199. *The Formation of Carbonium Ions by the Action of Metal Salts. Part III.* The Reaction of Mercuric Chloride with Triarylmethyl Chlorides in Nitromethane, Chlorobenzene, and Benzene.*

By J. W. Bayles, Alwyn G. Evans, and J. R. Jones.

Previous work on the ionization of triphenylmethyl chloride by mercuric chloride in nitromethane has been extended to chloro- and methyl-substituted triphenylmethyl chlorides in nitromethane, and to tri-*p*-tolylmethyl chloride in chlorobenzene and benzene. In the nitromethane the following equilibria exist: $RCl + HgCl_2 \rightleftharpoons R^+HgCl_3^-$; $R^+HgCl_3^- \rightleftharpoons R^+ + HgCl_3^-$. The changes in free energy have been obtained for the forward reactions. In this paper, the effect of the nature of R on these free-energy changes is given and discussed.

In the benzene and chlorobenzene, ion pairs, $R^+HgCl_3^-$, are formed but do not dissociate, and their solvation involves mercuric chloride molecules.

Stable crystalline complexes have been obtained from the RCl–$HgCl_2$ solutions in benzene. These complexes contain R^+ ions, as shown by their colour.

A study of the ionization of triphenylmethyl chloride by mercuric chloride in nitromethane [1a, b] showed that the solutions contain triphenylmethyl ions, partly as free ions ($Ph_3C^+ + HgCl_3^-$) and partly as ion pairs ($Ph_3C^+HgCl_3^-$). In this paper we describe a similar investigation of *o*-chloro-, *p*-chloro-, *o*-methyl-, and *p*-methyl-monosubstituted triphenylmethyl chlorides and of tri-*p*-chlorophenylmethyl chloride in nitromethane, and of tri-*p*-tolylmethyl chloride in chlorobenzene and benzene.

Experimental

Materials.—The triarylmethyl chlorides were prepared and purified as described by Evans, Jones, and Osborne,[2] and the m. p.s agreed well with those given by them.

Nitromethane was obtained from L. Light and Co. Ltd., and was purified as described earlier.[2a]

" AnalaR " benzene was obtained from British Drug Houses Ltd. and was dried over sodium wire and fractionated. The middle fraction distilling at 80° was collected.

Commercial chlorobenzene was kept overnight over phosphoric oxide, decanted on to a little fresh phosphoric oxide, and was fractionated from this through an 18 inch point-column; it had b. p. 132°.

Sulphuric acid was the 98% " AnalaR " reagent.

" AnalaR " mercuric chloride was twice sublimed in a high vacuum before use.

Spectra.—The light absorption of the solutions containing mercuric chloride and triarylmethyl chloride was measured on a Unicam S.P. 500 spectrophotometer, with an optical path length of 1 cm. The spectra are shown in Figs. 1*a*—*c*. The spectra of the sulphuric acid solutions of the corresponding alcohols were calculated from results at the concentrations used experimentally, so that the optical densities at the absorption peaks are the same as in the solvent used.

Effect of Concentration.—Master solutions, one of mercuric chloride and the other of triarylmethyl chloride, were mixed in various ratios, and the concentration of carbonium ions in the resulting solution was determined by assuming that $\int D_\lambda d\lambda$ is the same for these solutions as for 98% sulphuric acid solutions containing the same concentration of the carbonium ions. The same value for $\Delta G°$ ($\pm 0{\cdot}1$ kcal./mole) for the equilibria involved was obtained when the concentration of the ions was determined by making the alternative assumption that the height of the absorption peak is the same for these solutions as for 98% sulphuric acid solutions containing the same concentration of carbonium ions. In the nitromethane solutions of the

---

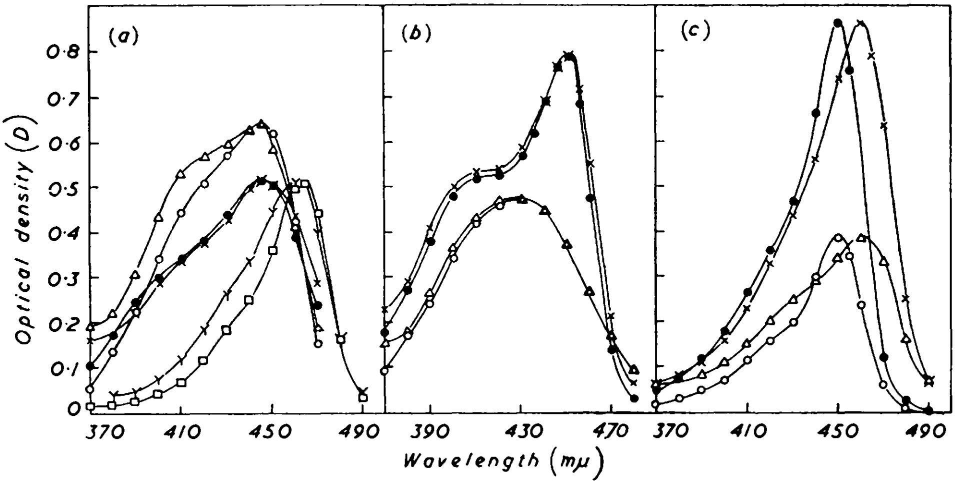
* Part II, Bayles, Cotter, and Evans, *J.*, 1955, 3104.

[1] (*a*) Bentley and Evans, *Research*, 1952, **5**, 535; (*b*) Bayles, Evans, and Jones, *J.*, 1955, 206; (*c*) Bayles, Cotter, and Evans, *J.*, 1955, 3104.

[2] Evans, Jones, and Osborne, (*a*) *Trans. Faraday Soc.*, 1954, **50**, 16, 470; (*b*) *J.*, 1954, 3803.

monosubstituted triphenylmethyl chlorides studied, the absorption peak occurs at the same wavelength as for the corresponding 98% sulphuric acid solution. For tri-*p*-chlorophenylmethyl chloride in nitromethane there is a small hypsochromic peak shift of 4 mμ and for solutions of tri-*p*-tolylmethyl chloride in chlorobenzene and benzene there is a bathochromic peak shift of 10 mμ in each case. In spite of these peak shifts, the shapes of the curves are very similar to those for the corresponding sulphuric acid solutions, so that there is no doubt that we are examining the spectrum of the carbonium ion. It has been shown earlier that the carbonium ion concentration can be determined as described above although there are these peak shifts.[3]

FIGS. 1*a*—*c*.



Compound	Total concn. of triarylmethyl cpd. (10^{-5} mole l.$^{-1}$)	Total concn. of mercuric chloride (10^{-4} mole l.$^{-1}$)	Solvent	Temp.
	FIG. 1*a*.			
○ *p*-Cl·C_6H_4·CPh_2·OH	1·305	—	98% H_2SO_4	
△ *p*-Cl·C_6H_4·CPh_2Cl	57·1	3·24	$MeNO_2$	17°
● *o*-Cl·C_6H_4·CPh_2·OH	1·052	—	98% H_2SO_4	
× *o*-Cl·C_6H_4·CPh_2Cl	25·5	3·035	$MeNO_2$	14
□ (*p*-Cl·C_6H_4)$_3$C·OH	0·495	—	98% H_2SO_4	
Y (*p*-Cl·C_6H_4)$_3$CCl	19·1	8·82	Me·NO_2	15
	FIG. 1*b*.			
○ *o*-Me·C_6H_4·CPh_2·OH	1·40	—	98% H_2SO_4	
△ *o*-Me·C_6H_4·CPh_2·Cl	8·12	0·791	$MeNO_2$	16
● *p*-Me·C_6H_4·CPh_2·OH	1·74	—	98% H_2SO_4	
× *p*-Me·C_6H_4·CPh_2Cl	6·72	0·603	$MeNO_2$	14
	FIG. 1*c*.			
○ (*p*-Me·C_6H_4)$_3$C·OH	0·494	—	98% H_2SO_4	
△ (*p*-Me(C_6H_4)$_3$CCl	640	35·1	C_6H_6	13
● (*p*-Me·C_6H_4)$_3$C·OH	1·102	—	98% H_2SO_4	
× (*p*-Me·C_6H_4)$_3$CCl	36·8	19·0	PhCl	16

Complex between Mercuric Chloride and Triarylmethyl Chloride.—When the benzene solutions of mercuric chloride and triarylmethyl chloride were mixed, the resulting solution was found to be stable during the measurement of its optical density. After about 6 hr., however, a trace of an orange-red complex had crystallized. When such a mixed solution was left to crystallize as much as possible, the supernatant liquid had an optical density of less than 0·1. Thus it was not possible to examine the reaction of mercuric chloride with tri-*p*-tolylmethyl chloride in benzene except under conditions for which the solution was supersaturated with respect to this complex. Since under these conditions no measurable change in optical density occurred for at least 15 min. after the solution had been made up we have confidence in the validity of the results obtained in benzene (which were completed within 5 min. of mixing) for the dependence

---

[3] Evans, McEwan, Price, and Thomas, *J.*, 1955, 3098.

of the carbonium-ion concentration on the concentrations of mercuric chloride and triarylmethyl chloride.

In order to examine the complex in more detail, highly concentrated benzene solutions of mercuric chloride and triarylmethyl chloride were mixed, and the composition of the orange-red complex which crystallized was determined as follows. A known weight of the $RCl-HgCl_2$ complex was treated with a known amount of 98% sulphuric acid, the solution decanted from the mercuric sulphate so formed, and the amount of triarylmethyl chloride determined spectrophotometrically, our previously determined values for the extinction coefficients of the triarylmethyl ions being used. (We find that when the triarylmethyl chloride is dissolved in 98% sulphuric acid it is completely converted into carbonium ions.) The results are given in Table 1, together with carbon, hydrogen, and chlorine content of the same complexes. It is seen that these two methods are in good agreement. Using the sulphuric acid method of estimating the $[HgCl_2] : [RCl]$ ratio in the complex we determined the effect on this of the $[HgCl_2] : [RCl]$ ratio in the solution from which the complex was precipitated. The results are given in Table 2 for the tri-*p*-tolylmethyl chloride–$HgCl_2$ complex.

TABLE 1. *Composition of* $RCl-HgCl_2$ *complex.*

Molar ratio $HgCl_2 : RCl$	$(p\text{-}Me{\cdot}C_6H_4)_3CCl$: Calc. % C	H	Cl	Molar ratio $HgCl_2 : RCl$	Ph_3CCl : Calc. % C	H	Cl
1	44·6	3·55	17·9	1	41·4	2·7	10·6
2·5	26·4	2·10	21·3	4·5	15·2	1·0	23·6
2·7	25·3	2·0	21·5	4·8	14·4	0·95	23·7
3·0	23·2	1·9	21·8	5·0	13·9	0·9	23·8
Found :	27·2	2·1	22·2	Found :	15·3	1·3	23·7

Ratio by H_2SO_4 method : $(p\text{-}Me{\cdot}C_6H_4)_3CCl$, 2·7; Ph_3CCl, 4·8.

TABLE 2. *Composition of* $HgCl_2-RCl$ *complex precipitated from solutions of varying* $HgCl_2$ *concentrations in benzene.* $[(p\text{-}Me{\cdot}C_6H_4)_3CCl] = 2{\cdot}013 \times 10^{-3}$ mole l.$^{-1}$.

$[HgCl_2]$ (10^{-3} mole l.$^{-1}$)	3·75	7·49	13·65
Ratio, $HgCl_2 : RCl$ (molar) (± 0·05)	2·45	2·77	2·8

These complexes melted at 90—110° (with decomp.). The tri-*p*-tolylmethyl chloride–mercuric chloride complex crystallized as six-sided plates.

No such complexes were obtained from the nitromethane and chlorobenzene solutions.

Molecular-weight Determination of Mercuric Chloride in Benezene.—A number of cryoscopic experiments were carried out on benzene solutions of mercuric chloride (25 ml. of the solution in a Beckmann freezing-point apparatus). The apparatus was thermally insulated by means of asbestos. The freezing point was read within ±0·005°. Concentrations were used which gave freezing point depressions of 0·03—0·08°. Higher concentrations could not be used owing to the possibility of crystallization of the mercuric chloride, so the accuracy of the molecular-weight determinations was ±50 units. In spite of this, the molecular weights so obtained were in no case greater than that corresponding to $HgCl_2$, showing that there is no measurable association of mercuric chloride in benzene.

DISCUSSION

Nitromethane Solutions.—*Stability of solutions.* The use of nitromethane as a solvent for these ionization reactions has been criticized by Smith and Leffler [4] on the grounds that when they made up triphenylmethyl chloride solutions in nitromethane the optical density decreased rapidly during 40 min. and a precipitate of ammonium chloride was formed. We always obtained stable solutions, whenever the rigorous method of purification developed in our earlier work was followed.[2a] This stability is strikingly demonstrated in the diagrams given earlier [2a, b] for the temperature-dependence of various triarylmethyl chloride solutions in nitromethane. In these experiments such solutions having optical densities from 0·2 to 0·5 (for an optical path length of 1 cm.) were heated and cooled within the temperature range 15—40° for 2—3 hr., the optical density at any temperature being always reproducible; the solutions remained perfectly clear.

---

[4] Smith and Leffler, *J. Amer. Chem. Soc.*, 1955, **77**, 1700.

In Part I[1b] temperature-dependence was investigated for mercuric chloride–triphenylmethyl chloride–nitromethane solutions, of optical density 0·2—0·7; these solutions were also heated and cooled within the temperature range of 15—40° for 2—3 hr., and again the optical density at any temperature was reproducible, the solutions remaining clear throughout the experiment.

We have kept a solution of triphenylmethyl chloride in nitromethane sealed in an optical cell for 10 days. The optical density of the solution initially was 0·178, the optical path length being 1 cm. After 10 days the optical density was 0·170, the solution remaining clear throughout the period. The stability of these solutions is further supported by the reproducibility of the results obtained with this solvent, especially the close correlation, discussed later in this paper, between the present values of ΔG°_{1a} for ionization by mercuric chloride in nitromethane, and those obtained previously for ionization in nitromethane in absence of mercuric chloride.

We have found [1c] that, when mercuric bromide is added to a nitromethane solution of tri-*p*-tolylmethyl bromide until no further ionization occurs, the bromide is 100% ionized (±15%) if the extinction coefficient obtained for the carbonium ion in sulphuric acid is used. This again supports the stability of the carbonium ions in these solutions.

FIG. 2a.

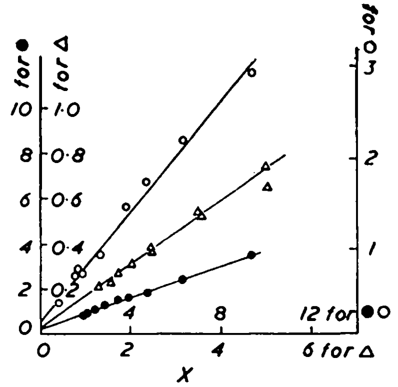


FIG. 2b.

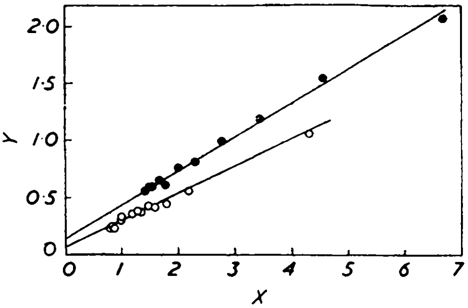


FIG. 2a. *Plot of* (*X*) $10^{-3}/([HgCl_2][RCl])^{\frac{1}{2}}$ (l. mole^{-1}) *against* (*Y*) $10^{-3}\{[R^+] + [R^+(HgCl_3)^-]\}/([RCl][HgCl_2]$ (l. mole^{-1}).
○ o-Cl·C_6H_4·CPh_2Cl. ● p-Cl·C_6H_4·CPh_2Cl. △ (p-Cl·$C_6H_4)_3CCl$.

FIG. 2b. *Plot of* (*X*) $10^{-4}/([HgCl_2][RCl])^{\frac{1}{2}}$ (l. mole^{-1}) *against* (*Y*) $\{[R^+] + [R^+(HgCl_3)^-]\}/([RCl][HgCl_2])$ (l. mole^{-1}).
○ o-Me·C_6H_4·CPh_2Cl. ● p-Me·C_6H_4·CPh_2Cl.

The results obtained for the ionization of triarylmethyl chlorides in nitromethane are further substantiated by their correlation with the corresponding results in nitroethane, 2-nitropropane, nitrobenzene, and *m*-nitrotoluene.[2a, 5]

Nature of the equilibrium. The curves obtained when the ionic concentration is plotted against the product of the reactant concentrations are of the same form as those obtained for the triphenylmethyl chloride–mercuric chloride system reported earlier.[1b] The points obtained when the mercuric chloride concentration is kept constant and the triarylmethyl chloride concentration is varied fall on the same curve as those found when the triarylmethyl chloride concentration is kept constant for a variation in the mercuric chloride concentration. Thus the reaction producing the carbonium ion is of the same order with respect to each reactant. It is therefore suggested that the equilibria involved are of the same form as those postulated in Part I for triphenylmethyl chloride.[1b]

This is established by the plots shown in Figs. 2*a* and *b*, obtained by analysing the

---

[5] Evans, Price, and Thomas, *Trans. Faraday Soc.*, 1954, **50**, 568.

results according to these equations as described in Part I. The fact that such good straight lines are obtained for these systems very strongly supports this method of analysis.

In Table 3 are given the mean values for the free-energy changes of reactions (1*a*) and (2*a*) (ΔG°_{1a} and ΔG°_{2a}), obtained from these plots as described in Part I. The variation in

$$\mathrm{RCl} + \mathrm{HgCl_2} \underset{b}{\overset{a}{\rightleftharpoons}} \mathrm{R^+HgCl_3^-} \quad . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$\mathrm{R^+HgCl_3^-} \underset{b}{\overset{a}{\rightleftharpoons}} \mathrm{R^+} + \mathrm{HgCl_3^-} \quad . \; . \; . \; . \; . \; . \quad (2)$$

ΔG°_{1a} [the free energy of ion-pair formation according to equation (1)], as substituents are introduced, is given in column 6. It is seen that the introduction of methyl groups increases, whereas that of chlorine atoms reduces, the ease of ion-pair formation, this effect being very marked when three *p*-chlorines are introduced.

In nitromethane, in the absence of mercuric chloride, the carbonium chloride undergoes ion-pair formation, $\mathrm{RCl} \rightleftharpoons \mathrm{R^+Cl^-}$, without subsequent dissociation of the ion pairs. The effect of substituents on the free-energy change for this ion-pair formation, which was measured earlier,[2] is plotted in Fig. 3 against the corresponding values obtained in this paper for the $\mathrm{RCl} + \mathrm{HgCl_2} \rightleftharpoons \mathrm{R^+HgCl_3^-}$ reaction (Table 3, column 6), and it is seen that there is a very close parallelism between these two sets of values, as is to be expected.

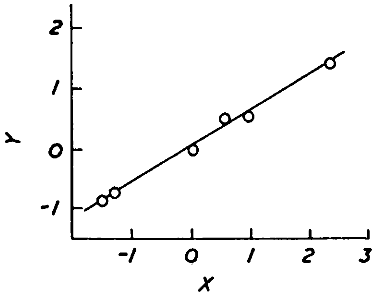


FIG. 3. *Plot of* (*X*) $\Delta G^\circ_{\mathrm{RCl}} - \Delta G^\circ_{\mathrm{Ph_3CCl}}$ *for* $\mathrm{RCl} + \mathrm{HgCl_2} \longrightarrow \mathrm{R^+HgCl_2^-}$ *in nitromethane against* (*Y*) $\Delta G^\circ_{\mathrm{RCl}} - \Delta G^\circ_{\mathrm{Ph_3CCl}}$ *for* $\mathrm{RCl} \longrightarrow \mathrm{R^+Cl^-}$ *in nitromethane*

In Table 3, column 7, are given the variations in ΔG°_{2a} [the free energy of dissociation of the ion pairs, according to equation (2)] as substituents are introduced. The error involved in measuring ΔG°_{2a} is greater than that for measuring ΔG°_{1a}, but we see that for the change of R which we have studied there is no parallel change in ΔG°_{2a}. This is to be expected since reaction (1*a*) involves the breaking and forming of bonds and the transfer of an electron, whereas reaction (2*a*) merely involves the separation of the charged bodies. Thus equilibrium (1) should be very markedly affected by a change in R, whereas equilibrium (2) should be independent of R except in so far as substituents in R increase the epuilibrium distance to which the ions can approach each other.

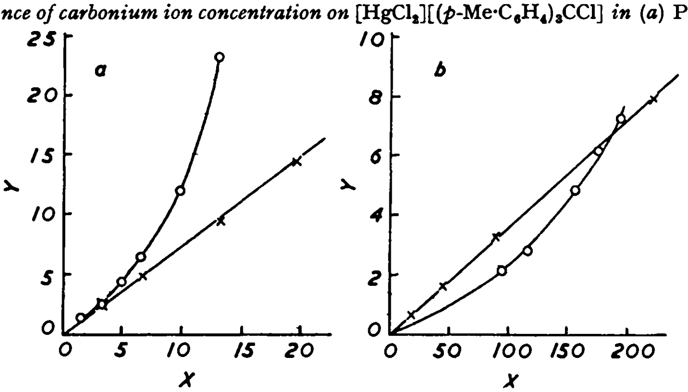
TABLE 3. *Thermodynamic values for reactions in nitromethane at* 17°.

$$\mathrm{RCl} + \mathrm{HgCl_2} \underset{b}{\overset{a}{\rightleftharpoons}} \mathrm{R^+HgCl_3^-} \; . \; . \; . \; (1), \text{ and } \mathrm{R^+HgCl_3^-} \underset{b}{\overset{a}{\rightleftharpoons}} \mathrm{R^+} + \mathrm{HgCl_3^-} \; . \; . \; . \; (2)$$

R	Mean K_1 (mole fraction)	Mean K_2 (mole fraction)	Mean ΔG°_{1a} (kcal./mole)	Mean ΔG°_{2a} (kcal./mole)	($\Delta G^\circ_{1a\,(\mathrm{RCl})} - \Delta G^\circ_{1a\,(\mathrm{Ph_3CCl})}$) (kcal./mole)	($\Delta G^\circ_{2a\,(\mathrm{RCl})} - \Delta G^\circ_{2a\,(\mathrm{Ph_3CCl})}$) (kcal./mole)
$\mathrm{Ph_3C}$	1.5×10^3	1.3×10^{-6}	-4.2 ± 0.2	7.8 ± 0.6	0	0
p-$\mathrm{Cl{\cdot}C_6H_4{\cdot}CPh_2}$	4.9×10^2	1.71×10^{-6}	-3.6 ± 0.2	7.8 ± 0.6	$+0.6 \pm 0.4$	0 ± 1.2
o-$\mathrm{Cl{\cdot}C_6H_4{\cdot}CPh_2}$	2.67×10^2	2.11×10^{-7}	-3.2 ± 0.2	9.3 ± 0.9	$+1.0 \pm 0.4$	$+1.5 \pm 1.5$
p-$\mathrm{Me{\cdot}C_6H_4{\cdot}CPh_2}$	2.14×10^4	3.95×10^{-6}	-5.7 ± 0.3	7.4 ± 1.2	-1.5 ± 0.5	-0.4 ± 1.8
o-$\mathrm{Me{\cdot}C_6H_4{\cdot}CPh_2}$	1.65×10^4	3.45×10^{-6}	-5.5 ± 0.5	7.4 ± 0.7	-1.3 ± 0.7	-0.4 ± 1.3
(*p*-$\mathrm{Cl{\cdot}C_6H_4)_3C}$ ...	3.0×10^1	8.02×10^{-6}	-1.9 ± 0.3	6.8 ± 0.3	$+2.3 \pm 0.5$	-1.0 ± 0.9

Solutions in Benzene and Chlorobenzene.—The results are shown in Fig. 4 for the tri-*p*-tolylmethyl chloride solutions in chlorobenzene and in benzene. In both solvents the carbonium-ion concentration varies linearly with the concentration of tri-*p*-tolylmethyl chloride when the mercuric chloride concentration is kept constant. This indicates that the ionisation involves only one molecule of tri-*p*-tolylmethyl chloride and, further, that no dissociation of ion pairs can be detected in these solutions since if this occurred the plot would be curved. The plot obtained when the mercuric chloride concentration is varied while the tri-*p*-tolylmethyl chloride concentration is kept constant shows that more than one molecule of mercuric chloride is involved in the reaction. This suggests that the mercuric chloride acts as a solvating agent for the ion pair $R^+HgCl_3^-$ when it is formed in these poorly solvating liquids. A similar effect has been found for the trichloroacetic acid-catalyzed dimerization of 1 : 1-diphenylethylene where, in a poorly ionizing solvent such as benzene, the order in acid is 3, one of these acid molecules being involved in proton donation to the olefin, and the other two helping to solvate the ion pair so formed.[6] Thus the ionization reaction in benzene and in chlorobenzene solution may be written as :

FIG. 4. *Dependence of carbonium ion concentration on* $[HgCl_2][(p\text{-Me}\cdot C_6H_4)_3CCl]$ *in* (*a*) PhCl *and* (*b*) C_6H_6.



Plot of (*X*) $10^7[HgCl_2][RCl]$ (*mole*^{2} *l.*$^{-2}$) *against* (*Y*) $10^6\ [R^+(HgCl_3)^-]$ (*g.-ion l.*$^{-1}$).

Fig.	Total tri-*p*-tolylmethyl chloride (10^{-4} mole l.$^{-1}$)	Total mercuric chloride (10^{-4} mole l.$^{-1}$)
4*a*	O, 6·92 (20°)	×, 4·73 (20°)
4*b*	O, 61·2 (17°)	×, 35·1 (13°)

$$RCl + nHgCl_2 \rightleftharpoons (R^+HgCl_3^-)_{\text{solv.}\ (n-1)\ HgCl_2}$$

where $(n - 1)$ molecules of mercuric chloride help in the solvating of the ion pair. The mercuric chloride involved in this solvation is loosely bound and n can on this account have a non-integral value.

There will be an equilibrium constant of the form $K = [\text{ions}]/[RCl][HgCl_2]^n$, and the value of n has been obtained by plotting $\log_{10}$ [ions] against $\log_{10}$ $[HgCl_2]$ for the solutions of constant RCl concentration. In this way the mean value for n is found to be 1·9 for the benzene solutions. In chlorobenzene n is found to increase from 1·0 to 2·4 as the mercuric chloride concentration increases within the limits used in our experiments. It is to be noticed that, although a variation of this kind has not been observed for the benzene solutions, a much smaller range of carbonium-ion concentration has been used in this solvent.

It is seen that the solvents lie in the following order as regards their ability to promote the ionization reaction : nitromethane > chlorobenzene > benzene.

Solid Complexes.—The fact that the crystalline complexes which separate from the

---

[6] Evans, Jones, and Thomas, *J.*, 1955, 1824.

benzene solutions containing RCl and mercuric chloride are orange-red shows that these crystals are ionic and contain R^+ ions.

Evidence for the tendency of mercuric chloride to associate with the ion pair is found in the composition of these orange-red crystalline complexes. Their analyses show an excess of mercuric chloride over the organic chloride, this excess increasing with increase of mercuric chloride concentration in the mother-liquor containing a given concentation of RCl (see Table 2).

We thank the D.S.I.R. for a Maintenance Allowance (to J. R. J.), and The Chemical Society for a grant from their Research Fund towards the cost of chemicals.

UNIVERSITY COLLEGE, CARDIFF.

[*Received, August 1st,* 1956.]