The Production of Carbonium Ions by the Action of Metal Salts. Part II.* The Extinction Coefficients of Carbonium Ions.

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The assumption that the extinction coefficient of triphenylmethyl ions in nitromethane solutions of mercuric chloride (whether as an ion pair $Ph_3C^+HgCl_3^-$ or as free ions $Ph_3C^+ + HgCl_3^-$) was the same as in concentrated sulphuric acid has been verified.

IN previous papers (Bentley and A. G. Evans, *Research*, 1952, **5**, 535; Part I *), the interaction of mercuric chloride with triphenylmethyl chloride in nitromethane was investigated. The concentration of the carbonium ions present under these conditions was measured spectrophotometrically, with the assumption that the extinction coefficient of this ion in

FIG. 1.
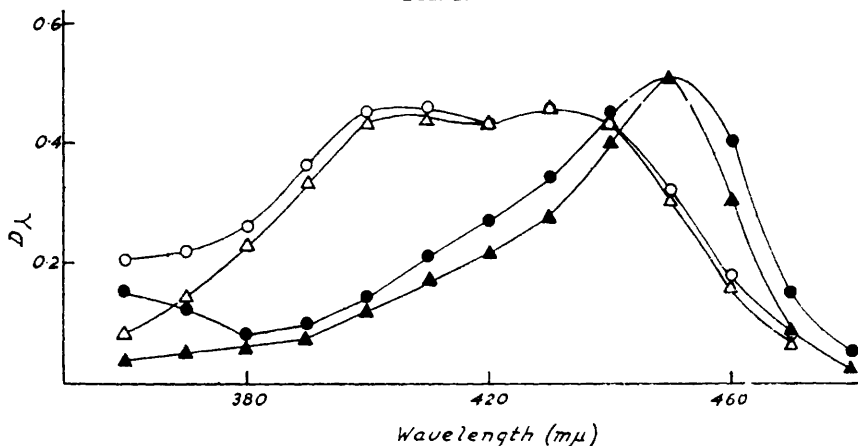
O Mercuric bromide (total concn. $1\cdot92 \times 10^{-2}$ mole $l.^{-1}$) and triphenylmethyl bromide (total concn. $1\cdot56 \times 10^{-5}$ mole $l.^{-1}$) in nitromethane at 16°.
△ Triphenylmethyl alcohol (concn. $1\cdot197 \times 10^{-5}$ mole $l.^{-1}$) in 98% sulphuric acid.
● Mercuric bromide (total concn. $1\cdot099 \times 10^{-2}$ mole $l.^{-1}$) and tri-p-tolylmethyl bromide (total concn. $7\cdot19 \times 10^{-6}$ mole $l.^{-1}$) in nitromethane at 16°.
▲ Tri-p-tolylmethyl alcohol (concn. $6\cdot538 \times 10^{-6}$ mole $l.^{-1}$) in 98% sulphuric acid.

these solutions was the same as in concentrated sulphuric acid. We justified this assumption on the grounds that the spectra of the ion in these solutions were almost identical. The assumption has now been tested as follows.

The addition of mercuric chloride to a nitromethane solution of triphenylmethyl chloride very markedly increases the ionization of the organic chloride. As shown in Part I, this involves the formation of ion pairs $Ph_3C^+HgCl_3^-$ and of free ions $Ph_3C^+ + HgCl_3^-$. If, in a given case, mercuric halide could be added to a triarylmethyl halide until no further increase in ionization occurred, we should know that complete ionization had been reached, and the calculated carbonium ion concentration for this solution should then indicate 100% ionization. These conditions are fulfilled for the addition of mercuric bromide to nitromethane solutions of triphenylmethyl or tri-*p*-tolylmethyl bromide. (The bromides, being more easily ionized than the chlorides, give complete ionization more easily.) For these solutions we find that when no further increase

in ionization occurs with increase in mercuric bromide concentration, our method of calculating the carbonium ion concentration gives 100% ionization, within the experimental accuracy.

EXPERIMENTAL

Materials and Purification.—Nitromethane was obtained and purified as described by A. G. Evans, Jones, and Osborne (*Trans. Faraday Soc.*, 1954, **50**, 16). Triphenylmethyl bromide and tri-*p*-tolylmethyl bromide were prepared from the corresponding alcohols as described by A. G. Evans, McEwan, Price, and Thomas (preceding paper).

Mercuric bromide was an " AnalaR " product, sublimed before use.

Experimental Procedure.—This was the same as previously described (for references see *idem, loc. cit.*).

Fig. 2.

$$10^3 \times \left[\textit{Total mercuric bromide} \right] \left(\textit{mole l.}^{-1} \right)$$
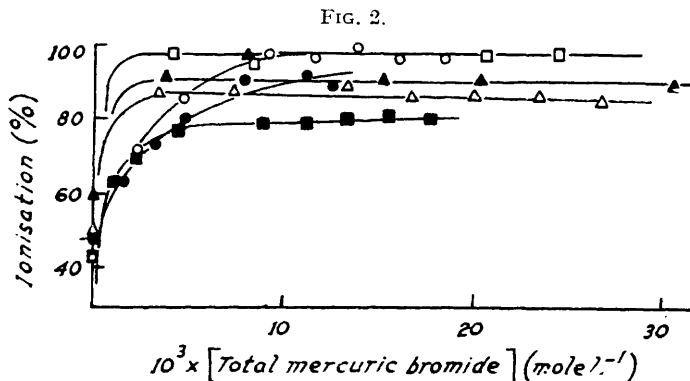
Tri-p-tolylmethyl bromide concn. : ○ 6·88, ● 7·19, △ 13·74, □ 13·76, ▲ 20·60 × 10^{-6} *mole l.*$^{-1}$.

Triphenylmethyl bromide concn. : 29·96 × 10^{-6} *mole l.*$^{-1}$.

Results.—Fig. 1 shows the spectra of the nitromethane solutions containing triarylmethyl bromide and mercuric bromide together with those of the corresponding alcohols in 98% sulphuric acid. The very close similarity for the two solvents establishes that the triarylmethyl ion is present in these nitromethane solutions. The percentage ionization has been calculated on the assumption that $\int D_\lambda d\lambda$ is the same for the two solutions containing the same concentration of triarylmethyl ions. [The alternative method of calculating the ionic concentration, by assuming $(D_\lambda)_{max.}$ to be the same for the same ionic concentration, leads to values which are identical, within experimental error, with the values used.] In Fig. 2 the percentage ionization, thus determined, is plotted against the total mercuric bromide concentration : when there is no further change of ionization the calculated percentage is between 80 and 100. This establishes that our method of calculating the carbonium ion concentration is correct within 20% and, therefore, that the values of $\Delta G°_{1a}$ and $\Delta G°_{2a}$ given in Part I are correct to within the experimental accuracy quoted there.

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