933. *The Effect of Solvents on the Ionisation of Organic Halides. Part V.*[1] *Ionisation in Mixed Solvents.*

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

The ionisation of triphenylmethyl chloride in *m*-cresol–benzene and –hexane, and of tri-*p*-tolylmethyl chloride in *m*-cresol–benzene, –hexane, and –acetic acid has been investigated spectrophotometrically.

We have extended work on the ionisation of triarylmethyl halides in *m*-cresol[1a] to the systems listed in the Summary.

Experimental and Results

Materials.—*m*-Cresol (Hopkin and Williams) was purified as described earlier.[1a] Triphenylmethyl chloride and tri-*p*-tolylmethyl chloride were obtained as described by A. G. Evans, Jones, and Osborne.[2] " AnalaR " acetic acid was purified by Eichelberger and La Mer's method.[3] It was refluxed for 10 hr. with 1% w/w of chromium trioxide, then fractionated between 117·5—118·5°, refluxed for 10 hr. with triacetyl borate, and finally fractionated; the fraction of b. p. 118·1° was collected (b. p. 118·1°/758 mm., f. p. 16·60°; lit.[4]: b. p. 118·1°, f. p. 16·58—16·60°). " AnalaR " benzene was kept over sodium wire and then fractionated from either phosphoric oxide or sodium. The fraction of b. p. 80·0—80·5° was collected. Benzene purified by both methods gave the same results. Hopkin and Williams's hexane (low in

---

[1] (*a*) Part III, Evans, McEwan, Price, and Thomas, *J.*, 1955, 3098; (*b*) Part IV, Evans, Price, and Thomas, *Trans. Faraday Soc.*, 1955, **52**, 332.

[2] A. G. Evans, Jones, and Osborne, *Trans. Faraday Soc.*, 1954, **50**, 16.

[3] Eichelberger and La Mer, *J. Amer. Chem. Soc.*, 1933, **55**, 3633.

[4] Timmermans, " Physico-Chemical Constants of Organic Compounds," Elsevier, 1950, p. 380.

FIG. 1.

▲ Triphenylmethyl chloride concn. 1·581 × 10^{-4} mole $l.^{-1}$ at 16°. *m*-Cresol mole fraction 1·0.
× Triphenylmethyl chloride concn. 4·872 × 10^{-4} mole $l.^{-1}$ at 15°. *m*-Cresol mole fraction 0·772. Benzene mole fraction 0·228.
Y Triphenylmethyl chloride concn. 22·41 × 10^{-4} mole $l.^{-1}$ at 15°. *m*-Cresol mole fraction 0·602. Benzene mole fraction 0·398.
△ Triphenylmethyl chloride concn. 14·83 × 10^{-4} mole $l.^{-1}$ at 15°. *m*-Cresol mole fraction 0·689. Hexane mole fraction 0·311.
□ Tri-*p*-tolylmethyl chloride concn. 1·521 × 10^{-5} mole $l.^{-1}$ at 19°. *m*-Cresol mole fraction 1·0.
○ Tri-*p*-tolylmethyl chloride concn. 1·521 × 10^{-5} mole $l.^{-1}$ at 19°. *m*-Cresol mole fraction 0·953. Benzene mole fraction 0·047.
◐ Tri-*p*-tolylmethyl chloride concn. 4·470 × 10^{-5} mole $l.^{-1}$ at 19°. *m*-Cresol mole fraction 0·286. Benzene mole fraction 0·714.
⅄ Tri-*p*-tolylmethyl chloride conc. 2·98 × 10^{-3} mole $l.^{-1}$ at 19°. Acetic acid mole fraction 1·0.
● Tri-*p*-tolylmethyl chloride concn. 6·143 × 10^{-5} mole $l.^{-1}$ at 21°. *m*-Cresol mole fraction 0·190. Acetic acid mole fraction 0·810.

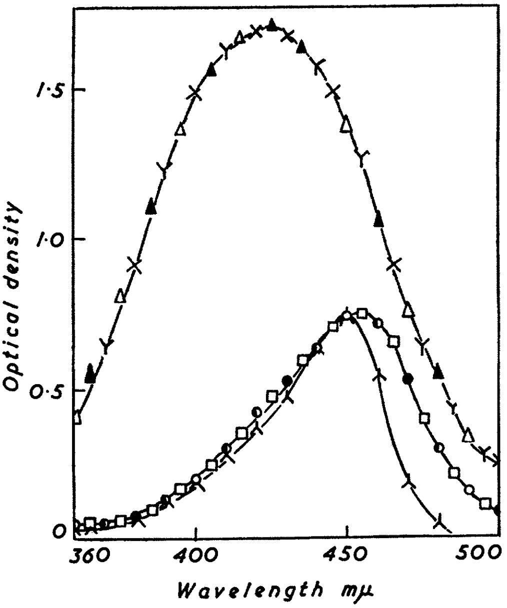


FIG. 2(*a*).

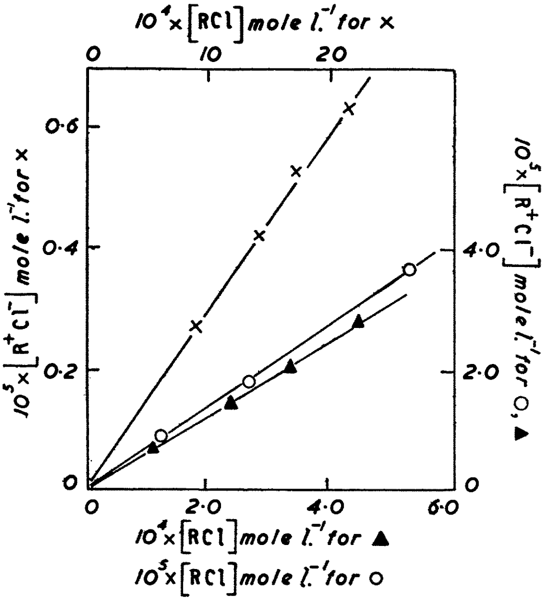


FIG. 2(*b*).

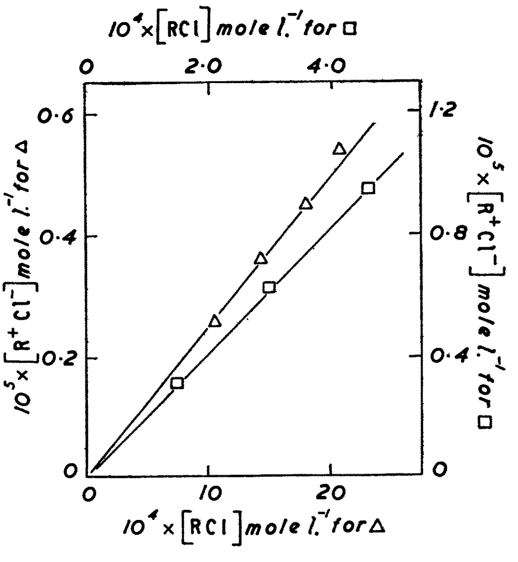


FIG. 2(*a*).

× Triphenylmethyl chloride in *m*-cresol (mole fraction 0·439)–benzene (mole fraction 0·561) at 15°.
○ Tri-*p*-tolylmethyl chloride in *m*-cresol (mole fraction 0·286)–benzene (mole fraction 0·714) at 15°.
▲ Tri-*p*-tolylmethyl chloride in *m*-cresol (mole fraction 0·079)–acetic acid (mole fraction 0·921) at 18°.

FIG. 2(*b*).

△ Triphenylmethyl chloride in *m*-cresol (mole fraction 0·370)–hexane (mole fraction 0·630) at 15°.
□ Triphenylmethyl chloride in *m*-cresol (mole fraction 0·641)–hexane (mole fraction 0·386) at 15°.

aromatic compounds) was purified in the same way as benzene, the fraction of b. p. 68—69° being collected.

Procedure.—The solutions were examined as described in Part III.

Spectra.—Fig. 1 shows typical absorption spectra (*a*) for solutions of triphenylmethyl chloride in pure *m*-cresol,[1a] in *m*-cresol–benzene and in *m*-cresol–hexane, scaled to give the same peak-height, and (*b*) for solutions of tri-*p*-tolylmethyl chloride in pure *m*-cresol, in *m*-cresol–benzene, in *m*-cresol–acetic acid, and in pure acetic acid scaled similarly. The shape of the spectrum in the mixed solvents is identical with that in pure *m*-cresol, and does not have the usual double peak but shows the single broad peak which is obtained in pure *m*-cresol.[1a]

FIG. 3(*a*).

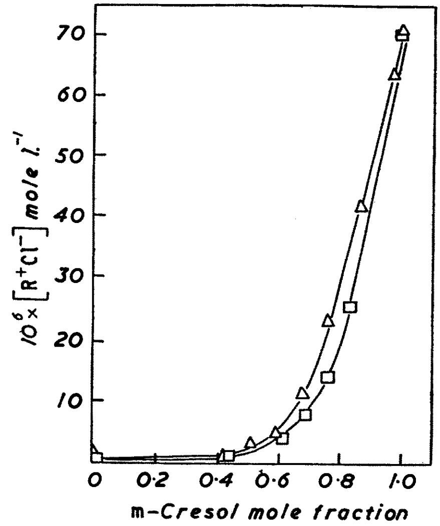


FIG. 3(*c*).

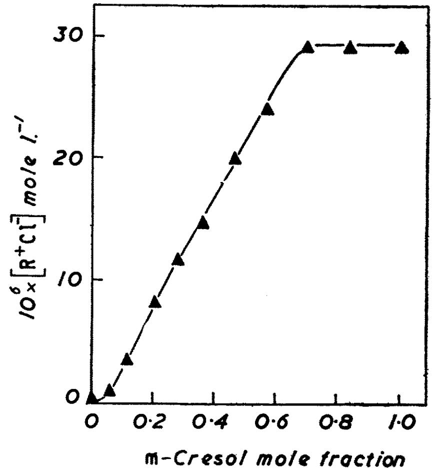


FIG. 3(*b*).

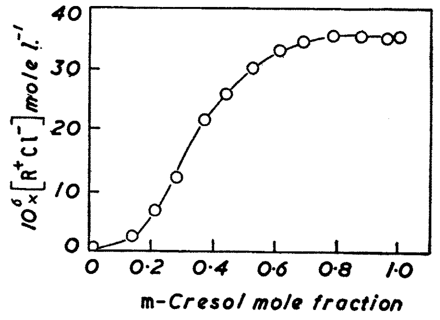


FIG. 3(*a*).

△ Triphenylmethyl chloride in *m*-cresol–benzene (total concn. $1{\cdot}864 \times 10^{-4}$ mole l.$^{-1}$) at 15°.

□ Triphenylmethyl chloride in *m*-cresol–hexane (total concn. $1{\cdot}841 \times 10^{-4}$ mole l.$^{-1}$) at 15°.

FIG. 3(*b*).

m-Cresol–benzene solution of tri-*p*-tolylmethyl chloride (total concn. $3{\cdot}531 \times 10^{-5}$ mole l.$^{-1}$) at 15°.

FIG. 3(*c*).

m-Cresol–acetic acid solution of tri-*p*-tolylmethyl chloride (total concn. $= 2{\cdot}94 \times 10^{-5}$ mole l.$^{-1}$) at 18°.

Dependence of Carbonium-ion Concentration on Triarylmethyl Halide Concentration.—The carbonium-ion concentration was calculated by the $\int D_\lambda d\lambda$ method described in Part III, and in Fig. 2 is plotted against the concentration of un-ionised triarylmethyl halide, obtained by subtracting the ionised from the total triarylmethyl chloride concentration. These good straight lines show that ionisation leads to the formation of ion pairs.

Dependence of Carbonium-ion Concentration on m-*Cresol Concentration.*—Figs. 3*a*, 3*b*, and 3*c* show the effect of changing the *m*-cresol concentration on the carbonium-ion concentration. The mole fractions are calculated on the basis of monomeric molecules.

Cryoscopic Measurements on the m-*Cresol–Acetic Acid System.*—The depression of the freezing point of acetic acid by *m*-cresol, measured in the normal way, shows that in this system the *m*-cresol exists as monomer (Table).

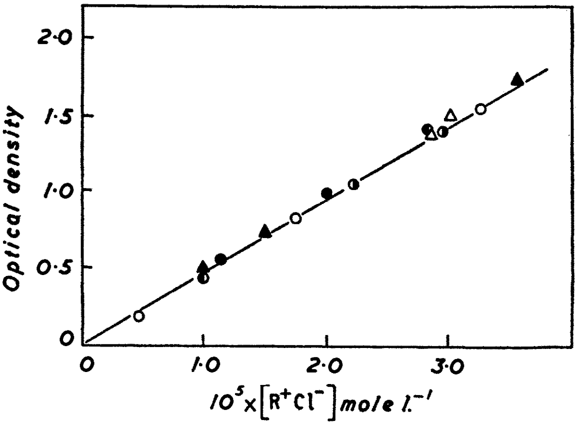
Cryoscopic determination of the molecular weight of m-*cresol in acetic acid.*
(*Calc. for* C_7H_8O; *M*, 108).

m-Cresol (g./1000 g. of acetic acid)	*m*-Cresol (mole fraction)	Δt	*M*
78·16	0·04165	2·71°	111
21·50	0·0118	0·79	107
33·21	0·01811	1·22	106

DISCUSSION

Measurement of Carbonium-ion Concentration.—For triphenylmethyl chloride, the addition of *m*-cresol to a hexane or benzene solution markedly increased the ionisation up to a value of 38% in pure *m*-cresol (Fig. 3*a*). For tri-*p*-tolylmethyl chloride, the addition of *m*-cresol to a benzene or acetic acid solution rapidly increased the ionisation up to an *m*-cresol mole fraction of about 0·7, after which the degree of ionisation is constant (Figs. 3*b* and 3*c*). This constancy shows that in solutions for which the *m*-cresol mole fraction is >0·7 the tri-*p*-tolylmethyl chloride is fully ionised. For these solutions our method[1a] of determining the carbonium-ion concentration gives a value which is the same to within ±5% of that corresponding to 100% ionisation. This fact justifies our $\int D_\lambda d\lambda$ method of obtaining the ionic concentrations. Further, this region of complete ionisation has been obtained for different total tri-*p*-tolylmethyl chloride concentrations, and in Fig. 4 we plot the optical density, D_λ, of these completely ionised solutions of tri-*p*-tolylmethyl chloride against their carbonium-ion concentration. The very good straight line obtained demonstrates that for the optical-density range used, Beer's law is accurately obeyed.

FIG. 4.



D_λ values for completely ionised solutions of tri-*p*-tolylmethyl chloride.

m-Cresol (mole fraction)	▲ 0·953	● 0·862	△ 0·772	◑ 0·843	◐ 0·701	○ 1·0
Benzene (mole fraction)	0·047	0·138	0·228	—	—	—
Acetic acid (mole fraction) ...	—	—	—	0·157	0·299	—

Ionisation Equilibria.—The plot of carbonium-ion concentration against the un-ionised halide gives a straight line (Fig. 2), which shows that ionisation leads to the formation of ion pairs [according to eqn. (1)]. For those tri-*p*-tolylmethyl chloride solutions in which ionisation is complete, it is, of course, impossible to tell by this spectrophotometric method what proportion of the ions are present as ion pairs or as free ions.

Order of Ionisation in m-*Cresol.*—Any analysis of the results obtained in the *m*-cresol–benzene and *m*-cresol–hexane systems is rendered difficult by the considerable complexing to dimers and higher polymers that is a feature of hydroxylic groups in non-polar solvents like benzene and hexane.[5] Thus, when log $[R^+Cl^-]/[RCl]$ is plotted against log [*m*-cresol]

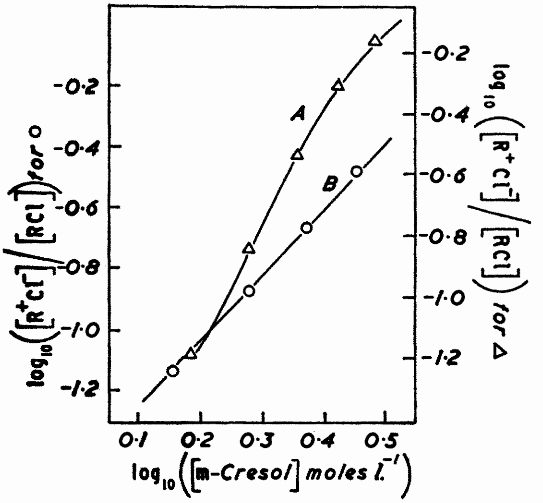
---

[5] Coggeshall and Saier, *J. Amer. Chem. Soc.*, 1951, **73**, 5416.

for the ionisation of tri-*p*-tolylmethyl chloride in *m*-cresol–benzene and *m*-cresol–hexane, under conditions of <25% ionisation (*i.e.* of *m*-cresol mole fraction <0·2; see, *e.g.*, Fig. 5, curve *A*), the slope varies continuously over the concentration range, and this could be due to the various equilibria existing between *m*-cresol monomer and polymer in these inert solvents, and to their differing powers of solvation.

There is considerable evidence, however, that when dissolved in oxygenated solvents, where solvent–hydroxyl complexes may arise (*e.g.* benzoic acid in acetic acid [6]), *m*-cresol is monomeric. We have now shown cryoscopically that *m*-cresol is monomeric in acetic acid up to a mole fraction of 0·04. (Recent work by Boozer, Robinson, Soldatos, Trisler, and Wiley uses the fact that formic and chloroacetic acids are monomeric in acetic acid.[7])

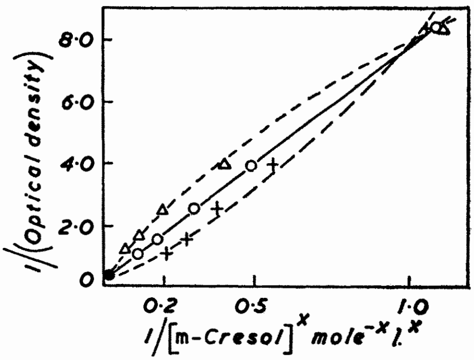
FIG. 5.



○ Tri-*p*-tolylmethyl chloride in *m*-cresol–acetic acid at 20°.

△ Tri-*p*-tolylmethyl chloride in *m*-cresol–benzene at 20°.

FIG. 6.



Tri-*p*-tolylmethyl chloride in *m*-cresol/acetic acid solution at 20°.
△, $x = 2·5$; ○, $x = 2·0$; +, $x = 1·5$; ● Intercept calculated from 1/[total RCl] × ε.

The plot of log [R$^+$Cl$^-$]/[RCl] against log [*m*-cresol] for tri-*p*-tolylmethyl chloride in *m*-cresol–acetic acid under conditions of <25% ionisation (*i.e.*, *m*-cresol mole fraction <0·2) gives a straight line of slope 2 (curve *B*, Fig. 5), showing that in these mixtures the order in *m*-cresol for the production of ion pairs is 2·1 ± 0·1. Confirmation of this is obtained from the Benesi–Hildebrand plot [8] (Fig. 6) when $1/D_{\lambda,\text{max.}}$ is plotted against $1/[m\text{-cresol}]^x$ over the same range of *m*-cresol concentration for a constant total tri-*p*-tolylmethyl chloride concentration of $8·477 \times 10^{-5}$ mole l.$^{-1}$. [The intercept on the $1/D_{\lambda,\text{max.}}$ axis has been evaluated from the extinction coefficient ε ($4·8 \times 10^{+4}$) of the ion in *m*-cresol (see Fig. 4).] When $x = 2$, a good straight line is obtained, but when $x = 1·5$ or 2·5, deviation from linearity is evident.

Thus in *m*-cresol–acetic acid solution of tri-*p*-tolylmethyl chloride (mole fraction <0·2) we have an ionisation equilibrium of the type

$$(p\text{-Me}\cdot\text{C}_6\text{H}_4)_3\text{CCl} + 2m\text{-CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{OH} \underset{b}{\overset{a}{\rightleftharpoons}} \{(p\text{-Me}\cdot\text{C}_6\text{H}_4)_3\text{C}^+\text{Cl}^-\}_{\text{solv.}} \quad . \quad (4)$$

in which 2 *m*-cresol molecules are involved in the solvation of the ion pair. The thermodynamic constants for this equilibrium at 21° are as follows, for acetic acid solution: K_4 (mole-fraction units), 8·9; ΔG°_{4a}, $-1·3 \pm 0·2$ kcal. mole^{-1}.

---

[6] Lassetre, *Chem. Rev.*, 1938, **20**, 259.
[7] Boozer, Robinson, Soldatos, Trisler, and Wiley, *J. Amer. Chem. Soc.*, 1956, **78**, 3428.
[8] Benesi and Hildebrand, *ibid.*, 1948, **70**, 2703.

Hudson and Saville,[9] in their study of the ionisation of triphenylmethyl chloride in carbon tetrachloride solutions of phenol, have tentatively suggested that the order in phenol for the ionisation is 2 at very low phenol concentration.

We thank the University College, Cardiff, for a British Nylon Spinners Post-graduate Scholarship (to I. H. McE.).

UNIVERSITY COLLEGE, CARDIFF.

[*Received, May* 30*th*, 1957.]

[9] Hudson and Saville, *J.*, 1955, 4130.