Nuclear Magnetic Resonance Study of the Ionization Kinetics of Triphenylmethanols in Concentrated Acid Solutions

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The n.m.r. line shape method is used to determine the rate constants for the appearance and disappearance of substituted triphenylmethyl ions in concentrated H_2SO_4 and $HClO_4$ solutions. The ionization reaction of tris-(4-methylphenyl)methanol is studied in 60% (w/w) dioxan–water solutions and that of tris-(4-methyl-3-sulphophenyl)methanol in water. From the closer correlation of log k_f (for ion formation) with H_0 than with H_R, it is concluded that the transition state approximates much more closely to a protonated alcohol than to the carbonium ion structure. Further evidence for a special interaction between perchlorate and triphenylmethyl ions is also provided by the n.m.r. chemical shifts observed in solutions of tris-(4-methylphenyl) and triphenylmethyl carbonium ions in mixtures of 98% H_2SO_4 with 70% $HClO_4$. The shifts observed are concordant with those calculated from Buckingham's equation when the perchlorate ion is assumed to be *ca.* 6 Å from the charged carbon atom.

THE H_R acidity function is based on reaction (1) and, unlike H_0,[1] it is not a common function of water activity for different strong acids.[2] In particular, on the H_R scale perchloric acid is relatively much stronger than the other strong acids. The proton hydration explanation of the H_0 dependence on water activity[1] is therefore

$$R_3COH + H^+ \underset{k_b}{\overset{k_f}{\rightleftharpoons}} R_3C^+ + H_2O \qquad (1)$$

inadequate for H_R, so other interactions could be important.

Two accounts of the effects of added salts on the kinetics and equilibrium of the ionization of tris-(4-methoxyphenyl)methanol in aqueous solution have been published recently.[3,4] Both concluded that the presence of the perchlorate ion gave an unusual extra stability to triarylmethyl ions in aqueous solutions, such as could arise from ion pair formation, *e.g.* of the ' solvent structure enforced ' type.[5]

A good correlation between log k_f and H_0 was also observed,[3] but since the acid concentrations did not exceed 1M the difference between H_0 and H_R was not large. One obstacle to an extension to higher acidities

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[1] P. A. H. Wyatt, *Discuss. Faraday Soc.*, 1957, **24**, 162.

[2] E. Högfeldt, *Acta Chim. Scand.*, 1962, **16**, 1054.

[3] M. J. Postle and P. A. H. Wyatt, *J.C.S. Perkin II*, 1972, 474.

[4] C. A. Bunton and S. K. Huang, *J. Amer. Chem. Soc.*, 1972, **94**, 3536.

[5] R. M. Diamond, *J. Phys. Chem.*, 1963, **67**, 2513.

(greater $H_0 - H_R$ differences) was that the reaction rates became too fast for the stopped-flow technique. We have therefore adopted an n.m.r. line shape method. This approach has also been used by Brauman and Archie[6] in a study of tris-(2,4,6-trideuteriophenyl)-methanol, but their solvent was acetonitrile containing only small amounts of water and the kinetic results are not directly relevant to a predominantly aqueous system. Since n.m.r. measurements require greater triphenylmethanol concentrations than the stopped-flow technique, our solubility difficulties had to be overcome in two ways: (a) by modifying the solvent: k_f and k_b were determined for tris-(4-methylphenyl)methanol in 60% (w/w) dioxan–water solutions of perchloric and sulphuric acids; (b) by sulphonating the solute to increase its solubility in water: k_f and k_b were determined for tris-(4-methyl-3-sulphophenyl)methanol in aqueous perchloric and sulphuric acids.

We have also sought further evidence for ion pairing between perchlorate and triarylmethyl ions. N.m.r. chemical shift measurements were made on the tris-(4-methylphenyl) and triphenylmethyl carbonium ions in concentrated sulphuric acid and sulphuric acid–perchloric acid mixtures.

EXPERIMENTAL

Tris-(4-*methylphenyl*)*methanol.*—This was prepared by reaction of diethyl carbonate and 4-methylphenylmagnesium bromide as described by Newman and Deno.[7] After several recrystallizations from light petroleum the product had m.p. 92—94 °C (lit.,[7] 93—94 °C).

Sulphonation of Tris-(4-*methylphenyl*)*methanol.*—Tris-(4-methylphenyl)methanol (1 g) was dissolved in 20% oleum (10 ml) and left on a steam-bath for 1·5 h. The solution was diluted, neutralized with barium carbonate, filtered, and the filtrate was evaporated to dryness. The product was redissolved in water, filtered, and evaporated to dryness again. The very high solubility of the product made further purification extremely difficult.

The sulphonated compound could be identified by its 100 MHz n.m.r. spectrum in 98% sulphuric acid. The high viscosity of this solvent broadens n.m.r. lines to at least 3—4 Hz so that fine structure is easily lost. [For example, the aromatic region of the n.m.r. spectrum of the unsulphonated tris-(4-methylphenyl)methyl carbonium ion is reduced to a simple AB type quartet with J 8·3 Hz, and chemical shift difference δ 11·5 Hz. Any finer detail of the real AA′BB′ system is not visible.]

The aromatic region of the spectrum of the sulphonated compound, tris-(4-methyl-3-sulphophenyl)methyl carbonium ion, consists of a one-proton line, 23·5 Hz downfield from a two-proton AB type quartet with J 8·1 and δ 11·8 Hz. This quartet is very similar to that described for the tris-(4-methylphenyl)methyl carbonium ion but is shifted downfield by 60 Hz. The methyl groups give rise to a single peak indicating that the same substitution pattern is present in each ring.

Sulphonation would be expected to occur in the 3-position and this appears to be confirmed by the chemical shift of the methyl group, which is downfield from its position in the unsulphonated compound in both the alcohol and the carbonium ion. This is consistent with the results of de Vries and Cerfontain[8] who found that with toluenesulphonic acids *ortho*-substitution caused downfield shifts in the methyl resonance, while *meta*- or *para*-substitution caused a smaller but upfield shift.

The ionization of tris-(4-methyl-3-sulphophenyl)methanol at 25 °C was followed spectrophotometrically using the carbonium ion maximum at 457 nm. The ionization followed H_R in both sulphuric and perchloric acids with pK_R values of $-9{\cdot}18$ and $-8{\cdot}96$ respectively.

N.m.r. Kinetic Measurements.—The methyl groups in both compounds provide a convenient two-site exchange system for measuring the rate constants in reaction (1). In both cases the fast exchange limit is approached and only a single line is observed over all acid concentrations. The shift of the line and its width vary with the relative amounts of carbinol and carbonium ion present and with the rate constants for their interconversion.

The complete two-site exchange equation[9] was used for the analysis. A computer program was used to calculate line widths at half height as a function of the fraction of alcohol present, $p(R_3COH)$, and its lifetime, $\tau\ (R_3COH) = 1/k_f$. It was then possible to construct a grid of lines of constant $p(R_3COH)$ and lines of constant $\tau\ (R_3COH)$ on a graph of the line width against chemical shift. When experimental values of line width and shift were located on the grid, $p(R_3COH)$ and $\tau\ (R_3COH)$ could be read off directly.

All n.m.r. measurements were made on a Varian HA 100 spectrometer at 34 °C. The probe temperature was determined from the methanol shift difference using van Geet's calibration.[10] The reference for the work in dioxan–water was the sodium salt of 4,4-dimethyl-4-silapentane-sulphonic acid (DSS). In aqueous solutions and for the shift measurements in concentrated acids the reference was the tetramethylammonium ion (TMA). The width of the DSS line, or the resolution of the TMA triplet, provided a good check of the instrument resolution when the other peaks were broadened by exchange. All solutions were made up by weight. Alcohol concentrations were in the range $1—4 \times 10^{-2}$M.

With very broad n.m.r. lines it is often difficult to decide where the true baseline lies and this can lead to uncertainties in measuring line widths. For Lorentzian lines this problem can be overcome by a simple transformation of the line shape equation.

If $2(\nu_i - \nu_0)$ is the width of a Lorentzian line corresponding to a distance x_i below the maximum it can be shown that the true width at half height $(1/\pi T_2)$ is given by equation (2). Equation (2) is easily included in a computer

$$(1/\pi T_2)^2 = \frac{4(\nu_i - \nu_0)^2(\nu_j - \nu_0)^2(x_j - x_i)}{(\nu_i - \nu_0)^2 x_j - (\nu_j - \nu_0)^2 x_i} \qquad (2)$$

program so that the true line width can be calculated for any number of pairs of points around an experimental curve without reference to a baseline.

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[6] J. I. Brauman and W. C. Archie, *J. Amer. Chem. Soc.*, 1970, **92**, 5981.

[7] M. S. Newman and N. C. Deno, *J. Amer. Chem. Soc.*, 1951, **73**, 3644.

[8] H. de Vries and H. Cerfontain, *Rec. Trav. chim.*, 1967, **86**, 873.

[9] H. M. McConnell, *J. Chem. Phys.*, 1958, **28**, 430.

[10] A. L. van Geet, *Analyt. Chem.*, 1970, **42**, 679.

RESULTS

Kinetics of the Ionization of Tris-(4-methylphenyl)methanol in 60% (w/w) Dioxan–Water.—The methyl group line widths and chemical shift in perchloric and sulphuric acid solutions in 60% dioxan–water are shown in Figure 1. The constants for the line shape equation for the perchloric acid solutions were $T_2(R_3COH)$ = 0·31 s, $T_2(R_3C^+)$ = 0·149 s and an $R_3COH - R_3C^+$ methyl shift difference of 35·2 Hz. In the sulphuric acid solutions T_2 varied with the acid concentration, presumably because of the increasing viscosity. Thus the T_2 values for R_3COH and R_3C^+ were assumed to be equal and to vary linearly with the acid molarity between 0 and 7·15M. The alternative procedure of taking $T_2(R_3COH)$ from a low acid concentration and $T_2(R_3C^+)$ from a high acid concentration gives the same result. The R_3COH–R_3C^+ chemical shift difference in sulphuric acid was 36·0 Hz. The results are set out in Table 1. The experimental ionization ratios in perchloric acid are consistent with the known pK_R[11] and H_R scale in this solvent.[12]

TABLE 1

Kinetic results for tris-(4-methylphenyl)methanol in 60% dioxan–water

Acid concentration/ M	log $[R_3C^+]$/ $[R_3COH]$	k_f/s^{-1}	k_b/s^{-1}
Perchloric acid			
2·35	−1·13	49	670
2·55	−0·85	87	600
2·78	−0·30	250	500
3·00	−0·04	390	430
3·26	0·40	740	290
3·47	0·62	1150	275
3·72	1·17	2380	160
Sulphuric acid			
2·99	−1·81	23	1470
3·29	−1·43	61	1620
3·52	−1·21	85	1370
3·96	−0·55	170	610
4·24	−0·13	370	500
4·34	0·04	430	392
4·61	0·44	660	240
5·04	1·09	760	63
5·20	1·39	1590	65

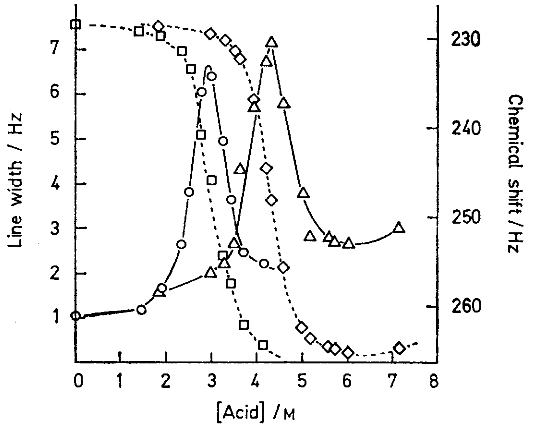

FIGURE 1 N.m.r. line widths and chemical shifts of tris-(4-methylphenyl) methanol in 60% dioxan–water: ○, line width in $HClO_4$ solutions; △, line width in H_2SO_4 solutions; □, shift in $HClO_4$ solutions; and ◇, shift in H_2SO_4 solutions

Kinetics of the Ionization of Tris-(4-methyl-3-sulphophenyl)-methanol in Aqueous Acid Solutions.—Methyl group line widths and chemical shifts upfield from TMA in aqueous perchloric and sulphuric acids are shown in Figure 2. For sulphuric acid the parameters for the line shape equation were $T_2(R_3COH)$ = 0·123 s, $T_2(R_3C^+)$ = 0·094 s, with a methyl shift difference of 44 Hz.

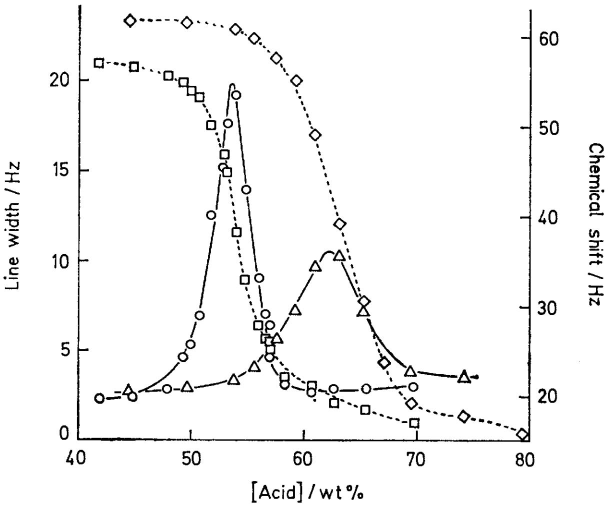

FIGURE 2 N.m.r. line widths and chemical shifts of tris-4-methyl-3-sulphophenyl)methanol in aqueous $HClO_4$ and H_2SO_4. The symbols are as in Figure 1

In perchloric acid $T_2(R_3COH)$ = 0·142 s, $T_2(R_3C^+)$ = 0·116 s, and the shift difference was 33·5 Hz. This value was obtained by extrapolating the shifts on either side of the ionization region back to the centre of the large change caused by the ionization (see Figure 2). The full kinetic results are set out in Table 2.

TABLE 2

Kinetic results for tris-(4-methyl-3-sulphophenyl)-methanol at 34 °C

Acid concentration/ wt %	log $[R_3C^+]$/ $[R_2COH]$	k_f/s^{-1}	k_b/s^{-1}
Perchloric acid			
49·42	−1·13	15·5	210
50·05	−0·99	26	260
50·79	−0·80	29	186
51·91	−0·44	56	155
52·91	−0·30	81	160
53·34	−0·21	91	148
54·14	0·01	120	123
54·95	0·22	195	118
56·13	0·56	290	80
56·70	0·69	330	68
57·00	0·69	410	83
Sulphuric acid			
55·96	−1·63	17	730
55·70	−1·28	35	670
57·62	−0·94	74	645
59·39	−0·71	115	585
61·00	−0·37	225	525
63·25	0·02	444	420
65·38	0·38	885	370
67·30	0·80	2400	370

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[11] N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Amer. Chem. Soc.*, 1955, **77**, 3044.

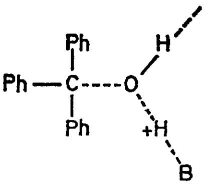
[12] H. Dahn, L. Lowe, and G. Rotzler, *Chem. Ber.*, 1960, **93**, 1572.

DISCUSSION

Acid Dependence.—The ionization of triphenylmethanols has generally been considered to follow the scheme shown in equation (3), which includes the protonated alcohol as an intermediate.[3,4] However general base

$$R_3COH + H^+ \rightleftharpoons R_3COH_2^+ \rightleftharpoons [‡] \rightleftharpoons R_3C^+ + H_2O \quad (3)$$

catalysis has recently been observed in the addition of water to the Malachite Green cation.[13] Thus the mechanism for the reverse reaction must be a concerted process in which the proton is being removed from the attacking water molecule at the same time as the carbon–oxygen bond is being formed, through a transition state of the form (1). A similar transition state with water acting as the general base would be expected for the reactions studied here. The acidity dependence of the reaction can give some information about its nature.



(1)

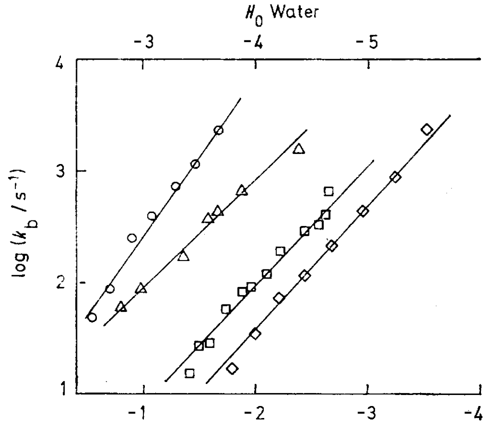


FIGURE 3 The correlation of log (k_f/s^{-1}) with H_0: ○, $HClO_4$ and △, H_2SO_4 in 60% dioxan–water; □, $HClO_4$ and ◇, H_2SO_4 in water

For the reaction scheme (3), with or without the $R_3COH_2^+$ step, equations (4) and (5) follow from transition state theory so that $\log k_b/a_{H_2O} = \log k_b^0 +$

$$\log k_f = \log k_f^0 + \log\left(\frac{y_{R_3COH} \times y_{H^+}}{y_‡}\right) \quad (4)$$

$$\log k_b = \log k_b^0 + \log\left(\frac{y_{R_3C^+} \times a_{H_2O}}{y_‡}\right) \quad (5)$$

$\log y_{R_3O^+}/y_‡$, where k_f^0 and k_b^0 are the standard state rate constants and y_i is the molar activity coefficient of the i species.

If the transition state resembles a protonated alcohol the hydration requirements of its formation from the left side of equation (3) (the forward reaction) should not be greatly different from those of the protonation of primary amines, and log k_f should follow H_0. Conversely, if the transition state is very like a carbonium ion, log k_f should follow H_R' ($H_R' = H_R - \log a_{H_2O}$).

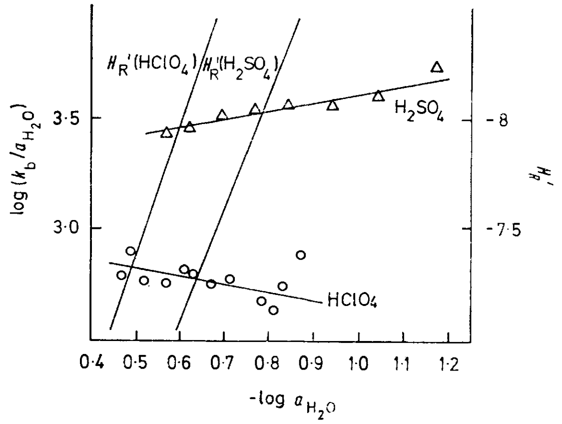


FIGURE 4 The variation of log (k_b/a_{H_2O}) and H_R' with log a_{H_2O} in $HClO_4$ and H_2SO_4 solutions

Plots of log k_f *versus* H_0 are shown in Figure 3. Similar correlations are obtained for H_R' or H_R. The slopes of these lines are collected in Table 3. With one exception, the slopes of log k_f *versus* $-H_0$ are much closer to unity, suggesting that the transition state resembles the protonated alcohol.

TABLE 3

Correlations of log k_f with acidity functions

Solvent	dlog k_f/ d($-H_0$)	dlog k_f/ d($-H_R$)	dlog k_f/ d($-H_R'$)
$HClO_4$/60% Dioxan–water	1·5 [a]	0·7	
H_2SO_4/60% Dioxan–water	1·0 [b]	0·6	
$HClO_4/H_2O$	1·1	0·6	0·7
H_2SO_4/H_2O	1·1	0·6	0·7
$HClO_4$/60% Dioxan–water [c]	1·2	0·5	
H_2O [d]	1·0		

[a] H_0 Data from C. A. Bunton, J. B. Ley, A. J. Rhind-Tutt, and C. A. Vernon, *J. Chem. Soc.*, 1957, 2327. [b] H_0 Data from B. Torck, M. Hellin, and F. Coussemant, *Bull. Soc, chim. France*, 1962, 1657. [c] H. Nicholson and P. A. H. Wyatt, *J. Chem. Soc. (B)*, 1968, 198. [d] Ref. 2.

This conclusion is reinforced by Figure 4 in which log k_b/a_{H_2O} is plotted against log a_{H_2O} for aqueous perchloric and sulphuric acids. The difference between the logarithms of the rate constants in the two acids is almost as large as the difference in H_R'.

This can be simply explained if the perchlorate is stabilizing the hydrophobic carbonium ion by structure enforced ion pairing but not greatly influencing the equally large transition state. If the transition state had significant carbonium ion character it would also be stabilized. However if it is very much like a protonated alcohol it will be involved in strong hydrogen

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[13] C. D. Ritchie, *J. Amer. Chem. Soc.*, 1972, **94**, 3275.

bonding with the solvent and as such would not be susceptible to structure enforced ion pairing.

Perchlorate–Triarylcarbonium Ion Interactions.—The formation of ion pairs between perchlorate and triarylcarbonium ions, invoked to explain the kinetic observations,[3] also provides a simple explanation of some distribution phenomena.

For example, Malachite Green and several other stable triarylcarbonium ions are readily extracted into organic solvents by perchlorate and a few other large anions. In fact this system has even been suggested as the basis for an analytical method for perchlorate.[14,15] Similarly the triphenylmethyl carbonium ion is easily extracted from concentrated perchloric acid into dichloromethane, but very little is extracted from sulphuric acid.

Brauman and Archie[6] have reported some n.m.r. measurements in acetonitrile which show that the triphenylmethyl cation and the large tetrafluoroborate ion are associated in some way. However until now there has been no direct experimental evidence for such R_3C^+ ion pairing in aqueous systems.

The high electric fields experienced by a counter ion in an ion pair are capable of affecting n.m.r. chemical shifts and the magnitude of this effect for protons can be estimated using equation (6) derived by Buckingham[16] where $\Delta\sigma$ is the change in the n.m.r. screening

$$\Delta\sigma = -2 \times 10^{-12}(E_z/\text{e.s.u.}) - 10^{-18}(E/\text{e.s.u.})^2 \qquad (6)$$

constant, E_z is the electric field along the carbon–hydrogen bond, and E is the magnitude of the field at the proton.

Counter-ion induced shifts have been observed for a number of large organic anions associated with the alkali metal cations.[17,18] These shifts are generally highly temperature dependent because they follow the ion pair–free ion, or contact–solvent separated ion pair equilibria. As expected, they also depend on the size of the metal ion as this affects the electric field intensity.

In this work shift measurements have been made on the tris-(4-methylphenyl)methyl and triphenylmethyl carbonium ions. The solvents were 98% sulphuric acid, 70% perchloric acid, and some mixtures of these. The shifts which are given in Table 4 were measured relative to internal TMA. Downfield shifts are taken to be negative. The spectrum of the ring protons of the tris-(4-methylphenyl)methyl ion was analysed as an AB system and the shifts are assigned to 'proton A' and 'proton B' in Tables 4 and 5, since one cannot be more specific here as to which proton is in the 2- and which is in the 3-position. For the triphenylmethyl ion only the *para*-proton shift is given. Analysis of the remainder of the spectrum was not undertaken.

Equation (6) was used to calculate the chemical shifts induced by placing a negative charge 5 or 6 Å above the central carbon atom of the carbonium ion. These calculations were repeated for several orientations of the aromatic rings. In Table 5 the calculated values are compared with the observed shifts induced by perchlorate, the shift of each proton in sulphuric acid being taken as its reference position.

TABLE 4

Chemical shifts in Hz from TMA

A Tris-(4-methylphenyl)methyl cation

Solvent	Proton A	Proton B	J_{AB}/Hz	Methyl group
98% H_2SO_4	−449·0	−437·2	8·3	47·4
5 : 1 (v/v) 98% H_2SO_4–70% $HClO_4$	−446·7	−434·2	8·4	49·8
1 : 1 (v/v) 98% H_2SO_4–70% $HClO_4$	−443·4	−429·4	8·2	51·6
70% $HClO_4$				50·7

B Triphenylmethyl cation

Solvent	*para*-Proton
98% H_2SO_4	−511·4
70% $HClO_4$	−502·8

TABLE 5

A Calculated shifts (Hz): ClO_4^-–C separation 6 Å

Aromatic ring twist (°)	*ortho*	*meta*	4-Methyl group	*para*
45	−6·0	+6·0	3·5	9·3
30	−1·3	6·4	3·5	9·3
0	1·4	7·3	3·5	9·3

B Calculated shifts (Hz): ClO_4^-–C separation 5 Å

Aromatic ring twist (°)	*ortho*	*meta*	4-Methyl group	*para*
45	−12·1	7·9	3·2	12·6
30	−1·4	9·4	3·2	12·6
0	3·2	10·3	3·2	12·6

C Observed shifts (Hz): shift in H_2SO_4 taken as reference

Solvent	Proton A	Proton B	4-Methyl group	*para*
5 : 1 H_2SO_4–$HClO_4$	2·3	2·9	2·4	
1 : 1 H_2SO_4–$HClO_4$ [a]	5·6	7·8	4·2	
70% $HClO_4$ [a]			3·3	
70% $HClO_4$ [b]				8·6

[a] Tris-(4-methylphenyl)methyl carbonium ion. [b] Triphenylmethyl carbonium ion.

Except for the *ortho*-proton there is fair agreement between the calculated and observed shifts. The indication is therefore that the perchlorate ion does associate with triaryl carbonium ions in aqueous solution. Such a specific interaction would be quite sufficient to upset any simple correlation of H_R with water activity for the different strong acids.

We thank the Leverhulme Trust for the award of a Research Fellowship to J. N. R.

[2/2624 *Received, 20th November, 1972*]

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