The Formation of Carbonium Ions by the Action of Metal Salts. Part I. The Reaction of Mercuric Chloride with Triphenylmethyl Chloride in Nitromethane.

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In the reaction between mercuric chloride and triphenylmethyl chloride in nitromethane, equilibria exist involving triphenylmethyl ions. The concentration of these ions has been measured spectrophotometrically and the results show that the ionization of triphenylmethyl chloride involves the equilibria :

$$Ph_3CCl + HgCl_2 \rightleftharpoons Ph_3C^+HgCl_3^-$$

and

$$Ph_3C^+HgCl_3^- \rightleftharpoons Ph_3C^+ + HgCl_3^-$$

We have determined the changes in free energy and heat content for the forward reactions.

IN a preliminary communication (Bentley and Evans, *Research*, 1952, **5**, 535), it was shown that in nitromethane the ionization of triphenylmethyl chloride is very markedly enhanced by the presence of mercuric chloride, and the changes in free energy and heat content for the reaction between these two compounds were estimated spectrophotometrically. The measurements on this reaction have now been extended, and in this paper we give a detailed account of the results.

EXPERIMENTAL

Materials.—Nitromethane and triphenylmethyl chloride were obtained and purified as described by Evans, Jones, and Osborne (*Trans. Faraday Soc.*, 1954, **50**, 16). Mercuric chloride (B.D.H.) was purified by sublimation *in vacuo*, and stored in sealed capsules.

Spectra.—A solution of triphenylmethyl chloride in nitromethane was made up which was so dilute that the absorption of light by triphenylmethyl ions was not measurable. A solution of mercuric chloride in nitromethane was also prepared; this showed no light absorption in the spectral region used for estimating the triphenylmethyl ions. These colourless solutions became intensely yellow on mixing, and their light absorption was measured on a Unicam S.P. 500 Spectrophotometer. The spectrum is given in Fig. 1, curve *A*, together with that for triphenylmethyl alcohol in 98% sulphuric acid (curve *B*). In order that the shape of the two spectra may be easily compared, curve *B* has been calculated from results at other concentrations so that the optical density at the 430 mμ peak is the same as that of curve *A*. These calculations were carried out by using the direct proportionality between optical density and carbonium-ion concentration which has been established at all wave-lengths involved in the absorption for the sulphuric acid solution of triphenylmethyl alcohol (*idem, ibid.*, p. 470). It is seen that these two spectra are very similar, and since triphenylmethyl alcohol is completely ionized in 98% sulphuric acid (Hantzsch, *Z. physikal. Chem.*, 1908, **61**, 257; Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1933, **55**, 1900) according to the equation: $Ph_3C{\cdot}OH + 2H_2SO_4 \longrightarrow Ph_3C^+ + H_3O^+ + 2HSO_4^-$, this close similarity demonstrates the presence of triphenylmethyl ions in the nitromethane solutions of triphenylmethyl chloride and mercuric chloride.

Effect of Concentration.—Solutions containing different concentrations of reactants were made up by mixing, in various ratios, the nitromethane solutions of mercuric chloride and triphenylmethyl chloride described above. The concentration of triphenylmethyl ions in a mixed solution was calculated by assuming that $\int D_\lambda d\lambda$ is the same in this solution as in 98% sulphuric acid for the same carbonium-ion concentration. An alternative method of calculating the carbonium-ion concentration is to assume that $(D_\lambda)_{max.}$ is the same in the nitromethane solution as in 98% sulphuric acid for the same carbonium-ion concentration. Since the spectra shown in Fig. 1 are so similar this alternative method leads to values which are the same, within experimental error, as those obtained by the above method.

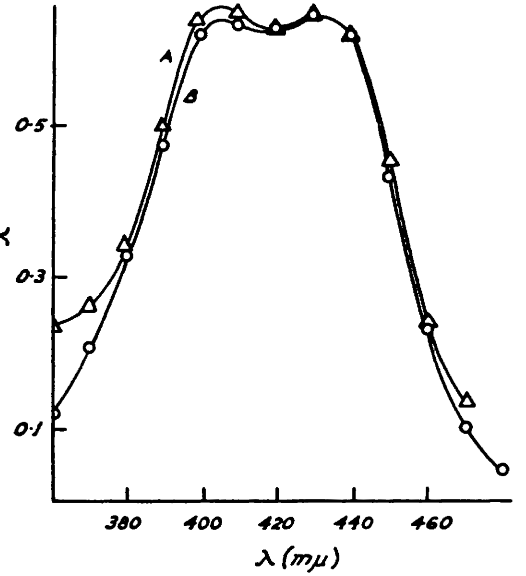

FIG. 1.

A, Mercuric chloride (total concn. 2·542 × 10^{-4} mole $l.^{-1}$) and triphenylmethyl chloride (total concn. 2·754 × 10^{-4} mole $l.^{-1}$) in nitromethane at 18°.

B. Triphenylmethyl alcohol (concn. 1·711 × 10^{-5} mole $l.^{-1}$) in 98% sulphuric acid.

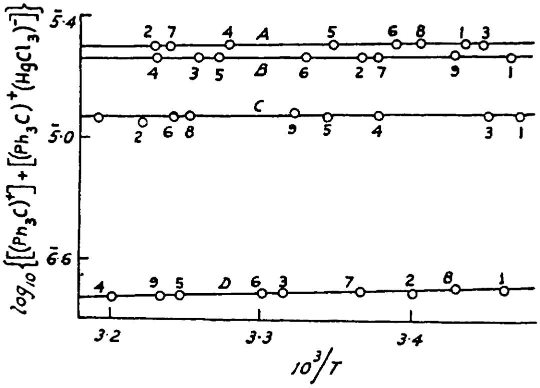

FIG. 2. *Total concentrations* × 10^4 (*moles* $l.^{-1}$).

	A	*B*	*C*	*D*
Ph_3CCl ...	3·14	3·32	2·21	0·628
$HgCl_2$	3·62	3·41	2·28	0·725

The carbonium-ion concentration was subtracted from the total mercuric chloride and total triphenylmethyl chloride concentrations to give the concentrations of these two reactants at equilibrium; this carbonium-ion concentration never amounted to more than 10% of the total triphenylmethyl chloride present. In Table 1 we give the results so obtained for two typical experiments.

Effect of Temperature.—Five solutions were made up in which the total amounts of mercuric chloride and triphenylmethyl chloride were known, and the product of the equilibrium concentrations $[HgCl_2][Ph_3CCl]$, varied between $0{\cdot}4 \times 10^{-8}$ and $1{\cdot}0 \times 10^{-7}$ mole² l.⁻². The change of optical density of these solutions with change in temperature was measured as described by

TABLE 1. *Equilibrium concentrations of reactants in nitromethane.*

$10^5\{[Ph_3C^+] + [Ph_3C^+HgCl_3^-]\}$ (g.-ions l.⁻¹)	$10^4[HgCl_2]$ (mole l.⁻¹)	$10^4[Ph_3CCl]$ (mole l.⁻¹)	$10^5\{[Ph_3C^+] + [Ph_3C^+HgCl_3^-]\}$ (g.-ions l.⁻¹)	$10^4[HgCl_2]$ (mole l.⁻¹)	$10^4[Ph_3CCl]$ (mole l.⁻¹)
	Experiment 1.			*Experiment* 2.	
3·84	5·04	4·74	3·95	5·36	5·85
2·70	5·15	2·80	3·71	5·39	4·63
2·04	5·22	1·84	3·18	5·44	3·43
3·56	3·98	4·76	2·53	5·51	2·25
3·13	2·94	4·81	1·35	5·62	1·11
2·39	1·93	4·88	0·81	5·68	0·55
1·66	2·54	2·39	4·02	4·21	5·85
1·18	2·59	1·41	3·40	3·12	5·91
0·815	2·63	0·94	2·63	2·04	5·99
0·464	1·03	0·97	1·91	2·69	2·93
			1·31	2·75	1·74
			0·563	1·09	1·19

Bentley and Evans (*J.*, 1952, 3468) by using a photomultiplier with an Ilford 601 filter having a maximum transmission in the region 400—460 mμ. The optical density of the solution was measured at various temperatures, and this was converted into carbonium-ion concentration as described above. Typical results are shown in Fig. 2, the points being numbered to show the sequence in which the temperature was varied.

DISCUSSION

Nature of Equilibria.—If the equilibrium involved in these experiments was of the form the plot of the total carbonium-ion concentration against the product of the equilibrium concentrations of triphenylmethyl chloride and mercuric chloride should be linear, and its slope should give the equilibrium constant for reaction (1). This plot is shown in Fig. 3,

$$Ph_3CCl + HgCl_2 \underset{(b)}{\overset{(a)}{\rightleftharpoons}} Ph_3C^+HgCl_3^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

curve *A*, for Experiment 2, Table 1, and it is seen that there is a marked departure from linearity. This experiment was carried out five times, and the curved plot was found to be quite reproducible. Because this plot is curved we conclude that an additional equilibrium exists which is of the form:

$$Ph_3C^+HgCl_3^- \underset{(b)}{\overset{(a)}{\rightleftharpoons}} Ph_3C^+ + HgCl_3^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and that the ionic concentration which is measured spectrophotometrically and plotted in Fig. 3, curve *A*, is the sum of the concentrations of the free ions Ph_3C^+ and of the ion pairs $Ph_3C^+HgCl_3^-$.

The equilibrium constants K_1 and K_2 for reactions (1) and (2) respectively may be written:

$$K_1 = [Ph_3C^+HgCl_3^-]/\{[Ph_3CCl][HgCl_2]\}$$

and

$$K_2 = \frac{[Ph_3C^+][HgCl_3^-]}{[Ph_3C^+HgCl_3^-]} = \frac{[Ph_3C^+]^2}{[Ph_3C^+HgCl_3^-]}$$

from which

$$K_1\,K_2 = [Ph_3C^+]^2/\{[Ph_3CCl][HgCl_2]\}$$

and

$$\frac{\{[Ph_3C^+] + [Ph_3C^+HgCl_3^-]\}}{[Ph_3CCl][HgCl_2]} = K_1 + \{K_1K_2/[Ph_3CCl][HgCl_2]\}^{\frac{1}{2}} \quad . \quad . \quad (3)$$

Thus, if instead of plotting the total carbonium-ion concentration

$$\{[Ph_3C^+] + [Ph_3C^+HgCl_3^-]\}$$

against $[Ph_3CCl][HgCl]$, as in Fig. 3, we plot $\{[Ph_3C^+] + [Ph_3C^+HgCl_3^-]\}/[Ph_3CCl][HgCl_2]$ against $\{[Ph_3CCl][HgCl_2]\}^{-\frac{1}{2}}$ we should obtain a straight line, according to equation (3), of slope $\sqrt{K_1K_2}$ and of intercept K_1. This plot is shown in Fig. 4 for the two experiments

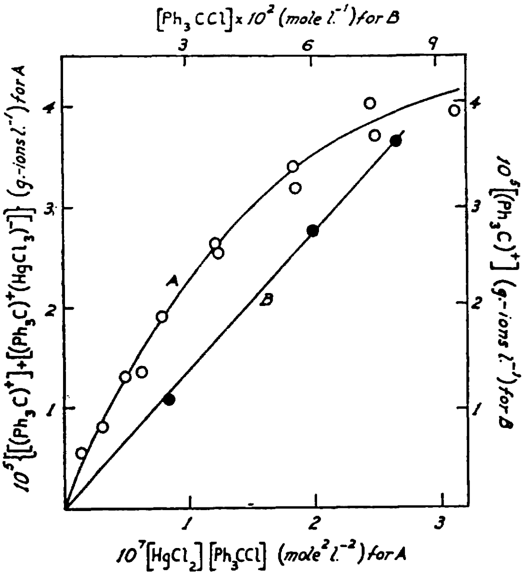

FIG. 3.

A, Nitromethane solution containing Ph_3CCl and $HgCl_2$.

Dependence of carbonium-ion concentration on $[Ph_3CCl][HgCl_2]$.

B, Nitromethane solution containing only Ph_3CCl.

Dependence of carbonium-ion concentration on $[Ph_3CCl]$.

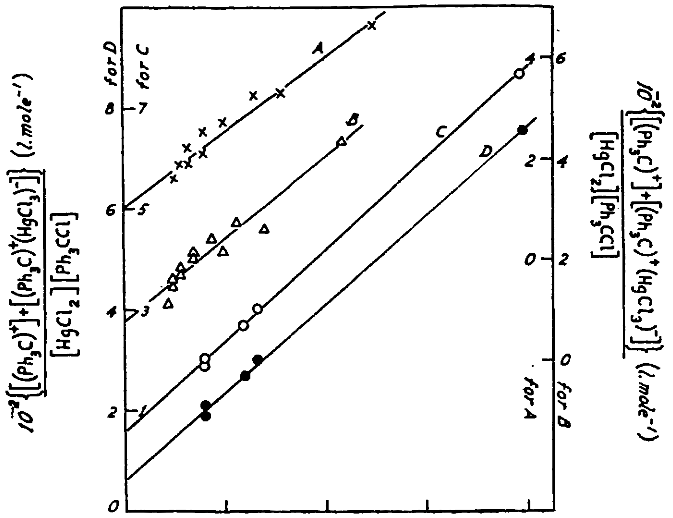

FIG. 4. *Plot of equation* (3).

The figures on the four vertical scales refer from left to right, respectively, to

^{1} ● 40°.
^{2} ○ 30°.
^{3} × 17° (Experiment 1, Table 1).
^{4} △ 17° (Experiment 2, Table 1).

given in Table 1. The fact that good straight lines are obtained demonstrates the existence of the two equilibria (1) and (2) in these solutions. {The assumption that the extinction coefficients of the ion pair $Ph_3C^+HgCl_3^-$ and of the free ion Ph_3C^+ in nitromethane are the same as for the free ion in concentrated sulphuric acid is strongly supported by the following facts : (*a*) the shapes of the spectra in these two solvents are very similar ; (*b*) we find that the shape of the spectrum is constant over the whole range of the concentration product, $[Ph_3CCl][HgCl_2]$, used in the experiments.} The experiments were carried out five times, and values of K_1 and K_2 were determined as described above for each experiment. The concentrations of reactants used in these plots are expressed in the units mole l.$^{-1}$ and g.-ion l.$^{-1}$, and the average values of K_1 and K_2 so obtained are 80·4 mole^{-1} l. and $2{\cdot}39 \times 10^{-5}$ mole l.$^{-1}$ respectively. We have converted these average values to mole fraction units, using the known values for the density of nitromethane at different temperatures (Int. Crit. Tables, **3**, 28) and K_1 and K_2 are given in these units in Table 2. The corresponding free-energy changes ΔG_{1a}° ($= -\boldsymbol{R}T \ln K_1$) and ΔG_{2a}° ($= -\boldsymbol{R}T \ln K_2$) for reactions (1*a*) and (2*a*) have been calculated from the values in mole fraction units of K_1 and K_2, and the average values so obtained are $\Delta G_{1a}^\circ = -4{\cdot}2$ kcal. mole^{-1} and $\Delta G_{2a}^\circ =$ 7·8 kcal. mole^{-1} at 17°. (The assumption is made here, that the reactants have unit activity coefficient. This we believe to be valid because of the very small ionic concentrations involved in these solutions.) The values of ΔG_{1a}° and ΔG_{2a}° obtained in these five experiments differed from the average values by less than $\pm 0{\cdot}2$ and $\pm 0{\cdot}6$ kcal. mole^{-1} respectively. In the preliminary communication (Bentley and Evans, *loc. cit.*) it was concluded that the reaction occurring in these solutions was that shown in equation (1) since a linear graph of $[Ph_3C^+]$ against $[Ph_3CCl][HgCl_2]$ was obtained. In the present more detailed work, however, it has been possible to detect the dissociation of ion pairs into free ions. [In the preliminary communication, ΔG_{1a}° was calculated from the average value of K_1 ($1{\cdot}46 \times 10^2$), expressed in the units l. mole^{-1}, and this gave the value of ΔG_{1a}° (−2·9 kcal. mole^{-1}) which appeared in that communication. If the method of first converting K into mole fraction units is used the ΔG_{1a}° obtained from this K_1 value is −4·6 kcal. mole^{-1}.]

Heats of Reaction.—We have determined ΔH_{1a}° and ΔH_{2a}° for reactions (1*a*) and (2*a*) as follows. Each curve in Fig. 2 corresponds to a solution for which the total concentrations of mercuric chloride and triphenylmethyl chloride are known at 17°, the temperature at which the solution was made up. The total concentrations of mercuric chloride and triphenylmethyl chloride have been calculated at 15°, 20°, 30°, and 40° by allowing for the small change in concentration due to the change in volume of the solvent with changing temperature (Int. Crit. Tables, *loc. cit.*). The equilibrium concentrations of these reactants were obtained by subtracting the spectrophotometrically determined total triphenylmethyl-ion concentration from these total concentrations of mercuric chloride and triphenylmethyl chloride. In this way, we have evaluated the ratio

$$\{[Ph_3C^+] + [Ph_3C^+HgCl_3^-]\}/[Ph_3CCl][HgCl_2]$$

at 15°, 20°, 30°, and 40° for each curve of Fig. 2, and have plotted it against $\{[Ph_3CCl][HgCl_2]\}^{-\frac{1}{2}}$ as in the analysis described above. These plots are good straight lines, which within experimental error are the same as those obtained at 17° (Fig. 4). As an example, we give in Fig. 4 the plots so obtained for 30° and 40°. The values of ΔG_{1a}° and ΔG_{2a}° obtained from Fig. 4 by the method described above are −4·2 and 7·9 kcal. mole^{-1} at 30°, and −4·4 and 8·3 kcal. mole^{-1} at 40°. These values at 30° and 40° taken together with the corresponding values of −4·2 and 7·8 kcal. mole^{-1} obtained at 17°, as described above, show that ΔH_{1a}° and ΔH_{2a}° are zero within the accuracy of our experimental method. We have considered the possible errors in these ΔH° values and estimate that $\Delta H_{1a}^\circ =$ $0{\cdot}0 \pm 2$ kcal. mole^{-1} and $\Delta H_{2a}^\circ = 0{\cdot}0 \mp 4$ kcal. mole^{-1}, the possible variations from zero being in opposite directions. The values of ΔS_{1a}° and ΔS_{2a}° calculated from the ΔG° and ΔH° values are given in Table 2. The possible variations in the values of ΔH° result in the limits of accuracy for the ΔS_{1a}° and ΔS_{2a}° values being 15 ± 7 and -27 ∓ 14 cal. deg.$^{-1}$ mole^{-1} respectively.

TABLE 2. *Thermodynamic quantities for reactions* (1) *and* (2) *in nitromethane at* 17·0°.

Reaction	K_1 (mole fraction)	K_2 (mole fraction)	ΔG_{1a}° (kcal. mole^{-1})	ΔG_{2a}° (kcal. mole^{-1})	ΔH_{1a}° (kcal. mole^{-1})	ΔH_{2a}° (kcal. mole^{-1})	ΔS_{1a}° (cal. deg.$^{-1}$ mole^{-1})	ΔS_{2a}° (cal. deg.$^{-1}$ mole^{-1})
1	$1{\cdot}5 \times 10^3$	—	−4·2	—	0·0	—	15	—
2	—	$1{\cdot}3 \times 10^{-6}$	—	7·8	—	0·0	—	−27

Dissociation of Ion Pairs.—It is interesting that in the nitromethane solution of triphenylmethyl chloride and mercuric chloride the dissociation of the ion pairs

$Ph_3C^+HgCl_3$ can be detected, since for nitromethane solutions containing only RCl no dissociation of ion pairs has been detected over a wide variety of types of R (Bentley, Evans, and Halpern, *Trans. Faraday Soc.*, 1951, **47**, 711; Evans, Jones, and Osborne, *loc. cit.*).* We have repeated the earlier work on nitromethane solutions containing only triphenylmethyl chloride (Bentley, Evans, and Halpern, *loc. cit.*), to see if we could obtain any indication of ion-pair dissociation, but none was detectable (see Fig. 3, curve *B*). This observed difference in the occurrence of ion-pair dissociation for these two systems might be caused if the distance apart of the positive and negative centres in the ion pair $Ph_3C^+HgCl_3^-$ were greater than in the ion pair $Ph_3C^+Cl^-$. To test this, and to elucidate other points, we are extending these experiments to different organic halides and metallic compounds, since a knowledge of the factors governing the formation and dissociation of such ion-pair complexes is fundamental to the understanding of the action of Friedel–Crafts catalysts.

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