49. *The Ionisation of Triphenylmethyl Chloride in Nitromethane.*

By Y. Pocker.

The work of A. G. Evans and his co-workers on the ionisation of triphenylmethyl chloride is revised. Triphenylmethyl chloride, on dissolving in nitromethane, instantaneously develops hydrogen chloride to an extent determined by a simple equation of mass-law type. The hydrogen chloride contributes significantly to the electrical conductance of these solutions, and is concerned with the development of colour.

The addition of tetraethylammonium chloride completely discharges the colour associated with the carbonium ion, whilst the corresponding perchlorate has no effect. The colour discharge by added chloride ions, taken in conjunction with the experimental observations of Evans *et al.*, indicates that the ionised triphenylmethyl chloride in nitromethane is in the form of free ions, rather than ion-pairs, though the chloride ion is largely combined in, or with, hydrogen chloride.

When triphenylmethyl chloride dissolves in nitromethane, the characteristic greenish-yellow colour of the carbonium ion appears to be produced instantaneously. Bentley, A. G. Evans, and Halpern showed [1a] that the ratio of coloured to colourless material is constant, independent of stoicheiometric concentration, so they concluded that the colour arises from the conversion of a small portion of solute molecules into ion-pairs:

$$\mathrm{Ph_3CCl} \rightleftharpoons \mathrm{Ph_3C^+Cl^-};\quad K = [\mathrm{Ph_3C^+Cl^-}]/[\mathrm{Ph_3CCl}]$$

Evans *et al.* developed this further in relation to the effects of substituents on the energetics of this ionisation by use of different triarylmethyl chlorides in various nitroalkanes.[1b–1e]

Formation of Hydrogen Chloride.—When triphenylmethyl chloride dissolves in nitromethane some hydrogen chloride appears to be produced instantaneously (Table 1), in addition to the greenish-yellow colour of the carbonium ion. The optical density of such solutions remained constant for at least one day, notwithstanding the presence of hydrogen chloride. On very long standing in stoppered containers (for about six months) at room temperature, the nitromethane slowly disproportionates to give a white crystalline precipitate, identical with that obtained on leaving dry hydrogen chloride in nitromethane—it is most probably hydroxylamine hydrogen dichloride.

Table 1. *The amounts of hydrogen chloride present in freshly prepared solutions of triphenylmethyl chloride in nitromethane at 25·0°.*

$10^3[\mathrm{Ph_3CCl}]$	120	90·0	60·0	30·0	15·0	15·0	10·0	7·5	3·25
$10^4[\mathrm{HCl}]$	25·5	22	18	12·7	8·8	9·0	7·2	6·25	4·0
10^5k_a	5·52	5·51	5·57	5·66	5·49	5·74	5·58	5·67	5·61

The observed constancy in the $[\mathrm{HCl}]^2/[\mathrm{Ph_3CCl}]$ (bottom row) ratio strongly suggests that hydrogen chloride is formed *via* a route of the type:

$$(a)\ \mathrm{Ph_3CCl} + \mathrm{CH_3{\cdot}NO_2} = \mathrm{X} + \mathrm{HCl};\quad K_a = [\mathrm{HCl}]^2/[\mathrm{Ph_3CCl}]$$

The nature of X has not yet been established, but it might be the triphenylmethyl ester of *aci*-nitromethane.

---

[1] (*a*) Bentley, Evans, and Halpern, *Trans. Faraday Soc.*, 1951, **47**, 711; (*b*) Evans, Price, and Thomas, *ibid.*, 1954, **50**, 568; (*c*) Evans, Jones, and Osborne, *ibid.*, 1954, **50**, 16, 470; (*d*) *idem*, *J.*, 1954, 3803; (*e*) Bayles, Evans, and Jones, *ibid.*, 1957, 1020.

Spectrophotometric measurements, similar to those of Evans and his co-workers,[1a-1e] indicate (Table 3) that triphenylmethyl chloride in nitromethane at 25·0° is ionised to an extent of 0·027%, independently of concentration. A 0·010M-solution has an initial specific conductance, $\kappa = 0{\cdot}185 \times 10^{-5}$ ohm^{-1} cm.$^{-1}$ at 25·0°, when water is rigorously excluded. Conductance registers free ions as opposed to ion-pairs and molecules. If diagnostic, the conductivity test would have indicated a dissociation of about 0·155% to free ions. However, there is no real discrepancy here, since this solution is 0·00072M in hydrogen chloride. An independent test shows that 0·00072M-hydrogen chloride in nitromethane has a specific conductance $\kappa = 0{\cdot}150 \times 10^{-5}$ ohm^{-1} cm.$^{-1}$, so that the specific conductance due to dissociated triphenylmethyl chloride is $0{\cdot}035 \times 10^{-5}$ ohm^{-1} cm.$^{-1}$. The equivalent conductance Λ of many tetra-alkylammonium halides at high dilution [5] is about 120 ohm^{-1} cm.^{2} mole^{-1}; using this value one obtains $2{\cdot}9 \times 10^{-6}$ mole l.$^{-1}$ as the concentration of dissociated triphenylmethyl chloride and the extent of ionisation as 0·029%, in good agreement with the spectrophotometric value.

Effects of Added Tetra-alkylammonium Salts.—According to the ion-pair hypothesis suggested by Evans and his co-workers, solutions of triphenylmethyl chloride in nitromethane should show no " common-ion " depression of the ionisation when a saline chloride is added. However, added tetraethylammonium chloride discharges the colour of the carbonium ion, whilst the perchlorate has no observable effect on the colour. The results are summarised in Table 2 where the calibration of colour in terms of the concentration of triphenylcarbonium ion, $[\mathrm{Ph_3C^+}]$, is made on the assumption [1a-e] that the extinction coefficient of the carbonium ions in nitromethane is the same as in 98% sulphuric acid, where triphenylmethanol is taken to be completely ionised.[2a, b, 3]

TABLE 2. *The effect of added tetra-alkylammonium salts on solutions of triphenylmethyl chloride in nitromethane;* $[\mathrm{Ph_3CCl}] = 0{\cdot}0150$ *and contains* $8{\cdot}8 \times 10^{-4}$M-HCl.

$10^5[\mathrm{NEt_4Cl}]$	$10^6[\mathrm{Ph_3C^+}]$ (g.-ions l.$^{-1}$)	$10^3[\mathrm{NEt_4ClO_4}]$	$10^6[\mathrm{Ph_3C^+}]$
None	4·0	1	4·0
0·75	3·2	2·5	4·0
7·5	0·82	5·0	4·0
75	$<0{\cdot}02$		
750	Indistinguishable experimentally at 430 mμ from pure nitromethane		

The following salts (0·001M) reduced the concentration of spectrophotometrically observable carbonium ions to 1% or less of the original: $\mathrm{Bu^n_4NN_3}$, $\mathrm{NEt_4NO_2}$, $\mathrm{NEt_4F}$, $\mathrm{NEt_4O{\cdot}COCH_3}$, $\mathrm{NEt_4O{\cdot}COPh}$, $\mathrm{NEt_4O{\cdot}CO{\cdot}C_6H_4{\cdot}NO_2}$ (*p*).

In contrast to the perchlorate the anions which discharge the colour are derived from acids weaker than hydrogen chloride, and so they liberate chloride ions from undissociated hydrogen chloride. Also, in contrast to the perchlorate, these anions can capture the carbonium ions more efficiently than do chloride ions, leading to products which dissociate negligibly in nitromethane. In addition, the liberated chloride ions would further suppress the concentration of carbonium ions by a mass-law effect.

Nature of Equilibrium.—Evans and his co-workers' observations cannot accommodate a simple equilibrium between molecules and free ions, but their ion-pair hypothesis cannot account for the observed chloride-ion effect. This dilemma can be resolved if one takes into account that hydrogen chloride is present in much larger concentration than the triphenylcarbonium ions and also that the hydrogen dichloride ion is stable in nitromethane.*

---

* Smith and Hammett (*J. Amer. Chem. Soc.*, 1945, **67**, 23) measured the acidity function H_0 of sulphuric acid and hydrogen chloride in nitromethane and had to postulate what they described as new and unexpected effects on the activity coefficients. As far as can be seen from their figures, ionisation schemes similar to the ones now suggested for the acid would fit the results.

[2] (*a*) Hantzsch, *Z. phys. Chem.*, 1908, **61**, 257; (*b*) *idem*, *Ber.*, 1922, **55**, 953.

[3] Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1933, **55**, 1900.

The following three equilibria are considered

$$(1)\quad \mathrm{HCl} \rightleftharpoons \mathrm{H^+ + Cl^-};\ K_1 = [\mathrm{H^+}][\mathrm{Cl^-}]/[\mathrm{HCl}]$$

$$(2)\quad \mathrm{Cl^- + HCl} \rightleftharpoons \mathrm{HCl_2^-};\ K_2 = [\mathrm{HCl_2^-}]/([\mathrm{Cl^-}][\mathrm{HCl}])$$

$$(3)\quad \mathrm{Ph_3CCl} \rightleftharpoons \mathrm{Ph_3C^+ + Cl^-};\ K_3 = [\mathrm{Ph_3C^+}][\mathrm{Cl^-}]/[\mathrm{Ph_3CCl}]$$

In the absence of added chloride ions, $[\mathrm{HCl_2^-}] > [\mathrm{Cl^-}]$, *i.e.*, $K_2 > K_1$. In the region where $[\mathrm{H^+}] > [\mathrm{Ph_3C^+}]$ one obtains $[\mathrm{H^+}] \approx [\mathrm{HCl_2^-}]$.

Then from equilibria (1) and (2)

$$K_1K_2 \approx [\mathrm{H^+}]^2/[\mathrm{HCl}]^2 \approx [\mathrm{HCl_2^-}]^2/[\mathrm{HCl}]^2 \text{ and } [\mathrm{Cl^-}] \approx \sqrt{(K_1/K_2)}$$

Thus equilibria (1) and (2) act as a " buffer " with respect to chloride ions, keeping the latter approximately * constant. Hence

$$K_3 \approx [\mathrm{Ph_3C^+}]/[\mathrm{Ph_3CCl}] \,.\, \sqrt{(K_1/K_2)}$$

Two additional ionisation schemes involving electrophilic catalysis, (3*a*) and (3*b*), are derivable from previous equilibria:

$$(3a)\quad \mathrm{Ph_3CCl + H^+ = Ph_3C^+ + HCl};\ K_{3a} = [\mathrm{Ph_3C^+}][\mathrm{HCl}]/([\mathrm{Ph_3CCl}][\mathrm{H^+}]) \approx [\mathrm{Ph_3C^+}]/[\mathrm{Ph_3CCl}] \,.\, 1/\sqrt{(K_1K_2)}$$

$$(3b)\quad \mathrm{Ph_3CCl + HCl = Ph_3C^+ + HCl_2^-};\ K_{3b} = [\mathrm{Ph_3C^+}][\mathrm{HCl_2^-}]/([\mathrm{Ph_3CCl}][\mathrm{HCl}]) \approx [\mathrm{Ph_3C^+}]/[\mathrm{Ph_3CCl}] \,.\, \sqrt{(K_1K_2)}$$

The equilibrium constants K_3, K_{3a}, and K_{3b} agree with the experimental findings of Evans and his co-workers and with the salt effects now observed, but are independent of the way in which hydrogen chloride is originally produced.

In benzene solution, a necessary elaboration of kinetic [4c] and thermodynamic [4a] schemes is the explicit recognition of an ion-pair form. No such elaboration is necessary with regard to the thermodynamic equilibria governing the spectrophotometrically observable triphenylcarbonium ions present in solutions of triphenylmethyl chloride in nitromethane, with its relatively high dielectric constant. On the other hand, specific interaction of chloride ions with the hydrogen chloride present in such solutions plays an important rôle.

EXPERIMENTAL

Materials.—Special care was taken to purify the starting materials. No method was found to purify commercial triphenylmethyl chloride for use as starting point for the preparation of spectrophotometrically satisfactory samples, even though it could be easily purified to have the correct m. p., give good analtytical data, and afford reproducibility in measurements within a given batch. It was therefore prepared as described previously.[4b]

Commercial nitromethane was refluxed under nitrogen with activated charcoal and dried ($\mathrm{CaCl_2}$, then $\mathrm{P_2O_5}$) with filtration after each stage. It was fractionated (b. p. 100·5—101·0°), passed through a column of freshly dried chromatographic alumina, then again fractionated, and passed through alumina. The nitromethane so obtained was tested for traces of acids and aldehydes and was gas-chromatographed. Its specific conductance was $0{\cdot}132 \times 10^{-7}$ ohm^{-1} cm.$^{-1}$ at 25·0°.[5]

---

* A rigorous calculation by use of (1), (2), and the charge-balance relation $[\mathrm{Ph_3C^+}] + [\mathrm{H^+}] = [\mathrm{HCl_2^-}] + [\mathrm{Cl^-}]$ gives

$$[\mathrm{Cl^-}] = \sqrt{(K_1/K_2)} \,.\, \sqrt{\{([\mathrm{H^+}] + [\mathrm{Ph_3C^+}] - [\mathrm{Cl^-}])/[\mathrm{H^+}]\}}$$

This relation shows that even when $[\mathrm{H^+}]$ is only moderately large relative to $[\mathrm{Ph_3C^+}]$, one obtains $[\mathrm{Cl^-}$ approximately constant.

[4] (*a*) de la Mare, Hughes, Ingold, and Pocker, *J.*, 1954, 2930; (*b*) Hughes, Ingold, Patai, and Pocker, *J.*, 1957, 1206; (*c*) Hughes, Ingold, Mok, Patai, and Pocker, *ibid.*, p. 1220; (*d*) *idem*, *ibid.*, p. 1265.

[5] Wright, Murray-Rust, and Hartley, *ibid.*, 1931, 199.

Tetra-alkylammonium salts were prepared and purified as described previously.[4a, c]

TABLE 3. *Triphenylcarbonium-ion concentration in nitromethane solutions of triphenylmethyl chloride at* 25·0°; $K = [Ph_3C^+]/[Ph_3CCl]$.

$10^2[Ph_3CCl]$	6·0	5·0	4·0	3·0	2·0	1·5	1·0
$10^6[Ph_3C^+]$ (g.-ions l.$^{-1}$)	16·1	13·4	10·8	8·0	5·3	4·0	2·67
10^4K	2·68	2·68	2·70	2·665	2·65	2·66	2·67

Spectrophotometry.—The optical density of nitromethane solutions of triphenylmethyl chloride was determined on a Unicam spectrophotometer at 430 mμ.[1a–e] Details of some measurements are given in Table 3, where the calibration of colour in terms of $[Ph_3C^+]$ is as discussed previously.

Acid Determinations.—Aliquot portions removed from freshly prepared solutions were quenched in cool dry benzene and titrated quickly with 0·001M- and 0·005M-triethylamine in benzene, bromophenol-blue being the indicator. Some samples were quenched in a benzene solution of triethylamine and titrated with dry hydrogen chloride in ether. The results of this method were the same. The titratable acid was shown to be hydrogen chloride by pumping off freshly prepared solutions, isolating the vapour in a cold trap, and analysing it for acidity and chloride.

The author is indebted to Professors E. D. Hughes, F.R.S., C. K. Ingold, F.R.S., and F. A. Long for valuable advice.

WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON, W.C.1.

[*Received, July 4th,* 1957.]