

IONIZATION AND DISSOCIATION EQUILIBRIA OF SOME
TRIPHENYLCHLOROMETHANE DERIVATIVES IN NITROBENZENE AT 25°

E. Price and N. N. Lichtin

Department of Chemistry

Boston University, Boston, Mass.

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EVANS and his associates have reported numerous data on ionization equilibria of derivatives of triphenylchloromethane in solution in nitroalkanes,¹ nitroaromatics,² chlorinated ethanes³ and acetic and formic acids⁴ based on spectrophotometric measurements. They conclude that the only equilibrium involved in many of these solvents is between the covalently bonded molecules and associated ion pairs. Thus, with nitro compounds (dielectric constant, D, in the range 24-35) as solvents, they report that dissociation to free ions is not detectable, a result which has been questioned⁵ because

¹A. Bentley, A. G. Evans and J. Halpern, Trans. Faraday Soc. 47, 711 (1951); A. Bentley and A. G. Evans, J. Chem. Soc. 3468 (1952); A. G. Evans, J. A. G. Jones and G. O. Osborne, Trans. Faraday Soc. 50, 16 (1954); A. G. Evans, J. A. G. Jones and G. O. Osborne, Ibid. 470 (1954); A. G. Evans, J. A. G. Jones and G. O. Osborne, J. Chem. Soc. 3803 (1954).

²A. G. Evans, A. Price and J. H. Thomas, Trans. Faraday Soc. 50, 568 (1954).

³A. G. Evans, A. Price and J. H. Thomas, Trans. Faraday Soc. 52, 332 (1956).

⁴A. G. Evans, A. Price and J. H. Thomas, Trans. Faraday Soc. 51, 481 (1955).

⁵N.N. Lichtin and H.P. Leftin, J. Phys. Chem. 60, 164 (1956).

conductivity data demonstrate extensive dissociation of many wholly ionic solutes in solution in nitromethane⁶ and nitrobenzene⁷ at concentrations cited by these workers. Other data⁸ for solutions of triphenylchloromethane in nitromethane cast doubt on Evans' results in this solvent. Evans *et al.*⁴ report that in the solvent formic acid ($D_{16} = 58.5$) at 21.5° triphenyl carbonium chloride ion pair is detectably dissociated but the "extent was too small for estimation". Electrostatic ionic association in a medium of such high dielectric constant would be expected to be negligible.⁹

Evans and his coworkers report dissociation of ion pairs in several solvents of lower dielectric constant, however. Thus, the dissociation constant of the ion pair tri-*p*-tolycarbonium chloride in acetic acid solution at 21.5° ($D_{20} = 6.15$), was found⁴ to be 6×10^{-8} mole fraction. The value of this constant in several chlorinated ethanes in which $3.6 \ll D_{20} \ll 11.9$ fell³ in the range 3×10^{-7} to 3×10^{-6} mole fraction.

Because of its relatively high dielectric constant ($D_{25} = 34.5$) and the absence of reaction between this solvent and solutes of the type discussed here, we undertook to reinvestigate the ionization and dissociation behavior of triphenylchloromethane and some of its derivatives in nitrobenzene solution at 25°. In this study, the final degassing and distillation of

⁶ C. P. Wright, D. M. Murray-Rust and H. Hartley, J. Chem. Soc. 199 (1931); R. C. Miller and R. M. Fuoss, J. Amer. Chem. Soc. 75, 3076 (1953).

⁷ C. R. Witschonke and C. A. Kraus, J. Amer. Chem. Soc. 69, 2472 (1947).

⁸ cf. B. B. Smith and J. E. Leffler, J. Amer. Chem. Soc. 77, 1700 (1955); Y. Pocker, J. Chem. Soc. 240 (1958), for evidence of the instability of solutions of trityl chloride in nitromethane.

⁹ The significance of this result is somewhat obscured by the fact that formic acid is known to reduce trityl chloride fairly rapidly at 100°C. cf. S.T. Bowden and T.F. Watkins, J. Chem. Soc. 1333 (1940).

solvent and the preparation of solutions were carried out on the high vacuum line under an atmosphere of solvent. Optical density and electrical conductivity were determined on the same solution in cells which had been sealed under vacuum. Free ion concentrations were calculated from conductivity data while the sums of free and associated ion concentrations were calculated from optical densities. It was found that, in solutions up to 1×10^{-5} M in carbonium ion, the concentration of free ions is indistinguishable from the total ionic concentration. This result conflicts with that of Evans et al.² who report only paired ions in 10^{-6} to 2×10^{-5} M solutions of triaryl carbonium ions in nitrobenzene.

No significant spectrophotometric data could be obtained with solutions of unsubstituted triphenylchloromethane because nitrobenzene absorbs strongly at the wave length of the carbonium ion maximum. Conductance data indicate a very low degree of dissociation.

With 0.002 to 0.015 M mono-p-tolylidiphenylchloromethane the concentration of carbonium ion was too small to measure accurately. The absorbancy, A_s^{10} , of a 0.015 M solution at λ_{max} (462 m μ) was 0.04 initially and tripled in 24 hr. Evans et al.² report $A_s = 1.21$ for a 0.088 M solution of this compound at 16.5° in what appears to have been a 1 cm cell and that ΔH° of ionization is + 0.5 kcal mole⁻¹.

Solutions of tri-p-t-butylphenylchloromethane were investigated in an attempt to obtain solutions of higher conductivity and optical density. Work with this solute was limited because of its extremely slow rate of

¹⁰ All A_s values are in 1 cm cells and were determined against a solvent blank in a double beam instrument. The solvent cell was always charged on the vacuum line at the time when the solutions were prepared.

dissolution. The equivalent conductance, Λ ,¹¹ of a 6.2×10^{-4} M solution was $0.12 \text{ mho cm}^2 \text{ mole}^{-1}$ and A_s at λ_{max} (469 m μ in nitrobenzene) was 0.204. These data yield crude estimates of the concentrations of free ions and total ions. Thus, if $\Lambda^{\circ 7}$ and a_m^{12} are assumed to be 30 and 8.31×10^4 respectively, the free ion and total ion concentrations are both 2.5×10^{-6} M. Analogous results were obtained with a 2.3×10^{-4} M solution.

More conclusive results were obtained with solutions of tri-p-anisylchloromethane. Conductivity data were obtained in the concentration range 4.55×10^{-5} to 8.18×10^{-4} M¹³ where A_s was too large to measure accurately. The limiting equivalent conductance, Λ° , and the equilibrium constant, K_{exp} ,¹⁴ were found by Shedlovsky's procedure¹⁵ to be $31 \pm 3 \text{ mho cm}^2 \text{ mole}^{-1}$ and $(4.2 \pm 1) \times 10^{-5} \text{ mole l}^{-1}$, respectively.

Spectrophotometric measurements distinguish between free ions and ion

¹¹All conductivity data are corrected for solvent conductivity.

¹²N. C. Deno, J. J. Jaruzelski and A. Schriesheim, J. Org. Chem. 19, 155 (1955).

¹³The conductivities of these solutions did not increase over a period of 24 hr.

¹⁴

$$K_{\text{exp}} = \frac{[R^+][Cl^-]}{[RCl] + [R^+Cl^-]} = \frac{K_1 K_2}{1 + K_1}$$

$$K_1 = \frac{[R^+Cl^-]}{[RCl]} \quad K_2 = \frac{[R^+][Cl^-]}{[R^+Cl^-]}$$

The terms in brackets are activities.

¹⁵T. Shedlovsky, J. Frank. Inst. 225, 739 (1938).

pairs on the one hand, and covalent molecules on the other,^{16,17,18} so that, for these solutions, $A_s = a_m b [(R^+) + \overline{(R^+Cl^-)}]$.¹⁹ The value of a_m for trianisyl carbonium ion at λ_{max} in nitrobenzene was found by adding an excess of mercuric chloride to solutions of the organic halide²⁰ to be $(10.4 \pm 0.8) \times 10^4$ at 498 m μ . This procedure was employed because a_m for sulfuric acid solutions of this chloride or its carbinol was lower²¹ than that reported in the literature¹² and the solutions were unstable. Solutions of tri-*p*-anisylchloromethane adhered to Beer's Law over the concentration range 1.52×10^{-6} to 11.8×10^{-6} M in the presence of either 1.6 or 5 moles of HgCl₂ per mole of organic solute.

The measurements summarized in Table 1 were made at such low concentrations that the equation $(R^+) = 10^3 k / \Lambda^0$, where k is the specific conductance of the solute, can be used to estimate the concentration of free ions, (R^+) .

From the data of Witschonke and Kraus⁷ it can be estimated that K_2 ¹⁴ is of the order of 10^{-2} mole l⁻¹ for these solutes in nitrobenzene. At the very low solute concentrations of Table 1 ion pairing would, thus, be negligible even if ionization were complete. The data of Table 1 are in

¹⁶ L. P. Hammett, Physical Organic Chemistry p. 50. McGraw-Hill, New York (1940).

¹⁷ G. N. Lewis, T. T. Magel and D. Lipkin, J. Amer. Chem. Soc. **64**, 1774 (1942).

¹⁸ A. G. Evans, I. H. McEwan, A. Price and J. H. Thomas, J. Chem. Soc. 3098 (1955).

¹⁹ $A_s = \log_{10} (I_0/I)$; $a_m = A_s/bc$, where b = cell path length in cm; c = concentration in moles l⁻¹.

²⁰ cf. J. L. Cotter and A. G. Evans, J. Chem. Soc. 2988 (1959).

²¹ With this value, $a_m = 7.43 \times 10^4$, the concentrations of carbonium ion appeared to be greater than the stoichiometric concentrations of organic chloride.

agreement with this conclusion. Differences between free ion concentration measured by electrical conductivity and total ion concentration measured by spectrophotometry are within experimental error, in direct disagreement with Evans et al.²

An interesting comparison between the "ionizing power" of nitrobenzene ($D_{25} = 34.5$) and SO_2 ($D_0 = 15.4$) can be made. Assuming that $K_2 = 10^{-2}$ in nitrobenzene, K_1^{14} of tri-p-anisylchloromethane is about 4×10^{-3} . The value of K_1 for this solute in liquid SO_2 at 0° , calculated from $\rho = -4.41^5$, $K_1 = 1.5 \times 10^{-2}$ for triphenylchloromethane²² and $\sigma^+ = -0.764$ for p-methoxy,²³

TABLE 1

Free and Total Ion Concentrations in Very Dilute Solutions of
tri-p-Anisylchloromethane in Nitrobenzene at 25°

| $10^5 c_s^a$ (mole l ⁻¹) | $10^5 (R^+)^b$ (mole l ⁻¹) | $10^5 [(R^+) + \overline{(R^+Cl)}]^b$ (mole l ⁻¹) |
|---|---|--|
| 0.37 | 0.22 ± 0.02 | 0.24 ± 0.02 |
| 0.67 | 0.52 ± 0.05 | 0.66 ± 0.05 |
| 0.71 | 0.53 ± 0.05 | 0.59 ± 0.05 |
| 1.73 | 0.98 ± 0.10 | 1.14 ± 0.10 |

a Stoichiometric concentration of solute.

b Uncertainties based on uncertainty in Λ^0 and a_s , respectively.

²² N. N. Lichtin and M. J. Vignale, J. Amer. Chem. Soc. 79, 579 (1957).

²³ H. C. Brown and Y. Okamoto, J. Amer. Chem. Soc. 79, 1913 (1957).

is $2 \times 10^{+8}$. The 5×10^{10} fold difference is a measure of the immensely greater "ionizing power" of SO_2 , a property which is not related even approximately to its dielectric constant. The relative abilities of nitrobenzene and liquid SO_2 to promote the dissociation of ion pairs are related in a qualitative fashion to their dielectric constant, however.^{7,24} We wish to emphasize the necessity of distinguishing carefully between these two functions of the solvent in the elucidation of chemical mechanisms.

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²⁴ cf. N. N. Lichtin and H. P. Leftin, J. Phys. Chem. 60, 160 (1956);
N. N. Lichtin and P. Pappas, Trans. N.Y. Acad. Sci. 20, 143 (1957).