## *Reactivities of organic poly-halogen compounds*

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ABSTRACT.

Two recent investigations have shown that an $\alpha$-chlorine substituent increases $S_N1$ reactivity, but analysis of the trends in $E_A$ and $\Delta S^{\ddagger}$ values in each case, shows that serious discrepancies exist between them.

In view of this it was considered that the role of an $\alpha$-chlorine substituent was still uncertain and it was decided to look into the matter further.

Towards this end, the solvolyses of benzyl chloride, benzal chloride, benzotrichloride, diphenylmethyl chloride and diphenylmethylene chloride have been examined in various solvents, over as wide a range of temperatures as possible, consistent with accurate results, it being considered that the mechanism of solvolysis was $S_N1$ in all cases, with the possible exception of benzyl chloride.

Analysis of the $E_A$ and $\Delta S^{\ddagger}$ values for the solvolyses of these compounds shows, in the first place, that the solvolysis of benzyl chloride is not straightforward $S_N1$. Its mechanism of solvolysis is discussed in chapter VII where it is concluded that it proceeds by a single, predominantly $S_N2$ mechanism.

Further analysis of the $E_A$ and $\Delta S^{\ddagger}$ values (and in some cases $\Delta C_p^{\ddagger}$ values) of the other compounds, in chapter VI, indicates that the primary role of an $\alpha$-chlorine

substituent in $S_N1$ reactions is electron release, although, as a second order effect it appears to cause an increase in the extent of solvation of the transition state.

The disturbing effects in the hydrolysis of diphenylmethylene chloride in aqueous acetone are analysed in part II where it is shown that they can be quantitatively explained, over a wide range of experimental conditions, on the basis of the mass law and ionic strength effects, proposed by Hughes and Ingold, in $S_N1$ reactions.

The exceptionally large mass law effect for diphenylmethylene chloride is ascribed to powerful electron release by the $\alpha$-chlorine atom, so confirming the conclusions reached in part I.

# REACTIVITIES OF ORGANIC POLY-HALOGEN COMPOUNDS.

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

-by-

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ABSTRACT.

Two recent investigations have shown that an α-chlorine substituent increases $S_N1$ reactivity, but analysis of the trends in $E_A$ and $\Delta S^{\ddagger}$ values in each case, shows that serious discrepancies exist between them.

In view of this it was considered that the role of an α-chlorine substituent was still uncertain and it was decided to look into the matter further.

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Analysis of the $E_A$ and $\Delta S^{\ddagger}$ values for the solvolyses of these compounds shows, in the first place, that the solvolysis of benzyl chloride is not straightforward $S_N1$. Its mechanism of solvolysis is discussed in chapter VII where it is concluded that it proceeds by a single, predominantly $S_N2$ mechanism.

Further analysis of the $E_A$ and $\Delta S^{\ddagger}$ values (and in some cases $\Delta C_p^{\ddagger}$ values) of the other compounds, in chapter VI, indicates that the primary role of an α-chlorine

substituent in $S_N1$ reactions is electron release, although, as a second order effect it appears to cause an increase in the extent of solvation of the transition state.

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# PART I

## REACTIVITIES OF ORGANIC POLY-HALOGEN COMPOUNDS.

# CHAPTER I

## INTRODUCTION.

### Electronic Theory of Reactions. (1)

Organic substitution reactions are electrical phenomena and reagents react by virtue of a constitutional affinity either for electrons (electrophilic), or for atomic nuclei (nucleophilic). An electrophilic reagent will attack a molecule provided there is at some point a sufficiently high electron density. A nucleophilic reagent will attack a molecule provided there is at some point a sufficiently low electron density. The development of the critical electron density at the reaction centre is considered as an essential feature of the activation energy. The replacement of one group by another at some point other than the reaction centre will affect the ease of reaction according to the effect each has on the electron density at the reaction centre.

### Mechanisms of Electron Displacement. (1)

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

In the General Inductive mechanism the electrical

dissymmetry arising out of the unequal sharing of the bonding electrons between two linked atoms can be propagated along the molecule by a process analogous to electrostatic induction. The mechanism was first proposed by Lewis (2) and is represented thus,

$$Cl \leftarrow CH_2 \leftarrow CH_2 \leftarrow CH_3,$$

the arrows pointing in the direction of electron concentration. In the case shown, the effect is caused by the electron dissymmetry of the C - Cl bond. In so far as the inductive mechanism enters into the description of the normal states of molecules it is called the Inductive effect.

The second method of electron displacement, now called the Conjugative mechanism (3a), since it can be regarded as a development of the early concept of conjugation in unsaturated systems, is characterised by the substitution of one duplet for another in the electron octet. This type of displacement was assumed by Lowry (4), who showed how the entrance into an octet of an unshared duplet possessed by a neighbouring atom could cause the ejection of another duplet which would then either become unshared or initiate a similar change further along the molecule. This effect is represented by a curved arrow pointing from the duplet to the point towards which the displacement is assumed to occur. The effect can be propagated along a

conjugated chain thus,

$$R_2\overset{\curvearrowright}{N} - C = \overset{\curvearrowright}{C} - C = \overset{\curvearrowright}{O} \quad \text{Structure I.}$$

The arrows indicate duplet displacement which, if carried to completion would lead to the formula,

$$R_2\overset{+}{N} = C - C = C - \overset{-}{O} \quad \text{Structure II.}$$

The true structure is considered to be the resonance hybrid of the above two canonical forms. The greater the conjugative release of the group $R_2N$, the greater will be the contribution of II to the structure of the molecule. It is evident that maximum relay of this effect will be achieved when the releasing group is connected to a conjugated system. In so far as the conjugative mechanism applies to the normal states of molecules it is called the Mesomeric effect.

Dependence of Polar Effects on Environment.

The polar effects of groups are not constant but vary according to their environment. For instance if, in the two molecules,

$$\overset{\cdot\cdot}{X}\overset{\curvearrowright}{} - C = C \rightarrow Y$$

$$\overset{\cdot\cdot}{X}\overset{\curvearrowright}{} - C = C \rightarrow Y'$$

X is capable of electron release by the mesomeric effect and Y and Y' are capable of electron attraction by the inductive effect, with Y' having the stronger attraction, interaction polarisation between the groups X and Y (or Y')

will cause each effect to be enhanced. The enhancement of the mesomeric effect of X will be greater in the second case however, due to the extra electron attraction of Y' compared with Y. In view of this it is desirable, when comparing the polar effects of groups, to effect the comparison when they are attached to similar structures so that any modification of the polar effects by the rest of the structure should be as nearly as possible constant.

Polarisability Effects.

A special case of the modification of polar effects by changes in environment is that caused, not by a variation of attached groups, but by a particular molecule (or molecules) entering the transition state of some reaction. In the transition state there will be extra electron displacements in consequence of the electrical demands of the reaction centre on the surrounding structure. As these extra electron displacements in the transition state depend on the polarisability of the structure with respect to the electrical forces exerted by the reaction centre they are collectively termed polarisability effects.

A polarisability effect occuring by the conjugative mechanism is called the Electromeric effect. A polarisability effect occuring by the inductive mechanism is called the Inductomeric effect (5).

The two mechanisms of electron displacement and the four effects arising therefrom are summarised in table I-1.

Table I-1.

| Mechanism | Polarisation | Polarisability |
|---|---|---|
| General Inductive(I) ($\rightsquigarrow$) | Inductive(I or $I_s$) | Inductomeric($I_d$) |
| Conjugative(T) ($\curvearrowright$) | Mesomeric(M) | Electromeric(E) |

A positive sign in front of the symbol for any effect indicates that it results in electron repulsion by the group concerned, a negative sign shows electron attraction.

Combination of Effects.

An important phase in the development of the theory of electron displacement was that concerned with the synthesis of the various polar effects into a single theoretical picture.

The first step in this direction was taken by Lucas and his collaborators (6), who brought together the inductive and electromeric effects, showing how the former might be supposed to assist and give direction to the latter, as for example in the activation of the olefins in their addition reactions,

$$CH_3 \rightarrow CH = \overset{\curvearrowright}{C}H_2.$$

Here, the inductive effect of the methyl group promotes

electromeric activation of the double bond as shown, leading to the uptake of a proton, derived from an adding hydrogen halide molecule, at the terminal carbon atom. Similar combinations of inductive and electromeric effects were assumed by Robinson and coworkers (7), notably in explanation of orientation in aromatic substitution. In the case of groups capable of mesomerism their I and T effects will operate, either in concert or in opposition, depending on their signs. For instance, the methoxy group has a +T effect and a -I effect while the nitro group has a -T effect and a -I effect.

Predicted Polar Effects of Bound Atoms and Groups. (1)(3b)

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

Inductive Effect.

The forces causing inductive electron displacement are essentially electrostatic. They depend on the strength

of attraction of an atomic nucleus for its valency electrons and the resultant underscreening or overscreening of the nucleus. Therefore, negatively charged groups will, as a class, repel electrons more strongly than neutral groups which will in turn repel electrons more strongly than positively charged groups. Groups with formal dipoles, e.g. $\overset{+-}{NO_2}$, are always bound to the remainder of the molecule through their cationic centres and should attract electrons relative to neutral groups.

Along the series,

$$CH_3 \quad NH_2 \quad OH \quad F,$$

the central atoms become progressively more electronegative and thus the groups should attract electrons progressively more strongly. This relationship may be expected to repeat itself among similar groups whose central atoms belong to the periods which, in Mendeléjeff's periodic table, end in halogen.

As we pass down a Mendélejeff group, e.g. the halogens, the electrical dissymetry of the bound atoms may be expected to be progressively reduced by a compensating polarisation of the core electrons. Thus we should expect the electron attraction of the halogens to decrease in the order,

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

Inductomeric Effect.

By inductomeric polarisability is meant the polarisability which atoms and groups in saturated combination exhibit along the lines of their bonds. Such polarisability must depend generally on the strength of binding of the valency electrons, the more strongly they are bound, the less they are polarisable. For isoelectronic atoms with completed valency shells, inductomeric polarisability should thus decrease with increasing electronegativity.

Firstly, therefore, inductomeric polarisability should be strongly increased by a negative charge and strongly decreased by a positive charge. Secondly, for atoms having the same formal charge it should decrease towards the right hand side of a Mendelejeff period,

e.g. $CR_3 > NR_2 > OR > F$.

Thirdly, as the polarisability of the valency electrons increases with a rise in principle quantum number, it may be expected that inductomeric polarisability should increase as we pass down a Mendelejeff group,

e.g. $F < Cl < Br < I$.

Mesomeric Effect in Unsaturated Systems.

In a system in which mesomeric release has occured, one of the terminal atoms increases its covalency becoming positively charged, while the other decreases its covalency becoming negatively charged.

Increases of covalency depend on the possession of unshared electron pairs, and on their power of interaction with an adjacent atomic nucleus. This affinity of the unshared electrons for the nucleus of another atom in turn depends on the strength of their binding, i.e. on the electronegativity of the atom to which they belong. Negatively charged groups should as a whole, therefore, tend to increase their covalency to a greater extent than neutral groups which, in turn, should tend to increase their covalency more than positively charged groups. For atoms in the same state of formal charge, the tendency to increase covalency should diminish along a Mendelejeff period,

$$NR_2 > OR > F.$$

The increase in covalency involved in the mesomeric effect is partial double bond formation, and, because of the overlap principle, double bonds are more easily formed when the atoms concerned, in particular the p orbitals of their valency shells, are about the same size (8). Therefore it is to be expected that the halogens stand in the following order with respect to their capacity to increase covalency in the mesomeric effect,

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

Similar arguments can be proposed to predict the tendency of a multiply bound atom towards a reduction in

covalency.

Electromeric Effect in Unsaturated Systems.

The origin of this effect is exactly the same as that of the mesomeric effect. It may be considered simply as an enhancement of that effect in the transition state of a reaction due to the extra electrical demands thereof. In consequence, the considerations discussed above in connection with the mesomeric effect will apply to the electromeric effect also.

Evidence for Polar Effects.

Three types of phenomena are available for consideration in relation to theories of electron displacement, namely, physical properties of molecules, reaction equilibria and the kinetic aspects of reactions. For the sake of brevity, the main emphasis will be placed on the halogens as they are the concern of the present investigation.

Physical Properties.

The dipole moments of the methyl halides, $CH_3X$, are related to the permanent polarisation of the molecule due to the inductive effect of the group X. Sutton's values (9), which are given in table I-2, show that the effect results in electron attraction decreasing in the order Cl > F > Br > I. Dipole moments are, however, a function of charge and distance. Assuming that here they arise

out of the existance of formal electric charges on the carbon and halogen atoms, these charges (c.f. table I-2), which can be obtained from the dipole moments and C - X distances (10), will reflect the magnitude of the permanent polarisation. The sequence for the -I effect then becomes F > Cl > Br > I.

Table I-2.

| X = | F | Cl | Br | I |
|---|---|---|---|---|
| Dipole Moment (Debyes) | -1.81 | -1.87 | -1.80 | -1.64 |
| Formal Charge(e.s.u. x $10^{-10}$) | -1.28 | -1.06 | -0.94 | -0.78 |

---

In the monohalogeno benzenes, PhX, the halogen group is linked to a conjugated system and therefore both the I and M effect of X will contribute to the permanent polarisation. In view of the presence of unshared electrons on the halogens the mesomeric effect should result in electron release. A comparison of the dipole moments of the corresponding methyl and phenyl halides led Sutton (9a) to conclude that the halogens were subject to a +M effect varying in the order F > Cl > Br > I. More recent values for the dipole moments of PhX (11) are given in table I-3 and show

that such a comparison leads to the irregular sequence F > Cl ~ I > Br but it has already been pointed out that dipole moments do not necessarily reflect the relative magnitudes of the polar effects.

Table I-3.

| X = | F | Cl | Br | I |
|---|---|---|---|---|
| Dipole Moment of MeX | -1.81 | -1.87 | -1.80 | -1.64 |
| Dipole Moment of PhX | -1.57 | -1.73 | -1.71 | -1.50 |
| Difference | 0.24 | 0.14 | 0.09 | 0.14 |

---

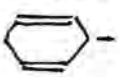
In PhX, mesomeric electron release results in the canonical form $\overset{+}{X}$ =  contributing to the structure of the molecule. As the C = X bond is shorter than the C - X bond, a comparison of the bond lengths in the corresponding alkyl and aryl halides should give the contribution of the double bond structure, i.e. it should reflect the magnitude of the +M effect. The percentage shortening of the aryl bond has been determind (12) and is given in table I-4.

Table I-4.

| X = | F | Cl | Br | I |
|---|---|---|---|---|
| % Contraction | 7.1 | 4.0 | 1.6 | 3.8 |

These results lead to the irregular sequence F > Cl ~ I > Br for the +M effect, but, as it is obviously greatest for F it is not improbable that the inversion of the last two members of the series is due to experimental error in obtaining the interatomic distances.

Summing up the physical data available it can be said to indicate that the polarisation effects of the halogens are +M and -I, both decreasing in the order F > Cl > Br > I.

Reaction Equilibria.

Consider the equilibrium,

$$RCOOH \leftrightharpoons RCOO^- + H^+$$

and side by side with it consider a similar case in which R has been constitutionally modified to R'

$$R'COOH \leftrightharpoons R'COO^- + H^+.$$

The group $COO^-$ is more electropositive than the group COOH so that if R' is more electronegative that R, the extra polarisation of $COO^-$ as compared with COOH and the extra polarisation of R' compared with R will co-operate in the product molecule $R'COO^-$ to produce extra stability. That is, the product molecule $R'COO^-$ will be more stable relative to its factor than the product molecule $RCOO^-$ was relative to its factor. Therefore, as we pass from the first system to the second the position of equilibrium should be shifted in the direction of products. If the group R' had

been less electronegative than R, the position would have been reversed. These conclusions should hold provided that, as seems very often the case, the difference of entropy differences between two such systems can be neglected.

The above picture was simplified inasmuch as group polarisations were treated as though they could be carried unaltered from one compound into another. It was implied that the extra polarisation of R' compared with R was carried unaltered from R'COOH into $R'COO^-$ while the extra polarisation of $COO^-$ compared with COOH was carried unaltered from $RCOO^-$ to $R'COO^-$ so that one had only to consider the interaction of these unaltered extra polarisations in $R'COO^-$. Group polarisations are not constant however, but become modified by the electrical state of the molecule in which they are located, which in turn is determined by the other groups present, as pointed out earlier. For instance, if R and R' differed in that R' contained a group capable of mesomeric release, and that group was conjugated with the COOH group, the mesomeric effect in R' would be stronger when R' was attached to COOH than when it was attached to $COO^-$ due to mutual repulsion of polar effects in the latter case. This would have the effect of giving extra stability to the undissociated acid so that the ionisation constant would be even lower than

that expected from the simplified picture.

Using the principles outlined above, it is possible to predict trends in ionisation constants due to the introduction into molecules of substituents whose polar effects are known, and conversely, to deduce the polar effects of substituents by their effect on ionisation constants.

The relative ionisation constants, $K_X/K_H$ (where the subscript refers to the substituent), for a number of halogen compounds are summarised in table I-5.

The ionisation of the monohalogeno-acetic acids is facilitated by electron attraction by the group X and the $K_X/K_H$ values therefore indicate electron attraction by the halogens in the order F > Cl > Br > I. Since the halogens are not conjugated with the reaction centre this must be due to the -I effect alone.

In the p-halogeno phenols and p-halogeno anilines, where the substituent is conjugated to the reaction centre, the ionisation constants indicate that the overall electron release, due here to the combined -I and +M effects, decreases in the order F > Cl > Br > I. As electron attraction by the -I effect follows this sequence the same must apply for electron release by the +M effect. (It is to be noted that electron releasing groups decrease the

Table I-5.

RELATIVE IONISATION CONSTANTS $K_X/K_H$ OF HALOGEN COMPOUNDS IN AQUEOUS SOLVENTS.

| Compound | H | F | Cl | Br | I |
|---|---|---|---|---|---|
| (A) Halogeno-acetic Acids (13) | 1 | 12.1 | 8.6 | 7.7 | 4.2 |
| (B) p-Halogeno-phenols (14) | 1 | 0.81 | 4.0 | 5.0 | 6.6 |
| (C) p-Halogeno-anilines (14) | 1 | 0.95 | 0.23 | 0.17 | 0.12 |
| (D) p-Halogeno-benzoic Acids (15) | 1 | 1.15 | 1.67 | 1.69 | - |
| (E) p-Halogeno-phenyl Acetic Acids (15) | 1 | 1.15 | 1.32 | 1.33 | 1.37 |

ionisation of the phenols but have the opposite effect on the proton accepting powers of the anilines).

In the ionisation of the p-halogeno benzoic acids and p-halogeno phenyl acetic acids, the substituents are not conjugated to the reaction centre. However, the $K_X/K_H$ values indicate overall electron release decreasing in the order F > Cl > Br > I and consequently point to the sequence F > Cl > Br > I for the +M effect which must be operating by some second order effect.

The evidence from reaction equilibria thus confirms that from the physical data, i.e. that the halogens exert a +M and -I effect, both decreasing in the order F > Cl > Br > I.

Kinetic Aspects of Reactions.

The situation with respect to the kinetic aspects of reactions is different to the other two cases. Account must be taken of the polarisation effects of the reactants, which as a first formal step may be considered to be carried unchanged into the transition state. There remains the interaction polarisation in the transition state, i.e. the extra electron displacements which accompany activation in consequence of the electrical demands of the reaction centre on the surrounding structure, i.e. the polarisability effects.

The polarisability effects may be expected to operate

to an appreciable extent only in those reactions in which the transition state has strong electrical requirements, either for low electron density or for high electron density, and will always be such as to facilitate reaction.

Before deductions about the polar effects of groups can be made from observations of their effects on reaction rates, it is obviously necessary to deduce the electrical requirements of the transition states of the reactions in question. For instance, reactions whose transition states require a high electron density will be facilitated by substituents which can release electrons to the reaction centre and retarded by substituents which attract electrons from the reaction centre.

In the next chapter, the various types of reaction met with in the present investigation will be discussed in detail and the requirements of their transition states will be deduced.

## CHAPTER II.

### MECHANISMS OF SUBSTITUTION AT SATURATED CARBON. (1) (16) (3c)

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

#### Reaction Types.

In a simple substitution reaction of the form,

$$Y + R - X \rightarrow Y - R + X,$$

in which only one bond is exchanged, it is necessary to distinguish between two main types of bond fission, defined as follows, (the dots representing electrons) (17),

$R\bullet\,|\,\bullet X$ (homolytic fission)

$R\,|\,\bullet\bullet X$ (heterolytic fission)

Processes involving the first type of rupture are

common in gas phase reactions and produce or consume atoms or other neutral particles.

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

Such reactions are not the concern of the present investigation and will not be considered further.

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

Nucleophilic Substitution,

$Y: + R|:X \rightarrow Y:R + :X$ (Termed $S_N$),

Electrophilic Substitution,

$Y + R:|X \rightarrow Y:R + X$ (Termed $S_E$).

In the first type, the expelled group X carries the bonding electrons away with it and the deficit on R is made up by electrons from the attacking group which is termed "nucleophilic",

e.g. $I^- + R - Cl \rightarrow I - R + Cl^-.$

In the second type, the expelled group leaves the bonding electrons behind. The attacking agent has a deficit of electrons which is made up by the excess on R. The attacking group is thus termed "electrophilic",

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

Again, only the nucleophilic type is the concern of the present investigation. The old bond, as stated above, is broken by heterolysis and the new bond is formed by co-ordination. There is an electron transfer from the substituting agent Y to the centre of substitution in R, and from this centre to the expelled group X, so that, in consequence of the substitution, Y becomes formally one electronic unit more positive and X one unit more negative. Subject to this there need be no restriction on the states of electrification of the species involved. For example, Y may be neutral as in the hydrolysis of an alkyl halide,

$$RCl + H_2O \longrightarrow ROH + HCl,$$

or negative, as in the Finklestein reaction,

$$RCl + I^- \longrightarrow RI + Cl^-.$$

Mechanisms of Nucleophilic Substitution.

Two mechanisms have been proposed for nucleophilic substitution. The first is a bimolecular process which occurs in a single stage and involves the direct attack of Y on RX, the two molecules simultaneously undergoing covalency change. This mechanism is labelled $S_N2$ and may be represented thus, in the case where Y is a negative ion,

$$\overline{Y}: + R - X \rightarrow \left[ Y^{\delta-} \cdots R \cdots X^{\delta-} \right] \rightarrow Y - R + :\overline{X} \quad (S_N2).$$

In the case where Y is neutral the charge distribution in

the transition state will be appropriately different. This type of process had already been suggested by Lewis (18) and was also used by London (19) in a discussion of the reaction $H + H_2 \rightleftharpoons H_2 + H$, which, although not a heterolytic reaction, involves an analogous synchronous bond forming and breaking process.

The second method of nucleophilic substitution involves two stages, a slow heterolysis of the compound substituted is followed by a rapid co-ordination between the formed carbonium ion and the substituting agent. The rate determining stage is the first, and since in that stage only one molecule is undergoing covalency change, the mechanism is called unimolecular and labelled $S_N1$. It may be represented thus, in the case where Y is a negative ion,

$$R - X \rightarrow \left[ R^{\delta+} \text{-------} X^{\delta-} \right] \rightarrow R^+ + X^- \quad \text{(Slow)}$$
$$R^+ + Y^- \rightarrow R - Y \quad \text{(Fast)} \qquad (S_N1).$$

The rate controlling ionisation is slow because it must pass through an energy maximum for a certain extension of the bond and a certain critical degree of charge transfer. The very large energy values required for the formation of gaseous ions accounts for the fact that thermal ionisation does not occur at ordinary temperatures, but is is considered that in the $S_N1$ reaction, which occurs in solution,

the energy maximum is reduced to accessible values by solvation forces which increase as the charge transfer increases.

The Kinetic Criterion of Mechanism.

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

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

However there are circumstances in which the $S_N2$ mechanism will lead to first order kinetics as, for instance, when the substituting agent is in constant excess, e.g. the solvent. In such a case the first order rate constant $k_1$ would be equal to $k_2 [Y]$.

The unimolecular mechanism of substitution will lead to first order kinetics, with an overall rate equal to the heterolysis rate, if the rate of reversal of the heterolysis is much smaller than the rate of co-ordination of the carbonium ion with the substituting agent. When the above condition does not apply, the $S_N1$ reaction will proceed by a complex kinetic form (20) as discussed in the second part of this thesis.

Determination of Mechanism.

As shown above, the kinetics of reaction do not

necessarily give a clear indication of the mechanism. Various supplementary methods are available which are summarised below.

(i) Effect of structural changes in the compound substituted on reaction rate.

(ii) Effect of systematic changes in the substituting agent on reaction rate.

(iii) Effect of solvent changes on reaction rate and on the products.

(iv) The stereochemical course of the substitution.

(v) The kinetic form of the substitution reaction.

(vi) Effect of salt additions on rate and products.

Method (i) involves the effect of substituent groups on reaction rate as a result of changes of the electron density at the reaction centre due to their introduction. This is of considerable importance in this investigation as it can also be used to examine the electron displacements due to substituents by noting their effects on the rate of a reaction where the mechanism, and therefore the electron configuration of the activated complex are already established. This is elaborated for substituted alkyl halides later in this chapter.

Full details of the general methods, mentioned above, for the elucidation of the mechanism of nucleophilic

substitution may be obtained by reference to a review by Hughes (21). The experimental results are invariably in accordance with the theoretical picture.

Further reference to the effect of changes in the solvent composition on rate, however, seems suitable at this stage as the principles involved are applied in later discussions.

Solvent Effects.

It has already been pointed out that most of the transition states and some of the reactants involved in nucleophilic substitution reactions possess formal electric charges. Such species will be solvated to some extent in solution. Solvation is essentially an electrostatic phenomenon. When an ion or polar molecule is put into a solvent having polar molecules, it orientates and attracts the molecules of the solvent thereby doing electrostatic work, and work done means energy lost so that the system becomes more stable. The energy of solvation of an ion in a polar solvent can be very large, often of the order of the strength of a covalent bond. It follows that a change from a less polar to a more polar solvent will increase or decrease the exothermicity of the reaction according as the products are more or less polar than the factors.

The nucleophilic reactions considered here are charac-

terised by important electrical transferences in the reactant species. The influence of the solvent may therefore be expected to be highly important in these reactions and since the effect must depend on the precise manner in which the electrical transferences take place, a change of medium should affect the two mechanisms both absolutely and relative to one another.

The influence of the solvent may be assessed by considering the magnitude and distribution of the charges in the transition state of each mechanism in relation to those of the reactants. It is reasonable to assume that strongly solvating (ionising) solvents facilitate an increase in the magnitude of the charges, inhibit a decrease and retard the distribution of a given charge, and that furthermore, a reaction in which the formation of the transition state involves an increase or decrease in the magnitude of the charges will be subject to a stronger solvent influence than one wherein a given charge is distributed in the transition state. On the basis of these assumptions, the solvent effect can be predicted for the various nucleophilic charge types. The three main charge types are set out in table II-1 where it is shown that the predictions are wholly in agreement with the experimental observations, in all three cases.

Table II-1.

PREDICTED AND OBSERVED SOLVENT EFFECTS. (22)

| Type | Mechanism | Charges in Rate Determining Stage | | | Predicted Effects of Polar Media on Reaction Rates |
|---|---|---|---|---|---|
| | | Reactants | Transition State | Products | |
| A | $S_N1$ | R - X | $^{\delta+}R\text{-------}X^{\delta-}$ | $R^+ + X^-$ | Strong Acceleration |
| B | $S_N2$ | $\bar{Y}$ + R - X | $^{\delta-}Y\text{---}R\text{---}X^{\delta-}$ | Y - R+$X^-$ | Weak Retardation |
| C | $S_N2$ | $^{\cdot\cdot}Y$ + R - X | $^{\delta+}Y\text{---}R\text{---}X^{\delta-}$ | Y - $^{+}R$ +$X^-$ | Strong Acceleration |

| Type | Example | Mechanism | Rate Constant | Vol. % of $H_2O$ in aq.EtOH | | | | | Observed Effect |
|---|---|---|---|---|---|---|---|---|---|
| | | | | 0 | 10 | 20 | 30 | 40 | |
| A | tBuCl+$H_2O$ | $S_N1$ | $10^6k_1$ at 25° | - | 1.71 | 9.14 | 40.3 | 126. | Strong Accelern. |
| B | iPrBr+$OH^-$ | $S_N2$ | $10^5k_2$ at 55° | 6.0 | - | 4.9 | - | 3.0 | Weak Retardation. |
| C | iPrBr+$H_2O$ | Mainly $S_N2$ | $10^7k_1$ at 55° | 1.73 | - | 23.6 | - | 66.7 | Strong Accelern. |

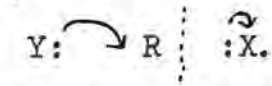
NOTE. The rate constants given for reaction by the bimolecular mechanism refer to substitution only, accompanying olefin elimination having, where necessary, been allowed for. Second order rate constants, $k_2$, are given in $sec^{-1}$ $mole^{-1}$ l, first order rate constants, $k_1$, in $sec^{-1}$.

The Effect of Substituents on Reactivity.

As stated earlier, the effect of substituents on reactivity will depend on the mechanism in operation.

Bimolecular Substitution.

Bimolecular substitution involves simultaneous electron transfers from the substituting agent to the reaction centre and from the latter to the expelled group. The first process will be favoured by a low electron density at the reaction centre and the second process will be favoured by a high electron density at the reaction centre, as illustrated below,



Thus, electron releasing substituents some distance from the reaction centre facilitate removal of the group X but oppose approach of the group Y. Electron attracting groups will have the opposite effect. (Substituents near to the reaction centre may, in addition, exert a steric effect). In general, one of these two opposing processes will predominate so that substituents may be expected to affect the rate by altering the electron density at the reaction centre, but since such an alteration affects the outgoing and incoming groups in an opposite manner, the resultant of two such opposing effects will be small and its direction will be ambiguous. This ambiguity is illustrated by the data

in table II-2 refering to the exchange between p-substituted benzyl bromides and radioactive bromide ions in ethylene diacetate, obtained by Sugden and Willis. (23).

Table II-2.

EFFECT OF SUBSTITUENTS ON $S_N2$ REACTIVITY.

(Relative 2nd order rates $k_X/k_H$ at 25°-Arrhenius parameters)

| Reaction | $k_X/k_H$ | $E_A$ | B/2.303 |
|---|---|---|---|
| p-$NO_2$-Benzyl bromide + $Br^{*-}$ | 11.2 | 15.11 | 7.77 |
| p-CN-Benzyl bromide + $Br^{*-}$ | 10.0 | 16.57 | 8.79 |
| Benzyl bromide + $Br^{*-}$ | 1. | 14.97 | 6.62 |
| p-MeO-Benzyl bromide + $Br^{*-}$ | 6.2 | 13.66 | 6.45 |

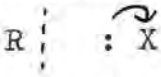
Note. Arrhenius parameters calculated from the modified equation $\ln(k/T^{\frac{1}{2}}) = B - E_A/RT$. Units of $E_A$ kilocals/mole.

It can be seen that both electron repelling groups, such as MeO, and electron attracting groups, such as CN and $NO_2$, increase the rate relative to the parent compound. Examination of Arrhenius parameters shows that electron releasing groups affect the rate by reducing $E_A$, i.e. by facilitating the breaking of the existing bond, and leaving the B factor virtually unchanged. Electron attracting groups, c.f. $NO_2$, in the first place affect the B factor, which is related to the entropy of activation, and we can therefore

consider that their primary effect is to increase the chance of bond formation with the approaching ion. Sugden and Willis considered this might be due to thinning of the $\overline{\pi}$ electron screen round the ring. Electron withdrawal from the reaction centre is sufficiently powerful in the case of the CN substituted compound to increase the energy required to break the original bond as well.

Unimolecular Substitution.

In the rate determining stage of a unimolecular substitution reaction there is an electron transfer from the reaction centre to the displaced group without any compensating gain of electrons by the reaction centre,



A large polar effect is thus to be expected and its direction is unambiguous. Electron release must facilitate such substitutions by stabilising the transition state and polarisability effects resulting in electron release can be expected to operate. An example of the facilitation of the unimolecular rate by electron release is to be found in the hydrolysis in aqueous formic acid (a medium favourable to the $S_N1$ mechanism due to its high ionising power) of alkyl bromides. The order of reactivity is MeBr < EtBr < iso-PrBr< tert-BuBr (24) which is also the order of increasing electron release by the alkyl groups. In less ionising solvents,

e.g. 80% aq.alcohol (25), the position of the first two members of the series is inverted due to the fact that they are now undergoing reaction by the bimolecular mechanism.

The results obtained by Branch and Nixon (26) for the alcoholysis of the para substituted triphenyl-methyl chlorides, and by Kohnstam (27) (28) for the hydrolysis in aq.acetone of the para substituted benzhydryl chlorides, both of which reactions are unimolecular, indicate clearly the polar effects of the various substituents when in the para position of a phenyl group attached to the reaction centre. Their results are summarised in table II-3, relative first order rates, $k_X/k_H$, are given together with the Arrhenius parameters.

The results for the triphenyl-methyl chlorides are probably not very accurate due to the high rates (e.g. $k_H$ = 0.0936 $min^{-1}$ at 0°). The result for the p-$NO_2$ compound in particular seems doubtful. Consideration of these results, together with those for the benzhydryl chlorides indicates, however, that the effect of the para substituents is largely shown in the $E_A$ values, a point of difference with the bimolecular case quoted earlier.

It is to be noted that fluorine, unlike the other halogens, is capable of acting as an overall electron releasing group compared with H, in the benzhydryl chlorides. The

Table II-3.

EFFECT OF SUBSTITUENTS ON $S_N1$ REACTIVITY.

(Relative first order rates, $k_X/k_H$, and Arrhenius parameters).

| Reaction | X= | $NO_2$ | I | Br | Cl | F | H | Me |
|---|---|---|---|---|---|---|---|---|
| Triphenyl-methyl chlorides in 40% EtOH-60% ether (26) | $k_X/k_H$ at 0° | 0.007 | 0.35 | 0.26 | 0.32 | 0.74 | 1. | 4.61 |
| | $E_A$ } 0°-25° | 17.95 | 13.20 | 14.05 | 13.48 | 13.57 | 13.43 | 12.28† |
| | B/2.303) | 9.36 | 7.30 | 7.83 | 7.47 | 7.91 | 7.93 | 7.67† |
| Benzhydryl chlorides in 70% aq.acetone (27) (28) | $k_X/k_H$ at 25° | 0.001‡ | 0.28 | 0.25 | 0.32 | 1.9 | 1. | 21.1† |
| | $E_A$ } 0°-25° | 25.25‡ | 21.4 | 21.4 | 21.3 | 20.2 | 20.8 | - |
| | B/2.303) | 12.14‡ | 11.89 | 11.82 | 11.88 | 11.84 | 12.00 | - |

NOTE. Arrhenius parameters calculated from the equation $\ln k = B - E_A/RT$.
Units of $E_A$ kilocals/mole.

† These results were calculated from data at 0° and 10°.

‡ This comparison was made in 85% aq.acetone.

‡ These results were extrapolated from data at higher temperatures.

order of the reactivity of the benzhydryl chlorides, and in particular the fact that fluorine can act as an overall electron releasing group, indicates that there is electromeric release operating in the order F ) Cl ) Br > I.

The inductive and conjugative effects of the halogens act in opposition, i.e. the inductive effect attracts electrons and the conjugative effect releases electrons. In the above examples, the predominant effect is the inductive effect except for fluorine in the case mentioned. This overall electron release by fluorine in the para position has been observed by Bennett (29) in the hydrolysis of the para sustituted benzyl chlorides but the mechanism is in doubt in that case.

Summary of Polar Effects of the Halogens.

The data on physical properties and reaction equilibria, discussed in chapter I, and on the effects of substituents on reactivity just discussed here, indicate the following for the polar effect of the halogens,

$-I_s$ decreasing in the order F > Cl > Br > I,

+M decreasing in the order F > Cl > Br > I,

+E decreasing in the order F > Cl > Br > I.

No evidence has been obtained for the inductomeric effect, from kinetic data, because in the cases so far considered, where the substituent is at a distance from the

reaction centre, it is unlikely to have any appreciable effect, but it may be illustrated for the halogens by the hydrolysis of the tert-butyl halides (30). This reaction proceeds by the $S_N1$ mechanism and the transition state is therefore facilitated by electron attraction by the halide group. As this group contains unshared electrons, attraction due to the -E effect is likely to be small and, other things being equal, the reaction should be controlled by the combined -I and inductomeric effects of X. Both rate constants and Arrhenius activation energies indicate overall electron attraction in the order I > Br > Cl > F and this leads to the conclusion that the inductomeric effect must follow the same sequence, since the -I effect follows the reverse sequence.

The variation of polar effects within the halogen series has thus been shown in every case to be as predicted in chapter I.

## CHAPTER III.

## EFFECT OF SUBSTITUENTS IN RELATION TO THEIR POSITION.

It has been shown in the previous chapter that $S_N1$ reactions give a clear indication of the polar effects of substituents. Substituents which release electrons to the reaction centre facilitate reaction and substituents which attract electrons from the reaction centre retard reaction. These statements have been shown to be true by considering cases in which the substituent was at a distance from the reaction centre and it is now proposed to consider what additional effects, or what modification of the polar effects, result from the substituent being directly attached to the reaction centre.

Table III-1 compares the effects of several electron releasing groups on $S_N1$ reactivity, (a) at the reaction centre and (b) in the para position of a phenyl group attached to the reaction centre. In all cases the results show, even though they are only order of magnitude calculations, that there is a more effective relay of polar effects when the substituent is directly attached to the reaction centre.

It was shown in the previous chapter that all of the halogens except fluorine are overall electron attractors

Table III-1.

EFFECT OF SUBSTITUENTS IN RELATION TO THEIR POSITION.

Relative first order rate constants, $k_X/k_H$.

| Position of Substituent | $k_X/k_H$ | Reactions Compared | |
|---|---|---|---|
| METHYL. | | | |
| p | 21 | $Ph_2CHCl$ in 85% aq. acetone.<br>p-Me-$Ph_2CHCl$ in 85% aq. acetone. | (28) |
| $\alpha$ | $\sim 10^6$ | iso-PrBr in moist formic acid.<br>tert-BuBr in moist formic acid. | (24) |
| PHENYL | | | |
| p | 7 | $Ph_2CHCl$ in 85% aq. acetone.<br>p-Ph-$Ph_2CHCl$ in 85% aq. Acetone. | (28) |
| $\alpha$ | $\sim 10^4$ | $Ph_2CHCl$ in 40% EtOH-60% ether.<br>$Ph_3CCl$ in 40% EtOH-60% ether. | (26) |
| METHOXY. | | | |
| p | 5500 | $Ph_2CHCl$ in 60% EtOH-40% ether.<br>p-MeO-$Ph_2CHCl$ in 60% EtOH-40% ether. | (28) |
| $\alpha$ | $\sim 10^8$ | †$CH_3Cl$ in 90% ether-10% EtOH.<br>$CH_2(MeO)Cl$ in 90% ether-10% EtOH. | (28) |

NOTE. Symbol p refers to substituents in para positions of phenyl groups attached to reaction centre. Symbol $\alpha$ refers to substituents directly attached to reaction centre.

† Rate for MeCl estimated from rate of MeBr in absolute alcohol. (This rate will be mainly $S_N2$ but will represent a top limit for the $S_N1$ rate).

when in the para position of a phenyl group attached to the reaction centre and that their introduction influences the rate mainly by their effect on $E_A$. In view of the fact that electron release by substituents is enhanced when they are situated at the reaction centre it was of interest to determine whether other halogens, and in particular chlorine, could act as overall electron releasing groups under these conditions.

Chlorine Substitution at the Reaction Centre.

It was found that the only published work on the effect of $\alpha$-chlorine substitution on $S_N1$ reactivity was on the hydrolysis of the side chain chlorine substituted toluenes, benzyl chloride, benzal chloride and benzotrichloride. Although in each case all of the halogen atoms are hydrolysed off, it is considered that, after the first has been replaced by an OH group, the others will come off immediately owing to the strong electron release of the OH group. The observed rate will thus be the rate of ionisation of the first chlorine atom and the polar effects of the others will be likely to affect that rate.

Olivier and Weber (31) have examined the hydrolysis of all three compounds in 50% aqueous acetone. Their results, which are summarised in table III-2, show that the order of reactivity is $PhCCl_3 > PhCHCl_2 > PhCH_2Cl$.

The rate of hydrolysis of benzyl chloride is accelerated by hydroxyl ions, which fact makes its mechanism of hydrolysis doubtful. In the case of the other two compounds hydroxyl ions have no effect on the rate and the mechanism of hydrolysis of each is therefore probably $S_N1$.

Table III-2.

HYDROLYSIS OF $PhCH_2Cl$, $PhCHCl_2$ AND $PhCCl_3$ IN 50% AQ.ACETONE.

(Olivier and Weber).

(First order rate constants x $10^5$ & Arrhenius parameters).

| Compound | $k_{30}$ | $k_{60}$ | $E_A$ | B/2.303 |
|---|---|---|---|---|
| $PhCH_2Cl$ | 2.2 | 48. | 20.64 | 8.43 |
| $PhCHCl_2$ | 23. | 660. | 22.48 | 10.78 |
| $PhCCl_3$ | 1100. | - | - | - |
| Units of $E_A$ kilocals/mole. Units of k $min^{-1}$. | | | | |

The large difference in B factor between benzyl chloride and benzal chloride may be due to a change in mechanism, in which case a comparison of activation energies would not be legitimate in order to decide whether the increased reactivity of benzal chloride was due to electron release by the additional chlorine or to some other effect, e.g. steric or solvation. In the case of benzotrichloride no Arrhenius

parameters were available.

Two recent investigations of the hydrolysis of benzal chloride and benzotrichloride have lead to conflicting results as to the variation of arrhenius parameters.

Hine and Lee (32), in an investigation of many of the side chain halogen substituted derivatives of toluene in 50% aqueous acetone, obtained results which were in good agreement with those of Olivier and Weber. Their results for benzyl chloride, benzal chloride and benzotrichloride are given in table III-3 (B and $\Delta S^{\ddagger}$ values calculated here).

Table III-3.

HYDROLYSIS OF $PhCH_2Cl$, $PhCHCl_2$ AND $PhCCl_3$ IN 50% AQ. ACETONE.

(Hine and Lee).

(First order rate constants x $10^4$. $E_A$, B and $\Delta S^{\ddagger}$ values).

| Compound | $k_{20}$ | $k_{30}$ | $k_{45}$ | $E_A$ | B/2.303 | $\Delta S^{\ddagger}$ |
|---|---|---|---|---|---|---|
| $PhCH_2Cl$ | - | 0.2231 | 1.174 | 21.23 | 8.87 | -20.0 |
| $PhCHCl_2$ | - | 2.214 | 13.66 | 23.26 | 11.33 | - 8.75 |
| $PhCCl_3$ | 34.55 | 110.5 | - | 20.54 | 11.06 | - 9.80 |

$\Delta S^{\ddagger}$, entropy of activation from Eyring equation (33), in cals/mole/deg. $E_A$ in kilocals/mole. k in $min^{-1}$.

Ignoring benzyl chloride because of its doubtful mechanism, these results show that $\alpha$-chlorination of benzal

chloride reduces $E_A$ and has little effect on B (and therefore $\Delta S^{\ddagger}$). This, Hine and Lee attribute to resonance stabilisation of the transition state by the additional chlorine atom due to electron release via the conjugative mechanism.

Evans and Hamann (34) have studied the hydrolysis of benzal chloride and benzotrichloride in 80% aqueous alcohol conductimetrically, the mechanism being considered $S_N1$ in both cases. The rate constants they obtained, together with the activation energies and $\Delta S^{\ddagger}$ values as quoted by them, are given in table III-4.

Table III-4

HYDROLYSIS OF $PhCHCl_2$ AND $PhCCl_3$ IN 80% AQUEOUS ALCOHOL.

(Evans and Hamann).

(First order rate constants x $10^7$. $E_A$ and $\Delta S^{\ddagger}$ values).

| Compound | $k_0$ | $k_{20}$ | $k_{60}$ | $k_{80}$ | $E_A$ | $\Delta S^{\ddagger}$ |
|---|---|---|---|---|---|---|
| $PhCHCl_2$ | 0.122 | 2.69 | 269 | 1780 | 22.7 | -12.8 |
| $PhCCl_3$ | 1.20 | 25.8 | - | - | 24.4 | - 2.7 |

Units of k $sec^{-1}$. Units of $E_A$ and $\Delta S^{\ddagger}$ as in table III-3.

Evans and Hamann actually quoted $\Delta H^{\ddagger}$ values but these have been converted to $E_A$ values in order to facilitate comparison with the other results. ($E_A = \Delta H^{\ddagger} + RT$).

These results show that $\alpha$-chlorination increases $E_A$ and increases $\Delta S^{\ddagger}$. Evans and Hamann consider that, since the $S_N1$ mechanism involves the development of charges on the R and X groups in the transition state, it might be expected that the entropy of activation would run parallel with the entropy of solvation of the free $R^+$ and $X^-$ ions. They consider that it is the change in these entropies of solvation which largely determine the change in $\Delta S^{\ddagger}$ for these reactions. Further, they consider that an $\alpha$-substituent will reduce the "freezing" of solvating water in the first solvation shell of an ion by an amount proportional to its volume, $v_s$, within that shell. For a number of alkyl chlorides they have estimated the values of $v_s$ for each $\alpha$-substituent in the alkyl groups and the sum of these, $V_s$, for each alkyl group. They have shown that a plot of $V_s$ vs. $\Delta S^{\ddagger}$ of hydrolysis is roughly linear, which fact would seem to justify their treatment.

A comparison of the values of $E_A$ and $\Delta S^{\ddagger}$ obtained by Hine and Lee on the one hand and Evans and Hamann on the other is given in table III-5. It will be observed that there are serious discrepancies and it is extremely unlikely that they can be wholly attributed to the difference in solvent.

It has been shown in the hydrolysis of organic halides

Table III-5.

HYDROLYSIS OF $PhCHCl_2$ AND $PhCCl_3$

($E_A$ in kilocals/mole. $\Delta S^{\ddagger}$ in cals/mole/deg).

| Investigators | $E_A$ | | $\Delta S^{\ddagger}$ | |
|---|---|---|---|---|
| | $PhCHCl_2$ | $PhCCl_3$ | $PhCHCl_2$ | $PhCCl_3$ |
| Hine and Lee | 23.26 | 20.54 | - 8.75 | -9.80 |
| Evans and Hamann | 22.7 | 24.4 | -12.8 | -2.7 |

by the $S_N1$ mechanism, that the activation energy decreases approximately linearly as the temperature rises, and this has been interpreted as due to the difference in heat capacities of the initial and activated states due to solvation of the latter (27). Neither of the above pairs of investigators took into consideration such a variation of $E_A$ (and in consequence $\Delta S^{\ddagger}$) with temperature and therefore some errors may be caused by comparing values obtained for different temperature ranges. In the case of Hine and Lee, rate constants were obtained for benzal chloride and benzotrichloride at two temperatures only in each case so that it is not possible to determine whether their values did vary with temperature or not. However, as the temperature ranges used for both compounds were fairly close, no serious errors are likely to be introduced by comparing the results as they stand.

In the case of Evans and Hamann, benzal chloride was investigated at four temperatures. Calculation of $E_A$ and $\Delta S^{\ddagger}$ for adjacent temperature intervals indicated that they do vary with temperature. The revised values are given in table III-6.

Table III-6.

HYDROLYSIS OF $PhCHCl_2$ AND $PhCCl_3$ IN 80% AQUEOUS ALCOHOL.

(Revised $E_A$ and $\Delta S^{\ddagger}$ values from rates of Evans and Hamann).

| $PhCHCl_2$ | | | | | $PhCCl_3$ |
|---|---|---|---|---|---|
| Temp. range | $0^\circ$-$20^\circ$ | $20^\circ$-$60^\circ$ | $60^\circ$-$80^\circ$ | | $0^\circ$-$20^\circ$ |
| $E_A$ | 24.63 | 22.35 | 22.10 | | 24.42 |
| $\Delta S^{\ddagger}$ | -6.5 | -14 | -15 | | -2.7 |
| Units as in table III-5. | | | | | |

The activation energy for benzal chloride decreases with rise in temperature but in an erratic way. This is probably due to errors in the rate constants at one or more temperatures, but it is not possible to decide from the quoted data which results might be inaccurate. However, the $E_A$ and $\Delta S^{\ddagger}$ values for the temperature range $0^\circ$ - $20^\circ$ seem most likely to be in error and it is probable that they should both be lower than given. This would probably make

them not very different from the values quoted by Evans and Hamann for the complete temperature range, which were presumably calculated by graphical methods. It follows therefore that even after taking into account the variation of $E_A$ and $\Delta S^{\ddagger}$ with temperature, the results of these two investigations show considerable deviations.

Both investigations showed that benzotrichloride hydrolyses more quickly than benzal chloride, Hine and Lee obtaining a rate ratio of about 50 while Evans and Hamann obtained a rate ratio of about 10. If electron release to the reaction centre is the predominant factor in the increased rate of benzotrichloride, it is to be expected that its $E_A$ would be lower than that for benzal chloride. The two investigations conflict on this point. In addition, Evans and Hamann obtained a much lower $\Delta S^{\ddagger}$ for the dichloride as compared with the trichloride. As mentioned above this lower $\Delta S^{\ddagger}$ for the dichloride they explain as due to greater solvation of its transition state. If the value of $\Delta S^{\ddagger}$ can be taken as a measure of solvation in the transition state, then $\Delta S^{\ddagger}$ for the dichloride should presumably be much lower than $\Delta S^{\ddagger}$ for the trichloride in the aqueous acetone solvent also. This lower $\Delta S^{\ddagger}$ for the dichloride is not reported by Hine and Lee.

In view of the discrepancies between the trends of $E_A$ and $\Delta S^{\ddagger}$ in these two investigations, the role of an $\alpha$-chlorine substituent cannot be regarded as clear and it was considered desirable to look into the matter again.

Towards the end of the present investigation, Vernon (35) published his results on the reactivities of various substituted allyl chlorides, the $\alpha$-chlorine substituted compound being one of them. These results will be discussed in relation to the results obtained here in a later chapter.

## CHAPTER IV.

## EFFECT OF α-CHLORINE SUBSTITUTION ON REACTIVITY.

### SUMMARY OF RESULTS.

The problem concerns α-chlorine substitution generally and it was initially decided to examine the hydrolysis of diphenylmethyl chloride and diphenylmethylene chloride since, as is shown below, they both undoubtedly react by the $S_N1$ mechanism. It was found however, that for the dichloride in aqueous solvents, the integrated rate constants dropped as the reaction proceeded. This effect, which was still in evidence when the concentration of reactant was reduced to about 0.0025M, can be accounted for on the basis of mass-law and ionic strength effects (20) as described in the second part of this thesis. Only in absolute alcohol could steady first order rate constants be obtained of a convenient speed.

In view of this, the main investigation was switched to the series benzyl chloride, benzal chloride, benzotrichloride, although, as stated earlier, the mechanism of hydrolysis of benzyl chloride is doubtful. The reactions of these three compounds have been investigated in 50% aq. alcohol, 50% aq.acetone and, excluding benzyl chloride, in 80% aq.alcohol. The reactions of diphenylmethyl chloride

and diphenylmethylene chloride have been investigated, in lesser detail than in the other cases, in absolute alcohol. The disturbing effects in the hydrolysis of diphenylmethylene-chloride in aqueous acetone have been investigated in the second part of this thesis.

a) Alcoholysis of Diphenylmethyl and Diphenylmethylene Chlorides.

It has been shown that the alcoholysis and hydrolysis in aqueous acetone of diphenylmethyl chloride is unimolecular and irreversible (36) (37) (38). This is to be expected since it has been shown (27) that the $S_N2$ transition state for its hydrolysis would be appreciably strained. In the case of diphenylmethylene chloride there would be even more strain and, anticipating the results of the second part of this thesis, it can be said that it shows salt effects in aq.acetone, precisely as expected in the unimolecular mechanism. The operation of the unimolecular mechanism in the hydrolysis of diphenylmethylene chloride is confirmed by the fact that the addition of a strong base, such as triethylamine, produces no increase in the rate in aq.acetone (c.f. experiments 2 and 20 in part II). It has been established here that its reactions are irreversible.

Steady first order rate constants were obtained for

both diphenylmethyl chloride and diphenylmethylene chloride in absolute alcohol and kinetic runs were carried out in this solvent for both compounds at $0^{\circ}$ and $20^{\circ}$C. The investigation was not continued at further temperatures since these would have had to be under $0^{\circ}$, a region difficult to work in with a highly hygroscopic solvent such as absolute alcohol. The average rate constants for this set of runs are given in table IV-1 together with Arrhenius parameters, calculated from the equation $\ln k = B - E_A/RT$ (39) and entropies of activation calculated from the Eyring equation for solution reactions, $k = \frac{ekT}{h} e^{-E_A/RT} e^{\Delta S^{\ddagger}/R}$ (33). Full run details are available in the experimental chapter.

Table IV-1.

HYDROLYSIS OF $Ph_2CHCl$ AND $Ph_2CCl_2$ IN ABSOLUTE ALCOHOL.

| Compound | $k_0$ | $k_{19.97}$ | $E_A$ | B/2.303 | $\Delta S^{\ddagger}$ |
|---|---|---|---|---|---|
| $Ph_2CHCl$ | $1.732 \times 10^{-6}$ | $2.820 \times 10^{-5}$ | 22.23 | 12.02 | -5.43 |
| $Ph_2CCl_2$ | $3.169 \times 10^{-5}$ | $4.183 \times 10^{-4}$ | 20.56 | 11.95 | -5.74 |

First order rate constants in $sec^{-1}$. Subscripts to k's refer to temp. in deg.C. $E_A$ in kilocals/mole. $\Delta S^{\ddagger}$ in cals/mole/deg.

b) Reactions of Benzyl Chloride, Benzal Chloride and Benzotrichloride in 50% (by volume) aq.Alcohol.

It has been shown that the hydrolysis in aqueous solvents of benzal chloride and benzotrichloride is not accelerated by hydroxyl ions (31). This is strong evidence that the unimolecular mechanism is in operation. The hydrolysis of benzyl chloride is accelerated by hydroxyl ions in aqueous solvents (31) (40). This makes the mechanism doubtful and it will be discussed in a later chapter.

Steady first order rate constants were obtained for all three compounds, the initial concentration of reactant always being such as to produce a final HCl concentration of about 0.015N, for convenience of analysis.

The effect of an approximately 100% increase in the initial concentration of reactant on rate is given for benzal chloride and benzotrichloride in table IV-2. In the case of benzal chloride, such an increase produces a drop of about 1% in the rate, and in the case of benzotrichloride a drop of 2 - 3%. The variation for the trichloride is not appreciably temperature dependent. The actual variation of initial concentration of any one reactant in this investigation was always under 30% in practice, so that any error due to this effect will be negligible.. This small concentration dependence of the rates is probably due to slight mass-law and ionic strength effects (20), which, although they balance each other in a particular run,

may produce an overall concentration effect.

Table IV-2.

EFFECT OF CONCENTRATION OF REACTANT ON RATE IN 50% AQ.ALCOHOL.

(Average first order rate constants in $sec^{-1}$ corrected to solvent I).

| Expt. No. | Compound | Initial Concentration | Temp°C. | k x $10^4$ |
|---|---|---|---|---|
| 15 | $PhCHCl_2$ | 0.008125M | 60.07 | 4.491 |
| 16 | $PhCHCl_2$ | 0.01647M | 60.07 | 4.453 |
| 20 | $PhCCl_3$ | 0.005586M | 20.04 | 1.282 |
| 22 | $PhCCl_3$ | 0.01014M | 20.04 | 1.248 |
| 23 | $PhCCl_3$ | 0.005190M | 29.99 | 4.390 |
| 24 | $PhCCl_3$ | 0.01147M | 29.99 | 4.322 |

Rate constants were obtained for each compound at $10^o$ intervals over $40^o$. All rate constants refer to the same solvent, a correction having been applied to those cases where different batches of solvent were used, as described in the experimental chapter. Values of the activation energy and B factor were calculated from the Arrhenius equation for adjacent temperature intervals. It was found that the values of both were dependent on the

TABLE IV-3.

HYDROLYSIS OF BENZYL CHLORIDE IN 50% AQUEOUS ALCOHOL.

| EXPERIMENTAL VALUES. | | | | LEAST SQUARE VALUES. | | | |
|---|---|---|---|---|---|---|---|
| Temp. | k | Mean Temp. | $E_A$ | Mean Temp. | $E_A$ | B/2.303 | $\Delta S^*$ |
| 39.99 | $4.521 \times 10^{-6}$ | 44.99 | 20.83 | 45.00 | 20.74 | 9.132 | -18.9 |
| 49.99 | $1.274 \times 10^{-5}$ | 55.02 | 20.44 | 55.00 | 20.46 | 8.940 | -19.8 |
| 60.05 | $3.332 \times 10^{-5}$ | 64.90 | 20.06 | 65.00 | 20.17 | 8.752 | -20.7 |
| 69.75 | $7.852 \times 10^{-5}$ | 74.90 | 19.83 | 75.00 | 19.88 | 8.567 | -21.6 |
| 80.06 | $1.836 \times 10^{-4}$ | 85.04 | 19.70 | 85.00 | 19.60 | 8.389 | -22.5 |
| 90.02 | $3.968 \times 10^{-4}$ | $d(E_A)/dT = -29$ cals/mole/deg. | | | | | |

NOTE. Mean first order rate constants in $sec^{-1}$ - Average of at least two runs. Units of $E_A$, kilocals/mole. Units of $\Delta S^*$, cals/mole/deg. Temperature in degrees centigrade. Rate constants corrected to solvent I.

TABLE IV-4.

HYDROLYSIS OF BENZAL CHLORIDE IN 50% AQUEOUS ALCOHOL.

| EXPERIMENTAL VALUES. | | | | LEAST SQUARE VALUES. | | | |
|---|---|---|---|---|---|---|---|
| Temp. | k | Mean Temp. | $E_A$ | Mean Temp. | $E_A$ | B/2.303 | $\Delta S^*$ |
| 20.04 | $3.604 \times 10^{-6}$ | 25.02 | 24.15 | 25.00 | 24.20 | 12.59 | -2.90 |
| 30.01 | $1.408 \times 10^{-5}$ | 35.00 | 23.69 | 35.00 | 23.63 | 12.18 | -4.84 |
| 39.99 | $4.928 \times 10^{-5}$ | 44.99 | 23.10 | 45.00 | 23.06 | 11.79 | -6.72 |
| 49.99 | $1.555 \times 10^{-4}$ | 55.03 | 22.45 | 55.00 | 22.49 | 11.40 | -8.54 |
| 60.07 | $4.477 \times 10^{-4}$ | $d(E_A)/dT = -57$ cals/mole/deg. | | | | | |

NOTE. Rate constants corrected to solvent I. Units, etc. as before.

TABLE IV-5.

HYDROLYSIS OF BENZOTRICHLORIDE IN 50 % AQUEOUS ALCOHOL.

| EXPERIMENTAL VALUES. | | | | LEAST SQUARE VALUES. | | | |
|---|---|---|---|---|---|---|---|
| Temp. | k | Mean Temp. | $E_A$ | Mean Temp. | $E_A$ | B/2.303 | $\Delta S^{\ddagger}$ |
| 0.00 | $7.043 \times 10^{-6}$ | 5.04 | 23.29 | 5.00 | 23.37 | 13.54 | +1.57 |
| 10.08 | $3.240 \times 10^{-5}$ | 15.06 | 22.79 | 15.00 | 22.66 | 12.99 | -1.01 |
| 20.04 | $1.283 \times 10^{-4}$ | 25.01 | 21.90 | 25.00 | 21.95 | 12.47 | -3.48 |
| 29.99 | $4.399 \times 10^{-4}$ | 35.01 | 21.23 | 35.00 | 21.24 | 11.96 | -5.88 |
| 40.04 | $1.362 \times 10^{-3}$ | $d(E_A)/dT$ = -71 cals/mole/deg. | | | | | |

NOTE. Rate constants corrected to solvent I. Units, etc. as before.

temperature range under consideration. This point is discussed in more detail in chapter V where it is shown that the value of the activation energy and B factor so determined can be identified with their values at the mean temperature of the particular interval.

This allows the relationship between $E_A$ and T to be determined. It was found that, within the limits of experimental error, this relationship was linear and hence smoothed values of $E_A$, B and $\Delta S^{\ddagger}$ were calculated from the best straight line, $E_A$ vs. T. this line being calculated by statistical methods. Values of the average rate constants and $E_A$, B, $\Delta S^{\ddagger}$ and $d(E_A)/dT$ values for the hydrolysis of the three compounds are given in tables IV-3, IV-4 and IV-5, full details of runs being available in the experimental chapter.

c) Reactions of Benzyl Chloride, Benzal Chloride and Benzotrichloride in 50% (by volume) aq.Acetone.

The foregoing remarks about mechanism in the case of the aqueous alcohol solvent will apply in this solvent also. Steady first order rate constants were calculated for all three compounds, the initial concentrations being the same as in aqueous alcohol. Rate constants were obtained for each compound at $10^{\circ}$ intervals over $40^{\circ}$.

Values of $E_A$, B, $\Delta S^{\ddagger}$ and $d(E_A)/dT$ were calculated as

TABLE IV-6.

HYDROLYSIS OF BENZYL CHLORIDE IN 50% AQUEOUS ACETONE

| EXPERIMENTAL VALUES. | | | | LEAST SQUARE VALUES. | | | |
|---|---|---|---|---|---|---|---|
| Temp. | k | Mean Temp. | $E_A$ | Mean Temp. | $E_A$ | B/2.303 | $\Delta S^{\ddagger}$ |
| 50.01 | $3.103 \times 10^{-6}$ | 55.04 | 20.45 | 55.00 | 20.50 | 8.351 | -22.5 |
| 60.08 | $8.115 \times 10^{-6}$ | 64.98 | 20.37 | 65,00 | 20.30 | 8.225 | -23.1 |
| 69.89 | $1.958 \times 10^{-5}$ | 74.95 | 20.12 | 75.00 | 20.11 | 8.104 | -23.7 |
| 80.01 | $4.556 \times 10^{-5}$ | 84.95 | 19.90 | 85.00 | 19.92 | 7.987 | -24.3 |
| 89.90 | $9.861 \times 10^{-5}$ | $d(E_A)/dT = -19$ cals/mole/deg. | | | | | |

NOTE. Rate constants corrected to solvent I. Units, etc. as before.

TABLE IV-7.

HYDROLYSIS OF BENZAL CHLORIDE IN 50% AQUEOUS ACETONE.

| EXPERIMENTAL VALUES. | | | | LEAST SQUARE VALUES. | | | |
|---|---|---|---|---|---|---|---|
| Temp. | k | Mean Temp. | $E_A$ | Mean Temp. | $E_A$ | B/2.303 | $\Delta S^*$ |
| 30.04 | $3.661 \times 10^{-6}$ | 34.98 | 23.36 | 35.00 | 23.31 | 11.36 | -8.59 |
| 39.92 | $1.245 \times 10^{-5}$ | 44.98 | 23.08 | 45.00 | 23.04 | 11.18 | -9.51 |
| 50.04 | $3.976 \times 10^{-5}$ | 55.04 | 22.64 | 55.00 | 22.77 | 11.00 | -10.4 |
| 60.04 | $1.144 \times 10^{-4}$ | 64.89 | 22.46 | 65.00 | 22.50 | 10.82 | -11.3 |
| 69.74 | $2.988 \times 10^{-4}$ | 74.91 | 22.33 | 75.00 | 22.24 | 10.65 | -12.1 |
| 80.08 | $7.798 \times 10^{-4}$ | $d(E_A)/dT = -27$ cals/mole/deg. | | | | | |

NOTE. Rate constants corrected to solvent I. Units, etc. as before.

TABLE IV-8.

HYDROLYSIS OF BENZOTRICHLORIDE IN 50% AQUEOUS ACETONE.

| EXPERIMENTAL VALUES. | | | | LEAST SQUARE VALUES. | | | |
|---|---|---|---|---|---|---|---|
| Temp. | k | Mean Temp. | $E_A$ | Mean Temp. | $E_A$ | B/2.303 | $\Delta S^{\ddagger}$ |
| 0.00 | $4.076 \times 10^{-6}$ | 4.97 | 21.28 | 5.00 | 21.29 | 11.64 | -7.12 |
| 9.94 | $1.614 \times 10^{-5}$ | 14.97 | 20.81 | 15.00 | 20.85 | 11.30 | -8.75 |
| 20.00 | $5.743 \times 10^{-5}$ | 25.02 | 20.52 | 25.00 | 20.41 | 10.97 | -10.3 |
| 30.05 | $1.846 \times 10^{-4}$ | 34.98 | 19.91 | 35.00 | 19.97 | 10.66 | -11.8 |
| 39.92 | $5.233 \times 10^{-4}$ | $d(E_A)/dT$ = -44 cals/mole/deg. | | | | | |

NOTE. Rate constants corrected to solvent I. Units, etc. as before.

before. A summary of results is given in tables IV-6, IV-7 and IV-8, full run details being available in the experimental chapter.

d) Reactions of Benzal Chloride and Benzotrichloride in 80% (by volume) aq.Alcohol.

Owing to the slowness of the reactions in this solvent only benzotrichloride was examined over the usual temperature range of 40°. Benzal chloride was examined at two temperatures only so that no value of $d(E_A)/dT$ for it was available in this solvent. The concentrations of reactants were the same as before, steady first order rate constants being obtained for both compounds. Values of $E_A$, B, $\Delta S^{\ddagger}$ (and $d(E_A)/dT$ for benzotrichloride) were calculated as before. A summary of results is given in tables IV-9 and IV-10, full details of runs being available in the experimental chapter.

Table IV-9.

HYDROLYSIS OF $PhCHCl_2$ AND $PhCCl_3$ IN 80% AQ. ALCOHOL I

| Compound | $k_{50.00}$ | $k_{60.13}$ | $E_A$ | B/2.303 | $\Delta S^{\ddagger}$ |
|---|---|---|---|---|---|
| $PhCHCl_2$ | $4.978 \times 10^{-6}$ | $1.557 \times 10^{-5}$ | 24.11 | 11.00 | -10.4 |
| $PhCCl_3$ | $1.033 \times 10^{-4}$ | $2.984 \times 10^{-4}$ | 22.43 | 11.17 | -9.59 |
| Units etc. as before. | | | | | |

TABLE IV-10.

HYDROLYSIS OF BENZOTRICHLORIDE IN 80% AQUEOUS ALCOHOL II.

| EXPERIMENTAL VALUES. | | | | LEAST SQUARE VALUES. | | | |
|---|---|---|---|---|---|---|---|
| Temp. | k | Mean Temp. | $E_A$ | Mean Temp. | $E_A$ | B/2.303 | $\Delta S^{\ddagger}$ |
| 25.02 | $4.898 \times 10^{-6}$ | 30.01 | 23.47 | 30.00 | 23.51 | 11.92 | -6.01 |
| 35.00 | $1.765 \times 10^{-5}$ | 40.00 | 23.16 | 40.00 | 23.10 | 11.63 | -7.42 |
| 45.01 | $5.795 \times 10^{-5}$ | 49.98 | 22.69 | 50.00 | 22.69 | 11.35 | -8.77 |
| 54.96 | $1.720 \times 10^{-4}$ | 59.88 | 22.26 | 60.00 | 22.28 | 11.07 | -10.1 |
| 64.81 | $4.651 \times 10^{-4}$ | $d(E_A)/dT = -41$ cals/mole/deg. | | | | | |

NOTE. Units, etc. as before.

The results obtained in the present investigation agree reasonably well with those of Hine and Lee (32) and Olivier and Weber (31), as shown in table IV-11.

Table IV-11.

HYDROLYSIS OF $PhCH_2Cl$, $PhCHCl_2$ AND $PhCCl_3$ IN 50% AQ. ACETONE.

(A comparison).

| Compound | Olivier & Weber | Hine & Lee | This Investigation |
|---|---|---|---|
| First order rate constants x $10^6$ in $sec^{-1}$ at 30°. | | | |
| $PhCH_2Cl$ | 0.37 | 0.3718 | 0.3670 † |
| $PhCHCl_2$ | 3.83 | 3.690 | 3.661 |
| $PhCCl_3$ | 183. | 184.2 | 184.6 |
| $E_A$'s in kilocals/mole for temperature range stated. | | | |
| $PhCH_2Cl$ | 20.64(30°-60°) | 21.23(30-45) | 20.70(45°)† |
| $PhCHCl_2$ | 22.48(30°-60°) | 23.26(30-45) | 23.04(45°) |
| $PhCCl_3$ | - | 20.54(20-30) | 20.41(25°) |
| † Calculated from data at higher temperatures. | | | |

A comparison between the results obtained in the present investigation and those of Evans and Hamann (34) is

given in table IV-12.

Table IV-12.

HYDROLYSIS OF $PhCHCl_2$ AND $PhCCl_3$ IN 80% AQ. ALCOHOL.

(A comparison).

| Compound | Evans and Hamann | This Investigation |
|---|---|---|
| First order rates x $10^6$ in $sec^{-1}$ at temperature stated. | | |
| $PhCHCl_2$ | 26.9 (60°) | 15.57 (60°) |
| $PhCCl_3$ | 2.58 (20°) | 2.47 (20°) † |
| $E_A$'s in kilocals/mole for temperature range stated. | | |
| $PhCHCl_2$ | 22.7 (0°-80°) | 24.6 (40°) † |
| $PhCCl_3$ | 24.4 (0°-20°) | 24.29 (10°) † |
| $\Delta S^{\neq}$ values in cals/mole/deg for temp. range stated. | | |
| $PhCHCl_2$ | -12.8 (0°-80°) | -9.0 (40°) † |
| $PhCCl_3$ | -2.7 (0°-20°) | -3.0 (10°) † |
| † Estimated from data at higher temperatures. | | |

In the case of benzotrichloride, the agreement between

rate constants, $E_A$ and $\Delta S^{\ddagger}$ values is good. Considerable deviations occur, however, in the case of benzal chloride between the rate constants. A sample run for benzal chloride quoted by Evans and Hamann shows that the reaction was only followed over about 0.4%, starting with an initial concentration of reactant of about 0.13M. A disadvantage of working over such a small range is that a small error in determining the initial concentration of reactant causes an appreciable error in the integrated rate constants. If the reaction is followed over some distance, this might be detected by a drift in the rate constants, but such a drift would not be evident over the limited range employed by Evans and Hamann. They would therefore get no indication from their rate constants if a particular run was spoilt due to the above cause.

As it is uncertain how Evans and Hamann obtained their values of $E_A$ and $\Delta S^{\ddagger}$ for benzal chloride, the comparison with the values obtained in the present investigation has been made at the mid-point of the temperature range used by them, i.e. 40°. The value of $E_A$ quoted by Evans and Hamann is 2 kilocals. lower than that obtained in the present investigation and the value of $\Delta S^{\ddagger}$ is about 4 cals/mole/deg. lower.

The present results show that, at the same temperature,

the values of the activation energies of the two compounds are reversed in order from the values quoted by Evans and Hamann and, contrary to their report, the entropies of activation are about the same (c.f. table IV-9). It must be concluded that the values of $E_A$ and $\Delta S^{\ddagger}$ quoted by Evans and Hamann are in part obtained from inaccurate data and are misleading in view of the fact that they neglected the temperature dependence of $E_A$ and $\Delta S^{\ddagger}$. (The temperature dependence of $\Delta S^{\ddagger}$ is particularly large, as indicated in the preceeding tables). The conclusions which they have drawn, therefore, concerning the solvation of the transition states must be considered unproved. This point will be considered further in the following chapters in the light of the present results.

## CHAPTER V.

## THE TEMPERATURE DEPENDENCE OF THE ARRHENIUS PARAMETERS.

In the previous chapter it was pointed out that the Arrhenius parameters in the solvolysis of benzyl chloride, benzal chloride and benzotrichloride were not independent of temperature. Temperature dependent Arrhenius parameters have been reported for other reactions, (for literature up to 1948 c.f. ref.27), including the solvolysis of the methyl halides (41) and the substituted benzhydryl chlorides (27), reactions which are very similar to those of the present investigation.

As the Arrhenius parameters were originally defined as constant it is necessary to see how these temperature coefficients arise. The Arrhenius equation can be written in two ways,

$$d(\ln k)/dT = E_A/RT^2 \qquad \text{V-A,}$$

$$\ln k = B - E_A/RT \qquad \text{V-B,}$$

where $E_A$ is called the activation energy and B equals lnA, where A is the so-called non exponential term. It is worth noting that if $E_A$ is a constant, B is also a constant, but that the two equations are still mutually consistent if $E_A$ is a function of T, provided that B is also temperature dependent in such a way that,

$$dB/dT = (RT)^{-1}.d(E_A)/dT \qquad \text{V-C.}$$

It is thus only necessary to account for the temperature coefficient of one of the Arrhenius parameters.

As the Arrhenius equation is entirely empirical, a theoretical rate equation must be accepted in order to interpret the significance and behaviour of the Arrhenius parameters. The most satisfactory equation of this type is due to Eyring, who assumed the reactants to be in equilibrium with the activated complex and treated this equilibrium by normal thermodynamic methods, assuming that the activated complex was a normal molecule except that translation along the reaction co-ordinate leads to decomposition. This enabled him to derive the absolute rate equation (33),

$$\ln k = \ln(\bar{k}T/h) + \Delta S^{\ddagger}/R - \Delta H^{\ddagger}/RT \qquad \text{V-D.}$$

where, $\bar{k}$ is the Boltzmann constant, R is the Gas constant,

h is the Planck constant, T is the temperature,

$\Delta S^{\ddagger}$ is the entropy of activation,

$\Delta H^{\ddagger}$ is the enthalpy of activation.

For reactions in condensed systems $\Delta H^{\ddagger} = \Delta U^{\ddagger}$ (where $\Delta U^{\ddagger}$ is the increase of internal energy for the activation process) and hence differentiation with respect to T leads to,

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

Comparison with the Arrhenius equation V-A shows that,

$$E_A = \Delta H^{\ddagger} + RT \qquad \text{V-E.}$$

As $\Delta H^{\ddagger}$ is a perfectly normal enthalpy change, Kirchoff's law must apply and we therefore have,

$$\partial(E_A)/dT = \Delta C_p^{\ddagger} + R \quad \text{V-F},$$

where $\Delta C_p^{\ddagger}$ is called the heat capacity of activation. It is also worth noting that substitution in equation V-D for $E_A$ (from equation V-E) and comparing with equation V-B leads to,

$$B = \ln(\bar{k}T/h) + \Delta S^{\ddagger}/R + 1 \quad \text{V-G},$$

that is, the Arrhenius parameters can be expressed in terms of the entropy and enthalpy of activation.

The concept of a heat capacity difference between the initial and activated states, leading to a temperature dependent $E_A$, was recognised by Trautz (42) in developing the theory of reaction rates. The rate equation derived by La Mer (43) by the methods of statistical mechanics leads to the same conclusion.

If the Eyring equation can be accepted, the existence of a temperature dependent activation energy arises out of a difference in heat capacity between the activated complex and the reactants. In the $S_N1$ solvolysis of alkyl halides, these two states appear, at first sight, to have rather similar structures and it is therefore necessary to decide why this difference should be large enough to lead to an

observable temperature coefficient of $E_A$.

The formation of the transition state in the systems under consideration in the present investigation implies the formation and separation of electric charges from initially neutral reactants (c.f. chapter II). A charged particle in a medium of dielectric constant D has a free energy and hence an enthalpy which depends on the value of D. Hence there will be a contribution to the heat capacity of such a particle which depends on the dielectric constant of the medium and its temperature coefficient dD/dT.

The uncharged reactant and activated complex have similar structures so there will be no appreciable difference in their heat capacities on that score. There will, however, be an additional contribution to the heat capacity of the transition state due to its charge and calculations based on extensions of the Debye-Huckel theory show that in such a system negative $d(E_A)/dT$ values should be observed; a prediction which holds in practice.

Confirmation of this view appears to be afforded by the work of Warner and his co-workers (44), who examined the formation of urea from ammonium cyanate on the assumption that a diminution of charge occurred as the system passed over into the transition state. Their results lead to quantitative agreement with theories developed on the basis of this

view, the constancy of $E_A$ in a series of isodielectric solvents being particularly striking. On the other hand, Weil and Morris (45) have pointed out that the ionic mechanism prpposed for this reaction cannot be regarded as established, an equally valid alternative being available. The rate constants quoted by Warner have also been criticised recently by Kemp and Kohnstam (46).

In any case it seems strange that the dielectric constant of a mixed solvent, a bulk property, should control the very short range forces which act between electric charges in the transition state of a reaction. This point is emphasised by Eyring and Ri (47) who, in their calculations on the nitration of substituted benzenes in polar solvents, obtained results in good agreement with experiment by assuming D = 1. Furthermore, Everett and Wynne-Jones have shown that analogous considerations to those used by Warner, when applied to the standard enthalpy change in the ionisation of weak acids in water, lead to $-\Delta C_p^{\bullet}$ values which are too small. (48)

An alternative explanation for the appreciable $\Delta C_p^{\ddagger}$ values in $S_N1$ hydrolysis (of the order of-40 cals/mole/deg.) has been proposed by Kohnstam (27). This author considers that solvation of the transition state is the cause of the large value of $-\Delta C_p^{\ddagger}$. In the transition state, the polar

water molecules may be considered to be bound electrostatically to the partial charges present. This binding will cause a loss of rotational degrees of freedom and hence a lowering of heat capacity. The value of $\Delta C_p^{\ddagger}$ will be the difference between the heat capacity of the bound water and the partial molar heat capacity of that water in the medium as a whole. In the parallel case of the ionisation of weak acids in water, already mentioned above, Everett and Wynne-Jones showed that $\Delta C_p^{o}$ was also of the order of -40 cals/mole/deg. and concluded that this was due mainly to solvation of the ions formed.

More recently Moelwyn-Hughes (41) has accounted for the value of $\Delta C_p^{\ddagger}$ by assuming that the transition state has zero heat capacity and that $\Delta C_p^{\ddagger}$ is thus equal to $-C_p^{o}$ of the initial state. Moelwyn-Hughes considers that in solution reactions the partial molar enthalpy of the transition state, $H^{\ddagger}$, is constant with temperature being the limiting value of the total energy which the molecule(s) can possess in solution. If H is the partial molar heat content of the initial state, then $E_A = H^{\ddagger} - H$ and $d/dT(E_A) = -dH/dT$. He thus explains the variation of $E_A$ with T as being due to the variation of H with T. Moelwyn-Hughes has determined this variation of $E_A$ with T in the hydrolysis of methylchloride, bromide and iodide in water and has found that $E_A$ drops at first,

passes through a minimum and begins to rise again as the temperature is increased, and states that, insofar as the partial molar heat content of the solute can be measured, it appears to rise, pass through a maximum and drop by nearly the same amount as the activation energy varies in the opposite sense.

The above postulate that $H^{*}$ should be constant with temperature seems unjustified. It may be reasonable to assume that the energy contained in the breaking bond is at its limiting value, but as the temperature rises, the energy distributed throughout the various degrees of freedom in the rest of the molecule must surely rise. It is rather difficult to imagine the partial molar enthalpy in water of the methyl halides to rise, pass through a maximum and decrease with rise in temperature and it seems remarkable that for three different compounds the maximum should be at about the same temperature. This must be so since the $E_A$ minimum for all three compounds is at about the same temperature. In view of this it is not improbable that the observed minima in $E_A$ values were due to some systematic experimental error and the calculated maxima in partial molar enthalpies of the methyl halides were due to errors in the data employed.

In view of the objections to the interpretations of the value of $\Delta C_p^{*}$ on the basis of the temperature dependence of the

dielectric constant and the partial molar heat content of the initial state, it is considered that the heat capacity of activation, as observed in the present investigation in the solvolysis of benzyl chloride, benzal chloride and benzotrichloride can best be explained as due to solvation of the partially ionised transition states.

The solvation concept, while originally developed for $S_N1$ solvolysis, may be expected to be valid for $S_N2$ solvolysis also, since in both cases a partially charged transition state is derived from initially neutral reactants. In the $S_N2$ transition state, one of the water molecules will admittedly be covalently attached to the activated complex, but in becoming so attached its heat capacity will probably not be reduced much more than if it were a solvating water molecule.

The extent of solvation in the $S_N1$ case will depend primarily on the magnitude of the partial charges developed in the transition state. The magnitude of the charges will in turn depend on the R - Cl bond stretching. Coulson and Everett (49) have developed a model for the solvation of an ion and have achieved moderate success in calculating the $\Delta C_p$ of solvation for the ionisation of weak acids. In the case of the $S_N1$ transition state, which is in effect a dipole, and in which, as stated above, the extent of solvation and

the charge development are interelated, it would be extremely difficult to derive a precise treatment. In any case the model used by the above authors was simplified in that it assumed no solvation outside of the first solvation shell. A more probable state of affairs would be to envisage an atmosphere of affected molecules surrounding the transition state, the degree of attachment and therefore the extent of heat capacity reduction decreasing as the distance between the transition state and the water molecules increased. In such a case, only qualitative conclusions can be reached based on the postulate that, the more negative is the $\Delta C_p^{\ddagger}$ value, the more solvated is the transition state.

Determination of Arrhenius Parameters.

It was assumed in chapter IV that the experimentally determined activation energies and B factors could be associated with the values of the true Arrhenius parameters at the mean temperature of the interval for which they were calculated. In view of the fact that the values of the experimentally determined parameters are temperature dependent it is necessary to justify this assumption. This is done in the appendix to this chapter.

## Appendix to Chapter V.

### Identity of Experimentally Determined Activation Energies and B Factors.

The experimental activation energy, $E_X$, for the temperature range $T_1 - T_2$ was calculated from the equation,

$$\ln(k_2/k_1) = E_X.\Delta T/RT_1T_2 \qquad \text{V-H,}$$

and the B factor, $B_X$, for that temperature range was calculated from the equation,

$$\ln k_1 = B_X - E_X/RT_1 \qquad \text{V-I.}$$

The relationship between these values and the true Arrhenius parameters at the mid-point of the temperature interval will now be determined.

### Activation Energy.

The true Arrhenius activation energy, $E_A$, at the temperature T is given by the differential form of the Arrhenius equation,

$$d(\ln k)/dT = E_{A(T)}/RT^2 \qquad \text{V-A,}$$

where the subscript to $E_A$ refers to the temperature.
As stated above, the experimental activation energy, $E_X$, for the temperature range $T_1 - T_2$ is given be the equation,

$$\ln(k_2/k_1) = E_X.\Delta T/RT_1T_2 \qquad \text{V-H.}$$

On the assumption that $E_A$ varies linearly with temperature over the range $T_1 - T_2$ we can write,

$$E_{A(T)} = E_{A(T_1)} + c(T - T_1) \qquad \text{V-J},$$

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

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

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

$$\frac{E_{A(T_1)}}{R} \cdot \frac{\Delta T}{T_1 T_2} + \frac{c}{R} \cdot \ln(T_2/T_1) - \frac{cT_1}{R} \cdot \frac{\Delta T}{T_1 T_2} = \ln(k_2/k_1) = E_X \cdot \frac{\Delta T}{RT_1 T_2}.$$

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

From equation V-J,

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

$$\therefore E_X = E_{A\left\{\frac{T_1 + T_2}{2}\right\}} + c \cdot \ln(T_2/T_1) \cdot \frac{T_1 T_2}{\Delta T} - c\left\{\frac{T_1 + T_2}{2}\right\}$$

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

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

Typical values of $\Delta T$ and $T_1$ are 10 and 300 respectively which would give the first three terms of the series the following values,

0.03333, -0.00056, +0.00001.

It is therefore only necessary to consider the first two terms.

It follows that,

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

A typical value for c is 50 cals/mole/deg. so that $c\left(\frac{\Delta T}{2T_1}\right)^2$ is of the order of 10 cals. Compared with activation energies of the order of 20,000 cals. this is negligible so that we may identify $E_X$ with $E_{A\left\{\frac{T_1 + T_2}{2}\right\}}$

$E_A$, thus determined, varies linearly with temperature, over the whole range covered, within the limits of experimental error, so that the assumption that $E_A$ varies linearly between $T_1$ and $T_2$ was justified. $E_X$ can thus be identified with the true Arrhenius activation energy at the mean temperature of the interval for which it was calculated.

B Factor.

The true Arrhenius B factor at the temperature T is given by the integrated form of the Arrhenius equation,

$$\ln k_{(T)} = B - \frac{E_{A(T)}}{RT} \qquad \text{V-B},$$

and the temperature coefficient of B when $E_A$ varies linearly with temperature is c/RT (from equation V-C). If follows that,

$$B_{\left\{\frac{T_1 + T_2}{2}\right\}} - B_{(T_1)} = \frac{c}{R}.\ln\left\{\frac{T_1 + T_2}{2T_1}\right\} \qquad \text{V-K}.$$

The experimental B factor, $B_X$, for the temperature range $T_1 - T_2$ is given by the equation,

$$B_X = \ln k_1 + E_X/RT_1 \qquad \text{V-I,}$$

and since it has been shown that $E_X = E_{A\left(\frac{T_1 + T_2}{2}\right)}$ it follows that,

$$B_X = \ln k_1 + E_{A\left(\frac{T_1 + T_2}{2}\right)} \cdot \frac{1}{RT_1}$$

$$= \ln k_1 + E_{A(T_1)}/RT_1 + \frac{c}{RT_1} \cdot \left(\frac{T_2 - T_1}{2}\right)$$

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

and from equation V-K it follows that,

$$B_X = B_{\left(\frac{T_1 + T_2}{2}\right)} + \frac{c}{RT_1} \cdot \left(\frac{T_2 - T_1}{2}\right) - \frac{c}{R} \cdot \ln\left(\frac{T_1 + T_2}{2T_1}\right)$$

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

Expanding the log as before and taking only the first two terms we have,

$$B_X = B_{\left(\frac{T_1 + T_2}{2}\right)} + \frac{c}{R} \cdot \frac{(\Delta T)^2}{8T_1^2}$$

A typical value for B is 25 and if c, $\Delta T$ and $T_1$ have values of the same order as before,

$$\frac{c}{R} \cdot \frac{(\Delta T)^2}{8T_1^2} = 0.0035, \text{ i.e. negligible.}$$

so that we may identify $B_X$ with $B_{\left\{\frac{T_1 + T_2}{2}\right\}}$,

That is to say, the experimentally determined B factor can be identified with the true Arrhenius B factor at the mean temperature of the interval for which it was calculated.

It follows that as $\Delta S^{\ddagger}$ is calculated from B it too must correspond to the mean temperature of the interval.

## CHAPTER VI.

## ROLE OF AN $\alpha$-CHLORINE SUBSTITUENT IN $S_N1$ REACTIONS.

A summary of the results obtained in the present investigation for the solvolysis of benzyl chloride, benzal chloride, benzotrichloride, diphenylmethyl chloride and diphenylmethylene chloride in the various solvents used is given in tables VI-1, 2, 3 and 4. Rate constants and $\Delta S^{\ddagger}$ values now contain a statistical correction factor. This arises from the fact that there are two equivalent hydrolysable chlorine atoms in the dichlorides and therefore two equivalent reaction paths and transition states are possible. This means that the rate per chlorine atom will be one half of the observed rate. Similarly, in the case of the trichloride, the rate per chlorine atom will be one third of the observed rate. These corrections will bring about alterations in the $\Delta S^{\ddagger}$ values, though not of course in the $E_A$ values.

Table VI-1.

$PhCHCl_2$ AND $PhCCl_3$ IN 80% AQ. ALCOHOL.

($E_A$ and $\Delta S^{\ddagger}$ values at 55°. All units as previously used).

| Compound | $E_A$ | $\Delta S^{\ddagger}$ | $\Delta C_p^{\ddagger}$ | Relative rates at 50°, $PhCHCl_2$ = 1. |
|---|---|---|---|---|
| $PhCHCl_2$ | 24.11 | -11.8 | - | 1. |
| $PhCCl_3$ | 22.43 | -11.8 | -43. | 13.8 |

Table VI-2.

$PhCH_2Cl$, $PhCHCl_2$ AND $PhCCl_3$ IN 50% AQ. ALCOHOL.

($E_A$ and $\Delta S^{\ddagger}$ values at 45°. All units as previously used).

| Compound | $E_A$ | $\Delta S^{\ddagger}$ | $\Delta C_p^{\ddagger}$ | Relative rates at 40°, $PhCH_2Cl$ = 1. |
|---|---|---|---|---|
| $PhCH_2Cl$ | 20.74 | -18.9 | -31. | 1. |
| $PhCHCl_2$ | 23.06 | -8.10 | -59. | 5.4 |
| $PhCCl_3$ | 20.53 † | -10.4 † | -73. | 100. |
| † Calculated from data at other temperatures. | | | | |

Table VI-3.

$PhCH_2Cl$, $PhCHCl_2$ AND $PhCCl_3$ IN 50% AQ. ACETONE.

($E_A$ and $\Delta S^{\ddagger}$ values at 45°. All units as previously used).

| Compound | $E_A$ | $\Delta S^{\ddagger}$ | $\Delta C_p^{\ddagger}$ | Relative rates at 40°, $PhCH_2Cl$ = 1. |
|---|---|---|---|---|
| $PhCH_2Cl$ | 20.69 † | -21.9 † | -21. | 1. † |
| $PhCHCl_2$ | 23.04 | -10.9 | -29. | 5.6 † |
| $PhCCl_3$ | 19.53 † | -15.4 † | -46. | 157. † |
| † Calculated from data at other temperatures. | | | | |

The results in all cases show that α-chlorine substitution causes an increase in rate. Although there is

some doubt as to whether the mechanism of solvolysis of

Table VI-4.

$Ph_2CHCl$ AND $Ph_2CCl_2$ IN ABSOLUTE ALCOHOL.

($E_A$ and $\Delta S^{\ddagger}$ values at $10^{\circ}$. All units as previously used).

| Compound | $E_A$ | $\Delta S^{\ddagger}$ | Relative rates at $0^{\circ}$, $Ph_2CHCl$ = 1. |
|---|---|---|---|
| $Ph_2CHCl$ | 22.23 | -5.43 | 1. |
| $Ph_2CCl_2$ | 20.56 | -7.12 | 9.1 |

benzyl chloride is $S_N1$ or $S_N2$, it was examined in the present investigation as it was thought that in solvolysis, the electrical requirements of the transition states of both mechanisms might be similar as in each case the predominant process would probably be the breaking of the R - Cl bond.

The present results show, however, that in all cases except benzyl chloride, $\alpha$-chlorine substitution produces a decrease in $E_A$ and a relatively small change in $\Delta S^{\ddagger}$. In the case of benzyl chloride, $\alpha$-chlorine substitution produces an increase in $E_A$ and also an appreciable increase in $\Delta S^{\ddagger}$. It would appear, therefore, that there may well be some $S_N2$ contribution to the solvolysis of benzyl chloride and that the assumption that in any case it would be comparable with the other cases was incorrect.

This point is further illustrated by Bennett's data (29) for the solvolysis of the para substituted benzyl chlorides

in 50% aq.acetone given in table VI-5.

Table VI-5.

SOLVOLYSIS OF p-SUBSTITUTED BENZYL CHLORIDES IN 50% AQ.ACETONE.

(Arrhenius parameters and relative rates. Units as before).

| Substituent | $CH_3$ | H | F | Cl | $NO_2$ |
|---|---|---|---|---|---|
| $E_A$ ) $69.8^\circ$ | 21.15 † | 20.58 | 20.07 | 20.19 | 20.71 |
| $B/2.303$) $84.5^\circ$ | 9.70 † | 8.38 | 8.28 | 7.90 | 7.49 |
| $k_X/k_H$ at $69.8^\circ$ | 9.1 | 1. | 1.7 | 0.59 | 0.11 |
| † Calculated for the temperature range $69.8^\circ$ - $54.8^\circ$. | | | | | |

Although the variation in rate with substituent is as obtained for $S_N1$ reactions (c.f. table II-3) it is due here mainly to a variation in the B factor, whereas in the $S_N1$ reactions, the rate variation is due almost entirely to a variation in the activation energy.

In view of the fact that, for benzyl chloride, the variation of Arrhenius parameters, on substitution, is not typical of $S_N1$ reactions, it will not be further considered here. Its mechanism of solvolysis will, however, be discussed in the next chapter.

The increased reactivity which $\alpha$-chlorine substitution produces in $S_N1$ reactions may be considered to be due to the

effect which it has on three factors, namely, steric compression in the initial state, solvation in the transition state and internal electron displacements (due to its polar effects). These three factors will now be discussed in turn in the light of the present results and other relevant data.

Steric Factors

Brown and Fletcher (50) have suggested that compression in the initial state of a molecule is capable of producing enhanced reactivity by the $S_N1$ mechanism. They cite two cases, the solvolysis of $RMe_2CCl$ and $REt_2CCl$. In each case there is an increase in reactivity as R changes from isopropyl to tert.-butyl. The change is considered to be too far removed from the reaction centre for the inductive effect to make any appreciable difference and the effect is attributed to steric compression, the relief of which, on passing into the transition state, causes the increased reactivity.

Hine and Lee (32) considered that the extra chlorine atom in benzotrichloride, compared with benzal chloride, might cause compressions in the molecule which could account, at least in part, for the greater rate of $S_N1$ solvolysis of the trichloride. After examining models, however, they came to the conclusion that no strain existed in the benzotrichloride molecule.

More detailed examination of benzotrichloride shows that there are some compressions and an attempt will be made to estimate them and the energy associated with them using the approach employed by Dostrovsky, Hughes and Ingold (51) to calculate non-bonding energy in the transition states of $S_N2$ reactions.

Compressions in the Benzotrichloride Molecule.

The orientation of the side chain of benzotrichloride for a minimum of non-bonding energy is as shown in figure I. The touching distance* sum for $H_I$ and $Cl_I$ (and $H_{II}$ and $Cl_{II}$) is 2.96 A. The actual separation is 2.53 A in each case and there is, therefore, compression amounting to 0.43 A for both pairs of H and Cl atoms.

Determination of Non-bonding Energy.

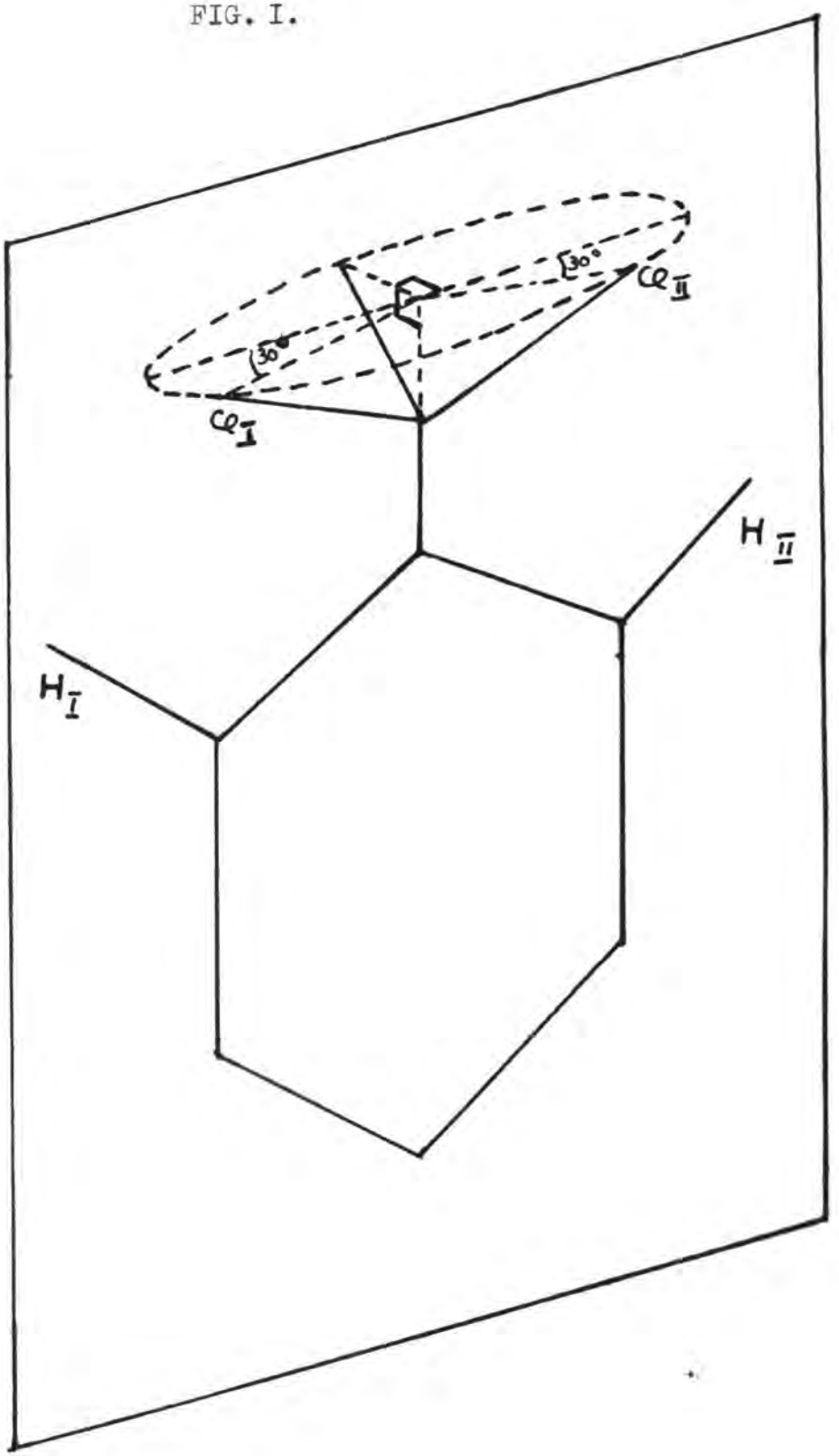
The energy of interaction between each pair of H and Cl atoms is, assuming no bond bending or stretching, given by the sum of three terms,

$$W = W_E + W_D + W_I.$$

$W_E$ is the electrostatic energy and in this case would be due

* The touching distance is defined as the effective van der Waals radius and, following Dostrovsky, Hughes and Ingold (51), is given by the equation $\rho_{max.} = \rho_{eff.} + 0.4(1+\cos 2\theta)$ at an angle $\theta$ to a bond. Van der Waal radii used are as quoted by Pauling (10).

FIG. I.



to interaction between the formal charges on the H and Cl atoms due to the dipoles of the C - H and C - Cl bonds. The electrostatic energy involved will be small and in view of the controversy existing as to the sign of the C - H dipole (for review cf. ref.52) it will be safer to ignore it here. $W_D$ and $W_I$ are the dispersion energy and the atomic interpenetration energy respectively and will be considered in turn.

Dispersion Energy.

The dispersion energy, $W_D$, is given by London's formula

$$\frac{-3\alpha_1\alpha_2 I_1 I_2}{2(I_1 + I_2)r^6} \qquad \text{VI-A,}$$

where r is the distance of seperation, $\alpha_1$ and $\alpha_2$ are the polarisabilities and $I_1$ and $I_2$ are the ionisation potentials of the two atoms. The polarisabilities are given by the equation,

$$\alpha = 3R/4\pi N \qquad \text{VI-B,}$$

where R is the atomic refraction constant and N is the Avogadro number.

$R_H$ = 1.09 c.c. leading to $\alpha_H = 4.320 \times 10^{-25}$ (53).

$R_{Cl}$ = 5.93 c.c. leading to $\alpha_{Cl} = 2.350 \times 10^{-24}$ (53).

$I_H$ = 14.5 e.v. in ethane (54).

$I_{Cl}$ = 11.17 e.v. in methyl chloride (55).

Substitution of these values into equation VI-A gives,

$$W_D = \frac{-9.614 \times 10^{-48}}{r^6} \text{ e.v.} \qquad \text{VI-C.}$$

Atomic Interpenetration Energy.

The estimation of the atomic interpenetration energy, $W_I$, is a matter of some difficulty and it will be necessary to consider extreme cases.

Fowler and Guggenheim (56) give,

$$W_I = R(r)e^{-r/a} \qquad \text{VI-D,}$$

where r is the atomic separation, a is a constant and R(r) is a polynomial containing powers of r. This equation, however, is not amenable to calculation and they state that the empirical formula,

$$W_I = br^{-n} \qquad \text{VI-E,}$$

where b and n are constants, is satisfactory over a limited range. Buckingham (57) used the expression,

$$W_I = Pe^{-r/a} \qquad \text{VI-F,}$$

where P and a are constants. This expression is nearer to the theoretical equation, VI-D, than is VI-E.

$W_I$ will be calculated here using both equations VI-E and VI-F. The value of n in equation VI-E will be that used by Urey and Bradley (58) i.e. 9. Dostrovsky, Hughes and Ingold (51) used equation VI-F taking a as 0.345 A as used by Born and Meyer (59) for alkali metal halide crystals and this value will be taken as one extreme here. It is

considered by Westheimer (60), however, that the larger alkali metal ions will be more easily compressed than will H and the value of a = 0.218 A as used by Slator (61) for two helium atoms will be taken as the other extreme. Three equations will be used therefore to calculate $W_I$,

$$br^{-9} \quad ; \quad Pe^{-r/0.345} \quad ; \quad Pe^{-r/0.218}$$

The values of b and P are obtained by equating dW/dr to zero at the touching distance.

Table VI-6 gives the value of W for both sets of compressions in the benzotrichloride molecule using the three equations quoted above in combination with equation VI-C.

Table VI-6.

(W in kilocals/mole).

| Using equations VI-C and F | | Using equations VI-C and E. |
|---|---|---|
| a = 0.218 A (P = 4981.) | a = 0.345 A (P = 53.29) | ($b = 1.662 \times 10^{-70}$) |
| 0.80 | 0.11 | 0.34 |

Conclusion.

These results, which at best are only approximate, show a wide divergence for the non-bonding energy. However, as Dostrovsky, Hughes and Ingold (51) obtained reasonable success by using the method giving the lower limit, we are

probably justified here in not going beyond the middle values. Taking the middle estimate as correct, therefore, it is obvious that only a small fraction of the drop in activation energy on passing from benzal chloride to benzotrichloride can be accounted for by steric compression in the initial state of benzotrichloride.

Consideration of diphenylmethyl chloride and diphenylmethylene chloride on the same lines as above shows that there is a small amount of compression in each case but the change in non-bonding energy on passing from one to the other is negligible.

It must therefore be concluded that in both sets of compounds considered here, $\alpha$-chlorine substitution introduces no appreciable increase in the non-bonding energy and that its effect on reactivity must be due to some other cause.

Solvation in the Transition State.

In the previous chapter it was concluded that the value of $\Delta C_p^*$ could be taken as a measure of the extent of solvation in the transition state of an $S_N1$ reaction. The values of $\Delta C_p^*$ for the solvolysis of benzal chloride and benzotrichloride, in the solvents used in the present investigation are given in table VI-7.

These results indicate that the transition state for the solvolysis of benzotrichloride is more solvated than that

Table VI-7.

( $\Delta C_p^{\ddagger}$ in cals/mole/deg).

| Compound | 80% aq.EtOH | 50% aq.acetone | 50% aq.EtOH |
|---|---|---|---|
| $PhCHCl_2$ | - | -29. | -59. |
| $PhCCl_3$ | -43. | -46. | -73. |

of benzal chloride in all of the solvents used. Evans and Hamann (34) consider, contrary to this view, that in reactions of this type, $\alpha$-substituents will sterically hinder solvation. Although, in the case of benzal chloride and benzotrichloride, their conclusions were based on inaccurate data, it seems reasonable to suppose that, other things being equal, an $\alpha$-substituent will tend to hinder solvation in the transition state, just as a bulky carbonium ion would be expected to be less solvated than a small carbonium ion due to shielding of its charge by the additional groups. In the transition states under consideration here, it is evident, however, that others factors are of more importance in determining their extent of solvation and in consequence steric hindrance to solvation is a second order effect.

It is suggested here that the most important factor governing the extent of solvation of the transition states is the extent of charge development and that the present

results indicate, in consequence, that $\alpha$-chlorine substitution leads to greater charge development in the transition state. This, in turn, can only come about by greater R - Cl bond stretching in the transition state.

$\Delta S^{\ddagger}$ as a Measure of Transition State Solvation.

Evans and Hamann (34) used the entropy of activation as a measure of transition state solvation, considering that a more negative $\Delta S^{\ddagger}$ indicated a more solvated transition state. It is to be expected that solvation will contribute a negative amount to the entropy of activation but that internal loosening of structure within the R - Cl molecule on passing into the $S_N1$ transition state will contribute a positive amount to the entropy of activation.

For the complete ionisation of two organic chlorides, RCl and R'Cl, the contribution to the entropy of ionisation due to configurational factors is probably the same in each case, being essentially the entropy change on breaking a C - Cl bond, so that it is legitimate to attribute any difference in $\Delta S^{\circ}$ of ionisation between two such compounds to differences in solvation. In the case of the $S_N1$ transition states of two such chlorides, however, it cannot be assumed that the R - Cl bond will be stretched to the same extent in each case (indeed, the present $\Delta C_p^{\ddagger}$ values indicate that in the cases of benzal chloride and

benzotrichloride the stretching is not the same). The contribution to $\Delta S^{\ddagger}$ due to bond stretching will therefore be different in each case and the differences between the total values of $\Delta S^{\ddagger}$ in each case cannot be taken as a measure of differences in transition state solvation.

The unreliability of $\Delta S^{\ddagger}$ as a measure of transition state solvation is further illustrated by the present results for benzal chloride and benzotrichloride. They show that $\Delta S^{\ddagger}$ varies with temperature and has a different temperature coefficient in each case (c.f. figures II and III†). The difference between the values of $\Delta S^{\ddagger}$ for the solvolysis of these two compounds therefore varies with temperature, and furthermore, in the 50% aq.alcohol solvent, the relative magnitudes of the $\Delta S^{\ddagger}$ values change at about $0^{\circ}$.

Polar Effects of $\alpha$-Chlorine.

The $E_A$ and $\Delta S^{\ddagger}$ values for the solvolysis of the compounds examined in the present investigation (excluding benzyl chloride) in the various solvents used, are given in table VI-8, 9 and 10.

These results show that the main effect of $\alpha$-chlorine substitution is on the activation energy although the entropy values (and therefore B factors) are not as steady

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† These $\Delta S^{\ddagger}$ values include a statistical correction factor as explained earlier.

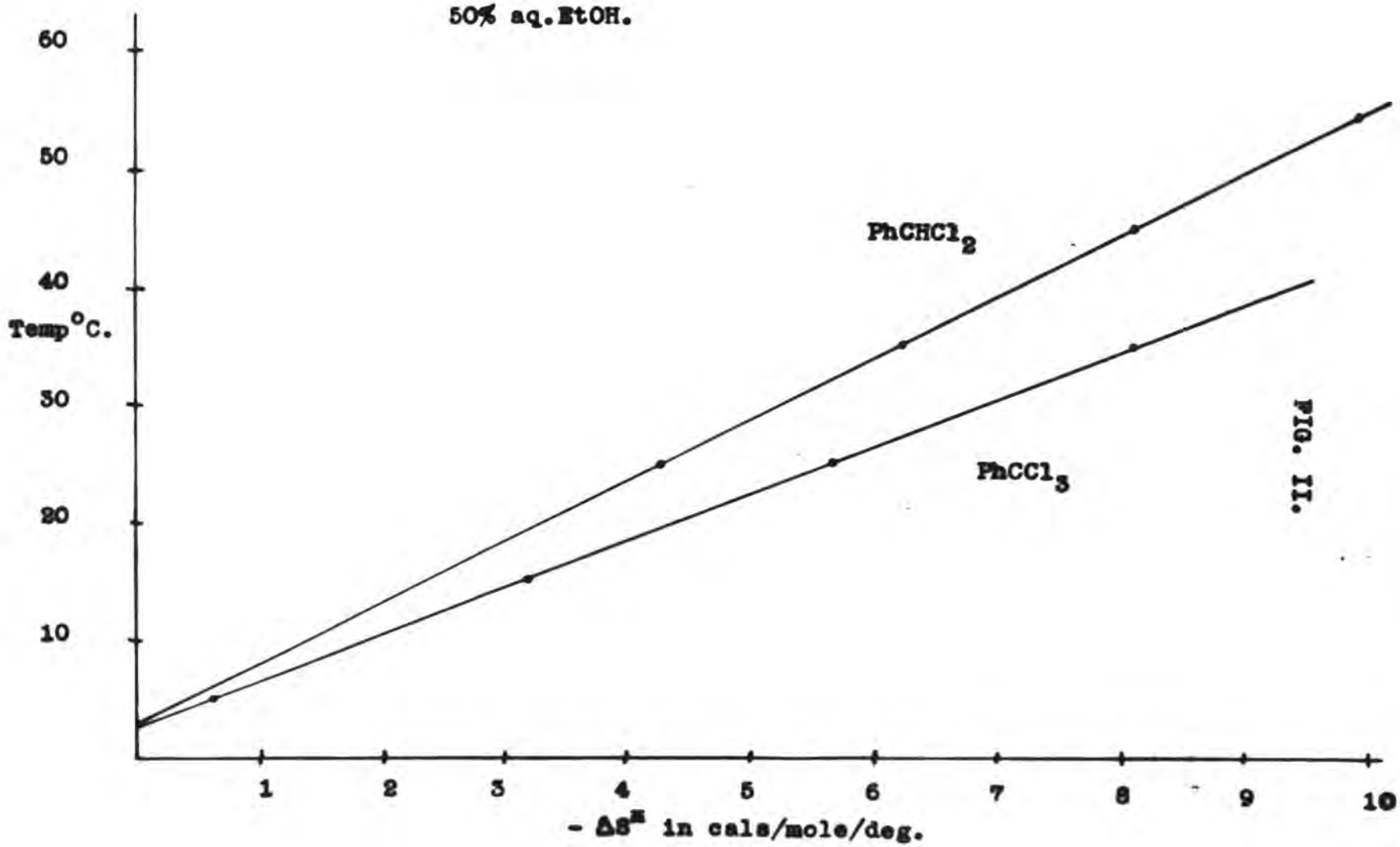

50% aq.EtOH.
60
50
40
30
20
10
Temp °C.
PhCHCl2
PhCCl3
1
2
3
4
5
6
7
8
9
10
- ΔS‡ in cals/mole/deg.

FIG. II.

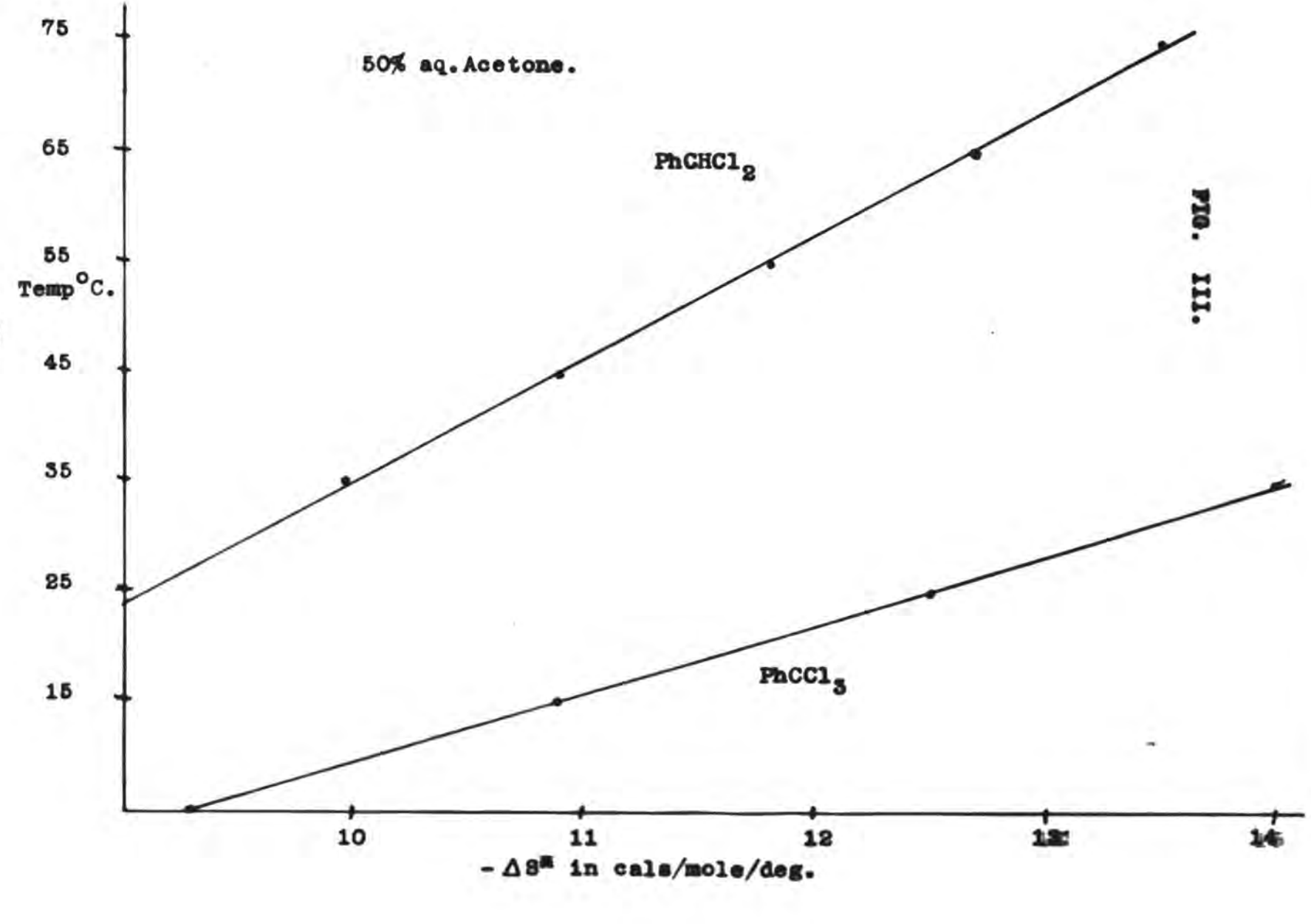

75
65
55
45
35
25
15
Temp °C.
50% aq. Acetone.
PhCHCl2
PhCCl3
10
11
12
13
14
- ΔS‡ in cals/mole/deg.

FIG. III.

Table VI-8.

$E_A$ VALUES FOR THE SOLVOLYSIS OF $PhCHCl_2$ AND $PhCCl_3$.

(in kilocals/mole)

| Compound | $E_A$ at 55° | $E_A$ at 35° | |
|---|---|---|---|
| | 80% aq.EtOH | 50% aq.acetone | 50% aq.EtOH |
| $PhCHCl_2$ | 24.11 | 23.31 | 23.63 |
| $PhCCl_3$ | 22.43 | 19.97 | 21.24 |

Table VI-9.

$\Delta S^{\ddagger}$ VALUES FOR THE SOLVOLYSIS OF $PhCHCl_2$ AND $PhCCl_3$.

(in cals/mole/deg)

| Compound | $\Delta S^{\ddagger}$ at 55° | $\Delta S^{\ddagger}$ at 35° | |
|---|---|---|---|
| | 80% aq.EtOH | 50% aq.acetone | 50% aq.EtOH |
| $PhCHCl_2$ | -11.8 | -9.97 | -6.22 |
| $PhCCl_3$ | -11.8 | -14.0 | -8.07 |

Table VI-10.

$E_A$ AND $\Delta S^{\ddagger}$ VALUES FOR ALCOHOLYSIS OF $Ph_2CHCl$ & $Ph_2CCl_2$ AT 10°.

($E_A$ in kilocals/mole. $\Delta S^{\ddagger}$ in cals/mole/deg)

| Compound | $E_A$ | $\Delta S^{\ddagger}$ |
|---|---|---|
| $Ph_2CHCl$ | 22.23 | -5.43 |
| $Ph_2CCl_2$ | 20.56 | -7.12 |

as in the case of substitution in the para position of a phenyl group attached to the reaction centre (c.f. table II-3).

This small variation in $\Delta S^{\ddagger}$, which varies with solvent and , as mentioned earlier, with temperature, is probably due to the fact that $\alpha$-chlorine substitution may cause an increase in the R- Cl distance in the transition state (as indicated by the present $\Delta C_p^{\ddagger}$ values for benzal chloride and benzotrichloride). While such extra bond stretching will cause a positive contribution to $\Delta S^{\ddagger}$, the extra charge development and solvation associated with it will cause a negative contribution to $\Delta S^{\ddagger}$, as pointed out before. The relative contributions of these two factors will probably depend on the system in question, the solvent and the temperature.

Despite the indicated increase in R -Cl bond stretching in benzotrichloride, compared with benzal chloride, the activation energy of benzotrichloride is lower than that for benzal chloride in all of the solvents investigated. This can only be due to greater ease of R - Cl bond stretching in the trichloride which must be due to electron release to the reaction centre by the additional $\alpha$-chlorine atom.

In the cases of diphenylmethyl and diphenylmenthylene chlorides, no $\Delta C_p^{\ddagger}$ values are available to estimate the variation of solvation and hence R -Cl bond stretching

in their transition states, but as the variation of $E_A$ and $\Delta S^{\ddagger}$ on $\alpha$-chlorination of the monochloride is similar to that for benzal chloride, it is probable that the position is similar.

Vernon (35) has recently published data on the $S_N1$ solvolysis of allyl chloride and its $\alpha$-chlorine substituted derivative in moist formic acid. He gives $E_A$ and B values (from which $\Delta S^{\ddagger}$ values have been calculated here) but unfortunately does not state the temperature ranges for which they were calculated. It is likely that the temperature range used for the monochloride was higher than that used for the dichloride so that his activation energies, as given in table VI-11, would diverge and his B factors (and $\Delta S^{\ddagger}$ values) would converge if they were corrected to the same temperature, assuming that they varied in the usual way with temperature.

Table VI-11.

SOLVOLYSIS OF $CH_2$:$CHCH_2Cl$ AND $CH_2$:$CHCHCl_2$ IN MOIST FORMIC ACID.

($E_A$, B and $\Delta S^{\ddagger}$ values, units as previously used)

| Compound | $E_A$ | B | $\Delta S^{\ddagger}$ |
|---|---|---|---|
| $CH_2$:$CHCH_2Cl$ | 24.8 | 11.48 | -8.3 |
| $CH_2$:$CHCHCl_2$ | 23.6 | 12.44 | -3.9 |

The small difference in B (and therefore $\Delta S^{\ddagger}$) resulting in this modification would bring his results into line with those of the present investigation as to the effect of $\alpha$-chlorine substitution on $E_A$ and $\Delta S^{\ddagger}$.

Vernon has also shown in his recent paper (35) that the $\gamma$-chlorine substituted allyl chlorides hydrolyse slightly faster than the parent compound in moist formic acid by the $S_N1$ mechanism as illustrated in table VI-12.

Table VI-12.

SOLVOLYSIS OF $CH_2$:$CHCH_2Cl$ & ClCH:$CHCH_2Cl$ IN MOIST FORMIC ACID.

(relative first order rates at 100°)

| Compound | Relative Rate (allyl chloride = 1) |
|---|---|
| $CH_2$:$CHCH_2Cl$ | 1. |
| ClCH:$CHCH_2Cl$ (cis) | 1.9 |
| ClCH:$CHCH_2Cl$ (trans) | 2.8 |

In so far as the rate can be taken as an indication of the polar effects of substituents, this indicates that a chlorine substituent in the $\gamma$-position results in slight electron release.

It would seem, therefore, that the +T effect of chlorine is less effectively relayed over distance than is its -I effect so that as a chlorine substituent is moved further

and further away from the reaction centre in an $S_N1$ reaction, its overall effect is changed from electron release to electron attraction.

Conclusion.

The evidence in the previous two sections indicates that the increase in $S_N1$ rate caused by an $\alpha$-chlorine substituent is due mainly to electron release by the chlorine. A second order effect is that $\alpha$-chlorine substitution produces greater solvation of the $S_N1$ transition state by creating greater R - Cl seperation therein. This point is discussed further in the next section.

Further Considerations.

Effect of Substituents on $\Delta S^{\ddagger}$ and $\Delta C_p^{\ddagger}$.

The variations in $S_N1$ reactivity caused by substituents in the para position of a phenyl group attached to the reaction centre are due almost entirely to variations in $E_A$, the B factor (and therefore $\Delta S^{\ddagger}$) being almost independent of substituent. In the case of an $\alpha$-chlorine substituent, although the main effect is again on $E_A$, $\Delta S^{\ddagger}$ also varies slightly and in an ambiguous manner. This variation of $\Delta S^{\ddagger}$ was attributed earlier to increased R - Cl bond stretching in the transition state, on introducing an $\alpha$-chlorine substituent, leading to a positive configurational contribution to $\Delta S^{\ddagger}$ and a negative con-

tribution due to increased solvation.

Since $\Delta S^{\ddagger}$ does not vary on introducing a substituent away from the reaction centre, it would appear that neither of the above two contributions to it have been affected by the substituent and that the extent of R - Cl bond stretching in the transition state has not been altered either. Confirmation of the view that a substituent away from the reaction centre does not affect the extent of solvation of the transition state is afforded by the reasonable constancy of the $\Delta C_p^{\ddagger}$ values, obtained by Kohnstam (28), for the solvolysis of the para substituted benzhydryl chlorides, given in table VI-13.

Table VI-13.

( $\Delta C_p^{\ddagger}$ in cals/mole/deg).

| Compound | Solvent | $\Delta C_p^{\ddagger}$ |
|---|---|---|
| $Ph_2CHCl$ | 70% aq.acetone | -38. |
| $pNO_2$-$Ph_2CHCl$ | 70% aq.acetone | -39. |
| $Ph_2CHCl$ | 85% aq.acetone | -41. |
| pMe-$Ph_2CHCl$ | 85% aq.acetone | -47. |
| pPh-$Ph_2CHCl$ | 85% aq.acetone | -25. |

It is possible, however, that on $\alpha$-chlorine substitution, the steric hindrance to solvation, which the $\alpha$-chlorine

substituent must exert, coupled with its strong electron releasing powers, together cause the energy maximum for R - Cl bond stretching to be reached at a greater seperation with the result that, despite the fact that the $\alpha$-chlorine substituent would result in less solvation for a given R - Cl seperation, solvation of the transition state is actually increased.

Variation of $E_A$, $\Delta S^{\ddagger}$ and $\Delta C_p^{\ddagger}$ of $PhCHCl_2$ and $PhCCl_3$ with Solvent.

Table VI-14 shows the variation of $E_A$, $\Delta S^{\ddagger}$ and $\Delta C_p^{\ddagger}$ for the solvolysis of benzal chloride and benzotrichloride on passing from 80% aq.EtOH to 50% aq.EtOH.

Table VI-14.

($E_A$ and $\Delta S^{\ddagger}$(statistically corrected) at 55°. Units as previously used)

| Compound | 80% aq.EtOH | | | 50% aq.EtOH | | |
|---|---|---|---|---|---|---|
| | $E_A$ | $\Delta S^{\ddagger}$ | $\Delta C_p^{\ddagger}$ | $E_A$ | $\Delta S^{\ddagger}$ | $\Delta C_p^{\ddagger}$ |
| $PhCHCl_2$ | 24.11 | -11.8 | - | 22.49 | - 9.92 | -59 |
| $PhCCl_3$ | 22.43 | -11.8 | -43 | 19.82† | -12.9† | -73 |

† Calculated from data at other temperatures.

For both compounds, the predominant variation is in the activation energy. In aqueous alcoholic solvents, the

transition state is presumably solvated by both water and alcohol molecules, and though the proportion of each will not be the same as in the bulk of the solvent, it is to be expected that, the lower is the proportion of water in the solvent, the lower will be the proportion of water in the solvation shell of the transition state. In view of this, and since alcohol is a less efficient solvating agent than water, due to its greater bulk and more screened dipole, it is to be expected that the heat capacity and energy of solvation of the transition state will be less negative in the less aqueous solvent. This will result in a higher value for $\Delta C_p^{\ddagger}$ and $E_A$, as observed.

Again, due to its greater solvating power, the water in the solvation shell can be expected to be the main determinant of the entropy of solvation of the transition state. The partial molar entropy of water will be higher in the less aqueous solvent so tending to decrease the entropy of solvation of the transition state (and therefore $\Delta S^{\ddagger}$) therein. On the other hand, there will be less water in the solvation shell of the transition state in this solvent. This will tend to increase its entropy of solvation (and therefore $\Delta S^{\ddagger}$). The small solvent dependence of $\Delta S^{\ddagger}$ for benzal chloride and benzotrichloride between 50% and 80% aq.EtOH indicates that these two effects about balance.

Table VI-15 shows the variation of $E_A$, $\Delta S^{\ddagger}$ and $\Delta C_p^{\ddagger}$ for the solvolysis of benzal chloride and benzotrichloride on passing from 50% aq.acetone to 50% aq.EtOH.

Table VI-15.

($E_A$ and $\Delta S^{\ddagger}$ (statistically corrected) at 35°. Units as previously used)

| Compound | 50% aq.acetone | | | 50% aq.EtOH | | |
|---|---|---|---|---|---|---|
| | $E_A$ | $\Delta S^{\ddagger}$ | $\Delta C_p^{\ddagger}$ | $E_A$ | $\Delta S^{\ddagger}$ | $\Delta C_p^{\ddagger}$ |
| $PhCHCl_2$ | 23.31 | - 9.97 | -29 | 23.63 | -6.22 | -59 |
| $PhCCl_3$ | 19.97 | -14.0 | -46 | 21.24 | -8.07 | -73 |

Although the alcohol solvent would normally be considered the more ionising (due to the more polar nature of alcohol than of acetone) it can be seen that the activation energies of both compounds are higher in this solvent and the small increase in rate in passing from the aq.acetone solvent to the aq.alcohol solvent is brought about by a rise in $\Delta S^{\ddagger}$.

It would appear, therefore, that as far as these two reactions are concerned, the aqueous acetone solvent is the more ionising (from the energetic standpoint). This may be due to the possibility that in the aq.acetone solvent, solvation is almost exclusively brought about by water

molecules (due to the low polar nature of acetone) whereas in the aq.alcohol solvent, solvation is probably caused by both water and alcohol molecules, as suggested earlier. While this would lead to more solvation in the case of a simple ion, in the transition state of an $S_N1$ reaction, which is in effect a dipole, steric hindrance might selectively impede solvation by the larger alcohol molecules so causing, in consequence, a less negative solvation energy and a higher activation energy. The increase in $E_A$ is larger for benzotrichloride than for benzal chloride, presumably due to the trichloride offering the greater steric hindrance to solvation.

The appreciable increase in $\Delta S^*$ for both compounds, in passing from the aq.acetone to the aq.alcohol solvent, could be due, partly to lower solvation of the transition states in the alcohol solvent and partly to appreciable differences between the partial molar entropies of the solvating agents (mainly the water) in the two media. The trichloride has a more negative $\Delta S^*$ than the dichloride in both solvents. $\Delta S^*$ values are composed partly of a positive configurational contribution and partly of a negative contribution due to solvation. The fact that $\Delta S^*$ for the trichloride is relatively less negative, compared with the dichloride, in the aq.alcohol solvent than in the

aq.acetone solvent, is consistent with the view that the solvation of the transition state of the trichloride, on passing from the aq.acetone to the aq.alcohol solvent is reduced to a greater extent than is the solvation of the transition state of the dichloride.

Since the partial molar heat capacities of the solvating agents (again mainly the water) are probably appreciably different in two solvents of such diverse composition, it is probably not legitimate to compare $\Delta C_p^{\ddagger}$ values between them.

Conclusion.

Further consideration of the solvolysis of benzal chloride and benzotrichloride indicates that the observed results can be accounted for by assuming that their transition states are sterically hindered to solvation to a degree which may cause selective exclusion of bulky solvating agents (such as alcohol) and that an $\alpha$-chlorine substituent further increases the extent of this hindrance. As indicated earlier, however, this extra steric hindrance to solvation, due to an $\alpha$-chlorine substituent, is more than outweighed by greater charge development, due in turn to greater R - Cl bond stretching in the transition state, induced by powerful electron release by the chlorine.

Polar Effects of Bromine and Fluorine at the Reaction Centre.

Hine and Lee (32) have investigated the solvolysis of

benzyl bromide, benzal bromide and benzotribromide in 50% aq.acetone. Their results, which are given in table VI-16, (B and $\Delta S^{*}$ values calculated here) show that the variation of $E_A$ and $\Delta S^{*}$ along this series is similar to that obtained by them, and in the present investigation, for the corresponding chlorine compounds, although, if the rate constants given in table VI-16 were statistically corrected, there would be a small drop in rate from benzyl bromide to benzal bromide.

Table VI-16.

$PhCH_2Br$, $PhCHBr_2$ AND $PhCBr_3$ IN 50% AQ. ACETONE.

(First order rate constants in $min^{-1} \times 10^4$. Other units as previously used)

| Compound | $k_{20}$ | $k_{30}$ | $k_{45}$ | $E_A$ | B/2.303 | $\Delta S^{*}$ |
|---|---|---|---|---|---|---|
| $PhCH_2Br$ | - | 5.684 | 25.07 | 18.97 | 8.646 | -21.0 |
| $PhCHBr_2$ | — | 6.847 | 47.06 | 24.64 | 12.82 | - 1.96 |
| $PhCBr_3$ | 362.3 | 1131. | - | 20.12 | 11.77 | - 6.67 |
| k, B and $\Delta S^{*}$ values not statistically corrected. | | | | | | |

Bromine in the $\alpha$-position apparently behaves like chlorine and can act as an overall electron releasing group. In the case of benzyl bromide, the low values of $E_A$ and $\Delta S^{*}$ indicate an $S_N2$ mechanism, as in the case of benzyl chloride

(c.f. chapter VII), but in the absence of further evidence, such as the effect of hydroxyl ions on the rate, the mechanism of solvolysis of benzyl bromide must be regarded as unproved

Hine has also investigated the solvolysis of chlorodifluoro-phenyl-methane in 50% aq.acetone (62). His results are given in table VI-17, together with the results obtained by him (32) for benzyl chloride and benzotrichloride in the same solvent.

Table VI-17.

$PhCH_2Cl$, $PhCCl_3$ AND $PhCF_2Cl$ IN 50% AQ.ACETONE.

(First order rate constants in $min^{-1}$ x $10^4$. Other units as used previously)

| Compound | $k_{30}$ | $k_{45}$ | $E_A$ | B/2.303 | $\Delta S^{\ddagger}$ |
|---|---|---|---|---|---|
| $PhCH_2Cl$ | 0.2231 | 1.174 | 21.23 | 8.87 | -20.0 |
| $PhCCl_3$ | 110.5 | - | 20.54 | 11.06 | - 9.80 |
| $PhCF_2Cl$ | 0.0419 | 0.2232 | 21.50 | 8.33 | -22.5 |
| k, B and $\Delta S^{\ddagger}$ values not statistically corrected. | | | | | |

The results show that $PhCF_2Cl$ is slightly less reactive than $PHCH_2Cl$ and very much less reactive than $PhCCl_3$. There is no evidence to show whether the mechanism of solvolysis of $PhCF_2Cl$ is $S_N1$ or $S_N2$ so that it is not possible to decide from the data available whether $\alpha$-fluorine

is capable of overall electron release or not since, if $PhCF_2Cl$ reacts by a predominantly $S_N2$ mechanism the +T release process of F could not be expected to be fully operative.

In view of this, further study of the effect of $\alpha$-fluorine substituents in reactions whose mechanisms are undoubtedly $S_N1$ is required in order to decide whether F is capable of overall electron release when attached to the reaction centre.

## CHAPTER VII.

### MECHANISM OF SOLVOLYSIS OF BENZYL CHLORIDE.

The mechanism of solvolysis of all of the compounds examined in the present investigation is $S_N1$ with the exception of benzyl chloride whose mechanism is doubtful, exhibiting characteristics of both the $S_N1$ and $S_N2$ mechanisms. The previous evidence available concerning the mechanism of solvolysis of benzyl chloride is discussed here, together with indications from the present results and other relevant data.

#### Salt Effects.

The solvolysis of benzyl chloride has been studied by Beste and Hammett (40) in aqueous dioxane. Salt effects were observed. Table VII-1 shows the percentage change in solvolysis rate of 0.075M. benzyl chloride caused by addition of the indicated solutes at 0.05M. strength.

Table VII-1.

| HCl | NaCl | $NaClO_4$ | $HClO_4$ |
|---|---|---|---|
| -2.9 | -4.3 | +7.6 | +8.0 |

The retarding effect of chloride ion is typical of the mass law effect in the $S_N1$ mechanism (20). The

accelerating effect of perchlorate ion was considered to be due either to a straightforward ionic strength effect (20) or to a bimolecular reaction between the perchlorate ion and the benzyl chloride to form benzyl perchlorate which would hydrolyse very quickly.

Effect of Substituents on Reactivity.

In the previous chapter it was pointed out that the effect of para substituents on the rate of solvolysis of benzyl chloride was similar to that observed in undoubted $S_N1$ reactions (c.f. tables II-3 and VI-5). That is to say, electron repelling groups increased the rate and electron attracting groups decreased the rate. Inspection of the Arrhenius parameters showed, however, that unlike the $S_N1$ cases, the main effect of para substituents was on the B factor. This is a strong indication that the mechanism of solvolysis of the benzyl chlorides is not straightforward $S_N1$.

Effect of Hydroxyl Ions on Rate.

Acceleration by hydroxyl ions is usually used as a test for $S_N2$ contribution to hydrolysis. Both Olivier and Weber (31) and Beste and Hammett (40) have observed such an acceleration in the case of benzyl chloride, each pair of investigators obtaining a value of about $10^3$-$10^4$ for the ratio $k_{2(OH^-)}/k_{2(H_2O)}$. This value is lower than the ratio

for methyl bromide in aq.EtOH (25), $10^4$-$10^5$, which is a typical $S_N2$ reaction, but is nevertheless significant.

Variation of Solvolysis Rate with Solvent.

Winstein, Grunwald and Jones (63) consider that some indication of mechanism of solvolysis can be obtained from the effect of a change of solvent on reactivity. They have shown that for many alkyl halides, a linear relationship exists between the free energy of activation of the alkyl halide and the free energy of activation of tert.-butyl chloride in the same solvent,

i.e. $\Delta G^{\ddagger}_{RX} = m \Delta G^{\ddagger}_{t.BuCl} + \text{constant.}$

They define two mechanistic categories, LIM and N, in preference to, but corresponding roughly with, $S_N1$ and $S_N2$ and consider that, when RX solvolyses by the LIM mechanism $m \sim 1$ and when RX solvolyses by the N mechanism $m \sim 0.3$. For benzyl chloride m = 0.425 which consequently places it in the N class.

This method is, however, open to some criticism since the free energy of activation relationship is not altogether linear for compounds solvolysing by the N mechanism (e.g. methyl bromide). It is also surprising that for benzhydryl chloride, which could be expected to be a pure LIM case, m is as low as 0.757.

The foregoing evidence has indicated that there is an

appreciable $S_N2$ contribution to the mechanism of solvolysis of benzyl chloride and an attempt will now be made to confirm this by considering the effect of an $\alpha$-chlorine substituent on $E_A$ and $\Delta S^{\ddagger}$ for the solvolysis of benzyl chloride and other relevant compounds.

Effect of $\alpha$-Chlorine Substitution on $E_A$ and $\Delta S^{\ddagger}$.

Variation of $E_A$.

Table VII-2 shows the effect of an $\alpha$-chlorine substituent of the activation energy for the solvolysis of benzal chloride and benzhydryl chloride, as found in the present investigation. Only one solvent is quoted for benzal chloride and benzotrichloride as the trends in $E_A$ in the other solvents investigated were similar.

Table VII-2.

($E_A$ in kilocals/mole at temperature stated).

| Compound | Solvent | $E_A$ |
|---|---|---|
| $PhCHCl_2$ | 50% aq.EtOH | 23.63 at 35° |
| $PhCCl_3$ | 50% aq.EtOH | 21.24 at 35° |
| $Ph_2CHCl$ | Abs.alcohol | 22.23 at 10° |
| $Ph_2CCl_2$ | Abs.alcohol | 20.56 at 10° |

For both pairs of compounds the mechanism of solvolysis

is undoubtedly $S_N1$ and $\alpha$-chlorine substitution results in a drop in activation energy of about 2 kilocals/mole in each case, due to electron release by the chlorine to the reaction centre.

Table VII-3 shows that in the case of benzyl chloride, however, $\alpha$-chlorine substitution results in an increase of about 2 kilocals/mole in the activation energy in both solvents used. This was also observed by Hine and Lee (32) and Olivier and Weber (31).

Table VII-3.

($E_A$ in kilocals/mole at 55°).

| Compound | Solvent | $E_A$ |
|---|---|---|
| $PhCH_2Cl$ | 50% aq.EtOH | 20.46 |
| $PhCHCl_2$ | 50% aq.EtOH | 22.49 |
| $PhCH_2Cl$ | 50% aq.acetone | 20.50 |
| $PhCHCl_2$ | 50% aq.acetone | 22.77 |

This is indicative of a mechanistic change from benzyl chloride to benzal chloride. If the mechanism of solvolysis of benzyl chloride is bimolecular, there will be attack by a solvent molecule on the benzyl chloride molecule before its C-Cl bond has stretched to the

separation required for the $S_N1$ transition state. This will result in a low activation energy, as observed.

Vernon's recent data (35) on the solvolysis of allyl chloride and its ∝-chlorine substituted derivative are given in table VII-4, and provide a striking confirmation of the above conclusions.

Table VII-4.

($E_A$ in kilocals/mole)

| Compound | $E_A$ | |
|---|---|---|
| | Moist formic acid | 50% aq.EtOH |
| $CH_2:CHCH_2Cl$ | 24.8 | 20.4 |
| $CH_2:CHCHCl_2$ | 23.6 | 23.5 |

In 50% aq.EtOH the rate of solvolysis of allyl chloride is accelerated by hydroxyl ions, so indicating that it proceeds by a predominantly $S_N2$ mechanism. There is an increase in activation energy from allyl chloride to its ∝-chlorine substituted derivative, whose rate is not appreciably accelerated by hydroxyl ions and is therefore predominantly $S_N1$. On the other hand, when these compounds are solvolysed in moist formic acid, where their mechanisms can be expected to be $S_N1$, due to the high ionising power of the solvent, there is a decrease in activation energy on

passing from allyl chloride to its $\alpha$-chlorine substituted derivative.

Variation of $\Delta S^{\ddagger}$.

Table VII-5 shows the effect of an $\alpha$-chlorine substituent on the entropy of activation of benzal chloride and benzhydryl chloride.

Table VII-5.

( $\Delta S^{\ddagger}$ in cals/mole/deg at temperature stated).

| Compound | $\Delta S^{\ddagger}$ at 10° | $\Delta S^{\ddagger}$ at 35° | | $\Delta S^{\ddagger}$ at 55° |
|---|---|---|---|---|
| | Abs. alcohol | 50% aq. EtOH | 50% aq. acetone | 80% aq. EtOH |
| $PhCHCl_2$ | - | -6.22 | -9.97 | -11.8 |
| $PhCCl_3$ | - | -8.07 | -14.0 | -11.8 |
| $Ph_2CHCl$ | -5.43 | - | - | - |
| $Ph_2CCl_2$ | -7.12 | - | - | - |
| Statistical | correction factors included. | | | |

As was pointed out in chapter VI, variations in $\Delta S^{\ddagger}$ on $\alpha$-chlorine substitution in $S_N1$ reactions are unpredictable, seeming to depend on the system under consideration, the solvent and the temperature. All that can be said is that these variations are relatively small; in no case considered here are the variations greater than 5 cals/mole/deg.

Table VII-6 shows the effect of an $\alpha$-chlorine substituent on the entropy of activation of benzyl chloride, in the solvents used in the present investigation.

Table VII-6.

( $\Delta S^{\ddagger}$ in cals/mole/deg at 55°)

| Compound | Solvent | $\Delta S^{\ddagger}$ |
|---|---|---|
| $PhCH_2Cl$ | 50% aq.acetone | -22.5 |
| $PhCHCl_2$ | 50% aq.acetone | -11.8 |
| $PhCH_2Cl$ | 50% aq.EtOH | -19.8 |
| $PhCHCl_2$ | 50% aq.EtOH | -9.92 |
| Statistical correction factors included. | | |

In the case of benzyl chloride, $\alpha$-chlorine substitution produces a marked increase in $\Delta S^{\ddagger}$, in both solvents, of about 10 cals/mole/deg. This may also be indicative of a mechanistic change from benzyl chloride to benzal chloride. If benzyl chloride solvolyses by the bimolecular mechanism, one of the solvent molecules surrounding the benzyl chloride molecule in the transition state will be covalently attached thereto, and in consequence, its position in space, relative to the benzyl chloride molecule, will be fixed. This, coupled with the smaller C-Cl bond extension to be expected

in the $S_N2$ transition state, should result in a more rigid and ordered transition state, compared with the $S_N1$ transition state. This greater rigidity and order in the transition state may produce a negative contribution to $\Delta S^{\ddagger}$ which more than makes up for the smaller negative contribution to $\Delta S^{\ddagger}$ due to less solvation of the $S_N2$ transition state.

The Arrhenius parameters and $\Delta S^{\ddagger}$ values for the solvolysis of a number of compounds are given in table VII-7. In general, the figures refer to various solvents and various temperatures, both of which factors affect the values of these parameters. Comparisons can therefore be order of magnitude only, but despite this, there seems to be a marked difference in the values of $\Delta S^{\ddagger}$ for $S_N1$ and $S_N2$ reactions. Whereas it is always dangerous to generalise, the occurrence of a relatively low value for $\Delta S^{\ddagger}$ would seem to be typical of the $S_N2$ mechanism.

This tentative view is given some support by the $\Delta S^{\ddagger}$ values, calculated from Vernon's (35) B factors, for the solvolysis of allyl chloride and its $\alpha$-chlorine substituted derivative, given in table VII-8.

As pointed out in chapter VI, the $\Delta S^{\ddagger}$ values in moist formic acid would probably have been closer if they had been compared at the same temperature. Bearing this in mind, it can be seen that in moist formic acid, in which both

## TABLE VII-7.

ARRHENIUS PARAMETERS AND $\Delta S^{*}$ VALUES FOR THE HYDROLYSIS OF ALKYL HALIDES IN AQ. ALCOHOL.

| Compound | Ref. | Solvent | Temp°C. | $E_A$ | B/2.303 | $\Delta S^{*}$ | Mechanism |
|---|---|---|---|---|---|---|---|
| MeBr | 63, 64 | 50% aq. Alcohol | 72.42 | 20.7 | 8.72 | -22. | $S_N2$ |
| EtBr | 63, 64 | 50% aq. Alcohol | 74, 92 | 19.8 | 7.92 | -26. | Mainly $S_N2$ |
| tert.-BuBr | 65 | 80% aq. Alcohol | 12.52 | 22.9 | 13.32 | +0.5 | $S_N1$ |
| tert.-BuCl | 66 | 80% aq. Alcohol | 26.5 | 23.0 | 11.82 | -6.5 | $S_N1$ |
| tert.-BuCl | 66 | 50% aq. Alcohol | ? | 22.9 | 13.35 | +0.6 | $S_N1$ |

compounds are considered to proceed by the $S_N1$ mechanism, their $\Delta S^{\ddagger}$ values are fairly close (as in the purely $S_N1$ cases considered in the present investigation). In aqueous alcohol the monochloride, which Vernon considers to proceed by the $S_N2$ mechanism, has a considerably lower $\Delta S^{\ddagger}$ value than the dichloride, which is considered to proceed by the $S_N1$ mechanism. This case is therefore similar to the case of benzyl chloride and benzal chloride.

Table VII-8.

($\Delta S^{\ddagger}$ in cals/mole/deg)

| Compound | $\Delta S^{\ddagger}$ | |
|---|---|---|
| | Moist formic acid | 50% aq.EtOH |
| $CH_2:CHCH_2Cl$ | -8.3 | -15. |
| $CH_2:CHCHCl_2$ | -3.9 | -4.3 |

Conclusion.

Comparison of the changes brought about by $\alpha$-chlorine substitution on $E_A$ and $\Delta S^{\ddagger}$ for the solvolysis of benzyl chloride, with the changes brought about in these properties by $\alpha$-chlorine substitution in other alkyl halides, has added confirmation to the view that its mechanism of solvolysis is predominantly $S_N2$.

Possibility of Two Separate Mechanisms.

The foregoing evidence has established that there is a considerable, though not exclusive, bimolecular contribution to the mechanism of solvolysis of benzyl chloride. There remains the question of whether two separate mechanisms co-exist, one unimolecular, one bimolecular, each with its own transition state, or whether there is only one mechanism of intermediate character.

Winstein, Grunwald and Jones (63) have considered, in the case of iso-propyl bromide, the possibility of two separate mechanisms. By assuming that each mechanism obeys their linear free energy of activation relationship, the unimolecular contribution having a typical m value of 0.94 and the bimolecular contribution having a typical m value of 0.34, they have calculated the overall rate in a number of solvents and compared it with the observed rate. The lack of success of the comparison is considered as evidence against two separate mechanisms and, therefore, in favour of one intermediate mechanism.

Bird, Hughes and Ingold (67). in a recent investigation, while agreeing with the above conclusion, consider that the test is not necessarily valid because of the assumption that the free energy of activation relationship is linear for the bimolecular contribution, even though it is appreciably not so in the case of methyl bromide.

These authors have studied the reactions of m-chlorobenzhydryl chloride with fluoride ion, triethylamine and pyridine in liquid sulphur dioxide. The substitutions showed common ion retardations, a characteristic feature of the unimolecular mechanism, but the rates were sensitive to the nature and concentration of the substituting agent. A plot of initial rate against concentration of substituting agent for the three cases, gave rates in the order, $Et_3N > C_6H_5N > F^-$. The rates did not converge to zero with decreasing concentration of substituting agent, as would be expected in a completely bimolecular reaction. The rates were not equal, as would be expected in a completely unimolecular reaction. The rates did not converge to some fixed value with decreasing concentration of substituting agent, as would be expected for a mixture of mechanisms. These authors therefore consider a single mechanism, intermediate in nature between the two extremes, to be in operation.

Since, in the two borderline cases cited above, there would seem to be no evidence for two separate mechanisms, the same probably applies in the case of the solvolysis of benzyl chloride.

This view is supported by the observation in the present investigation that $d(E_A)/dT$ for the solvolysis of benzyl chloride is negative. If two mechanisms were in operation, each with a different activation energy, the mechanism with the higher activation energy would become more prominant as the temperature rose and the observed composite activation energy could be expected to rise with temperature.

It must be concluded, therefore, that the weight of evidence indicates that the solvolysis of benzyl chloride is predominantly, but not exclusively, $S_N2$ and that only one mechanism, of intermediate character, is in operation.

## CHAPTER VIII.

## EXPERIMENTAL.

### Preparation and Purification of Materials.

### Reactants.

a) Diphenylmethylene Chloride.

Diphenylmethylene chloride was prepared by the action of $PCl_5$ on benzophenone, $Ph_2CO + PCl_5 \rightarrow Ph_2CCl_2 + POCl_3$ (68). Recrystallised benzophenone (48 gm.) was heated on an oil bath with $PCl_5$ (80 gm.) at about 165° for 5 hours. The mixture was then distilled at 200° to remove the $PCl_5$ and $POCl_3$. The residue was heated in vacuo (0.5 mm.). Further quantities of volatile phosphorus compounds came over initially and the product distilled at about 160°. The hydrolysable chloride, obtained from the acidity of solutions in aqueous acetone, was 99.6% of the theoretical amount.

b) Diphenylmethyl (Benzhydryl) Chloride.

A sample of this compound was kindly given to the author by Dr G. Kohnstam. The hydrolysable chloride was 99.8% of the theoretical amount.

c) Benzyl Chloride.

A sample of this compound, kindly given by the General Chemicals Division of I.C.I., was distilled from calcium chloride under reduced pressure (14 mm.) at about 70°.

The hydrolysable chloride was 99.5% of the theoretical amount.

d) Benzal Chloride.

B.D.H. benzal chloride (prepared from benzaldehyde) was distilled from calcium chloride in vacuo (0.5 mm.) at about 60°. The hydrolysable chloride was 99.8% of the theoretical amount.

e) Benzotrichloride.

Lights benzotrichloride was distilled in vacuo (0.5 mm.) at about 80°. The hydrolysable chloride was 99.6% of the theoretical amount.

All these compounds were stored in stoppered bottles in dessicators in the dark, diphenylmethyl chloride and diphenylmethylene chloride over $P_2O_5$, the others over $CaCl_2$.

Solvents.

a) Acetone.

Commercial acetone was refluxed over potassium permanganate and caustic soda for two hours (69) and fractionated, large head and tail fractions being discarded.

b) Ethyl Alcohol.

Pure alcohol was obtained by refluxing a dilute solution of sodium ethoxide in commercial absolute alcohol with a little diethyl phthalate and fractionating (70).

The various aqueous solvents used were made up by volume, e.g. 50% aqueous acetone was composed of 50 volumes

of acetone added to 50 volumes of water.

Procedure of Hydrolysis.

Kinetic runs were carried out at temperature ranging from 0° to 90°C. The thermostat for use at 0° consisted of an insulated bath containing a mixture of crushed ice and water which was kept in a constant state of agitation by a fast stirrer. The other thermostats were of the usual type, i.e. toluene-mercury regulators and electric lamp bulb heaters. Thermostats operated between 0° and room temperature contained, in addition, a coil of copper tubing through which cooled water was circulated. The temperature of the 0° thermostat was constant at 0° and the others showed a variation of up to ± 0.02° at the higher temperatures.

The hydrolysis of the chlorides examined always proceeded to completion and the velocity constants could therefore be calculated from a knowledge of the acid produced at various times and the acidity at 100% reaction without the necessity of using weighed amounts of reactants.

A special method of sampling was required for the absolute alcohol runs owing to the hygroscopic nature of the solvent. The runs in the aqueous solvents were sampled by one of two methods, depending on the temperature, and will be referred to as tube and flask runs.

Absolute Alcohol Runs.

The method of sampling in the case of the absolute alcohol runs was by means of the apparatus shown in figure IVa. About 100 ml. of solvent was allowed to reach the temperature of the thermostat in the flask A which was closed with a B14 stopper treated with silicone grease. Reactant was introduced into the flask which was shaken and then quickly connected to the rest of the apparatus at the ground joint. The pipette was filled by applying suction at B. The liquid was run back into the flask as far as the mark C and then run into a receiver as far as the mark D. The reaction mixture in the vertical tube F was returned to the flask A and that in the delivery tube was run to waste. Two apparati were used. Model A had a capacity of 4.110 ml. at room temperature and model B a capacity of 4.111 ml.

Flask Runs.

In general, at temperatures of $30^{\circ}$ and under the reactant was added to about 100 ml. of solvent in a stoppered flask at the thermostat temperature. The flask was thoroughly shaken and samples removed from time to time by means of a 5 ml. pipette.

Tube Runs.

Above $30^{\circ}$, where evaporation during extraction made

FIG IVa.

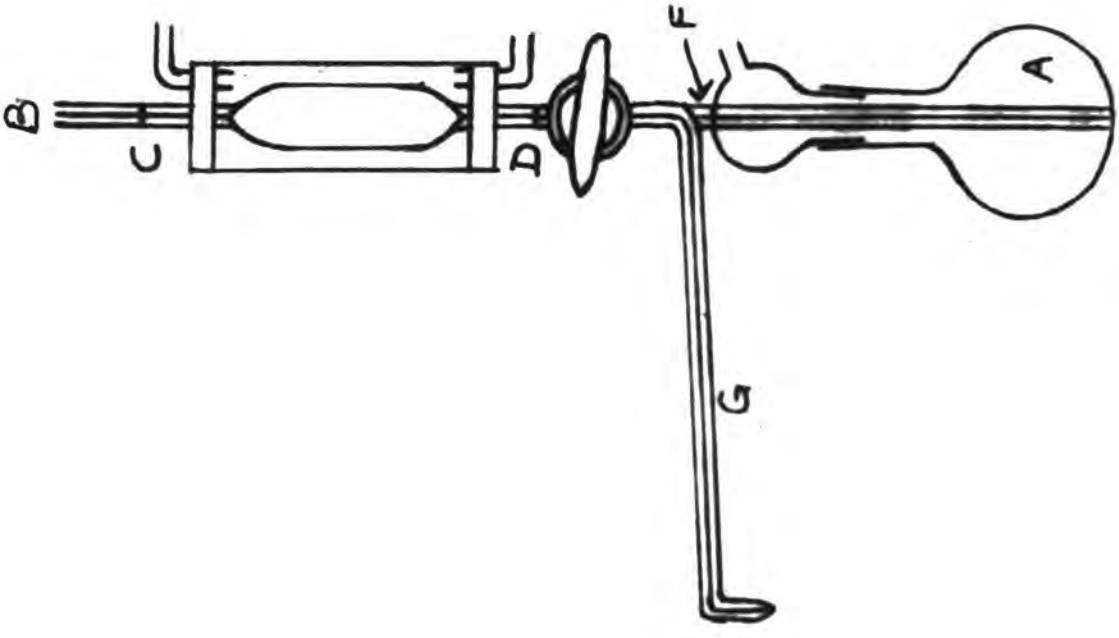
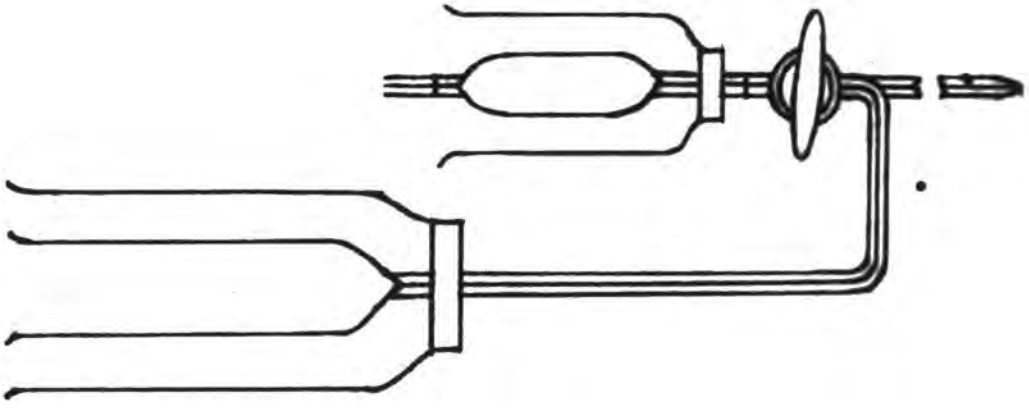



FIG IVb.



the use of the above method undesirable, the reaction was carried out in sealed tubes. The reactant was added to about 100 ml. of solvent at either room temperature or $0^{\circ}$, depending on the speed of the reaction, and was well shaken. The reaction mixture was then pipetted into tubes by means of the apparatus shown in figure IVb which could be jacketed at $0^{\circ}$ if necessary. The tubes were sealed off, attached to sinkers and introduced into the thermostat in batches of about seven. Each batch was vigorously shaken for a given time (usually two minutes) and a tube was removed from the thermostat to give the zero reading. Further tubes were removed at various times. Usually a run consisted of two batches of seven tubes each. The tube filler had a capacity of 3.765 ml. at $0^{\circ}$.

Analysis of Sample.

In the case of the absolute alcohol and flask runs the extracted samples were run into about 200 ml. of acetone to stop the reaction. The acid produced was then titrated against standard caustic soda, the acetone having been previously treated with the indicator lacmoid and neutralised. In the case of the tube runs the reaction was stopped by plunging the tubes into a $CO_2$-alcohol bath. They were then cleaned, broken under neutralised, lacmoid treated acetone and the acid titrated as before.

Calculation of Rate Constants.

First order rate constants were calculated from the equation $k = 2.303/t.\log_{10}(a/a-x)$ where t is the time in seconds and a and a-x are the concentrations of the organic halide at t = 0 and t = t respectively. The time of the first reading was taken as zero, a being the difference between the first reading and the reading when the reaction had gone to completion (10 times the half life period). Detailed results of individual runs are given at the end of this chapter.

Usually the amount of solvent prepared was not sufficient to carry out all of the experiments in a particular series and fresh solvent had to be prepared. In such cases the results in one solvent were made comparable with those in another by carrying out identical runs in each, i.e. the same chloride at the same temperature, comparing the rate constants so obtained, and applying the necessary factor to subsequent runs carried out in the second solvent.

Products of Hydrolysis.

a) Diphenylmethylene Chloride.

A weighed amount of $Ph_2CCl_2$ was allowed to react in 85% aqueous acetone. After the completion of the reaction the solution was made alkaline with ammonia and most of the acetone pumped off at room temperature. The

concentrate was poured into ice-water and the precipitated product was filtered into a sintered glass crucible, washed and weighed.

Weight of $Ph_2CCl_2$ 0.2214 gm.

Weight of product 0.1624 gm.

Theoretical yield of benzophenone 0.1701 gm.

The melting point of the product, an authentic sample of benzophenone and a mixture of the two was 47.5°. Extraction of the residues with ether failed to yield any further product.

b) Benzhydryl Chloride.

Benzhydryl chloride has been shown (38) to be hydrolysed to benzhydrol quantitatively in 80% aqueous acetone.

c) Benzyl Chloride.

Olivier (71) has shown that in addition to benzyl ~~chloride~~ alcohol, benzyl-ethyl-ether is formed in the hydrolysis of benzyl chloride in 50% aqueous ~~acetone~~ alcohol. It is likely that alcoholysis takes place to some extent in alcoholic solvents in the case of some of the other compounds studied.

d) Benzal Chloride.

A weighed amount of $PhCHCl_2$ was hydrolysed in 50% aqueous alcohol. A two times excess of p-nitro-phenyl-hydrazine was added in 30 ml. of 30% acetic acid and the precipitate allowed to stand for five hours. The

precipitate was then filtered through a sintered glass crucible, washed with 10% acetic acid, dried at 110° and weighed.

Weight of $PhCHCl_2$ 0.1902 gm.

Weight of product 0.2691 gm.

Theoretical yield of benzal-p-nitro-phenylhydrazone 0.2847 gm.

The melting point of the product, an authentic sample of the hydrazone and a mixture of the two was 192°.

e) Benzotrichloride.

A weighed amount of $PhCCl_3$ was hydrolysed in 50% aqueous acetone. The solution was made alkaline with caustic soda and the acetone was distilled off. The solution was made acid with HCl and extracted three times with chloroform. The extracts were poured into a weighed vessel and the chloroform evaporated off with warm air. The vessel was reweighed.

Weight of benzotrichloride 0.2098 gm.

Weight of product 0.1321 gm.

Theoretical yield of benzoic acid 0.1310 gm.

The melting point of the product, an authentic sample of benzoic acid and a mixture of the two was 121°.

The benzoic acid produced in the benzotrichloride runs did not titrate in acetone using lacmoid as indicator.

## Appendix to Chapter VIII.

### Alcoholysis of Diphenylmethyl and Diphenylmethylene Chlorides. Solvolysis of Benzyl Chloride, Benzal Chloride and Benzotrichloride in Aqueous Acetone and Aqueous Alcohol.

Details of Individual Runs.

First order rate constants were calculated from the equation,

$$k = 2.303/t.\ \log_{10}(a/a-x)$$

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

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

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

t is the time in seconds.

Rate constants with superscripts, i.e. k', k" etc., refer to repeat runs, which are not quoted in detail. Values of a-x are expressed in ml. of NaOH per sample. It was assumed that after the first chlorine atom had been hydrolysed off the others, if any, instantly followed it.

Expt. 1. Diphenylmethyl Chloride in abs. Alcohol at 0.00°.

Initial concentration 0.01302M

4.110 ml. titrated with 0.004945N NaOH.

| Time | a-x | k x $10^6$ |
|---|---|---|
| 0 | 10.81 | - |
| 67380 | 9.62 | 1.726 |
| 97740 | 9.09 | 1.772 |
| 154200 | 8.22 | 1.776 |
| 184020 | 7.83 | 1.752 |
| 239100 | 7.11 | 1.752 |
| 268800 | 6.82 | 1.714 |
| 329640 | 6.14 | 1.716 |
| 355500 | 5.84 | 1.733 |
| 412080 | 5.32 | 1.721 |
| 412440 | 5.30 | 1.729 |
| $\infty$ | 0.00 | - |

k = 1.739

k' = 1.728

k" = 1.729

Expt. 2. Diphenylmethyl Chloride in abs.Alcohol at 19.97°.

Initial concentration 0.01334M

4.110 ml. titrated with 0.004945N NaOH.

| Time | a-x | $k \times 10^5$ |
|---|---|---|
| 0 | 10.87 | - |
| 3605 | 9.84 | 2.760 |
| 7440 | 8.82 | 2.807 |
| 10260 | 8.18 | 2.770 |
| 15600 | 7.01 | 2.812 |
| 28260 | 4.90 | 2.821 |
| 28980 | 4.78 | 2.835 |
| 29220 | 4.75 | 2.833 |
| 32160 | 4.36 | 2.841 |
| 35700 | 3.96 | 2.828 |
| 35880 | 3.89 | 2.864 |
| 38820 | 3.59 | 2.854 |
| 39180 | 3.57 | 2.841 |
| ∞ | 0.00 | - |

---

k = 2.822

k'= 2.807

k"= 2.831

Expt. 3. Diphenylmethylene Chloride in abs.Alcohol at 0.00°.

Initial concentration 0.006434M

4.110 ml. titrated with 0.004933N NaOH.

| Time | a-x | $k \times 10^5$ |
|---|---|---|
| 0 | 10.38 | - |
| 3660 | 9.22 | (3.241) |
| 7980 | 8.05 | 3.186 |
| 14580 | 6.52 | 3.192 |
| 16020 | 6.23 | 3.187 |
| 18840 | 5.73 | 3.153 |
| 21960 | 5.16 | 3.184 |
| 24550 | 4.78 | 3.159 |
| 28620 | 4.19 | 3.170 |
| 31620 | 3.82 | 3.162 |
| 35040 | 3.41 | 3.176 |
| 37500 | 3.16 | 3.172 |
| $\infty$ | 0.00 | - |

k = 3.174

k'= 3.164

Expt. 4. Diphenylmethylene Chloride in abs.Alcohol at 19.97°.

Initial concentration 0.006315M

4.110 ml. titrated with 0.004933N NaOH.

| Time | a-x | k x $10^4$ |
|---|---|---|
| 0 | 9.51 | - |
| 300 | 8.42 | 4.062 |
| 640 | 7.31 | 4.114 |
| 975 | 6.33 | 4.177 |
| 1260 | 5.62 | 4.177 |
| 1500 | 5.11 | 4.143 |
| 1860 | 4.33 | 4.232 |
| 2090 | 3.93 | 4.230 |
| 2405 | 3.46 | 4.206 |
| 3120 | 2.60 | 4.158 |
| 3590 | 2.11 | 4.195 |
| 4380 | 1.38 | (4.407) |
| 4800 | 1.22 | 4.280 |
| $\infty$ | 0.00 | - |

k = 4.179

k' = 4.187

Expt. 5. Benzyl Chloride in 50% aq.Alcohol II at 39.99°.

Initial concentration 0.01375M

3.765 ml. titrated with 0.005013N NaOH. Tube run.

| Time | a-x | k x $10^6$ |
|---|---|---|
| 0 | 10.30 | - |
| 80400 | 7.08 | 4.662 |
| 99960 | 6.47 | 4.650 |
| 160440 | 4.93 | 4.594 |
| 274080 | 2.92 | 4.598 |
| 329280 | 2.23 | 4.647 |
| 415080 | 1.53 | 4.595 |
| ∞ | 0.00 | - |
| 0 | 10.25 | - |
| 56040 | 7.92 | 4.602 |
| 143340 | 5.34 | 4.552 |
| 177780 | 4.52 | 4.604 |
| 229260 | 3.60 | 4.564 |
| 254160 | 3.13 | (4.669) |
| 404820 | 1.62 | 4.557 |
| ∞ | 0.00 | - |

k =4.602

Corrected to solvent I k =4.531

Corrected to solvent I k'=4.512

Expt. 6. Benzyl Chloride in 50% aq.Alcohol II at 49.99°.

Initial concentration 0.01395M

3.765 ml. titrated with 0.005237N NaOH. Tube run.

| Time | a-x | $k \times 10^5$ |
|---|---|---|
| 0 | 10.00 | - |
| 52260 | 5.13 | 1.278 |
| 63060 | 4.43 | 1.292 |
| 73860 | 3.89 | 1.286 |
| 88140 | 3.22 | 1.282 |
| 145860 | 1.59 | (1.260) |
| 167460 | 1.13 | 1.302 |
| $\infty$ | 0.00 | - |
| 0 | 9.99 | - |
| 10800 | 8.70 | 1.282 |
| 18000 | 7.93 | 1.286 |
| 28800 | 6.91 | 1.280 |
| 35520 | 6.28 | 1.308 |
| 104040 | 2.63 | 1.284 |
| 117840 | 2.13 | 1.312 |
| $\infty$ | 0.00 | - |

k = 1.290

Corrected to solvent I k = 1.270

Corrected to solvent I k' = 1.279

Expt. 7. Benzyl Chloride in 50% aq.Alcohol II at 60.05°.

Initial concentration 0.01371M

3.765 ml. titrated with 0.005013N NaOH. Tube run.

| Time | a-x | $k \times 10^5$ |
|---|---|---|
| 0 | 10.20 | - |
| 49500 | 1.90 | 3.395 |
| 57000 | 1.49 | 3.375 |
| 63600 | 1.16 | 3.418 |
| 71400 | 0.90 | 3.399 |
| ∞ | 0.00 | - |
| 0 | 10.20 | - |
| 3600 | 9.00 | 3.480 |
| 7140 | 7.99 | 3.422 |
| 10740 | 7.09 | 3.389 |
| 13740 | 6.39 | 3.404 |
| ∞ | 0.00 | - |
| 0 | 10.19 | - |
| 17940 | 5.58 | 3.358 |
| 21540 | 4.91 | 3.391 |
| 34200 | 3.20 | 3.389 |
| ∞ | 0.00 | - |

k = 3.394
Corrected to solvent I k = 3.342
Corrected to solvent I k' = 3.322

Expt. 8. Benzyl Chloride in 50% aq.Alcohol III at 69.75°.

Initial concentration 0.01421M

3.765 ml. titrated with 0.005279N NaOH. Tube run.

| Time | a-x | k x $10^5$ |
|---|---|---|
| 0 | 9.95 | - |
| 9600 | 4.64 | 7.947 |
| 12240 | 3.79 | 7.887 |
| 16800 | 2.64 | 7.900 |
| 19980 | 2.05 | 7.905 |
| 20040 | 1.95 | 8.133 |
| ∞ | 0.00 | - |
| 0 | 9.99 | - |
| 1200 | 9.08 | 7.963 |
| 2460 | 8.20 | 8.033 |
| 3600 | 7.51 | 7.931 |
| 4800 | 6.84 | 7.891 |
| 6060 | 6.16 | 7.980 |
| 7200 | 5.73 | (7.721) |
| ∞ | 0.00 | - |

k = 7.937

Corrected to solvent I k = 7.845

Corrected to solvent I k'= 7.860

Expt. 9. Benzyl Chloride in 50% aq.Alcohol III at 80.06°.

Initial concentration 0.01529M

3.765 ml. titrated with 0.005279N NaOH. Tube run.

| Time | a-x | $k \times 10^4$ |
|---|---|---|
| 0 | 10.50 | - |
| 4500 | 4.56 | 1.853 |
| 5700 | 3.63 | 1.864 |
| 6900 | 2.90 | 1.865 |
| 8100 | 2.37 | 1.838 |
| 9360 | 1.89 | 1.832 |
| 10920 | 1.37 | 1.865 |
| ∞ | 0.00 | - |
| 0 | 10.49 | - |
| 600 | 9.39 | 1.846 |
| 1200 | 8.39 | 1.862 |
| 1800 | 7.50 | 1.864 |
| 2400 | 6.70 | 1.870 |
| 3000 | 6.06 | 1.830 |
| ∞ | 0.00 | - |

$k = 1.854$

Corrected to solvent I $k = 1.832$

Corrected to solvent I $k' = 1.841$

Expt. 10. Benzyl Chloride in 50% aq.Alcohol III at 90.02°.

Initial concentration 0.001465M

3.765 ml. titrated with 0.005279N NaOH. Tube run.

| Time | a-x | k x $10^4$ |
|---|---|---|
| 0 | 9.55 | - |
| 240 | 8.65 | (4.127) |
| 480 | 7.87 | 4.031 |
| 720 | 7.15 | 4.021 |
| 960 | 6.52 | 3.977 |
| 1200 | 5.95 | 3.945 |
| 1440 | 5.35 | 4.024 |
| ∞ | 0.00 | - |
| 0 | 9.54 | - |
| 2100 | 4.14 | 3.975 |
| 2400 | 3.64 | 4.016 |
| 2880 | 3.02 | 3.995 |
| 3360 | 2.45 | 4.046 |
| 3840 | 2.04 | 4.018 |
| 4320 | 1.65 | 4.063 |
| ∞ | 0.00 | - |

k = 4.010

Corrected to solvent I k = 3.963

Corrected to solvent I k'= 3,974

Expt. 11. Benzal Chloride in 50% aq.Alcohol I at 20.04°.

Initial concentration 0.009272M

3.765 ml. titrated with 0.005371N NaOH. Tube run.

| Time | a-x | k x $10^6$ |
|---|---|---|
| 0 | 12.96 | - |
| 71700 | 10.00 | 3.619 |
| 82500 | 9.67 | 3.553 |
| 82500 | 9.63 | 3.603 |
| 93300 | 9.27 | 3.594 |
| 105600 | 8.89 | 3.572 |
| 157800 | 7.35 | 3.596 |
| ∞ | 0.00 | - |
| 0 | 12.95 | - |
| 168300 | 7.07 | 3.597 |
| 190200 | 6.50 | 3.626 |
| 244200 | 5.33 | 3.637 |
| 278700 | 4.80 | 3.563 |
| 330600 | 3.95 | 3.593 |
| 363180 | 3.50 | 3.603 |
| ∞ | 0.00 | - |

k = 3.600

k'= 3.593

k"= 3.619

Expt. 12. Benzal Chloride in 50% aq.Alcohol I at 30.01°.

Initial concentration 0.009286M

3.765 ml. titrated with 0.005371N NaOH. Tube run.

| Time | a-x | k x $10^5$ |
|---|---|---|
| 0 | 12.89 | - |
| 10800 | 11.08 | 1.405 |
| 21600 | 9.52 | 1.404 |
| 28920 | 8.63 | 1.388 |
| 97200 | 3.27 | 1.411 |
| 108000 | 2.81 | 1.411 |
| 117420 | 2.42 | 1.425 |
| $\infty$ | 0.00 | - |
| 0 | 12.89 | - |
| 10500 | 11.12 | 1.408 |
| 21300 | 9.56 | 1.404 |
| 28620 | 8.59 | 1.418 |
| 96900 | 3.23 | 1.429 |
| 107700 | 2.81 | 1.415 |
| 117120 | 2.41 | 1.432 |
| $\infty$ | 0.00 | - |

k = 1.413

k' = 1.403

Expt. 13. Benzal Chloride in 50% aq.Alcohol I at 39.99°.

Initial concentration 0.008593M

3.765 ml. titrated with 0.005371N NaOH. Tube run.

| Time | a-x | k x $10^5$ |
|---|---|---|
| 0 | 11.95 | - |
| 2400 | 10.60 | 4.999 |
| 4500 | 9.58 | 4.913 |
| 6600 | 8.64 | 4.916 |
| 8700 | 7.76 | 4.963 |
| 10800 | 7.01 | 4.941 |
| 12900 | 6.33 | 4.927 |
| ∞ | 0.00 | - |
| 0 | 11.95 | - |
| 14400 | 5.85 | 4.961 |
| 18000 | 4.92 | 4.932 |
| 21600 | 4.15 | 4.898 |
| 25200 | 3.45 | 4.932 |
| 28800 | 2.90 | 4.918 |
| 30600 | 2.60 | 4.987 |
| ∞ | 0.00 | - |

k = 4.940

k' = 4.915

Expt. 14. Benzal Chloride in 50% aq.Alcohol I at 49.99°.

Initial concentration 0.008840M

3.765 ml. titrated with 0.005230N NaOH. Tube run.

| Time | a-x | k x $10^4$ |
|---|---|---|
| 0 | 12.47 | - |
| 7920 | 3.63 | 1.559 |
| 9480 | 2.83 | 1.565 |
| 11040 | 2.22 | 1.564 |
| 12600 | 1.72 | 1.572 |
| 14160 | 1.33 | 1.581 |
| ∞ | 0.00 | - |
| 0 | 12.47 | - |
| 840 | 11.03 | (1.461) |
| 1620 | 9.73 | 1.532 |
| 2400 | 8.63 | 1.535 |
| 3180 | 7.62 | 1.549 |
| 3960 | 6.78 | 1.539 |
| 4695 | 6.01 | 1.555 |
| ∞ | 0.00 | - |

k = 1.555

k' = 1.556

Expt. 15. Benzal Chloride in 50% aq.Alcohol I at 60.07°.

Initial concentration 0.008125M

3.765 ml. titrated with 0.005230N NaOH. Tube run.

| Time | a-x | k x $10^4$ |
|---|---|---|
| 0 | 11.19 | - |
| 1920 | 4.80 | 4.410 |
| 2400 | 3.80 | 4.501 |
| 2880 | 3.09 | 4.468 |
| 3365 | 2.49 | 4.467 |
| 3840 | 2.01 | 4.473 |
| 4320 | 1.60 | 4.503 |
| ∞ | 0.00 | - |
| 0 | 11.17 | - |
| 240 | 10.02 | 4.520 |
| 480 | 8.99 | 4.521 |
| 720 | 8.09 | 4.481 |
| 960 | 7.26 | 4.487 |
| 1200 | 6.50 | 4.512 |
| 1440 | 5.80 | 4.551 |
| ∞ | 0.00 | - |

k = 4.491

k'= 4.464

Expt. 16. Benzal Chloride in 50% aq.Alcohol III at 60.07°.

Initial concentration 0.01647M.

3.765 ml. titrated with 0.01188N NaOH. Tube run.

| Time | a-x | k x $10^4$ |
|---|---|---|
| 0 | 9.75 | - |
| 1925 | 4.10 | 4.501 |
| 2400 | 3.30 | 4.515 |
| 2880 | 2.69 | 4.472 |
| 3360 | 2.10 | 4.571 |
| 3840 | 1.70 | 4.550 |
| 4320 | 1.36 | 4.561 |
| ∞ | 0.00 | - |
| 0 | 9.75 | - |
| 240 | 8.74 | 4.558 |
| 480 | 7.89 | 4.410 |
| 720 | 7.09 | 4.428 |
| 960 | 6.32 | 4.517 |
| 1200 | 5.69 | 4.490 |
| 1440 | 5.10 | 4.500 |
| ∞ | 0.00 | - |

k = 4.506

Corrected to solvent I k = 4.453

Expt. 17. Benzotrichloride in 50% aq.Alcohol II at 0.00°.

Initial concentration 0.004853M

5 ml. titrated with 0.005013N NaOH. Flask run.

| Time | a-x | $k \times 10^6$ |
|---|---|---|
| 0 | 14.19 | - |
| 51540 | 9.81 | 7.159 |
| 54600 | 9.59 | 7.173 |
| 72600 | 8.46 | 7.121 |
| 87000 | 7.57 | 7.223 |
| 87300 | 7.57 | 7.199 |
| 138540 | 5.22 | 7.220 |
| 148500 | 4.88 | 7.188 |
| 165180 | 4.32 | 7.198 |
| 174540 | 4.09 | 7.131 |
| 174840 | 4.06 | 7.160 |
| 223800 | 2.82 | 7.188 |
| $\infty$ | 0.00 | - |

$k = 7.178$

Corrected to solvent I $k = 7.066$

Corrected to solvent I $k' = 7.021$

Expt. 18. Benzotrichloride in 50% aq.Alcohol II at 10.08°.

Initial concentration 0.005143M

5 ml. titrated with 0.005013N NaOH. Flask run.

| Time | a-x | $k \times 10^5$ |
|---|---|---|
| 0 | 14.19 | - |
| 3600 | 12.60 | 3.295 |
| 8100 | 10.88 | 3.276 |
| 12900 | 9.28 | 3.291 |
| 14400 | 8.81 | 3.309 |
| 16200 | 8.30 | 3.310 |
| 18000 | 7.87 | 3.274 |
| 21600 | 6.99 | 3.278 |
| 25260 | 6.18 | 3.291 |
| 28500 | 5.58 | 3.276 |
| 32400 | 4.92 | 3.270 |
| 34920 | 4.50 | 3.288 |
| $\infty$ | 0.00 | - |

$k = 3.287$

Corrected to solvent I $k = 3.236$

Corrected to solvent I $k' = 3.245$

Expt. 19. Benzotrichloride in 50% aq.Alcohol I at 20.04°.

Initial concentration 0.004620M

5 ml. titrated with 0.005371N NaOH. Flask run.

| Time | a-x | $k \times 10^4$ |
|---|---|---|
| 0 | 10.88 | - |
| 780 | 9.88 | (1.237) |
| 1680 | 8.78 | 1.277 |
| 2580 | 7.80 | 1.291 |
| 3480 | 6.92 | 1.301 |
| 4440 | 6.12 | 1.296 |
| 5640 | 5.29 | 1.279 |
| 6840 | 4.53 | 1.282 |
| 8160 | 3.85 | 1.273 |
| 10380 | 2.90 | 1.274 |
| 12180 | 2.30 | 1.276 |
| 13980 | 1.84 | 1.272 |
| ∞ | 0.00 | - |

k = 1.282

k' = 1.281

II/I = 1.016

Expt. 20. Benzotrichloride in 50% aq.Alcohol II at 20.04°.

Initial concentration 0.005586M

5 ml. titrated with 0.005237N NaOH. Flask run.

| Time | a-x | k x $10^4$ |
|---|---|---|
| 0 | 13.40 | - |
| 900 | 11.92 | 1.300 |
| 1800 | 10.60 | 1.302 |
| 2720 | 9.40 | 1.304 |
| 3600 | 8.39 | 1.301 |
| 4500 | 7.43 | 1.311 |
| 5405 | 6.66 | 1.293 |
| 7205 | 5.23 | 1.306 |
| 9000 | 4.14 | 1.306 |
| 10805 | 3.30 | 1.297 |
| 12780 | 2.56 | 1.295 |
| 14640 | 1.98 | 1.306 |
| $\infty$ | 0.00 | - |

k = 1.302

Corrected to solvent I k = 1.282

Corrected to solvent I k' = 1.284

Expt. 21. Benzotrichloride in 50% aq.Alcohol III at 20.04°.

Initial concentration 0.004440M

5 ml. titrated with 0.004898N NaOH. Flask run.

| Time | a-x | $k \times 10^4$ |
|---|---|---|
| 0 | 12.07 | - |
| 900 | 10.71 | (1.325) |
| 2100 | 9.20 | 1.292 |
| 2700 | 8.49 | 1.302 |
| 3600 | 7.57 | 1.295 |
| 4495 | 6.69 | 1.312 |
| 5400 | 5.99 | 1.297 |
| 7200 | 4.79 | 1.283 |
| 9000 | 3.73 | 1.305 |
| 10805 | 2.97 | 1.298 |
| 12600 | 2.40 | 1.282 |
| 14400 | 1.86 | 1.299 |
| $\infty$ | 0.00 | - |

k = 1.296

k' = 1.297

III/I = 1.012

Expt. 22. Benzotrichloride in 50% aq.Alcohol I at 20.04°.

Initial concentration 0.01014M.

5 ml. titrated with 0.01188N NaOH. Flask run.

| Time | a-x | $k \times 10^4$ |
|---|---|---|
| 0 | 10.82 | - |
| 1080 | 9.50 | (1.205) |
| 1800 | 8.67 | 1.231 |
| 2700 | 7.70 | 1.260 |
| 3660 | 6.83 | 1.257 |
| 4860 | 5.89 | 1.252 |
| 5400 | 5.48 | 1.260 |
| 7200 | 4.40 | 1.250 |
| 9002 | 3.51 | 1.251 |
| 10800 | 2.79 | 1.255 |
| 12600 | 2.29 | 1.233 |
| 14105 | 1.89 | 1.238 |
| 14520 | 1.78 | 1.243 |
| $\infty$ | 0.00 | - |

k = 1.248

Expt. 23. Benzotrichloride in 50% aq.Alcohol II at 29.99°.

Initial concentration 0.005190M

5 ml. titrated with 0.005013N NaOH. Flask run.

| Time | a-x | k x $10^4$ |
|---|---|---|
| 0 | 12.49 | - |
| 300 | 10.91 | 4.506 |
| 600 | 9.56 | 4.452 |
| 900 | 8.33 | 4.501 |
| 1200 | 7.29 | 4.487 |
| 1500 | 6.42 | 4.437 |
| 1800 | 5.60 | 4.456 |
| 2525 | 4.03 | 4.480 |
| 3000 | 3.30 | 4.437 |
| 3605 | 2.55 | 4.407 |
| 4260 | 1.87 | 4.458 |
| 4800 | 1.48 | 4.444 |
| $\infty$ | 0.00 | - |

k = 4.460

Corrected to solvent I k = 4.390

Corrected to solvent I k'= 4.408

Expt. 24. Benzotrichloride in 50% aq.Alcohol III at 29.99°.

Initial concentration 0.01147M.

5 ml. titrated with 0.01007N NaOH. Flask run.

| Time | a-x | k x $10^4$ |
|---|---|---|
| 0 | 14.08 | - |
| 300 | 12.34 | 4.391 |
| 600 | 10.80 | 4.418 |
| 902 | 9.49 | 4.371 |
| 1205 | 8.29 | 4.394 |
| 1480 | 7.35 | 4.390 |
| 1900 | 6.13 | 4.375 |
| 3120 | 3.59 | 4.380 |
| 3425 | 3.15 | 4.372 |
| 3760 | 2.77 | 4.324 |
| 4200 | 2.26 | 4.356 |
| 4960 | 1.64 | 4.335 |
| $\infty$ | 0.00 | - |

k = 4.373

Corrected to solvent I k = 4.322

Expt. 25. Benzotrichloride in 50% aq.Alcohol III at 40.04°.

Initial concentration 0.005842M.

3.765 ml. titrated with 0.005279N NaOH. Tube run.

| Time | a-x | $k \times 10^3$ |
|---|---|---|
| 0 | 10.37 | - |
| 90 | 9.14 | 1.405 |
| 180 | 8.10 | 1.373 |
| 270 | 7.09 | 1.409 |
| 360 | 6.22 | (1.421) |
| 450 | 5.51 | 1.406 |
| 540 | 4.90 | 1.388 |
| ∞ | 0.00 | - |
| 0 | 10.27 | - |
| 658 | 4.12 | 1.388 |
| 778 | 3.53 | 1.373 |
| 898 | 3.00 | 1.371 |
| 1018 | 2.57 | 1.362 |
| 1198 | 2.00 | 1.366 |
| 1275 | 1.76 | 1.384 |
| ∞ | 0.00 | - |

k = 1.384

Corrected to solvent I k = 1.368

Corrected to solvent I k' = 1.357

Expt. 26. Benzyl Chloride in 50% aq.Acetone III at 50.01°

Initial concentration 0.01431M

3.765 ml. titrated with 0.005033N NaOH. Tube run

| Time | a-x | k x $10^6$ |
|---|---|---|
| 0 | 10.70 | - |
| 59400 | 8.91 | 3.082 |
| 94680 | 8.01 | 3.059 |
| 146520 | 6.80 | 3.095 |
| 166560 | 6.35 | 3.133 |
| 181500 | 6.09 | 3.106 |
| 231480 | 5.20 | 3.118 |
| ∞ | 0.00 | - |
| 0 | 10.70 | - |
| 267720 | 4.67 | 3.098 |
| 318420 | 3.90 | 3.170 |
| 411840 | 2.96 | 3.122 |
| 501120 | 2.20 | 3.158 |
| 579420 | 1.70 | 3.175 |
| 579540 | 1.66 | (3.216) |
| ∞ | 0.00 | - |

k = 3.120

Corrected to solvent I k = 3.117

Corrected to solvent I k'= 3.090

Expt. 27. Benzyl Chloride in 50% aq.Acetone III at 60.08°.

Initial concentration 0.01431M

3.765 ml. titrated with 0.005033N NaOH. Tube run.

| Time | a-x | k x $10^6$ |
|---|---|---|
| 0 | 10.70 | - |
| 53100 | 7.00 | 7.993 |
| 63900 | 6.36 | 8.141 |
| 76560 | 5.74 | 8.138 |
| 141360 | 3.40 | 8.111 |
| 163200 | 2.87 | 8.063 |
| 225240 | 1.70 | 8.170 |
| ∞ | 0.00 | - |
| 0 | 10.70 | - |
| 12600 | 9.66 | 8.115 |
| 24360 | 8.72 | (8.403) |
| 35700 | 8.01 | 8.113 |
| 96240 | 4.89 | 8.137 |
| 118380 | 4.09 | 8.121 |
| 182860 | 2.44 | 8.083 |
| ∞ | 0.00 | - |

k = 8.108

Corrected to solvent I k = 8.100
Corrected to solvent I k'= 8.123
Corrected to solvent I k"= 8.122

Expt. 28. Benzyl Chloride in 50% aq.Acetone III at 69.89°.

Initial concentration 0.01465M

3.765 ml. titrated with 0.005033N NaOH. Tube run.

| Time | a-x | k x $10^5$ |
|---|---|---|
| 0 | 10.95 | - |
| 52620 | 3.88 | 1.972 |
| 59340 | 3.44 | 1.951 |
| 64800 | 3.16 | 1.919 |
| 70140 | 2.76 | 1.965 |
| 78840 | 2.23 | 1.963 |
| 85320 | 2.08 | 1.947 |
| ∞ | 0.00 | - |
| 0 | 10.95 | - |
| 6240 | 9.66 | 2.008 |
| 11700 | 8.67 | 1.995 |
| 17040 | 7.79 | 1.999 |
| 23040 | 6.97 | 1.961 |
| 32400 | 5.82 | 1.952 |
| ∞ | 0.00 | - |

k = 1.967

Corrected to solvent I k = 1.965

Corrected to solvent I k' = 1.951

Expt. 29. Benzyl Chloride in 50% aq.Acetone III at 80.01°

Initial concentration 0.01382M

3.765 ml. titrated with 0.004903N NaOH. Tube run.

| Time | a-x | k x $10^5$ |
|---|---|---|
| 0 | 10.51 | - |
| 17700 | 4.69 | 4.559 |
| 22800 | 3.71 | 4.567 |
| 26460 | 3.12 | 4.590 |
| 28560 | 2.91 | 4.498 |
| 32100 | 2.41 | 4.517 |
| 35700 | 2.01 | 4.633 |
| ∞ | 0.00 | - |
| 0 | 10.51 | - |
| 2400 | 9.41 | 4.605 |
| 4560 | 8.52 | 4.606 |
| 6960 | 7.62 | 4.620 |
| 9360 | 6.88 | 4.528 |
| 12360 | 6.04 | 4.483 |
| 14160 | 5.58 | 4.472 |
| ∞ | 0.00 | - |

| | |
|---|---|
| | k = 4.556 |
| Corrected to solvent I | k = 4.552 |
| Corrected to solvent I | k'= 4.526 |
| Corrected to solvent I | k"= 4.571 |
| Corrected to solvent I | k"= 4.577 |

Expt. 30. Benzyl Chloride in 50% aq.Acetone III at 89.90°

Initial concentration 0.01226M

3.765 ml titrated with 0.004903N NaOH. Tube run.

| Time | a-x | k x $10^5$ |
|---|---|---|
| 0 | 9.23 | - |
| 8160 | 4.20 | 9.652 |
| 9900 | 3.51 | 9.769 |
| 11700 | 2.97 | 9.695 |
| 14100 | 2.30 | 9.859 |
| 16500 | 1.79 | 9.942 |
| 18900 | 1.41 | 9.942 |
| ∞ | 0.00 | - |
| 0 | 9.21 | - |
| 1200 | 8.16 | 10.10 |
| 2100 | 7.51 | 9.727 |
| 3300 | 6.63 | 9.965 |
| 4200 | 6.10 | 9.816 |
| 5400 | 5.41 | 9.856 |
| 6300 | 4.92 | 9.956 |

k = 9.857

Corrected to solvent I k = 9.847

Corrected to solvent I k'= 9.876

Expt. 31. Benzal Chloride in 50% aq.Acetone II at 30.04°.

Initial concentration 0.007903M.

5 ml. titrated with 0.005825N NaOH. Flask run.

| Time | a-x | k x $10^6$ |
|---|---|---|
| 0 | 13.53 | - |
| 32160 | 12.06 | 3.581 |
| 84360 | 9.97 | 3.616 |
| 99000 | 9.44 | 3.636 |
| 114840 | 8.92 | 3.628 |
| 115140 | 8.91 | 3.628 |
| 176520 | 7.17 | 3.598 |
| 187740 | 6.87 | 3.610 |
| 204840 | 6.47 | 3.602 |
| 265020 | 5.17 | 3.630 |
| 359040 | 3.69 | 3.620 |
| 359520 | 3.67 | 3.630 |
| 358800 | 3.67 | 3.637 |
| $\infty$ | 0.00 | - |

k = 3.618

Corrected to solvent I k = 3.665

Corrected to solvent I k'= 3.658

Expt. 32. Benzal Chloride in 50% aq.Acetone II at 39.92°.

Initial concentration 0.007890M

3.765 ml. titrated with 0.005825N NaOH. Tube run.

| Time | a-x | $k \times 10^5$ |
|---|---|---|
| 0 | 10.19 | - |
| 50880 | 5.43 | 1.237 |
| 61380 | 4.77 | 1.237 |
| 72180 | 4.20 | 1.228 |
| 86340 | 3.75 | (1.158) |
| 137100 | 1.89 | 1.229 |
| 154860 | 1.50 | 1.237 |
| ∞ | 0.00 | - |
| 0 | 10.17 | - |
| 18540 | 8.09 | 1.235 |
| 24600 | 7.50 | 1.238 |
| 28560 | 7.19 | 1.215 |
| 79860 | 3.79 | 1.236 |
| 97620 | 3.06 | 1.231 |
| 116340 | 2.41 | 1.238 |
| ∞ | 0.00 | - |

k = 1.233

Corrected to solvent I k = 1.249

Corrected to solvent I k' = 1.242

Expt. 33. Benzal Chloride in 50% aq.Acetone II at 50.04°.

Initial concentration 0.008303M.

3.765 ml. titrated with 0.006185N NaOH. Tube run.

| Time | a-x | k x $10^5$ |
|---|---|---|
| 0 | 10.08 | - |
| 51660 | 1.31 | 3.950 |
| 51660 | 1.31 | 3.950 |
| ∞ | 0.00 | - |
| 0 | 10.02 | - |
| 5460 | 8.11 | 3.872 |
| 7260 | 7.57 | 3.860 |
| 10860 | 6.56 | 3.900 |
| 14460 | 5.71 | 3.899 |
| 19080 | 4.74 | 3.923 |
| 21660 | 4.29 | 3.915 |
| 25260 | 3.71 | 3.934 |
| 28980 | 3.21 | 3.928 |
| 32460 | 2.82 | 3.907 |
| 36240 | 2.39 | 3.955 |
| ∞ | 0.00 | - |

k = 3.916

Corrected to solvent I k = 3.967

Corrected to solvent I k' = 3.985

Expt. 34. Benzal Chloride in 50% aq.Acetone III at 50.04°.

Initial concentration 0.007701M

3.765 ml. titrated with 0.005026N NaOH. Tube run.

| Time | a-x | $k \times 10^5$ |
|---|---|---|
| 0 | 11.41 | - |
| 20220 | 5.11 | 3.974 |
| 25020 | 4.23 | 3.968 |
| 29100 | 3.57 | 3.993 |
| 32580 | 3.13 | 3.971 |
| 35880 | 2.78 | 3.936 |
| 36000 | 2.72 | 3.984 |
| ∞ | 0.00 | - |
| 0 | 11.39 | - |
| 4860 | 9.40 | 3.957 |
| 6540 | 8.76 | 4.018 |
| 9360 | 7.84 | 3.993 |
| 12780 | 6.84 | 3.992 |
| 16860 | 5.84 | 3.964 |
| 19140 | 5.29 | 4.007 |
| ∞ | 0.00 | - |

k = 3.980

k' = 3.977

III/I = 1.001

Expt. 35. Benzal Chloride in 50% aq.Acetone II at 60.04°.

Initial concentration 0.007975M

3.765 ml. titrated with 0.005825N NaOH. Tube run.

| Time | a-x | k x $10^4$ |
|---|---|---|
| 0 | 10.14 | - |
| 7200 | 4.51 | 1.125 |
| 9000 | 3.63 | 1.141 |
| 10800 | 3.00 | 1.128 |
| 12600 | 2.41 | 1.140 |
| 14400 | 1.99 | 1.131 |
| 16430 | 1.56 | 1.140 |
| ∞ | 0.00 | - |
| 0 | 10.17 | - |
| 1180 | 8.90 | 1.130 |
| 2110 | 8.01 | 1.132 |
| 3000 | 7.30 | (1.106) |
| 3900 | 6.50 | 1.148 |
| 4800 | 5.91 | 1.131 |
| 5700 | 5.31 | 1.140 |
| ∞ | 0.00 | - |

k = 1.135

Corrected to solvent I k = 1.150

Corrected to solvent I k'= 1.138

Expt. 36. Benzal Chloride in 50% aq.Acetone II at 69.74°.

Initial concentration 0.008149M

3.765 ml. titrated with 0.006185N NaOH. Tube run.

| Time | a-x | k x $10^4$ |
|---|---|---|
| 0 | 9.61 | - |
| 2760 | 4.23 | 2.973 |
| 3510 | 3.41 | 2.952 |
| 4200 | 2.80 | 2.937 |
| 4920 | 2.23 | 2.970 |
| 5640 | 1.82 | 2.951 |
| 6420 | 1.42 | 2.979 |
| ∞ | 0.00 | - |
| 0 | 9.59 | - |
| 390 | 8.59 | (2.822) |
| 720 | 7.77 | 2.924 |
| 1065 | 7.01 | 2.946 |
| 1440 | 6.29 | 2.928 |
| 1815 | 5.59 | 2.973 |
| 2160 | 5.08 | 2.942 |
| ∞ | 0.00 | - |

k = 2.953

Corrected to solvent I k = 2.991

Corrected to solvent I k'= 2.986

Expt. 37. Benzal Chloride in 50% aq.Acetone II at 80.08°.

Initial concentration 0.007641M

3.765 ml. titrated with 0.005038N NaOH. Tube run.

| Time | a-x | k x $10^4$ |
|---|---|---|
| 0 | 10.55 | - |
| 120 | 9.61 | 7.773 |
| 300 | 8.39 | 7.631 |
| 300 | 8.40 | 7.593 |
| ∞ | 0.00 | - |
| 0 | 10.53 | - |
| 480 | 7.31 | 7.607 |
| 600 | 6.67 | 7.610 |
| 720 | 6.06 | 7.675 |
| ∞ | 0.00 | - |
| 0 | 10.53 | - |
| 1740 | 2.72 | 7.780 |
| 2040 | 2.13 | 7.835 |
| 2340 | 1.82 | 7.503 |
| ∞ | 0.00 | - |
| 0 | 10.53 | - |
| 960 | 5.02 | 7.715 |
| 1210 | 4.18 | 7.633 |
| 1440 | 3.51 | 7.630 |
| ∞ | 0.00 | - |
| | | k = 7.665 |
| Corrected to solvent I | | k = 7.764 |
| Corrected to solvent I | | k'= 7.833 |

Expt. 38. Benzotrichloride in 50% aq.Acetone I at 0.00°.

Initial concentration 0.005438M

5 ml. titrated with 0.006427N NaOH. Flask run.

| Time | a-x | k x $10^6$ |
|---|---|---|
| 0 | 12.69 | - |
| 53220 | 10.19 | 4.132 |
| 70440 | 9.49 | 4.127 |
| 85740 | 8.92 | 4.113 |
| 137580 | 7.27 | 4.050 |
| 157320 | 6.69 | 4.072 |
| 172500 | 6.28 | 4.079 |
| 227340 | 5.03 | 4.072 |
| 258000 | 4.48 | 4.036 |
| 323100 | 3.44 | 4.041 |
| 398820 | 2.50 | 4.075 |
| 399120 | 2.53 | 4.041 |
| $\infty$ | 0.00 | - |

k = 4.076

k'= 4.077

Expt. 39. Benzotrichloride in 50% aq.Acetone I at 9.94°.

Initial concentration 0.005638M

5 ml. titrated with 0.006427N NaOH. Flask run.

| Time | a-x | k x $10^5$ |
|---|---|---|
| 0 | 13.06 | - |
| 7200 | 11.63 | 1.606 |
| 15600 | 10.15 | 1.615 |
| 22500 | 9.05 | 1.630 |
| 30060 | 8.02 | 1.621 |
| 36000 | 7.32 | 1.608 |
| 89220 | 3.06 | 1.626 |
| 99300 | 2.62 | 1.618 |
| 108660 | 2.25 | 1.618 |
| 119520 | 1.95 | 1.592 |
| $\infty$ | 0.00 | - |

k = 1.615

k' = 1.606

k" (for 50,000-80,000 seconds) = 1.622

Expt. 40. Benzotrichloride in 50% aq.Acetone I at 20.00°.

Initial concentration 0.004927M

5 ml. titrated with 0.006427N NaOH. Flask run.

| Time | a-x | k x $10^5$ |
|---|---|---|
| 0 | 11.18 | - |
| 2700 | 9.55 | 5.825 |
| 4800 | 8.48 | 5.754 |
| 7200 | 7.38 | 5.765 |
| 9360 | 6.50 | 5.791 |
| 12900 | 5.30 | 5.782 |
| 15600 | 4.57 | 5.734 |
| 19200 | 3.72 | 5.729 |
| 23160 | 3.00 | 5.681 |
| 27000 | 2.40 | 5.699 |
| 30900 | 1.90 | 5.734 |
| $\infty$ | 0.00 | - |

k = 5.749

k'= 5.738

Expt. 41. Benzotrichloride in 50% aq.Acetone I at 30.05°.

Initial concentration 0.005060M

5 ml. titrated with 0.006427N NaOH. Flask run.

| Time | a-x | k x $10^4$ |
|---|---|---|
| 0 | 9.90 | - |
| 900 | 9.21 | 1.871 |
| 1620 | 8.06 | 1.864 |
| 2340 | 7.08 | 1.844 |
| 3055 | 6.21 | 1.842 |
| 3955 | 5.29 | 1.827 |
| 5165 | 4.21 | 1.842 |
| 6435 | 3.38 | 1.820 |
| 7740 | 2.61 | 1.847 |
| 9120 | 2.07 | 1.821 |
| 10500 | 1.56 | 1.852 |
| $\infty$ | 0.00 | - |

k = 1.843

k'= 1.850

Expt. 42. Benzotrichloride in 50% aq.Acetone II at 30.05°.

Initial concentration 0.005359M

5 ml. titrated with 0.006427N NaOH. Flask run.

| Time | a-x | k x $10^4$ |
|---|---|---|
| 0 | 11.53 | - |
| 900 | 9.80 | 1.807 |
| 1620 | 8.56 | 1.838 |
| 2335 | 7.51 | 1.838 |
| 3055 | 6.56 | 1.846 |
| 3970 | 5.60 | 1.819 |
| 5160 | 4.50 | 1.824 |
| 6425 | 3.58 | 1.821 |
| 7680 | 2.81 | 1.838 |
| 8940 | 2.22 | 1.843 |
| 10200 | 1.79 | 1.826 |
| $\infty$ | 0.00 | - |

k = 1.830

k'= 1.814

I/II = 1.013

Expt. 43. Benzotrichloride in 50% aq.Acetone I at 39.92°.

Initial concentration 0.005585M
3.765 ml. titrated with 0.006427N NaOH. Tube run.

| Time | a-x | $k \times 10^4$ |
|---|---|---|
| 0 | 9.02 | - |
| 180 | 8.21 | 5.232 |
| 390 | 7.33 | 5.320 |
| 540 | 6.80 | 5.234 |
| 720 | 6.27 | 5.051 |
| 900 | 5.62 | 5.260 |
| 1080 | 5.17 | 5.154 |
| ∞ | 0.00 | - |
| 0 | 9.00 | - |
| 1320 | 4.47 | 5.301 |
| 1685 | 3.70 | 5.276 |
| 2040 | 3.11 | 5.210 |
| 2520 | 2.42 | 5.214 |
| 3000 | 1.91 | 5.168 |
| 3540 | 1.35 | (5.360) |
| ∞ | 0.00 | - |

k = 5.237

k' = 5.229

Expt. 44. Benzal Chloride in 80% aq.Alcohol I at 50.00°.

Initial concentration 0.008051M

3.765 ml. titrated with 0.004887N NaOH. Tube run.

| Time | a-x | k x $10^6$ |
|---|---|---|
| 0 | 12.36 | - |
| 21360 | 11.11 | 4.992 |
| 30180 | 10.66 | 4.899 |
| 85980 | 8.07 | 4.958 |
| 86040 | 8.06 | 4.970 |
| 102420 | 7.51 | (4.868) |
| 116040 | 6.92 | 5.000 |
| ∞ | 0.00 | - |
| 0 | 12.37 | - |
| 174780 | 5.20 | 4.958 |
| 230460 | 3.90 | 5.008 |
| 258240 | 3.40 | 5.002 |
| 317340 | 2.58 | 4.940 |
| 317520 | 2.52 | 5.011 |
| 323640 | 2.48 | 4.966 |
| ∞ | 0.00 | - |

k = 4.973

k' = 4.984

Expt. 45. Benzal Chloride in 80% aq.Alcohol I at 60.13°.

Initial concentration 0.007923M.

3.765 ml. titrated with 0.004887N NaOH. Tube run.

| Time | a-x | k x $10^5$ |
|---|---|---|
| 0 | 12.15 | - |
| 52800 | 5.33 | 1.561 |
| 59520 | 4.81 | 1.557 |
| 73920 | 3.88 | 1.545 |
| 85860 | 3.20 | 1.554 |
| ∞ | 0.00 | - |
| 0 | 12.16 | - |
| 10080 | 10.41 | 1.543 |
| 16320 | 9.46 | 1.538 |
| 20880 | 8.77 | 1.565 |
| 28140 | 7.81 | 1.573 |
| 32820 | 7.28 | 1.563 |
| 98040 | 2.67 | 1.547 |
| 107820 | 2.29 | 1.549 |
| 114720 | 2.03 | 1.561 |
| ∞ | 0.00 | - |

k = 1.555

k' = 1.559

Expt. 46. Benzotrichloride in 80% aq.Alcohol I at 50.00°.

Initial concentration 0.005762M

3.765 ml. titrated with 0.004887N NaOH. Tube run.

| Time | a-x | k x $10^4$ |
|---|---|---|
| 0 | 13.11 | - |
| 8400 | 5.52 | 1.030 |
| 9600 | 4.86 | 1.034 |
| 12060 | 3.73 | 1.042 |
| 14400 | 2.92 | 1.043 |
| 16800 | 2.28 | 1.041 |
| 19200 | 1.81 | 1.031 |
| ∞ | 0.00 | - |
| 0 | 13.11 | - |
| 1260 | 11.52 | 1.027 |
| 2400 | 10.26 | 1.021 |
| 3600 | 9.02 | 1.039 |
| 4440 | 8.30 | 1.030 |
| 6000 | 7.02 | 1.041 |
| 7200 | 6.21 | 1.038 |
| ∞ | 0.00 | - |

k = 1.035

k'= 1.031

Expt. 47. Benzotrichloride in 80% aq.Alcohol I at 60.13°.

Initial concentration 0.005191M

3.765 ml. titrated with 0.004887N NaOH. Tube run.

| Time | a-x | k x $10^4$ |
|---|---|---|
| 0 | 11.60 | - |
| 2760 | 5.08 | 2.992 |
| 3360 | 4.21 | 3.018 |
| 3965 | 3.53 | 3.001 |
| 4560 | 3.00 | 2.966 |
| 5160 | 2.48 | 2.991 |
| 5760 | 2.02 | 3.036 |
| ∞ | 0.00 | - |
| 0 | 11.59 | - |
| 540 | 9.89 | 2.938 |
| 1080 | 8.37 | 3.015 |
| 1440 | 7.52 | 3.005 |
| 1800 | 6.80 | 2.963 |
| 2160 | 6.08 | 2.988 |
| ∞ | 0.00 | - |

k = 2.992

k'= 2.977

Expt. 48. Benzotrichloride in 80% aq.Alcohol II at 25.02°.

Initial concentration 0.005881M.

3.765 ml. titrated with 0.005528N NaOH. Tube run.

| Time | a-x | k x $10^6$ |
|---|---|---|
| 0 | 12.02 | - |
| 162600 | 5.47 | 4.843 |
| 195600 | 4.66 | 4.846 |
| 249840 | 3.61 | 4.817 |
| 280740 | 3.01 | 4.933 |
| 336180 | 2.30 | 4.919 |
| 367200 | 2.00 | 4.886 |
| ∞ | 0.00 | - |
| 0 | 12.02 | - |
| 162300 | 5.47 | 4.852 |
| 195300 | 4.62 | 4.898 |
| 249540 | 3.59 | 4.844 |
| 280440 | 3.00 | 4.951 |
| 335880 | 2.23 | (5.017) |
| 366900 | 2.00 | 4.889 |
| ∞ | 0.00 | - |

k = 4.880

k' (for 0-120,000 seconds) = 4.920

Expt. 49. Benzotrichloride in 80% aq.Alcohol II at 35.00°.

Initial concentration 0.006410M.

3.765 ml. titrated with 0.005528N NaOH. Tube run.

| Time | a-x | k x $10^5$ |
|---|---|---|
| 0 | 13.09 | - |
| 50700 | 5.41 | 1.743 |
| 60300 | 4.50 | 1.771 |
| 72300 | 3.59 | 1.789 |
| 84300 | 3.00 | 1.748 |
| ∞ | 0.00 | - |
| 0 | 13.01 | - |
| 6600 | 11.60 | 1.735 |
| 18000 | 9.56 | (1.711) |
| 23400 | 8.60 | 1.769 |
| 29400 | 7.72 | 1.775 |
| 34500 | 7.10 | 1.755 |
| 96600 | 2.40 | 1.750 |
| 107400 | 1.91 | 1.786 |
| ∞ | 0.00 | - |

k = 1.762

k' = 1.769

Expt. 50. Benzotrichloride in 80% aq.Alcohol II at 45.01°.

Initial concentration 0.005542M.

3.765 ml. titrated with 0.005895N NaOH. Tube run.

| Time | a-x | k x $10^5$ |
|---|---|---|
| 0 | 10.59 | - |
| 9540 | 6.10 | 5.782 |
| 18000 | 3.72 | 5.813 |
| 21600 | 3.01 | 5.824 |
| 25500 | 2.42 | 5.790 |
| 28800 | 1.92 | 5.929 |
| 31980 | 1.62 | 5.873 |
| ∞ | 0.00 | - |
| 0 | 10.60 | - |
| 2100 | 9.40 | 5.725 |
| 3600 | 8.62 | 5.745 |
| 5400 | 7.78 | 5.728 |
| 7260 | 6.93 | 5.855 |
| 9000 | 6.31 | 5.766 |
| 14400 | 4.58 | 5.828 |
| ∞ | 0.00 | - |

k = 5.805

k' = 5.785

Expt. 51. Benzotrichloride in 80% aq.Alcohol II at 54.96°.

Initial concentration 0.005542M.

3.765 ml. titrated with 0.005895N NaOH. Tube run.

| Time | a-x | k x $10^4$ |
|---|---|---|
| 0 | 10.47 | - |
| 900 | 9.00 | 1.684 |
| 1200 | 8.52 | 1.720 |
| 1800 | 7.71 | 1.700 |
| 2460 | 6.83 | 1.738 |
| 3120 | 6.12 | 1.721 |
| 3840 | 5.40 | 1.725 |
| $\infty$ | 0.00 | - |
| 0 | 10.47 | - |
| 4800 | 4.61 | 1.710 |
| 6000 | 3.71 | 1.730 |
| 7200 | 3.00 | 1.737 |
| 8400 | 2.44 | 1.734 |
| 9600 | 2.01 | 1.720 |
| 11400 | 1.42 | 1.753 |
| $\infty$ | 0.00 | - |

k = 1.723

k'= 1.718

Expt. 52. Benzotrichloride in 80% aq.Alcohol II at 64.81°.

Initial concentration 0.005741M.

3.765 ml. titrated with 0.005895N NaOH. Tube run.

| Time | a-x | k x $10^4$ |
|---|---|---|
| 0 | 10.46 | - |
| 240 | 9.36 | 4.634 |
| 420 | 8.60 | 4.666 |
| 600 | 7.91 | 4.659 |
| 780 | 7.26 | 4.686 |
| 960 | 6.69 | 4.658 |
| 1260 | 5.86 | 4.600 |
| ∞ | 0.00 | - |
| 0 | 10.42 | - |
| 1500 | 5.21 | 4.623 |
| 1860 | 4.41 | 4.625 |
| 2220 | 3.69 | 4.677 |
| 2580 | 3.16 | 4.626 |
| 3060 | 2.55 | 4.601 |
| 3600 | 1.96 | 4.642 |
| ∞ | 0.00 | - |

k = 4.641

k' = 4.662

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# PART II

## SALT EFFECTS IN THE HYDROLYSIS OF DIPHENYL-METHYLENE CHLORIDE IN AQUEOUS ACETONE.

## CHAPTER I.

## SALT EFFECTS IN NUCLEOPHILIC ALIPHATIC SUBSTITUTION.

It was pointed out in part I, chapter IV, that deviations from the expected straight forward first order kinetics are observed in the solvolysis of diphenylmethylene chloride in aqueous acetone solvents. Such deviations are well known for substances undergoing solvolysis by the $S_N1$ mechanism and a detailed examination of their nature has in fact been used to demonstrate the existence of this mechanism beyond all doubt by Hughes, Ingold and co-workers (1,2).

An outline of the treatment applied by these workers is given below and further details may be obtained by reference to the original literature.

The $S_N1$ hydrolysis of an alkyl halide is considered to occur via a reversible ionisation followed by a reaction between the carbonium ion and the solvent.

$$RX \underset{(2)}{\overset{(1)}{\rightleftharpoons}} R^+ + X^-$$

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

Stage (1) is assumed to be slow, compared with stages (2) and (3) which involve the unstable carbonium ion, and therefore largely controls the rate. The carbonium ion reacts by either stage (2) or stage (3) almost as soon as it

is formed and can therefore be assumed to be in a stationary state, i.e.

$$v_1 = v_2 + v_3.$$

The instantaneous rates of the three stages are as follows,

$$v_1 = k_1 [RX] \ , \ v_2 = k_2 [R^+][X^-] \text{ and } v_3 = k_3 [R^+] \ .$$

The measured rate,

$$dx/dt = v_3 = \frac{v_1 v_3}{v_2 + v_3} \qquad \text{I - A,}$$

$$= \frac{k_1 [RX]}{k_2/k_3 . [X^-] + 1}$$

If $v_2 \ll v_3$, i.e. $k_2/k_3 [X^-] \ll 1$, ordinary first order kinetics will be observed. If this condition is not obeyed, deviations from the first order rate law will be found. These deviations may be regarded as due to the operation of two effects which may act singly or in combination.

Mass Law Effect.

As the reaction proceeds, more and more halide ions are produced and consequently a stage may be reached when the term $k_2/k_3 . [X^-]$ is no longer negligible compared with unity. This results in a retardation of the rate below the value predicted by the simple first order rate equation. This effect is called the mass law effect and can cause a progressive retardation of rate as the reaction proceeds.

The addition of $X^-$ ions to such a system should, of course, enhance this effect and, generally, the addition of a common ion salt should retard the $S_N1$ solvolysis of an alkyl halide. Salts not possessing such a common ion will have no influence on the operation of this effect.

Ionic Strength Effect.

The ionic concentration of the solution will also affect the rate of $S_N1$ solvolysis. If we consider the rate of stage (1) - the ionisation of the alkyl halide - we note that this stage involves a charged transition state formed from an initially neutral reactant. The stability of this transition state, relative to its initial state, will therefore increase as the ionising power of the solvent is increased, i.e. the rate of stage (1) will increase. An increase in ionic strength increases the ionising power of the solvent and as the reaction under consideration involves the formation of ions we can expect that the ionic strength effect should result in a progressive rise in rate, as stage (1) largely determines the solvolytic rate. The addition of any ionisable salt should enhance this effect unconditionally.

Analagous considerations will make it clear that the ionic strength of the solution will also affect the rates of stages (2) and (3) but this will only affect the observed rate of solvolysis to a small extent.

Combination of Effects.

It will be apparent that the retarding mass law effect and the accelerating ionic strength effect may act simultaneously and hence during the solvolysis of an alkyl halide we may find,

(i) increasing first order rate constants due to a significant ionic strength effect and a negligible mass law effect, c.f. tert.-butyl bromide in aqueous acetone (1a),

(ii) constant first order rate constants due to a cancelling out of these two effects, or due to negligibly small effects, c.f. benzhydryl chloride in 80% aq.acetone (1b),

(iii) decreasing first order rate constants resulting from a mass law effect sufficiently large to more than balance the ionic strength effect, c.f. pp'-dimethyl-benzhydryl chloride in aq.acetone (1d).

It is worthy of note that in general the magnitude of both of these effects increases as the carbonium ion is increasingly stabilised by resonance and that the greater increase is observed in the case of the mass law effect.

Observed Effects of Added Salts on the Initial Overall Rate of Ionisation.

Observations of the effects of added salts on the initial $S_N1$ rate are given in table I-1. In all cases the rates of liberation of the appropriate halide ions were measured to give the overall ionisation rates, so that even in the cases

where the anion of the added salt intervened to form a stable product the results were valid. The effect of common ion

Table I-1.

EFFECTS OF ADDED SALTS ON THE INITIAL OVERALL RATES OF IONISATION OF ALKYL HALIDES IN AQUEOUS ACETONE.

| Aqueous acetone | Temp. | Salt | Concn. of salt | % Change of rate |
|---|---|---|---|---|
| tert.-Butyl Bromide (1a) | | | | |
| 90% | 50° | $NaN_3$ | 0.10 | +40. |
| 90% | 50° | LiCl | 0.10 | +29. |
| 90% | 50° | LiBr | 0.10 | +42. |
| Benzhydryl Chloride (2) | | | | |
| 80% | 25° | LiCl | 0.10 | -13. |
| 80% | 25° | LiBr | 0.10 | +17. |
| Benzhydryl Bromide (2) | | | | |
| 80% | 25° | LiCl | 0.10 | +27. |
| 80% | 25° | LiBr | 0.10 | -13. |
| pp'-Dimethylbenzhydryl Chloride (1d) | | | | |
| 85% | 0° | $NaN_3$ | 0.05 | +48. |
| 85% | 0° | LiCl | 0.05 | -46. |
| 85% | 0° | LiBr | 0.05 | +46. |

salts was to depress the rate in all cases except tert.-

butyl bromide, which, as stated above has a negligible mass law effect.

Lucas and Hammett (3) have suggested that the rate depressions given by some of these salts might be due to an attraction by the salt for the reactive component of the solvent, i.e. the water. Some salts might attract water more than others rendering the solvent effectively "drier", and thereby reducing the reaction rate. Such an explanation, though plausible, could not account for the reversed effect of lithium chloride and bromide on the rates of reaction of benzhydryl chloride and bromide. Identity of anion between the salt and the alkyl halide is evidently necessary for these rate depressions (2).

The above conclusion of Lucas and Hammett was based on their observation that hydroxyl ions reduced the rate of unimolecular hydrolysis of tert.-butyl nitrate in aq.dioxane. Benfey, Hughes and Ingold (4) have studied anomalies of this type and have found them to be general for "salts" having anions in common with the solvent. This they explain as due to the ability of the hydroxyl ions to distribute their proton defect over a number of solvent molecules. The distributed proton defect in the solvent then apparently impairs the solvation of the forming halide ion more than it aids the solvation of the developing car-

bonium ion. This would be likely to reduce the reaction rate.

Kinetics of Salt Effects in Unimolecular Hydrolysis.

The above considerations of the deviations from first order kinetics in $S_N1$ reactions, which are essentially of a qualitative nature, have been put on a more quantitative basis by Hughes, Ingold and co-workers (1e) who developed a rate equation which allowed for the operation of mass law and ionic strength effects by considering the effect of varying ionic strength on the terms, $v_1$, $v_2$, and $v_3$ of equation I-A, which is written again for convenience,

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

Using the formalism of Polanyi, Evans and Eyring (5) and assuming that the activity coefficient of the transition state differs from unity by so much more than does the activity coefficient of RX that the latter may be set equal to unity, it can be shown that,

$$v_1 = k_1^o(a-x)/f_T \qquad \text{I-B,}$$

where $k_1^o$ is the first order rate constant at zero ionic strength, $f_T$ is the activity coefficient of the transition state and a-x is the concentration of RX. The activity coefficient of the transition state can be calculated, on the same principle as used by Debye for the activity

coefficient of an ion, by treating it as a permanent dipole consisting of two point charges $\pm ze$ seperated by a fixed distance d and surrounded by a dilute atmosphere of point charges $\pm e$. It follows that, for dilute solutions,

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

where N is the Avogadro number, e is the electronic charge, $\bar{k}$ is the Botzmann constant, $\mu$ is the ionic strength, D is the dielectric constant of the medium and T is the temperature. For ease of writing $z^2 d$ will be termed $\sigma$ and $\frac{4\Pi}{1000} \cdot \frac{Ne^4}{\bar{k}^2} \cdot \frac{1}{(DT)^2}$ will be termed B.

Combining equations I-B and I-C gives,

$$v_1 = k_1^o (a-x) \exp \left[ B\sigma\mu \right] \qquad \text{I-D.}$$

The effect of ionic strength on stage (2) is obtained by introducing the Brönsted activity correction, $f_+ \cdot f_- / f_T$, where $f_T$ is given by equation I-C and $f_+$ and $f_-$, the activity coefficients of the ions are given at great dilution by Debye's formula,

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

$\sqrt{\frac{2}{1000}} \cdot \frac{N^{\frac{1}{2}} e^3}{\bar{k}^{3/2}} \cdot \frac{1}{(DT)^{3/2}}$ will be termed A so that,

$$v_2 = k_2^o \left[R^+\right]\left[X^-\right] \exp \left[ B\sigma\mu - 2A\mu^{\frac{1}{2}} \right] \qquad \text{I-F,}$$

where $k_2^o$ is the second order rate constant at zero ionic

strength.

Stage (3) is unimolecular with respect to the ion $R^+$ and has been shown by trial to be multimolecular with respect to water, the reaction being considered to go to completion by the collapse of the solvation shell around $R^+$. There will, in consequence, be a very large spatial distribution of the positive charge in the transition state for the collapse of the shell and the activity coefficient cannot be calculated by means of Debye's limiting law. As the spatial distribution is increased, the extra factor which enters into the Debye-Hückel law causes $-\ln f_{aq}$ + to approach zero and it will be given that value here. The Brönsted correction factor, $f_+/f_{aq}+$, then becomes $f_+$ and,

$$v_3 = k_3^o \left[R^+\right] \quad \exp \left[-A\mu^{\frac{1}{2}}\right] \qquad \text{I-G.}$$

Substitution of the corrected values of $v_1$, $v_2$ and $v_3$ into equation I-A gives,

$$dx/dt = \frac{k_1^o\,(a-x)}{\left[X^-\right] \alpha^o \exp\left[-A\mu^{\frac{1}{2}}\right] + \exp\left[-B\sigma\mu\right]} \qquad \text{I-H,}$$

where $\alpha^o = k_2^o/k_3^o$.

This equation was further modified for the presence of non common ions which,

(i) react with $R^+$ to give a stable product,

e.g. $N_3^-$ added to RCl or RBr,

(ii) react with $R^+$ to give a product which itself hydrolyses.

e.g. $Br^-$ added to RCl.

The validity of the approach was checked by applying equation I-H, or its modified forms for the presence of non common ions, to the observed results for the solvolytic rate of an alkyl halide under a number of different conditions, as follows. The parameter $\sigma$ was determined from the effect of salt additions on the initial rate. Equation I-H was then numerically determined and t was eliminated between it and the first order rate equation, $k't = \ln(a/a-x)$. The ratio $k'/k_1^o$ could thus be obtained and it was plotted against 100x/a. The procedure was carried out for several values of $\alpha^o$. From the experimentally obtained intergrated rate constants, the value of $k_1^o$ could be obtained by extrapolating to zero time. The experimentally obtained $k'/k_1^o$ values were also plotted against 100x/a. The value of $\alpha^o$ which gave the best fit between the experimental and calculated curves for the plot $k'/k_1^o$ vs. 100x/a was taken as correct.

For a number of alkyl halides, under a variety of experimental conditions, it was found that the values of $\alpha^o$ and $\sigma$ depended only on the nature of the organic halide, i.e. the method leads to consistent results and the treatment could be accepted as valid.

## CHAPTER II.

## SALT EFFECTS IN THE UNIMOLECULAR HYDROLYSIS OF DIPHENYLMETHYLENE CHLORIDE IN AQUEOUS ACETONE.

It has already been mentioned that the solvolysis of diphenylmethylene chloride shows deviations from first order kinetics, the rate constants dropping as reaction proceeds. The solvolysis of this compound was therefore examined in more detail in 75% and 85% aqueous acetone and also in the presence of chloride and bromide ions, in order to determine whether its behaviour was consistent with the operation of mass law and ionic strength effects as predicted by Hughes, Ingold and co-workers (1).

These authors, on the basis of their electrostatic theory, derived the rate equation,

$$dx/dt = \frac{k_1^o(a-x)}{[Cl^-]\alpha^o \exp[-A\mu^{\frac{1}{2}}] + \exp[-B\sigma\mu]} \quad \text{I-H,}$$

for the $S_N1$ solvolysis of an alkyl chloride and showed that, for any one chloride, one value of $\alpha^o$ and one of $\sigma$ allowed the rate to be expressed by this equation under a variety of experimental conditions in any one solvent. Their method, which was outlined in the previous chapter, involved the evaluation of $k_1^o$ from the value of the integrated first order rate constant at zero time for solvolytic runs in the

absence of added salts.

This method was not employed here as it was found that the k' values for the early stages of runs were not very accurate, thus making an accurate extrapolation to zero time difficult, especially as the early stages of the present runs were always associated with the largest curvature of the k' vs. t plot.

An attempt was made to obtain $k_1^o$ by expressing the instantaneous rate constant, $^{*}k_1$, as a power series in $\sqrt{\mu}$,

i.e. $k_1 = a + b\sqrt{\mu} + c\,\mu$,

where $k_1^o$ is equal to a. Again, the consistency of $k_1^o$ values obtained for a number of different runs was not particularly good.

A different method was therefore adopted. The ionic strength in all of the reactions carried out here was rather lower than that used by Hughes, Ingold and co-workers, being always under 0.06 mole/l and in the majority of cases under 0.01 mole/l. This means that under the present conditions the term $e^{-B\sigma\mu}$ in equation I-H is relatively insensitive to the value of $\sigma$ and for $\mu < 0.01$ consistent values of $\alpha^o$ and $k_1^o$ were obtained for any value of $\sigma$ between 0 and $2 \times 10^{-8}$.

*Instantaneous rate constants were obtained from integrated rate constants using the equation, $k_1 = k' + dk'/d\ln t$, the differential being obtained from the k' vs. lnt plot.

The runs at $\mu \sim 0.06$ led, by trial and error, to $1.1 \times 10^{-8}$ as the most likely value of this parameter, but even so, this value must be regarded as only approximate though sufficiently accurate for the purposes of this investigation. Accepting this value of $\sigma$, $k_1^o$ and $\alpha^o$ may be obtained from the integrated form of equation I-H by the method outlined below.

Before discussing this method it must be pointed out that the use of equation I-H in the presence of bromide ions implies that any $Ph_2CClBr$ formed by the reaction,

$$Ph_2CCl^+ + Br^- \rightarrow Ph_2CClBr,$$

is hydrolysed almost as soon as it is formed so that its concentration at any time is negligibly small. This assumption appears to be justified as no systematic difference could be detected between $\alpha^o$ and $k_1^o$ values determined from runs with and without bromide ions added.

Present Method.

Assuming instantaneous hydrolysis of $Ph_2C(OH)Cl$ and complete ionisation of all electrolytes present we have, at any one time,

$[Ph_2CCl_2] = a-x$, $[Cl^-] = c + 2x$, $\mu = b + c + 2x$,

where,

a = initial concentration of $Ph_2CCl_2$,

x = amount decomposed at time t,

b = concentration of added bromide and

c = concentration of chloride at t = 0.

Integration of equation I-H between the limits t = 0, x = 0 and t = t, x = x then gives,

$$k_1^o t = \alpha^o \int_o^x \left(\frac{c + 2x}{a - x}\right) e^{-A(b + c + 2x)^{\frac{1}{2}}} dx + e^{-B\sigma (b+c)} \int_o^x \frac{e^{-B\sigma 2x} dx}{a - x}$$

$$= \alpha^o X + Y$$

and hence,

$$Y/t = k_1^o - \alpha^o X/t \qquad \text{II-A.}$$

Thus the plot of Y/t vs. X/t gives a straight line of slope $-\alpha^o$ and intercept $k_1^o$ on the Y/t axis at X/t = 0.

In practice the method of least squares was employed to determine the best straight line for the results for any one run. Consistent values of $k_1^o$ and $\alpha^o$ were obtained by means of equation II-A for reaction mixtures containing no added chloride ions (both with and without bromide ions added). Here, the functions Y/t and X/t were subject to appreciable variations over the experimental range and the extrapolation to X/t = 0 did not involve too great a departure beyond the experimental points, c.f. figure I.

This is not the case, however, for runs in the presence of appreciable amounts of added chloride ions. Here the observed variations of these functions are very much smaller

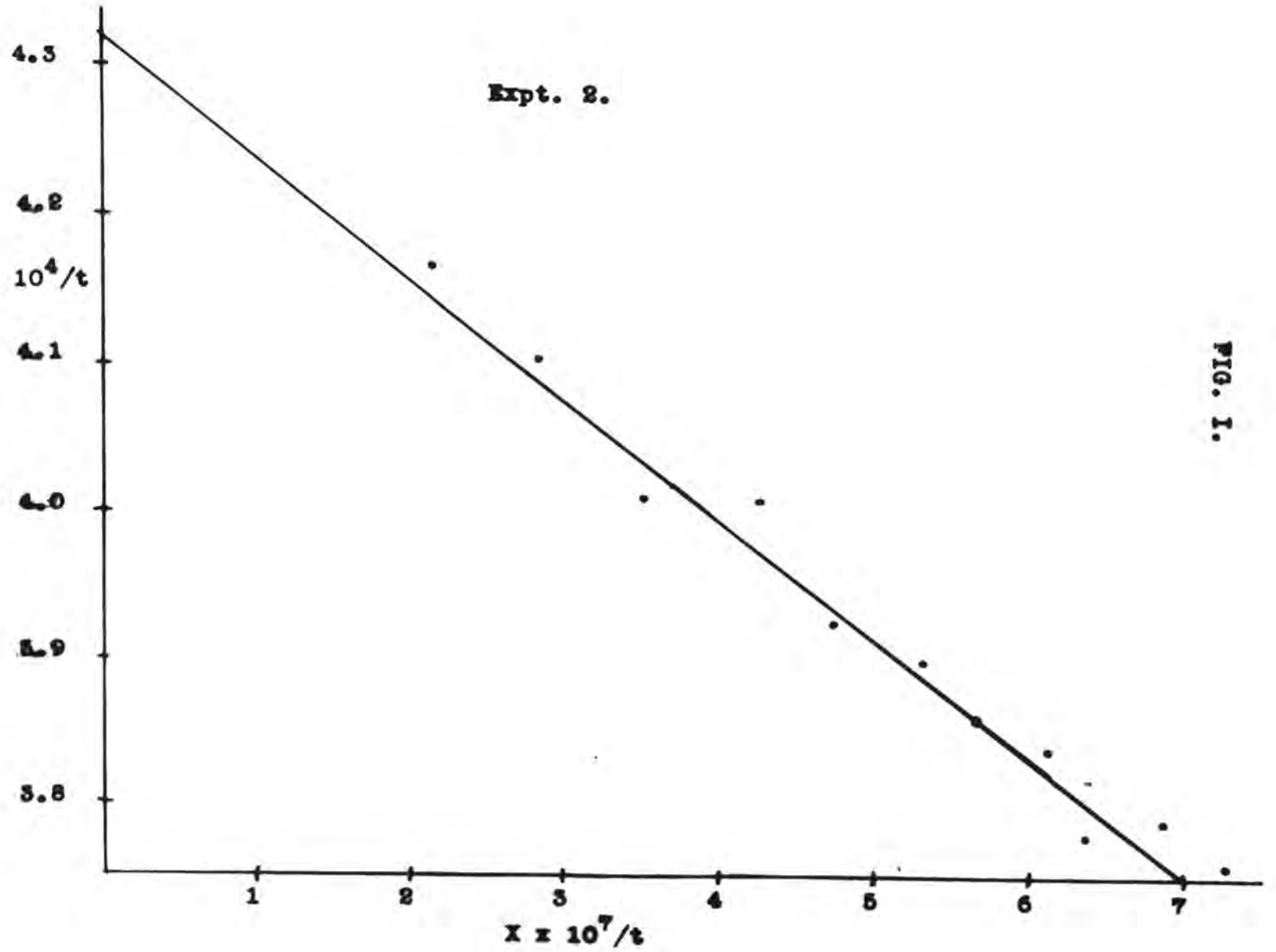



FIG. 1.

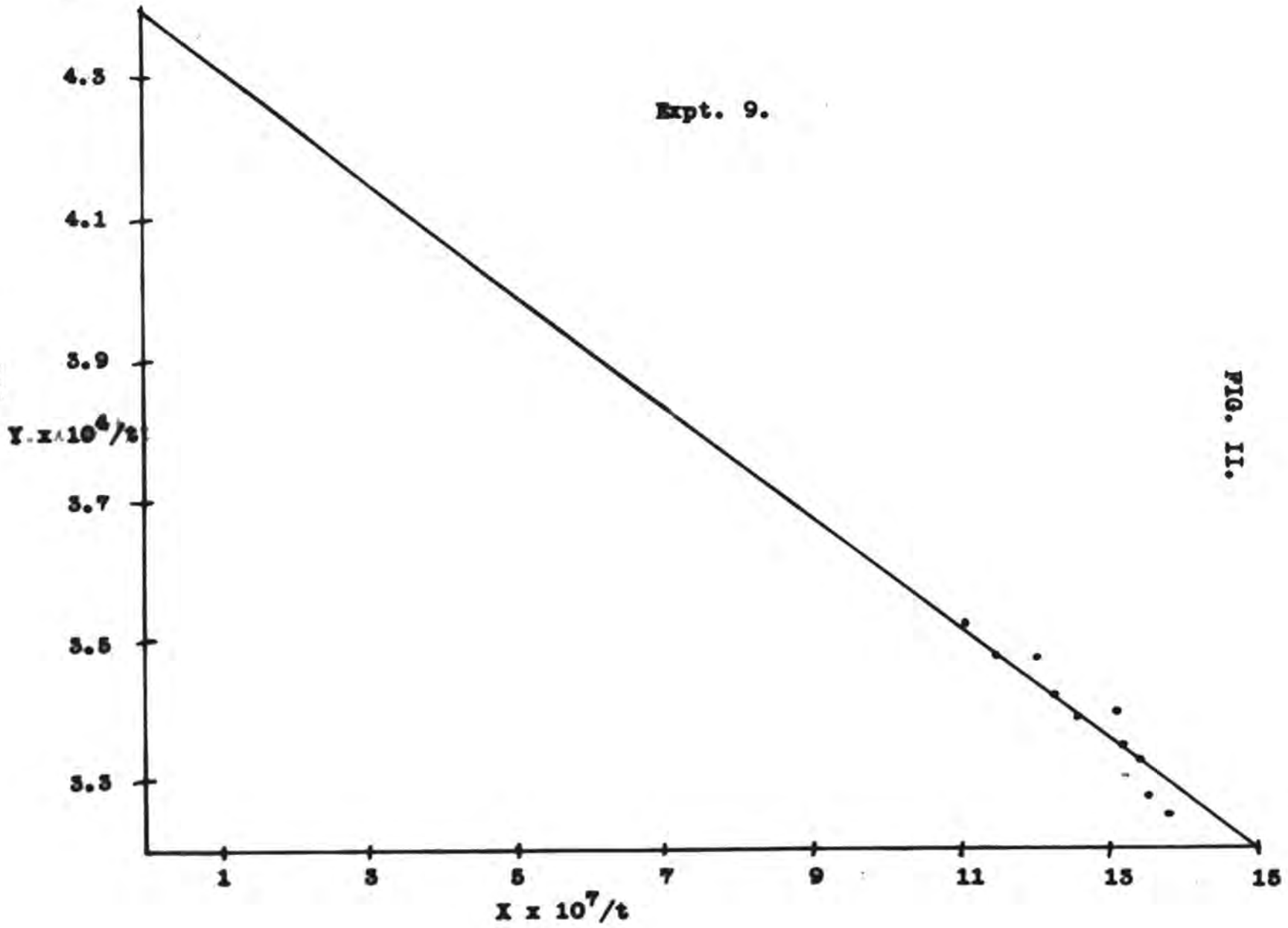



FIG. 11.

and a much longer extrapolation to $X/t = 0$ is involved, c.f. figure II. As the experimental error is the same as before, its influence on the slope and intercept will be greater and $k_1^o$ and $\alpha^o$ values determined by equation II-A will therefore not be so reliable. For this reason, $k_1^o$ values obtained from other runs were accepted in the chloride runs, $\alpha^o$ being calculated from equation II-A written in the form,

$$\alpha^o = \frac{k_1^o t - Y}{X} .$$

Values of $\alpha^o$ could thus be calculated for each point in a particular run and the average taken.

The integral,

$$X = \int_o^x \left( \frac{c + 2x}{a - x} \right) e^{-A(b + c + 2x)^{\frac{1}{2}}} dx$$

was evaluated graphically.

The integral,

$$Y = e^{-B\sigma (b + c)} \int_o^x \frac{e^{-2B\sigma x}}{a - x} dx$$

can also be integrated graphically but it can be shown (c.f. appendix to chapter III) that no accuracy is lost in writing,

$$Y = e^{-B\sigma (b + c + 2a)} \left[ k't + 2B\sigma x + (B\sigma)^2 x(2a - x) \right] ,$$

where $k'$ is the integrated first order rate constant.

Values of $\alpha^o$ (and $k_1^o$ for runs containing no added chloride ion) obtained under a wide variety of conditions

are listed in tables II-1, 2, 3 and 4. All data in table II-1 refer to the same medium (75% aq.acetone I) although in practice two batches of solvent were used. The same applies for data in table II-4 (referring to 85% aq.acetone I). One batch of solvent was standardised against another by measuring the rate of solvolysis of benzhydryl chloride in each and assuming that the same factor applied to the $k_1^o$ values for diphenylmethylene chloride. The effect of small changes in solvent composition on $\alpha^o$ was ignored but this proceedure appeared to be justified as a change from 75% to 85% aq.acetone affects $k_1^o$ by a factor of 10 while $\alpha^o$ is less than doubled (c.f. expts.1 and 21). By an inadvertence, solvents 75% aq.acetone I and II and 85% aq.-acetone I and II were not standardised with respect to each other, but the $k_1^o$ values obtained in each are internally consistent.

Discussion.

The values of $k_1^o$ and $\alpha^o$ obtained in the present investigation for diphenylmethylene chloride are reasonably constant, for a particular temperature and solvent, over a wide range of conditions and this can be regarded as proof that the disturbing effects in the hydrolysis of diphenylmethylene chloride are due to the salt effects encountered in the $S_N1$ mechanism.

Table II-1.

HYDROLYSIS OF $Ph_2CCl_2$ IN 75% AQ.ACETONE I AT 0°.

| Expt. No. | Initial $[Ph_2CCl_2]$ | Added salt | Concn. of added salt | $k_1^o \times 10^4$ | $\alpha^o$ |
|---|---|---|---|---|---|
| 1 | 0.002603 | - | - | 4.36 | 85. |
| 2 | 0.002464 | - | - | 4.32 | 81. |
| 3 | 0.01707 | - | - | 4.34 | 78. |
| 4 | 0.01718 | - | - | 4.31 | 77. |
| 5 | 0.002307 | LiBr | 0.004811 | 4.50 | 78. |
| 6 | 0.002501 | NaBr | 0.003744 | 4.42 | 80. |
| 7 | 0.02051 | NaBr | 0.01674 | 4.45 | 82. |
| 8 | 0.002556 | NaCl | 0.002917 | - | 79. |
| 9 | 0.002788 | NaCl | 0.003053 | - | 79. |
| 10 | 0.01685 | NaCl | 0.01653 | - | 82. |
| 11 | 0.01627 | NaCl | 0.008129 | - | 78. |
| Mean $k_1^o = 4.39 \times 10^{-4}$ sec$^{-1}$. Mean $\alpha^o = 80$. | | | | | |

Some discrepancies do occur in the case of runs in 85% aq.acetone with lithium bromide added, c.f. expts. 29 and 30. This is probably due to the fact that the treatment used assumed complete ionisation of salts whereas the data of Olson and Konecny (6) show that lithium bromide is not completely ionised in aqueous acetone. Rough

Table II-2.

HYDROLYSIS OF $Ph_2CCl_2$ IN 75% AQ. ACETONE II AT 0°.

| Expt. No. | Initial $[Ph_2CCl_2]$ | Concn. of KBr | Concn. of KCl | $k_1^o \times 10^4$ | $\alpha^o$ |
|---|---|---|---|---|---|
| 12 | 0.004437 | - | - | 4.06 | 75. |
| 13 | 0.004511 | 0.05075 | - | 4.04 | 85. |
| 14 | 0.004284 | 0.05075 | - | 4.03 | 82. |
| 15 | 0.004485 | 0.04960 | 0.01015 | - | 77. |
| 16 | 0.004398 | 0.03553 | 0.01522 | - | 79. |
| 17 | 0.004174 | 0.02538 | 0.02537 | - | 77. |
| Mean $k_1^o = 4.04 \times 10^{-4}$ sec$^{-1}$. Mean $\alpha^o = 79$. | | | | | |

Table II-3.

HYDROLYSIS OF $Ph_2CCl_2$ IN 85% AQ. ACETONE II AT 0°.

| Expt. No. | Initial $[Ph_2CCl_2]$ | Added salt | Concn. of added salt | $k_1^o \times 10^5$ | $\alpha^o$ |
|---|---|---|---|---|---|
| 21 | 0.005575 | - | - | 5.29 | 119. |
| 22 | 0.005650 | - | - | 5.31 | 132. |
| Mean $k_1^o = 5.30 \times 10^{-5}$ sec$^{-1}$. Mean $\alpha^o = 126$. | | | | | |

Table II-4.

HYDROLYSIS OF $Ph_2CCl_2$ IN 85% AQ.ACETONE I AT 24.76°.

| Expt. No. | Initial $[Ph_2CCl_2]$ | Added salt | Concn. of added salt | $k_1^o \times 10^4$ | $\alpha^o$ |
|---|---|---|---|---|---|
| 23 | 0.01677 | - | - | 7.93 | 166. |
| 24 | 0.01747 | - | - | 7.57 | 141. |
| 25 | 0.002828 | - | - | 7.82 | 134. |
| 26 | 0.003159 | - | - | 7.97 | 146. |
| 27 | 0.002265 | - | - | 8.15 | 136. |
| 28 | 0.002394 | - | - | 8.00 | 140. |
| 29 | 0.002496 | LiBr | 0.006644 | 8.46 | 132. |
| 30 | 0.002470 | LiBr | 0.01862 | 9.04 | 100. |

Mean $k_1^o$ (excluding expts.29 and 30) = $7.91 \times 10^{-4}$ $sec^{-1}$.

Mean $\alpha^o$ (excluding expts. 29 and 30) = 144.

calculations, based on their data, (neglecting activity effects) shown that in 75% aq.acetone, at the concentrations used here, the amount of lithium bromide undissociated is negligible, but this is not so in 85% aq.acetone. In expt. 29 the degree of ionisation is about 0.8 and in expt. 30, about 0.7.

Variation of $\alpha^o$ with Temperature.

Comparison of the values of $\alpha^o$ at 0° and 25° in

85% aq.acetone indicates that there is a small variation of $\alpha^{o}$ with temperature (although at 0° there are only two rather discordant values to go by). However, assuming that the variation is genuine, it indicates that there is a difference of about 0.9 kilocals/mole between the activation energies of stages (2) and (3) of the unimolecular mechanism as set out below,

$$RCl \underset{(2)}{\overset{(1)}{\rightleftharpoons}} R^{+} + Cl^{-} \xrightarrow[(4)]{H_2O,\ (3)} ROH + H^{+} + Cl^{-}$$

$$Cl^{-} \xrightarrow{N_3^{-}} RN_3 + Cl^{-}$$

Since processes (4) and (2) can be expected to have comparable activation energies, such a conclusion may be compared with that of Hawdon, Hughes and Ingold (7) who have shown that the difference between the activation energies of stages (4) and (3) is only 4 kilocals/mole in the hydrolysis of pp'-dimethyl-benzhydryl chloride in aqueous acetone.

Variation of $\alpha^{o}$ with Solvent.

Comparison of the values of $\alpha^{o}$ in 75% and 85% aq.acetone at 0° shows that $\alpha^{o}$ becomes smaller as the solvent becomes more aqueous. $\alpha^{o}$ is equal to $k_2^{o}/k_3^{o}$ and so it would appear that a variation in the ionising (i.e. solvating) power of the medium has not the same effect on $k_2^{o}$ as on $k_3^{o}$. $k_2^{o}$ is the rate constants for process (2) i.e. $R^{+} + Cl^{-} \rightarrow RCl$. It

is reasonable to assume that the transition state of this reaction will be less charged than the reactants were, and in consequence less solvated. $k_3^o$ is the rate constant for stage (3) i.e. $R^+ + H_2O \rightarrow ROH + H^+$. Here, the transition state can be expected to carry the same charge as the initial state but the charge will be more dispersed. This again will result in a less solvated transition state.

The effect of decreasing the ionising power of the medium will thus be to increase the rates of both processes. However, in process (2) there will be a greater reduction in solvation from the initial state to the transition state than in process (3) since, in the former there is a charge reduction whereas in the latter there is merely charge dispersion. The solvent influence can thus be expected to be greater for process (2) than process (3) and a decrease in ionising power of the medium will increase $k_2^o$ to a greater extent than $k_3^o$, i.e. $\alpha^o$ will rise. This is as observed.

Such a solvent dependence of $\alpha^o$ was not observed by Hughes, Ingold and co-workers (1), but in the case where it might have been expected to appear, i.e. the hydrolysis of pp'-dimethylbenzhydryl chloride, their rates where uncomfortably high with the result that, as they themselves point out, their experimental points show a considerable scatter about the theoretical curves. It is possible,

therefore, that because of these unavoidable experimental errors, the effect was missed.

Variation of $\alpha^{o}$ with R.

The value of $\alpha^{o}$ represents the efficacy with which the solvated cations are destroyed by their own anions. This is dependent on the length of time the solvation shell of $R^{+}$ survives before internal collapse, which in turn depends on the extent of electron release to the reaction centre. Increased electron release to the reaction centre will cause an increase in stability of $R^{+}$, a longer time of survival and hence a greater chance of destruction by penetration of its solvation shell by a halide ion.

Table II-5 gives values of $\alpha^{o}$ for several substituted benzhydryl chlorides obtained by Hughes, Ingold and coworkers (1) and for diphenylmethylene chloride obtained in the present investigation. The values of $\alpha^{o}$ for diphenylmethylene chloride are greater than those obtained for any of the other compounds and this indicates powerful electron release to the reaction centre, by the extra $\alpha$-chlorine atom, as shown in the first part of this thesis.

Variation of $\sigma$ with R.

The magnitude of $\sigma^{*}(=z^{2}d)$ for diphenylmethylene chloride is lower than in any of the other cases mentioned in table II-5, although its value for $\alpha^{o}$ is the greatest. Hughes,

Table II-5.

p-SUBSTITUTED BENZHYDRYL CHLORIDES (1) AND DIPHENYLMETHYLENE CHLORIDE.

(Ionic Strength and Mass Law Constants).

| Reaction | $\alpha^{o}$ | $\sigma \times 10^{8}$ |
|---|---|---|
| Benzhydryl Chloride in aq.acetone | 10. | 1.62 |
| p-Tert.-butyl-benzhydryl Chloride in aq.acetone | 20. | 2.22 |
| p-Methyl-benzhydryl Chloride in aq.acetone | 35. | 2.22 |
| pp'-Dimethyl-benzhydryl Chloride in aq.acetone | 69. | 2.73 |
| Diphenylmethylene Chloride in 75% aq.acetone at $0^{o}$ | 80. | 1.1 |
| Diphenylmethylene Chloride in 85% aq.acetone at $0^{o}$ | 126. | 1.1 |
| Diphenylmethylene Chloride in 85% aq.acetone at $24.76^{o}$ | 144. | 1. 1 |

Ingold and co-workers (1e) have attributed the high $\sigma^-$ values for the para substituted benzhydryl chlorides, as compared with tert.-butyl bromide where it is about $0.74 \times 10^{-8}$, to mesomerism in the transition state. This would tend to move the effective position of the positive charge from the aliphatic carbon atom into the benzene rings, so increasing d and hence $\sigma^-$.

Electron release by para substituents would tend to move the positive charge even further into the benzene rings and so increase $\sigma^-$ still further, as observed. In the case of dipheylmethylene chloride, however, the electron releasing substituent is not remote from the reaction centre but is directly attached to it. Electron release by the $\alpha$-chlorine atom will tend to move the effective position of the positive charge (in the transition state) towards itself and therefore out of the benzene rings, so reducing d and therefore $\sigma^-$.

## CHAPTER III.

## EXPERIMENTAL.

### Preparation and Purification of Materials.

#### Reactants.

a) Diphenylmethylene Chloride.

This compound was prepared and purified as detailed in part I, chapter III of this thesis.

b) Lithium, Sodium and Potassium Chlorides and Bromides.

These salts were dried, by heating in an oven at 250°, cooled and stored over $P_2O_5$ in a desicator.

#### Solvents.

Acetone.

Commercial acetone was purified as described in part I. The solvents were made up by volume, e.g. 75% aq.acetone was composed of 75 volumes of acetone added to 25 volumes of water.

#### Procedure of Hydrolysis.

Kinetic runs were carried out at 0° and 24.76°, the thermostats being as described in part I. The hydrolysis of diphenylmethylene chloride always went to completion and the rate constants could therefore be calculated from a knowledge of the acid produced at various times and the acidity at 100% reaction.

All runs were flask runs. About 100 ml. of solvent in a stoppered flask were allowed to come to the temperature of the thermostat. Reactant was added and the flask was thoroughly shaken. Samples were removed from time to time by means of a 5 ml. pipette.

Analysis of Samples for Acid.

The extracted samples were run into about 200 ml. of acetone to stop the reaction. The acid produced was then titrated against standard caustic soda, the acetone having been previously treated with the indicator lacmoid and neutralised.

Estimation of Added Salts.

The potassium bromide and chloride were weighed into a known volume of solvent. In all other cases the added halide was estimated from a knowledge of the total halide concentration and the acidity at complete reaction. The total halide at complete reaction was determined by differential potentiometric titration with silver nitrate as described below.

The Differential Potentiometric Titration Technique.

The procedure was as follows. Two silver - silver chloride electrodes were placed in the halide solution. One of the electrodes was protected from the bulk of the solution by being mounted in a capillary tube. At the

start, both electrodes were in contact with the same solution and there was thus no potential difference between them. Some silver nitrate was added whilst the bulk of the solution was stirred. The two electrodes were thus in contact with solutions of different composition and in effect a concentration cell was created with the result that a potential difference was also created between the electrodes. After each addition of silver nitrate, the E.M.F. was read, the capillary tube was flushed out and the two electrodes were once again brought into contact with the same solution.

At the equivalence point, the E.M.F. per unit titre was at a maximum.

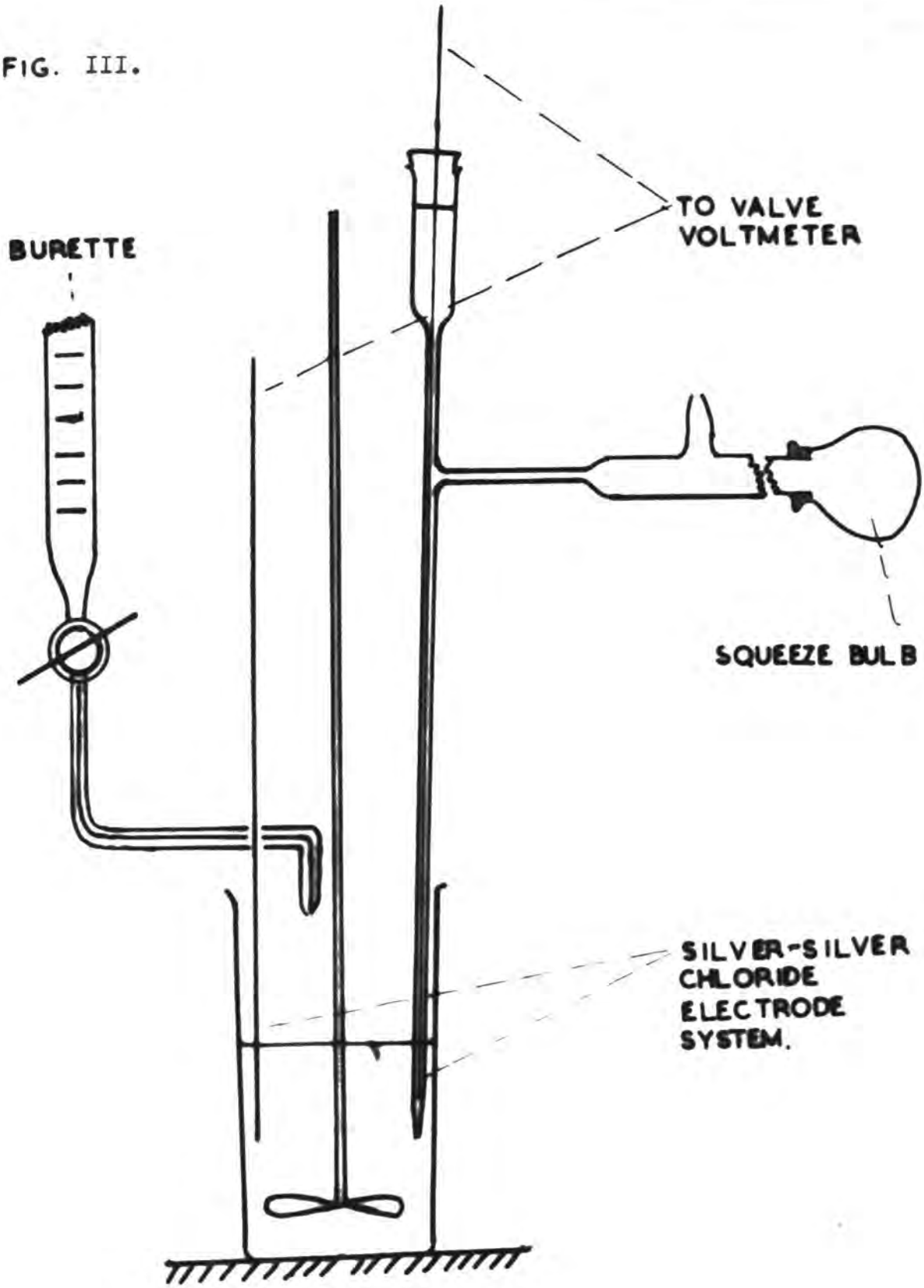
The apparatus was as illustrated in figure III. Silver nitrate was added from the burette into the halide solution in the beaker to which acetone had been added. The addition of the latter was found to give a sharper end-point. The E.M.F. was measured on a valve voltmeter, as illustrated in figure IV, which was capable of reading E.M.F. without taking any current. It was not calibrated as this was unnecessary for the present purpose.

Calculation of Rate Constants.

First order rate constants were calculated from the equation,

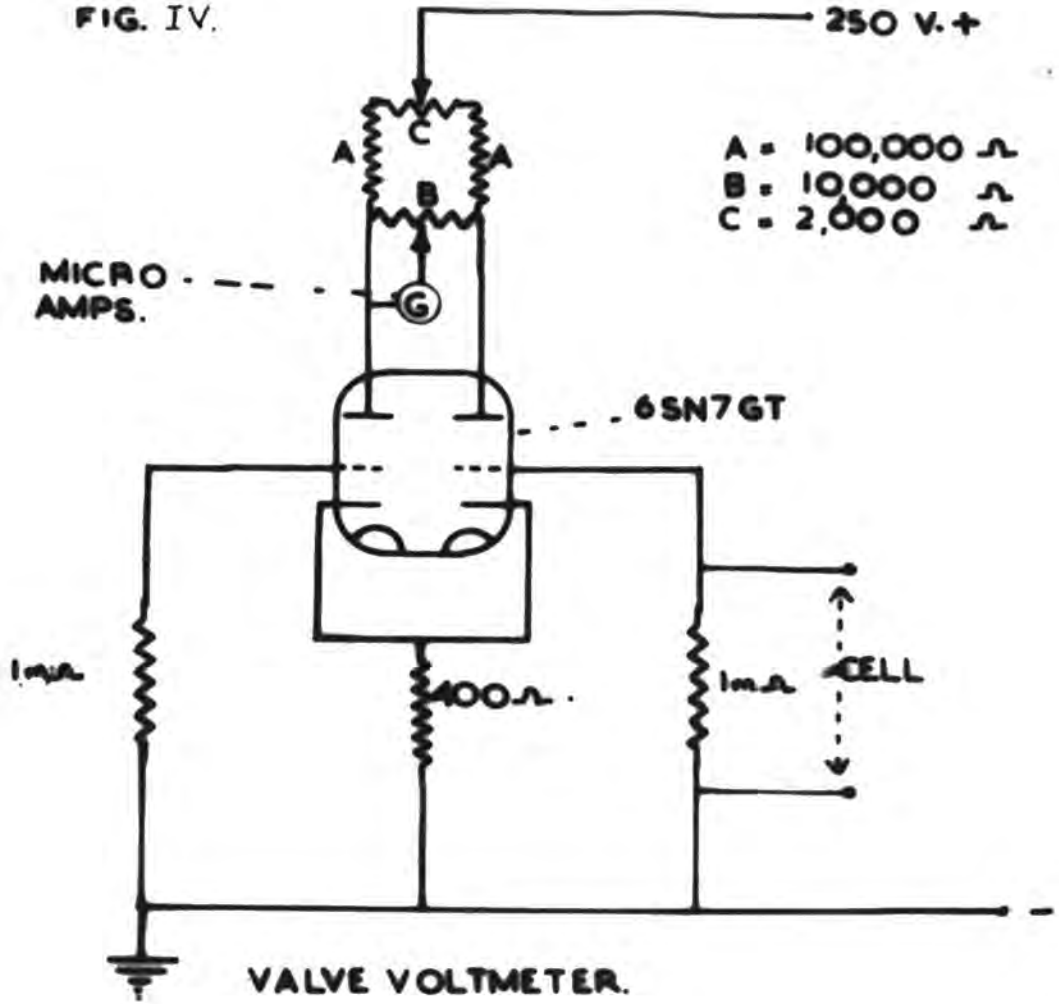
$$k't = \ln(a/a-x),$$

FIG. III.




DIFFERENTIAL TITRATION APPARATUS

FIG. IV.


250 V.+
A = 100,000 Ω
B = 10,000 Ω
C = 2,000 Ω
A
C
A
B
MICRO AMPS.
G
6SN7GT
1mΩ
100Ω
1mΩ
CELL
-
VALVE VOLTMETER.

where t is the time in seconds, and a and a-x are the concentrations of organic halide at t = 0 and t = t respectively. The time of the first reading was taken as zero, a being the difference between the first reading and the reading when the reaction had gone to completion. Detailed results of individual runs are given in the second appendix to this chapter.

First Appendix to Chapter III.

Values of A,B and D.

The values of the parameters A and B and the dielectric constant D for the solvents and temperatures used in the present investigation are given in table III-1.

Table III-1.

| Solvent and Temperature. | D | A | B x $10^{-8}$ |
|---|---|---|---|
| 75% aq. acetone at $0^{\circ}$ | 40.00 | 3.657 | 1.759 |
| 85% aq. acetone at $24.76^{\circ}$ | 28.60 | 5.315 | 2.893 |
| 85% aq. acetone at $0^{\circ}$ | 32.28 | 5.048 | 2.701 |
| Dielectric constants estimated from Åkerlöf's data (8). | | | |

Evaluation of Integral.

$$Y = e^{-B\sigma (b + c)} \int_0^x \frac{e^{-2B\sigma x}}{a - x}\, dx.$$

$$= e^{-B\sigma (b + c)} I,$$

where $I = \int_0^x \frac{e^{-2B\sigma x}}{a - x}\, dx.$

Writing $2B\sigma = L$ and $(a-x) = Z$ we have,

$$I = -\int \left( e^{-L(a - Z)}/Z \right) dZ$$

$$= -e^{-La} \int \left( e^{+LZ}/Z \right) dZ$$

$$= -e^{-La} \int (1/Z + L + L^2 Z/2 \text{ ----}) dZ.$$

$$= e^{-La}(-\ln Z - LZ - L^2Z^2/4 \text{ ------ }) + K$$

Substitution back for L and Z gives,

$$I = e^{-2B\sigma a}\left[ -\ln(a - x) - 2B\sigma (a - x) - (B\sigma)^2(a - x)^2 \text{---} \right.$$

$$\left. \text{------} \right]_0^x$$

$$= e^{-2B\sigma a}\left[ k't + 2B\sigma x + (B\sigma)^2 x(2a - x) \text{ ---- } \right]$$

where k' is the integrated first order rate constant.

Therefore,

$$Y = e^{-B\sigma (b + c + 2a)}\left[ k't + 2B\sigma x + (B\sigma)^2 x(2a - x)\text{---} \right]$$

and,

$$Y/t = e^{-B\sigma (b + c + 2a)}\left[ k' + 2B\sigma x/t + (B\sigma)^2 x(2a - x)/t\text{--} \right]$$

Only the first three terms of this series were taken, further terms being negligible as shown by table II-2 which contains these three terms for the first points (where the second and third terms were the most important) for several runs.

Table III-2.

| Expt. No. | $k' . 10^4$ | $2B\sigma x . 10^4/t$ | $(B\sigma)^2 x(2a - x) . 10^4/t$ |
|---|---|---|---|
| 2 | 4.169 | 0.034 | 0. |
| 4 | 3.512 | 0.207 | 0.006 |
| 5 | 4.420 | 0.036 | 0. |
| 7 | 3.873 | 0.277 | 0.010 |
| 9 | 3.553 | 0.033 | 0. |
| 12 | 3.654 | 0.051 | 0. |
| 13 | 4.261 | 0.061 | 0. |
| 24 | 5.206 | 0.499 | 0.024 |
| 26 | 6.941 | 0.112 | 0.001 |
| 29 | 8.455 | 0.113 | 0.001 |
| 21 | 4.818 | 0.145 | 0.002 |

## Second Appendix to Chapter III.

### Hydrolysis of Diphenylmethylene Chloride in Aqueous Acetone.

Details of Individual Runs.

First order rate constants were calculated from the equation,

$$k' = 2.303/t \log_{10}(a/a-x)$$

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

t is the time in seconds,

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

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

The values of a and a-x were obtained from the titration results, expressed in ml. of NaOH per sample. It was assumed that after the first chlorine atom had been hydrolysed off the other instantly followed it.

Expt. 1. Diphenylmethylene Chloride in 75% aq.Acetone Ia at 0°.

Initial concentration 0.002603M.

5 ml. titrated with 0.002160N NaOH.

| Time | Titn | $k' \times 10^4$ |
|---|---|---|
| 0 | 1.01 | - |
| 225 | 2.00 | 4.186 |
| 530 | 3.15 | 4.067 |
| 1130 | 4.99 | 3.957 |
| 1430 | 5.73 | 3.902 |
| 1730 | 6.43 | 3.905 |
| 2090 | 6.90 | (3.650) |
| 2455 | 7.70 | 3.794 |
| 2875 | 8.29 | 3.746 |
| 3300 | 8.81 | 3.716 |
| 3725 | 9.30 | 3.733 |
| 4205 | 9.70 | 3.681 |
| $\infty$ | 12.05 | - |

Expt. 2. Diphenylmethylene Chloride in 75% aq.Acetone Ib at 0°.

Initial concentration 0.002464M.

5 ml. titrated with 0.002010N NaOH.

| Time | Titn | $k' \times 10^4$ |
|---|---|---|
| 0 | 0.70 | - |
| 300 | 2.06 | 4.169 |
| 540 | 3.00 | 4.107 |
| 840 | 4.01 | 4.015 |
| 1145 | 4.96 | 4.015 |
| 1445 | 5.71 | 3.931 |
| 1760 | 6.45 | 3.908 |
| 2040 | 7.01 | 3.868 |
| 2350 | 7.58 | 3.849 |
| 2640 | 8.01 | 3.791 |
| 3005 | 8.57 | 3.801 |
| 3425 | 9.08 | 3.770 |
| ∞ | 12.26 | - |

Expt. 3. Diphenylmethylene Chloride in 75% aq.Acetone Ib at 0°.

Initial concentration 0.01707M.

5 ml. titrated with 0.01109N NaOH.

| Time | Titn | $k' \times 10^4$ |
|---|---|---|
| 0 | 0.84 | - |
| 240 | 2.02 | (3.512) |
| 540 | 3.30 | 3.430 |
| 840 | 4.30 | 3.232 |
| 1145 | 5.23 | 3.135 |
| 1460 | 6.03 | 3.020 |
| 1750 | 6.71 | 2.952 |
| 2040 | 7.31 | 2.883 |
| 2355 | 7.90 | 2.820 |
| 2680 | 8.40 | 2.735 |
| 3100 | 9.10 | 2.705 |
| 3515 | 9.70 | 2.672 |
| ∞ | 15.39 | - |

Expt. 4. Diphenylmethylene Chloride in 75% aq. Acetone Ib at 0°.

Initial concentration 0.01718M.

5 ml. titrated with 0.01109N NaOH.

| Time | Titn | $k' \times 10^4$ |
|---|---|---|
| 0 | 1.11 | - |
| 240 | 2.27 | 3.512 |
| 535 | 3.46 | 3.336 |
| 835 | 4.48 | 3.200 |
| 1135 | 5.33 | 3.062 |
| 1435 | 6.10 | 2.971 |
| 1770 | 6.87 | 2.893 |
| 2090 | 7.56 | 2.849 |
| 2445 | 8.20 | 2.779 |
| 2845 | 8.81 | 2.695 |
| 3245 | 9.42 | 2.659 |
| 3665 | 9.99 | 2.622 |
| $\infty$ | 15.49 | - |

Expt. 5. Diphenylmethylene Chloride in 75% aq.Acetone Ia at 0°.

Initial concentration 0.002307M. Added LiBr 0.004811N.

5 ml. titrated with 0.002189N NaOH.

| Time | Titn | $k' \times 10^4$ |
|---|---|---|
| 0 | 0.51 | - |
| 235 | 1.50 | 4.420 |
| 495 | 2.42 | (4.267) |
| 780 | 3.39 | 4.340 |
| 1090 | 4.24 | 4.269 |
| 1385 | 4.95 | 4.221 |
| 1685 | 5.60 | 4.205 |
| 1985 | 6.11 | 4.118 |
| 2295 | 6.67 | 4.151 |
| 2675 | 7.15 | 4.056 |
| 3035 | 7.60 | 4.045 |
| 3455 | 8.02 | 3.999 |
| 3875 | 8.44 | 4.036 |
| 4350 | 8.79 | 4.016 |
| $\infty$ | 10.54 | - |

Expt. 6. Diphenylmethylene Chloride in 75% aq.Acetone Ia at 0°.

Initial concentration 0.002501M. Added NaBr 0.003744N.

5 ml. titrated with 0.002175N NaOH.

| Time | Titn | k' x $10^4$ |
|---|---|---|
| 0 | 0.60 | - |
| 230 | 1.61 | 4.226 |
| 490 | 2.65 | 4.253 |
| 775 | 3.60 | 4.155 |
| 1065 | 4.50 | 4.160 |
| 1335 | 5.20 | 4.118 |
| 1610 | 5.83 | 4.060 |
| 1945 | 6.50 | 4.006 |
| 2230 | 7.00 | 3.967 |
| 2610 | 7.61 | 3.949 |
| 2970 | 8.08 | 3.903 |
| 3395 | 8.51 | 3.811 |
| 3830 | 9.00 | 3.845 |
| ∞ | 11.50 | - |

Expt. 7. Diphenylmethylene Chloride in 75% aq.Acetone Ib at 0°.

Initial concentration 0.02051M. Added NaBr 0.01674N.

5 ml. titrated with 0.01109N NaOH.

| Time | Titn | $k' \times 10^4$ |
|---|---|---|
| 0 | 0.80 | - |
| 305 | 2.77 | 3.873 |
| 600 | 4.22 | 3.576 |
| 895 | 5.50 | 3.451 |
| 1200 | 6.61 | 3.316 |
| 1505 | 7.61 | 3.229 |
| 1860 | 8.60 | 3.125 |
| 2280 | 9.54 | 2.987 |
| 2700 | 10.42 | 2.907 |
| 3185 | 11.31 | 2.830 |
| 3660 | 12.05 | 2.759 |
| 4515 | 13.19 | 2.667 |
| ∞ | 18.50 | - |

Expt. 8. Diphenylmethylene Chloride in 75% aq.Acetone Ib at $0^{\circ}$.

Initial concentration 0.002556M. Added NaCl 0.002917N.

5 ml. titrated with 0.002010N NaOH.

| Time | Titn | $k' \times 10^4$ |
|---|---|---|
| 0 | 0.71 | - |
| 240 | 1.77 | (3.839) |
| 535 | 2.80 | 3.572 |
| 835 | 3.80 | 3.561 |
| 1140 | 4.70 | 3.542 |
| 1440 | 5.45 | 3.486 |
| 1740 | 6.15 | 3.466 |
| 2035 | 6.73 | 3.418 |
| 2340 | 7.35 | 3.440 |
| 2705 | 7.91 | 3.383 |
| 3140 | 8.51 | 3.339 |
| 3535 | 9.04 | 3.347 |
| 4020 | 9.57 | 3.330 |
| $\infty$ | 12.72 | - |

Expt. 9. Diphenylmethylene Chloride in 75% aq.Acetone Ib at 0°.

Initial concentration 0.002788M. Added NaCl 0.003053N.

5 ml. titrated with 0.002010N NaOH.

| Time | Titn | k x $10^4$ |
|---|---|---|
| 0 | 0.79 | - |
| 305 | 2.20 | (3.730) |
| 610 | 3.34 | 3.553 |
| 905 | 4.35 | 3.510 |
| 1205 | 5.30 | 3.507 |
| 1535 | 6.17 | 3.451 |
| 1835 | 6.89 | 3.421 |
| 2135 | 7.59 | 3.435 |
| 2460 | 8.18 | 3.384 |
| 2760 | 8.70 | 3.363 |
| 3120 | 9.22 | 3.314 |
| 3545 | 9.79 | 3.286 |
| ∞ | 13.87 | - |

Expt. 10. Diphenylmethylene Chloride in 75% aq.Acetone Ib at 0°.

Initial concentration 0.01685M. Added NaCl 0.01653N.

5 ml. titrated with 0.01109N NaOH.

| Time | Titn | k x $10^4$ |
|---|---|---|
| 0 | 0.58 | - |
| 240 | 1.38 | 2.341 |
| 540 | 2.31 | (2.332) |
| 840 | 3.11 | 2.265 |
| 1125 | 3.81 | 2.219 |
| 1495 | 4.63 | 2.172 |
| 1750 | 5.20 | 2.171 |
| 2150 | 5.99 | 2.150 |
| 2635 | 6.81 | 2.108 |
| 3125 | 7.58 | 2.085 |
| 3595 | 8.14 | 2.025 |
| 4195 | 8.90 | 2.008 |
| 4800 | 9.56 | 1.985 |
| 5395 | 10.10 | 1.953 |
| $\infty$ | 15.20 | - |

Expt. 11. Diphenylmethylene Chloride in 75% aq.Acetone Ib at $0^{o}$.

Initial concentration 0.01627M. Added NaCl 0.008129N.

5 ml. titrated with 0.01109N NaOH.

| Time | Titn | $k' \times 10^4$ |
|---|---|---|
| 0 | 1.10 | - |
| 240 | 2.01 | 2.888 |
| 720 | 3.49 | 2.690 |
| 1015 | 4.22 | 2.574 |
| 1320 | 4.98 | 2.551 |
| 1680 | 5.80 | 2.530 |
| 2035 | 6.42 | 2.445 |
| 2395 | 7.02 | 2.392 |
| 2805 | 7.70 | 2.375 |
| 3240 | 8.28 | 2.325 |
| 3660 | 8.82 | 2.299 |
| 4260 | 9.51 | 2.270 |
| $\infty$ | 14.67 | - |

Expt. 12. Diphenylmethylene Chloride in 75% aq.Acetone II at 0°.

Initial concentration 0.004437M.

5 ml. titrated with 0.003825N NaOH.

| Time | Titn | $k' \times 10^4$ |
|---|---|---|
| 0 | 1.68 | - |
| 300 | 2.71 | 3.654 |
| 725 | 3.92 | 3.530 |
| 1080 | 4.80 | 3.497 |
| 1441 | 5.57 | 3.455 |
| 1795 | 6.20 | 3.389 |
| 2157 | 6.79 | 3.358 |
| 2880 | 7.73 | 3.270 |
| 3475 | 8.38 | 3.238 |
| 4320 | 9.10 | 3.191 |
| 5042 | 9.60 | 3.176 |
| 5760 | 9.97 | 3.136 |
| 6480 | 10.24 | 3.067 |
| ∞ | 11.60 | - |

Expt. 13. Diphenylmethylene Chloride in 75% aq.Acetone II at 0°.

Initial concentration 0.004511M. Added KBr 0.05075N

5 ml. titrated with 0.003798N NaOH.

| Time | Titn | $k' \times 10^4$ |
|---|---|---|
| 0 | 1.21 | - |
| 300 | 2.49 | 4.261 |
| 595 | 3.51 | 4.084 |
| 905 | 4.50 | 4.075 |
| 1200 | 5.30 | 4.030 |
| 1500 | 6.01 | 3.985 |
| 1800 | 6.63 | 3.941 |
| 2400 | 7.69 | 3.896 |
| 3000 | 8.50 | 3.834 |
| 3600 | 9.10 | 3.737 |
| 4500 | 9.90 | 3.743 |
| 5100 | 10.22 | 3.649 |
| $\infty$ | 11.88 | - |

Expt. 14. Diphenylmethylene Chloride in 75% aq.Acetone II at 0°.

Initial concentration 0.004284M. Added KBr 0.05075N.

5 ml. titrated with 0.003798N NaOH.

| Time | Titn | $k' \times 10^4$ |
|---|---|---|
| 0 | 1.13 | - |
| 305 | 2.40 | (4.387) |
| 605 | 3.41 | 4.207 |
| 900 | 4.25 | 4.082 |
| 1200 | 5.08 | 4.109 |
| 1500 | 5.71 | 4.001 |
| 1800 | 6.34 | 4.002 |
| 2462 | 7.42 | 3.927 |
| 3005 | 8.10 | 3.863 |
| 3603 | 8.72 | 3.823 |
| 4200 | 9.24 | 3.822 |
| 4620 | 9.49 | 3.757 |
| 4935 | 9.70 | 3.771 |
| $\infty$ | 11.28 | - |

Expt. 15. Diphenylmethylene Chloride in 75% aq.Acetone II at 0°.

Initial concentration 0.004485M.

Added KBr 0.04060N. Added KCl 0.01015N.

5 ml. titrated with 0.003798N NaOH.

| Time | Titn | $k' \times 10^4$ |
|---|---|---|
| 0 | 1.08 | - |
| 422 | 2.41 | 3.139 |
| 855 | 3.59 | 3.116 |
| 1260 | 4.52 | 3.069 |
| 1680 | 5.41 | 3.076 |
| 2100 | 6.11 | 3.013 |
| 2525 | 6.80 | 3.016 |
| 3360 | 7.85 | 2.968 |
| 4200 | 8.67 | 2.927 |
| 5050 | 9.31 | 2.885 |
| 6015 | 9.90 | 2.870 |
| 6305 | 10.06 | (2.877) |
| 7140 | 10.40 | 2.843 |
| $\infty$ | 11.81 | - |

Expt. 16. Diphenylmethylene Chloride in 75% aq.Acetone II at 0°.

Initial concentration 0.004398M.

Added KBr 0.03553N  Added KCl 0.01522N.

5 ml. titrated with 0.003798N NaOH.

| Time | Titn | $k' \times 10^4$ |
|---|---|---|
| 0 | 1.10 | - |
| 480 | 2.40 | 2.760 |
| 955 | 3.51 | 2.735 |
| 1440 | 4.46 | 2.683 |
| 1925 | 5.34 | 2.693 |
| 2405 | 6.07 | 2.673 |
| 2885 | 6.70 | 2.649 |
| 3780 | 7.70 | 2.629 |
| 4745 | 8.52 | 2.594 |
| 5585 | 9.08 | 2.567 |
| 6487 | 9.60 | 2.569 |
| 7440 | 10.00 | 2.543 |
| 8295 | 10.28 | 2.516 |
| ∞ | 11.58 | - |

Expt. 17. Diphenylmethylene Chloride in 75% aq.Acetone II at 0°.

Initial concentration 0.004174M.

Added KBr 0.02538N. Added KCl 0.02537N.

5 ml. titrated with 0.003798N NaOH.

| Time | Titn | $k' \times 10^4$ |
|---|---|---|
| 0 | 0.82 | - |
| 605 | 2.12 | 2.257 |
| 1202 | 3.23 | 2.246 |
| 1745 | 4.10 | 2.231 |
| 2401 | 5.01 | 2.210 |
| 3005 | 5.74 | 2.200 |
| 3644 | 6.40 | 2.182 |
| 4802 | 7.41 | 2.174 |
| 6001 | 8.19 | 2.146 |
| 7202 | 8.80 | 2.132 |
| 8040 | 9.15 | 2.126 |
| 8300 | 9.24 | 2.120 |
| 8640 | 9.32 | (2.092) |
| $\infty$ | 10.99 | - |

Expt. 18. Diphenylmethyl Chloride in 75% aq.Acetone Ib at 0°.

Initial concentration 0.005652M

5 ml. titrated with 0.002175N NaOH.

| Time | Titn | $k' \times 10^6$ |
|---|---|---|
| 0 | 0.00 | - |
| 21000 | 1.94 | 7.710 |
| 32100 | 2.81 | 7.605 |
| 36300 | 3.10 | 7.519 |
| 81540 | 6.00 | 7.603 |
| 91500 | 6.50 | 7.590 |
| 103980 | 7.09 | 7.591 |
| 168060 | 9.44 | 7.720 |
| 185520 | 9.82 | 7.607 |
| 197640 | 10.07 | 7.557 |
| ∞ | 12.99 | - |

$k' = 7.611$

Expt. 19. Diphenylmethyl Chloride in 75% aq.Acetone Ia at 0°.

Initial concentration 0.005915M.

5 ml. titrated with 0.002175N NaOH.

| Time | Titn | $k' \times 10^6$ |
|---|---|---|
| 0 | 0.00 | - |
| 9960 | 1.00 | 7.651 |
| 14400 | 1.41 | 7.597 |
| 21960 | 2.10 | 7.635 |
| 81480 | 6.28 | 7.605 |
| 91440 | 6.81 | 7.599 |
| 103920 | 7.47 | 7.670 |
| 168000 | 9.82 | 7.621 |
| 185460 | 10.30 | 7.637 |
| 198060 | 10.60 | 7.631 |
| $\infty$ | 13.60 | - |

$k' = 7.627$

Expt. 20. Diphenylmethylene Chloride in 75% aq.Acetone Ib at 0°.

Initial concentration 0.002907M. Added $Et_3N$ 0.003556N.
5 ml. titrated with 0.002288N NaOH.
The $Et_3N$ could be titrated with HCl in acetone. Until the reaction had produced enough acid to neutralise the $Et_3N$ 5 ml. of 0.004333N HCl were added before titration to each sample. This was not necessary beyond the dotted line.

| Time | Titn | $k' \times 10^4$ |
|---|---|---|
| 0 | 2.39 | - |
| 630 | 5.20 | 4.226 |
| 900 | 6.19 | 4.223 |
| 1195 | 7.11 | 4.176 |
| 1495 | 7.91 | 4.114 |
| 1810 | 8.65 | 4.066 |
| 2105 | 9.19 | 3.963 |
| 2460 | 0.38 | 3.940 |
| 2820 | 0.91 | 3.876 |
| 3240 | 1.42 | 3.792 |
| 3735 | 2.02 | 3.790 |
| ∞ | 4.94 | - |

Expt.21. Diphenylmethylene Chloride in 85% aq.Acetone II at $0^{o}$.

Initial concentration 0.005575M.

5 ml. titrated with 0.005528N NaOH.

| Time | Titn | $k' \times 10^5$ |
|---|---|---|
| 0 | 0.11 | - |
| 2700 | 1.40 | (5.126) |
| 3600 | 1.70 | 4.818 |
| 5400 | 2.33 | 4.656 |
| 7200 | 2.90 | 4.555 |
| 10815 | 3.89 | 4.404 |
| 16545 | 5.08 | 4.168 |
| 20160 | 5.70 | 4.073 |
| 24960 | 6.40 | 3.986 |
| 29820 | 6.92 | 3.846 |
| 34560 | 7.40 | 3.793 |
| $\infty$ | 10.09 | - |

Expt.22. Diphenylmethylene Chloride in 85% aq.Acetone II at 0°.

Initial concentration 0.005650M.

5 ml. titrated with 0.005528N NaOH.

| Time | Titn | $k' \times 10^5$ |
|---|---|---|
| 0 | 0.13 | - |
| 1800 | 1.00 | 5.002 |
| 2700 | 1.39 | 4.930 |
| 3600 | 1.72 | 4.760 |
| 5400 | 2.33 | 4.550 |
| 7200 | 2.91 | 4.476 |
| 10800 | 3.88 | 4.301 |
| 16200 | 5.01 | 4.080 |
| 19800 | 5.60 | 3.945 |
| 24600 | 6.35 | 3.897 |
| 29400 | 6.91 | 3.792 |
| 34200 | 7.40 | 3.729 |
| $\infty$ | 10.22 | - |

Expt.23. Diphenylmethylene Chloride in 85% aq.Acetone Ia at 24.76°

Initial concentration 0.01677M.

5 ml. titrated with 0.01118N NaOH.

| Time | Titn | $k' \times 10^4$ |
|---|---|---|
| 0 | 1.25 | - |
| 310 | 3.25 | 5.073 |
| 630 | 4.72 | 4.617 |
| 935 | 5.88 | 4.391 |
| 1235 | 6.82 | 4.206 |
| 1535 | 7.64 | 4.072 |
| 1975 | 8.65 | 3.911 |
| 2585 | 9.80 | 3.762 |
| 3210 | 10.70 | 3.622 |
| 4070 | 11.60 | 3.434 |
| 4425 | 11.98 | 3.426 |
| 5225 | 12.55 | 3.302 |
| $\infty$ | 15.00 | - |

Expt.24. Diphenylmethylene Chloride in 85% aq. Acetone Ia at 24.76°

Initial concentration 0.01747M.

5 ml. titrated with 0.01126N NaOH.

| Time | Titn | $k' \times 10^4$ |
|---|---|---|
| 0 | 1.14 | - |
| 280 | 3.09 | 5.206 |
| 595 | 4.70 | 4.784 |
| 885 | 5.88 | 4.521 |
| 1250 | 7.10 | 4.284 |
| 1580 | 8.01 | 4.113 |
| 2005 | 9.00 | 3.947 |
| 2485 | 9.95 | 3.816 |
| 3090 | 10.95 | 3.711 |
| 3690 | 11.70 | 3.593 |
| 4315 | 12.32 | 3.483 |
| 4935 | 12.90 | 3.451 |
| $\infty$ | 15.52 | - |

Expt.25. Diphenylmethylene Chloride in 85% aq.Acetone Ia at 24.76°

Initial concentration 0.002828M.

5 ml. titrated with 0.002316N NaOH.

| Time | Titn | $k' \times 10^4$ |
|---|---|---|
| 0 | 0.97 | - |
| 225 | 2.65 | 7.197 |
| 455 | 4.00 | 6.909 |
| 690 | 5.13 | 6.701 |
| 1010 | 6.42 | 6.570 |
| 1405 | 7.64 | 6.409 |
| 1785 | 8.50 | 6.221 |
| 2230 | 9.32 | 6.093 |
| 2800 | 10.10 | 5.974 |
| 3400 | 10.73 | 5.964 |
| 4010 | 11.13 | 5.841 |
| $\infty$ | 12.21 | - |

Expt.26. Diphenylmethylene Chloride in 85% aq.Acetone Ia at 24.76°

Initial concentration 0.003159M.

5 ml. titrated with 0.002316N NaOH.

| Time | Titn | $k' \times 10^4$ |
|---|---|---|
| 0 | 1.03 | - |
| 175 | 2.58 | (7.502) |
| 405 | 4.12 | 6.941 |
| 635 | 5.43 | 6.760 |
| 930 | 6.80 | 6.576 |
| 1240 | 7.91 | 6.360 |
| 1555 | 8.88 | 6.266 |
| 1965 | 9.82 | 6.077 |
| 2440 | 10.70 | 5.969 |
| 3040 | 11.46 | 5.774 |
| 3645 | 12.07 | 5.718 |
| 4250 | 12.51 | 5.680 |
| $\infty$ | 13.64 | - |

Expt.27. Diphenylmethylene Chloride in 85% aq.Acetone Ib at 24.76°

Initial concentration 0.002265M.

5 ml. titrated with 0.002184N NaOH.

| Time | Titn | $k' \times 10^4$ |
|---|---|---|
| 0 | 0.90 | - |
| 185 | 2.20 | 7.980 |
| 395 | 3.37 | 7.649 |
| 655 | 4.58 | 7.511 |
| 940 | 5.60 | 7.299 |
| 1175 | 6.31 | 7.211 |
| 1440 | 6.93 | 7.031 |
| 1705 | 7.50 | 7.001 |
| 2005 | 8.00 | 6.910 |
| 2300 | 8.41 | 6.850 |
| 2595 | 8.77 | 6.851 |
| 3060 | 9.20 | (6.834) |
| ∞ | 10.37 | - |

Expt.28. Diphenylmethylene Chloride in 85% aq.Acetone Ib at 24.76°

Initial concentration 0.002394M.

5 ml. titrated with 0.002177N NaOH.

| Time | Titn | $k' \times 10^4$ |
|---|---|---|
| 0 | 0.90 | - |
| 210 | 2.41 | 7.710 |
| 455 | 3.81 | 7.470 |
| 685 | 4.89 | 7.340 |
| 940 | 5.80 | 7.065 |
| 1170 | 6.54 | 6.987 |
| 1405 | 7.14 | 6.846 |
| 1665 | 7.76 | 6.830 |
| 1935 | 8.28 | 6.780 |
| 2200 | 8.68 | 6.686 |
| 2455 | 9.00 | 6.598 |
| 2710 | 9.33 | (6.641) |
| 2950 | 9.51 | 6.490 |
| $\infty$ | 11.00 | - |

Expt.29. Diphenylmethylene Chloride in 85% aq.Acetone Ib at 24.76°

Initial concentration 0.002496M. Added LiBr 0.006644N.

5 ml. titrated with 0.002146N NaOH.

| Time | Titn | $k' \times 10^4$ |
|---|---|---|
| 0 | 1.08 | - |
| 180 | 2.57 | 8.455 |
| 365 | 3.84 | 8.310 |
| 600 | 5.20 | (8.250) |
| 810 | 6.11 | 7.999 |
| 1000 | 6.83 | 7.875 |
| 1230 | 7.58 | 7.781 |
| 1500 | 8.30 | 7.690 |
| 1735 | 8.78 | 7.543 |
| 1990 | 9.29 | 7.569 |
| 2250 | 9.65 | 7.435 |
| 2520 | 9.96 | 7.316 |
| ∞ | 11.63 | - |

Expt.30. Diphenylmethylene Chloride in 85% aq.Acetone Ib at 24.76°.

Initial concentration 0.002470M. Added LiBr 0.01862N.

5 ml. titrated with 0.002146N NaOH.

| Time | Titn | $k' \times 10^4$ |
|---|---|---|
| 0 | 0.73 | - |
| 185 | 2.43 | 9.274 |
| 370 | 3.82 | 9.130 |
| 580 | 5.12 | 9.018 |
| 795 | 6.21 | 8.930 |
| 981 | 6.98 | 8.840 |
| 1250 | 7.90 | 8.755 |
| 1490 | 8.55 | 8.675 |
| 1750 | 9.10 | 8.561 |
| 1930 | 9.44 | 8.550 |
| 2165 | 9.80 | 8.503 |
| 2410 | 10.10 | 8.443 |
| ∞ | 11.51 | - |

Expt.31. Diphenylmethyl Chloride in 85% aq.Acetone Ia at 24.76°.

Initial concentration 0.01926M

5 ml. titrated with 0.007350N NaOH.

| Time | Titn | $k' \times 10^5$ |
|---|---|---|
| 0 | 0.01 | - |
| 3270 | 0.87 | 2.064 |
| 6930 | 1.79 | 2.104 |
| 10470 | 2.59 | 2.094 |
| 13530 | 3.25 | 2.100 |
| 18330 | 4.16 | 2.079 |
| 21900 | 4.85 | 2.106 |
| 25500 | 5.40 | 2.080 |
| 29070 | 6.00 | 2.103 |
| 32670 | 6.50 | 2.096 |
| 40050 | 7.45 | 2.098 |
| 45450 | 8.10 | 2.116 |
| 93150 | 11.31 | 2.136 |
| 107670 | 11.80 | 2.145 |
| ∞ | 13.10 | - |

$k' = 2.102$

Expt.32. Diphenylmethyl Chloride in 85% aq.Acetone Ib at 24.76°.

Initial concentration 0.01886M.

5 ml. titrated with 0.007306N NaOH.

| Time | Titn | $k' \times 10^5$ |
|---|---|---|
| 0 | 0.01 | - |
| 3690 | 1.01 | 2.190 |
| 7110 | 1.87 | 2.189 |
| 11460 | 2.87 | 2.188 |
| 19890 | 4.60 | 2.211 |
| 24090 | 5.31 | 2.197 |
| 28485 | 6.03 | 2.208 |
| 31260 | 6.41 | 2.193 |
| 38650 | 7.40 | 2.201 |
| 44060 | 8.01 | 2.197 |
| 82260 | 10.93 | (2.279) |
| $\infty$ | 12.91 | - |

$k' = 2.197$

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