04	2.956
1,080	5.13	3.028
1,800	6.83	2.977
2,160	7.61	3.002
3,060	9.21	3.045
3,900	10.30	3.021
4,800	11.20	3.011
5,700	11.90	3.010
6,660	12.43	2.980
∞	14.15	-

10^4k = 2.997 (10 readings)

10^4k^1 = 2.983 (9 readings)

Mean k= (2.990 ± 0.00859) x 10^4

Corrected to 70% Acetone k = (1.873 ± 0.00538) x 10^4

/158...

Exp. 5 <u>Benzyl Toluenesulphonate in 70% Acetone (2) at 50.26°C</u>

6.220 mls titrated with 0.02205N NaOH

Time	Titre	10^4k
0	2.27	-
360	5.04	8.009
540	6.16	8.048
720	7.00	2.773
900	7.82	7.805
1,260	9.20	7.845
1,620	10.23	7.881
1,980	11.05	8.013
2,340	11.63	8.048
2,700	12.03	7.982
3,060	12.35	7.986
∞	13.31	-

10^4k = 7.936 (10 readings)

10^4k^1 = 7.936 (10 readings)

Mean k = $(7.936 \pm 0.0231) \times 10^4$

Corrected to 70% Acetone k = $(4.971 \pm 0.0155) \times 10^4$

/159...

Expt. 6 p-Nitrobenzyl Toluenesulphonate in 70% Acetone (3) at 50.64°C

6.220 mls titrated with 0.005176 N NaOH

Time	Titre	10^5k
0	0.09	-
3,600	1.10	3.205
7,200	2.01	3.194
10,800	2.80	3.204
14,400	3.52	3.204
18,000	4.13	3.181
25,200	5.11	3.095
32,400	6.14	3.264
39,600	6.76	3.210
0	0.10	-
46,800	7.27	3.170
54,000	7.72	3.203
∞	9.36	-

10^5k = 3.193 (10 readings)

10^5k^1 = 3.176 (9 readings)

Mean k = $(3.185 \pm 0.011) \times 10^5$

Corrected to 70% Acetone k = $(2.139 \pm 0.00745) \times 10^5$

/160...

Exp. 7 p-Nitrobenzyl Toluenesulphonate in 70% Acetone (3) at 60.15°C

6.220 mls titrated with 0.005176 N NaOH

Time	Titre	10^5k
0	0.08	-
1,800	1,33	7.778
3,600	2.39	7.670
5,400	3.34	7.707
7,200	4.16	7.709
9,000	4.85	7.660
12,000	5.85	7.686
15,000	6.64	7.668
21,000	7.76	7.705
24,000	8.13	7.645
∞	9.66	-

10^5k = 7.692 (10 readings)

10^5k^1 = 7.748 (10 readings)

Mean k = $(7.721 \pm 0.0108) \times 10^4$

Corrected to 70% Acetone k = $(5.185 \pm 0.00725) \times 10^4$

Exp. 8 p-Nitrobenzyl Toluenesulphonate in 70% Acetone (3) at 69.90 °C

6.220 mls titrated with 0.005176 N NaOH

Time	Titre	10^4k
0	0.10	-
1,200	1,82	1.791
2,400	3.22	1.799
3,600	4.37	1.815
4,800	5.25	1.801
6,000	6.07	1.851
7,800	6.80	1.793
9,600	7.36	1.766
10,400	7.72	1.865
13,200	8.11	1.745
15,000	8.49	1.787
∞	9.00	-

10^4k = 1.801 (10 readings)

10^4k^1 = 1.795 (10readings)

Mean k = $(1.798 \pm 0.00910) \times 10^4$

Corrected to 70% Acetone k = $(1.208 \pm 0.00611) \times 10^4$

/162...

Exp. 9 p-Nitrobenzyl Toluenesulphonate in 70% Acetone (3) at 79.91°C

6.220 mls titrated with 0.005176N NaOH

Time	Titre	10^4k
0	0.15	-
300	1.15	3.985
600	2.07	4.064
900	2.89	4.105
1,200	3.54	4.106
1,500	4.16	4.012
2,100	5.18	3.987
2,700	6.03	4.027
3,600	6.85	3.911
4,800	7.71	3.986
6,000	8.24	4.052
∞	9.02	-

10^4k = 4.033 (10 readings)

10^4k^1 = 4.031 (10 readings)

Mean k = $(4.032 \pm 0.0110) \times 10^4$

Corrected to 70% Acetone k = $(2.707 \pm 0.00739) \times 10^4$

/163...

Exp. 10 p-Nitrobenzyl Toluenesulphonate in 70% Acetone (3) at 89.71°C

6.220 mls titrated with 0.005176 N NaOH

Time	Titre	10^4k
0	0.23	-
120	1.09	8.407
240	1.87	8.412
360	2.57	8.401
480	3.20	8.360
600	3.81	8.489
720	4.34	8.399
960	5.21	8.437
1,200	5.90	8.335
1,620	6.90	8.405
2,100	7.66	8.395
∞	9.20	-

10^4k = 8.404 (10 readings)

10^4k^1 = 8.417 (10 readings)

Mean k = $(8.411 \pm 0.0112) \times 10^4$

Corrected to 70% Acetone k = $(5.649 \pm 0.00752) \times 10^4$

/164...

Expt. 11 p-Methylbenzyl Toluenesulphonate in 70% Acetone (4) at 19.99°C

5.00 mls titrated with 0.005186N NaOH

Time	Titre	10^6k
0	0.63	-
36,520	1.71	3.355
74,100	2.68	3.350
109,270	3.54	3.406
144,160	4.28	3.422
180,760	4.92	3.393
212,340	5.43	3.389
284,590	6.39	3.361
357,720	7.16	3.341
∞	9.99	-

10^6k = 3.377 (8 readings)
10^6k^1 = 3.352 (8 readings)
10^6k^{11} = (3.367) (5 readings)
Mean k = $(3.365 \pm 0.0423) \times 10^6$

Corrected to 70% Acetone k = $(2.949 \pm 0.0370) \times 10^6$

/165...

Exp. 12 p-Methylbenzyl Toluenesulphonate in 70% Acetone (4) at -10.23°C

5.00 mls titrated with 0.005186N NaOH.

Time	Titre	10^5k
0	0.31	-
1815	0.68	1.472
3625	1.11	1.531
5445	1.48	1.514
7220	1.83	1.503
9015	2.20	1.517
10815	2.54	1.512
12720	2.89	1.506
14890	3.27	1.501
16275	3.51	1.500
18195	3.84	1.499
19915	4.11	1.491
∞	15.09	-

10^5k = 1.504 (11 readings)
10^5k^1 = 1.497 (9 readings)
Mean k = $(1.500 \pm 0.00485) \times 10^5$

Corrected to 70% Acetone k = $(1.312 \pm 0.00425) \times 10^5$

/166...

Exp. 13 p-Methylbenzyl Toluenesulphonate in 70% Acetone (3) at 0°C

5.00 mls titrated with 0.005186N NaOH

Time	Titre	10^5k
0	0.58	-
195	0.73	8.032
1,262	1.53	8.158
2,420	2.32	8.156
3,634	3.10	8.262
4,840	3.79	8.285
6,066	4.41	8.262
7,230	4.95	8.260
9,650	5.90	8.217
12,015	6.71	8.292
14,417	7.32	8.239
17,188	7.89	8.112
19,215	8.31	8.258
20,982	8.50	8.041
∞	10.30	

10^5k = 8.199 (13 readings)

10^5k^1 = 8.208 (12 readings)

Mean k= $(8.204 \pm 0.0214) \times 10^5$

Corrected to 70% Acetone k= $(5.510 \pm 0.0144) \times 10^5$

/167...

Exp. 14 p-Methylbenzyl Toluenesulphonate in 70% Acetone (3) at 10.13°C

5.00 mls titrated with 0.005186N NaOH

Time	Titre	10^4k
0	0.40	-
330	1.52	3.015
695	2.67	3.065
1,035	3.58	3.026
1,415	4.50	3.008
1,815	5.37	3.001
2,160	6.05	3.004
2,875	7.20	2.976
3,655	8.24	2.974
4,200	8.89	3.011
5,000	9.58	2.993
5,710	10.11	3.011
7,200	10.87	3.005
∞	12.23	

10^4k = 3.007 (12 readings)

10^4k^1 = 3.008 (11 readings)

Mean k= $(3.008 \pm 0.00394) \times 10^4$

Corrected to 70% Acetone k= $(2.020 \pm 0.00265) \times 10^4$

/168...

Exp. 15 p-Methylbenzyl Toluenesulphonate in 70% Acetone (3) at 20.57°C

5.00 mls titrated with 0.005186N NaOH

Time	Titre	10^3k
0	0.79	-
168	2.26	1.021
380	2.79	1.021
570	4.94	1.032
762	5.87	1.032
950	6.62	1.032
1,270	7.63	1.041
1,464	8.07	1.035
1,880	8.73	1.013
2,331	9.26	1.023
∞	10.12	-

10^3k = 1.028 (9 readings)

10^3k^1 = 1.024 (11 readings)

Mean k = (1.026 ± 0.00242) x 10^3

Corrected to 70% Acetone k = (0.6891 ± 0.00163) x 10^3

/169...

Exp. 16 p-Phenoxybenzyl Toluenesulphonate in 85% Acetone (1) at - 30.15°C

5.00 mls titrated with .004716N NaOH

Time	Titre	10^6k
0	0.87	-
13,530	1.31	3.897
41,150	2.32	4.002
58,630	2.90	4.011
79,560	3.50	3.934
100,980	4.09	4.041
127,520	4.81	3.944
157,460	5.47	3.964
186,580	6.05	3.955
231,800	6.85	3.965
307,540	7.84	3.909
∞	10.87	

10^6k = 3.962 (10 readings)

10^6k^1 = 3.940 (10 readings)

Mean k = (3.951 ± 0.0165) x 10^6

Corrected to 85% Acetone k = (3.985 ± 0.0166) x 10^6

/170...

Exp. 17 p-Phenoxybenzyl Toluenesulphonate in 85% (1) at -20.14°C

5.00 mls titrated with 0.004716N NaOH

Time	Titre	10^5k
0	0.63	-
3,320	1.17	2.005
7,690	1.82	2.004
13,700	2.68	2.059
15,790	2.94	2.055
20,680	3.50	2.039
27,220	4.21	2.060
32,640	4.70	2.050
41,640	5.47	2.096
46,700	5.80	2.072
63,210	6.69	2.073
∞	8.97	

10^5k = 2.050 (10 readings)

10^5k^1 = 2.020 (11 readings)

Mean k = $(2.035 \pm 0.00671) \times 10^5$

Corrected to 85% Acetone k = $(2.053 \pm 0.00677) \times 10^5$

/171...

Exp. 18. p-Phenoxybenzyl Toluenesulphonate in 85% Acetone (1) at -9.94°C

5.00 mls titrated with 0.004716N NaOH

Time	Titre	10^5k
0	1.61	-
1,530	2.85	8.806
2,720	3.74	8.958
3,060	3.96	8.903
4,310	4.74	8.929
5,720	5.57	8.987
6,630	5.99	8.875
7,350	6.35	8.933
8,510	6.88	9.001
10,880	7.75	9.000
14,520	8.75	8.890
16,650	9.25	8.989
∞	11.46	-

10^5k = 8.935 (11 readings)

10^5k^1 = 8.896 (11 readings)

Mean K= $(8.915 \pm 0.0153) \times 10^5$

Corrected to 85% Acetone k = $(8.993 \pm 0.0154) \times 10^5$

/172...

Expt. 19 p-Phenoxybenzyl Toluenesulphonate in 85% Acetone (1) at 0°C

5.00 mls titrated with 0.004716N NaOH

Time	Titre	10^4k
0	1.57	-
344	2.41	3.542
714	3.18	3.480
927	3.62	3.553
1, 222	4.13	3.524
1, 540	4.65	3.544
1, 811	5.01	3.561
2, 122	5.40	3.490
2, 374	5,78	3.607
2, 795	6.24	3.635
3, 266	6.61	3.576
4, 583	7.51	3.642
∞	8.89	-

10^4k = 3.560 (11 readings)

10^4k^1 = 3.576 (10 readings)

Mean k = $(3.568 \pm 0.00981) \times 10^4$

Corrected to 85% Acetone k = $(3.599 \pm 0.00990) \times 10^4$

/173...

Expt. 20 p-Phenoxybenzyl Toluenesulphonate in 85% Acetone (1) at 10.14°C

5.00 mls titrated with 0.004176N NaOH

Time	Titre	10^3k
0	1.51	-
150	3.31	1.254
240	4.24	1.257
360	5.38	1.282
480	6.24	1.251
720	8.08	1.263
900	8.66	1.273
1,080	9.35	1.277
1,260	9.82	1.250
1,500	10.47	1.287
1,800	10.97	1.295
∞	11.99	-

$10^3k = 1.269$ (10 readings)

$10^3k^1 = 1.256$ (10 readings)

Mean $k = (1.263 \pm 0.00359) \times 10^3$

Corrected to 85% Acetone $k = (1.274 \pm 0.00362) \times 10^{-3}$

Exp. 21 p-Anisylbenzyl Toluenesulphonate in 85% Acetone (2) at -10.02°C

5.00 mls titrated with 0.004215N NaOH

Time	Titre	10^6k
0	3.10	-
75,240	5.89	9.005
81,320	6.03	8.944
100,020	6.45	8.936
145,500	7.29	9.233
173,280	7.60	9.108
∞	8.77	-
0	2.18	-
14,460	2.79	8.871
26,220	3.24	8.950
80,840	4.84	9.199
113,160	5.39	8.863
155,400	5.99	8.960
∞	7.25	-

$10^6k = 9.007$ (1o readings)

$10^6k^1 = 9.053$ (10 readings)

Mean $k = (9.030 \pm 0.0270) \times 10^6$

Corrected to 85% Acetone $k = (4.762 \pm 0.0142) \times 10^6$

/175...

Exp. 22 <u>p-Anisylbenzyl Toluenesulphonate in 85% Acetone(2) at 0°C</u>

5.00 mls titrated with 0.004215N NaOH

Time	Titre	10^5k
0	1.23	-
1,980	1.86	3.873
4,830	2.69	3.873
7,550	2.27	3.868
10,000	4.01	3.928
14,480	4.87	3.823
17,920	5.56	3.932
21,620	6.10	3.893
26,380	6.71	3.876
31,680	7.30	3.898
41,360	8.07	3.881
oo	9.79	-

10^5k = 3.884 (10 readings)
10^5k^1 = 3.878 (10 readings)
Mean k= (3.881 ± 0.0131) x 10^5

Corrected to 85% Acetone k = (2.046 ± 0.00691) x 10^5

/176...

Expt. 23 p-Anisylbenzyl Toluenesulphonate in 85% Acetone (2) at 10.13°C

5.00 mls titrated with 0.004215N NaOH

Time	Titre	10^4k
0	2.12	-
660	2.79	1.518
1,390	3.47	1.536
2,045	3.98	1.506
2,660	4.42	1.492
3,375	4.87	1.473
4,090	5.35	1.518
5,290	5.97	1.486
5,880	6.25	1.472
7,200	6.73	1.501
8,630	7.17	1.506
9,770	7.52	1.500
10,800	7.76	1.503
∞	9.14	

10^4k = 1.501 (12 readings)

10^4k^1 = 1.496 (12 readings)

Mean k= $(1.498 \pm 0.00520) \times 10^4$

Corrected to 85% Acetone k = $(0.7899 \pm 0.00274) \times 10^4$

/177...

Expt. 24 p-Anisylbenzyl Toluenesulphonate in 85% Acetone (2) at 20.57°C

Time	Titre	10^4k
0	4.19	-
340	6.39	5.364
520	7.44	5.439
777	8.71	5.401
1,036	9.77	5.308
1,277	10.75	5.387
1,628	11,89	5.385
1,875	12.55	5.360
2,240	13.43	5.383
2,725	14.39	5.447
3,010	14.75	5.357
∞	17.38	-

10^4k = 5.383 (10 readings)

10^4k^1= 5.402 (10 readings)

Mean k= $(5.393 \pm 0.0100) \times 10^4$

Corrected to 85% Acetone k = $(2.844 \pm 0.0052) \times 10^4$

/178...

Expt. 25 p-Anisylbenzyl Toluenesulphonate in 85% Acetone (2) at 30.27°C

5.00 mls titrated with 0.004215N NaOH

Time	Titre	10^3k
0	2.76	-
113	3.74	1.624
211	4.43	1.596
307	5.07	1.640
540	6.13	1.593
702	6.68	1.583
824	7.03	1.594
930	7.29	1.608
987	7.38	1.603
1,130	7.62	1.580
1,390	7.91	1.626
∞	8.60	-

10^3k = 1.605 (10 readings)

10^3k^1 = 1.602 (11 readings)

Mean k = $(1.603 \pm 0.00379) \times 10^3$

Corrected to 85% Acetone k = $(8.453 \pm 0.00200) \times 10^3$

/179...

Expt. 26 p-Nitrobenzhydryl Toluenesulphonate in 85% Acetone(3) at -19.72° C

5.00 mls titrated with 0.004233N NaOH

Time	Titre	10^6k
0	0.66	-
89,400	2.49	2.657
114,000	2.92	2.653
200,400	4.23	2.652
∞	9.32	-
0	1.05	-
62,700	2.82	2.707
77,500	3.17	2.699
149,400	4.76	2.650
174,000	5.29	2.691
234,000	6.30	2.653
∞	12.40	-

$10^6k = 2.666$ (8 readings)

$10^6k^1 = 2.654$ (10 readings)

Mean $k = (2.660 \pm 0.00877) \times 10^6$

Corrected to 85% Acetone $k = (2.340 \pm 0.00771) \times 10^6$

/180...

Expt. 27 p-Nitrobenzhydryl Toluenesulphonate in 85% Acetone(3) at -9.80°C

5.00 mls titrated with 0.004233N NaOH

Time	Titre	10^5k
0	0.50	-
60,960	7.07	1.318
65,400	7.42	1.333
68,400	7.61	1.331
72,000	8.82	1.326
81,600	8.33	1.315
85,200	8.52	1.316
97,200	9.10	1.319
∞	12.40	

0	0.54	-
20,400	3.50	1.346
24,000	3.97	1.359
36,000	5.30	1.355
86,400	9.00	1.341
∞	12.87	-

10^5k = 1.333 (11 readings)

10^5k^1 = 1.334 (9 readings)

Mean k= (1.334 ± 0.00326) x 10^5

Corrected to 85% Acetone k= (1.173 ± 0.00287) x 10^5

Expt. 28 p-Nitrobenzhydryl Toluenesulphonate in 85% Acetone (3) at 0°C

5.00 mls titrated with 0.004233N NaOH

Time	Titre	10^5k
0	0.69	-
3,000	2.81	5.642
4,500	3.75	5.537
6,000	4.65	5.558
7,500	5.50	5.598
9,000	6.21	5.537
10,800	7.08	5.591
13,200	8.03	5.553
18,000	9.60	5.513
20,400	10.28	5.536
∞	14.91	-

10^5k = 5.585 (9 readings)

10^5k^1 = 5.619 (13 readings)

Mean k= $(5.602 \pm 0.0143) \times 10^5$

Corrected to 85% Acetone k= $(4.928 \pm 0.0126) \times 10^5$

/182...

Expt. 28 p-Nitrobenzhydryl Toluenesulphonate in 85% Acetone(3) at 0°C

5.00 mls titrated with 0.004233N NaOH

Time	Titre	10^5k
0	0.69	-
3,000	2.81	5.642
4,500	3.75	5.537
6,000	4.65	5.558
7,500	5.50	5.598
9,000	6.21	5.537
10,800	7.08	5,591
13,200	8.03	5.553
18,000	9.60	5.513
20,400	10.28	5.536
∞	14.91	-

10^5k = 5.585 (9 readings)

10^5k^1 = 5.619 (13 readings)

Mean k = (5.602 ± 0.0143) x 10^5

Corrected to 85% Acetone k = (4.928   0.0126) x 10^5

Expt. 29. p-Nitrobenzhydryl Toluenesulphonate in 85% Acetone (3) at 10.38°C

5.00 mls titrated with 0.004233N NaOH

Time	Titre	10^4k
0	0.66	-
860	2.64	2.308
1,270	3.41	2.267
1,690	4.15	2.259
2,160	4.88	2.241
2,540	5.45	2.251
2,950	5.99	2.247
3,610	6.79	2.257
4,270	7.46	2.255
5,020	8.10	2.248
6,020	8.78	2.223
7,210	9.47	2.239
∞	11.66	-

10^4k = 2.254 (11 readings)

10^4k^1 = 2.262 (9 readings)

Mean k= $(2.258 \pm 0.00482) \times 10^4$

Corrected to 85% Acetone k= $(1.986 \pm 0.00424) \times 10^4$

/184...

Expt. 30. p-Nitrobenzhydryl Toluenesulphonate in 85% Acetone (3) at 20.57°C

5.00 mls titrated with 0.004233N NaOH

Time	Titre	10^4k
0	1.04	-
160	2.36	7.845
365	3.85	7.915
565	5.09	7.944
795	6.30	7.978
1,190	7.90	7.968
1,1430	8.64	7.938
1,750	9.44	7.924
2,335	10.48	7.861
2,735	10.96	7.932
∞	12.24	-

10^4k = 7.943 (9 readings)

10^4k^1 = 7.946 (13 readings)

Mean k = $(7.944 \pm 0.0141) \times 10^4$

Corrected to 85% Acetone k = $(6.987 \pm 0.0124) \times 10^4$

/185...

Expt. 31. Benzyl Toluenesulphonate in 85% Acetone (3) at 34.16°C

6.220 mls titrated with 0.005124N NaOH

Time	Titre	10^5k
0	0.34	-
3,600	1.19	2.022
7,200	1.98	2.025
10,800	2.72	2.030
14,400	3.42	2.042
18,000	4.06	2.043
25,200	5.20	2.038
32,400	6.18	2.037
∞	12.43	-
0	0.30	-
49,500	6.79	2.020
54,000	7.12	2.021
57,600	7.38	2.030
∞	10.57	-

10^5k = 2.033 (10 readings)

10^5k^1 = 2.042 (12 readings)

Mean k = $(2.038 \pm 0.00465) \times 10^5$

Corrected to 85% Acetone k = $(1.793 \pm 0.00409) \times 10^5$

/186...

Expt. 32 Benzyl Toluenesulphonate in 85% Acetone (3) at 44.09°C

6.220 mls titrated with 0.005124N NaOH

Time	Titre	10^5k
0	1.22	-
1,800	2.96	5.566
5,400	5.88	5.455
7,200	7.17	5.479
9,000	8.40	5.553
10,800	9.45	5.587
14,400	11.29	5.569
18,000	12.66	5.476
21,600	13.93	5.514
25,200	15.01	5.586
28,800	15.79	5.554
∞	19.48	-

10^5k = 5.534 (10 readings)

10^5k^1 = 5.556 (11 readings)

Mean k = $(5.545 \pm 0.00839) \times 10^5$

Corrected to 85% Acetone k = $(4.877 \pm 0.00738) \times 10^5$

/187...

Expt. 33 **Benzyl Toluenesulphonate in 85% Acetone (3) at 54.29°C**

6.220 mls titrated with 0.005124N NaOH

Time	Titre	10^4k
0	0.62	-
900	1.94	1.418
1,800	3.10	1.416
2,700	4.19	1.449
3,660	5.09	1.421
4,500	5.90	1.450
8,100	8.22	1.445
9,060	8.65	1.440
10,020	9.06	1.449
13,500	10.05	1.434
16,500	10.62	1.443
∞	11.64	-

10^4k = 1.436 (10 readings)

10^4k^1 = 1.438 (8 readings)

Mean k = $(1.437 \pm 0.00324) \times 10^4$

Corrected to 85% Acetone k = $(1.264 \pm 0.00285) \times 10^4$

/188...

Expt. 34 Benzyl Toluenesulphonate in 85% Acetone (3) at 64.15°C

6.220 mls titrated with 0.005124N NaOH

Time	Titre	10^4k
0	0.69	-
300	1.80	3.316
900	3.71	3.311
1,200	4.61	3.395
1,500	5.34	3.370
1,800	6.06	3.405
2,100	6.69	3.416
2,700	7.75	3.417
3,360	8.66	3.392
3,900	9.32	3.418
5,400	10.50	3.360
∞	12.41	-

10^4k = 3.380 (10 readings)
10^4k^1 = 3.378 (11 readings)
Mean k = $(3.379 \pm 0.00789) \times 10^4$

Corrected to 85% acetone k = $(2.972 \pm 0.00694) \times 10^4$

/189...

Expt. 35 **Benzyl Toluenesulphonate in 85% Acetone (3) at 74.56°C**

6.220 mls titrated with 0.005124N NaOH

Time	Titre	10^4k
0	1.19	-
430	3.99	7.921
680	5.18	7.793
903	6.15	7.932
1,130	6.83	7.710
1,350	7.50	7.789
1,590	8.12	7.884
1,810	8.59	7.952
2,040	8.87	7.652
2,280	9.26	7.692
2,530	9.53	7.766
∞	10.89	-

10^4k = 7.826 (10 readings)

10^4k^1 = 7.812 (9 readings)

Mean k = $(7.819 \pm 0.0193) \times 10^4$

Corrected to 85% Acetone k = $(6.878 \pm 0.0170) \times 10^4$

/190...

Expt. 36 iso-Propyl Toluenesulphonate in 85% Acetone (4) at 60.38°C

6.220 mls titrated with 0.005047N NaOH

Time	Titre	10^5k
0	0.12	-
61,200	7.20	1.199
72,000	8.04	1.210
86,400	9.02	1.225
147,600	11.48	1.217
158,400	11.80	1.230
169,200	12.01	1.220
0	0.14	-
14,400	2.29	1.193
21,600	3.29	1.220
28,800	4.18	1.224
93,600	9.32	1.200
111,600	10.26	1.222
∞	13.74	-

10^5k = 1.217 (11 readings)
10^5k^1 = 1.222 (12 readings)
Mean k= (1.219 ± 0.00280) x 10^5

Corrected to 85% Acetone k= (1.170 ± 0.00269) x 10^5

/191...

Expt. 37 iso-Propyl Toluenesulphonate in 85% Acetone (4) at 70.49°C

6.220 mls titrated with 0.005047N NaOH

Time	Titre	10^5k
0	0.69	-
59,400	9.54	3.311
63,000	9.70	3.309
64,800	9.82	3.369
0	0.13	-
3,600	1.36	3.346
7,200	2.45	3.343
10,860	3.43	3.321
13,200	4.03	3.374
15,600	4.56	3.364
18,060	5.15	3.439
21,600	5.70	3.336
25,260	6.38	3.398
28,800	6.87	3.371
∞	10.98	-

$10^5k = 3.357$ (12 readings)

$10^5k^1 = 3.352$ (12 readings)

Mean $k = (3,355 \pm 0.00748) \times 10^5$

Corrected to 85% Acetone $k = (3.219 \pm 0.00718) \times 10^5$

/192...

Expt. 38 iso-Propyl Toluenesulphonate in 85% Acetone (4) at 79.60°C

6.220 mls titrated with 0.005047N NaOH

Time	Titre	10^5k
0	0.27	-
1,800	2.06	7.881
3,300	3.35	7.823
4,500	4.29	7.840
6,300	5.58	7.918
7,800	6.47	7.869
10,200	7.79	7.966
12,600	8.81	7.922
14,400	9.46	7.902
16,200	10.09	8.001
18,900	10.85	8.075
21,615	11.43	8.077
∞	13.79	

10^5k = 7.935 (11 readings)

10^5k^1 = 7.895 (11 readings)

Mean k = $(7.915 \pm 0.0189) \times 10^5$

Corrected to 85% Acetone k = $(7.594 \pm 0.0181) \times 10^5$

/193...

Expt. 39 iso-Propyl Toluenesulphonate in 85% Acetone (4) at 89.73°C

6.220 mls titrated with 0.005047N NaOH

Time	Titre	10^4k
0	0.60	-
600	1.87	1.945
1,200	2.98	1.929
1,800	3.94	1.901
2,400	4.84	1.913
3,000	5.62	1.908
3,600	6.37	1.931
4,500	7.27	1.923
5,400	8.03	1.918
6,600	8.86	1.914
7,800	9.58	1.938
9,000	10.10	1.935
10,800	10.70	1.938
∞	12.12	-

10^4k = 1.924

10^4k^1 = 1.937

Mean k = (1.930 ± 0.00342) x 10^4

Corrected to 85% Acetone k = (1.852 ± 0.00328) x 10^4

/194...

Expt. 40 iso-Propyl Toluenesulphonate in 85% Acetone (4) at 99.85°C

6.220 mls titrated with 0.005047N NaOH

Time	Titre	10^4k
0	1.44	-
180	2.25	4.350
360	3.02	4.465
720	4.32	4.392
900	4.89	4.363
1,140	5.60	4.355
1,380	6.28	4.404
1,680	7.04	4.454
2,100	7.91	4.468
2,520	8,59	4.432
2,940	9.21	4.467
∞	12.07	

$10^4k = 4.415$ (10 readings)

$10^4k^1 = 4.437$ (9 readings)

Mean $k = (4.426 \pm 0.0113) \times 10^4$

Corrected to 85% Acetone $k = (4.246 \pm 0.0108) \times 10^4$

/195...

Expt. 41 iso-Propyl Toluenesulphonate in 50% Acetone (1) at 20.18°C

5 mls titrated with 0.004995N NaOH

Time	Titre	10^6k
0	0.47	-
57,600	2.86	3.819
81,000	3.70	3.842
144,000	5.61	3.850
169,200	6.26	3.858
230,400	7.59	3.860
316,800	8.93	3.806
0	0.60	-
86,400	3.94	3.794
111,600	4.76	3.833
172,800	6.38	3.825
194,400	6.84	3.800
259,200	8.16	3.864
∞	12.55	-

10^6k = 3.832 (11 readings)

10^6k^1 = 3.806 (12 readings)

Mean k = $(3.819 \pm 0.00551) \times 10^6$

Corrected to 50% Acetone k = $(3.715 \pm 0.00536) \times 10^6$

/196...

Expt. 42 iso-Propyl Toluenesulphonate in 50% Acetone (1) at 29.91°C

5 mls titrated with 0.004995 NaOH

Time	Titre	10^5k
0	0.33	-
61,200	6.36	1.332
68,400	6.84	1.346
75,600	7.30	1.367
0	0.40	-
10,800	1.84	1.333
14,400	2.28	1.335
18,000	2.68	1.324
21,600	3.12	1.356
86,400	7.78	1.343
98,100	8.33	1.362
10,800	8.65	1.351
oo	11.15	-

10^5k = 1.345 (10 readings)
10^5k^1 = 1.350 (11 readings)
Mean k = $(1.347 \pm 0.00271) \times 10^{5}$
Corrected to 50% Acetone k = $(1.310 \pm 0.00264) \times 10^{5}$

/197...

Expt. 43 iso-Propyl Toluenesulphonate in 50% Acetone(1) at 39.86°C

6.220 mls titrated with 0.004995N NaOH

Time	Titre	10^5k
0	1.06	-
2,400	2.17	4.472
4,200	2.92	4.452
6,000	3.61	4.433
7,860	4.29	4.468
9,600	4.88	4.493
11,400	5.41	4.463
13,200	5.90	4.442
15,000	6.41	4.493
16,800	6.84	4.492
18,900	7.29	4.480
21,000	7.72	4.490
23,100	9.09	4.477
∞	11.97	-

10^5k = 4.472 (12 readings)

10^5k^1 = 4.452 (11 readings)

Mean k = $(4.462 \pm 0.00506) \times 10^5$

Corrected to 50% Acetone k = $(4,341 \pm 0.00492) \times 10^5$

Expt. 44 iso-Propyl Toluenesulphonate in 50% Acetone (1) at 50.13°C

6.220 mls titrated with 0.004995N NaOH

Time	Titre	10^4k
0	3.53	-
720	4.41	1.388
1,440	5.22	1.399
2,160	5.95	1.400
2,940	6.66	1.402
3,900	7.39	1.403
4,920	8.10	1.398
6,000	8.72	1.396
7,500	9.49	1.397
9,300	10.21	1.389
11,700	10.94	1.395
∞	12.80	-

10^4k = 1.397 (10 readings)

10^4k^1 = 1.392 (11 readings)

Mean k = $(1.394 \pm 0.00152) \times 10^4$

Corrected to 50% Acetone k = $(1.356 \pm 0.00148) \times 10^4$

Expt. 45 iso-Propyl Toluenesulphonate in 50% Acetone (1) at 59.97°C

6.220 mls titrated with 0.004995N NaOH

Time	Titre	10^4k
0	0.84	-
360	2.12	3.915
720	3.22	3.899
1,083	4.08	3.745
1,440	4.95	3.811
1,800	5.68	3.824
2,160	6.36	3.879
2,700	7.10	3.820
3,300	7.85	3.863
3,900	8.41	3.860
4,500	8.85	3.840
∞	10.57	-

10^4k = 3.846 (10 readings)
10^4k^1 = 3.836 (8 readings)
Mean k = $(3.841 \pm 0.0119) \times 10^4$

Corrected to 50% Acetone k = $(3.737 \pm 0.0116) \times 10^4$

/200...

Expt. 46 p-Phenylbenzyl Toluenesulphonate in 70% Acetone (5) at -9.83°C

5 mls titrated with 0.004316N NaOH

Time	Titre	10^6k
0	0.11	-
43,200	0.68	3.589
75,600	1.02	3.508
129,600	1.52	3.461
216,000	2.14	3.528
302,400	2.65	3.486
∞	4.01	-
0	0.15	-
82,800	1.03	3.489
108,000	1.26	3.522
172,800	1.74	3.492
257,400	2.26	3.569
∞	3.66	-

10^6k = 3.517 (9 readings)

10^6k^1 = 3.514 (9 readings)

Mean k = $(3.515 \pm 0.0107) \times 10^6$

Corrected to 70% Acetone k = $(3.029 \pm 0.00922) \times 10^6$

/201...

Expt. 47 p-Phenylbenzyl Toluenesulphonate in 70% Acetone (5) at 0°C

5 mls titrated with 0.004316N NaOH

Time	Titre	10^5k
0	0.25	-
46,800	2.67	1.464
57,000	2.99	1.455
714,000	3.38	1.447
∞	5.11	-
0	0.62	-
7,200	1.33	1.507
14,400	1.98	1.523
16,800	2.18	1.523
19,200	2.31	1.462
21,000	2.46	1.475
∞	7.53	-

10^5k = 1.482 (8readings)

10^5k^1 = 1.472 (8 readings)

Mean k = $(1.477 \pm 0.00581) \times 10^5$

Corrected to 70% Acetone k = $(1.273 \pm 0.00501) \times 10^5$

/202...

Expt. 48 p-Phenylbenzyl Toluenesulphonate in 70% Acetone (5) at 10.22°C

5 mls titrated with 0.004316N NaOH

Time	Titre	10^5k
0	0.55	-
1,800	1.12	5.848
3,600	1.64	5.898
5,400	2.10	5.877
7,200	2.50	5.815
9,000	2.90	5.907
10,800	3.20	5.792
13,200	3.62	5.860
15,600	3.92	5.735
18,600	4.28	5.713
21,600	4.59	5.713
∞	6.25	-

10^5k = 5.817 (10 readings)

10^5k^1 = 5.815 (9 readings)

Mean k = $(5.816 \pm 0.0162) \times 10^5$

Corrected to 70% Acetone k = $(5.012 \pm 0.0140) \times 10^5$

/203...

Expt. 49 p-Phenylbenzyl Toluenesulphonate in 70% Acetone (5) at 20.20°C

5.00 mls titrated with 0.004316N NaOH

Time	Titre	10^4k
0	1.03	-
271	1.50	1.997
705	2.21	2.019
1,817	3.72	1.984
2,507	4.52	1.988
3,307	5.41	2.005
4,392	6.24	2.009
5,845	7.11	1.971
7,380	7.84	1.968
9,462	8.53	1.962
∞	9.92	-

10^4k = 1.989 (9readings)

10^4k^1 = 1.976 (9readings)

Mean k = $(1.982 \pm 0.00487) \times 10^4$

Corrected to 70% Acetone k = $(1.708 \pm 0.00420) \times 10^4$

/204...

Expt. 50 p-Phenylbenzyl Toluenesulphonate in 70% Acetone (5) at 30.13°C

5.00 mls titrated with 0.004316N NaOH

Time	Titre	10^4k
0	1.09	-
335	2.39	6.180
651	3.37	6.108
903	4.05	6.148
1,091	4.48	6.130
1,338	4.97	6.109
1,693	5.55	6.064
2,348	6.35	6.022
2,630	6.61	6.012
∞	8.04	-

10^4k = 6.098 (8 readings)

10^4k^1 = 6.128 (8 readings)

Mean k = $(6.113 \pm 0.0167) \times 10^4$

Corrected to 70% Acetone k = $(5.268 \pm 0.0144) \times 10^4$

Expt. 51 p-Phenoxybenzyl Chloride in 50% Acetone (3) at 9.99°C

5 mls titrated with 0.004421N NaOH

Time	Titre	10^5k
0	0.21	-
45,020	3.14	1.130
54,040	3.55	1.122
61,200	3.85	1.117
68,400	4.17	1.132
72,000	4.30	1.129
82,800	4.67	1.136
133,200	5.92	1.126
147,600	6.19	1.138
∞	7.56	-
0	0.11	-
7,200	0.64	1.129
14,400	1.11	1.108
21,600	1.57	1.123
27,060	1.88	1.117
36,300	2.36	1.110
90,000	4.40	1.113
105,000	4.80	1.121
111,600	4.94	1.117
174,600	5.93	1.120
∞	6.89	-

10^5k = 1.123 (17 readings)

10^5k^1 = 1.125 (17 readings)

Mean k = $(1.124 \pm 0.00157) \times 10^5$

Corrected to 50% Acetone k = $(1.171 \pm 0.00164) \times 10^5$

/206...

Expt. 52 p-Phenoxybenzyl Chloride in 50% Acetone (3) at 20.20°C

5 mls titrated with 0.004421N NaOH

Time	Titre	10^5k
0	0.31	-
2,400	1.08	4.174
4,800	1.79	4.222
7,200	2.40	4.165
12,000	3.48	4.159
14,400	3.94	4.150
16,800	4.34	4.119
19,200	4.77	4.191
22,200	5.20	4.196
25,200	5.53	4.132
28,200	5.89	4.170
31,800	6.23	4.160
35,400	6.54	4.177
39,000	6.82	4.215
∞	8.38	-

10^5k = 4.172 (13 readings)

10^5k^1 = 4.157 (12 readings)

Mean k = $(4.164 \pm 0.00816) \times 10^5$

Corrected to 50% Acetone k = $(4.338 \pm 0.00850) \times 10^5$

/207...

Expt. 53 p-Phenoxybenzyl Chloride in 50% Acetone (3) at 30.02°C

5 mls titrated with 0.004421N NaOH

Time	Titre	10^4k
0	1.79	-
900	2.62	1.336
1,800	3.36	1.340
2,700	4.02	1.343
3,600	4.58	1.331
4,500	5.09	1.330
5,400	5.56	1.338
6,300	5.97	1.341
7,500	6.47	1.357
9,000	6.92	1.338
10,500	7.36	1.359
∞	9.12	-

10^4k = 1.341 (10 readings)

10^4k^1 = 1.338 (13 readings)

Mean k = $(1.340 \pm 0.00227) \times 10^4$

Corrected to 50% Acetone k = $(1.398 \pm 0.00237) \times 10^4$

/208...

Expt. 54 p-Phenoxybenzyl Chloride in 50% Acetone (3) at 40.16°C

6.220 mls titrated with 0.004421N NaOH

Time	Titre	10^4k
0	1.25	-
660	3.74	4.149
1,020	4.75	4.028
1,330	5.61	4.092
1,620	6.29	4.097
1,890	6.90	4.153
2,220	7.41	4.051
2,580	7.98	4.045
3,100	8.74	4.118
3,600	9.28	4.119
4,200	9.75	4.059
4,800	10.19	4.104
∞	11.64	-

10^4k = 4.092 (11 readings)

10^4k^1 = 4.092 (10 readings

Mean k = $(4.092 \pm 0.00982) \times 10^4$

Corrected to 50% Acetone k = $(4.263 \pm 0.0102) \times 10^4$

/209...

Expt. 55 p-Phenoxybenzyl Chloride in 50% Acetone (3) at 49.93°C

6.220 mls titrated with 0.004421N NaOH

Time	Titre	10^3k
0	1.30	-
180	2.96	1.086
540	5.40	1.070
660	6.15	1.110
780	6.68	1.100
900	7.18	1.104
1,080	7.75	1.086
1,265	8.37	1.118
1,440	8.87	1.117
1,620	9.05	1.093
∞	10.64	-

10^3k = 1.098 (9readings)

10^3k^1 = 1.105 (9readings)

Mean k = $(1.102 \pm 0.00366) \times 10^3$

Corrected to 50% Acetone k = $(1.148 \pm 0.00381) \times 10^3$

/210...

Expt. 56 n-Propyl Toluenesulphonate in 50% Acetone (3) at 60.34°C

6.220 mls titrated with 0.004421N NaOH

Time	Titre	10^5k
0	0.32	-
12,600	2.73	1.599
21,600	4.18	1.600
27,000	4.90	1.578
36,000	6.00	1.562
43,200	6.77	1.552
100,800	10.83	1.578
111,600	11.27	1.586
0	0.30	-
59,400	8.30	1.564
66,600	8.86	1.566
86,400	10.18	1.593
153,000	12.39	1.608
∞	13.52	-

10^5k = 1.581 (11 readings)

10^5k^1 = 1.583 (8 readings)

Mean k = $(1.582 \pm 0.00350) \times 10^5$

Corrected to 50% Acetone k = $(1.647 \pm 0.00365) \times 10^5$

/211...

Expt. 57 n-Propyl Toluenesulphonate in 50% Acetone (3) at 69.78°C

6.220 mls titrated with 0.004421N NaOH

Time	Titre	10^5k
0	0.34	-
3,600	2.10	3.966
7,200	3.60	3.931
11,100	4.93	3.845
14,400	5.97	3.854
19,800	7.40	3.857
23,400	8.22	3.876
32,400	9.77	3.857
∞	13.56	-
0	0.33	-
38,700	9.71	3.829
42,300	10.17	3.934
45,900	10.45	3.908
49,560	10.80	4.003
53,100	10.98	3.951
∞	12.47	-

10^5k = 3.901 (12 readings)
10^5k^1 = 3.916 (12 readings)
Mean k = (3.908 ± 0.0103) x 10^5

Corrected to 50% Acetone k = (4.071 ± 0.0107) x 10^5

/212...

Expt. 58 n-Propyl Toluenesulphonate in 50% Acetone (3) at 79.88°C

6.220 mls titrated with 0.004421N NaOH

Time	Titre	10^5k
0	0.39	-
2,400	2.94	0.644
3,600	3.97	9.513
4,800	4.92	9.533
6,000	5.75	9.500
7,000	6.50	9.768
8,100	7.11	9.594
10,800	8.32	9.530
12,800	9.20	9.781
15,600	9.94	9.534
17,600	10.50	9.722
20,400	11.00	9.633
∞	12.73	-

10^5k = 9.614 (11 readings)
10^5k^1 = 9.650 (9 readings)
Mean k = $(9.632 \pm 0.0235) \times 10^5$

Corrected to 50% Acetone k = $(10.04 \pm 0.0245) \times 10^5$

/213...

Expt. 59 n-Propyl Toluenesulphonate in 50% Acetone (3) at 90.89°C

6.220 mls titrated with 0.004421N NaOH

Time	Titre	10^4k
0	0.75	-
420	1.94	2.413
840	3.03	2.435
1,260	3.99	2.416
1,680	4.82	2.387
2,100	5.65	2.413
2,520	6.33	2.391
2,940	6.97	2.388
3,600	7.80	2.356
4,200	8.58	2.401
5,400	9.64	2.364
7,200	10.82	2.357
∞	13.08	-

10^4k = 2.393 (11 readings)

10^4k^1 = 2.380 (10 readgins)

Mean k = $(2.387 \pm 0.00502) \times 10^4$

Corrected to 50% Acetone k = $(2.487 \pm 0.00523) \times 10^4$

/ 214...

Expt. 60 <u>n-Propyl Toluenesulphonate in 50% Acetone (3) at 97.85°C</u>

6.220 mls titrated with 0.004421N NaOH

Time	Titre	10^4k
0	0.82	-
600	3.62	4.168
900	4.81	4.212
1,200	5.72	4.082
1,500	6.66	4.125
1,800	7.44	4.117
2,100	8.14	4.116
2,400	8.68	4.048
3,000	9.78	4.107
3,720	10.74	4.123
4,200	11.22	4.112
5,040	11.88	4.116
∞	13.47	-

10^4k = 4.111 (10 readings)
10^4k^1 = 4.099 (11 readings)
Mean k = $(4.105 \pm 0.0177) \times 10^4$

Corrected to 50% Acetone k = $(4.282 \pm 0.0184) \times 10^4$

Expt. 61 p-Nitrobenzyl Toluenesulphonate in 50% Acetone (5) at 26.00°C

21.34 mls titrated with 0.003861 N NaOH

Time	Titre	10^6k
-	4.39	-
18,000	3.14	8.906
27,900	3.44	8.733
86,400	2.05	8.814
97,200	1.82	9.061
108,000	1.69	8.842
121,400	1.53	8.672
∞	6.64	-
-	2.30	-
43,812	1.56	8.864
61,200	1.33	8.961
74,700	1.19	8.828
∞	3.20	-

10^6k = (9 readings)

10^6k^1 = (9 readings)

Mean k = $(8.858 \pm 0.0366) \times 10^6$

Corrected to 50% Acetone k = $(9.142 \pm 0.0378) \times 10^6$

/216...

Expt. 62 p-Nitrobenzyl Toluenesulphonate in 50% Acetone (5) at 45.32°C

21.34 mls titrated with 0.003861N NaOH

Time	Titre	10^5k
-	1.82	-
2,700	2.59	6.428
5,400	3.23	6.405
7,200	3.60	6.407
10,800	4.21	6.343
12,600	4.53	6.557
14,400	4.75	6.508
16,200	4.99	6.470
18,000	5.13	6.450
20,400	5.32	6.350
∞	6.64	-

10^5k = 6.437 (9 readings)

10^5k^1 = 6.432 (6 readings)

10^5k^{11} = 6.438 (6 readings)

Mean k = $(6.435 \pm 0.0144) \times 10^5$

Corrected to 50% Acetone k = $(6.642 \pm 0.0149) \times 10^5$

/217...

Expt. 63 p-Nitrobenzyl Toluenesulphonate in 50% Acetone (5) at 59.92°C

21.34 mls titrated with 0.003861N NaOH

Time	Titre	10^4k
-	1.59	-
300	1.96	2.457
660	2.36	2.428
1,020	2.73	2.427
1,560	3.22	2.412
1,920	3.50	2.385
2,340	3.85	2.438
2,820	4.16	2.418
3,720	4.65	2.387
4,620	5.08	2.409
5,520	5.41	2.403
6,420	5.68	2.407
7,320	5.92	2.443
8,220	6.11	2.475
∞	6.79	-

10^4k = 2.422 (13 readings)

10^4k^1 = 2.428 (10 readings)

Mean k = $(2.425 \pm 0.00530) \times 10^4$

Corrected to 50% Acetone k = $(2.503 \pm 0.00547) \times 10^4$

Expt. 64 Benzyl Toluenesulphonate in 50% Acetone (4) at 0° C

10 mls titrated with 0.003861N NaOH

Time	Titre	10^5k
-	1.78	-
7,200	2.85	2.182
10,800	3.31	2.158
14,400	3.78	2.202
18,000	4.20	2.217
19,800	4.41	2.233
25,200	4.96	2.248
28,800	5.30	2.268
32,400	5.56	2.225
79,200	7.81	2.160
82,800	8.01	2.263
∞	9.14	-

10^5k = 2.215 (10 readings)

10^5k^1 = 2.213 (15 readings)

Mean k = (2.213 ± 0.00668) x 10^5

Corrected to 50% Acetone k = (2.221 ± 0.00670) x 10^5

/219...

Expt. 65 **Benzyl Toluenesulphonate in 50% Acetone (4) at 20.19°C**

10 mls titrated with 0.003861N NaOH

Time	Titre	10^4k
-	1.12	-
540	1.72	2.444
1,030	2.21	2.473
1,520	2.63	2.455
2,060	3.05	2.464
2,670	3.45	2.452
3,300	3.80	2.438
4,260	4.22	2.393
5,160	4.60	2.450
6,090	4.87	2.436
7,320	5.13	2.396
9,060	5.42	2.416
∞	5.97	-

10^4k = 2.437 (11 readings)

10^4k^1 = 2.437 (10 readings)

Mean $k = (2.437 \pm 0.00546) \times 10^4$

Corrected to 50% Acetone $k = (2.446 \pm 0.00548) \times 10^4$

Expt. 66 Benzyl Toluenesulphonate in 50% Acetone (4) at 39.61°C

10 mls titrated with 0.003861N NaOH

Time	Titre	10^3k
0	3.32	-
247	6.42	1.716
360	7.56	1.778
450	8.29	1.795
550	8.86	1.732
646	9.39	1.748
730	9.81	1.761
860	10.36	1.787
1,060	10.86	1.733
∞	12.29	-

10^3k = 1.756 (8 readings)
10^3k^1 = 1.748 (12 readings)
Mean k = $(1.752 \pm 0.00577) \times 10^3$

Corrected to 50% Acetone k = $(1.758 \pm 0.00579) \times 10^3$

/221...

Expt. 67 p-Methoxybenzyl Toluenesulphonate in 85% Acetone (5) at - 20.44°C

Time	10^4(HOTs)	10^3k
-	1.61	-
56.75	3.56	2.772
85.50	4.46	2.791
110.25	5.16	2.782
144.5	6.05	2.784
172.67	6.75	2.798
207.0	7.46	2.773
242.0	8.16	2.771
272.0	8.68	2.756
313.75	9.40	2.771
350.0	9.92	2.761
389.0	10.45	2.770
434.75	10.97	2.756
466.0	11.31	2.760
540.0	11.85	2.769
∞	15.02	-

10^3k = 2.772 (14 readings)

10^3k^1 = 2.776 (14 readings)

Mean k = (2.774 ± 0.00196) x 10^3

Corrected to 85% Acetone k = (3.171 ± 0.00224) x 10^3

/222...

Expt, 68 p-Methoxybenzyl Toluenesulphonate in 85% Acetone (5) at -10.63°C

Time	10^4(HOTs)	10^3k
-	2.92	-
7.7	3.63	9.900
16.1	4.43	10.06
42.4	6.45	10.17
64.7	7.74	10.04
116.3	9.84	9.947
176.5	11.26	9.948
238.0	12.05	9.900
∞	13.00	-

10^3k = 9.995 (7 readings)
10^3k^1 = 9.968 (7 readings)
10^3k^{11} = 9.979 (7 readings)
Mean k = $(9.981 \pm 0.0129) \times 10^3$

Corrected to 85% Acetone k = $(11.41 \pm 0.0147) \times 10^3$

/223...

Expt. 69 p-Methoxybenzyl Toluenesulphonate in 85% Acetone (5) at -32.42°C

Time	10^4(HOTs)	10^4k
-	1.77	-
379.25	4.45	4.864
522.5	5.50	4.905
675.5	6.38	4.859
841.5	7.33	4.885
1023.5	8.25	4.871
1221.25	9.20	4.898
1554.0	10.62	4.947
1675.0	11.06	4.945
1942.0	11.94	4.940
2090.5	12.39	4.938
2428.5	13.24	4.896
3119.0	14.60	4.822
∞	18.26	-

10^4k = 4.897 (12 readings)
10^4k^1 = 4.891 (13 readings)
Mean k = $(4.894 \pm 0.00713) \times 10^4$

Corrected to 85% Acetone k = $(5.594 \pm 0.00815) \times 10^4$

/224...

Expt. 70 Benzyl Toluenesulphonate in 70% Acetone (6) at 20.04°C

5 mls titrated with 0.01055N NaOH

Time	Titre	10^5k
-	0.15	-
5,100	0.89	3.432
8,870	1.35	3.398
10,840	1.56	3.370
13,320	1.81	3.350
15,105	1.99	3.373
16,420	2.14	3.442
18,540	2.30	3.389
23,640	2.70	3.408
26,520	2.91	3.443
36,780	3.43	3.379
∞	4.76	-

10^5k = 3.399 (10 readings)
10^5k^1 = 3.387 (11 readings)
Mean k = $(3.393 \pm 0.0102) \times 10^5$

/225...

Expt. 71 Benzyl Toluenesulphonate in 70% Acetone (6) at 20.04°C

5 mls titrated with 0.01055N NaOH

Added 0.100 N NaCl

Time	Titre	10^5k
-	0.26	-
2,700	0.80	6.687
5,460	1.28	6.846
8,100	1.63	6.704
10,800	1.97	6.854
13,500	2.22	6.788
16,200	2.42	6.748
18,600	2.60	6.760
36,660	3.24	6.609
∞Ts'	3.53	-

Complete hydrolysis 7.21

10^5k = 6.748 (8 readings)

10^5k^1 = 6.758 (9 readings)

Mean k = $(6.753 \pm 0.0315) \times 10^5$

/226...

Expt. 72 <u>Benzyl Toluenesulphonate in 70% Acetone (6) at 20.04°C</u>

5 mls titrated with 0.005482N NaOH

Added 0.1005 KNO_3

Time	Titre	10^5k
-	0.25	-
2,105	1.49	3.983
4,080	2.57	3.996
6,305	3.62	3.916
10,800	5.52	3.872
14,400	6.88	3.902
18,180	8.10	3.914
21,605	9.09	3.942
28,800	10.74	3.961
45,000	13.14	4.017
∞B'	15.67	-
Complete hydrolysis	18.20	

10^5k = 3.983 (9 readings)
10^5k^1 = 3.987 (9 readings)
Mean k = (3.985 ± 0.0207) x 10^5

/227...

Expt. 73 Benzyl Toluenesulphonate in 70% Acetone (6) at 20.04°C

5 mls titrated with 0.005482N NaOH

Added 0.2572 KNO_3

Time	Titre	10^5k
-	0.30	-
3,664	1.68	4.845
7,740	2.97	4.881
10,800	8.75	4.831
14,880	4.63	4.795
18,000	5.26	4.875
21,600	5.80	4.832
36,000	7.33	4.891
82,810	8.63	4.797
$^{\infty}T_{s}'$	8.79	
Complete hydrolysis	12.02	

10^5k = 4.843 (8 readings)

10^5k^1 = 4.851 (10 readings)

Mean k = $(4.847 \pm 0.0106) \times 10^5$

/228...

Expt. 74 Benzyl Toluenesulphonate in 70% Acetone (6) at 20.04°C

5 mls titrated with 0.005482N NaOH

Added 0.1002N $NaClO_4$

Time	Titre	10^5k
-	1.94	-
3,600	3.35	3.525
5,400	3.97	3.484
7,204	4.55	3.459
9,000	5.16	3.529
10,830	5.72	3.577
12,615	6.23	3.562
14,460	6.72	3.576
16,260	7.15	3.568
18,090	7.59	3.586
38,400	10.87	3.655
79,230	13.11	3.625
∞	13.78	-

10^5k = 3.559 (11 readings)
10^5k^1 = 3.547 (10 readings)
Mean k = (3.553 ± 0.0165) x 10^5

/229...

Expt. 75 Benzyl Toluenesulphonate in 70% Acetone (6) at 20.04°C

5 mls titrated with 0.005482N NaOH

Added 0.2567N $NaClO_4$

Time	Titre	10^5k
-	0.30	-
7,200	2.63	3.803
9,000	3.13	3.818
10,800	3.58	3.804
12,600	4.01	3.809
14,405	4.47	3.885
16,200	4.80	3.831
18,000	5.20	3.891
19,800	5.53	3.895
21,615	5.82	3.876
41,940	8.20	3.885
82,800	9.62	3.825
∞	10.03	-

10^5k = 3.857 (11 readings)

10^5k^1 = 3.847 (11 readings)

Mean k = $(3.852 \pm 0.0161) \times 10^5$

/230...

Expt. 76 m-Chlorobenzyl Toluenesulphonate in 70% Acetone (6) at 69.86°C

6.220 mls titrated with 0.005482N NaOH

Time	Titre	10^4k
-	0.71	-
900	3.55	3.490
1,800	5.51	3.376
2,280	6.46	3.459
2,550	6.82	3.399
2,760	7.21	3.475
3,255	7.84	3.468
3,660	8.30	3.480
4,290	8.87	3.470
4,860	9.36	3.537
5,580	9.80	3.555
∞	11.25	-

10^5k = 3.471 (10 readings)
10^5k^1 = 3.460 (11 readings)
Mean k = $(3.465 \pm 0.0162) \times 10^4$

/231...

Expt. 77 m-Chlorobenzyl Toluenesulphonate in 70% Acetone (6) at 69.86°C

6.220 mls titrated with 0.005482N NaOH

Added 0.09901N KNO_3

Time	Titre	10^4k
-	0.66	-
257	1.71	5.840
600	2.88	5.823
990	3.96	5.866
1,175	4.41	5.748
1,500	5.01	5.888
1,800	5.58	5.895
2,400	6.36	5.803
3,720	7.32	5.830
∞Ts'	8.19	-
Complete hydrolysis	10.80	

10^4k = 5.835 (8 readings)

10^4k^1 = 5.851 (11 readings)

Mean k = $(5.843 \pm 0.0211) \times 10^4$

/232...

Expt. 78 m-Chlorobenzyl Toluenesulphonate in 70% Acetone (6) at 69.86°C

6.220 mls titrated with 0.005482N NaOH
Added 0.2685N KNO_3

Time	Titre	10^4k
-	0.41	-
325	1.36	8.131
600	2.00	8.151
900	2.57	8.287
1,200	2.98	8.181
1,500	3.30	8.097
1,800	3.56	8.078
2,100	3.79	8.231
2,420	3.94	8.093
2,700	4.04	7.954
3,450	4.27	8.117
∞_{Ts}'	4.52	-
Complete hydrolysis	7.86	

10^4k = 8.132 (10 readings)
10^4k^1 = 8.134 (9 readings)
Mean k = $(8.133 \pm 0.0303) \times 10^4$

/233...

Expt. 79 m-Chlorobenzyl Toluenesulphonate in 70% Acetone (6) at 69.86°C

6.220 mls titrated with 0.005482N NaOH

Added 0.1001N $NaClO_4$

Time	Titre	10^4k
-	0.29	-
390	1.31	4.246
720	2.06	4.273
1,080	2.74	4.231
1,440	3.34	4.235
1,760	3.80	4.234
2,190	4.32	4.223
2,850	4.97	4.232
3,520	5.48	4.263
4,240	5.86	4.234
5,540	6.33	4.234
∞	6.97	-

10^4k = 4.240 (10 readings)

10^4k^1 = 4.222 (10 readings)

Mean k = $(4.231 \pm 0.047) \times 10^4$

/234...

Expt. 80 m-Chlorobenzyl Toluenesulphonate in 70% Acetone (6) at 69.86°C

6.220 mls titrated with 0.005482N NaOH

Added 0.2585N $NaClO_4$

Time	Titre	10^4k
-	1.15	-
180	2.49	4.836
420	4.10	4.834
600	5.20	4.836
900	6.88	4.887
1,200	8.25	4.859
1,560	9.62	4.796
1,890	10.76	4.818
2,160	11.57	4.835
2,700	12.82	4.797
3,600	14.39	4.817
∞	17.23	-

10^4k = 4.831 (10 readings)
10^4k^1 = 4.825 (12 readings)
Mean k= (4.828 ± 0.0091) x 10^4

/235...

Expt. 81 p-Nitrobenzhydryl Chloride in 70% Acetone (7) at 90°C

6.220 mls titrated with 0.005411N NaOH

Time	Titre	10^4k
-	1.95	-
240	3.22	6.304
480	4.36	6.453
740	5.33	6.321
920	5.99	6.428
1,200	6.75	6.299
1,560	7.58	6.239
1,800	8.14	6.401
2,100	8.64	6.402
2,460	9.10	6.346
2,760	9.41	6.302
∞	11.00	-

10^4k = 6.350 (10 readings)

10^4k^1 = 6.396 (9 readings)

Mean k = $(6.373 \pm 0.0200) \times 10^4$

/236...

Expt. 82 p-Nitrobenzhydryl Chloride in 70% Acetone (7) at 90°C

6.220 mls titrated with 0.005411N NaOH

Added 0.1000N KCl

Time	Titre	10^4k
-	1.00	-
240	2.43	5.892
480	3.67	5.877
720	4.78	5.949
960	5.69	5.897
1,220	6.48	5.767
1,500	7.31	5.810
1,800	8.02	5.798
2,100	8.62	5.771
2,400	9.19	5.859
2,700	9.66	5.928
3,060	10.02	5.818
∞	11.85	-

10^4k = 5.851 (11 readings)
10^4k^1 = 5.878 (8 readings)
Mean k = (5.864 ± 0.0141)

/237...

Expt. 83 p-Nitrobenzhydryl Chloride in 70% Acetone (7) at 50°C

6.220 mls titrated with 0.005411N NaOH

Time	Titre	10^6k
-	0.13	-
61,200	6.22	9.875
68,400	6.69	9.800
81,000	7.47	9.764
145,800	10.27	9.633
172,800	11.04	9.683
-	0.08	-
10,800	1.43	9.661
25,200	3.01	9.725
100,800	8.49	9.703
113,400	9.15	9.856
∞	13.56	-

10^6k = 9.745 (9 readings)

σ = 0.0389

/238...

Expt. 84 <u>p-Nitrobenzhydryl Chloride in 70% Acetone (7) at 50°C</u>

6.220 mls titrated with 0.005411N NaOH

Time	Titre	10^6k
-	0.15	-
61,200	6.35	9.350
81,000	7.71	9.364
145,800	10.60	9.095
172,800	11.64	9.536
-	0.09	-
10,800	1.43	9.128
18,000	2.31	9.392
25,200	3.09	9.350
100,800	8.77	9.275
113,400	9.44	9.370
∞	14.38	-

10^6k = 9.317 (9 readings)

σ = 0.0589

/239...

Expt.	T°C	Substrate	KCl Added	(ROH)	(ROTs)	$(\overline{Cl})$ $(\overline{ROTs})$
85	20.04	$C_6H_5CH_2OTs$	0.0962N	3.53	7.21	10.8
86	25.00	p-$MeC_6H_4CH_2OTs$	0.100N	2.42	3.15	3.02
87	25.00	p-$PhOC_6H_4CH_2OTs$	0.100N	3.61	4.08	1.30
88	20.19	p-$MeOC_6H_4CH_2OTs$	0.100N	4.55	5.67	2.68
89	25.00	p-$NO_2C_6H_4CH.PhOTs$	0.100N	9.09	9.60	0.56
90	25.00	PrOTs	0.100N	13.20	18.64	4.12

/240...

Expt. 91 Benzhydryl Chloride in 70% Acetone (8) at 20.19°C

5 mls titrated against 0.009653N after addition of 5mls 0.02155N HCl

Added 0.02N NaOH

Time	Titre	10^4k
-	0.29	-
300	1.56	3.634
587	2.66	3.665
895	3.71	3.659
1,208	4.69	3.683
1,520	5.55	3.689
1,920	6.51	3.692
2,416	7.58	3.741
3,000	8.51	3.707
3,678	9.38	3.684
4,205	9.91	3.660
5,235	10.76	3.685
∞	12.54	-

10^4k = 3.682 (11 readings)

10^4k^1 = 3.684 (10 readings)

Mean k = $(3.683 \pm 0.0082) \times 10^4$

/241...

Expt. 92 Benzhydryl Chloride in 70% Acetone (8) at 20.19°C

5 mls + 5 mls 0.03174N HCl titrated against 0.009653N NaOH

Added 0.03N NaOH

Time	Titre	10^4k
-	1.04	-
615	3.18	3.565
915	4.05	3.546
1,200	4.81	3.550
1,470	5.49	3.583
1,936	6.47	3.576
2,260	7.05	3.563
2,750	7.88	3.609
3,280	8.58	3.607
3,805	9.14	3.593
5,370	10.35	3.616
∞	11.91	-

$10^4k = 3.581 \pm 0.0083$ (11 readings)

/242...

Expt. 93 Benzhydryl Chloride in 70% Acetone (9) at 20.19°C

5 mls + 5 mls 0.01031N HCl titrated with 0.009653N NaOH

Added 0.009207N NaOH

Time	Titre	10^4k
-	1.24	-
560	2.73	3.093
828	3.37	3.115
1,100	3.96	3.117
1,407	4.59	3.144
1,723	5.15	3.134
2,067	5.69	3.117
2,506	6.30	3.100
3,175	7.15	3.139
4,174	8.11	3.166
∞	10.61	-

$10^4k = 3.125 \pm 0.0072$ (9 readings)

/243...

Expt. 94 Benzhydryl Chloride in 70% Acetone (10) at 20.19°C

5 mls + 5 mls 0.02173N HCl titrated with 0.009653N NaOH

Added 0.02142N NaOH+

Time	Titre	10^4k
-	1.12	-
301	2.07	3.229
675	3.07	3.122
1,030	3.97	3.162
1,370	4.74	3.175
1,735	5.49	3.199
2,215	6.35	3.219
2,960	7.43	3.226
3,680	8.27	3.244
4,345	8.89	3.259
5,038	9.40	3.266
5,650	9.75	3.257
∞	11.38	-

10^4k = 3.214 ± 0.0064 (11 readings)

+ NaOH added 15 mins before start of run

/244...

Expt. 95 Benzhydryl Chloride in 70% Acetone (10) at 20.19°C

5 mls + 5 mls 02301 NHCl titrated with 0.009653N NaOH

Added 0.02292 N NaOH[+]

Time	Titre	10^4k
-	1.09	-
311	2.25	3.488
625	3.25	3.405
960	4.30	3.490
1,292	5.17	3.474
1,650	5.98	3.443
1,956	6.64	3.463
2,385	7.41	3.445
3,105	8.57	3.505
3,810	9.37	3.477
4,500	10.01	3.477
5,400	10.65	3.483
6,320	11.12	3.481
∞	12.37	-

$10^4k = 3.469 \pm 0.0081$ (12 readings)

+ NaOH added 16 hrs before start of run

/245...

Expt. 96 Benzhydryl Chloride in 70% Acetone at 20.19°C

5 mls + 5 mls 0.01813N HCl titrated with 0.009653N NaOH

Added 0.01758N NaOH

Time	Titre	10^4k
-	2.48	-
321	3.99	3.501
662	5.44	3.528
1,000	6.70	3.521
1,315	7.81	3.574
1,695	8.90	3.546
2,061	9.87	3.562
2,833	11.50	3.551
3,527	12.58	3.518
4,500	13.87	3.595
∞	16.69	-

$10^4k = 3.545 \pm 0.0094$ (9 readings)

Duplicate 0.02736 NaOH $10^4k = 3.555$

0.02736 NaCl $10^4k = 3.602$

No salt 10^4k (calc) $= 3.790$

/246...

Expt. 97 Benzhydryl Chloride in 70% Acetone at 20.19°C

5 mls titrated with 0.009653N NaOH

Added 0.01758N NaCl+

Time	Titre	10^4k
-	0.06	-
633	1.78	3.624
925	2.44	3.633
1,245	3.09	3.598
1,595	3.72	3.595
1,910	4.26	3.634
2,303	4.80	3.614
2,845	5.45	3.615
3,402	6.02	3.643
4,200	6.62	3.627
5,478	7.32	3.677
∞	8.45	-

$10^4k = 3.626 \pm 0.0071$ (10 readings)

No salt:- 10^4k (calc) $= 3.715 \pm 0.0073$

+ By neutralising the alkaline solvent in experiment 96 with HCl

/247...

Expt. 98 Benzyl Toluenesulphonate in 70% Acetone at 20.19°C

5 mls + 5 mls 0.01991 NHCl titrated with 0.009653N NaOH

Added 0.01877N NaOH

Time	Titre	10^5k	10^5k(calc)
-	1.77	-	-
4,500	3.29	4.278	4.242
6,900	3.90	4.112	4.080
9,900	4.62	4.022	4.038
13,500	5.38	3.938	3.993
17,100	6.00	3.907	3.953
20,700	6.56	3.877	3.915
23,400	6.95	3.883	3.890
26,100	7.29	3.873	3.867
31,500	7.85	3.827	3.822
35,100	8.20	3.848	3.797
38,700	8.45	3.793	3.772
∞	10. 45	-	-

10^4k_2 = 5.029 $(m/l)^{-1}s^{-1}$

10^5k_1 = 3.288 s^{-1}

No salt 10^5k_1(calc) = 3.352 s^{-1}

Duplicate 0.01922N NaOH 10^4k_2 = 4.553 $(m/l)^{-1}s^{-1}$

10^5k_1 = 2.997 s^{-1}

No salt 10^5k_1(calc) = 3.008 s^{-1}

Expt. 99 Benzyl Toluenesulphonate in 70% Acetone at 20.19°C

5 mls titrated with 0.00965sN NaOH

Added 0.01877N NaOTs +

Time	Titre	10^5k
-	0.79	-
4,500	1.68	3.337
6,900	2.13	3.418
9,900	2.59	3.350
13,500	3.11	3.348
17,100	3.56	3.317
20,700	3.99	3.363
23,400	4.26	3.355
26,100	4.54	3.397
31,500	4.98	3.395
35,100	5.21	3.363
38,700	5.41	3.328
∞	7.17	-

$10^5k = 3.362 \pm 0.0090$ (11 readings)

\+ By neutralising solution 98

Added 01922N NaOTs ++ $10^5k = 3.017 \pm 0.00517$ (9 readings)

++ By neutralising duplicate solution 98

/249...

Expt. 100 Benzyl Toluenesulphonate in 70% Acetone (11) at 20.19°C

5 mls titrated with 0.009653N

Added 0.02064N NaOTs

Time	Titre	10^5k
-	2.22	-
1,800	2.59	2.533
3,600	2.96	2.585
5,400	3.31	2.602
7,200	3.61	2.537
9,000	3.96	2.605
10,800	4.26	2.605
13,560	4.69	2.597
16,200	5.08	2.600
18,900	5.48	2.630
21,720	5.82	2.512
∞	10.54	-

10^5k = 2.590 ± 0.0095 (10 readings)

/250...

Expt. 101 Benzyl Toluenesulphonate in 50% Acetone (2) at 20.19°C

10 mls titrated with 0.003861N NaOH

Added 0.100N KCl

Time	Titre	10^4k
-	1.60	-
660	2.29	3.102
1,440	2.93	3.061
1,860	3.21	3.037
2,460	3.59	3.100
3,180	3.97	3.174
3,785	4.18	3.109
4,290	4.34	3.093
4,740	4.48	3.121
5,555	4.65	3.065
∞Ts	5.33	-
Complete Hydrolysis	7.28	-

10^4k = 3.096 (9 readings)

10^4k^1 = 3.088 (9 readings)

Mean k = (3.092 ± 0.0147) x 10^4

No salt 10^4k = 2.314 ± 0.0125

Expt. 102 Benzyl Toluenesulphonate in 50% Acetone (6) at 20.19°C

10 mls titrated with 0.004669N NaOH

Added 0100 $NaClO_4$

Time	Titre	10^4k
-	1.60	-
480	2.84	2.418
917	3.90	2.476
1,415	4.95	2.479
2,111	6.15	2.439
2,520	6.82	2.454
3,105	7.61	2.439
3,530	8.11	2.425
3,915	8.57	2.443
4,435	9.10	2.449
5,100	9.64	2.429
5,580	10.03	2.447
6,065	10.32	2.426
∞		

10^4k = 2.446 (12 readings)

10^4k^1 = 2.435 (12 readings)

Mean k = $(2.442 \pm 0.0126) \times 10^4$

No salt 10^4k = 2.408 ± 0.0125

/252...

Expt. 103 p-Methoxybenzyl Chloride in 70% Acetone at 20.10°C

5 mls + 5 mls 0.02147N NaOH titrated with 0.009921N NaOH

Added 02089N NaOH

Time	Titre	10^4k
-	0.52	-
997	3.23	2.936
1,540	4.50	3.028
2,046	5.47	3.044
2,550	6.23	3.000
3,090	6.93	2.967
3,600	7.55	2.987
4,137	8.10	2.991
4,733	8.58	2.969
5,321	8.95	2.928
5,846	9.31	2.963
6,420	9.55	2.910
∞	11.20	-

10^4k = 2.974 (11 readings)
10^4k^1 = 2.987 (11 readings)
Mean k = $(2.980 \pm 0.0151) \times 10^4$
No salt 10^4k (calc) = 2.974

/253...

LIST OF SOLVENTS

Solvent	T°C	Substrate	10^4k
70%(2)	20.59	pMeOC$_6$H$_4$CH$_2$Cl	4.303
70%(3)	20.59	pMeOC$_6$H$_4$CH$_2$Cl	4.005
70%(3)	20.57	pMeC$_6$H$_4$CH$_2$OTs	10.26
70%(4)	20.57	pMeC$_6$H$_4$CH$_2$OTs	7.869
70%(5)	10.13	pMeC$_6$H$_4$CH$_2$OTs	2.345
70%(6)	20.04	C$_6$H$_5$CH$_2$OTs	33.93
70%(8)	20.19	(C$_6$H$_5$)$_2$CHCl	3.054
70%(9)	20.19	(C$_6$H$_5$)$_2$CHCl	2.529
70%(10)	20.19	(C$_6$H$_5$)$_2$CHCl	2.905
70%(11)	20.19	(C$_6$H$_5$)$_2$CHCl	2.582
85%(1)	60.21	(C$_6$H$_5$)$_2$CHCl	8.014
85%(2)	20.57	pMeC$_6$H$_4$CH.PhCl	5.488
85%(3)	20.57	pMeC$_6$H$_4$CH.PhCl	3.290
85%(4)	20.57	pMeC$_6$H$_4$CH.PhCl	3.016
85%(5)	20.57	pMeC$_6$H$_4$CH.PhCl	2.532
50%(1)	60.41	pNO$_2$C$_6$H$_4$CH.PhCl	4.934
50%(2)	20.19	C$_6$H$_5$CH$_2$OTs	2.314
50%(3)	60.41	pNO$_2$C$_6$H$_4$CH.PhCl	4.613
50%(4)	60.41	pNO$_2$C$_6$H$_4$CH.PhCl	4.637
50%(5)	60.41	pNO$_2$C$_6$H$_4$CH.PhCl	3.501
50%(6)	20.19	C$_6$H$_5$CH$_2$OTs	2.408

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