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SOLVOLYTIC STUDIES OF SOME  
ORGANIC CHLORIDES AND FLUORIDES.

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

BY

M. HALLAS.

HATFIELD COLLEGE

1967.



ACKNOWLEDGEMENTS.

The author wishes to thank Dr. G. Kohnstam for his advice and encouragement throughout the course of this work, Dr. D.L.H. Williams for help at various times, Eric Jackson and Denis Routledge for their assistance with the rapid conductance runs.

Thanks are also due to the Science Research Council for the award of a Research Studentship.

### ABSTRACT.

Rates, (with mass-law constants where appropriate), and activation parameters have been determined for the reactions of triphenylmethyl chloride, its p-nitro derivative, the corresponding fluorides and methoxymethyl chloride with aqueous acetone. Thus information has been obtained on the effects of replacing chlorine by fluorine as leaving group in  $S_N1$  reactions.

The rapid  $S_N1$  reactions of the triphenylmethyl chlorides with 85% aqueous acetone at low temperatures showed the expected large mass-law effects.<sup>1</sup> Mass-law constants and rates of ionisation at zero ionic strength were obtained for each experimental temperature, account being taken of the influence of changing ionic strength during reaction. The substituent effects on the rate of ionisation and the activation parameters, attending the introduction of the p-nitro group into triphenylmethyl chloride, were consistent with earlier results for diphenylmethyl chlorides,<sup>2</sup> although both reactions showed extremely negative entropies of activation.

The relatively slow reactions of triphenylmethyl fluoride and its p-nitro derivatives with 70% aqueous acetone have been studied. As in the case of the chlorides, the p-nitro group reduced the rate almost entirely though an increase in the energy of activation. The entropies

of activation when compared to those obtained for the chlorides provide support for the hypothesis<sup>3</sup> that the transition states for the reactions of the fluorides are stabilised by hydrogen bonding between a water molecule and the incipient fluoride ion. The  $\Delta C_p^\ddagger / \Delta S^\ddagger$  ratio for the hydrolysis of triphenylmethyl fluoride can also be interpreted in terms of this hypothesis.

Contrary to expectations,<sup>4</sup> several features of the reaction of methoxymethyl chloride suggested that the reaction does not proceed by mechanism  $S_N1$ . The observed values of the entropy and heat capacity of activation were consistent with a transition state involving covalent attachment of a water molecule.<sup>5</sup> Further, the reaction although rapid was not subject to mass-law effects, indicating that the carbonium ion ( $\text{MeOCH}_2^+ \leftrightarrow \text{MeO}^+ = \text{CH}_2$ ) is not a reaction intermediate. Thus as the purpose of the present work was to study the effect of a change in leaving group on  $S_N1$  reactions, no attempt was made to prepare methoxymethyl fluoride.

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2. Fox, Ph.D. Thesis, Durham, 1962.
3. R.E. Parker, "Advances in Fluorine Chemistry", Butterworth's, London, Vol.3, (1963), p.63.
4. Ballinger, de la Mare, Kohnstam and Presst, J.C.S., 1955, 3641.
5. Kohnstam, "The Transition State", Chem.Soc. Special Publ. No.16, p.179.

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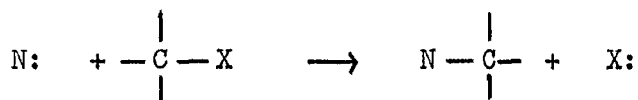
## CHAPTER I.

### INTRODUCTION.

#### I.1. Nucleophilic Substitution Reactions.

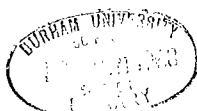
This thesis describes some studies of the solvolytic reactions of selected organic chlorides and fluorides in aqueous acetone. In each case the halogen atom is attached to a saturated carbon atom and all the reactions studied are nucleophilic substitution reactions. The work is aimed at establishing, by kinetic methods, any mechanistic differences in behaviour, of structurally analogous chlorides and fluorides, in their reactions with aqueous acetone solvents.

The essential feature of a nucleophilic substitution reaction ( $S_N$ )<sup>1</sup> is that a group X (termed the leaving group) is displaced from the reaction centre\* by a reagent N (termed the nucleophile), with the transfer of a pair of electrons, from N to the reaction centre, and also from the reaction centre to X. X therefore departs with both the electrons originally forming the bond attaching it to the reaction centre. Thus in general terms we have:

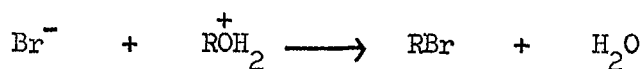
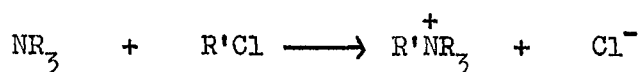


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\* In this thesis the reaction centre will always be a carbon atom.



A variety of situations as regards the charges on N, C and X are possible. Thus all the following are nucleophilic substitution reactions. <sup>1,2</sup>

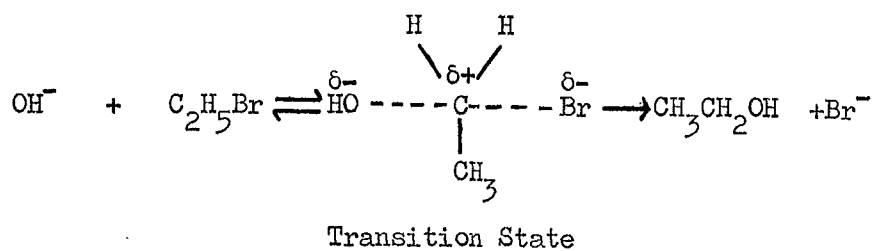


where R and R' represent alkyl groups.

### I.2. Mechanisms of S<sub>N</sub> Reactions.

The two reaction paths by which nucleophilic substitution reactions are considered to proceed, were first elucidated by Hughes and Ingold and co-workers. <sup>1</sup>

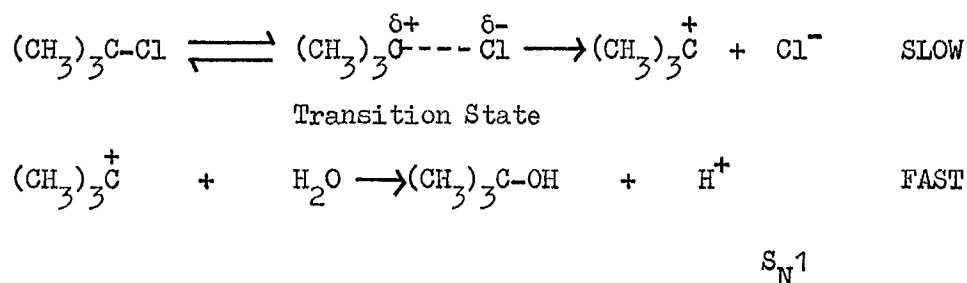
(a) The products are formed in a single rate determining step in which the substrate RX and the nucleophile N undergo simultaneous covalency change. Thus the reaction is bimolecular and is labelled S<sub>N</sub>2. An example of this mechanism is furnished by the reaction of ethyl bromide with hydroxide ions in ethanol. <sup>3</sup>



S<sub>N</sub>2

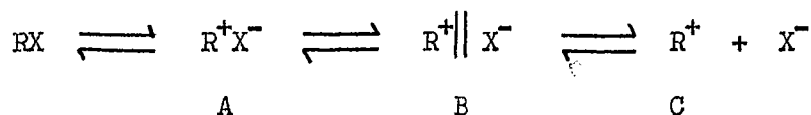
(b) The products are formed by a two step process. In the first and rate determining step, the substrate, RX, ionises to give the very reactive carbonium ion R<sup>+</sup> which then in the second step, reacts rapidly with the nucleophile, which may be a solvent molecule. Here, only the substrate undergoes a covalency change in the rate-determining step and hence the reaction is unimolecular, being labelled S<sub>N</sub>1.

However an essential feature of this mechanism is the stabilisation of the polar transition state of the first step by its interaction with solvent dipoles.<sup>4</sup> This reduces the activation energy for this step as compared with the relatively high values required for the gas phase ionisation of RX where no such stabilisation is possible. Tertiary butyl chloride is hydrolysed in aqueous acetone by this mechanism.<sup>5</sup>



### I.3. Ion-Pair Intermediates in Solvolysis.

Winstein<sup>6</sup> has proposed that for the S<sub>N</sub>1 solvolysis of certain substrates in acetic acid, the following representation of the ionisation step is appropriate.



Here A is an "intimate" ion-pair, the charged species sharing the same solvation shell, B is a "solvent separated" ion pair and C is the free carbonium ion. Thus for some optically active compounds it has been found that racemisation occurs more rapidly than solvolysis in this solvent suggesting that the former process may occur by ion-pair return as well as by solvolysis. Further in the presence of low concentrations of electrolytes marked increases in the rate of solvolysis have been observed in some cases. Once a certain critical salt concentration has been reached however further additions produced much smaller increases. Nevertheless, under these conditions the racemisation rate still exceeded that for acetolysis. These results have been interpreted as meaning that the low salt concentrations suppress ion-pair return from stage B (and thus "abnormally" increasing the rate of solvolysis) while ion-pair return from stage A is unaffected. The larger salt concentrations then increase the solvolysis rate by a normal salt effect (see Section I.4).

Racemisation rates exceeding the corresponding rates of substitution have also been reported for other solvents.<sup>7</sup> When aqueous organic solvents have been involved <sup>7b,c,d</sup> the ratio of the two rates has been closer to unity than has generally been the case for non-aqueous solvents.

According to Winstein's scheme chemical capture by nucleophiles can in principle occur with either A, B or C. However for aqueous

acetone solvents there is no evidence to suggest that ion-pair species react to form solvolysis products. Indeed the results of Kohnstam and Shillaker<sup>8</sup> for the solvolysis of dichlorodiphenylmethane in 70% aqueous acetone in the presence of chloride and bromide ions require that only the free carbonium ion reacts with water and anions in this solvent.

Also Winstein and Appel<sup>9</sup> studying the rates of hydrolysis, azide formation and  $^{18}\text{O}$  equilibration for triphenylmethyl benzoate in acetone containing small amounts of water have concluded that the proportion of chemical capture occurring via the free carbonium ion increases steeply with increasing water content of the solvent. Further, Sneen and co-workers<sup>10</sup> have recently suggested, from a consideration of the data relating to competition between hydrolysis and azide formation in 80% aqueous acetone containing azide ions, that for substrates generally supposed to give rise to stable carbonium ions, only free carbonium ions react to form hydrolysis products under these conditions.

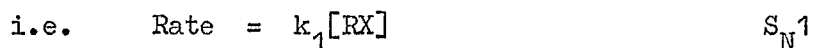
It therefore seems reasonable to assume that for  $\text{S}_{\text{N}}1$  reactions in aqueous acetone solvents, chemical capture occurs only via the free carbonium ion as originally envisaged by Hughes, Ingold and their co-workers.<sup>11</sup>

#### I.4. Recognition of Mechanism.

##### A The Kinetic Criterion.

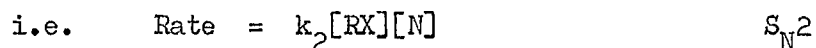
If the reacting species are in small and controllable concentrations then it is evident from the description in Section 1 that the  $\text{S}_{\text{N}}1$

mechanism will lead to first-order kinetics.



Deviations from first-order kinetics which can sometimes occur in  $S_N1$  reactions will be discussed in Section I.6.

Similarly the  $S_N2$  mechanism will lead to second-order kinetics.



However in solvolytic reactions the nucleophile is a major component of the solvent and is usually in virtually constant excess over the substrate. Such reactions are therefore first-order, independent of the mechanism and the kinetic criterion of mechanism is inapplicable.

#### B Other Criteria.

Hughes<sup>12</sup> has discussed several methods which are useful in the determination of the mechanism of a solvolytic reaction. These should be applied in conjunction, as far as possible, as each on its own is of limited use and may not be unambiguous in a given case.

##### (1) Variations in the Substituting Agent.

In an  $S_N1$  reaction the rate is controlled by the ionisation of RX. Thus if a nucleophile which is stronger than the solvent is added the rate should not be substantially altered. However if the nucleophile is an ionic species there may be a small "medium effect" on the rate (See I.4. B (2)).

By contrast the  $S_N2$  mechanism involves nucleophilic attack in the rate determining stage and the rate of such a reaction will be substantially increased by the addition to the solvent of a stronger nucleophile.

Thus the addition of hydroxide ions to 80% aqueous ethanol has a large effect on the rate of reaction of methyl bromide but virtually no effect on the rate of t-butyl bromide which is sterically hindered to bimolecular attack.<sup>13</sup> (Table I.1.)

TABLE I. 1. <sup>13</sup>

<u>RX</u>	<u><math>10^5 k_1 \text{ sec}^{-1} ([\text{NaOH}] = 0)</math></u>	<u><math>10^5 k_1 [\text{NaOH} = 1]</math></u>
MeBr	0.349	2140
Bu <sup>t</sup> Br	1010	1010

The apparent absence of a medium effect on the solvolysis of t-butyl bromide in the presence of molar sodium hydroxide is perhaps surprising but the quoted rate constants for this compound are calculated from results at other temperatures and this may not be precisely correct.

In general if no substantial rate\* increase is observed on the addition of a strong nucleophile to the solvent then the reaction of RX

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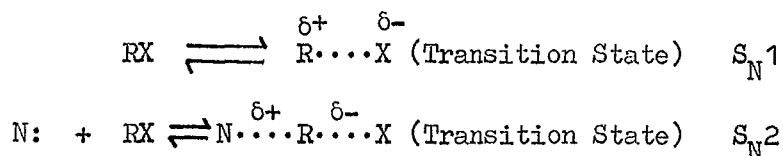
\* By rate is meant here the rate of disappearance of RX.



with the solvent is unimolecular but the observation of a substantial rate increase does not necessarily mean that the solvolysis is bimolecular since RX may react unimolecularly with the solvent but bimolecularly with a stronger nucleophile.

(2) Electrolyte Effects.

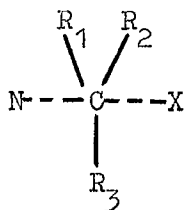
It was originally suggested <sup>11</sup> that the transition states of both  $S_N1$  and  $S_N2$  solvolyses are more polar than the corresponding initial states.



The addition of an inert electrolyte to the solvent should therefore stabilise the transition states for both mechanisms by analogy with ion-atmosphere stabilisation of fully developed ions. An increase in rate should result in both cases but the increase should be greater for an  $S_N1$  reaction since in this case the degree of charge development in the transition state is greater. For the effect of "common-ion" electrolyte additions see Section I.4. B (3).

Recent work <sup>14,15b</sup> has shown that the actual behaviour of electrolytes is more complex in that some electrolytes can reduce the rate of a solvolysis by "drying" the solvent (i.e. through solvation of the added electrolyte by the more polar component of the solvent) and that electrolytes have specific effects on both the initial and transition

shown in the diagram which refers to an asymmetric reaction centre.



$R_1$ ,  $R_2$  and  $R_3$  are considered to be co-planar and N attacks at the opposite side from which X leaves. This is consistent with the inversion of configuration observed for a large variety of  $S_N2$  solvolyses.

On the other hand there is no unique rule for determining the steric course of an  $S_N1$  reaction. Carbonium ions are generally considered to have a planar configuration and in many cases therefore a racemic substitution product is formed. However if the substrate gives rise to a relatively unstable carbonium ion then the product may be partially inverted. Further, a neighbouring group may interact with the carbonium ion centre resulting in the formation of a product showing net retention of configuration. The stereochemistry of nucleophilic substitution reactions has been discussed by Bunton.<sup>16</sup>

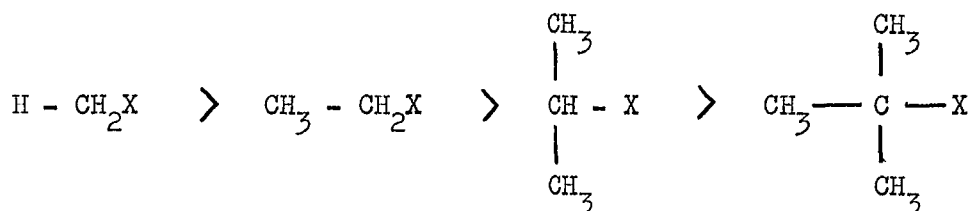
#### (6) Structural Variations in R.



In nucleophilic substitution, the leaving group departs with the electron pair formerly binding it to the reaction centre. Co-ordination

with the nucleophile makes up the electron deficiency either simultaneously in an  $S_N2$  reaction, or afterwards in an  $S_N1$  reaction.

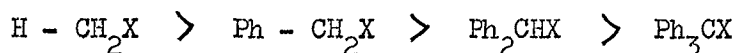
Thus variations in R which increase electron release towards the reaction centre will increase the tendency for reaction by the  $S_N1$  mechanism. For example methyl groups release electrons by the inductive effect and therefore the following series should show an increasing tendency for reaction by this mechanism.



For this series of bromides in aqueous ethanol, the rate is at a minimum for the isopropyl compound while hydroxide ions accelerate the reaction of the first three compounds in the order  $\text{CH}_3\text{X} > \text{CH}_3\text{CH}_2\text{X} > (\text{CH}_3)_2\text{CHX}$  but do not affect the rate of solvolysis of  $(\text{CH}_3)_3\text{C-X}$ .<sup>13</sup> These facts indicate that the tertiary butyl compound undergoes  $S_N1$  solvolysis and that the  $S_N2$  reactivity of the others decreases along the series methyl, ethyl, isopropyl. The solvolytic rate minimum and the small accelerating effect of hydroxide ions when isopropyl bromide is the substrate, indicate that the solvolysis of this compound is not entirely  $S_N2$  but that the reaction lies in the region of mechanistic change between  $S_N2$  and  $S_N1$  mechanisms. This region, described as the "borderline region", will be discussed in detail in

Section I.5.

A similar mechanistic transition is found for the solvolytic reactions of the series:

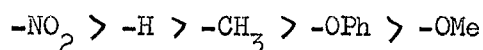


Here tendency to react by the  $S_N1$  mechanism is increased by the successive introduction of phenyl groups into the molecule, as this group can release electrons towards the reaction centre by a conjugative effect. The region of mechanistic change here lies between the benzyl and diphenylmethyl compounds and rates increase throughout the series. The methyl compounds as described above react by the  $S_N2$  mechanism. The solvolyses of diphenylmethyl halides are unimolecular, <sup>17</sup> hydroxide ions having little effect on the rate <sup>18</sup> while triphenylmethyl halides react very rapidly in aqueous solvents and the mass law retardation of common ions has been observed.<sup>19</sup> It has also been concluded that the chloride reacts unimolecularly in ethanol-ether mixtures.<sup>20</sup>

The hydrolysis of benzyl chloride in aqueous solvents furnishes a good example of the need to apply these criteria with care. Thus the acceleration produced by added hydroxide ions <sup>21</sup> indicates a bimolecular incursion by the stronger nucleophile but does not necessarily mean that the solvolysis is bimolecular. Similarly the slight retardation caused by added chloride ion may not be a mass law effect but a salt induced

medium effect.<sup>15b,22</sup> Bensley and Kohnstam<sup>23</sup> have concluded from their measurements of the  $\frac{\Delta C^\ddagger}{\Delta S^\ddagger}$  ratio (see Section I.4. B (7) and Chapter 2) in 50% aqueous ethanol and 50% aqueous acetone that in these solvents the solvolysis is mainly if not entirely  $S_N2$ .

Electron release towards the reaction centre in a series of structurally similar compounds may be varied by the introduction of p-substituents in a benzene ring attached to the reaction centre. Thus steric complications are eliminated and both inductive and mesomeric effects come into play. The series,



shows an increasing facility for electron release towards such a centre. Thus the p-methoxy and p-phenoxy benzyl chlorides<sup>24a</sup> hydrolyse in 70% aqueous acetone by the unimolecular mechanism, while the p-methyl compound is "borderline" and the p-nitro compound (in 50% aqueous acetone) is hydrolysed by the  $S_N2$  mechanism.<sup>24b</sup>

For the bimolecular mechanism electron release towards the reaction centre will assist the heterolysis of the C-X bond but will hinder the formation of the new bond between N and the reaction centre, especially when N carries a negative charge. Thus the effect of polar substituents depend on which process is dominant in the transition state for the reaction concerned. This ambiguity is illustrated by the results of Sugden and Willis<sup>25</sup> for the Finkelstein reactions of p-substituted benzyl bromides in ethylene diacetate.

TABLE I.2. <sup>25</sup>

Substituent Effects,  $\frac{k_X}{k_H}$  for p-X Benzyl Bromides in Ethylene Diacetate.

RBr	<sup>82</sup> Br	<sup>82</sup> R Br	+ Br <sup>-</sup>	
X	NO <sub>2</sub>	CN	H	OMe
$\frac{k_X}{k_H}$	11.2	10.0	1	6.2

A rate minimum is found for the parent compound. These results are consistent with the theory that the electron withdrawing p-nitro and p-cyano groups increase the rate by facilitating the approach of the bromide ion and the p-methoxy group by facilitating the heterolysis of the C-Br bond. It might be argued that the powerfully electron releasing p-methoxy group alters the mechanism from S<sub>N</sub>2 to S<sub>N</sub>1 as in the solvolysis reaction previously referred to, but there is evidence for bimolecular reaction of the latter compound with azide ions in aqueous acetone <sup>26</sup> and therefore it is reasonable to suppose that in ethylene diacetate, p-methoxybenzyl bromide could be subject to bimolecular attack by bromide ion which is a good nucleophile.

In cases where the nucleophile is a neutral molecule, one might expect that in the bimolecular transition state, bond breaking will predominate. Thus electron release towards the reaction centre will

facilitate reaction but the effect will be smaller than for an  $S_N1$  reaction where there is no bond making in the transition state. This is illustrated by the data in Table I.3.

TABLE I. 3.

Substituent Effects,  $\frac{k_X}{k_H}$ , for the Solvolyses of p-X Benzyl

Chlorides and p-X Diphenylmethyl Chlorides.

	X = NO <sub>2</sub>	H	Me	Mechanism
p-XC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Cl (a)	9.16x10 <sup>-2</sup>	1	8.13	S <sub>N</sub> 2
p-XC <sub>6</sub> H <sub>4</sub> CHCl.Ph (b)	1.25x10 <sup>-4</sup>	1	21.2	S <sub>N</sub> 1

(a) in 50% \* aqueous acetone at 50°C. 24b

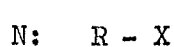
(b) in 70% \* aqueous acetone at 25°C. 28

The influence of bond formation on the substituent effects in the S<sub>N</sub>2 case is thus demonstrated.

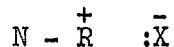
(7) Activation Parameters.

Although the value of the entropy of activation  $\Delta S^\ddagger$  can sometimes furnish information about the mechanism of a solvolytic reaction, the value of the ratio  $\frac{\Delta C_p^\ddagger}{\Delta S^\ddagger}$  where  $\Delta C_p^\ddagger$  is the heat capacity of activation

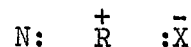
\* In this thesis x% aqueous acetone always refers to the solvent resulting from the addition of x volumes of acetone to (100-x) volumes of water.



I



II



III

For an  $S_N1$  transition state there is no contribution from II and for the extreme  $S_N2$  transition state there is no contribution from III. If all three structures contribute then the reaction must be considered bimolecular within the meaning of that term.<sup>30</sup>

Two mechanisms for borderline reactions have been proposed.<sup>27</sup>

(1) The reaction proceeds via a single transition state with structural contributions from I, II and III.

(2) The individual molecular substitutions making up the reaction, occur via a variety of transition states some of which have structures with no contribution from II, i.e. the reaction takes place with a concurrence of both mechanisms. A simplified model of this proposal involves one unimolecular and one bimolecular path. The supporting evidence for both these views will now be discussed.

Winstein, Grunwald and Jones<sup>29,31</sup> studied the effects of solvent changes on a number of solvolytic reactions thought to proceed via mechanism  $S_N1$ . They proposed the following linear free energy relationship as a means of expressing quantitatively the effects of such changes.



$$\log k = \log k_0 + mY \quad \text{Equation I.1.}$$

$k$  and  $k_0$  are the rate constants for solvolysis in a given solvent and in a standard solvent (80% aqueous ethanol) respectively,  $Y$  is a measure of the ionising power of the solvent ( i.e.  $Y = \log \frac{k}{k_0}$  with  $t$ -butyl chloride as substrate) and  $m$  is the slope of the  $\log k$  v  $Y$  plot for the substrate concerned. It was found that for the solvolytic reactions of primary alkyl halides application of Equation I. 1 led to lower  $m$  values than those found for the unimolecular reactions.

The solvolysis of isopropyl bromide in ethanol-water mixtures was then taken as an example of a reaction whose mechanism was thought to lie in the borderline region and Equation I. 1 applied to the rate data in two ways. Firstly, two concurrent mechanisms were assumed to be operating. An equation of the above form was assumed (with an appropriate  $m$  value) to be appropriate for each reaction path. On combination of the two equations however, a poor fit to the experimental data was obtained. A much superior fit was obtained using a single equation with an intermediate  $m$  value. Thus the authors favoured a description of solvolytic reactions in the borderline region involving a single mechanistic path for a given reaction.

This argument has been criticised<sup>32</sup> on the grounds that the plots of  $\log k$  v  $Y$  for methyl and ethyl bromides are not linear and that the resulting  $m$  values are not independent of those obtained for the  $S_N 1$  reactions.

In any case Streitwieser<sup>33</sup> has pointed out that equations like I.1 have a limited range of applicability as different solvent systems yield different correlation lines. Further limitations have also been pointed out by other authors.<sup>34</sup>

Swain and his co-workers<sup>34-37</sup> have taken the view that one mechanism is sufficient for all solvolysis reactions, the variations in behaviour being accounted for by gradual changes in nucleophilic and electrophilic participation by the solvent in the transition state. This view denies even the existence of a mechanistic borderline. Three main pieces of evidence were put forward.

The reaction between triphenylmethyl chloride and methanol in benzene<sup>35</sup> was found to be first-order in the halide and second-order in methanol and this was interpreted as resulting from a termolecular "push-pull" mechanism. A similar mechanism was assigned to the nucleophilic substitution reactions of methyl halides in benzene<sup>37b</sup> and from the behaviour of these systems it was inferred that solvolyses in general proceeded by a similar mechanism.

A similar conclusion was reached from the gradual variation of values of the Hammett reaction constant,  $\rho$ , for a wide range of solvolytic reactions.<sup>36</sup>

Finally the application of equation I.1<sup>34</sup> revealed large deviations from linearity for the rates of triphenylmethyl fluoride in various

common solvents.

The deviations were such as to lead the authors to conclude that t-butyl chloride was intermediate in its mechanistic behaviour between n-butyl bromide and triphenylmethyl fluoride. They then tried treating t-butyl chloride as an intermediate case as Grunwald and Winstein had treated isopropyl bromide and the results of their calculations for the solvent variation of the total rate and the fraction (in each solvent) proceeding by the  $S_N1$  mechanism were not consistent with the variations expected on the basis of the Hughes-Ingold duality of mechanism.

However the generalisation made from the third-order kinetics observed in benzene is rather sweeping and later work <sup>37b,38</sup> casts doubt on both the results and the conclusions for these reactions. Gold <sup>30</sup> has pointed out that the spread of the  $\rho$  values would be expected on the basis of the assumption that, on approaching the borderline region,  $S_N2$  reactions will become gradually more " $S_N1$  like" as regards substituent effects as the bond breaking process becomes progressively more important in the transition state. The third piece of evidence seems merely to emphasise the limitations of equation I.1.

Kornblum and co-workers <sup>39</sup> have studied the reactions of silver nitrite with alkyl chlorides in various solvents. On the assumption that  $S_N1$  reaction would give the nitrite ester R-ONO and  $S_N2$  reaction the nitro-compound  $RNO_2$  the authors have concluded that such reactions in general exhibit carbonium ion character and bimolecular nucleophilic

displacement character in proportions which vary continuously with structural variation in the halides and that borderline substitutions proceed via a single intermediate mechanism. However, as silver nitrite is insoluble in most of the solvents employed, as was shown by the extraction experiments described by these workers some of the reactions appear to be heterogeneous and thus the conclusions drawn do not seem to be relevant to general nucleophilic substitution reactions.

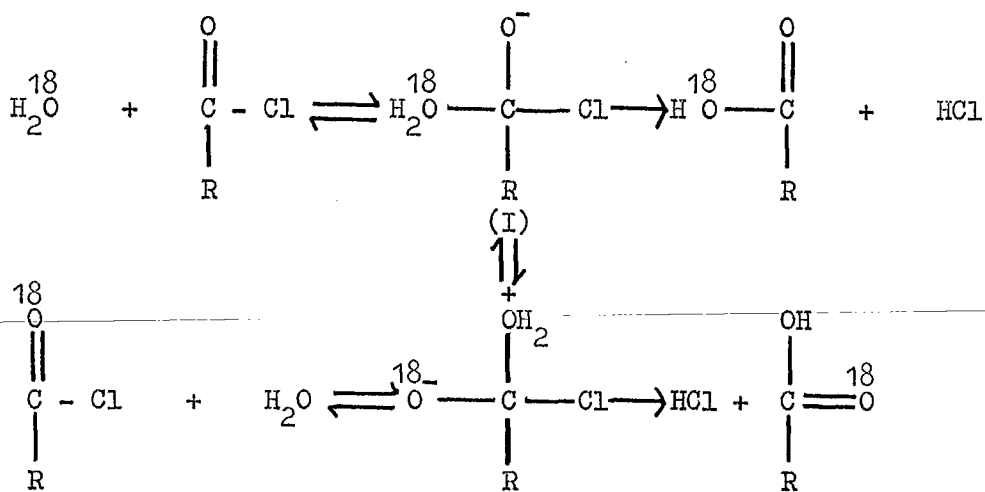
Bird, Hughes and Ingold<sup>32</sup> examined the rates of reaction of *m*-chlorobenzhydryl chloride with fluoride ion and with pyridine and triethylamine in liquid sulphur dioxide. They found that the reactions were subject to mass law retardations by added chloride ion, indicative of  $S_N1$  character. But the initial rates were dependent on the amine used yet did not vary for a given amine at different concentrations in the way expected for bimolecular reactions. Moreover the initial rates did not converge to zero as the amine concentrations were reduced to zero ( $S_N2$  behaviour) nor to a common finite value (concurrent  $S_N1/S_N2$  behaviour). Apart from the mass law effect the results are consistent with an intermediate transition state although no allowance was made for medium effects or ion pair formation which may have had a serious effect on the results.

Gold<sup>30</sup> has criticised the conclusions of some of the above workers, pointing out that any transition state in which there is a covalent interaction of a nucleophile, however weak, is bimolecular and that a

molecule either interacts covalently or does not.

Crunden and Hudson<sup>40</sup> measured the rates of p-substituted benzoyl chlorides in 65% aqueous acetone and formic acid, solvents having similar Y values on the Grunwald-Winstein classification. On the assumption that the nucleophilic power of formic acid is very small, they considered that the excess rate of a compound in 65% acetone over its rate in formic acid was due to an additional bimolecular reaction with the water. On this basis the p-methyl compound underwent solvolysis in 65% acetone with 70% S<sub>N</sub>1 reaction, the parent compound with 40%, and the p-nitro compound entirely by the S<sub>N</sub>2 mechanism. They further considered that concurrent S<sub>N</sub>1 and S<sub>N</sub>2 reactions were more likely than an intermediate mechanism because of the statistical nature of chemical reactions. This approach is in agreement with the results of Gold, Hilton and Jefferson<sup>41</sup> which pointed to the operation of two physically distinct mechanisms in the hydrolysis of benzoyl chloride in 50% aqueous acetone.

However, Bunton, Lewis and Llewellyn<sup>42</sup> have shown that the reaction of benzoyl chloride with water can involve other paths than nucleophilic substitution. They found that for reaction in aqueous dioxan containing <sup>18</sup>H<sub>2</sub>O, samples of starting material extracted from the reaction mixture contained <sup>18</sup>O and the mechanism proposed to account for this was as follows.



If the intermediate (I) is sufficiently stable then proton exchange can take place before it decomposes and this would explain the  $^{18}\text{O}$  in the starting material. (An exchange of  $^{18}\text{O}$  between solvent and substrate has also been reported by Bender for the hydrolysis of esters in aqueous solvents and he has proposed a similar mechanism to account for his results). In general the amount of exchange would here depend on the stability of the C-X bond involved (here a C-Cl bond) and this reaction will be referred to again in connection with the hydrolysis of acyl fluorides (I.8). Thus it appears that the hydrolysis of acyl chlorides may not occur entirely by  $S_N$  mechanisms.

Kohnstam, Queen and Shillaker<sup>26a</sup> showed that azide ions reduced the rate of hydrolysis but increased the rate of ionisation of p-methoxybenzyl chloride in 70% aqueous acetone which was always less than the total rate of disappearance of substrate. Thus under these

conditions p-methoxybenzyl azide appears to be formed by both an  $S_N1$  and an  $S_N2$  process. Further, Kohnstam, Queen and Ribar <sup>26b</sup> showed that p-methoxy and p-phenoxy benzyl chlorides were bimolecularly attacked by nucleophiles in 70% aqueous acetone. From the relative bimolecular rates of the two compounds with the nucleophiles it was concluded that some ionisation of the C-Cl bond takes place before nucleophilic attack and that for the weakest nucleophiles, nitrate and benzene-sulphonate ions the transition state for ionisation has almost been reached before the covalent interaction begins.

Weiner and Sneed <sup>44a</sup> from the results of their work on the intervention of azide ions in the solvolysis of 2-octyl-brosylate in 70% aqueous dioxan originally concluded that the solvolysis proceeds by concurrent  $S_N1$  and  $S_N2$  mechanisms but they have subsequently <sup>44b</sup> shown that the solvolysis proceeds by two bimolecular mechanisms, one of which involves attack by the "inert" component of the solvent in aqueous dioxan and that acetone also intervened when the solvolysis was studied in aqueous acetone.

Le Roux and Swart <sup>45</sup> reported evidence for concurrent of mechanisms in the exchange reaction between t-butyl bromide with radio active bromide ions in acetone but de la Mare <sup>45</sup> concluded that the same reaction was almost wholly  $S_N2$  with a small amount of interference from an elimination side reaction. However, Winstein, Smith and Darwish

have recently taken the view that this compound eliminates HBr nearly quantitatively in acetone and that exchange probably occurs through re-addition of HBr.<sup>46</sup>

Casapieri and Swart<sup>48</sup> have studied the exchange reactions of benzyl and diphenylmethyl chlorides with chloride and bromide ions in various polar solvents. For benzyl chloride the results were consistent with bimolecular reaction for all solvents. For diphenylmethyl chloride the results were consistent with a concurrence of unimolecular and bimolecular mechanisms. For reaction in dimethylformamide the unimolecular rate constant was independent of the nucleophile and increased solvent polarity increased the unimolecular rate constant for chloride exchange while decreasing that for the bimolecular component. However, for the reaction between diphenylmethyl chloride and chloride ions in dimethylformamide the entropy of activation for the bimolecular reaction was substantially the same as for the unimolecular component. The authors did not comment on this. Nevertheless their conclusions are supported by similar work by Pocker in nitromethane.<sup>49</sup>

From their recent results for the exchange reactions of substituted diphenylmethyl thiocyanates (with thiocyanate ions) and substituted triphenylmethyl chlorides (with chloride ions) in polar solvents Fava and his co-workers<sup>50,51</sup> have reached similar conclusions concerning concurrent mechanisms. However their conclusions as regards the triphenylmethyl compounds are perhaps open to question and



will be referred to again in Chapter 4.

Okamoto and co-workers<sup>52</sup> have determined the degree of inversion ( $\alpha$ ) of both products (alcohol and ether) in the solvolysis of optically pure 1-phenylethyl chloride in the complete range of aqueous ethanol solvents. Plots were made of  $\alpha$  v % of water in the solvent for each product. The resultant curves intersected near the 100% alcohol end of the graph. Assuming that both the ethanolysis and hydrolysis are borderline substitutions and react by a concurrence of mechanism in this solvent region then the intersection could arise out of a concurrence of the  $\alpha$  values (each made up of  $S_N1$  and  $S_N2$  components) for ethanolysis and hydrolysis. On the other hand if each solvolysis proceeds by a single mechanism one would expect the alcohol curve to approach the ether curve tangentially as the water content of the solvent increases. Thus one might tentatively conclude that a concurrence of mechanisms is occurring in this case.

In conclusion then, the available evidence<sup>26,48-51</sup> tends to support the operation of concurrent  $S_N1$  and  $S_N2$  mechanisms in borderline substitution involving non-solvolytic nucleophiles. For solvolytic reaction however persuasive evidence in favour of either view has not yet appeared.

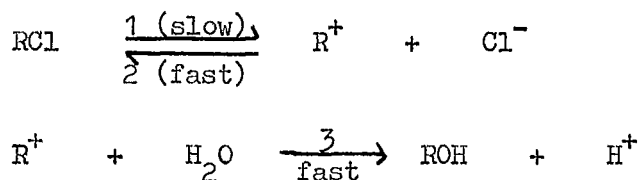
Many of the criteria discussed in Section I.4 are clearly of limited use in or near the borderline region as an  $S_N2$  transition state will be dominated by the bond breaking process and will therefore show

considerable "S<sub>N</sub>1 character" as regards solvent changes, structural effects and ionic strength effects whereas an S<sub>N</sub>1 reaction involving a very unstable carbonium ion may show a negligibly small mass law effect and uncharacteristic stereochemical effects.

Clearly the  $\frac{\Delta C_p}{\Delta S^\ddagger}$  criteria is useful for reactions thought to be in or near the borderline region as it does not depend on the effects of changes in the reaction system.

#### I.6. Mass Law Effects in S<sub>N</sub>1 Reactions.

Bateman, Hughes and Ingold<sup>11</sup> first pointed out that the unimolecular (S<sub>N</sub>1) mechanism for solvolysis would lead to first-order kinetics only under limiting conditions. Neglecting ion-pair formation the reaction scheme for an organic chloride reacting with an aqueous solvent is,



Thus the rate determining ionisation is reversible and the application of the stationary state principle to the highly reactive carbonium ion R<sup>+</sup>, gives the rate law,

$$-\frac{d[\text{RCl}]}{dt} = \frac{k_1[\text{RCl}]}{1 + \frac{k_2}{k_3}[\text{Cl}^-]} \quad \text{Equation I.2.}$$

First-order kinetics will only result if  $k_2 \ll k_3$  i.e. if the carbonium ion is very unstable so that the solvation shell (containing water molecules) collapses, generating alcohol before it can be penetrated by chloride ions with consequent substrate regeneration. This scheme predicts that in general an  $S_N1$  reaction rate should be depressed by addition of a common ion and that for a substrate giving rise to a very stable carbonium ion a fall in the calculated integrated first-order rate coefficients should be found as the reaction proceeds. The first prediction has been confirmed for a number of organic chlorides <sup>11,18</sup> and the expected deviations from first-order kinetics during a run have been observed for the solvolyses of substituted diphenylmethyl chlorides <sup>8,11,53,54</sup> and for substituted 9-fluorenyl chlorides, <sup>55</sup> all in aqueous acetone solvents.

Lucas and Hammett <sup>56</sup> suggested that the interpretation of common ion retardation on the basis of a mass law effect was questionable in view of their results concerning electrolyte effects on the solvolyses of t-butyl nitrate and benzyl nitrate in aqueous dioxan. They found that perchlorate ions accelerated while hydroxide ions retarded and other ions had effects which paralleled their effects on the activity of water in the medium. However Benfey, Hughes and Ingold <sup>5</sup> showed that chloride ions depressed the rate of hydrolysis of diphenylmethyl chloride in aqueous acetone and enhanced that of diphenylmethyl bromide in the same solvent in accordance with the previously established mass law and

ionic strength effects <sup>11</sup> while bromide ions enhanced the rate of diphenylmethyl chloride yet depressed that of diphenylmethyl bromide, account being taken where necessary of the exchange reactions accompanying solvolysis. Thus the reality of the mass law effect was established.

Ingold and co-workers <sup>11</sup> observed no variation in the mass law constant  $[\alpha^{\circ} = k_2^{\circ} / k_3^{\circ}]^*$  for p,p' dimethyl diphenylmethyl chloride over a range of acetone/water solvents but later work <sup>8,53</sup> has shown that  $\alpha^{\circ}$  for dichlorodiphenylmethane decreased as the water content of the solvent increased in the aqueous acetone solvents employed. This was explained in terms of the different effects of solvent changes on  $k_2^{\circ}$  and  $k_3^{\circ}$ .

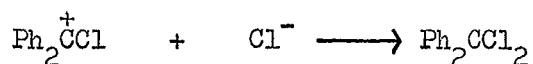
It would be expected that structural changes in the substrate which enhance the stability of the intermediate carbonium ion (and hence increase the rate of solvolysis) would also increase the value of  $\alpha$ . Although this behaviour has been demonstrated for a number of compounds <sup>11,53,54</sup> cases have been reported in which changes in  $\alpha^{\circ}$  resulting from a structural alteration in the substrate, are greater than would be expected from the corresponding changes in hydrolysis rate, <sup>53,54</sup> and the rate of ionisation of p,p' dimethyldiphenylmethyl chloride is a factor of 10 greater than that of dichlorodiphenylmethane in 85%

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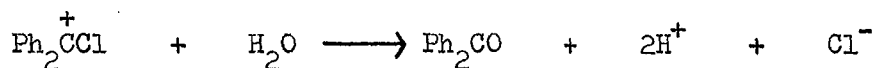
\* The superscript o refers to zero ionic strength.

acetone whereas  $\alpha$  for the latter compound is 140 and for the former 74.<sup>53</sup> These results have been interpreted as meaning that in these cases the fully developed carbonium ion is being stabilised by electron releasing substituents more than is the transition state for solvolysis. This is consistent with the fact that the "anomalously" large  $\alpha$  values are associated with substituents having a greater response to increased electron demand at the reaction centre due to the presence in the group of unshared electron pairs. It has further been reported that the change from diphenylmethyl chloride to the corresponding bromide, which increases the nucleophilic power of the leaving group, also increases the value of  $\alpha^{\circ}$ ,<sup>11</sup> but more recent work<sup>57</sup> has suggested that the carbonium ion involved here may not be able to discriminate between different nucleophiles unless they are of widely differing strengths.

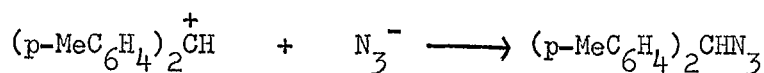
The variation of  $\alpha$  with temperature leads to the value of the difference in activation energy for reactions 2 and 3 (see the beginning of this section). Thus Bensley and Kohnstam<sup>53</sup> found that the activation energy for the reaction



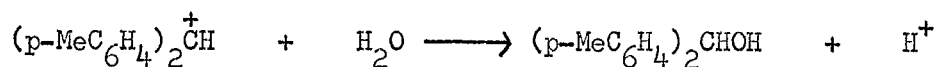
was about 0.9 k.cal. greater than that for the reaction



This result is consistent with the conclusion of Hawdon, Hughes and Ingold<sup>59</sup> that the activation energy for the reaction



is 4 k.cal. greater than that for the reaction,



in 90% aqueous acetone. The implication is that at least the ionic reactions cited above have an activation energy and this is consistent with the view that the solvation shells of both ions involved must be broken down before combination can occur.

It must be stressed that ionic strength and mass law effects usually operate together and that the precise determination of  $\alpha^\circ$  and initial rates of ionisation when high substrate concentrations or added salts are involved, can only be affected by complex procedures allowing if necessary for the interaction of the two effects and for activity coefficient corrections.<sup>8,11,53</sup> These will be further discussed in Chapter 4.

#### I.7. The Effect of Changing the Leaving Group on Rate and Mechanism.

Limited changes in the nature of the leaving group often have comparable effects on the rates of both  $\text{S}_{\text{N}}1$  and  $\text{S}_{\text{N}}2$  reactions and usually have only a small effect on the relative importance of the two mechanisms.<sup>60</sup>

However broad generalisations are not possible as the effects can be dependent on the solvent, the nature of the reaction centre and the

nucleophile involved. For example for some  $S_N2$  reaction of halides with anions and amines, change from a dipolar aprotic solvent, <sup>58,61</sup> (e.g. dimethylformamide), to a hydrogen bonding solvent, (methanol), exerts a "levelling" effect on the relative rates since hydrogen bonding more strongly stabilises the transition states involving the smaller more strongly bound leaving groups. <sup>62</sup>

An examination of the solvolysis of structurally analogous chlorides and bromides in aqueous acetone <sup>63</sup> solvents has shown that the (solvent dependent) enhanced reactivity of the bromides is due mainly to a decrease in the activation energy for both  $S_N1$  and  $S_N2$  mechanism and also that when Cl is replaced by Br in benzyl chloride (which reacts in aqueous acetone by  $S_N2$  mechanism which is close to the borderline region), <sup>23</sup> the change to a better leaving group does not alter the mechanism. Similarly Kohnstam and Tidy <sup>64</sup> have shown that replacement of Cl by the toluene p-sulphonate group in a series of p-substituted benzyl compounds hardly alters the point of mechanistic change for solvolysis in aqueous acetone although the latter compounds were more reactive.

Hoffmann <sup>65</sup> has discussed the mechanistic conclusions to be drawn from the values of the ratio  $\frac{k_{ROTS}}{k_{RBr}}$  i.e. the ratio of the rate constant for the reaction of an alkyl toluene p-sulphonate to the rate constant for the same reaction of the corresponding bromide. The reactions

involved were nucleophilic displacements involving anionic nucleophiles and some solvolytic reactions. He found that the ratio was small for  $S_N2$  reactions and large for  $S_N1$  reactions. Further the ratio increased for  $S_N2$  reactions as the strength of the nucleophile decreased. The versatility of the toluene p-sulphonate ion as a leaving group was considered to arise mainly from its capacity for delocalising charge in the transition state. Thus a large  $\frac{k_{ROTs}}{k_{RBr}}$  ratio indicates a high degree of charge separation in the transition state. For solvolytic reactions however, differences in the solvation of initial and transition states for bromides and toluene p-sulphonates are important.

#### I.8. Fluorine as a Leaving Group.

The behaviour of fluorine as a leaving group may be expected to be singular among the halogens because of the extreme properties of the element. However the nucleophilic substitution reactions of alkyl and aralkyl fluorides have not been studied in the same detail as have the corresponding reactions of chlorides and bromides. Examples of this singular behaviour will now be considered under 3 main headings.

##### (1) Relative Rates

In view of the greater amount of energy required to break a carbon fluorine bond as compared to a carbon-chloride bond [e.g.  $D_{MeF} = 123$  k.cal. mole<sup>-1</sup>,  $D_{MeCl} = 81$  k.cal. mole<sup>-1</sup>]<sup>66</sup> an alkyl fluoride would be expected to undergo nucleophilic substitution much more slowly than the



corresponding chloride under the same conditions.\*

The available data have been reviewed by R.E. Parker,<sup>67</sup> and results for five substrate pairs are shown in the following table.

TABLE I. 4.

The Rate Ratios ( $k_{\text{RCl}}/k_{\text{RF}}$ ) for some Alkyl Fluorides and Chlorides.

<u>Halides</u>	<u>Reagent</u>	<u>Solvent</u>	<u>Temperature</u>	<u><math>k_{\text{RCl}}/k_{\text{RF}}</math></u>
MeX <sup>68</sup>	H <sub>2</sub> O	H <sub>2</sub> O	100°C	25
MeX <sup>69</sup>	HO <sup>-</sup>	H <sub>2</sub> O	100°C	27
PhCH <sub>2</sub> X <sup>70</sup>	H <sub>2</sub> O	10% aq. acetone	50°C	300
t-BuX <sup>71</sup>	H <sub>2</sub> O/EtOH	80% aq. ethanol	25°C	10 <sup>5</sup>
Ph <sub>3</sub> CX <sup>72</sup>	H <sub>2</sub> O	85% aq. acetone	25°C	10 <sup>6</sup>

Although some of the above data are approximate it is clear that the  $k_{\text{RCl}}/k_{\text{RF}}$  ratio increases on passing from conditions which are conducive to the operation of the S<sub>N</sub>2 mechanism to those where the unimolecular mechanism might be expected to operate, i.e. as the C-X bond breaking process becomes

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\* This is not the case for certain nucleophilic substitutions involving activated aryl fluorides which are often more reactive than the corresponding chlorides presumably because there is very little C-F bond breaking in the transition state.<sup>67</sup>

increasingly dominant in the transition state. Thus the influence of C-X bond strength makes itself felt increasingly strongly down the series.

(2) Activation Parameters.

It is of further interest to enquire how the much diminished reactivity of the fluorides is reflected in the activation parameters for their reactions as compared to those calculated for the corresponding reactions involving chlorides.<sup>67</sup> The increased capacity of the incipient fluoride ion in the transition state to form hydrogen bonds with the solvent (relative to the substrate) as compared to the incipient chloride ion, might be expected to result in a more negative entropy of activation relative to the chloride. Similarly the resultant stabilisation of the transition state should lower the activation energy as compared to the high value expected on the basis of the C-F bond strength only.\* Not very many precise data are available to test this hypothesis. Swain and co-workers have determined the activation energies for the solvolysis of triphenylmethyl fluoride in various acetone-water solvents as recorded below.

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\* The transition states for both chloride and fluoride solvolysis will of course both be stabilised by solvation.

TABLE I.5.

Activation Energies in the Solvolysis of Triphenylmethyl Fluoride.

<u>Solvent</u>	<u>Temperature</u>	<u>E(k.cal.)</u>	<u>Refs.</u>
50%	25°C	13.0 ± .6	73
70%	25°C	24.4	34b
85%	25°C	22.6	72

Winstein's data <sup>74</sup> for the variation of activation energy with water content for the solvolysis of t-butyl chloride in aqueous acetone show a shallow minimum near the aqueous end of the scale. If this represents typical S<sub>N</sub>1 behaviour then the solvent variation reported above would seem to be anomalous. In any case the data provided by Swain and Scott <sup>72</sup> for triphenylmethyl chloride relate to the 85% solvent.

TABLE I.6.

The Hydrolyses of Triphenylmethyl Chloride and Fluoride in 85%

Aqueous Acetone at 25°C. <sup>72</sup>

<u>Compound</u>	<u>k<sub>1</sub> sec.<sup>-1</sup></u>	<u>E(k.cal.)</u>	<u>-ΔS<sup>‡</sup> cals/°K/mole</u>
Ph <sub>3</sub> CCl	2.7	12.5	17
Ph <sub>3</sub> C-F	2.7x10 <sup>-6</sup>	22.6	10

Thus, taken at face value the results for this substrate pair are not consistent with the hypothesis. However it is not clear how the values for the chloride were obtained. An unexplained extrapolation procedure was used using rates obtained at  $-34^{\circ}\text{C}$  and  $-14^{\circ}\text{C}$ . Even at  $-14^{\circ}\text{C}$  the value of  $k_1$  was  $1.1 \times 10^{-1} \text{ sec.}^{-1}$  (half life 7 sec.) although the kinetic procedure described involved an acid-base titration technique. Thus the figures for triphenylmethyl chloride may be seriously in error.

In the bimolecular reactions of the methyl halides with water and with hydroxide ion the slower rates for the fluoride result from a lowering of the entropy of activation.<sup>68,69</sup> Here the activation energy was lower for the fluoride in both reactions. Care must here be exercised in the interpretation of these results as it appears that solvolysis reactions in water are governed by different factors than those which operate in aqueous organic solvents (see Chapter 2).

Chapman and Levy<sup>75</sup> studied the bimolecular reactions of various simple alkyl fluorides with ethanolic sodium ethoxide. They found for the primary and secondary fluorides studied, the activation energies differed little from that for isobutyl bromide, the relatively slow rates for the fluorides again being due to lower pre-exponential factors, i.e. more negative entropies of activation. In the case of the tertiary fluorides there was also a substantial increase in the energy of activation, as compared to t-butyl bromide.

(3) Acid Catalysis

Acid catalysis would be expected for the nucleophilic substitution reactions of alkyl fluorides since an acid should assist the heterolysis of a C-F bond by hydrogen bonding. The phenomenon has been observed for the solvolysis of substituted benzyl fluorides in aqueous ethanol,<sup>76</sup> for various aliphatic fluorides in the same solvent<sup>77</sup> and for the solvolysis of 1,3,5,7,7,7, hexafluoro-1-heptene in moist formic acid.<sup>78</sup>

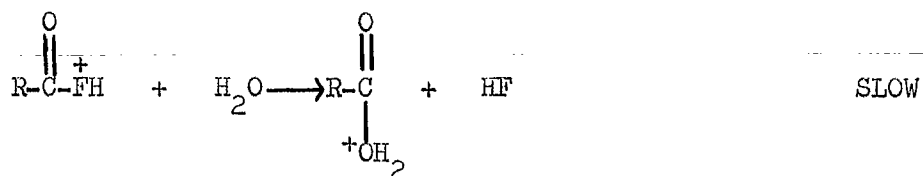
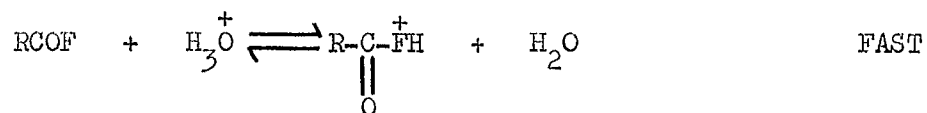
There have also been some more detailed studies. Bevan and Hudson<sup>79</sup> studied the acid catalysed solvolysis of benzoyl fluoride in aqueous acetone. No auto-catalysis was observed and the rate of the acid catalysed reaction was less responsive to increases of water concentration in the solvent than was the uncatalysed reaction, from which the authors concluded that acid catalysis reduced the importance of solvation by water in the transition state. The catalytic effect of the hydrochloric acid employed was attributed to the hydrogen ions as no rate increase resulted from the addition of lithium chloride.

Satchell<sup>80</sup> has extended these studies to the solvolyses of other acyl fluorides in aqueous dioxan.

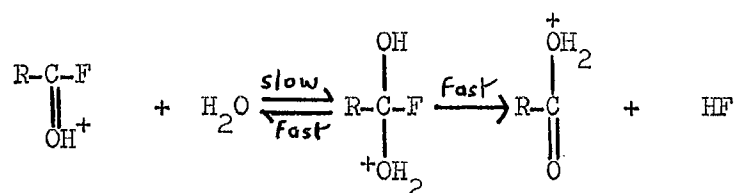
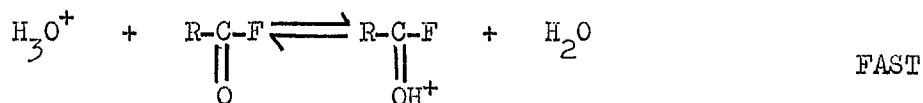
The general rate law was,

$$-\frac{d}{dt}[\text{ROCF}] = (k_0 + k_0[\text{H}_3\text{O}^+]) [\text{ROCF}]$$

the suggested mechanism being,

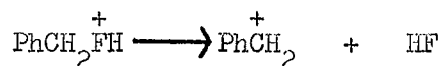


Acid catalysis for acyl chlorides has not been observed under these conditions and so proton attachment to fluorine rather than to the carbonyl oxygen was preferred. The latter mechanism would be

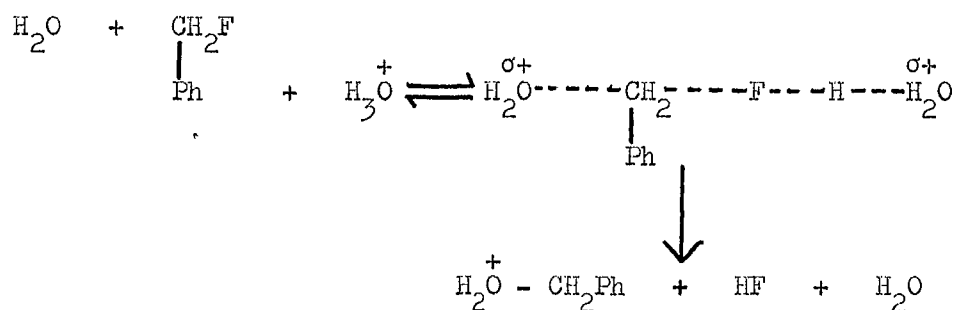


Here, the second step is very similar to that proposed by Bunton and co-workers<sup>42</sup> to explain his isotopic exchange results for acyl compounds in aqueous dioxan (see Section I.5) and it would be of interest to see if exchange occurs more readily with a fluoride than with a chloride as it should on Bunton's hypothesis.<sup>42</sup>

Swain and Spalding<sup>70</sup> found that the rate of solvolysis of benzyl fluoride in 10% aqueous acetone was very nearly proportional to  $h_0$  (the Hammett acidity function). They suggested as the rate determining step (after an initial proton transfer),



R.E. Parker<sup>67</sup> has criticised this view and has suggested that the following mechanism is more likely.



However this mechanism is not consistent with the absence of a solvent

isotope effect. Swain<sup>70</sup> found that  $\frac{k_{\text{D}_2\text{O}}}{k_{\text{H}_2\text{O}}}$  was unity within experimental error.

It is noteworthy that the activation energy of the catalysed reaction was found to be greater than that of the uncatalysed but that the entropy of activation was 15 e.u. less negative. The fact that the solvent used was so highly aqueous (see Chapter 2) may partly account for these rather surprising results. The solvolysis of benzyl

fluoride in 99.86% formic acid has recently been examined by Delpeuch and co-workers<sup>81</sup> who observed autocatalysis at high substrate concentrations.

The nature of the acid catalysis of the solvolysis of triphenylmethyl fluoride in 70% aqueous acetone has been investigated in some detail<sup>82</sup> by Coverdale and Kohnstam. The rate law was found to be,

$$\frac{d}{dt}[\text{Ph}_3\text{COH}] = -\frac{d}{dt}[\text{Ph}_3\text{CF}] = \left\{ k_0 + k_{\text{HF}}[\text{HF}] + k_{\text{H}}[\text{H}^+] \right\} [\text{Ph}_3\text{CF}]$$

The integrated form of this equation gave rate coefficients in good agreement with those observed under all the experimental conditions employed. Thus the reaction was autocatalysed by the HF produced in the solvolysis as well as by hydrogen ions in the form of added HCl. Sodium chloride and sodium fluoride had little effect on the rate. Autocatalysis had previously been reported in the solvolyses of some primary and secondary alkyl fluorides in aqueous ethanol.<sup>77</sup>

Swain and co-workers<sup>19,73</sup> had previously reported no acid catalysis in the solvolysis of triphenylmethyl fluoride in 50% aqueous acetone with an (added)  $\text{HNO}_3$  concentration of  $5 \times 10^{-3} \text{M}$ ; whereas in the 70% solvent Coverdale and Kohnstam found that this concentration of HCl doubled the rate.<sup>82</sup> However in a later paper Swain and co-workers<sup>83</sup> reported specific hydronium ion catalysis in the 50% solvent. It is curious that Moelwyn-Hughes did not observe any acid catalysis in the hydrolysis of methyl fluoride in aqueous solution 0.03M in perchloric acid.<sup>68</sup>



### I.9. The Present Study.

In view of the lack of precise reliable information concerning the solvolytic reaction of alkyl fluorides, especially in relation to the corresponding chlorides, it was decided at the outset to examine the solvolysis of triphenylmethyl chloride and methoxymethyl chloride in 85% aqueous acetone. Both these reactions were expected, from consideration of earlier work,<sup>20</sup> to react rapidly and by the S<sub>N</sub>1 mechanism.

Thus the corresponding fluorides were also expected to solvolyse unimolecularly in aqueous acetone solvents, and to do so at convenient rates. Also it was hoped that the results would provide a test of the mechanistic criterion based on the value of the  $\frac{\Delta C^\ddagger}{\Delta S^\ddagger}$  ratio when fluorine is the leaving group.

In the event the results for methoxymethyl chloride indicated that its solvolysis in 85% aqueous acetone does not proceed by an S<sub>N</sub>1 mechanism and so the fluoride was not studied. Various attempted syntheses of diphenylmethyl fluoride proved unsuccessful (see Chapter 6) and so the information obtained as regards substrate pairs has been restricted to the triphenylmethyl and p-nitrotriphenylmethyl compounds. The reactions of both triphenylmethyl chlorides were subject to considerable mass law effects. The mass law constants at each temperature were evaluated in order to obtain the corresponding rates of ionisation at zero ionic strength, necessary for the calculation of the required activation parameters.

CHAPTER II.

ENTROPIES AND HEAT CAPACITIES OF ACTIVATION IN SOLVOLYTIC REACTIONS.

II.1. The Arrhenius Law.<sup>84</sup>

In 1887 Van't Hoff suggested that the relationship between the rate of a chemical reaction and the temperature should be of a form similar to that known to hold for the relationship between equilibrium constants and temperature. He proposed the equation,

$$k = A \exp(-E/RT) \qquad \text{Equation II.1}$$

where  $k$  is the rate constant for a particular reaction,  $T$  is the absolute temperature and  $A$  and  $E$  are constants for the reaction concerned. Arrhenius showed that the equation fitted the data for a large number of reactions and it thus became known as the Arrhenius Equation. He also suggested that during the course of reaction, molecules must become activated by collisions, that there is an equilibrium between normal and activated molecules, and that  $E$  was identified with the energy difference between the normal and activated molecules. The development of the collision theory of reactions later identified  $A$  as being related to the collision frequency of molecules.

However it has long been predicted on theoretical grounds<sup>85</sup> that  $E$  should be temperature dependent and it is therefore better defined by the differential form of Equation II. 1.

$$\frac{d \ln k}{dT} = \frac{E}{RT^2} \quad \text{Equation II. 2}$$

## II.2. The Transition State Theory.<sup>86</sup>

At the present time the most satisfactory theory of reaction rates is that proposed by Eyring<sup>86</sup> and other workers in which the reactants in a chemical reaction are considered to pass through a continuous series of configurations en route to the formation of products. At some intermediate stage a critical configuration of maximum free energy is reached, the transition state or activated complex. Reactant molecules are in equilibrium with the activated complexes and the reaction rate is determined by the rate of decomposition of the latter species.

The activated complex is regarded as a normal molecule with the usual thermodynamic properties except that motion in one direction, i.e. along the reaction co-ordinate, leads to product formation. The difference in free energy between the activated complex and the reactants, (all species being in their standard states), is the free energy of activation,  $\Delta G^\ddagger$ , and it can be shown that this quantity is related to

the rate coefficient for the reaction by the equation,

$$k = \frac{\bar{k}T}{h} \exp(-\Delta G^\ddagger/RT) \quad \text{Equation II. 3.}$$

where  $\bar{k}$ ,  $h$ , and  $R$  have their usual significance and  $T$  is the absolute temperature.

Thus applying the thermodynamic relationship between  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  for a chemical process and taking logs, we have

$$\ln k = \ln \frac{\bar{k}T}{h} + \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} \quad \text{Equation II. 4}$$

where  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  are the enthalpy and entropy of activation.

Differentiation of Equation II. 4 with respect to temperature, at constant pressure, gives

$$\frac{d \ln k}{dT} = \frac{RT + \Delta H^\ddagger}{RT^2} \quad \text{Equation II. 5}$$

and comparison with Equation II. 2 shows that

$$E = \Delta H^\ddagger + RT \quad \text{Equation II. 6}$$

and therefore

$$\frac{dE}{dT} = \Delta C_p^\ddagger + R \quad \text{Equation II. 7}$$

where

$$\Delta C_p^\ddagger = \frac{d(\Delta H^\ddagger)}{dT}$$

Thus  $E$  is shown to be closely related to the enthalpy of activation and is thus called the energy of activation and  $\Delta C_p^\ddagger$ , the heat capacity of activation at constant pressure is related to the temperature coefficient of  $E$ . Further, if  $\Delta C_p^\ddagger$  differs significantly from zero then both  $E$  and  $\Delta S^\ddagger$  will vary with temperature.

Many workers have ignored the possibility of such variations, probably because a  $dE/dT$  value of 100 cal. deg.<sup>-1</sup> mole<sup>-1</sup>, which is larger than usually observed, would give rise to only small deviation from linearity in a plot of  $\log k$  against  $1/T$ .

Thus, the inadequacy of equation II.1 may have escaped notice due to insufficient precision in the rate measurements.

Nevertheless, in the last few years, the number of reports of  $dE/dT$  values has increased.<sup>87</sup> Except in two early cases,<sup>88,89</sup> and some examples in which quantum mechanical "tunnelling" through the free energy barrier has been postulated,<sup>87</sup> all the values are negative and mostly relate to solvolytic reactions. Since this thesis is concerned with such reactions further discussion of the significance of heat capacities of activation will be restricted to these systems.

The methods used in the evaluation of energies and entropies of activation from rate measurements for cases in which  $\Delta C_p^\ddagger$  does differ significantly from zero are discussed in Chapter 6.

### II.3. Heat Capacities of Activation in Solvolytic Reactions.

As mentioned in the previous section, if  $\Delta C_p^\ddagger$  for a reaction differs significantly from zero, then values of  $E$  and  $\Delta S^\ddagger$  may be strongly temperature dependant. For example in the hydrolysis of diphenylmethyl chloride in 70% aqueous acetone <sup>27</sup>  $\Delta C_p^\ddagger$  is  $-38 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$  and  $\Delta S^\ddagger$  at  $0^\circ\text{C}$  is  $-3.88 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ , while at  $50^\circ\text{C}$ ,  $\Delta S^\ddagger$  is 6.4 entropy units more negative.

In general therefore, since for solvolytic reactions heat capacities of activation are not usually zero, comparisons of  $E$  and  $\Delta S^\ddagger$  values for different reactions must relate to the same temperature and  $\Delta C_p^\ddagger$  values are essential if different temperatures have been used in the rate measurements for the reactions concerned.

In practice  $\Delta C_p^\ddagger$  is constant within the limits of experimental error but there is no fundamental reason why this should be so. An experimentally determined  $\Delta C_p^\ddagger$  represents the mean value over the range of temperatures studied and is probably most reliable at the mean temperature. Consequently values of  $E$  and  $\Delta S^\ddagger$  calculated for temperatures outside the experimental range may be subject to indeterminate errors and in comparing activation parameters for a series of reactions it is clearly best, to employ a temperature as close as possible to all the experimental ranges involved in the rate measurements.

Values of  $\Delta C_p^\ddagger$  for solvolytic reactions in water and a number of

aqueous organic solvents are available <sup>27</sup> and are generally in the range -20 to -70 cal. deg.<sup>-1</sup> mole<sup>-1</sup>. Where several compounds have been studied in the same aqueous organic solvent the results show the striking feature that for the S<sub>N</sub>1 reactions of a variety of alkyl chlorides and bromides, <sup>27</sup> two toluene-p-sulphonates <sup>64</sup> and diphenylmethyl p-nitrobenzoate, <sup>63b</sup> the ratio  $\frac{\Delta C_p^\ddagger}{\Delta S^\ddagger}$ , is independent of the substrate for a given solvent and temperature, and has a smaller value for compounds reacting by mechanism S<sub>N</sub>2 under the same conditions. <sup>27,63a</sup> The constancy of the ratio for S<sub>N</sub>1 reactions is unlikely to be fortuitous as some of the entropy values differ widely. The results provide additional evidence to support the original proposal of Binsley and Kohnstam <sup>23</sup> that the value of this ratio for a given solvent and temperature can be used on a test of mechanism for solvolytic reactions.

However a consideration of the results for solvolytic reactions in water shows quite clearly that the above test of mechanism does not apply in this solvent. The values of  $\Delta C_p^\ddagger / \Delta S^\ddagger$  at 50° for three substrates whose reactions with water would be expected to occur by mechanism S<sub>N</sub>1 are recorded below:

<u>Compound</u>	<u><math>[\Delta C_p^\ddagger / \Delta S^\ddagger]_{50^\circ C}</math></u>
Bu <sup>t</sup> CH <sub>2</sub> O <sub>3</sub> SPh <sup>90</sup>	10.7
Bu <sup>t</sup> CH <sub>2</sub> O <sub>3</sub> SMe <sup>90</sup>	6.77
Bu <sup>t</sup> Cl <sup>91</sup>	-22.2

Thus the ratio varies widely from substrate to substrate. This, together with the fact that  $\Delta S^\ddagger$  for t-butyl chloride is positive in water whereas negative  $\Delta S^\ddagger$  values are the rule in aqueous organic solvents, strongly suggests that the values of these parameters are controlled by different factors in the two solvent systems. The nature of these differences will be discussed later, (Section II.5).

The use of  $\frac{\Delta C_p^\ddagger}{\Delta S^\ddagger}$  values as a criterion of mechanism in aqueous organic solvents has been criticised<sup>92</sup> on the grounds that as  $\Delta S^\ddagger$  becomes less negative with decreasing temperatures, the function  $\frac{\Delta C_p^\ddagger}{\Delta S^\ddagger}$  will be discontinuous at low temperatures. However, it is found experimentally that the variations of  $\Delta S^\ddagger$  with temperatures is of the form

$$\Delta S_T^\ddagger = A + \Delta C_p^\ddagger \ln T$$

where A and  $\Delta C_p^\ddagger$  are empirical constants relating only to the experimentally accessible temperature range for the reaction in question. Thus the temperature ( $T_0$ ) at which  $\Delta S^\ddagger$  becomes zero is given by

$$\ln T_0 = \frac{-A}{\Delta C_p^\ddagger}$$

and it is found that for the systems under consideration this temperature is always well outside the experimental range. Indeed,  $T_0$  often lies below the freezing point of the solvent concerned and is therefore of no physical significance.



In view of the constant value of the  $\frac{\Delta C_p^\ddagger}{\Delta S^\ddagger}$  ratio observed for  $S_N1$  solvolyses under given conditions, it seems reasonable to suppose that the same factors control the magnitude of both parameters for such reactions in aqueous organic solvents. Clearly, any explanation of the observed values must take account of the fact that  $\Delta C_p^\ddagger$  and  $\Delta S^\ddagger$  are invariably negative in these solvents as well as of the constancy of the above ratio.

#### II.4. The Interpretation of Entropies and Heat Capacities of Activation for Solvolytic Reactions in Aqueous Organic Solvents.

In this section, two theoretical approaches will be discussed.

##### (a) The Electrostatic Approach.

All the reactions discussed in this section involve an increase in polarity in passing from a weakly dipolar initial state to a much more polar transition state. Such systems may be discussed in terms of Kirkwoods equation<sup>93</sup> for the electrostatic contribution to the change in free energy  $\Delta G_D$  involved in transferring a polar molecule from a medium of unit dielectric constant to one of dielectric constant D.

Thus,

$$\Delta G_D = \frac{-\mu^2}{r^3} \left( \frac{D-1}{2D+1} \right) \quad \text{Equation II.8}$$

where  $\mu$  is the dipole moment and r the radius of the molecule. This equation then leads to the following expressions for the electrostatic

contributions ( $\Delta S_D^\ddagger$  and  $\Delta C_D^\ddagger$ ) to  $\Delta S^\ddagger$  and  $\Delta C_p^\ddagger$  for  $S_N1$  solvolysis,

$$\Delta S_D^\ddagger = \left\{ \frac{\mu_\ddagger^2}{r_\ddagger^3} - \frac{\mu_i^2}{r_i^3} \right\} \frac{3D}{(2D+1)^2} \cdot \frac{d \ln D}{dT} \quad \text{Equation II.9}$$

$$\Delta C_D^\ddagger = - \left\{ \frac{\mu_\ddagger^2}{r_\ddagger^3} - \frac{\mu_i^2}{r_i^3} \right\} \frac{3DT(2D-1)}{(2D+1)^3} \cdot \left[ \frac{d \ln D}{dT} \right]^2 \quad \text{Equation II.10}$$

Here the subscripts  $i$  and  $\ddagger$  refer to the initial and transition states and  $D$  is the dielectric constant of the solvent concerned.

If contributions to  $\Delta S^\ddagger$  and  $\Delta C_p^\ddagger$  from bond stretching are negligible as seems likely then the above equations show that a purely electrostatic approach predicts negative values for both parameters ( $\frac{d \ln D}{dT}$  is negative for all known solvents) and a ratio independent of the substrate as observed.

A comparison of some observed values for  $\frac{\Delta C_p^\ddagger}{\Delta S^\ddagger}$  and the values calculated on the basis of the electrostatic approach, for a variety of solvents, is given in Table II.1.

Clearly the electrostatic approach is quantitatively inadequate. Observed values are always larger than those calculated and widely different values are observed for solvents of similar dielectric constant. It must therefore be concluded that electrostatic factors are not the dominant ones in determining the magnitude of  $\Delta C_p^\ddagger$  and  $\Delta S^\ddagger$  for these reaction conditions and it is noteworthy that a similar failure of the

electrostatic approach to account for the observed values of activation parameters in Menschutkin reactions has been reported.<sup>95</sup>

TABLE II. 1.<sup>27</sup>

Electrostatic and Observed Values of  $\frac{\Delta C_p^\ddagger}{\Delta S^\ddagger}$  for S<sub>N</sub>1 Solvolysis at 50°C.

<u>Aqueous Solvent</u>	D.	$\frac{\Delta C_p^\ddagger}{\Delta S^\ddagger}$	
		calc.	observed
50% EtOH	46.2	1.71	6.42
50% Acetone	46.0	1.56	2.89
70% Acetone	34.2	1.55	3.68
80% Acetone	28.0	1.54	2.75
80% EtOH	27.8	1.90	3.86
85% Acetone	24.8	1.53	2.81

(b) The Solvation Model.

It has long been recognised<sup>1</sup> that an essential feature of an S<sub>N</sub>1 solvolysis is the stabilisation of the highly polar transition state by solvation interactions with solvent dipoles. Thus the activation energy is very much reduced as compared to that for the corresponding gas phase ionisation.

If it is assumed that in aqueous acetone, the additional solvation requirements of the transition state are met by the more polar water molecules then these molecules will be less free to move in the transition state, relative to the initial state, and consequently their entropies and heat capacities will be reduced. Hence if contributions to  $\Delta S^\ddagger$  and  $\Delta C_p^\ddagger$  from bond stretching and electrostatic effects<sup>27</sup> are small, then solvation will control the magnitudes of these parameters. Both will be negative and on this view the ratio  $\frac{\Delta C_p^\ddagger}{\Delta S^\ddagger}$  could well be independent of the substrate.

$\Delta C_p^\ddagger$  values for  $S_N2$  reactions are in general less negative than those for  $S_N1$  solvolysis and the former reactions are also associated with more negative entropies of activation. Thus  $\frac{\Delta C_p^\ddagger}{\Delta S^\ddagger}$  ratios are smaller than those for  $S_N1$  reactions under the same conditions. The transition state for an  $S_N2$  reaction requires a greater spread of charge and possibly less charge development than an  $S_N1$  transition state. Consequently the increase in solvation on activation should be smaller and on this view would give rise to a smaller  $\Delta C_p^\ddagger$  as observed, if the loss of heat capacity on covalent attachment of a water molecule is of the same order as the loss when a water molecule solvates the transition state. This assumption is reasonable since there could be compensation for translational and librational heat capacity losses through new modes of vibration involving the attached molecule in the transition state. Covalent attachment of a water molecule could however give

rise to substantial loss of entropy explaining the more highly negative entropies of activation (relative to  $S_{N1}$  values), observed for  $S_{N2}$  reactions. Thus the solvation model can be used to interpret qualitatively the observed values of  $\Delta C_p^\ddagger$  and  $\Delta S^\ddagger$  for both  $S_{N1}$  and  $S_{N2}$  solvolytic reactions.

For  $S_{N1}$  reactions in aqueous acetone solvents, a quantitative discussion of the solvation model is possible.<sup>27</sup> We can write

$$\begin{aligned} \Delta S^\ddagger &= n \left[ (S_T - S_i^o) - (S_i - S_i^o) \right] \\ \Delta C_p^\ddagger &= n \left[ (C_T - C_i^o) - (C_i - C_i^o) \right] \end{aligned} \quad \text{Equation II.11}$$

where  $n$  is the effective increase in solvation number associated with the activation process,  $S_T$  and  $C_T$  are the molar contributions of a solvating molecule to the entropy and heat capacity of the transition state, (assumed to be independent of the solvent),  $S_i$  and  $C_i$  the partial molar heat capacity of water in the solvent and the superscript  $o$  refers to pure water. Equation II.11 predicts a value of  $\frac{\Delta C_p^\ddagger}{\Delta S^\ddagger}$  which is independent of  $n$  and hence, of the substrate. Also, as the following table shows the observed and calculated values of  $\frac{\Delta C_p^\ddagger}{\Delta S^\ddagger}$  for various aqueous acetone solvents agree tolerably well with each other if  $S_T - S_i^o = -1.79 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$  and  $C_T - C_i^o = -2.65 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ .

TABLE II. 2.<sup>96</sup>

Observed and Calculated Values of  $\frac{\Delta C^\ddagger}{\Delta S^\ddagger}$  for S<sub>N</sub>1 Solvolysis at 25°C.

<u>% Acetone</u>	<u>C<sub>i</sub>-C<sub>i</sub><sup>0</sup></u>	<u>S<sub>i</sub>-S<sub>i</sub><sup>0</sup></u>	$\frac{\Delta C^\ddagger}{\Delta S^\ddagger}$ <u>obs.</u>	$\frac{\Delta C^\ddagger}{\Delta S^\ddagger}$ <u>calc.</u>
50	1.75	-0.34	3.77	3.03
70	3.31	-0.68	5.24	5.37
80	3.53	-0.28	3.53	4.09
85	3.32	-0.13	3.58	3.62

The values of  $S_T-S_i^0$  and  $C_T-C_i^0$  employed are approximately one third of the values for the freezing of water. This seems reasonable since the loss of freedom by water molecules when solvating the transition state would not be expected to be as great as in the process of freezing to ice. It thus appears that the solvation model is applicable to solvolysis in aqueous organic solvents.

There is some evidence that in aqueous acetone, the substrate is solvated by both components of the solvent.<sup>15a</sup> This would not however invalidate the above model provided that the transition state for solvolysis is solvated by acetone to the same extent as is the initial state.

## II.5. S<sub>N</sub> Reactions in Water.<sup>27</sup>

It has already been suggested that different factors control the values of  $\Delta C_p^\ddagger$  and  $\Delta S^\ddagger$  for solvolysis in water and the results obtained in this solvent cannot be accommodated within the solvation model discussed above.

Robertson<sup>90,97,98</sup> has suggested that in this solvent the initial state entropy and heat capacity are dependent on contributions from solvent-solvent interactions which are increased in the neighbourhood of the organic solute. Such interactions increase with the size of the solute and result in a negative contribution to the entropy of the initial state and a positive contribution to the corresponding heat capacity since these interactions are diminished at higher temperatures. Thus a positive  $\Delta S$  may result if the initial state interactions are very strong and has been observed for the hydrolysis of t-butyl chloride.<sup>91</sup> Clearly then for these reactions  $\frac{\Delta C_p^\ddagger}{\Delta S^\ddagger}$  is dependent on the size of the substrate.

Robertson and co-workers<sup>91,99,100,101</sup> have further suggested that these initial state interactions should give rise to a more negative  $\Delta C_p^\ddagger$  for S<sub>N</sub>1 reactions in water than for S<sub>N</sub>2 reactions but the supporting evidence for this proposal, is not at the present time, very conclusive.

It may well be that both the Robertson approaches and the solvation model are applicable to the systems for which they were developed. Thus, in water, a substrate containing polar or polarisable groups which can reduce solvent-solvent interactions in the initial state should give rise to a more negative  $\Delta S^\ddagger$  and a less negative  $\Delta C^\ddagger$ . In agreement with this view it is found that  $\Delta S^\ddagger$  for benzyl chloride is more negative than for normal alkyl halides<sup>90</sup> and also more negative for n-alkyl sulphonates than for the corresponding halides. Further the introduction of a methoxy group into t-butyl chloride reduces the value of  $-\Delta C_p^\ddagger$  for hydrolysis by 21 cal. deg.<sup>-1</sup> mole.<sup>-1</sup><sup>99</sup> In aqueous organic solvents  $\Delta S^\ddagger$  is virtually the same for normal alkyl halides as for benzyl halides and reactions of sulphonates show more positive  $\Delta S^\ddagger$  values than do the corresponding chlorides.<sup>27</sup>

Kohnstam has suggested<sup>27</sup> that the differences between hydrolysis in water and in an aqueous organic solvent may be that in the latter case initial state solvation by the organic component of the solvent reduces the solvent-solvent interactions induced by the presence of the substrate. Thus addition of relatively small amounts of dioxan or acetone to water results in a fall in the value of  $\Delta S^\ddagger$  for the hydrolysis of t-butyl chloride<sup>74</sup> and this may be because the solvent-solvent interactions are so reduced by the added organic component that they are not further reduced by the activation process. If so then the



solvation model would then be applicable to the solvolysis. Also Robertson and his co-workers<sup>103</sup> have found that  $-\Delta C_p^\ddagger$  for the reaction of t-butyl chloride with water and various aqueous ethanol solvents shows a sharp maximum in the region of solvent composition where the structure of the solvent is thought to change rapidly with its composition.

The difference in behaviour between water and aqueous organic solvents is further illustrated by the  $\frac{\Delta C_p^\circ}{\Delta S^\circ}$  values for the ionisation of formic, acetic, propionic and butyric acids in aqueous dioxan solvents.<sup>102</sup> These ionisations in that they involve charge separation, may be compared to the ionisation step in  $S_N1$  solvolysis. It is found that the value of  $\frac{\Delta C_p^\circ}{\Delta S^\circ}$  at 25° is independent of the acid concerned for the 45%, 70% and 82% solvent but not in water or the 20% solvent.

In the work described in this thesis the solvents employed have been 70% and 85% aqueous acetone. The solvation model described in this chapter represents the best working hypothesis available at the present time for the explanation of the results of solvolytic studies in these solvents and it will therefore be employed in the discussion of the present results.

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were very rapid. Good first-order kinetics were always obtained and runs at the various temperatures were generally duplicated. Although there was good reason to expect the reaction to proceed by the unimolecular mechanism,<sup>20,104,106</sup> an analysis of the results showed that, for reaction under the present conditions, this view could not be maintained. Consequently, as the main purpose of the present study was to compare the features of the  $S_N1$  reactions of corresponding chlorides and fluorides, no attempt was made to study methoxymethyl fluoride.

### III.2. Results.

The rates and activation parameters obtained in three different batches of solvent are recorded in Table III. 1. The quoted energies and entropies of activation refer in each case to the mean of the adjacent temperatures.

Although the  $\Delta C_p^\ddagger$  values differ for the three solvents there is substantial agreement in the values of  $E$  and  $\Delta S^\ddagger$  as the following summary shows.

<u>Solvent.</u>	<u>Temp. °C.</u>	<u>E(k.cal.)</u>	<u><math>-\Delta S^\ddagger</math> cal. deg.<sup>-1</sup> mole<sup>-1</sup></u>
1	-8.74	13.42	18.76
2	-8.34	13.26	19.29
3	-7.48	13.25	19.32

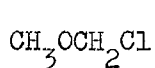
TABLE III. 1.  
Rates and Activation Parameters for the Solvolysis of  
Methoxymethyl Chloride in 85% Aqueous Acetone.

<u>Solvent No. 1.</u>			
<u>T °C.</u>	<u>10<sup>4</sup> k<sub>1</sub> sec.<sup>-1</sup></u>	<u>E(k.cal.)</u>	<u>-ΔS<sup>‡</sup> calcs. mole<sup>-1</sup> deg.<sup>-1</sup></u>
+0.04	218.9 ± 0.27		
		13.42 ± 0.015	18.76 ± 0.056
-17.44	40.42 ± 0.058 (a)		
		13.18 ± 0.011	19.56 ± 0.045
-33.85	6.826 ± 0.0037 (a)		
	ΔC <sub>p</sub> <sup>‡</sup> = 12 ± 1.1 calcs. deg. <sup>-1</sup> mole <sup>-1</sup>		
<u>Solvent No. 2.</u>			
0.00	221.0 ± 0.20 (a)		
		13.27 ± 0.017	19.29 ± 0.064
-16.69	45.02 ± 0.075		
		13.26 ± 0.018	19.21 ± 0.072
-33.85	6.975 ± 0.0128		
	ΔC <sub>p</sub> <sup>‡</sup> = -1 ± 1.5 calcs. deg. <sup>-1</sup> mole <sup>-1</sup>		
<u>Solvent No. 3.</u>			
-0.09	224.4 ± 0.32		
		13.25 ± 0.018	19.32 ± 0.069
-15.06	54.41 ± 0.073		
		13.47 ± 0.012	18.37 ± 0.047
-29.99	10.85 ± 0.005		
	ΔC <sub>p</sub> <sup>‡</sup> = -16.6 ± 1.4 calcs. deg. <sup>-1</sup> mole <sup>-1</sup>		

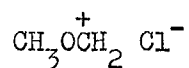
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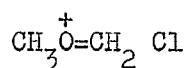
about  $10^{14}$  times greater than that of methyl chloride.<sup>20</sup> This enormous difference in reactivity has been attributed to the powerful capacity of the methoxy group for mesomeric electron release towards the developing carbonium ion centre in the transition state for  $S_N1$  solvolysis. On this view the transition state would be a resonance hybrid of the three canonical forms,



I



II



III

and there would be a strong contribution from III.

The present results cast doubts on the validity of these assumptions as several features of the reaction of this compound with 85% aqueous acetone are inconsistent with the operation of mechanism  $S_N1$  under the conditions employed.

An examination of the activation parameters shows that the entropy of activation is much more negative than for other chlorides reacting at similar rates under the same conditions. A comparison is given in Table III. 2., with some other reactive chlorides which react with aqueous acetone by mechanism  $S_N1$

TABLE III. 2.

Rates and Activation Parameters for the Hydrolyses of  
Reactive Alkyl Chlorides at 0°C in 85% Aqueous Acetone.

<u>Compound</u>	<u><math>10^2 k_1 \text{ sec.}^{-1}</math></u>	<u>E(k.cal.)</u>	<u><math>-\Delta S^\ddagger \text{ cal. deg.}^{-1} \text{ mole}^{-1}</math></u>
p-MeOC <sub>6</sub> H <sub>4</sub> CHCl.Ph (a)	3.007	15.81	9.41
p-MeO,p'-Cl(C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> CHCl (a)	1.289	16.73	7.77
MeOCH <sub>2</sub> Cl	2.244	13.14	19.78

(a) Ref. 28.

If the highly negative entropy of activation for methoxymethyl chloride arises out of a very highly solvated transition state then the value of the  $\frac{\Delta C_p^\ddagger}{\Delta S^\ddagger}$  ratio<sup>27</sup> for S<sub>N</sub>1 reactions under these conditions requires that the corresponding  $\Delta C_p^\ddagger$  value should be -120 cal. deg.<sup>-1</sup> mole<sup>-1</sup>. Clearly the experimental value is much less negative than this. The constancy of the above ratio under these conditions has been demonstrated for a wide variety of substrates<sup>27</sup> reacting by mechanism S<sub>N</sub>1 and there is no reason to suppose that it does not apply here. However it is conceivable that some unknown factor may invalidate the application of this criterion of mechanism in the present case.

In the absence of such a factor, the observed  $\Delta S^\ddagger$  suggests that the transition state requires covalent attachment of a water molecule,<sup>27</sup> in which case the reaction is bimolecular. The value of  $\Delta S^\ddagger$  at 50° would be -22.56 cal. deg.<sup>-1</sup> mole<sup>-1</sup> which is of the same order as the values obtained for the S<sub>N</sub>2 reactions of alkyl chlorides in more aqueous solvents.<sup>27,63</sup> From the observed effects of solvent changes on the  $\Delta S^\ddagger$  values for the S<sub>N</sub>1 reactions of alkyl chlorides<sup>27,28</sup> one might expect, assuming a similar pattern of behaviour for S<sub>N</sub>2 reactions, that the present value at 50° might be 3 or 4 entropy less negative than the value expected for an S<sub>N</sub>2 reaction under these conditions. This then leads to the tentative conclusion that the present reaction may occur by a borderline mechanism and this view is supported by the fact that the  $\Delta C_p^\ddagger$  value obtained in the present work is close to zero. Such  $\Delta C_p^\ddagger$  values have been interpreted in terms of concurrent mechanisms or temperature dependent transition state structures.<sup>24b,27</sup>

The good first-order kinetics always observed in the present work indicate that the reaction, if S<sub>N</sub>1, has a very small mass law constant (Section I.6.) i.e. that there is no significant reversal of the initial ionisation step as the concentration of chloride ions builds up during the reaction. Such a reversal leads to a drop in the value of the integrated first order rate coefficient as the reaction proceeds.<sup>11</sup>

The value of the mass law constant,  $\alpha$ , controls the magnitude of the

mass law effect, and  $\alpha$  increases with the stability of the carbonium ion involved in the reaction. The rate of an  $S_N1$  reaction is also in general dependent on the stability of the carbonium ion intermediate and there is a rough correlation between the rate and the mass law constant for such a reaction, (but see section I.6 for exceptions).

However the rate for p-methoxydiphenylmethyl chloride is of the same order as that for methoxymethyl chloride in 85% aqueous acetone but the reaction of the former compound shows considerable deviations from first-order kinetics. The kinetics of the 2 reactions at 0°C are compared below. Quoted rate coefficients are integrated first order values, and exactly the same kinetic procedure was used in both cases.

<u>MeOCH<sub>2</sub>Cl</u>		<u>p-MeOC<sub>6</sub>H<sub>4</sub>CHPhCl</u>	
<u>% Reaction</u>	<u>10<sup>4</sup> k<sub>1</sub> sec.<sup>-1</sup></u>	<u>% Reaction</u>	<u>10<sup>4</sup> k<sub>1</sub> sec.<sup>-1</sup></u>
11.3	219.3	14.8	230.6
30.1	217.4	39.3	210.9
59.7	218.6	58.4	198.4
79.0	218.2	86.4	181.9

The behaviour of p-methoxydiphenylmethyl chloride in the present case is quantitatively consistent with that observed previously under the same conditions <sup>28</sup> when it was shown that the deviations from first-order

kinetics were due to the operation of the mass law effect.

Further, the rate of reaction of p-methoxy, p'-nitrodiphenylmethyl chloride in the 85% solvent is slower by a factor of 100 than that of methoxymethyl chloride and yet the former reaction has a mass law constant of sufficient magnitude that the initial rate is depressed by more than 20% in the presence of  $8 \times 10^{-4} \text{M HCl}$ .<sup>28</sup> By contrast the same concentration of HCl had no effect on the rate for methoxymethyl chloride.

Clearly then, it appears that the present reaction is not subject to a significant mass law effect and this is consistent with the view that no significant proportion of the reaction proceeds via a carbonium ion intermediate. It is conceivable however, that because of the open structure of the  $\text{MeOCH}_2^+$  carbonium ion, solvation effectively prevents attack by chloride ion before the collapse of the solvation shell.

#### III.4. Results in Other Solvents.

##### (a) Activation Parameters.

From the rate measurements of Leimu and Salomaa,<sup>106</sup> activation parameters calculated for the solvolysis of methoxymethyl chloride in ethanol at  $7.5^\circ$  are compared below to those for diphenylmethyl chloride<sup>107</sup> which would be expected to react with this solvent by mechanism  $S_N1$ .



<u>Compound</u>	<u>E(k.cal.)</u>	<u><math>\Delta S^\ddagger</math> cal. deg.<sup>-1</sup> mole<sup>-1</sup></u>
MeOCH <sub>2</sub> Cl	14.7	14.8
Ph <sub>2</sub> CHCl	22.9	2.81

The values for diphenylmethyl chloride are consistent with the results obtained by Bolton, Chapman and Shorter<sup>108</sup> for diphenylmethyl halides in methanol and ethanol at somewhat higher temperatures. Clearly the behaviour of methoxymethyl chloride in this solvent parallels that in 85% aqueous acetone and once again the highly negative entropy of activation can be interpreted in terms of a transition state in which there is covalent attachment of the nucleophile.

(b) The Effects of Solvent Changes.

Table III. 3 shows the effect,  $k_{\text{MeOH}}/k_{\text{EtOH}}$ , of changing the solvent from ethanol to methanol on the solvolytic rates for the reactions of methoxymethyl chloride and three other compounds for which the data are available.

The value for methoxymethyl chloride has been put forward<sup>106</sup> as part of the evidence for the operation of the unimolecular mechanism in its reaction with ethanol. The isopropanol-methanol ratio for this compound is 19.6 at 5°C<sup>106</sup> while for diphenylmethyl chloride at 25° it is 142. Thus the evidence based on the effects of solvent changes is not very conclusive.

TABLE III. 3.

Relative Rates  $k_{\text{MeOH}}/k_{\text{EtOH}}$  for some Solvolytic Reactions.

<u>Compound</u>	<u>Temp °C.</u>	<u><math>k_{\text{MeOH}}/k_{\text{EtOH}}</math></u>	<u>Mechanism</u>	<u>Reference</u>
$\text{Pr}^i\text{OSO}_2\text{C}_6\text{H}_4\text{Br}$	70	2.8	Borderline	29
$\text{MeOCH}_2\text{Cl}$	5	6.8		106
$\text{Bu}^t\text{Cl}$	25	7.7	$\text{S}_{\text{N}}1$	29, 109
$\text{Ph}_2\text{CHCl}$	25	15.5	$\text{S}_{\text{N}}1$	29, 110

(c) The Effects of Electrolyte Additions.

The effects of added lithium ethoxide on the rates of solvolysis of methoxymethyl chloride, acetyl chloride and triphenylmethyl chloride in 90% ether-ethanol at 25° are recorded below, <sup>20</sup>

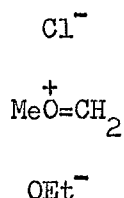
<u>Compound</u>	<u>First Order Rate Constants <math>10^4 k_1 \text{ sec}^{-1}</math></u>	
	<u>Without LiOEt</u>	<u>Added LiOEt = 0.02M</u>
$\text{MeOCH}_2\text{Cl}$	0.69	4.8
$\text{CH}_3\text{COCl}$	8.8	150 (a)
$\text{Ph}_3\text{C-Cl}$	1.04	4 (b)

(a) Rate measured at 0°C.

(b) With sodium ethoxide.

Since the magnitude of the rate increase in the presence of added base for methoxymethyl chloride was much closer to that observed for triphenylmethyl chloride than to the rate increase in the reaction of acetyl chloride it was concluded that the methoxy compound undergoes solvolysis in 90% ether-ethanol by mechanism  $S_N1$ .

In ethanol the addition of sodium and lithium ethoxide has been found to result in a rapid bimolecular reaction between the substrate and ethoxide ions<sup>20, 106</sup> and it has been calculated that for this reaction the rate for methoxymethyl chloride is about  $10^5$  times greater than when the substrate is methyl chloride.<sup>20</sup> This very considerable enhancement of reactivity was explained in terms of a contribution from the structure



in the transition state of this reaction, no structure of corresponding importance being possible for the reaction of methyl chloride.

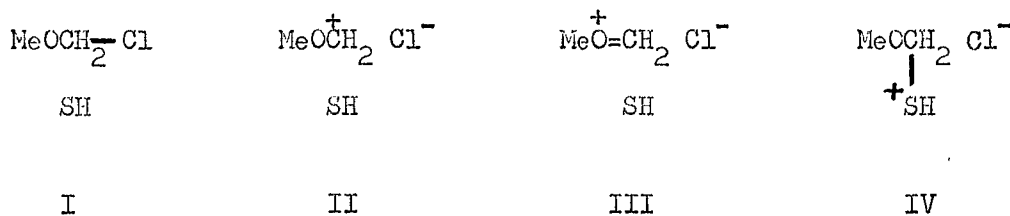
A brief investigation of the very rapid exchange reaction between methoxymethyl chloride and chloride ions in acetone<sup>20</sup> showed that again the reactivity of this compound was  $10^5$  times that of methyl chloride for these conditions and so it was presumed that the exchange reaction of the methoxy compound is bimolecular also. The catalysis of the

ethanolysis of methoxymethyl chloride by added mercuric chloride <sup>106</sup> has been advanced as evidence for the unimolecular nature of the uncatalysed reaction. However Benfey <sup>111</sup> has shown that the S<sub>N</sub>2 hydrolyses of primary alkyl bromides in aqueous dioxan are also catalysed by this reagent.

"Catalysis" by HCl has also been observed, in solvents of low ionising power <sup>106,113</sup> but this phenomenon is probably a salt effect <sup>112</sup> as it decreases in importance as the ionising power of the solvent increases and is not observed in ethanol. <sup>106</sup> Positive salt effects have also been observed in the presence of lithium chloride, <sup>20</sup> in ethanol and ethanol-ether solvents.

### III.5. Conclusions.

From a consideration of the present results and the evidence in the preceding section, it appears that the assumption of the unimolecular mechanism for the solvolytic reactions of methoxymethyl chloride is not justified. In general terms the transition state for the reaction of methoxymethyl chloride with a solvent whose nucleophilic component is SH, may best be represented as a resonance hybrid of the following canonical structures:



If there is a contribution from IV, ( and the substrate is sterically very susceptible to nucleophilic attack), then the reaction is bimolecular. On the other hand a solvolysis may involve a concurrence of mechanisms (Section I.5) i.e. a variety of reaction paths some involving transition states whose structures do not have any contribution from IV.

In the present case the absence of mass law effects strongly suggests that a single transition state, with a strong contribution from III, is involved in the reaction with 85% aqueous acetone. The contribution from IV would be expected to diminish as the temperature is raised <sup>24b,27</sup> so that at a high enough temperature the reaction would proceed by mechanism  $S_N1$ .

Such a view would also explain the " $S_N1$  like" behaviour, e.g. the relative reactivities of methyl and methoxymethyl chlorides,<sup>20</sup> and the effects of solvent changes<sup>106</sup> and added base<sup>20</sup> on the rates of solvolysis of the methoxy compound, observed by other workers. All these results are consistent with a bimolecular mechanism provided that the structures of the transition states involved have substantial contributions from III. The available evidence however does not rule out the possibility of concurrent mechanisms for reaction in the other solvents.

CHAPTER IV.

THE HYDROLYSIS OF TRIPHENYLMETHYL CHLORIDES

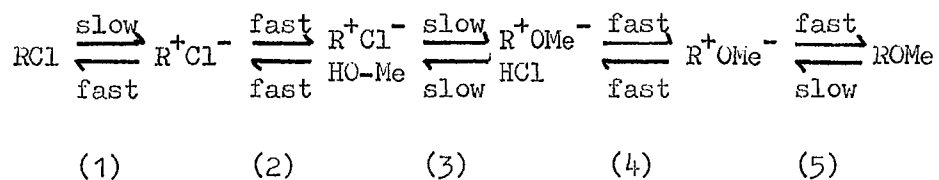
IN 85% AQUEOUS ACETONE.

IV.1. Introduction.

Triphenylmethyl halides are among the most reactive of neutral substrates towards nucleophiles <sup>115</sup> and consequently detailed studies have in the main been confined to solvents of relatively low polarity. For the purposes of a brief review it is convenient to discuss solvolytic and non-solvolytic studies separately, although the dividing line is necessarily an arbitrary one.

(a) Non-Solvolytic Studies.

The reactions of triphenylmethyl chloride with anions and polar molecules in solvent benzene have been investigated by several workers.<sup>38a</sup> Ingold and his co-workers <sup>38b</sup> have concluded that in general the results may be interpreted in terms of the following reaction scheme (particularised here for reaction with methanol).



$R^+Cl^-$  is a triphenylmethyl carbonium ion-pair and step (3) is a quadrupole rearrangement.

On the other hand Swain and Pegues,<sup>37b</sup> disagreeing with Ingold's results and conclusions, have proposed that at least for low methanol concentrations the rate determining step is attack by methanol on the triphenylmethyl carbonium ion-pair.

Patai and Zabicky,<sup>116</sup> studying the exchange of p,p',p'', trinitro-triphenylmethyl chlorides with anions (as  $M^+X^-$ ) in acetic acid have proposed the formation of the ion pair  $R^+(MXCl)^-$  as rate determining step while Hudson and Saville<sup>117</sup> have proposed a variety of alcohol assisted ionisation steps to account for the results of their alcoholysis studies in carbon tetrachloride and polar solvents.

Recently, Fava and Miotti<sup>50</sup> have reported mixed first and second order kinetics for the exchange reactions of p,p' dinitro- and p,p',p'' trinitrotriphenylmethyl chlorides with chloride ions in acetone and aceto-nitrile. The second order component they ascribed tentatively to an  $S_N2$  reaction but the available evidence (salt and solvent effects on the second order rate constant) does not favour this mechanism conclusively against the alternative rate determining attack by chloride ion on the ion-pair. An analogous mechanism has been suggested to describe the alcoholysis<sup>118</sup> and acetolysis<sup>119</sup> of the unsubstituted compound in nitromethane and carbon tetrachloride respectively.

(b) Solvolytic Studies.

De la Mare and his co-workers,<sup>20</sup> Branch and Nixon,<sup>114</sup> and Bolton, Chapman and Shorter<sup>108</sup> have studied the ethanolsis of triphenylmethyl chloride in various solvent mixtures.

The measurements of de la Mare have been discussed in Chapter 3. Branch and Nixon<sup>114</sup> measured rates and activation parameters for a number of substituted triphenylmethyl chlorides in 60% ether/ethanol. Variations in rate with substrate and with added hydrogen chloride concentration may have been due to the operation of mass law effects and the reactions of all the triphenylmethyl chlorides studied showed low frequency factors as compared to the reaction of diphenylmethyl chloride under the same conditions. Bolton, Chapman and Shorter<sup>108</sup> observed a similar decrease in the entropy of activation for solvolysis on passing from diphenylmethyl to triphenylmethyl chloride in 9-1 ethanol-acetone. Errors which may have been introduced in the extrapolation of measurements at low temperatures in the case of the solvolysis of triphenylmethyl chloride would probably make the reported  $\Delta S^\ddagger$  too large and do not therefore invalidate the conclusion.

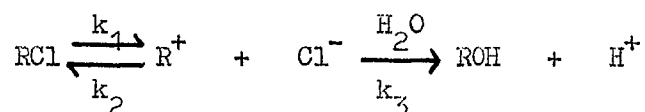
Swain, Scott and Lohmann<sup>19</sup> have observed the expected depression of the rate of solvolysis of triphenylmethyl chloride in 85% aqueous acetone by added chloride ions and have determined activation parameters, (see Section IV. 4). Finally Swain and McLachlan<sup>120</sup> have measured



solvolysis rates for the above compound in a variety of solvent systems fitting the data to a 4 parameter equation. They also concluded that in acetic acid the rate determining step is nucleophilic attack by the solvent on an ion-pair intermediate.

IV.2. The Evaluation of Initial Rates of Ionisation and Mass Law Constants for the Hydrolysis of Reactive Alkyl Chlorides in Aqueous Acetone.

It has already been pointed out (Section I.6) that for the  $S_N1$  hydrolysis of an alkyl chloride (RCl) the reaction scheme is,



and that only if  $k_2 \ll k_3$  will the reaction show first-order kinetics.

The rate law (equation I.2) can be written

$$\frac{dx}{dt} = \frac{k_1(a-x)}{1 + \alpha(c+x)} \quad \text{Equation IV. 1}$$

where  $a$  and  $a-x$  are the concentration of RCl at zero time and time  $t$  respectively,  $c$  is the concentration of chloride ion at zero time and  $\alpha$  is  $\frac{k_2}{k_3}$ .

If the effect of increasing ionic strength (as the reaction proceeds) on  $k_1$  and  $\alpha$  can be neglected then integration of IV. 1 gives

$$k_1^0 = \bar{k}_1 + \alpha^0 [\bar{k}_1(a+c) - x/t] \quad \text{Equation IV. 2}$$

where  $\bar{k}_1 = \frac{2.303}{t} \log \frac{a}{a-x}$  and the superscript o denotes zero ionic strength. Equation IV. 2 predicts that a plot of  $\bar{k}_1$  against  $[\bar{k}_1(a+c) - x/t]$  should be linear and such a plot has previously been employed in the evaluation of  $k_1^o$  and  $\alpha^o$  values for the reaction of p-substituted diphenylmethyl chlorides in 85% aqueous acetone.<sup>28,54</sup>

However other workers<sup>8,11,53</sup> using relatively high substrate concentrations and investigating the effects of added salts had taken account of changing ionic strength on the activity coefficients of the reacting species in studies of similar reactions.

Thus, Ingold and co-workers<sup>11</sup> applied the Brönsted relationship<sup>121</sup> to the effect of changing ionic strength during a given run on the values of  $k_1$ ,  $k_2$  and  $k_3$ . They calculated the required activity coefficients (for chloride ion and the quasi-ionic transition state for steps 1 and 2) on the basis of the Debye-Huckel limiting law. This treatment led to the following modification of Equation IV. 1.

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

Here  $\sigma$  is the "ionic strength constant" which depends on the degree of charge development and the charge separation in the transition state for steps 1 and 2.  $A = -1.815 \times 10^6 (DT)^{-3/2}$ ,  $B = -0.912 \times 10^1 (DT)^{-2}$ ,  $\mu$  and  $D$  are the ionic strength and dielectric constant of the solution and  $T$  is the absolute temperature.

For 85% aqueous acetone solvents at low temperatures, (the present experimental conditions), B is approximately  $1-2 \times 10^8$  and  $\sigma$  values are usually <sup>11</sup> of the order of  $10^{-8}$ . Thus for reactions studied under conditions of low ionic strength the first term of the denominator in Equation IV. 3 may be set equal to unity without serious error. Then writing  $f_{Cl^-}$  for  $\text{antilog}_{10}(A\mu^{\frac{1}{2}})$  we have

$$\frac{dx}{dt} = \frac{k_1^0(a-x)}{1 + \alpha^0(c+x)f_{Cl^-}} \quad \text{Equation IV. 4}$$

where  $f_{Cl^-}$  is the activity coefficient for chloride ion at time t. The integrated form of Equation IV. 4 is

$$k_1^0 = \bar{k}_1 + \alpha^0 \frac{J}{t} \quad \text{Equation IV. 5}$$

where

$$J = \int_0^x \frac{c+x}{a-x} f_{Cl^-} dx$$

In the present work (see Section IV. 3)  $f_{Cl^-}$  was evaluated from the Davies equation,<sup>122</sup>

$$f_{Cl^-} = \exp \left[ \frac{A(c+x)^{\frac{1}{2}}}{1 + (c+x)^{\frac{1}{2}}} + 0.4606(c+x) \right]$$

where A is the Debye limiting slope. In aqueous solution this expression is valid up to ionic strengths of ca. 0.1. The evaluation of the integral J is discussed in Appendix IV. 1.

#### IV.3. The Present Results.

The reactions of triphenylmethyl chloride and its p-nitro derivative with 85% aqueous acetone have been studied at low temperatures and substrate concentrations of ca.  $2 \times 10^{-3} M$  using the conductance technique described in Chapter 6. In view of the high stabilities of triphenylmethyl carbonium ions<sup>123</sup> and the steric hindrance to bimolecular attack for these systems, both substrates were expected to hydrolyse rapidly by the unimolecular mechanism and to show pronounced deviations from first-order kinetics due to the operation of mass law effects.

These expectations were fully confirmed. Both reactions were very rapid, the p-nitro group exerting a powerful retarding effect on the rate. For all runs the values of the integrated first-order rate coefficients fell as reaction proceeded, the effect being more pronounced in the case of the unsubstituted compound. Further, within experimental error the data for each run gave a linear plot of  $\bar{k}_1 V$  [ $\bar{k}_1(a + c) - x/t$ ] as required by Equation IV. 2 and the  $k_1^0$  values thus obtained from duplicate runs generally agreed satisfactorily. It should be stressed however that any slight curvature in the plots would be difficult to detect because of the scatter of the individual points.

For each run, values of  $k_1^0$  and  $\alpha^0$  were obtained from the least squares fit of the data to Equation IV. 2. The weighted mean values for both quantities (with standard errors) were calculated for each

temperature, using in every case the  $k_1^{\circ}$  and  $\alpha^{\circ}$  values obtained from duplicate runs. This procedure was adopted in all cases as it was found that when for a given pair of duplicate runs all the data was combined and a least squares value for  $k_1^{\circ}$  calculated, the resultant value always differed from the weighted mean of the duplicate  $k_1^{\circ}$ 's unless the duplicate  $\alpha^{\circ}$ 's were almost identical. An example of this behaviour is shown below. Details of the runs concerned can be found in Appendix IV. 2.

TABLE IV. 1.

The Hydrolysis of  $(C_6H_5)_3CCl$  in 85% Aqueous Acetone at  $-25.44^{\circ}$ .

<u>Expt.</u>	<u><math>10^2 k_1^{\circ} \text{ sec.}^{-1}</math></u>	<u><math>\alpha^{\circ}</math></u>	<u><math>10^2 k_1^{\circ} \text{ (mean) sec.}^{-1}</math></u>
11	$9.502 \pm 0.29$	$734 \pm 22$	(a) $9.583 \pm .18$ (b) $9.123 \pm .80$
12	$9.643 \pm 0.21$	$654 \pm 15$	

(a) Weighted mean of values from experiments 11 and 12

(b) Value from a single least squares treatment of the combined data from experiments 11 and 12.

It is however noteworthy that in general two duplicate runs can give rise to  $\alpha^{\circ}$  values differing significantly from each other (as in

Table IV. 1) and yet the discrepancy in the  $k_1^{\circ}$  values for the same runs is very much less.

Initial rates of ionisation and mass law constants were also obtained via Equation IV. 5. Weighted mean values of  $k_1^{\circ}$  and  $\alpha^{\circ}$  were obtained for each temperature using the same procedure as regards duplicate runs as described above. Rates and mass law constants obtained from the two equations are compared in Table IV. 2. It can be seen that allowance for ionic strength effects in accordance with Equation IV. 5, results in a small increase, (generally 1-2%), compared with the value obtained from Equation IV. 2, in  $k_1^{\circ}$ , accompanied by a relatively substantial increase, (20-27%), in  $\alpha^{\circ}$ . These systematic increases are not obscured by the standard errors involved.

Equation IV. 5 may be derived from Equation IV. 1 by making the assumption that small changes in ionic strength do not affect the activity coefficients for the initial and transition states of step 1 (i.e. both are always unity). It thus allows only for ionic strength effects on steps 2 and 3 and thus on  $k_2$  and  $k_3$ . It is also necessary to assume that the activity coefficient of the transition state for step 3 is unity.<sup>11</sup>

Thus the smaller values of  $\alpha^{\circ}$  obtained via Equation IV. 2 are probably a reflection of the fact that the mass law constant in this equation is the  $\alpha^{\circ}$  of Equation IV. 5 multiplied by a mean value of  $f_{Cl^-}$

TABLE IV. 2.

Rates of Ionisation and Mass Law Constants at Zero Ionic Strength,  
for Triphenylmethyl Chlorides in 85% Aqueous Acetone.

<u>Compound</u>	<u>Temp. °C.</u>	<u>Equation</u>	<u><math>10^4 k_1^0 \text{ sec.}^{-1}</math></u>	<u><math>\alpha^0</math></u>
$\text{Ph}_3\text{CCl}$	-25.44	IV. 2	$958.3 \pm 18$	$688 \pm 31$
		IV. 5	$967.6 \pm 25$	$823 \pm 33$
	-36.25	IV. 2	$259.2 \pm 2.9$	$580 \pm 30$
		IV. 5	$267.1 \pm 4.3$	$739 \pm 46$
	+ .17	IV. 2	$126.8 \pm 0.8$	$384 \pm 19$
		IV. 5	$128.0 \pm 0.7$	$465 \pm 22$
	-15.48	IV. 2	$20.54 \pm 0.13$	$342 \pm 13$
		IV. 5	$20.76 \pm .08$	$411 \pm 9$
(a)	-29.50	IV. 2	$3.235 \pm 0.015$	$296 \pm 10$
		IV. 5	$3.262 \pm 0.025$	$356 \pm 6$
$\text{p-NO}_2\text{C}_6\text{H}_4\text{Ph}_2\text{CCl}$	+ .03	IV. 2	$122.8 \pm 1.2$	$369 \pm 12$
		IV. 5	$124.4 \pm 1.1$	$453 \pm 11$
	-29.98	IV. 2	$3.075 \pm .022$	$373 \pm 26$
		IV. 5	$3.120 \pm .020$	$458 \pm 29$

(a) and (b) refer to different batches of 85% solvent.

for the appropriate reaction conditions (see Equations IV. 1 and IV. 4). The consistently slightly lower values of  $k_1^0$  obtained via Equation IV. 2 would then reflect the effect of changing ionic strength on the linearity of the plot involved in the use of Equation IV. 2.

It therefore seems reasonable to accept the values of both parameters obtained via Equation IV. 5 as being the better approximation to the required mass law constants and rates of ionisation at zero ionic strength respectively.

The quoted standard errors in Table IV. 2 represents the fit of the data concerned to the chosen equation and are not necessarily a reflection of the true errors. For a given run the difference between two consecutive  $\bar{k}_1$  values is not large in relation to the errors involved in their determination and hence the data may well fit a different equation which gives rise to a slightly different  $k_1^0$  value. Also, neglect of the ionic strength effects mentioned above, the possible incomplete dissociation of  $\text{HCl}^{28}$  and the fact that for rapid reactions "zero time" does not correspond to zero ionic strength, all introduce additional small uncertainties. In view of these considerations the standard errors quoted in Table IV. 2 could well underestimate the true errors and the results are consequently to be treated with caution.



IV.4. Discussion.

(a) Relative Rates and Substituent Effects.

Interpolation of the present results for triphenylmethyl chloride gives a  $k_1^0$  value for this compound at  $-34.5^\circ$  of  $3.317 \times 10^{-2} \text{ sec.}^{-1}$ . Swain and his co-workers<sup>19</sup> have found the rate of solvolysis\* in the same solvent at this temperature to be  $1.3 \times 10^{-2} \text{ sec.}^{-1}$ . The discrepancy is greater than might be expected from the use of different solvent batches made up by volume. Such discrepancies in these laboratories do not normally exceed ca. 30%. However the accuracy of the titration method employed by Swain must be limited for half lives of the order of 30 sec. and no allowance for mass law effects was reported. Since temperature control was only  $\pm 0.5^\circ\text{C}$ , a combination of these factors could well explain the discrepancy.

In Table IV. 3, some substituent effects on rates of ionisation in 85% aqueous acetone, calculated from the present results and extrapolations of previous results to the temperatures presently employed, are shown.

It was considered best to extrapolate the rate constants for the diphenylmethyl compounds to  $-25^\circ\text{C}$  rather than to compare rates at more normal temperatures as the  $\Delta C_p^\ddagger$  values for the hydrolyses of the diphenylmethyl chlorides were known.

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\* The rate of solvolysis is only equal to the rate of ionisation if mass law effects are absent.

TABLE IV. 3.

Substituent Effects on the Rates of Ionisation of some Aralkyl Chlorides in 85% Aqueous Acetone at -25°C.

<u>Compounds</u>	<u><math>k_x/k_y</math></u>
X = Ph <sub>3</sub> CCl	8.03x10 <sup>6</sup>
Y = Ph <sub>2</sub> CHCl	
X = p-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CPh <sub>2</sub> Cl	5.64x10 <sup>-3</sup>
Y = Ph <sub>3</sub> CCl	
X = p-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CHClPh	3.39x10 <sup>-4</sup> (28)
Y = Ph <sub>2</sub> CHCl	

The very large increase in rate on passing from diphenylmethyl to triphenylmethyl chloride greatly exceeds the increase quoted for this solvent by Streitwieser<sup>25</sup> which appears to be a calculated value. It is very probably due to the increase in resonance stabilisation of the transition state brought about by the extra phenyl group. Inasmuch as the transition state for solvolysis resembles the corresponding carbonium ion, the present results support the "propellor" model for

the triphenylmethyl cation <sup>108,125</sup> (steric hindrance prevents the ion from assuming a completely planar configuration) rather than the proposal of Deno <sup>126</sup> that in this ion one phenyl group is perpendicular to the plane containing the other two. On the latter view the difference in the ease of formation of  $\text{Ph}_2\overset{+}{\text{C}}\text{H}$  and  $\text{Ph}_3\overset{+}{\text{C}}$  from the corresponding chlorides is due to steric repulsion energy effects. <sup>126</sup> However it seems unlikely that the large difference in the energy of activation for solvolysis of  $\text{Ph}_2\text{CHCl}$  and  $\text{Ph}_3\text{CCl}$  (see Table IV. 5) can be accounted for on such a basis.

The introduction of a p-nitro group results in a smaller reduction in the rate of ionisation of triphenylmethyl chloride than in the case of diphenylmethyl chloride. This is consistent with previous results <sup>28,127</sup> which suggest that the magnitude of the effect on a rate of ionisation, exerted by an electron releasing or withdrawing group, decreases as the electron demand at the reaction centre decreases.

(b) Activation Parameters.

Energies and entropies of activation for the ionisation of triphenylmethyl chloride and its p-nitro derivative are shown in Table IV. 4.

It has already been pointed out that the standard errors in Table IV. 2 may very well underestimate the true errors which for the  $k_1^0$  values could well be as high as  $\pm 2\%$ . Thus it is not possible to calculate a

TABLE IV. 4.

Rates and Activation Parameters for the Ionisation of  
Triphenylmethyl Chlorides in 85% Aqueous Acetone.

1. Triphenylmethyl Chloride.

<u>Temp. °C.</u>	<u><math>10^2 k_1^0 \text{ sec.}^{-1}</math></u>	<u>E(k.cal.)</u>	<u><math>-\Delta S^\ddagger \text{ cal. deg.}^{-1} \text{ mole}^{-1}</math></u>
-25.44	$9.676 \pm .25$	$13.89 \pm .33$	$8.69 \pm 1.4$
-36.25	$2.671 \pm .043$		

2. p-Nitrotriphenylmethyl Chloride.

Series a.

<u>Temp. °C.</u>	<u><math>10^4 k_1^0 \text{ sec.}^{-1}</math></u>	<u>E(k.cal.)</u>	<u><math>-\Delta S^\ddagger \text{ cal. deg.}^{-1} \text{ mole}^{-1}</math></u>
+ .17	$128.0 \pm .70$	$16.26 \pm .070$	$9.45 \pm .25$
-15.48	$20.76 \pm .080$	$16.46 \pm .080$	$8.64 \pm .29$
-29.50	$3.262 \pm .025$		

Series b.

<u>Temp. °C.</u>	<u><math>10^4 k_1^0 \text{ sec.}^{-1}</math></u>	<u>E(k.cal.)</u>	<u><math>-\Delta S^\ddagger \text{ cal. deg.}^{-1} \text{ mole}^{-1}</math></u>
+ .03	$124.4 \pm 1.1$	$16.24 \pm .05$	$9.50 \pm .20$
-29.98	$3.120 \pm .020$		

Series 'a' and 'b' refer to different solvent batches.

meaningful  $\Delta C_p^\ddagger$  for the ionisation of p-nitrophenylmethyl chloride even though this reaction was studied at three temperatures. The results in series 'b' for this compound were obtained in a different batch of solvent, in order to confirm the extremely negative entropy of activation arising from the results of series 'a'. It is once again instructive to compare these values with those previously obtained<sup>28</sup> for the corresponding diphenylmethyl compounds. As before, the latter have been extrapolated to the present working temperatures using the appropriate  $\Delta C_p^\ddagger$  data.

TABLE IV. 5.

Activation Parameters for the Ionisation of some Aralkyl  
in 85% Aqueous Acetone at -30°

<u>Compound</u>	$\text{Ph}_2\text{CHCl}$ <sup>28</sup>	$\text{p-NO}_2\text{C}_6\text{H}_4\text{CHPhCl}$ <sup>28</sup>	$\text{Ph}_3\text{CCl}$ <sup>a</sup>	$\text{p-NO}_2\text{C}_6\text{H}_4\text{CPh}_2\text{Cl}$
<u>E(k.cal.)</u>	23.13	27.16	13.89	16.56
<u><math>-\Delta S^\ddagger</math> e.u.</u>	2.96	2.89	8.69	8.18

a. values at -30.84°C.

Inspection of Table IV. 5 shows that in agreement with the earlier results,<sup>28</sup> the decrease in rate, on the introduction of a p-nitro

group into triphenylmethyl chloride, results from an increase in the energy of activation, the entropy of activation being virtually unaffected. This is consistent with the general behaviour of p-substituents (except alkoxy groups) in  $S_N1$  reactions<sup>28,128</sup> and indicates that p-substitution does not affect the degree of charge development and hence the solvation in the transition state.

The extremely negative entropies of activation found for the triphenylmethyl chlorides require comment. The probable limitations in accuracy of Swain's rate data<sup>19</sup> for the solvolysis of triphenylmethyl chloride in 85% aqueous acetone have already been discussed and this unreliability must extend also to the  $\Delta S^\ddagger$  value arising from this data ( $\Delta S^\ddagger = -6.8 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$  at  $-24^\circ$ ).

Nevertheless this result together with those of Branch and Nixon<sup>114</sup> and Chapman<sup>108</sup> described in Section IV. 1 all point in the same direction and are qualitatively consistent with the results now obtained in 85% aqueous acetone.

At least part of the explanation may be that the introduction of the third phenyl group results in an increased carbon-chlorine separation in the transition state for ionisation as compared to that for diphenylmethyl chloride. This would increase the solvation requirements of the transition state and the accompanying steric hindrance to solvation could be outweighed by this factor. Bensley and Kohnstam<sup>129</sup> used an analogous argument to explain a similar effect

observed for the solvolyses of benzylidene chloride and benzotrichloride in aqueous acetone and ethanol solvents and the observed solvent effects were consistent with their interpretation.

(c) Mass-Law Constants.

The values of  $\alpha^{\circ}$  recorded in Table IV. 2, although like the  $k_1^{\circ}$  values subject to indeterminate errors over and above the standard errors quoted, can still be regarded as a reflection of the stability of the corresponding carbonium ion intermediates.

Table IV. 6 compares some  $\alpha^{\circ}$  values for structurally related aralkyl chlorides. For comparison purposes values obtained via Equation IV. 2 are shown as well as appropriate rate coefficients. The temperature dependence of  $\alpha^{\circ}$  is generally small compared to its size <sup>53</sup> and hence temperature differences recorded in the table do not affect the conclusions which may be drawn from the quoted values.

The large increase in  $\alpha^{\circ}$  on passing from diphenylmethyl chloride to the triphenylmethyl compound lends further support to the "propellor" model for the  $\text{Ph}_3\text{C}^+$  ion (Section IV. 4 a). As expected the introduction of a p-nitro group into triphenylmethyl chloride results in a substantial decrease in  $\alpha$  and by inference a less stable carbonium ion.

An interesting feature of Table IV. 5 is that although triphenylmethyl chloride is more reactive than p-phenoxy, p'-methoxydiphenylmethyl chloride the latter compound is associated with a very much

state involves the breaking down of the solvation shells of  $R^+$  and  $Cl^-$ .

It should be stressed however that at the present time the real nature of the temperature dependence of  $\alpha^0$  could be obscured by the indeterminate errors involved in its determination.



CHAPTER V.

THE HYDROLYSIS OF TRIPHENYLMETHYL FLUORIDES

IN 70% AQUEOUS ACETONE.

V.1. The Present Results.

Previous work on the solvolysis of alkyl and aralkyl fluorides has been described in Section I. 8. This chapter describes studies of the neutral hydrolysis of triphenylmethyl fluoride and its p-nitro derivative in 70% aqueous acetone.

Within experimental error the reactions of both compounds showed first-order kinetics at all temperatures studied. The rates were obtained by following the development of acidity of 0.005 - 0.01M solutions, and because in these cases the product (HF) is a weak acid, a different and rather more involved analytical technique was necessary (see Section VI. 5) than that usually employed when the substrate is a chloride or a sulphonate. This, together with the fact that it was necessary to allow for loss of hydrogen fluoride at the higher temperatures, resulted in less precise rate coefficients than can usually be obtained in the case of substrates containing leaving groups which are inert weak bases.

Nevertheless, the results for the unsubstituted compound were accurate enough to permit the calculation of the heat capacity of activation ( $\Delta C_p^\ddagger$ )

from rates at five temperatures but for the p-nitro derivative, studied at three elevated temperatures, the extremely small numerical value for  $\Delta C_p^\ddagger$  arising from the data is perhaps of doubtful validity and probably underestimates the true value. Nevertheless the energies and entropies of activation reported for this compound are considered to be reliable for the temperature range concerned. Table V. 1 shows the rates and activation parameters obtained for both reactions together with the appropriate standard errors.

## V.2. Discussion.

### (a) Kinetics.

The first-order kinetics now obtained for the hydrolysis of triphenylmethyl fluoride in 70% aqueous acetone indicate that the autocatalytic effects observed previously<sup>82</sup> at higher substrate concentrations than those employed in the present work, are now insignificantly small. Coverdale and Kohnstam<sup>82</sup> observed an increase of ca. 12% in the values of the integrated first-order rate coefficients during the course of the reaction in the 70% solvent when the substrate concentration was ca. 0.02M. The triphenylmethyl fluoride concentrations used in the present work were ca. 0.01M and the spread of the individual rate coefficients during a run was often as high as 7-8%. Under these conditions then, any autocatalytic effects could well be negligible compared to the experimental errors. For the p-nitro compound substrate

TABLE V. 1.

Rates and Activation Parameters for the Hydrolysis of  
Triphenylmethyl Fluorides in 70% Aqueous Acetone.

a. Triphenylmethyl Fluoride.

<u>Temp. °C.</u>	<u>10<sup>5</sup> k<sub>1</sub> sec.<sup>-1</sup></u>	<u>E(k.cal.)</u>	<u>-ΔS<sup>‡</sup> cal. deg.<sup>-1</sup> mole<sup>-1</sup></u>
60.52	61.22 ± 0.33	17.86 ± .13	21.90 ± .40
50.82	27.32 ± .070	18.27 ± .085	20.58 ± .26
40.42	10.67 ± .038	18.71 ± .093	19.11 ± .30
29.74	3.699 ± .018	19.25 ± .17	17.27 ± .57
20.79 *	1.397 ± .010		

$$\Delta S^{\ddagger} \text{ at } 50^{\circ} = -21.23 \pm .34 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta C_p^{\ddagger} = -47 \pm 6 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

b. p-Nitrotriphenylmethyl Fluoride.

<u>Temp. °C.</u>	<u>10<sup>6</sup> k<sub>1</sub> sec.<sup>-1</sup></u>	<u>E(k.cal.)</u>	<u>-ΔS<sup>‡</sup> cal. deg.<sup>-1</sup> mole<sup>-1</sup></u>
90.66	199.6 ± 1.1	19.93 ± .11	23.01 ± .32
69.84	37.44 ± .23	20.15 ± .11	22.26 ± .33
50.03	6.115 ± .036		

$$\Delta S^{\ddagger} \text{ at } 50^{\circ} = -21.93 \pm .57 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta C_p^{\ddagger} = -13 \pm 8 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

\* This temperature is exactly half a degree higher than that originally recorded. Since the latter value gives an activation energy which is inconsistent with the others in Table V. 1 it has been assumed that a mistake was made in reading the thermometer scale.

concentrations were always ca. 0.005M and thus here also no significant autocatalytic effect would be expected.

In the absence of autocatalytic effects then, the first-order kinetics preclude the operation of significant mass law effects in these reactions even though the same carbonium ion intermediates are almost certainly involved as in the reactions of the corresponding chlorides.

Temperature and solvent changes are most unlikely to be responsible for this difference in behaviour (in any case they would probably have opposing affects on the magnitude of the mass law effects.<sup>8,53</sup>) It must therefore be attributed to the change in leaving group from chloride to fluoride and it may be explained in terms of the different properties of the two ions.

Firstly fluoride ion is a weaker nucleophile than chloride in solvents which can form hydrogen bonds to it<sup>61</sup> and thus fluoride ion will compete less effectively with solvent molecules for the carbonium ion than will chloride ion under the same conditions. Secondly fluoride ions will combine with the hydrogen ions produced by the reaction of the carbonium ion with the solvent to form undissociated hydrofluoric acid. Indeed the probable value of the dissociation constant for this acid in 70% aqueous acetone<sup>82</sup> suggests that under the present conditions the concentration of fluoride ion never exceeds ca.  $10^{-4}$  gm. ions  $l^{-1}$

On these grounds then, no detectable deviations from first-order kinetics due to mass law effects would be expected and hence it is most unlikely that in the present results there has been a mutual cancellation between mass law retardation and autocatalytic acceleration.

(b) Relative Rates and Substituent Effects.

The results now observed for triphenylmethyl fluoride lead to rate coefficients at 25° and 40°, which are in satisfactory agreement with those obtained by previous workers.<sup>82,34b</sup> The p-nitro derivative has not been studied before.

Direct comparison of the present rates obtained for the two triphenylmethyl fluorides, with those for the corresponding chlorides involves large temperature extrapolations and allowance for solvent effects. However some qualitative conclusion may be drawn, based on the data in Table V. 2.

All the rate coefficients in the above table have been calculated using the appropriate activation parameters. The value for p-nitro-triphenylmethyl fluoride is perhaps a little uncertain as it was obtained from the rate at +50°C and the  $\Delta C_p^\ddagger$  found for this reaction may well be too low (see Section V. 2. c).

The ratios  $\frac{k_{RC1}}{k_{RF}}$  have been calculated on the assumption that a change from 85% aqueous acetone to the 70% solvent will increase the rates of hydrolysis of the fluorides by a factor of ca. 20. This conclusion

TABLE V. 2.

Relative Rates and Substituent Effects for the  
Hydrolysis of Triphenylmethyl Halides at -25°C.

Compound	10 k sec. <sup>-1</sup>	$\frac{k_{RCl}}{k_{RF}}$ <sup>a</sup>	$\frac{k_X}{k_H}$ X = p-NO <sub>2</sub>
Ph <sub>3</sub> CCl	a 1.003		
		1.0x10 <sup>8</sup>	
Ph <sub>3</sub> CF	b 2.23x10 <sup>-7</sup>		
p-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CClPh <sub>2</sub>	a 5.661x10 <sup>-3</sup>		a 5.66x10 <sup>-3</sup>
		3x10 <sup>7</sup>	
p-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CFPh <sub>2</sub>	b 3.655x10 <sup>-9</sup>		b 1.63x10 <sup>-2</sup>

a in 85% aqueous acetone

b in 70% aqueous acetone

was reached by considering the magnitudes of the effects of the same solvent change on the rates for diphenylmethyl chlorides of comparable reactivity.<sup>28</sup> Thus these ratios may be subject to some error but they are considered to be of the correct order of magnitude. The value of  $\frac{k_{\text{RCl}}}{k_{\text{RF}}}$  for the p-nitro compounds may well be somewhat high relative to that for the unsubstituted halides in view of the uncertainty of the rate for the fluoride (see above) and the possibility that the solvent effect may decrease with decreasing reactivity of the substrate.

As expected<sup>67</sup> the ratio  $\frac{k_{\text{RCl}}}{k_{\text{RF}}}$  is greater for the compounds showing greater  $S_{\text{N}}1$  reactivity. A value of  $10^6$  for the triphenylmethyl compounds at  $25^\circ$  in 85% aqueous acetone has previously been reported<sup>72</sup> based on data at other temperatures (for the chloride) and in other solvents (for the fluoride).

The effect of the p-nitro group on the rate of hydrolysis of triphenylmethyl fluoride is less than when the leaving group is chloride (Table V. 2) but once again errors in temperature extrapolation and incorrect allowance for solvent effects may exaggerate the difference in the present case.

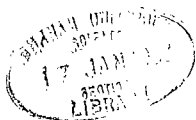
(c) Activation Parameters.

Very few data are available in the literature with which to compare the activation parameters in Table V. 1. Swain and Mosely<sup>34b</sup> have reported an activation energy of 24.4 k.cal. for the reaction of

triphenylmethyl fluoride with 70% aqueous acetone at 25°. The present value for this temperature is  $19.25 \pm .17$  k.cal. The present experimental values show the expected decrease with increasing temperature and are substantially less than those for the p-nitro compound under the same conditions, consistent with the electron withdrawing properties of the nitro group. Moreover the value of Swain and Mosely together with their rate coefficient at 25° lead to an entropy of activation of  $-0.65$  cal. deg.<sup>-1</sup> mole<sup>-1</sup> which would represent a singularly high (less negative) value for this solvent although it has already been pointed out that fluorides are expected to show lower (more negative) entropies of activation as compared to other halides. Thus it appears that Swain's data may be seriously in error.

It can be seen from Table V. 1 that the introduction of a p-nitro group into triphenylmethyl fluoride reduces the rate almost entirely by increasing the activation energy, the entropy of activation being substantially unaffected. This is consistent with previous observations for S<sub>N</sub>1 reactions and with the present results for the corresponding chlorides described in Chapter 4.

It is clear that relative C-Cl and C-F bond strengths<sup>66</sup> are reflected in the very large differences in activation energy  $E_{RF} - E_{RCl}$  for both R groups. Neglecting solvents effects<sup>74</sup> the values are (at least) 6.7 k.cal. for R = p-nitrotriphenylmethyl at  $-7.5^{\circ}$  and 7.3 k.cal.





for R = triphenylmethyl at  $-30^{\circ}$ .

It seems best to examine the effect of the change in leaving group on the entropies of activation for the present compounds by comparing values at  $50^{\circ}$  where the sensitivity of this parameter to solvent changes may be more easily evaluated from other data.

For p-nitrotriphenylmethyl chloride the experimental data at low temperatures may be used (see Equation VI. 13) to calculate the entropy of activation at  $50^{\circ}$  in the 85% solvent. The value is  $-21 \pm 2$  e.u. \* This method cannot be employed to calculate the corresponding value for triphenylmethyl chloride as the temperature difference now involved is such as to make the denominator in Equation VI. 13 very small and subject to a very large error. However there seems no reason to suppose the entropy values at  $50^{\circ}$  for the two chlorides are very different and a value of  $-21$  or  $-22$  e.u. for the triphenylmethyl compound could certainly be consistent with the present data at low temperatures.

Previous results <sup>27,28,74</sup> for  $S_N1$  solvolysis involving a variety of chlorides indicate that on passing from 85% aqueous acetone to the 70% solvent the entropies of activation for such reactions increase by about 5 e.u. On this basis,  $\Delta S^{\ddagger}$  at  $50^{\circ}$  for the triphenylmethyl chlorides would be  $-16$  e.u. and represents an increase of 5 e.u. as compared to the corresponding fluorides. Such a conclusion is necessarily tentative

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\* This probably represents a minimum value for the error.

but provides support for the hypothesis that the entropy of activation for the solvolysis of a fluoride should be more negative than that for the reaction of the corresponding chloride because of hydrogen bonding between a water molecule and the incipient fluoride ion in the transition state.

As mentioned in Chapter 1 (Section I. 8) the data of Swain and Scott<sup>72</sup> relating to 85% aqueous acetone do not support this hypothesis. However possible errors in the rate coefficients for triphenylmethyl chloride have already been pointed out (Sections I. 8 and IV. 4). Further the data for triphenylmethyl fluoride are calculated from runs in the 70% solvent and may also be subject to serious errors. Hence the quoted activation parameters must be of doubtful validity.

The entropies of activation at 50° for the fluorides, suggest on the basis of the  $\frac{\Delta C_p^\ddagger}{\Delta S^\ddagger}$  ratio for S<sub>N</sub>1 reactions under the present conditions,<sup>27</sup> that both reactions should show a  $\Delta C_p^\ddagger$  of about -80 cal. deg.<sup>-1</sup> mole.<sup>-1</sup> The observed values are significantly less than this. For the p-nitro compound the value is very low (-13 cal.) but is based on rates at only three temperatures and under conditions (low substrate concentrations and high temperatures) not conducive to great accuracy and it is quite possible that it underestimates the real value.

For triphenylmethyl fluoride the observed  $\Delta C_p^\ddagger$  of -47 cal. is not abnormal for S<sub>N</sub>1 solvolysis in this solvent.<sup>27</sup> The low  $\frac{\Delta C_p^\ddagger}{\Delta S^\ddagger}$  ratio is

therefore due mainly to the extremely negative entropy of activation. In the case of an  $S_N2$  solvolysis it has been pointed out (Section II. 4) that covalent attachment of a water molecule in the transition state probably results in a substantial loss of entropy for this molecule which is not paralleled by the corresponding decrease in heat capacity.

It could well be that hydrogen bonding between a water molecule and the incipient fluoride ion in the transition state could affect  $\Delta S^\ddagger$  and  $\Delta C_p^\ddagger$  in an analogous way and be responsible for the low  $\frac{\Delta C_p^\ddagger}{\Delta S^\ddagger}$  ratio now observed for the solvolysis of triphenylmethyl fluoride.

If the contribution to  $\Delta S^\ddagger$  for this reaction from the hydrogen bonding is as much as -7 e.u. and the remainder is attributed to additional solvation on activation then the ratio  $\frac{\Delta C_p^\ddagger}{\Delta S_{solv}^\ddagger}$  is then consistent with the accepted value for  $S_N1$  solvolysis under these conditions. Comparison with the reaction of the corresponding chloride suggests that this "hydrogen bonding" contribution is about -5 e.u. but in view of the uncertainty in the quoted  $\Delta S^\ddagger$  for the chloride, a contribution of -7 e.u. is not inconceivable. However this argument depends on the assumption that the additional solvation requirements of the transition states for the chloride and the fluoride are the same, which may not be justified.

CHAPTER VI.

EXPERIMENTAL

VI.1. Preparation and Purification of Materials.

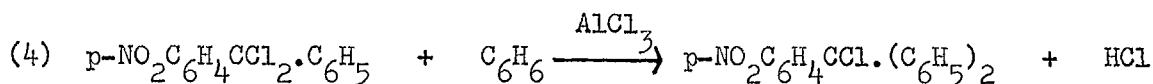
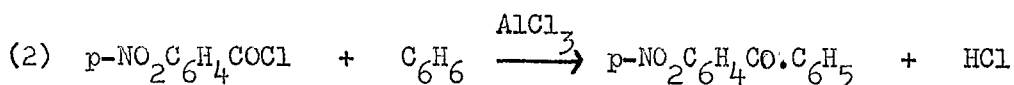
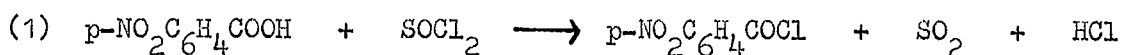
A. ALKYL CHLORIDES.

i. Methoxymethyl chloride was prepared by the reaction between gaseous HCl and a mixture of methanol and formalin.<sup>130a</sup> The formaldehyde content of the formalin was first determined iodometrically<sup>131</sup> and usually contained about 40 g. formaldehyde per litre. The best results were obtained when equimolar amounts of formaldehyde and methanol were present. After passing a rapid stream of gaseous HCl through the reaction mixture for 6 hours, two layers were formed, and after a further 3 hours the top layer was separated from the aqueous layer. More product was obtained by "salting out" from the aqueous layer with calcium chloride. The crude methoxymethyl chloride was dried and fractionated, b.pt. 59.0 (Lit. 58.9<sup>20</sup>). The samples used for kinetic purposes contained 98.9% and 100.0% of the theoretical amount of hydrolysable chloride respectively.

ii. Triphenylmethyl Chloride.<sup>130b</sup> Triphenylmethanol in dry benzene was heated on a water bath and acetyl chloride added. The mixture was refluxed for an hour and protected from atmospheric moisture by means of

a calcium chloride tube. On cooling and addition of excess petroleum ether, yellow crystals of triphenylmethyl chloride separated. The product was recrystallised from dry petroleum ether (b.pt. 80 - 100°C) and washed with more volatile petroleum ether (b.pt. 40 - 60°) and vacuum dried, m.pt. 109 - 110°C (Lit.<sup>20</sup> 111 - 112°). Found: C, 81.7%, H, 5.23%; calc. for (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>CCl, C, 81.8%, H, 5.42%. The hydrolysable chloride was 100.2% of the theoretical amount.

iii. p-Nitrotriphenylmethyl chloride was prepared by a variation of the method of Bayer and Willinger.<sup>132</sup> The reaction path was as follows.



Experimental details for the individual stages are given below.

Stage (1).

p-Nitrobenzoic acid (200 g.) was heated on a water bath with freshly distilled thionyl chloride (250 ml.) until no more gases were evolved. After removal of the excess thionyl chloride, the product was purified by vacuum distillation and recrystallisation from petroleum ether.

Melting point after vacuum drying 72 - 73° (Lit.<sup>133</sup> 73°).

Stage (2).

p-Nitrobenzoyl chloride (180 g.) was dissolved in dry A.R. benzene (1750 ml.) and aluminium trichloride (160 g.) added. The mixture was refluxed for 8 hours, (by which time the evolution of HCl gas had ceased), kept well stirred, and was protected from atmospheric moisture. After cooling, the mixture was poured into 2 litres of cold aqueous HCl and the product extracted with benzene, washed with sodium bicarbonate solution and dried. The benzene was then removed, the crude product recrystallised from glacial acetic acid,\* washed with low boiling petroleum ether and vacuum dried, m.pt.  $136 - 137^{\circ}$  (Lit.<sup>132</sup>  $138^{\circ}$ ). Found: C, 68.8%, H, 4.11%; calculated for  $p\text{-NO}_2\text{C}_6\text{H}_4\text{COC}_6\text{H}_5$ , C, 68.7%, H, 4.00%.

Stage (3).

p-Nitrobenzophenone (110 g.) and phosphorus pentachloride (130 g.) were kept at  $150^{\circ}$  for 2 hours without stirring in a flask fitted with a reflux condenser. After removal of the phosphorus pentachloride by vacuum distillation the solid residue was dissolved in benzene, washed with water and dried. Evaporation of the benzene left a dark brown oily residue which could only be induced to crystallise by an exhaustive series of extractions with low boiling petroleum ether, concentration of the resulting solution and cooling to low temperatures. The final product

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\* Several common solvents were tried but acetic acid gave the best results.

(a brown solid) was dried under vacuum, m.pt. 55 - 56° (Lit.<sup>132</sup> 56 - 57°), Found: C, 55.2%, H, 3.4%; calculated for p-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CCl<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, C, 55.7%, H, 3.2%. The hydrolysable chloride was 100.2% of the theoretical amount.

Stage (4).

p-Nitrodichlorodiphenylmethane (60 g.), dry A.R. benzene (350 ml.) and aluminium trichloride (40 g.) were refluxed with efficient stirring for 6 hours and were protected from atmospheric moisture. The product was a heavy black oil below a benzene layer which according to Bayer and Willinger<sup>132</sup> should contain some starting material. As much as possible of this layer was decanted off and the residue worked up in the usual manner for Friedel-Crafts reactions. A black solid insoluble in both benzene and water made the extraction process difficult. After drying the benzene extract was evaporated leaving a very dark red solid.\*

All attempts at recrystallisation from petroleum ether produced either oils or crystals contaminated with a red tar. Soxhlet extraction, as recommended by Bayer and Willinger,<sup>132</sup> recrystallisation from various solvents and solvent mixtures, and vacuum sublimation were all found to be unsatisfactory as methods of purification.†

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\* The whole synthesis was performed as far as this point, four times with the same final product independent of the rigour of purification of the intermediate compounds.

† Professor Cadogan (private communication) also encountered extreme difficulty in the recrystallisation of the product from this reaction.

The product and impurities were eluted down a celite column too rapidly for effective separation even with petroleum ether as eluent and both were tenaciously absorbed on an alumina column. However using a deactivated alumina column (prepared by washing the alumina with water and drying) a yellow solid was separated from the dark red tar. This solid contained no hydrolysable chloride and the infra red spectrum indicated that it was p-nitrotriphenylmethanol.

Therefore the least tarry of the recrystallised products were combined and hydrolysed by refluxing in aqueous acetone. After removal of the solvent the impure alcohol was then dissolved in benzene and the solution stirred with de-activated alumina on which most of the red tar was absorbed. The residual alcohol was recrystallised from petroleum ether. This alcohol was then chlorinated by dissolving it in benzene adding anhydrous zinc chloride to the solution and passing dry HCl gas through the mixture.<sup>28</sup> The resultant triphenylmethyl chloride, (after filtration and removal of the benzene), was recrystallised from petroleum ether and separated as pale yellow crystals, m.pt.  $91 - 91.5^{\circ}$  (Lit.<sup>132</sup>  $92-93^{\circ}$ ). The hydrolysable chloride was 99.3% of the theoretical amount.

iv. p-Methoxydiphenylmethyl chloride was prepared by chlorination of the corresponding alcohol.<sup>28</sup> Gaseous HCl was passed through a petroleum ether solution of the alcohol over phosphorus pentoxide. The product was recrystallised twice from petroleum ether at low temperatures,



m.pt. 62 - 63° (Lit.<sup>28</sup> 64°). The hydrolysable chloride was 98.9% of the theoretical amount.

## B. ALKYL FLUORIDES.

The methods commonly employed for the introduction of fluorine into organic compounds have been reviewed by Stevens and Tatlow.<sup>134</sup> In the present work the relevant methods were the replacement of chlorine and hydroxyl by fluorine. The application of these methods to the attempted synthesis of diphenylmethyl fluoride and to the synthesis of triphenylmethyl fluoride and its p-nitro derivative are described below.

### i. Diphenylmethyl Fluoride.

The reactions of diphenylmethyl chloride with antimony trifluoride, ammonium fluoride, tetramethylammonium fluoride and anhydrous hydrofluoric acid were tried. Experimental details are given below.

Antimony trifluoride was first purified by Soxhlet extraction with freshly dried methanol. It was then heated with diphenylmethyl chloride and the tarry product extracted with carbon tetrachloride. This procedure had been used previously in an analogous synthesis of diphenyldifluoromethane.<sup>131</sup> The residue after removal of the carbon tetrachloride was distilled in vacuo but the infra red spectrum of the distillate showed no carbon-fluorine peaks.

Ammonium fluoride was dried by azeotropic distillation using carbon

tetrachloride and then refluxed in dry acetone with diphenylmethyl chloride for 13 hours. Infra red evidence again indicated that no diphenylmethyl fluoride was present in the reaction product.

Tetramethylammonium fluoride was prepared by careful neutralisation of the corresponding alcohol with hydrofluoric acid and concentration of the resulting solution till the fluoride salt crystallised. It was then dried under vacuum and heated with the organic chloride in dry acetone for 11 hours. The infra red spectrum of the organic product was the same as that of diphenylmethyl chloride.

When the solvent was changed to sulphur dioxide which had been dried by repeated passage through towers filled with calcium sulphate, no identifiable organic products were obtained from the reaction mixture.

Anhydrous hydrogen fluoride was condensed from a cylinder into the first of a series of interconnected polythene bottles. The final bottle was a moisture trap and the rest of the apparatus was protected from the atmosphere by sealing all the joints with molten polythene. Any leaks were repaired with paraffin wax. The acid was distilled from the first bottle into the second which contained diphenylmethyl chloride. The mixture was kept at  $-10^{\circ}$  for several hours and overnight at room temperature. The acid was then distilled into the moisture trap in a stream of dry nitrogen. The residue was dissolved in dry ether, any remaining hydrogen fluoride removed by shaking with anhydrous potassium fluoride and the ether solution evaporated. During the evaporation a

curious blue-yellow fluorescence was observed. The product was a light fluffy solid \* which contained no halogen and which could have been polymeric.

Occasionally during the work described in the last two paragraphs there were indications of traces of a possible alkyl fluoride product but no workable amounts were ever obtained and no further possible synthetic routes to diphenylmethyl fluorides were investigated.

ii. Triphenylmethyl Fluoride. Triphenylmethyl chloride, prepared as previously described, was treated with anhydrous hydrofluoric acid.<sup>82</sup> the apparatus and procedure were as described for the reaction of the acid with diphenylmethyl chloride. The product was recrystallised from petroleum ether containing a little dry ether at low temperatures, m.pt. 103 - 103.3 (Lit.<sup>82</sup> 103°). The hydrolysable fluoride was found to be 96% of the theoretical amount and no hydrolysable chloride was found in the product. Samples on solvolysis did not show significant deviations from first-order kinetics and the impurity was presumed to be triphenylmethanol. Swain and his co-workers<sup>73</sup> reported a similar failure to separate small amounts of this alcohol from triphenylmethyl fluoride by recrystallisation from a variety of solvents and their product also melted at 103°.

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\* An earlier preparation had resulted in a "glassy" product.

In view of the hazards involved in working with anhydrous hydrofluoric acid while attempting to achieve moisture free conditions an alternative method of preparation was also used. This involved the reaction of triphenylmethanol with acetyl fluoride.<sup>136</sup>

Acetyl fluoride was prepared by the reaction between carefully dried potassium fluoride and benzotrichloride in glacial acetic acid.<sup>137</sup> After refluxing the mixture for 2 hours the acetyl fluoride (b.pt. 20°) was distilled off. A large excess was added to a solution of triphenylmethanol in dry benzene. The mixture was refluxed at 70° for 14 hours and then left for two days at room temperature. After removal of the volatile components of the reaction mixture, the product was recrystallised from petroleum ether and dried in vacuo. m.pt. 103 - 103.5°. The hydrolysable fluoride was 93.5% of the theoretical amount.

Once again the product contained no hydrolysable chloride and the infra red spectrum indicated that a small proportion of an alcohol was present. That the impurity was triphenylmethanol was again suggested by the fact that the sample on solvolysis showed first-order kinetics. An attempted separation by vacuum sublimation was not successful nor could it be achieved by column chromatography since the fluoride was completely converted to the alcohol.

iii. p-Nitrotriphenylmethyl fluoride. p-Nitrotriphenylmethanol was prepared from the impure chloride as described previously. m.pt. 96 - 98°

(Lit.<sup>131</sup> 98°). Found: C, 74.7%, H, 4.5%; calculated for  
 $p\text{-NO}_2\text{C}_6\text{H}_4\text{COH}(\text{C}_6\text{H}_5)_2$  C, 74.7%, H, 4.95%.

The alcohol in benzene solution was sealed up with a large excess of acetyl fluoride in a steel bomb and kept at 140° for five days. The contents were then evaporated to a small volume, excess benzene added, and the solution was washed with sodium bicarbonate and dried. After removal of the solvent a brown solid was obtained which was recrystallised from petroleum ether, (this removed most of the colour), and dried in vacuo. Found: C, 74.4%, H, 4.6%; calculated for  $p\text{-NO}_2\text{C}_6\text{H}_4\text{CF}(\text{C}_6\text{H}_5)_2$  C, 74.3%, H, 4.6%. The alcohol and the fluoride would give rise to almost identical carbon and hydrogen analyses. The hydrolysable fluoride was 78% of the theoretical amount. Infra red measurements on solutions of the pure alcohol and the reaction product in carbon tetrachloride indicated that about 20% of the latter was unconverted alcohol. The infra red spectrum of the reaction product also showed the expected peaks for an aromatic nitro compound<sup>139</sup> at 6.6 and 7.4  $\mu$  and peaks at 8.2 and 10.1  $\mu$ , (also present in the spectrum of  $(\text{C}_6\text{H}_5)_3\text{C-F}$ ), attributable to a carbon-fluorine linkage.<sup>139</sup> The product melted at 105 - 108°. A second bomb reaction resulted in a product with very similar properties and both samples on hydrolysis showed first-order kinetics with identical rate coefficients. Thus there was every reason to suppose that both samples were suitable for use in the study of the hydrolysis of p-nitrotriphenylmethyl fluoride.

## VI.2. Rate Measurements.

All kinetic runs were carried out in thermostats of conventional design and temperature control was to  $\pm 0.01^\circ$ . For low temperatures ( $0 - -35^\circ\text{C}$ ) a refrigeration unit was used in conjunction with a mercury-toluene regulator, heating elements and a relay. The thermostat was filled with a mixture of ethylene glycol and water. For higher temperatures the thermostat bath was filled with water covered by a layer of oil and contact thermometers were used for temperature control again in conjunction with relays and heating elements. Thermometers usually standardised to  $\pm 0.02$  by the National Physical Laboratory were used for temperature measurements.

Aqueous acetone solvents were made up using A.R. acetone refluxed over sodium hydroxide and potassium permanganate and fractionally distilled over small amounts of hydroquinone. The water used was distilled water from which the excess carbon dioxide had been removed. "x" % aqueous acetone was made up by mixing x volumes of acetone with (100 - x) volumes of water. Each batch of solvent was "monitored" by measuring the rate of hydrolysis of diphenylmethyl chloride in the batch, at a suitable temperature. The runs for triphenylmethyl fluoride were spread over two solvent batches and in order that all the rate coefficients should refer to the "same" solvent a correction factor was applied to those measured in the second batch. This correction

factor was based on the rates of hydrolysis of triphenylmethyl fluoride at 50° in both batches.

All reactions were followed by the development of acidity over three "half-lives". An initial reading, taken when the reaction mixture had reached thermal equilibrium with the thermostat, marked zero time and the difference between this reading and that taken after ten "half-lives" gave the concentration of the substrate. The acidity of the reaction mixture was determined by means of one of the techniques described in the following sections.

### VI.3. Conductimetric Determination of Hydrochloric Acid.

For the hydrolyses of the very reactive chlorides a conductance technique was employed. The cell, (200 ml.), had baffled sides to assist the stirring provided by 1200 r.p.m. motor, in conjunction with a ground glass stirrer fitted with a carefully lubricated glass sleeve. The platinum electrodes, (sealed into glass), were 1 sq. cm. in area and 0.5 cm. apart. About 150 ml. solvent was allowed to reach the thermostat temperature and the organic chloride, (sufficient to make the solution  $1.8 \times 10^{-3} M$ ), dissolved in dry acetone, (0.4 ml.), was rapidly introduced with maximum stirring. It was found necessary to make up a fresh solution of the chloride in acetone for each run, as it was found that the mean rate coefficients from successive runs, using a stock solution of methoxymethyl chloride in acetone, decreased, even though the

stock solution was kept at  $-20^{\circ}$ . The solvent was "compensated" by the addition of the appropriate amount of water prior to the addition of the substrate.

The use of a Pye conductance bridge, (Type 11700), in conjunction with an accurate mechanical counter allowed the determination of the time required for the resistance of the reaction mixture to attain the value of an external resistance. A series of external resistances covering an appropriate range for the temperature involved could be switched rapidly into the bridge circuit. The time required for each resistance value to be reached was determined by using a cine camera to record simultaneously the position of the oscilloscope trace on the screen of the instrument, and the reading on the counter, which could be read to 0.02 sec. For all experimental temperatures the solvent was calibrated for conductance with known concentrations of hydrochloric acid. The conductance of the reaction solution after ten "half-lives" could be read directly and the conductance at "zero" time was always a value reached after allowing adequate time for the mixing of the reagents.

#### VI.4. Titrimetric Determination of Hydrochloric Acid.

All solvents were monitored (see VI. 2) by determining the rate of hydrolysis of diphenylmethyl chloride in each batch. For 85% aqueous acetone at  $50^{\circ}$  a sealed ampoule technique was used. Ampoules were



withdrawn from time to time, cooled rapidly to  $-70^{\circ}\text{C}$ , cleaned and broken under neutral acetone and titrated against standard sodium hydroxide using lacmoid as indicator.

For the 70% solvent runs were carried out at 20 or  $25^{\circ}$  and in this case aliquots were withdrawn from the reaction mixture by pipette, quenched in neutral acetone and titrated as indicated above. The acetone employed for quenching was the commercial product which had been distilled from potassium permanganate and sodium hydroxide. Samples used for quenching were always first neutralised.

#### VI.5. Titrimetric Determination of Hydrofluoric Acid.

The hydrolyses of the two relatively unreactive alkyl fluorides were studied by means of the sealed ampoule technique, but the determination of the acidity of the samples presented difficulties. Neither of the techniques used for the other reactions was appropriate, mainly because HF is a weak acid. Further the methods used by previous workers<sup>73,77,79</sup> for runs in aqueous organic solvents were not considered to be of the precision hoped for in the present work. Thus several possible methods were investigated as described below.

Dilute solutions (ca. 0.01M) of HF in acetone containing an excess of calcium ions were made up. It was hoped that precipitation of calcium fluoride would leave HCl in solution which could then be titrated as previously described. Although this method has been used before

for more concentrated solutions,<sup>82</sup> it was found that the end points for the concentration now employed were poor and subject to "drifting". No improvement was effected when lithium perchlorate was used as precipitating agent.

Potentiometric titration of HF was difficult and inaccurate in water and not possible at all in acetone.

Samples of HF were shaken up with petroleum ether and then extracted with large quantities of water and titrated against sodium hydroxide using methyl red-methylene blue as indicator. Comparison with samples titrated directly, indicated that the extraction was not quantitative.

When a solution of HF in acetone was passed down an Amberlite I.R.A. 400 anion exchange column only a small proportion of the acid was converted to HCl.

Aliquots of an HF solution in 70% aqueous acetone were added to 20 ml. carbon tetrachloride and 100 ml. water added. The acid was extracted into the water layer by stirring and bubbling nitrogen through the mixture. The titration of the HF in the water layer was made difficult when methyl red-methylene blue was the indicator as the methyl red was absorbed into the carbon tetrachloride. No such difficulty was encountered when phenol red-bromothymol blue was used as indicator and reproducible titres were obtained which agreed with

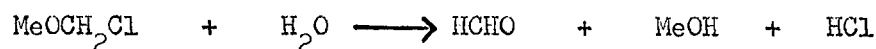
those obtained in the absence of the organic solvent.

However the success of these titrations depended on the rigorous exclusion of atmospheric  $\text{CO}_2$  at all stages. In the kinetic runs the sealed ampoules were broken under 20 ml. carbon tetrachloride and 100 ml. of neutral carbonate free water added. After a few minutes stirring to complete the extraction of the HF into the aqueous layer, the solution was titrated against sodium hydroxide. Throughout the process  $\text{CO}_2$  free compressed air was bubbled through the mixture. Check experiments showed that no significant hydrolysis of unreacted triphenylmethyl fluoride from the ampoules occurred during titration. Addition of calcium chloride to the aqueous extract did not improve the end points which could be estimated to  $\pm 0.02$  ml.

Additional experiments showed that over ten "half-lives" at  $60^\circ$  a 0.01M solution of HF lost 0.5% of its acidity, presumably by attack on the glass or solvent. "Infinity" titres were thus corrected for this loss. However higher temperatures were required for the study of p-nitrotriphenylmethyl fluoride. Over ten "half-lives" at  $100^\circ\text{C}$  1% acidity loss occurred from a 0.01M solution of HF but for a concentration of 0.005M negligible loss occurred under these conditions. Thus in the kinetic runs involving this compound 0.005M solutions were employed.

VI.6. The Products of the Reaction between Methoxymethyl Chloride and 85% Aqueous Acetone.

In view of the unexpected features of the results obtained in the present study of the hydrolysis of methoxymethyl chloride in 85% aqueous acetone it was decided to investigate the products of this reaction in order to confirm that reaction under study was in fact



This stoichiometry had previously been assumed for reaction with water in aqueous ethanol.<sup>105</sup>

Analysis of the hydrolysis product for acid indicated that HCl was formed quantitatively according to the above equation. Aliquots were titrated against standard sodium hydroxide in acetone using lacnoid as indicator.

The method of Bricker and Vail<sup>140</sup> was used to determine formaldehyde in the hydrolysis product. They had shown that chromotropic acid (1,8 di-hydroxy, 3,6 naphthalene disulphonic acid) forms a complex with formaldehyde which when heated with sulphuric acid gives a purple coloured solution. The intensity of colour produced is proportional to the amount of formaldehyde initially present and a large excess of acetone does not interfere.

In the present case, 1 ml. of each of a series of standard formaldehyde solutions was heated to 170° with 100 mg. of chromotropic

acid. After 10 minutes the samples were cooled and 5 ml. of concentrated sulphuric acid added. The samples were then heated for 30 minutes on a water bath during which time the purple colour developed. The optical density of each solution at 570 m. $\mu$ . was then measured after cooling and dilution to an appropriate volume with water. The blank was prepared by using 1 ml. of water instead of formaldehyde in an otherwise identical procedure. A linear plot of initial formaldehyde concentration against optical density was obtained.

A standard solution of methoxymethyl chloride in 85% aqueous acetone was allowed to reach equilibrium and the resulting concentration of formaldehyde determined by making use of the procedure and results described above. The concentration found was 102% of the theoretical, based on the assumed stoichiometry.

These analyses show that 1 mole of methoxymethyl chloride reacts with aqueous acetone to produce 1 mole of HCl and 1 mole of formaldehyde. This is very convincing evidence that the above stoichiometry is correct.

#### VI.7. Calculations.

##### (i) Rate Coefficients.

First-order rate coefficients were calculated from the integrated rate equation,

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

Equation VI. 1

where  $a$  is the substrate concentration at zero time and  $a - x$  its concentration at time  $t$ . A given run was usually duplicated or triplicated and the standard error  $\sigma(k)$  of the final mean rate coefficient  $k_m$  was calculated from the expression,

$$\sigma(k) = \frac{1}{n} [\sum (k - k_m)^2]^{1/2} \quad \text{Equation VI. 2}$$

where  $n$  was the number of separate determinations of  $k$ . Individual rate coefficients differing from the mean by more than  $2\frac{1}{2}\sigma$  (each) where  $\sigma$  (each) =  $n^{1/2}\sigma(k)$  were rejected and the appropriate values of  $k_m$  and  $\sigma(k)$  recalculated.

(ii) Rate Coefficients for runs showing deviation from first-order kinetics due to the operation of mass law effects.

(a) For each run the experimental data was first fitted to Equation IV. 2 (Section IV. 3). If  $\bar{k}_1 \equiv Y$  and  $[\bar{k}_1(a + c) - \frac{x}{t}] \equiv X$  then by the method of least squares <sup>141</sup> we have

$$k_1^o = \frac{\sum Y \sum X^2 - \sum X \sum XY}{n \sum X^2 - (\sum X)^2} \quad \text{Equation IV. 3a}$$

where  $n$  is the number of determinations of  $\bar{k}_1$ .

Similarly the mass law constant is obtained from,

$$\alpha^o = \frac{n \sum XY - \sum X \sum Y}{n \sum X^2 - (\sum X)^2} \quad \text{Equation VI. 3b}$$

The standard errors in  $k_1^0$  and  $\alpha^0$  are given by,<sup>141</sup>

$$\frac{\sigma^2(\alpha^0)}{n} = \frac{\sigma^2(k_1^0)}{\sum X^2} = \frac{\sum(\alpha^0 X + k_1^0 - Y)^2}{(n-2)[n\sum X^2 - (\sum X)^2]} \quad \text{Equation VI. 4a}$$

The standard error  $\sigma(k_m^0)$  of a final value ( $k_m^0$ ) calculated as a weighted mean of values from two duplicate runs giving values  $k_1^0 \pm \sigma_1$  ( $w_1$  readings) and  $k_2^0 \pm \sigma_2$  ( $w_2$  readings) was calculated from the equation,

$$\sigma^2(k_m^0) = \frac{w_1 \sigma_1^2 + w_2 \sigma_2^2 + w_1 \Delta_1^2 + w_2 \Delta_2^2}{2(w_1 + w_2)} \quad \text{Equation VI. 4b}$$

where

$$\Delta_1^2 = (k_m^0 - k_1^0)^2 \quad \text{and} \quad \Delta_2^2 = (k_m^0 - k_2^0)^2$$

An analogous equation gives  $\sigma(\alpha_m^0)$ .

(b) When the experimental data were fitted to Equation IV. 5 appropriate forms of Equation VI. 3 and VI. 4 were used.

(iii) Activation Parameters.

The activation energy (E) for a reaction was calculated from the expression,

$$E = \frac{2.303 k T_a T_b}{T_a - T_b} \log \frac{k_a}{k_b} \quad \text{Equation VI. 5}$$

where  $k_a$  and  $k_b$  are the first-order rate coefficients at the absolute temperatures  $T_a$  and  $T_b$  and  $E$  refers <sup>24b</sup> to  $\frac{T_a + T_b}{2}$ .

The standard error in  $E$  is given by,

$$\sigma(E) = \frac{RT_a T_b}{T_a - T_b} \left[ \left( \frac{\sigma_a}{k_a} \right)^2 + \left( \frac{\sigma_b}{k_b} \right)^2 \right]^{\frac{1}{2}} \quad \text{Equation VI. 6}$$

The entropy of activation  $\Delta S^\ddagger$  for a reaction was obtained from

$$\ln k_a = \ln \frac{A}{h} + \ln \frac{T_a + T_b}{2} + \frac{\Delta S^\ddagger}{R} - \frac{E}{RT_a} \quad \text{Equation VI. 7}$$

where  $E$  and  $\Delta S^\ddagger$  refer <sup>24b</sup> to  $\frac{T_a + T_b}{2}$ ,

and the standard error in  $\Delta S^\ddagger$  is approximately given by

$$\sigma(\Delta S^\ddagger) = \frac{\sigma(E)}{T} \quad \text{Equation VI. 8}$$

The heat capacity of activation for a reaction was obtained from the expression

$$\Delta C_p^\ddagger = \frac{dE}{dT} - R \quad \text{Equation II. 7}$$

where  $\frac{dE}{dT}$  was obtained by the method of least squares from the  $E$ 's at the experimental temperatures using the equation

$$E = E^0 + T \frac{dE}{dT} \quad \text{Equation VI. 9}$$

where  $E^0$  is a constant for the experimental conditions concerned. This



equation assumes that  $\frac{dE}{dT}$  is independent of temperature over the experimental range concerned.

The standard error in  $\frac{dE}{dT}$  was obtained in two ways.

(a) From the standard error in the slope of the best straight line of E against T using an appropriate form of Equation VI. 4a.

(b) From the standard errors of the individual E's using,

$$\sigma\left(\frac{dE}{dT}\right) = \frac{\left(\sum[\sigma(E)(T - T_m)]^2\right)^{\frac{1}{2}}}{\sum(T - T_m)^2} \quad \text{Equation VI. 10}$$

where  $T_m$  is the mean of the experimental temperatures. The larger of the  $\sigma\left(\frac{dE}{dT}\right)$  values was accepted.

(iv) Activation Parameters at Temperatures not studied experimentally.

The activation energy for a reaction at a temperature T outside the experimental range was calculated from,

$$E = E_m + (T - T_m)\frac{dE}{dT} \quad \text{Equation VI. 11}$$

where  $E_m$  and  $T_m$  are the mean values for the experimental range of temperatures.

Similarly  $\Delta S_T^\ddagger$  at any temperature T was obtained from,

$$\Delta S_T^\ddagger = \Delta S_m^\ddagger + 2.303 \Delta C_p^\ddagger \log\left(\frac{T}{T_m}\right) \quad \text{Equation VI. 12}$$

If  $\Delta C_p^\ddagger$  for the reaction is not known then the entropy of activation

$\Delta S_{T_2}^\ddagger$  for an  $S_N1$  reaction at a temperature  $T_2$ , may be calculated from an experimental value  $\Delta S_{T_1}^\ddagger$  at a temperature  $T_1$  from the equation,

$$\Delta S_{T_2}^\ddagger = \frac{\Delta S_{T_1}^\ddagger}{1 - 2.303 a \log \frac{T_2}{T_1}} \quad \text{Equation VI. 13}$$

where  $a = \frac{\Delta C_p^\ddagger}{\Delta S^\ddagger}$  at the temperature  $T_2$  for  $S_N1$  reaction in the solvent concerned.

APPENDIX VI. 1.

THE EVALUATION OF THE INTEGRAL "J" IN EQUATION IV. 5.

(See Section IV. 2).

$$J = \int_0^x \frac{c+x}{a-x} f_{Cl}^- dx \quad (\text{See Equation IV. 5})$$

and

$$f_{Cl}^- = \exp \left[ \frac{A(c+x)^{\frac{1}{2}}}{1+(c+x)^{\frac{1}{2}}} + 0.4606(c+x) \right]$$

expanding we have without error (since  $c+x$  is  $\ll 1$ )

$$f_{Cl}^- = 1 + A(c+x)^{\frac{1}{2}} + B_3(c+x) + B_4(c+x)^{\frac{3}{2}} + B_5(c+x)^2$$

$$B_3 = 0.4606 - A + A^2/2$$

$$B_4 = A + A(0.4606 - A) + A^3/6$$

$$B_5 = A^2 + (0.4606 - A)A^2/2 + A^4/24 + \frac{(0.4606 - A)^2}{2}$$

The above integral can now be written,

$$J = I_1 + AI_2 + B_3 I_3 + B_4 I_4 + B_5 I_5$$

$$I_1 = (a + c) \ln \frac{a}{a-x} - x$$

$$I_2 = (a + c)^{3/2} \ln \frac{(a + c)^{1/2} + (c + x)^{1/2}}{(a + c)^{1/2} - (c + x)^{1/2}} x \frac{(a + c)^{1/2} - c^{1/2}}{(a + c)^{1/2} + c^{1/2}}$$

$$= (a + c)^{3/2} \ln F$$

$$I_3 = (a + c)^2 \ln \frac{a}{a-x} - 2(a + c)x - \frac{1}{2} (a - x)^2 - a^2$$

$$I_4 = (a + c)^{5/2} \ln F - 2(a + c)^2 [(c + x)^{1/2} - c^{1/2}]$$

$$- \frac{2}{3}(a + c) [(c + x)^{3/2} - c^{3/2}] - \frac{2}{5}[(c + x)^{5/2} - c^{5/2}]$$

$$I_5 = (a + c)^3 \ln \frac{a}{a-x} - 3(a + c)^2 x - \frac{3}{2}(a + c) [(a - x)^2 - a^2]$$

$$+ \frac{1}{3}[(a - x)^3 - a^3]$$

A computer programme was available for the evaluation of the values of  $\frac{J}{t}$  corresponding to the  $\bar{k}_1$  values in a given run and the resulting values of  $k_1^0$  and  $\alpha^0$ , with standard errors.

APPENDIX VI. 2.

DETAILS OF INDIVIDUAL RUNS.

First order rate coefficients were calculated from the equation

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

where  $k$  is the integrated rate coefficient in  $\text{sec}^{-1}$   $t$  is the time in seconds,  $a$  is the concentration of substrate at zero time and  $a - x$  is its concentration at time  $t$ . Titres are expressed in ml. of NaOH.

In each case details of one run are given and the mean rate coefficients  $k'$ ,  $k''$  etc. of duplicate runs are quoted. For the runs involving the triphenylmethyl chlorides values of  $k_1^0$  and  $\alpha^0$  from both Equations IV. 2 and IV. 5 are quoted.

Experiment 1.

Methoxymethyl Chloride in 85% Aqueous Acetone (1) at 0.04°.

<u>Time</u>	<u><math>10^4 C_{\text{HCl}}</math></u>	<u><math>10^2 k_1</math></u>
0	3.170	
2.45	3.901	2.200
3.49	4.752	2.193
7.46	5.274	2.186
9.82	5.857	2.183
16.51	7.380	2.174
21.34	8.362	2.179
27.20	9.410	2.176
41.54	11.506	2.186
49.48	12.422	2.193
59.23	13.328	2.193
70.82	14.164	2.182
128.0	16.306	2.202
$\infty$	17.41	

$$10^2 k_1 = 2.187 \pm 0.0025 \text{ (12 readings)}$$

$$10^2 k_1' = 2.192 \pm 0.0042 \text{ ( 8 readings)}$$

$$10^2 k_1 \text{ (mean)} = 2.189 \pm 0.0027$$

Experiment 2.

Methoxymethyl Chloride in 85% Aqueous Acetone (1) at  $-17.44^{\circ}$ .

<u>Time</u>	<u><math>10^4 C_{\text{HCl}}</math></u>	<u><math>10^3 k_1</math></u>
0	1.791	
24.6	3.289	4.007
55.6	4.995	4.018
78.8	6.154	4.042
108.9	7.502	4.057
129.8	8.329	4.052
155.4	9.254	4.043
237.6	11.677	4.057
310.4	13.242	4.062
426.7	14.933	4.045
$\infty$	17.773	

$$10^3 k_1 = 4.042 \pm .0058 \text{ (9 readings)}$$

Experiment 3.

Methoxymethyl Chloride in 85% Aqueous Acetone (1) at  $-33.85^{\circ}$ .

<u>Time</u>	<u><math>10^4 C_{HCl}</math></u>	<u><math>10^4 k_1</math></u>
0	2.37	
209.8	4.47	6.806
304.3	5.34	6.849
408.6	6.21	6.814
520.5	7.10	6.846
644.2	8.00	6.845
779.6	8.88	6.815
930.0	9.80	6.834
1100	10.72	6.835
1294	11.63	6.818
1523	12.58	6.822
1790	13.51	6.821
2128	14.46	6.809
2566	15.43	6.828
$\infty$	18.17	

$$10^4 k_1 = 6.826 \pm 0.0037 \text{ (13 readings)}$$



Experiment 4.

Methoxymethyl Chloride in 85% Aqueous Acetone (2) at  $-33.85^{\circ}$ .

<u>Time</u>	<u><math>10^4 C_{\text{HCl}}</math></u>	<u><math>10^4 k_1</math></u>
0	2.18	
153.0	3.65	7.104
251.8	4.50	7.033
358.7	5.35	6.998
476.9	6.22	6.983
606.0	7.04	6.863
749.5	7.98	6.954
908.0	8.86	6.948
1095	9.77	6.926
1307	10.69	6.934
1561	11.61	6.920
1867	12.57	6.909
2265	13.46	6.891
$\infty$	16.46	

$$10^4 k_1 = 6.955 \pm .018 \text{ (12 readings)}$$

$$10^4 k_1' = 7.000 \pm .013 \text{ ( 9 readings)}$$

$$10^4 k_1 \text{ (mean)} = 6.975 \pm .0128$$

Experiment 6.

Methoxymethyl Chloride in 85% Aqueous Acetone (2) at 0.00°.

<u>Time</u>	<u><math>10^4 C_{\text{HCl}}</math></u>	<u><math>10^2 k_1</math></u>
0	3.63	
4.55	4.91	2.210
6.63	5.46	2.220
12.59	6.88	2.214
16.85	7.79	2.211
22.02	8.78	2.208
34.10	10.71	2.209
40.70	11.54	2.198
47.80	12.38	2.220
56.81	13.17	2.199
96.8	13.20	(2.067)
$\infty$	17.01	

$$10^2 k_1 = 2.210 \pm 0.0024 \text{ (9 readings)}$$

Experiment 7.

Methoxymethyl Chloride in 85% Aqueous Acetone (3) at -29.99°.

<u>Time</u>	<u><math>10^4 C_{HCl}</math></u>	<u><math>10^3 k_1</math></u>
0	1.40	
119.5	3.42	1.083
158.0	4.01	1.082
198.6	4.62	1.084
242.1	5.23	1.082
287.6	5.85	1.083
335.7	6.48	1.086
387.6	7.10	1.084
441.9	7.73	1.085
501.5	8.37	1.084
637.4	9.69	1.084
840.7	11.36	1.087
990.8	12.38	1.091
1246	13.73	1.086
1408	14.43	1.088
1606	15.13	1.089
$\infty$	18.02	

$$10^3 k_1 = 1.085 \pm 0.0007 \text{ (15 readings)}$$

$$10^3 k_1' = 1.085 \pm 0.0007 \text{ (10 readings)}$$

$$10^3 k_1 \text{ (mean)} = 1.085 \pm 0.0005$$

Experiment 8.

Methoxymethyl Chloride in 85% Aqueous Acetone (3) at -15.06°.

<u>Time</u>	<u><math>10^4 C_{\text{HCl}}</math></u>	<u><math>10^3 k_1</math></u>
0	1.345	
23.61	3.200	5.489
35.43	4.045	5.524
48.66	4.900	5.462
62.67	5.760	5.465
78.02	6.635	5.472
95.12	7.510	5.457
114.4	8.405	5.445
136.1	9.330	5.462
191.1	11.205	5.458
272.2	13.105	5.439
333.8	14.080	5.425
425.8	15.045	5.404
$\infty$	16.570	

$$10^3 k_1 = 5.458 \pm .0069 \text{ (12 readings)}$$

$$10^3 k_1' = 5.422 \pm .0092 \text{ (11 readings)}$$

$$10^3 k_1 \text{ (mean)} = 5.441 \pm .0073$$

Experiment 9.

Methoxymethyl Chloride in 85% Aqueous Acetone (3) at  $-0.09^{\circ}$ .

<u>Time</u>	<u><math>10^4 C_{\text{HCl}}</math></u>	<u><math>10^2 k_1</math></u>
0	3.140	
6.09	3.055	2.254
8.10	6.020	2.238
11.93	6.650	2.243
21.07	8.770	2.240
25.00	9.540	2.232
30.87	10.615	2.242
46.56	12.885	2.261
57.36	14.045	2.274
66.70	14.740	2.237
107.9	16.825	2.273
$\infty$	18.110	

$$10^2 k_1 = 2.249 \pm .0046 \text{ (10 readings)}$$

$$10^2 k_1' = 2.238 \pm .0034 \text{ ( 9 readings)}$$

$$10^2 k_1 \text{ (mean)} = 2.244 \pm .0032$$

Experiment 10.

Triphenylmethyl Chloride in 85% Aqueous Acetone (5) at  $-36.25^{\circ}$ .

<u>Time</u>	<u><math>10^4 C_{HCl}</math></u>	<u><math>10^2 \bar{k}_1</math></u>
0	2.50	
2.88	3.61	2.199
6.50	4.89	2.168
10.09	5.97	2.100
14.93	3.14	1.974
23.99	9.18	1.906
33.89	10.89	1.827
50.96	13.11	1.722
65.19	14.61	1.683
88.60	16.30	1.607
121.3	17.86	1.537
$\infty$	20.68	

$$10^2 k_1^{\circ} = 2.570 \pm .035 \quad \alpha^{\circ} = 532 \pm 26 \text{ (10 readings)}$$

$$10^2 k_1^{\circ'} = 2.630 \pm .016 \quad \alpha^{\circ'} = 627 \pm 14 \text{ ( 6 readings) Equation IV. 2}$$

$$10^2 k_1^{\circ} \text{ (mean)} = 2.592 \pm .029 \quad \alpha^{\circ} \text{ (mean)} = 580 \pm 30$$

$$10^2 k_1^{\circ} = 2.630 \pm .035 \quad \alpha^{\circ} = 693 \pm 31 \text{ (10 readings)}$$

$$10^2 k_1^{\circ'} = 2.731 \pm .036 \quad \alpha^{\circ'} = 805 \pm 37 \text{ ( 7 readings) Equation IV. 5}$$

$$10^2 k_1^{\circ} \text{ (mean)} = 2.671 \pm .043 \quad \alpha^{\circ} \text{ (mean)} = 739 \pm 46$$

Experiment 11.

Triphenylmethyl Chloride in 85% Aqueous Acetone (5) at  $-25.44^{\circ}$ .

<u>Time</u>	<u><math>10^4 C_{\text{HCl}}</math></u>	<u><math>10^2 \bar{k}_1</math></u>
0	1.88	
1.50	3.40	7.554
3.55	5.19	7.480
5.27	6.38	7.232
7.80	7.78	6.886
12.30	9.67	6.467
21.74	12.22	5.993
30.75	13.54	5.598
43.90	14.71	5.328
$\infty$	16.08	

$$10^2 k_1^{\circ} = 9.502 \pm .29 \quad \alpha^{\circ} = 734 \pm 22 \text{ (6 readings) Equation IV. 2.}$$

$$10^2 k_1^{\circ} = 9.335 \pm .21 \quad \alpha^{\circ} = 811 \pm 61 \text{ (8 readings) Equation IV. 5.}$$

Experiment 12.

Triphenylmethyl Chloride in 85% Aqueous Acetone (5) at -25.44°.

<u>Time</u>	<u><math>10^4 C_{\text{HCl}}</math></u>	<u><math>10^2 \bar{k}_1</math></u>
0	1.88	
2.60	5.19	7.946
3.90	6.38	7.505
5.60	7.78	7.221
8.41	9.67	6.879
13.70	12.22	6.384
17.50	13.54	6.121
21.78	14.71	5.899
28.73	16.12	5.651
42.25	17.76	5.339
$\infty$	19.62	

$$10^2 k_1^0 = 9.643 \pm .21 \quad \alpha^0 = 654 \pm 15 \text{ (8 readings) Equation IV. 2}$$

$$10^2 k_1^0 = 9.979 \pm .09 \quad \alpha^0 = 834 \pm 22 \text{ (9 readings) Equation IV. 5}$$



Experiment 13.

p-Nitrotriphenylmethyl Chloride in 85% Aqueous Acetone (4) at -29.50°.

<u>Time</u>	<u><math>10^4 c_{\text{HCl}}</math></u>	<u><math>10^4 \bar{k}_1</math></u>
0	0.96	
362	3.06	3.099
540	3.99	3.080
843	5.34	2.973
1140	6.56	2.925
1500	7.80	2.834
1800	8.80	2.811
2100	9.70	2.783
2300	11.21	2.711
3300	12.67	(2.725)
4140	14.00	2.608
4860	15.04	2.570
5525	15.81	2.525
6240	16.54	2.495
7020	17.24	2.480
7680	17.70	2.453
$\infty$	20.70	

$$10^4 k_1^{\circ} = 3.253 \pm .017 \quad \alpha^{\circ} = 283 \pm 9 \text{ (14 readings)}$$

$$10^4 k_1^{\circ'} = 3.220 \pm .009 \quad \alpha^{\circ'} = 307 \pm 5 \text{ (16 readings) Equation IV. 2}$$

$$10^4 k_1^{\circ} \text{ (mean)} = 3.235 \pm .015 \quad \alpha^{\circ} \text{ (mean)} = 296 \pm 10$$

$$10^4 k_1^{\circ} = 3.297 \pm .016 \quad \alpha^{\circ} = 353 \pm 9 \text{ (15 readings)}$$

$$10^4 k_1^{\circ'} = 3.232 \pm .0078 \quad \alpha^{\circ'} = 359 \pm 5 \text{ (17 readings) Equation IV. 5}$$

$$10^4 k_1^{\circ} \text{ (mean)} = 3.262 \pm .025 \quad \alpha^{\circ} \text{ (mean)} = 356 \pm 6$$

Experiment 14.

p-Nitrotriphenylmethyl Chloride in 85% Aqueous Acetone at -15.48°.

<u>Time</u>	<u><math>10^4 C_{HCl}</math></u>	<u><math>10^3 \bar{k}_1</math></u>
0	1.39	
58.11	2.84	1.922
77.25	3.26	1.899
97.3	3.69	1.889
118.6	4.11	1.866
165.3	4.97	1.834
218.2	5.87	1.819
279.1	6.77	1.787
349.2	7.68	1.760
432.6	8.60	1.727
552.9	9.73	1.697
650.6	10.41	1.651
804.2	11.36	1.618
1000	12.35	1.605
1313	13.33	1.563
$\infty$	15.08	

$$10^3 k_1^{\circ} = 2.051 \pm .0078 \quad \alpha^{\circ} = 346 \pm 9 \text{ (14 readings)}$$

$$10^3 k_1^{\circ'} = 2.059 \pm .026 \quad \alpha^{\circ'} = 337 \pm 25 \text{ (10 readings) Equation IV. 2}$$

$$10^3 k_1^{\circ} \text{ (mean)} = 20.54 \pm 0.13 \quad \alpha^{\circ} \text{ (mean)} = 342 \pm 13$$

$$10^3 k_1^{\circ} = 2.072 \pm .0091 \quad \alpha^{\circ} = 412 \pm 11 \text{ (14 readings)}$$

$$10^3 k_1^{\circ'} = 2.080 \pm .013 \quad \alpha^{\circ'} = 409 \pm 15 \text{ (11 readings) Equation IV. 5}$$

$$10^3 k_1^{\circ} \text{ (mean)} = 2.076 \pm .08 \quad \alpha^{\circ} \text{ (mean)} = 411 \pm 9$$

Experiment 15.

p-Nitrotriphenylmethyl Chloride in 85% Aqueous Acetone (4) at +0.17°.

<u>Time</u>	<u><math>10^4 C_{HCl}</math></u>	<u><math>10^2 \bar{k}_1</math></u>
0	1.01	
11.42	2.83	1.198
16.11	3.46	1.171
22.01	4.21	1.156
30.76	5.16	1.123
44.59	6.51	1.094
53.04	7.21	1.075
60.95	7.83	1.069
71.44	8.55	1.054
85.80	9.45	1.046
106.8	10.47	1.026
141.3	11.76	0.9936
214.4	13.40	0.9501
$\infty$	15.26	

$$10^2 k_1^0 = 1.265 \pm .010 \quad \alpha^0 = 368 \pm 16 \text{ (12 readings)}$$

$$10^2 k_1^{0'} = 1.271 \pm .013 \quad \alpha^{0'} = 404 \pm 23 \text{ (10 readings) Equation IV. 2}$$

$$10^2 k_1^0 \text{ (mean)} = 1.268 \pm .008 \quad \alpha^0 \text{ (mean)} = 384 \pm 19$$

$$10^2 k_1^0 = 1.275 \pm .0080 \quad \alpha^0 = 444 \pm 17 \text{ (12 readings)}$$

$$10^2 k_1^{0'} = 1.286 \pm .010 \quad \alpha^{0'} = 491 \pm 24 \text{ (10 readings) Equation IV. 5}$$

$$10^2 k_1^0 \text{ (mean)} = 1.280 \pm .007 \quad \alpha^0 \text{ (mean)} = 465 \pm 22$$

Experiment 16.

p-Nitrotriphenylmethyl Chloride in 85% Aqueous Acetone (3) at -29.98°.

<u>Time</u>	<u><math>10^4 c_{HCl}</math></u>	<u><math>10^4 \bar{k}_1</math></u>
0	1.025	
360	2.545	(2.943)
659	3.605	2.838
971	4.600	2.796
1270	3.460	2.729
1709	6.605	2.690
1980	7.200	2.647
2314	7.785	(2.557)
2549	8.340	2.589
3155	9.340	2.526
3588	10.025	2.515
4160	10.770	2.480
4625	11.305	2.457
5609	12.253	2.414
6548	12.990	2.385
7230	13.400	2.351
$\infty$	16.165	

$$10^4 k_1^o = 3.049 \pm .018 \quad \alpha^o = 338 \pm 12 \text{ (13 readings)}$$

$$10^4 k_1^{o'} = 3.104 \pm .010 \quad \alpha^{o'} = 410 \pm 8 \text{ (12 readings) Equation IV. 2}$$

$$10^4 k_1^o \text{ (mean)} = 3.075 \pm .022 \quad \alpha^o \text{ (mean)} = 373 \pm 26$$

$$10^4 k_1^o = 3.098 \pm .018 \quad \alpha^o = 420 \pm 14 \text{ (14 readings)}$$

$$10^4 k_1^{o'} = 3.144 \pm .012 \quad \alpha^{o'} = 499 \pm 12 \text{ (13 readings) Equation IV. 5}$$

$$10^4 k_1^o \text{ (mean)} = 3.120 \pm .020 \quad \alpha^o \text{ (mean)} = 458 \pm 29$$

Experiment 17.

p-Nitrotriphenylmethyl Chloride in 85% Aqueous Acetone (3) at +0.3°.

<u>Time</u>	<u><math>10^4 C_{HCl}</math></u>	<u><math>10^2 \bar{k}_1</math></u>
0	1.140	
10.36	3.135	1.131
22.32	5.040	1.091
26.48	5.605	1.074
34.20	6.635	1.061
53.61	8.720	1.015
61.95	9.510	1.005
74.87	10.550	0.9834
110.3	12.830	0.9449
132.8	13.920	0.9262
148.6	14.535	0.9110
223.7	16.570	0.8614
$\infty$	19.200	

$$10^2 k_1^{\circ} = 1.215 \pm .0040 \quad \alpha^{\circ} = 363 \pm 7 \text{ (11 readings)}$$

$$10^2 k_1^{\circ'} = 1.246 \pm .0080 \quad \alpha^{\circ'} = 376 \pm 13 \text{ (9 readings) Equation IV. 2}$$

$$10^2 k_1^{\circ} \text{ (mean)} = 1.228 \pm .012 \quad \alpha^{\circ} \text{ (mean)} = 369 \pm 12$$

$$10^2 k_1^{\circ} = 1.229 \pm .0040 \quad \alpha^{\circ} = 444 \pm 8 \text{ (11 readings)}$$

$$10^2 k_1^{\circ'} = 1.262 \pm .0080 \quad \alpha^{\circ'} = 464 \pm 15 \text{ (9 readings) Equation IV. 5}$$

$$10^2 k_1^{\circ} \text{ (mean)} = 1.244 \pm .012 \quad \alpha^{\circ} \text{ (mean)} = 453 \pm 11$$

Experiment 18.

Triphenylmethyl Fluoride in 70% Aqueous Acetone (2) at 20.79°.

10.11 ml. titrated with .00937M NaOH

<u>Time</u>	<u>Titre</u>	<u><math>10^5 k_1</math></u>
0	1.46	
6840	2.38	1.713
14100	3.21	1.673
21240	4.00	1.715
28440	4.68	1.720
35220	5.28	1.745
41940	5.87	1.807
100440	8.40	1.789
116040	8.66	1.728
118080	8.75	1.770
0	1.62	
57240	6.91	1.825
72120	7.56	1.805
78900	7.88	1.848
$\infty$	9.78	

$$10^5 k_1 = 1.762 \pm 0.0143 \text{ (12 readings)}$$

$$10^5 k_1' = 1.748 \pm 0.0113 \text{ (10 readings)}$$

$$10^5 k_1 \text{ (mean)} = 1.755 \pm 0.012$$

$$\text{corrected to 70\% Acetone (1)} = 1.397 \pm 0.010$$

Experiment 19.

Triphenylmethyl Fluoride in 70% Aqueous Acetone (1) at 29.74°.

10.11 ml. titrated with .00896M NaOH

<u>Time</u>	<u>Titre</u>	<u>10<sup>5</sup> k<sub>1</sub></u>
0	0.60	
4860	1.95	3.843
9660	2.91	3.567
13560	3.70	3.658
24060	5.29	3.722
28200	5.67	3.617
0	0.94	
28980	5.89	3.645
34020	6.39	3.722
37620	6.67	3.738
42240	6.92	3.672
47400	7.29	3.822
52260	7.45	3.732
∞	8.53	

$$10^5 k_1 = 3.702 \pm .024 \text{ (11 readings)}$$

$$10^5 k_1' = 3.695 \pm .019 \text{ ( 9 readings)}$$

$$10^5 k_1 \text{ (mean)} = 3.699 \pm .018$$

Experiment 20.

Triphenylmethyl Fluoride in 70% Aqueous Acetone (1) at 40.42°.

10.11 ml. titrated with .00917M NaOH

<u>Time</u>	<u>Titre</u>	<u>10<sup>4</sup> k<sub>1</sub></u>
0	0.99	
2580	3.02	1.071
3780	3.76	1.057
4920	4.38	1.048
6120	5.05	1.077
7380	5.61	1.080
9660	6.37	1.057
12000	7.05	1.062
14460	7.52	1.036
16860	8.07	1.093
19260	8.32	1.066
21060	8.57	1.100
∞	9.40	

$$10^4 k_1 = 1.068 \pm .0054 \text{ (11 readings)}$$

$$10^4 k_1' = 1.066 \pm .0052 \text{ ( 8 readings)}$$

$$10^4 k_1 \text{ (mean)} = 1.067 \pm .038$$



Experiment 21.

Triphenylmethyl Fluoride in 70% Aqueous Acetone (1) at 50.82°.

10.11 ml. titrated with .00917M NaOH

<u>Time</u>	<u>Titre</u>	<u>10<sup>4</sup> k<sub>1</sub></u>
0	2.20	
420	3.05	2.743
840	3.77	2.668
1260	4.47	2.722
1680	5.00	2.638
2200	5.57	2.684
4020	7.40	7.721
4620	7.81	2.736
5460	8.31	2.784
6130	8.52	2.693
$\infty$	10.02	

$$10^4 k_1 = 2.710 \pm .013 \text{ (9 readings)}$$

$$10^4 k_1' = 2.754 \pm .0050 \text{ (9 readings)}$$

$$10^4 k_1 \text{ (mean)} = 2.732 \pm .0070 \text{ (from 4 runs)}$$

Experiment 22.

Triphenylmethyl Fluoride in 70% Aqueous Acetone (2) at 60.52°.

10.11 ml. titrated with .00937M NaOH

<u>Time</u>	<u>Titre</u>	<u>10<sup>4</sup> k<sub>1</sub></u>
0	2.61	
300	4.15	7.830
600	5.31	7.618
1110	6.87	7.790
1350	7.45	7.947
1655	8.09	8.247
0	1.79	
300	3.43	7.463
620	4.85	7.560
900	5.81	7.515
2100	8.32	7.624
2520	8.83	7.822
2792	9.15	8.239
∞	9.97	

$$10^4 k_1 = 7.787 \pm .078 \text{ (11 readings)}$$

$$10^4 k_1' = 7.358 \pm .049 \text{ ( 9 readings)}$$

$$10^4 k_1'' = 7.790 \pm .047 \text{ ( 9 readings)}$$

$$10^4 k_1''' = 7.797 \pm .055 \text{ (11 readings)}$$

$$10^4 k_1 \text{ (mean)} = 7.693 \pm .042$$

$$\text{corrected to 70\% aqueous acetone (1) } 10^4 k_1 = 6.122 \pm .033$$

Experiment 23.

Triphenylmethyl Fluoride in 70% Aqueous Acetone (2) at 50.40°.

(Standardisation Run).

10.11 ml. titrated with .00971M NaOH

<u>Time</u>	<u>Titre</u>	<u><math>10^4 k_1</math></u>
0	1.05	
482	2.27	3.443
900	3.05	3.207
1363	3.91	3.354
1740	4.59	3.369
2160	5.10	3.280
2640	5.68	3.289
3420	6.39	3.234
4260	7.08	3.308
5880	7.88	3.295
6540	8.10	3.287
$\infty$	9.03	

$$10^4 k_1 = 3.306 \quad (10 \text{ readings})$$

$$10^4 k_1' = 3.310 \quad (6 \text{ readings})$$

$$10^4 k_1 (\text{mean}) = 3.307 \quad (16 \text{ readings})$$

Experiment 24.

p-Nitrotriphenylmethyl Fluoride in 70% Aqueous Acetone (3) at 90.66°.

10.11 ml. titrated with .01019M NaOH

<u>Time</u>	<u>Titre</u>	<u><math>10^4 k_1</math></u>
0	0.50	
630	1.01	1.964
1200	1.48	2.104
1980	1.90	1.939
2406	2.14	1.945
3242	2.58	1.982
3660	2.71	1.913
5100	3.29	1.980
5880	3.57	2.044
8280	4.09	2.057
9600	4.28	2.056
10740	4.38	2.005
$\infty$	4.89	

$$10^4 k_1 = 1.999 \pm .017 \text{ (11 readings)}$$

$$10^4 k_1' = 1.992 \pm .011 \text{ ( 8 readings)}$$

$$10^4 k_1 \text{ (mean)} = 1.996 \pm .011$$

Experiment 25.

p-Nitrotriphenylmethyl Fluoride in 70% Aqueous Acetone (3) at 69.84°.

10.11 ml. titrated with .01019M NaOH

<u>Time</u>	<u>Titre</u>	<u><math>10^5 k_1</math></u>
0	0.29	
5280	1.10	3.598
7873	1.50	3.800
12420	2.08	3.880
15780	2.42	3.845
19320	2.70	3.745
23880	3.01	3.644
31080	3.50	3.726
36120	3.77	3.768
41700	3.99	3.751
47220	4.13	3.638
51600	4.27	3.682
$\infty$	4.97	

$$10^5 k_1 = 3.734 \pm .025 \text{ (11 readings)}$$

$$10^5 k_1' = 3.747 \pm .062 \text{ ( 8 readings)}$$

$$10^5 k_1'' = 3.754 \pm .035 \text{ (10 readings)}$$

$$10^5 k_1 \text{ (mean)} = 3.744 \pm .023$$

Experiment 26.

p-Nitrotriphenylmethyl Fluoride in 70% Aqueous Acetone (3) at 50.03°.

10.11 ml. titrated with .00971M NaOH

<u>Time</u>	<u>Titre</u>	<u>10<sup>6</sup> k<sub>1</sub></u>
0	0.10	
19200	0.69	6.547
37020	1.10	6.040
73920	1.89	6.013
91800	2.25	6.142
110580	2.52	6.002
123360	2.70	5.969
169200	3.36	6.265
198360	3.69	6.408
247380	4.00	6.152
299640	4.24	5.908
349620	4.48	6.012
349620	4.49	6.061
<b>∞</b>	5.09	

$$10^6 k_1 = 6.127 \pm .053 \text{ (12 readings)}$$

$$10^6 k_1' = 6.104 \pm .049 \text{ (12 readings)}$$

$$10^6 k_1 \text{ (mean)} = 6.115 \pm .036$$

SOLVENTS.

All solvents were monitored using diphenylmethyl chloride and the rate for this compound in each solvent is recorded below

<u>Solvent</u>	<u>Temp. °C</u>	<u><math>10^4 k_1 \text{ sec.}^{-1}</math></u>
85% (1)	40.00	1.085
85% (2)	40.00	0.8786
85% (3)	40.00	1.143
85% (4)	40.00	1.157
85% (5)	40.00	1.083
70% (1)	25.13	4.802
70% (2)	25.13	6.349
70% (3)	20.29	3.032

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