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THE EFFECT OF SUBSTITUENTS ON SIDE-CHAIN REACTIVITY

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

BY

JOHN R. FOX

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ABSTRACT.

The investigation is concerned with the effect of p-substituents on the rates and activation parameters in the ionisation (S_N1 reaction) of phenylmethyl halides. In these systems, substituents exert their effect on the rate almost entirely by altering the electron density at the reaction centre[1]. The work was designed to yield information about the effect of changing electron demand at the site of p-substitution in the transition state.

The reaction of p-substituted benzyl halides with slightly moist formic acid was studied initially. In this system, the electron demand at the site of p-substitution can be expected to be large but the results were unsuitable for discussion of substituent effects in S_N1 reactions since this mechanism did not operate throughout the series. Completely S_N1 solvolysis appears to require the presence of an electron donating substituent and may not be attained by the p-methyl derivative. An extension to aqueous organic solvents showed that completely S_N1 hydrolysis requires the presence of a p-phenoxy, or better electron releasing substituent.

The hydrolysis of p-substituted p'-nitro-, p'-hydrogen-, and p'-methoxy-benzhydryl chlorides undoubtedly occurs by the ionisation mechanism. The electron demand at the site of p-substitution was expected to decrease in the order,

p'-nitro > p'-hydrogen > p'-methoxy

and it is consistent with this view that the effect of any one p-substituent on the rate follows the same sequence. The kinetic effect of these p-substituents arises almost entirely from changes in the activation energy although the entropy of activation is significantly reduced by the introduction of p-phenoxy and p-methoxy substituents.

In all three series, reaction is facilitated by electron releasing p-substituents, particularly by those which are polarisable with respect to electron demand at the reaction centre. There is, however, no simple relation between the magnitude of these polarisability effects and the electron demand at the site of p-substitution. As a result, simple free-energy relations of the Hammett type[2] are inadequate in accounting for the effect of p-substituents on the rates, even in the present three similar series. The Tsuno-Yukawa equation[3], which attempts to allow for polarisation and polarisability effects separately, describes the present rates more satisfactorily, if the reaction constants are derived from the results for the two p-substituents with extreme polar properties. However, this equation assumes a linear relation for the response of substituents to a demand for electrons. It is concluded that the effects of p-substituents are more profitably discussed by using Ingold's approach[4] of considering the polarisation and polarisability effects, and the reaction mechanism.

1. Ingold, "Structure and Mechanism in Organic Chemistry", Bell, London, 1953, p.316.
2. Hammett, "Physical Organic Chemistry", McGraw-Hill, New York, 1940, p.188.
   Brown and Okamoto, J.Amer.Chem.Soc., 1957, 79, 1913, 1958, 80, 4979; J.Org.Chem., 1957, 22, 485.
3. Tsuno and Yukawa, Bull.Chem.Soc.Japan, 1959, 32, 971.
4. Ref. 1, Chapters 6, 7 and 13.

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INTRODUCTION

THE ELECTRONIC THEORY OF REACTIONS [1]

Organic substitution reactions are essentially electrical phenomena and reagents react by a constitutional affinity for electrons (electrophilic reagents) or for atomic nuclei (nucleophilic reagents). Thus, providing there is at some point in a molecule a sufficiently high electron density, then an electrophilic reagent will attack that point. Conversely, a nucleophilic reagent will attack a molecule provided that there is at some point a sufficiently low electron density. The replacement of one group by another at some point in the molecule, other than the reaction centre, will affect the facility of reaction depending on the effect each has on the electron density at the reaction centre. A substituent group can alter this electron density by virtue of its capacity for attracting or repelling electrons.

The effect of a particular substituent on the facility of reaction will, therefore, be decided by the polar character of the substituent, the efficiency with which the electron shift initiated by the substituent is relayed to the

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reaction centre (controlled by the structure of the system) and the polar requirements at the reaction centre.

MECHANISMS OF NUCLEOPHILIC SUBSTITUTION AT A SATURATED CARBON ATOM.

In any reaction, the polar requirements at the reaction centre depend on the detailed nature of the transition state, i.e. on the reaction mechanism. The various mechanisms of substitution will, therefore, be considered below.

Types of substitution[2].

Chemical bonding involves interactions between the bonded centres and an associated pair of electrons. Formation or rupture of bonds must therefore be accompanied by modifications of the bonding electron pair.

In a substitution of the form

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

in which a single bond is exchanged, there are two main types of bond fission.

In homolytic or symmetric fission,

$$Y. + R. \mid . X \longrightarrow Y. \, . R + .X$$

(The dots represent electrons)

the departing group separates with one of the bonding electrons and a new bond is formed by the pairing of an electron on the reagent with that left on R. Such reactions, although common in the gas phase, are not the concern of the present studies and will not be given any further consideration.

In heterolytic or dissymmetric fission, which is frequently observed for reactions in solution, the departing group either leaves behind, or separates with the pair of "bonding" electrons. It is therefore necessary to subdivide heterolytic fission into two classes.

(i) When the reagent is electron deficient and makes up a complete "octet" by utilising the discarded pair at the reaction centre, the process is termed <u>electrophilic</u> substitution (S_E).

$$Y + R.\,.\,|\,X \longrightarrow Y : R + X$$

(ii) When the deficiency of electrons arises at the reaction centre and the product is formed by co-ordination with a pair of electrons on the reagent, the process is termed a <u>nucleophilic</u> substitution (S_N).

$$Y{:} + R\,|\,.\;.X \longrightarrow Y : R + {:}X$$

Nucleophilic substitution reactions are accompanied by a transfer of electrons from the substituting group Y to the substitution centre and from here to the expelled group X.

Thus Y becomes one unit more positive and X one unit more negative, and provided that this condition is fulfilled the charged states of the species involved need not be restricted. Since the present studies are restricted to nucleophilic substitutions, a more detailed consideration of this class of reactions will now be given.

Mechanisms of nucleophilic substitution.

Two mechanisms are recognised for nucleophilic substitution.

When the product is formed from the reagents in a single step in which two molecules simultaneously undergo covalency change, the reaction is bimolecular and labelled S_N2. For an ionic reagent the reaction is

$$Y^{-} + RX \longrightarrow \underset{\text{transition state}}{\left[Y^{-}\text{-----}R\text{-----}X^{-}\right]} \longrightarrow YR + X^{-}$$

For a non-ionic reagent, the charge distributions are suitably modified. The hydrolysis of methyl bromide in aqueous ethanol follows this mechanism[3].

When the rate of reaction is determined by a preliminary slow ionisation of the compound RX, to give a highly reactive carbonium ion which then rapidly co-ordinates with the reagent, the mechanism is labelled S_N1. Since only one molecule is undergoing covalency change in the rate determining step, the process is regarded as unimolecular[2, 3].

$$RX \longrightarrow \underset{\text{transition state}}{\left[R^{+}\text{------}X^{-}\right]} \longrightarrow R^{+} + X^{-}$$

$$R^{+} + Y^{-} \longrightarrow RY$$

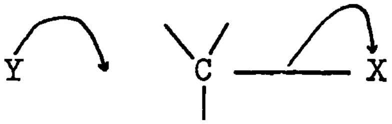
It is postulated that the large activation energy required for the ionisation of C - X in the gaseous phase is reduced to an accessible value in solution by solvation of the polar transition state[3]. Tert.-butyl chloride in aqueous acetone hydrolyses by this mechanism[4].

Since this chapter is mainly concerned with the effect of substituents on reactivity, the various criteria of mechanism available for solvolytic reactions will not be discussed here. A comprehensive review of this subject has been published by Hughes[5].

The effect of substituents on the rates of nucleophilic substitution reactions[2b, 6].

The reaction mechanism is an important factor in determining the effect of a polar substituent on the rate.

In reaction by mechanism S_N2, electron release towards the reaction centre facilitates fission of the C - X bond but, at the same time, hinders the approach of the nucleophilic reagent Y; electron withdrawal from the reaction centre will reverse these effects.



The overall effect of substituents on the rate of reaction will therefore depend on whether bond-making or bond-breaking is the predominant process, but this effect will usually be small since it depends on the difference between the polar requirements of bond-making and bond-breaking.

In reaction by mechanism S_N1, only the fission of the C - X bond is involved. Thus the polar requirements are quite unambiguous; electron release towards the reaction centre gives rise to an acceleration in the rate of reaction, and electron attraction to a retardation. Thus reactions which occur by this mechanism are highly suitable for studying the polar effects of substituents, provided that the relay of these effects through the system to the reaction centre is efficient.

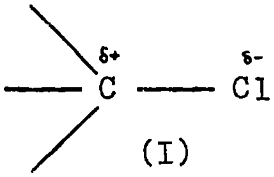
POLAR EFFECTS OF SUBSTITUENT GROUPS.

Mechanisms of electron displacement[1, 7].

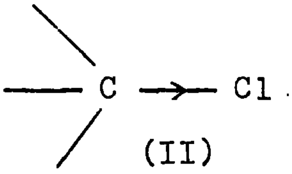
Substituent groups in a molecule can alter the electron density at the reaction centre by virtue of their capacity for attracting or repelling electrons. Two mechanisms have been recognised for such electron displacements; both preserve the pairing of electrons, and the "octets" or other stable electronic configurations in the atoms.

(i) The inductive mechanism.

Lewis[8] first showed how electrical dissymmetry, arising from the unequal sharing of electrons between unlike atoms, could be propagated along a chain of bound atoms by a mechanism of electrostatic induction. This is called the inductive mechanism of electron displacement. Thus in an alkyl halide,



(I)



(II)

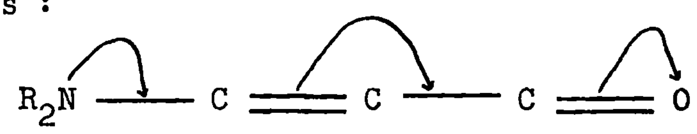
the electron density tends to be greater nearer chlorine than carbon as the former is the more electronegative; this is generally represented by the structures I or II, the arrow pointing in the direction of electron concentration. If the carbon atom bonded to chlorine is itself attached to further carbon atoms, the effect can be relayed further :

$$\underset{4}{C} - \underset{3}{C} - \underset{2}{C} \rightarrow \underset{1}{C} \twoheadrightarrow Cl$$

The effect of the chlorine atom's partial appropriation of the electrons of the carbon-chlorine bond is to leave C_1 slightly electron deficient; this atom attempts to compensate for this deficiency by appropriating slightly more than its share of the electrons of the bond joining it to C_2, and so on along the chain of carbon atoms. The effect of C_1 on C_2 is less than the effect of Cl on C_1, however, and the transmission quickly dies away in a saturated chain.

(ii) The conjugative mechanism.

The second method of electron displacement which preserves duplets and octets is characterised by the substitution of one duplet for another in the same electron octet, and is known as the conjugative mechanism. This type of displacement was first proposed by Lowry[9], 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 :



(III)

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

$$\overset{+}{R_2N} = C - C = C - \overset{-}{O} \qquad (IV)$$

Clearly, efficient relay of this effect only takes place when the releasing group is connected to a conjugated system.

In more modern language, the structure of the molecule can be considered as the resonance hybrid of the two canonical forms,(III)and (IV). The greater the conjugative release of the group R_2N, the greater will be the contribution of (IV) to the structure of the molecule.

Polar effects of substituents in the initial and transition states of chemical reactions[1, 7, 10].

In so far as the inductive and conjugative mechanisms apply to the ground-states of molecules, they are called the inductive and mesomeric effects respectively and are collectively known as polarisation effects. These permanent polarisations are manifested in the physical properties of the compounds in which they occur, e.g. dipole moments.

The effect of substituents on reactivity, however, arises from the difference in their effect on the stabilities of the initial and transition states. As a first approximation polarisation effects may be considered to be carried unchanged into the transition state. However, additional electron displacements will come into play on activation as a result in the change in electron demand at the reaction centre. These displacements are usually termed polarisability effects, and are regarded as time-variable analogues of the permanent polarisations.

The mesomeric effect (M) and its time-variable analogue, the electromeric effect (E), operate in the same manner. Thus the conjugative (T) electron release of a substituent is controlled by the electron demand at the site of substitution, irrespective of whether this demand occurs in the transition state of reaction, or not.

This does not apply to the general inductive effect where the permanent polarisation, the inductive effect (I_s), arises from the electronegativities of two adjacent groups while the time-variable analogue, the inductomeric effect (I_d), is a consequence of the polarisability of the outer electrons of the substituent. For a series of substituents, the inductive and inductomeric effects need not, therefore, vary in the same manner.

The various polar effects which substituents can exert are considered in more detail in the following sections.

The inductive effect (I_s)[7].

The inductive effect exerted by a substituent depends on its electronegativity and that of the group to which it is joined. For a substituent which can attract or release electrons by the inductive effect, the magnitude of its effect on the rate of a chemical reation depends on the sensitivity of the rate to electron accession and withdrawal. However, the relative magnitudes of the I_s effects of substituents can be deduced from the relatively simple considerations outlined below. These deductions are fully confirmed by physical properties, e.g. dipole moments.

The most powerful electron-attracting or repelling powers are exhibited by formally charged entities, for example $-\overset{+}{N}R_3$. Somewhat less powerful are the I_s effects resulting from dipoles in co-ordinate covalence, e.g. $O = \overset{+}{N} - \overset{-}{O}$ which will strongly attract electrons from any group R in a compound $R - NO_2$. The I_s effects arising from normal covalence between atoms of unequal electronegativity, e.g. $C - Cl$, are weaker still. If an atom or group attracts electrons, relative to hydrogen, it is said to exhibit a $-I_s$ effect; if it repels them, it exhibits a $+I_s$ effect and is known as an electron-releasing group.

Individual variations, as opposed to the broad variations arising from formal electric charges, become apparent on considering a series of different groups in the same state of formal charge, and will be illustrated by reference to neutral groups. Along the isoelectronic series,

$$— CH_3, \quad \rightarrow NH_2, \quad \rightarrow OH, \quad \longrightarrow F,$$

the total nuclear charge becomes progressively centralised, and thus the groups attract electrons progressively more strongly.

The electrical dissymmetry of the bound fluorine atom is reduced in similarly bound chlorine by a compensating polarisation of the core electrons of the latter. This compensation will increase with the size of the core in the heavier halogens. Thus the electron attraction, and the $-I_s$ effect, of the halogens increases along the series,

$$I < Br < Cl < F$$

On this basis, the inductive effect of the alkyl groups would appear to be zero. However, such groups will exert essentially those polar effects which are impressed on them by the other polar groups present in the molecule. The alkyl groups are more polarisable than hydrogen, so that $-CH_3$, although non-polar when $CH_3 - CH_3$ is compared with $H - CH_3$, becomes weakly electron-repelling when the comparison is between $CH_3 \longrightarrow CH_2Cl$ and $H — CH_2Cl$. Since the majority of common substituents are inductive attractors, alkyl groups normally function as weakly electron-repelling groups.

The mesomeric effect (M)[7].

Mesomeric effects are determined by the affinity of unshared electron pairs for the nucleus of another atom. This in turn depends on the electronegativity of the atom to which they belong. Thus negatively charged groups tend to increase their covalency more than neutral groups whilst neutral groups tend to increase their covalency more than positively charged groups. This affinity also decreases with increasing electronegativity of the central atom along an isoelectronic series. Hence the tendency to increase covalency diminishes along a row of the periodic table,

e.g., $-NR_2 > -OR > -F$.

Electron release by the mesomeric (+M) effect requires an increase in covalency between the substituent and the atom to which it is attached . The principle of maximum overlap shows that such an increase becomes progressively more facile as the sizes of the atomic orbitals concerned become more nearly the same. The +M effect for halogens attached to carbon will therefore decrease in the sequence,

— F > — Cl > — Br > — I

When any group X, which is capable of mesomeric electron release, is attached to an unsaturated residue, the conjugative mechanism always operates to decrease the electron content of X, and increase that of the unsaturated residue. The group X is acting electropositively and the resulting mesomeric effect is labelled +M.

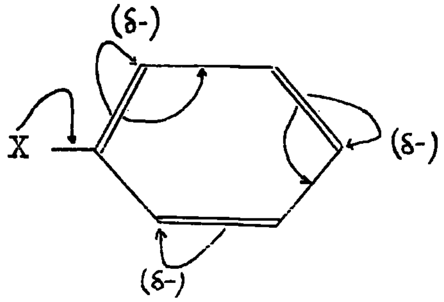


FIGURE I-1. THE +M EFFECT.

These predicitions are confirmed by a comparison of physical properties, e.g. the dipole moments of substituted benzenes and methanes[12]; only inductive effects can operate in the latter compounds.

Time-variable effects.[7]

The electron movements, indicated by the arrows in figure I-1, will be amplified by the presence of electron attracting substituents in the ortho and para positions of the benzene ring, or by passage into the transition state of a reaction which is facilitated by electron release to these positions. Generally speaking, electromeric polarisability (E) has similar characteristics to those of mesomeric polarisation and will therefore vary in the same manner as the mesomeric effect with the nature of the substituent.

The time-variable analogue of the inductive effect, the inductomeric polarisability (I_d) is likely to be[10],

(a) of importance only when the substituent is very close to the point of attack on the molecule;

(b) larger for charged than for dipolar or neutral reagents; and

(c) larger for more polarisable substituents (e.g. to increase in the order F $<$ Cl $<$ Br $<$ I).

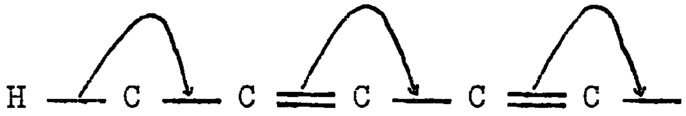
Hyperconjugation[7, 11].

The inductive mechanism leads us to expect that alkyl groups will accelerate reaction in the order,

$$+I : (CH_3)_3C \longrightarrow (CH_3)_2CH \longrightarrow CH_3.CH_2 \longrightarrow CH_3 \longrightarrow H.$$

This is shown, for example, in the strengths of substituted acetic acids[45]. When alkyl groups are attached to unsaturated systems, the inductive order of electron-release is sometimes found, as in the dipole moments of tert.-

butylbenzene and methylbenzene[12], and in the gas-phase excitation energies of p-alkyl substituted acetophenones and nitrobenzenes[13]. More frequently, however, especially when electron-release is being estimated from rates of reaction, a reversed order of effectiveness is often observed. This effect was first recognised by Baker and Nathan[11] in 1935 and is demonstrated convincingly by the solvolysis of benzhydryl[14] and phenyldimethylcarbinyl[15a] chlorides. Baker and Nathan[11] postulated that the electron pairs of the C-H bonds are less localised than the electrons of C-C bonds and are able to conjugate with an unsaturated system.



This type of electron release is called hyperconjugative release and can only occur for C-H bonds which are attached to a conjugated system. The magnitude of this effect therefore decreases in the order,

$$CH_3 - > CH_3CH_2 - > (CH_3)_2CH - > (CH_3)_3C -$$

when alkyl groups are attached to such a system.

Other types of hyperconjugation have also been suggested[16]. From his work on the alkylphenyldimethylcarbinyl chlorides, Brown[15a] concludes that C-C hyperconjugation must be nearly as important as C -H hyperconjugation. The participation of the electron pairs of C-Halogen bonds in electron-attracting hyperconjugative effects (-M) has also been postulated by de la Mare, Hughes and Ingold[17].

The effect of substituents on the rates of S_N1 reactions.

The electron-demand of the reaction centre in the transition state of solvolysis by mechanism S_N1 is much greater than in the initial state, so that any substituent with a capacity for conjugative or hyperconjugative electron release will tend to satisfy this demand. Unimolecular nucleophilic substitution reactions are thus particularly suitable for a study of the +M and +E effects of substituents, provided that substituent and reaction centre are connected by a conjugated system.

Para-substituted phenylmethyl halides fulfil this requirement but the corresponding meta-substituted derivatives do not. The S_N1 reactions of such systems have been reported and the results are briefly discussed below to illustrate the way in which substituent effects may be qualitatively explained in terms of the electrical effects outlined in the preceding sections.

Roberts, Clement and Drysdale[20] have shown that the inductive effect of a substituent group on an aromatic ring is probably best regarded as falling off smoothly with distance in accord with the Coulomb law. The effect of inductive attractions or repulsions on the reaction centre is therefore somewhat larger when the substituent is in the meta- than when it is in the para-position.

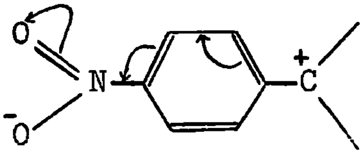
Whilst a polarisable para-substituent is capable of direct resonance with a suitable reaction centre, a similar meta-substituent is unable to do so. However, there is considerable evidence[21] that an electron demanding reaction centre occasions some electron demand at the position ortho to this centre and that a meta-substituent can satisfy this demand by the conjugative mechanism. The effect will clearly be very much smaller than that resulting from direct interaction between a para-substituent and the reaction centre.

The alkoxy, phenyl and related substituents all exhibit a small electron withdrawing inductive effect. Thus m-methoxyphenyldimethylcarbinyl chloride solvolyses at a rate of 0·6 that of the parent compound in 90% acetone at 25°C[15c], and m-phenyltriphenylcarbinyl chloride ionises more slowly than the parent compound in liquid sulphur dioxide by a similar amount[22]. However, when these substituents are placed in the para-position, they promote a large rate increase in the order of their decreasing polarisability,

$$CH_3O- > C_6H_5O- \gg C_6H_5- > H.$$

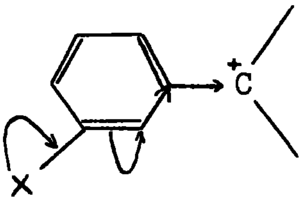
This is attributed to resonance stabilisation of the electron demanding centre, i.e., the operation of the +E effect.

The marked decrease in rate generally observed on the introduction of nitro-substituents is in accord with the powerful electron withdrawing inductive effect of these substituents. The slightly greater effect of the more distant para-substituent is attributed to a small conjugative contribution which increases the electron deficiency of the reaction centre, thus



(-M effect)

Halogen substituents in the meta-position also give rise to a reduced reactivity, attributed to their -I effect, although this effect is not so marked as in the case of the nitro-compounds. However, the observed order of rates in the electron demanding solvolysis of m-halophenyldimethylcarbinyl chlorides[15b], F > Cl > Br < I, does not agree with that anticipated on the basis of the decrease in electronegativity with increasing atomic weight, F < Cl < Br < I. An accompanying, small, electron supplying conjugative effect F > Cl > Br > I relayed by induction from the ortho-position has been postulated to account for these and similar results, i.e.,



The relatively small overall effects of para-halogen substituents on rates have been readily explained[15b, 23] in terms of opposing conjugative and inductive components of comparable magnitude. In the case of fluorine, it is postulated that the +M (or E) effect outweighs the -I effect, giving rise to a greater reactivity than in the parent compound.

The unimolecular solvolyses of p-alkyl substituted phenylmethyl halides[14, 15a] provide a convincing demonstration of the importance of C - H hyperconjugation. This effect stabilises the electron demanding transition state so that the reactions are strongly accelerated by the p-alkyl substituents, and considerably more by methyl than by tert.-butyl. Sweeney and Schubert[18], however, suggested that bulky alkyl groups in the para-position give rise to steric hindrance to solvation in the transition state of S_N1 reactions and therefore retard the rate of reaction, so accounting for the hyperconjugative order. Burawoy and Spinner[19], on the other hand, consider alkyl groups to release electrons by the inductive mechanism only and according to their view, steric hindrance to bond contraction accompanying inductive release acts to invert the order of electron release as the electron demand is increased.

The behaviour of meta-alkyl substituents can be explained in a similar way to that of the meta-halogen substituents in that hyperconjugative contributions appear to be relayed inductively from the ortho position to the reaction centre.

The effects of ortho-substituents on the type of reaction considered above have not been discussed since the picture is now complicated by steric effects. A comprehensive study of this subject has been made by Brown[15].

The Hammett equation[24, 25].

It was illustrated in the preceding section that a qualitative explanation of substituent effects can be developed in terms of the polar properties of substituents, the structure of the system and the mechanism of reaction.

Attempts have been made, however, to put the correlation of rate and equilibrium constants on a quantitative basis. The most successful conception is due to Hammett[24] and his linear free-energy relation, equation I-1, has often been used to predict the effects of meta- and para-substituents on the rates of chemical reactions.

$$\log \frac{k_X}{k_H} = \sigma\rho \qquad \text{. . . . . Eqn. I-1.}$$

The σ-value represents the effect of the substituent on the electron density at the reaction centre and depends only on the substituent; the quantity ρ represents the sensitivity of the reaction to such electron shifts and depends only on the nature of the reaction, k_X is the rate (or equilibrium) constant when the reactant contains a substituent, X, and k_H is the corresponding rate (or equilibrium) constant for the unsubstituted compound. The σ-values were determined from the ionisation constants of meta- and para-substituted benzoic acids by making the assumption that $\rho = 1$ for this reaction. In view of the fundamental nature of the assumptions inherent in the Hammett equation, even the limited success that this relation attained must be regarded as surprising.

One criticism is that the influence of reaction mechanism on the behaviour of substituents is ignored. In reaction by mechanism S_N2, electron-release towards the reaction centre will facilitate the fission of the R-X bond but will, at the same time, tend to inhibit the approach of the reagent by electrostatic interaction with its bond-forming electron pair, the effect being more pronounced for anionic reagents. Depending, therefore, on whether the bond-forming or bond-breaking tendency predominates in the activation process, electron release to the reaction centre can increase or decrease the rates of S_N2 substitutions. A striking demonstration of this effect, has been given for the bimolecular exchange between para-substituted benzyl bromides and radio-active bromide ions in ethylene diacetate[26], and for the Finkelstein reaction with benzyl chlorides in acetone[27] where the S_N2 mechanism also operates. Similar observations have recently been published by Klopman and Hudson[28] who measured the rates of bimolecular exchange between para-substituted benzyl bromides and thiophenate and methylate ions in methanol (see Table I-1). Although the Hammett σ-values predict that the p-bromo and p-nitro substituents will act in the opposite direction to the p-methoxy and p-methyl substituents, all four substituents have been found to accelerate the reaction. The rate of reaction is thus a minimum for the parent compound.

TABLE I - 1.

Rates of substitution of para-substituted benzyl bromides in methanol at 20°C.[28]

Substituent R	log k Reaction A	log k Reaction B	Hammett σ
CH_3O -	0.693	- 2.02	- 0.268
CH_3 -	0.212	- 3.14	- 0.170
H -	0.032	- 3.26	0
Br -	0.410	- 3.11	0.232
NO_2 -	0.874	- 2.85	0.778

Reaction A : (p-) $R - C_6H_4 - CH_2Br + C_6H_5S^-$

Reaction B : (p-) $R - C_6H_4 - CH_2Br + CH_3O^-$

Other objections to the Hammett equation arise from the following considerations.

If the mechanism of a reaction is changed by the introduction of more polar substituents, the same reaction constants cannot be expected to apply to both mechanisms as the polar requirements of the reaction centre will not be the same in the two cases[32].

Electron deficient reaction centres invoke a considerable electron-demand on substituents at the para-position in an aromatic ring. Therefore any polarisable substituent in this position will be encouraged to release electrons conjugatively. No allowance for this type of behaviour is inherent in the σ-values based on the substituted benzoic acids. Thus several authors[15, 29] have found that the behaviour of meta-substituents can be adequately described by the Hammett σ-constants whereas many of the para-substituents promote a higher reactivity than predicted by their σ-values.

Kochi and Hammond[29] studied the rates of solvolysis of meta- and para-substituted benzyl tosylates in aqueous acetone. The σ-values which they obtained for the p-methyl and p-methoxy substituents were more negative than the standard σ-values, the divergence being greater for the p-methoxy group. The authors ascribed this effect to an exceptional increase in the resonance stabilisation of the electron deficient transition states due to the conjugation of these groups with the aromatic ring.

Roberts, Sanford, Sixma, Cerfontain and Zagt[30] compared the relative reactivity in aromatic nitration reactions with the σ-constants and found that those substituents which would be expected to show significant transition state resonance effects deviated considerably from the acceptable correlation line defined by the meta-substituents. Similarly, de la Mare[31] emphasised that the σ-values reflect to a greater extent the inductive than the electromeric effect of substituents.

Brown and his co-workers[15] observed serious divergencies from the Hammett σ-values for polarisable para-substituents (ρ being defined by the results for meta-substituents) in the solvolysis of phenyldimethylcarbinyl chlorides in aqueous acetone, a reaction which proceeds by mechanism S_N1. This lack of correlation was again attributed to resonance interactions between the para-substituents and the electron deficient centre in the transition state. In an attempt to include both the conjugative and inductive effects in the substituent constants, the reaction constant was calculated from the rate data for meta-substituents and their standard σ-values. A new set of substituent constants, σ^+, were calculated from the modified Hammett equation, equation I - 2,

$$\log \frac{k_X}{k_H} = \sigma^+\rho \qquad \ldots\ldots\ \text{Eqn. I - 2.}$$

These σ^+-values allow for the resonance interactions referred to above. The treatment makes the reasonable assumption that meta-substituents have little conjugative effect.

Brown[15d, 15g, 32] applied these σ^+-values to a variety of reactions including the solvolysis of triphenylcarbinyl chlorides in 40% ethanol - 60% ethyl ether[33] and substituted benzhydryl chlorides in ethanol[34] and iso-propanol[35]. The

σ^+-values were shown to give a very much better correlation than the Hammett σ-constants.

There are, however, serious theoretical objections to Brown's treatment which implies that the overall electron release of a substituent is proportional to the electron demand at the site of substitution; the magnitude of this release is controlled by the value of σ^+ and the proportionality constant which is implicitly assumed to be the same for all substituents. The overall electron release by a substituent, however, arises from the operation of inductive and conjugative effects and only the latter can be expected to respond significantly to a demand for electrons. Moreover, there is no guarantee that even the magnitude of conjugative electron release varies in the same manner with electron demand for all substituents.

Similar criticisms of the Brown relation have already been put forward by Eaborn[37] on the basis of the behaviour of p-halogeno and p-phenyl substituents, and by Wepster and his co-workers[36] who suggested that the effect of para substituents on the rates of electron demanding reactions can only be accommodated by a 'sliding scale' or 'multiplicity' of substituent constants of the σ^+ type. These authors have also pointed out[36] that the value of σ^+ of substituents is not by itself a measure of the electron release but that the value of ρ and the temperature must be taken into account in such discussions.

Tsuno and Yukawa[39] attempt to allow for the fact that increasing electron demand only increases electron release by the conjugative mechanism. They assume that the Hammett σ-values (derived from the ionisation of benzoic acids) reflect the magnitude of the inductive effect and that, therefore, $\Delta\sigma_R^+$ ($\equiv \sigma^+ - \sigma$) is proportional to the magnitude of the conjugative effect. It follows that the appropriate proportionality constant, r, is unity for the solvolysis of the phenyldimethylcarbinyl chlorides, the reaction employed by Brown[15] to establish the scale of σ^+-values, and hence

$$\log \frac{k_X}{k_H} = \rho\,(\sigma + r\,\Delta\sigma_R^+) \quad \ldots\ldots \text{Eqn. I - 3.}$$

Tsuno and Yukawa[39c] applied this relation to some thirty-five reaction series and found a very adequate fit. Eaborn and Pande[40] have recently applied this equation to their results for the rates of cleavage of substituted aryltriethylgermanes, $X\cdot C_6H_4\cdot GeEt_3$, and found 'precise' correlation.

The Tsuno-Yukawa equation assumes the response of all para-substituents to be linearly proportional to the demand. This assumption is supported, for p-alkyl substituents, by the evidence of Schubert, Robins and Haun[13] who have reported the gas-phase excitation energies of a series of p-alkyl acetophenones and nitrobenzenes. These workers conclude, from the linearity of a plot of maximum frequencies for p-alkylacetophenones against p-alkylnitrobenzenes, that within this change in electron demand the alkyl groups respond in linear proportion to demand. On the other hand it is difficult to see why this should always be the case. It is possible to visualise a group which is easily polarised and will not require as large an electron demand as a less polarisable group to reach its limit for electron donation.

THE PRESENT STUDY.

At the beginning of the present study, the contributions of Wepster[36] and Tsuno and Yukawa[39] had not been published. Brown's σ^+-values[15g] (based on his data for the S_N1 solvolysis of substituted phenyldimethylcarbinyl chlorides) were, however, available for a wide range of substituents.[†] Some other S_N1 reactions had been studied[14, 33, 34, 35], but only with a limited number of substituents. There was not, therefore, sufficient information to establish conclusively whether his

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[†] The most electron attracting and releasing substituents, however, were studied in solvents different to those for the other substituents[15c], and no attempt was made to allow for the temperature dependence of the activation parameters when comparing rates of reactions which had been studied over different ranges of temperature.

relation, equation I - 2, was valid for a variety of S_N1 reactions with different electron demands at the site of substitution. In view of the criticisms of the Brown relation expressed on page 27, it was felt that this information should be obtained.

The present study therefore aimed at obtaining further information about the effect of para-substituents on the rates of the unimolecular solvolysis of phenylmethyl halides. In these systems, the conjugative effects of substituents can be transmitted through the aromatic ring to the reaction centre, the polar requirements of the activated complex are unambiguous (see p. 5) and substituents exert their effect on the rate almost entirely by altering the electron density at the reaction centre.

It was originally intended to obtain information about systems with a large electron demand at the site of substitution from a study of the solvolysis of benzyl halides as it is generally believed that mechanism S_N1 operates for solvolysis in slightly aqueous formic acid. The results observed with a number of substituents, however, indicated that this assumption was not valid (see Chapter II) and it was therefore decided to study the hydrolysis of para-substituted p'-nitrobenzhydryl chlorides where the electron demand at the site of substitution is also large. Para-substituted benzhydryl chlorides (for which some information was already available[23, 41]) and para-substituted p'-methoxybenzhydryl chlorides were chosen to furnish information about systems with moderate and small electron demand at the site of substitution, respectively. This choice has the considerable advantage that all three series are highly similar so that all differences are polar and uncomplicated by steric or structural factors.

That these reactions occur by mechanism S_N1 is beyond doubt. In reaction by this mechanism, the rate is controlled by the ionisation of RX (see p. 4) and a powerful nucleophilic reagent, such as hydroxide ion, should therefore have no effect on the rate (although it may influence the rate slightly by the operation of "medium" effects). The bimolecular mechanism requires covalent attachment of the reagent in the rate-determining step and its presence is thus an important factor governing the rate of reaction by this mechanism. It follows that if the addition of a strong nucleophile does not alter the rate of reaction, the reaction must occur unimolecularly.[5] It has been observed[42] that the hydrolysis of benzhydryl chloride in aqueous alcohol containing hydroxide ion proceeds independently of the hydroxide ion. Also, the solvolysis of benzhydryl chlorides is subject to "mass-law" and "ionic-strength" effects[43] which are characteristic of reaction by mechanism S_N1 (see also Chapter III). Furthermore, the benzhydryl system is sterically hindered to bimolecular attack[44].

It was clear that the study of substituents with widely different properties would yield a wide range of reactivities and that all reactions could therefore not be studied at the same temperature. Comparisons of the effect of substituents on the rate must be carried out at the same temperature and a knowledge of the activation parameters was therefore essential. It was expected that the determination of these parameters would be of value since relatively little information about the effect of substituents on the activation parameters in S_N1 solvolysis was available at the beginning of the present work.

CHAPTER II

THE SOLVOLYSIS OF BENZYL HALIDES IN 70% AQUEOUS ACETONE AND 99.5% AQUEOUS FORMIC ACID.[≠]

MECHANISM IN THE "BORDER-LINE" REGION.

Results obtained for the formolysis of substituted benzyl halides were found to be inconsistent with the operation of mechanism S_N1 throughout the series (see p. 50). This observation stimulated interest in that region of mechanism which marks the transition from reaction by mechanism S_N2 to reaction by mechanism S_N1, known as the "border-line" region.

It is instructive to consider the transition state in nucleophilic substitution as the resonance hybrid of the canonical forms (I), (II) and (III)[46].

$$\underset{\text{(I)}}{Y{:}\quad R-X}\qquad\qquad \underset{\text{(II)}}{Y-R\quad {:}X}\qquad\qquad \underset{\text{(III)}}{Y{:}\quad R\quad {:}X}$$

In reaction by mechanism S_N1, only structures (I) and (III) contribute to the transition state. On the other hand, if structure (II) also makes a significant contribution, the

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[≠] Throughout this work an "x%" solvent refers to the mixture made up in the proportion x ml. of the solvent named last and (100 - x) ml. of the other component.

mechanism must be regarded as bimolecular since covalent participation by the reagent is still an essential feature of the activation process[47]; this applies irrespective of any contribution by structure (III).

Two possibilities must be considered for reactions occuring in the mechanistic border-line region; both have been proposed[46b, 48, 49].

(i) It has been suggested that such reactions may proceed via a single reaction path. The transition state has contributions from all three canonical forms and the mechanism must therefore be bimolecular. The greater the contribution from (III) relative to (II), the more does the reaction tend to be S_N1 in character.

(ii) The second alternative postulates that the individual acts of substitution may occur through a 'continuous spectrum' of transition states. The contributions from the canonical forms vary for each transition state and some transition states may have no contributions from (II). On this view, mechanisms S_N1 and S_N2 operate concurrently. Such a concurrence has been demonstrated for the reaction of azide ions with p-methoxybenzyl chloride in aqueous acetone[50] and there are very strong indications that this also applies to the hydrolysis of p-methylbenzyl chloride in 50% aqueous acetone[51].

Substituted benzyl halides are particularly suitable for studying the mechanistic border-line region.

The introduction of electron releasing substituents in the p-position will facilitate ionisation of the C - Cl linkage, i.e. mechanism S_N1, and it is therefore to be expected that unimolecular reaction will be observed when the p-substituent is a sufficiently powerful donor of electrons, while mechanism S_N2 will operate when it is not. These predictions have already been confirmed by a previous study of the solvolysis of p-substituted benzyl halides[51], but only two electron releasing substituents were studied in this work. Further substituents have now been investigated in order to allow a discussion of the finely graded mechanistic series to be expected in these systems.

SOLVOLYSIS OF p-SUBSTITUTED BENZYL CHLORIDES IN 70% AQUEOUS ACETONE.

Details of the experimental procedures and methods of calculation are given in Chapter IV. As in Shillaker's work[51], rate measurements were made at five temperatures to allow the determination of dE/dT (where T is the absolute temperature) and hence activation parameters at comparable temperatures. First-order rate constants (k) and activation energies (E) and entropies (ΔS^{*}) at 50°C are given in Table II - 1 together with heat capacities of activation (ΔC^{*}). The data from which these quantities were derived are given in Appendices II - 1 and II - 2 at the end of this Chapter.

TABLE II - 1.

The solvolysis of p-substituted benzyl chlorides in 70% aqueous acetone at 50°C.

(k in sec.^{-1}, E in kcal. mole^{-1}, ΔS^{*} in cal. $^{\circ}K^{-1}$,
ΔC^{*} in cal. $^{\circ}K^{-1}$)

Substituent	H.^{b}	Me.^{a}	An.^{c}	PhO.	MeO.^{a}
$10^{6}k$.	0.4168	2.001	6.768	66.98	5814
E.	21.31±.11	22.39±.08	23.11±.02	21.91±.00	18.98±.14
$-\Delta S^{*}$.	23.96±.32	17.49±.23	12.82±.06	11.98±.00	11.99±.44
$-\Delta C^{*}$.	21.7 ± 2.5	20.8 ± 2.7	29.6 ± 1.4	43.1 ± 2.9	45.9 ± 4.5

a) Calculated from the results of Shillaker[51].

b) Calculated from the results of Cowie and Kohnstam[52].

c) An = p- $MeO.C_6H_4$-.

Table II - 1 shows that as the facility for electron donation to the reaction centre by the substituents is increased, the heat capacity of activation becomes more negative and the entropy of activation becomes more positive. A constant value is reached for the two most reactive substrates.

Information about the mechanism of solvolysis in this series can be obtained from an examination of the effect of substituents on the rate of solvolysis and on the activation parameters.

Relative rates.

The changes in the rate of solvolysis resulting from p-methyl substitution are given in Table II - 2 for benzyl chloride and also for a number of compounds known to react by mechanism S_N1.

It can be seen from Table II - 2 that the relative rates (k_{Me}/k_H) vary considerably. This is to be expected since the effect of the substituent on the rate depends on the electron demand at the site of substitution. This demand will clearly be affected by the nature of the other groups attached to the reaction centre since these groups may also help to satisfy the electron demand at the reaction centre and thus reduce the demand at the site of substitution. On this view, the accelerating effect of the p-methyl

TABLE II - 2.

The effect of p-methyl substituents on the rates of solvolysis of various compounds at 25°C [53].

Compound	Ph.CH_2Cl	Ph.$CHCl_2$[53]	Ph.CHMe.Cl[54]	Ph.CHPh.Cl[c]	Ph.CMe_2.Cl[15a]	Ph.CPh_2.Cl[33]
Solvent	70% Acetone[a]	50% Acetone[a]	79.5% Dioxan[a]	85% Acetone[a]	90% Acetone[a]	60% Ether[b]
Mechanism	?	S_N1	S_N1	S_N1	S_N1	S_N1
k_{Me}/k_H	4.2	79.2	56.2	21.2	26.0	4.1

a) Water as second component.

b) Ethanol as second component.

c) From Table III - 9.

substituent in reactions which proceed by mechanism S_N1 should decrease with increasing polarisability of the other groups attached to the reaction centre, as observed in Table II - 2. Admittedly, the largest value of (k_{Me}/k_H) also corresponds to the best ionising solvent in this series but the effect of para-substituents on the rates of S_N1 reactions is usually fairly insensitive to changes in solvent[15c, 23].

It is, however, an essential requirement of this interpretation that the p-methyl substituent should show the largest acceleration in benzyl chloride if this compound undergoes S_N1 solvolysis as there are now no other polarisable groups attached to the reaction centre. Since this requirement is not met, we may conclude that, at least in the case of the parent compound, the solvolysis does not proceed by mechanism S_N1.

Similar comparisons are made in Table II - 3 where the effects of several electron releasing substituents, relative to others, are compared for the benzyl (A) and p'-nitrobenzhydryl (B) series; mechanism S_N1 operates throughout series B.

TABLE II - 3.

The effect of electron releasing substituents on the rates of solvolysis of benzyl chloride (A) and p'-nitrobenzhydryl chloride (B) at 50°C.

Compound	$k_{An.}/k_{Me.}$	$k_{PhO.}/k_{An.}$	$k_{MeO.}/k_{PhO.}$
$Ph\cdot CH_2Cl$ (A).	3.38[a]	9.90[a]	86.8[a]
$NO_2\cdot C_6H_4\cdot CHPh\cdot Cl$(B).	5.07[a,c]	5.00[b]	47.9[b]

a) In 70% aqueous acetone.

b) In 85% aqueous acetone. c) Assumes $\frac{k_{An.}\ 70\%\ \text{acetone}}{k_{An.}\ 85\%\ \text{acetone}} = 16.5$

For the more powerful electron releasing substituents, the rate ratios ($k_{PhO.}/k_{An.}$ and $k_{MeO.}/k_{PhO.}$) are about twice as large in series A as in series B. However, ($k_{An.}/k_{Me.}$) has the lower value in series A and it can therefore be concluded that p-methylbenzyl chloride does not undergo entirely S_N1 solvolysis.

The effect of substituents on the activation parameters.

Table II - 4 shows the effect of para-substituents on the entropy of activation in the solvolysis of benzyl chloride and of benzhydryl chloride.

TABLE II - 4.

The effect of para-substituents on the activation entropy ($\Delta S^{\ast}$) in the solvolysis of benzyl and benzhydryl chlorides.

Compound	$-\Delta S^{\ast}$ (cal. $^{o}K^{-1}$ at $50^{o}C$) for the p-substituted compounds				
	H	Me	An	PhO	MeO
$Ph\cdot CH_2Cl$[a]	23.96±.32[52]	17.49±.23[51]	12.82±.06	11.98±.00	11.99±.44[51]
$Ph\cdot CHPh\cdot Cl$[b] (S_N1)	15.55±.10[41b]	16.78±.29[41b]	14.51±.30	19.75±.40	17.62±.95

a) in 70% aqueous acetone. (from Table II - 1).

b) in 85% aqueous acetone. (see Chapter III).

The entropy is virtually constant throughout the series of benzhydryl chlorides (thus substituents here affect the rate of solvolysis mainly through the activation energy, see p. 85). This constant entropy is to be expected in S_N1 reactions if the transition state has the same degree of charge development and the same degree of solvation for all the compounds under consideration[23]; the small entropy variations in the benzhydryl series (e.g. the slightly more negative value for p-phenoxy and p-methoxy) are discussed in Chapter III. It is worth noting that the corresponding p'-nitrobenzhydryl chlorides (see p. 85) and, over a more limited range of substituents, the phenyldimethylcarbinyl chlorides[15] also exhibit a substantially constant entropy of activation.

The benzyl chlorides, however, (Table II - 4) show an increasingly positive entropy as the facility of the substituent for electron donation to the reaction centre is increased, until a final constant value is achieved for the two most reactive compounds. Such a gradation is consistent with a change from mechanism S_N2 to S_N1[55] as the polarity of the substituents is increased and it is reasonable to suggest that the final constant entropy value indicates that mechanism S_N1 operates in the solvolysis of the p-phenoxy and p-methoxy derivatives. On this basis, the mechanism of solvolysis of the p-methyl and p-anisyl derivatives lies in the "borderline" region, with the solvolysis of the more reactive compound showing a greater S_N1 character.

A similar interpretation of changing entropy has been applied by Tommila and his co-workers to the solvolysis of alkyl substituted benzyl chlorides[56].

The ratio $\Delta C^{\ast}/\Delta S^{\ast}$.

Bensley and Kohnstam[55] suggested that the ratio $\Delta C^{\ast}/\Delta S^{\ast}$ should be independent of the nature of the substrate in S_N1 solvolysis and that the ratio should have a lower value for solvolysis by mechanism S_N2 under the same experimental conditions. In a recent communication[57], the validity of these predictions has been confirmed for the solvolysis of a variety of chlorides and bromides in aqueous acetone. The value of $\Delta C^{\ast}/\Delta S^{\ast}$ therefore appears to afford an additional method for recognising solvolytic mechanism.

The values of $\Delta C^{\ast}/\Delta S^{\ast}$ found in the solvolysis of p-substituted benzyl halides are given in Table II - 5 together with the S_N1 value[57] (the mean for eight reactions where the mechanism is indisputably unimolecular).

TABLE II - 5.

$\Delta C^{\ast}/\Delta S^{\ast}$ for the solvolysis of para-substituted benzyl chlorides in 70% aqueous acetone at 50°C.

p-Substituents	H[52]	Me[51]	An	PhO	MeO[51]
$C^{\ast}/\ S^{\ast}$ [a]	0.91±.11	1.19±.15	2.31±.04	3.60±.24	3.83 ±.39
S_N1 value[57]	3.68				

a) From Table II - 1.

The results in Table II - 5 show that only the most powerful electron donating substituents (MeO. and PhO.) yield completely S_N1 solvolysis and that $\Delta C^{\ast}/\Delta S^{\ast}$ for the other three derivatives is less than the S_N1 value. The figures for the p-methyl and p-anisyl compounds can be explained either in terms of reaction via a single transition state or in terms of concurrent mechanisms, but the present information does not permit a distinction between these alternatives.

Thus the results suggest that within the present series of benzyl chlorides, solvolysis in 70% aqueous acetone only occurs by mechanism S_N1 for the p-phenoxy and p-methoxy derivatives. All the available evidence is consistent with this view.

Robertson and Scott[58] have recently criticised mechanistic interpretations based on values of $\Delta C^{\ast}/\Delta S^{\ast}$ on the grounds that $\Delta S^{\ast}$ for solvolysis in water passes through zero and becomes positive as the temperature is reduced. However, the constancy of this ratio for S_N1 solvolysis in water has never been claimed or established as there are insufficient data available at present to form any conclusions. It has also been emphasised[53, 57] that the factors controlling the magnitude of $\Delta C^{\ast}$ and $\Delta S^{\ast}$ may not be the same in water as in aqueous acetone where one of the solvent components can "solvate" an organic substrate.

SOLVOLYSIS OF BENZYL HALIDES IN 99.5% AQUEOUS FORMIC ACID.

The reaction of substituted benzyl halides with slightly aqueous formic acid was studied as it was anticipated that the reaction would proceed by mechanism S_N1 and that the system would therefore provide an opportunity for obtaining information about the behaviour of substituents in a situation where the electron demand at the site of substitution was large (see Chapter I).

The solvolysis of benzyl compounds in nearly anhydrous formic acid has been studied in the past by two sets of workers. Evans and Hamann[59] made a brief conductimetric study of the formolysis of benzyl chloride but at only one temperature and Bevan[60] investigated the substituent effects of the p-methyl and p-tert.-butyl groups on the formolysis of benzyl bromide, also at only one temperature. Both these workers relied on initial rate data, for different reasons. Evans and Hamann could only utilise the conductance data for hydrogen chloride in formic acid given by Schlesinger and Martin[61] below a certain HCl concentration, whilst Bevan found that equilibrium was attained at an early stage in the reaction. The present investigation also showed that the reaction was significantly reversible since the first-order rate constants for the solvolysis of benzyl bromide in

99.5% formic acid gradually fell to about half their initial value after two half-lives (Appendix IV - 2, Expt. 11). That this was due to the reverse reaction with the product HCl was confirmed when it was found that the introduction of an organic base gave rise to constant rate coefficients having similar values to the initial rates observed in the absence of base,

In all cases, except that of p-nitrobenzyl bromide, varying base concentration had little effect on the rate provided that concentration was in excess of that of the organic halide (when the base concentration was less than that of the substrate, falling rate coefficients resulted). Experiments were conducted with two bases, piperidine and triethylamine, and since the rates obtained were very similar it was concluded that the base merely acts as an acceptor of protons. The effect of changing base concentration on the rates of formolysis of three compounds is shown in Table II - 6. All subsequent experiments were carried out with .02 - .025 M organic halide in the presence of .05 M piperidine.

TABLE II - 6.

The effect of changing base and base concentration on the formolysis rate of .02 - .025 M benzyl halides at 80.17°C.

Substrate	Base	Base Concn. (M).	10^5k(sec^{-1})	Per-cent change in rate relative to .05M. piperidine
$PhCH_2Br$	$C_5H_{11}N$	.033	16.21	- 2.84
	$C_5H_{11}N$	.05	16.67	-
	$C_5H_{11}N$	.1	17.76	+ 6.14
	NEt_3	.033	15.74	- 5.91
	NEt_3	.1	16.34	- 2.02
$PhCH_2Cl$	$C_5H_{11}N$	.05	6.603	-
	$C_5H_{11}N$	.1	6.976	+ 5.35
$p\text{-}NO_2C_6H_4CH_2Br$	$C_5H_{11}N$	.05	0.2184	-
	$C_5H_{11}N$	.1	0.2898	+ 24.64

Reaction products.

From Table II - 6, it can be seen that a doubled base concentration in the formolysis of p-nitrobenzyl bromide gives rise to a 25% increase in rate. This could arise from the abstraction of an α-hydrogen atom by the base as a first step, which would ultimately result in the formation of a stilbene, as in the reaction of p-nitro benzyl chloride with hydroxide ions in aqueous solvents. Hanna, Iskander and Riad[62] consider this latter reaction to follow the path,

$$O_2N\cdot C_6H_4\cdot CH_2Cl \;+\; OH^- \rightleftharpoons O_2N\cdot C_6H_4\cdot CHCl^- \;+\; H_2O$$

$$O_2N\cdot C_6H_4\cdot CHCl^- \xrightarrow{\text{slow}} O_2N\cdot C_6H_4\cdot CH : \;+\; Cl^-$$

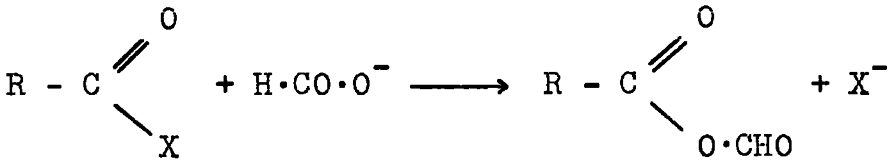
$$2\ O_2N\cdot C_6H_4\cdot CH : \longrightarrow O_2N\cdot C_6H_4\cdot CH : CH\cdot C_6H_4\cdot NO_2$$

involving the free biradical p-nitrophenylmethylene. However, p-nitrobenzyl chloride is found to react 60 times faster than the parent compound in 50% aqueous acetone in the presence of alkali. In the present system the substituent effect is in the opposite direction (see Table II - 7).

Analysis of the products of reaction between p-nitrobenzyl bromide, piperidine and 99.5% formic acid under similar conditions to those of the kinetic experiments (Appendix IV - 3) showed that no p, p'-dinitrostilbene was formed. The product consisted of piperidine hydrobromide, p-nitrobenzyl formate and p-nitrobenzyl alcohol, as required by an S_N mechanism.

Crunden and Hudson[63] studied the effect of added formate ions on the rate of solvolysis of p-methyl, p-bromo and p-nitro benzoyl chloride and the parent compound in slightly aqueous formic acid. They found that the rate of reaction of the p-nitro compound increased rapidly on the addition of formate ions whereas the rates of reaction of the parent and p-methyl compounds were unaffected, and considered the possibility that the reaction might have proceeded with formate ions due to the ionisation of formic acid promoted by water :

$$H{\cdot}CO_2H \rightleftharpoons H^+ + H{\cdot}CO{\cdot}O^-$$



$$R-C(=O)X + H{\cdot}CO{\cdot}O^- \longrightarrow R-C(=O)O{\cdot}CHO + X^-$$

However, these authors rejected this possibility since the rate of hydrolysis was found to be strictly first-order over the whole course of the reaction. They pointed out that if the reaction involved formate ions, the rate constant would decrease continuously owing to the common ion effect provided that the hydrogen ion concentration produced in the hydrolysis was greater than that produced by ionisation of the formic acid. This requirement was fulfilled in their experiments.

The experimental conditions prevalent in the present study, however, are somewhat different. The reactions are effected in the presence of an excess of piperidine so that a large increase in formate ion concentration, proportional to the piperidine concentration, is likely to occur as the base concentration is doubled. It is felt that under these circumstances, especially where reaction with the solvent is relatively slow, bimolecular attack of the p-nitrobenzyl bromide by formate ions is a distinct possibility.

Mechanism of formolysis of benzyl halides.

Substituted benzyl bromides were mainly used as the substrates for this series of experiments as the chlorides were thought to be too unreactive for convenience. The effects of the following seven substituents on rates and activation parameters were studied : p-nitro, m-chloro, hydrogen, p-fluoro, p-phenyl, p-methyl and p-methoxy. The relative reactivities of substituted benzyl chlorides and bromides were also briefly examined. Most compounds were studied at two temperatures, thus yielding activation parameters at the mean temperature. Benzyl bromide was, however, studied at three temperatures to give dE/dT.

This allowed a comparison of the rate of formolysis of each substituted derivative with that of the parent compound at the same temperature. Details of the experimental procedures and methods of calculation are given in Chapter IV.

Relative rates.

Relative rates in the formolysis of benzyl bromides are set out in Table II - 7 together with similar data for the hydrolysis of two series of compounds known to proceed by mechanism S_N1.

TABLE II - 7.

Relative rates (k/k_H) in the formolysis of substituted benzyl bromides and in the hydrolysis of benzhydryl and phenyldimethylcarbinyl chlorides.

(All temperatures are 25.00° unless otherwise stated).

Substituent	$Ph\cdot CH_2Cl$ (Formolysis)	$Ph_2\cdot CHCl$ [a] (Hydrolysis)	$Ph\cdot C\cdot Me_2Cl$ [b] (Hydrolysis)
$p-NO_2$	.0131 (80.17°)	8.896×10^{-4}	2.57×10^{-4}
m-Cl	.114 (80.17°)	.0125 [c]	.0156
p-F	1.611 (80.17°)	1.857	2.14
p-Ph	21.81 (40.15°)	6.993	6.52
p-Bu$^{t.}$	28.0 [d]	11.20	14.4
p-Me	50.35 (40.15°)	21.19	26.0
p-MeO	3.7×10^6 (9.70°) [e]	1.435×10^4	3.36×10^3

a) From Table III - 9. b) Ref. 15 c) Methanolysis; Ref. 35.

d) Ref. 60. e) From ratio of chlorides (see Chapter IV, p.167).

It has already been shown (see p. 37) that the electron demand at the site of substitution is somewhat greater in the benzyl than in the benzhydryl and phenyldimethylcarbinyl series. Thus if the formolysis of benzyl bromides proceeds by mechanism S_N1, the relative rates (k/k_H) in Table II - 7 should be somewhat larger in the benzyl series. This is observed for the p-phenyl, p-tert. butyl, p-methyl and p-methoxy substituents but the acceleration produced by the p-fluoro group is similar to that in the benzhydryl and phenyldimethylcarbinyl series whereas a larger effect is to be expected on the basis of the present interpretation. This would seem to suggest that the formolysis of the parent benzyl bromide does not occur by mechanism S_N1 although mechanistic interpretations based on the behaviour of p-halogen substituents must be used with caution due to the roughly equal but opposite inductive and mesomeric capacities of the substituents (see Chapter I, p.20 and Chapter III, p. 95). On the present scheme, (k/k_H) for the retarding substituents p-nitro and m-chloro is expected to be somewhat smaller in the benzyl case than in the unimolecular examples if these groups induce the formolysis of benzyl bromide to occur by mechanism S_N1. This requirement is not fulfilled and it is therefore highly probable that these two derivatives do not react by mechanism S_N1 in moist formic acid.

It is worth noting, at this point, that the effect of p-methylation on the rate in the benzyl residue is a factor of ten larger in formolysis (Table II - 7) than for reaction in aqueous acetone (Table II - 2). This is in agreement with the assignment of a bimolecular contribution to the mechanism of solvolysis of benzyl chloride in aqueous acetone (p. 39).

The effect of substituents on the activation parameters.

Table II - 8 shows the effect of substituents on the entropy of activation in the formolysis of benzyl bromide and in the S_N1 solvolysis of benzhydryl chloride. The activation parameters for the formolysis of p-nitro and m-chloro benzyl bromides were not measured since the relative rate results clearly indicated that these derivatives did not react by the unimolecular mechanism.

The variations in the entropy of activation in the formolysis of substituted benzyl bromides are reminiscent of similar results for the solvolysis of benzyl chlorides (Table II - 4) in that, in general, the entropy becomes more positive as the facility for electron donation by the substituent to the reaction centre increases. There is no such variation in the unimolecular solvolysis of substituted

TABLE II - 8.

The effect of substituents on the entropy of activation in formolysis of benzyl bromide and in the S_N1 hydrolysis of benzhydryl chloride.

(All temperatures are 25.00° unless otherwise stated).

Substituent X	$\Delta S_X^{\ast} - \Delta S_H^{\ast}$ (cal.°k^{-1})	
	$Ph.CH_2Cl$ [a] (Formolysis)	$Ph_2.CHCl$ (Hydrolysis)
p-F	1.82 ± .16 (70.18°)	- 0.94 ± .11[c]
p-Ph	8.21 ± .22 (30.33°)[b]	0.97 ± .07[d]
p-Me	3.89 ± .23 (30.33°)[b]	- 0.96 ± .12[d]

a) Activation parameters cannot be compared at the same temperature as dE/dT is available only for the parent compound.

b) Using calculated values of $\Delta S_H^{\ast}$

c) In 70% aqueous acetone[23].

d) In 85% aqueous acetone[41b].

benzhydryl chlorides. It therefore seems safe to conclude that benzyl bromide does not react by mechanism S_N1 in moist formic acid. The abnormally positive entropy of the p-methyl derivative, and also the fact that it is less positive than that of the p-phenyl derivative, would seem to cast some doubt on whether even the p-methyl substituent is able to promote unimolecular formolysis. Although p-phenylbenzyl bromide undergoes formolysis more slowly than the p-methyl compound (Table II - 7), it is possible that the more positive entropy of the former substrate indicates that the mechanism of formolysis of this compound is nearer the S_N1 limit than that of the latter. This could be explained in terms of the larger polarisability of the phenyl group.

The present conclusions contradict the assumptions which are usually made in the literature and it is therefore of interest to consider the evidence favouring the view that benzyl halides undergo unimolecular formolysis.

Reaction mechanism in formic acid.

Bateman and Hughes[67] observed that the rate of formolysis of alkyl halides increased along the series Me. $<$ Et. $<$ iso.-Pr. $<$ tert.-Bu., the order expected for reaction by mechanism S_N1. However, the rate increase on passing from the methyl to the ethyl compound was not large. Addition of small amounts of water increased the rate of reaction of methyl and other n-alkyl halides[65, 67] but did not alter the rate of formolysis of tert.-butyl chloride[64], a compound which can certainly be expected to react unimolecularly in this solvent.

These authors therefore concluded that nucleophilic interaction with the solvent (i.e. S_N2 reaction) was still of importance in the formolysis of the n-alkyl halides. These conclusions were supported by the observation that added formate ions increased the rate of decomposition of n-alkyl halides[65], but not the rate of reaction of tert,-butyl halides[66]. The rate sequence of a series of α -methylated alkyl halides, however, shows that solvolysis by mechanism S_N1 is more likely to occur in formic acid than in water.

This conclusion has also been reached by Vernon[68] but this worker showed that the reaction of 1-methylallyl chloride with formic acid can be accelerated by the addition of small amounts of water even though solvolysis in aqueous solvents occurred unimolecularly. It would therefore appear that the exact stage in a series of alkyl halides at which formolysis occurs entirely by mechanism S_N1 has still to be established. It is also noteworthy that benzoyl chloride and its more reactive derivatives are considered to react unimolecularly with formic acid[63]. The evidence is based on the effects of water and formate ions on the rate.

Streitwieser[70] found that the formolysis of the p-bromobenzenesulphonate of butanol-1-D, $H_3C{\cdot}H_2C{\cdot}H_2C{\cdot}HDC{\cdot}OH$, proceeds with inversion of configuration accompanied by little, if any, racemisation and pointed out that this is consistent with the operation of mechanism S_N2. This author considered that such a mechanistic assignment is not supported by the observation that a change from methyl to the ethyl halide or sulphonate decreases the rate by a factor of ca. 2 in aqueous and ethanolic solvents[71], and increases the rate by a similar factor in formic acid[72]. He therefore proposed that solvolysis occurs via intermediates of the type put forward by Doering and Zeiss[73], but it must be stressed that such a hypothesis is unnecessary. Rates of bimolecular substitution depend on the relative importance of bond-making and bond-breaking processes and it is very likely that α-methyl substituents in methyl halides will have different effects on the rates of reaction with formic acid and aqueous solvents since the bond-breaking process appears to be of greater importance in the former solvent.

The recent work by Deitz, quoted by Crunden and Hudson[74], has shown that a secondary sulphonate gave a completely racemised product on formolysis and it would therefore seem that this compound undergoes reaction by mechanism S_N1. It is noteworthy that the solvolysis of iso.-propyl tosylate in 50% aqueous acetone also occurs entirely by mechanism S_N1[79] while benzyl chloride reacts bimolecularly with this solvent[55].

Since sulphonates are more likely to undergo unimolecular solvolysis than the corresponding chlorides, the fact that a secondary sulphonate reacts by this mechanism with formic acid does not demand a similar mechanism for benzyl chloride. The mechanistic conclusion based on the activation parameters in the formolysis of this compound does not, therefore, contradict the available evidence.

Comparison of the formolysis of benzyl bromides with the hydrolysis of benzyl tosylates in aqueous acetone.

The present results for the formolysis of substituted benzyl bromides show a remarkable similarity to those of Hammond[29, 75, 76, 77] for the solvolysis of substituted benzyl toluene-p-sulphonates (Table II - 9). The relative rates suggest that the electron demand at the site of substitution is greater in the formolysis of the bromides than in the hydrolysis of the sulphonates. This is consistent with the greater ease of ionisation of the sulphonate group when attached to carbon. The changes in the entropy of activation caused by the introduction of substituents show the same features, i.e. an increase on the introduction of a p-methyl group and a larger increase on the introduction of the more weakly electron donating p-phenyl group. Hammond[76] assumed that all the compounds, except for the p-nitro derivative, underwent S_N1 solvolysis and attributed the abnormally positive entropy of p-phenylbenzyl tosylate (which was not found for the m-phenyl derivative) to a spreading of the positive charge

TABLE II - 9.

Substituent effects in the formolysis of benzyl bromide (reaction A) and in the solvolysis of benzyl toluene-p-sulphonate in aqueous acetone (reaction B).

(entropies are in cal. $^{\circ}k^{-1}$).

Substituents	k/k_H		$\Delta S^{\ddagger} - \Delta S^{\ddagger}_H$	
	A	B[d]	A	B[d]
p-NO_2	.0131 (80.17°)	.0562 (25.00°)[a]	-	-7.17 (35.00°)[a]
p-F	1.611 (80.17°)	2.042 (25.00°)[a]	1.82 (70.18°)	-0.76 (35.00°)[a]
p-Ph	21.81 (40.15°)	8.527 (25.00°)[a]	8.21 (30.33°)[e]	9.85 (35.00°)[a]
p-Me	50.35 (40.15°)	21.37 (25.00°)[a]	3.89 (30.33°)[e]	6.82 (35.00°)[a]
p-MeO	3.7 x 10^6(9.70°)[c]	2.6 x 10^4(25.00°)[b]	-	-

a) In 83.3% aqueous acetone. b) In 96% aqueous acetone. c) From ratio of chlorides (Chapter IV, p.167)

d) Recalculated from Hammond's data, Ref. 29, 75, 76, 77.

e) Using calculated values for the parent compound.

in the p-phenylbenzyl cation which was reflected in an unusually small tendency for the ion to orient solvent[77]. However, no such abnormally positive entropy is observed in the S_N1 solvolysis of p-phenylbenzhydryl chloride (see Chapter III) and it is difficult to see why Hammond's explanation, if correct, should not also apply to this compound.

Recent work in this department[79] suggests that the hydrolysis of benzyl tosylates only occurs entirely by mechanism S_N1 for the p-anisyl and more reactive derivatives[≠]. Thus, if there is a genuine parallel between the formolysis of benzyl bromides and the solvolysis of benzyl tosylates, it is reasonable to suppose that the stage at which a bimolecular contribution to the mechanism occurs is similar for the two reactions.

[≠] The most convincing claim for S_N1 hydrolysis of the less reactive compounds is based on the formation of chlorides and nitrates on the addition of the appropriate anions without any significant effect on the overall rate of decomposition of the substrate[78]. Recent work in this department[79] does not confirm this conclusion and Professor Hammond has now found errors in the calculation of some of his results[89].

The influence of the displaced group on the formolysis of benzyl halides.

Inclusion of the p-methoxy substituent in the present formolysis work necessitated the use of the chloride rather than the bromide. It was therefore necessary to examine the formolysis of another benzyl chloride, for which a result for the corresponding bromide was available, in order to obtain an estimate of the effect of this substituent on the rate of formolysis of benzyl bromide; benzyl chloride was chosen for this purpose. The result showed that the replacement of a chloride by the corresponding bromide had only a relatively small effect on the rate, both here and in the p-methylbenzyl compound. The results are summarised in Table II - 10.

TABLE II - 10.

Bromide/Chloride rate ratios in the formolysis of benzyl halides.

Substrate	Temp. ^{o}C.	k_{Br} [a]	k_{Cl} [a]	k_{Br}/k_{Cl}
Benzyl halide	80.17	1.667×10^{-4}	6.603×10^{-5}	2.52
p-Methylbenzyl halide	40.15	1.519×10^{-4}	1.073×10^{-4}	1.42

a) First-order rate constants in sec^{-1}.

Ingold[38] surveyed the available figures for both bimolecular and unimolecular rates of hydrolysis or alcoholysis and found that a given alkyl bromide substituted by the bimolecular mechanism some 30-40 times faster than the corresponding chloride while the iodide substituted about 2.0-2.5 times faster than the bromide. Bromides were found to ionise about 25-60 times faster than the chlorides and iodides some 1.5-4.5 times faster than the bromides.

Hughes and Shapiro[80] pointed out that the much larger velocity difference between chloride and bromide than between bromide and iodide would not be expected for gas-phase reactions since the C-Hal. bond strengths and stretching force-constants vary in a fairly regular manner in the series Cl, Br, I. Reactions in solution, however, would be considerably influenced by polarisation, polarisability and solvation factors so that the authors did not consider the absence of any obvious relationship between bond strengths or force-constants and reaction rate to be surprising.

The present results (Table II - 10) show that the bromide/chloride rate ratio is a factor of ten or so smaller than is usual in solvolytic reactions; that this is not due to preferential bimolecular attack by formate ions has already been shown (see Table II - 6). Heppolette and Robertson[81] observed a similar anomaly for the hydrolysis of methyl halides in water, where the bromide reacted 11.50 times faster than the chloride whilst the corresponding figure for the iodide was only 3.88.

Miller and Parker[69] reported that aromatic nucleophilic substitution reactions were up to 10^5 times faster in nine dipolar aprotic solvents than they were in three protic solvents and suggested that in dipolar aprotic solvents, solvation of anions was in the reverse order to that accepted for protic solvents, i.e. solvation decreased in the series,

$$I^- > Br^- > Cl^-$$

Analogous considerations may apply in the present solvent, which is protic but not hydroxylic, and the solvation forces may well be different in formic acid to those in the hydroxylic solvents for which the relative rate generalisations for chlorides, bromides and iodides were established. It is possible that such a solvation difference could counteract the lower ionisation energy of bromine relative to chlorine and thus give rise to the observed, small, bromide-chloride rate ratios.

APPENDIX TO CHAPTER II

Summary of Rate Constants and Derived Data for the Reaction of Substituted Benzyl Halides with 70% Aqueous Acetone and 99·5% Aqueous Formic Acid

The results are summarised in Appendices II - 1 to II - 4, details of the experimental procedures and methods employed in calculation being given in Chapter IV. Throughout the Tables k represents the first-order rate coefficient (in sec^{-1}), σ the standard error in k, E the activation energy (in kcal. mole^{-1}), $\Delta S^{\ne}$ the entropy (in cal. deg.$^{-1}$) and $\Delta C^{\ne}$ the heat capacity of activation (in cal. deg.$^{-1}$). The units of temperature are degrees centigrade and dE/dT values are in cal. deg.$^{-1}$. σ (dE/dT), the standard error in dE/dT, was obtained in two ways.

(i) From the deviations of experimental values of E from the 'best' straight line, E vs. T.

(ii) From the standard deviations of E (σ (E)),

and only the larger value is quoted in the following tables.

APPENDIX II - 1

Hydrolysis of p-anisylbenzyl chloride in 70% aqueous acetone.

(Expts. 1 - 5, Appendix IV - 2)

Experimental Values						'Least Squares' Values	
Temp.	k	$\frac{\sigma}{k}$	Mean Temp.	E	$-\Delta S^{*}$	E	$-\Delta S^{*}$
95·40	$4{\cdot}914 \times 10^{-4}$	0·0014					
			87·81	22·054 ± ·029	16·21	22·068	16·19
80·21	$1{\cdot}347 \times 10^{-4}$	0·0011					
			73·06	22·503 ± ·048	14·86	22·475	14·95
65·91	$3{\cdot}487 \times 10^{-5}$	0·0027					
			58·25	22·868 ± ·044	13·70	22·884	13·65
50·58	$6{\cdot}992 \times 10^{-6}$	0·0016					
			45·31	23·244 ± ·059	12·46	23·241	12·47
40·04	$2{\cdot}073 \times 10^{-6}$	0·0027					

$\frac{dE}{dT} = -27{\cdot}6 \pm 1{\cdot}4\ (\sigma(E))$

$\Delta S^{*}\ (50^{\circ}) = -12{\cdot}82 \pm {\cdot}06$ (in 70% Acetone A)

$k\ (50^{\circ}) = 6{\cdot}768 \times 10^{-6}$ (in 70% Acetone A)

$\Delta C^{*} = -29{\cdot}6 \pm 1{\cdot}4$

$E\ (50^{\circ}) = 23{\cdot}112 \pm {\cdot}022$

$\frac{\Delta C^{*}}{\Delta S^{*}}\ (50^{\circ}) = 2{\cdot}31 \pm {\cdot}04$

APPENDIX II - 2

Hydrolysis of p-phenoxybenzyl chloride in 70% aqueous acetone

(Expts. 6 - 10, Appendix IV - 2)

Experimental Values						'Least Squares' Values	
Temp.	k	$\frac{\sigma}{k}$	Mean Temp.	E	$-\Delta S^{\ddagger}$	E	$-\Delta S^{\ddagger}$
69·47	$4{\cdot}353 \times 10^{-4}$	0·0021					
			64·83	21·290 ± ·081	14·03	21·300	14·00
60·19	$1{\cdot}823 \times 10^{-4}$	0·0026					
			55·43	21·686 ± ·075	12·78	21·686	12·80
50·68	$6{\cdot}971 \times 10^{-5}$	0·0021					
			45·38	22·128 ± ·058	11·35	22·099	11·44
40·07	$2{\cdot}175 \times 10^{-5}$	0·0022					
			34·74	22·518 ± ·045	10·04	22·536	9·98
29·41	$6{\cdot}082 \times 10^{-6}$	0·0013					

$\frac{dE}{dT} = -41{\cdot}1 \pm 2{\cdot}9\ (\sigma(E))$

$\Delta S^{\ddagger}\ (50^{\circ}) = -11{\cdot}98$ (in 70% Acetone A)

$k\ (50^{\circ}) = 6{\cdot}698 \times 10^{-5}$ (in 70% Acetone A)

$\Delta C^{\ddagger} = -43{\cdot}1 \pm 2{\cdot}9$

$E\ (50^{\circ}) = 21{\cdot}909$

$\frac{\Delta C^{\ddagger}}{\Delta S^{\ddagger}}\ (50^{\circ}) = 3{\cdot}60 \pm {\cdot}24$

APPENDIX II - 3

Solvolysis of Benzyl Bromide in 99·5% Aqueous Formic Acid.

(Added Base: 0·05M Piperidine).

(Expts. 17 - 19, Appendix IV-2)

Experimental Values					
Temp.	k	$\frac{\sigma}{k}$	Mean Temp.	E	$-\Delta S^{\ddagger}$
80·17	$1\cdot667 \times 10^{-4}$	0·0027	70·18	$21\cdot494 \pm \cdot036$	17·27
60·18	$2\cdot659 \times 10^{-5}$	0·0015	50·17	$22\cdot550 \pm \cdot044$	13·98
40·15	$3\cdot017 \times 10^{-6}$	0·0039			

$$\frac{dE}{dT} = -52\cdot8 \pm 2\cdot8 \ (\sigma\,(E))$$

$$\Delta S^{\ddagger}\ (50^{o}) = -13\cdot92 \pm \cdot09$$

$$\Delta S^{\ddagger}\ (30\cdot33^{o}) = -10\cdot48 \pm \cdot22$$

$$k\ (9\cdot70^{o}) = 4\cdot857 \times 10^{-8}$$

$$\Delta C^{\ddagger} = -54\cdot8 \pm 2\cdot8$$

$$E\ (50^{o}) = 22\cdot559 \pm \cdot029$$

$$E\ (30\cdot33^{o}) = 23\cdot597 \pm \cdot071$$

APPENDIX II - 4

Solvolysis of p-methyl, p-phenyl, p-fluoro, m-chloro and p-nitro benzyl bromides and p-methoxy benzyl chloride in 99·5% aqueous formic acid.

(Added base: ·05M Piperidine).

Experimental Values of k, E and ΔS^{*}

Substituent	Temp.	k	$\frac{\sigma}{k}$	Mean Temp.	E	$-\Delta S^{*}$	Expt.[b] Nos.
p-CH_3	40·15	$1{\cdot}519 \times 10^{-4}$	0·0016	30·33	22·386 ± ·025	6·59 ± ·08	21
	20·51	$1{\cdot}372 \times 10^{-5}$	0·0021				20
p-C_6H_5	40·15	$6{\cdot}580 \times 10^{-5}$	0·0010	30·33	24·261 ± ·011	2·27 ± ·04	23
	20·51	$4{\cdot}859 \times 10^{-6}$	0·0014				22
p-F	80·17	$2{\cdot}686 \times 10^{-4}$	0·0029	70·18	21·801 ± ·045	15·45 ± ·13	24
	60·18	$4{\cdot}174 \times 10^{-5}$	0·0026				25
m-Cl	80·17	$1{\cdot}901 \times 10^{-5}$	0·0054	-	-	-	26
p-NO_2	80·17	$2{\cdot}184 \times 10^{-6}$	0·0098	-	-	-	27
p-CH_3O (benzyl chloride)	9·70	$7{\cdot}182 \times 10^{-2}$ [a]	0·0558	-	-	-	33

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[a] Method of Rate determination, p. 158.
Method of Calculation of bromide rate, p. 167.

[b] Appendix IV - 2

CHAPTER III.

THE SOLVOLYSIS OF SUBSTITUTED BENZHYDRYL CHLORIDES IN AQUEOUS ACETONE.

The effect of p-nitro, p-chloro, p-fluoro, p-phenyl, p-tert.-butyl, p-methyl, p-anisyl, p-phenoxy and p-methoxy substituents on the rates of hydrolysis of p'-nitrobenzhydryl chloride, benzhydryl chloride and p'-methoxybenzhydryl chloride was examined[≠]. These reactions all proceed by the ionisation mechanism, S_N1, and the three series involve differing demands for electrons at the site of p-substitution in the activated complex; this demand is relatively large for the p'-nitro-compounds, relatively small for the p'-methoxy-compounds and intermediate when no p'-substituent is present.

The less reactive compounds were studied at an initial concentration of approximately .01 M and the reactions followed by titrating aliquots with standard alkali. Constant integrated first-order rate coefficients were observed and it was assumed that these rate coefficients corresponded to the rate of ionisation (see p. 82). The more reactive compounds

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[≠] The effect of p-nitro, p-chloro, p-fluoro, p-phenyl, p-tert.-butyl and p-methyl substituents on the rate of hydrolysis of benzhydryl chloride was previously studied by Kohnstam[23, 41]; these results are included in the present discussion.

were studied by noting the conductance of initially ca. .002 M solutions. Check experiments showed no difference in rate on changing the initial concentration from .01 M to .0017 M (see Expt. 63, Appendix IV-2). Full details of the experimental methods employed are given in Chapter IV.

In the solvolysis of the more reactive compounds, the integrated first-order rate coefficients decreased as the reaction proceeded and this decrease became more marked as the reactivity of the substrate increased. This suggests the incursion of the "mass-law effect" which is characteristic of reaction by mechanism S_N1. This effect is considered in more detail in the following pages.

"MASS-LAW EFFECTS".

"Mass-law constants" in the solvolysis of substituted benzhydryl chlorides.

In the S_N1 hydrolysis of an organic chloride, RCl[82],

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

the unstable carbonium ion, R^+, is considered to react almost as soon as it is formed. Application of the stationary state principle then yields, for the first-order disappearance of the substrate,

$$- \frac{1}{[RCl]} \cdot \frac{d\,[RCl]}{dt} = \frac{k_1}{1 + \alpha[Cl^-]} \quad . \quad . \quad . \quad . \quad . \text{ Eqn. III - 1.}$$

where $\alpha = k_2/k_3$ is called the "mass-law constant"[82] and represents the efficiency of attack by Cl^- ions on R^+, relative to the attack by water.

Equation III - 1 shows that added chloride ions will reduce the first-order rate in reaction by this mechanism and that, even in the absence of added electrolytes, the production of Cl^- ions as the reaction proceeds may lead to a progressive reduction in this rate. These predictions have been confirmed for the S_N1 hydrolysis of a number of organic chlorides and it was found that the "mass-law constant" increased with increasing stability of the carbonium ion R^+[43b, 83], probably because increasing stability of the carbonium ion allows a greater probability for the penetration of its solvation shell by chloride ions before this shell collapses to give the alcohol[82]. The present observation of decreasing first-order rate coefficients as the reaction proceeds therefore appears to be consistent with the operation of the "mass-law effect". Support for this interpretation arises from the following considerations.

(i) The decrease in the rate coefficients increased with increasing reactivity of the substrate, i.e. with increasing stability of the carbonium ion.

(ii) The addition of HCl to the reaction mixture decreased the first-order rate coefficients (compare Expts. 58 and 59; 61 and 62, Appendix IV-2).

(iii) An increase in the initial concentration of the substrate decreased the initial first-order rates (compare Expts. 58 and 59A, Appendix IV-2), consistent with the greater initial chloride ion concentration of the more concentrated solution.

(iv) The decreases in the first-order rates on the addition of HCl and on increasing the initial concentration of the substrate were quantitatively consistent with equation III - 1 which assumes the operation of the "mass-law effect". (See Expts. 59, 59A and 62, Appendix IV-2).

It was therefore assumed that the rate of reaction was given by equation III - 1 and rates of ionisation were obtained from the integrated form of this equation, viz.,

$$k_1^o = \bar{k}_1 + \alpha^o \left[\bar{k}_1 (a + c) - x/t\right] \quad . \; . \; . \; . \text{ Eqn. III -2.}$$

where $\bar{k}_1 = (2.303/t) \cdot \log [a/(a - x)]$, a is the concentration of RCl at zero time, $a - x$ its concentration at time t and c the concentration of chloride ions at zero time. k_1^o and α^o

represent $\underline{k_1}$ and $\underline{\alpha}$ of equation III - 1, respectively, the superscript $\underline{o}$ indicating zero ionic strength as equation III - 2 was derived from equation III - 1 on the assumption that all activity coefficients were equal to unity. Strictly, this only applies at zero ionic strength but it was assumed, as a first approximation, that this assumption would not cause any great error in the present very dilute solutions,

Values of $\underline{\alpha^o}$ obtained from equation III - 2 are shown in Table III - 1 for those compounds which did not show constant values for the integrated first-order rate coefficient $\bar{k}_1$. It can be seen that $\underline{\alpha}^o$ generally increases with increasing stability of the carbonium ion in agreement with the observations of Hughes, Ingold and their co-workers[82] which have already been discussed. Similar observations have been reported by Eaborn, Golesworthy and Lilly[85] who suggest that a stabler carbonium ion can discriminate more effectively between the weakly nucleophilic water, present in high concentration, and the more strongly nucleophilic chloride ion present in low concentration.

The p-methoxy $\underline{p}'$-nitro compound, however, has a larger "mass-law constant" than the p-phenoxy $\underline{p}'$-hydrogen compound although the latter ionises twice as rapidly as the former. This may arise from inaccuracies in the values of $\underline{\alpha^o}$ (see below) but it must also be stressed that the rate of ionisation

TABLE III - 1.

"Mass-law constants" in the hydrolysis of substituted benzhydryl chlorides in 85% aqueous acetone.

Substituents. p-	 p'-	$-\log k_1^{o}$ (0°)	α^{o}
H.	H.	6.086	11.5[a]
MeO.	NO_2	3.533	309 (20.61°), 346 (0.10°).
PhO.	H.	3.257	162 (20.61°), 145 (0.10°).
Cl.	MeO.	1.890	879 (0.10°), 778 (-19.90°).
H.	MeO.	1.522	680 (0.10°), 673 (-19.90°), 769 (-32.90°).
F.	MeO.	1.412	825 (0.10°), 788 (-19.90°).
Ph.	MeO.	1.024	1081 (0.10°), 1052 (-19.90°), 1283 (-32.90°).
Bu^t.	MeO.	0.840	1002 (-19.90°), 1193 (-32.90°).
Me.	MeO	0.652	1514 (-19.90°), 1802 (-32.90°).
An.	MeO.	0.519	2275 (-32.90°).
PhO.	MeO.	0.158	2275 (-32.90°), 2106 (-37.34°).
MeO.	MeO.	-0.800	2570 (-37.34°).

a) Mean value for 80% and 90% acetone, 25° and 50°[82].

does not necessarily always reflect the stability of the resulting carbonium ion. Relative to a p-phenoxy group, the more polarisable p-methoxy may well stabilise the fully developed carbonium ion, R^+, more than it stabilises the transition state of ionisation. This type of behaviour has been reported before, for example an α-chloro substituent in benzhydryl chloride yields a greater "mass-law constant" and a lower rate of ionisation than a p-methyl substituent[87].

The results in Table III - 1 often show an increase of $\underline{\alpha}^o$ with decreasing temperature, contrary to previous observations[87, 129] which have suggested that reaction of a carbonium ion with water has a lower activation energy than its reaction with an anion. It therefore seems that the approximations inherent in equation III - 2 may yield inaccurate "mass-law constants". This point is discussed in more detail below.

Errors in α^o calculated from equation III - 2.

Hughes, Ingold and their co-workers[82] have pointed out that the highly dipolar transition state in the ionisation of an organic chloride will be subject to ion-atmosphere stabilisation in the presence of electrolytes, A simple electrostatic treatment of this effect showed that the acceleration of ionisation caused by the presence of a uni-

univalent electrolyte was independent of the nature of the electrolyte[82]. The assumption that the Debye limiting law applies to fully developed ions yields equation III - 1 in the form (Ref. 82, Eqn. 14),

$$\frac{dx}{dt} = \frac{k_1^o(a - x)}{\text{antilog}_{10}(B\sigma\mu) + \alpha^o(c + x)\ \text{antilog}_{10}(A\mu^{\frac{1}{2}})} \quad \ldots \text{Eqn. III - 3}$$

where σ, the "ionic strength constant", depends only on the degree of charge development and the separation of charges in the transition state, $A = -1.815 \times 10^6\ (DT)^{-3/2}$, $B = -0.912 \times 10^{16}\ (DT)^{-2}$ and μ, D and T are the ionic strength, dielectric constant, and absolute temperature, respectively. The integrated form of equation III - 3 can be written,

$$I/t = k_1^o - \alpha^o\ (J/t) \quad \ldots\ldots\ldots \text{Eqn. III - 4.}$$

$$\text{where } I = \int_0^x \frac{\text{antilog}_{10}\ B\sigma\ (c + x)}{a - x}\, dx \quad \text{and}$$

$$J = \int_0^x \frac{(c + x)\ \text{antilog}_{10}\ A\ (c + x)^{\frac{1}{2}}}{a - x} \cdot dx$$

The "ionic strength constant", σ, is usually of the order of 10^{-8} and B is approximately $1 - 2 \times 10^8$ under the present experimental conditions. The error in the integral I caused by taking σ as zero will therefore be very small in the dilute solutions now employed ($c \simeq o$, $x \leqslant .002$). Thus equation III - 3 may now be written,

$$\frac{dx}{dt} = \frac{k_1^{o}\ (a - x)}{1 + \alpha^{o}(c + x)\ \text{antilog}_{10}\, A(c + x)^{\frac{1}{2}}} \quad . \ . \ \text{Eqn. III - 5}$$

Integration of equation III - 5 gives,

$$k_1^{o} = \bar{k}_1 + \frac{\alpha^{o}}{t} \int_{0}^{x} \left[\frac{(c + x)}{(a - x)}\ \text{antilog}_{10}\, A(c + x)^{\frac{1}{2}} \right] . \, dx \quad . \ . \text{Eqn. III-6}$$

A further error arises from the assumption that HCl is completely ionised under the present experimental conditions. Conductance experiments (see Appendix IV - 1) show that this assumption is not valid in 85% acetone and that the degree of association increases as the temperature rises. It can readily be shown that this requires writing equation III - 6 in the form,

$$k_1^{o} = \bar{k}_1 + \frac{\alpha^{o}}{t} \int_{0}^{x} \left[\frac{\gamma(c + x)}{(a - x)} .\ \text{antilog}_{10}\, A\ \left[\gamma(c + x)\right]^{\frac{1}{2}} \right] . \ dx \quad . \ . \ . \ \text{Eqn. III - 7}$$

where γ is the degree of dissociation of HCl at the concentration $(c + x)$.

Values of α^{o} and k_1^{o} derived from equations III - 2, III - 6 and III - 7 are compared in Table III - 2 for the hydrolysis of p-methoxybenzhydryl chloride in 85% acetone at -20° (Expt. 66B, Appendix IV - 2)[≠]. It can be seen that

TABLE III - 2.

Equations III-2, III-6 and III-7 applied to the results of Expt. 66B (Appendix IV-2).

Equation.	α^0	$10^3 k_1^0$(sec.$^{-1}$)
III-2	679.5	2.930
III-6	820.9	2.980
III-7	871.7	3.004

the approximations which have been made can cause significant errors in α^0 but that the corresponding error in k_1^0 is very

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[≠] The method of least squares was employed in each case to give the 'best' straight line of slope α^0 and intercept k_1^0. A was evaluated from Akerlof's data for the dielectric constants of acetone-water mixtures[84] (equation IV-25) and J was obtained by graphical integration.

Unfortunately, the present conductance measurements were not sufficiently accurate to allow the precise determination of the dissociation constant of HCl which is required for the evaluation of γ in equation III - 7. A value of K_{HCl} = 2×10^{-2} at 20° was therefore assumed; the conductance measurements and the values of Atkins and Monk[130] at 25° for 80% and 90% acetone suggest that this value is approximately correct.

much smaller. Errors arising from the neglect of the ionic activity coefficients ($\underline{f} = \text{antilog}_{10} A \mu^{\frac{1}{2}}$) are virtually independent of the temperature since $\underline{f}$ only changes by ca. 2% over the experimental temperature range when $\mu = .001$. The dissociation constant of HCl is approximately halved on going from -33° to +20° so that the neglect of the association of this acid could cause errors of ca.12% in $\underline{\alpha}^{o}$ and 1.3% in $\underline{k}_1^{o}$ at the higher temperature.

It must be stressed that the results quoted in Table III - 2 refer to a run in which only 5% of the reaction had occurred at zero time. In reactions with shorter half-lives, more reaction had occurred after the 1.5 sec. which were always allowed to ensure complete mixing of the reactants (see p.162) and the calculations suggest that under these conditions (i.e. higher initial chloride ion concentration), equation III - 2 underestimates $\underline{\alpha}^{o}$ to an even greater extent than in Expt. 66B. As reactions occur more rapidly on increasing the temperature, this factor and the neglect of the association of HCl may well account for the increase of $\underline{\alpha}^{o}$ with decreasing temperature which was observed in some cases (see Table III - 1). It must therefore be concluded that the values of $\underline{\alpha}^{o}$ recorded in Table III - 1 may be underestimated by as much as 50% but it is thought that the relative scale of the $\underline{\alpha}^{o}$ values is reliable.

It has already been stressed that the approximations inherent in equation III - 2 only cause small errors in $\underline{k}_1^0$, the rate coefficients for ionisation at zero ionic strength. Values of this rate coefficient may be between 3 and 4% too small but this error should be independent of temperature and should therefore only have a slight effect on the corresponding values of the activation parameters.

The magnitude of α^0 when no decrease in rate was observed.

The lowest value of $\underline{\alpha}^0$ reported in Table III - 1 was ca. 150. Other compounds did not show decreasing first-order rate coefficients even in .01 M solutions and it is of interest to consider the maximum value of $\underline{\alpha}^0$ under these conditions. A 5% decrease in $\bar{\underline{k}}_1$ over the course of a kinetic run could easily have been detected and this yields a maximum value of ca. 25 for $\underline{\alpha}^0$ in the reaction of p-phenoxy p'-nitrobenzhydryl chloride with 85% acetone at 0° (Expt.54, Appendix IV - 2; methods employed in the calculation are outlined in Appendix IV - 4).

Table III - 3 shows the rates at 0° and the "mass-law" constants for the two least reactive compounds for which $\underline{\alpha}^0$ could be measured and for the two most reactive compounds which gave constant values of $\bar{\underline{k}}_1$ even in .01 M solution. It can be seen that the hundred-fold reduction in the rate on passing from p-methoxy p'-nitrobenzhydryl chloride to the p-phenoxy p'-nitro compound is associated with at least a thirteen-fold

TABLE III - 3.

(Results in 85% acetone)

Substituents. p-	p'-	-log k (0°)	$\underline{\alpha}^{o}$
PhO.	H.	3.2574	~150
MeO.	NO_2.	3.5325	~320
An.	H.	4.1687	< 25
PhO.	NO_2.	5.5793	< 25

decrease in $\underline{\alpha}^{o}$ and that eight-fold reduction in the rate on passing from the p-phenoxy p'-hydrogen to the p-anisyl p'-hydrogen derivative yields at least a six-fold decrease in $\underline{\alpha}^{o}$. These figures correspond to a greater sensitivity of $\underline{\alpha}^{o}$ to the rate of ionisation than most of the results quoted in Table III-1. If the values of $\underline{\alpha}^{o}$ reflect the stability of the carbonium ion it must be concluded that, relative to a p-phenoxy substituent, a p-methoxy substituent stabilises the carbonium ion more than the activated complex in ionisation (see also p. 75) and that analagous considerations apply when a p-phenoxy substituent is compared with a p-anisyl substituent. These conclusions are consistent with the known order of conjugative polarisability of these substituents.

ACTIVATION PARAMETERS IN THE IONISATION OF SUBSTITUTED BENZHYDRYL CHLORIDES.

The activation parameters were obtained from the rate coefficients for ionisation at zero ionic strength, $\underline{k}_1^0$, where this parameter had been determined (see p. 72) or from the constant integrated first-order rate coefficients for hydrolysis which were assumed to be equal to $\underline{k}_1^0$; this assumption implies that "mass-law" and "ionic-strength" effects cancel each other.

Any comparison of activation parameters must be carried out at the same temperature. Consequently, a knowledge of the temperature coefficient of these parameters (dE/dT or ΔC^{*}) is essential in any discussion of reactions which have been studied over different ranges of temperature. Previous work, however, had shown that the ratio $\Delta C^{*}/\Delta S^{*}$ is independent of the nature of the substrate in S_N1 reactions[57] and values of this ratio were known for both the present solvents, 70% and 85% aqueous acetone. Most of the reactions were, therefore, studied at only two temperatures, thus yielding values of E and ΔS^{*} which refer to the mean of the temperature range. ΔC^{*} was then calculated from the known value of $\Delta C^{*}/\Delta S^{*}$ for S_N1 reactions at this temperature and from the experimental value of ΔS^{*}. In order to ensure uniformity, this method was also applied to reactions which had been studied at more than two temperatures. Here $\Delta C^{\ast}$ was obtained from $\Delta S^{\ast}$ at the mean of the experimental temperature range. Full details are given in Chapter IV.

Only three compounds were studied at more than two temperatures[≠], thus allowing the determination of $\Delta C^{\ast}$. The results confirm the conclusion that $\Delta C^{\ast}/\Delta S^{\ast}$ is independent of the nature of the substrate in S_N1 reactions (see Table III-4), at least for 85% acetone.

Energies and entropies of activation.

The calculated values of k, E and $\Delta S^{\ast}$ at 0°C for the p'-nitro-, p'-hydrogen- and p'-methoxy - benzhydryl series are set out in Tables III-5, III-6 and III-7, respectively. The comparisons are made at 0°C, rather than at 25°C or 50°C, as this involves a minimum of extrapolation for the more reactive compounds. The standard errors in $\Delta S^{\ast}$ for the p'-methoxybenzhydryl series (Table III-7) may be too

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[≠] Benzhydryl chloride and its p-nitro, p-chloro, p-fluoro, p-phenyl, p-tert.-butyl and p-methyl derivatives were also studied at more than two temperatures. Although the results are included in this thesis, the experiments were carried out by other workers[23, 41].

TABLE III - 4.

$\Delta C^{*}/\Delta S^{*}$ in 85% aqueous acetone at 50°.

(All substituents are in the p-position).

Compound.	$MeO\cdot C_6H_4\cdot CHCl\cdot Ph$ [a]	$MeO\cdot C_6H_4\cdot CHCl\cdot C_6H_4\cdot Ph$ [a]	$PhO\cdot C_6H_4\cdot CHCl\cdot C_6H_4\cdot NO_2$ [a]	Other (57) S_N1 reactions
$\Delta C^{*}/\Delta S^{*}$	3.09 ± .19	2.74 ± .51	2.80 ± .08	2.77 ± .14

a) From Appendices III - 4 to III - 6.

small as a result of ignoring the activity coefficients and dissociation corrections (see p. 75). For this reason, little weight can be attached to the activation entropies for this series. The abnormal value of ΔS^{*} for the p-chloro derivative appears to arise from some additional error. Unfortunately, this was only realised when the present work had been completed and it is clear that the rates of solvolysis of this compound must be studied again. It is, however, unlikely that the experimental rate at 0^{o} is greatly in error and relative rates based on this figure are therefore regarded as accurate.

It is noteworthy that in all three benzhydryl series, substituents affect the rates of solvolysis almost entirely through the activation energy (with virtually constant entropy) in agreement with previous findings for p-alkyl substituents[14] and p-halogen substituents[23] in the p'-hydrogen series. This behaviour is to be expected in S_N1 reactions if the transition state has the same degree of charge development and the same degree of solvation for all the compounds under consideration[23]. In both the p'-nitro- and p'-hydrogen-benzhydryl series, however, the introduction of p-phenoxy and p-methoxy substituents significantly decreases ΔS^{*}. This could arise from the fact that these highly polarisable substituents yield a

TABLE III - 5.

First-order rate constants (k), energies (E) and entropies (ΔS^{*}) of activation for the solvolysis of p-substituted p'-nitrobenzhydryl chlorides in aqueous acetone at 0°C. [d]

(Errors quoted are standard deviations from the final mean; k in sec^{-1}; E in $kcal.mole^{-1}$; ΔS^{*} in $cal.^{o}K^{-1}$).

Substituent	k	σ/k [c]	E	$-\Delta S^{*}$	Solvent % acetone.
NO_2.	8.182×10^{-13}	.0493	30.61 ± .15	3.91 ± .45	70
Cl.	3.543×10^{-9}	.0299	26.01 ± .11	3.94 ± .35	70
H.[a]	9.205×10^{-9}	.0134	25.47 ± .07	3.88 ± .24	70
F.	3.412×10^{-8}	.0172	24.72 ± .09	4.09 ± .28	70
Ph.	2.000×10^{-7}	.0096	23.94 ± .06	3.41 ± .19	70
Bu^t.	2.434×10^{-7}	.0090	23.85 ± .06	3.34 ± .18	70
Me.	7.711×10^{-7}	.0043	23.10 ± .04	3.81 ± .15	70
PhO.	5.577×10^{-5} б	.0019 б	20.10 ± .03	6.28 ± .12	70
H.	5.837×10^{-10}	.0629	25.84 ± .22	8.23 ± .69	85
An.	3.064×10^{-7}	.0164	22.38 ± .11	8.29 ± .35	85
PhO.	2.634×10^{-6} б	.0023 б	20.69 ± .05	10.15 ± .19	85
MeO.[b]	2.934×10^{-4}	.0028	17.86 ± .05	11.18 ± .20	85

a) The result of Kohnstam[41b].   b) Reaction subject to "mass-law" retardation.

c) The standard deviation from the final mean k is denoted by σ.

d) All values are calculated from data at other temperatures, except those marked б. A summary of the experimental data is given in Appendix III - 1.

TABLE III - 6.

First-order rate constants (k), energies (E) and entropies (ΔS^*) of activation for the solvolysis of p-substituted benzhydryl chlorides in aqueous acetone at 0°C.[d]

(Errors quoted are standard deviations from the final mean; k in sec^{-1}, E in Kcal.mole^{-1}, ΔS^* in $\text{cal.}^\circ\text{K}^{-1}$.)

Substituent.	k	σ/k[c]	E	$-\Delta S^*$	Solvent % acetone
NO_2. [a]	9.205×10^{-9}	.0134	25.47 ± .07	3.88 ± .24	70
Cl. [e]	5.886×10^{-6} ø	.0021 ø	21.92 ± .03	4.06 ± .12	70
H. [e]	1.963×10^{-5} ø	.0040 ø	21.30 ± .02	3.91 ± .08	70
F. [e]	3.962×10^{-5} ø	.0016 ø	20.79 ± .03	4.43 ± .09	70
NO_2.	5.837×10^{-10}	.0629	25.84 ± .22	8.23 ± .69	85
H. [a]	8.211×10^{-7}	.0061	21.81 ± .08	8.30 ± .25	85
Ph. [a]	6.626×10^{-6} ø	.0018 ø	20.88 ± .05	7.63 ± .16	85
Bu.^{t} [f]	1.087×10^{-5} ø	.0021 ø	20.63 ± .04	7.51 ± .13	85
Me. [a]	2.375×10^{-5} ø	.0028 ø	19.81 ± .03	8.96 ± .11	85
An.	6.782×10^{-5} ø	.0028 ø	19.59 ± .04	7.75 ± .13	85
PhO. [b]	5.530×10^{-4} ø	.0019 ø	17.93 ± .04	10.55 ± .16	85
MeO. [b]	3.007×10^{-2}	.0045	15.81 ± .07	9.41 ± .28	85

a) The results of Kohnstam[41b]. b) Reaction subject to "mass-law" retardation,

c) The standard deviation from the final mean k is denoted by σ.

d) All values are calculated from data at other temperatures, except those marked ø . A summary of the experimental data is given in Appendix III-2.

e) The results of Kohnstam[23]. f) The result of Kohnstam and Hooton[41a].

TABLE III - 7.

First-order rate constants (k), energies (E) and entropies ($\Delta S^{\neq}$) of activation for the solvolysis of p-substituted p'-methoxybenzhydryl chlorides in 85% aqueous acetone at 0°C.[d]

(Errors[g] quoted are standard deviations from the final mean; k in sec^{-1}, E in $Kcal.mole^{-1}$, $\Delta S^{\neq}$ in $cal.^{o}K^{-1}$).

Substituent.	k	σ/k[c]	E	$-\Delta S^{\neq}$
NO_2.[b]	2.934×10^{-4}	.0028	17.86 ± .06	11.18 ± .20
Cl.[b]	1.289×10^{-2}	.0052	16.73 ± .05	7.77 ± .19
H.[b]	3.007×10^{-2}	.0045	15.81 ± .07	9.41 ± .28
F.[b]	3.877×10^{-2}	.0111	15.62 ± .09	9.67 ± .33
Ph.[b]	9.462×10^{-2}	.0127	15.20 ± .10	9.41 ± .38
$Bu.^{t}$ (b)	1.445×10^{-1}	.0167	14.63 ± .17	10.68 ± .67
Me.[b]	2.227×10^{-1}	.0252	14.50 ± .22	10.30 ± .87
An.[b]	3.031×10^{-1}	.0178	-	-
PhO.[b]	6.944×10^{-1}	.0928	13.06 ± .63	13.26 ± 2.50
MeO.[b]	6.314×10^{0}	.0927	-	-

b) Reaction subject to "mass-law" retardation.

c) The standard deviation from the final mean k is denoted by σ.

d) All values are calculated from data at other temperatures. A summary of the experimental data is given in Appendix III - 3.

g) These errors do not include those resulting from ignoring activity coefficient and dissociation corrections (see p. 75).

transition state for ionisation which is associated with a greater degree of charge development, and hence with a greater degree of solvation than the transition state for other substituted derivatives.

Bulky substituents (p-phenyl, p-tert.-butyl and p-anisyl) yield a slightly more positive value of $\Delta S^{\ast}$ than the parent compound. This has already been reported for the p-tert.-butyl derivative in the p'-hydrogen series[14] and has been ascribed[18] to steric hindrance to solvation at the site of substitution.

POLAR EFFECTS IN THE SOLVOLYSIS OF SUBSTITUTED BENZHYDRYL CHLORIDES.

In this section, information about the polar effects of substituents from their effect on the rates of ionisation of p'-nitro-, p'-hydrogen- and p'-methoxy-benzhydryl chlorides (k_X/k_H) is discussed.

Comparison with previous results.

The effect of p-substituents on the rate of solvolysis of benzhydryl chloride has been reported on several previous occasions, usually in solvents different to those now employed. A brief comparison with the present results is given in Table III - 8.

TABLE III - 8.

Relative rates (k_X/k_H) for p-substituted benzhydryl chlorides at 25°.

Previous work.				Present work.	
Substituent.	Solvent.	(k_X/k_H).	Ref.	Solvent % acetone.	(k_X/k_H).
NO_2.	Methanol.	6.8×10^{-4}	35	70 [b]	8.896×10^{-4}
				85	1.247×10^{-3}
Cl.	Methanol.	0.47	35	70 [b]	0.3275
	iso-Propanol.	0.51	35		
	Ethanol.	0.27	34 [a]		
Ph.	Ethanol.	9.3	34 [a]	85 [b]	6.993
$Bu.^t$	Ethanol.	18.6	14	85 [b]	11.20
	80% acetone.	10.9	14		
Me.	Ethanol.	23.4	14	85 [b]	21.19
	80% acetone.	21.4	14		
PhO.	Ethanol.	216.3	34 [a]	85	362.5
MeO.	iso-Propanol.	ca.5000	35	85	1.435×10^{4}

a) The results of Norris[34] as corrected by Packer, Vaughan and Wilson[88].

b) The results of Kohnstam[23, 41].

The satisfactory measure of agreement between the two sets of results in Table III-8 suggests that the nature of the solvent does not greatly affect the relative rates of ionisation of these compounds. However, Hughes, Ingold and Taher[14] pointed out that the spacing of the rates amongst the alkyl compounds was closer for ethanolysis than for hydrolysis. This was attributed to a reduction of electron demand on the alkyl group in the transition state for ethanolysis since the developing positive charge on the carbonium ion was likely to be more compensated by solvation in ethanolysis than in hydrolysis. It was also noticeable in the present study that, for those compounds which were studied in both 70% and 85% aqueous acetone, the effect of the substituent on the rate of ionisation of the parent compound was slightly greater in the more aqueous solvent (c.f. the p-nitro substituent in Table III-8 and the p-phenoxy substituent in series A of Table III-9).

The present results.

(i) Polar effects of substituents.

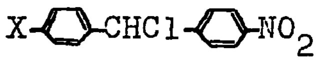
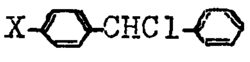
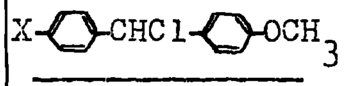
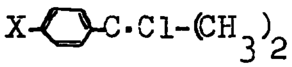
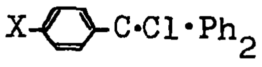
The present results for the solvolysis of p'-nitro-, p'-hydrogen- and p'-methoxy-benzhydryl chlorides are summarised in Table III-9 (series A, B and C, respectively). It can be seen that in all three series, the rates of ionisation of the p-substituted derivatives follow the sequence,

$$CH_3O- > C_6H_5O- > p\text{-}CH_3O\cdot C_6H_4- > CH_3- > t.\text{-}C_4H_9- > C_6H_5- >$$
$$F- > H- > Cl- > NO_2- .$$

TABLE III - 9.

Polar effects of substituents in solvolysis by mechanism S_N1.

Relative rates at 25°C.

Substituent X	Series A.[d,e]		Series B.[d,e]		Series C.[d,e]	Series D.[15]	Series E.[33]
							
	k_X/k_H		k_X/k_H		k_X/k_H	k_X/k_H	k_X/k_H
	70% acetone	85% acetone	70% acetone	85% acetone	85% acetone	90% acetone	60% ethanolic ether.
NO_2.	1.830×10^{-4}	-	8.896×10^{-4} [c]	1.247×10^{-3}	1.317×10^{-2}	2.57×10^{-4} [b]	1.1×10^{-2}
Cl.	0.4072	-	0.3275 [c]	-	0.5025	0.305	0.32
H.	1	1	1	1	1	1	1
F.	3.260	-	1.857 [c]	-	1.248	2.14	0.76
Ph.	17.37	-	-	6.993 [c]	2.865	6.52	-
$Bu.^t$	20.91	-	-	11.20 [c]	3.895	14.4	-
Me.	58.66	-	-	21.19 [c]	5.909	26.0	4.1
An.	-	325.3	-	59.03	8.318	-	-
PhO.	2555	2130	-	362.5	13.96	-	-
MeO.	-	1.516×10^{5}	-	1.435×10^{4}	105.4	3.360×10^{3} [a]	>90

a) By extrapolation from 94.8% (W/W) aqueous acetone. b) By extrapolation from 60% (W/W) aqueous acetone.
c) The results of Kohnstam[23, 41].
d) Calculated from results at different temperatures (Chapter IV, p. 172).
e) Experimental results are summarised in Appendix III at end of this chapter.

It can therefore be concluded that this is also the order of overall electron release in these systems. Similar rate sequences in S_N1 reactions have been observed and discussed previously; the present sequence therefore needs little general comment. There are, however, several points of interest.

It is, perhaps, surprising that the p-methyl derivative ionises more rapidly than the p-phenyl compound, since this order is reversed in the solvolysis of α-methyl and α-phenyl substituted phenylmethyl chlorides[15e]. This anomaly was noted by Brown[15e], who suggested that the unexpectedly low resonance stablilisation of the transition state by the p-phenyl substituent might be due to the non-coplanarity of the biphenyl system.

The effect of the p-phenoxy substituent on the rates of S_N1 reactions has received little attention in the past; its effect on the ethanolysis of benzhydryl chloride was, however, studied by Norris[34a] who found, in agreement with the present results, that its activating effect was less than that of the p-methoxy group and greater than that of the p-methyl group. The effect of the p-anisyl substituent (p-methoxyphenyl) on the rates of ionisation of phenylmethyl chlorides has not been studied before, and it is noteworthy (Table III-9A) that a p-methoxy group has a very much smaller activating effect in a biphenylcarbinyl than in a phenylcarbinyl system. This can be explained in terms of hindered relay of the +E effect through the non-coplanar biphenyl[15e] or by a poor relay of this effect through a long, conjugated system[23]; the latter explanation was given by Kohnstam[23] to account for the different behaviour of the α-, γ- and p-chloro groups in S_N1 reactions.

TABLE III - 9A.

The effect of p-methoxy substituents on rates of ionisation of benzhydryl and p-phenylbenzhydryl chlorides at 25°.

Series	p'-NO_2	p'-H	p'-CH_3O
k_{An}/k_{Ph}	22.5 [a]	8.44	2.90
k_{MeO}/k_H	1.516×10^5	1.435×10^4	105.4

a) Assuming k_{An}/k_{PhO} has same value in 70% and 85% acetone.

It can be seen from Table III-9 that going from the p-nitro to the p-methoxy derivative increases the rate by a factor of 10^9 in the p'-nitro series, 10^7 in the p'-hydrogen series and 10^4 in the p'-methoxy series. The accelerating effect of electron releasing substituents is greatest in the p'-nitro series and least in the p'-methoxy series while electron attracting substituents (e.g. p-nitro) show the greatest retardation in the p'-nitro series. These observations are fully consistent with the polar properties of the p'-substituents which require that the electron demand at the reaction centre in the transition state of ionisation is satisfied by these substituents in the order,

$$\text{p'-CH}_3\text{O} > \text{p'-H} > \text{p'-NO}_2$$

As a result, the electron demand at the site of p-substitution will follow the converse of this order. The p-chloro group, however, does not show the largest retardation in the p'-nitro series, as expected for electron attracting substituents. This probably arises from the fact that the overall polar effects of the halogens represent a small difference between two large opposing effects, namely conjugative release and inductive attraction (see Chapter I, p. 20). As the magnitude of the conjugative release depends on the electron demand at the site of p-substitution, it can easily be visualised that a large demand (as in the p'-nitro series) can invoke more than sufficient electron release to counterbalance the retarding effect of the inductive attraction.

It is useful to compare the present results (series A, B and C in Table III-9) with those of Brown[15] for the solvolysis of p-substituted phenyldimethylcarbinyl chlorides (series D). Relative rates for the p-fluoro, p-tert.-butyl and p-methyl substituents in series D and B suggest that the electron demand at the site of p-substitution is almost the same in the two series; it is also noteworthy that the parent compounds of series D and B ionise at roughly the same rate. However, highly polar substituents (p-nitro and p-methoxy) do not show the same results for series D and B. In series D the retarding effect of the p-nitro substituent is greater than the accelerating effect of the p-methoxy substituent, contrary to the present observations in series B, or in series C where a much smaller electron demand exists at the site of p-substitution. This discrepancy probably arises from the fact that these two substituted derivatives in series D were studied in solvents which differed from those employed in the other experiments; the p-nitro compound was studied in 60% acetone and the p-methoxy in 94.8% acetone. Rates in the standard solvent, 90% acetone, were obtained by assuming a linear relation between log k and (D-1)/(2D+1) (where D is the dielectric constant of the solvent) with the same slope for all compounds[15c]. The slope of the line was obtained from experiments with m-halogeno derivatives in the more aqueous solvents. Our experiments, however, indicate (see Table III-9) that changes in the water content of aqueous acetone do not have the same effect on the rates of ionisation of all the substituted compounds; the overall effect of a substituent on the rate is enhanced as the solvent is made more aqueous. Thus, Brown's procedure for series D probably results in too large a retardation for the p-nitro substituent and too small an acceleration for the p-methoxy substituent. An allowance for these errors would bring the results more into line with those now observed. It is also possible that the hydrolysis of the p-methoxy derivative in series D is retarded by "mass-law effects". This would also partly obscure the accelerating effect of this substituent but it has also been pointed out that HCl is only slightly ionised in acetone containing small amounts of water[131].

The substituent effects in series C (p'-methoxybenzhydryl) and E (triphenylmethyl)[33] are very close and it therefore seems likely that the electron demand at the site of p-substitution is similar in the two cases. This similarity in behaviour between a p'-methoxy and an α-phenyl group has been observed before, for example, in the solvolysis of p-methoxybenzyl chloride and of benzhydryl chloride[51, 86]. On the basis of this interpretation, the retarding effect of the p-fluoro group in series E is a little puzzling. However, the effect of this substituent is small in both series C and E and the observed results may arise from small differences in the two opposing polar effects of fluorine.

(ii) Polarisability effects.

The effect of substituents on the rate of reaction by mechanism S_N1 can be expressed by the equation[41b],

$$\log \frac{k_X}{k_H} = \frac{\Delta G_X^{*} - \Delta G_H^{*}}{RT} = \sigma_X'' \rho'' \,.\;.\;.\;.\;.\;.\;.\;.\;.\;. \quad \text{Eqn.III - 8.}$$

where $\underline{\Delta G_H^{*}}$ and $\underline{\Delta G_X^{*}}$ are the free energies of activation of the parent compound and its substituted derivative, respectively. $\underline{\sigma_X''}$ represents the magnitude of electron release towards, or electron withdrawal from, the reaction centre by the substituent, X, and depends on the nature of the reaction, i.e. on ρ'' ; positive values of σ_X'' are associated with electron attraction and negative values with electron donation. $\underline{\rho''}$ represents the electron demand at the site of substitution and the sensitivity of the rate of reaction to electron release to the reaction centre (which is probably constant in the present series of similar compounds). ρ'' is independent of σ_X''. This relation, which cannot be proved, seems reasonable and represents the most general form of the various interpretations based on linear free energy relations (see Chapter I, p.21). However, equation III-8 represents a quantitative statement of the suggestion of a sliding scale of σ values which was made by Wepster[36] after the beginning of the present work.

If a substituent, X, is not polarisable with respect to electron demand at the reaction centre, the value of σ''_X will be independent of the nature of the reaction, i.e. of ρ''. This condition is met by the p-nitro group and consequently the ratio,

$$\log (k_X/k_H)/\log (k_{p-NO_2}/k_H) = (\sigma''_X)/(\sigma''_{p-NO_2})$$

will be independent of ρ'', and will therefore have the same value in series A, B and C, if X is also not polarisable with respect to an electron demanding reaction centre. If X is polarisable, however, the value of this ratio will decrease in the order,

$$p'-CH_3O > p'-H > p'-NO_2$$

i.e. the order of increasing electron demand at the site of p-substitution[≠].

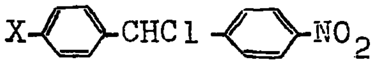
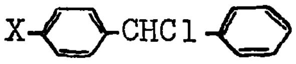
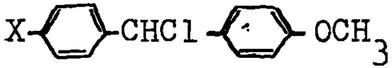
Values of this ratio are given in Table III-10 and it can be seen that,

---

[≠] σ''_X is negative when X is an overall releasing group, relative to hydrogen. Hence decreasing values of $\sigma''_X/\sigma''_{p-NO_2}$ indicate increasing electron release by X, relative to p-NO_2.

TABLE III - 10.

log (k_X/k_H)/log $(k_{p\text{-}NO_2}/k_H)$ values, and standard errors, at 0°C.

p-Substituent X	Series A 	Series B 	Series C [a] 
Cl.	0.1023 ± .0036 [b]	0.1571 ± .0006 [b]	0.1829 ± .0015
F.	-0.1405 ± .0025 [b]	-0.0916 ± .0006 [b]	-0.0549 ± .0026
Ph.	-0.3300 ± .0026 [b]	-0.2881 ± .0027 [a]	-0.2476 ± .0029
$Bu.^t$	-0.3511 ± .0026 [b]	-0.3563 ± .0032 [a]	-0.3391 ± .0038
Me.	-0.4747 ± .0031 [b]	-0.4641 ± .0041 [a]	-0.4326 ± .0055
An.	-0.6950 ± .0083 [a]	-0.6089 ± .0054 [a]	-0.4991 ± .0040
PhO.	-0.9337 ± .0054 [a b]	-0.8984 ± .0079 [a]	-0.6782 ± .0197
MeO.	-1.4566 ± .0108 [a]	-1.4496 ± .0126 [a]	-1.1550 ± .0201

a) From results in 85% acetone. b) From results in 70% acetone.

log $(k_{p\text{-}NO_2}/k_H)$ in 85% acetone for series A was obtained by assuming that log $(k_{p\text{-}PhO}/k_H)$/log $(k_{p\text{-}NO_2}/k_H)$ has the same value in both solvents.

(i) the ratio is virtually constant for the p-tert.-butyl substituent but rises for the p-methyl group on passing from series A to series C. If the present view is correct, this suggests that the p-tert.-butyl group is not polarisable and that the p-methyl group is polarisable with respect to the reaction centre, in agreement with the widely accepted views of hyperconjugative electron release by alkyl groups. These views have been challenged by Schubert[18] who considers that alkyl groups release electrons in the inductive order (t.-Bu > Me) and that the observed rate sequence in the hydrolysis of benzhydryl chlorides (p-Me > p-t.-Bu) is due to steric hindrance to solvation at the p-position by the more bulky group. The present evidence, however, suggests that this view is incorrect and that hyperconjugation (see ChapterI) is responsible for the observed rate sequence. Furthermore, it is very doubtful if the slightly more positive entropy of activation observed in the solvolysis of p-tert.-butylbenzhydryl chloride (see p. 87) reflects a sufficient degree of steric hindrance to solvation to make Schubert's explanation feasible.

(ii) The increase in the ratio for the p-methyl group on passing from series A to series C is small. This suggests that the p-methyl group is not very polarisable.

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(iii) The ratio increases markedly from series A to series C for all the other substituents, suggesting that they are all highly polarisable. It is noteworthy that all the variations are in the same expected direction, even for the halogen substituents where the rates, relative to hydrogen, do not yield unambiguous answers (see p. 95).

(iv) For p-methoxy and p-phenoxy substituents, the ratio does not change greatly on passing from series A to series B but increases markedly on passing from B to C. It is well known that these two groups are relatively easily polarised and it seems that a limit for this polarisation has almost been reached when the electron demand reaches the value associated with series B. A very large increase in electron demand, larger than that associated with series A, may of course invoke further conjugative electron release by these substituents.

(v) The p-phenyl, p-anisyl and p-halogen substituents, however, show roughly the same increase in the ratio on passing from A to B and from B to C. This suggests that these groups are less easily polarised than p-alkoxy and p-aryloxy substituents and that the limit for conjugative electron release is now only reached when the demand for electrons is more substantial. Such differences in the response of substituents to electron demand at the reaction centre contradict the theoretical assumptions implicit in the Tsuno-Yukawa equation[39] (see p. 28).

THE HAMMETT EQUATION AND ITS MODIFICATIONS.

Frequent attempts have been made in the past to interpret substituent effects quantitatively and the development of the most successful of these, the Hammett equation[24], over the past twenty years was traced in Chapter I of this thesis. The Hammett equation, equation I - 1, has already been shown to be inapplicable to the present reaction series (p. 24) and consequently will receive no further attention. However, substituent effects in such reactions are still often discussed in terms of the Brown relation[15], equation I - 2.

The Brown relation.

The value of the Brown relation, $\log (k_X/k_H) = \rho\,\sigma^+$, for predicting the effect of para-substituents on the solvolysis of benzhydryl chloride under conditions of changing electron demand is now considered. In Figure III-1 the correlation of the present data for p-substituted p'-nitrobenzhydryl chlorides in 70% aqueous acetone with σ^+ is demonstrated. Line A is the 'best' straight line passing through the mean of the ordinates and the mean of the abscissae. The correlation is considerably better than would be given by the

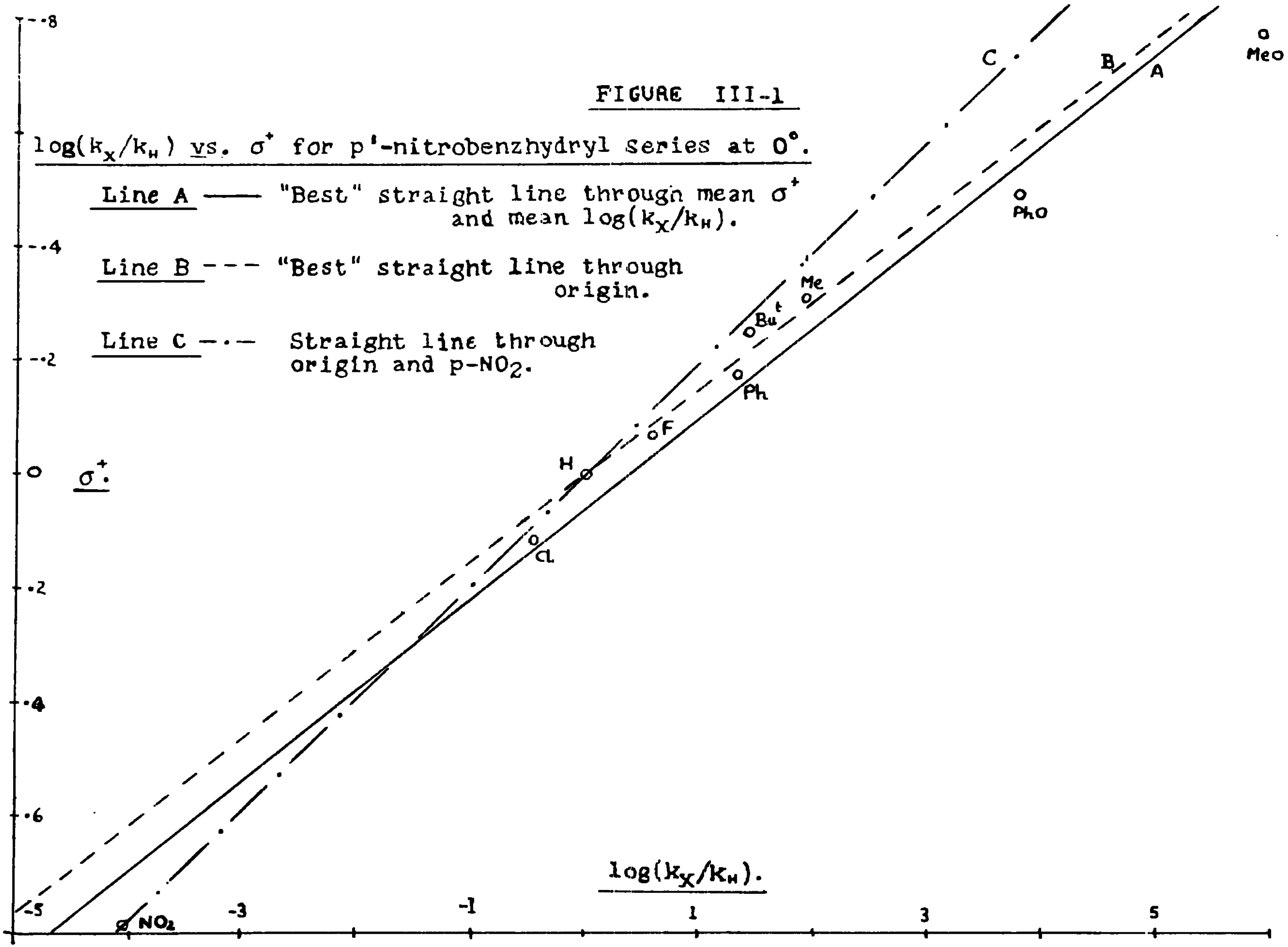


FIGURE III-1

$\log(k_X/k_H)$ vs. σ^+ for p'-nitrobenzhydryl series at 0°.

Line A —— "Best" straight line through mean σ^+ and mean $\log(k_X/k_H)$.

Line B - - - "Best" straight line through origin.

Line C —·— Straight line through origin and p-NO$_2$.

Hammett equation and is at least as good as some of those chosen by Brown[15d, 15g, 32] to support his preference for the σ^+ values over the Hammett σ constants. The most serious deviation is for the p-methoxy group where the rate is underestimated by a factor of five in a system where the reactivity covers a range of 10^{10}. Doubt has already been expressed about the accuracy of the relative rates for the p-methoxy and p-nitro substituents in the phenyldimethylcarbinyl series (see p. 96). Correction for these errors should lead to a more negative value for σ^+ (p-MeO) and a smaller value for σ^+ (p-NO_2); this would give a better correlation.

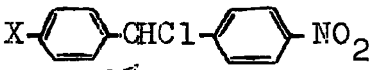
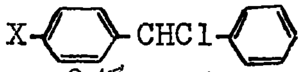
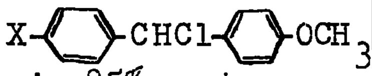
However, line A quite clearly does not pass through the origin so that the equation describing it becomes $\log (k_X/k_H) = \rho \sigma^+ +$ 'a constant'. This is contrary to the requirements of the Brown equation. Even in several of Brown's published examples[15d] (e.g. the chlorination of monosubstituted benzenes in acetic acid and the brominolysis of benzeneboronic acids in 20% acetic acid), the best line of correlation does not pass through the origin and in others (e.g. the bromination of monosubstituted benzenes in acetic acid) a reduction in the rate of the p-methoxy derivative by a factor of a hundred would probably not seriously impair the 'goodness of fit'.

It might then be argued that in a correlation, such as that in Figure III-1, the 'best' line should be assumed to pass through the origin (line B), in accordance with the requirements of the Brown relation. Not only is the reaction constant, ρ, altered slightly but the majority of the points lie above the line. The most serious deviations again occur for the p-nitro and p-methoxy groups, where the 'predicted' rates now differ by factors of twelve and seven respectively from those determined.

It must be stressed that the value of any successful quantitative relation for substituent effects lies in the ability of such a relation to predict the effects of substituents which have not yet been studied and not in noting how far the experimental points deviate from the best straight line which has been drawn through them. A more valid test of the Brown relation therefore involves a knowledge of the reaction parameter, ρ, from independent data. While this is not possible in the present systems, many previous workers have pointed out[15d, 36, 39, 76] that the p-nitro substituent, which is not polarisable with respect to an electron demanding reaction centre, can be employed to determine the ρ value for an electron demanding reaction from the relation $\log k_{p\text{-}NO_2} - \log k_H = \rho\sigma^+_{p\text{-}NO_2}$. This value of ρ gives a very poor correlation between σ^+ and $\log (k_X/k_H)$ in the p'-nitro series (Line C, Figure III-1). The observed

TABLE III - 11.

Application of the Brown relation, equation I-2, to the present data at 0°C.

p-Substituent, X	$\sigma^{+}_{(\text{Brown})}$ [b]	Series A.  in 70% acetone. $\frac{k_X(\text{obs.})}{k_X(\text{calc.})}$ [a]	Series B.  in 85% acetone. $\frac{k_X(\text{obs.})}{k_X(\text{calc.})}$ [a]	Series C.  in 85% acetone. $\frac{k_X(\text{obs.})}{k_X(\text{calc.})}$ [a]
NO_2.	.790	1.00 [c]	1.00 [c]	1.00 [c]
Cl.	.114	1.48	0.91 [e]	0.84
F.	-.073	1.57	0.99 [e]	0.84
Ph.	-.179	2.63	1.56	1.10
$Bu.^t$	-.256	1.29	1.26	1.07
Me.	-.311	2.13	1.67	1.20
PhO.	-.500	16.54	6.85	1.23
MeO.	-.778	81.55 [d]	29.06	2.20
	ρ	- 5.128	- 3.985	- 2.545
Overall rate spread (approx).		10^{10}	10^{7}	10^{4}

a) ρ defined by $\rho . \sigma^{+}_{p\text{-}NO_2} = \log k_{p\text{-}NO_2} - \log k_H$. b) Ref. 15g.

c) Value required by assumption (a)

d) Using calculated values of k_X(obs.) in 70% acetone from results in 85% (see Appendix III - 10).

e) Using calculated values of k_X(obs.) in 85% acetone from results in 70% (see Appendix III -10).

rate coefficients are compared with those calculated by this procedure in Table III-11 and it can be seen that the Brown relation is certainly not suitable for the prediction of reaction rates for highly polarisable substituents (p-MeO and p-PhO) when the electron demand at the site of substitution is significant (series A and B). On the other hand, rates are predicted reasonably well when this demand is small (series C) i.e. when polarisability effects do not exert such a large influence on the rates.

It is also noteworthy that the Brown relation requires that the ratio $\log (k_X/k_H)/\log (k_{p\text{-}NO_2}/k_H) = \sigma^+_X/\sigma^+_{p\text{-}NO_2}$ is constant and independent of the nature of the reaction. The ratio, however, varies from reaction to reaction (see. Table III-10). It has already been suggested (Chapter I) that the Brown relation is theoretically unsound and it may now be concluded that the relation is of very limited practical value.

The Tsuno-Yukawa relation[39].

Tsuno and Yukawa[39] suggested that the behaviour of para-substituents will only be described by the σ^+ constants when the electron demand at the site of substitution is similar to that in Brown's reference reaction (see Chapter I). They proposed that a 'sliding scale' of σ values be adopted, as described by their equation (equation I - 3),

$$\log \frac{k_X}{k_H} = \rho\,(\sigma + r\ [\sigma^+ - \sigma]\ ).$$

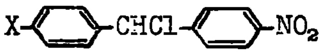
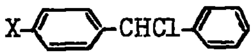
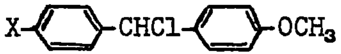
which assumes that no polarisability effects are embodied in the Hammett σ values (obtained from the ionisation of substituted benzoic acids, see p.22) and that the response of all substituents to the electron demand at the site of substitution is linearly proportional to the demand.

Good correlations have been obtained from the use of this expression[39c, 40]. However, this was probably ensured by using a mean value of r, the resonance reaction constant, determined from the results for all the substituents investigated. It must be stressed that such a procedure is profitless although an estimate of the two reaction constants, ρ and r, from the results for two or three substituents might be useful for the prediction of rates.

The validity of equation I-3 for the three present reaction series is examined in Table III-12 where the reaction constants are determined from the results for the most accelerating and decelerating substituents, p-methoxy and p-nitro. The agreement between observed and calculated rates is considerably better than that in Table III-11 and always within a factor of ca. 2-3. However, discrepancies of this magnitude are serious for the p-halogen substituents,

TABLE III - 12

Application of the Tsuno-Yukawa relation, equation I-3, to the present data at 0°C.

p-Substituent, X	σ^{c}	σ^{+d}	$\sigma^{+} - \sigma$	 in 70% acetone $\frac{k_x \text{ (obs.)}}{k_x \text{ (calc.)}}^{a}$	 in 85% acetone $\frac{k_x \text{ (obs.)}}{k_x \text{ (calc.)}}^{a}$	 in 85% acetone $\frac{k_x \text{ (obs.)}}{k_x \text{ (calc.)}}^{a}$
NO_2	·778	·790	·012	$1{\cdot}00^{g}$	$1{\cdot}00^{g}$	$1{\cdot}00^{g}$
Cl	·227	·114	-·113	0·54	$0{\cdot}42^{f}$	0·70
F	·062	-·073	-·135	0·48	$0{\cdot}40^{f}$	0·68
Ph	-·010	-·179	-·169	0·60	0·51	0·85
Bu^{t}	-·197	-·256	-·051	0·93	0·99	1·04
Me	-·170	-·311	-·141	0·64	0·66	0·97
An^{b}	-·020	-·316	-·296	$1{\cdot}20^{e}$	0·64	$1{\cdot}00^{g}$
PhO	-·320	-·500	-·180	3·61	2·13	0·94
MeO	-·268	-·778	-·510	$1{\cdot}00^{eg}$	$1{\cdot}00^{g}$	$1{\cdot}00^{g}$
			ρ	-5·069	-3·940	-2·535
			r	1·757	1·745	1·270
Overall rate spread (approx.)				10^{10}	10^{7}	10^{4}

[a] ρ and r calculated from log (k_{MeO}/k_H) and log (k_{NO_2}/k_H).

[b] σ^{+} for p-anisyl by taking log $(k_{An}/k_H)_{obs.}$ = $\rho(\sigma + r[\sigma^{+} - \sigma])$ in p'-methoxy series and by assuming $\sigma = -{\cdot}020$ (analogy with p-phenyl).

[c] From ionisation of substituted benzoic acids, Ref.90.

[d] Ref.15g.

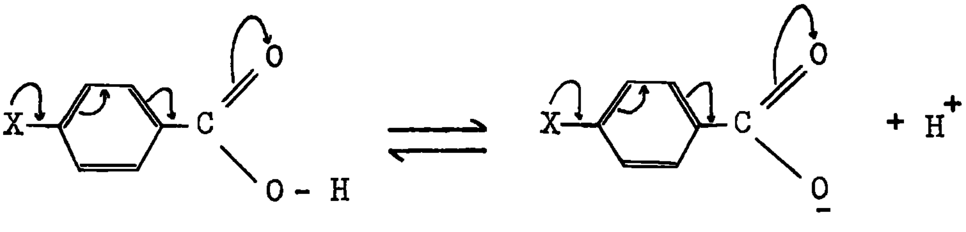
[e] Using calculated values of k_x (obs.) in 70% acetone from results in 85% (Appendix III - 10.)

[f] Using calculated values of k_x (obs.) in 85% acetone from results in 70% (Appendix III - 10.)

[g] Value required by assumptions a) or b).

where they are of the same order as the changes in rate produced by these substituents (Table III-9). The Tsuno-Yukawa relation also predicts that the p-phenyl substituent will be more accelerating than the p-tert.-butyl substituent in the two less reactive series, contrary to the present observation.

It must be said, however, that the reasonable agreement for the intermediate substituents probably arises from using the results for the extreme substituents to give ρ and r, and would undoubtedly have been very much worse if, say, the halogen substituents had been used for this purpose. Moreover, there are serious theoretical objections to the Tsuno-Yukawa equation. The assumption that the response to demand by different groups was similar was discussed earlier (see p. 98) and shown to be unreasonable; the further assumption that polarisability effects do not occur in the benzoic acids, from which the Hammett σ values were obtained, is probably false since there is no guarantee that any increased stability caused by possible conjugative interaction,



is the same in the initial and ionised states.

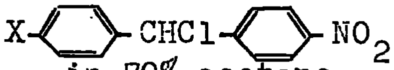
In an attempt to overcome the latter difficulty, Taft[91] proposed a series of polar substituent constants, σ', to represent only inductive effects.[≠] If this proposition is sound, replacement of the Hammett σ values in the Tsuno-Yukawa relation by σ' should give an improved correlation. This possibility is examined in Table III-13 for the p'-nitrobenzhydryl series at 0°C where the reaction constants are calculated in a similar way to those in the previous Table. The agreement between observed and calculated rates, although marginally superior to that in Table III-12 for the phenyl, methyl and phenoxy derivatives, is generally of poorer precision and it is noticeable that the rates are always overestimated, (seriously for the halogens). Apart from the assumption that response and demand are linearly related for all substituents, it may well be that Roberts' σ' values[92] do not reflect the inductive effect in the benzene system.

[≠] Taft[91] arrived at the σ' values by modifying his polar substituent constants for aliphatic series, σ^*, on the basis of Roberts' σ' scale[92] which was thought to correspond to the inductive effect in the benzene system.

TABLE III - 13.

Examination of the use of Taft's σ' values[91] for representing inductive effects.

(Hammett σ values replaced by Taft σ' values in the Tsuno-Yukawa equation.[a])

p-Substituent, X	σ'	σ^+	$\sigma^+ - \sigma'$	Series A  in 70% acetone. $\frac{k_X \text{ (obs.)}}{k_X \text{ (calc.)}}$
NO_2.	0.63	0.79	0.16	1.00[b]
Cl.	0.47	0.11	-0.36	0.20
F.	0.50	-0.07	-0.57	0.09
Ph.	0.10	-0.18	-0.28	0.75
$Bu.^t$	-0.07	-0.26	-0.19	0.61
Me.	-0.05	-0.31	-0.26	0.79
PhO.	+0.38	-0.50	-0.88	0.31
MeO.	+0.23	-0.78	-1.01	1.00[b]
			ρ	-4.673
			r	1.476

a) Making the same assumptions as in Table III-12.

b) Value required by assumptions.

General conclusion.

The arguments advanced in the preceding pages show that the quantitative prediction of substituent effects is extremely difficult. The behaviour of intermediate substituents in the solvolysis of benzhydryl chloride can be reasonably described by the Tsuno-Yukawa equation[39], provided that the extreme substituents are used to define the reaction parameters; relations with only one reaction parameter are of very limited use for predicting rates. Wepster[36], after the commencement of the present work, also pointed out the need for a 'sliding scale' of σ values depending on the polar requirements of the reaction and stressed that substituent effects could not be discussed in terms of σ values alone but that the reaction parameter and the temperature should also be considered. It is therefore felt that Ingold's approach[93] of considering the polarisation and polarisability effects, and the reaction mechanism, is more profitable, in agreement with the similar conclusion of Wepster.

APPENDIX TO CHAPTER III

Summary of Rate Constants and Derived Data for the Reaction of Substituted Benzhydryl Chlorides with 70% and 85% Aqueous Acetone.

The results are summarised in Appendices III - 1 to III - 10, details of the experimental procedures and methods employed in calculation being given in Chapter IV. Throughout the tables k (in sec.$^{-1}$) represents the rate coefficient for ionisation at zero ionic strength, where this parameter had been determined, or the constant integrated first-order rate coefficient for hydrolysis. Those compounds which were subject to mass-law deviations are marked ∅. σ denotes the standard error in k, E the activation energy (in kcal. mole^{-1}), $\Delta S^{\ddagger}$ the entropy (in cal. deg.$^{-1}$) and $\Delta C^{\ddagger}$ the calculated heat capacity of activation (in cal. deg.$^{-1}$). $\sigma(dE/dT)$, the standard error in dE/dT, was obtained from the standard deviations of $E(\sigma(E))$. The units of temperature are degrees centigrade.

APPENDIX III - 1

Solvolysis of p-substituted p'-nitrobenzhydryl chlorides in aqueous acetone

Substituent	Temp.	k	10^3 (σ/k)	Mean temp.	E	$-\Delta S^{\neq}$	$-\Delta C^{\neq}$ calc.	Solvent, % acetone
NO_2	147·18	$6{\cdot}387 \times 10^{-5}$	1·48	134·39	25·908 ± ·032	18·71 ± ·08	37·0 ± 1·1	70
	121·60	$8{\cdot}559 \times 10^{-6}$	1·98					
Cl	94·66	$3{\cdot}709 \times 10^{-4}$	2·32	87·00	22·908 ± ·044	14·33 ± ·12	37·6 ± 1·2	70
	79·33	$9{\cdot}490 \times 10^{-5}$	1·19					
F	79·32	$5{\cdot}406 \times 10^{-4}$	1·64	69·61	22·161 ± ·021	12·89 ± ·06	38·8 ± 1·2	70
	59·90	$8{\cdot}546 \times 10^{-5}$	0·55					
Ph	60·03	$4{\cdot}222 \times 10^{-4}$	1·43	50·04	22·412 ± ·023	8·87 ± ·07	32·5 ± 1·1	70
	40·05	$4{\cdot}873 \times 10^{-5}$	1·70					
Bu^t	59·90	$4{\cdot}966 \times 10^{-4}$	1·95	49·98	22·363 ± ·024	8·67 ± ·07	31·8 ± 1·0	70
	40·05	$5{\cdot}835 \times 10^{-5}$	1·16					
Me	40·05	$1{\cdot}521 \times 10^{-4}$	1·32	30·31	22·059 ± ·018	7·61 ± ·06	36·2 ± 1·3	70
	20·57	$1{\cdot}450 \times 10^{-5}$	1·40					

/cont.

APPENDIX III - 1 (cont.)

Substituent	Temp.	k	10^3 (%k)	Mean temp.	E	$-\Delta S^{\neq}$	$-\Delta C^{\neq}$ calc.	Solvent, % acetone
PhO	20·60	$6{\cdot}930 \times 10^{-4}$	1·26	10·30	19·506 ± ·017	8·49 ± ·06	59·7 ± 2·8	70
	0·00	$5{\cdot}577 \times 10^{-5}$	1·86					
H	120·96	$3{\cdot}428 \times 10^{-4}$	2·11	110·21	21·354 ± ·042	22·71 ± ·11	42·7 ± 2·0	85
	99·45	$7{\cdot}105 \times 10^{-5}$	2·24					
An	59·92	$3{\cdot}453 \times 10^{-4}$	2·79	49·99	20·326 ± ·034	15·52 ± ·10	43·0 ± 2·0	85
	40·05	$4{\cdot}921 \times 10^{-5}$	1·63					
PhO	See Appendix III - 4			20·32	19·660 ± 0	13·93 ± 0	52·7 ± 2·6	85
MeO ø	20·61	$2{\cdot}738 \times 10^{-3}$	5·68	10·36	17·282 ± ·049	13·33 ± ·17	58·0 ± 3·1	85
	0·10	$2{\cdot}969 \times 10^{-4}$	2·83					

APPENDIX III - 2

Solvolysis of p-substituted benzhydryl chlorides in 85% aqueous acetone.

Substituents	Temp.	k	$10^3(\sigma/k)$	Mean temp.	E	$-\Delta S^{\ddagger}$	$-\Delta C^{\ddagger}$ calc.
An	20·28	$7{\cdot}813 \times 10^{-4}$	2·14	10·14	19·201 ± ·028	9·21 ± ·10	40·2 ± 2·1
	0·00	$6{\cdot}782 \times 10^{-5}$	2·82				
PhO ϕ	20·61	$5{\cdot}232 \times 10^{-3}$	3·42	10·36	17·388 ± ·031	12·58 ± ·11	54·7 ± 2·9
	0·10	$5{\cdot}597 \times 10^{-4}$	1·91				
MeO ϕ	See Appendix III - 6			-18·15	16·657 ± ·000	6·04 ± ·00	48·8 ± 4·0

APPENDIX III - 3

Solvolysis of p-substituted p'-methoxybenzhydryl chlorides in 85% aqueous acetone

Substituents	Temp.	k	10^3 (σ/k)	Mean temp.	E	$-\Delta S^{\ddagger}$	$-\Delta C^{\ddagger}$ calc.
NO_2 ϕ	See Appendix III - 1						
Cl ϕ	+0·10	$1{\cdot}304 \times 10^{-2}$	5·23	-9·90	17·111 ± ·043	6·29 ± ·16	40·3 ± 2·9
	-19·90	$1{\cdot}083 \times 10^{-3}$	3·35				
H ϕ	See Appendices III - 2 and III - 6						
F ϕ	+0·10	$3{\cdot}918 \times 10^{-2}$	11·08	-9·90	16·096 ± ·078	7·82 ± ·30	50·2 ± 3·9
	-19·90	$3{\cdot}773 \times 10^{-3}$	2·59				
Ph ϕ	See Appendix III - 5			-18·15	16·052 ± ·061	6·04 ± ·24	48·8 ± 4·4
Bu^t ϕ	-32·90	$2{\cdot}873 \times 10^{-3}$	2·70	-26·40	16·036 ± ·041	5·04 ± ·17	55·4 ± 6·4
	-19·90	$1{\cdot}611 \times 10^{-2}$	3·49				
Me ϕ	-32·90	$4{\cdot}618 \times 10^{-3}$	6·68	-26·40	15·852 ± ·105	4·86 ± ·43	53·4 ± 7·5
	-19·90	$2{\cdot}538 \times 10^{-2}$	9·12				
An ϕ	-32·90	$6{\cdot}283 \times 10^{-3}$	11·18	-	-	-	-

/cont.

APPENDIX III - 3 (cont.)

Substituents	Temp.	k	$10^3\,(\sigma/k)$	Mean temp.	E	$-\Delta S^{\ddagger}$	$-\Delta C^{\ddagger}$ calc.
PhO ϕ	-37·34	$1{\cdot}062 \times 10^{-2}$	4·72	-35·12	15·410 ± ·176	3·77 ± ·74	68·8 ± 17·3
	-32·90	$1{\cdot}950 \times 10^{-2}$	5·11				
MeO ϕ	-37·34	$1{\cdot}370 \times 10^{-1}$	17·00	-	-	-	-

APPENDIX III - 4

$\Delta C^{\ddagger}/\Delta S^{\ddagger}$ for the solvolysis of p-phenoxy p'-nitrobenzhydryl chloride in 85% acetone.

Experimental Values					
Temp.	k	$\frac{\sigma}{k}$	Mean Temp.	E	$-\Delta S^{\ddagger}$
40·06	$2{\cdot}725 \times 10^{-4}$	0·0020			
			30·33	19·144 ± ·023	15·76
20·59	$3{\cdot}549 \times 10^{-5}$	0·0015			
			10·30	20·175 ± ·021	12·11
0·00	$2{\cdot}623 \times 10^{-6}$	0·0023			

$dE/dT = -51{\cdot}5 \pm 1{\cdot}6$.

$\Delta C^{\ddagger} = -53{\cdot}5 \pm 1{\cdot}6$

$-\Delta S^{\ddagger}\ (50^{\circ}) = 19{\cdot}09 \pm {\cdot}15$

$\Delta C^{\ddagger}/\Delta S^{\ddagger}\ (50^{\circ}) = 2{\cdot}80 \pm {\cdot}08$

APPENDIX III - 5

$\Delta C^{\ddagger}/\Delta S^{\ddagger}$ for the solvolysis of p-phenyl p'-methoxybenzhydryl chloride$^{\phi}$ in 85% acetone.

Experimental Values					
Temp.	k	$\frac{\sigma}{k}$	Mean Temp.	E	$-\Delta S^{\ddagger}$
0·10	$9{\cdot}560 \times 10^{-2}$	0·0127			
			-9·90	15·679 ± ·093	7·57
-19·90	$9{\cdot}780 \times 10^{-3}$	0·0045			
			-26·40	16·424 ± ·079	4·50
-32·90	$1{\cdot}673 \times 10^{-3}$	0·0073			

$dE/dT = -45{\cdot}2 \pm 7{\cdot}4$

$\Delta C^{\ddagger} = -47{\cdot}1 \pm 7{\cdot}4$

$-\Delta S^{\ddagger}\ (50^{\circ}) = 17{\cdot}22 \pm 1{\cdot}76$

$\Delta C^{\ddagger}/\Delta S^{\ddagger}\ (50^{\circ}) = 2{\cdot}74 \pm {\cdot}51$

APPENDIX III - 6

$\Delta C^{\ddagger}/\Delta S^{\ddagger}$ for the solvolysis of p-methoxybenzhydryl chloride$^{\phi}$ in 85% acetone.

Experimental Values					
Temp.	k	$\frac{\sigma}{k}$	Mean Temp.	E	$-\Delta S^{\ddagger}$
0·10	$3{\cdot}039 \times 10^{-2}$	0·0045	-9·90	16·094 ± ·036	8·33
-19·90	$2{\cdot}926 \times 10^{-3}$	0·0027	-26·40	17·219 ± ·045	3·76
-32·90	$4{\cdot}596 \times 10^{-4}$	0·0040			

$dE/dT = -68{\cdot}2 \pm 3{\cdot}5$

$\Delta C^{\ddagger} = -70{\cdot}2 \pm 3{\cdot}5$

$-\Delta S^{\ddagger}\ (50^{\circ}) = 22{\cdot}72 \pm {\cdot}83$

$\Delta C^{\ddagger}/\Delta S^{\ddagger}\ (50^{\circ}) = 3{\cdot}09 \pm {\cdot}19$

APPENDIX III - 7

Rates of reaction of p-substituted p′-nitrobenzhydryl chlorides, calculated at 0°C and 25°C

Substituents	0·00°C		25·00°C		Solvent, % acetone
	k	$\sigma/_k$	k	$\sigma/_k$	
NO_2	$8{\cdot}182 \times 10^{-13}$	·0493	$7{\cdot}982 \times 10^{-11}$	·0306	70
Cl	$3{\cdot}543 \times 10^{-9}$	·0299	$1{\cdot}776 \times 10^{-7}$	·0159	
H [a]	$9{\cdot}205 \times 10^{-9}$	·0134	$4{\cdot}361 \times 10^{-7}$	·0054	
F	$3{\cdot}412 \times 10^{-8}$	·0172	$1{\cdot}422 \times 10^{-6}$	·0069	
Ph	$2{\cdot}000 \times 10^{-7}$	·0096	$7{\cdot}573 \times 10^{-6}$	·0030	
Bu^t	$2{\cdot}434 \times 10^{-7}$	·0090	$9{\cdot}120 \times 10^{-6}$	·0026	
Me	$7{\cdot}711 \times 10^{-7}$	·0043	$2{\cdot}559 \times 10^{-5}$	·0015	
PhO	$5{\cdot}577 \times 10^{-5}$	·0019	$1{\cdot}114 \times 10^{-3}$	·0016	
H	$5{\cdot}837 \times 10^{-10}$	·0629	$2{\cdot}743 \times 10^{-8}$	·0355	85
An	$3{\cdot}064 \times 10^{-7}$	·0164	$8{\cdot}922 \times 10^{-6}$	·0043	
PhO	$2{\cdot}634 \times 10^{-6}$	·0023	$5{\cdot}845 \times 10^{-5}$	·0015	
MeO ø	$2{\cdot}934 \times 10^{-4}$	·0028	$4{\cdot}159 \times 10^{-3}$	·0059	

[a] From the results of Kohnstam.[23]

APPENDIX III - 8

Rates of reaction of p-substituted benzhydryl chlorides, calculated at 0°C and 25°C

Substituents	0·00°C		25·00°C		Solvent, % acetone
	k	σ/k	k	σ/k	
NO_2 [a]	$9{\cdot}205 \times 10^{-9}$	·0134	$4{\cdot}361 \times 10^{-7}$	·0054	70
Cl [b]	$5{\cdot}886 \times 10^{-6}$	·0021	$1{\cdot}606 \times 10^{-4}$	·0025	
H [b]	$1{\cdot}963 \times 10^{-5}$	·0040	$4{\cdot}902 \times 10^{-4}$	·0023	
F [b]	$3{\cdot}962 \times 10^{-5}$	·0016	$9{\cdot}099 \times 10^{-4}$	·0018	
NO_2	$5{\cdot}837 \times 10^{-10}$	·0629	$2{\cdot}743 \times 10^{-8}$	·0355	85
H [a]	$8{\cdot}211 \times 10^{-7}$	·0061	$2{\cdot}201 \times 10^{-5}$	·0019	
Ph [a]	$6{\cdot}626 \times 10^{-6}$	·0018	$1{\cdot}539 \times 10^{-4}$	·0019	
Bu^t [c]	$1{\cdot}087 \times 10^{-5}$	·0021	$2{\cdot}462 \times 10^{-4}$	·0019	
Me [a]	$2{\cdot}375 \times 10^{-5}$	·0028	$4{\cdot}665 \times 10^{-4}$	·0024	
An	$6{\cdot}782 \times 10^{-5}$	·0028	$1{\cdot}299 \times 10^{-3}$	·0024	
PhO ø	$5{\cdot}530 \times 10^{-4}$	·0019	$7{\cdot}979 \times 10^{-3}$	·0036	
MeO ø	$3{\cdot}007 \times 10^{-2}$	·0045	$3{\cdot}158 \times 10^{-1}$	·0194	

[a] From the results of Kohnstam.[41b]

[b] From the results of Kohnstam.[23]

[c] From the results of Kohnstam & Hooton.[41a]

APPENDIX III - 9

Rates of reaction of p-substituted p'-methoxybenzhydryl chlorides, calculated at 0°C and 25°C.

Substituents	0·00°C		25·00°C		Solvent, % acetone
	k	$\sigma/_k$	k	$\sigma/_k$	
NO_2 ϕ	2·934 x 10^{-4}	·0028	4·159 x 10^{-3}	·0059	85
Cl ϕ	1·289 x 10^{-2}	·0052	1·587 x 10^{-1}	·0131	
H ϕ	3·007 x 10^{-2}	·0045	3·158 x 10^{-1}	·0194	
F ϕ	3·877 x 10^{-2}	·0111	3·942 x 10^{-1}	·0213	
Ph ϕ	9·462 x 10^{-2}	·0127	9·046 x 10^{-1}	·0261	
Bu^t ϕ	1·445 x 10^{-1}	·0167	1·230 x 10^{0}	·0569	
Me ϕ	2·227 x 10^{-1}	·0252	1·866 x 10^{0}	·0721	
An ϕ	3·031 x 10^{-1}	·0178	2·627 x 10^{0}	·0291	
PhO ϕ	6·944 x 10^{-1}	·0928	4·407 x 10^{0}	·2305	
MeO ϕ	6·314 x 10^{0}	·0927	3·331 x 10^{+1}	·2276	

APPENDIX III - 10

Logarithms (to base 10) of relative rates of p-substituted benzhydryl chlorides at 0°C.

Substituent	p'-NO_2 benzhydryl chlorides. solvent, % acetone		benzhydryl chlorides. solvent, % acetone		p'-MeO benzhydryl chlorides. solvent, % acetone
	70	85	70	85	85
NO_2	-4·0511 ± ·0222	-	-3·3289 ± ·0060[c]	-3·1482 ± ·0274	-2·0106 ± ·0023
Cl	-0·4146 ± ·0142	-	-0·5231 ± ·0019[c]	(-0·495)[b]	-0·3678 ± ·0030
H	0[c]	0	0[c]	0[c]	0
F	0·5691 ± ·0095	-	0·3050 ± ·0018[c]	(+0·288)[b]	0·1104 ± ·0052
Ph	1·3370 ± ·0072	-	-	0·9069 ± ·0028[c]	0·4979 ± ·0059
Bu^t	1·4223 ± ·0070	-	-	1·1218 ± ·0028[c]	0·6818 ± ·0076
Me	1·9232 ± ·0061	-	-	1·4612 ± ·0030[c]	0·8697 ± ·0111
An	(2·815)[a]	2·7201 ± ·0282	-	1·9169 ± ·0030	1·0034 ± ·0080
PhO	3·7824 ± ·0059	3·6545 ± ·0273	-	2·8283 ± ·0028	1·3635 ± ·0404
MeO	(5·901)[a]	5·7013 ± ·0273	-	4·5637 ± ·0034	2·3222 ± ·0404

/cont.

APPENDIX III - 10 (cont.)

[a] Calculated values from results in 85% Acetone, assuming $\dfrac{\log(k_X/k_H)\ 70\%}{\log(k_X/k_H)\ 85\%} = \dfrac{\log(k_{PhO}/k_H)\ 70\%}{\log(k_{PhO}/k_H)\ 85\%}$

[b] Calculated values from results in 70% Acetone by a similar method.

[c] From the results of other workers (see Appendices III - 7 and III - 8).

CHAPTER IV.

EXPERIMENTAL.

PREPARATION AND PURIFICATION OF MATERIALS.

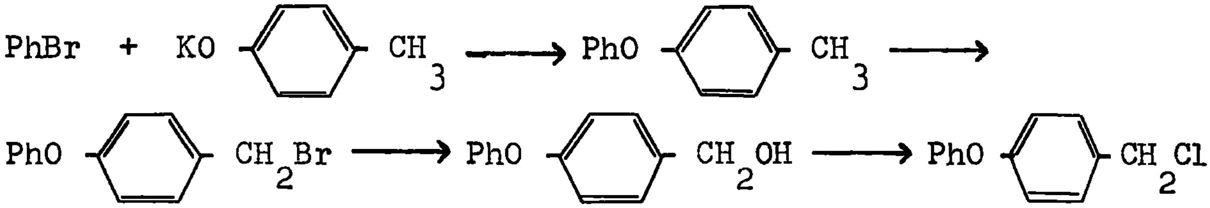
In this section, full preparative details are only given for new compounds and for substances which have been synthesised by new synthetic routes; compounds which have not been synthesised before are indicated by an asterisk (e.g. p-phenoxybenzyl alcohol*). For all halides, purities were determined by noting the amount of acid produced by complete hydrolysis.

SUBSTITUTED BENZYL HALIDES.

p-Methoxybenzyl chloride was prepared by passing dry hydrogen chloride through an ethereal solution of p-Methoxybenzyl alcohol, as previously described[51, 86, 94].

b.p. 84.5° (0.5 mm.); refractive index 1.5491 (20°); purity 99.6%

p-Phenoxybenzyl chloride* was prepared via the following reactions;



a). p-tolylphenyl ether was obtained[95, 96] by heating dry potassium cresate (37·8 gm.), bromobenzene (31.4 gm.) and copper bronze (0.2 gm.) for 24 hours at 230-250°. After extracting with ether and working up in the usual manner, the product was fractionally distilled under reduced pressure; unchanged bromobenzene came over at 25-30° (0.8 mm.) :

b.p. 96° (0.8 mm.); refractive index 1.5697 (22°);

yield 14 gm.

b). p-phenoxybenzyl bromide*. The aromatic ether was converted to p-phenoxybenzyl bromide with a slight excess of N-bromosuccinimide[97]. The crude product was dissolved in petrol (40-60°), shaken with dry alumina, filtered and evaporated; the resulting bromide had a purity of 99·5%.

c). p-phenoxybenzyl alcohol* was obtained by refluxing the bromide (10 gm.) with aqueous acetone. The solution was neutralised, evaporated, extracted with ether, and the ethereal extract washed and dried. After removal of the ether, the pure alcohol was obtained by recrystallisation from petrol (60-80°) as white plates.

m.p. 53°; yield 7 gm.; found C 78.1%; H 6.0%;
$C_{13}H_{12}O_2$ requires C 78.0%; H 6.0%.

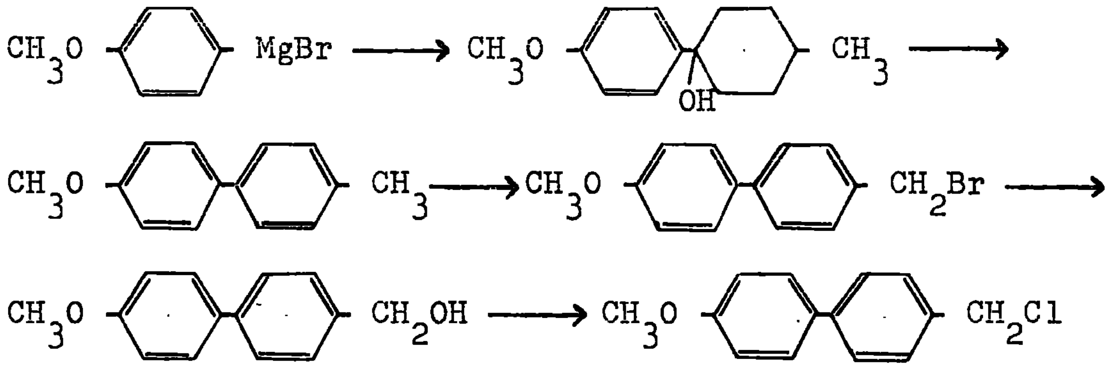
The infrared spectrum of this compound shows a broad -OH band at 3390 cm^{-1}, (cf. benzyl alcohol, sharp at 3510 cm^{-1};

p-nitrobenzyl alcohol, sharp at 3509 cm^{-1}) indicative of intermolecular hydrogen bonding giving rise to polymeric association[98]. This helps to explain why the alcohol cannot be purified by distillation under reduced pressure, when loss of water and polymerisation occurs.

d). p-phenoxybenzyl chloride* was obtained from the alcohol by the method used for the preparation of the p-methoxy compound.

b.p. 114° (0.5 mm.); refractive index 1.5990 (20°); purity 99.4%.

p-Anisylbenzyl chloride was prepared via the following reactions;



a). 4-methyl 1-(p-anisyl) cyclohexanol* was prepared[99] by the addition of a solution of 4-methyl cyclohexanone (12.4 gm.) in dry ether (150 ml.) to the Grignard compound of p-bromanisole (21 gm.) in the same solvent (250 ml.). The product was worked up in the usual way and purified by fractional distillation under reduced pressure.

b.p. 108-109° (0.35 mm.); m.p. 68-69°; yield 18.5 gm.; found C 76.4%; H 9.0%; $C_{14}H_{20}O_2$ requires C 76.4%; H 9.1%.

b). p-methoxy p'-methyldiphenyl was prepared[99] by heating the alcohol (17.63 gm.) with sulphur (5.13 gm.) at 180-250°. The residue was extracted with ether, the extract washed with alkali and water, dried and the solvent evaporated. The residue was purified by recrystallisation from ethanol (after boiling with charcoal) and further purified by sublimation at 110° (0.4 mm.).

m.p. 114° (lit.[100] 112°); yield 9 gm.; found C 84.9%; H 7.3%; $C_{14}H_{14}O$ requires C 84.8%; H 7.1%.

c). p-anisylbenzyl bromide was prepared from this compound with N-bromosuccinimide (cf. p.130) and recrystallised from petrol (80-100°).

m.p. 114° (lit.[101] 114°); purity 99.9%.

d). p-anisylbenzyl alcohol was prepared by refluxing the bromide with aqueous acetone; the crude alcohol which separated on cooling was recrystallised from ethanol as white plates.

m.p. 164° (lit.[101] 164°).

e). p-anisylbenzyl chloride was prepared from the alcohol and dry hydrogen chloride as for the p-methoxy derivative; chlorination was, however, now carried out in a 1:1 ether-chloroform solvent and the product recrystallised from petrol (80-100°) and sublimed at 110° (0.3 mm.).

m.p. 103-104° (lit.[101] 103.5-104°); purity 100.3%;
yield 4 gm.(from 9 gm. p-methoxy p'-methyldiphenyl).

Direct chlorination of p-methoxy p'-methyldiphenyl (with N, 2, 4, 6 - tetrachloro-acetanilide[102]) was attempted but a pure product could not be obtained by this method.

p-Methylbenzyl chloride was prepared by chlorination of p-methylbenzyl alcohol in the usual manner (see p.129). The alcohol was obtained by reduction of the ethyl ester of p-toluic acid with lithium aluminium hydride in ether; full details have been given by Shillaker[51].

b,p. 38° (0.3 mm.); purity 99.8%.

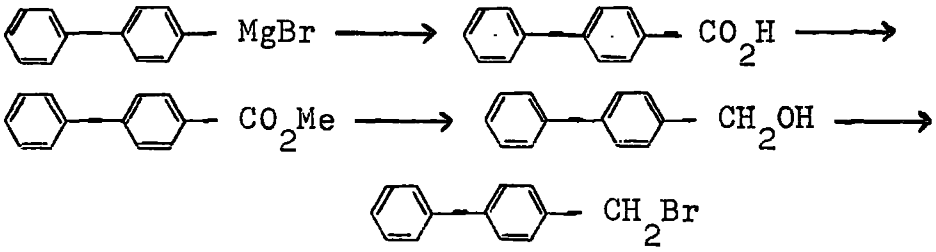
Benzyl chloride. The B.D.H. product was dried ($CaCl_2$) and distilled under reduced pressure.

b.p. 50° (3.5 mm.); purity 100.0%.

p-Methylbenzyl bromide was prepared by passing dry hydrogen bromide (from bromine and tetralin) for 3 hours through a petrol (60-80°) solution of p-methylbenzyl alcohol over anhydrous lithium bromide. The solution was filtered, washed with sodium bicarbonate solution and water, dried ($MgSO_4$) and evaporated. The residue was purified by distillation under reduced pressure.

m.p. 35° (lit.[103] 35.5°); b.p. 74° (0.5 mm.); purity 99.4%.

p-Phenylbenzyl bromide was prepared via the following reactions;



a). p-phenylbenzoic acid was prepared by the addition of solid CO_2 (50 gm.) to the Grignard compound of p-bromdiphenyl (100 gm.) in dry ether (400 ml.). The product was worked up in the usual manner and purified via the sparingly soluble sodium salt.

m.p. 220.5° (lit.[106] 220-221°); yield 53 gm.

b). methyl p-phenylbenzoate. The acid (50 gm.) was esterified by azeotropic distillation of a solution in 1:1 methanol-chloroform (600 ml.) containing conc. sulphuric acid (5 ml.). The precipitated product was filtered, washed with cold methanol and recrystallised from methyl cyclohexane.

m.p. 116-117° (lit.[106] 116.5-117°); yield 30 gm.

c). <u>p-phenylbenzyl alcohol</u> was obtained from the ester (30 gm.) by lithium aluminium hydride (7 gm.) reduction in ether (400 ml.) under nitrogen. The product was worked up in the usual manner and purified by recrystallisation from petrol (80-100°).

m.p. 101° (lit.[77] 100.5-101°); yield 20 gm.;

found C 84.7%; H 6.7%;

$C_{13}H_{12}O$ requires C 84.8%; H 6.5%.

d). <u>p-phenylbenzyl bromide</u> was prepared from the alcohol and dry hydrogen bromide as for the p-methyl derivative; bromination was, however, now carried in ether and the product recrystallised from petrol (80-100°) to give white plates.

m.p. 85° (lit.[104] 85°); purity 100.2%.

<u>p-Fluorobenzyl bromide</u> was prepared by brominating the corresponding alcohol in the same way as the p-phenyl derivative; p-fluorobenzyl alcohol was obtained by refluxing p-fluorobenzyl chloride (Light's) in aqueous acetone. The bromide was purified by distillation under reduced pressure.

b,p. 41° (0.25 mm.) cf. lit.[105] 85° (15 mm.);

purity 99.7%.

Benzyl bromide. The B.D.H. product was dried (LiBr) and distilled under reduced pressure.

b.p. 98° (3.5 mm.); purity 99.6%.

m-Chlorobenzyl bromide. The Light's product was dried (LiBr) and distilled under reduced pressure.

b.p. 72° (1.5 mm.) cf. lit.[105] 109° (10 mm.); purity 100.2%.

p-Nitrobenzyl bromide. The B.D.H. product was purified by sublimation at 100° (1 mm.).

m.p. 99° (lit.[107] 99-100°); purity 99.6%.

Miscellaneous materials used in the formolysis of benzyl halides.

Piperidine. The commercial product was purified by distillation over sodium followed by fractional distillation.

b.p. 105.9-106.5°.

Triethylamine. The commercial product was purified by distillation.

b.p. 88.5-89°.

SUBSTITUTED BENZHYDRYL CHLORIDES.

All benzhydryl chlorides were prepared by chlorinating the benzhydrols with hydrogen chloride (details p.153). The three general methods employed for the synthesis of the benzhydrols are outlined below.

1. The appropriate benzophenone was prepared by Friedel-Crafts reaction between an acid chloride and benzene (or substituted benzene) and reduced to the benzhydrol with aluminium isopropoxide or lithium aluminium hydride (the latter cannot be used for the reduction of ketones containing nitro groups) viz.,

$$\mathrm{R\cdot C_6H_4\cdot COCl + R'\cdot Ph \longrightarrow R\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot R' \longrightarrow}$$

$$\mathrm{R\cdot C_6H_4\cdot CH(OH)\cdot C_6H_4\cdot R'}$$

2. The appropriate diphenylmethane was prepared by Friedel-Crafts reaction between a benzyl halide and benzene, brominated with N-bromosuccinimide and the benzhydryl bromide hydrolysed, viz.,

$$\mathrm{R\cdot C_6H_4\cdot CH_2Cl + C_6H_6 \longrightarrow R\cdot C_6H_4\cdot CH_2\cdot C_6H_5 \longrightarrow R\cdot C_6H_4\cdot CHBr\cdot C_6H_5}$$

$$\mathrm{\longrightarrow R\cdot C_6H_4\cdot CH(OH)\cdot C_6H_5}$$

3. The appropriate benzhydrol was prepared by Grignard reaction between a bromobenzene and a benzaldehyde, viz.,

$$\mathrm{R\cdot C_6H_4\cdot MgBr + R'\cdot C_6H_4\cdot CHO \longrightarrow R\cdot C_6H_4\cdot CH(OH)\cdot C_6H_4\cdot R'}$$

This method cannot be used for the preparation of benzhydrols containing nitro groups.

A summary of the methods employed in the individual syntheses together with the physical properties of the products is given in Tables IV - 1 to IV - 9. The purity of the chlorides, estimated from the acid produced by complete hydrolysis was never less than 99.0%. Details of the synthesis of starting materials which were prepared in the laboratory are given in pp. 155 ; most of these compounds, however, were commercial products and were purified by standard methods.

TABLE IV - 1.

p-Substituted p'-Nitro benzophenones.

Substituents	Route (see p.137)	Starting materials[b]	Yield %	m.p.	Method of purification	Infrared C = O (cm^{-1})	Found % C	Found % H	Calc.% C	Calc.% H
MeO	1	$NO_2\cdot C_6H_4\cdot COCl$ $CH_3O\cdot C_6H_5$	60	121.5° (lit.[111] 121°)	R.(ethanol)	1663	64.9	4.4	65.4	4.3
PhO.*	1	$NO_2\cdot C_6H_4\cdot COCl$ $PhO\cdot C_6H_5$	49	117-118°	G.(2:1 $CHCl_3$-petrol 60-80°) R.(petrol 80-100°)	1672	71.6	4.1	71.5	4.1
An.*	1	$NO_2\cdot C_6H_4\cdot COCl$ $CH_3O\cdot C_6H_4\cdot C_6H_5$	26	199-200°	F.(benzene)	1658	71.7	4.6	72.1	4.5
Me.	1	$NO_2\cdot C_6H_4\cdot COCl$ $CH_3\cdot C_6H_5$	47	125° (lit.[112] 122-124°)	R.(ethanol) G.(benzene) R.(petrol 80-100°)	1660	70.1	4.4	69.7	4.6
$Bu.^t$ *	1	$NO_2\cdot C_6H_4\cdot COCl$ t.-$Bu\cdot C_6H_5$	53	115°	G.(4:1 benzene-petrol 60-80°) R.(petrol 80-100°)	1660	71.2	5.8	72.1	6.0
Ph.*	1	$NO_2\cdot C_6H_4\cdot COCl$ $C_6H_5\cdot C_6H_5$	50	169-170°	G.(1:1 $CHCl_3$ - benzene) R.(petrol 80-100°)	1647	75.4	4.4	75.2	4.3

-cont'd./

TABLE IV - 1 (cont'd.)

p-Substituted p'-Nitro benzophenones.

Substituents	Route (see p.137)	Starting materials[b]	Yield %	m.p.	Method of purification	Infrared $C=O$ (cm^{-1})	Found %		Calc. %	
							C	H	C	H
F.*	1	$NO_2 \cdot C_6H_4 \cdot COCl$ $F \cdot C_6H_5$	44	87°	G.(2:1 benzene-petrol 40-60°) R.(petrol 80-100°)	1675	63.7	3.1	63.7	3.3
Cl.	1	$NO_2 \cdot C_6H_4 \cdot COCl$ $Cl \cdot C_6H_5$	48	106° (lit.[113] 107.5°)	R.(petrol 80-100°) R.(ethanol)	1675	60.1	3.1	59.7	3.1

* = new compound.

b) all substituents in p-position.

R.= recrystallised.

G.= chromatographed on alumina column.

F.= fractionally crystallised.

TABLE IV - 2.

p-substituted p'-nitro benzhydrols.

Substituent	Route (see p.137)	Reducing agent	Yield %	m.p.	Method of purification	Crystalline form.	Infrared -OH (cm^{-1})	Found % C	Found % H	Calc.% C	Calc.% H
MeO.*	1	Al isopropoxide	81	79°	R.(petrol 60-80° + benzene + charcoal)	White clusters	3528	63.9	5.1	64.9	5.0
PhO.*	1	"	76	102.5°	R.(petrol 80-100°)	Pale-yellow plates	3521	71.4	4.9	71.0	4.7
An.*	1	"	80	149-150°	R.(1:1 benzene - petrol 60-80°)	Pale-yellow needles	3553	71.1	4.9	71.6	5.1
Me.*	1	"	75	104.5°	R.(petrol 80-100°)	White clusters	3534	68.6	5.7	69.1	5.3
Bu.^{t}*	1	"	71	109°	R.(petrol 60-80° + benzene + charcoal)	White clusters	3521	70.8	7.0	71.6	6.7
Ph.*	1	"	84	143°	R.(petrol 80-100° + benzene)	White needles	3509	74.9	4.7	74.8	4.9

-cont'd/

TABLE IV - 2 (cont'd.)

p-substituted p'-nitro benzhydrols.

Substituent	Route (see p.137)	Reducing agent	Yield %	m.p.	Method of purification	Crystalline form	Infrared -OH (cm^{-1})	Found %		Calc. %	
								C	H	C	H
F.*	1	Al isopropoxide	79	78.5°	R. (petrol 80-100°)	White needles	3521	63.6	4.4	63.2	4.0
Cl.*	1	"	82	135°	R. (4:1 petrol 80-100° -benzene)	White needles	3509	58.7	3.9	59.2	3.8
NO_2.*	2	-[a]	61	170°	R. (1:1 benzene-petrol 80-100°)	White powder	3534	56.4	3.7	56.9	3.6

* = new compound. R. = recrystallised.

a) from p, p'-dinitrodiphenylmethane (Kodak).

TABLE IV - 3.

p-substituted p'-nitro benzhydryl chlorides.

Substituent	Chlorination method(p.153)	Yield %	m.p.	Method of purification	Crystalline form
MeO.*	C	71	Liquid[a]	Z.(petrol 40-60°)	(Colourless oil)
PhO.*	B	75	79°	R.(petrol 60-80°)	Pale green powder
An.*	B	82	120°	R.(ether)	White plates
Me.*	B	80	50°	R.(petrol 40-60°)	White needles
Bu.^{t}*	B	77	Liquid[a]	Z.(petrol 40-60°)	(Colourless oil)
Ph.*	A	67	115°	R.(petrol 80-100°)	White needles
F.*	A	90	Liquid[a]	Z.(petrol 40-60°)	(Colourless oil)
Cl.*	A	76	44°	R.(petrol 60-80°)	White needles
NO$_2$.*	A	76	100.5°	R.(petrol 80-100°)	Pale green cubes

* = new compound.

a) see p.154.

R. = recrystallised.

Z. = frozen out at -20°C.

TABLE IV - 4.

p-substituted p'-hydrogen benzophenones.

Substituent	Route (see p.137)	Starting materials[b]	Yield %	m.p.	Method of purification	Infrared C=O (cm.$^{-1}$)
PhO.	1	$C_6H_5\cdot COCl$ $PhO\cdot C_6H_5$	59	71°(lit.[114] 71°)	R.(ethanol)	1644
An.	1	$C_6H_5\cdot COCl$ $CH_3O\cdot C_6H_4\cdot C_6H_5$	21	165-166°(lit.[115] 165-167°)	F.(benzene)	-
Me.	1	$CH_3\cdot C_6H_4\cdot COCl$ C_6H_6	83	54-55°(lit.[14] 54-55°)	R.D.	-

b) All substituents in p-position.

R.= recrystallised.

F.= fractionally crystallised.

R.D. = distilled under reduced pressure.

TABLE IV - 5.

p-substituted p'-hydrogen benzhydrols.

Substituent	Route (see p.137)	Reducing agent in route 1	Starting matls.[b] in routes 2 & 3	Method of purification	m.p.	Infrared - OH (cm.$^{-1}$)
MeO.	3	-	C_6H_5Br. $CH_3O \cdot C_6H_4 \cdot CHO$	R.(petrol 80-100° + benzene)	68°(lit.[41b] 68°)	3411
PhO.	1 and 3	$LiAlH_4$	$PhO \cdot C_6H_4 \cdot Br$. $C_6H_5 \cdot CHO$	R.(petrol 60-80°)	78°(lit.[34a] 75°)	3381
An.[a.*]	1	$LiAlH_4$	-	R.(petrol 80-100°)	109.5-110°	3378
Me.	1	$LiAlH_4$	-	R.(petrol 40-60°)	52-53°(lit.[14] 52-53°)	3413
H.	-	-	-	R.(petrol 60-80°)	68°(lit.[23] 67.8°)	3407
NO_2.	2	-	$NO_2 \cdot C_6H_4 \cdot CH_2Cl$ C_6H_6	R.(petrol 80-100°)	73-74°(lit.[53] 73-74°)	3478 & 3425 (split peak)

* = new compound.

R.= recrystallised.

a) found % C 82.5; H 6.4
   calc. % C 82.8; H 6.2

b) all substituents in p-position.

TABLE IV - 6.

p-substituted p'-hydrogen benzhydryl chlorides.

Substituent	Chlorination method (p. 153)	Method of purification	m,p. or b.p./mm.
MeO.	C	R.(petrol 80-100°)	64° (lit.[116] 64°)
PhO.	C	R.(petrol 80-100°)	52° (lit.[34a] 49-50°)
An.*	B	R.(ether)	124-125°
Me.	B	R.D.	125°/0.2 mm. (lit.[14] 136°/0.4 mm.)
H.	B	R.D.	19.4°(lit.[23] 19.6°)
NO_2.	A	R.(petrol 40-60°)	44-44.5°(lit.[53] 43.5-44.5°)

* = new compound.

R.= recrystallised.

R.D.= distilled under reduced pressure.

TABLE IV - 7.

p-substituted p'-methoxy benzophenone.

Substituent	Route (see p.137)	Starting materials[b]	Yield %	m.p.	Method of purification	Infrared C=O (cm.$^{-1}$)	Found % C	Found % H	Calc.% C	Calc.% H
An.*	1	$CH_3O\cdot C_6H_4\cdot COCl$ $CH_3O\cdot C_6H_4\cdot C_6H_5$	15	213°	F.(benzene)	1645	78.6	5.6	79.2	5.7

* = new compound.

F. = fractionally crystallised.

b) All substituents in p-position.

TABLE IV - 8

p-substituted p'methoxy benzhydrols

Substituent	Route (see p.137)	Starting materials [b]	Yield %	m.p. or b.p./m.m.	Method of purification	Crystalline form	Infrared -OH, (cm.$^{-1}$)	Found %		Calc. %	
								C	H	C	H
MeO	3	$CH_3O \cdot C_6H_4Br$ $CH_3O \cdot C_6H_4CHO$	41	71-72° (lit.[116] 71-72°)	F. (petrol 60 - 80° + benzene	White needles	3425	74·6	6·8	73·8	6·6
PhO *	3	$PhO \cdot C_6H_4Br$ $CH_3O \cdot C_6H_4CHO$	32	60-61°	F. (petrol 80 - 100°)	White clusters	3311	78·1	5·8	78·4	5·9
An *	1 [a]	$CH_3O \cdot C_6H_4COCl$ $CH_3O \cdot C_6H_4 \cdot C_6H_5$	95	110°	R. (benzene)	White needles	3372	78·7	6·3	78·8	6·3
Me *	3	$CH_3O \cdot C_6H_4Br$ $CH_3 \cdot C_6H_4CHO$	66	57°	F. (petrol (60-80°)	White granular crystals	3378	78·3	6·8	78·9	7·0
Bu^t *	3	$t \cdot Bu \cdot C_6H_4Br$ $CH_3O \cdot C_6H_4CHO$	71	82-83°	R. (petrol 60 - 80°)	White needles	3268	80·2	8·0	80·0	8·1
Ph *	3	$C_6H_5 \cdot C_6H_4Br$ $CH_3O \cdot C_6H_4CHO$	83	89°	R. (petrol 60 - 80°)	White plates	3378	82·9	6·5	82·8	6·2

/continued

TABLE IV - 8 (cont.)

Substituent	Route (see p.137)	Starting materials [b]	Yield %	m.p. or b.p./m.m.	Method of purification	Crystalline form	Infrared -OH (cm.$^{-1}$)	Found %		Calc. %	
								C	H	C	H
F [*]	3	$CH_3O\cdot C_6H_4Br$ $F\cdot C_6H_4CHO$	57	138° (·05 mm.)	R.D.	(pale green liquid)	3413	72·7	5·9	72·4	5·6
Cl [*]	3	$CH_3O\cdot C_6H_4Br$ $Cl\cdot C_6H_4CHO$	70	39·5°	F. (petrol 60 - 80°)	White granular crystals	3333	67·6	5·2	67·6	5·2

[*] = new compound.

a) Using $LiAlH_4$ as reducing agent.

b) All substituents in p-position.

R. = recrystallised.

F. = fractionally crystallised.

R.D. = distilled under reduced pressure.

TABLE IV - 9.

p-substituted p'-methoxy benzhydryl chlorides.

Substituent	Chlorination method (p.153)	Yield %	m.p.	Refractive index	Method of purification	Crystalline form
MeO.	C	89	82.5-83.5° (lit.[116] 83-84°)	-	R. (petrol 80-100°)	White needles (turning pink slowly)
PhO.*	C	49	47°	1.6060 (20°) (before crystallis'n)	R. (petrol 80-100°)	Pale green cubes
An.*	B	69	147°	-	P. (petrol 40-60°)	White needles.
Me.*	C	65	Liquid[a]	1.5851 (20°)	Z. (petrol 80-100°)	(Colourless oil)
Bu.^{t}*	C	64	56°	-	R. (petrol 80-100°)	Pale green powder
Ph.*	C	61	102°	-	R. (petrol 80-100°)	Pale green powder
F.*	C	68	Liquid[a]	1.5649 (22°)	Z. (petrol 80-100°)	(Colourless oil)
Cl.*	C	60	Liquid[a]	1.5930 (22°)	Z. (petrol 80-100°)	(Colourless oil)

* new compound.

a) see p. 154.

R. = recrystallised.

Z. = frozen out at -20°.

P. = precipitated by the addition of petrol to ethereal solution.

Preparative details.

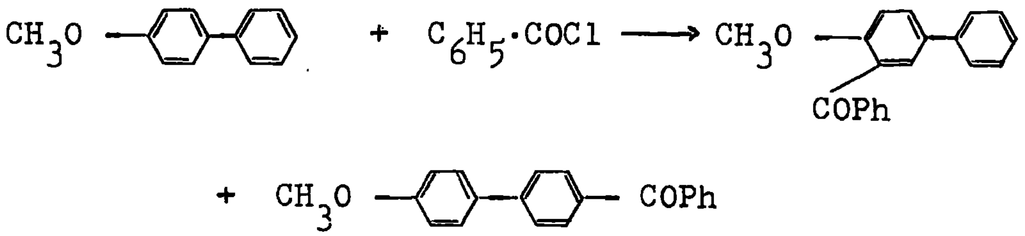
The routes by which the substituted benzhydrols were obtained were given on p. 137. Preparative details have been given fully in the literature; reference to them is given below together with any observations of special interest. Details of the methods employed in the chlorination of these compounds follow.

Route 1.

a). Friedel-Crafts reaction between an acid chloride and benzene (or substituted benzene).

This reaction was carried out in carbon disulphide by Montagne's method[119]. Equimolar proportions of anhydrous aluminium chloride (Hopkins and Williams), acid chloride and benzene were used. Unreacted materials were removed from the reaction mixture, whenever possible, by using only a small quantity of carbon disulphide and separating the aluminium-ketone complex from the solvent before hydrolysis. Sometimes, several crystallisations were sufficient to yield a pure product but often, especially in the case of nitro-compounds, chromatographic purification on an alumina column was necessary.

Attack by the acid chloride occurs mainly in the p-position in these reactions[111, 112, 113]. Small amounts of the o-compounds may also be formed but, as they are more soluble, they are removed in the working-up stages. However, the methoxy group in p-methoxydiphenyl has been found to activate the o-position as well as the p'-position[115], e.g.,



(I)

Fieser and Bradsher[115] found that, in this case, the p'-derivative only constituted about half the total product. However, the much greater solubility of the o-derivative easily allowed separation by fractional crystallisation. This solubility effect is quite general for aromatic compounds but is very marked in the present case[115, 117, 118]. For instance, the low solubility of p-bromo-p'-methoxydiphenyl in ether prevents the preparation of the corresponding Grignard reagent, whilst the o-compound is easily synthesised[117]. p-Anisylbenzhydryl chloride was prepared from the known ketone I, above, and the same principles were applied to the isolation of p-anisyl p'-nitrobenzhydryl chloride and p-anisyl p'-methoxybenzhydryl chloride. The respective ketones were crystallised to constant melting point and the observation of good first-order kinetics in the hydrolysis of the chlorides formed from the ketones in the two least reactive series confirmed that no o-derivatives were present in the products; the progressive fall in rate observed for p-anisyl p'-methoxybenzhydryl chloride was fully consistent with the "mass-law effect" in this series.

b). Meerwein-Ponndorf reduction of the ketone.

This method, which was employed to reduce all ketones having nitro-substituents, has been fully described[120]. The fractionating column was two feet in length, packed with 'dixon rings' and jacketed at 60°. A 50% excess of reducing agent was employed.

or c). Lithium aluminium hydride reduction of the ketone.

This reagent was employed to reduce all other ketones. The reaction, which has also been fully described[121], was carried out in ether and under nitrogen. A 50% excess of reducing agent was employed.

Route 2.

This route was only employed in the preparation of p-nitrobenzhydrol and p, p'-dinitrobenzhydrol; the former preparation has been described[53]. Kodak p, p'-dinitrodiphenylmethane was brominated and hydrolysed, in a similar manner to that described for the mononitro compound, to give p, p'-dinitrobenzhydrol.

Route 3.

Grignard reaction between a bromobenzene and a benzaldehyde.

The method employed was exactly as described by Bachmann for the preparation of p-methoxybenzhydrol.[122]

Methods of Chlorination (see Tables IV - 3, IV - 6 and IV-9).

As has already been stated (p.136) all benzhydryl chlorides were prepared by chlorinating the benzhydrols with hydrogen chloride. Three general variations were used, the choice depending on the reactivity of the product with water or of the benzhydrol with hydrogen chloride.

Method A.

The least reactive benzhydryl chlorides were formed by chlorination of the alcohols in benzene, over anhydrous zinc chloride. Hydrogen chloride was passed for 8 hours, the benzene solution filtered, washed, dried ($MgSO_4$) and evaporated. The crude product was then purified by crystallising or freezing-out, usually from petrol.

Method B.

Most benzhydrols were chlorinated in ether over granular anhydrous calcium chloride as in the preparation of p-methoxy benzyl chloride (see p.129). The product was worked up in the usual manner and usually purified by distillation under reduced pressure or by recrystallisation from petrol. In the preparation of p-anisyl p'-methoxybenzhydryl chloride (Table IV - 9), chlorination was carried out in fairly dilute solution (1 gm. in 200 ml.) and the chloride precipitated by the addition of petrol (40-60°) after the excess hydrogen chloride and much of the ether had been removed under reduced pressure.

Method C.

The most reactive chlorides were formed by chlorination for about 6 hours in petrol (80-100°) over phosphorous pentoxide. Excess hydrogen chloride was removed by boiling under reduced pressure over fresh P_2O_5. The product was then allowed to crystallise at -20°C from the filtered solution.

Crystallisation of the benzhydryl chlorides.

Some of the chlorides could not be obtained as solids at room temperature (see Tables IV-3 and IV-9), and could not be distilled or sublimed without decomposition, even at very low pressures (0.001 mm.). These compounds were therefore separated from their solutions in petrol by cooling to -80° and removing excess solvent at low pressures. In all cases, complete hydrolysis indicated that the products were sufficiently pure. The methoxybenzhydryl chlorides were all stored under vaccuum and at -20°, as decomposition was quite rapid at room temperature.

Preparation of starting materials.

Most starting materials (Tables IV - 1, - 4, - 5, - 7, - 8) were the purified commercial products. However, p-brom tert.-butylbenzene had to be prepared in the laboratory.

p-brom tert.-butylbenzene was prepared[123] by the dropwise addition of bromine (36 gm.) to tert,-butylbenzene (30 gm.) in carbon tetrachloride (100 ml.) containing a little iodine. The mixture was refluxed for 6 hours, the solvent removed and the residue washed, dried and distilled under reduced pressure, generous head and tail fractions being discarded.

b.p. 95° (10 mm.); m.p. 10° (lit.[123] 10°);
refractive index 1.5317 (19°).

SOLVENTS.

Acetone was the 'Analar' product which had been refluxed with sodium hydroxide and potassium permanganate for two hours[124] before being fractionated from hydroquinone. 70% aqueous acetone was made up by mixing 700 volumes acetone and 300 volumes distilled water which had been passed down a column containing mixed ion exchange resin. 85% aqueous acetone was made up in an analagous manner.

Formic acid was the 'Analar' product which had been dried over successive quantities of boric anhydride[125] and distilled under reduced pressure.

m.p. 8.38° (lit.[126] 8.39°).

99.5% formic acid was made up by mixing 995 volumes formic acid and 5 volumes water, purified as above.

Titration acetone was the commercial product which was distilled after being refluxed with sodium hydroxide and potassium permanganate for two hours. The indicator lacmoid was added and the solution neutralised before use.

THERMOSTATS.

These were of conventional design. The low temperature thermostat had a refrigerator unit to cool the liquid (ethylene glycol-water) below the required temperature. Temperature control was to ±.01° by contact thermometers or toluene-mercury regulators. The 0° thermostat consisted of a well stirred ice-water mixture; no temperature variation could be detected. Thermometers standardised to ± .02° (-10 - 100°); ±.05° (100-150°); ±. 1° (-35 — -10°) by the National Physical Laboratory were used for temperature measurement. Temperatures below -35° were measured with the help of a standard thermometer and a Beckmann thermometer.

METHODS OF RATE MEASUREMENT.

The slower runs were followed by titrating the acid or halide produced and the faster runs by measuring the conductance of the solutions. The hydrolysis of the halides always went to completion and velocity constants could therefore be calculated from a knowledge of the acidity or halide concentration after various time intervals and at 100% reaction without the necessity of using weighed amounts of organic halides.

Titrimetric runs.

The sealed ampoule technique was used for runs at the higher temperatures (above 20°). 12-15 tubes were allowed to attain thermostat temperature; single tubes were then removed from time to time, cleaned and broken in neutral acetone. Runs at lower temperatures were carried out in stoppered flasks and 5 ml. samples pipetted into neutral acetone. For the hydrolysis of benzyl and benzhydryl chlorides, the quenched solutions were titrated with sodium hydroxide solution (lacmoid as indicator); for the formolysis of benzyl halides, where piperidine was also present (see p. 46), the quenched solutions were titrated potentiometrically with silver nitrate solution after the addition of several drops of conc. nitric acid[86].

A special, approximate, method was employed for the rapid formolysis of p-methoxybenzyl chloride. A micrometer syringe was used to introduce a small, constant, amount of organic chloride into a beaker which had attained thermostat temperature (10°). A series of stoppered test tubes containing 5 ml. of solvent was also allowed to reach thermostat temperature. Rate measurements were then made by pouring the solvent onto the organic chloride, shaking, and then swiftly adding 200 ml. of dry acetone; the interval between these two operations being timed with a stopwatch. The acetone solutions were then estimated for chloride as above.

Conductimetric runs.

The more rapid reactions were followed by noting the conductance of the solution at various times. A Pye (No. 11700) conductance bridge was employed; this bridge had several advantages.

(1) When phase balance was exact, the equivalence point was indicated by a horizontal line on an oscilloscope screen but check experiments showed that this point was also indicated accurately by an ellipse whose major axis was horizontal even when exact phase balance was not obtained. The time consumed in adjusting phase balance could therefore be avoided.

(2) The bridge contained a circuit which allowed the unknown conductance to be compared with a known external resistance. A series of such resistances was therefore prepared so that the unknown conductance could be compared with various resistances by turning a switch.

In the kinetic experiments, a mechanical counter driven by a 1 rev. per sec. synchronous motor was placed next to the oscilloscope screen. This counter indicated time to 0.1 sec. During a run, the oscilloscope screen and counter were filmed at up to 64 frames per sec. (Kodak K-100, 16 mm. cine camera). The film then showed the exact time (which could be estimated to 0.02 sec.) at which the reaction solution had the same resistance as that of the external standard. As soon as the resistance of the solution had dropped below that of the first standard resistance, the next standard resistance was brought into circuit, this process being repeated 12-15 times throughout a kinetic run. The concentrations of hydrochloric acid corresponding to the various resistances were obtained by separate experiments with standard solutions of hydrochloric acid in the solvents employed. Good, reproducible conductance-concentration curves could be obtained in this manner provided that a small amount (10^{-4} M.) of hydrochloric acid was initially present. This was found necessary in spite of precautions in the purification of acetone, and attempts to remove any dissolved carbon dioxide from the solvent. The conductance was not affected by the presence of benzhydrols in the concentrations encountered during a run.

For reactions with half-lives down to ca. 30 sec., this procedure gave first order rate coefficients of the same precision as the titrimetric runs (standard error of final mean $\ngtr$ 0.3%). For reactions with half-lives down to ca. 7 sec., the precision was acceptable (standard error of final mean $\ngtr$ 1.2%). The conductimetric runs were carried out in more dilute solution (.002 M) than the titrimetric runs (.01 M) but this did not affect the value of the rate coefficient (see Appendix IV - 2; Expt. 63).

Conductance cell (see Figure IV - 1).

Smooth, parallel platinum electrodes ca. 1 cm. square and 0.5 cm. apart were employed. The electrodes were made from 0.5 mm. thick platinum sheet and their platinum leads of wire 0.5 mm. diameter to provide maximum rigidity. They were sealed into soda glass and connected to the bridge via mercury wells; all leads were screened. A 'spot' welding technique was found to be the most satisfactory for adjoining the platinum wire and sheet; in order to prevent the platinum sticking to the copper welding electrodes, it was necessary to place two thin pieces of copper sheet on either side of the

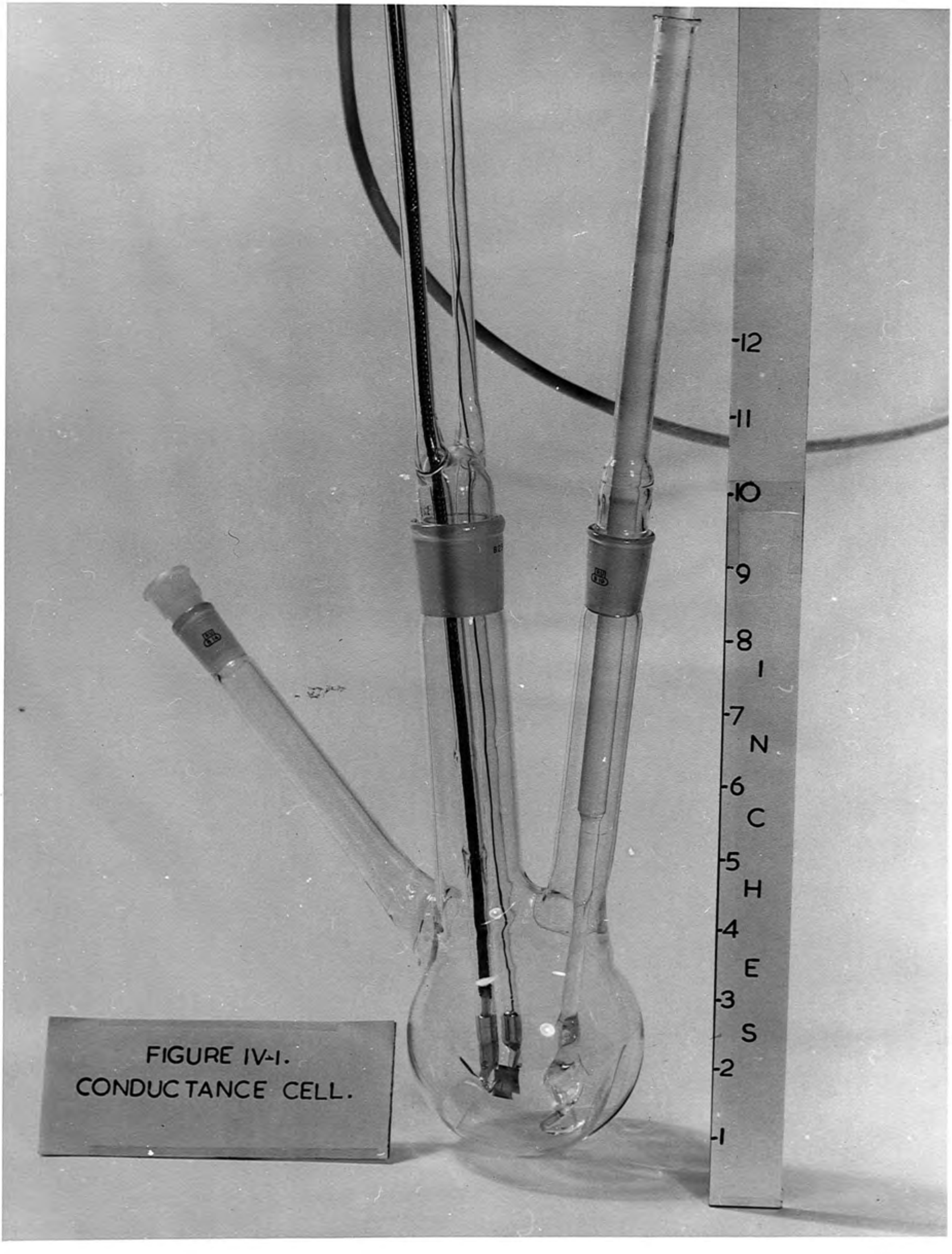


FIGURE IV-1.
CONDUCTANCE CELL.

platinum prior to welding. Most of this could be pulled from the platinum afterwards but the remainder was dissolved off with 50% aqua regia. Prior to sealing in the glass, the electrodes were cleaned and etched by dipping in aqua regia.

The pyrex reaction vessel (capacity ca. 200 ml.) is depicted in Figure IV - 1. A stirrer (1200 r.p.m.) with a long ground glass sleeve was inserted in the B.19 socket; the sleeve was lubricated by a thin film of glycerine on top of a film of stopcock grease as this gave the smoothest running. Baffles were suitably placed in the flask to facilitate stirring; check experiments showed the mixing of the reactants to be complete within *ca.* 1.5 sec. after the introduction of the chloride.

External resistances were high stability resistances (values 1-30 KΩ) with a tolerance of ± 1%, enclosed in an earthed tin box. The resistances did not vary over the period of the experiments.

Introduction of samples. A portion of the organic chloride was dissolved in a small quantity (usually 0.2 ml.) of anhydrous acetone (distilled from molecular sieves) and the appropriate quantity of water added to the solvent to restore solvent composition on the introduction of the sample. To initiate a run, the chloride in acetone was squirted into the cell through the smallest neck, the stirrer being run at its fastest.

Four compounds were insoluble in the usual 0.2 ml. acetone; p-anisyl p'-hydrogen-, p-phenoxy p'-nitro- and p-phenyl p'-methoxy-benzhydryl chlorides were each dissolved in 0.7 ml. acetone at 20°. p-anisyl p'-methoxy benzhydryl chloride was dissolved in 2.0 ml. acetone at 30° (it was not sufficiently soluble in 5.0 ml. acetone at 20°). Satisfactory results with this compound were obtained at -33°, but at -20° the reaction was so fast that the heat supplied to the cell was not dissipated quickly enough to allow the observation of satisfactory rate coefficients.

Temperature measurement was made as described on p. 156. However, it was found that, at low temperatures, the temperature of the reacting solution was slightly greater than that of the thermostat, due to incomplete immersion of the conductance cell (to allow the injection of reactant to be observed). This temperature difference was measured by means of a shielded copper-constantan thermocouple; the temperatures quoted in this thesis have been corrected for this effect.

METHODS OF CALCULATION.

Rate coefficients.

First-order rate coefficients were calculated from equation IV - 1,

$$k = (2.303/t) \cdot \log [a/(a - x)] \quad . \quad . \quad . \quad . \quad \text{Eqn. IV - 1.}$$

where t is the time in seconds and a and a-x are the organic halide concentrations at t = o and t = t, respectively. The time of the first reading was taken as zero, a being the difference between the first reading and that at infinity (10 times the half-life period). Constant first-order rate coefficients were obtained for most titrimetric runs over the first 80% reaction except for the formolysis of benzyl halides (see p.45). The observed hydrolysis rate coefficients were therefore assumed to be identical to the rate of ionisation in S_N1 reactions ('mass-law' and 'ionic strength' effects cancelling). All experiments were carried out in duplicate or triplicate, and the standard error of the final mean rate coefficient (km) obtained from equation IV - 2,

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

where n was the number of separate determinations of k. Individual rate constants differing from the mean by more than $2\frac{1}{2}\ \sigma(\text{each})$, where $\sigma(\text{each}) = n^{\frac{1}{2}}\sigma(k)$, were rejected and a new $\sigma(k)$ found.

In the hydrolysis of the more reactive compounds, first-order rate coefficients decreased as the reaction proceeded. This arose from a large value of α^{o} (see p. 70) which controls the reversal of the rate-determining ionisation by the chloride ions produced. This was observed for the reactions studied by the conductimetric technique in very dilute solution; activity coefficients of all charged species were therefore assumed to be unity, as a first approximation. On this view, the rate of reaction is given by equation IV - 3,

$$\frac{dx}{dt} = \frac{k_1^o\,(a - x)}{1 + \alpha^o(c + x)} \quad . \quad . \quad . \quad . \quad \text{Eqn. IV - 3.}$$

which, on integration between the usual limits, yields equation IV - 4 where $\bar{k}_1 = (2.303/t).\log\,[a/(a - x)]$,

$$k_1^o = \bar{k}_1 + \alpha^o \left[\bar{k}_1\,(a + c) - \frac{x}{t} \right] . \quad . \text{ Eqn. IV - 4.}$$

Thus the mass-law constant, α^o, and the rate coefficient at zero ionic strength, k_1^o, were calculated from the 'best' straight line $\bar{k}_1$ vs. $\left[\bar{k}_1\,(a + c) - \frac{x}{t}\right]$ by the method of least squares. Before any such calculation, however, the results were investigated graphically to make sure of the linearity of the relation for every compound. Any points which deviated considerably from linearity were discarded at this stage to avoid repetition of a lengthy calculation and recalculation of k_1^o and α^o.* The least squares value of α^o is given by equation IV - 5,

$$\alpha^o = \frac{\sum \left[\bar{k}_1 - km\right]\left[A - Am\right]}{\sum \left[A - Am\right]^2} \quad . \quad . \quad . \quad . \quad \text{Eqn. IV - 5}$$

where $A = \left[\bar{k}_1\,(a + c) - \frac{x}{t}\right]$, $Am = \frac{1}{n}\sum A$, n = number of determinations.

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* It was never necessary to discard more than two points in any run.

k_1^o is then given by equation IV - 6,

$$k_1^o = km + \alpha^o Am, \left(km = \frac{1}{n}\sum \bar{k}_1\right) \quad . \quad . \quad \text{Eqn. IV - 6.}$$

The standard error of α^o is then given by equation IV - 7,

$$\sigma(\alpha^o) = \left[\frac{\sum(\bar{k}_1 - \bar{k}_1 \,\text{calc.})^2}{(n - 2)\sum[A - Am]^2}\right]^{\frac{1}{2}} \quad . \quad . \quad \text{Eqn. IV - 7.}$$

and the standard error of k_1^o by $\sigma(k_1^o) = \sigma(\alpha^o)\ Am$.

Rate coefficients in the reactions of p-nitro- and m-chlorobenzyl bromides with 99.5% formic acid (Appendix IV - 2, Expts. 26, 27, 28).

The reactions of p-nitro- and m-chloro-benzyl bromides with 99.5% formic acid were only followed over the first 30% reaction for the following reasons:

(i) The reactions were so slow that prolonged heating of tube samples gave rise to explosions due to the decomposition of formic acid (to water and carbon monoxide).

(ii) The water produced in this decomposition will have an unknown effect on the rate.

Rate coefficients over the first 10% reaction were obtained from the expression k = x/at, the usual approximation of the integrated first-order rate equation when $x \ll a$. Rate coefficients in the range 10-30% reaction were obtained in the normal manner.

The Rate of formolysis of p-methoxybenzyl bromide at 9.70°

was calculated from the rate of formolysis of p-methoxybenzyl chloride at 9.70° (see p. 61) by making the very rough assumption that,

$$\left(k_{Ph\cdot CH_2Br} \Big/ k_{Ph\cdot CH_2Cl}\right)_{80.17^\circ} = 2.5246 =$$

$$\left(k_{p\text{-}MeO\cdot C_6H_4\cdot CH_2Br} \Big/ k_{p\text{-}MeO\cdot C_6H_4\cdot CH_2Cl}\right)_{9.70^\circ}$$

Activation parameters.

Rate coefficients, k_1^o, for the ionisation at zero ionic strength were employed in calculating the activation parameters. It has already been pointed out (p. 164) that the observed integrated first-order rate coefficients were equal to this quantity when they did not vary over the course of a run. In the following discussion, the parameter k represents k_1^o.

The activation energy, E, was calculated from the values of k at adjacent temperatures and refers to the mean temperature,

$$E = \frac{2.303\ RT_aT_b}{T_b - T_a} \log \frac{k_a}{k_b} \quad \ldots\ldots\ldots\ldots \quad \text{Eqn. IV - 8.}$$

where k_a and k_b are the values of k at the absolute temperatures T_a and T_b.

The standard error in E was obtained from equation IV - 9,

$$\sigma\ (E) = \frac{RT_aT_b}{T_b - T_a}\left[\left(\frac{\sigma_a}{k_a}\right)^2 + \left(\frac{\sigma_b}{k_b}\right)^2\right]^{\frac{1}{2}} \quad . . \text{Eqn. IV - 9.}$$

where σ_a and σ_b are the standard errors of the final mean k_a and k_b.

The entropy of activation, ΔS^{*}, at the temperature $(T_a + T_b)/2$ was calculated from equation IV - 10,

$$\ln k_a = \ln\left(\frac{\bar{k}}{h}\right) + \ln\frac{(T_a + T_b)}{2} + 1 + \frac{\Delta S^{*}}{R} - \frac{E}{RT_a} \quad .. \text{Eqn. IV - 10.}$$

where k_a refers to the temperature T_a, and E to $(T_a + T_b)/2$.

The standard error in ΔS^{*}, $\sigma(\Delta S^{*})$, was obtained from the approximation,

$$\sigma\ (\Delta S^{*}) \simeq \frac{\sigma\ (E)}{T} \quad . . . . \text{Eqn. IV - 11.}$$

Heat capacity of activation.

The heat capacity of activation, ΔC^{*}, is given by equation IV - 12,

$$\Delta C^{*} = dE/dT - R \quad . . . . \text{Eqn. IV - 12.}$$

For compounds which were studied at three or more temperatures, dE/dT was obtained from equation IV - 13,

$$E = E_o + \frac{dE}{dT} . T$$

by the method of least squares (cf. p.165). This procedure assumes dE/dT to be independent of temperature, but this has been found to be true within the limits of experimental error[53].

The standard error in dE/dT was obtained in two ways:-

(i) From the 'best' straight line E vs. T using equation IV - 13,

$$\sigma\left(\frac{dE}{dT}\right) = \left[\frac{\sum (E_{obs} - E_{calc})^2}{(n - 2) \sum (T - T_m)^2}\right]^{\frac{1}{2}} \quad \ldots\ldots\ldots \text{Eqn. IV - 13.}$$

where n is the number of determinations of E.

(ii) From σ (E) using equation IV - 14.

$$\sigma\left(\frac{dE}{dT}\right) = \frac{\left[\sum (\sigma(E))\ (T - Tm)^2\right]^{\frac{1}{2}}}{\sum (T - Tm)^2} \quad \ldots\ldots\ldots \text{Eqn. IV - 14.}$$

Only the larger value is quoted in this work.

$\Delta C^{\ast}$ in reactions studied at only two temperatures.

It has already been pointed out (p. 82) that for S_N1 reactions in the present solvents, $\Delta C^{\ast}/\Delta S^{\ast}$ is independent of the nature of the substrate[57] and the value of this ratio in a given solvent at any temperature can easily be calculated. When the hydrolysis of a compound is studied at only two temperatures, the calculated value of $\Delta S^{\ast}$ refers to the mean of those temperatures and as the value of $\Delta C^{\ast}/\Delta S^{\ast}$ at this temperature is also known, ΔC^{*} can easily be obtained. Hence,

$$\frac{\Delta S^{*}}{\Delta C^{*}} = \frac{\Delta S^{*}_{o}}{\Delta C^{*}} + 2.303 \log T$$

where ΔS^{*}_{o} is a constant. Since $\Delta S^{*}/\Delta C^{*}$ is constant, independent of the substrate and $\Delta S^{*}_{o}/\Delta C^{*}$ is constant, independent of temperature, then

$$\frac{\Delta S^{*}}{\Delta C^{*}} - 2.303 \log T$$

is constant and independent of substrate and temperature. Hence $\Delta S^{*}/\Delta C^{*}$ or $\Delta C^{*}/\Delta S^{*}$ can be calculated at any temperature. Mean values of this quantity for a number of substrates in 70% and 85% aqueous acetone are shown in Table IV - 10.

TABLE IV - 10.

Mean values of ($\Delta S^{*}/\Delta C^{*} - 2.303 \log T$) in 70% and 85% aqueous acetone[57, 79].

% acetone.	No. of substrates from which mean value obtained.	($\Delta S^{*}/\Delta C^{*} - 2.303 \log T$)mean.
70	10	- 5.5061
85	6	- 5.4185

Rates and activation parameters at temperatures not studied experimentally.

(a) Activation parameters.

As an experimental value of ΔC^{*} was not available for all reactions, a calculated value of this parameter was always employed. ΔC^{*} was obtained from the value of $\Delta C^{*}/\Delta S^{*}$ at the temperature T_m' and the value of ΔS^{*} at this temperature, where

(1) T_m' is the temperature corresponding to the mean value of log T where T is the temperature to which the experimental value of ΔS^{*} refers, and $\Delta S^{*}_{T_m'}$ is the mean of the experimental values of ΔS^{*}. This only applies when the reaction was studied at three or more temperatures.

(2) T_m' is the mean of the experimental temperatures and $\Delta S^{*}_{T_m'}$ is the experimental value. This applies when the reaction was studied at only two temperatures.

Hence E and ΔS^{*} at any temperature, T, were calculated from equations IV - 15 and IV - 16,

$$E_T = E_{T_m'} + (\Delta C^{*} + R)(T - T_m') \quad \ldots\ldots \text{Eqn. IV - 15.}$$

$$\Delta S^{*}_{T} = \Delta S^{*}_{T_m'} + 2.303\,\Delta C^{*} \log \frac{T}{T_m'} \quad \ldots\ldots \text{Eqn. IV - 16.}$$

The standard error in ΔC^{*}, $\sigma_{\Delta C^{*}}$, which arises from the error in the experimental ΔS^{*} and from the error in $\Delta C^{*}/\Delta S^{*}$ was calculated from equation IV - 17,

$$\sigma_{\Delta C^{*}} = \frac{\Delta S^{*}_{T'm}}{(\Delta S^{*}/\Delta C^{*})_{T'm}} \left[\left(\frac{\sigma_{\Delta S^{*}}}{\Delta S^{*}} \right)^{2}_{T'm} + \left(\frac{\sigma}{\Delta S^{*}/\Delta C^{*}} \right)^{2}_{T'm} \right]^{\frac{1}{2}} \quad \ldots \quad \text{Eqn. IV - 17.}$$

The standard errors in E and ΔS^{*} at T were then calculated from equations IV - 18 and IV - 19,

$$\sigma (E_T) = \sigma_{\Delta C^{*}} (T - T'm) \quad \ldots\ldots\ldots \quad \text{Eqn. IV - 18.}$$

$$\sigma (\Delta S^{*}_{T}) = 2.303\, \sigma_{\Delta C^{*}} \log \frac{T}{T'm} \quad \ldots\ldots \quad \text{Eqn. IV - 19.}$$

(b) Rate coefficients.

The rate coefficient at any temperature T, k_T, was calculated from that at the nearest experimental temperature T'', $k_{T''}$, by equation IV - 20.

$$\log \frac{k_T}{k_{T''}} = \frac{\left[E_{T'm} + (\Delta C^{*} + R) \left\{ \frac{T + T''}{2} - T'm \right\} \right] (T - T'')}{2.303\, RTT''} \pm \frac{\sigma_{\Delta C^{*}} \left(\frac{T + T''}{2} - T'm \right) (T - T'')}{2.303\, RTT''} \quad \ldots \text{Eqn. IV - 20}$$

$$= \quad a \quad \pm \quad b \text{ (say).}$$

$$\frac{k_T}{k_T''} = \text{antilog } a \qquad \sigma\left(\frac{k_T}{k_T''}\right) = 2.303\, b \cdot \frac{k_T}{k_T''}$$

Then $k_T = k_T''(k_T/k_T'')$ and the standard error in k_T, $\sigma(k_T)$, is given by equation IV - 20,

$$\sigma(k_T) = k_T'' \, (k_T/k_T'') \left[\left(\sigma''/k_T''\right)^2 + (2.303\, b)^2 \right]^{\frac{1}{2}} \quad \text{.. Eqn. IV - 20.}$$

where σ'' is the experimental error in k_T''.

$\Delta C^{\ast}$ in reactions studied at only one temperature.

In the case of the two substituted p'-methoxybenzhydryl compounds, p-anisyl and p-methoxy, rate measurements were made at only one temperature for each compound due to solubility difficulties for the anisyl compound (see p. 163), and because the rate of the methoxy compound was too fast to be measured at all but the lowest temperature available. In the calculations it was assumed that the p-anisyl compound would have the same $\Delta S^{\ast}$ and error as the p-phenyl compound and that $\Delta S^{\ast}$ and its error for the p-methoxy compound were identical with that of the p-phenoxy compound. These assumptions are borne out by the results for these substituents in the parent and p'-nitro series (see p. 83).

APPENDIX IV - 1.

THE DISSOCIATION OF HCl IN 85% AQUEOUS ACETONE.

(see Chapter III, p.77).

The Onsager Limiting Law[127].

The Onsager limiting law for a uni-univalent electrolyte is described by Equation IV-21

$$\Lambda = \Lambda_\infty - (B_1 \Lambda_\infty + B_2)\sqrt{c} \quad \ldots\ldots\ldots \text{Equation IV-21}$$

$$\text{where } B_1 = \frac{8.204 \times 10^5}{(DT)^{3/2}} \quad ; \quad B_2 = \frac{82.5}{\eta(DT)^{1/2}}$$

and Λ = Equivalent conductance of the electrolyte.

Λ_∞ = Equivalent conductance of the electrolyte at infinite dilution.

C = Concentration of the electrolyte (in gram equivalents per litre).

D = Dielectric constant of the solvent.

η = Viscosity of the solvent (in poise).

T = Absolute temperature.

If the dissociation of the electrolyte is incomplete, the $\underline{\sqrt{c}}$ term in Equation IV-21 is replaced by $\underline{\sqrt{\gamma c}}$ where $\underline{\gamma}$ denotes the degree of dissociation of the electrolyte.

The Determination of γ.

The effect of the successive addition of HCl to 85% acetone on the conductance of the solution at various temperatures was determined in connection with the evaluation of kinetic data (see p. 159). If C is the concentration of HCl added, then

$$\Lambda = \frac{1000\ k}{C} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{Equation IV-22}$$

where k is the observed specific conductance of the solution.

The theoretical conductance, Λ', is given by Equation IV-23

$$\Lambda' = \frac{1000\ k}{C'} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{Equation IV-23}$$

where C' is the actual ionic concentration, i.e. $C' = \gamma C$. Combination of Equations IV-22 and IV-23, gives

$$\frac{\Lambda}{\Lambda'} = \frac{C'}{C} = \gamma \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{Equation IV-24}$$

γ may then be obtained by successive approximation from Equations IV-21 and IV-24. The Viscosities and Dielectric constants of 85% acetone at the required temperatures can be obtained from Equations IV-25 and IV-26.

Application to the present Conductance Data.

Λ_∞ was obtained by graphical extrapolation of the conductance data to infinite dilution. The results did not appear to be sufficiently accurate to merit a 'least squares' treatment, or even a detailed study of all temperatures used in the kinetic work. The conductance data for two temperatures was selected (+ 20.61°C and -32.90°C) and $\underline{\gamma}$ calculated at several concentrations. The results are summarised in Table IV-11

TABLE IV - 11

THE DEGREE OF DISSOCIATION OF HCl IN 85% ACETONE AT VARIOUS CONCENTRATIONS AND TEMPERATURES.

Λ_∞ at 20.61°C $\simeq 0.594 \times 10^{-2}$; Λ_∞ at -32.90°C $\simeq 0.168 \times 10^{-2}$

HCl concn. (N).	γ	
	+20.61°C	-32.90°C
2.5×10^{-4}	0.97	0.98
4.3×10^{-4}	0.96	0.98
9.8×10^{-4}	0.94	0.98
28.3×10^{-4}	0.89	0.94

Whilst it must be emphasised that these values are only approximate, it is clear that there is almost complete dissociation at the lower temperature but at 20°C, there is a distinguishable amount of association over this, same, concentration range. Also, the degree of dissociation decreases as the concentration rises, as expected.

Experimental.

The viscosities and dielectric constants of 85% acetone were required at temperatures from +20° to -37° (see equation IV-21).

Dielectric constants of 85% acetone were found by extrapolation of Akerlof's data,[84] using equation IV-25[41b],

$$\log D = 1.4594 - .00214\ (T - 293.16) \quad . \quad . \quad \text{Eqn. IV-25}$$

where D is the dielectric constant of 85% acetone at the absolute temperature, T.

Viscosities of 85% acetone were measured at five temperatures from +20° to -27° by means of a conventional Ostwald relative viscometer, the time taken for a constant volume of liquid to pass through a capillary under the force of gravity being determined with a stopwatch. Water was used as the standard for comparison. The method also required a knowledge of the density of 85% acetone at the various temperatures; this was determined pyknometrically. The results are shown in Table IV-12. A plot of $1/\eta$ against $1/T$, where η is in centipoises and T is the absolute temperature, is linear and can be represented by equation IV-26,

TABLE IV-12.

The density and viscosity of 85% acetone from +20° to - 27°.

Temp. °C	Density (gm./ml.)[a]	Time of liquid fall (sec.)[a] Water	Time of liquid fall (sec.)[a] 85% acetone	Viscosity (cp.)[b] (observed)	Viscosity (cp.) (calc. Eqn. IV-26).
20.00	0.8434	25.42	21.96	0.731	0.730
0.00	0.8637	-	25.78	0.879	0.880
-10.00	0.8729	-	28.78	0.990	0.991
-19.90	0.8820	-	32.98	1.146	1.148
-26.90	0.8893	-	37.32	1.308	1.311

a) The mean of several experiments.

b) Assuming viscosity of water at 20° = 1.0019 cp.[128] and density of water at 20° = 0.99823 gm./ml.[128]

$$1/\eta = 1.031 - 925.6\ ({}^{1}/T - .003776) \quad . \quad . \quad . \quad \text{Eqn.IV-26.}$$

The values of η at the required temperatures could thus be obtained.

APPENDIX IV-2.

Details of Individual Runs.

First order rate constants were calculated from the equation,

$$k = (2.303 / t).\log \left[a/(a-x)\right]$$

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

t is the time in seconds,

a is the concentration of organic halide at t = 0,

a-x is the concentration of organic halide at t = t.

Titres are expressed in ml. of NaOH or $AgNO_3$ per sample.

In each case details of one run are given and the mean rate coefficients, k', of duplicate runs are also quoted.

Expt.1 p-Anisylbenzyl Chloride in 70% aq.Acetone I at 40.04°C

5.817 ml. titrated with 0.004065 N NaOH.

Time	Titre	$10^6 k$
0	0.03	-
60000	1.33	2.068
86400	1.86	2.076
149400	3.05	2.114
183600	3.59	2.096
234000	4.27	2.046
320400	5.39	2.046
493200	7.12	2.049
579600	7.80	2.059
666000	8.43	2.102
748800	8.87	2.102
∞	11.18	-

$10^6 k$ = 2.076 (10 readings)
$10^6 k'$ = 2.069 (10 readings)
Mean k = $(2.073 \pm 0.00550).10^{-6}$.

Expt.2 p-Anisylbenzyl Chloride in 70% aq.Acetone I at 50.58°C

5.817 ml. titrated with 0.004065 N NaOH.

Time	Titre	10^6 k
0	0.09	-
13740	1.06	6.939
25680	1.83	6.933
83400	4.82	7.030
111600	5.91	7.076
171900	7.57	7.037
256500	8.95	6.934
∞	10.75	-
0	0.11	-
57000	3.63	7.046
75900	4.47	6.945
145500	6.93	7.042
230100	8.64	7.033
∞	10.75	-

10^6 k = 7.002 (10 readings)
10^6 k' = 6.982 (10 readings)
Mean k = (6.992 ± 0.0114).10^{-6}.

Expt.3 p-Anisylbenzyl Chloride in 70% aq.Acetone I at 65.91°C

5.817 ml. titrated with 0.004065 N NaOH.

Time	Titre	10^5 k
0	0.16	-
3600	1.36	3.430
6300	2.22	3.532
9900	3.18	3.494
13500	4.01	3.455
18900	5.21	3.551
24300	6.03	3.457
31500	7.01	3.454
38700	7.78	3.458
∞	10.49	-
0	0.10	-
46200	8.42	3.493
54000	8.89	3.465
∞	10.49	-

10^5 k = 3.479 (10 readings)
10^5 k' = 3.495 (10 readings)
Mean k =$(3.487 \pm 0.00936).10^{-5}$.

Expt.4 p-Anisylbenzyl Chloride in 70% aq.Acetone I at 80.21°C

5.817 ml. titrated with 0.003906 N NaOH.

Time	Titre	10^4 k
0	0.11	-
600	1.01	1.347
1260	1.92	1.347
1980	2.82	1.345
2880	3.83	1.344
3600	4.57	1.349
4680	5.49	1.333
5940	6.50	1.349
7380	7.40	1.344
9660	8.57	1.355
11940	9.38	1.348
∞	11.70	-

10^4 k = 1.346 (10 readings)

10^4 k' = 1.349 (5 readings)

Mean k = $(1.347 \pm 0.00145).10^{-4}$.

Expt.5 p-Anisylbenzyl Chloride in 70% aq.Acetone I at 95.40°C

5.817 ml. titrated with 0.003906 N NaOH.

Time	Titre	10^4 k
0	0.35	-
240	1.62	4.914
425	2.50	4.899
600	3.29	4.951
780	4.02	4.957
1020	4.89	4.953
∞	11.80	-
0	0.34	-
1380	5.98	4.910
1740	6.90	4.884
2100	7.70	4.896
2520	8.45	4.882
3120	9.35	4.945
3720	9.95	4.904
∞	11.80	-

10^4 k = 4.918 (11 readings)
10^4 k' = 4.910 (11 readings)
Mean k $= (4.914 \pm 0.00684).10^{-4}$.

Expt.6 p-Phenoxybenzyl Chloride in 70% aq.Acetone I at 29.41°C

5.817 ml. titrated with 0.004006 N NaOH.

Time	Titre	10^6 k
0	0.13	-
10800	0.80	6.056
26100	1.68	6.071
82500	4.31	6.099
95760	4.80	6.087
108780	5.27	6.122
169200	6.91	6.063
193500	7.45	6.095
255300	8.45	6.060
∞	10.70	-
0	0.14	-
55500	3.18	6.116
68760	3.78	6.146
142200	6.26	6.092
∞	10.70	-

10^6 k = 6.092 (11 readings)
10^6 k' = 6.072 (11 readings)
Mean k $= (6.082 \pm 0.00802).10^{-6}$

Expt.7 p-Phenoxybenzyl Chloride in 70% aq.Acetone I at 40.07°C

5.817 ml. titrated with 0.004065 N NaOH.

Time	Titre	10^5 k
0	0.25	-
3600	1.04	2.201
7200	1.73	2.143
14400	3.02	2.162
21600	4.15	2.189
28800	5.08	2.183
36000	5.87	2.175
86100	8.98	2.154
97200	9.34	2.166
∞	10.60	-

0	0.30	-
49200	7.07	2.177
60300	7.83	2.178
∞	10.60	-

10^5 k = 2.173 (10 readings)

10^5 k' = 2.178 (10 readings)

Mean k $=(2.175 \pm 0.00476).10^{-5}$

Expt.8 p-Phenoxybenzyl Chloride in 70% aq.Acetone I at 50.68°C

5.817 ml. titrated with 0.004006 N NaOH.

Time	Titre	10^5 k
0	0.24	-
1800	1.49	6.972
3600	2.59	6.966
5400	3.59	7.042
7200	4.42	6.971
9000	5.20	7.021
10800	5.81	6.910
13200	6.38	(6.567)
15900	7.31	6.928
18300	7.83	6.893
21900	8.57	7.055
∞	10.83	-

10^5k = 6.973 (9 readings)
10^5k' = 6.969 (10 readings)
Mean k =(6.971 ± 0.0147).10^{-5}

Expt.9 p-Phenoxybenzyl Chloride in 70% aq.AcetoneIat 60.19°C

5.817 ml. titrated with 0.004065 N NaOH.

Time	Titre	10^4 k
0	0.34	-
480	1.17	1.784
1080	2.13	1.806
1800	3.15	1.813
2460	3.98	1.818
3240	4.84	1.823
4020	5.58	1.823
5700	6.90	1.843
6720	7.41	1.795
7680	8.01	1.859
8160	8.19	1.845
∞	10.43	-

10^4k = 1.821 (10 readings)
10^4k' = 1.824 (10 readings)
Mean k = $(1.823 \pm 0.00468).10^{-4}$

Expt.10 p-Phenoxybenzyl Chloride in 70% aq. Acetone I at 69.47°C

5.817 ml. titrated with 0.004006 N NaOH.

Time	Titre	10^4 k
0	0.27	-
240	1.32	4.357
420	2.03	4.332
660	2.89	4.313
1080	4.20	4.303
1320	4.89	4.353
1800	6.07	4.420
2220	6.82	4.354
2820	7.72	4.328
3300	8.39	4.430
3780	8.79	4.339
∞	10.84	-

10^4 k = 4.353 (10 readings)
10^4 k' = 4.354 (9 readings)
Mean k = $(4.353 \pm 0.00895).10^{-4}$

Expt. 11 Benzyl Bromide in 99.5% Formic Acid I at 80.17°C

6.216 ml. titrated with 0.01071 N $AgNO_3$.
No added base.

Time	Titre	10^4 k
0	0.12	-
1260	2.62	1.707
2100	3.82	1.608
2700	4.54	1.552
3600	5.36	1.445
4200	5.86	1.399
4800	6.24	1.338
5400	6.40	1.233
6300	6.79	1.153
7200	6.99	1.054
9000	7.19	0.881
∞	13.04	-

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Expt. 12 Benzyl Bromide in 99.5% Formic Acid I at 80.17°C

6.216 ml. titrated with 0.01071 N $AgNO_3$.
Added Piperidine 0.016 M.

Time	Titre	10^4 k
0	2.02	-
600	2.97	1.520
1200	3.94	1.615
2100	5.10	1.582
2700	5.78	1.569
3600	6.65	1.538
4500	7.39	1.510
5400	8.02	1.483
6360	8.59	1.453
7440	9.27	1.473
9060	9.57	1.305
10740	9.97	1.219
∞	12.91	-

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Expt. 13 Benzyl Bromide in 99.5% Formic Acid I at 80.17°C

6.216 ml. titrated with 0.009775 N $AgNO_3$.
Added Piperidine 0.033 M.

Time	Titre	10^4 k
0	0.35	-
600	1.53	1.624
1200	2.63	1.646
1800	3.54	1.604
2460	4.53	1.619
3000	5.22	1.609
3600	6.03	1.644
4500	6.93	1.619
5520	7.80	1.597
7140	8.92	1.569
9060	10.09	1.603
∞	13.07	-

10^4 k = 1.613 ± 0.00681 (10 readings)

Expt. 14 Benzyl Bromide in 99.5% Formic Acid I at 80.17°C

6.216 ml. titrated with 0.009311 N $AgNO_3$.
Added Piperidine 0.1 M.

Time	Titre	10^4 k
0	0.64	-
600	1.95	1.754
1200	3.15	1.773
1800	4.23	1.779
2460	5.34	1.807
3000	6.09	1.795
3600	6.83	1.778
4500	7.82	1.767
5520	8.82	1.776
7620	10.37	1.784
9060	11.10	1.771
∞	13.73	-

10^4 k = 1.778 ± 0.00441 (10 readings)

Expt. 15 Benzyl Bromide in 99.5% Formic Acid I at 80.17°C.

6.216 ml. titrated with 0.009311 N $AgNO_3$.
Added Triethylamine 0.033 M.

Time	Titre	10^4 k
0	0.32	-
600	1.43	(1.481)
1200	2.54	1.556
1800	3.53	1.571
2460	4.49	1.570
3000	5.23	1.578
3600	6.02	1.599
4500	6.97	1.589
5520	7.83	1.557
7620	9.37	1.559
9060	10.24	1.584
∞	13.34	-

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10^4 k = 1.574 ± 0.00475 (9 readings)

Expt. 16 Benzyl Bromide in 99.5% Formic Acid I at 80.17°C.

6.216 ml. titrated with 0.009311 N $AgNO_3$.
Added Triethylamine 0.05 M.

Time	Titre	10^4 k
0	0.31	-
600	1.55	1.581
1200	2.73	1.617
1800	3.81	1.636
2460	4.88	1.647
3000	5.68	1.656
3600	6.43	1.642
4500	7.49	1.647
5520	8.35	1.599
7620	10.06	1.628
9060	10.92	1.639
∞	14.03	-

10^4 k = 1.629 ± 0.00710 (10 readings)

Expt.17 Benzyl Bromide in 99.5% Formic Acid I at 40.15°C.

6.216 ml. titrated with 0.009311 N $AgNO_3$.
Added Piperidine 0.05 M.

Time	Titre	10^6 k
0	0.24	-
22080	1.05	2.994
55800	2.23	3.067
84600	3.13	3.063
111300	3.93	3.095
141000	4.64	3.028
169800	5.32	3.021
198400	6.00	3.061
226800	6.55	3.043
255600	7.06	3.028
345600	8.45	3.026
432000	9.53	3.064
∞	12.90	-

10^6 k = 3.045 (11 readings)
10^6 k' = 2.988 (11 readings)
Mean k =$(3.017 \pm 0.0118).10^{-6}$

Expt.18 Benzyl Bromide in 99.5% Formic Acid I at 60.18°C.

6.216 ml. titrated with 0.009311 N $AgNO_3$.
Added Piperidine 0.05 M.

Time	Titre	10^5 k
0	0.28	-
5400	2.11	2.696
14400	4.59	2.671
18120	5.46	2.671
22500	6.34	2.648
27000	7.24	2.684
32760	8.12	2.655
39600	9.10	2.676
48180	10.00	2.642
58200	10.91	2.662
73800	11.90	2.672
90030	12.56	2.671
oo	13.78	-

10^5 k = 2.668 (11 readings)
10^5 k' = 2.651 (11 readings)
Mean k =(2.659 ± 0.00398).10^{-5}

Expt.19 Benzyl Bromide in 99.5% Formic Acid I at 80.17°C.

6.216 ml. titrated with 0.009311 N $AgNO_3$.
Added Piperidine 0.05 M.

Time	Titre	10^4 k
0	0.36	-
600	1.53	(1.592)
1200	2.67	1.652
1800	3.66	1.649
2460	4.67	1.662
3000	5.42	1.669
3600	6.15	1.664
4500	7.13	1.663
5520	8.06	1.657
7620	9.59	1.663
9060	10.37	1.666
∞	13.21	-

10^4 k = 1.661 (9 readings)
10^4 k' = 1.672 (10 readings)
Mean k $= (1.667 \pm 0.00443).10^{-4}$

Expt.20 p-Methylbenzyl Bromide in 99.5% Formic Acid I at 20.51°C

5.00 ml. titrated with 0.009311 N $AgNO_3$.
Added Piperidine 0.05 M.

Time	Titre	10^5 k
0	0.44	-
8085	1.54	1.396
14745	2.33	1.374
20100	2.92	1.369
27540	3.65	1.355
36240	4.46	1.363
47490	5.35	1.362
60330	6.20	1.356
68610	6.67	1.351
76470	7.15	1.376
88350	7.66	1.364
95970	7.95	1.358
oo	10.75	-

10^5 k = 1.366 (11 readings)
10^5 k' = 1.377 (11 readings)
Mean k $=(1.372 \pm 0.00293).10^{-5}$

Expt.21 p-Methylbenzyl Bromide in 99.5% Formic Acid I at 40.15°C

5.00 ml. titrated with 0.009311 N $AgNO_3$.
Added Piperidine 0.05 M.

Time	Titre	10^4 k
0	0.61	-
585	1.58	(1.386)
930	2.23	1.496
1260	2.76	1.501
1725	3.46	1.502
2340	4.35	1.522
3060	5.29	1.535
3780	6.07	1.521
4800	7.08	1.522
6255	8.33	1.539
7845	9.32	1.524
9825	10.30	1.523
11190	10.83	1.524
∞	13.10	-

10^4k = 1.519 (11 readings)
$10^4k'$ = 1.518 (10 readings)
Mean k $= (1.519 \pm 0.00246).10^{-4}$

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Expt.22 p-Phenylbenzyl Bromide in 99.5% Formic Acid I at 20.51°C

5.00 ml. titrated with 0.009311 N $AgNO_3$.
Added Piperidine 0.05 M.

Time	Titre	10^6 k
0	0.67	-
14340	1.23	(4.690)
27540	1.76	4.884
83700	3.56	4.852
107000	4.20	4.895
169200	5.52	4.853
193400	5.91	4.804
256100	6.84	4.867
345600	7.71	4.851
∞	9.33	-
0	0.97	-
45120	2.63	4.905
67680	3.30	4.829
132900	4.96	4.882
∞	9.33	-

10^6 k = 4.862 (10 readings)
10^6 k' = 4.856 (10 readings)
Mean k = $(4.859 \pm 0.00692).10^{-6}$

Expt.23 p-Phenylbenzyl Bromide in 99.5% Formic Acid I at 40.15°C.

5.00 ml. titrated with 0.009311 N $AgNO_3$.
Added Piperidine 0.05 M.

Time	Titre	10^5 k
0	1.33	-
1260	2.01	6.598
1920	2.35	6.633
2955	2.83	6.555
4020	3.33	6.658
6000	4.10	6.551
9000	5.13	6.564
12360	6.07	6.575
16320	6.93	6.561
19740	7.52	6.569
23220	8.00	6.577
∞	9.85	-

10^5 k = 6.584 (10 readings)
10^5 k' = 6.577 (11 readings)
Mean k =(6.580 ± 0.00678).10^{-5}

Expt.24 p-Fluorobenzyl Bromide in 99.5% Formic Acid I at 60.18°C

3.712 ml. titrated with 0.009311 N $AgNO_3$.
Added Piperidine 0.05 M.

Time	Titre	10^5 k
0	0.39	-
1080	0.98	(5.480)
2280	1.33	4.223
3660	1.85	4.197
5760	2.63	4.283
7920	3.27	4.164
10800	4.10	4.160
14400	4.98	4.124
18000	5.83	4.205
22320	6.55	4.117
25920	7.14	4.147
29880	7.64	4.112
∞	10.64	-

10^5 k = 4.173 (10 readings)
10^5 k' = 4.174 (10 readings)
Mean k =(4.174 ± 0.0107).10^{-5}

Expt.25 p-Fluorobenzyl Bromide in 99.5% Formic Acid I at 80.17°C

3.712 ml. titrated with 0.009311 N $AgNO_3$.
Added Piperidine 0.05 M.

Time	Titre	10^4 k
0	0.53	-
540	1.90	2.700
960	2.84	2.706
1380	3.72	2.754
1800	4.45	2.732
2280	5.19	2.717
2820	5.88	2.679
3420	6.56	2.662
3840	6.96	2.641
4740	7.76	2.660
5820	8.50	2.681
6960	9.04	2.665
∞	10.62	-

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10^4 k = 2.691 (11 readings)
10^4 k' = 2.681 (11 readings)
Mean k =$(2.686 \pm 0.00781).10^{-4}$

Expt.26 m-Chlorobenzyl Bromide in 99.5% Formic Acid I at 80.17°C

3.712 ml. titrated with 0.009206 N $AgNO_3$.
Added Piperidine 0.05 M .

Time	Titre	10^5 k
0	0.31	-
600	0.44	1.880*
1200	0.58	1.954*
1800	0.71	1.930*
2400	0.83	1.881*
3000	0.97	1.910*
7740	1.89	1.904
11580	2.62	1.932
14820	3.05	1.832
18420	3.64	1.852
22320	4.20	1.846
∞	11.83	-

10^5 k = 1.892 (10 readings)
10^5 k' = 1.910 (10 readings)
Mean k =$(1.901 \pm 0.0104).10^{-5}$

Note. *Signifies first order rate constant calculated according to the approximation $k = \frac{x}{at}$ for initial rates (see p. 166).

k is the rate constant in sec^{-1}.
a is the concentration of organic halide at t = 0.
t is the time in seconds.

Expt.27 p-Nitrobenzyl Bromide in 99.5% Formic Acid I at 80.17°C.

3.712 ml. titrated with 0.009206 N $AgNO_3$.
Added Piperidine 0.05 M.

Time	Titre	10^6 k
0	0.24	-
6300	0.37	2.005*
12360	0.54	2.359*
16800	0.63	2.256*
21600	0.73	2.205*
25200	0.84	2.314*
28800	0.91	2.261*
77400	1.85	2.199
102600	2.33	2.213
164700	3.37	2.203
248400	4.52	2.165
∞	10.53	-

10^6 k = 2.218 (10 readings)
10^6 k' = 2.150 (10 readings)
Mean k =$(2.184 \pm 0.0213).10^{-6}$

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* See footnote, p.206

Expt.28 p-Nitrobenzyl Bromide in 99.5% Formic Acid I at 80.17°C

3.712 ml. titrated with 0.009206 N $AgNO_3$.
Added Piperidine 0.1 M.

Time	Titre	10^6 k
0	0.24	-
3600	0.36	2.822*
7200	0.48	2.822*
10800	0.60	2.822*
14400	0.76	3.057*
18000	0.86	2.916*
21600	0.98	2.900*
25200	1.10	2.889*
86400	2.90	2.956
∞	12.05	-

Mean k = $(2.898 \pm 0.0269).10^{-6}$

* See footnote, p. 206

Expt.29 p-Methylbenzyl Chloride in 99.5% Formic Acid II at 20.56°C.

5.00 ml. titrated with 0.009206 N $AgNO_3$.
Added Piperidine 0.05 M.

Time	Titre	10^6 k
0	0.25	-
18000	1.83	9.365
25200	2.36	9.210
32400	2.90	9.303
37800	3.28	9.346
85200	5.78	9.198
95220	6.24	9.326
108000	6.73	9.374
172800	8.40	9.333
∞	10.43	-

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Time	Titre	10^6 k
0	0.76	-
49200	4.33	9.365
57720	4.78	9.311
140400	7.82	9.330
∞	10.43	-

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10^6 k = 9.315 (11 readings)
10^6 k' = 9.306 (11 readings)
Mean k = $(9.311 \pm 0.0136).10^{-6}$
Corrected to Formic Acid I, k = $(9.509 \pm 0.0139).10^{-6}$

Expt.30 p-Methylbenzyl Chloride in 99.5% Formic Acid II at 40.15°C.

5.00 ml. titrated with 0.009206 N $AgNO_3$.
Added Piperidine 0.05 M.

Time	Titre	10^4 k
0	0.59	-
1560	2.13	1.042
3000	3.37	1.052
4680	4.58	1.052
6300	5.54	1.044
8100	6.44	1.041
10200	7.34	1.051
12300	7.97	1.031
14400	8.55	1.036
17100	9.14	1.046
19800	9.54	1.036
∞	10.86	-

10^4 k = 1.043 (10 readings)
10^4 k' = 1.059 (10 readings)
Mean k =(1.051 ± 0.00264).10^{-4}
Corrected to Formic Acid I, k =(1.073 ± 0.00270).10^{-4}

Expt. 31 Benzyl Chloride in 99.5% Formic Acid II at 80.17°C

3.712 ml. titrated with 0.009206 N $AgNO_3$.
Added Piperidine 0.05 M.

Time	Titre	10^5 k
0	0.42	-
1200	1.14	6.409
2700	1.97	6.422
4200	2.76	6.552
6000	3.58	6.543
8700	4.61	6.476
12000	5.70	6.519
15600	6.63	6.519
18600	7.23	6.473
22260	7.82	6.421
25800	8.28	6.395
∞	10.15	-

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10^5 k = 6.473 (10 readings)
10^5 k' = 6.459 (10 readings)
Mean k =(6.466 ± 0.0121).10^{-5}
Corrected to Formic Acid I, k =(6.603 ± 0.0123).10^{-5}

Expt.32 Benzyl Chloride in 99.5% Formic Acid II at 80.17°C.

3.712 ml. titrated with 0.009206 N $AgNO_3$.
Added Piperidine 0.1 M.

Time	Titre	10^5 k
0	0.22	-
1500	1.21	6.863
3000	2.08	6.772
5400	3.33	6.803
7200	4.14	6.806
9000	4.92	6.940
10860	5.53	6.852
13500	6.32	6.841
16800	7.12	6.819
20100	7.74	6.763
23400	8.30	6.847
∞	10.34	-

Mean k = 6.831 ± 0.0153 (10 readings)

Corrected to Formic Acid I, 10^5 k = 6.976 ± 0.0156

Expt.33 p-Methoxybenzyl Chloride in 99.5% Formic Acid II at 9.70°C.

Samples titrated with 0.009206 N $AgNO_3$.

Added Piperidine 0.05 M.

The technique of rate measurement is described in Chapter IV, (p. 158)

Time	Titre	10^2 k
0	0.00	-
6.1	4.74	7.261
9.3	6.33	6.985
10.5	6.94	7.068
13.7	8.22	7.069
16.8	9.16	6.998
20.5	9.97	6.811
∞	13.25	-

Mean k = 7.032 ± 0.0546 (6 readings)

Corrected to Formic Acid I, k =(7.182 ± 0.0558).10^{-2}

Expt.34 pp'-Dinitro-benzhydryl Chloride in 70% Acetone III at 147.18°C.

5.817 ml. titrated with 0.004170 N NaOH.

Time	Titre	10^5 k
0	0.10	-
1200	0.82	6.026
3000	1.84	6.149
4800	2.72	6.094
7200	3.76	6.078
10500	4.99	6.108
∞	10.43	-

Time	Titre	10^5 k
0	0.12	-
12960	5.72	6.047
15960	6.53	6.091
19260	7.21	6.043
22500	7.81	6.089
24300	8.10	6.122
∞	10.43	-

10^5 k = 6.085 (10 readings)

10^5 k' = 6.060 (9 readings)

Mean k =$(6.073 \pm 0.00898).10^{-5}$

Corrected to 70% Acetone A, k =$(6.387 \pm 0.00944).10^{-5}$

Expt.35 pp'-Dinitro-benzhydryl Chloride in 70% AcetoneIII at 121.60°C.

5.817 ml. titrated with 0.004170 N NaOH.

Time	Titre	10^6 k
0	0.00	-
29340	2.26	8.155
40140	2.98	8.206
86820	5.40	8.183
113700	6.46	8.243
189060	8.30	8.044
∞	10.62	-

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Time	Titre	10^6 k
0	0.00	-
50580	3.58	8.127
62940	4.23	8.071
75000	4.91	8.275
133200	7.01	8.102
150720	7.52	8.172
∞	10.62	-

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10^6 k = 8.158 (10 readings)

10^6 k' = 8.119 (10 readings)

Mean k =$(8.138 \pm 0.0161).10^{-6}$

Corrected to 70% Acetone A, k =$(8.559 \pm 0.0170).10^{-6}$

Expt.36 p-Chloro p'-Nitro-benzhydryl Chloride in 70% AcetoneIII at 94.66°C.

5.817 ml. titrated with 0.004181 N NaOH.

Time	Titre	10^4 k
0	0.18	-
540	2.17	3.544
900	3.29	3.532
1260	4.27	3.517
1680	5.24	3.481
2100	6.14	3.510
2640	7.05	3.481
3240	7.91	3.482
3840	8.70	3.563
4800	9.54	3.561
5640	10.04	3.521
∞	11.61	-

10^4 k = 3.519 (10 readings)

10^4 k' = 3.526 (10 readings)

Mean k $=(3.523 \pm 0.00819).10^{-4}$

Corrected to 70% Acetone A, k $=(3.709 \pm 0.00862).10^{-4}$

Expt.37 p-Chloro p'-Nitro-benzhydryl Chloride in 70% AcetoneIII at 79.33°C.

5.817 ml. titrated with 0.004181 N NaOH.

Time	Titre	10^5 k
0	0.03	-
2220	2.13	9.003
3300	3.00	8.974
4560	3.94	9.031
5880	4.82	9.074
7260	5.56	8.939
8760	6.37	9.053
10440	7.11	9.053
12840	7.96	8.991
15540	8.76	9.024
19140	9.56	9.046
∞	11.61	-

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10^5 k = 9.019 (10 readings)
10^5 k' = 9.011 (10 readings)
Mean k =(9.015 ± 0.0107).10^{-5}
Corrected to 70% Acetone A, k =(9.490 ± 0.0113).10^{-5}

Expt.38 p-Fluoro p'-Nitro-benzhydryl Chloride in 70% Acetone II at 79.32°C.

5.817 ml. titrated with 0.004181 N NaOH.

Time	Titre	10^4 k
0	0.40	-
180	1.47	5.093
360	2.44	5.079
600	3.63	5.121
900	4.93	5.151
1200	6.02	5.140
1440	6.80	5.158
1740	7.62	5.144
2100	8.50	5.186
2460	9.20	5.186
3000	9.97	5.106
∞	12.61	-

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10^4k = 5.136 (10 readings)
$10^4k'$ = 5.133 (10 readings)
Mean k =$(5.135 \pm 0.00844)\cdot 10^{-4}$
Corrected to 70% Acetone A, k =$(5.406 \pm 0.00889).10^{-4}$

Expt.39 p-Fluoro p'-Nitro-benzhydryl Chloride in 70% Acetone II at 59.90°C.

5.817 ml. titrated with 0.004181 N NaOH.

Time	Titre	10^5 k
0	0.24	-
2760	2.52	(7.936)
4020	3.47	8.125
5340	4.32	8.127
6720	5.11	8.108
8160	5.85	8.110
9960	6.68	8.141
11760	7.36	8.102
14340	8.20	8.097
17520	9.05	8.151
21180	9.79	(8.204)
∞	11.83	-

10^5k = 8.120 (8 readings)

$10^5k'$ = 8.117 (10 readings)

Mean k =$(8.118 \pm 0.00447).10^{-5}$.

Corrected to 70% Acetone A, k =$(8.546 \pm 0.00471).10^{-5}$.

Expt.40 p-Phenyl p'-Nitro-benzhydryl Chloride in 70% AcetoneIII at 60.03°C.

5.817 ml. titrated with 0.004170 N NaOH.

Time	Titre	10^4 k
0	0.71	-
300	1.82	3.977
600	2.81	3.987
900	3.70	4.010
1200	4.47	3.997
1500	5.20	4.046
1920	6.00	3.998
2340	6.67	3.958
2820	7.41	4.028
3300	7.96	4.020
3900	8.52	4.018
4860	9.19	4.034
∞	10.58	-

10^4k = 4.007 (11 readings)

$10^4k'$ = 4.021 (11 readings)

Mean k =(4.014 ± 0.00576).10^{-4}.

Corrected to 70% Acetone A, k =(4.222 ± 0.00606).10^{-4}.

Expt.41 p-Phenyl p'-Nitro-benzhydryl Chloride in 70% AcetoneIII at 40.05°C.

5.817 ml. titrated with 0.004170 N NaOH.

Time	Titre	10^5 k
0	0.40	-
2940	1.66	4.567
4920	2.44	4.625
6780	3.10	4.627
9660	4.01	4.620
13380	5.04	4.641
17100	5.92	4.674
21900	6.78	4.617
26100	7.45	4.651
30300	7.99	4.667
35640	8.52	4.655
∞	10.43	-

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10^5k = 4.624 (10 readings)
$10^5k'$ =(4.642 (10 readings)
Mean k =(4.633 ± 0.00788).10^{-5}.
Corrected to 70% Acetone A, k = 4.873 ± 0.00829).10^{-5}.

Expt.42 p-Tert.-butyl p'-Nitro-benzhydryl Chloride in 70% Acetone II at 59.90°C.

5.817 ml. titrated with 0.004181 N NaOH.

Time	Titre	10^4 k
0	0.48	-
180	1.40	(4.388)
380	2.48	4.745
580	3.35	4.658
840	4.46	4.735
1200	5.70	4.690
1560	6.82	4.742
1980	7.82	4.693
2460	8.85	4.763
3000	9.73	4.794
3600	10.41	4.743
∞	12.61	-

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10^4k = 4.729 (9 readings)

$10^4k'$ = 4.706 (10 readings)

Mean k =(4.717 ± 0.00920).10^{-4}.

Corrected to 70% Acetone A, k =(4.966 ± 0.00969).10^{-4}.

Expt.43 p-Tert.-butyl p'-Nitro-benzhydryl Chloride in 70% Acetone II at 40.05°C.

5.817 ml. titrated with 0.004181 N NaOH.

Time	Titre	10^5 k
0	0.42	-
1800	1.69	(5.654)
3600	2.79	5.540
5640	3.91	5.488
7620	4.92	5.518
9660	5.86	5.550
12360	6.92	5.543
15840	8.12	5.589
19740	9.12	5.522
22860	9.84	5.547
26580	10.56	5.588
∞	13.53	-

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10^5k = 5.543 (9 readings)

10^5k' = 5.543 (10 readings)

Mean k =(5.543 ± 0.00641).10^{-5}.

Corrected to 70% Acetone A, k =(5.835 ± 0.00675).10^{-5}.

Expt.44 p-Methyl p'-Nitro-benzhydryl Chloride in 70% Acetone II at 40.05°C.

5.817 ml. titrated with 0.004141 N NaOH.

Time	Titre	10^4 k
0	0.37	-
600	1.27	1.443
1200	2.09	1.440
1980	3.05	1.434
2760	3.90	1.428
3600	4.75	1.437
4440	5.51	1.447
6000	6.67	1.450
7260	7.40	1.441
8580	8.10	1.455
10080	8.70	1.452
12900	9.53	1.445
∞	11.21	-

10^4k = 1.443 (11 readings)

10^4k' = 1.448 (11 readings)

Mean k =(1.445 ± 0.00191).10^{-4}.

Corrected to 70% Acetone A, k =(1.521 ± 0.00201).10^{-4}.

Expt.45 p-Methyl p'-Nitro-benzhydryl Chloride in 70% Acetone II at 20.57°C.

5.00 ml. titrated with 0.004141 N NaOH.

Time	Titre	10^5 k
0	0.10	-
11580	1.56	1.373
16980	2.18	1.383
23820	2.88	1.379
29460	3.43	1.387
35100	3.93	1.389
115200	8.01	1.382
∞	10.03	-

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Time	Titre	10^5 k
0	0.20	-
45600	4.78	1.376
53460	5.32	1.377
63900	5.92	1.366
71640	6.34	1.369
∞	10.03	-

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10^5k = 1.378 (10 readings)
10^5k' = 1.376 (10 readings)
Mean k =$(1.377 \pm 0.00193).10^{-5}$.
Corrected to 70% Acetone A, k =$(1.450 \pm 0.00203).10^{-5}$.

Expt.46 p-Phenoxy p'-Nitro-benzhydryl Chloride in 70% AcetoneII at 20.60°C.

5.00 ml. titrated with 0.004405 N NaOH.

Time	Titre	10^4 k
0	0.82	-
180	1.80	(6.754)
365	2.65	6.582
572	3.50	6.558
765	4.20	6.557
1002	4.95	6.563
1245	5.59	6.533
1551	6.33	6.642
1876	6.91	6.612
2472	7.68	6.521
2930	8.16	6.627
3455	8.52	6.622
∞	9.39	-

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10^4k = 6.582 (10 readings)

$10^4k'$ = 6.584 (11 readings)

Mean k =$(6.583 \pm 0.00827).10^{-4}$.

Corrected to 70% Acetone A, k =$(6.930 \pm 0.00871).10^{-4}$.

Expt.47 p-Phenoxy p'-Nitro-benzhydryl Chloride in 70% AcetoneII at 0.00°C.

5.00 ml. titrated with 0.004405 N NaOH.

Time	Titre	10^5 k
0	0.19	-
2440	1.02	5.360
4550	1.64	5.301
6095	2.06	5.304
8695	2.71	5.356
12660	3.49	5.281
16825	4.15	5.225
20070	4.60	5.253
24210	5.06	5.249
27765	5.41	5.310
∞	6.96	-

$10^5 k$ = 5.293 (9 readings)
$10^5 k'$ = 5.302 (9 readings)
Mean k $= (5.298 \pm 0.00984) . 10^{-5}$.
Corrected to 70% Acetone A, k $= (5.577 \pm 0.0104) . 10^{-5}$.

Expt.48 p-Nitro-benzhydryl Chloride in 85% Acetone II at 120.96°

5.817 ml. titrated with 0.004170 N NaOH.

Time	Titre	10^4 k
0	0.21	-
300	0.98	(2.695)
600	1.83	2.979
900	2.53	2.966
1200	3.17	2.959
1560	3.91	3.000
1980	4.63	2.986
2520	5.50	3.033
3180	6.31	3.011
3960	7.10	3.007
4920	7.88	3.030
5520	8.22	3.000
∞	10.11	-

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10^4k = 2.997 (10 readings)

$10^4k'$ = 2.987 (11 readings)

Mean k =$(2.992 \pm 0.00632).10^{-4}$.

Corrected to 85% Acetone A, k =$(3.428 \pm 0.00724).10^{-4}$.

Expt.49 p-Nitro-benzhydryl Chloride in 85% Acetone II at 99.45°C

5.817 ml. titrated with 0.004170 N NaOH.

Time	Titre	10^5 k
0	0.06	-
1920	1.22	6.130
3900	2.30	6.183
5640	3.18	6.285
7560	3.98	6.215
9660	4.78	6.215
12180	5.62	6.229
14760	6.30	6.153
18600	7.18	6.141
22440	7.87	6.120
25560	8.39	6.229
∞	10.52	-

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10^5k = 6.190 (10 readings)

$10^5k'$ = 6.215 (10 readings)

Mean k =$(6.202 \pm 0.0139).10^{-5}$.

Corrected to 85% Acetone A, k =$(7.105 \pm 0.0159).10^{-5}$.

Expt.50 p-Anisyl p'-Nitro-benzhydryl Chloride in 85% Acetone II at 59.92°C.

5.817 ml. titrated with 0.004405 N NaOH.

Time	Titre	10^4 k
0	0.53	-
420	1.72	2.988
660	2.38	3.071
960	3.10	3.066
1320	3.90	3.082
1680	4.49	2.970
2100	5.22	2.982
2760	6.16	2.962
3360	6.91	2.984
4020	7.60	3.007
4800	8.23	3.008
5400	8.61	2.995
∞	10.61	-

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10^4k = 3.010 (11 readings)
$10^4k'$ = 3.018 (10 readings)
Mean k =$(3.014 \pm 0.00841).10^{-4}$
Corrected to 85% Acetone A, k =$(3.453 \pm 0.00963).10^{-4}$

Expt.51 p-Anisyl p'-Nitro-benzhydryl Chloride in 85% Acetone II at 40.05°C.

5.817 ml. titrated with 0.004405 N NaOH.

Time	Titre	10^5 k
0	0.25	-
3660	1.63	4.310
5820	2.32	4.246
7500	2.84	4.271
10140	3.59	4.302
13080	4.28	4.251
16680	5.13	4.356
20760	5.83	4.300
24960	6.48	4.313
28380	6.90	4.286
32700	7.35	4.256
∞	9.70	-

10^5k = 4.289 (10 readings)

10^5k' = 4.302 (10 readings)

Mean k =(4.296 ± 0.00702).10^{-5}

Corrected to 85% Acetone A, k =(4.921 ± 0.00804).10^{-5}

Expt.52 p-Phenoxy p'-Nitro-benzhydryl Chloride in 85% AcetoneII at 40.06°C.

5.817 ml. titrated with 0.004405 N NaOH.

Time	Titre	10^4 k
0	1.70	-
480	2.84	2.418
960	3.83	2.386
1380	4.64	2.406
2340	6.21	2.428
2940	7.01	2.429
3660	7.77	2.391
4380	8.41	2.362
5220	9.10	2.378
6060	9.63	2.368
7200	10.20	2.356
∞	12.11	-

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10^4k = 2.392 (10 readings)

$10^4k'$ = 2.386 (11 readings)

Mean k =$(2.389 \pm 0.00469).10^{-4}$

Corrected to 85% Acetone A, k =$(2.737 \pm 0.00537).10^{-4}$

Expt.53 p-Phenoxy p'-Nitro-benzhydryl Chloride in 85% Acetone II at 20.59°C.

5.00 ml. titrated with 0.004405 N NaOH.

Time	Titre	10^5 k
0	0.13	-
4720	1.60	3.128
7130	2.27	3.127
9840	2.97	3.132
12500	3.56	3.089
16680	4.50	3.145
21220	5.28	3.090
26665	6.20	3.137
31875	6.87	3.114
36970	7.44	3.105
43225	8.02	3.088
∞	10.84	-

10^5k = 3.116 (10 readings)
$10^5k'$ = 3.106 (10 readings)
Mean k =$(3.111 \pm 0.00454).10^{-5}$
Corrected to 85% Acetone A, k =$(3.564 \pm 0.00520).10^{-5}$

Expt.54 p-Phenoxy p'-Nitro-benzhydryl Chloride in 85% AcetoneII at 0.00°C.

5.00 ml. titrated with 0.004405 N NaOH.

Time	Titre	10^6 k
0	0.05	-
83236	1.81	2.286
108320	2.28	2.289
170700	3.38	2.328
195300	3.75	2.320
255720	4.55	2.289
281640	4.87	2.285
343140	5.55	2.272
367680	5.85	2.301
426900	6.48	2.348
∞	10.21	-

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10^6k = 2.302 (9 readings)

10^6k' = 2.295 (9 readings)

Mean k =(2.299 ± 0.00533).10^{-6}

Corrected to 85% Acetone A, k =(2.634 ± 0.00611).10^{-6}

Expt.55 p-Anisyl-benzhydryl Chloride in 85% Acetone I at 20.28°C

5.00 ml. titrated with 0.004115 N NaOH.

Time	Titre	10^4 k
0	0.61	-
150	1.69	6.817
320	2.82	6.939
466	3.67	6.918
593	4.31	6.839
725	4.90	6.741
905	5.69	6.761
1215	6.82	6.747
1506	7.78	6.896
1825	8.50	6.798
2185	9.23	6.858
2630	9.90	6.896
∞	11.71	-

10^4k = 6.837 (11 readings)

10^4k' = 6.843 (11 readings)

Mean k =$(6.840 \pm 0.0147).10^{-4}$

Corrected to 85% Acetone A, k =$(7.813 \pm 0.0168).10^{-4}$

Expt.56 *p*-Anisyl-benzhydryl Chloride in 85% Acetone I at 0.00°C.

5.00 ml. titrated with 0.004115 N NaOH.

Time	Titre	10^5 k
0	0.17	-
1070	0.84	5.855
2735	1.85	6.037
4650	2.85	5.981
6715	3.81	5.961
8420	4.49	5.896
11145	5.43	5.806
14270	6.39	5.809
17220	7.27	5.985
19810	7.83	5.977
23525	8.46	5.907
∞	11.21	-

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10^5k = 5.921 (10 readings)

$10^5k'$ = 5.955 (10 readings)

Mean k =$(5.938 \pm 0.0168).10^{-5}$

Corrected to 85% Acetone A, k =$(6.782 \pm 0.0192).10^{-5}$

RATE DETERMINATION BY CONDUCTIMETRIC METHODS.

Full details of the method employed are given in Chapter IV.

First order rate constants were calculated from the equation,

$$\bar{k}_1 = (2.303 / t).\log [a/(a-x)]$$

where $\bar{k}_1$ is the rate constant in $sec.^{-1}$

t is the time in seconds,

a is the concentration of organic chloride at $t = 0$,

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

The units of concentration are $mole.l.^{-1}$

For each experiment, details of two runs are given. The rate coefficient at zero ionic strength, k_1^o , and the mass-law constant, α^o , are also quoted where applicable. (The method of calculation is shown in Chapter IV.)

All conductimetric runs were carried out in the presence of approximately 7.10^{-5} N HCl as backing electrolyte, except where stated.

Expt.57 p-Phenoxy-benzhydryl Chloride in 85% Acetone VI at 20.61°C.

Time	$\frac{10^4}{0.9750}[\mathrm{HCl}]$*	$10^3\bar{k}_1$	Time	$\frac{10^4}{0.9750}[\mathrm{HCl}]$	$10^3\bar{k}_1$
0.00	1.05	-	0.00	1.05	-
7.25	1.46	(5.114)	6.00	1.46	(5.334)
15.25	1.92	5.271	13.25	1.92	5.214
20.50	2.20	5.246	18.00	2.20	5.142
27.00	2.51	5.142	23.00	2.51	5.177
44.00	3.34	5.165	37.75	3.34	5.131
55.75	3.87	5.171	48.50	3.87	5.043
69.25	4.41	5.119	59.75	4.41	5.002
99.75	5.52	5.070	84.25	5.52	5.002
114.25	5.99	5.053	96.00	5.99	4.980
130.00	6.48	5.063	108.75	6.48	4.971
146.25	6.92	5.035	121.50	6.92	4.943
194.50	8.03	4.974	157.50	8.03	4.888
244.75	8.95	4.942	192.50	8.95	4.861
338.00	10.10	4.818	250.00	10.10	4.766
399.00	10.64	4.783	281.75	10.65	4.750
558.00	11.50	4.719	343.25	11.50	4.744
			507.00	12.83	4.670
∞	12.31	-	∞	14.05	-

$$10^3k_1^o = 5.321 \pm 0.0182 \text{ (31 readings)}$$

Corrected to 85% Acetone A, ... $= 5.232 \pm 0.0179$

$$\alpha^o = 162.4 \pm 9.1$$

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[*] The factor 0.9750, and similar factors in subsequent experiments, arises from the strength of the HCl used to calibrate conductance against HCl concentration.

Expt.58 p-Phenoxy-benzhydryl Chloride in 85% Acetone IV at 0.10°C.

Time	$\frac{10^4}{1.083}$ [HCl]	$10^4 \bar{k}_1$	Time	$\frac{10^4}{1.083}$ [HCl]	$10^4 \bar{k}_1$
0	1.73	-	0	1.71	-
106	2.41	5.106	96	2.40	5.157
239	3.20	5.069	298	3.71	5.039
334	3.72	5.027	400	4.32	5.020
451	4.34	5.020	467	4.70	5.000
528	4.71	4.986	545	5.13	4.995
619	5.14	4.971	762	6.23	4.963
873	6.24	4.938	917	6.93	4.929
1055	6.94	4.915	1096	7.65	4.873
1275	7.67	4.850	1507	9.13	4.826
1788	9.15	4.799	1720	9.77	4.793
2063	9.79	4.765	1953	10.41	4.769
2380	10.43	4.729	2200	11.02	4.752
2720	11.04	4.719	2986	12.50	4.662
3945	12.52	4.612			
∞	14.61	-	∞	16.07	-

$10^4 k_1^0$ $= 5.272 \pm 0.0101$ (27 readings)

Corrected to
85% Acetone A, ... $= 5.597 \pm 0.0107$

α^0 $= 148.9 \pm 4.0$

Note. On going from 0.10° to 0.00°, the $\bar{k}_1$ values decrease by ca.1%. Thus the initial rate for an initially ca..0015 M solution at 0.00° is $10^4 \bar{k}_1 \simeq 5.1$. The initial rate for an initially .018 M solution at 0.00° was $10^4 \bar{k}_1 \simeq 4.3$ (see Expt.59A).

Expt.59 p-Phenoxy-benzhydryl Chloride in 85% Acetone IV at 0.10°C.

Added HCl in 85% Acetone, $(8.140).10^{-4}$ N.

Time	$\frac{10^4\,[\text{HCl}]}{1.099}$	$10^4\,\bar{k}_1$	$10^4\,\bar{k}_1$(calc.)*
0	8.83	-	-
186	10.04	4.668	4.584
408	11.28	4.527	4.524
940	13.81	4.462	4.441
1218	14.90	4.438	4.404
1550	16.02	4.402	4.363
1903	17.05	4.379	4.325
3170	19.59	4.251	4.215
4680	21.30	4.167	4.129
∞	23.37	-	-

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Time	$\frac{10^4\,[\text{HCl}]}{1.099}$	$10^4\,\bar{k}_1$	$10^4\,\bar{k}_1$(calc.)*
0	7.87	-	-
134	8.83	4.676	4.644
316	10.04	4.672	4.608
536	11.28	4.528	4.549
1050	13.81	4.480	4.466
1323	14.90	4.438	4.425
1642	16.02	4.404	4.384
1995	17.05	4.348	4.342
3210	19.59	4.203	4.229
4095	20.78	4.130	4.171
∞	23.70	-	-

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*Calculated from Eqn. III-2, p. 72, taking $\alpha^0 = 148.9$ and $10^4\,\overset{o}{k}_1{}^0 = 5.272$ (from Expt.58)

Expt.59A p-Phenoxy-benzhydryl Chloride in 85% Acetone IV at 0.00°C.

ORGANIC CHLORIDE INITIALLY 0.01787 M.

5.00 ml. titrated with 0.008333 N NaOH.

Time	Titre	$10^4\ \bar{k}_1$	$10^4\ \bar{k}_{1(calc.)}$*
0	0.80	-	-
143	1.39	4.285	4.256
300	2.03	4.345	4.219
520	2.76	4.235	3.998
775	3.50	4.102	3.802
1097	4.20	3.827	3.543
1403	4.88	3.778	3.412
1855	5.62	3.588	3.203
2251	6.20	3.493	3.068
2700	6.79	3.430	2.945
3316	7.43	3.329	2.797
∞	10.72	-	-

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*Calculated from Eqn. III-2 , p. 72 , taking α^o = 148.9 and $10^4 k_1^o$ = 5.272 (from Expt.58).

Expt.60 p-Methoxy p'-Nitro-benzhydryl Chloride in 85% Acetone V at 20.61°C.

Time	$\frac{10^4\,[HCl]}{0.9750}$	$10^3\,\bar{k}_1$	Time	$\frac{10^4\,[HCl]}{0.9750}$	$10^3\,\bar{k}_1$
0.00	1.46	-	0.00	1.46	-
14.50	1.92	2.509	12.60	1.92	2.467
24.25	2.20	2.441	20.80	2.20	2.446
35.50	2.51	2.394	30.00	2.51	2.426
66.00	3.34	2.394	55.80	3.34	2.418
87.50	3.87	2.371	73.60	3.87	2.394
112.50	4.41	2.315	93.00	4.41	2.368
165.80	5.52	2.288	136.60	5.52	2.324
191.80	5.99	2.266	157.20	5.99	2.298
219.50	6.48	2.255	179.00	6.48	2.289
247.50	6.92	2.233	200.20	6.92	2.274
326.30	8.03	2.192	258.60	8.03	2.242
404.50	8.95	2.159	314.80	8.95	2.211
533.30	10.10	2.089	401.40	10.10	2.152
663.00	11.07	2.075	465.20	10.85	2.129
830.30	11.94	2.032	571.00	11.94	2.118
1070.00	12.83	2.015	683.00	12.83	2.096
			830.00	13.72	2.070
			1035.00	14.61	2.050
∞	14.32	-	∞	16.40	-

$10^3 k_1^{\circ}$ = 2.571 ± 0.0146 (34 readings)

Corrected to 85% Acetone A, = 2.738 ± 0.0155

α° = 308.9 ± 14.4

Expt.61 p-Methoxy p'-Nitro-benzhydryl Chloride in 85% Acetone V at 0.10°C.

Time	$\frac{10^4}{1.083}$ [HCl]	$10^4\ \bar{k}_1$	Time	$\frac{10^4}{1.083}$ [HCl]	$10^4\ \bar{k}_1$
0	1.73	-	0	1.73	-
192	2.41	2.578	194	2.41	2.599
434	3.20	2.552	438	3.20	2.561
608	3.72	2.519	613	3.72	2.528
824	4.34	2.501	831	4.34	2.511
967	4.71	2.473	975	4.71	2.485
1136	5.14	2.455	1147	5.14	2.463
1611	6.24	2.412	1627	6.24	2.420
1957	6.94	2.376	1974	6.94	2.390
2363	7.67	2.334	2394	7.67	2.339
3255	9.15	2.317	3360	9.15	2.282
3815	9.79	2.245	3865	9.79	2.255
4380	10.43	2.215	4440	10.43	2.226
4985	11.04	2.192	5050	11.04	2.206
6930	12.52	2.121	7050	12.52	2.139
9600	13.72	2.018			
11160	14.28	2.027			
∞	15.74	-	∞	15.59	-

$10^4 k_1^o = 2.788 \pm 0.0079$ (30 readings)

Corrected to 85% Acetone A, ... $= 2.969 \pm 0.0084$

$\alpha^o = 345.9 \pm 6.3$

Expt.62 p-Methoxy p'-Nitro-benzhydryl Chloride in 85% Acetone V

Added HCl in 85% Acetone, (8.140).10^{-4} N. at 0.10°C.

Time	$\frac{10^4}{1.099}[\mathrm{HCl}]$	$10^4\ \bar{k}_1$	$10^4\ \bar{k}_1$(calc.)*
0	7.87	-	-
336	8.83	2.097	2.111
802	10.04	2.084	2.080
1375	11.28	2.015	2.033
2040	12.53	1.966	1.992
2785	13.81	1.963	1.961
3575	14.90	1.932	1.926
4520	16.02	1.909	1.893
5605	17.05	1.878	1.859
8220	18.87	1.843	1.797
∞	21.97	-	-

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0	7.87	-	-
303	8.83	2.030	2.090
709	10.04	2.046	2.068
1206	11.28	1.976	2.022
2400	13.81	1.922	1.952
3045	14.90	1.888	1.919
3800	16.02	1.861	1.886
4630	17.05	1.828	1.854
7560	19.59	1.727	1.768
8775	20.39	1.719	1.743
∞	23.95	-	-

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*Calculated from Eqn. III-2 , p. 72 , taking α^{o} = 345.9 and $10^4 k_1^{o}$ = 2.788 (from Expt.61)

Expt.63 p-Phenoxy p'-Nitro-benzhydryl Chloride in 85% Acetone V at 20.61°C.

Time	$\frac{10^4 [HCl]}{0.9750}$	$10^5 k_1$
0	0.08	-
2477	1.46	3.357
3348	1.92	3.364
3895	2.20	3.358
4531	2.51	3.344
6215	3.34	3.365
7350	3.87	3.368
8620	4.41	3.345
11265	5.52	3.354
12500	5.99	3.346
13785	6.48	3.353
15045	6.92	3.347
18410	8.03	3.347
21540	8.95	3.342
26120	10.10	3.318
29340	10.86	3.330
40260	12.82	3.317
∞	17.37	-

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Mean $10^5 k_1$ = 3.347 ± 0.00366 (16 readings)

Corrected to 85% Acetone A,..... = 3.564 ± 0.00390

When Organic halide initially 0.0096 M,
$10^5 k$ = 3.572 ± 0.00521 at 20.61°C
in 85% Acetone A (from Expt.53).

Expt.64 p-Anisyl-benzhydryl Chloride in 85% Acetone V at 0.10°C.

Time	$\frac{10^4}{1.083}$ [HCl]	$10^5 \bar{k}_1$
0	1.73	-
1625	3.20	6.732
2265	3.72	6.670
3048	4.34	6.673
3557	4.71	6.624
4154	5.14	6.615
5800	6.24	6.592
6965	6.94	6.564
8325	7.67	6.510
11385	9.15	6.506
12950	9.79	6.474
14700	10.43	6.452
16560	11.04	6.439
∞	15.93	-

Mean $10^5\bar{k}_1$ = 6.571 ± 0.0267 (12 readings)

Corrected to 85% Acetone A, ... = 6.997 ± 0.0284

When Organic halide initially 0.0092 M,

10^5k = 6.893 ± 0.0194 at 0.10°C

in 85% Acetone A (from Expt.56).

Expt.65 p-Methoxy-benzhydryl Chloride in 85% Acetone VI at 0.10°

Time	$\frac{10^4\,[HCl]}{1.083}$	$10^2\,\bar{k}_1$	Time	$\frac{10^4\,[HCl]}{1.083}$	$10^2\,\bar{k}_1$
0.00	3.20	-	0.00	3.20	-
3.60	4.34	2.412	1.70	3.72	2.466
4.90	4.71	2.383	3.80	4.34	(2.478)
6.50	5.14	2.349	5.25	4.71	2.413
11.00	6.24	2.284	7.00	5.14	2.369
14.25	6.94	2.241	11.95	6.24	2.290
18.15	7.67	2.179	15.55	6.94	2.244
27.25	9.15	2.094	19.90	7.67	2.180
32.05	9.79	2.050	30.20	9.15	2.093
37.40	10.43	2.009	35.65	9.79	2.053
43.05	11.04	1.977	41.85	10.43	2.013
60.60	12.52	1.887	48.65	11.04	1.975
81.70	13.71	1.789	70.15	12.52	1.888
128.60	15.30	1.678	97.95	13.71	1.795
oo	16.88	-	∞	15.90	-

$10^2k_1^0 = 3.091 \pm 0.0138$ (25 readings)

Corrected to 85% Acetone A, ... $= 3.039 \pm 0.0136$

$\alpha^0 = 679.9 \pm 9.7$

Expt.66 p-Methoxy-benzhydryl Chloride in 85% Acetone VI at -19.90°C.

Expt.66A			**Expt.66B**		
Time	$\frac{10^4\,[\mathrm{HCl}]}{0.9845}$	$10^3\,\bar{k}_1$	Time	$\frac{10^4\,[\mathrm{HCl}]}{0.9845}$	$10^3\,\bar{k}_1$
0.00	0.98	-	0.00	0.98	-
18.50	1.81	2.726	17.50	1.81	2.764
32.00	2.36	2.671	30.25	2.36	2.703
48.75	3.00	2.617	46.75	3.00	2.611
59.50	3.40	2.605	57.00	3.40	2.598
72.75	3.87	2.586	70.00	3.87	2.566
109.80	4.97	2.462	105.30	4.97	2.447
136.00	5.69	2.412	130.00	5.69	2.401
167.50	6.46	2.348	159.50	6.46	2.343
238.00	8.02	2.273	225.80	8.02	2.268
273.30	8.65	2.223	259.30	8.65	2.213
312.00	9.30	2.182	295.30	9.30	2.173
352.50	9.90	2.138	332.80	9.90	2.129
471.00	11.38	2.039	440.50	11.38	2.034
596.50	12.60	1.962	554.00	12.60	1.954
821.50	14.15	1.852	748.30	14.15	1.850
			908.00	15.15	1.809
∞	17.83	-	∞	18.55	-

$10^3 k_1^0 = 2.976 \pm 0.00796$ (31 readings)

Corrected to 85% Acetone A,··· $= 2.926 \pm 0.00782$

$\alpha^0 = 672.6 \pm 8.2$

Expt.67 p-Methoxy-benzhydryl Chloride in 85% Acetone VII at -32.90°C.

Time	$\frac{10^4\,[HCl]}{0.9835}$	$10^4\,\bar{k}_1$	Time	$\frac{10^4\,[HCl]}{0.9835}$	$10^4\,\bar{k}_1$
0.0	0.95	-	0.0	0.95	-
109.7	1.78	(4.158)	113.3	1.78	4.207
189.6	2.34	4.105	195.2	2.34	4.154
288.4	2.99	4.041	296.5	2.99	4.079
354.0	3.38	3.968	363.7	3.38	4.015
431.2	3.82	3.904	442.7	3.82	3.949
646.4	4.96	3.769	665.9	4.96	3.805
800.2	5.68	3.681	825.7	5.68	3.712
979.0	6.42	3.574	1012.0	6.42	3.600
1379.0	7.94	3.434	1430.0	7.94	3.457
1577.0	8.55	3.346	1639.0	8.55	3.367
1795.0	9.20	3.280	1865.0	9.20	3.308
2016.0	9.80	3.219	2101.0	9.80	3.241
4355.0	14.24	(2.897)	3485.0	12.62	(3.021)
∞	19.49	-	∞	18.88	-

$10^4k_1^0$ = 4.660 ± 0.0185 (23 readings)

Corrected to 85% Acetone A, ... = 4.596 ± 0.0182

α^0 = 768.8 ± 14.9

Expt.68 p-Chloro p'-Methoxy-benzhydryl Chloride in 85% Acetone at 0.10°C.

VIII

Time	$\frac{10^4\,[HCl]}{1.083}$	$10^3\,\bar{k}_1$	Time	$\frac{10^4\,[HCl]}{1.083}$	$10^3\,\bar{k}_1$
0.00	2.41	-	0.00	2.41	-
5.72	3.20	10.23	5.56	3.20	10.28
9.90	3.72	9.982	9.60	3.72	10.05
15.20	4.34	9.833	14.73	4.34	9.897
18.76	4.71	9.625	18.18	4.71	9.692
23.00	5.14	9.504	22.22	5.14	9.576
35.24	6.24	9.145	34.02	6.24	9.204
44.26	6.94	8.904	42.66	6.94	8.978
55.24	7.67	8.602	53.06	7.67	8.688
81.21	9.15	8.160	77.64	9.15	8.256
95.12	9.79	7.950	90.56	9.79	8.069
111.05	10.43	7.736	105.42	10.43	7.861
128.22	11.04	7.556	121.20	11.04	7.686
260.06	13.71	(6.433)	172.14	12.52	7.193
			236.76	13.71	(6.664)
∞	16.32	-	∞	16.65	-

$10^2 k_1^0 = 1.300 \pm 0.00679$ (25 readings)

Corrected to 85% Acetone A,··· $= 1.304 \pm 0.00681$

$\alpha^0 = 879.4 \pm 14.6$

Expt.69 p-Chloro p'-Methoxy-benzhydryl Chloride in 85% Acetone VIII at -19.90°C.

Time	$\frac{10^4}{0.9845}[HCl]$	$10^4 \bar{k}_1$	Time	$\frac{10^4}{0.9845}[HCl]$	$10^4 \bar{k}_1$
0.0	0.98	-	0.0	0.98	-
51.4	1.81	9.811	51.3	1.81	9.699
88.7	2.36	9.607	88.7	2.36	9.504
135.6	3.00	9.376	135.4	3.00	9.305
166.8	3.40	9.251	166.1	3.40	9.206
203.4	3.87	(9.217)	202.9	3.87	9.137
307.3	4.97	8.754	306.7	4.97	8.688
382.7	5.69	8.527	381.1	5.69	8.472
470.8	6.46	8.312	469.3	6.46	8.252
672.2	8.02	8.004	668.6	8,02	7.952
775.7	8.65	7.787	770.2	8.65	7.749
889.3	9.30	7.612	882.7	9.30	7.571
1005.7	9.90	7.447	997.5	9.90	7.411
1356.9	11.38	7.031	1342.8	11.38	6.998
1735.5	12.60	6.688	1716.0	12.60	6.655
∞	17.90	-	∞	18.05	-

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$10^3 k_1^0 = 1.080 \pm 0.00361$ (27 readings)

Corrected to 85% Acetone A,... $= 1.083 \pm 0.00363$

$\alpha^0 = 778.0 \pm 11.4$

Expt.70 p-Fluoro p'-Methoxy-benzhydryl Chloride in 85% Acetone VIII at 0.10°C.

Time	$\frac{10^4 [HCl]}{1.083}$	$10^2 \bar{k}_1$	Time	$\frac{10^4 [HCl]}{1.083}$	$10^2 \bar{k}_1$
0.00	3.72	-	0.00	2.41	-
1.93	4.34	2.828	3.52	3.72	(3.166)
3.20	4.71	(2.764)	6.82	4.71	3.002
4.69	5.14	2.759	8.47	5.14	2.928
8.96	6.24	2.709	13.15	6.24	2.802
12.12	6.94	2.657	16.67	6.94	2.720
16.00	7.67	2.575	20.95	7.67	2.627
25.40	9.15	2.457	31.25	9.15	2.501
30.40	9.79	2.407	37.08	9.79	2.430
36.20	10.43	2.355	43.69	10.43	2.372
42.60	11.04	2.307	51.15	11.04	2.318
64.14	12.52	2.175	77.75	12.52	2.159
94.84	13.71	2.028	122.05	13.71	(1.963)
∞	15.42	-	∞	14.84	-

$10^2 k_1^0 = 3.906 \pm 0.0433$ (21 readings)

Corrected to 85% Acetone A, $\cdots$ $= 3.918 \pm 0.0434$

$\alpha^0 = 824.5 \pm 25.9$

Expt.71 p-Fluoro p'-Methoxy-benzhydryl Chloride in 85% Acetone VIII at -19.90°C.

Time	$\frac{10^4}{0.9845}[HCl]$	$10^3\ \bar{k}_1$	Time	$\frac{10^4}{0.9845}[HCl]$	$10^3\ \bar{k}_1$
0.0	0.98	-	0.0	0.98	-
13.8	1.81	3.404	13.4	1.81	3.421
23.8	2.36	3.329	35.4	3.00	3.259
36.2	3.00	3.271	44.0	3.40	3.182
44.8	3.40	3.207	80.1	4.97	3.028
82.1	4.97	3.035	99.7	5.69	2.941
102.5	5.69	2.941	122.2	6.46	2.872
125.6	6.46	2.874	173.3	8.02	2.758
178.4	8.02	2.763	199.0	8.65	2.686
204.6	8.65	2.696	226.0	9.30	2.637
233.5	9.30	2.638	255.5	9.90	2.570
263.1	9.90	2.581	336.5	11.38	2.450
348.3	11.38	2.457	421.5	12.60	2.341
436.2	12.60	2.357	561.0	14.15	2.212
586.1	14.15	2.221			
∞	19.07	-	∞	19.51	-

$10^3k_1^o$ = 3.761 ± 0.00974 (27 readings)

Corrected to 85% Acetone A, ... = 3.773 ± 0.00977

α^o = 787.7 ± 8.2

Expt.72 p-Phenyl p'-Methoxy-benzhydryl Chloride in 85% Acetone VII at 0.10°C.

Time	$\frac{10^4}{1.083}[\text{HCl}]$	$10^2\,\bar{k}_1$	Time	$\frac{10^4}{1.083}[\text{HCl}]$	$10^2\,\bar{k}_1$
0.00	4.71	-	0.00	4.71	-
2.49	6.24	(6.012)	3.80	6.94	(5.860)
5.62	7.67	5.573	9.56	9.15	5.299
9.79	9.15	5.273	11.76	9.79	5.159
11.97	9.79	5.169	14.30	10.43	5.019
14.56	10.43	5.035	16.99	11.04	4.922
17.33	11.04	4.939	26.07	12.52	4.609
26.61	12.52	4.645	37.78	13.71	4.338
39.15	13.71	4.346	74.32	15.30	3.982
84.26	15.30	(3.879)			
∞	15.72	-	∞	15.88	-

$10^2 k_1^o$ = 9.693 ± 0.124 (14 readings)

Corrected to 85% Acetone A,.... = 9.560 ± 0.122

α^o = 1081.2 ± 27.7

Expt.73 p-Phenyl p'-Methoxy-benzhydryl Chloride in 85% Acetone VI at -19.90°C.

Time	$\frac{10^4}{0.9845}[\mathrm{HCl}]$	$10^3\ \bar{k}_1$	Time	$\frac{10^4}{0.9845}[\mathrm{HCl}]$	$10^3\ \bar{k}_1$
0.00	0.98	-	0.00	0.98	-
7.15	1.81	(8.666)	6.15	1.81	(8.874)
12.52	2.36	8.426	10.78	2.36	8.588
19.40	3.00	8.179	16.70	3.00	8.316
24.10	3.40	8.007	20.70	3.40	8.155
29.70	3.87	7.932	25.50	3.87	8.048
46.00	4.97	7.439	39.25	4.97	7.546
58.00	5.69	7.219	49.40	5.69	7.291
72.80	6.46	6.969	61.55	6.46	7.049
108.10	8.02	6.624	89.90	8.02	6.692
126.80	8.65	6.422	104.80	8.65	6.473
148.80	9.30	6.229	121.40	9.30	6.296
172.10	9.90	6.064	138.90	9.90	6.124
250.00	11.38	5.631	192.90	11.38	5.715
351.20	12.60	5.289	253.30	12.60	5.416
∞	14.75	-	∞	16.55	-

$10^3k_1^o$ = 9.947 ± 0.0444 (26 readings)

Corrected to 85% Acetone A, ... = 9.780 ± 0.0437

α^o = 1051.6 ± 15.9

Expt.74 p-Phenyl p'-Methoxy-benzhydryl Chloride in 85% Acetone VII at -32.90°C.

Time	$\frac{10^4}{0.9835}$[HCl]	$10^3\ \bar{k}_1$	Time	$\frac{10^4}{0.9835}$[HCl]	$10^3\ \bar{k}_1$
0.0	0.95	-	0.0	0.95	-
39.8	1.78	1.423	41.2	1.78	1.459
69.6	2.34	1.387	72.4	2.34	1.416
107.4	2.99	1.353	112.4	2.99	1.371
133.4	3.38	1.314	139.6	3.38	1.337
164.4	3.82	1.280	172.2	3.82	1.303
254.4	4.96	1.212	267.6	4.96	1.231
321.1	5.68	1.169	338.5	5.68	1.188
402.1	6.42	1.116	425.0	6.42	1.136
592.1	7.94	1.047	629.0	7.94	1.069
691.9	8.55	1.009	735.9	8.55	1.031
805.2	9.20	0.9790	859.3	9.20	1.002
923.6	9.80	0.9521	987.1	9.80	0.9788
1291.0	11.34	0.8993	1402.0	11.34	(0.8898)
1723.0	12.62	(0.8565)			
∞	16.08	-	∞	15.24	-

$10^3 k_1^o = 1.696 \pm 0.0123$ (25 readings)

Corrected to 85% Acetone A,.... $= 1.673 \pm 0.0122$

$\alpha^o = 1282.9 \pm 31.1$

Expt.75 p-Tert.-butyl p'-Methoxy-benzhydryl Chloride in 85% Acetone VII at -19.90°C.

Time	$\frac{10^4}{0.9845}[\mathrm{HCl}]$	$10^2\,\bar{k}_1$	Time	$\frac{10^4}{0.9845}[\mathrm{HCl}]$	$10^2\,\bar{k}_1$
0.00	0.98	-	0.00	0.98	-
3.75	1.81	1.450	3.85	1.81	1.423
6.55	2.36	1.410	6.71	2.36	1.383
10.10	3.00	1.371	10.28	3.00	1.353
12.50	3.40	1.345	12.68	3.40	1.336
15.35	3.87	1.330	15.52	3.87	1.325
23.67	4.97	1.245	23.80	4.97	1.247
29.65	5.69	1.209	29.87	5.69	1.209
36.90	6.46	1.170	37.20	6.46	1.169
53.70	8.02	1.114	54.00	8.02	1.118
62.50	8.65	1.080	62.90	8.65	1.081
72.30	9.30	1.052	72.90	9.30	1.052
82.70	9.90	1.023	83.27	9.90	1.024
113.90	11.38	0.9612	115.30	11.38	0.9596
150.00	12.60	0.9072	151.80	12.60	0.9074
220.90	14.15	0.8373	226.20	14.15	0.8316
∞	16.61	-	∞	16.52	-

$10^2k_1^o$ = 1.633 ± 0.00570 (30 readings)

Corrected to 85% Acetone A,.... = 1.611 ± 0.00562

α^o = 1001.9 ± 12.2

Expt.76 p-Tert.-butyl p'-Methoxy-benzhydryl Chloride in 85% Acetone VII at -32.90°C.

Time	$\frac{10^4\,[HCl]}{0.9835}$	$10^3\,\bar{k}_1$	Time	$\frac{10^4\,[HCl]}{0.9835}$	$10^3\,\bar{k}_1$
0.0	0.95	-	0.0	0.95	-
20.4	1.78	2.518	19.0	1.78	2.509
36.0	2.34	2.431	33.2	2.34	2.435
55.3	2.99	2.374	51.0	2.99	2.375
68.3	3.38	2.324	63.3	3.38	2.311
84.1	3.82	2.262	77.5	3.82	2.258
129.1	4.96	2.146	118.2	4.96	2.149
161.9	5.68	2.075	148.0	5.68	2.077
201.0	6.42	1.993	183.0	6.42	1.997
292.2	7.94	1.874	264.7	7.94	1.875
339.2	8.55	1.808	306.0	8.55	1.810
391.3	9.20	1.760	350.7	9.20	1.766
445.5	9.80	1.713	397.8	9.80	1.719
610.4	11.34	1.614	535.1	11.34	1.628
1129.0	14.24	(1.432)	933.5	14.24	(1.458)
∞	17.53	-	∞	18.82	-

$10^3k_1^o$ = 2.913 ± 0.00787 (26 readings)

Corrected to 85% Acetone A,.... = 2.873 ± 0.00777

α^o = 1193.0 ± 11.1

Expt.77 p-Methyl p'-Methoxy-benzhydryl Chloride in 85% Acetone VII at -19.90°C.

Time	$\frac{10^4}{0.9845}$[HCl]	$10^2\ \bar{k}_1$	Time	$\frac{10^4}{0.9845}$[HCl]	$10^2\ \bar{k}_1$
0.00	0.98	-	0.00	0.98	-
2.65	1.81	(1.972)	2.22	1.81	2.168
4.50	2.36	(1.960)	3.96	2.36	2.053
8.46	3.40	1.892	6.17	3.00	1.971
10.38	3.87	1.873	7.64	3.40	1.930
15.92	4.97	1.755	9.43	3.87	1.898
20.00	5.69	1.696	14.60	4.97	1.756
24.98	6.46	1.632	18.42	5.69	1.685
36.70	8.02	1.532	23.06	6.46	1.612
42.90	8.65	1.473	33.80	8.02	1.506
49.88	9.30	1.422	39.36	8.65	1.449
57.25	9.90	1.375	45.70	9.30	1.395
80.05	11.38	1.259	52.20	9.90	1.349
106.70	12.60	1.159	72.24	11.38	1.232
161.50	14.15	(1.009)	94.70	12.60	(1.134)
∞	17.36	-	∞	18.63	-

- -

$10^2k_1^0 = 2.573 \pm 0.0235$ (24 readings)

Corrected to 85% Acetone A,..... $= 2.538 \pm 0.0232$

$\alpha^0 = 1513.6 \pm 37.6$

Expt.78 p-Methyl p'-Methoxy-benzhydryl Chloride in 85% Acetone VIII at -32.90^{o}C.

Time	$\frac{10^4}{0.9835}$ [HCl]	$10^3\ \bar{k}_1$	Time	$\frac{10^4}{0.9835}$ [HCl]	$10^3\ \bar{k}_1$
0.0	0.95	-	0.0	0.95	-
13.0	1.78	3.667	12.2	1.78	3.681
23.2	2.34	3.504	33.4	2.99	3.421
35.6	2.99	3.416	51.2	3.82	3.221
44.4	3.38	3.299	78.5	4.96	3.040
54.8	3.82	3.206	99.1	5.68	2.907
84.8	4.96	3.006	124.1	6.42	2.755
107.6	5.68	2.870	181.5	7.94	2.545
134.4	6.42	2.729	211.1	8.55	2.437
198.0	7.94	2.516	244.9	9.20	2.344
231.2	8.55	2.404	279.1	9.80	2.264
268.6	9.20	2.315	383.7	11.34	2.081
308.7	9.80	2.223	496.0	12.62	1.937
430.9	11.34	2.030	705.4	14.24	(1.722)
850.6	14.24	(1.611)			
∞	18.77	-	∞	19.85	-

$10^3 k_1^o$ = 4.604 ± 0.0308 (25 readings)

Corrected to 85% Acetone A, ... = 4.618 ± 0.0309

α^o = 1801.6 ± 30.6

Expt.79 p-Anisyl p'-Methoxy-benzhydryl Chloride in 85% Acetone VIII at -32.90°C.

Time	$\frac{10^4}{0.9835}[HCl]$	$10^3 \bar{k}_1$	Time	$\frac{10^4}{0.9835}[HCl]$	$10^3 \bar{k}_1$
0.00	1.78	-	0.00	1.78	-
9.53	2.34	(4.567)	12.60	2.34	4.331
23.12	2.99	4.194	29.93	2.99	4.070
32.52	3.38	4.007	41.74	3.38	3.946
44.14	3.82	3.841	56.48	3.82	3.808
78.92	4.96	3.531	102.10	4.96	3.516
105.50	5.68	3.360	138.10	5.68	3.345
139.00	6.42	3.156	183.90	6.42	3.154
220.90	7.94	2.889	304.06	7.94	2.887
265.30	8.55	2.753	374.20	8.55	2.748
318.70	9.20	2.634	460.80	9.20	2.642
372.80	9.80	2.555	563.80	9.80	2.539
556.60	11.34	2.364	999.40	11.34	(2.378)
∞	14.84	-	∞	12.32	-

$10^3k_1^o$ = 6.263 ± 0.0700 (22 readings)

Corrected to 85% Acetone A,.... = 6.283 ± 0.0703

α^o = 2274.8 ± 53.5

Expt.80 p-Phenoxy p'-Methoxy-benzhydryl Chloride in 85% Acetone VIII at -32.90°C.

Time	$\frac{10^4}{0.9835}[HCl]$	$10^2 \bar{k}_1$	Time	$\frac{10^4}{0.9835}[HCl]$	$10^2 \bar{k}_1$
0.00	0.95	-	0.00	0.95	-
3.67	1.78	1.481	3.55	1.78	1.505
6.50	2.34	1.432	6.45	2.34	1.418
10.35	2.99	1.351	10.15	2.99	1.350
12.97	3.38	1.301	12.70	3.38	1.302
16.20	3.82	1.252	15.85	3.82	1.254
25.75	4.96	1.151	25.05	4.96	1.156
32.95	5.68	1.093	32.10	5.68	1.096
41.80	6.42	1.030	40.60	6.42	1.035
63.10	7.94	0.9396	60.90	7.94	0.9473
74.55	8.55	0.8933	71.70	8.55	0.9031
87.40	9.20	0.8586	83.80	9.20	0.8694
101.00	9.80	0.8269	96.60	9.80	0.8379
143.90	11.34	0.7595	182.50	12.62	(0.7209)
298.50	14.24	(0.6363)			
∞	16.58	-	∞	16.90	-

$10^2k_1^o = 1.944 \pm 0.00993$ (25 readings)

Corrected to 85% Acetone A, ... $= 1.950 \pm 0.00997$

$\alpha^o = 2275.3 \pm 27.5$

Expt.81 p-Phenoxy p'-Methoxy-benzhydryl Chloride in 85% Acetone VIII at -37.34°C.

Time	$\frac{10^4}{0.9608}[HCl]$	$10^3 \bar{k}_1$	Time	$\frac{10^4}{0.9608}[HCl]$	$10^3 \bar{k}_1$
0.00	0.71	-	0.00	0.71	-
5.70	1.49	(8.971)	6.00	1.49	8.636
10.20	2.01	(8.511)	10.55	2.01	8.318
16.20	2.61	7.989	16.55	2.61	7.932
20.30	2.98	7.714	20.65	2.98	7.683
25.25	3.40	7.469	25.70	3.40	7.439
39.80	4.45	6.863	40.60	4.45	6.819
50.90	5.14	6.539	51.80	5.14	6.513
64.30	5.85	6.193	65.50	5.85	6.167
96.10	7.29	5.678	97.70	7.29	5.671
112.90	7.87	5.418	115.10	7.87	5.401
131.20	8.48	5.231	134.20	8.48	5.200
151.50	9.05	5.025	154.20	9.05	5.023
210.00	10.44	4.630	215.90	10.44	4.594
275.70	11.62	4.333	286.60	11.62	4.263
398.30	13.15	3.978	415.70	13.15	3.923
∞	16.36	-	∞	16.18	-

- -

$10^2 k_1^o$ = 1.059 ± 0.00499 (28 readings)

Corrected to 85% Acetone A, ... = 1.062 ± 0.00501

α^o = 2106.4 ± 23.4

Expt.82* pp'-Dimethoxy-benzhydryl Chloride in 85% Acetone VIII at -37.34°C.

Time	$\frac{10^4}{0.9608}[HCl]$	$10^2\ \bar{k}_1$	Time	$\frac{10^4}{0.9608}[HCl]$	$10^2\ \bar{k}_1$
0.00	3.40	-	0.00	3.40	-
1.32	4.45	(6.769)	1.27	4.45	7.000
2.31	5.14	6.621	2.29	5.14	6.637
3.53	5.85	6.302	3.50	5.85	6.323
6.43	7.29	(5.924)	6.39	7.29	(5.921)
8.03	7.87	5.636	7.99	7.87	5.626
9.83	8.48	5.433	9.74	8.48	5.443
11.71	9.05	5.264	11.66	9.05	5.246
17.55	10.44	4.842	17.51	10.44	4.821
24.25	11.62	4.564	24.25	11.62	4.517
37.53	13.15	(4.211)	37.51	13.15	(4.156)
∞	15.68	-	∞	15.75	-

(P.T.O.)

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*This experiment was carried out in triplicate as only a limited number of readings could be obtained from one run.

Expt.82 (continued) pp'-Dimethoxy-benzhydryl Chloride in 85% Acetone VIII at $-37.34^{\circ}C$.

Time	$\frac{10^4}{0.9608}[HCl]$	$10^2\ \bar{k}_1$
0.00	3.40	-
1.30	4.45	(7.158)
2.34	5.14	(6.811)
3.65	5.85	6.359
6.83	7.29	5.839
8.53	7.87	5.565
10.53	8.48	5.330
12.57	9.05	5.166
19.07	10.44	4.742
26.68	11.62	4.449
42.88	13.15	4.055
∞	15.23	-

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$10^1 k_1^{o} = 1.366 \pm 0.0232$ (23 readings)

Corrected to 85% Acetone A,.. $= 1.370 \pm 0.0233$

$\alpha^{o} = 2569.8 \pm 72.8$

LIST OF SOLVENTS.

p-Phenylbenzyl Bromide in 99.5% Formic Acid.

Temp. °C.	Solvent	10^5 k (sec.^{-1})
40.15	I	6.580
40.15	II	6.445

- -

p-Methoxybenzyl Chloride in 70% aq. Acetone.

Temp. °C.	Solvent	10^4 k (sec.^{-1})
20.58	I	2.603
20.38	A	2.624

- -

Benzhydryl Chloride in 70% aq. Acetone.

Temp. °C.	Solvent	10^4 k (sec.^{-1})
20.24	II	2.656
20.57	III	2.766
25.00	A	4.931

- -

Benzhydryl Chloride in 85% aq. Acetone.

Temp. °C.	Solvent	10^4 k (sec.^{-1})
40.14	I	1.027
40.06	II	1.044
25.00	A	0.2201

LIST OF SOLVENTS (continued).

p-Methyl-benzhydryl Chloride in 85% aq. Acetone .

Temp. °C.	Solvent	10^4 k ($sec.^{-1}$)
20.53	IV	2.707
20.53	V	2.699
20.53	VI	2.923
20.53	VII	2.914
20.53	VIII	2.865
25.00	A	4.660

- -

APPENDIX IV - 3.

IDENTIFICATION OF THE PRODUCTS OF FORMOLYSIS OF p-NITROBENZYL BROMIDE IN THE PRESENCE OF 0.1M PIPERIDINE.

(see Chapter II, p. 48)

p-Nitrobenzyl bromide (5.4 gm., .05M) and piperidine (4.26 gm., 0.1M) were refluxed in 99.5% formic acid (500 ml.) for 10 days. The formic acid and excess piperidine were removed by distillation under reduced pressure. The resulting green sludge was then dried at room temperature (0.1 mm.) and extracted with cold benzene. Piperidine hydrobromide remained in the form of small white crystals:

yield 3.8 gm. (calculated yield 4.16 gm.);
m.p. 233° (lit.[108] 235°);
found C 36.2%; H 7.4% : $C_5H_{12}Br\,N$ requires C 36.2%;
H 7.2%

The benzene extract was evaporated and the residue dissolved in chloroform. The solution was washed, dried ($MgSO_4$) and evaporated to yield a green liquid (4 gm.). This second product (X) was identified as a mixture of p-nitrobenzyl alcohol and p-nitrobenzyl formate by comparison with the known compounds, and did not contain any p, p'-dinitrostilbene. The results on which this conclusion is based are given below.

p-nitrobenzyl formate was prepared from p-nitrobenzyl bromide and sodium formate in aqueous ethanol[109]; m.p. 31° (lit.[109] 31°). Recrystallised p-nitrobenzyl alcohol had m.p. 93° (lit.[110] 93°). p, p'-dinitrostilbene was made by the addition of aqueous potassium hydroxide to p-nitrobenzyl chloride in acetone. The solution was allowed to stand at room temperature overnight and the yellow crystals filtered and dried; m.p. 290° (lit.[62] 288°). The infrared spectra of these three compounds and that of compound (X) were examined.

1. The spectrum of p, p'-dinitrostilbene bore little relation to that of compound (X). Peaks at 1502 $cm.^{-1}$ and 1335 $cm.^{-1}$ were assigned to the nitro group and the strong band at 1592 $cm.^{-1}$ to the C = C double bond. This latter frequency was absent in the spectrum of compound (X).
2. The spectrum of compound (X) showed considerable similarity to that of p-nitrobenzyl alcohol, e.g. -OH band at 3448 $cm.^{-1}$. However, the unknown compound showed a sharp band at 1733 $cm.^{-1}$ and a broad band at about 1156 $cm.^{-1}$ with the semblance of a shoulder at 1176 $cm.^{-1}$ The first of these frequencies could be assigned to C = O stretching vibrations in formates (usually 1724 $cm.^{-1}$)[98] and the second to similar C - O vibrations (usually 1200 $cm.^{-1}$ - 1179 $cm.^{-1}$)[98], bearing

in mind the considerable influence of conjugation on these vibrations.

3. Examination of the spectrum of p-nitrobenzyl formate showed these predictions to be correct. Strong bands were present at 1733 $cm.^{-1}$ and 1160 $cm.^{-1}$ It was also clear that the superimposition of the spectra of p-nitrobenzyl alcohol and p-nitrobenzyl formate would give rise to the spectrum of compound (X), almost exactly.

Accordingly, a portion of compound (X)(1 gm.) was hydrolysed in boiling water (100 ml.) for 18 hours. The volume was then reduced at the pump, when white needles crystallised. These were filtered and dried in vacuo.

m.p. 93°; mixed m.p. with p-nitrobenzyl alcohol 93°. The infrared spectrum was identical with that of p-nitrobenzyl alcohol.

APPENDIX IV - 4.

THE MAXIMUM VALUE OF THE "MASS-LAW CONSTANT", α^{o}, IN CASES WHERE CONSTANT FIRST-ORDER RATE COEFFICIENTS WERE OBSERVED THROUGHOUT A RUN.

(see Chapter III, p. 80)

For reactions in which no decrease in the first-order rate coefficients was observed, the integrated rate coefficient for the time interval o-t can be assumed to represent the instantaneous value at $(t/2)^{86}$, and the concentration of organic halide, RCl, at time (t/2) can be shown to be[86],

$$[\mathrm{RCl}]_{t/2} = \left([\mathrm{RCl}_o]\ [\mathrm{RCl}_t] \right)^{\frac{1}{2}}$$

$$\text{i.e., } (a-x)_{t/2} = a^{\frac{1}{2}}(a-x)_t^{\frac{1}{2}}$$

Thus the concentration of chloride ion formed by hydrolysis at time t/2, $x_{t/2}$, can be obtained. Equation III-5 (see p.77) gives,

$$k_{\text{instantaneous}} = \frac{1}{a-x} \cdot \frac{dx}{dt} = \frac{k_1^o}{1 + \alpha^o (x + c)\,\text{antilog}_{10} A (c + x)^{\frac{1}{2}}}$$

.... Eqn.IV-27

and if it is assumed that a 5% drop (say) in the integrated rate between the first ($\bar{k}_{t_1}$) and last reading ($\bar{k}_{t_n}$) is distinguishable,

$$\text{i.e., } \left(k_{\frac{t_1}{2}}\right) \Big/ \left(k_{\frac{t_n}{2}}\right) = 1.05 \,,$$

then, $$\frac{1 + \alpha^{o}(x + c)_{\frac{t_n}{2}} \text{ antilog}_{10} \, A(x + c)^{\frac{1}{2}}_{\frac{t_n}{2}}}{1 + \alpha^{o}(x + c)_{\frac{t_1}{2}} \text{ antilog}_{10} \, A(x + c)^{\frac{1}{2}}_{\frac{t_1}{2}}} = 1.05 \; . \; . \; . \qquad \text{Eqn. IV-28}$$

Equation IV-28 can be solved for α^{o} (in the present experiments, $a \simeq 0.01$ mole. litre^{-1}) and the value obtained will depend on the magnitudes of c and x. For an experiment where $c = 0.30 \times 10^{-3}$ mole. litre^{-1},

$\left(\frac{x}{a}\right)_{t_1} = .15$, $\left(\frac{x}{a}\right)_{t_n} = .66$ and $A = -2.4$; then $\alpha^{o} = 23$.

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