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THE EFFECT OF TETRA-ALKYL-AMMONIUM SALTS ON THE RATES OF S_N1 REACTIONS

by

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SUMMARY

The effect of electrolytes on the rates of reaction by mechanism S_N1 have been partially explained by the electrostatic theory of Hughes and Ingold, which is based on the view that electrolytes alter the rate by ion-atmosphere stabilisation of the transition state. This theory requires acceleration of reaction by all electrolytes and that the magnitude of this acceleration is independent of the nature of the electrolyte. Contrary to the requirements of this approach, specific electrolyte effects have been reported and can normally be explained by an additional effect, originally suggested by Hammett, arising from the change in the "effective" solvent composition which is caused by the specific solvation of the electrolyte by the solvent components.

Recent results for the addition of tetra-n-butyl ammonium salts cannot be explained by the "solvation" hypothesis, although tetra-methylammonium salts behave in the expected manner. The effects of tetra-alkyl ammonium salts, containing a variety of different alkyl groups, on the rate of decomposition of benzhydryl chloride in an aqueous organic solvent (70% aqueous acetone) have been investigated in this work in an attempt to obtain information about the effect of these salts on the rates of S_N1 reactions.

The work has shown that tetra-alkyl ammonium salts have specific effects on the rate of ionisation of benzhydryl chloride in 70% aqueous acetone. There is an additive nature to the results which shows that the effects are a consequence of the individual ions. The order of the effect of anions on the rate agrees with the predictions of the solvation model of Lucas and Hammett. The effects of the cations cannot be reconciled with this approach but can be explained if short range specific interactions occur with the substrate in the initial state.

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CONTENTS

CHAPTER ONE

INTRODUCTION

This investigation is concerned with the effect of salt additions on the rate of solvolysis of benzhydryl chloride in 70% aqueous acetone.

$$Ph_2CHCl + H_2O \longrightarrow Ph_2CHOH + HCl$$

This reaction is one of a group of displacement reactions in which valency electrons are removed from the reaction centre by the departing group, in this case, chloride. This type of displacement reaction is known as a nucleophilic substitution.[1]

In general nucleophilic substitution reactions can be depicted by the following equation, where the reaction centre is designated by a vertical line.

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

The electron deficiency at the reaction centre, resulting from the removal of the valency electrons by the departing group, is made good by coordination with the reagent Y. Thus Y becomes one unit more positive and X, the expelled group, one unit more negative. This takes place irrespective of the charges carried by the reacting species. e.g.

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

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

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

Two general mechanisms are recognised for nucleophilic substitution reactions.[1] The bimolecular mechanism (S_N2) involves reaction in a single step in which bond formation with Y and the fission of the bond linking the departing group to the reaction centre occur simultaneously.

$$\text{e.g.}\quad Y^- + RX \longrightarrow \underset{\text{Transition state}}{{}^-Y\;\_\,\_\,\_\;R\;\_\,\_\,\_\;X^-} \longrightarrow YR + X^- \quad (S_N2)$$

This process involves a covalency change of two species, Y^- and RX. When the reactant Y^- is not ionic, the charge distribution in the given example will be modified accordingly.

In reaction by the unimolecular process (S_N1), the rate-determining hydrolysis of the substrate forms a carbonium ion which can react rapidly with the nucleophilic reagent:

$$\left.\begin{array}{l} RX \rightleftharpoons \underset{\text{Transition state}}{R^+\;\_\,\_\,\_\,\_\,\_\,\_\,\_\;X^-} \longrightarrow R^+ + X^- \text{ (Slow)} \\ \qquad R^+ + Y^- \longrightarrow RY \text{ (rapid)} \end{array}\right\} S_N1$$

As only one species undergoes covalency change in the rate-determining step, the reaction is regarded as unimolecular.

S_N1 reactions do not occur readily in the gas phase as the energy required for ionisation of the substrate molecule is too high. However, in solution, the substantial solvation of the highly polar transition state (relative to the non-polar initial state) reduces the free energy of activation to accessible values.[2] Many reactions in solution have been shown to proceed in this manner.

Determination of the mechanism

Reaction by mechanism S_N2 should lead to second order kinetics, if both species are in small and comparable concentrations, and first order kinetics, if the reaction proceeds by the S_N1 mechanism,

i.e. Rate = $k_a [RX] [Y]$ (S_N2)

Rate = $k_b [RX]$ (S_N1)

However, when the nucleophilic reagent Y is the solvent, as in this study, then it is present in virtually constant excess. Consequently, first order kinetics will be obeyed, irrespective of whether mechanism S_N1 or S_N2 is operating. Clearly then, in solvolytic reactions different operating criteria have to be employed in order to establish the mechanism, although it is noteworthy that characteristic deviations from first order kinetics can be expected in some S_N1 reactions (see page 12).

These additional tests of solvolytic mechanism have been summarised by Hughes:[3]

(1) The effect of structural changes in the compound substituted.

(2) The effect of variations in the substituting reagent.

(3) The effect of solvent changes on reaction rates and products.

(4) The stereochemical course of the substitution e.g. mechanism S_N2 leads to an inversion effect.

(5) The kinetic form of the substitution reaction.

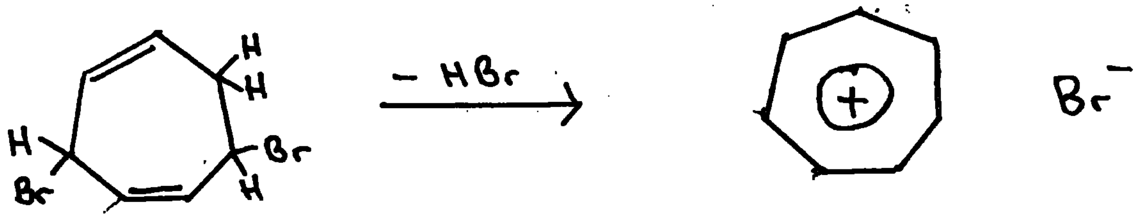
(6) The effect of salt additions on rates and products.

Recently it has been suggested that the ratio of the heat capacity of activation to the entropy of activation $\frac{\Delta C^*}{\Delta S^*}$ is independent of the nature of the substrate in S_N1 reactions, and that the value of this ratio is different when mechanism S_N2 is operating under the same experimental conditions.[4]

It is now generally accepted that the solvolysis of benzhydryl chloride in 70% aqueous acetone proceeds entirely by the S_N1 mechanism.[4,5,6] Therefore, it is not proposed to discuss in detail the criteria for the determination of mechanism, except for the effect of salt additions (6, see page 9) on S_N1 solvolysis, which will be considered later in this chapter.

The Carbonium Ion

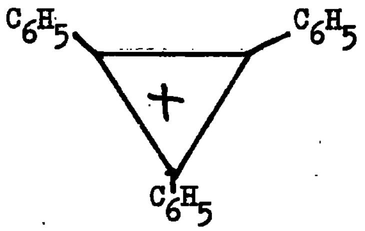
Solvolysis by the S_N1 mechanism requires the formation of a carbonium ion (R^+). This species is generally highly reactive but certain stable carbonium salts have been prepared in solution or isolated as ionic solids. For example, cycloheptatrienylium bromide,[7] has been obtained from dibromotropilidene, by thermal elimination of HBr, as yellow crystals when crystallised from ethanol (M.Pt. 198 - 200°C).



Dibromotropilidene

Cycloheptatrienylium bromide

The mixed salt of sym-triphenylcyclo-propenylium fluoroborate-hydroxylfluoroborate has been isolated as a crystalline solid (M.Pt. 300°C) when 1,2,3 triphenylcyclopropenyl cyanide was refluxed with boron-trifluoride-etherate.[8] The cation may be represented as



Conductance and spectral measurements have provided evidence for the existence of carbonium ions from measurements on the dissociation of some organic halides in various solvents. The presence of (a) t-butyl and (b)triphenyl methyl cations has been detected by spectral measurements on solutions of the alcohols in concentrated sulphuric acid.[(a)9, (b)10]

There is no direct evidence for the existence of carbonium ions in the majority of reactions proceeding by the S_N1 mechanism. However, the kinetic evidence suggests that the mechanism is correct and so it is thought to be certain that carbonium ions are involved as intermediates.

The Effect of Electrolytes on the rates of S_N1 reactions

Hughes, Ingold and their co-workers[11] pointed out that the rates of S_N1 reactions could be modified by the presence of electrolytes. Two general effects were envisaged.

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

$$R^+ + H_2O \xrightarrow{3} ROH + H^+$$

The rate determining ionisation of the substrate (step 1) proceeds via a highly polar transition state, $(R^{\sim\frac{1}{2}+} ---- Cl^{\sim\frac{1}{2}-})$, which can therefore be expected to be subject to ion-atmosphere stabilisation by analogy with the similar stabilisation of fully developed ions in solution. This ionic strength effect will tend to accelerate the reaction and will be invoked by the addition of electrolytes. However, one of the reaction products (hydrochloric acid in the example quoted above) is an electrolyte, so that, even when no salts have been added, the operation of the ionic strength effect should progressively increase the observed first-order rate coefficient as reaction proceeds. The quantitative treatment of this effect is discussed on page 18 but a simple electrostatic treatment[11] suggested that its magnitude would depend only on the degree of charge development in the transition state (regarded as a linear dipole) and on the ionic strength, at least in very dilute Solutions.

A further effect arises in the presence of common anions (chloride in the example quoted on page 12) which will accelerate the reversal of the ionisation (step 2) and can therefore be expected to decrease the observed rate of reaction since some of the carbonium ions (R^+) will have reverted to the original substrate (RCl) before they have captured a water molecule to form the alcohol by step 3. This retarding mass-law effect will be invoked by the addition of common ions, and also by their production as reaction proceeds. The magnitude of this effect is given by the mass law constant $\alpha = \frac{k_2}{k_3}$, and there is ample evidence (see Table Ii) in support of the original suggestion[11] that α should increase with increasing stability of the intermediate carbonium ion.

Table Ii[11]

Values of α for various alkyl halides in 85% acetone

Halide	α
Triphenyl methyl chloride	~ 400[19]
p,p' dimethyl benzhydryl chloride	68 - 69
p methylbenzhydryl chloride	28 - 35
p-t-butylbenzhydryl chloride	20 - 43
Benzhydryl chloride	10 - 16

It was envisaged that the stabler this ion, the longer could it persist in solution and therefore the greater the chance of its reaction with an anion before the solvation shell collapses to give the alcohol by step 3.

When no electrolyte is initially present, in an S_N1 mechanism both effects operate during the hydrolysis of an organic halide, because halide and hydrogen ions are produced as the reaction proceeds. Since the effects influence the rate of reaction in differing manners, the ionic strength effect leading to an increase, and the mass law effect to a reduction in rate, the overall result will depend on the relative importance of the two effects. Constant first-order rates have been observed for the solvolysis of benzhydryl chloride in aqueous acetone[12] and the solvolysis of tert. butyl bromide is accelerated as the reaction proceeds[13] since, in both cases, the mass law effects are small. The solvolysis of dichlorodiphenyl methane is progressively retarded due to a high mass law effect.[14] (18)

Similar considerations apply to reactions in other solvents e.g. the reaction of benzhydryl chloride with either fluoride ions, pyridine or triethylamine always occured initially at the same rate apart from a small medium effect.[15] This observation is fully consistent with the rate determining ionisation of benzhydryl chloride, which is, of course, not affected by the nature of the other species present:

e.g. $$RCl \rightleftharpoons R^+ + Cl^-$$

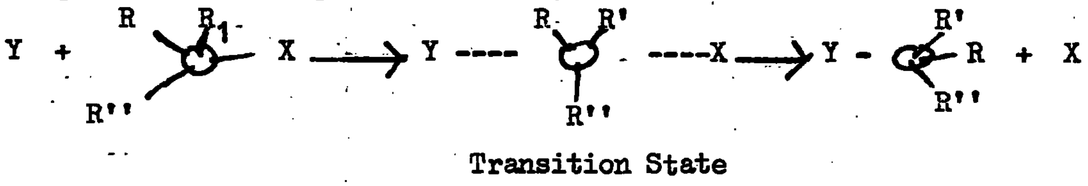
$$R^+ + F^- \longrightarrow RF$$

At later stages in the reaction, the rate of disappearance of benzhydryl chloride depends on the nature of the nucleophile, which must now compete with the product chloride ions for the reactive carbonium ion. Similarly the addition of chloride ions will retard the reaction. These observations are fully consistent with the operation of the mass law effect.[15,16]

S_N2 solvolysis also involves an increase in polarity on passage into the transition state and should, therefore, also be subject to an accelerating ionic strength effect. Owing to the more diffuse charge distribution in the transition state of an S_N2 reaction than in an S_N1 reaction, the accelerating effect is less marked. No mass law effect can operate in a reaction by mechanism S_N2 and common ion salts should therefore not affect the rate in any special manner.

Ion-pair intermediates in solvolysis

The statement is generally accepted that the energetically most favoured path for S_N2 reactions involves attack of the reagent on that side of the molecule which is opposite to the displaced group. The resulting inversion effect can readily be seen from the diagram below (charges are omitted).



Under these conditions an optically active substrate should give a completely inverted product.

In S_N1 reactions, however, the optical configuration of the product is controlled by reaction between the nucleophile and the intermediate carbonium ion, R^+. In general this ion should possess a planar configuration, so that there is no favoured direction for attack by the nucleophile, resulting in a racemic product.[1]

There was, initially, a considerable amount of evidence consistent with this prediction, but the S_N1 solvolysis of α phenylethyl chloride gave a partially inverted product.[20,21,22] Hughes, Ingold and their co-workers, suggested that this result could arise from the fact that the intermediate carbonium ion was highly reactive so that attack by a solvent molecule could occur whilst one side of the molecule was still partially shielded by the departing group.

An alternative suggestion was made by Hammett[23] who proposed that an "ion-pair" intermediate could be formed, before the substrate was fully ionised, and that this ion pair could react with the solvent to give an inverted product. The relative rates of reaction of the carbonium ion and the ion-pair would control the ratio of racemisation to inversion.

Hammett's suggestion of ion-pair intermediates has been used by Winstein and others to explain the results of the solvolyses of optically active sulphonates in acetic acid; which are thought to proceed by the S_N1 mechanism. [24,25]

Winstein and his co-workers[25] have obtained much evidence for the existence of internal ion-pairs in S_N1 reactions, largely from observations that the loss of optical activity occurs more rapidly than solvolysis or other reactions. The majority of their work involved study of the acetolysis of the esters of sulphonic acids, where they concluded that two different types of ion-pair intermediates preceded the formation of the fully developed carbonium ion. In acetic acid these intermediates were also considered to be capable of reaction with the solvent and the nucleophile.

Similarly, halogen ion exchange and solvolysis of the benzhydryl halides in aqueous acetone were found to occur more slowly than the loss of optical activity, suggesting that here too the heterolysis proceeded via one or more intermediate ion-pairs. There is, however, no evidence that these intermediates react with the solvent or nucleophiles and it has recently been shown[26,27] that any such processes make only a negligibly small contribution to the overall rate of reaction of dichlorodiphenyl methane in this solvent. Here, the evidence suggests that the products are only formed by the reaction with the fully developed carbonium ion, and there is no reason to believe that this should not also apply to benzhydryl chloride. For this reason the present reactions are discussed on the basis of the original scheme proposed by Hughes, Ingold and their coworkers.[11]

Quantitative treatment of electrolyte effects in S_N1 solvolysis[11]

In the hydrolysis of an organic halide by mechanism S_N1 the steps are:

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

$$\mathrm{R}^+ + \mathrm{H_2O} \xrightarrow{3} \mathrm{ROH} + \mathrm{H}^+$$

The intermediate carbonium ion, R^+, is highly reactive and will therefore participate in step 2 or 3 almost as soon as it is formed.

The stationary state principle can therefore be applied to this species so that the instantaneous rate coefficient for hydrolysis is given by

$$k_h = \frac{1}{[\mathrm{ROH}]} \cdot \frac{d[\mathrm{ROH}]}{dt} = -\frac{1}{[\mathrm{RCl}]} \cdot \frac{d[\mathrm{RCl}]}{dt} = \frac{k_1}{1 + \alpha[\mathrm{Cl}^-]} \qquad (1)$$

where the mass law constant, α, $= \frac{k_2}{k_3}$. This parameter is a measure of the competition between Cl^- and water for reaction with the fully developed carbonium ion.

The addition of electrolytes will alter the rate coefficients, k_1, k_2 and k_3, by changing the value of the activity coefficients, γ, of the appropriate initial and transition states. Application of the Brønsted equation to the individual reaction steps then shows that:

$$k_1 = k_1^o \frac{\gamma_{RCl}}{\gamma_1^*} \qquad (2)$$

$$k_2 = k_2^o \frac{\gamma_{R^+}\gamma_{Cl^-}}{\gamma_1^*} \qquad (\text{since } \gamma_1^* = \gamma_2^*) \quad (3)$$

$$k_3 = k_3^o \frac{\gamma_{R^+}\gamma_{H_2O}}{\gamma_3^*} \qquad (4)$$

where the γ's are the activity coefficients relative to unity at zero ionic strength, superscript ^{o} refers to zero ionic strength and superscript * to the transition states of the individual reaction steps.

Hughes, Ingold and their co-workers considered that electrolytes have only a negligibly small effect on the stability of the very weakly polar organic halide (i.e. $\gamma_{RCl} = 1$). The transition state of the rate determining ionisation (step 1) was regarded as a linear dipole consisting of two point charges ($\pm ze$) separated by a distance d. An electrostatic treatment, based on the electric potential in the vicinity of this dipole and similar to that employed by Debye and Huckel for the calculation of the activity coefficients of ions, showed that

$$\log_{10} \gamma_1^* = B \sigma \mu \qquad (5)$$

where μ is the ionic strength, B is a constant for a given solvent and temperature (see Chapter III page 55) and the ionic strength constant, σ, is equal to $z^2 d$. σ is a measure of the charge development in the transition state and controls the magnitude of the ion atmosphere stabilisation of this state. It is noteworthy that on this view γ_1^* is independent of the nature of any electrolyte present.

Substitution into equation 2 for k_1 then shows that

$$\log \frac{k_1}{k_1^0} = -B \sigma \mu \qquad (\text{as } \gamma_{RCl} = 1) \qquad (6)$$

This expression predicts the effect of electrolytes on the rate determining ionisation.

Hughes and Ingold further assumed that the activity coefficient of a fully developed ion was given by Debye's limiting law:

$$-\log_{10} \gamma_X = A z_X^2 \mu^{\frac{1}{2}} \qquad (7)$$

where z_X is the valency of the ion X and A is the Debye limiting slope. They noted that the transition state in step 3 could be regarded as a central carbonium ion surrounded by a sheath of solvating water molecules with the charge spread over the whole system. They therefore considered that $\gamma_{s}^{*} = \gamma_{H_2O}$ so that from equation 4

$$k_3 = k_3^{o} \gamma_{R^+} \qquad (8)$$

Substituting from equations 8, 6 and 7 into equation 3 for k_2 and hence into equation 1 for k_h we obtain

$$k_h = \frac{k_1^{o}}{\text{antilog } B\sigma\mu + [Cl^-]\alpha^{o} \text{ antilog } A\mu^{\frac{1}{2}}} \qquad (9)$$

where $\alpha^{o} = \dfrac{k_2^{o}}{k_3^{o}}$ i.e. the mass law constant at zero ionic strength.

The application of equation 9 to data for a number of S_N1 reactions[11,28,14] showed that the ionic strength constant σ and the mass law constant α^{o} varied in the expected manner with changes in the structure of the substrate, i.e. σ increases where the distance between the charges in the transition state can be expected to be great and α^{o} is largest for compounds which can be expected to form the most stable carbonium ion. The mass law constants quoted in table Ii are in fact values at zero ionic strength (α^{o}).

Specific electrolyte effects in S_N1 reactions

The electrostatic approach of Hughes and Ingold predicts that the effect of electrolytes on the rate of hydrolysis should depend only on the ionic strength and be independent of the nature of the electrolyte, except in so far as common chloride ions would alter the rate by operation of the mass law effect. They did, however, stress that the approach was a limiting one which was strictly valid only in very dilute solutions. This requirement becomes progressively more important as the dielectric constant of the solvent decreases and may well account for some of the relatively small differences which have been reported for the rates in the presence of different electrolytes.[26]

Similarly deviations from the requirements of equation 9 could occur if ion-pairing by the electrolyte is significant under the experimental conditions. Thus, Nash and Monk,[29] have shown that the effect of inorganic bromides on the hydrolysis of tert. butyl bromide is consistent with equation 9 provided that ion-pair association is taken into account. Similar considerations could apply to Olsen's results.[26]

On the other hand, highly specific salt effects, which cannot be accommodated by corrections to equation 9 have been reported for solvolysis of different systems on a number of occasions.[30,31,32,33]

Although the actual magnitudes of the effects depend on the system studied, there appears to be general agreement about the order of the accelerating effect of different electrolytes in the solvolysis of halides, sulphonates and nitrates. The accelerating effect of anions on the rate determining ionisation decreases in the order $ClO_4^- > BF_4^- > Br^- > NO_3^- > PhSO_3^- > Cl^- > F^- > OH^-$.[27,32,33,34,35,36] For cations the sequence appears to be $H^+ > Na^+ \; Li^+ \; K^+ \; Me_4N^+ > nBu_4N^+$.[31,28,34,35,36]

Contrary to the requirements of an accelerating ionic strength effect, fluoride and hydroxide ions invariably retard the reaction and a decreased rate for the ionisation step due to added chloride ions has also been reported on some occasions. It is also noteworthy that tetra-n-butyl ammonium perchlorate has only a very small effect on the rate in contrast to other perchlorates.[39,28]

The retarding effect of hydroxide ion was regarded as a special case by Hughes, Ingold and ~~Hawden~~ Bentley[50] but their explanation would not account for the behaviour of ionised fluorides. While admitting the existence of an ionic strength effect, Lucas and Hammett[32] pointed out that the different degrees of solvation of different electrolytes by water would change the "effective" composition of mixed aqueous solvents by differing amounts. Since rates of ionisation of organic esters are very sensitive to changes in solvent composition, this salt induced medium effect[33] could account for the specific salt effects which have been observed. Thus the highly hydrated hydroxide and fluoride ions would tend to retard ionisation by 'drying' the solvent while the less effective drying action of, say, perchlorate ions would allow the accelerating ionic strength effect to predominate.

More recent experiments suggest that electrolytes are in fact solvated by both components of a mixed aqueous solvent[37] but this conclusion requires only a slight modification of Lucas and Hammett's simple solvation model. It is now conceivable that an electrolyte which is heavily solvated by the organic component will lead to an "effectively" more aqueous solvent and would therefore accelerate ionisation by the salt induced medium effect. The proportion of water "removed" from 50% dioxan by anions decreases in the order $OH^- > Cl^- > Br^- > NO_3^- > ClO_4^-$.[37] Except for the inversion of the position of bromide and nitrate ions this sequence represents the converse of that generally found for the acceleration of ionisation (see page 13) suggesting that salt induced medium effects are indeed of importance in these reactions. This conclusion implies that the relative solvation of electrolytes in aqueous organic solvents parallels that in 50% dioxan.

The electrostatic approach of Hughes and Ingold assumed that the effect of electrolytes on the initial state in S_N1 reactions could be neglected. Grunwald and others[50] found that the activity coefficients of sparingly soluble non-electrolytes in aqueous dioxan were significantly altered by the addition of electrolytes in a manner which depended on the nature of the ions involved. In qualitative terms these authors' explanation of their results can be summarised as requiring the operation of an electrostatic effect (independent of the nature of the electrolyte) and a salt-induced medium effect which can be considered to arise from the fact that the solubility of a non-electrolyte in an aqueous organic solvent will be increased by decreasing the "effective" water content. On this view most of their results are consistent with the relative solvating properties of the electrolytes employed.[37]

By assuming that similar considerations apply to the stability (activity coefficients) of the transition state for ionisation, the effect of electrolytes on the rates of these processes could be placed on a semi-quantitative basis,[33] thus confirming the essential features of the simple solvation model originally proposed by Lucas and Hammett. The specific effects of many electrolytes on the rate of ionisation of substituted benzhydryl chlorides in aqueous acetone[34,35,36] are also consistent with this interpretation, provided that the relative drying effect of the ions in this solvent follows the same sequence as in 50% dioxan.

The extremely poor accelerating effect of tetra-n-butyl ammonium salts[38,39] cannot be explained on the same basis since it might have been expected that the cation would favour solvation by an organic solvent rather than by water. The cation should therefore accelerate ionisation rather more than, say, sodium ion. Anomalous effects with salts containing large organic ions have already been observed in other reactions[33] but these include tetramethyl ammonium salts which were found to behave normally in the hydrolysis of benzhydryl chlorides.[35,36]

It was therefore decided to obtain more extensive information about salt effects invoked by tetraalkyl ammonium salts in the hydrolysis of benzhydryl chloride by studying a greater variety of these salts than had previously been examined.

CHAPTER TWO

RESULTS AND DISCUSSION

The effect of quaternary ammonium salts ($R_4N^+Y^-$, R = Me, Et, n - Pr, n - Bu, $Y^- = Cl^-$, Br^-, ClO_4^-) on the rate of hydrolysis of benzhydryl chloride was studied in 70% aqueous acetone at 20.13°C. Solutions initially 0.02M with respect to substrate were examined in the presence of 0.05M and 0.1M salts. Reactions were followed by noting the development of acidity, full details of the methods employed are given in the next chapter. All the reactions gave good first-order kinetics.

Effects of salts on the rate of hydrolysis

The effect of the various salts on the rate of hydrolysis are summarised in Table II.1 where the figures refer to the percentage change of the integrated rate coefficient for hydrolysis, k_x, on addition of the salt.

Table II 1

The effect of added electrolytes on the rate of hydrolysis of benzhydryl chloride

The figures refer to the % change in k_x on addition of salt.
All errors are standard errors.

	.05M salts			0.10M salts		
	Cl^-	Br^-	ClO_4^-	Cl^-	Br^-	ClO_4^-
Me_4N^+	-6.82±.27	+8.15±.40	+13.25±.24	-13.75±.33	+14.93±.58	+27.56±.71
Et_4N^+	-9.33±.18	+3.26±.18	-	-19.31±.30	+6.38±.29	-
Pr_4N^+	-12.54±.17	+0.585±.21	-	-22.83±.15	+0.59±.16	-
Bu_4N^+	-16.74±.35	-2.22±.25	-0.51±.24	-26.43±.13	-4.60±.23	-1.87±.29

For all salt additions, the rates decrease in the order $Me_4N^+ > Et_4N^+ > nPr_4N^+ > nBu_4N^+$. Thus there is a decrease in the rate as the chain length of the alkyl groups increases. It is noteworthy that all tetra-n-butyl salts retard, even the perchlorate, which is the most strongly ~~clearing~~ accelerating anion so that the results confirm the abnormal retarding effect of the tetra-n-butyl.

The results for the tetra~~-n-~~methyl salts are similar to those obtained by Queen,[34,35] Shillaker and others for sodium salts e.g. from table II 1 tetra~~-n-~~methyl ammonium perchlorate accelerates the reaction by +13.25%, and Queen gives a value of +15.08% for sodium perchlorate in 0.05M solution.

Anions accelerate the hydrolysis in the order $ClO_4^- > Br^- > Cl^-$. These results also agree with those of Queen, Shillaker and Jackson[34,35,36]. It must be remembered that the retarding effect of the chloride is partly due to a mass law effect. Nevertheless when the effect of the ions on the rate determining ionisation of the substrate (page 37) is calculated, the same anion sequence is obtained.

When the salt concentration is doubled the effect on the rate is increased by the same factor to a first approximation. A number of possible reasons can be advanced to explain the generally low figures for the 0.1M salts. Firstly, ion-pair association[42] could occur. Secondly, since ions are produced during the run, the ionic strength is not necessarily doubled on doubling the salt concentration. Lastly, chloride ions give a mass law retardation of the form $\frac{1}{1 + \alpha[Cl^-]}$, where α is the mass law constant, so that doubling the chloride concentration does not result in a similar change in the rate.

On the solvation model, the effect of the salt on the rate of ionisation should be an additive property. Thus the difference between the % effects on the rate for Et_4NY and Me_4NY ~~and tetramethyl ammonium~~ as added salts, should be equal to the difference between Et_4NY and Me_4NY where Y, say, is chloride in the first pair and bromide ion in the second pair, as a check on cation additivity. Anion additivity would be shown by the difference between the % effects on the rate when R_4NCl and R_4NBr are the added salts, being independent of the cation.

These additivity relationships can be calculated from Table II 1 but it is more profitable to calculate additivity relationships from the effects of electrolytes on the rates of ionisation, k_1, where there is no complication from the mass law effect on the chlorides. This has been done on page 38.

Effect of salts on the rate of ionisation.

Since all the various kinetic theories lead to simpler expressions for instantaneous rates than for integra~~l~~ted rates, it is necessary to consider the effect of electrolyte additions on the rate coefficient for ionisation, k_1. The mean integrated rate coefficient, k_x, is related to the instantaneous rate coefficient for hydrolysis, k_h, by the expression $k_x = \frac{1}{t}\int_0^t k_h dt$

and according to the Hughes-Ingold electrostatic approach (Chapter 1)

$$k_h = \frac{k_1}{1 + \alpha[Cl^-]} = \frac{k_1^{\,o}}{\text{antilog } B\sigma\mu + [Cl^-]\alpha^o \text{ antilog } A\mu^{\frac{1}{2}}} \qquad (1)$$

Thus if k_h were known, the effect of electrolyte additions could be discussed either in terms of the ratio $\frac{k_1}{k_1^{\,o}}$ or in terms of σ, the ionic strength constant.

Hydrochloric acid is produced as the solvolysis proceeds. There should thus be a variation in k_h since k_1 and α will alter under these conditions. The fact that the integrated rate coefficient, k_x, was constant merely implies a cancellation of the relatively small mass law and ionic strength effects within the limits of experimental error.

It is therefore necessary to establish the experimental conditions under which the instantaneous rate coefficient, k_h, can be identified with the integrated rate coefficient, k_x. When an integrated rate coefficient varies only slightly as reaction proceeds, its value for the time interval o - t can be identified with the instantaneous rate coefficient at time t/2.[43] Since the reaction follows first order rate law:

$$[RCl]_t = [RCl]_o e^{-kt}$$

where [RCl] is the concentration of the substrate at the time t, k is the integrated rate coefficient for the run and subscript $_o$ refers to the concentration at the time zero.

The concentration of substrate at time t/2 is given by the expression

$$[\mathrm{RCl}]\ t/2 = [\mathrm{RCl}]_o^{\frac{1}{2}}\ [\mathrm{RCl}]_t^{\frac{1}{2}}$$

and so can be obtained from the experimentally observed values of $[\mathrm{RCl}]_t$. It is then possible to obtain values for the concentrations of chloride and hydrochloric acid at the time t/2. (See Chapter III). Thus the individual integrated rate coefficient, k_i, can be identified with the instantaneous value, k_h, corresponding to the ionic concentrations at times t/2. The mean integrated rate coefficient, k_x, can then be taken as identical with the instantaneous rate coefficient, k_h, at the mean of the electrolyte concentrations at the times t/2.

The calculation of k_1, the rate coefficient for ionisation, from equation II1, however, also requires a knowledge of the mass law constant α, at the concentration to which k_h refers. The resulting calculations would be extremely lengthy but fortunately they can be greatly simplified since Queen[35,44] found that the assumption of a constant value of α for increasing ionic strength up to 0.1M caused no significant error. On this assumption, substitution of $k_1 = k_1^o$ antilog $B\sigma\text{-}\mu$ (Chapter 1) into equation II1 gives:

$$k_h = \frac{k_1^o \text{ antilog } B\sigma - \mu}{1 + \alpha[\mathrm{Cl}^-]}$$

It must also be recognised that contrary to the requirement $\log \frac{k_1}{k_1^o} = B\sigma\mu$, different electrolytes have differing effects on the rate of ionisation. The difficulty can be overcome by retaining the formalism of Hughes and Ingold's electrostatic approach but redefining σ as a parameter whose value depends on the nature of the electrolyte and replacing the expression $\log \frac{k_1}{k_1^o} = B\sigma\mu$ by the equation $\log \frac{k_1}{k_1^o} = \sum_{MX} \sigma_{MX} B\mu_{MX}$ where Mx refers to a particular electrolyte and the expression is summed over all the electrolytes present. In the present systems, only added electrolytes and the hydrochloric acid produced by the reaction need be considered.

Equation II1 can be modified to give:

$$k_h = \frac{k_1^o \text{ antilog } B\sigma\mu}{1 + \alpha^o [\text{Cl}^-] \text{ antilog } (-A\mu^{\frac{1}{2}} + B\sigma\mu)} \qquad \text{II2}$$

Queen and Shillaker[34,35] have obtained good results, for a variety of electrolytes, by accepting the approximation: $\text{antilog}(-A\mu^{\frac{1}{2}} + B\sigma\mu) = 1$. This approximation has also been assumed in the present work. Utilizing also the assumption that α is constant, equation II2 becomes:

$$k_h = \frac{k_1^{\circ}\ \text{antilog}\ B\left[\sigma_{HCl}\,\mu_{HCl} + \sigma_{MX}\,\mu_{MX}\right]}{1 + \alpha\left[Cl^-\right]} \qquad \text{II3}$$

where μ_{MX} is the ionic strength of the quaternary ammonium salt. σ_{MX} now represents a measure of the effect of the quaternary ammonium salt on the rate of ionisation, which can also be expressed in the form $k_1 = k_1^{\circ}$ antilog $B\sigma_{MX}\,\mu_{MX}$.

The unknown value of k_1° can be eliminated from equation II3 by comparison with results for hydrolysis in the absence of added electrolytes, where:

$$k_h^+ = \frac{k_1^{\circ}\ \text{antilog}\ \left[B\sigma_{HCl}\,\mu^+_{HCl}\right]}{1 + \alpha\left[Cl^-\right]^+}$$

where + means with no added salt.

Hence,

$$\frac{k_h}{k_h^+} = \frac{\text{antilog}\ B\left[\sigma_{HCl}\left(\mu_{HCl} - \mu^+_{HCl}\right) + \sigma_{MX}\,\mu_{MX}\right]}{\dfrac{1 + \alpha\left[Cl^-\right]}{1 + \alpha\left[Cl^-\right]^+}} \qquad \text{II4}$$

In equation II4 $\dfrac{k_h}{k_h^+} = \dfrac{k_x}{kx_o}$ provided the concentrations are the mean values at the time t/2 (see page 32).

On rearranging equation II4 and taking logarithms, an expression for σ_{MX} is obtained:-

$$\sigma_{MX} = \frac{\log\left[\dfrac{k_h}{k_h^+}\cdot\dfrac{(1 + \alpha\left[Cl^-\right])}{(1 + \alpha\left[Cl^-\right]^+)}\right] - B\sigma_{HCl}\left(\mu_{HCl} - \mu^+_{HCl}\right)}{B\mu_{MX}} \qquad \text{II5}$$

σ_{MX} was determined for each salt from known values of B, σ_{HCl} and α for this reaction (See Chapter III). The effect of electrolytes on the rate of ionisation for this reaction can then be studied, either by means of σ values, or by values of antilog $B\sigma_{MX}\mu_{MX}$ i.e. $\frac{k_1}{k_1^o}$.

Effect of quaternary ammonium salts on the rate of ionisation of benzhydryl chloride

The values of the electrolyte parameter, σ_{MX}, as calculated from equation II5 are summarised below.

Table II2

σ values (All errors are standard errors)

Salt	0.05M	0.1M
Me_4NCl	+0.522 ± .036	+0.392 ± 0.024
$Me_4N\ Br$	+1.009 ± .047	+0.892 ± 0.032
Me_4NClO_4	+1.604 ± .027	+1.560 ± 0.036
Et_4NCl	+0.191 ± .025	-0.059 ± 0.024
Et_4NBr	+0.412 ± .022	+0.396 ± 0.017
nPr_4NCl	-0.338 ± .025	-0.340 ± 0.011
nPr_4NBr	+0.075 ± .031	+0.044 ± 0.010
nBu_4NCl	-0.956 ± .054	-0.642 ± 0.011
nBu_4NBr	-0.289 ± .033	-0.305 ± 0.015
nBu_4NClO_4	-0.088 ± .031	-0.126 ± 0.019

If the σ values are reliable to within ± twice the standard error (95% confidence limit) most of the results give the same value of σ_{MX} for 0.05 and 0.1M solutions. It is therefore assumed that some fortuitous error is responsible for the differing results in the values for tetramethyl ammonium chloride and tetra-n-butyl ammonium chloride.

After allowance for mass law retardation in the calculation of σ, the σ values are negative for salts which retard the rate of ionisation of the benzhydryl chloride. Negative values of σ are obtained for tetra-propyl ammonium chloride and the tetra-n-butyl ammonium chloride, bromide and perchlorate.

Tetramethyl ammonium chloride has a positive σ value in 0.05M solution (+0.191 ± .025) but a negative one in the 0.1M solution (-0.059 ± .024). This effect could be due to ion pair formation, which would occur to a larger extent in the 0.1M solution. It can be deduced that the salt would have relatively less effect on the rate of ionisation in a 0.1M solution, than in a 0.05M solution, if ion-pair formation occurs. The results do, in general, give a smaller σ value for 0.1M solution and thus a relatively smaller effect upon the rate (since $\frac{k_1}{k_1^o}$ = antilog $B\sigma_{MX}\mu_{MX}$) than would be expected if ion-pair formation did not occur.

The mean σ values are given in the table below.

Table II3

Mean σ values

Mean of 0.05M and 0.1M σ values.

All errors are standard errors.

Salt	σ_m
Me_4NCl	+0.457 ± .072
Me_4NBr	+0.951 ± .071
Me_4NClO_4	+1.582 ± .039
Et_4NCl	+0.066 ± .127
Et_4NBr	+0.404 ± .021
nPr_4NCl	-0.339 ± .019
nPr_4NBr	+0.060 ± .028
nBu_4NCl	-0.799 ± .162
nBu_4NBr	-0.297 ± .027
nBu_4NClO_4	-0.107 ± .032

It can be seen that the sequence in which the cations and anions affect the rate is unchanged from Table II1. It is useful, however, to obtain additivity relationships for the ions. This has been done in table II4.

Table II4

Ionic Contributions to σ

Cation Additivity	Cl^-	Br^-	ClO_4^-
$Et_4N^+ - Me_4N^+$	-0.391 ± .146	-0.547 ± .074	-
$n\text{Pr}_4N^+ - Et_4N^+$	-0.405 ± .130	-0.344 ± .035	-
$n\text{Bu}_4N^+ - n\text{Pr}_4N^+$	-0.460 ± .163	-0.357 ± .039	-
$n\text{Bu}_4N^+ - Me_4N^+$	-1.256 ± .177	-1.248 ± .076	-1.689 ± .050
Anion Additivity	$Br^- - Cl^-$	$ClO_4^- - Cl^-$	
Me_4N^+	+0.494 ± .101	+1.125 ± .082	
Et_4N^+	+0.338 ± .129	-	
$n\text{Pr}_4N^+$	+0.399 ± .034	-	
$n\text{Bu}_4N^+$	+0.502 ± .164	+0.692 ± .165	

If the effect of the electrolytes depends on the individual ions, it would be expected that σ would be additive with respect to the individual ions. The differences between the values of σ of pairs of salts having a common ion are given above in the table. It can be seen that $\sigma_{MX} - \sigma_{M'X}$ for a pair of cations is independent of the nature of the anion, X, and that similarly for a pair of anions, $\sigma_{MX} - \sigma_{MX'}$ is independent of the nature of the cation M.

The two outstanding exceptions both involve comparison with $\overline{\sigma}$ for tetramethyl ammonium perchlorate and both suggest the value for this parameter is too large. However, as only two perchlorates were studied, it is difficult to decide whether this observation is genuine or fortuitous, especially as $\overline{\sigma}$ for tetra-n-butyl ammonium perchlorate differs from the value for the chloride by the expected amount, although the limits of experimental error are rather large.

The values of the electrolyte parameter $\overline{\sigma}$, obtained from the experimental work in 0.05 and 0.1M solutions, were employed to calculate the effect of salts on the initial rates of ionisation of benzhydryl chloride. The relationship connecting the rates with $\overline{\sigma}$ values is

$$\frac{k_1}{k_1^o} = \text{antilog } B\overline{\sigma}_{MX}\mu_{MX}$$

Table II5 shows the resulting values expressed as a percentage change in the initial rate of ionisation.

Table II5

% Acceleration of the rate from $\frac{k_1}{k_1^o}$

	0.05M salt			0.1M salt		
	Cl^-	Br^-	ClO_4^-	Cl^-	Br^-	ClO_4^-
Me_4N^+	4.16±.29	8.20±.40	13.34±.24	6.31±.40	14.94±.57	27.58±.72
Et_4N^+	1.50±.20	3.27±.18	-	-0.92±.37	6.38±.28	-
n-Pr_4N^+	-2.604±.19	0.58±.24	-	-5.17±.16	0.69±.16	-
n-Bu_4N^+	-7.19±.39	-2.23±.25	0.68 ~~-2.23~~±.25	-9.54±.16	-4.65±.22	-1.95±.29

The results again show the very striking decrease of the accelerating effect of the cations with increasing chain length of the alkyl groups. Similarly the accelerating effect of anions decreases in the order $Cl^- > Br^- > ClO_4^-$ as already reported for sodium salts by Queen, Shillaker and Jackson.[34,35,36] The results in Table II5 agree with those calculated from the ratio $\frac{kx}{kx_o}$ in Table IIi for bromide and perchlorate. The chloride results differ significantly from those based on the mean integrated values due to the mass law effect of the chlorides.

As might have been expected, doubling the salt concentration generally doubles the effect on the rate. Exceptions to this are tetra-ethyl ammonium and tetra - n - butyl ammonium chlorides for which anomalous σ values have already been reported (page 36).

DISCUSSION OF RESULTS

The present results confirm and extend previous observations that the effect of tetra-alkyl ammonium salts on rates of ionisation depends markedly on the structure of the salts. The accelerating power of the salt decreases as the alkyl chain length increases (Table IIi).

The results for anions follow the same sequence as found by other workers[34,35,39] and are fully consistent with the simultaneous operation of the ionic strength effect and a salt induced medium effect. This medium effect can be qualitatively rationalised in terms of the simple solvation model (see page 23). In agreement with the results of fugacity measurements on aqueous dioxan solutions,[37] the present results suggest that solvation of the anions by water relative to solvation by acetone, decreases in the order $Cl^- > Br^- > ClO_4^-$. It seems possible that perchlorate ions are solvated to some extent by the organic component since sodium perchlorate is remarkably soluble in acetone and other organic solvents and since the crystals obtained from solutions of aqueous dioxan contain significant amounts of dioxan[37].

Also, if the solvation theory is correct, the results for anions should be additive i.e. each anion should make its own contribution, irrespective of the nature of the cation. The results show that this additivity effect for anions does exist (see Table II4).

The cation results however cannot be explained by the same considerations as were used for the anions. The simple solvation model would suggest the least solvation by water and the largest by acetone for the cations containing the bulkiest alkyl groups. The effective water content of the solvent should therefore be increased in the order $Me_4N^+ < Et_4N^+ < Pr_4N^+ < nBu_4N^+$. This should then also be the order of the acceleration of ionisation, in direct contrast to the observations (Table II5).

Alternative hypotheses, based on the consequences of changes in solvent structure by adding bulky solutes, similarly fail to account for the present results, since the largest of the anions also has the greatest accelerating effect (Table II5).
Admittedly the charge on the tetra-n-butyl cation is so well

shielded from contact with the solvent that the effect of this ion might be considered to parallel more closely the effects of added nonelectrolytes, but these are generally small[35].

Similarly, the present results cannot be explained by assuming that the higher tetra-alkyl ammonium salts undergo more extensive ion-association in solution, thus causing a smaller acceleration resulting from the reduced ionic strength, as such a hypothesis is contradicted by the retardation of ionisation by added tetra-n-butyl ammonium bromide.

Grunwald and others[33] explained the anomalous effect of large ions on the rate of ionisation of sulphonates in terms of specific short range interactions, analogous to complex formation, between the ion and the substrate in the initial and transition states. If it is possible for the initial state of the substrate to be stabilised relative to the transition state, then the rate of ionisation of the substrate would be lowered.

Short range interactions could occur between the phenyl rings of the substrate and the organic group of the electrolyte in the initial state. As the alkyl chain length increases, the central charge on the nitrogen atom is progressively hidden, leading to an increase in the extent of possible attractive short range interactions between the non polar alkyl chain and the phenyl ring of the substrate.

In the transition state, two effects could occur. The short range interactions could be destroyed in passing into this state. Thus the greater the extent of the interaction with the initial state, the more will this state be stabilised relative to the transition state, and the greater will be the retarding effect of the added electrolyte. Alternatively, the interactions could persist in the transition state but it is difficult to see how interaction with positive ions could stabilise a positive transition state to the same extent as interaction with the non-polar initial state. Consequently, any increase in short range interaction will again cause a greater retardation of the reaction.

If these views are correct, tetrabutyl ammonium would stabilise the initial state relative to the transition state rather more than tetramethyl ammonium cation. The order of retardation of the reaction would be $n\text{Bu}_4\text{N}^+ > n\text{Pr}_4\text{N}^+ > \text{Et}_4\text{N}^+ > \text{Me}_4\text{N}^+$ for any anion series. This is in agreement with the observed results, so that the idea of short range interactions with the substrate for the cations seems to be justified.

Jackson and Kohnstam[36], in their work on the stabilities of initial and transition states in S_N1 reactions have shown that the combination of ionic strength and solvation effects accounts for the observed rates with a variety of anions, including the perchlorate ion. They also found an abnormally large and similar stabilisation of both the initial and transition state by perchlorate ions. This is possibly due to specific short range interactions with the substrate as now postulated for cations.. However since both the initial and transition states are stabilised to about the same extent by perchlorate ions, the effects cancel and perchlorate fits into the kinetic sequence of anions predicted by the solvation model. The fact that perchlorate apparently stabilises the transition state to a greater extent than any of the other anions could possibly account for the anomalous additivity figures for perchlorate (page 38).

It is concluded that the tetra-alkyl ammonium salts show specific effects on the rate of ionisation of benzhydryl chloride in 70% aqueous acetone. The additive nature of the results shows that the effects are a consequence of the individual ions and are not merely a property of the electrolyte as a whole. The kinetic results agree with the predictions of the solvation model of Lucas and Hammett's for the order of the effect of anions on the rate, but it is difficult to reconcile the behaviour of the cations with this approach. The effects of the cations can, however, be explained if short range specific interactions occur with the substrate in the initial state.

CHAPTER THREE

EXPERIMENTAL

KINETIC RUNS

All kinetic runs were carried out at 20.13°C. A conventional thermostat was used, with a Shandon-Jumat contact thermometer operating through a GK10/NC relay controlling an intermittent heater. Since ambient temperature was about 20°C, a copper cooling coil was immersed in the thermostat through which was circulated cold water. The thermostat was well stirred and temperature variation, as recorded on a Beckmann thermometer, was never more than ± 0.01°C.

The solvolysis of the benzhydryl chloride was carried out in a flask immersed in the thermostat following the procedure given below.

(a) Runs with no salt addition.

Sufficient benzhydryl chloride to give a 0.02M solution in 100 ml (approximately 0.44 gm)was weighed into a 100 ml flask. Solvent acetone (70% aqueous acetone) at thermostat temperature, was then added. A 5 ml sample was withdrawn immediately by pipette.

This extracted sample was quenched by pouring into 150 ml acetone to which had been added Lacmoid indicator. Timing was started when the pipette began to empty. The sample was titrated with 0.01M NaOH from a 50 ml burette. Further 5 ml samples were withdrawn from the reaction flask about every 10 minutes until

2 - 3 half lives had elapsed (1 - $2\frac{1}{2}$ hours). Approximately 12 readings were obtained for each run.

The initial concentration of benzhydryl chloride was determined from an "infinity" reading which was taken from a sample removed from the reaction vessel when not less than 10 half lives had elapsed, (normally over 24 hours).

(b) Runs with a salt addition.

The procedure was the same as in (a) except that the solvent acetone which was added to the reaction vessel contained sufficient dissolved salt to give a 0.05M or 0.1M solution.

The burette containing sodium hydroxide was connected to a Winchester of standard solution and the whole system was sealed by means of soda-lime tubes to prevent carbon dioxide absorption.

The method thus measures the extent of reaction by determining the development of acidity due to the formation of hydrochloric acid as solvolysis proceeds.

Preparation of Materials

Solvent acetone

The solvent acetone was obtained by refluxing Analar acetone with 20 g sodium hydroxide and 20 g potassium permanganate per litre for 3 hours and then fractionally distilling. The distilled acetone was refluxed for a further 3 hours with hydroquinone and fractionally distilled.

An infra-red spectrum of this acetone is given (Spectrum 1). The acetone was made into a 70% aqueous acetone solution (70% acetone, 30% water) by adding the required amount of water by volume.

Quenching acetone

The acetone used for quenching was recovered after use and purified in the same manner as the solvent acetone, omitting the reflux over hydroquinone. 5 ml of a saturated solution of Lacmoid indicator in acetone was added to each 2½ litres of quenching acetone. The quenching acetone was normally alkaline and was neutralised by adding small amounts of 0.01N hydrochloric acid immediately before each kinetic run. An infra-red spectrum of a sample of recovered quenching acetone is included (Spectrum 2).

Benzhydryl chloride

Some difficulty was experienced in obtaining pure benzhydryl chloride. Several commercial samples were obtained and attempts were made to purify them by vacuum distillation. The purity was then estimated by carrying out a blank kinetic run and using the amount of hydrochloric acid produced at 100% hydrolysis as a criterion of purity. Normally it was impossible to obtain benzhydryl chloride of purity greater than 96 - 98% on repeated vacuum distillation.

Benzhydryl chloride was then made from benzhydrol by the following method[35]. Hydrogen chloride was prepared from conc. sulphuric acid and ammonium chloride. The gas was dried by passing through conc. sulphuric acid and then through a carbon dioxide - acetone cold trap.

The hydrogen chloride was bubbled into 25 g benzhydrol dissolved in dry ether (200 ml), containing granular calcium chloride, for 10 hours at 0°C. Excess hydrogen chloride and most of the ether were then removed at the water pump.

200 ml of dry pet. ether (40 - 60°C) was added to the residue, the resulting solution was washed with water, 5% sodium bicarbonate, water and dried over potassium carbonate.

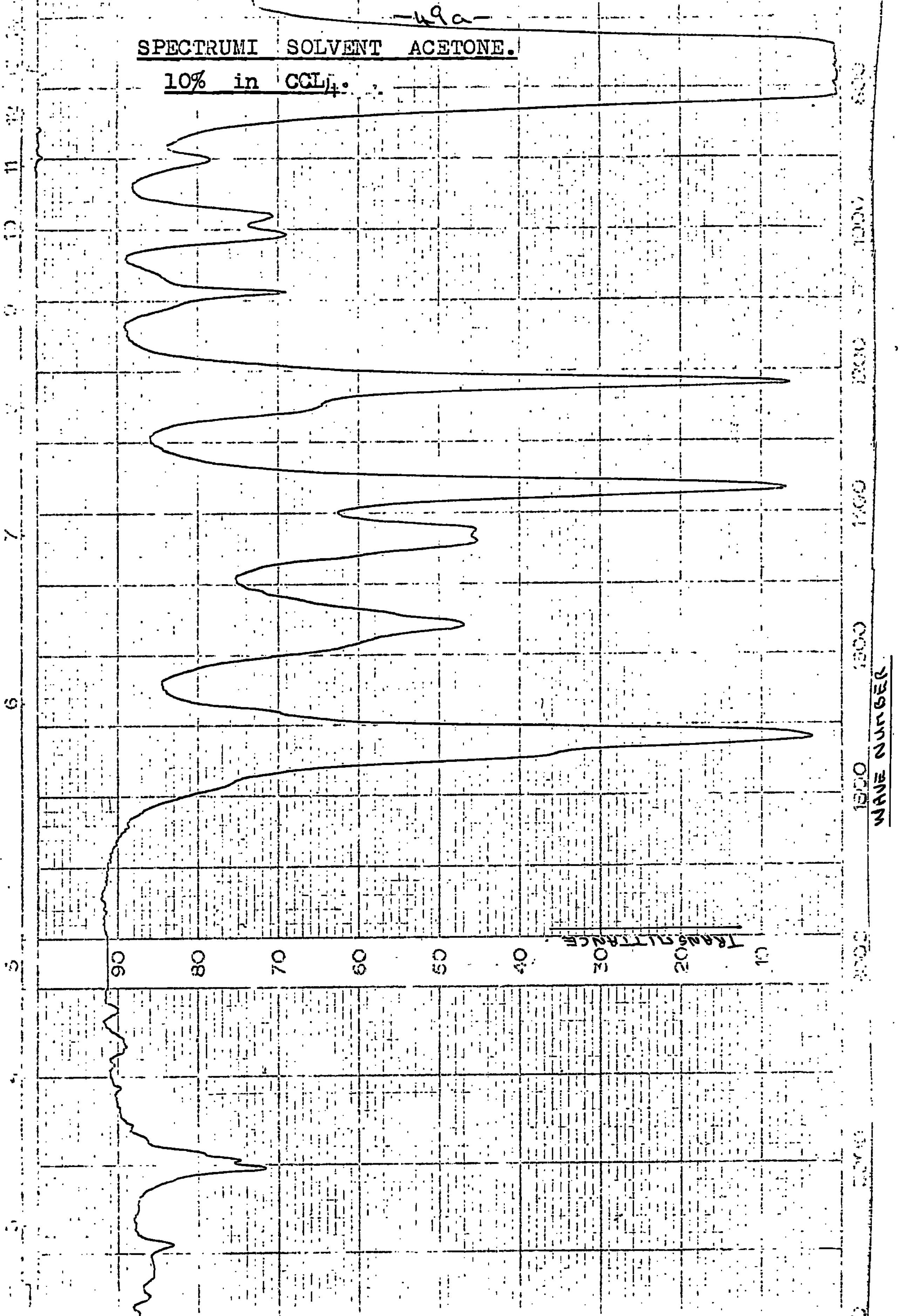
Solvent was removed on the water bath and the resulting oil purified by vacuum distillation. A colourless liquid was obtained. Again, purities estimated by complete hydrolysis were not higher than 97%.

As an alternative procedure a solution of benzhydrol in methanol (40 gm/50 mls) was passed through an alumina column (chromatographic grade). The solution was diluted with water until the benzhydrol precipitated, warmed to redissolve and cooled in ice to reprecipitate the benzhydrol. Fine white plate crystals of benzhydrol were obtained (M.Pt. 68 - 69°C). An infra-red spectrum indicated the removal of an alcohol, as there were less bonded OH groups indicated.(Spectra 3 and 4 show benzhydrol before and after this treatment).

When this benzhydrol was used for the preparation of benzhydryl chloride a consistent purity figure of 99 - 100% on complete hydrolysis was obtained.

SPECTRUMI SOLVENT ACETONE.

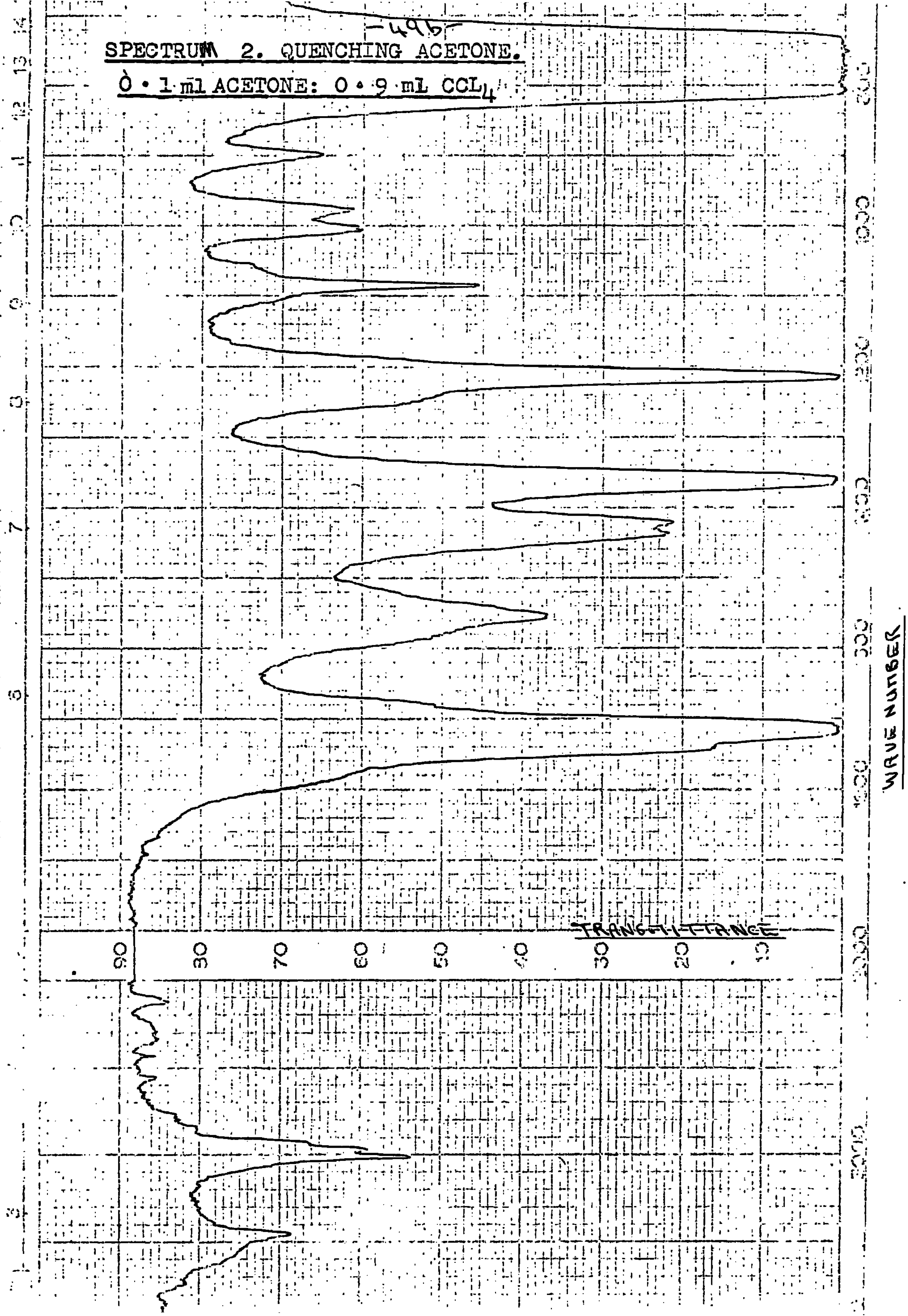
10% in CCl_4.



-49b-

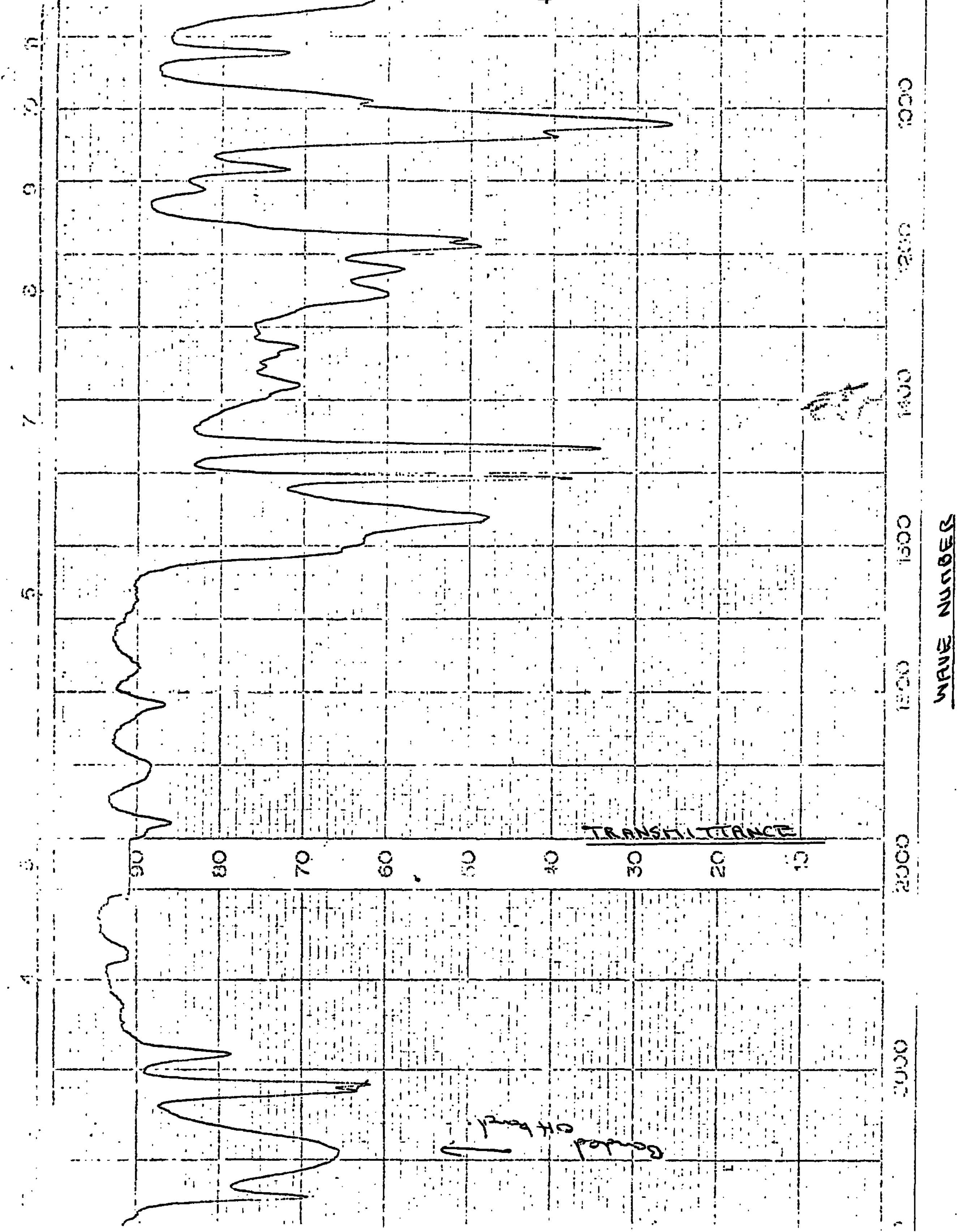
SPECTRUM 2. QUENCHING ACETONE.

0 • 1 ml ACETONE: 0 • 9 mL CCL$_4$



SPECTRUM 3 BENZHYDROL BEFORE PASSING THROUGH ALUMINA COLUMN.

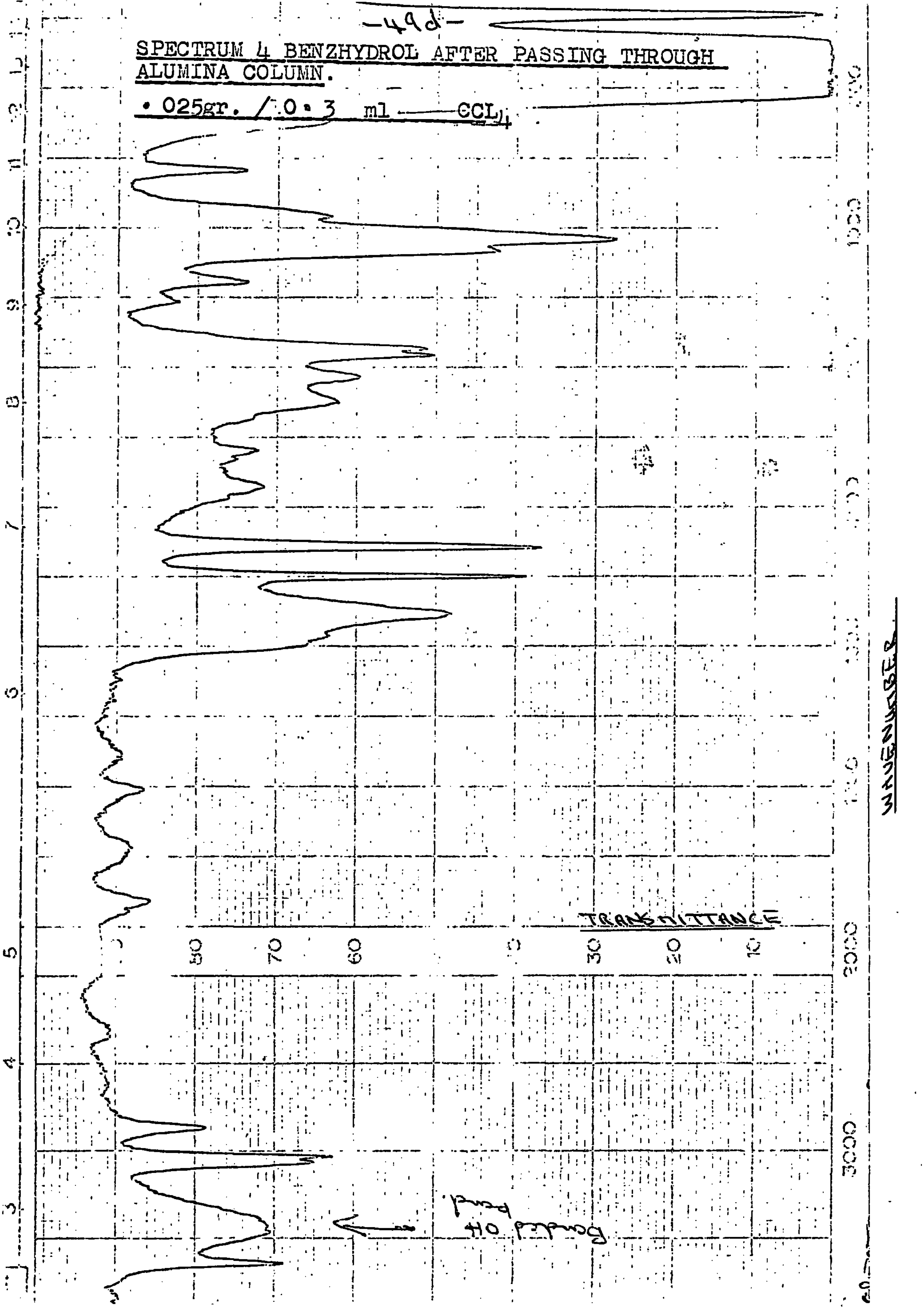
.025 gr. / 0.3 ml CCL_4.



-49d-

SPECTRUM 4 BENZHYDROL AFTER PASSING THROUGH ALUMINA COLUMN.

.025gr. / 0.3 ml — CCl_4



Benzhydryl chloride was stored in stoppered tubes in a refrigerated vacuum container. The estimated purity of any sample remained above 99% for at least four months.

Salts

All salts were dried and stored in vacuo at room temperature over phosphorus pentoxide except where stated. The chloride and bromide purities were determined by titration with silver nitrate using dichlorofluorescein as indicator. Perchlorate purities were obtained by estimating with standard alkali the perchloric acid which was liberated when a solution of the perchlorate was passed through a cation exchange column.

Tetramethyl ammonium chloride

Commercial sample (B.D.H.) Purity 99.75%

(Purity also determined by a conductimetric titration).

Tetramethyl ammonium bromide

Commercial sample (B.D.H.) Purity 100%

Tetramethyl ammonium perchlorate

Tetramethyl ammonium perchlorate was prepared by methathesis of tetramethyl ammonium bromide with silver perchlorate in alcoholic solution. Purity 99.30%.

Tetraethyl ammonium chloride

Commercial sample (B.D.H.) Purity 99.89%

Tetraethyl ammonium bromide

Commercial sample (B.D.H.) Purity 99.84%.

Tetra-n-propyl ammonium chloride

Tetra-n-propyl ammonium chloride was prepared by shaking tetra-n-propyl ammonium iodide (B.D.H.) with silver oxide in aqueous ethanol for several hours. The solution was then filtered and titrated to pH7 with hydrochloric acid. After evaporation to dryness, the resulting brown crystals were dissolved in ethanol and the solution was passed through an alumina column. The solution was evaporated to dryness and the crystals produced were recrystallised from ethyl acetate (Soxhlet extraction). The substance was extremely deliquescent and was stored over magnesium perchlorate. Purity 99.15%.

Tetra-n-propyl ammonium bromide[45,46]

Tri-n-propylamine was refluxed continuously with a slight excess of n-propyl bromide. A white solid was produced at the rate of 5 g per day, which was extracted (Sohxlet) with ethyl acetate.

Purity 99.88%.

Tetra-n-butyl ammonium chloride

Two methods were used.

(a) Tri-n-butylamine and n-butyl chloride were purified by distillation. The Menschutkin reaction was attempted with various solvents (ethanol, methanol, acetone and no solvent).

$$\underset{92.57}{C_4H_9Cl} \quad + \quad \underset{185.36}{(C_4H_9)_3N} \longrightarrow \underset{277.93}{(C_4H_9)_4NCl}$$

The method yielded small amounts of a dark brown immiscible liquid which could have been tetra-n-butyl ammonium chloride.

(b) Richardson and Stern's method[47] was more successful.

50 g tetrabutyl ammonium iodide and 21 g silver oxide were dissolved in 200 ml water and 250 ml ethanol. The mixture was shaken for two hours, filtered and the filtrate titrated to pH7 with 2N hydrochloric acid. Ethanol was removed on the steam bath and water by vacuum distillation. The residual brown viscous oil was dissolved in ethyl acetate and precipitated with diethyl ether to give the product as a whitish-yellow solid. The product was dried over magnesium perchlorate. Purity 98.0%.

Tetra-n-butyl ammonium bromide

The Menschutkin reaction was used

$$C_4H_9Br \; + \; (C_4H_9)_3N \longrightarrow (C_4H_9)_4N\,Br$$

50 ml of tri-n-butylamine were refluxed with a small excess of n-butyl bromide (50 ml) in the presence of 50 ml acetone for several hours. After removal of solvent on the water bath, the resulting brown oil was triturated with sodium-dried ether to obtain the product as white crystals. The product was dried over magnesium perchlorate. Purity 99.5%.

Tetra-n-butyl ammonium perchlorate[48]

Tetra-n-butyl ammonium perchlorate was obtained from the methathesis of tetra-n-butyl ammonium iodide with silver perchlorate in alcoholic solution. Purity 100%.

CALCULATION OF PARAMETERS

Rate Constants

Each kinetic run gave an average of 10 values of the integrated rate constant. These were calculated from the formula

$$k_i = \frac{2.303}{t_i} \log_{10} \frac{T_\infty - T_o}{T_\infty - T_i}$$

where t_i is the time in seconds of each determination.

T_∞ is the titre of sodium hydroxide at the end of the reaction.

To is the initial titre of sodium hydroxide.

Tt is the titre after a time interval t_i seconds.

The mean value of the integrated rate constant of hydrolysis for any given kinetic run was obtained from the expression

$$k_m = \frac{\sum k_i}{n}$$

where n is the number of determinations of Ki.

The value of the overall integrated rate constant for any given salt, kx, was obtained from

$$k_x = \frac{\sum_j n_j (k_m)_j}{\sum n_j}$$

where j is the number of duplicated kinetic runs on the particular salt and n is the number of determinations in any one run.

A similar expression was used when no salt was present. The ratio $\frac{k_x}{k_{x_o}}$ was evaluated for each salt so that the % acceleration or retardation of the hydrolysis due to the added salt, could be determined. (See Table II1).

Errors

The individual values of ki_o from all the kinetic runs on any solvent were treated as one set of results, in order to determine the standard error of the mean value of kx_o, i.e.

$$\sigma_m{}^o = \frac{\left[\sum(ki_o - km_o)^2\right]^{\frac{1}{2}}}{n}$$

where n is the number of determinations of ki_o.

When a salt was present, σ_m of k_m was obtained from each kinetic run from the relationship

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

The error in $\frac{km}{km_o}$ for each run was calculated from the equation

$$\text{error} = \sigma\left(\frac{km}{km_o}\right) = \frac{km}{km_o}\left[\left(\frac{\sigma m}{km}\right)^2 + \left(\frac{\sigma^o m}{km_o}\right)^2\right]^{\frac{1}{2}}$$

The ratio $\frac{km}{kx_o}$ was obtained as the arithmetic mean of n values of $\frac{km}{km_o}$ each with an error $\sigma\left(\frac{km}{km_o}\right)$

$\frac{kx}{kx_o}$ has an error given by:-

$$(\text{Error})_{\frac{kx}{kx_o}} = \left[\sigma\left(\frac{km}{km_o}\right)_1^2 + \sigma\left(\frac{km}{km_o}\right)_2^2 + \text{----} + \Delta_1^2 + \Delta_2^2 + \text{----}\right]^{\frac{1}{2}}$$

where $\Delta_1 = \left(\frac{km}{km_o}\right)_1 - \left(\frac{km}{km_o}\right)_m$

$\left(\frac{km}{km_o}\right)_m$ is the mean value of the ratio.

The error in the difference of two $\frac{kx}{kx_o}$ ratios A and B, was determined from the relationship:-

$$\text{error} = (\sigma_A^2 + \sigma_B^2)^{\frac{1}{2}}$$

Calculation of the ionic strength constant, σ_{MX}

As shown in Chapter II, the ionic strength constants, σ_{MX}, for each salt were obtained from:-

$$\sigma_{MX} = \frac{\log\left[\frac{kh}{kh^+} \cdot \frac{1 + \alpha[Cl^-]}{1 + \alpha[Cl^-]^+}\right] - B\sigma_{HCl}\,(\mu_{HCl} - \mu^+_{HCl})}{B\mu_{MX}}$$

where $\frac{kh}{kh^+}$ can be equated with $\frac{kx}{kx_o}$ if appropriate concentrations are used (See Chapter II, page 32 and below). Queen's values,[35] as given below, of α, B and σ_{HCl} were used to calculate σ_{MX}.

$\alpha = 2.35$

$B = 0.678 \times 10^8$

$\sigma_{HCl} = 0.89 \times 10^{-8}$

The error in σ_{MX} was calculated from:-

$$\text{Error}(\sigma_{MX}) = \frac{\pm \dfrac{x}{2.303 \frac{kx}{kx_o}}}{{}^{B}\nu_{MX}}$$

where x is the error in $\left(\frac{kx}{kx_o}\right)_m$.

The error in the mean value of σ_{MX} for 0.05 and 0.1M solutions was obtained from the expression

$$\text{Error}\left(\frac{\sigma_A + \sigma_B}{2}\right) = \left[(\sigma_a - m)^2 + (\sigma_b - m)^2 + \text{Error}\,\sigma_A{}^2 + \text{Error}\,\sigma_B{}^2\right]^{\frac{1}{2}} / \sqrt{2}$$

where m is the mean value of σ_A and σ_B.

Instantaneous and Integrated Rates

In Chapter II page 32 it was shown that the integrated rate coefficient for hydrolysis k_i for the time interval $0 - t_i$ is identical with the instantaneous rate coefficient at time $t_i/_2$. In order to evaluate σ_{MX} from the equation on page 55 using integrated rate coefficients it is necessary to know the concentrations at the time $\frac{t}{2}$.

The concentration of RCl at time $\frac{t}{2}$ was shown on page 32 Chapter II to be given by

$$[RCl]_{\frac{t}{2}} = [RCl]_o^{\frac{1}{2}} \; [RCl]_t^{\frac{1}{2}}$$

The chloride ion concentration at $\frac{t}{2}$ is therefore as below

$$\left[Cl^-\right]_{\frac{t}{2}} = \left[Cl^-\right]_{\infty} - \left[\left[RCl\right]_o \left[RCl\right]_t\right]^{\frac{1}{2}}$$

Thus the mean of the integrated rate coefficients corresponds to the instantaneous value when the mean chloride ion concentration is given by:-

$$\left[Cl^-\right]_m = \frac{1}{n}\left[Cl^-\right]_{\frac{t}{2}} = \left[Cl^-\right]_{\infty} - \frac{\left[RCl\right]_o^{\frac{1}{2}}}{n}\sum\left[RCl\right]_t^{\frac{1}{2}}$$

where n is the number of determinations of the integrated rate coefficient, and t refers to the experimental times at which individual values of k_i were determined.

This expression can be formulated in terms of the titration figures obtained, if a conversion factor for ml $\rightarrow$ concentration is included.

i.e. $\left[HCl\right]_m = \text{conv.}\left[T_{\infty} - \frac{(T_{\infty} - T_o)^{\frac{1}{2}}}{n}\sum(T_{\infty} - T)^{\frac{1}{2}}\right] = Y$

In the calculation of the mean concentrations of the species present, the following possibilities exist.

(a) <u>Cation M^+, Anion $X^- \neq Cl^-$</u>

k_x refers to $\left[MX\right]_m = \left[MX\right]_{initial}$

$\left[HCl\right]_m = Y$ (above)

$\left[Cl^-\right]_m = Y$

(b) Cation M^+, Anion $X^- = Cl^-$

$$k_x \text{ refers to } [MCl]_m = [MCl]_{initial}$$

$$[HCl]_m = Y$$

$$[Cl^-]_m = Y + [MCl]_{initial}$$

where the suffix m represents mean.

For every salt mean values of the chloride and HCl concentrations were evaluated and substituted into the expression for σ_{MX} for the condition $k_h = k_x$ where k_x is the mean integrated rate coefficient for each salt.

$\frac{k_1}{k_1^o}$ was then given from $\frac{k_1}{k_1^o}$ = antilog $B\sigma_{MX}\mu_{MX}$ (Chapter II, page 32).

Table III1

General Table of Results

The table contains the results of all the kinetic runs. Column 2 (Solvent) is of importance since for comparison the runs with and without salt must be performed in the same solvent. Column 4 (n) gives the number of determinations of the rate constant in the run. Column 5 gives the value of the integrated rate constant for the run (k_m) with salt present, and column 6 the value without salt (km_o). The seventh column contains the values of the ratios $\frac{km}{km_o}$ and column 8 the standard error in km. The standard error in $\frac{km}{km_o}$ is tabulated in the last column.

Values of $\frac{kx}{kx_o}$ were obtained as the mean of the $\frac{km}{km_o}$ values.

Exp. 1	Solvent 2	Addition 3	n 4	$10^4 k_m$ 5	$10^4 k_{m_0}$ 6	$\frac{k_m}{k_{m_0}}$ 7	$10^3 \sigma_m$ 8	$10^3 \sigma_{\frac{k_m}{k_{m_0}}}$ 9
1a	V	None	8		2.737			
1b	V	None	8		2.750			
1c	V	None	10		2.722			
2a	VI	None	10		2.578			
2b	VI	None	8		2.586			
2c	VI	None	10		2.565			
3a	VII	None	9		2.508			
3b	VII	None	7		2.495			
4a	VIII	None	9		2.544			
4b	VIII	None	8		2.538			
4c	VIII	None	9		2.551			
5a	IX	None	10		2.568			
5b	IX	None	9		2.563			
5c	IX	None	8		2.580			
6a	X	None	9		2.415			
6b	X	None	8		2.426			
7a	V	Me_4NCl 0.0505M	9	2.557		.9349	1.61	1.892
7b	V	Me_4NCl 0.05014M	8	2.540		.9287	5.30	2.637
8a	V	Me_4NCl 0.1019M	9	2.363		.8640	3.809	2.170
8b	V	Me_4NCl 0.1005M	9	2.340		.8556	8.886	3.641

contd.

1	2	3	4	5	6	7	8	9
8c	V	Me_4NCl 0.1006M	7	2.374		.8680	2.703	1.942
9a	VI	Me_4NBr 0.05005M	9	2.794		1.0846	9.587	4.033
9b	VI	Me_4NBr 0.04998M	7	2.765		1.0734	6.809	3.057
9c	VI	Me_4NBr 0.0500M	8	2.799		1.0866	10.356	4.309
10a	VI	Me_4NBr 0.1001M	8	2.963		1.1502	4.235	2.326
10b	VI	Me_4NBr 0.1001M	8	2.932		1.1382	19.81	7.860
10c	VI	Me_4NBr 0.1001M	8	2.987		1.1596	4.119	2.304
11a	IX	$Me_4NClO_4$0.05005M	7	2.910		1.1323	4.667	2.543
11b	IX	$Me_4NClO_4$0.05005M	7	2.911		1.1327	9.249	4.014
12a	IX	$Me_4NClO_4$0.09991M	10	3.256		1.2669	11.22	4.800
12b	IX	$Me_4NClO_4$0.09994M	8	3.301		1.2844	11.433	4.885
13a	V	Et_4NCl 0.05075M	8	2.482		.9075	4.104	2.303
13b	V	Et_4NCl 0.05098M	7	2.483		.9079	6.771	3.031
13c	V	Et_4NCl 0.05113M	9	2.475		.9049	5.994	2.800
14a	VI	Et_4NCl 0.09909M	10	2.082		.8082	3.954	1.922
14b	VI	Et_4NCl 0.09937M	8	2.062		.8004	5.309	2.357
14c	VI	Et_4NCl 0.09946M	8	2.092		.8121	2.945	1.630
15a	IX	Et_4NBr 0.0500M	9	2.655		1.0331	4.549	2.402
15b	IX	Et_4NBr 0.05000M	9	2.652		1.0319	5.153	2.579
16a	IX	Et_4NBr 0.1000M	9	2.734		1.0638	3.630	2.189
16b	IX	Et_4NBr 0.1000M	6	2.734		1.0638	12.917	5.298
17a	VIII	Pr_4NCl 0.5005M	9	2.222		.8731	1.686	1.443
17b	VIII	Pr_4NCl 0.05015M	9	2.229		.8758	4.760	2.338

contd.

1	2	3	4	5	6	7	8	9
18a	VIII	Pr_4NCl 0.100M	8	1.967		.7729	3.623	1.821
18b	VIII	Pr_4NCl 0.1000M	7	1.961		.7705	3.296	1.721
19a	IX	Pr_4NBr 0.04998M	10	2.582		1.0047	6.899	3.115
19b	IX	Pr_4NBr 0.0500M	7	2.588		1.0070	3.984	2.215
20	IX	Pr_4NBr 0.1000M	10	2.585		1.0058	4.963	2.495
21a	X	Pr_4NBr 0.10001M	10	2.438		1.0070	6.174	2.828
21b	X	Pr_4NBr 0.10001M	8	2.433		1.0050	5. 774	2.679
22a	VII	Bu_4NCl 0.04992M	8	2.074		.8289	2.359	1.924
22b	VII	Bu_4NCl 0.04996M	9	2.095		.8373	5.804	2.873
23a	VII	B u_4NCl 0.1000M	10	1.839		.7351	3.570	2.062
23b	VII	Bu_4NCl 0.1001M	9	1.841		.7358	5.297	2.588
24	IX	Bu_4NCl 0.1001M	10	1.892		.7362	3.231	1.709
25a	VII	Bu_4NBr 0.04999M	8	2.450		.9792	4.3787	2.644
25b	VII	Bu_4NBr 0.05001M	9	2.443		.9764	7.788	3.687
26a	VII	Bu_4NBr 0.09998M	10	2.391		.9556	4.969	2.772
26b	VII	Bu_4NBr 0.09995M	7	2.383		.9524	4.950	2.762
27a	VIII	Bu_4NClO_4 0.04998M	10	2.534		.9957	3.314	1.959
27b	VIII	Bu_4NClO_4 0.05001M	10	2.530		.9941	9.914	4.160
28a	VIII	Bu_4NClO_4 0.1000M	7	2.498		.9815	2.969	1.8541
28b	VIII	Bu_4NClO_4 0.1000M	10	2.497		.9811	13.533	5.509

The following table is a summary of Table III1 with results expressed as % changes in rate from the $\frac{km}{km_o}$ values. Table II1 lists $\frac{kx}{kx_o}$ values which are the means of the values in this table for each salt.

Table III2

Summary of results.

Cation	Anion	Exp.	Conc.(M)	%	Exp.	Conc.(M)	%
Me_4N^+	Cl^-	7a	.0515	-6.51±.19	8a	.1019	-13.60±.22
Me_4N^+	Cl^-	7b	.0501	-7.13±.26	8b	.1005	-14.44±.36
Me_4N^+	Cl^-				8c	.1006	-13.20±.19
Me_4N^+	Br^-	9a	.0501	+8.46±.40	10a	.1001	+15.02±.23
		9b	.0500	+7.34±.31	10b	.1001	+13.82±.77
		9c	.0500	+8.66±.43	10c	.1001	+15.96±.23
Me_4N^+	ClO_4^-	11a	.0501	+13.23±.25	12a	.0999	+26.69±.48
		11b	.0501	+13.27±.40	12b	.0999	+28.44±.49
Et_4N^+	Cl^-	13a	.0508	-9.25±.23	14a	.0991	-19.18±.19
		13b	.0510	-9.21±.30	14b	.0994	-19.96±.24
		13c	.0511	-9.51±.28	14c	.0995	-18.79±.16
Et_4N^+	Br^-	15a	.0500	+3.33±.24	16a	.1000	+6.38±.22
		15b	.0500	+3.19±.26	16b	.1000	+6.38±.53
Pr_4N^+	Cl^-	17a	.0501	-12.69±.14	18a	.1000	-22.71±.18
		17b	.0502	-12.42±.23	18b	.1000	-22.95±.17

contd.

Cation	Anion	Exp.	Conc(M)	%	Exp.	Conc(M)	%
Pr_4N^+	Br^-	19a	.0500	+0.47±.31	20	.1000	+0.58±.25
		19b	.0500	+0.70±.22	21a	.1000	+0.70
					21b	.1000	+0.50
nBu_4N^+	Cl^-	22a	.0499	-17.21±.19	23a	.1000	-26.49±.21
		22b	.0500	-16.27±.29	23b	.1000	-26.42±.26
					24	.1001	-26.38±.17
nBu_4N^+	Br^-	25a	.0500	-2.08±.26	26a	.1000	-4.44±.28
		25b	.0500	-2.36±.37	26b	.0999	-4.76±.28
nBu_4N^+	ClO_4^-	27a	.0500	-0.43±.20	28a	.1000	-1.85±.19
		27b	.0500	-0.59±.42	28b	.1000	-1.89±.55

APPENDIX

Details of kinetic runs

All runs are in 70% aqueous acetone at 20.13°C. Full details are given of one run in each experiment. The mean rate coefficients only are quoted for duplicates. The rate coefficients are all first order and were obtained from the rate expression $k = \frac{2.303}{t} \log \frac{a}{a - x}$.

The order of experiments in this summary is one of convenience for reference and not the chronological order of the work.

APPENDIX

Details of Kinetic Runs

Experiment 1 Benzhydryl chloride in Solvent V.

No Salt.

5 ml. titrated with .009785N NaOH

Time (secs)	Titre (mls)	10^4k (sec^{-1})
0	0.12	-
603	1.59	2.693
1210	2.84	2.687
1815	3.88	2.662
2423	4.78	2.660
3042	5.67	2.743
3606	6.25	2.720
4308	6.91	2.735
5155	7.58	2.772
6053	8.09	2.766
6907	8.49	2.778
∞	9.93	-

$10^4k = 2.737$ (8 readings)

Duplicate Experiments

$10^4k = 2.750$ (8 readings)

$10^4k = 2.722$ (10 readings)

Mean k in Solvent V

$10^4k = 2.735 \pm .0053$

Experiment 2 Benzhydryl-chloride in Solvent VI acetone.

No Salt.

5 ml. titrated with 0.010096 N NaOH

Time (secs)	Titre (ml)	$10^4k(sec^{-1})$
0	0.38	-
600	1.97	2.618
1870	4.57	2.586
2580	5.63	2.537
3150	6.48	2.593
3640	7.02	2.570
4255	7.67	2.584
4872	8.22	2.594
5460	8.61	2.562
6004	8.98	2.575
6650	9.32	2.562
∞	11.31	-

$10^4k = 2.578$ (10 readings)

Duplicate experiments

$10^4k = 2.586$ (8 readings)

$10^4k = 2.565$ (10 readings)

Mean k in Solvent VI

$10^4k = 2.576 \pm .0037$

Experiment 3 Benzhydryl chloride in Solvent VII acetone.

No Salt.

5 ml. titrated with 0.010215 N NaOH

Time (secs)	Titre (ml)	$10^4k(\text{sec}^{-1})$
0	0.30	-
798	2.38	2.534
1480	3.80	2.484
2200	5.10	2.488
2796	6.03	2.504
3588	7.02	2.489
4365	7.88	2.514
5189	8.60	2.519
6049	9.20	2.519
6750	9.61	2.525
∞	11.68	-

$10^4k = 2.508$ (9 readings)

Duplicate Experiment

$10^4k = 2.495$ (7 readings)

Mean k in Solvent VII

$10^4k = 2.502 \pm .0051$

Experiment 4 Benzhydryl chloride in Solvent VIII acetone

No Salt.

5 ml. titrated with 0.00977 N NaOH

Time (secs)	Titre (ml)	10^4k (sec^{-1})
0	0.27	-
990	2.80	2.638
1550	3.90	2.578
2140	4.90	2.542
2822	5.95	2.565
3967	7.25	2.526
4620	7.89	2.542
5110	8.28	2.535
5736	8.76	2.561
6341	9.06	2.515
7034	9.44	2.531
∞	11.30	-

$10^4k = 2.544$ (9 readings)

Duplicate Experiments

$10^4k = 2.538$ (8 readings)

$10^4k = 2.551$ (9 readings)

Mean k in Solvent VIII

$10^4k = 2.545 \pm 0.0037$

Experiment 5 Benzhydryl chloride in Solvent IX acetone.

No Salt.

5 ml. titrated with 0.01049N NaOH

Time (sec)	Titre (ml)	10^4k (sec^{-1})
0	0.32	-
902	2.53	2.563
1500	3.79	2.610
2130	4.85	2.579
2700	5.69	2.574
3305	6.40	2.534
3840	6.99	2.535
4240	7.43	2.568
4860	7.98	2.580
5310	8.31	2.577
5729	8.56	2.556
∞	11.04	-

$10^4k = 2.568$ (10 readings)

Duplicate Experiments

$10^4k = 2.563$ (9 readings)

$10^4k = 2.580$ (8 readings)

Mean k in Solvent IX

$10^4k = 2.570 \pm 0.0040$

Experiment 6. Benzhydryl chloride in Solvent X acetone

No Salt.

5 ml titrated with 0.009766 N NaOH

Time (secs)	Titre (ml)	10^4k (sec^{-1})
0	0.19	-
1350	3.17	2.409
1728	3.87	2.427
2100	4.45	2.403
2413	4.95	2.425
2770	5.44	2.420
3184	5.95	2.410
3620	6.45	2.412
4290	7.09	2.394
5085	7.73	2.377
6084	8.49	2.431
∞	10.94	-

10^4k = 2.415 (9 readings)

Duplicate Experiment

10^4k = 2.426 (8 readings)

Mean k in Solvent X

10^4k = 2.421 ± 0.0029

Experiment 7 Benzhydryl chloride in Solvent V

Added Me_4NCl 0.0515M

5 ml. titrated with 0.009804N NaOH

Time (secs)	Titre (ml)	10^4k (sec^{-1})
0	0.31	-
607	1.75	2.576
1204	2.92	2.523
1870	4.10	2.557
2409	4.89	2.554
3608	6.32	2.560
4218	6.90	2.565
4808	7.37	2.562
5404	7.78	2.560
6005	8.12	2.548
6927	8.58	2.554
7800	8.92	2.555
∞	10.28	-

$10^4k = 2.557 \pm 0.0016$ (9 readings)

Duplicate Experiment

Added Me_4NCl 0.05014M

$10^4k = 2.540 \pm 0.0053$ (8 readings)

Experiment 8 Benzhydryl chloride in Solvent V

Added Me_4NCl 0.1019M

5 ml. titrated with 0.009785N NaOH

Time (secs)	Titre (ml)	10^4k (sec^{-1})
0	0.36	-
613	1.70	2.393
1210	2.80	2.370
1830	3.79	2.352
2409	4.60	2.354
3210	5.57	2.363
3685	6.09	2.385
4230	6.51	2.335
4810	7.01	2.360
5418	8.41	2.346
6034	7.82	2.374
6918	8.25	2.364
∞	10.16	-

$10^4k = 2.363 \pm 0.0038$ (9 readings)

Duplicate Experiments

Added Me_4NCl 0.10054M $10^4k = 2.340 \pm 0.0088$ (9 readings)

Added Me_4NCl 0.1006M $10^4k = 2.374 \pm 0.0027$ (7 readings)

Experiment 9 Benzhydryl chloride in Solvent VI

Added Me_4N Br 0.05005M

5 ml. titrated with 0.010096N NaOH

Time (secs)	Titre (ml)	10^4k (sec^{-1})
0	0.44	-
966	2.80	2.761
1504	3.86	2.758
2104	4.96	2.831
2764	5.87	2.804
3308	6.48	2.769
3927	7.13	2.780
4508	7.75	2.872
5128	8.17	2.846
5754	8.50	2.801
6465	8.86	2.798
∞	10.51	-

$10^4k = 2.794 \pm 0.0096$ (9 readings)

Duplicate Experiments

Added Me_4N Br 0.04998M $10^4k = 2.765 \pm 0.0068$ (7 readings)

Added Me_4N Br 0.05000M $10^4k = 2.799 \pm 0.0100$ (8 readings)

Experiment 10 Benzhydryl chloride in Solvent VI

Added Me_4N Br 0.1001M

5 ml. titrated with .010096N NaOH

Time (sec)	Titre (ml)	10^4k (sec^{-1})
0	0.28	-
610	1.98	2.937
1216	3.40	2.941
1810	4.60	2.977
2734	6.02	2.950
3303	6.77	2.977
3923	7.40	2.958
4622	8.01	2.961
5168	8.46	3.010
5824	8.81	2.970
6607	9.19	2.968
∞	10.65	-

$10^4k = 2.963 \pm 0.0042$ (8 readings)

Duplicate Experiments

Added Me_4N Br 0.1001M $10^4k = 2.932 \pm 0.0019$ (8 readings)

Added Me_4N Br 0.1001M $10^4k = 2.987 \pm 0.0041$ (8 readings)

Experiment 11 Benzhydryl chloride in Solvent IX

Added Me_4NClO_4 0.05005M

5 ml. titrated with 0.009804N NaOH

Time (sec)	Titre (ml)	10^4k (sec^{-1})
0	0.37	-
1060	3.64	2.950
1421	4.49	2.911
1815	5.35	2.902
2437	6.56	2.916
2955	7.31	2.859
3345	7.94	2.909
3738	8.47	2.932
4502	9.27	2.919
4958	9.62	2.880
∞	12.54	-

$10^4k = 2.910 \pm 0.0047$ (7 readings)

Duplicate Experiment

Added Me_4NClO_4 0.05005M $10^4k = 2.911 \pm 0.0092$ (7 readings)

Experiment 12 Benzhydryl chloride in Solvent IX

Added Me_4NClO_4 0.09991M

5 ml. titrated with 0.009804N NaOH

Time (sec)	Titre (ml)	10^4k (sec^{-1})
0	0.44	-
1124	3.99	3.319
1555	5.00	3.286
1920	5.66	3.191
2250	6.36	3.256
2711	7.12	3.253
3267	7.89	3.246
3665	8.35	3.230
3978	8.74	3.274
4330	9.09	3.284
4924	9.50	3.216
∞	11.84	-

$10^4k = 3.256 \pm 0.0112$ (10 readings)

Duplicate Experiment

Added Me_4NClO_4 0.09994M $10^4k = 3.301 \pm 0.0114$ (8 readings)

Experiment 13 Benzhydryl chloride in Solvent V.

Added Et_4NCl 0.05075M

5 ml. titrated with 0.009785N NaOH

Time (sec)	Titre (ml)	10^4k (sec^{-1})
0	0.57	-
614	2.70	2.599
1261	4.47	2.497
1924	6.05	2.481
2422	7.11	2.491
3054	8.27	2.495
3720	9.19	2.444
4212	9.93	2.481
4851	10.67	2.478
5407	11.21	2.470
6012	11.72	2.461
6930	12.35	2.442
∞	15.01	-

$10^4k = 2.482 \pm 0.0041$ (8 readings)

Duplicate Experiments

Added Et_4NCl 0.05098M $10^4k = 2.483 \pm 0.0068$

Added Et_4NCl 0.05113M $10^4k = 2.475 \pm 0.0060$

Experiment 14 Benzhydryl chloride in Solvent VI

Added Et_4NCl 0.09909M

5 ml. titrated with 0.010096N NaOH

Time (sec)	Titre (ml)	10^4k (sec^{-1})
0	0.41	-
950	2.07	2.065
1594	3.02	2.066
2130	3.76	2.096
2708	4.40	2.068
3333	5.07	2.085
3915	5.59	2.080
4524	6.07	2.074
5100	6.52	2.098
5702	6.90	2.099
6306	7.21	2.084
∞	9.71	

$10^4k = 2.082 \pm 0.0039$ (10 readings)

Duplicate Experiments.

Added Et_4NCl 0.09937M $10^4k = 2.062 \pm 0.0053$ (8 readings)

Added Et_4NCl 0.09946M $10^4k = 2.092 \pm 0.0029$ (8 readings)

Experiment 15 Benzhydryl chloride in Solvent IX

Added Et_4N Br 0.05001M

5 ml. titrated with 0.009804N NaOH

Time (sec)	Titre (ml)	10^4k (sec^{-1})
0	0.32	-
906	3.05	2.733
1306	3.99	2.673
1800	5.09	2.680
2408	6.20	2.653
2717	6.71	2.648
3154	7.38	2.653
3660	8.03	2.635
4287	8.80	2.662
5025	9.49	2.650
5681	10.00	2.641
∞	12.78	-

$10^4k = 2.655 \pm 0.0045$ (9 readings)

Duplicate Experiment

Added Et_4N Br 0.0500M $10^4k = 2.652 \pm 0.0052$ (9 readings)

Experiment 16 Benzhydryl chloride in Solvent IX

Added Et_4N Br 0.1000M

5 ml. titrated with 0.009804N NaOH

Time (sec)	Titre (ml)	10^4k (sec^{-1})
0	0.42	-
810	2.62	2.735
1204	3.55	2.760
1839	4.79	2.730
3071	6.71	2.735
3745	7.51	2.732
4535	8.29	2.737
5038	8.70	2.736
5490	9.00	2.718
6510	9.61	2.724
∞	11.49	-

$10^4k = 2.734 \pm 0.0036$ (9 readings)

Duplicate Experiment

Added Et_4N Br 0.1000M $10^4k = 2.734 \pm 0.0129$ (6 readings)

Experiment 17 Benzhydryl chloride in Solvent VIII

Added Pr_4NCl 0.05005M

5 ml. titrated with 0.00977N NaOH

Time (sec)	Titre (ml)	10^4k (sec^{-1})
0	0.19	-
1050	2.49	2.224
1510	3.38	2.260
2112	4.33	2.229
2455	4.82	2.216
2755	5.23	2.215
3309	5.92	2.215
3710	6.39	2.227
4200	6.88	2.221
4770	7.40	2.223
5120	7.69	2.226
∞	11.22	-

10^4k = 2.222 ± 0.0017 (9 readings)

Duplicate Experiment

Added Pr_4NCl 0.05015M 10^4k = 2.229 ± 0.0048 (9 readings)

Experiment 18 Benzhydryl chloride in Solvent VIII

Added Pr_4NCl 0.1000M

5 ml. titrated with 0.00977N NaOH

Time (sec)	Titre (ml)	10^4k (sec^{-1})
0	0.28	-
609	1.59	2.065
1200	2.67	2.025
1809	3.60	1.966
2405	4.49	1.985
3050	5.27	1.960
3605	5.90	1.961
4809	7.03	1.951
5412	7.54	1.965
6018	8.00	1.980
6643	8.37	1.968
∞	11.37	-

$10^4k = 1.967 \pm 0.0036$ (8 readings)

Duplicate Experiment

Added Pr_4NCl 0.1000M $10^4k = 1.961 \pm 0.0033$ (7 readings)

Experiment 19 Benzhydryl chloride in Solvent IX

Added Pr_4N Br 0.04998M

5 ml. titrated with 0.010499N NaOH

Time (sec)	Titre (ml)	10^4k (sec^{-1})
0	0.37	-
690	2.09	2.607
1285	3.34	2.609
1800	4.28	2.609
3103	6.10	2.566
3600	6.69	2.583
4136	7.19	2.561
4526	7.58	2.593
4983	7.88	2.550
5460	8.27	2.589
6009	8.56	2.554
∞	10.81	-

$10^4k = 2.582 \pm 0.0069$ (10 readings)

Duplicate Experiment

Added Pr_4N Br 0.05000M $10^4k = 2.588 \pm 0.0040$ (7 readings)

Experiment 20 Benzhydryl chloride in Solvent IX.

Added Pr_4N Br 0.1000M

5ml. titrated with 0.009804N NaOH

Time (sec)	Titre (ml)	10^4k (sec^{-1})
0	0.21	-
1430	3.92	2.561
1815	4.78	2.610
2240	5.50	2.565
2764	6.39	2.583
3113	6.88	2.572
3662	7.61	2.579
4525	8.59	2.603
4857	8.87	2.586
5250	9.20	2.583
5599	9.50	2.603
∞	12.32	-

$10^4k = 2.585 \pm 0.0049$ (10 readings)

Experiment 21 Benzhydryl chloride in Solvent X.

Added Pr_4N Br 0.10001M

5 ml. titrated with 0.009766N NaOH

Time (sec)	Titre (ml)	10^4k (sec^{-1})
0	0.14	-
1915	4.12	2.420
2216	4.67	2.470
2617	5.20	2.435
2916	5.61	2.442
3540	6.32	2.420
4005	6.80	2.417
4380	7.20	2.445
4697	7.52	2.474
5250	7.89	2.436
5910	8.31	2.420
∞	10.88	-

$10^4k = 2.438 \pm 0.0062$ (10 readings)

Duplicate Experiment

ADDED Pr_4N Br 0.10001M $10^4k = 2.433 \pm 0.0058$ (8 readings)

Experiment 22 Benzhydryl chloride in Solvent VII

Added nBu_4NCl 0.04992M

5 ml. titrated with 0.0100N NaOH

Time (sec)	Titre (ml)	10^4k (sec^{-1})
0	0.27	-
804	2.01	2.039
1610	3.55	2.078
2106	4.40	2.105
2710	5.24	2.079
3324	6.00	2.068
3910	6.69	2.082
4645	7.38	2.065
5100	7.80	2.076
5710	8.25	2.063
6918	9.06	2.077
∞	11.80	-

$10^4k = 2.074 \pm 0.0024$ (8 readings)

Duplicate Experiment

Added nBu_4NCl 0.04996M $10^4k = 2.095 \pm 0.0058$ (9 readings)

Experiment 23 Benzhydryl chloride in Solvent VII

Added nBu_4NCl 0.1000M

5 ml. titrated with 0.100N NaOH

Time (sec)	Titre (ml)	10^4k (sec^{-1})
0	0.19	-
903	1.90	1.826
1465	2.83	1.824
2230	3.99	1.848
2712	4.62	1.844
3304	5.30	1.833
3905	5.99	1.856
4515	6.57	1.854
5102	7.01	1.827
6016	7.70	1.831
6720	8.18	1.843
∞	11.44	-

$10^4k = 1.839 \pm 0.0036$ (10 readings)

Duplicate Experiment

Added nBu_4NCl 0.1001M $10^4k = 1.841 \pm 0.0053$ (9 readings)

Experiment 24 Benzhydryl chloride in Solvent IX

Added nBu_4NCl 0.1001M

5 ml. titrated with 0.009804N NaOH

Time (secs)	Titre (ml)	10^4k (sec^{-1})
0	0.19	-
1800	3.30	1.904
2390	4.10	1.898
2867	4.70	1.904
3339	5.19	1.881
3859	5.73	1.885
4373	6.19	1.876
4888	6.65	1.888
5430	7.07	1.891
6084	7.50	1.883
6990	8.08	1.906
∞	10.91	-

10^4k = 1.892 ± 0.0032 (10 readings)

Experiment 25 Benzhydryl chloride in Solvent VII

Added nBu_4NBr 0.04999M

5 ml. titrated with 0.0100N NaOH

Time (sec)	Titre (ml)	10^4k (sec^{-1})
0	0.11	-
913	2.29	2.427
1518	3.52	2.449
1131	4.58	2.454
2708	5.42	2.442
3308	6.23	2.464
3933	6.89	2.444
4518	7.50	2.474
5409	8.15	2.437
6013	8.51	2.409
6615	8.90	2.437
∞	11.09	-

$10^4k = 2.450 \pm 0.0044$ (8 readings)

Duplicate Experiment

Added nBu_4NBr 0.05001M $10^4k = 2.443 \pm 0.0078$ (9 readings)

Experiment 26 Benzhydryl chloride in Solvent VII

Added nBu_4NBr 0.09998M

5 ml. titrated with 0.0100N NaOH

Time (sec)	Titre (ml)	10^4k (sec^{-1})
0	0.30	-
901	2.37	2.369
1590	3.67	2.368
2106	4.54	2.382
2745	5.49	2.402
3350	6.22	2.389
3955	6.85	2.376
4536	7.45	2.412
5096	7.90	2.409
5760	8.35	2.399
6870	8.99	2.405
∞	11.05	-

$10^4k = 2.391 \pm 0.0049$ (10 readings)

Duplicate Experiment

Added nBu_4NBr 0.09995M $10^4k = 2.383 \pm 0.0050$ (7 readings)

Experiment 27 Benzhydryl chloride in Solvent VIII

Added nBu_4NClO_4 0.04998M

5 ml. titrated with 0.00977N NaOH

Time (sec)	Titre (ml)	10^4k (sec^{-1})
0	0.28	-
822	2.29	2.547
1219	3.10	2.528
1704	4.01	2.538
2284	4.93	2.521
2951	5.87	2.528
3525	6.58	2.549
3924	6.98	2.537
4523	7.51	2.520
5121	7.99	2.523
5718	8.43	2.545
∞	10.91	-

$10^4k = 2.534 \pm 0.0033$ (10 readings)

Duplicate experiment

Added nBu_4NClO_4 0.05001M $10^4k = 2.530 \pm 0.0099$ (10 readings)

Experiment 28 Benzhydryl chloride in Solvent VIII

Added nBu_4NClO_4 0.1000M

5 ml. titrated with 0.00977N NaOH

Time (sec)	Titre (ml)	10^4k (sec^{-1})
0	0.31	-
925	2.81	2.577
1554	4.17	2.555
1877	4.72	2.498
3124	6.70	2.499
3605	7.29	2.488
4205	7.83	2.416
4595	8.35	2.493
5100	8.83	2.515
5745	9.29	2.497
6300	9.65	2.494
∞	12.10	-

$10^4k = 2.498 \pm 0.0030$ (7 readings)

Duplicate Experiment

Added nBu_4NClO_4 0.100M $10^4k = 2.497 \pm 0.0135$ (10 readings)

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