224. *The Ionisation of Triphenylmethyl Bromide by Stannic Bromide.*

By Fred Fairbrother and Bernard Wright.

The ionisation of triphenylmethyl bromide by stannic bromide has been measured spectrophotographically in several solvents, and the equilibrium constants for the respective ionogenic and dissociation reactions calculated. The percentage ionisation in a given solvent varies linearly with the concentration of the solute, and varies with the solvent, from about 0·03% in very dilute benzene solution to about 8% in 5 × 10^{-3} M-ethyl bromide. Substitution of one bromine atom by a methyl radical destroys the ionising power in benzene solution.

In a previous communication (Fairbrother, *J.*, 1945, 503) the ionisation of the carbon–halogen bond in triphenylmethyl bromide by a catalytic inorganic halide was discussed, and a rough estimate of the extent of the ionisation by stannic bromide and by boron tribromide obtained from a study of the colour intensities of a few solutions of the respective complex compounds

* The size of the samples was restricted to 10 g. by the limited amount of pure ester available.

in benzene. An extended series of quantitative measurements of this ionisation by stannic bromide has now been made, and the equilibrium constants of the ionogenic and dissociation reactions :

$$(C_6H_5)_3CBr + SnBr_4 \rightleftharpoons [(C_6H_5)_3C^+\cdot SnBr_5^-]^0 \rightleftharpoons (C_6H_5)_3C^+ + SnBr_5^-$$

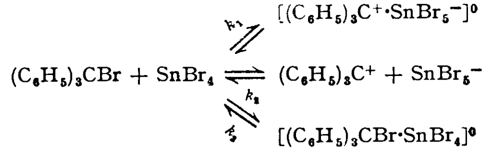
determined in several solvents. The percentage of the triphenylmethyl bromide–stannic bromide complex which, on dissolution, is ionised, varies from about 0·03% in very dilute benzene solution to about 8% in 5 × 10⁻³ M-ethyl bromide solution : most of the remainder appears to revert to the original components.

In the present work the ionisation was determined by the measurement, in the several solvents, of the molar extinction coefficient of the complex at the maximum of the absorption band in the neighbourhood of $\nu = 2300$ mm.$^{-1}$ and the comparison of this with the molar extinction coefficient of completely ionised triphenylmethyl salts. The latter was re-determined by the measurement of the light absorption by solutions of triphenylcarbinol in concentrated sulphuric acid and a value of 35,000 obtained, which is in good agreement with the work of Anderson (*J. Amer. Chem. Soc.*, 1935, **57**, 1673) on the light absorption of the triphenylmethyl cation. Moreover, the characteristic double-humped maximum of the absorption band was also observed in the present work, confirming that the absorption measured was in fact due to the triphenylmethyl cation.

Extinction measurements were made in each solvent at six or seven concentrations, an average of seven separate determinations at each concentration being made for benzene solutions, and from one to four in the remaining solvents. Control determinations showed that the ionisation of pure triphenylmethyl bromide in the several solvents was negligible in comparison with the ionisation of the complex.

The molar extinction coefficient of the complex in the several solutions is observed to vary almost linearly with the concentration of the solution, the slopes of the lines, which do not pass through the origin, varying with the nature of the solvent. The relationship, shown in the figure, may most easily be explained as follows. The dissolution of the triphenylmethyl bromide–stannic bromide complex is equivalent to the addition of equimolar quantities of stannic bromide and triphenylmethyl bromide, and indeed is prepared in this manner. At equilibrium we may conceivably have in solution free components, components which are in dipolar association or as some non-ionically bound complex, ion pairs, and free ions. Only the last two give rise to the visible colour, and the total concentration of carbonium ions as measured spectrophotographically is made up of their sum, since the absorption bands of associated ions (ion pairs) and of the same ions when dissociated are usually so alike as to be indistinguishable.

If we write the equilibria formally in terms of the free components, then



$$\begin{array}{lcl} & \overset{k_1}{\rightleftharpoons} & [(C_6H_5)_3C^+\cdot SnBr_5^-]^0 \\ (C_6H_5)_3CBr + SnBr_4 & \overset{k_2}{\rightleftharpoons} & (C_6H_5)_3C^+ + SnBr_5^- \\ & \underset{k_3}{\rightleftharpoons} & [(C_6H_5)_3CBr\cdot SnBr_4]^0 \end{array}$$

the free ions being actually in direct equilibrium with the ionised but undissociated complex, *viz.*,

$$[(C_6H_5)_3C^+\cdot SnBr_5^-]^0 \underset{k'}{\rightleftharpoons} (C_6H_5)_3C^+ + SnBr_5^-$$

We cannot at present evaluate k_3, but the evidence indicates that it is small. If the non-ionic fraction of the solute remained substantially as a dipolar or co-ordinate complex rather than as free components, then the ionic fraction would vary in a manner different from that observed. The dielectric behaviour of the solutions in benzene is also against any massive formation of such a covalent complex (cf. Fairbrother, *loc. cit.*).

Let the total concentration of double compound dissolved be $[C]$, and the fraction present respectively as ionised but undissociated complex, as free ions, and as un-ionised complex, be α, β, and γ. Also, let the equilibrium constants as written be k_1, k_2, k_3, the numerical magnitudes of which are associated with the expression of all concentrations as molalities, then

$$k_1 = \alpha[C]/\{[C](1-\alpha-\beta-\gamma)\}^2 \text{ and } k_2 = (\beta[C])^2/\{[C](1-\alpha-\beta-\gamma)\}^2$$

Since the percentage of the solute which is ionised is in general small (0·3% in the most concentrated benzene solution, 3—4% in other solvents, and some 4—8% in ethyl bromide), and, since the experimental variations inherent in the spectrophotographic method do not justify a more exact treatment, we can write :

$$k_1 \approx \alpha/[C] \text{ and } k_2 \approx \beta^2 \text{ for } (\alpha + \beta + \gamma) \ll 1$$

Moreover, since the molar extinction coefficient of the triphenylmethyl cation is 35,000 and the fraction of the solute which is ionised is $(\alpha + \beta)$, then the molar extinction coefficient of the solution is

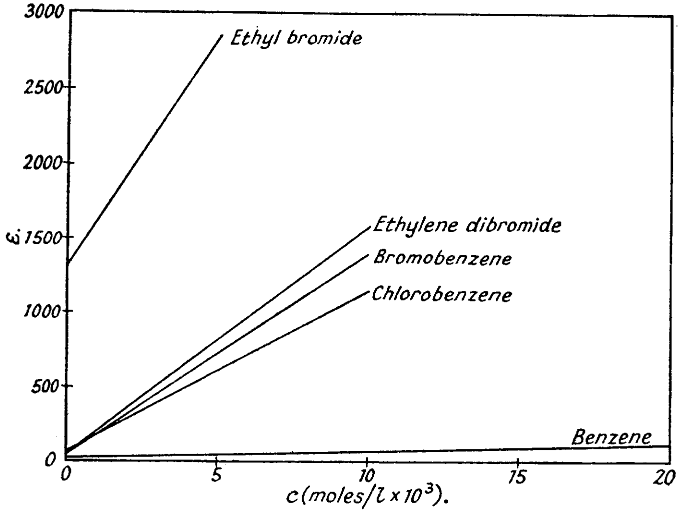
$$\varepsilon = 35{,}000 \times (\alpha + \beta)$$

and as

$$(\alpha + \beta) = k_1 C + \sqrt{k_2}$$

$$\varepsilon = 35{,}000 \times (k_1 C + \sqrt{k_2})$$

Hence, if the molar extinction coefficient is plotted against the molar concentration of the solution we should expect to obtain an approximately straight line with a slope of $35{,}000 \times k_1$ and an intercept at zero concentration of $35{,}000 \times \sqrt{k_2}$.



This does in fact obtain, as can be seen from the figure. These lines, calculated by the method of least squares from the experimental data, have the general form $y = a + bx$, in which for benzene $a = 8{\cdot}88$, $b = 5000$; for ethylene dibromide $a = 55$, $b = 152{,}000$; for bromobenzene $a = 53$, $b = 134{,}000$; for chlorobenzene $a = 78$, $b = 106{,}500$; and for ethyl bromide $a = 1320$, $b = 301{,}000$. Values of k_1 and k_2 calculated from these slopes and intercepts are given in the table, in which also are given $k' = k_2/k_1$, the dissociation constants of the ion pairs, the dielectric constants (D) of the solvents, and, for comparison, the fraction of the solute ionised in 5×10^{-3} M-solution (the highest concentration examined in ethyl bromide solution).

Solvent.	D.	k_1.	k_2.	k'.	Fraction ionised at 0·005M.
Benzene	2·28	0·14	$6{\cdot}4 \times 10^{-8}$	$4{\cdot}6 \times 10^{-7}$	0·0009
Ethylene dibromide	4·9	4·3	$2{\cdot}4 \times 10^{-6}$	$5{\cdot}6 \times 10^{-7}$	0·023
Bromobenzene	5·4	3·8	$2{\cdot}3 \times 10^{-6}$	$6{\cdot}1 \times 10^{-7}$	0·021
Chlorobenzene	5·9	3·0	$5{\cdot}0 \times 10^{-6}$	$1{\cdot}7 \times 10^{-6}$	0·017
Ethyl bromide	9·5	8·6	$1{\cdot}4 \times 10^{-3}$	$1{\cdot}6 \times 10^{-4}$	0·081

It must be concluded from the above considerations that even in benzene solutions a small fraction of the ions are free. It is possible that the existence of these free ions may contribute more to the abnormally high apparent molar dielectric polarisation of the ionic form, previously noted, than the presence of an un-ionised complex. The actual concentration of such free ions, however, is so small that, coupled with their large volume and therefore low mobility, the conductivities of the benzene solutions are too low to introduce any observable damping in the dielectric-constant measurements by the heterodyne method. A small conductivity in dry benzene solution, however, can be observed with a sensitive galvanometer.

It may be observed that both the total amount of ionisation and the fraction of this which is present as free ions show a general increase with the dielectric constant of the solvent. The choice of solvent was restricted to those which did not interact with the stannic bromide.

A few experiments similar to those described above were carried out with mixtures of triphenylmethyl bromide and methyltribromotin in benzene solution. The results were sufficient to show that, at all events in benzene solution, little if any ionisation of the triphenylmethyl bromide occurs. Thus, the substitution of a methyl radical for a bromine atom in stannic bromide practically destroys the catalytic activity of the stannic compound. This result is to be attributed to a redistribution of electronic charge within the molecule, in the direction of a lessened ionic character of the Sn⁻Br bonds, an effect which is also manifested in the extension of carbon–halogen bond length when three of the halogen atoms in a stannic halide are successively replaced by methyl radicals (Skinner and Sutton, *Trans. Faraday Soc.*, 1944, **40**, 164).

EXPERIMENTAL.

Materials.—The triphenylmethyl bromide–stannic bromide double compound was prepared as before (Fairbrother, *loc. cit.*) by mixing equimolar quantities of the components, dissolved in sufficient warm benzene to prevent immediate precipitation, and allowing the solution to cool slowly. Solvents were purified and dried by methods appropriate to each.

Measurements.—The molar light-extinction coefficients were measured with the aid of a Hilger E2 quartz spectrograph, iron arc, and rotating-sector photometer, in the usual manner, with the following modifications. The photographic plates ordinarily used for ultra-violet spectrophotography proved to be inconveniently slow in the region of the absorption band of the triphenylmethyl cation, which is in the visible region of the spectrum, and we are indebted to Messrs. Ilford Ltd. for a specially cut supply of Ilford Press Ortho (Series II) which greatly speeded the determinations and minimised any change in the solutions during measurement. The location of the match points was greatly facilitated by printing positives on a glossy high-contrast contact paper. Pure solvent was used in the comparison cells except in measurements on mixtures of triphenylmethyl bromide and methyltribromotin, for which a solution of the tin compound was used for comparison in order to compensate for a slight colour instability of the latter. The cells varied in depth from 4 cm. for dilute benzene solutions to 1 mm. for the most concentrated ethyl bromide solutions. Measurements were made in a basement room of even temperature (*ca.* 15°) : control measurements showed that effects of variation of temperature on the ionisation, far greater that those experienced, would not be detected.

We are indebted to the Anglo Iranian Oil Co, Ltd., for a grant to one of us (B. W.) during this work.

THE UNIVERSITY OF MANCHESTER. [*Received, September 25th,* 1948.]