

## THE IONIZATION OF ORGANIC HALIDES IN NITROALKANES

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*Received 27th May, 1953; in final form, 18th September, 1953*

The thermodynamics of the equilibrium  $\text{RCl}_{(s)} \rightleftharpoons \text{R}^+\text{Cl}^-_{(s)}$  in nitromethane have been studied for various R groups. The values of  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  for this reaction have been obtained, and the results are discussed in relation to corresponding  $\text{S}_{\text{N}}1$  reactions.

A knowledge of the thermodynamics of the equilibrium



is important for the understanding of organic halide reactivity. This type of reaction has been studied by a spectroscopic method, and values of  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  obtained.<sup>1, 2, 3</sup> A conductimetric method has also been used to study the ionization of organic halides in liquid sulphur dioxide.<sup>4</sup> In our present paper we give the results obtained for reaction (1) for various types of RCl in nitromethane as solvent.

### EXPERIMENTAL

**MATERIALS.**—*Nitromethane.*—Since the reproducibility of successive batches of nitromethane is very important, we prepared samples of this solvent by different methods, and compared these samples by measuring the ionization of tri-*p*-tolylmethyl chloride in them. A sample was obtained by drying the nitromethane for 10 h over phosphorus pentoxide, distilling off at 20 mm pressure, then distilling at atmospheric pressure through a 40-cm long fractionating column, and collecting the fraction distilling over the range 100.5°–101.5°.  $\Delta G^\circ$  for the ionization of tri-*p*-tolylmethyl chloride in this solvent was found to be 1.7 kcal using the method previously described.<sup>1, 2</sup> The value of  $\Delta G^\circ$  for this reaction was not affected by treating this solvent (i) to subsequent distillation, (ii) to further treatment with phosphorus pentoxide, (iii) to subsequent treatment with  $\text{K}_2\text{CO}_3$  or (iv) by changing the source of supply. It is by this method that we purified our solvent, and each new batch has been accurately overlapped with the previous one.

*Sulphuric acid.*—This was 98 % A.R. material supplied by Hopkin and Williams.

*Triaryl carbinols.*—These were prepared from the appropriate Grignard reagent and carbonyl compound by boiling in ether solution for 4–8 h, decomposing the complex with ice and dilute sulphuric acid, and steam distilling. Recrystallization, generally from low boiling petroleum ether, gave pale coloured solids, which were repeatedly crystallized to constant melting points. The emphasis in each experiment was on purity rather than on maximum yield, and each carbinol was finally obtained as a white crystalline solid.

The melting points of all but four of the carbinols have been reported previously. The analyses and melting points which we obtained for the four carbinols which have not been reported previously are as follows: mono-*p*-*tert*-butyltriphenylcarbinol: found, C, 87.3; H, 7.50; calculated, C, 87.3; H, 7.64 %; m.p. 80–81°. Di-*p*-*tert*-butyltriphenyl-

carbinol; found, C, 86.9; H, 8.71; calculated, C, 87.0; H, 8.66; m.p. 111-112°. Mono-*p*-iso-propyltriphenylcarbinol; found, C, 86.5; H, 7.25; calculated: C, 87.4, H, 7.33; m.p. 66-67°. Tri-*p*-isopropyltriphenylcarbinol: found, C, 86.0; H, 8.78; calculated: C, 86.9, H, 8.86; m.p. 96-97°. (The analyses were carried out by Messrs. Weiler and Strauss, Oxford.)

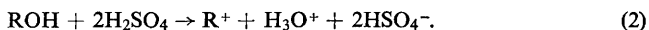
**Triarylmethyl chlorides.**—These were prepared by boiling the carbinols with acetyl chloride + petroleum ether mixture for 15-60 min. On cooling, the solid chloride was deposited, and this was recrystallized from a solution of 10 % acetyl chloride in petroleum ether. The resulting white crystals were carefully washed free from acetyl chloride with petroleum ether, and then dried in a desiccator over calcium chloride. In no case was the chloride stored; each was prepared from the carbinol just before it was used. All these chlorides had been prepared earlier, and the melting points of our materials agreed well with those given in the literature.

**PROCEDURE.**—The method of studying the equilibrium shown in eqn. (1) was the same as described previously.<sup>1, 2</sup>

## RESULTS

### CARBONIUM ION SPECTRA.

In fig. 1 to 4 the optical density  $D_\lambda$  is plotted against wavelength  $\lambda$  for the solutions of RCl in nitromethane and of ROH in 98 %  $\text{H}_2\text{SO}_4$ . In these latter solutions we assume that the following reaction goes to completion :



The completeness of reaction (2) has been established by Hantzsch<sup>5</sup> and Hammett and Deyrup<sup>6</sup> when R is triphenylmethyl, and by Newman and Deno<sup>7</sup> when R is tri-*p*-tolylmethyl and tri-*p*-nitro-triphenylmethyl. Since the *para*-groups which we have used fall within this series as regards their tendency to promote the formation of the  $\text{R}^+$  ion, we are justified in assuming reaction (2) to be complete for the carbinols we have used. The very marked similarity between the spectra of RCl in nitromethane and in conc.  $\text{H}_2\text{SO}_4$  establishes the presence of the  $\text{R}^+$  ion in the nitromethane solution of RCl. We may obtain the concentration of these ions in the nitromethane solution by assuming that the maximum extinction coefficient  $\epsilon$  of  $\text{R}^+$  is the same in conc.  $\text{H}_2\text{SO}_4$  as it is in nitromethane.

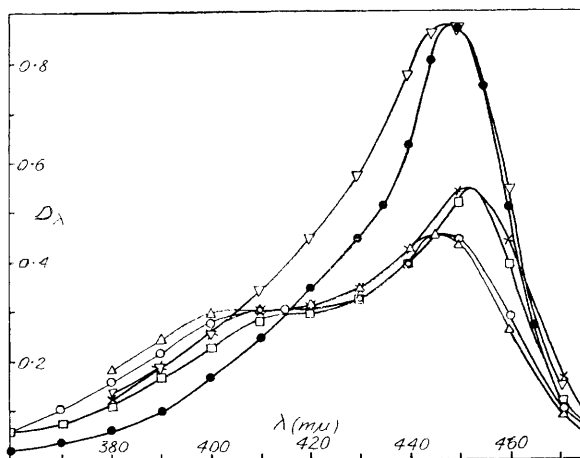


FIG. 1.

Δ	( <i>p</i> -Me C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> CCl in nitromethane	5.30 × 10 <sup>-3</sup> mole/l. at 18.5° C
○	( <i>p</i> -Me C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> COH in 98 % H <sub>2</sub> SO <sub>4</sub>	1.0 × 10 <sup>-5</sup> mole/l.
×	( <i>p</i> -Me C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> CCl in nitromethane	9.56 × 10 <sup>-4</sup> mole/l. at 17.5° C
□	( <i>p</i> -Me C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> COH in 98 % H <sub>2</sub> SO <sub>4</sub>	1.0 × 10 <sup>-5</sup> mole/l.
▽	( <i>p</i> -Me C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> CCl in nitromethane	2.18 × 10 <sup>-4</sup> mole/l. at 20° C
●	( <i>p</i> -Me C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> COH in 98 % H <sub>2</sub> SO <sub>4</sub>	1.13 × 10 <sup>-5</sup> mole/l.

## NATURE OF THE EQUILIBRIUM

The change in the optical density  $D_\lambda$  at the peak of the spectrum with change of RCl concentration in nitromethane gave a straight line relationship in all cases (see for example, fig. 5). This demonstrates that the ions  $R^+$  and  $Cl^-$  do not dissociate in this solvent but remain together as a solvated ion pair as shown in eqn. (1). The value of the equilibrium constant  $K = [R^+Cl^-]/[RCl]$  was obtained from the slope of the  $[R^+]$  against  $[RCl]$  line. The value of  $[R^+]$  used in this plot was obtained by assuming the maximum value of  $\epsilon$  to be the same in conc.  $H_2SO_4$  as it is in nitromethane, and

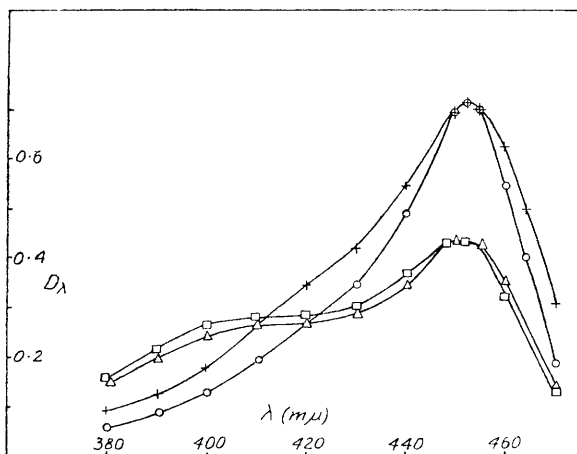


FIG. 2.

□	( <i>p</i> -iso-Pr $C_6H_4$ ) $_2$ CCl in nitromethane	$4.07 \times 10^{-3}$ mole/l. at $21^\circ C$
Δ	( <i>p</i> -iso-Pr $C_6H_4$ ) $_2$ COH in 98 % $H_2SO_4$	$0.85 \times 10^{-5}$ mole/l.
+	( <i>p</i> -iso-Pr $C_6H_4$ ) $_3$ CCl in nitromethane	$2.07 \times 10^{-4}$ mole/l. at $21.5^\circ C$
○	( <i>p</i> -iso-Pr $C_6H_4$ ) $_3$ COH in 98 % $H_2SO_4$	$0.85 \times 10^{-5}$ mole/l.

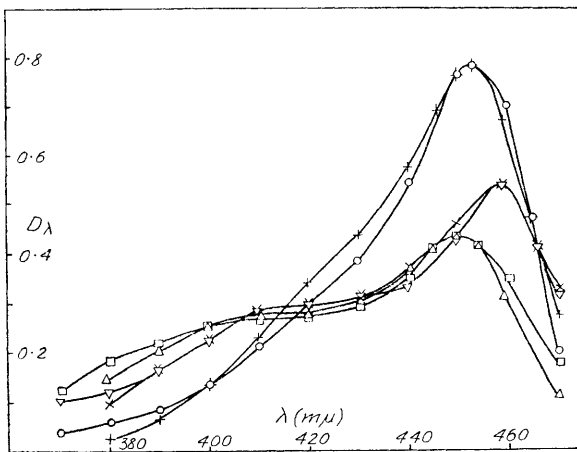


FIG. 3.

Δ	( <i>p</i> -tert.-Bu $C_6H_4$ ) $_2$ CCl in nitromethane	$5.36 \times 10^{-3}$ mole/l. at $21.5^\circ C$
□	( <i>p</i> -tert.-Bu $C_6H_4$ ) $_2$ COH in 98 % $H_2SO_4$	$0.83 \times 10^{-5}$ mole/l.
×	( <i>p</i> -tert.-Bu $C_6H_4$ ) $_2$ CCl in nitromethane	$0.87 \times 10^{-3}$ mole/l. at $21^\circ C$
▽	( <i>p</i> -tert.-Bu $C_6H_4$ ) $_2$ COH in 98 % $H_2SO_4$	$0.83 \times 10^{-5}$ mole/l.
+	( <i>p</i> -tert.-Bu $C_6H_4$ ) $_3$ CCl in nitromethane	$0.25 \times 10^{-3}$ mole/l. at $20^\circ C$
○	( <i>p</i> -tert.-Bu $C_6H_4$ ) $_3$ COH in 98 % $H_2SO_4$	$0.83 \times 10^{-5}$ mole/l.

the values of  $\Delta G^\circ = -RT \ln([R^+Cl^-]/[RCl])$  so obtained were reproducible to  $-0.1$  kcal. (Making the alternative assumption that  $\int \epsilon d\lambda$  is the same in the two solvents would not change these  $\Delta G^\circ$  values by more than  $0.1$  kcal.)

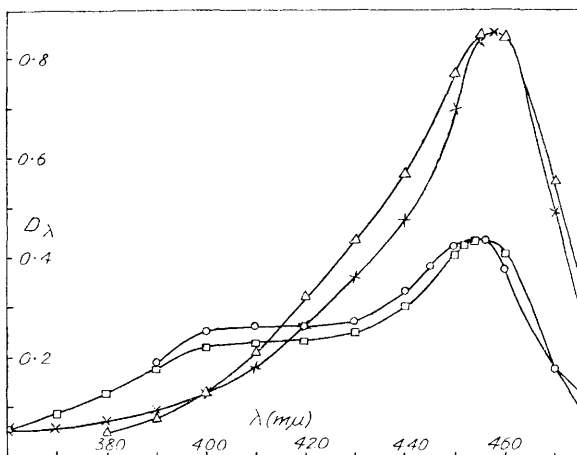


FIG. 4.

- |   |   |   |
|---|---|---|
| ○ | $(p\text{-C}_6\text{H}_{11}\text{C}_6\text{H}_4)_2\text{CCl}$ in nitromethane                 | $3.07 \times 10^{-3}$ mole/l. at $19^\circ\text{C}$ |
| □ | $(p\text{-C}_6\text{H}_{11}\text{C}_6\text{H}_4)_2\text{COH}$ in 98 % $\text{H}_2\text{SO}_4$ | $7.80 \times 10^{-6}$ mole/l.                       |
| Δ | $(p\text{-C}_6\text{H}_{11}\text{C}_6\text{H}_4)_3\text{CCl}$ in nitromethane                 | $1.54 \times 10^{-4}$ mole/l. at $23^\circ\text{C}$ |
| × | $(p\text{-C}_6\text{H}_{11}\text{C}_6\text{H}_4)_3\text{COH}$ in 98 % $\text{H}_2\text{SO}_4$ | $7.80 \times 10^{-6}$ mole/l.                       |

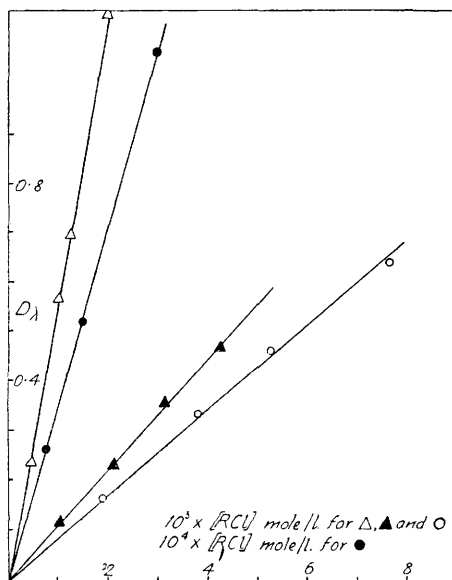


FIG. 5.

- |   |  |
|---|--|
| ○ | $(p\text{-Me C}_6\text{H}_4)_2\text{CCl}$ in nitromethane      |
| Δ | $(p\text{-Me C}_6\text{H}_4)_2\text{CCl}$ in nitromethane      |
| ▲ | $(p\text{-iso-Pr C}_6\text{H}_4)_2\text{CCl}$ in nitromethane  |
| ● | $(p\text{-iso-Pr C}_6\text{H}_4)_3\text{CCl}$ in nitromethane. |

CHANGE OF  $K$  WITH TEMPERATURE

The change of  $K$  with temperature was determined as described earlier,<sup>1,2</sup> and in all cases the plot of  $\log D_{\max}$  against  $1/T$  gave a good straight line (see for example, fig. 6). Since the fraction of  $RCl$  which is ionized is small in all cases, this plot gives the same slope as the  $\log K$  against  $1/T$  line, if we assume that the maximum extinction coefficient of  $R^+$  is temperature independent. (We have tested this assumption with a solution of di- $p$ -methyltriphenylcarbinol in sulphuric acid, and find that there is no change in

the maximum extinction coefficient of this carbonium ion over the temperature range normally used in these experiments.\*) The change in the concentration of the carbonium ions due to expansion of the solvent has been allowed for in all these plots. The solution was sealed in the cell, and the points in the figures are numbered to show the sequence in which the temperature of the solution was varied.

The expression  $d \ln K/dT = \Delta H/RT^2$  at a given temperature is true, whether  $\Delta H^\circ$  and  $\Delta S^\circ$  for the reaction are constant with temperature, or whether they vary, due for example to a change in dielectric constant with temperature. Our plots of  $\log K$  against  $1/T$  have the form:  $\log K = A - (B/T)$ , where  $A$  and  $B$  are constants. It is seen from the figures that any departure of the experimental points from the straight line is quite random, and there is no indication whatever of any curvature. Thus our results have the form  $d \ln K/dT = B/T^2$  and comparison of this with the earlier expression establishes that for our reactions  $\Delta H^\circ$  is constant over the experimental temperature range. This being so, we have plotted  $\log K$  against  $1/T$ , and found  $\Delta H^\circ$  from the slope of this plot.

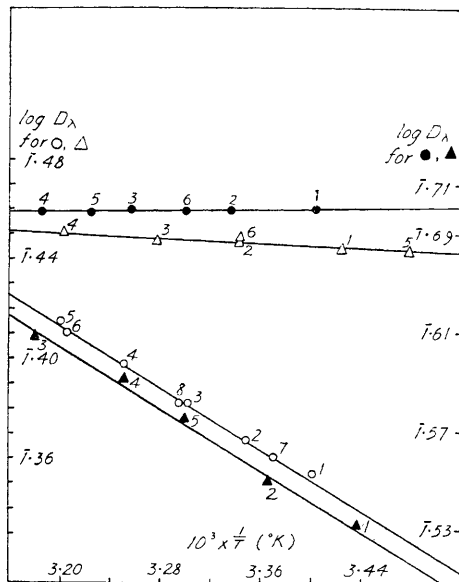


FIG. 6.

- (*p*-Me C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CCl in nitromethane  
 Δ (*p*-Me C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CCl in nitromethane  
 ▲ (*p*-iso-Pr C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CCl in nitromethane  
 ● (*p*-iso-Pr C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>CCl in nitromethane.

The value of  $\Delta H^\circ$  so obtained gives the actual change in heat content for the reaction at the temperature of our experiments. In all cases the temperature-dependence experiment was done at least twice (in most cases three or more determinations were made), except for tri-*p*-cyclohexyltriphenylmethyl chloride, and it was found that the  $\Delta H^\circ$  values so obtained for any compound never differed by more than 0.4 kcal. The mean values of  $\Delta H^\circ$  so obtained are given in table 1, and we consider these to be accurate to within  $\pm 0.2$  kcal. The value of the standard entropy change  $\Delta S^\circ$  for reaction (1) was determined from the values of  $\Delta G^\circ$  and  $\Delta H^\circ$ , and the results are given in table 1. We consider these values to be accurate to within  $\pm 1.0$  cal/deg. mole.

Using the more standardized method of purifying the solvent we have redetermined the  $\Delta G^\circ$  and  $\Delta H^\circ$  values which we gave previously for triphenylmethyl chloride<sup>1</sup> and tri-*p*-tolylmethyl chloride<sup>2</sup> in nitromethane, nitroethane and  $\beta$ -nitropropane. In these redetermination experiments we have also made sure that the results are not affected by the presence of traces of metal halides in the RCl. (We have recently determined the very marked effect which a trace of Friedel-Crafts catalyst has on the ionization of triphenylmethyl chloride.)<sup>3</sup> Since the preparation of the commercial triphenylmethyl chloride involves the use of aluminium chloride, the triphenylmethyl chloride used in these redetermination experiments was obtained (i) from B.D.H. triphenylcarbinol and (ii) from benzophenone by means of phenyl magnesium bromide. The tri-*p*-tolylmethyl chloride used in the redetermination experiments was obtained from Mersey Chemicals

\* This experiment was carried out by Mr. A. Price.

Ltd. It was purified by boiling with water for 10 h, recrystallizing the carbinol so produced (m.p. 93°) and reconvertng this to the chloride by acetyl chloride. It was found that boiling with water for more than 10 h made no difference to the results obtained. In addition to this, since magnesium has been used in the commercial preparation of the material, the effect on  $\Delta G^\circ$  was examined when the nitromethane was saturated with magnesium sulphate. No measurable effect was found.

The redetermined values are given in table 1 along with the new ones which we have obtained in the present work. The  $\Delta G^\circ$  values redetermined in this way for triphenylmethyl chloride in nitromethane, nitroethane, and  $\beta$ -nitropropane, and for tri-*p*-tolylmethyl chloride in nitroethane and  $\beta$ -nitropropane are exactly the same as those which we have obtained previously. The redetermined value of  $\Delta G^\circ$  for tri-*p*-tolylmethyl chloride in nitromethane is higher than our earlier value, 1.7 kcal as compared with 1.0 kcal, but this change does not affect our previous conclusions. (The tri-*p*-tolylmethyl curves are shown in fig. 1).

TABLE 1\*

## A. Thermodynamic constants for the ionization of triphenylethyl chloride

solvent	$\Delta G^\circ(T^\circ\text{C})$ kcal/mole	$\Delta H^\circ$ kcal/mole	$\Delta S^\circ$ cal/deg. mole.
nitromethane	4.5 (20.0°)	1.4	— 10.5 (20.0°)
nitroethane	5.7 (20.0°)		
$\beta$ -nitropropane	6.3 (20.0°)		

## B. Thermodynamic constants for the ionization of substituted triphenylmethyl chloride

solvent	substituents	$\Delta G^\circ(T^\circ\text{C})$ kcal/mole	$\Delta H^\circ$ kcal/mole	$\Delta S^\circ$ cal/deg. mole.
nitromethane	mono- <i>p</i> -methyl	3.6 (19.0°)	1.4	— 7.6 (19.0°)
„	di- <i>p</i> -methyl	2.6 (20.5°)	0.2	— 8.3 (20.5°)
„	tri- <i>p</i> -methyl	1.7 (20.0°)	— 0.2	— 6.4 (20.0°)
nitroethane	tri- <i>p</i> -methyl	3.1 (18.1°)	— 0.1	— 11.0 (18.1°)
$\beta$ -nitropropane	tri- <i>p</i> -methyl	3.7 (19.0°)	— 0.1	— 13.0 (19.0°)
nitromethane	mono- <i>p</i> -isopropyl	3.6 (21.0°)	1.4	— 7.6 (21.0°)
„	tri- <i>p</i> -isopropyl	1.9 (21.0°)	— 0.1	— 6.8 (21.0°)
nitromethane	mono- <i>p</i> - <i>tert</i> -butyl	3.7 (21.0°)	1.1	— 8.8 (21.0°)
„	di- <i>p</i> - <i>tert</i> -butyl	2.7 (21.0°)	0.8	— 6.5 (21.0°)
„	tri- <i>p</i> - <i>tert</i> -butyl	2.0 (20.0°)	0.2	— 6.2 (20.0°)
nitromethane	mono- <i>p</i> -C <sub>6</sub> H <sub>11</sub>	3.5 (21.0°)	1.2	— 7.7 (21.0°)
„	tri- <i>p</i> -C <sub>6</sub> H <sub>11</sub>	1.7 (23.0°)	0.2	— 5.1 (23.0°)

As regards the redetermination of  $\Delta H^\circ$ , the value obtained for triphenylmethyl chloride is lower than that given previously; 1.4 kcal instead of 2.75 kcal. This value of 1.4 kcal to within  $\pm 0.2$  kcal was obtained in twelve experiments, when the triphenylmethyl chloride was made by the method described above. When, however, a sample of the commercial triphenylmethyl chloride was purified by the method used in our earlier work <sup>1</sup> (by recrystallizing from petrol ether containing 10 % acetyl chloride, to give a product with the correct melting point of 111° C), it was found to give a  $\Delta H^\circ$  value of 2.4 kcal in nitromethane which agreed with the value we gave earlier, but a test on it for aluminium using the aluminon spot test gave a positive result. When, however, this commercial

\* The  $\Delta G^\circ$  values in this table are calculated assuming that the maximum value of  $\epsilon$  is the same in conc. H<sub>2</sub>SO<sub>4</sub> as it is in the nitroalkane. Making the alternative assumption that  $\int \epsilon d\lambda$  is the same in the two solvents would not change the  $\Delta G^\circ$  values for the nitromethane solutions by more than 0.1 kcal, but would reduce the  $\Delta G^\circ$  values for tri-*p*-tolylmethyl chloride in nitroethane and  $\beta$ -nitropropane by 0.1 and 0.2 kcal respectively; and reduce the  $\Delta G^\circ$  values for triphenylmethyl chloride in nitroethane and  $\beta$ -nitropropane by about 0.2 and 0.4 kcal respectively.

triphenylmethyl chloride was first boiled with dilute acid to convert it to carbinol, the carbinol twice recrystallized from benzene plus charcoal, and then reconverted to the chloride by boiling with 100 % acetyl chloride and washing with petroleum ether, it was found that this chloride did not give the test for aluminium and that  $\Delta H^\circ$  now had a value of 1.5 kcal. A repeat of this experiment gave a  $\Delta H^\circ$  of 1.4 kcal.\* We conclude, therefore, that the value of  $\Delta H^\circ$  for the ionization reaction of triphenylmethyl chloride in nitromethane is 1.4 kcal; the higher value obtained earlier being due to a small trace of aluminium in the triphenylmethyl chloride which was not eliminated in the purification process.

The  $\Delta H^\circ$  value redetermined for tri-*p*-tolylmethyl chloride in nitroethane is the same (i.e. thermoneutral), within experimental error, as that we obtained previously. The new value of  $\Delta H^\circ$  for tri-*p*-tolylmethyl chloride in nitromethane is -0.2, compared with our earlier value of -0.65 kcal/mole. The new value of  $\Delta H^\circ$  for tri-*p*-tolylmethyl chloride in  $\beta$ -nitropropane is -0.1 compared with our earlier value of 0.6 kcal/mole. We believe that these later values are more accurate because of the greater precautions taken in the standardization of the solvent batches and in the purification of the tri-*p*-tolylmethyl chloride.

## DISCUSSION

### SPECTRUM OF R<sup>+</sup>

It is found that there is a close agreement between the spectrum determined for a di-*p*-substituted triarylcannabinol in conc. H<sub>2</sub>SO<sub>4</sub> and the curve calculated from the corresponding spectra of the unsubstituted and tri-substituted carbinols by adding one-third the  $D_\lambda$  of the unsubstituted carbinol to two-thirds the  $D_\lambda$  of the tri-*p*-substituted carbinol for solutions of the same concentration. With the mono-*p*-substituted carbinols, however, although the spectrum calculated in this way (by adding two-thirds the  $D_\lambda$  of the unsubstituted carbinol to one-third the  $D_\lambda$  of the tri-*p*-substituted carbinol) is of a similar shape to that experimentally determined, the fit between the two curves is not good.

For the tri-substituted ions we find that the wavelength of the peak increases along the series of the substituents: methyl, *isopropyl*, *tert*.-butyl, cyclohexyl. For any one substituent, the wavelength of the peaks are in order: di- > tri- > mono-.

### EFFECT OF SUBSTITUENT GROUPS

From the results in table 1 we may make the following points. (i) For a given alkyl group, as each successive *para*-alkyl group is introduced, there is a decrease in  $\Delta G^\circ$  corresponding to an increase in the equilibrium constant  $K$  of the ionization reaction (1). This is accompanied by an overall decrease in  $\Delta H^\circ$  (i.e. an increase in the exothermicity of reaction). (ii) The introduction of a *para*-alkyl group into triphenylmethyl chloride causes a slight but definite increase in  $\Delta S^\circ$ . (iii) The increase in  $\Delta G^\circ$  as the solvent changes from nitromethane to  $\beta$ -nitropropane is mainly due to a decrease in  $\Delta S^\circ$ .

It is of interest to compare the effect of substituent groups on  $\Delta G^\circ$  for the reaction (1) with their effect on  $\Delta G^\ddagger$  of  $S_N1$  reactions. Nixon and Branch<sup>8</sup> have measured the velocity constants  $k_r$  for the alcoholysis of triphenylmethyl chloride and mono-*p*-methyltriphenylmethyl chloride. These reactions are most certainly of the  $S_N1$  type. From their results we have calculated the corresponding values of  $\Delta G^\ddagger$ , the free energy of activation of the alcoholysis, using the equation<sup>9</sup>  $\Delta G^\ddagger = -RT \ln(k_r/hkT)$ , where  $k$  is the Boltzmann constant. The  $\Delta G^\ddagger$  values so calculated are: 17.2 kcal for triphenylmethyl chloride and 16.43 kcal for mono-*p*-methyltriphenylmethyl chloride at 0°C. Our  $\Delta G^\circ$  values for the same compounds in nitromethane are 4.5 and 3.6 kcal respectively. Thus the effect of a *p*-methyl group on the  $\Delta G^\circ$  of reaction (1) is very similar to its effect on the  $\Delta G^\ddagger$  of the corresponding  $S_N1$  reaction, a decrease of some 0.9 kcal occurring in each case.

\* Mr. A. Bentley assisted with these experiments.

Hughes, Ingold and Taher<sup>10</sup> have measured the velocity constants  $k_r$  for the  $S_N1$  hydrolysis at 0° C of mono-*p*-alkyl substituted benzhydryl chlorides in 80 % aqueous acetone. We have calculated the  $\Delta G^\ddagger$  values from their results as follows: unsubstituted, 22.9; *p*-methyl, 21.1; *p*-isopropyl, 21.4; *p*-tert.-butyl, 21.53 kcal. In fig. 7 we plot the difference between our  $\Delta G^\circ$  values for unsubstituted and substituted triphenylmethyl chloride in nitromethane against the corresponding differences in the  $\Delta G^\ddagger$  values given above. The parallelism between the two sets of values is seen to be quite close. Not only do our values of  $\Delta G^\circ$  show the Baker and Nathan effect, but the changes in  $\Delta G^\circ$  produced by these substituent groups are of a similar order of magnitude to the corresponding changes in  $\Delta G^\ddagger$ .

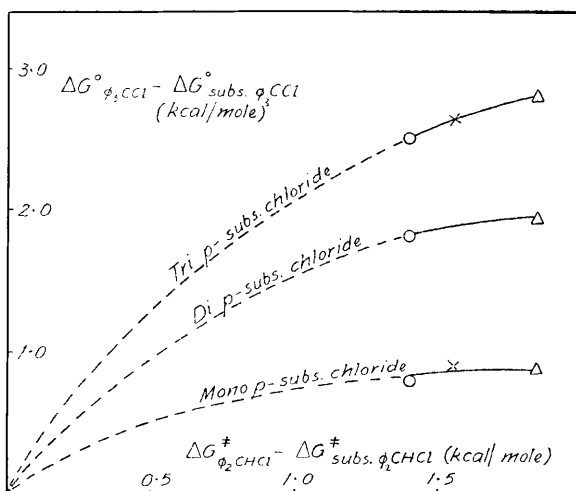


FIG. 7.

Nature of *para*-substituent.

Δ methyl

× isopropyl

○ tert.-butyl.

This parallelism between the changes in  $\Delta G^\ddagger$  for the  $S_N1$  reaction, and the changes in  $\Delta G^\circ$  for the corresponding reaction of type (1) is to be expected. Changes in R which lower the free energy difference between the initial and final states of the reaction,  $RCl_{(s)} \rightleftharpoons R^+Cl^-_{(s)}$ , will also lower the free energy difference between the initial and transition states of the  $S_N1$  reaction of RCl.

We wish to thank the D. S. I. R. for the Maintenance Allowances held by two of us (J. A. G. J. and G. O. O.).

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<sup>2</sup> Bentley and Evans, A. G., *J. Chem. Soc.*, 1952, 3468.

<sup>3</sup> Bentley and Evans, A. G., *Research*, 1952, **5**, 535.

<sup>4</sup> Lichtin and Bartlett, *J. Amer. Chem. Soc.*, 1951, **78**, 5530.

<sup>5</sup> Hantzsch, *Z. physik. Chem.*, 1908, **61**, 257.

<sup>6</sup> Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1933, **55**, 1900.

<sup>7</sup> Newman and Deno, *J. Amer. Chem. Soc.*, 1951, **73**, 3644.

<sup>8</sup> Nixon and Branch, *J. Amer. Chem. Soc.*, 1936, **58**, 492.

<sup>9</sup> Wynne-Jones and Eyring, *J. Chem. Physics*, 1935, **3**, 492; see also Glasstone, Laidler and Eyring, *Theory of Rate Processes* (McGraw-Hill Inc., 1941), p. 195.

<sup>10</sup> Hughes, Ingold and Taher, *J. Chem. Soc.*, 1940, 949.