The Ionization of Organic Halides in Nitroalkanes. Part V.*

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We have studied the effect of *ortho*- and *meta*-substitution on the thermodynamics of the ionization equilibrium of triphenylmethyl chloride in nitromethane. This equilibrium, which is of the type $RCl \rightleftharpoons R^+Cl^-$, was examined by a spectrophotometric method.

In our earlier papers, we have studied the ionization of *para*-substituted triphenylmethyl chlorides in nitroalkanes by a spectrophotometric method (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). This study is now extended to *ortho*- and *meta*-methyl, -chloro-, and -bromo-substituted triphenylmethyl chlorides.

Experimental

Materials.—The nitromethane, sulphuric acid, substituted triarylmethyl alcohols, and substituted triarylmethyl chlorides were obtained as described previously (A. G. Evans, Jones, and Osborne, *locc. cit.*). Two of the alcohols not previously described had the following characteristics: 2-*chloro*-4′ : 4″-*dimethyltriphenylmethanol*, m. p. 98—99° (Found: C, 77·9; H, 6·3; Cl, 11·3. $C_{21}H_{19}OCl$ requires C, 78·1; H, 5·9; Cl, 11·0%); 2 : 4′ : 4″-*trimethyltriphenylmethanol*, m. p. 88° (Found: C, 87·1; H, 7·34. $C_{22}H_{22}O$ requires C, 87·4; H, 7·3%). Two of the chlorides not previously prepared had the following characteristics: 2-*chloro*-4′ : 4″-*dimethyltriphenylmethyl chloride*, m. p. 128—129° (Found: hydrolysable chlorine, 10·2. $C_{21}H_{18}Cl_2$ requires Cl^-, 10·4%); 2 : 4′ : 4″-*trimethyltriphenylmethyl chloride*, m. p. 111° (Found: hydrolysable chlorine, 11·5. $C_{22}H_{21}Cl$ requires Cl^-, 11·1%).

Results

Spectra.—The spectra are shown in Figs. 1 and 2. All the alcohols except 2 : 5-dimethyl- and 2 : 4′ : 4″-trimethyl-triphenylmethanol were examined in 98% sulphuric acid in which solvent we assume that they are completely ionized. Evidence that this assumption is justified is quoted in Part IV (*loc. cit.*). 2 : 5-Dimethyl- and 2 : 4′ : 4″-trimethyl-triphenylmethanol appeared to undergo sulphonation in 98% sulphuric acid, so their spectra were measured in 85% sulphuric acid in which solution they are stable. Gold and Hawes (*J.*, 1951, 2102) have demonstrated that triphenylmethanol is fully ionized in 60% sulphuric acid, so we are justified in assuming that these alcohols are completely ionized in 85% sulphuric acid. The very close similarity seen in Figs. 1 and 2 between the spectrum of RCl in nitromethane and that of the corresponding ROH in sulphuric acid establishes the presence of the R^+ ion in the nitromethane solutions.

Nature of Equilibrium.—In Fig. 3 we plot $(D_\lambda)_{max.}$ against the concentration of un-ionized RCl. These lines are straight, demonstrating that the equilibrium is of the type

$$RCl \rightleftharpoons R^+Cl^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which the ion pairs are not dissociated. The values of the equilibrium constant, K, and of the free-energy change, ΔG° ($= -\boldsymbol{R}T \ln K$), for reaction (1) have been obtained as described in Part IV, and the values of ΔG° are considered to be accurate to within $\pm 0{\cdot}1$ kcal./mole. (Again, the two methods of obtaining the R^+-ion concentration give the same ΔG° value to within $\pm 0{\cdot}1$ kcal./mole.)

Change of K *with Temperature.*—The plots of $\log_{10} D$ against $1/T$ are shown in Fig. 4. The expansion of the solvent with temperature has been allowed for in these plots. Values of ΔH° calculated from the slopes of these lines are given in Table 1. (For 2-chlorotriphenylmethyl chloride, for example, the change of optical density with temperature was determined for six solutions of different concentrations, these concentrations varying over a 2½-fold range.) For all chlorides studied, ΔH° was reproducible to within $\pm 0{\cdot}2$ kcal./mole.

* Part IV, *Trans. Faraday Soc.*, 1954, **50**, 470.

TABLE 1.

Substituents	Thermodynamic constants for ionization of substituted triphenylmethyl chlorides in nitromethane 10^4K (T°C)	$\Delta G°$ (T°C), kcal./mole	$\Delta H°$, kcal./mole	$\Delta S°$, cal./deg.-mole	$\Delta G‡$ for alcoholysis of substituted diphenylmethyl chlorides $\Delta G‡$, kcal./mole
Unsubstituted	4·4 (20·0°) [a]	4·5 (20·0°) [a]	1·4 [a]	−10·5 (20·0°) [a]	21·0 [d]
2-Methyl	18 (20·0°)	3·7 (20·0°)	1·6	−7·2 (20·0°)	20·2 [d]
3-Methyl	8·6 (19·0°)	4·1 (19·0°)	1·4	−9·2 (19·0°)	20·6 [d]
4-Methyl	20 (19·0°) [b]	3·6 (19·0°) [b]	1·4 [b]	−7·6 (19·0°) [b]	19·3 [d]
2 : 5-Dimethyl	49 (20·0°)	3·1 (20·0°)	1·7	−4·8 (20·0°)	—
2 : 4′ : 4″-Trimethyl	910 (20·0°)	1·4 (20·0°)	0·7	−2·4 (20·0°)	—
4 : 4′ : 4″-Trimethyl	540 (20·0°) [b]	1·7 (20·0°) [b]	−0·2 [b]	−6·4 (20·0°) [b]	—
2-Chloro	1·8 (21·0°)	5·0 (21·0°)	2·5	−8·5 (21·0°)	23·8 [d]
4-Chloro	1·9 (21·5°) [c]	5·0 (21·5°) [c]	1·7 [c]	−11·2 (21·5°) [c]	21·5 [d]
2-Chloro-4′ : 4″-dimethyl	81 (18·0°)	2·8 (18·0°)	0·8	−6·9 (18·0°)	—
4-Chloro-4′ : 4″-dimethyl	46·8 (18·0°) [c]	3·1 (18·0°) [c]	0·2 [c]	−10·0 (18·0°) [c]	—
2-Bromo	3·1 (18·0°)	4·7 (18·0°)	2·1	−8·9 (18·0°)	—
4-Bromo	1·9 (21·5°) [c]	5·0 (21·5°) [c]	1·6 [c]	−11·5 (21·5°) [c]	—

[a] Bentley, A. G. Evans, and Halpern, *Trans. Faraday Soc.*, 1951, **47**, 711. [b] A. G. Evans, Jones, and Osborne, *ibid.*, 1954, **50**, 16. [c] *Idem, ibid.*, p. 470. [d] Calculated from results of Norris and Banta (*J. Amer. Chem. Soc.*, 1928, **50**, 1804).

FIG. 1.

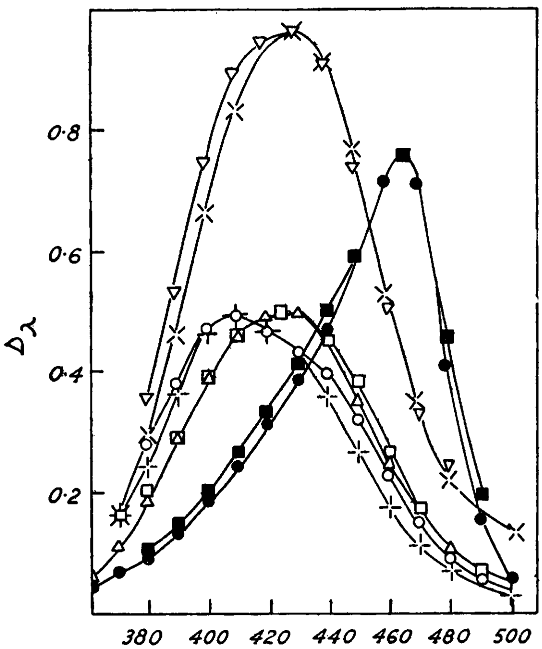

FIG. 2.

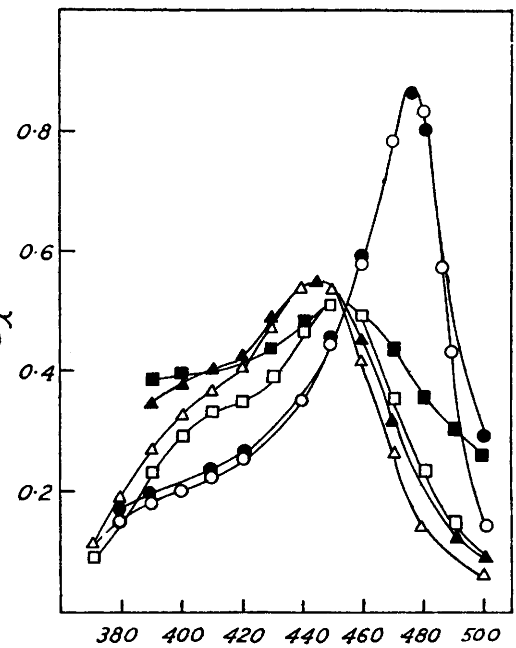

FIG. 1.	△	2-Methyltriphenylmethanol in 98% H_2SO_4	$1·49 \times 10^{-5}$ mole/l.
	□	2-Methyltriphenylmethyl chloride in $MeNO_2$	$9·1 \times 10^{-3}$ mole/l.
	+	3-Methyltriphenylmethanol in 98% H_2SO_4	$1·53 \times 10^{-5}$ mole/l.
	○	3-Methyltriphenylmethyl chloride in $MeNO_2$	$1·80 \times 10^{-2}$ mole/l.
	×	2 : 5-Dimethyltriphenylmethanol in 85% H_2SO_4	$2·98 \times 10^{-5}$ mole/l.
	▽	2 : 5-Dimethyltriphenylmethyl chloride in $MeNO_2$	$5·87 \times 10^{-3}$ mole/l.
	●	2 : 4′ : 4″-Trimethyltriphenylmethanol in 85% H_2SO_4	$1·48 \times 10^{-5}$ mole/l.
	■	2 : 4′ : 4″-Trimethyltriphenylmethyl chloride in $MeNO_2$	$1·50 \times 10^{-5}$ mole/l.
FIG. 2.	△	2-Chlorotriphenylmethanol in 98% H_2SO_4	$1·50 \times 10^{-5}$ mole/l.
	▲	2-Chlorotriphenylmethyl chloride in $MeNO_2$	$1·00 \times 10^{-1}$ mole/l.
	□	2-Bromotriphenylmethanol in 98% H_2SO_4	$1·49 \times 10^{-5}$ mole/l.
	■	2-Bromotriphenylmethyl chloride in $MeNO_2$	$4·90 \times 10^{-2}$ mole/l.
	○	2-Chloro-4′ : 4″-dimethyltriphenylmethanol in 98% H_2SO_4	$1·50 \times 10^{-5}$ mole/l.
	●	2-Chloro-4′ : 4″-dimethyltriphenylmethyl chloride in $MeNO_2$	$1·85 \times 10^{-3}$ mole/l.

TABLE 2. *Maximum extinction coefficients of substituted triphenylmethyl chlorides.*

Substituents	$10^{-4}\varepsilon_{max.}$	λ, mμ	Substituents	$10^{-4}\varepsilon_{max.}$	λ, mμ
Unsubstituted	3·8	430	4-Chloro	4·9	442
2-Methyl	3·4	425	2-Bromo	3·5	452
4-Methyl	4·6	446	4-Bromo	5·1	450
2 : 2′ : 2″-Trimethyl *	2·5	460	4 : 4′-Dimethyl	5·6	452
4 : 4′ : 4″-Trimethyl	7·8	450	2-Chloro-4′ : 4″-dimethyl	5·8	476
2-Chloro	3·7	444	4-Chloro-4′ : 4″-dimethyl	7·8	455

* Newman and Deno (*J. Amer. Chem. Soc.*, 1951, **73**, 3645).

FIG. 3.

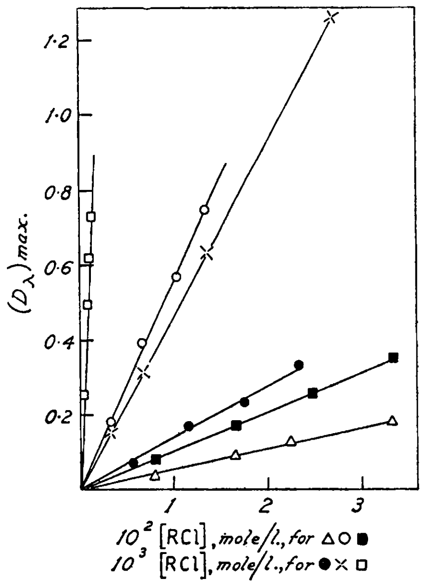

FIG. 4.

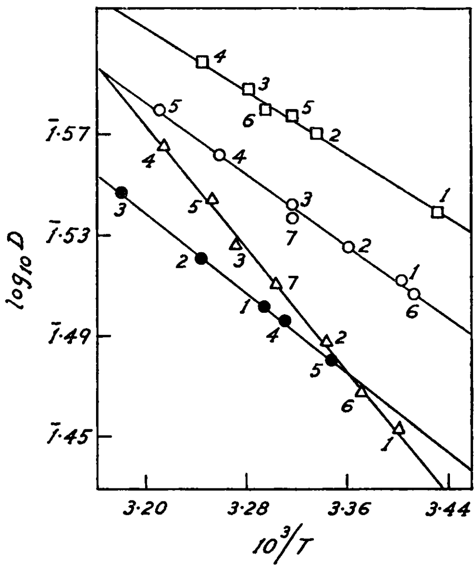

FIG. 3.

○ 2-Methyltriphenylmethyl chloride in $MeNO_2$ at 18°.
● 2 : 5-Dimethyltriphenylmethyl chloride in $MeNO_2$ at 18°.
□ 2 : 4′ : 4″-Trimethyltriphenylmethyl chloride in $MeNO_2$ at 19°.
△ 2-Chlorotriphenylmethyl chloride in $MeNO_2$ at 19°.
■ 2-Bromotriphenylmethyl chloride in $MeNO_2$ at 18°.
× 2-Chloro-4′ : 4″-dimethyltriphenylmethyl chloride in $MeNO_2$ at 18°.

FIG. 4.

○ 2-Methyltriphenylmethyl chloride.
□ 3-Methyltriphenylmethyl chloride.
● 2 : 5-Dimethyltriphenylmethyl chloride.
△ 2-Chlorotriphenylmethyl chloride.

DISCUSSION

Spectra.—From the values given in Table 2, which we obtain for the maximum extinction coefficients, ε, we see that the introduction of *para*-substituents increases the extinction coefficient of the triphenylmethyl ion, but changing the substituent from the *para*- to the *ortho*-position causes a marked decrease in the extinction coefficient, reducing it to a value similar to or even less than that of the unsubstituted ion. This effect in the 2 : 2′ : 2″-tritolylmethyl ion has been attributed by Newman and Deno (*loc. cit.*, 1951, **73**, 3645) to steric inhibition of resonance by the *ortho*-group, an effect which does not operate in the *para*-substituted ion.

Effect of Substituent Groups.—From Table 1 we see that the effects of 2-methyl, 2-chloro-, and 2-bromo-substituents upon $\Delta G°$ for the ionization are similar (to within

0·3 kcal./mole) to the effects obtained when the corresponding groups are introduced into the 4-position. We have calculated the values of $\Delta G^{\ddagger}$, the free energy of activation for the alcoholysis of substituted diphenylmethyl chlorides, from the velocity constants obtained by Norris and Banta (*J. Amer. Chem. Soc.*, 1928, **50**, 1804), and these values are given in Table 1. It is seen that for the introduction of *ortho*- and *para*-chloro-groups, the change in $\Delta G^{\ddagger}$ is in the same direction as is the corresponding change in ΔG°. The chlorine atom, however, produces a greater increase in $\Delta G^{\ddagger}$ (*i.e.*, a more marked slowing down of the reaction rate) when introduced into the *ortho*- than into the *para*-position although the corresponding effects on ΔG° are the same. In the same way, the methyl group appears to produce a smaller decrease in $\Delta G^{\ddagger}$ (*i.e.*, a less marked speeding up of the reaction) when introduced into the *ortho*- than into the *para*-position, although again the corresponding effects on ΔG° are the same. This means that if the alcoholysis were S_N1 in mechanism, the reaction of the *ortho*-substituted compound is slower than one would expect from the consideration of the fact that ΔG° is the same for both *ortho*- and *para*-substituted triphenylmethyl chlorides.

The value of ΔG° for 2 : 5-dimethyltriphenylmethyl chloride calculated from the ΔG° values of 2-methyl- and 3-methyl-substituted triphenylmethyl chlorides is 3·3 kcal./mole, which is close to that observed, *viz.*, 3·1 kcal./mole. The ΔG° value for 2-chloro-4′ : 4″-dimethyltriphenylmethyl chloride calculated from the ΔG° value of 2-chloro- and that of 4 : 4′-dimethyl-triphenylmethyl chloride (A. G. Evans, Jones, and Osborne, *Trans. Faraday Soc.*, 1954, **50**, 16), is 3·1 kcal./mole compared with the observed value of 2·8 kcal./mole. The ΔG° value of 2 : 4′ : 4″-trimethyltriphenylmethyl chloride calculated from the ΔG° value of 2-methyl- and of 4 : 4′-dimethyl-triphenylmethyl chloride is 1·8 kcal./mole, compared with the observed value of 1·4 kcal./mole. Thus, although the effect of *ortho*-groups is not so strictly additive as for *para*-groups, a fair degree of additivity still holds for the effect of these groups on ΔG°.

The ΔH° values of the *ortho*-substituted compounds are seen to be in general somewhat greater (*i.e.*, the ionization is more endothermic) than those of the corresponding *para*-substituted compounds.

Values of ΔS° for the *ortho*- are somewhat less negative than those obtained for the corresponding *para*-substituted compounds. This effect may be attributed to the intrusion of the *ortho*-group into the solvation shell around the carbon atom which has the formal positive charge, thus reducing the extent to which the solvent is " frozen " around the ion. Such a reduction in the extent to which the solvent interacts with the ion may account for the higher endothermicity of ionization of the *ortho*-compounds.

The introduction of a *meta*-methyl group into triphenylmethyl chloride causes a slight increase in ionization, as shown by the small decrease of 0·4 kcal./mole in ΔG° (compared with the decrease of 0·8 kcal./mole for the introduction of an *ortho*-methyl group). This introduction of a *meta*-methyl group involves practically no change in ΔH° or ΔS°. Lichtin and Bartlett (*J. Amer. Chem. Soc.*, 1951, **73**, 5530) have also obtained a ΔG° change of 0·4 kcal./mole for this effect in their conductimetric study of substituted triphenylmethyl chlorides in liquid sulphur dioxide. This decrease in ΔG° is paralleled by a decrease of 0·45 kcal./mole in the free energy of alcoholysis, $\Delta G^{\ddagger}$, which occurs when a *meta*-methyl group is introduced into diphenylmethyl chloride (Table 1). This parallelism has been found in Parts III and IV (*locc. cit.*) for *para*-substituent groups.

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