Solvent Participation in Nucleophilic Displacement Reactions. Part III. Ionisation Reactions with Particular Reference to the Alcoholysis of Triphenylmethyl Chloride.*

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The high reactivity of triphenylmethyl chloride in the presence of electrophilic reagents and the very slow reaction with primary amines in carbon tetrachloride and in acetone suggest strongly that reaction involves pre-ionisation. In carbon tetrachloride the rate is proportional to the concentration of associated alcohol over the 0·05—0·5M concentration range, showing that a minimum of three alcohol molecules are involved in the overall reaction.

In more concentrated solutions the rate increases rapidly with alcohol concentration, and this is attributed to further solvation of the initial ion-pair, which, however, remains associated as shown by the absence of mass-action repression of the rate. In contrast to the reaction of acid chlorides, the rate of reaction in dilute alcohol solutions is increased considerably by increase in the polarity of the solvent, *e.g.*, by replacing ether by acetone. Evidence is presented for a change in mechanism in acetone involving rate-determining substitution of the cation.

The kinetics of the ethanolysis of chlorodimethyl ether and 2 : 4 : 6-trimethylbenzoyl chloride have been followed in carbon tetrachloride and ether, and the influence of solvation has been discussed.

TRIARYLMETHANE derivatives are amongst the most readily ionised organic compounds, and stable salts have been known for a long time (see Burton and Praill, *Quart. Rev.*, 1952, **6**, 302). In addition, the covalent halides are rapidly ionised in polar aprotic solvents, *e.g.*, sulphur dioxide (Walden, *Ber.*, 1902, **35**, 2018) and nitromethane (Bentley, Evans, and Halpern, *Trans. Faraday Soc.*, 1951, **47**, 711). The ionisation of compounds of this type in non-polar media is strongly promoted by electrophilic reagents in benzene (Swain, *J. Amer. Chem. Soc.*, 1948, **70**, 1119; Hawthorne and Cram, *ibid.*, 1954, **76**, 3451). Recent observations have shown that ionisation occurs more readily than hitherto suspected. For example, 1-phenylethyl chloride is racemised by stannic chloride in carbon tetrachloride (Heald and Gwyn-Williams, *J.*, 1954, 362), and 1-mesitylethyl chloride by acetone alone (Charlton and Hughes, *J.*, 1954, 2939). These observations suggest that ionisation may require a relatively small energy of solvation compared with earlier estimates (Evans, *Trans. Faraday Soc.*, 1946, **42**, 719), a view which is supported by the recent work of Swain and Kreevoy (*J. Amer. Chem. Soc.*, 1955, **77**, 1122) using ^{36}Cl ions. It was shown that in very dilute solutions of chloride ions in benzene, the exchange of Cl^- in triphenylmethyl chloride is of first order. The obvious inference is that the exchange follows a slow ionisation of the halide promoted by benzene solvent alone. It is therefore preferable to regard the ionisation as a covalent–ionic transition, as the energy of the ionic state must be lowered considerably by the electrostatic interaction between the two ions in intimate contact. This stabilisation energy (which may be of the order of 50 kcal./mole) is unimportant in systems leading to fully solvated ions.

The triarylmethyl cation is an exceptionally stable carbonium ion, and under some conditions where it is rapidly pre-formed the rate of substitution may be determined by the rate of the subsequent reaction with the nucleophilic reagent (Gelles, Hughes, and Ingold, *J.*, 1954, 2918). These workers have differentiated between such a case and the more frequent S_N1 process in which the slow ionisation controls the substitution rate.

In general, the ease of ionisation will be related simply to the stability of the cation as reflected in the ionisation potential. We are concerned here more closely with the significance of the kinetic order of the solvation process in various solvents in terms of the

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* Parts I and II, preceding papers.

ease of ionisation. Most of the experimental results given below refer to the alcoholysis of triphenylmethyl chloride, as the kinetics are relatively simple in this case, but brief consideration is given to the solvent effect in other reactions which, at least in solvolytic media, are thought to proceed by rate-determining ionisation.

EXPERIMENTAL

The solvents were purified as in the previous paper and the same method of following the rate was used. Triphenylmethyl chloride (B.D.H.), recrystallised from light petroleum (b. p. 60—80°)–acetyl chloride (9 : 1), had m. p. 112°. "AnalaR" chlorodimethyl ether, purified by fractional distillation, had b. p. 59·5°. 2 : 4 : 6-Trimethylbenzoyl chloride was prepared and purified as given by Brown and Hudson (*J.*, 1953, 3352); it had b. p. 130°/22 mm.

Analysis of Results.—The reversibility of the reaction of triphenylmethyl chloride in ethanol–carbon tetrachloride mixtures is shown by the % reaction–time curves for various initial concentrations of ethanol (Fig. 1). Preliminary analysis showed that the rate is not given by the appropriate equation for a forward first-order and backward second-order process as expected for the reaction

$$Ph_3CCl + \underset{\text{(excess)}}{EtOH} \rightleftharpoons Ph_3{\cdot}COEt + HCl$$

In the more concentrated solutions (0·69—6·9M-ethanol) the pseudo-unimolecular rate constant k_0 was found to obey a first-order reversal equation accurately * (Fig. 2) and hence k_1 could be obtained by assuming that $k_1 = k'T_e/T_\infty$, where k' is the experimental rate constant, T_∞ is the concentration of products equivalent to the initial concentration of triphenylmethyl chloride, and T_e is the corresponding concentration at equilibrium. For concentrations of ethanol less than 0·690M, the rate constants were obtained from initial rates, as the reaction does not follow the first-order rate equation accurately. A summary of the rate constants and position of equilibrium is given in Table 1. The accuracy is somewhat less than for the rate measurements of the acid chlorides, owing possibly to the reversibility of the reaction and the large molecular weight of the chloride. Change in concentration of the latter therefore has a significant effect on the medium. The change in rate constant with halide concentration is relatively small, and hence the reaction is approximately of first order with respect to this reactant. The results of Table 1 show that the graphical method used previously leads to significantly different results from the initial rates, and it was not used for this reaction.

The effect of temperature in the more concentrated solutions is given by the results in Table 2.

TABLE 1. *Ethanolysis of triphenylmethyl chloride in carbon tetrachloride at 20·0°.*

[EtOH] (mole/l.)	[R_3CCl] (mole/l.)	10^4k_0 (min.$^{-1}$)	Method *	Equilibrium (% reaction)
0·086	0·0093	6·1	I	23·8
,,	0·0215	5·6	,,	18·2
,,	0·0333	5·7	,,	16·0
0·172	0·0110	25·0	,,	36·0
,,	0·0473	27·1	,,	22·4
,,	,,	30·0	A	—
0·345	0·0273	79·2	I	61·0
,,	0·0250	86·0	A	60·7
,,	,,	83·0	I	—
0·690	0·0250	197	I	75·0
,,	—	203	E	—
1·380	0·0476	639	E	82·2
2·412	0·0494	1725	L	—
3·450	0·0470	3450	,,	—
5·175	0·0480	8220	,,	—

* I = Initial rate method; A = graphical method; E = reversible first-order equation; L = first-order equation.

The following additional rate constants for reactions of triphenylmethyl chloride (0·025M) in acetone were obtained:

Hydrolysis in 1·11M-water in acetone at 21°: k_1 = 0·0847 (0·0856) min.$^{-1}$

The rates of reaction of 0·025M-*n*-butylamine and 0·025M-di-*n*-butylamine in acetone were too slow to be followed (less than 5% reaction detected in 24 hr.).

In the alcoholysis of 2 : 4 : 6-trimethylbenzoyl chloride and chlorodimethyl ether strong autocatalysis was detected in the more dilute solutions. This was shown to be due to the

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* This is presumably due to the strong basicity of $Ph_3C{\cdot}OEt$ which associates preferentially with the HCl.

hydrogen chloride produced in the reaction. The extent of the autocatalysis can be defined in terms of the initial and the maximum rate of reaction. As shown by the results in Table 5 the variation between these two rates decreased with increasing concentration of alcohol and became negligible in solutions more concentrated than 1·0M.

TABLE 2. *Effect of temperature on the rate of ethanolysis of triphenylmethyl chloride in carbon tetrachloride.*

[EtOH] (mole/l.)	[Ph_3CCl] (mole/l.)	Temp.	10^4k_1 (min.$^{-1}$)	E (kcal./mole)	[EtOH] (mole/l.)	[Ph_3CCl] (mole/l.)	Temp.	10^4k_1 (min.$^{-1}$)	E (kcal./mole)
0·690	0·0250	20·0°	198	12·8	5·175	0·0480	20·0°	8220	13·6
,,	0·0248	10·3	97·8		,,	,,	10·8	3930	
,,	0·0251	0·0	41·1		,,	,,	0·5	1590	

TABLE 3. *Rate of* iso*propanolysis of triphenylmethyl chloride in carbon tetrachloride at* 21°.

[$CHMe_2$·OH] (mole/l.)	[Ph_3CCl] (mole/l.)	10^4k_1 (min.$^{-1}$)	Method	[$CHMe_2$·OH] (mole/l.)	[Ph_3CCl] (mole/l.)	10^4k_1 (min.$^{-1}$)	Method
0·657	0·0250	11·4	I	7·88	0·0250	585	E
3·94	,,	103	E			562	I
				13·14	,,	3480	E

TABLE 4. *Rates of ethanolysis of triphenylmethyl chloride and chlorodimethyl ether in semipolar solvents.*

[EtOH] (mole/l.)	[RCl] (mole/l.)	Temp.	10^4k_1 (min.$^{-1}$)	Method	[EtOH] (mole/l.)	[RCl] (mole/l.)	Temp.	10^4k_1 (min.$^{-1}$)	Method
			Triphenylmethyl chloride in ether						
0·828	0·050	20·0°	7·93	E	5·175	0·052	20°	1040	L
1·725	0·051	,,	45·5	L	6·900 *	—	,,	6045	L
3·450	0·047	,,	281	L					
			Triphenylmethyl chloride in acetone						
0·172	0·0250	21·0	62	I	0·690	0·025	21·0	507	E
0·345	0·0265	,,	173	I	0·690	0·025	0·5	92·6	E
			171	E	1·725	0·028	21·0	1445	L
			Chlorodimethyl ether in ether						
0·690	0·050	20·0	1·16 †	I	5·175	,,	20·0	949	L
1·725	,,	,,	31·1	L	5·175	,,	,,	951	L
3·45	,,	,,	274	L				944	I
			266	I					

* Obtained from Nixon and Branch's results (*loc. cit.*).
† Slight autocatalysis observed.

TABLE 5. *Rates of ethanolysis of chlorodimethyl ether and* 2 : 4 : 6-*trimethylbenzoyl chloride in carbon tetrachloride at* 20°.

[EtOH] (moles/l.)	[RCl] (moles/l.)	10^4min.$^{-1}$ $\frac{dx/dt}{(a-x)} = k_1$ as $x \rightarrow 0$	10^4min.$^{-1}$ $\frac{\partial x}{\partial t(a-x)}$ at $\frac{d^2x}{dt^2} = 0$ when $x = a$ *	a *
		Chlorodimethyl ether		
0·050	0·0467	1·63	4·32	0·00598
0·100	0·0501	8·78	29·4	0·0100
0·172	0·0440	31·9	78·3	0·0136
0·345	0·0436	116	191	0·0166
0·690	0·0457	351	492	0·0228
2·59	0·0500	2820	—	—
		2 : 4 : 6-Trimethylbenzoyl chloride		
0·172	0·0400	8·0	25·4	0·012
0·690	0·0400	132	168	0·020
2·59	,,	1670	1670	—
5·175	,,	7200	7200	—
5·175	,,	1140	1140	—

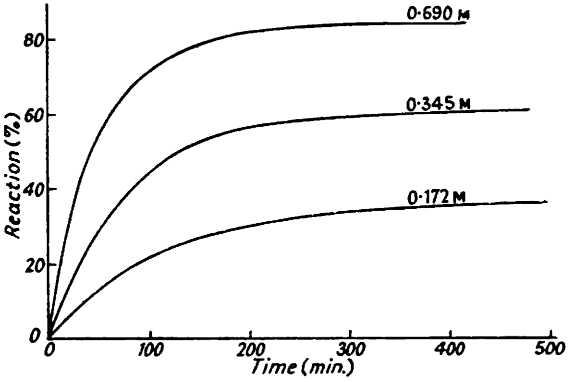
Owing to the complexity of the system, possible rate laws were not examined for these reactions.

DISCUSSION

Reactions of Triphenylmethyl Chloride.—(a) *With dilute alcohol solutions in carbon tetrachloride.* Before an interpretation of the effect of solvent on the rate can be advanced, the mechanism of reaction under non-solvolytic conditions must be considered. Swain *et al.* (*loc. cit.*) described the mechanism in benzene as a termolecular process involving simultaneous nucleophilic and electrophilic solvation of the halide. These results are, however, inconclusive, as pointed out by Gelles, Hughes, and Ingold, (*loc. cit.*), and it is necessary therefore to investigate this reaction further.

The exceptional reactivity of triphenylmethyl chloride compared with aliphatic halides under these conditions suggests strongly that the driving forces in solvolytic and non-solvolytic media are similar, and further rate measurements with nucleophilic and electrophilic reagents support this view (Hudson and Saville, *Chem. and Ind.*, 1954, 1423). It is found that even in dilute solutions of alcohol in carbon tetrachloride, the addition of *n*-butylamine has a negligible effect on the reaction rate (see Table 6). The similar stereochemical configuration of the primary alcohol and amine discounts the possibility that steric hindrance prevents reaction in one case and not in the other. Neither can the lack of reactivity be attributed to the thermodynamic instability of the product as in the corresponding reaction of a tertiary amine (Ingold, " Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, 1953, p. 356), since compounds of the type $Ph_3C{\cdot}NHR$ are normally prepared by heating triphenylmethyl chloride and the amine together in benzene.

FIG. 1. *Rates of ethanolysis of* 0·025M-*triphenylmethyl chloride in* CCl_4–EtOH *solution.* (Concn. of EtOH given against corresponding curve).



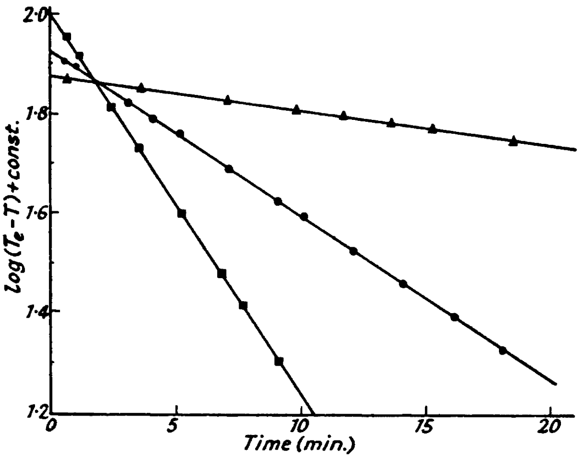


FIG. 2.

First-order reversal equation.

▲ 0·690M-EtOH, 0·025M-Ph_3CCl
● 1·380M- „ 0·050M- „

First-order plot.

■ 2·412M- „

As the influence of the amine would be much greater under these conditions than in solvolytic media, it follows that the substitution rate is not determined primarily by the bond-forming process, *i.e.*, the reaction is probably not of the S_N2 type. On the other hand, the rate of alcoholysis and amination is increased considerably by electrophilic reagents, *e.g.*, phenol, as observed by Swain (*loc. cit.*), and the magnitude of the rate increases shows the dominating importance of the bond-breaking process.

TABLE 6. *The effect of electrophilic and nucleophilic reagents on the rate of reaction of triphenylmethyl chloride* (0·01—0·02M). Temp. = 20°.

[EtOH] (mole/l.)	Amine	10^4k (min^{-1}.)	[Phenol] (mole/l.)	Reactant	10^4k (min.$^{-1}$)
0·690	0·025M-NEt$_3$	178	0·10	0·10M-EtOH	1970
0·690	0·025M-Bu·NH$_2$	255	Nil	0·20M-EtOH	34·6
0·690	Nil	197	0·10	0·10M-BuOH	1590
0·172	0·023M-Bu·NH$_2$	22·3	0·10	0·10M-Bu·NH$_2$	6500
0·172	Nil	25	—	—	—

We are led to the conclusion, therefore, that the reaction proceeds by a slow ionisation, as in more polar solvents, forming a primary ion-pair which either decomposes to the reaction products or returns to the covalent form. In dilute solutions (up to 0·69M) of alcohol in carbon tetrachloride, the rate of reaction follows the trimer concentration as in the case of the acid chlorides (Fig. 3). No evidence of hydrogen-ion catalysis was found (see p. 4137) and consequently it follows that the reaction proceeds by interaction of at the most three (and possibly two, but not one) alcohol molecules to give the ion-pair. The formation of a similar ion-pair may be observed directly in dilute solutions of phenol in carbon tetrachloride; the nucleophilic power of phenol is low, and the equilibrium constant of the substitution process is very small. Colorimetric analysis indicated that the concentration of carbonium ions is proportional to the square of phenol concentration * over the concentration range 0·05—1·0M (Table 7). Under these conditions the associated phenol is largely in the form of dimers (Fox and Martin, *Proc. Roy. Soc.*, 1937, *A*, **162**, 419; Kreuzer and Mecke, *Z. phys. Chem.*, 1941, **49**, *B*, 309), and consequently the ionisation proceeds by the encounter of a molecule of chloride with either a dimer or two phenol monomers. The contribution of the solvent (carbon tetrachloride) to the solvation energy cannot be ascertained, but this is likely to be small owing to the small electrostatic field of the molecules. Thus salts which dissolve in benzene are insoluble in carbon tetrachloride, and it is probably satisfactory to attribute the solvation energy to the interaction of the two phenol or three alcohol molecules as a first approximation.

TABLE 7. *Change in carbonium-ion concentration with phenol concentration in carbon tetrachloride at* 18° (0·028M-Ph$_3$CCl).

Optical density at 410 mμ	0·018	0·029	0·084	0·192	0·358	0·425
[PhOH], M	0·0062	0·201	0·657	1·205	1·61	1·97

(b) *With dilute alcohol solutions in polar solvents.* The kinetic data in ether show that the order with respect to alcohol approaches 2 as the concentration decreases (Fig. 4), in agreement with the previous conclusion that a minimum of two ROH molecules are required for ionisation. Owing to the slow rate and reversibility, the reaction was not followed in solutions more dilute than 0·82M. The rate is increased considerably on changing to a more polar solvent; *e.g.*, the rate in acetone is of the order of 50 times greater than that in ether containing an equivalent alcohol concentration. This increase is attributed to the increased contribution of the solvent (acetone) to the solvation energy. This is in contrast to the corresponding reaction of *p*-nitrobenzoyl chloride (see Part II) as in this case the two rates are of the same order of magnitude. The difference lies in the greater polarity of the transition state of triphenylmethyl chloride which probably resembles an " intimate ion-pair " (see Winstein and Schreiber, *J. Amer. Chem. Soc.*, 1952, **74**, 2129).

The results of Table 4 show further that the apparent order in acetone is less than that in ether, and moreover this decreases with increasing alcohol concentration in contrast to the usually observed increase (*e.g.*, in ether) attributed to progressive solvation by hydroxylic molecules. The reaction in acetone probably involves a change in mechanism involving the

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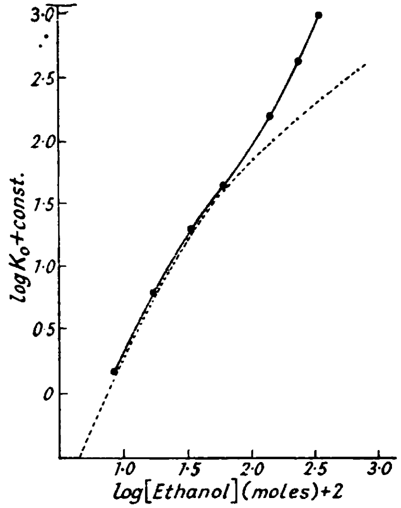
* Deduced by correlation of the results in Table 7 with the infrared data of Kreuzer and Mecke (*loc. cit.*). These systems are being investigated further.

nucleophilic process in the rate-determining step as recently detected by Gelles, Hughes, and Ingold (*loc. cit.*) for the reaction in nitromethane. Thus equimolar solutions of water and alcohol react at almost equal rates although water is a stronger electrophilic solvating agent. The rate with *n*-butylamine alone, however, remains low, so it may be inferred that the electrophilic process is the more important. There is no doubt that, by analogy with similar systems, ion-pairs are formed in acetone alone, but the concentration must be small compared with that of the electrophilically solvated species as shown by their low reactivity towards butylamine, itself a strong nucleophilic reagent. It may be concluded therefore that the mechanism is intermediate between that of *tert.*-butyl bromide and triphenylmethyl chloride in nitromethane (Gelles *et al.*, *loc. cit.*). Accordingly, the reaction is controlled primarily by electrophilic action which has the effect of separating the ion-pair and hence reducing the rate of internal return (see Winstein and Schreiber, *loc. cit.*).

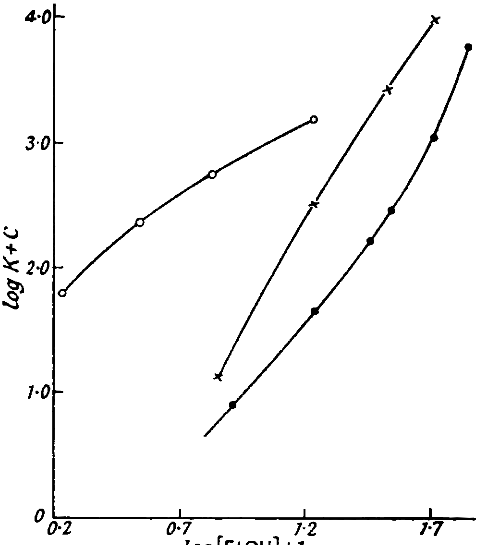
FIG. 3.



——— *Relation between rate of ethanolysis of* Ph_3CCl *in* CCl_4 *at 20° and ethanol concn.*

- - - - *Superimposition of log [Trimers] ordinate* v. *log* [EtOH] (*same abscissæ*).

FIG. 4.



Rate–concentration relationships for ethanolysis of:
○ $0{\cdot}025\text{M}\text{-}Ph_3CCl$ *in* $COMe_2$ (c = 4).
× $0{\cdot}050\text{M}\text{-}CH_2Cl{\cdot}O{\cdot}CH_3$ *in* Et_2O (c = 5).
● $0{\cdot}025\text{M}\text{-}Ph_3CCl$ *in* Et_2O (c = 4).

This mechanism may be represented as follows :

$$R'X + ROH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R^+ \ldots X^- \ldots HOR \xrightarrow{ROH;\ k_3} R'OR + H^+$$

In general, the solvated ion-pair can decompose internally or by reaction with a nucleophilic reagent. The second alternative is more likely, as the former process would be expected to proceed at a rate similar to that of the direct interaction of an ROH molecule with the ion-pairs stabilised by acetone alone. The participation of a second alcohol molecule being assumed, the rate is given by

$$-d[RX]/dt = k_1k_3[R'X][ROH]^2/(k_2 + k_3[ROH])$$

This explanation is supported by examining the change in apparent reaction order with alcohol concentration in terms of the relative nucleophilic and electrophilic reactivities of triphenylmethyl chloride towards water and alcohol given by Gelles *et al.* (*loc. cit.*). We have observed that the rates of reaction in 1M-alcohol and 1M-water solutions are approximately equal, hence it follows that

$$k_1k_3/(k_2 + k_3) = k_1'k_3'/(k_2 + k_3') \text{ (}k\text{ refers to alcohol and }k'\text{ to water)}$$

the assumption being made that the rates of internal return of the two ion-pairs $R'\cdots X\cdots HOR$ and $R'\cdots X\cdots HOH$ are equal. The results of Gelles *et al.* show that $k_3 = 4k_3'$, and if it is further assumed that the relative solvating power of water to alcohol is the same for triphenylmethyl chloride and *tert.*-butyl bromide, it follows that $k_1' = 2k_1$, and hence $k_2 = 2k_3'$.

The rate of the alcoholysis is then given simply by

$$-d[RX]/dt = 4k_1[ROH]^3/(1 + 2[ROH])$$

This enables the apparent order over a particular concentration range to be calculated. Over the 0·34—0·69M-alcohol range the observed and calculated orders are both 1·55; over the 0·69—1·725M-concentration range the experimental order is 1·12 compared with the predicted order of 1·29.

In view of the assumptions made, the fact that the observed and calculated reaction orders are of similar magnitude lends some support to this interpretation of the reaction mechanism which merits further investigation in the light of more experimental results. It seems reasonable to conclude tentatively, however, that under these conditions the mechanism is intermediate between the two types of ionisation process designated S_N1 and S_{NC+} by Gelles, Hughes, and Ingold (*loc. cit.*).

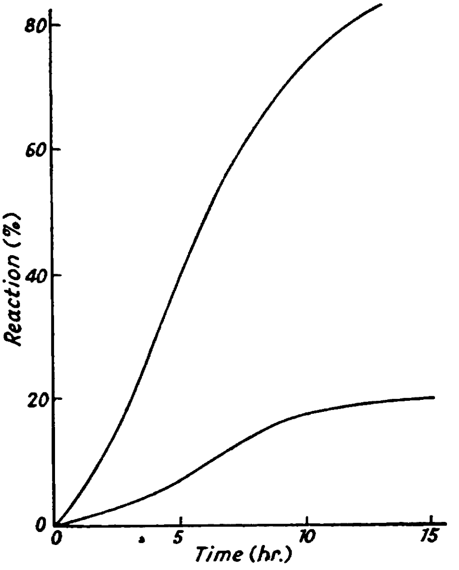
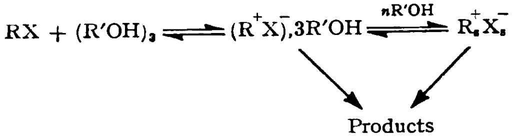


FIG. 5. *Rates of ethanolysis of* 2 : 4 : 6-*trimethylbenzoyl chloride* (0·05M) *in* 0·172M-EtOH *in* CCl_4 (*upper curve*) *and chlorodimethyl ether* (0·05M) *in* 0·050M-EtOH *in* CCl_4 (*lower curve*).

(c) *With concentrated alcohol solutions.* As already mentioned, the rate of alcoholysis in carbon tetrachloride is proportional to the trimer concentration (or more strictly the concentration of alcohol in the associated form) in the more dilute solutions, but above 0·69M a strong additional solvent effect is observed (Fig. 3) in contrast to the corresponding reaction of the acid chlorides. This is in agreement with the previous observation that the rate increases considerably with increase in polarity of the solvent. Similarly, in ether the order of reaction with respect to alcohol increases regularly from *ca.* 2 in the dilute solutions to *ca.* 6 in the most concentrated solutions used (Fig. 4). Again the order of the corresponding reaction of *p*-nitrobenzoyl chloride remains 2 over most of this concentration range.

Although the order changes rapidly little change in activation energy is observed above 0·69M-ethanol, and again this limiting value is almost equal to that in alcohol–ether mixtures. This is perhaps surprising since further interaction between the medium and transition state would be expected to reduce the energy of the system (see Glasstone, Laidler, and Eyring, " Theory of Rate Processes," McGraw-Hill Book Co., 1941, Chapter 8). It may be significant that the activation energy in hydrogen-bonded solvents is approximately equal to the sum of the heat of ionisation in nitromethane (Bentley, Evans, and Halpern, *loc. cit.*) and the energy of two hydrogen bonds, in view of the fact that a minimum of two ROH molecules are necessary for reaction.

The constancy of the activation energy above 0·69M with increasing kinetic order of the solvation process indicates a change in structure of the transition state or reaction intermediates, such that the additional solvation energy is compensated by an energy increase in the reacting system. Such a situation is possible if the additional solvent molecules solvate the primary ion-pair, thus effectively separating the ions further, and reducing the rate of internal return similar to the scheme of Winstein, Clippinger, Fainberg, and Robinson (*Chem. and Ind.*, **1954**, 664) :



No information on the relative effect on the rate of ionisation and subsequent substitution can be obtained but both will be affected. Owing to the high kinetic order of the reaction, however, it may be concluded that the additional solvation process must be important, and the reduction in the rate of return probably accounts for most of the rate increase. The relatively long life of the primary ion-pair increases its " collision radius," since all molecules of solvent or solute lying within a hypothetical radius r given $r = \bar{V}\tau$, were $\bar{V}$ is the mean velocity of the molecules and τ the life of the primary ion-pair, have a chance of colliding with the latter and stabilising the ion further.

Examination of the rate curves shows that the reaction in concentrated solutions is strictly of first order over the whole course of the reaction (Fig. 2). This shows that the solvated ion-pairs remain associated in concentrated alcohol solutions, whereas in aqueous acetone the ions are largely dissociated as shown by the large mass-action effect (Scott, Swain, and Lohmann, *J. Amer. Chem. Soc.*, **1953**, 75, 136). The latter observation also shows that the carbonium ion is stable when solvated by nucleophilic hydroxylic molecules, which further supports the interpretations of the reaction mechanism given above in terms of independent nucleophilic and electrophilic processes.

Chlorodimethyl Ether and 2 : 4 : 6-*Trimethylbenzoyl Chloride*.—Solvent participation was also examined in the alcoholysis of other reactive chlorides which are usually considered to react by an ionisation mechanism in solvolytic media. As already mentioned, triarylmethyl halides give exceptionally stable carbonium ions. This is reflected in the solvent effect in dilute alcohol solutions, as the relatively low energy required to ionise the halide enables the reaction to proceed in the presence of a small number of electrophilic molecules. In this case the high kinetic order in solvolysis may be attributed to the further solvation of the preformed ion-pair. As the C–X bond energy increases, however, one might expect that a greater number of hydroxylic molecules are necessary to provide the required solvation energy.

In order to examine this possibility, the effect of alcohol concentration on the rate of reaction of chlorodimethyl ether (Ingold, *op. cit.*, p. 333) and 2 : 4 : 6-trimethylbenzoyl chloride (Hudson and Brown, *J.*, **1953**, 3352), which are normally considered to react by an ionisation mechanism, was determined. The rates of reaction are sufficiently great to be followed in dilute alcohol solution, and the reactions are largely irreversible, in contrast to the alcoholysis of tertiary alkyl halides. In carbon tetrachloride the measurements show that both reactions are strongly catalysed by acid (Table 5). The variation in initial rate with alcohol concentration is at least as pronounced as in the case of triphenylmethyl chloride, where no acid catalysis is observed. The autocatalysis becomes less pronounced as the alcohol concentration increases, and the initial rate becomes proportional to the square or cube of the trimer concentration. (It is realised that the associated alcohol is not in the form of trimers only in the concentration range under consideration, but it is convenient to refer to the order of the reaction in terms of trimer concentration for the purpose of comparison with the other reactions already considered.)

The general rate expression for these reactions therefore becomes of the form

$$-\mathrm{d}[\mathrm{RX}]/\mathrm{d}t = k_1[\mathrm{RX}]\{[\mathrm{HCl},n\mathrm{ROH}] + k_2[(\mathrm{ROH})_3] + k_3[(\mathrm{ROH})_3]^2 + \ldots\}$$

The participation of the second term cannot be detected in the present examples since the first term completely defines the rate in dilute solution as far as can be detected, and as the catalysis disappears the third term becomes important. In dilute solution, the reaction probably proceeds by proton transfer from a hydrogen chloride molecule which is itself solvated by a number of ROH molecules :

$$\mathrm{HCl} + \mathrm{RX} \xrightarrow{n\mathrm{R'OH}} \mathrm{R}^{+} \ldots \mathrm{X}^{-} \ldots \mathrm{H{-}Cl} \xrightarrow{\mathrm{R'OH}} \text{Products}$$

Similar catalysis has been observed in the hydrolysis of *tert.*-butyl bromide in acetone containing small quantities of water (Bateman, Cooper, and Hughes, *J.*, 1940, **913**) but this rapidly gives way to a solvation process involving water molecules and acetone only, and in the racemisation of 1-mesitylethyl chloride (Charlton and Hughes, *loc. cit.*).

Similarly, in ether solution a minimum of three ROH molecules are required in the alcoholysis of chlorodimethyl ether under conditions where the acid catalysis is negligible. This reaction order is similar to that estimated from Böhme's results (*Ber.*, 1941, **74**, 248) for the hydrolysis of this chloro-ether and the thio-ether in dioxan. In neither case is there evidence for an increase in the kinetic order of the solvation process, which may be attributed to the instability of the carbonium ion formed :

$$\mathrm{R{-}O{-}CH_2{-}Cl} \rightleftharpoons \left\{\begin{array}{l}\mathrm{R{-}\overset{+}{O}{=}CH_2} + \mathrm{Cl}^{-} \xrightarrow{\text{Very fast}} \text{Products} \\ \mathrm{R{-}O{-}\overset{+}{C}H_2}\end{array}\right.$$

This also explains the irreversibility of this process, and the reaction of 2 : 4 : 6-trimethylbenzoyl chloride under similar conditions, as no mass-action repression is observed in 5% aqueous acetone (Brown and Hudson, *loc. cit.*).

In these reactions where several hydroxylic molecules are required to produce an (unstable) cation, the substitution process probably takes place without further separation of the ion-pair even in dissociating media. Reaction in the primary ion-pair may be recognised by the complete absence of mass-action repression of the rate, and by the lack of formation of the product of reaction with a highly nucleophilic reagent in the solvolysis medium. Thus strongly nucleophilic ions (*e.g.*, I^-, CNS^-, $\mathrm{S_2O_3}^{2-}$) do not react to any appreciable extent with the *iso*propyl ion in aqueous acetone solution (Hudson and Marshall, unpublished work) and the hydrolysis of the tertiary butyl halides proceeds without mass-action repression (Bateman, Hughes, and Ingold, *J.*, 1940, 960). It has similarly been observed by Scott, Swain, and Lohmann (*loc. cit.*) that the competition factors (Ogston, *Trans. Faraday Soc.*, 1948, **44**, 45) of nucleophilic agents increase with the stability of the cation. The observations of Winstein *et al.* (*loc. cit.*) showing that the perchlorate ion interacts only with primary ion-pairs which are stabilised by neighbouring groups support the general interpretation.

This discussion shows that two kinetically distinct ionisation reactions may be recognised by studies of solvent participation, which correspond in general terms to the two mechanisms, termed $S_{\mathrm{N}}1$ and $S_{\mathrm{NC+}}$ by Gelles *et al.* (*loc. cit.*). These two mechanisms represent extreme cases of the general substitution process involving heterolytic bond fission, and differ mainly in the relative energy levels of ground state and intermediate cation. Thus a gradual change from one mechanism to the other is expected as in the corresponding transition from $S_{\mathrm{N}}1$ to $S_{\mathrm{N}}2$ mechanisms (Bird, Hughes, and Ingold, *J.*, 1954, 531 ; Winstein, Grunwald, and Jones, *J. Amer. Chem. Soc.*, 1951, **73**, 2700 ; Hudson and Brown, *loc. cit.*), depending on the structure of the reactant and on the relative nucleophilic and electrophilic power of the solvent.

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