665. *Ionisation of Tri*-p-*tolylmethyl Chloride in Nitroalkanes.*

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A study has been made of the thermodynamics of the equilibrium $(p\text{-}C_6H_4Me)_3CCl_{(s)} \rightleftarrows (p\text{-}C_6H_4Me)_3C^+Cl^-_{(s)}$ in nitromethane, nitroethane, and 2-nitropropane. The values of the equilibrium constant, and of ΔG°, ΔH°, and ΔS° for the forward reaction have been obtained in these three solvents. The effect of change of solvent on the ΔG°, ΔH°, and ΔS° values is discussed, and the results for $(p\text{-}C_6H_4Me)_3CCl$ are compared with those obtained earlier for Ph_3CCl.

Bentley, A. G. Evans, and Halpern recently (*Trans. Faraday Soc.*, 1951, **47**, 711) described a method for obtaining ΔG°, ΔH°, and ΔS° for the ionisation of triphenylmethyl chloride in nitroalkanes. In the present work we give the corresponding results for the ionisation of tri-*p*-tolylmethyl chloride in nitroalkanes. As discussed for the earlier case, the following conditions must be fulfilled in order that this method may be used.

(*a*) The carbonium ion R^+ must not react with the solvent. It was originally shown by Hantzsch (*Z. physikal. Chem.*, 1909, **65**, 41) that when nitromethane was dissolved in concentrated sulphuric acid the solution showed the normal depression of the freezing point. This indicated that nitromethane did not accept protons from the acid to any appreciable extent. It has been shown recently by Gillespie (*J.*, 1950, 2541) that nitromethane is ionised in 100% sulphuric acid to an extent which would correspond to about 21% at 0·1 molal concentration. This indicates that nitromethane is very slightly basic, and the question of its acceptance of R^+ ions in the solution we are using must therefore be considered. If the nitroalkane accepts the R^+ ion (as it does the proton to a small extent in concentrated sulphuric acid), giving the $(CH_3{\cdot}NO_2R)^+_{(s)}$ ion, the spectrum of this ion would be very different from that of the $R^+_{(s)}$ ion produced from ROH in concentrated sulphuric acid, where the presence of the $R^+_{(s)}$ ion has been established by freezing-point measurements for the case when R is Ph_3C (Hantzsch, *Z. physikal. Chem.*, 1908, **61**, 257; Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1933, **55**, 1600). The fact that we find the spectrum of RCl in nitromethane to be almost identical in shape with that of ROH in concentrated sulphuric acid establishes that what we are measuring spectrophotometrically is in fact the concentration of $R^+_{(s)}$ ions. If there were any interaction between R^+ and nitroalkane to give an ion of the type $(CH_3{\cdot}NO_2R)^+_{(s)}$, then under our conditions, where the concentration of R^+ is extremely small ($\lesssim 10^{-5}$ molal), its concentration would be negligible; in any case, it would not be included in our spectroscopically determined $R^+_{(s)}$

concentration, and so would not affect the validity of our equilibrium constant, $K = [\text{R}^+\text{Cl}^-_{(s)}]/[\text{RCl}]$.

(*b*) The R^+ ion must not rearrange or form an olefin by loss of a proton. This condition is fulfilled for the tri-*p*-tolylmethyl ion.

(*c*) The polarity of the nitroalkane solvents and the stability of the R^+ ions must be such as to give a measurable equilibrium concentration of R^+ ions at ordinary temperatures. This was found to be the case.

The effect of concentration, temperature and change of solvent on the equilibrium constant was determined for the reaction :

$$(p\text{-CH}_3\cdot\text{C}_6\text{H}_4)_3\text{CCl}_{(s)} \rightleftarrows (p\text{-CH}_3\cdot\text{C}_6\text{H}_4)_3\text{C}^+\text{Cl}^-_{(s)} \quad . \; . \; . \; . \; (1)$$

EXPERIMENTAL

Materials.—Tri-*p*-tolylmethyl chloride was a product of Mersey Chemicals Ltd. When received it had a good colour and m. p., and so a quantitative determination of the spectrum was made over the range 360—480 mμ, in nitromethane. A small amount of the chloride was then recrystallised from light petroleum, and the spectrum and m. p. were found to be unchanged. The measurements were therefore made on the material as received from Mersey Chemicals (m. p. 171°).

Tri-*p*-tolylmethyl alcohol was prepared by hydrolysis of the chloride. The chloride was dissolved in concentrated sulphuric acid and poured into ice-water. The alcohol was recrystallised from aqueous ethanol and had m. p. 93°.

Concentrated sulphuric acid was analytical-grade material from J. W. Towers Ltd.

Nitromethane and nitroethane were Light's products. The 2-nitropropane was kindly given by Imperial Chemical Industries Limited, Billingham Division. All the nitroalkanes were dried over phosphoric oxide and distilled under reduced pressure. B. p.s were 100·5°, 115°, and 121° respectively.

Procedure.—The dependence of optical density *D* on wave-length for tri-*p*-tolylmethyl chloride in each of the nitroalkanes and for the alcohol in 98% sulphuric acid was measured by a Unicam Spectrophotometer, and the results are shown in Figs. 1*a*, *b*, and *c*. The spectra of the chloride in the three nitroalkanes are seen to be very similar to that of the alcohol in concentrated sulphuric acid. The dependence of optical density on concentration of the chloride was measured (*a*) on a Spekker photometer with a filter with maximum transmission at wave-length 440 mμ, (*b*) on a photomultiplier with an Ilford 601 filter with maximum transmission in the region 400—460 mμ, and (*c*) on the Unicam spectrophotometer at wave-length 450 mμ.

The dependence of optical density on chloride concentration is shown in Figs. 2*a*, *b*, and *c*. It is seen that the optical densities measured on the Spekker photometer, and on the photomultiplier are directly proportional to those measured at wave-length 450 mμ on the Unicam instrument, and so the optical density obtained by the Spekker photometer and by the photomultiplier was taken as a measure of the carbonium ion concentration.

The dependence of optical density on temperature was measured by the photomultiplier. A new apparatus was designed for the temperature control of the cell liquid. This apparatus consisted of a metal box fitted with a heater, mercury–toluene regulator, stirrer, thermometer, and " Perspex " windows to allow passage of light. The entire box was surrounded by a wooden outer jacket to act as lagging. Two Beckman cells were used. One was filled with solvent, the other with solution; these were water-proofed and completely immersed in the bath. The cell carriage was moved by means of a rack and pinion. In this way there was no danger of temperature gradients within the cell, and temperatures are accurate to ±0·1°.

RESULTS

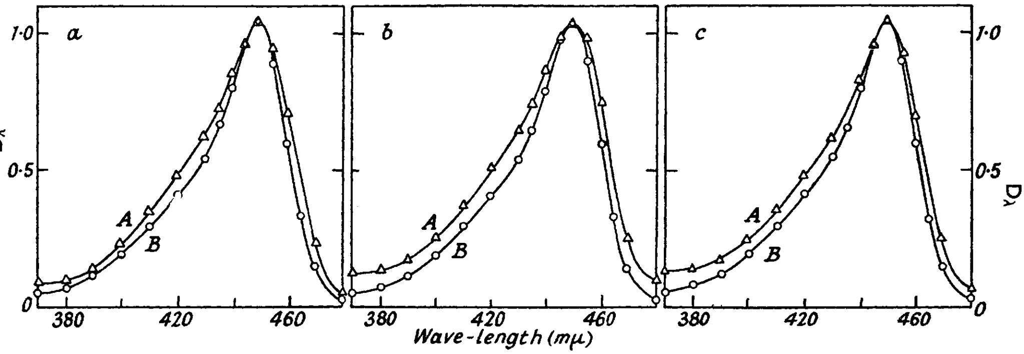
The shape of the absorption spectrum obtained for tri-*p*-tolylmethyl alcohol in 98% sulphuric acid (Figs. 1*a*, *b*, and *c*) is similar to that obtained previously by Newman and Deno (*J. Amer. Chem. Soc.*, 1951, **73**, 3644), who also showed by cryoscopic measurements that the reaction

$$(p\text{-}\cdot\text{CH}_3\cdot\text{C}_6\text{H}_4)_3\text{C}\cdot\text{OH} + 2\text{H}_2\text{SO}_4 \longrightarrow (p\text{-CH}_3\cdot\text{C}_6\text{H}_4)_3\text{C}^+ + 2\text{HSO}_4^- + \text{H}_3\text{O}^+ \quad . \quad (2)$$

goes to completion. On the basis of the completeness of reaction (2), our sulphuric acid solution containing $1\cdot195 \times 10^{-5}$ mole/l. of tri-*p*-tolylmethyl alcohol has a concentration of

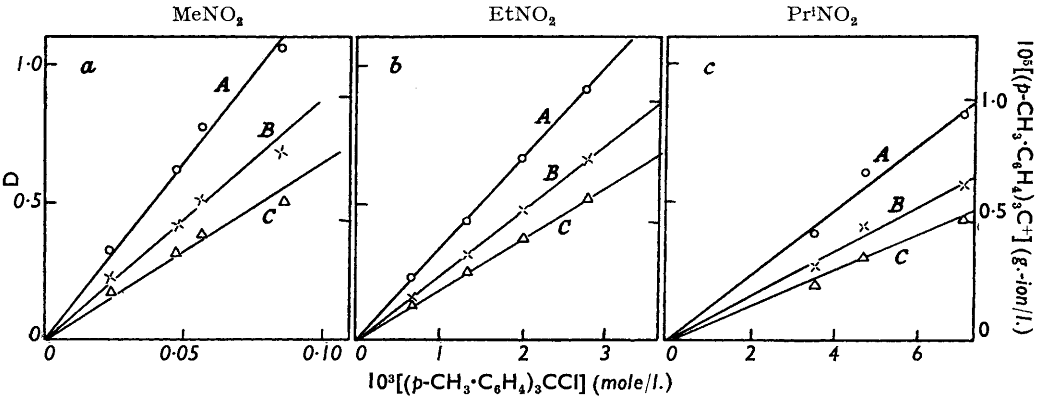
$(p\text{-}CH_3{\cdot}C_6H_4)_3C^+$ ions of $1{\cdot}195 \times 10^{-5}$ g.-ion/l. The spectra of tri-*p*-tolylmethyl chloride in nitromethane ($8{\cdot}63 \times 10^{-5}$ mole/l.), in nitroethane ($3{\cdot}1 \times 10^{-3}$ mole/l.), and in 2-nitropropane ($9{\cdot}05 \times 10^{-3}$ mole/l.) are shown in Figs. 1*a*, *b*, and *c*. These curves are calculated from results at other concentrations (by using the observed direct proportionality between optical density and the concentration of the chloride shown in Figs. 2), so that they coincide at 450 mμ with the curve for a solution of the alcohol in concentrated sulphuric acid of a concentration $1{\cdot}195 \times 10^{-5}$ mole/l.

FIG. 1.



Curve A (FIG. 1*a*), $(p\text{-}CH_3{\cdot}C_6H_4)_3CCl$ *in* $MeNO_2$, $8{\cdot}63 \times 10^{-5}$ *mole/l.*
Curve A (FIG. 1*b*), $(p\text{-}CH_3{\cdot}C_6H_4)_3CCl$ *in* $EtNO_2$, $3{\cdot}10 \times 10^{-3}$ *mole/l.*
Curve A (FIG. 1*c*), $(p\text{-}CH_3{\cdot}C_6H_4)_3CCl$ *in* Pr^iNO_2, $9{\cdot}05 \times 10^{-3}$ *mole/l.*
Curve B, $(p\text{-}CH_3{\cdot}C_6H_4)_3C{\cdot}OH$ *in* 98% H_2SO_4, $1{\cdot}195 \times 10^{-5}$ *mole-l.*

FIG. 2.



Curve A, D_{450} *and* $[(p\text{-}CH_3{\cdot}C_6H_4)_3C^+]$ *against* $[p\text{-}CH_3{\cdot}C_6H_4)_3CCl]$.
Curve B, *D* (*Photomultiplier*) *against* $[(p\text{-}CH_3{\cdot}C_6H_4)_3CCl]$.
Curve C, *D* (*Spekker*) *against* $[(p\text{-}CH_3{\cdot}C_6H_4)_3CCl]$.

These results establish that the spectrum which we measure in the nitroalkanes is that due to $(p\text{-}CH_3{\cdot}C_6H_4)_3C^+$ ion produced by ionisation of the chloride (a solution of the chloride has no absorption in this region when dissolved in a non-polar solvent). Further, in view of the close similarity of these spectra we assume that the extinction coefficient of $p\text{-}CH_3{\cdot}C_6H_4)_3C^+$ is the same in the three nitroalkanes as it is in concentrated sulphuric acid (in this respect tri-*p*-tolylmethyl chloride differs from triphenylmethyl chloride, the spectrum for which broadens appreciably from nitromethane to nitroethane to 2-nitropropane; Bentley, A. G. Evans, and Halpern, *loc. cit.*). Thus those solutions of tri-*p*-tolylmethyl chloride in nitroalkanes, for which the spectra are shown in Figs. 1*a*, *b*, and *c*, will each have a concentration of $(p\text{-}CH_3{\cdot}C_6H_4)_3C^+$ ions of $1{\cdot}195 \times 10^{-5}$ g.-ion/l.

Nature of the Equilibrium.—To find the nature of the equilibrium obtaining in these solutions of tri-*p*-tolylmethyl chloride in nitroalkanes, the same procedure was employed for each of the nitroalkane solvents as was used for the earlier experiments on triphenylmethyl chloride in nitromethane. The concentration of $(p\text{-}CH_3\cdot C_6H_4)_3C^+$ ions was measured for different total concentrations of the chloride. A set of typical results are shown in Figs. 2*a*, *b* and *c*. In each case curve *A* shows the absorption at 450 mμ (as measured on the Unicam spectrophotometer) and the $(p\text{-}CH_3\cdot C_6H_4)_3C^+$ concentration (calculated as above), plotted against the concentration of the chloride. In the case of tri-*p*-tolylmethyl chloride in nitromethane the concentration of un-ionised chloride is less than that of the total concentration of chloride and this has been allowed for, but in the solvents nitroethane and 2-nitropropane the ion concentration is so small that the concentration of un-ionised chloride has been taken as equal to the total concentration of chloride in solution. Curves *B* and *C* show the absorption of the same solutions, measured on the photomultiplier and on the Spekker photometer. A good linear relation is obtained between optical density and chloride concentration in each nitroalkane, and for each method of measurement.

The direct proportionality between the concentrations of $(p\text{-}CH_3\cdot C_6H_4)_3C^+$ and $(p\text{-}CH_3\cdot C_6H_4)_3CCl$ establishes that the equilibrium

$$(p\text{-}CH_3\cdot C_6H_4)_3CCl_{(s)} \rightleftarrows (p\text{-}CH_3\cdot C_6H_4)_3C^+Cl^-{}_{(s)} \quad . \quad . \quad . \quad (3)$$

exists over the range of concentration studied. Any dissociation of the ion pairs would cause a deviation from this direct proportionality relationship. Values of *K* defined by

$$K = [(p\text{-}CH_3\cdot C_6H_4)_3C^+Cl^-{}_{(s)}]/[(p\text{-}CH_3\cdot C_6H_4)_3CCl_{(s)}]$$

were obtained from the slopes of the curves *A*, and these are given in the annexed Table, together with the values of ΔG^o calculated from *K*. We estimate the accuracy of ΔG^o to be within the limits ±0·17 kcal./mole.

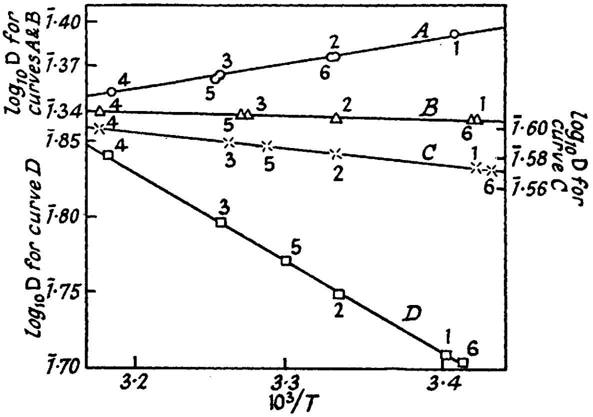


FIG. 3.

Curve A, $(p\text{-}CH_3\cdot C_6H_4)_3CCl$ *in* $MeNO_2$.
Curve B, $(p\text{-}CH_3\cdot C_6H_4)_3CCl$ *in* $EtNO_2$.
Curve C, $(p\text{-}CH_3C_6H_4)_3CCl$ *in* Pr^iNO_2.
Curve D, $(C_6H_5)_3CCl$ *in* $MeNO_2$.

Solvent	Temp.	*K*	ΔG^o (kcal./mole)
$MeNO_2$	16°	$1\cdot71 \times 10^{-1}$	1·0
$EtNO_2$	17	$3\cdot85 \times 10^{-3}$	3·2
Pr^iNO_2	17	$1\cdot33 \times 10^{-3}$	3·8

Dependence of K *on Temperature.*—The $(p\text{-}CH_3\cdot C_6H_4)_3C^+$ concentration of a solution of tri-*p*-tolylmethyl chloride in nitroalkane was measured at different temperatures as described earlier, the same solution being used at all temperatures. The same experiment was done with triphenylmethyl chloride in order to repeat the earlier experiments with the new apparatus. A set of typical plots for tri-*p*-tolylmethyl chloride in nitromethane, nitroethane, and 2-nitropropane, and for triphenylmethyl chloride in nitromethane are shown in Fig. 3, curves *A*, *B*, *C*, and *D* respectively. The points in Fig. 3 are numbered to show the sequence in which the temperature of the solution was varied. The plots are for log *D* against $1/T$, as it is not necessary to plot log *K* in order to obtain ΔH^o. The change in concentration of carbonium ions due to expansion of the solvent has been allowed for in each of these plots (in the case of nitromethane the change of density with temperature was known. For nitroethane and 2-nitropropane the required volume change was determined by dilatometer experiments). As in our earlier paper we have again assumed that the extinction coefficient, ε, is independent of temperature. The values of ΔH° were obtained from the slopes of these lines, and by combination of these values with ΔG°, values of ΔS° were obtained. The value of ΔG° for triphenylmethyl chloride is 4·46 ± 0·17 kcal./mole at 16° (Bentley, A. G. Evans, and Halpern, *loc. cit.*). The results are given in the annexed Table. We consider the ΔH° (av.) and the ΔS° values to be accurate to ±0·2 kcal./mole and ±1·3 cal./mole deg., respectively.

Solute	Solvent	ΔH° (exp.) (kcal./mole)	ΔH° (av.) (kcal./mole)	ΔS° (cal./mole deg.)	
Ph_3CCl	$MeNO_2$	2·68 2·72 2·85	2·75	− 5·9	at 16°
$(p\text{-}CH_3\cdot C_6H_4)_3CCl$	$MeNO_2$	−0·73 −0·72 −0·62 −0·69 −0·58 −0·58 −0·59 −0·70 −0·60 −0·71	−0·65	− 5·7	at 16°
,, ...	$EtNO_2$	0·131 0·101 0·150	0·13	−10·6	at 17°
,, ...	Pr^iNO_2	0·507 0·63 0·65	0·60	−11·0	at 17°

The value of ΔH° for triphenylmethyl chloride in nitromethane obtained with the new apparatus (2·75 kcal./mole) is greater than that obtained by our earlier technique (2·35 kcal./mole). We consider the present value to be the more accurate because in the new method the possibility of a temperature gradient in the cell solution has been eliminated.

Discussion

Change of Solvent.—The results in the second Table show that as the solvent changes from nitromethane to nitroethane to 2-nitropropane the ionisation of tri-*p*-tolylmethyl chloride becomes progressively less exothermic. This is to be expected for an ionisation reaction of this type [reaction (3)], since the dielectric constant of the solvent decreases along this sequence. [The dielectric constant is 39 for nitromethane and 30 for nitroethane (Intern. Crit. Tables, Vol. 6, pp. 83, 85). The value for 2-nitropropane is not known, but is very probably still smaller.]

Along this sequence of solvents the ΔS° value for the ionisation reaction becomes more negative. The change in ΔS° from one solvent to another will be mainly due to the change in the entropy of solvation of the ions formed in the reaction. Thus the results shown in the Table show that the smaller the dielectric constant of the solvent the more negative is the entropy of solvation of the ions. This effect is also shown for ions in aqueous methanol; increasing the methanol content causes the entropy of solvation of the ions to become more negative (Latimer and Slansky, *J. Amer. Chem. Soc.*, 1940, **62**, 2019).

*Comparison of Tri-*p*-tolyl- with Triphenyl-methyl Chloride.*—The only reliable comparison which can be made between these chlorides is in the solvent nitromethane. [The spectrum of triphenylmethyl chloride in nitroethane and 2-nitropropane was found to be appreciably broader than that of triphenylmethyl alcohol in concentrated sulphuric acid (Bentley, A. G. Evans, and Halpern, *loc. cit.*)]. It is seen from the Table that ΔS° for the ionisation of these two chlorides in nitromethane is the same. We expect this to be the case since the introduction of *para*-substituents will not affect the entropy of solvation of the positive and negative ions, the *para*-groups being too far away to interfere sterically with the " freezing " of solvent molecules around the charged atoms.

The change in ΔH° from triphenyl- to tri-*p*-tolylmethyl chloride is such that the ionisation of the latter is 3·4 kcal./mole more exothermic than that of the former (this difference of ΔH° was obtained using the same batch of solvent for each chloride). We hope to find out whether or not the effect of the *p*-methyl groups is additive by examining phenyldi-*p*-tolylmethyl chloride.

Shape of the Spectrum of R^+.—The introduction of three *p*-methyl groups into triphenylmethyl chloride produces a marked change in the spectrum of the carbonium ion. The two peaks at 410 and 430 mμ for the Ph_3C^+ ion are replaced by a single peak of more than twice the intensity at 450 mμ. We attribute this new peak to the presence of the $>\overset{+}{C}\cdot C_6H_4\cdot CH_3$ group, and the absence of the 410 and 430 mμ peaks to the absence of the $>\overset{+}{C}Ph$ group. This is confirmed by preliminary results for phenyldi-*p*-tolylmethyl chloride.

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