Arrhenius parameters in the solvolysis of alkyl chlorides and bromides

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UNIVERSITY OF DURHAM

DEGREE OF MASTER OF SCIENCE IN THE FACULTIES OF SCIENCE AND APPLIED SCIENCE

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ARRHENIUS PARAMETERS IN THE SOLVOLYSIS OF ALKYL CHLORIDES AND BROMIDES

BY

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Contents.

ABSTRACT.

The reactivities of alkyl halides, RX, in nucleophilic substitution reactions increase in the order RF < RCl < RBr < RI. It has been suggested that this reactivity sequence arises almost entirely from a decrease in activation energy, E, along this series, consistent with the decreasing ionisation energy of the C-halogen bonds, ie., C-F > C-Cl > C-Br > C-I. On the other hand some authors have concluded that a change in the entropy of activation, $\Delta S^{\ddagger}$, plays the most important part in controlling reaction rate in this series. In many cases, however, the activation parameters of the different halides referred to different temperatures. Such comparisons may be misleading since recent work has clearly shown that E and $\Delta S^{\ddagger}$ can vary with temperature; any valid comparison of these parameters must, therefore, involve quantities which all refer to the same temperature.

A study of the reactions of several pairs of alkyl chlorides and bromides with aqueous acetone is now reported. Reaction rates, activation parameters and the temperature coefficients of these parameters have been determined and the results show that, for hydrolysis at the same temperature, the change in rate caused by replacing an alkyl chloride by the corresponding bromide arises almost entirely from a change in the activation energy; this applies to both S_N1 and S_N2 reactions.

It has recently been suggested that the value of $\Delta C^{\ddagger}/\Delta S^{\ddagger}$, where $\Delta C^{\ddagger}$ is the heat capacity of activation, should be independent of the nature of the substrate in S_N1 solvolyses and that this ratio will have a lower value

for solvolysis by mechanism S_N2 under the same experimental conditions. This suggestion was based on results observed with alkyl chlorides. All the alkyl chlorides and bromides now studied behave in accordance with the requirements of this hypothesis.

During this work the solvolysis of benzyl bromide was studied and the results indicated that this substance reacted by mechanism S_N2. This is of interest, for although the hydrolysis of benzyl chloride occurs near the point which marks the transition from reaction by mechanism S_N2 to reaction by mechanism S_N1, the replacement of the chlorine atom by a bromine atom does not appear to cause a major mechanistic change.

CHAPTER I.

INTRODUCTION.

1. C-X Bond Fission.

A single covalent bond between carbon and some other atom comprises two electrons situated approximately midway between the atoms concerned. When such a bond is broken the products and subsequent reactions depend on the deployment of these two electrons - there are two possibilities.

(a). Homolytic fission.

Rupture of the bond may be homolytic, in which case the bonding electrons are equally shared between the fission products giving rise to free radicals. This type of fission, which is common to many gas phase reactions and peroxide catalysed polymerisations, can be illustrated by the decomposition of hexaphenyl ethane in non-ionising solvents.

$$(C_6H_5)\ C : C\ (C_6H_5) \longrightarrow 2(C_6H_5)\ C\cdot$$

(b) Heterolytic fission.

In heterolytic bond rupture both bonding electrons are retained by one of the fission products; two possibilities can be envisaged.

(i). The bonding electrons may be retained by the carbon atom which is thus rendered prone to attack by reagents which can accomodate the excess electrons present at the reaction centre. A reaction involving this type of fission is the nitration of an aromatic nucleus by $NO_2^{\oplus}$.

$$Ar : H + NO_2^{\oplus} \longrightarrow Ar : NO_2 + H^{\oplus}.$$

Reactions of this type are called electrophilic substitution, S_E.

(ii). The bonding electrons may be retained by the leaving group giving a carbon atom prone to attack by reagents which can supply electrons. This type of fission is involved in the reaction between an alkyl halide (RX) and $OH^{\ominus}$.

$$R{:}X + OH^{\ominus} \longrightarrow ROH + {:}X^{\ominus}.$$

This is an example of nucleophilic substitution, S_N, and is characteristic of many substitution processes taking place in solution.

This work is concerned with nucleophilic substitution and these reactions are, therefore, considered in some detail below.

2. <u>Nucleophilic Substitution Reactions.</u>

During the period 1927-35 Hughes, Ingold and their co-workers (1)(2) established the principal features of S_N processes and showed that reaction could occur by one of two mechanisms.

The first of these takes place in two stages and involves an initial ionisation of the R-X bond followed by the rapid co-ordination of the substituting agent; <u>viz</u>.,

$$RX \rightleftharpoons [\overset{\delta\oplus}{R}\cdots\overset{\delta\ominus}{X}] \rightleftharpoons R^{\oplus} + X^{\ominus} \xrightarrow{Y^{\ominus}} RY + X^{\ominus} \quad (S_N1)$$

The ionisation of RX is considered to be the slowest step in the reaction; since this rate-determining stage involves covalency change by only one molecule the reaction is regarded as unimolecular and described by the symbol S_N1.

The alternative mechanism involves reaction via a single stage; <u>viz</u>.,

$$RX + Y^{\ominus} \longrightarrow [\overset{\delta\ominus}{X}\cdots R\cdots\overset{\delta\ominus}{Y}] \longrightarrow RY + X^{\ominus} \quad (S_N2)$$

In this case two molecules undergo covalency change in the rate-determining step. The reaction is, therefore, regarded as bimolecular and labelled S_N2.

These two processes* can be distinguished from one another by the use of suitable mechanistic tests which are considered in the following section.

3. The Recognition of Mechanism in Nucleophilic Substitution Reactions.

(a) Kinetic form.

In an S_N1 reaction a single molecule, RX, is involved in the rate-determining step and, therefore, first order kinetics should be observed; ie.,

$$\text{Rate} = k\,[RX] .$$

Small deviations from strictly first-order kinetics may, however, be observed if the reversal of the rate-determining ionisation of RX occurs at a rate comparable to that for the formation of the product.

In the S_N2 reaction two molecules are involved in the rate-determining step and, therefore, second-order kinetics should be observed; ie.,

$$\text{Rate} = K[RX]\,[Y] .$$

(where Y is the substituting agent).

The present work is concerned with solvolytic reactions and as the nucleophilic reagent, the solvent, is present in large excess, its concentration will not change significantly over the course of reaction.

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* Winstein (3) has suggested that an 'ion-pair' may be involved in the S_N1 process; there is, however, no evidence for the intervention of 'ion-pairs' in solvolysis in partly aqueous solvents and S_N1 reactions will therefore be considered as occurring exclusively via a carbonium ion intermediate.

First-order kinetics will, therefore, be observed irrespective of the reaction mechanism.

(b) Influence of the solvent.

The formation of a highly polar transition state is an essential feature of S_N solvolysis and thus, in polar solvents, the transition state will be stabilised by solvation.

The extent of solvation depends upon two main factors; the polarity of the solvent, and the degree and nature of the charge development in the transition state. The power to solvate a charged solute will, in general, increase with increase in the molecular dipole moment of the solvent but will decrease with increased shielding of the dipolar charge(2). It must be emphasised, however, that the ionising or solvating power of a given solvent cannot be adequately measured in terms of its dielectric constant alone (4)(5). This is especially true for mixtures of water and inert solvents where the actual water content is of far greater importance than any function of the dielectric constant (6)(7)(8). With reference to the degree of charge development in the transition state, it is expected that solvation will increase with increasing magnitude of the charge but will decrease with its increased dispersal, although the latter effect will be less than that due to destruction of the charge (2).

Consideration of the S_N1 and S_N2 processes shows that the degree of charge dispersal is greatest in the S_N2 transition state; it is, therefore, to be expected that a bimolecular reaction will be less sensitive to changes in the ionising power of the solvent than the unimolecular process. This is illustrated in Table I-A.

Although this test is valuable for distinguishing between reactions

TABLE I-A

The Effect of a Change in Solvent Composition on the Rate of S_N1 and S_N2 Reactions.

System	10^5k (sec^{-1})		$\frac{k50\%}{k70\%}$	Ref.
	50% acetone	70% acetone		
Benzhydryl chloride in aqueous acetone at 25°C (S_N1).	1650	32	51.5	(9)
Benzyl chloride in aqueous acetone at 50°C (S_N2).	3.103	0.413	7.5	(10) (present work)

by the extreme forms of the two mechanisms it does not always give unambiguous results. In the mechanistic border line region which marks the transition from S_N2 to S_N1 solvolysis most of the positive charge in the transition state may be situated on the central carbon atom although covalent attachment of a solvent molecule is an essential feature of the process. Such a reaction must be considered as bimolecular yet the effect of solvent changes on the rate may be closer to those found in S_N1 solvolysis than in reaction by the more extreme form of mechanism S_N2. Moreover an extreme change in the ionising power of the solvent may cause a complete change in reaction mechanism (see Section 4(c)) which further limits the usefulness of this test.

(c) Stereochemistry (2)

In an S_N2 reaction the nucleophilic reagent participates in the formatio of the transition state and always approaches the reaction centre from a direction remote to the displaced group; ie.,

$\left[\overset{\delta\ominus}{Y}\text{---}R\text{---}\overset{\delta\ominus}{X}\right]$ (where X is the displaced group)

Thus for an optically active alkyl halide (RX), where the reacting carbon atom is a centre of asymmetry, an inversion of configuration will be produced on substitution.

In an S_N1 reaction the nucleophile reacts with a carbonium ion, $R^{\oplus}$ (see page 2). Since $R^{\oplus}$ is planar (11) the nucleophilic reagent can approach the reaction centre from both directions; thus a reaction carried out with an optically active compound whose centre of asymmetry is the reacting carbon atom will give a racemised product.

Although the stereochemical courses of the S_N1 and S_N2 reactions appear to be very different a more detailed examination of the S_N1 process shows that this mechanism can also give rise to an almost complete inversion of configuration. The scheme for an S_N1 solvolytic reaction may be written as:

$$RX + xSOH \underset{1a}{\overset{1}{\rightleftharpoons}} (R.xSOH)^{\oplus} + X^{\ominus} \xrightarrow{2} ROS + X^{\ominus} + H^{\oplus} + (x-1)\ SOH.$$

Where SOH is a solvent molecule and $(R.xSOH)^{\oplus}$ represents the carbonium ion surrounded by its solvation shell. If the carbonium ion is very unstable reaction with the solvent molecule may occur while the displaced group, $(X^{\ominus})$, is still very close to the carbonium ion. In such cases attack by the solvent molecule will occur from a single direction, that remote to the displaced group, and produce a net inversion of configuration (12).

Retention of configuration has been observed in S_N1 reactions and arises from the interaction between suitably placed 'protecting-groups' and the reaction centre. Thus certain groups having unshared electrons, such as the α-carboxylate ion (13), may form a weakly electrostatic bond with the reaction centre on the side remote to the displaced group; hence attack by a nucleophilic reagent is less likely from this direction and a net retention of configuration will result.

The usefulness of the stereochemical test is thus seen to be restricted; probably the most important factor for defining reaction mechanism is the identification of complete racemisation with the S_N1 mechanism.

(d) The influence of added electrolytes (2)

The polar transition state in S_N solvolysis is stabilised by solvation as described in Section 3(b). In the presence of ionic substances the transition state will also have the opportunity to form an ion-atmosphere similar to that envisaged in the Debye-Hückel treatment of fully developed ions. This will result in a greater stability of the transition state and hence an increase in reaction rate. This effect, which is known as the Ionic Strength Effect, does not influence S_N1 and S_N2 processes to the same extent but is greatest for S_N1 reactions due to the more concentrated nature of the electronic change in the transition state.

In S_N1 reactions the rate determining ionisation of RX is reversible; *ie.*,

$$RX \underset{1a}{\overset{1}{\rightleftharpoons}} R^{\oplus} + X^{\ominus}.$$

Thus if $X^{\ominus}$ ions are added to the reaction the rate of the reverse process, 1a, will increase and the overall rate of reaction will decrease. Even in the absence of added $X^{\ominus}$ ions a progressive fall in reaction rate may be observed; this is due to the increase in the concentration of $X^{\ominus}$ as reaction proceeds. This effect, which is specific to S_N1 reactions (the rate determining stage in S_N2 reactions being non-reversible), is known as the Mass Law Effect. It is apparent that for an S_N1 reaction in the presence of added common ions the Ionic Strength and Mass Law Effects will oppose one another - the resultant effect depending on the relative magnitudes of these two quantities.

The quantitative treatment of the effects of added electrolytes (2) thus indicates that all electrolytes should accelerate both S_N1 and S_N2 solvolysis, although common-ion electrolytes may retard the rate of an S_N1 reaction but not that of an S_N2 reaction. Recently, however, several observations contrary to this view have been reported. Thus the addition of non-common fluoride ions to the solvolysis of benzhydryl chloride and its p-nitro derivative in aqueous acetone is found to retard the ionisation of the substrate (14)(15), and a similar effect is noted for the addition of hydroxide and chloride ions to the solvolysis of neophyl p-toluene sulphonate in aqueous dioxan (16).

Lucas and Hammett (17) have noted that electrolytes having anions in common with those of the solvent (lyate ions) may reduce the rate of reaction. Thus the addition of hydroxide ions to the solvolysis of t-butyl nitrate reduces the rate of reaction and a similar effect has been observed by Benfey, Hughes and Ingold (18) in the unimolecular solvolysis of some t-butyl and diphenyl methyl halides. Furthermore a slight reduction of reaction rate by chloride ions has been reported for the hydrolysis of benzyl chloride in partly aqueous media (19)(20) although all other evidence indicates that this substance reacts by mechanism S_N2 in these solvents (19)(21). It should be noted that further complications may arise when the added electrolyte is also a nucleophilic reagent - this aspect is discussed on page 13.

In view of the limitations of the simple quantitative treatment probably the only valid test of reaction mechanism, arising from the addition of electrolytes to S_N solvolysis, is the identification of a large reduction in reaction rate by common ions with the S_N1 process.

(e) Activation parameters.

Evidence obtained in recent years has clearly shown that the activation parameters for the solvolysis of alkyl halides decrease with increasing temperature. (see Chapter II.).

Bensley and Kohnstam (10) have recently suggested that the value of the ratio $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ (the heat capacity and the entropy of activation, respectively) can provide useful information about the reaction mechanism. It was assumed that in S_N1 reactions the magnitudes of both $\Delta C^{\ddagger}$ and $\Delta S^{\ddagger}$ reflect almost entirely the increase in solvation on passage into the transition state. Thus, since both of these terms are controlled by the same factors, their ratio, $\Delta C^{\ddagger}/\Delta S^{\ddagger}$, should be independent of the nature of the substrate and dependent only on temperature and solvent composition. In S_N2 solvolysis the partial covalent attachment of a solvent molecule in the transition state should cause a greater decrease in entropy than its participation in solvation, although the value of $\Delta C^{\ddagger}$ should not be greatly affected. The value of $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ for an S_N2 reaction should, therefore, be substantially less than that for an S_N1 reaction.

The results available at the beginning of the present work indicated that these requirements were met in the solvolysis of alkyl chlorides. Further evidence is now available (22) which shows that this mechanistic test appears to be valid for both alkyl chlorides and bromides and may be of value in the study of 'border-line' reactions where classical tests do not always give unambiguous results.

In the preceding pages several mechanistic tests for distinguishing between the S_N1 and S_N2 mechanisms have been discussed; additional, although generally less definite, tests can be considered more conveniently in the following section.

4. Factors Influencing the Mechanism of Nucleophilic Processes.

(a) Structural factors (2).

The influence of the alkyl group structure can be discussed most conveniently by considering reactions by mechanisms S_N1 and S_N2 separately.

(i) S_N1 solvolysis: The essential feature of the S_N1 mechanism is a stretching of the R-X bond leading to the eventual formation of a carbonium ion. Thus any structural property which can increase the delocalisation of the electronic charge at the reaction centre in the transition state, via induction (23), conjugation (24) or hyperconjugation (25), will facilitate the S_N1 process. The tendency to react via ionisation will, therefore, depend upon the extent of electron release towards the reaction centre which for a series of alkyl halides, RX, is expected to increase in the order:

A. $CH_3X < C_2H_5X < (CH_3)_2.CHX < (CH_3)_3.CX$

B. $CH_3X < Ph.CH_2X < Ph_2.CHX < Ph_3.CX$

C. $p\text{-}NO_2.C_6H_4.CH_2X < Ph.CH_2X < p\text{-}(p\text{-}CH_3O.C_6H_4).C_6H_4.CH_2X < p\text{-}PhO.C_6H_4.CH_2X$
$< p\text{-}CH_3O.C_6H_4.CH_2X$.

As a result, in solvents of moderate polarity, a change in mechanistic behaviour can be observed in these series which is located in the region of the iso-propyl group in A, the benzyl group in B (2) and the $p\text{-}(p\text{-}MeO.C_6H_4).C_6H_4.CH_2\text{-}$ group in C(22).

The presence of substituents on the alkyl group can have a considerable effect upon the ionisation process provided their electron releasing or attracting properties can be effectively transmitted to the seat of reaction. A nitro group, being electron attracting, will hinder ionisation and cause a reduction in the rate of an S_N1 reaction - see Table I-B. On the other hand the carboxylate ion, phenoxy and methoxy groups, which are powerful electron donors, will increase the rate of ionisation and, in fact, their effect may be sufficient to cause a change in mechanism from S_N2 for the parent compound to S_N1 for the substituted compound. This behaviour has been observed by Hughes and Taher (26) for a series of α-bromo-carboxylate ions and by Kohnstam and his co-workers (22) for a series of p-substituted benzyl chlorides.

An additional structural factor which may cause some acceleration in S_N1 reactions arises from a reduction in atomic congestion on forming the transition state and has been described as Steric Acceleration (27). In branched systems up to Me_3C-CMe_2X there is, however, some doubt whether the increase in reaction rate should be attributed to a steric or a polar effect. With even more highly branched systems accelerative effects occur which are sufficiently large to indicate the possible operation of such a steric factor (28).

(ii) S_N2 Solvolysis: Bimolecular substitution reactions involve the simultaneous transfer of electrons from the substituting agent to the alkyl group and from the latter to the expelled group. The bimolecular reaction should therefore, in the absence of complicating steric effects, be less sensitive to the effects of electron attracting or releasing substituents on the alkyl group than the unimolecular process. Although a flow of electrons to the reaction centre facilitates ionisation it may hinder the approach of the substituting agent, especially when the latter is negatively charged, and may even retard the rate of reaction.

Tables I-B and I-C show the effects of substituents on some S_N1 and S_N2 reactions.

The stereochemical course of the S_N2 reaction suggests that atomic congestion in the molecule as a whole is increased by the formation of the transition state which may be represented as follows:

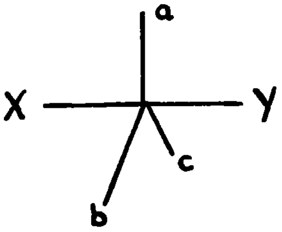

TABLE I-B.

The Effect of a p-NO_2 Group on Reaction Rate.

System	Mechanism	Relative Rates		Ref.
		p-H	p-NO_2.	
Benzhydryl chloride in 70% aqueous acetone at 45°C	S_N1	1.00	0.0014	(20)
Benzyl chloride in 50% aqueous acetone at 69.8°C	S_N2	1.00	0.105	(29)

TABLE I-C.

The Effect of p-Alkyl Groups on Reaction Rate.

System	Mechanism	Relative Rates			Ref.
		p-H	p-Me	p-tBu	
Benzhydryl chloride in 80% aqueous acetone at 0°C	S_N1	1.00	29.6	12.7	(30)
Benzyl bromide with pyridine in acetone at 20°C	S_N2	1.00	1.66	1.35	(25)

This effect, which can reduce the rate of reaction, is known as Steric Retardation (28)(31). A particular example of steric retardation is afforded by the neo-pentyl halides (32), $(CH_3)_3.C.CH_2X$, where congestion in the bimolecular transition state is so great that it almost inhibits reaction by this mechanism.

Consideration of the influence of the alkyl group structure on reaction mechanism shows clearly that the effects of suitable substituents can be used as a test of reaction mechanism as indicated in Tables I-B and I-C. The usefulness of this test, however, is limited since the substitution of certain groups on R- may bring about a complete change in reaction mechanism.

(b) Nucleophilicity of the substituting agent.

Since the rate-controlling factor in mechanism S_N1 is the ionisation of the R-X bond this process is clearly independent of the nucleophilicity of the substituting agent.

In the bimolecular reaction, however, the nucleophile is involved in the rate-determining stage and this process will, therefore, be dependent upon the nucleophilicity of the substituting agent. Thus, for a series of reactions in which the only variable is the nucleophile, the rate of the S_N2 process will decrease with decreasing nucleophilicity of the reagent and may eventually become lessthan that for ionisation. The mechanism will then become unimolecular and independent of the substituting agent. This type of behaviour has been demonstrated for the decomposition of trimethyl sulphonium salts in ethyl alcohol (33) for the reagents, (in order of decreasing nucleophilicity):

$$OH^{\ominus}, \quad OPh^{\ominus}, \quad CO_3^{\ominus\ominus}, \quad Br^{\ominus}, \quad Cl^{\ominus}.$$

The relatively rapid second-order reactions with hydroxide and phenoxide ions were interpretted as S_N2 reactions, while the carbonate, bromide and chloride ions reacted by first-order kinetics with the same rate constant and were regarded as occurring unimolecularly. This implies that the carbonate, bromide and chloride ions are such poor nucleophiles that they cannot compete adequately with an ionisation process. However these results could be explained equally well on the basis that the carbonate, bromide and chloride ions cannot compete with a bimolecular reaction between solvent ethanol and substrate (6).

The effect of varying the nucleophile in an otherwise constant bimolecular system can be used to obtain a comparative measure of the nucleophilicity of the substituting agent. From such data the following list of reagents, in order of decreasing nucleophilicity has been prepared. (34).

$C_6H_5S^{\ominus} > I^{\ominus} > C_2H_5O^{\ominus} > Br^{\ominus} > OPh^{\ominus} > Cl^{\ominus} > CH_3COO^{\ominus} > NO_3^{\ominus}$.

An alternative measure of the strength of a nucleophile has been proposed by Swain and Scott (35) in terms of a nucleophilic constant. This is defined as the logarithm of the rate of reaction of a nucleophile with methyl bromide in water, relative to the rate of the reaction of methyl bromide with water itself. The choice of water as the standard solvent may be a poor one but the results obtained are in fair agreement with those described above.

In the preceding pages it is clearly indicated that the effect of a nucleophile can provide a useful test for reaction mechanism. Thus the rate of an S_N2 reaction will be altered by a change in the nucleophilicity of the substituting agent, whereas the rate of an S_N1 reaction will not. However the addition of a powerful nucleophile to S_N1 solvolysis may give rise to a situation in which the substrate reacts bimolecularly with the nucleophile and unimolecularly with the solvent (36).

(c) The ionising power of the solvent.

The importance of solvation in increasing the stability of the transition state in S_N reactions has been stressed in earlier sections.

In powerfully ionising solvents the ease of ionisation may be increased to such an extent that it is possible that a reaction, which otherwise occurs by mechanism S_N2, will take place by mechanism S_N1. Thus Bateman and Hughes (37) who examined the hydrolysis of alkyl halides by water in formic acid, a good ionising solvent, observed that even for primary halides the reactions were only slightly dependent on the small amount of water present and gave rise to the first-order rate sequence:

$$Me < Et < i\text{-}Pr < t\text{-}Bu.$$

There is some evidence that in poorly ionising solvents the reverse of the above is true, the bimolecular reaction being preferred. For the system alkyl halide/halide ion in acetone (38) the rate of second-order displacement for a number of simple alkyl halides (RX) was found to decrease in the order;

$$Me > Et > i\text{-}Pr > t\text{-}Bu.$$

It is, however, doubtful whether the reactions of the t-butyl halides are, in fact, bimolecular since mixed first and second-order kinetics have been observed under these circumstances (39)(40), while recent work by Gall and Winstein (41) indicates that probably only a small fraction of these reactions of the t-butyl halides occur bimolecularly.

The relationship between ionising power and other properties of a solvent is complex. The simple model of a solvent as a continuous dielectric can often be used to predict the gross effect of a change in solvent composition for reactions of various charge types (42)(43) but there is little doubt that such a model is severely restricted. Thus mixed solvents can hardly be considered as continuous media since some segregation of the solvent components will undoubtably occur in the vicinity of the reactants. An additional factor which renders dielectric constant a poor guide to ionising power is the possibility of hydrogen bonding between hydroxylic, and similar solvents, and the ground and transition states of the organic substrate.

Numerous attempts to correlate the ionising powers of different solvents have been made (4)(44)(45)(46) but the methods employed can hardly be considered as having a sound theoretical basis and the principal value of the results obtained seems confined to a rough prediction of solvolysis rate.

Grunwald and Winstein (4), who have carried out extensive work in this field, have defined the ionising power of a solvent, Y, as the logarithm of the rate of solvolysis of t-butyl chloride in that solvent relative to its rate of solvolysis in 80% aqueous ethanol. It was found that the logarithms of the solvolysis rates of many compounds gave linear correlations in Y which could be expressed by:-

$$\log k = mY + \log k_0$$

Where k_0 is the rate of solvolysis in the standard solvent (80% aqueous ethanol), and m is a measure of the sensitivity of the substrate to the ionising power of the solvent relative to t-butyl chloride. This method of measuring ionising power is, however, subject to severe limitations (47)(48) and it has been observed that in systems different to t-butyl chloride different correlation lines are often obtained.

(d) <u>The influence of the displaced group.</u>

A feature common to both the S_N1 and S_N2 processes is the heterolysis of the R-X bond - the more facile this bond-breaking process the greater will be the reactivity of the compound RX in this type of reaction. On this basis a relationship between the ionisation energy of the C-X bond and reactivity might be expected. Examination of many solvolytic reactions, occurring by both S_N1 and S_N2 mechanisms, indicates that the ease of displacement of various groups decreases in the order:-

$I > Br > Cl > SR_2^{\oplus} > F$. (2)(6)(49)(50)(51)(52)(53)(54)(55)(56).

This sequence is also the sequence of increasing ionisation energy for the C-X bond (57). In both S_N1 and S_N2 reactions iodides, although occasionally behaving contrary to this reactivity sequence (51)(58)(59), generally react 1.5 - 4.5 times faster than the corresponding bromides which, in turn, react some 25-60 times faster than the corresponding chlorides.

Rates of chemical reactions are usually related to two experimentally determinable parameters, the energy and entropy of activation, E and $\Delta S^{\ddagger}$ respectively. Since a decrease in the value of E leads to an increase in reaction rate a tentative explanation of the halide reactivity sequence can be offered in terms of a reduction in E arising from the change in inductomeric polarisability of the displaced halogens which decrease in the order (2):-

$$I > Br > Cl > F.$$

On the other hand there seems no real reason why a change in $\Delta S^{\ddagger}$ should not be the dominant factor.

Values of E and $\Delta S^{\ddagger}$ for the solvolysis of many alkyl halides can be calculated from the published rate data*; examination of the results obtained for various pairs of alkyl chlorides and bromides does not, however, reveal any clear trends. In some systems the change in rate appears to result almost entirely from a change in E and in others almost entirely from a change in $\Delta S^{\ddagger}$; changes in rate arising from significant changes in both E and $\Delta S^{\ddagger}$ have also been reported. Typical examples are given below in Table I-D.

It will be noted from Table I-D that the values of E and $\Delta S^{\ddagger}$ do not necessarily refer to the same temperature for the chloride and bromide; in general this is true for most of the published rate data since the more reactive bromides are usually examined at lower temperatures than the corresponding chlorides. Recent work, however, has clearly indicated that the values of both E and $\Delta S^{\ddagger}$ can vary with temperature in S_N solvolysis** and thus a comparison of reactivities in terms of these parameters is only

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* See references quoted for the halide reactivity sequence - page 16.

** See Chapter II.

TABLE I-D.

Activation Parameters for the Solvolysis of Some Alkyl Halides.

System		E (kcal/mole)	$\Delta S^{\ddagger}$ (e.u)
t-Butyl halides in aqueous acetone (53)	Cl	23.0 at 27.4°	- 9.7 at 27.4°
	Br	20.2 " 15.0°	-10.6 " 15.0°
Methyl halides in water (51)	Cl	25.3 " 45.1°	-10.2 " 45.1°
	Br	24.7 " 45.1°	- 6.7 " 45.1°
Iso-propyl halides in aqueous ethanol (60)(61)	Cl	23.1 " 99.8°	-18.7 " 99.8°
	Br	23.3 " 70.0°	-11.1 " 70.0°

justified when their values refer to the same temperature for both chloride and bromide. Comparisons of the type shown in Table I-D. are therefore invalid and furthermore, as the temperature coefficients of E and $\Delta S^{\ddagger}$ are usually not available for these reactions, no comparisons of these parameters at the same temperature are possible.

It was therefore decided to investigate the hydrolysis of several pairs of alkyl chlorides and bromides in aqueous acetone over wide ranges of temperature so that the temperature coefficients of both E and $\Delta S^{\ddagger}$ could be obtained. Values of E and $\Delta S^{\ddagger}$ for the hydrolysis of these chlorides and bromides could then be compared at the same temperature. Before the results of the present work can be discussed, however, it is necessary to examine the variation of E with temperature; this is considered in the following chapter.

CHAPTER II.

THE TEMPERATURE DEPENDENCE OF ENERGY OF ACTIVATION.

1. The Arrhenius Equation (62).

The variation of rate constant (k) with temperature is expressed by the Arrhenius equation as:-

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

where E is the energy of activation.

On the assumption that E is a constant, equation 1 can be written in the integrated form:-

$$\ln k = \frac{-E_A}{RT} + B \text{ - - - - - - - - } 2$$

where $E_A = E$ when E is, in fact, constant.

The integrated equation 2 has been extensively used in chemical kinetics (63) and the value of E_A established as a constant for a given chemical reaction. In spite of the experimental evidence for the constancy of energy of activation the theoretical considerations of La Mer (64), Scheffer and Brandsma (65) and Trautz (66) have indicated that E should be temperature-dependent when the heat capacity of the activated complex differs appreciably from that of the initial reactants; the same conclusion arises from Eyring's (5) absolute rate equation.

Probably the first genuine observation of a variation of E with temperature was that of Moelwyn-Hughes (67) in the hydrolysis of methyl halides in water. More recently several workers, notably Kohnstam (10) (68)(69)(70), Moelwyn-Hughes (51)(71), Tommila (72)(73) and Robertson (52)(74)(75)(76) and their co-workers have reported a temperature-dependence of the energy of activation in many solvolytic reactions and have clearly shown that the value of E decreases with an increase in temperature. (see Table II-A).

TABLE II-A.

Values of dE/dT in Some Solvolytic Reactions.

System	-dE/dT (cal/deg).	Ref.
Methyl halides in water.	64	(67)
Substituted aryl sulphonates in water.	25-35	(74)
t-Butyl chloride in aqueous acetone.	60 (average)	(73)
Benzyl and substituted benzyl chlorides in aqueous acetone.	19-44	(10)
t-Butyl chloride in aqueous acetone.	25	(69)
Ethyl bromide in aqueous acetone.	33	(77)

At this point it is of interest to consider the reasons why a variation of energy of activation with temperature was not generally observed earlier for reactions of this type. There are probably two main reasons. The graphical determination of E from the Arrhenius equation by plotting ln k against 1/T may have completely obscured its variation with temperature, while the use of small temperature ranges and some inaccuracy in rate measurements can give rise to inaccurate values of E; values are often quoted as accurate to ±0.5 kcal. This would prevent the observation of any variation with temperature when dE/dT is numerically small.

2. The Variation of E With Temperature.

The evidence presented in Section 1 shows clearly that E is temperature-dependent; it is now necessary to consider the origin of this effect.

In the transition state theory of reactions (5) a sequence -

$$\text{Initial Reactants} \longrightarrow \text{Activated Complex} \longrightarrow \text{Products},$$

is envisaged. The activated complex, or transition state, is regarded as being in equilibrium with the initial reactants and similar to an ordinary molecule except that translational motion along the reaction co-ordinate leads to decomposition.

The absolute rate equation may be written in the form:-

$$\ln k = \ln \frac{(k'T)}{(h)} + \frac{\Delta S^{\ddagger}}{R} - \frac{\Delta H^{\ddagger}}{RT} \quad \text{--------} \; 3$$

Where k' = the Boltzmann constant.

h = Planck's constant.

$\Delta S^{\ddagger}$ = the entropy of activation and represents the difference in entropy between the initial and activated states.

$\Delta H^{\ddagger}$ = the enthalpy of activation and represents the difference in enthalpy between the initial and activated states.

Differentiation of equation 3 with respect to temperature gives

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

which, on comparison with equation 1 shows that

$$E = \Delta H^{\ddagger} + RT$$

and hence that

$$\frac{dE}{dT} = \frac{d(\Delta H^{\ddagger})}{dT} + R$$

$$= \Delta C^{\ddagger} + R.$$

where $\Delta C^{\ddagger}$ represents the difference in heat capacity between the initial and transition states, and is known as the heat capacity of activation.

Thus the variation of E with temperature can, according to the absolute rate equation, be attributed to a change in heat capacity on attaining the transition state. All the available experimental evidence shows that $\Delta C^{\ddagger}$ is negative in solvolytic reactions and it must therefore be concluded that the heat capacity of the activated complex must be less than that of the initial reactants. Several explanations have been proposed to account for this.

The electrostatic treatment of reaction rates, which envisages the solvent as a continuous dielectric, considers that there is an electrostatic contribution, E_D, to the energy of activation which depends on dielectric constant. For all known solvents the dielectric constant, D, decreases with increasing temperature and thus E_D, and therefore E can be expected to vary with temperature. The electrostatic approach has been used by many workers (5), especially Amis and La Mer (78)(79) and Warner (80) in the discussion of a large number of ionic and ion-dipole reactions, and is found to give a satisfactory explanation of a great deal of experimental data.

According to Pearson (81) the changes in energy and entropy for a reaction having a pseudo-ionic transition state can be interpretted using Kirkwood's equation (82). In this treatment, which assumes the Born charging process, the free energy (ΔG) of a dipole, of moment μ and molecular radius r, in a medium of dielectric constant D relative to its value in a vacuum is given by:

$$\Delta G = -\frac{\mu^2}{r^3}\frac{(D-1)}{(2D+1)} \qquad \text{- - - - - - - - - - 4}$$

ΔS for this process will be obtained by differentiating equation 4 with respect to temperature. However the electrostatic contribution to ΔS only arises when D varies with temperature. Hence ΔS, which refers to the transfer of a dipole from a vacuum to a medium of dielectric constant D, is equal to S_D, the electrostatic entropy of the dipole in the medium of dielectric constant D. Consequently ΔS_D, the electrostatic contribution to the entropy of activation, is given by:

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

The subscripts i and t refer to the initial and transition respectively. The electrostatic contribution to $\Delta C^{\ddagger}$ will then be:

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

Values of ΔC_D obtained in this manner are usually negative but in poor agreement with values of $\Delta C^{\ddagger}$ obtained experimentally (70)(83); this could, however, be due to the choice of an inappropiate value for $\left(\frac{\mu_t^2}{r_t^3} - \frac{\mu_i^2}{r_i^3}\right)$. On the other hand if the value of this term is adjusted to give the correct value of ΔC_D (ie. $\Delta C_D = \Delta C^{\ddagger}$) the corresponding value of ΔS_D does not then agree with the experimental value of $\Delta S^{\ddagger}$; furthermore, electrostatic factors do not control the changes in both $\Delta S^{\ddagger}$ and $\Delta C^{\ddagger}$ observed in going from one solvent to another (70). The failure of the electrostatic approach in the study of many reactions has already been referred to (page 4), and it is further note-worthy that temperature dependent E values are not generally associated with constant iso-dielectric activation energies as required by the theory (84)(85). Moreover the Born relationship assumed in this treatment does not satisfactorily account for the forces existing between a charged particle and its first solvation shell, although it accounts well for the long range forces between charged particles in solution (86)(87).

Moelwyn-Hughes (51) has suggested that the transition state for the hydrolysis of methyl halides has zero heat capacity and that $\Delta C^{\ddagger}$ is, therefore, numerically equal to the partial molar heat capacity of the initial reactant which was observed to vary with temperature. A temperature dependence of $\Delta C^{\ddagger}$ in these reactions is not, however, shown by the recent work of Heppolette and Robertson (52); furthermore there seems little reason why the heat capacity of the activated complex should be zero since parts of the molecule will be unaffected by the activation process. It is also difficult to accept a scheme for reactions of this type which does not envisage the participation of solvent molecules in the transition state.

Kohnstam (70) has explained the difference in the heat capacity of the initial and transition states for S_N reactions in terms of solvation. The effect of solvation in these reactions, which was discussed on page 4, causes a reduction in the energy of activation required for reaction; since solvent molecules involved in the solvation process are less free to move than those in the bulk of the solvent they will be less able to absorb heat, and their heat capacity will therefore decrease. On this view the degree of solvation of the transition state relative to that of the initial state is the most important factor controlling the magnitude of $\Delta C^{\ddagger}$; furthermore this solvation hypothesis can also be used to account for the different values of $\Delta S^{\ddagger}$ for S_N1 and S_N2 reactions and the constantcy of the ratio $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ in solvolysis by mechanism S_N1 - see Chapter I, Section 3 (e) and Chapter III, Section 2 (b).

This simple solvation hypothesis is not, however, supported by Robertson and his co-workers (88)(89) who believe that the interactions between the initial state and the solvent are not carried over into the transition state with the result that the values of $\Delta C^{\ddagger}$, and $\Delta S^{\ddagger}$, will depend upon the structure of the substrate for all nucleophilic substitution reactions. It should be noted, however, that most of Robertson's work refers to solvolysis in water and it may be that the factors controlling the magnitude of $\Delta C^{\ddagger}$, and $\Delta S^{\ddagger}$, in this solvent are not the same as in partly aqueous media (69). For example, $\Delta S^{\ddagger}$ for the hydrolysis of t-butyl chloride in water decreases rapidly when small amounts of water are added (73) although the partial molar entropy of water changes little under these conditions.

A 'freezing-out' of solvent molecules, as in solvation, has also been assumed to account for the negative partial molar heat capacities of electrolytes (90) and the negative heat capacities of ionisation of weak acids (86). Although these cases refer to fully developed ions it seems reasonable to expect a certain similarity in behaviour with the polar transition state of an S_N reaction. Negative values of $\Delta C^{\ddagger}$ have been observed in other reactions where the transition state is more polar than the initial reactants; eg., in the hydrolysis of acetic anhydride in water and aqueous acetone $\Delta C^{\ddagger}$ varies between -55 and -89 cal/deg (84), while for the solvolysis of 1-methallyl chloride in 50% aqueous ethanol (70) the value is about -60 cal/deg and about -45 cal/deg for the hydrolysis of methyl nitrate in water (91).

The solvation hypothesis proposed by Kohnstam also gives a satisfactory explanation why the value of the ratio $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ should be greater for solvolysis by mechanism S_N1 than by mechanism S_N2 (See Chapter I, Section 3 (e)), and furthermore, since the results obtained in the present work also show that the value of $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ is greatest for compounds reacting by mechanism S_N1, the solvation hypothesis will be used in the discussion of the results of this work in the following chapter.

CHAPTER III.

RESULTS AND DISCUSSION

In this work the hydrolysis of several alkyl chlorides (RCl) and bromides (RBr) in aqueous acetone was studied over a temperature range of 50° and rate constants were determined at 10° intervals. Rate constants determined in this fashion enable values of the activation parameters, E and $\Delta S^{\ddagger}$, to be calculated at several temperatures and thus allow the temperature-dependence of these parameters to be determined. In every case hydrolysis was followed measuring the acidity developed by titration with dilute sodium hydroxide; good first-order kinetics were always obtained.

The systems examined are shown below, where it can be seen that data for the hydrolysis of three pairs of alkyl chlorides and bromides, two of the pairs in two different solvents, are now available.

R	$PhCH_2$*	$PhCH_2$	t-Bu	t-Bu*	$p\text{-}NO_2.C_6H_4.CHPh$*
% Acetone	50	70	70	80	70
Mechanism	S_N2	S_N2	S_N1	S_N1	S_N1

1. Results.

The kinetic data for the reactions now studied are summarised in Tables III-A - III-G. Energies of activation (E_{OBS}) were calculated from rate coefficients (k) at adjacent temperatures via the integrated form of the Arrhenius equation, and refer to the mean temperature of the interval, $(T_1 + T_2)/2$ (70). Entropies of activation ($\Delta S^{\ddagger}_{OBS}$) at the

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* Results for benzyl chloride in 50% acetone, t-Butyl bromide in 80% acetone and p-nitrobenzhydryl chloride in 70% acetone were already available before the beginning of this work (20).

TABLE III-A.

Benzyl Bromide in 50% Solvent (Solvent F).

(Temp. in °C., k in sec.$^{-1}$, E in kcal., $\Delta S^{\ddagger}$ and $\Delta C^{\ddagger}$ in cal. deg.$^{-1}$).

Temp.	10^4k	Temp.	E_{OBS}	E_c	$\Delta S^{\ddagger}_{OBS}$	$\Delta S^{\ddagger}_c$
69.00	3.439 ±0.003					
		64.19	18.653±0.038	18.657±0.032	-22.11	-22.10
59.37	1.554 ±0.002					
		54.40	18.870±0.041	18.892±0.011	-21.40	-21.34
49.42	0.6439 ±0.0009					
		44.55	19.187±0.045	19.129±0.011	-20.36	-20.55
39.67	0.2533 ±0.0004					
		34.81	19.330±0.052	19.362±0.032	-19.84	-19.73
29.95	0.09347±0.0002					

$$\Delta C^{\ddagger} = -26.0 \pm 2.2.$$

TABLE III-B.

Benzyl Bromide in 70% Solvent (Solvent G).

(Temp. in °C., k in sec.$^{-1}$, E in kcal., $\Delta S^{\ddagger}$ and $\Delta C^{\ddagger}$ in cal. deg.$^{-1}$).

Temp.	10^4k	Temp.	E_{OBS}	E_c	$\Delta S^{\ddagger}_{OBS}$	$\Delta S^{\ddagger}_c$
84.88	2.320 ±0.003					
		79.91	18.441±0.055	18.477±0.039	-25.99	-25.90
74.94	1.107 ±0.002					
		69.98	18.754±0.057	18.686±0.013	-25.04	-25.23
65.01	0.4994 ±0.0007					
		59.94	18.869±0.040	18.898±0.013	-24.64	-24.55
54.86	0.2095 ±0.0002					
		49.84	19.106±0.038	19.111±0.039	-23.85	-23.84
44.82	0.08304±0.00003					

$$\Delta C^{\ddagger} = -23.1 \pm 2.6.$$

TABLE III-C.

Benzyl Chloride in 70% Solvent (Solvents H and I).

(Temp. in °C., k in sec.$^{-1}$, E in kcal., $\Delta S^{\ddagger}$ and $\Delta C^{\ddagger}$ in cal. deg.$^{-1}$).

Temp.	10^4k	Temp.	E_{OBS}	E_c	$\Delta S^{\ddagger}_{OBS}$	$\Delta S^{\ddagger}_c$
114.97	0.9066 ±0.0007					
		109.94	20.124±0.045	20.131±0.044	-27.68	-27.65
104.90	0.4525 ±0.0006					
		99.86	20.362±0.052	20.325±0.014	-27.00	-27.08
94.82	0.2154 ±0.0003					
		89.94	20.460±0.072	20.517±0.014	-26.68	-26.51
85.05	0.1004 ±0.0002					
		79.90	20.736±0.080	20.711±0.044	-25.80	-25.92
74.74	0.04234 ±0.0001					

$$\Delta C^{\ddagger} = -21.3 \pm 2.9.$$

TABLE III-D.

t-Butyl Bromide in 70% Solvent (Solvents B and C).

(Temp. in °C., k in sec.$^{-1}$, E in kcal., $\Delta S^{\ddagger}$ and $\Delta C^{\ddagger}$ in cal. deg.$^{-1}$).

Temp.	$10^4 k$	Temp.	E_{OBS}	E_c	$\Delta S^{\ddagger}_{OBS}$	$\Delta S^{\ddagger}_c$
38,25	28.11 $\pm$0.06					
		33.94	19.863$\pm$0.077	19.833$\pm$0.046	-8.48	-8.58
29.62	11.26 $\pm$0.03					
		24.85	20.131$\pm$0.061	20.206$\pm$0.016	-7.54	-7.29
20.07	3.788 $\pm$0.007					
		15.50	20.646$\pm$0.040	20.589$\pm$0.015	-5.72	-5.94
10.92	1.210 $\pm$0.001					
		5.45	20.988$\pm$0.038	21.001$\pm$0.048	-4.44	-4.39
-0.03	0.2726$\pm$0.0007					

$$\Delta C^{\ddagger} = 43.0 \pm 3.3$$

TABLE III-E.

t-Butyl Chloride in 70% Solvent (Solvent D).

(Temp. in °C., k in sec.$^{-1}$, E in kcal., $\Delta S^{\ddagger}$ and $\Delta C^{\ddagger}$ in cal. deg.$^{-1}$).

Temp.	10^4k	Temp.	E_{OBS}	E_c	$\Delta S^{\ddagger}_{OBS}$	$\Delta S^{\ddagger}_c$
54.90	3.455 ±0.007					
		49.84	21.257±0.064	21.319±0.064	-11.73	-11.55
44.78	1.224 ±0.003					
		39.93	21.767±0.062	21.710±0.021	-10.07	-10.26
35.07	0.4135 ±0.0008					
		30.08	22.174±0.058	22.098±0.023	- 8.68	- 8.93
25.08	0.1230 ±0.0003					
		20.94	22.387±0.073	22.458±0.063	- 7.91	- 7.66
16.79	0.04176±0.00010					

$$\Delta C^{\ddagger} = -41.4 \pm 4.4$$

TABLE III-F.

p-Nitrobenzhydryl Bromide in 70% Solvent(Solvent A)

(Temp. in °C., k in sec.$^{-1}$, E in kcal., $\Delta S^{\ddagger}$ and $\Delta C^{\ddagger}$ in cal. deg.$^{-1}$).

Temp.	10^4k	Temp.	E_{OBS}	E_c	$\Delta S^{\ddagger}_{OBS}$	$\Delta S^{\ddagger}_c$
54.87	3.408 ± 0.007					
		49.89	22.324$\pm$0.073	22.356$\pm$0.040	-8.50	-8.41
44.90	1.165 ± 0.003					
		40.12	22.675$\pm$0.071	22.640$\pm$0.014	-7.34	-7.45
35.34	0.3833 ± 0.0008					
		30.07	22.957$\pm$0.048	22.933$\pm$0.013	-6.36	-6.43
24.79	0.1018 ± 0.0002					
		20.00	23.199$\pm$0.043	23.226$\pm$0.041	-5.48	-5.39
15.21	0.02770$\pm$0.00004					

$$\Delta C^{\ddagger} = -31.1 \pm 2.7.$$

TABLE III-G.

t-Butyl Chloride in 80% Solvent (Solvent E).

(Temp. in °C., k in sec.$^{-1}$, E in kcal., $\Delta S^{\ddagger}$ and $\Delta C^{\ddagger}$ in cal. deg.$^{-1}$).

Temp.	10^4k	Temp.	E_{OBS}	E_c	$\Delta S^{\ddagger}_{OBS}$	$\Delta S^{\ddagger}_c$
69.95	2.543 $\pm$0.007					
		64.96	21.669$\pm$0.082	21.729$\pm$0.051	-14.08	-13.89
59.97	0.9815 $\pm$0.0027					
		55.12	22.079$\pm$0.078	22.028$\pm$0.018	-12.79	-12.95
50.27	0.3610 $\pm$0.0010					
		44.97	22.367$\pm$0.064	22.337$\pm$0.017	-11.83	-11.92
39.66	0.1109 $\pm$0.0003					
		34.83	22.623$\pm$0.069	22.645$\pm$0.051	-10.95	-10.88
29.99	0.03474$\pm$0.00010					

$$\Delta C^{\ddagger} = -32.4 \pm 3.4.$$

same temperature were obtained from the equation (70)

$$\ln k_1 = \ln \frac{k}{h} + \ln\left(\frac{T_1+T_2}{2}\right) + 1 + \frac{\Delta S^{\ddagger}_{OBS}}{R} - \frac{E_{OBS}}{RT_1}$$

where E_{OBS} is the activation energy calculated from the rate coefficients at T_1 and T_2, and the subscrip 1 refers to the temperature T_1. The temperature coefficient of the activation energy, dE/dT, was obtained from the slope of the 'best' straight line of E_{OBS} against T by the method of least squares, and the heat-capacity of activation, $\Delta C^{\ddagger}$, from the equation,

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

Full details of the methods employed for the determination of rate coefficients and in the calculations are given in the experimental section (pp 44-50).

The results show that dE/dT is always negative, and never zero, as expected (cf. Chapter II). For each compound dE/dT, and hence $\Delta C^{\ddagger}$, appears to be constant within the limits of experimental error over the temperature range studied since the observed and calculated values of the activation energy (E_{OBS} and E_c[*]) and of the entropy of activation ($\Delta S^{\ddagger}_{OBS}$ and $\Delta S^{\ddagger}_c$[**]) are in good agreement with each other.

Most of the reactions studied in this work have been examined previously by other workers and it is, therefore, possible to compare the various results. Although the earlier data are generally restricted to narrow ranges of temperature reasonable comparisons are possible since

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[*] E_c is calculated from the 'best' straight line of E_{OBS} against T.

[**] $\Delta S_c^{\ddagger}$ is calculated from the 'best' straight line of $\Delta S^{\ddagger}_{OBS}$ against log T.

the temperature coefficients of both E and $\Delta S^{\ddagger}$ have been determined in the present work. Hence the values of these parameters can be calculated at the temperatures to which the previous values refer. Exact agreement between the results of different workers is, however, extremely unlikely. This is mainly due to the slight differences in the composition of the solvents used which arises from the difficulty of preparing partly aqueous solvents of exact composition by volume. Examination of the data given in Table III-H shows, however, that there is fair agreement between the results of the present work and those of other workers. Suitable data for comparison with p-nitrobenzhydryl and benzyl bromides in the 70% solvent were not found in the literature.

2. Discussion.

(a) The kinetic effect of replacing a chlorine by a bromine atom in alkyl halides.

The present results for the hydrolysis of some alkyl chlorides and bromides at 50°C are given in Table III-I. It can be seen that the bromides invariably react some 25-40 times faster than the corresponding chlorides and that, irrespective of mechanism, this increase in reactivity is almost entirely due to a reduction in activation energy.

This observation is supported by the work of Hine and Lee (50) on the hydrolysis of benzyl chloride and bromide in aqueous acetone and by Robertson and Heppolette's work (52) on the hydrolysis of methyl halides in water. In both these cases a comparison of the activation parameters for the chloride and bromide is possible at the same temperature.

The conclusion is not supported by the work of Winstein and his co-workers (54)(55)(56) who have examined a wide variety of solvolytic reactions for purposes of solvent characterisation. Their data show

TABLE III-H.

Comparison of Rate Constants and Other Parameters.

(k in sec.$^{-1}$, E in kcal. and $\Delta S^{\ddagger}$ in cal.deg.$^{-1}$)

Halide	10^4k	E	$\Delta S^{\ddagger}$	Ref.
Benzyl bromide in 50% aqueous acetone	0.418 at 45°C	18.96 at 37.5°C	-21.1 at 37.5°C	(50)
	0.424 " "	19.30 " "	-20.0 " "	Present Work.
Benzyl chloride in 70% aqueous acetone	0.0367 at 71.5°C	21.0 at 66.7°C	-24.7 at 66.7°C	(92)
	0.0321 " "	21.0 " "	-25.1 " "	Present Work.
t-Butyl bromide in 70% aqueous acetone	5.37 at 25°C			(93)
	6.8 " "			Present Work.
	5.0 at 24.8°C	18.8 at 15°C	-12.5 at 15°C	(53)*
	6.65 " "	20.6 " "	- 5.9 " "	Present Work.
t-Butyl chloride in 70% aqueous acetone	2.15 at 50°C			(54)
	2.09 " "			Present Work.
	0.217 at 30°C	18.1 at 27.4°C	-22.0 at 27.4°C	(53)*
	0.229 at "	22.2 " "	- 8.6 " "	Present Work.
t-Butyl chloride in 80% aqueous acetone	0.066 at 35°C			(94)
	0.078 " "			Present Work.
	0.033 at 30°C	23.9 at 27.4°C	- 6.8 at 27.4°C	(53)*
	0.040 " "	22.9 " "	- 9.7 " "	Present Work.

*Calculated from data in other solvents.

that, in general, the difference in reactivity between an alkyl chloride and the corresponding bromide involves almost equal changes in both E and $\Delta S^{\ddagger}$, and that the greater reactivity of the bromide can be attributed to an average decrease in $\Delta H^{\ddagger}$ of 0.8 ± 0.3 kcal ($\Delta H^{\ddagger} = E - RT$) plus an average increase in $\Delta S^{\ddagger}$ of 3 ± 2 cal. This observation is, however, open to several objections. In many cases the bromides were examined at a lower temperature than the corresponding chlorides and the temperature coefficients of E and $\Delta S^{\ddagger}$ were not determined although when the value of $\Delta C^{\ddagger}$ is negative the value of $\Delta S^{\ddagger}$ will increase as the temperature decreases;* ie., the bromide at the lower temperature is expected to have a greater value of $\Delta S^{\ddagger}$ than the chloride at a higher temperature even if the value of $\Delta S^{\ddagger}$ is the same for both at the same temperature. Furthermore many of the data quoted by Winstein are taken from the results of other workers and were, in some cases, adjusted to refer to different temperatures and solvent compositions.

According to Cooper and Hughes (60)(61)(95) the different reactivities of iso-propyl and t-butyl chlorides and bromides in solvolysis by aqueous ethanol are mainly due to changes in entropy. This conclusion, which also contradicts that of the present work, is also open to objections. Examination of their data shows that the bromide was examined over a lower temperature range than the chloride and that in the case of iso-propyl bromide, where rate constants were determined over a 40° range of temperature, the value of E, calculated from rates at adjacent temperatures, did not decrease with increase in temperature as expected for reactions of this type (See Chapter II). Values of E for the hydrolysis

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* When $\Delta C^{\ddagger} = -30$ cal. deg.$^{-1}$, $\Delta S^{\ddagger}(37.5°) - \Delta S^{\ddagger}(12.5°) = 2.5$ cal.

TABLE III-I

Activation Parameters for Some Alkyl Chlorides (RCl) and Bromides (RBr) in Aqueous Acetone at 50°C.

Halides	Solvent	$\log k_{Br} - \log k_{Cl}$	$\dfrac{E_{Br} - E_{Cl}}{2.303\ RT}$	$\dfrac{\Delta S^{\ddagger}_{Br} - \Delta S^{\ddagger}_{Cl}}{2.303\ R}$
Benzyl	50%	1.39	-1.09	0.31
Benzyl	70%	1.51	-1.47	0.04
t-Butyl	70%	1.62	-1.45	0.17
p-Nitrobenzhydryl	70%	1.30	-0.96	0.34
t-Butyl	80%	1.72	-1.46	0.26

of iso-propyl bromide are given in Table III-J.

Table III-J.

Activation Energies for the Hydrolysis of Iso-Propyl Bromide in 80% Aqueous Ethanol.

Temperature (^{o}C)	E (kcal.)
70	23.25
60	23.28
50	23.10

Furthermore if the values of E and $\Delta S^{\ddagger}$ for the iso-propyl halides (See Table I-D) are adjusted to refer to the same temperature the results will be more in accord with those of the present work since the value of E for the chloride will increase while the value of $\Delta S^{\ddagger}$ will become less negative.

The principal conclusion of this work is, therefore, that the greater reactivities of alkyl bromides compared with the corresponding chlorides in S_N solvolysis is due mainly to changes in energy of activation, consistent with the reduction in the energy of ionisation in passing from the C-Cl to the C-Br bond. Changes in the entropy of activation are small and contribute little to the differences in the rates of hydrolysis of alkyl bromides and the corresponding chlorides.

(b) The use of $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ as a mechanistic test.

Bensley and Kohnstam (10) have recently suggested, from a study of the hydrolysis of alkyl chlorides in aqueous acetone, that the value of the ratio $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ can provide useful information about the mechanism of S_N reactions. The basis of this test can be explained in terms of the solvation hypothesis outlined in Chapter II. Thus the magnitude of $\Delta C^{\ddagger}$ and $\Delta S^{\ddagger}$ will, in the absence of complicating features, be almost entirely controlled by the degree of solvation of the transition state relative to that of the initial state. In an S_N1 reaction both $\Delta C^{\ddagger}$ and $\Delta S^{\ddagger}$ will be governed by the same factors and hence the value of $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ should be independent of the substrate and dependent only on solvent composition and temperature. In an S_N2 reaction the partial covalent attachment of a solvent molecule in the transition state causes a greater loss in entropy than its participation in solvation but the value of $\Delta C^{\ddagger}$ is not greatly altered; the S_N2 value of $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ will, therefore, be substantially less than the value for an S_N1 reaction. Values of $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ calculated from the results of the present work are given in Table III-K.

Table III-K.

Values of $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ at 50°C.

Compound	Solvent	Mechanism	$\Delta C^{\ddagger}/\Delta S^{\ddagger}$
Benzyl bromide	50%	S_N2	1.24±0.11
Benzyl bromide	70%	S_N2	0.97±0.11
Benzyl chloride	70%	S_N2	0.89±0.12
t-Butyl bromide	70%	S_N1	3.99±0.33
t-Butyl chloride	70%	S_N1	3.58±0.39
p-Nitrobenzhydryl bromide	70%	S_N1	3.69±0.33
t-Butyl chloride	80%	S_N1	2.60±0.27

(i) Values of $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ in S_N1 reactions.

Values of $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ for the S_N1 reactions now studied are compared with the values of this ratio for other reactions occurring by this mechanism in Tables III-L and III-M. It can be seen that, within the limits of experimental error, the values of $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ are the same for both chlorides and bromides under the same experimental conditions, and that the values of the ratio obtained in this work compare very favourably with those of other work on alkyl chlorides.

Table III-L.

Values of $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ for S_N1 Solvolysis in 70% Aqueous Acetone at $50^{\circ}C$.

Present Work		Other Work	
Halide	$\Delta C^{\ddagger}/\Delta S^{\ddagger}$	Halide	$\Delta C^{\ddagger}/\Delta S^{\ddagger}$
t-Butyl bromide t-Butyl chloride p-Nitrobenzhydryl bromide	3.99 ± 0.33 3.58 ± 0.39 3.69 ± 0.33	p-X Benzhydryl chloride (22) ($X=H, Cl, Br, I, NO_2$)	3.62 ± 0.13

Table III-M.

Values of $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ for S_N1 Solvolysis in 80% Aqueous Acetone at $50^{\circ}C$.

Present Work.		Other Work.	
Halide	$\Delta C^{\ddagger}/\Delta S^{\ddagger}$	Halide	$\Delta C^{\ddagger}/\Delta S^{\ddagger}$
t-Butyl chloride	2.60 ± 0.27	t-Butyl bromide Benzhydryl chloride (22)	2.80 ± 0.37 2.81 ± 0.27

(ii) Values of $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ in S_N2 reactions.

Values of $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ for the S_N2 reactions now studied are compared with the values of this ratio for other reactions occurring by this mechanism in Table III-N. It can be seen that the values of the ratio obtained in this work compare favourably with those of other work.

Values of $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ for the S_N1 reactions of both chlorides and bromides

Table III-N.

Values of $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ for S_N2 Solvolysis in 50% Aqueous Acetone at 50°C.

Present Work		Other Work	
Halide	$\Delta C^{\ddagger}/\Delta S^{\ddagger}$	Halide	$\Delta C^{\ddagger}/\Delta S^{\ddagger}$
Benzyl bromide	1.24 ± 0.11	n-Butyl bromide, n-propyl bromide. p-X Benzyl chloride ($X=H, NO_2$) (22).	1.20 ± 0.16 0.90 ± 0.11

under the same experimental conditions are very similar and considerably larger than the values of the ratio for S_N2 reactions. This conclusion is in agreement with Kohnstam's suggestion that the value of $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ for an S_N1 reaction will be considerably larger than that for an S_N2 reaction and that the value of the ratio will be independent of the nature of the substrate and dependent only on solvent composition and temperature. Thus the results of this work strengthen the validity of using the value of $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ as a test of reaction mechanism and indicate that the test is applicable to both alkyl chlorides and bromides.

It is noteworthy that for reactions occurring by the same mechanism under the same experimental conditions the values of $\Delta C^{\ddagger}$ and $\Delta S^{\ddagger}$ for bromides are only very slightly less than those for chlorides. This implies that the degree of solvation in the transition state of hydrolysis is very similar for chlorides and bromides. Values of $\Delta C^{\ddagger}$ and $\Delta S^{\ddagger}$ for some chlorides and bromides are given in Table III-O. This observation is rather surprising since it is normally considered that the fully developed bromide ion is solvated to a smaller degree than the chloride ion. In the present case, however, it must be remembered that partial bonds exist between the alkyl group and the displaced halogen with the

TABLE III-0.

Values of $\Delta C^{\ddagger}$ and $\Delta S^{\ddagger}$ for Some Alkyl Chlorides and Bromides at 50°c.

Halide		$-\Delta S^{\ddagger}$ (cal.deg.$^{-1}$)	$-\Delta C^{\ddagger}$ (cal.deg.$^{-1}$)
t-Butyl in 70% aqueous acetone (present work).	Cl	11.58 ± 0.21	41.4 ± 4.4
	Br	10.79 ± 0.33	43.0 ± 3.3
Benzyl in 70% aqueous acetone (present work).	Cl	24.03 ± 0.38	21.3 ± 2.9
	Br	23.86 ± 0.11	23.1 ± 2.6
Benzyl in 50% aqueous acetone (present work and (10)).	Cl	22.8	21.0 ± 2.5
	Br	20.99 ± 0.01	26.0 ± 2.2

result that direct comparison with the behaviour of fully developed ions may not be completely justified in this instance. On the other hand Shorter and Hinshelwood (58) have published data for the solvolysis of some alkyl chlorides and iodides in aqueous ethanol which show that there is a considerable difference in the degree of solvation of the transition states of these halides. This evidence must, however, be regarded as questionable since examination of their work, in which rate constants were determined over a range of temperatures, did not reveal the temperature dependence of E now expected for reactions of this type.

(c) The hydrolysis of benzyl bromide.

The available evidence suggests that the hydrolysis of benzyl chloride in partly aqueous solvents is mechanistically borderline (2)(10) and it might, therefore, be expected that benzyl bromide would react via the unimolecular mechanism since organic bromides are more readily ionised than chlorides.

The value of $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ for benzyl bromide obtained in this work does not support this view but indicates that reaction occurs by mechanism

S_N2. Additional evidence from the present work also supports this conclusion. Thus the value of $\Delta S^{\ddagger}$, which is usually more negative for an S_N2 than an S_N1 reaction (7)(96), compares favourably with the values of $\Delta S^{\ddagger}$ for other S_N2 reactions, as shown in Table III-P.

TABLE III-P.

Values of $\Delta S^{\ddagger}$ for Some S_N2 Reactions at 50°C.

Reaction	$-\Delta S^{\ddagger}$(cal. deg.$^{-1}$)	Ref.
Benzyl chloride in 50% aq. acetone	22.8	(10)
Ethyl bromide in 50% aq. acetone	18.3	(77)
n-Propyl bromide in 50% aq. acetone	20.79	(77)
Benzyl bromide in 50% aq. acetone	20.99	(present work)
Benzyl bromide in 70% aq. acetone	23.86	

The influence of a change in solvent composition on the rate of hydrolysi of benzyl bromide (See Chapter I Section 3 (b)) is also consistent with the view that this substance reacts bimolecularly since a change in solvent composition from 70% to 50% aqueous acetone only increases the reaction rate by a factor of 5, while for a similar change in solvent composition for the S_N1 hydrolysis of t-butyl chloride this factor is 15.

Data for the hydrolysis of benzyl bromide in partly aqueous solvents are limited but Hine and Lee (50) have also shown that the hydrolysis of this substance in aqueous acetone occurs bimolecularly. This observation was based upon the fact that no significant increase in reaction rate was produced by the α-bromination of benzyl bromide. If mechanism S_N1 had been operating a marked increase in reaction rate should have been noted due to the greater possibilities of electron release to the reaction centre.

It is of interest to establish to what extent, if any, S_N1 processes contribute to the overall rate of hydrolysis of benzyl bromide in the 50% solvent. An approximate value for the fraction of the total solvolysis which may proceed by mechanism S_N1, k_1/k[*], can be obtained by calculating the energy and entropy of activation for the S_N1 process (E_1 and $\Delta S_1^\ddagger$ respectively) with the aid of a priori reasonable assumptions. If it is assumed that α-chlorination in benzyl chloride lowers E_1 by the same amount as α-chlorination in benzylidene chloride (10), $E_1 = 26.5$ kcal. for the hydrolysis benzyl chloride at 50°. The rate of hydrolysis of benzyl bromide, relative to the chloride, is almost the same as for the S_N1 hydrolysis of other bromides and it was therefore assumed that

$$E_1(PhCH_2Br) - E_1(PhCH_2Cl) = E_{OBS}(PhCH_2Br) - E_{OBS}(PhCH_2Cl).$$

This yields $E_1(PhCH_2Br) = 24.9$ kcal. at 50°. $\Delta S_1^\ddagger$ was taken as -10 cal. deg.$^{-1}$ ($\Delta S^\ddagger$ for the S_N1 hydrolysis of t-butyl chloride in 50% aqueous acetone at 50°C is -10.28 cal. deg.$^{-1}$ (69)). Hence $k_1/k \simeq 0.03$; this value is much too small to permit the view that S_N1 processes contribute significantly to the overall solvolysis in the 50% solvent.

It therefore seems likely that the effect of exchanging a chlorine for a bromine atom in the benzyl halides is restricted to increasing the rate of hydrolysis without causing a change in reaction mechanism.

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[*] The subscript 1 refers to the S_N1 value.

CHAPTER IV.

EXPERIMENTAL.

1. Preparation and Purification of Materials.

(a) p-Nitrobenzhydryl bromide.

p-Nitrobenzophenone was prepared by Friedel-Crafts reaction between p-nitrobenzoyl chloride and benzene using anhydrous aluminium chloride as catalyst. The ketone was purified by shaking with activated charcoal in acetone followed by repeated recrystallisation from this solvent. It had mp. 135-137°C (138°C (97)) and infra-red analysis indicated a purity $\nless$ 98%.

p-Nitrobenzhydrol was obtained by Meerwein-Pondorf reduction of the ketone and was purified by shaking with activated charcoal in ethanol followed by repeated recrystallisation from this solvent. The purified alcohol had mp. 74-75.5°C (73-75.5°C (98)), and infra-red analysis indicated a purity of approximately 99%.

The alcohol was brominated by passing a stream of dry hydrogen bromide through a benzene solution for 4-6 hours in the presence of anhydrous lithium bromide. Hydrogen bromide was prepared by reaction of bromine with tetralin in the presence of iron filings and was passed through tetralin and concentrated sulphuric acid before use. The bromide was obtained by washing the benzene solution (water/dilute aqueous potassium bicarbonate/water), drying (anhydrous sodium sulphate), and removing the solvent by distillation under reduced pressure. Purification was carried out by passing a petroleum ether/di-ethyl ether solution of the bromide down a 'Celite' (alumina) column; the solvent was removed under reduced pressure and left a pale yellow liquid which slowly crystallised to a pale yellow solid mp. 31-33°C .[*]

(b) Benzyl bromide.

Commercial benzyl bromide was shaken with sodium bicarbonate, dried with anhydrous sodium sulphate and then purified by distillation under reduced pressure, large head and tail fractions being discarded.

mp. was -4.0°C (-3.9°C (99)).

A similar method was used to obtain the following halides in the required state of purity.

(c) Benzyl chloride.

$$n_D^{15} = 1.5420 \; (n_D^{15} = 1.5415 \; (97)).$$

(d) t-Butyl chloride.

$$n_D^{20} = 1.3870 \; (n_D^{20} = 1.3856 \; (97)).$$

(e) t-Butyl bromide.

$$n_D^{25} = 1.4260 \; (n_D = 1.428 \; (100)).$$

The purity of the halides was determined by estimation of the acid liberated on complete hydrolysis of a weighed sample in aqueous acetone by titration with standard sodium hydroxide. Only halides of purity ≮99% were used in the kinetic runs.

(f) Acetone.

Solvent acetone was prepared by refluxing A.R. material with potassium permanganate and sodium hydroxide for two hours; the bulk of the acetone was distilled off and then, after the addition of alittle hydroquinone, carefully fractionated, generous head and tail fractions being discarded (101). Acetone for titration purposes was obtained by treating commercial

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[*] Smith and Leffler (98) have also prepared this substance but obtained a liquid.

material in a similar fashion.

The aqueous solvent was prepared by volume; thus 70% aqueous acetone refers to a mixture of 70 volumes of acetone and 30 volumes of water.

2. Measurement of Reaction Rates.

The thermostats used were of conventional design except at 0°C where a well-stirred bath of melting ice was used. The temperatures were always maintained constant to within ± 0.01° and were measured with thermometers which had been checked against thermometers standardised by the National Physical Laboratory to ± 0.02°.

With the exception of t-butyl bromide in the 70% solvent the sealed ampoule technique was used throughout this work. The tubes containing the reaction mixture (0.02M. with respect to the halide) were placed in a suitable container and then introduced into the thermostat with vigorous shaking. When the thermostat had regained its original temperature, usually within two to eight minutes, two or three tubes were withdrawn and plunged into an acetone/'Drikold' freezing mixture; further tubes were withdrawn at various times and treated similarly. The amount of acid present in any tube was determined by breaking the cleaned tube under 200ml. of cold, neutral acetone and titrating with sodium hydroxide using lacmoid as indicator. Complete hydrolysis of the halide present in a tube was carried out by heating at an elevated temperature.

In the case of t-butyl bromide the reactant was added to the solvent in the thermostat and 5ml. samples withdrawn as required, run into 200ml. of cold, neutral acetone and titrated as before. The acidity produced on complete hydrolysis was determined by running a 5ml sample into a glass tube which was then sealed off, heated at an elevated temperature, and then treated as described above.

3. Calculation of Results.

(a) Reaction rate.

Rate constants were obtained from the integrated first-order rate equation

$$k = \frac{2.303}{t} \log \frac{a}{(a-x)},$$

where the symbols have their usual meaning.

In any one run, k was generally obtained as the mean of ten separate determinations and at least two runs were always carried out for a given set of experimental conditions.

The standard error, σ_m, of the mean k was calculated from

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

where k_m = mean value of k.

k = individual values of k.

n = number of k values.

Good first-order kinetics were always obtained and the value of σ_m/k_m never exceeded 0.003. Rate constants at 50°C were calculated from the calculated values of E and $\Delta S^{\ddagger}$ at 50°C.

In this work several batches of each solvent were used, and each batch was monitored by examining the rate of hydrolysis of a reactant which had been studied previously. The substance used for the 70 and 80% solvents was benzhydryl chloride and for the 50% solvent p-nitrobenzhydryl chloride; both of these compounds reacting by mechanism S_N1. In this manner rates of hydrolysis could be corrected to refer to the same batch of each solvent. For the S_N1 reactions of the t-butyl and p-nitrobenzhydryl halides a correction term was obtained by direct comparison of the rate of hydrolysis of benzhydryl chloride in the required solvent with standard values (20).

For the S_N2 reactions of the benzyl halides a similar procedure was adopted except that allowance was made for the fact that an S_N2 reaction is not altered to the same extent as an S_N1 reaction for a similar change in solvent composition (See Chapter I, Section 3b). An approximate value for this additional factor was obtained by comparing the effects of a similar change in solvent composition on the rates of hydrolysis of t-butyl chloride in benzyl chloride.

(b) Energy of activation.

Activation energies, E_{OBS}, were calculated from the equation

$$E_{OBS} = \frac{2.303RT_1T_2}{T_2 - T_1} \log \frac{k_2}{k_1},$$

which arises from the integrated form of the Arrhenius equation.

k_1 is the rate constant at T_1 and

k_2 is the rate constant at T_2.

Energies of activation calculated in this manner refer to the mean of the temperature interval, $(T_1 + T_2)/2$; this is shown in the Appendix.

The standard error in E_{OBS} is given by (102).

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

where σ_1 is the standard error in k_1 at T_1

and σ_2 is the standard error in k_2 at T_2.

The value of E at any particular temperature is calculated from

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

where E_m is the mean of the observed activation energies, ie.,$E_m = \sum(E_{OBS})/n$, and T_m is the mean of the temperatures to which the values of E_{OBS} refer, ie., $T_m = \sum(T)/n$. The standard error in E_c depends upon the standard error in dE/dT such that

$$\sigma(E_c) = \sigma(dE/dT)\ (T-Tm).$$

(c) Entropy of activation.

Entropies of activation, $\Delta S^{\ddagger}_{OBS}$, at the temperature $(T_1 + T_2)/2$ (see Appendix) were obtained from the expression

$$\Delta S^{\ddagger}_{OBS} = 2.303R \left[-\log \frac{k'}{h} - \frac{1}{2.303} + \log k_1 + \frac{E_{\frac{T_1+T_2}{2}}}{2.303RT_1} - \log \frac{T_1 + T_2}{2} \right]$$

which arises from the conventional form of the absolute rate equation for reactions in solution.

The value of $\Delta S^{\ddagger}$ at any particular temperature is calculated from

$$\Delta S^{\ddagger}_{c} = \Delta S^{\ddagger}_{m} + 2.303\, \Delta C^{\ddagger} (\log T - \log T_m)$$

where $\Delta S^{\ddagger}_{m}$ is the mean of the observed entropies of activation, ie.,

$$\Delta S^{\ddagger}_{m} = \sum(\Delta S^{\ddagger}_{OBS})/n \text{ and } \log Tm = \sum(\log T)/n.$$

The standard error in $\Delta S^{\ddagger}_{c}$ depends upon the standard error in dE/dT such that

$$\sigma(\Delta S^{\ddagger}_{c}) = 2.303\, \sigma(dE/dT)\, (\log T - \log Tm).$$

(d) Heat capacity of activation.

Values of dE/dT were obtained as the slope of the 'best' straight line of E_{OBS} against T from the expression

$$\frac{dE}{dT} = \frac{\sum(E-Em)(T-Tm)}{\sum(T-Tm)^2}$$

and heat capacities of activation, $\Delta C^{\ddagger}$, were calculated from the relationship

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

The standard error of dE/dT can be obtained in one of two ways:

(i) from the 'best' straight line of E_{OBS} against T.

$$\sigma\left(\frac{dE}{dT}\right) = \left[\frac{\sum(E_{OBS}-E_c)^2}{n-2\ \sum(T-Tm)^2}\right]^{\frac{1}{2}}$$

(ii) from the standard error in E_{OBS}

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

The values of σ(dE/dT) quoted in this thesis and employed to calculate the errors in E_c and $\Delta S^{\ddagger}_c$ were always the largest of the values obtained from (i) and (ii).

APPENDIX.

To Show that E_{OBS} and $\Delta S^{\ddagger}_{OBS}$ Refer to the Temperature $(T_1+T_2)/2$.

(a) E_{OBS}.

The value of E_{OBS} is calculated from the expression

$$E_{OBS} = \frac{RT_1T_2}{T_2-T_1} \ln \frac{k_2}{k_1} \quad \text{--------- } 1$$

Thus if E_{OBS} varies with temperature its value will depend on T_1 and T_2; this is in fact the case (see Table III-A, page 27) and it is, therefore, necessary to establish to what temperature E_{OBS} refers. The experimental results of this work indicate that the value of dE/dT is constant over the temperature range studied and therefore it may be assumed that E varies linearly with temperature.

Equation 1 may be written

$$E_{OBS} = \frac{RT_1T_2}{T_2-T_1}\left[\ln \frac{k^1}{h} + \ln T_2 + 1 + \frac{\Delta S^{\ddagger}_{T_2}}{R} - \frac{E_{T_2}}{RT_2} - \ln \frac{k^1}{h} - \ln T_1 - 1 - \frac{\Delta S^{\ddagger}_{T_1}}{R} + \frac{E_{T_1}}{RT_1}\right].$$

Noting that $\Delta C^{\ddagger} = (dE/dT)-R$ and $d(\Delta S^{\ddagger})/dT = \Delta C^{\ddagger}/T$

$$E_{OBS} = \frac{RT_1T_2}{T_2-T_1}\left[\ln \frac{T_2}{T_1} + \frac{\Delta C^{\ddagger}}{R} \ln \frac{T_2}{T_1} - \frac{E_{T_2}}{RT_2} + \frac{E_{T_1}}{RT_1}\right]$$

$$= E_{\frac{T_1+T_2}{2}} + \frac{T_1T_2}{T_2-T_1}\frac{dE}{dT}\left[\ln \frac{T_2}{T_1} - \frac{T_2-T_1}{2T_2} + \frac{T_1+T_2}{2T_1}\right]$$

$$= E_{\frac{T_1+T_2}{2}} + \frac{dE}{dT}\left[T_2 - \frac{T_2(T_2-T_1)}{2T_1} - \frac{(T_1+T_2)}{2}\right] \quad \text{------- } 2$$

Typical values of T_1, T_2 and dE/dT are 300, 310 and -30 respectively; substitution of these values in equation 2 shows that

$$E_{OBS} = E_{\frac{T_1+T_2}{2}} + 5 \text{ cal.}$$

Since 5 cal. is negligible compared with a value of E_{OBS} of 20 kcal. it follows that

$$E_{OBS} = E_{\frac{T_1+T_2}{2}}$$

(b) $\Delta S^{\ddagger}_{OBS}$.

From the absolute rate equation

$$\ln k_1 = \ln \frac{k^1}{h} + 1 + \ln T_1 + \frac{\Delta S^{\ddagger}_{T_1}}{R} - \frac{E_{T_1}}{RT_1} \text{ - - - - - - - } 3$$

If equation 3 is written

$$\ln k_1 = \ln \frac{k^1}{h} + 1 + \ln \frac{T_1+T_2}{2} + \frac{\Delta S^{\ddagger}_{OBS}}{R} - \frac{E_{\frac{T_1+T_2}{2}}}{RT_1} \text{ - - - - - } 4$$

it is necessary to establish to what temperature $\Delta S^{\ddagger}_{OBS}$ refers.

Comparison of equations 3 and 4 shows that

$$0 = \ln \frac{T_1+T_2}{2} - \ln T_1 + \frac{\Delta S^{\ddagger}_{OBS} - \Delta S^{\ddagger}_{T_1}}{R} - \frac{1}{RT_1}\left[E_{\frac{T_1+T_2}{2}} - E_{T_1}\right]$$

and that

$$\begin{aligned} \Delta S^{\ddagger}_{OBS} - \Delta S^{\ddagger}_{T_1} &= \frac{dE}{dT} \ln \frac{T_1+T_2}{2T_1} - R \ln \frac{T_1+T_2}{2T_1} \\ &= \Delta C^{\ddagger}\left[\ln \frac{T_1+T_2}{2} - \ln T_1\right] \\ &= \Delta S^{\ddagger}_{\frac{T_1+T_2}{2}} - \Delta S^{\ddagger}_{T_1} \end{aligned}$$

Hence $\Delta S^{\ddagger}_{OBS} = \Delta S^{\ddagger}_{\frac{T_1+T_2}{2}}$.

Details of Kinetic Runs.

(5 ml. samples titrated with *ca.* 0.01N sodium hydroxide).

Benzyl Bromide in 50% Aqueous Acetone

(Solvent F) at 69.00°C. Run Nos. 73/74.

Time (sec.)	Titre. (ml.)	10^4k (sec.$^{-1}$)
0	0.90	
0	0.90	
420	2.02	3.493
720	2.71	3.457
1020	3.36	3.490
1320	3.88	(3.416)
1620	4.38	(3.403)
1860	4.82	3.489
2220	5.30	3.457
2520	5.68	3.463
2760	5.98	3.494
3060	6.29	3.493
3300	6.50	3.473
3660	6.81	3.477
∞	9.11	
∞	9.10	

Mean k = 3.479×10^{-4}sec.$^{-1}$

Duplicate mean k (11 determinations) = 3.483×10^{-4}sec.$^{-1}$

Overall mean k; k_m = 3.481×10^{-4}sec.$^{-1}$

$$\frac{6_m}{k_m} = 0.0008$$

k_m corrected for the solvent = 3.439×10^{-4}sec.$^{-1}$

Benzyl Bromide in 50% Aqueous Acetone

(Solvent F) at 59.37°C. Run Nos. 68/69.

Time (sec.)	Titre. (ml.)	10^4k (sec.$^{-1}$)
0	0.89	
0	0.89	
1250	2.30	1.570
1905	3.04	1.572
2380	3.485	1.552
3035	4.06	1.557
3630	4.54	1.566
4345	5.05	1.568
4945	5.44	1.572
5605	5.81	1.566
7105	6.56	1.575
8905	7.24	1.576
10885	7.78	1.566
13105	8.24	1.572
∞	9.31	
∞	9.31	
∞	9.32	

Mean k = 1.568×10^{-4} sec.$^{-1}$

Duplicate mean k (12 determinations) = 1.578×10^{-4} sec.$^{-1}$

Overall mean k ; k_m = 1.573×10^{-4} sec.$^{-1}$

$$\frac{\sigma_m}{k_m} = 0.0014$$

k_m corrected for the solvent = 1.554×10^{-4} sec.$^{-1}$

Benzyl Bromide in 50% Aqueous Acetone (Solvent F) at 49.42°C. Run Nos. 66/67.

Time (sec.)	Titre. (ml.)	10^4k (sec.$^{-1}$)
0	0.34	
0	0.34	
3360	2.06	0.6451
6080	3.26	0.6606
8400	4.04	0.6469
10560	4.72	0.6491
12120	5.17	0.6534
14580	5.75	0.6507
17040	6.25	0.6495
19140	6.64	0.6533
21300	6.95	0.6482
22800	7.17	0.6516
24480	7.41	0.6591
26340	7.59	0.6534
∞	9.17	
∞	9.17	
∞	9.18	

Mean k = 0.6517 x 10^{-4}sec.$^{-1}$

Duplicate mean k (11 determinations) = 0.6516 x 10^{-4}sec.$^{-1}$

Overall mean k ; k_m = 0.6517 x 10^{-4}sec.$^{-1}$

$\frac{\sigma_m}{k_m}$ = 0.0013

k_m corrected for the solvent = 0.6439 x 10^{-4}sec.$^{-1}$

Benzyl Bromide in 50% Aqueous Acetone
(Solvent F) at 39.67°C. Run Nos. 71/72.

Time (sec.)	Titre. (ml.)	$10^4 k$ (sec.$^{-1}$)
0	0.57	
0	0.56	
7020	2.00	0.2546
12120	2.90	0.2558
14040	3.20	0.2551
17580	3.72	0.2543
21120	4.22	0.2561
23700	4.54	0.2557
26980	4.92	0.2552
28980	5.16	0.2571
31320	5.39	0.2561
0	0.19	
0	0.19	
61800	7.46	0.2581
67620	7.71	0.2574
74340	7.97	0.2580
∞	9.315	
∞	9.31	
∞	9.30	

Mean k = 0.2561×10^{-4} sec.$^{-1}$

Duplicate mean k (11 determinations) = 0.2567×10^{-4} sec.$^{-1}$

Overall mean k ; $k_m = 0.2564 \times 10^{-4}$ sec.$^{-1}$

$$\frac{\sigma_m}{k_m} = 0.0017$$

k_m corrected for the solvent = 0.2533×10^{-4} sec.$^{-1}$

Benzyl Bromide in 50% Aqueous Acetone

(Solvent F) at 29.95°C. Run Nos. 75/76.

Time (sec.)	Titre. (ml.)	10^4k (sec.$^{-1}$)
0	0.35	
0	0.36	
18900	1.90	0.09333
25500	2.38	0.09348
87360	5.72	0.09452
100920	6.19	0.09396
112200	6.64	0.09607
115980	8.11	0.09561
0	0.13	
0	0.16	
60480	4.39	0.09473
73740	5.07	0.09557
86640	5.63	0.09561
148500	7.47	0.09399
162060	7.85	(0.09638)
173340	8.04	0.09614
∞	9.88	
∞	9.88	

Mean k = 0.09482 x 10^{-4}sec.$^{-1}$

Duplicate mean k (11 determinations) = 0.09441 x 10^{-4}sec.$^{-1}$

Overall mean k ; k_m = 0.09461 x 10^{-4}sec.$^{-1}$

$\frac{\sigma_m}{k_m}$ = 0.0021

k_m corrected for the solvent = 0.09347 x 10^{-4}sec.$^{-1}$

p-Nitrobenzhydryl Chloride in 50% Aqueous Acetone (Solvent F) at 50.02°C. Run Nos. 95/96.

Time (sec.)	Titre. (ml.)	10^4k (sec.$^{-1}$)
0	0.69	
0	0.73	
1200	2.10	(1.694)
1800	2.73	1.730
2520	3.37	1.724
3300	4.01	1.742
4400	4.82	1.770
5220	5.22	1.743
6540	5.85	1.747
7800	6.37	1.776
8400	6.58	1.788
9060	6.77	1.792
9600	6.86	1.756
10320	7.10	(1.816)
∞	8.27	
∞	8.25	

Mean k = 1.757×10^{-4}sec.$^{-1}$

Duplicate mean k (10 determinations) = 1.763×10^{-4}sec.$^{-1}$

Overall mean k ; $k_m = 1.760 \times 10^{-4}$sec.$^{-1}$

$$\frac{\sigma_m}{k_m} = 0.003$$

Benzyl Bromide in 70% Aqueous Acetone

(Solvent G) at 84.88°C. Run Nos. 128/129.

Time (sec.)	Titre. (ml.)	10^4k (sec.$^{-1}$)
0	0.93	
0	0.92	
895	2.53	2.268
1495	3.40	2.233
2215	4.33	2.235
2695	4.89	2.250
3475	5.65	2.247
4315	6.36	2.263
5215	6.95	2.254
6055	7.43	2.265
6835	7.77	2.252
7433	8.01	2.254
8033	8.23	2.267
8451	8.35	2.250
∞	9.63	
∞	9.64	

Mean k = 2.254×10^{-4} sec.$^{-1}$

Duplicate mean k (10 determinations) = 2.265×10^{-4} sec.$^{-1}$

Overall mean k ; k_m = 2.259×10^{-4} sec.$^{-1}$

$$\frac{\sigma_m}{k_m} = 0.0011$$

k_m corrected for the solvent = 2.320×10^{-4} sec.$^{-1}$

Benzyl Bromide in 70% Aqueous Acetone
(Solvent G) at 74.94°C. Run Nos.140/141.

Time (sec.)	Titre. (ml.)	10^4k (sec.$^{-1}$)
0	0.38	
0	0.39	
0	0.41	
1320	1.61	(1.031)
2640	2.76	1.075
3600	3.47	1.075
4735	4.23	1.079
6240	5.11	1.048
7200	5.54	1.068
8820	6.29	1.081
10560	6.94	1.086
12300	7.45	1.081
13560	7.78	1.083
15360	8.20	1.093
16860	8.46	1.089
∞	9.99	
∞	9.99	

Mean k = 1.078×10^{-4} sec.$^{-1}$

Duplicate mean k (12 determinations) = 1.078×10^{-4} sec.$^{-1}$

Overall mean k ; k_m = 1.078×10^{-4} sec.$^{-1}$

$$\frac{\sigma_m}{k_m} = 0.0019$$

k_m corrected for the solvent = 1.107×10^{-4} sec.$^{-1}$

Benzyl Bromide in 70% Aqueous Acetone

(Solvent G) at 65.01°C. Run Nos. 130/131.

Time (sec.)	Titre. (ml.)	10^4k (sec.$^{-1}$)
0	0.20	
0	0.185	
2160	1.09	0.4841
4815	2.05	0.4831
7215	2.84	0.4861
10665	3.80	0.4833
12460	4.27	0.4870
14835	4.80	0.4862
16215	5.10	0.4897
17775	5.38	0.4870
19305	5.68	0.4914
21075	5.95	0.4887
27855	6.84	0.4867
35115	7.52	0.4854
∞	9.15	
∞	9.15	

Mean k = 0.4866×10^{-4} sec.$^{-1}$

Duplicate mean k (12 determinations) = 0.4860×10^{-4} sec.$^{-1}$

Overall mean k ; k_m = 0.4863×10^{-4} sec.$^{-1}$

$\frac{\sigma_m}{k_m}$ = 0.0015

k_m corrected for the solvent = 0.4994×10^{-4} sec.$^{-1}$

Benzyl Bromide in 70% Aqueous Acetone

(Solvent G) at 54.86°c. Run Nos. 142/143.

Time (sec.)	Titre. (ml.)	10^4k (sec.$^{-1}$)
0	0.25	
0	0.25	
4270	1.08	(0.2169)
7590	1.60	0.2046
11550	2.21	0.2027
17790	3.09	0.2026
23070	3.77	0.2037
28170	4.33	0.2024
0	0.08	
0	0.08	
57240	6.65	0.2031
60720	6.87	0.2041
65310	7.13	0.2047
70110	7.35	0.2039
78090	7.68	0.2030
84720	7.96	0.2052
∞	9.64	
∞	9.64	

Mean k = 0.2036×10^{-4}sec.$^{-1}$

Duplicate mean k (11 determinations) = 0.2044×10^{-4}sec.$^{-1}$

Overall mean k ; k_m = 0.2040×10^{-4}sec.$^{-1}$

$\frac{\sigma_m}{k_m}$ = 0.0012

k_m corrected for the solvent = 0.2095×10^{-4}sec.$^{-1}$

Benzyl Bromide in 70% Aqueous Acetone

(Solvent G) at 44.82°C. Run Nos.124/125.

Time (sec.)	Titre. (ml.)	10^4k (sec.$^{-1}$)
0	0.36	
0	0.35	
53850	3.54	0.08071
69360	4.22	0.08044
82350	4.76	0.08112
143100	6.55	0.08076
0	0.02	
0	0.02	
69390	4.06	0.08123
98190	5.06	(0.07848)
11540	5.64	0.07923
154350	6.73	0.08142
169935	7.04	0.08123
182910	7.28	0.08134
243630	8.14	(0.08241)
249750	8.16	0.08102
∞	9.40	
∞	9.40	

Mean k = 0.08085×10^{-4} sec.$^{-1}$

Duplicate mean k (12 determinations) = 0.08087×10^{-4} sec.$^{-1}$

Overall mean k ; k_m = 0.08086×10^{-4} sec.$^{-1}$

$$\frac{\sigma_m}{k_m} = 0.0015$$

k_m corrected for the solvent = 0.08304×10^{-4} sec.$^{-1}$

Benzhydryl Chloride in 70% Aqueous Acetone

(Solvent G) at 20.78°C. Run Nos. 134/135.

Time (sec.)	Titre. (ml.)	10^4k (sec.$^{-1}$)
0	0.37	
780	2.17	2.773
1260	3.12	2.797
1920	4.20	2.781
2220	4.71	2.775
3004	5.61	2.778
3530	6.13	2.756
4020	6.58	2.764
4920	7.25	2.762
5605	7.68	2.780
6085	7.91	2.767
6540	8.10	2.754
∞	9.64	
∞	9.62	

Mean k = 2.772×10^{-4}sec.$^{-1}$

Duplicate mean k (11 determinations) = 2.774×10^{-4}sec.$^{-1}$

Overall mean k ; k_m = 2.773×10^{-4}sec.$^{-1}$

$\frac{\sigma_m}{k_m}$ = 0.0019

Benzyl Chloride in 70% Aqueous Acetone
(Solvent II) at 114.97°C. Run Nos. 136/137.

Time (sec.)	Titre. (ml.)	$10^4 k$ (sec.$^{-1}$)
0	0.98	
0	0.96	
960	1.77	(0.9283)
1860	2.44	0.9175
3480	3.53	0.9173
4440	4.12	0.9223
5760	4.82	0.9187
7260	5.52	0.9160
9060	6.26	0.9177
11040	6.93	0.9156
12360	7.32	0.9162
13920	7.74	0.9210
15240	7.98	(0.9051)
16620	8.31	0.9204
∞	10.34	
∞	10.34	

Mean k = 0.9183×10^{-4} sec.$^{-1}$

Duplicate mean k (10 determinations) = 0.9207×10^{-4} sec.$^{-1}$

Overall mean k ; k_m = 0.9195×10^{-4} sec.$^{-1}$

$\frac{\sigma_m}{k_m}$ = 0.0008

k_m corrected for the solvent = 0.9066×10^{-4} sec.$^{-1}$

Benzyl Chloride in 70% Aqueous Acetone (Solvent H) at 104.90°C. Run Nos. 132/133.

Time (sec.)	Titre. (ml.)	10^4k (sec.$^{-1}$)
0	0.28	
0	0.28	
3945	1.92	(0.4483)
6945	3.02	0.4548
9375	3.79	0.4526
11985	4.56	0.4591
15165	5.36	0.4601
18465	6.05	0.4580
20265	6.42	0.4613
21835	6.73	0.4640
24075	7.06	0.4613
27645	7.58	0.4631
30285	7.90	0.4627
33285	8.20	0.4596
∞	10.39	
∞	10.39	

Mean k = 0.4597×10^{-4} sec.$^{-1}$

Duplicate mean k (10 determinations) = 0.4581×10^{-4} sec.$^{-1}$

Overall mean k ; k_m = 0.4589×10^{-4} sec.$^{-1}$

$\frac{\sigma_m}{k_m}$ = 0.0013

k_m corrected for the solvent = 0.4525×10^{-4} sec.$^{-1}$

Benzyl Chloride in 70% Aqueous Acetone

(Solvent B) at 94.82°C. Run Nos. 144/145.

Time (sec.)	Titre. (ml.)	$10^4 k$ (sec.$^{-1}$)
0	0.04	
0	0.05	
4890	1.09	0.2181
8230	1.74	0.2167
14130	2.75	0.2156
18150	3.40	0.2170
22170	4.00	0.2185
25590	4.47	0.2195
29610	4.98	0.2203
0	0.02	
0	0.02	
56610	7.33	0.2177
60720	7.62	0.2197
65160	7.90	0.2213
71760	8.20	0.2193
81000	8.60	0.2199
∞	10.35	
∞	10.32	

Mean k = 0.2186×10^{-4} sec.$^{-1}$

Duplicate mean k (11 determinations) = 0.2183×10^{-4} sec.$^{-1}$

Overall mean k ; k_m = 0.2185×10^{-4} sec.$^{-1}$

$$\frac{\sigma_m}{k_m} = 0.0014$$

k_m corrected for the solvent = 0.2154×10^{-4} sec.$^{-1}$

Benzyl Chloride in 70% Aqueous Acetone

(Solvent H) at 85.05°C. Run Nos. 146/147.

Time (sec.)	Titre. (ml.)	10^4k (sec.$^{-1}$)
0	0	
0	0	
10770	1.00	(0.09687)
19050	1.77	0.1013
77460	5.41	0.09933
101280	6.50	0.1022
120540	7.17	0.1031
175590	8.38	0.1014
0	0	
0	0	
57690	4.43	0.1003
67980	4.86	(0.09679)
81450	5.68	0.1017
100740	6.48	0.1023
143280	7.74	0.1020
155790	8.00	0.1014
∞	10.08	
∞	10.08	

Mean k = 0.1015×10^{-4} sec.$^{-1}$

Duplicate mean k (10 determinations) = 0.1020×10^{-4} sec.$^{-1}$

Overallmean k; k_m = 0.1018×10^{-4} sec.$^{-1}$

$$\frac{\sigma_m}{k_m} = 0.0023$$

k_m corrected for the solvent = 0.1004×10^{-4} sec.$^{-1}$

Benzyl Chloride in 70% Aqueous Acetone

(Solvent I) at 74.74°C. Run Nos. 152/153.

Time (sec.)	Titre. (ml.)	10^4k (sec.$^{-1}$)
0	0.05	
0	0.04	
27690	1.11	0.04017
86700	3.08	0.04138
99720	3.46	0.04156
115380	3.89	0.04170
129270	4.19	0.04105
172470	5.18	0.04141
185640	5.43	0.04129
204990	-	-
259650	6.66	0.04124
287700	7.10	0.04203
346320	7.72	0.04159
364860	8.00	(0.04291)
∞	10.10	
∞	10.10	

Mean k = 0.04134×10^{-4} sec.$^{-1}$

Duplicate mean k (10 determinations) = 0.04140×10^{-4} sec.$^{-1}$

Overall mean k; k_m = 0.04137×10^{-4} sec.$^{-1}$

$$\frac{\sigma_m}{k_m} = 0.0024$$

k_m corrected for the solvent = 0.04234×10^{-4} sec.$^{-1}$

Benzyl Chloride in 70% Aqueous Acetone

(Solvent I) at II4.90°C. Run Nos. 154/155.

Time (sec.)	Titre. (ml.)	10^4k (sec.$^{-1}$)
0	0.73	
0	0.74	
1360	1.81	0.8941
2385	2.49	0.8748
2840	2.79	0.8750
3485	3.08	(0.8221)
5015	4.09	0.8776
6375	4.80	0.8853
8360	5.65	0.8812
11525	6.72	0.8734
12838	7.11	0.8776
13907	7.41	0.8849
15605	7.81	0.8890
16637	8.00	0.8837
∞	10.15	
∞	10.19	
∞	10.18	

Mean k = 0.8815×10^{-4} sec.$^{-1}$

Duplicate mean k (10 determinations) = 0.8815×10^{-4} sec.$^{-1}$

Overall mean k ; k_m = 0.8815×10^{-4} sec.$^{-1}$

$$\frac{\sigma_m}{k_m} = 0.0016$$

Benzhydryl Chloride in 70% Aqueous Acetone

(Solvent H) at 20.72°C. Run Nos. 138/139.

Time (sec.)	Titre. (ml.)	10^4k (sec.$^{-1}$)
0	0.56	
510	1.98	(3.002)
925	3.01	3.041
1353	3.94	3.049
1680	4.57	3.052
2139	5.36	3.058
2635	6.09	3.056
3115	6.69	3.048
3485	7.10	3.052
3941	7.56	3.056
4440	7.99	3.061
4860	8.29	3.052
5553	8.77	3.098
∞	10.56	
∞	10.55	

Mean k = 3.057×10^{-4} sec.$^{-1}$

Duplicate mean k (10 determinations) = 3.063×10^{-4} sec.$^{-1}$

Overall mean k ; k_m = 3.060×10^{-4} sec.$^{-1}$

$$\frac{\sigma_m}{k_m} = 0.0014$$

t-Butyl Bromide in 70% Aqueous Acetone

(Solvent C) at 38.25°C. Run Nos. 118/119.

Time (sec.)	Titre. (ml.)	10^4k (sec.$^{-1}$)
0	1.43	
66	2.75	25.82
137	3.91	25.47
200	4.91	26.67
272	5.73	26.28
349	6.53	26.68
420	7.08	26.47
480	7.50	26.60
540	7.84	26.54
595	8.10	26.41
656	8.40	26.81
713	8.54	26.10
∞	9.84	
∞	9.85	

Mean k = 26.35×10^{-4}sec.$^{-1}$

Duplicate mean k (10 determinations) = 26.24×10^{-4}sec.$^{-1}$

Overall mean k ; k_m = 26.30×10^{-4}sec.$^{-1}$

$\frac{\sigma_m}{k_m}$ = 0.0023

k_m corrected for the solvent = 28.11×10^{-4}sec.$^{-1}$

t-Butyl Bromide in 70% Aqueous Acetone

(Solvent B) at 29.62°C. Run Nos. 100/101.

Time (sec.)	Titre. (ml.)	10^4k (sec.$^{-1}$)
0	1.57	
107	2.58	10.86
225	3.54	10.70
374	4.67	10.97
575	5.83	10.80
705	6.52	10.94
815	6.93	10.70
919	7.42	10.97
1107	7.98	10.76
1211	8.36	11.04
1396	8.74	10.80
1517	9.00	10.83
1649	9.20	10.69
∞	10.76	
∞	10.78	
∞	10.78	

Mean k = 10.84×10^{-4}sec.$^{-1}$

Duplicate mean k (11 determinations) = 10.85×10^{-4}sec.$^{-1}$

Overall mean k ; k_m = 10.84×10^{-4}sec.$^{-1}$

$$\frac{\sigma_m}{k_m} = 0.0027$$

k_m corrected for the solvent = 11.26×10^{-4}sec.$^{-1}$

t-Butyl Bromide in 70% Aqueous Acetone
(Solvent B) at 20.07°C. Run Nos. 104/105.

Time (sec.)	Titre. (ml.)	10^4k (sec.$^{-1}$)
0	0.72	
420	2.18	3.691
900	3.52	3.581
1200	4.32	3.645
1640	5.24	3.588
2126	6.24	3.687
2520	6.80	3.620
2910	7.41	3.693
3315	7.85	3.651
3885	8.42	3.651
4475	8.91	3.666
5130	9.42	(3.782)
5444	9.50	3.667
∞	10.87	
∞	10.88	
∞	10.88	

Mean k = 3.649×10^{-4}sec.$^{-1}$

Duplicate mean k (9 determinations) = 3.643×10^{-4}sec.$^{-1}$

Overall mean k ; k_m = 3.646×10^{-4}sec.$^{-1}$

$\frac{\sigma_m}{k_m}$ = 0.0019

k_m corrected for the solvent = 3.788×10^{-4}sec.$^{-1}$

t-Butyl Bromide in 70% Aqueous Acetone (Solvent B) at 10.92°C. Run Nos. 102/103.

Time (sec.)	Titre. (ml.)	10^4k (sec.$^{-1}$)
0	2.12	
975	3.04	1.153
1935	3.86	1.160
2775	4.51	1.163
3735	5.17	1.159
4995	5.93	1.161
6615	6.78	1.168
7945	7.34	1.162
8895	7.70	1.162
9975	8.07	1.165
10995	8.38	1.167
12075	8.66	1.165
13575	9.01	1.169
∞	10.78	
∞	10.77	

Mean k = 1.163×10^{-4} sec.$^{-1}$

Duplicate mean k (12 determinations) = 1.167×10^{-4} sec.$^{-1}$

Overall mean k ; k_m = 1.165×10^{-4} sec.$^{-1}$

$$\frac{\sigma_m}{k_m} = 0.0011$$

k_m corrected for the solvent = 1.210×10^{-4} sec.$^{-1}$

t-Butyl Bromide in 70% Aqueous Acetone

(Solvent B) at -0.03°C. Run Nos. 107/108.

Time (sec.)	Titre. (ml.)	10^4k (sec.$^{-1}$)
0	0.38	
4170	1.56	(0.2519)
8970	2.69	0.2631
12830	3.43	0.2588
15630	3.98	0.2623
19650	4.70	0.2644
22920	5.19	0.2646
29910	6.16	0.2666
33390	6.50	0.2617
0	0.18	
52320	8.12	0.2649
56490	8.38	0.2635
61380	8.57	0.2561
∞	10.78	
∞	10.77	

Mean k = 0.2626×10^{-4} sec.$^{-1}$

Duplicate mean k (11 determinations) = 0.2622×10^{-4} sec.$^{-1}$

Overall mean k ; k_m = 0.2624×10^{-4} sec.$^{-1}$

$\frac{\sigma_m}{k_m}$ = 0.0025

k_m corrected for the solvent = 0.2726×10^{-4} sec.$^{-1}$

Benzhydryl Chloride in 70% Aqueous Acetone
(Solvent C) at 20.43°C. Run Nos.116/117.

Time (sec.)	Titre. (ml.)	10^4k (sec.$^{-1}$)
0	0.37	
615	2.04	2.693
1052	3.04	2.660
1535	4.05	2.670
2293	5.40	2.685
2853	6.20	2.669
3489	7.00	2.670
3875	7.41	2.662
4345	7.88	2.669
5019	8.46	2.681
5730	8.92	2.655
6145	9.20	2.678
6699	9.49	2.678
∞	11.29	
∞	11.32	

Mean k = 2.673×10^{-4} sec.$^{-1}$

Duplicate mean k (12 determinations) = 2.678×10^{-4} sec.$^{-1}$

Overall mean k ; k_m = 2.676×10^{-4} sec.$^{-1}$

$\frac{\sigma_m}{k_m}$ = 0.0009

Benzhydryl Chloride in 70% Aqueous Acetone

(Solvent B) at 20.48°C. Run Nos.109/110.

Time (sec.)	Titre. (ml.)	$10^4 k$ (sec.$^{-1}$)
0	0.48	
900	2.04	2.779
1380	2.68	2.711
2040	3.51	2.755
2700	4.22	2.861
3300	4.72	2.789
4020	5.18	2.733
4560	5.60	2.841
5040	5.79	2.777
5460	6.06	(2.872)
5895	6.15	2.767
6720	6.44	2.778
∞	7.53	
∞	7.53	

Mean k = 2.773×10^{-4} sec.$^{-1}$

Duplicate mean k (10 determinations) = 2.769×10^{-4} sec.$^{-1}$

Overall mean k ; k_m = 2.771×10^{-4} sec.$^{-1}$

$$\frac{\sigma_m}{k_m} = 0.0025$$

t-Butyl Chloride in 70% Aqueous Acetone
(Solvent D) at 54.90°C. Run Nos. 87/88.

Time (sec.)	Titre. (ml.)	10^4k (sec.$^{-1}$)
0	1.82	
0	1.84	
480	3.11	(3.819)
840	3.88	3.719
1260	4.71	3.757
1620	5.27	3.695
1985	5.81	3.708
2400	6.31	3.680
2880	6.86	3.731
3420	7.35	3.750
3780	7.58	3.696
4260	7.88	3.684
4980	8.22	(3.636)
5700	8.57	3.753
∞	9.46	
∞	9.46	
∞	9.49	

Mean k = 3.717×10^{-4} sec.$^{-1}$

Duplicate mean k (11 determinations) = 3.713×10^{-4} sec.$^{-1}$

Overall mean k ; k_m = 3.715×10^{-4} sec.$^{-1}$

$\frac{\sigma_m}{k_m}$ = 0.0019

k_m corrected for the solvent = 3.455×10^{-4} sec.$^{-1}$

t-Butyl Chloride in 70% Aqueous Acetone

(Solvent D) at 44.78°C. Run Nos. 83/84.

Time (sec.)	Titre. (ml.)	10^4k (sec.$^{-1}$)
0	0.90	
0	0.90	
1200	2.32	1.326
2100	3.18	1.282
2880	3.92	1.302
3900	4.78	1.317
4920	5.54	1.330
6360	3.36	1.306
7620	7.04	1.325
9060	7.62	1.313
10260	8.08	1.326
11160	8.40	1.339
12180	-	-
12720	8.81	1.344
∞	10.56	
∞	10.52	
∞	10.57	

Mean k = 1.319×10^{-4} sec.$^{-1}$

Duplicate mean k (11 determinations) = 1.313×10^{-4} sec.$^{-1}$

Overall mean k;k_m = 1.316×10^{-4} sec.$^{-1}$

$$\frac{\sigma_m}{k_m} = 0.0025$$

k_m corrected for the solvent = 1.224×10^{-4} sec.$^{-1}$

t-Butyl Chloride in 70% Aqueous Acetone
(Solvent D) at 35.07°C. Run Nos. 85/86.

Time (sec.)	Titre. (ml.)	10^4k (sec.$^{-1}$)
0	1.00	
0	1.00	
2280	1.84	(0.4303)
4680	2.66	0.4355
7800	3.60	0.4379
10380	4.34	0.4477
12300	4.81	0.4484
14220	5.25	0.4430
16920	5.77	0.4472
21000	6.46	0.4452
23220	6.87	(0.4558)
26040	7.18	0.4468
30180	7.65	0.4461
34980	8.14	0.4521
∞	10.01	
∞	9.97	

Mean k = 0.4450×10^{-4} sec.$^{-1}$

Duplicate mean k (11 determinations) = 0.4442×10^{-4} sec.$^{-1}$

Overall mean k; k_m = 0.4446×10^{-4} sec.$^{-1}$

$$\frac{\sigma_m}{k_m} = 0.0018$$

k_m corrected for the solvent = 0.4135×10^{-4} sec.$^{-1}$

t-Butyl Chloride in 70% Aqueous Acetone

(Solvent D) at 25.08°C. Run Nos. 89/90.

Time (sec.)	Titre. (ml.)	10^4k (sec.$^{-1}$)
0	0.52	
0	0.54	
7980	1.43	(0.1281)
12300	1.94	0.1345
17100	2.38	0.1305
20940	2.78	0.1331
24960	3.11	0.1310
30990	3.61	0.1306
0	0.20	
0	0.22	
76080	6.26	0.1315
79920	6.39	0.1299
84660	6.70	0.1340
92280	6.95	0.1320
100080	7.22	0.1318
107700	7.48	0.1324
∞	9.805	
∞	9.785	

Mean k = 0.1319×10^{-4} sec.$^{-1}$

Duplicate mean k (10 determinations) = 0.1324×10^{-4} sec.$^{-1}$

Overall mean k ; k_m = 0.1322×10^{-4} sec.$^{-1}$

$\frac{\sigma_m}{k_m}$ = 0.0026

k_m corrected for the solvent = 0.1230×10^{-4} sec.$^{-1}$

t-Butyl Chloride in 70% Aqueous Acetone (Solvent D) at 16.79°C. Run Nos.91/92.

Time (sec.)	Titre. (ml.)	10^4k (sec.$^{-1}$)
0	0.55	
0	0.54	
27840	1.54	0.04468
82020	3.20	0.04468
107760	3.89	0.04533
172020	5.17	0.04449
194400	5.60	0.04519
277140	6.63	0.04389
0	0.15	
0	0.14	
66780	2.41	0.04311
87840	3.05	0.04404
107100	3.56	0.04424
149460	4.60	0.04535
175200	5.06	0.04473
255300	6.34	0.04523
344580	7.32	0.04574
∞	9.18	
∞	9.20	

Mean k = 0.04480×10^{-4} sec.$^{-1}$

Duplicate mean k (12 determinations) = 0.04501×10^{-4} sec.$^{-1}$

Overall mean k ; k_m = 0.04490×10^{-4} sec.$^{-1}$

$$\frac{\sigma_m}{k_m} = 0.0024$$

k_m corrected for the solvent = 0.04176×10^{-4} sec.$^{-1}$

Benzhydryl Chloride in 70% Aqueous Acetone

(Solvent D) at 21.35°C. Run Nos. 93/94.

Time (sec.)	Titre. (ml.)	$10^4 k$ (sec.$^{-1}$)
0	0.42	
660	1.61	(3.248)
1440	2.70	3.404
2100	3.38	3.388
2820	4.00	3.429
3420	4.41	3.453
4140	4.78	3.438
4980	5.10	3.401
5280	5.22	3.443
5700	5.35	3.459
6060	5.44	3.456
6240	5.48	3.451
∞	6.15	
∞	6.11	

Mean k = 3.432×10^{-4} sec.$^{-1}$

Duplicate mean k (10 determinations) = 3.436×10^{-4} sec.$^{-1}$

Overall mean k ; k_m = 3.434×10^{-4} sec.$^{-1}$

$$\frac{\sigma_m}{k_m} = 0.0028$$

p-Nitrobenzhydryl Bromide in 70% Aqueous Acetone (Solvent A) at 54.87°C. Run Nos. 7/8.

Time (sec.)	Titre. (ml.)	$10^4 k$ (sec.$^{-1}$)
0	1.10	
0	1.12	
600	2.65	3.370
1200	3.91	3.374
1860	5.03	3.375
2490	5.95	3.442
2700	6.16	3.399
3120	6.62	3.413
3600	7.09	3.449
4080	7.58	(3.595)
4560	7.75	3.418
5100	8.04	3.407
5580	8.27	3.418
6000	8.49	(3.500)
∞	9.52	
∞	9.52	

Mean k = 3407 x 10^{-4}sec.$^{-1}$

Duplicate mean k (11 determinations) = 3.397 x 10^{-4}sec.$^{-1}$

Overall mean k ; k_m = 3.401 x 10^{-4}sec.$^{-1}$

$\frac{\sigma_m}{k_m}$ = 0.0020

k_m corrected for the solvent = 3.408 x 10^{-4}sec.$^{-1}$

p-Nitrobenzhydryl Bromide in 70% Aqueous Acetone (Solvent A) at 44.90°C. Run Nos. 3/4.

Time (sec.)	Titre. (ml.)	10^4k (sec.$^{-1}$)
0	0.48	
0	0.48	
1260	1.59	1.159
2520	2.54	1.152
3720	3.35	1.162
5040	4.08	1.151
6300	4.72	1.160
7560	5.29	1.173
9060	5.75	1.141
10200	6.19	1.174
11340	6.52	1.182
12540	6.74	1.156
13620	7.01	1.176
14580	7.21	1.187
∞	8.67	
∞	8.65	

Mean k = 1.164×10^{-4}sec.$^{-1}$

Duplicate mean k (10 determinations) = 1.162×10^{-4}sec.$^{-1}$

Overall mean k ; k_m = 1.163×10^{-4}sec.$^{-1}$

$$\frac{\sigma_m}{k_m} = 0.0029$$

k_m corrected for the solvent = 1.165×10^{-4}sec.$^{-1}$

p-Nitrobenzhydryl Bromide in 70% Aqueous Acetone (Solvent A) at 35.34°C. Run Nos.14/15.

Time (sec.)	Titre. (ml.)	10^4k (sec.$^{-1}$)
0	0.24	
0	0.26	
2820	1.10	0.3789
5400	1.70	(0.3510)
8760	2.67	0.3881
11460	3.21	0.3792
14160	3.78	0.3852
16740	4.24	0.3851
19440	4.68	0.3857
22200	5.01	0.3767
25080	5.30	0.3775
27960	5.76	0.3818
30600	6.04	0.3821
33420	6.30	0.3813
∞	8.64	
∞	8.66	

Mean k = 0.3820×10^{-4} sec.$^{-1}$

Duplicate mean k (10 determinations) = 0.3830×10^{-4} sec.$^{-1}$

Overall mean k ; k_m = 0.3825×10^{-4} sec.$^{-1}$

$$\frac{\sigma_m}{k_m} = 0.0020$$

k_m corrected for the solvent = 0.3833×10^{-4} sec.$^{-1}$

p-Nitrobenzhydryl Bromide in 70% Aqueous Acetone (Solvent A) at 24.79°C. Run Nos.22/23.

Time (sec.)	Titre. (ml.)	10^4k (sec.$^{-1}$)
0	0.58	
0	0.61	
5700	1.08	0.09979
12270	1.63	0.1032
19560	2.12	(0.09868)
25560	2.60	0.1028
31350	2.94	0.1005
37680	3.36	0.1021
0	0.26	
0	0.24	
56940	4.22	0.1021
61260	4.42	0.1015
67830	4.72	0.1010
73410	4.98	0.1014
79320	5.21	0.1008
85860	5.49	0.1015
93060	5.77	0.1019
∞	9.28	
∞	9.24	

Mean k = 0.1015×10^{-4} sec.$^{-1}$

Duplicate mean k (12 determinations) = 0.1017×10^{-4} sec.$^{-1}$

Overall mean k ; k_m = 0.1016×10^{-4} sec.$^{-1}$

$\frac{\sigma_m}{k_m}$ = 0.0020

k_m corrected for the solvent = 0.1018×10^{-4} sec.$^{-1}$

p-Nitrobenzhydryl Bromide in 70% Aqueous Acetone (Solvent A) at 15.21°C. Run Nos. 20/21.

Time (sec.)	Titre. (ml.)	10^4k (sec.$^{-1}$)
0	0.14	
0	0.15	
77160	1.90	0.02734
106020	2.48	0.02755
163440	3.46	0.02730
199260	4.01	0.02730
249780	4.76	0.02784
275580	5.06	0.02769
339720	5.75	0.02764
0	0.16	
427980	6.46	(0.02704)
452340	6.69	0.02742
514140	7.13	0.02772
538380	7.30	0.02787
608700	7.64	0.02764
∞	9.35	
∞	9.34	

Mean k = 0.02757 x 10^{-4}sec.$^{-1}$

Duplicate mean k (12 determinations) = 0.02770 x 10^{-4}sec.$^{-1}$

Overall mean k ; k_m = 0.02764 x 10^{-4}sec.$^{-1}$

$$\frac{\sigma_m}{k_m} = 0.0013$$

k_m corrected for the solvent = 0.02770 x 10^{-4}sec.$^{-1}$

Benzhydryl Chloride in 70% Aqueous Acetone

(Solvent A) at 15.19°C. Run Nos. 18/19.

Time (sec.)	Titre. (ml.)	10^4k (sec.$^{-1}$)
0	0.85	
0	0.81	
1172	2.79	1.516
2040	3.96	1.521
2795	4.84	1.479
4265	6.48	1.489
5020	7.07	1.474
5780	7.90	1.462
6705	8.30	1.536
7440	8.86	1.482
8170	9.25	1.476
8940	-	-
9630	9.98	1.488
10447	10.28	1.477
∞	12.85	
∞	12.84	

Mean k = 1.491×10^{-4} sec.$^{-1}$

Duplicate mean k (12 determinations) = 1.498×10^{-4} sec.$^{-1}$

Overall mean k ; k_m = 1.495×10^{-4} sec.$^{-1}$

$$\frac{\sigma_m}{k_m} = 0.0026$$

t-Butyl Chloride in 80% Aqueous Acetone (Solvent E) at 69.95°C. Run Nos. 50/51.

Time (sec.)	Titre. (ml.)	10^4k (sec.$^{-1}$)
0	0.78	
0	0.78	
0	0.82	
900	2.78	2.874
1380	3.65	2.877
1800	4.31	2.868
2220	4.90	2.867
2820	5.66	2.895
3360	6.16	2.843
3780	6.59	2.889
4260	6.93	2.853
4800	7.36	2.911
5340	7.65	2.886
5940	7.95	2.889
6540	8.22	2.913
∞	9.53	
∞	9.52	
∞	9.50	

Mean k = 2.880×10^{-4} sec.$^{-1}$

Duplicate mean k (12 determinations) = 2.868×10^{-4} sec.$^{-1}$

Overall mean k ; km = 2.874×10^{-4} sec.$^{-1}$

$$\frac{\sigma_m}{k_m} = 0.0024$$

k_m corrected for the solvent = 2.543×10^{-4} sec.$^{-1}$

t-Butyl Chloride in 80% Aqueous Acetone

(Solvent E) at 59.97°C. Run Nos. 56/57.

Time (sec.)	Titre. (ml.)	10^4k (sec.$^{-1}$)
0	0.30	
0	0.32	
2160	2.31	1.098
3420	3.21	(1.069)
4680	4.10	1.095
6000	4.93	1.115
7440	5.64	1.113
8760	6.12	1.085
10080	6.70	1.114
11220	7.07	1.115
12480	7.42	1.114
13500	7.70	1.123
14520	8.00	(1.151)
15845	8.22	1.138
∞	9.78	
∞	9.77	

Mean k = 1.111×10^{-4}sec.$^{-1}$

Duplicate mean k (11 determinations) = 1.108×10^{-4}sec.$^{-1}$

Overall mean k ; k_m = 1.109×10^{-4}sec.$^{-1}$

$$\frac{\sigma_m}{k_m} = 0.0027$$

k_m corrected for the solvent = 0.9815×10^{-4}sec.$^{-1}$

t-Butyl Chloride in 80% Aqueous Acetone (Solvent E) at 50.27°C. Run Nos. 58/59.

Time (sec.)	Titre. (ml.)	10^4k (sec.$^{-1}$)
0	0.20	
0	0.18	
0	0.20	
4265	1.73	0.3993
7500	2.79	0.4041
11115	3.78	0.4032
13815	4.48	0.4094
17460	5.24	0.4070
20715	5.88	0.4111
23115	6.28	0.4112
26415	6.76	0.4109
29835	7.22	0.4131
33495	7.57	0.4065
36735	7.91	0.4085
∞	10.09	
∞	10.12	

Mean k = 0.4077×10^{-4}sec.$^{-1}$

Duplicate mean k (11 determinations) = 0.4081×10^{-4}sec.$^{-1}$

Overall mean k ; k_m = 0.4079×10^{-4}sec.$^{-1}$

$$\frac{\sigma_m}{k_m} = 0.0023$$

k_m corrected for the solvent = 0.3610×10^{-4}sec.$^{-1}$

t-Butyl Chloride in 80% Aqueous Acetone

(Solvent E) at 39.66°C. Run Nos. 60/61.

Time (sec.)	Titre. (ml.)	10^4k (sec.$^{-1}$)
0	0.19	
0	0.19	
13620	1.72	0.1233
20340	2.41	0.1248
24060	2.74	0.1238
87300	6.82	0.1269
94380	7.02	0.1241
101640	7.34	0.1261
110280	7.64	0.1266
0	0.13	
0	0.14	
54360	5.05	0.1251
63660	5.65	0.1268
73500	6.12	0.1250
79140	6.39	0.1250
142320	8.44	0.1263
∞	10.07	
∞	10.10	

Mean k = 0.1253×10^{-4} sec.$^{-1}$

Duplicate mean k (11 determinations) = 0.1252×10^{-4} sec.$^{-1}$

Overall mean k ; k_m = 0.1253×10^{-4} sec.$^{-1}$

$\frac{\sigma_m}{k_m}$ = 0.0025

k_m corrected for the solvent = 0.1109×10^{-4} sec.$^{-1}$

t-Butyl Chloride in 80% Aqueous Acetone

(Solvent E) at 29.99°C. Run Nos. 62/63.

Time (sec.)	Titre. (ml.)	10^4k (sec.$^{-1}$)
0	0.18	
0	0.18	
32700	1.39	0.03853
81930	2.96	0.03874
103700	3.58	0.03900
171780	5.20	0.03933
179220	5.48	(0.04079).
0	0.04	
0	0.025	
237360	6.36	0.03971
252180	6.60	0.03981
270660	6.86	0.03980
319920	7.48	0.03962
341640	-	-
409800	8.33	0.03931
424380	8.45	0.03938
∞	10.39	
∞	10.41	

Mean k = 0.03932×10^{-4} sec.$^{-1}$

Duplicate mean k (10 determinations) = 0.03917×10^{-4} sec.$^{-1}$

Overall mean k ; k_m = 0.03925×10^{-4} sec.$^{-1}$

$\frac{\sigma_m}{k_m}$ = 0.0025

k_m corrected for the solvent = 0.03474×10^{-4} sec.$^{-1}$

Benzhydryl Chloride in 80% Aqueous Acetone
(Solvent E) at 29.13°C. Run Nos. 64/65.

Time (sec.)	Titre. (ml.)	10^4k (sec.$^{-1}$)
0	0.24	
900	1.18	1.248
1620	1.79	1.251
2280	2.29	1.244
2880	2.73	1.250
3840	3.34	1.244
4710	3.86	1.252
5880	4.47	1.258
7320	5.12	1.269
8595	5.58	1.266
9480	5.86	1.266
10320	6.12	1.275
∞	8.22	
∞	8.25	

Mean k = 1.257×10^{-4} sec.$^{-1}$

Duplicate mean k (10 determinations) = 1.263×10^{-4} sec.$^{-1}$

Overall mean k ; k_m = 1.260×10^{-4} sec.$^{-1}$

$$\frac{\sigma_m}{k_m} = 0.0016$$

Data for the Hydrolysis of Alkyl Halides in Aqueous Acetone at 50°C.

(k in sec.$^{-1}$, E in kcal., $\Delta S^{\ddagger}$ and $\Delta C^{\ddagger}$ in cal. deg.$^{-1}$).

Alkyl Halide	Solvent	$10^4 k_c$ *	E_c *	$-\Delta S_c^{\ddagger}$ *	$-\Delta C^{\ddagger}$	$\Delta C^{\ddagger}/\Delta S^{\ddagger}$
Benzyl bromide	50%	0.6726	18.999±0.001	20.99±0.01	26.0±2.2	1.24±0.11
Benzyl bromide	70%	0.1340	19.108±0.039	23.86±0.11	23.1±2.6	0.97±0.11
Benzyl chloride	70%	0.004128	21.288±0.130	24.03±0.38	21.3±2.9	0.89±0.12
t-Butyl bromide	70%	86.82	19.174±0.099	10.79±0.33	43.0±3.3	3.99±0.33
t-Butyl chloride	70%	2.086	21.313±0.065	11.58±0.21	41.4±4.4	3.58±0.39
p-Nitrobenzhydryl bromide	70%	2.030	22.352±0.040	8.42±0.13	31.1±2.7	3.69±0.33
t-Butyl chloride	80%	0.3487	22.184±0.000	12.44±0.000	32.4±3.4	2.60±0.27

* Calculated values.

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