*The Effect of Solvent on the Ionization of Organic Halides.   Part III.**
The Extinction Coefficients of Carbonium Ions.

By Alwyn G. Evans, I. H. McEwan, A. Price, and J. H. Thomas.

[Reprint Order No. 6368.]

When the ionization of triarylmethyl chlorides, RCl, was studied by measuring the carbonium-ion concentration spectrophotometrically, it was assumed that the extinction coefficient of the ion R^+ was the same for ion pairs $R^+Cl^-_{solv.}$ or free ions $R^+_{solv.} + Cl^-_{solv.}$ as in concentrated sulphuric acid. We have now established that the value of $\int D_\lambda d\lambda$ for a m-cresol solution containing R^+ ions is the same as for a concentrated sulphuric acid solution of the same R^+ ion concentration.

In previous work (Bentley, A. G. Evans, and Halpern, *Trans. Faraday Soc.*, 1951, **47**, 711; Bentley and A. G. Evans, *J.*, 1952, 3468; A. G. Evans, Jones, and Osborne, *Trans. Faraday Soc.*, 1954, **50**, 16, 470; *J.*, 1954, 3803; A. G. Evans, Price, and Thomas, *Trans. Faraday Soc.*, 1954, **50**, 378), the ionization of triarylmethyl chlorides in various solvents has been studied by measuring the concentration of the carbonium ions spectrophotometrically, assuming that the extinction coefficient of the R^+ ion (whether as an ion pair $R^+Cl^-_{solv.}$ or as free ions $R^+_{solv.} + Cl^-_{solv.}$) is the same as it is in concentrated sulphuric acid. We justified

* Part II, A. G. Evans, Price, and Thomas, *Trans. Faraday Soc.*, 1955, **51**, 481.

this assumption by the fact that the spectrum of the R⁺ ion in all the solvents used was so very similar in shape to that in concentrated sulphuric acid. We have now confirmed this assumption.

We chose a solvent of high ionizing power and a triarylmethyl chloride of marked ionizing tendency in the hope that under these conditions there would be complete ionization of the chloride. If this were attained, then our method of calculating the R⁺ ion concentration should give 100% ionization. As a test for complete ionization, we have made use of the fact that, in general, a bromide RBr is more extensively ionized than is the corresponding chloride. Thus, when the latter is not completely ionized, the percentage ionization should increase on changing to the corresponding bromide. In contrast, when the chloride is completely ionized, the percentage ionization should not increase on changing to the bromide.

m-Cresol is a powerfully ionizing solvent, and in this solvent we find that the change from triphenylmethyl chloride to triphenylmethyl bromide gives a marked increase in optical density (for a given RHal concentration), showing incomplete ionization in the triphenylmethyl chloride solution. The change from tri-*p*-tolylmethyl chloride to tri-*p*-tolylmethyl bromide, on the other hand, causes no such increase, and this shows that both tri-*p*-tolylmethyl halides are completely ionized in these solutions. Calculation of the percentage ionization of tri-*p*-tolylmethyl halides in these solutions, by the $\int D_i \mathrm{d}\lambda$ method we have used previously, gave values of 100% within the experimental accuracy.

Materials.—*m*-Cresol, from Hopkin and Williams, was 98% pure. It was distilled, and the fraction boiling between 200° and 202° was collected. Further distillation had no effect on the results obtained. Triphenylmethyl bromide (m. p. 152°) and tri-*p*-tolylmethyl bromide [m. p. 170° (decomp.)] were obtained as white crystals by the action of redistilled acetyl bromide on the corresponding alcohol. The products were recrystallized, until colourless, from light petroleum (b. p. 40—60°) which had been dried over phosphoric oxide. Triphenylmethyl chloride and tri-*p*-tolylmethyl chloride were obtained as described by A. G. Evans, Jones, and Osborne (*Trans. Faraday Soc.*, 1954, **50**, 16).

m-Tolyl triphenylmethyl ether, m. p. 103°, was prepared from the sodium derivative of *m*-cresol and triphenylmethyl chloride (Schorigin, *Ber.*, 1926, **59**, 2506).

Procedure.—The solutions were examined as described in the papers quoted above.

RESULTS

Spectra.—The spectra of the solutions of triarylmethyl halides in *m*-cresol are shown in Fig. 1. It is seen that the spectrum of the *m*-cresol solution of RHal is much broader than that of the R⁺ ion in concentrated sulphuric acid. In the case of the triphenylmethyl halide, this broadening has resulted in the merging of the two peaks. For the tri-*p*-tolylmethyl halide, there is a slight peak shift. In spite of these small changes, however, it is quite clear that these spectra are those of the R⁺ ion.

Dependence of R⁺ Ion Concentration on RHal Concentration.—In Fig. 2 we show how the R⁺Hal⁻ concentration (calculated as described below) depends on the concentration of un-ionized halide for triphenylmethyl halide, and on the concentration of the total halide for tri-*p*-tolylmethyl halide. It is seen that all the solutions give good straight lines.

Dependence of [R⁺Hal⁻]/[RHal] *on Temperature.*—In Fig. 3 is shown the dependence of $\log_{10}$[R⁺Hal⁻]/[RHal] on $1/T$ for the triphenylmethyl halides. These plots have not been corrected for the small volume change of the solvent with temperature (Int. Crit. Tab., **3**, 29). This volume change has been taken into account in calculating the $\Delta H°_1$ values from these plots (see Table 2). (This correction is 0·2 kcal. mole⁻¹.) The slope of these plots does not vary with the total halide concentration. (It is seen that solutions of the halide having different optical densities at 21° give the same slope.)

At high temperatures it was found that for solutions of RHal in *m*-cresol the optical density decreased with time. This is due to the reaction between the halide and the solvent which gives hydroxy-substituted tetraphenylmethane (Hantzsch, *Ber.*, 1921, **54**, 2595). This reaction is so slow at room temperature that it did not cause any change of

FIG. 1.
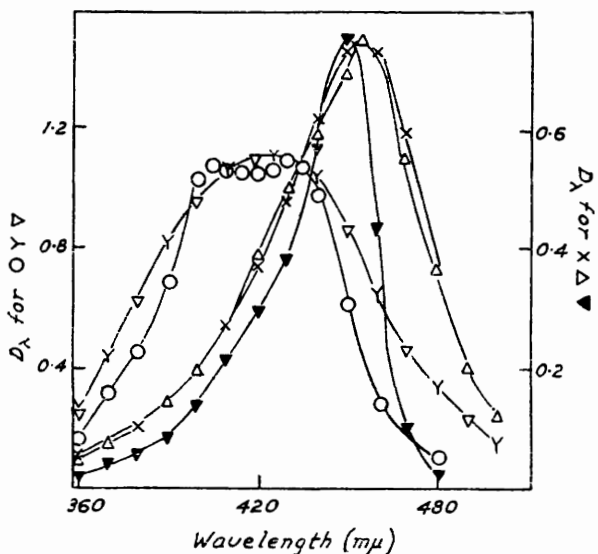
O *Triphenylmethyl alcohol in 98% H_2SO_4 (2.93×10^{-5} mole l.$^{-1}$).*
Y *Triphenylmethyl chloride in m-cresol at 18° (10.5×10^{-5} mole l.$^{-1}$).*
▽ *Triphenylmethyl bromide in m-cresol at 18° (5.6×10^{-5} mole l.$^{-1}$).*
▼ *Tri-p-tolylmethyl alcohol in 98% H_2SO_4 (0.96×10^{-5} mole l.$^{-1}$).*
✕ *Tri-p-tolylmethyl chloride in m-cresol at 18° (1.55×10^{-5} mole l.$^{-1}$).*
△ *Tri-p-tolylmethyl bromide in m-cresol at 18° (1.71×10^{-5} mole l.$^{-1}$).*

FIG. 2. *Solutions in m-cresol at 18°.*
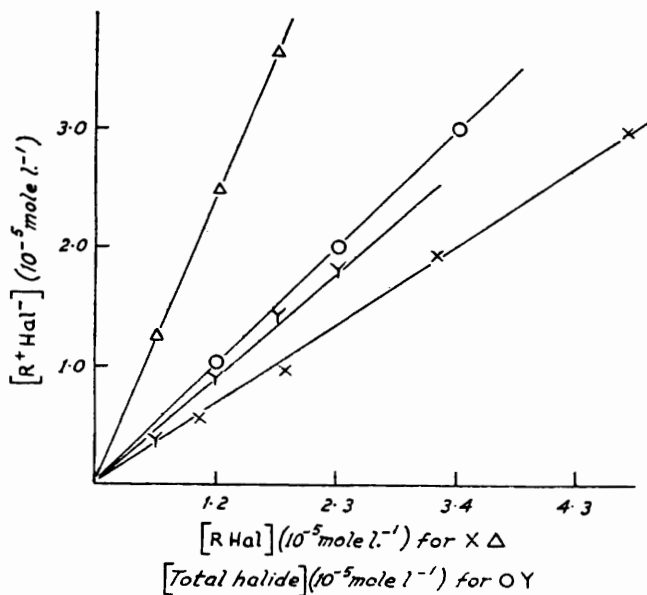
✕ *Triphenylmethyl chloride.*   O *Tri-p-tolylmethyl chloride.*
△ *Triphenylmethyl bromide.*   Y *Tri-p-tolylmethyl bromide.*

optical density over the time of our concentration-dependence experiments. The temperature-dependence experiments were carried out over a temperature range of 9—25° and the optical density of the solution at any temperature within this range was reproducible over the time of the experiments. (See Fig. 3, in which the points are numbered to show the sequence in which the temperature was varied.)

FIG. 3. *The actual value of* D_{21}, *the optical density at 21°, as measured on the photomultiplier is given below for each solution. The value of* D_{21} *is directly proportional to the concentration of ions, and this is directly proportional to the halide concentration.*
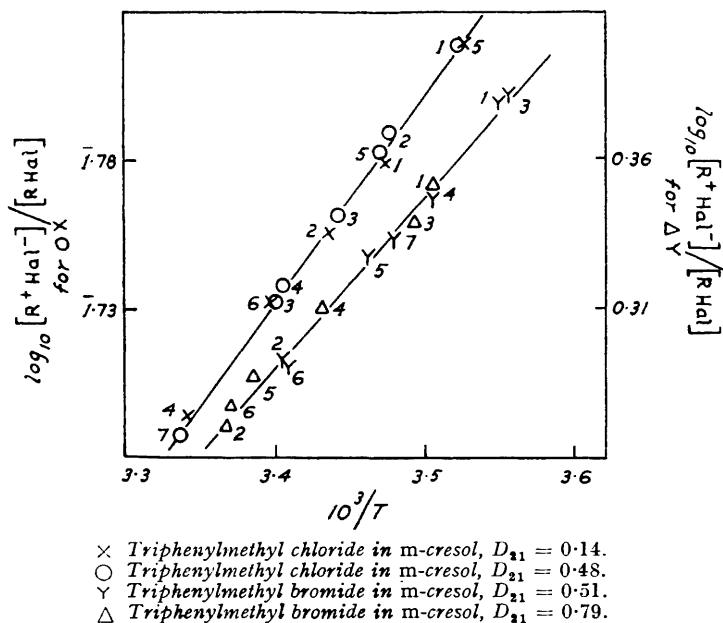

X *Triphenylmethyl chloride in* m-*cresol*, $D_{21} = 0.14$.
O *Triphenylmethyl chloride in* m-*cresol*, $D_{21} = 0.48$.
Y *Triphenylmethyl bromide in* m-*cresol*, $D_{21} = 0.51$.
△ *Triphenylmethyl bromide in* m-*cresol*, $D_{21} = 0.79$.

Table 1, column 3, gives the values of [R⁺Hal⁻]calculated for typical experiments on the assumption that $\int D_\lambda d\lambda$ is the same in these solutions as in concentrated sulphuric acid for the same concentration of carbonium ions. (This was the method used for calculating

TABLE 1.

	[Total halide] (10^{-5} mole l.$^{-1}$)	[R⁺Hal⁻] (10^{-5} g.-ion l.$^{-1}$)	Ionization (%)
Triphenylmethyl chloride	4·91	1·75	36 ± 4
Triphenylmethyl bromide	7·50	5·10	68 ± 7
Tri-*p*-tolylmethyl chloride	0·995	1·00	100 ± 10
Tri-*p*-tolylmethyl bromide	0·99	0·899	91 ± 10

[R⁺Hal⁻] in Figs. 2 and 3.) Using these values, we have calculated the percentage ionization in the various solutions (see column 4); these are reproducible to the limits given. For triphenylmethyl halides, where the change from chloride to bromide produces a twofold increase in the percentage ionization, it is seen that the calculated percentage ionization is much less than 100%. For tri-*p*-tolylmethyl halides, where the change from chloride to bromide causes no appreciable variation in percentage ionization, the calculated percentage ionization is 100%, within the experimental accuracy. This establishes that our method of calculating the concentration of carbonium ions is valid.

If we calculate the carbonium-ion concentration by the alternative assumption that $(D_\lambda)_{max.}$ is the same in these solutions as in concentrated sulphuric acid for the same concentration of ions, we obtain the following values for the percentage ionization at the total halide concentration given in parentheses : triphenylmethyl chloride ($4·91 \times 10^{-5}$ mole/l.)

30%; triphenylmethyl bromide $(7.50 \times 10^{-5}$ mole/l.) 55%; tri-*p*-tolylmethyl chloride $(0.995 \times 10^{-5}$ mole/l.) 63%; tri-*p*-tolylmethyl bromide $(0.99 \times 10^{-5}$ mole/l.) 55%. These values are smaller than those calculated by the $\int D_\lambda \mathrm{d}\lambda$ method. This is the first solvent we have studied in which these two methods give appreciably different results, and this difference arises because the carbonium-ion spectrum is so much broader in *m*-cresol than it is in concentrated sulphuric acid, and because the extent of ionization in this solvent is so high. Although these values are smaller than those obtained by the $\int D_\lambda \mathrm{d}\lambda$ method, they show the same features, that is, a marked increase (two-fold) in percentage ionization for the change from triphenylmethyl chloride to triphenylmethyl bromide, and no increase in percentage ionization (within the experimental accuracy) from tri-*p*-tolylmethyl chloride to tri-*p*-tolylmethyl bromide. Thus, in a case like this, when the shape of the absorption spectrum is such that the $\int D_\lambda \mathrm{d}\lambda$ and the $(D_\lambda)_{\max}$ method give appreciably different values for the carbonium-ion concentration, the fact that the $\int D_\lambda \mathrm{d}\lambda$ method gives a value of 100% ionization when we know the ionization to be complete shows that it is the better method.

Since for triphenylmethyl chloride and triphenylmethyl bromide the plots of $[\mathrm{R^+Hal^-}]$ against $[\mathrm{RHal}]$ are straight, and since further the slope of the plot of $\log_{10}([\mathrm{R^+Hal^-}]/[\mathrm{RHal}])$ against $1/T$ does not vary with the total halide concentration, the only detectable equilibrium present in these solutions is of the type :

$$\mathrm{RHal} \underset{(b)}{\overset{(a)}{\rightleftharpoons}} \mathrm{R^+Hal^-} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$
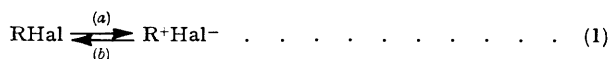
It is reasonable to assume that this will also be the case in the solutions of tri-*p*-tolyl-methyl chloride and bromide in *m*-cresol, although we cannot demonstrate this since there is complete ionization.

We can summarize the results given in Table 1 by saying that the value of $\int D_\lambda \mathrm{d}\lambda$ for the carbonium ion when it is present in $\mathrm{R^+Hal^-_{solv.}}$ ion pairs in *m*-cresol is the same, within experimental error, as when it exists in the absence of ion pairs in concentrated sulphuric acid. Thus this very great change in environment does not affect the light absorption of the carbonium ion appreciably.

In Table 2 are given the values of the thermodynamic constants for equilibrium (1) obtained from the results given in Figs. 2 and 3 in the way described in our earlier papers. We estimate the accuracy of ΔG°_{1a} to be within ± 0.1 and ± 0.2 kcal. mole^{-1} for triphenyl-methyl chloride and triphenylmethyl bromide respectively, and the accuracy of ΔH°_{1a} to be within ± 0.2 kcal. mole^{-1} for both halides. The corresponding thermodynamic constants cannot be given for the tri-*p*-tolylmethyl halides since, for these halides, there is complete ionization within experimental accuracy. From the results we see that *m*-cresol is a most powerful ionizing solvent. Comparing the values obtained at 20° for triphenyl-methyl chloride in nitromethane $(K_1 = 4.4 \times 10^{-4}, \Delta G^\circ_{1a} = 4.5$ kcal. mole^{-1}, $\Delta H^\circ_{1a} = 1.4$ kcal. mole^{-1}, and $\Delta S^\circ_{1a} = -10.5$ cal. deg.$^{-1}$ mole^{-1} (A. G. Evans, Bentley, and Halpern; A. G. Evans, Jones, and Osborne, *locc. cit.*) with those given in Table 2 for *m*-cresol, we see

TABLE 2.

	K_1 (18°)	ΔG°_{1a} (18°) (kcal. mole^{-1})	ΔH°_{1a} (kcal. mole^{-1})	ΔS°_{1a} (cal. deg.$^{-1}$ mole^{-1})
Triphenylmethyl chloride ...	0.56	0.34	-3.0	-11.5
Triphenylmethyl bromide ...	2.12	-0.43	-2.4	$- 6.9$

that the change from nitromethane to *m*-cresol gives a 1000-fold increase in K_1, the equilibrium constant of reaction (1). This marked increase in the degree of ionization corresponds to a decrease in ΔG°_{1a} of 4.16 kcal. mole^{-1}, and this involves ΔH°_{1a} becoming more negative by 4.4 kcal. mole^{-1} and ΔS°_{1a} remaining unchanged. Thus the entropy of ionization in *m*-cresol is much the same as it is in nitromethane, but the ionization is much more exothermic. The dielectric constant of *m*-cresol, 12.4, is much less than that of nitro-methane 37.4 (Maryott and Smith, U.S. Nat. Bur. Stand., Circular No. 514, 1951). Thus
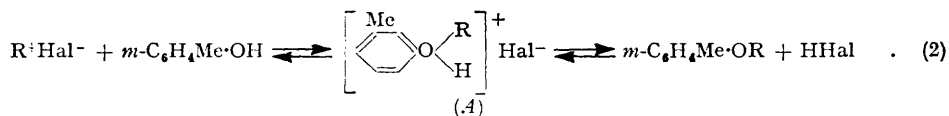
if the solvent effect of *m*-cresol were determined by its dielectric constant according to the relation between free energy of ionization and dielectric constant obtained for the nitro-solvents (A. G. Evans, Price, and Thomas *loc. cit.*), we should expect the ionization of triphenylmethyl chloride in *m*-cresol to be so low that it could not be measured. We attribute the exceptional ionizing power of this solvent to the formation of hydrogen bonds between the hydroxyl group of the *m*-cresol and the Hal^- ion of the R^+Hal^- ion pair. Hydrogen bonding of the solvent with the Hal^- ion has been postulated earlier (*idem, loc. cit.*), to account for the fact that acetic acid is a better ionizing solvent than one would expect from its low dielectric constant. Hammett ("Physical Organic Chemistry," McGraw-Hill, New York, 1940, p. 54) has referred to this effect in considering the action of solvents on the ionization of triphenylmethyl chloride.

We also see in Table 2 that the change from chloride to bromide causes a four-fold increase in K_1, which corresponds to a decrease of 0·77 kcal. mole^{-1} in $\Delta G°_{1a}$. This increase in ionization from chloride to bromide is seen to be due to the more positive entropy of ionization of the bromide than of the chloride. We believe this to be due to the increase in size of the negative ion and the consequent reduction in the extent of "freezing" of solvent around this ion.

We have calculated the $\Delta G^{\ddagger}$ values for the S_N1 reactions of *tert.*-butyl chloride and bromide in 80% aqueous ethyl alcohol from the velocity constants obtained by Hughes (*J.*, 1935, 225) and Cooper and Hughes (*J.*, 1937, 1183) at 25°. These show a decrease of 2·1 kcal. mole^{-1} from chloride to bromide, and this decrease runs parallel to the decrease of 0·77 kcal. mole^{-1} which we obtain in $\Delta G°_{1a}$.

Thus the change from chloride to bromide has an effect on the $\Delta G^{\ddagger}$ for S_N1 reactions which runs parallel to its effect on the $\Delta G°_{1a}$ value for reaction (1*a*) (cf. our previous papers).

The validity of our K values depends upon there being no appreciable concentration of uncoloured ions of the type (*A*) in which the R is covalently bonded to a solvent molecule (see Part II for a discussion of this point). If this ion were formed we should expect equilibria of the following type to exist :

$$R^+Hal^- + m\text{-}C_6H_4Me\cdot OH \rightleftharpoons \left[\begin{array}{c} Me \\ \bigcirc O \begin{array}{c} R \\ H \end{array} \end{array} \right]^+ Hal^- \rightleftharpoons m\text{-}C_6H_4Me\cdot OR + HHal \quad . \quad (2)$$
$$(A)$$

since we know that the action of hydrochloric acid on a *m*-cresol solution of *m*-tolyl triphenylmethyl ether produces the characteristic R^+ spectrum. If such equilibria involved an appreciable concentration of positive ions such as (*A*) we should expect that the addition of excess of *m*-tolyl triphenylmethyl ether would have a marked effect on the equilibrium concentration of the carbonium ions. We find that the addition of this substance in a concentration one hundred times greater than that of the chloride has no effect on the optical density of a solution of triphenylmethyl chloride in *m*-cresol. We believe this to be strong evidence for our assumption that ions such as (*A*), if present, are in negligible concentration, and hence that the concentration of un-ionized halide is equal to the total concentration of halide minus the concentration of carbonium ions as measured by our absorption experiments.

CHEMISTRY DEPARTMENT, UNIVERSITY COLLEGE, CARDIFF.