# 597. *The Formation of Carbonium Ions by the Action of Metal Salts. Part IV.*[1] *Ionisation of Triarylmethyl Chlorides by Friedel–Crafts Catalysts in Acetic Acid.*

By J. L. Cotter and Alwyn G. Evans.

The ionisation of triarylmethyl chlorides RCl by various Friedel–Crafts catalysts $MCl_x$ has been studied spectrophotometrically in acetic acid. The ionisation leads to the reversible formation of ion pairs $R^+MCl_{x+1}^-$. The ionising power of the metal chlorides decreases along the sequence $SbCl_5 \gg FeCl_3 \gg SnCl_4 \gg BiCl_3 > HgCl_2 > SbCl_3$.

## Experimental

*Materials.—Mercuric chloride.* The " AnalaR " reagent was twice sublimed under a high vacuum.

*Antimony trichloride.* The " AnalaR " reagent was sublimed three times under a high vacuum and portions were collected in sealed capsules.

*Stannic chloride.* The first sample, prepared by the action of chlorine on tin, was green; the colour was removed by keeping the sample over granulated tin for a few hours. The second sample, prepared by electrolysis of fused stannous chloride, was colourless.[2] A third sample was obtained from Messrs. Hopkin and Williams. The three samples, purified by six distillations under a high vacuum and collected in sealed capsules, gave identical results.

[1] Part III, Bayles, A. G. Evans, and Jones, *J.*, 1957, 1020.
[2] A. G. Evans and Lewis, *J.*, 1957, 2975.

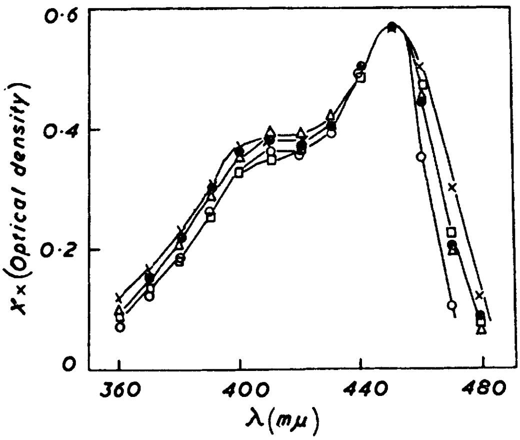
*Ferric chloride.* B.D.H. anhydrous material was pumped out under a high vacuum and collected in sealed capsules.

*Bismuth trichloride.* One sample was once sublimed under a high vacuum and a second treated in the same way as ferric chloride; both samples were collected in sealed capsules and gave the same results.

*Antimony pentachloride.* This was five times distilled under a high vacuum and collected in receivers by means of liquid-air traps; the receivers were then sealed.

*Triarylmethyl chlorides.* These were prepared from the corresponding carbinols as previously described.[3]

FIG. 1.




△ Antimony trichloride (total concn. 1·294 × $10^{-1}$ mole $l.^{-1}$) and diphenyl-*p*-tolylmethyl chloride (total concn. 3·498 × $10^{-3}$ mole $l.^{-1}$) in acetic acid at 19°; $X = 0·780$.

□ Mercuric chloride (total concn. (6·901 × $10^{-2}$ mole $l.^{-1}$) and diphenyl-*p*-tolylmethyl chloride (total concn. 4·574 × $10^{-3}$ mole $l.^{-1}$) in acetic acid at 20°; $X = 1·04$.

× Bismuth trichloride (total concn. 7·668 × $10^{-3}$ mole $l.^{-1}$) and diphenyl-*p*-tolylmethyl chloride (total concn. 1·268 × $10^{-2}$ mole $l.^{-1}$) in acetic acid at 19°; $X = 1·34$.

● Stannic chloride (total concn. 5·802 × $10^{-3}$ mole $l.^{-1}$) and diphenyl-*p*-tolylmethyl chloride (total concn. 4·636 × $10^{-4}$ mole $l.^{-1}$) in acetic acid at 20°; $X = 1·09$.

○ Diphenyl-*p*-tolylmethyl alcohol (concn. 1·238 × $10^{-5}$ mole $l.^{-1}$) in 98% $H_2SO_4$; $X = 1$.

$X$ is the factor which has been used to scale the spectra to the same peak height as that of the solution in 98% $H_2SO_4$.

Curves Δ and □ are examples of high $MCl_x$ concentrations (see section on Solvation of Ion Pairs by $MCl_x$).

*Acetic acid.* " AnalaR " reagent (f. p. 16·40°) was purified by Eichelberger and La Mer's method.[4] The solvent was refluxed for 14 hr. over triacetyl borate followed by a fractionation. The f. p. of this batch was 16·59° (lit., 16·58° for acetic acid used in conductivity work [4]). All solvent batches were purified by this method and were overlapped as far as possible.

*Procedure.*—Two master solutions were made up, one containing the organic chloride and the other the metal chloride. Both were of known concentration and so dilute that their light absorption was negligible. Metal chloride solutions were made up as follows. Since mercuric chloride is non-hygroscopic, it was weighed out directly and the solution made up in a graduated flask. For other metal chlorides a small file mark was made near one end of a weighed capsule containing it, which was broken under the solvent. The metal chloride usually dissolved rapidly and the solution was made up in a graduated flask. The capsule pieces were then dried and weighed. Acetic acid solutions of stannic chloride, antimony pentachloride, and ferric chloride so made were too concentrated and were diluted.

The triarylmethyl chloride and metal chloride solutions were then mixed in various ratios. These colourless solutions became intensely yellow on mixing, and their light absorption was measured on a Unicam SP.500 spectrophotometer. Fig. 1 shows typical spectra of the acetic acid solutions containing a triarylmethyl chloride and metal chloride together with the spectrum

[3] A. G. Evans, Jones, and Osborne, *Trans. Faraday Soc.*, 1954, **50**, 167.
[4] Eichelberger and La Mer, *J. Amer. Chem. Soc.*, 1933, **55**, 3633.

of the corresponding alcohol in 98% sulphuric acid. For convenience, these spectra have been scaled up or down to meet the spectrum of the sulphuric acid solution of the alcohol at the absorption maximum. The very close similarity between corresponding spectra for both solvents establishes that the triarylmethyl ion is present in these acetic acid solutions.

The carbonium-ion concentration has been calculated on the assumption that $\int D_\lambda \, d\lambda$ is the same for solutions containing the same concentration of triarylmethyl ions. The alternative method of calculating the ionic concentration, by assuming that $D_{\lambda(\max.)}$ is the same for the same ionic concentration, leads to values which are identical within experimental error with those used.

*Molecular-weight Determination.*—Cryoscopic measurements were made on the acetic acid solutions of the metal chlorides with a normal Beckmann apparatus, efficient stirring being maintained.

## Results

*When* $[R^+]$ *varies with* $[RCl]^1$ *and with* $[MCl_x]^1$.—The ionisation of diphenyl-*p*-tolylmethyl chloride in the presence of $HgCl_2$, $SbCl_3$, $FeCl_3$, $SnCl_4$, $SbCl_5$, and $BiCl_3$ occurs according to eqn. (1) as seen in Table 1. The values of $K_1 = [R^+MCl_{x+1}^-]/[RCl][MCl_x]$ and of $\Delta G^\circ_{1a}$ for this reaction are given in Table 2.

The ionisation of $Ph_3C{\cdot}Cl$ in the presence of $SnCl_4$ and $FeCl_3$ also obeys eqn. (1) as shown by Table 3. The equilibrium constants and the corresponding free-energy changes are given in Table 2.

$$RCl + MCl_x \underset{b}{\overset{a}{\rightleftharpoons}} R^+MCl_{x+1}^- \qquad (1)$$

*Equilibrium-constant Units.*—The concentrations of reactants used in these Tables are expressed in mole l.$^{-1}$ and g.-ion l.$^{-1}$ units. The free-energy changes have been calculated from

TABLE 1. *Some typical examples of the equilibrium concentrations for mixtures of* RCl *and* $MCl_x$ *in acetic acid where* R *is diphenyl*-p-*tolylmethyl.*

| $10^5[MCl_x]$ | $10^4[RCl]$ | $10^6[R^+MCl_{x+1}^-]$ | $\frac{[R^+MCl_{x+1}^-]}{[RCl][MCl_x]}$ |
|---|---|---|---|
| | | $BiCl_3$ at 20° | |
| 191·7 | 169·1 | 2·67 | $8·27 \times 10^{-2}$ |
| 383·4 | 169·1 | 5·17 | $8·00 \times 10^{-2}$ |
| 575·1 | 169·0 | 8·26 | $8·52 \times 10^{-2}$ |
| 766·8 | 169·0 | 11·19 | $8·73 \times 10^{-2}$ |
| 958·5 | 168·9 | 14·63 | $9·02 \times 10^{-2}$ |
| 766·8 | 422·1 | 3·34 | $10·34 \times 10^{-2}$ |
| 766·8 | 845·0 | 5·74 | $8·88 \times 10^{-2}$ |
| 766·8 | 211·3 | 13·69 | $8·48 \times 10^{-2}$ |
| 766·8 | 126·8 | 8·50 | $8·71 \times 10^{-2}$ |
| | | $FeCl_3$ at 19° | |
| 7·84 | 3·840 | 6·58 | 219 |
| 11·73 | 3·804 | 10·20 | 229 |
| 19·45 | 3·723 | 17·93 | 248 |
| 23·37 | 3·693 | 21·30 | 246 |
| 3·89 | 3·870 | 3·56 | 236 |
| 12·01 | 2·530 | 7·43 | 245 |
| 11·41 | 5·074 | 13·42 | 232 |
| 11·17 | 6·452 | 15·76 | 218 |
| 10·85 | 7·621 | 18·91 | 229 |
| 12·32 | 1·260 | 4·34 | 280 |
| 11·38 | 5·071 | 13·70 | 237 |
| | | $HgCl_2$ at 19° | |
| 568 | 239·2 | 2·54 | $18·7 \times 10^{-3}$ |
| 1136 | 239·2 | 5·32 | $19·5 \times 10^{-3}$ |
| 1704 | 239·2 | 8·04 | $19·7 \times 10^{-3}$ |
| 2272 | 239·2 | 11·78 | $21·6 \times 10^{-3}$ |
| 3408 | 239·2 | 18·08 | $22·1 \times 10^{-3}$ |
| 2272 | 59·8 | 3·54 | $26·0 \times 10^{-3}$ |
| 2272 | 119·6 | 6·21 | $22·8 \times 10^{-3}$ |
| 2272 | 179·4 | 8·90 | $21·8 \times 10^{-3}$ |
| 2272 | 358·8 | 15·82 | $19·4 \times 10^{-3}$ |
| | | $SbCl_5$ at 20·5° | |
| 12·13 | 1·471 | 8·70 | 489 |
| 18·34 | 1·442 | 11·56 | 423 |
| 11·90 | 2·227 | 11·00 | 415 |
| 6·17 | 1·525 | 3·26 | 345 |
| 12·51 | 0·730 | 4·86 | 532 |
| 24·31 | 1·389 | 16·90 | 500 |
| 11·74 | 2·990 | 12·60 | 357 |
| | | $SnCl_4$ at 20° | |
| 72·7 | 12·16 | 5·91 | 6·67 |
| 145·3 | 12·10 | 12·24 | 6·97 |
| 217·9 | 12·04 | 18·70 | 7·14 |
| 290·5 | 11·97 | 24·78 | 7·12 |
| 145·8 | 6·04 | 7·40 | 8·45 |
| 144·5 | 18·14 | 19·80 | 7·58 |
| 143·9 | 24·18 | 26·26 | 7·55 |
| 146·1 | 3·02 | 3·91 | 8·92 |
| | | $SbCl_3$ at 21° | |
| 428 | 243·1 | 1·345 | $1·29 \times 10^{-2}$ |
| 1284 | 243·1 | 2·717 | $0·895 \times 10^{-2}$ |
| 1284 | 567·2 | 4·652 | $0·639 \times 10^{-2}$ |
| 2140 | 405·2 | 6·174 | $0·711 \times 10^{-2}$ |
| 2140 | 324·1 | 5·282 | $0·761 \times 10^{-2}$ |
| 2140 | 243·1 | 4·565 | $0·875 \times 10^{-2}$ |
| 1712 | 405·2 | 5·087 | $0·735 \times 10^{-2}$ |
| 1284 | 405·2 | 3·891 | $0·754 \times 10^{-2}$ |
| 3424 | 162·0 | 5·39 | $0·973 \times 10^{-2}$ |
| 856 | 648·2 | 3·89 | $0·701 \times 10^{-2}$ |
| 856 | 405·2 | 2·847 | $0·821 \times 10^{-2}$ |

TABLE 2.

| RCl | Metal chloride | Mean $K_1$ * (mole fraction) | Mean $\Delta G_1^\circ$ (kcal. mole$^{-1}$) | Mean temp. |
|---|---|---|---|---|
| $p$-$CH_3 \cdot C_6H_4 \cdot CPh_2Cl$ ......... | $SbCl_3$ | 0·145 | 1·11 ± 0·15 | 20° |
| ,, ......... | $HgCl_2$ | 0·358 | 0·59 ± 0·1 | 18 |
| ,, ......... | $BiCl_3$ | 1·57 | −0·26 ± 0·1 | 19 |
| ,, ......... | $SnCl_4$ | 106·4 | −2·69 ± 0·4 | 17 |
| ,, ......... | $FeCl_3$ | 4,220 | −4·81 ± 0·1 | 18 |
| ,, ......... | $SbCl_5$ | 5,655 | −4·98 ± 0·2 | 20 |
| $Ph_3C \cdot Cl$ ......................... | $SnCl_4$ | 7·29 | −1·14 ± 0·3 | 18·5 |
| ,, ......................... | $FeCl_3$ | 353 | −3·40 ± 0·1 | 19·5 |

* The value of $K_1$ at 20° can be converted into mole$^{-1}$ l. units by dividing by 17·46.

TABLE 3. *Some typical examples of the equilibrium concentrations for mixtures of* RCl *and* $MCl_x$ *in acetic acid where* R *is triphenylmethyl.*

| $10^3[MCl_x]$ | $10^4[RCl]$ | $10^6[R^+MCl_{x+1}^-]$ | $\frac{[R^+MCl_{x+1}^-]}{[RCl][MCl_x]}$ | $10^3[MCl_x]$ | $10^4[RCl]$ | $10^6[R^+MCl_{x+1}^-]$ | $\frac{[R^+MCl_{x+1}^-]}{[RCl][MCl_x]}$ |
|---|---|---|---|---|---|---|---|
| | | $FeCl_3$ at 19° | | | | $SnCl_4$ at 18° | |
| 0·671 | 4·500 | 6·31 | 20·9 | 1·436 | 123·8 | 10·42 | 0·584 |
| 0·335 | 4·534 | 2·92 | 19·2 | 2·871 | 123·7 | 21·05 | 0·594 |
| 1·002 | 4·460 | 10·25 | 23·0 | 2·881 | 61·8 | 11·23 | 0·626 |
| 1·340 | 4·437 | 12·63 | 21·2 | 2·887 | 30·9 | 5·15 | 0·574 |
| 1·672 | 4·403 | 16·05 | 21·8 | 0·718 | 122·8 | 5·15 | 0·582 |
| 1·009 | 1·480 | 4·07 | 27·5 | 2·164 | 123·9 | 15·52 | 0·580 |
| 1·005 | 2·971 | 7·10 | 23·8 | 2·877 | 92·7 | 16·05 | 0·595 |
| 1·000 | 5·958 | 12·63 | 21·3 | 4·295 | 123·6 | 33·63 | 0·633 |
| 0·997 | 7·451 | 15·40 | 20·7 | 2·862 | 185·8 | 30·26 | 0·568 |
| | | | | 5·737 | 123·4 | 47·36 | 0·675 |
| | | | | 2·850 | 247·4 | 42·63 | 0·605 |

equilibrium constants expressed in mole-fraction units (the recorded values for the density of acetic acid at various temperatures being used).

*When* $[R^+]$ *varies with* $[RCl]^1$ *but with* $[MCl_x]^n$, *when* $n > 1$.—Mercuric chloride and antimony trichloride are the least effective ionising metal chlorides, and so to produce the same extent of ionisation higher concentrations of these are needed than of the others. When their concentrations are about equal to the concentration of the diphenyl-$p$-tolylmethyl chloride, $[R^+]$ varies with $[RCl]^1$ and with $[MCl_x]^1$ (see Table 1). When, however, the metal chloride is present in large excess $[R^+]$ varies with $[RCl]^1$ but with $[MCl_x]^n$ where $n > 1$. Over this higher concentration range the value of $n$ for $SbCl_3$ is 2·2 ± 0·2 and for $HgCl_2$ is 1·4 ± 0·2 for the interaction of these metal chlorides with diphenyl-$p$-tolylmethyl chloride, and for the interaction of $SbCl_3$ with triphenylmethyl chloride a value of $n$ of up to 3·0 ± 0·2 is found. A typical case is shown in Fig. 2.

*Molecular Weights.*—Molecular weights are given in Table 4. The freezing-point depressions obtained show that $HgCl_2$, $SbCl_3$, and $BiCl_3$ are monomeric in acetic acid. The depressions obtained for acetic acid solutions of $SnCl_4$, $FeCl_3$, and $SbCl_5$ respectively approximate to those expected for the dimeric species.

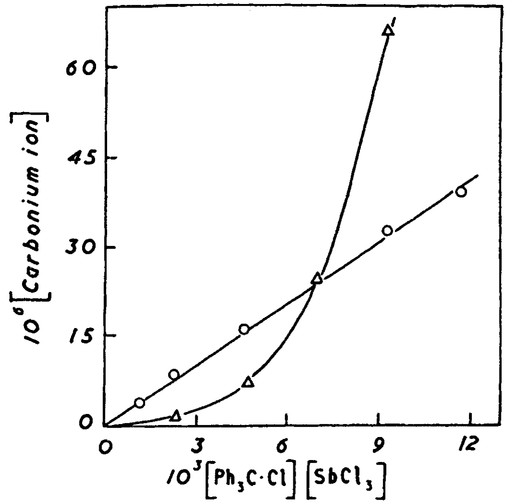
TABLE 4. *Molecular weights.*

| Metal halide ......................... | $HgCl_2$ | $BiCl_3$ | $SbCl_3$ | $SbCl_5$ | $SnCl_4$ | $FeCl_3$ |
|---|---|---|---|---|---|---|
| Concn. range ($10^{-2}$ mole l.$^{-1}$) ... | 6·2—16 | 7·1—16·7 | 21 | 9·4—32·8 | 3·2—12·8 | 1·3—5·3 |
| Mean $M$ (obs.) ..................... | 272·8 | 279·1 | 226·1 | 638·0 | 506·0 | 310·8 |
| $M$ (calc.) ............................. | 271·6 | 315·3 | 228·3 | 299·3 | 260·7 | 162·4 |

The actual concentrations of the $SnCl_4$, $FeCl_3$, and $SbCl_5$ used in the cryoscopic experiments had to be approximately 10, 100, and 1000 times as great respectively as those required for the ionisation experiments, since the depressions which would be obtained with molar concentrations equal to those used in the ionisation runs would be extremely small. Since the acetic acid solutions of these metal chlorides are so dilute in the spectroscopic work, we have calculated our results on the assumption that at these dilutions the metal chlorides will be monomeric.

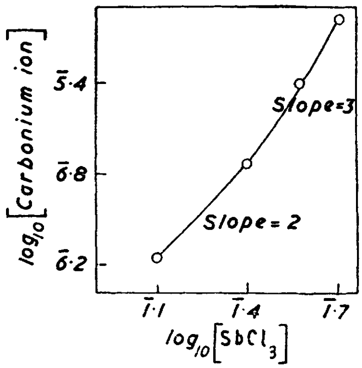
*Extinction Coefficients of Carbonium Ions.*—In Fig. 3 the ionisation is plotted against the total metal chloride concentration. When there is no further change of ionisation the calculated ionisation is between 90 and 100%. This was found in Part II [5] for nitromethane solutions of triphenylmethyl and tri-*p*-tolylmethyl bromides in presence of $HgBr_2$. This establishes that our method of calculating the carbonium-ion concentration, and the values of $\Delta G°$ so obtained, are correct within the experimental accuracy quoted. We have plotted the optical densities

FIG. 2*a*. *Dependence of carbonium-ion concentration on* $[SbCl_3][Ph_3C{\cdot}Cl]$.




△ At constant $[Ph_3C{\cdot}Cl] = 1{\cdot}821 \times 10^{-2}$ mole l.$^{-1}$.
○ At constant $[SbCl_3] = 3{\cdot}831 \times 10^{-1}$ mole l.$^{-1}$.

FIG. 2*b*. *Order in* $SbCl_3$ *at constant* $[Ph_3C{\cdot}Cl]$.



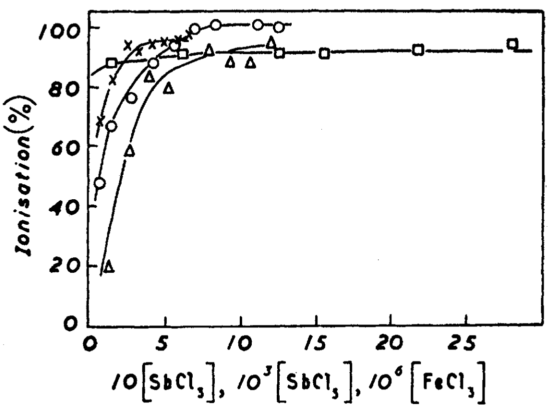




FIG. 3.

× Tri-*p*-tolylmethyl chloride (concn. $5{\cdot}840 \times 10^{-6}$ mole l.$^{-1}$) with ferric chloride.
□ Tri-*p*-tolylmethyl chloride (concn. $9{\cdot}360 \times 10^{-6}$ mole l.$^{-1}$) with antimony pentachloride.
○ Diphenyl-*p*-tolylmethyl chloride (conc. $(1{\cdot}235 \times 10^{-5}$ mole l.$^{-1}$) with antimony pentachloride.
△ Tri-*p*-tolylmethyl chloride (concn. $9{\cdot}360 \times 10^{-6}$ mole l.$^{-1}$) with antimony trichloride.

at maximum ionisation (Fig. 3) against the tri-*p*-tolylmethyl carbonium-ion concentration. This plot gives a straight line passing through the origin, and shows that Beer's law holds accurately for these solutions.

## DISCUSSION

*Free-energy Changes.*—In the absence of metal halide the free energy of ionisation of RCl in acetic acid was 5·8 kcal. mole$^{-1}$ for *p*-$CH_3{\cdot}C_6H_4{\cdot}CPh_2Cl$, and $Ph_3C{\cdot}Cl$ did not give a coloured solution.[6] Table 2 shows that the presence of the metal halide causes a great

[5] Bayles, Cotter, and A. G. Evans, *J.*, 1955, 3104.
[6] A. G. Evans, Price, and Thomas, *Trans. Faraday Soc.*, 1954, **50**, 534.

reduction in the free energy of ionisation. (No change in the heat of ionisation with change in concentration of reagent was observed in these metal halide systems.)

Using the free energy of ionisation as a measure of the ionising efficiency of a metal chloride, we obtain the sequence $SbCl_5 \geqslant FeCl_3 \gg SnCl_4 \gg BiCl_3 > HgCl_2 > SbCl_3$, which we may compare with those obtained for Friedel–Crafts-catalysed reactions. The conversion of pinene into bornyl chloride is accelerated by the presence of Friedel–Crafts catalysts.[7] This is considered to take place by means of a carbonium-ion mechanism and the sequence $SbCl_5 > SnCl_4 > FeCl_3 > HgCl_2 > SbCl_3$ was obtained for the catalyst efficiency, differing from our $\Delta G°$ sequence in the interchange of $SnCl_4$ with $FeCl_3$.

The racemisation of 1-phenylethyl chloride takes place in the presence of certain metal chlorides and probably involves a carbonium-ion mechanism.[8] The order of efficiency of the catalysts was $SbCl_5 > SnCl_4 > HgCl_2$, which is the same as our sequence.

An efficiency sequence obtained by Dermer [9] on the basis of yields of *p*-methylacetophenone obtained in the metal chloride-catalysed reaction of acetophenone with methyl chloride is $SbCl_5 > FeCl_3 > SnCl_4 > BiCl_3$, which again agrees with ours.

Jenson and Brown,[10] for the effect of Friedel–Crafts catalysts on the rates of the reaction of benzoyl chloride with toluene and with chlorobenzene, found $SbCl_5 > FeCl_3 \gg SnCl_4 \gg SbCl_3$.

*Solvation of Ion Pairs by Metal Halides.*—Although under normal conditions the ionisation occurred according to eqn. (1), when very high concentrations of $HgCl_2$ and $SbCl_3$ were used $[R^+]$ varied with $[RCl]^1$ and $[MCl_x]^n$ where $n > 1$. We have seen earlier that in poorly ionising solvents such as benzene and chlorobenzene, the metal chloride also helps to solvate the ion.[1] This effect is also found in the dimerisation of 1 : 1-diphenylethylene by trichloroacetic acid in benzene where the trichloroacetic acid helps to solvate the ions.[11] We attribute the dependence of $[R^+]$ on $[RCl]^1$ and $[MCl_x]^n$ to the fact that the metal halide helps to solvate the ions according to the equation:

$$RCl + nMCl_x \rightleftharpoons (R^+MCl^-_{x+1})_{solv.}$$

where solv. is $(n-1)MCl_x$ and $n$ is not necessarily an integer since it gives merely a statistical mean of the number of metal chloride molecules associated with an ion.

*Ionisation of* $Ph_3C{\cdot}Cl$ *in the Presence of* $SnCl_4$ *and* $FeCl_3$.—Ferric chloride is more efficient in promoting ionisation than is stannic chloride. The difference in efficiency as measured by the difference in free energy of ionisation is 2·12 kcal./mole when the organic chloride is diphenyl-*p*-tolylmethyl chloride and 2·26 kcal./mole when the organic chloride is triphenylmethyl chloride (Table 2). Thus the effect on $\Delta G°_1$ of a change in metal halide is the same for different RCl molecules.

The successive introduction of *p*-methyl groups into triphenylmethyl chloride decreases the free energy of ionisation by 1·3 kcal./mole in acetic acid.[5] The corresponding decrease for $FeCl_3$ and $SnCl_4$ in acetic acid solutions is 1·4 and 1·6 kcal./mole respectively (Table 2). Thus the effect on $\Delta G°_1$ of a change of R is the same for different metal halides, and in the absence of metal halides.

*Stability of Solutions.*—Acetic acid exists completely as the positive ion $(CH_3{\cdot}CO_2H_2^+)$ in concentrated sulphuric acid.[12] The possibility that acetic acid might accept carbonium ions to form the complex $(CH_3CO_2HR^+)$ has been previously considered [5] and it was concluded that if any such ions are formed then their concentration is too small to invalidate the determination of the ionisation equilibrium constants.

In order to detect any interaction between carbonium ions and acetic acid, a 1 cm.

[7] Meerwein and Van Emster, *Ber.*, 1922, **55**, 2500.
[8] Bodendorf and Bohme, *Annalen*, 1935, **516**, 1.
[9] Dermer, *J. Amer. Chem. Soc.*, 1941, **63**, 2881.
[10] Jenson and Brown, *J. Amer. Chem. Soc.*, 1958, **80**, 3039.
[11] A. G. Evans, Jones, and Thomas, *J.*, 1955, 2757.
[12] Hammett, " Physical Organic Chemistry," McGraw-Hill Book Company, Inc., 1940, p. 46.

glass cell containing an acetic acid solution of stannic chloride and diphenyl-*p*-tolylmethyl chloride was sealed and thermostatted at 55° for three weeks, after which time the optical density at the absorption maximum was unchanged, as it was after 12 months also. This is good evidence that no reaction takes place between the solvent and the carbonium ions in the presence of a Friedel–Crafts catalyst, since it is unlikely that any such reaction would be instantaneous.

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