Kinetic and Equilibrium Aspects of the Effects of Salts and Nonelectrolytes upon the Ionization Equilibrium of Tris-*p*-methoxyphenylmethanol in Aqueous Solution at 25°

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The rates of formation and disappearance of the R_3C^+ ion in aqueous solution at 25° are measured in the presence of several electrolytes and nonelectrolytes, the effects of which upon H_R, also reported, can therefore be interpreted in terms of these two opposing reactions. (It is first verified that the rate of disappearance of the ion is not complicated by general base catalysis.) Additives generally influence the forward and reverse reaction rates in opposite ways and thus produce still more marked effects upon the equilibrium $[R_3C^+]/[R_3COH]$ ratio and H_R.

Electrolytes and nonelectrolytes also have large and varied effects upon the solubility of R_3COH, but although these resemble the effects of the additives upon the rate of formation of the ion, no simple correlation with the latter emerges. Instead a good correlation is found between the rate of formation of R_3C^+ and the Hammett function H_0, implying that the reasons for the peculiarities in the H_R scale are to be sought in effects upon the reverse reaction. Perchlorates [which like $(CH_3)_4NCl$ behave similarly to the *non*electrolytes in their effects upon the solubility of R_3COH] have a very marked effect upon the reverse reaction even at quite low concentrations and this behaviour (interpreted tentatively in terms of a ' structure enforced association ' between R_3C^+ and ClO_4^-) is believed to hold the key to the absence of a simple correlation between H_R and water activity for strong acids.

A FORMER investigation of the tris-*p*-methoxyphenylmethyl carbonium ion (R_3C^+) was confined to dioxan–water mixtures.[1] Our stopped-flow technique was subsequently improved to permit rate measurements at higher dilutions of the coloured ion, thus extending the study to simple aqueous systems which solubility limits previously rendered inaccessible. Though still planned as a contribution towards the understanding of acidity functions, the present work is mainly a search for regularities in the kinetic and equilibrium effects produced by a broad range of salts and nonelectrolytes, to which the system is very sensitive. In this respect some of our findings resemble those of Ritchie, Skinner, and Badding,[2] who studied the effects of solvent changes in related systems. Whereas their forward and reverse rate constants for reaction (1) were always changed in

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

the same direction with a change of solvent however, our additives generally had opposite effects upon the two reaction rates, thus reinforcing their effects upon the overall equilibrium. For the addition of salts and nonelectrolytes to our aqueous system therefore, our general conclusion is that *those additives which hasten the disappearance of the carbonium ion always shift the equilibrium in favour of the carbinol and those which reduce the rate of disappearance of the ion shift the equilibrium the other way*.

Since the activity coefficient of the un-ionized tris-*p*-methoxyphenylmethanol (R_3COH) is directly obtainable from solubility measurements, the changes in this quantity are also compared with the kinetic effects of the additives.

During the course of our work, two other stopped-flow studies on the same aqueous system were reported [3,4] and more recently a related paper on n.m.r. line-broadening in the unsubstituted triphenylmethylcarbinol system has appeared.[5] From the reported entropy of activation [3] (-27 cal mol^{-1} K^{-1}) for the rate of disappearance of R_3C^+ [the reverse reaction in (1)], it appears that four or five water molecules are probably incorporated in the approach to the transition state,[6] as would be expected in the preparation for the formation of the hydrated proton in a single-step mechanism; but the small deuterium isotope effect nevertheless shows that the proton transfer is not appreciable in the slow step [4] and must occur very rapidly thereafter. Our failure to find evidence for general base catalysis is consistent with this latter conclusion.

For simplicity all kinetic results are expressed here in

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[1] H. Nicholson and P. A. H. Wyatt, *J. Chem. Soc.* (*B*), 1968, 198.

[2] C. D. Ritchie, G. A. Skinner, and V. G. Badding, *J. Amer. Chem. Soc.*, 1967, **89**, 2063.

[3] R. A. Diffenbach, K. Sano, and R. W. Taft, *J. Amer. Chem. Soc.*, 1966, **88**, 4447.

[4] E. A. Hill and W. J. Mueller, *Tetrahedron Letters*, 1968, 2565.

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

[6] L. L. Schaleger and F. A. Long, *Adv. Phys. Org. Chem.*, 1963, **1**, 1.

terms of the experimental first-order constants, k_f and k_b, corresponding to the forward and reverse reactions in (1). The acid and water dependence are therefore included in k_f and k_b, and the relationship of these constants to the rate constants for a supposed two-step mechanism involving $R_3COH_2^+$ can readily be derived if required.[1] The rate constant observed is always $(k_f + k_b)$, but k_f and k_b can be separated when k_f/k_b is known from the H_R determinations or (as in most of the measurements here) by making k_f so small at low acidities that k_b, the rate of disappearance of R_3C^+, is effectively measured directly.

The pH *Dependence of* k_b *and the Absence of General Base Catalysis.*—Although the rate of disappearance of R_3C^+ is sensitive to the concentration of the salt used to maintain a fixed ionic strength, the results in Table 1 show that the rate of the reaction is (within an experimental error of about ±10%) independent of the acetate ion concentration from 0·5 to 1·0M at a fixed pH. At the lower ionic strength of 0·3 mol dm^{-3}, k_b is somewhat greater but remains constant over the whole pH range from 4·4 to 9·3, quite independently of the nature of the buffer (acetate, phosphate, and borate), as the results in the first half of Table 2 show.

TABLE 1

Effect of acetate buffer concentration upon k_b for the disappearance of R_3C^+ at ionic strength 1·5M (made up with $NaClO_4$)

Buffer concentration (mol dm^{-3})	0·05	0·10	0·25	0·40
Mean k_b/s^{-1}	6·7	5·7	6·2	5·6
pH of cell effluent	4·55	4·50	4·43	4·40
Buffer concentration (mol dm^{-3})	0·50	0·60	0·75	1·00
Mean k_b/s^{-1}	6·5	6·8	6·5	7·0
pH of cell effluent	4·30	4·40	4·40	4·40

TABLE 2

Effect of pH on k_b for the disappearance of R_3C^+ at ionic strength 0·3M (made up with $NaClO_4$)

pH	Mean k_b/s^{-1}	(k_b/s^{-1}) − 10·2	Buffer
4·40	10·3		0·1M-Acetate
7·50	10·6		0·1M-Phosphate
7·70	10·2		0·1M-Borate
8·65	9·8		,,
9·10	10·0		,,
9·30	10·1		,,
10·70	13·4	3·2	0·05M-Triethylamine
10·70	13·5	3·3	0·1M-Triethylamine
11·40	28·1	17·9	,,
11·47	37·5	27·3	,,
11·59	50·1	39·9	,,
11·70	60·0	49·8	,,

Sharp increases in rate *are* observed with different bases at the alkaline end of the scale, but these are ascribed to direct nucleophilic attack upon the carbonium ion either by OH^-, to form the same product as the attack by water, or by NH_3 or Et_2NH to form different products with the loss of a proton (see Table 3). Significantly Et_3N, with no proton to lose, has no effect upon the rate of disappearance of R_3C^+ in pH regions (8—10·2) where marked effects are observed with low concentrations of NH_3 and Et_2NH (Table 3), despite the fact that it is the strongest base. When increases *are* observed with Et_3N (Table 2) they are dependent only upon the pH and not upon the buffer concentrations. The high pH Et_3N results in Table 2 therefore refer to the reaction of R_3C^+ with OH^-. The second-order constants for the reaction of R_3C^+ with NH_3 and Et_2NH were $1{\cdot}4 \times 10^3$ and $3{\cdot}3 \times 10^3$ l mol^{-1} s^{-1} at 25°, the former being consistent with $2{\cdot}1 \times 10^3$ l mol^{-1} s^{-1} at 30° obtained by Diffenbach, Sano, and Taft.[3]

TABLE 3

Effects of ammonia and diethylamine buffer concentrations on k_b at ionic strength 0·4M (with $NaClO_4$)

Molarity of NH_3	0·01	0·02	0·025	0·035	0·04	0·07
$[NH_3]/[NH_4^+]$	0·1	0·1	0·1	0·1	1	1
k_b/s^{-1}	14·1	41·5	45·7	58·7	67·9	125
pH	8·80	8·75	8·57	8·52	9·37	9·35
Molarity of Et_2NH	0·01	0·04				
k_b/s^{-1}	17	130				
pH	10·05	10·23				

Small temperature corrections were necessary in some of the above experiments and for this purpose a few experiments on the temperature dependence of k_b were carried out. Between 0 and 36° k_b could be represented by $1{\cdot}9 \times 10^8 \exp(-5000/T)$ s^{-1} at ionic strength 0·1M (0·05M-$LiClO_4$ and 0·05M-acetate buffer) and pH 4·50, and by $2{\cdot}5 \times 10^7 \exp(-4900/T)$ s^{-1} at ionic strength 2·0M ($NaClO_4$) and pH 4·15. The corresponding activation energies, *viz.* 41·5 kJ (9·9 kcal) and 40·7 kJ (9·7 kcal) respectively, agree within the experimental error despite the 8-fold decrease in rate due to the $NaClO_4$ concentration, thus suggesting that changes in the pre-exponential factor are probably dominant in the effects described below. Agreement of the activation energy with that of Diffenbach *et al.*[3] (8·1 kcal + RT ± 0·5 kcal) seems reasonable since our experimental error could easily be ±1 kcal here.

Effects of Additives on the Rate of Formation of R_3C^+ *in Acid Solution.*

$$R_3COH + H^+(H_2O)_n \xrightarrow{k_f}$$

In these experiments the two constants in $(k_f + k_b)$, the measured rate constant for the appearance of R_3C^+, were separated by means of the equilibrium ratio $[R_3C^+]/[R_3COH]$ $(= k_f/k_b)$ determined for each solution during the H_R study mentioned below. Values of k_b obtained in this way, though less precise than those obtained directly at higher pH values, agreed satisfactorily with the latter. The k_f results are recorded in Figure 1: two further points, with k_f inconveniently large, were obtained at 0·8M-$HClO_4$ alone (k_f = 92 s^{-1}) and at 1M-HCl in 2M-Me_4NCl (k_f = 53 s^{-1}).

As expected for a reaction involving the hydrogen ion, k_f is very sensitive to additives. It is significant however that the variation of k_f with acid concentration is very similar for HCl and $HClO_4$, in contrast to their effects upon k_b described below, and that H_0 and H_R are also very similar for HCl in this region of concentration. As a step towards resolving the difficulties in reconciling H_0 and H_R at higher acidities therefore, we now plot log k_f against $-H_0$ to see if at least the forward reaction in an H_R equilibrium behaves ‘ normally ’.

Figure 2 shows that a very good correlation is obtained, accommodating the effects of those salts for which the influence upon H_0 has been recorded.[7] Any explanation which serves for the salt effect on H_0 (*e.g.* in terms of effects upon proton hydration and base salting-out effects) will, therefore, serve as an explanation for the salt effects upon k_f and part of the effects upon H_R. The H_0 correlation is also clearly consistent with the hypothesis that $R_3COH_2^+$ occurs as a transient intermediate before the transition state.

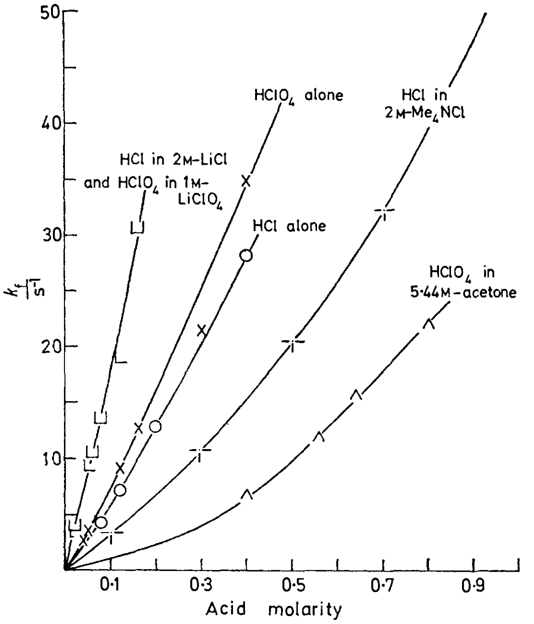

FIGURE 1 Effects of additives upon the rate constant k_f for the formation of the R_3C^+ ion

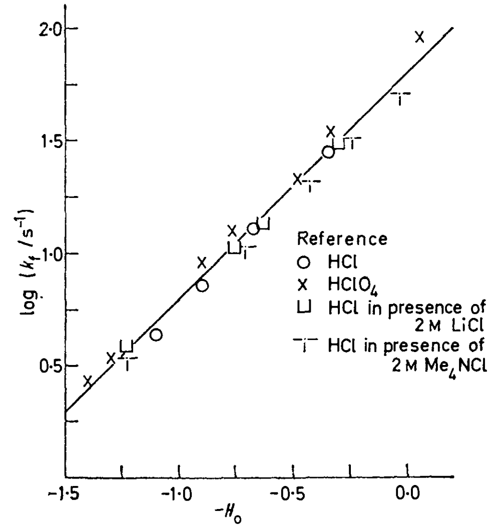

FIGURE 2 Correlation of log (k_f/s^{-1}) with H_0. The line is drawn with unit slope

Effects of Additives on the Rate of Disappearance of the R_3C^+ *Ion.*

$$R_3C^+ + (n + 1)H_2O \xrightarrow{k_b}$$

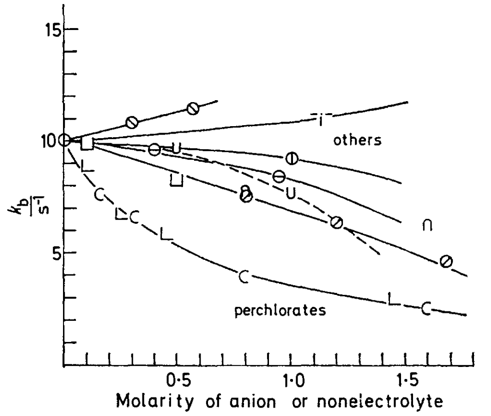

FIGURE 3 Effects of additives (<2M) upon the rate constant k_b for the disappearance of the R_3C^+ ion. Symbols as in Figure 4

Since k_b is independent of pH within the range 4—9, the pH of the solutions used here is not critical. One of the solutions mixed in the stopped-flow apparatus has nevertheless to be acid to provide the initial R_3C^+ concentration, and 0·2M-HCl containing the (freshly purified) indicator was therefore mixed with equimolar NaOH containing acetate buffer so that the final solution was always 0·1M in NaCl and 0·05M in acetate buffer and of pH about 4·7. Each of the solutions before mixing also contained the appropriate concentration of added electrolyte or nonelectrolyte to be studied. The results are displayed in Figures 3 and 4, where the full lines correspond to electrolytes and broken lines to nonelectrolytes.

Figures 1 and 4 show that roughly opposite effects are produced on k_f and k_b. It is also very noticeable that perchlorates have a much more marked effect at low concentrations than any other additives (a much larger effect of $NaClO_4$ than NaCl also appears in Figure 1 of

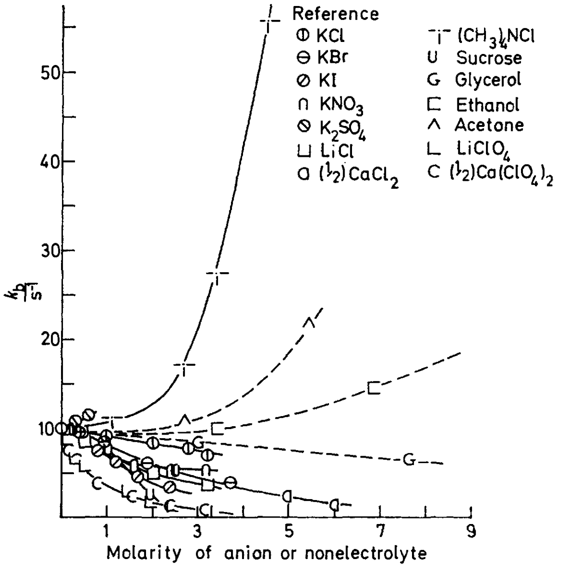

FIGURE 4 Effects of additives (up to 8M) upon the rate constant k_b for the disappearance of the R_3C^+ ion. Full lines are for electrolyte and broken lines for nonelectrolyte additives

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[7] M. A. Paul and F. A. Long, *Chem. Rev.*, 1957, **57**, 1.

ref. 4). Exactly the same effect is evident in the k_b results (determined together with k_f) for solutions of HCl and $HClO_4$ alone:

Molarity of HCl	0·08	0·12	0·20	0·40	
k_b/s^{-1}	9·1	9·8	10·3	9·6	
Molarity of $HClO_4$	0·12	0·16	0·30	0·40	0·80
k_b/s^{-1}	10·0	9·2	5·5	5·2	2·8

Since the reaction probably involves the attack upon the R_3C^+ of several water molecules, some correlation with water activity might be expected; but this factor clearly cannot be dominant here. Salts like K_2SO_4 and Me_4NCl, which certainly decrease the water activity, increase k_b, and at 1M the water activities of HCl (0·953) and $HClO_4$ solutions (0·958) are practically identical. [Even raised to the fifth power, to account for the production of $H^+(H_2O)_4$ near the transition state, a water activity of 0·96 would only account directly for a 20% lowering of k_b.]

The simplest explanation of the striking effect of perchlorate is that an ion pair between ClO_4^- and R_3C^+ reduces the concentration of free R_3C^+ and hence lowers k_b. On this basis, a concentration quotient of *ca.* 2 mol^{-1} dm^3 for $[R_3C^+{\cdot}ClO_4^-]/[R_3C^+][ClO_4^-]$ roughly satisfies the k_b results for $HClO_4$ both in the absence and presence of other perchlorates. More marked association of R_3C^+ (and possibly of other large molecules, charged or uncharged) with ClO_4^- than Cl^- is comprehensible in terms of Diamond's 'water structure enforced' association, in which the two species can ease their large separate effects upon the solvent structure by joining together.[8] In the case of the other large ion, Me_4N^+, which resembles ClO_4^- in its effects upon the solubility of R_3COH (see below), the positive charge would make such a complex with R_3C^+ less likely.

*Effects of Additives on the Solubility of Tris-*p*-methoxyphenylmethanol in Water at* 25°.—Solubilities (S) of the alcohol in the presence of a third component were always related to that in pure water ($S°$) by comparing the optical densities of aliquot volume samples acidified to convert R_3COH completely into R_3C^+. The ratio $S° : S$ is therefore a direct measure of the activity coefficient of the alcohol on the molarity scale, y_{R_3COH}. All the results are collected in Figure 5.

Except for the perchlorates, the additives display the same sequence in their effects upon the alcohol activity coefficient (Figure 5) as in their effects upon k_f, the rate constant for the reaction of the alcohol with the hydrogen ion (Figure 1). Division of k_f by y_{R_3COH} (removing the latter from the factor $y_{R_3COH}y_{H^+}/y_{\ddagger}$ formally contained in k_f) does not bring the k_f points onto a common line in Figure 1 however; but such a simple result is not expected since it leaves no room for effects upon y_{H^+} through the reduction of the water activity.

Most of the electrolytes show the normal, almost linear, log $(S°/S)$ plots, but the perchlorates and Me_4NCl 'salt out' like the other electrolytes only at low concentrations and in general follow the pattern of the bulky nonelectrolytes. Two possible explanations suggest themselves. (i) Because of the presence of ClO_4^-, Me_4N^+, or the bulky nonelectrolytes, the whole water structure undergoes a series of spatial modifications according to the concentration of the additive and these modifications act (everywhere) as worse or better solvents for R_3COH in a way that necessarily produces a log $(S°/S)$ curve of the general shape of that shown by glycerol, Me_4NCl, and the perchlorates. (ii) ClO_4^- and Me_4N^+ form 'solvent structure enforced' complexes with R_3COH, and the extra solubility over that in the presence of a similar concentration of salts like $CaCl_2$, KCl, or LiCl measures the concentration of the complex. On this basis, a formation constant $K \approx (S - S')/S°[ClO_4^-]$ or $(S - S')/S°[Me_4N^+]$ can be calculated as 0·5 mol^{-1} dm^3 for $R_3COH{\cdot}ClO_4^-$ or 0·9 mol^{-1} dm^3 for $R_3COH{\cdot}(CH_3)_4N^+$. [The activity of R_3COH is numerically $S°$ and constant throughout, the activity coefficient of the charged complex is assumed to balance that of ClO_4^- or Me_4N^+, and S and S' represent respectively the solubilities in the presence of the large ion and of the same concentration of a reference electrolyte—LiCl for $LiClO_4$ or $CaCl_2$ for $Ca(ClO_4)_2$ and $(CH_3)_4NCl$.]

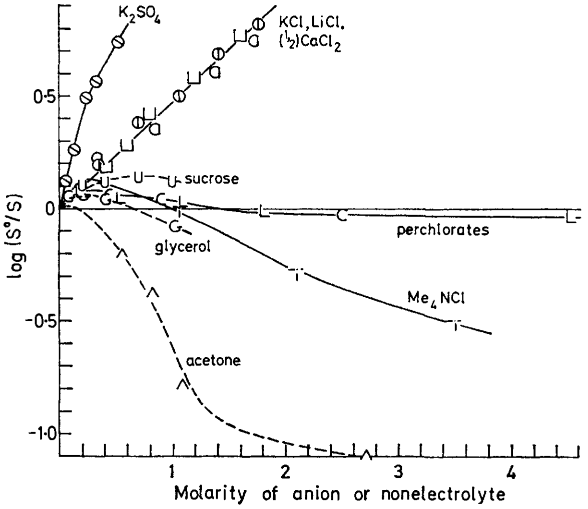

FIGURE 5 Effects of additives upon the solubility of R_3COH. Symbols as in Figure 4

Despite the independence of concentration shown by the calculated K values, we favour explanation (i) mainly because of the relative simplicity required of the parallel explanation of k_f effects: the influence of Me_4N^+ upon k_f is rendered 'normal' by correcting for its known effect upon H_0 (Figure 2), while the similarity of the influence of the perchlorates and chlorides upon k_f (Figure 1) is understandable if the special structural effect of perchlorate persists in the transition state and so cancels out of the kinetic activity factor in k_f. This effect upon the transition state has, of course, to be carried through to the reverse reaction, thus requiring an effect of ClO_4^- upon R_3C^+ larger than supposed above: if ion-pairing explains the diminution of k_b, either it has to be more extensive than previously calculated or it is accompanied by an additional structural

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

effect of ClO_4^- similar to that upon R_3COH and the transition state. On the ' complex ' explanation (ii), the increased reaction rate of H^+ with the anionic species $R_3COH{\cdot}ClO_4^-$ and the decreased rate with $R_3COH{\cdot}(Me)N^+$ seem reasonable enough, but the correlation of the Me_4N^+ effect on k_f with H_0 and the similarity of the effects of $LiClO_4$ and LiCl would then be completely accidental consequences of the relative extents of complexing of R_3COH in the reactant and transition states and of the relative rates of the reactions involving the complexed and free alcohol.

Effects of Additives upon H_R.

$$H_0 = pK_R - \log [R_3C^+]/[R_3COH] \qquad (2)$$

Direct measurements of the ratio $[R_3C^+]:[R_3COH]$ permit the calculation of H_R from (2) with $pK_R = +0{\cdot}81$, the mean value (with standard deviation $\pm0{\cdot}02$) obtained at low acid concentrations: *cf.* lit.[9] 0·82. The results for HCl and additives are collected in Figure 6 and those for $HClO_4$ in Figure 7.

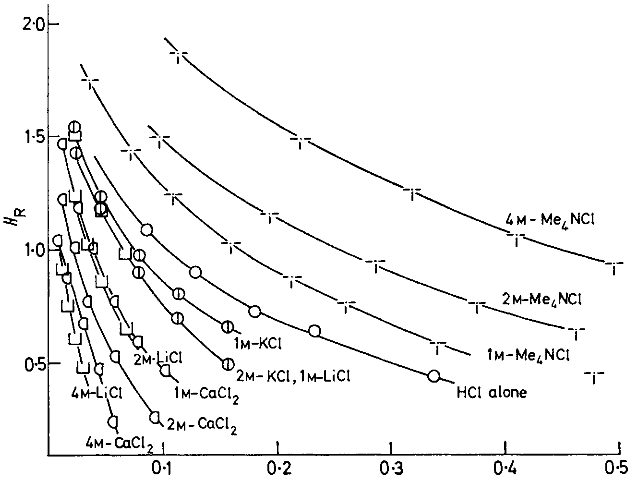

FIGURE 6 Effects of additives upon H_R in HCl solutions. ○ HCl alone; other symbols as in Figure 4

Since additives have opposite effects upon k_f and k_b, these effects reinforce in displacing the equilibrium. For example, at 5·44M-acetone, k_b is *ca.* 2·2 times as large as in pure water (Figure 4), but the H_R shift of 1·0 (Figure 7) corresponds to a change in k_b/k_f of a factor of 10, because of the associated diminution of k_f by a factor of 4·3 (Figure 1).

Although the range of solutions in which k_f was studied was more limited than that for the other properties, the success of the correlation of log k_f with H_0 (Figure 2) supports the conclusion that the differences between H_0 and H_R in the presence of electrolytes are due to the different effects of the electrolytes on k_b, the rate constant for the disappearance of R_3C^+. In particular, at concentrations below 1M, where k_b in the presence of HCl is practically constant, the difference in H_R between HCl and $HClO_4$ at a given concentration is certainly due to the special effect of ClO_4^- upon k_b, which we tentatively interpret in terms of the presence of $R_3C^+{\cdot}ClO_4^-$ ion pairs. In this region of concentration at least, it is significant that our H_R values for HCl solutions are very similar to H_0 for both HCl and $HClO_4$, while our values for H_R in $HClO_4$ (which agree well with those of Deno *et al.*[9]) deviate to the negative side of the HCl line at much lower concentrations than H_0. Part at least of the puzzling difference between H_R' (for $HClO_4$ [9] and H_2SO_4 [10] solutions) and H_0 at higher acid concentrations may, therefore, be attributed to the special effects of large anions upon the R_3C^+ ions; and, since such effects differ from anion to anion, a simple explanation emerges

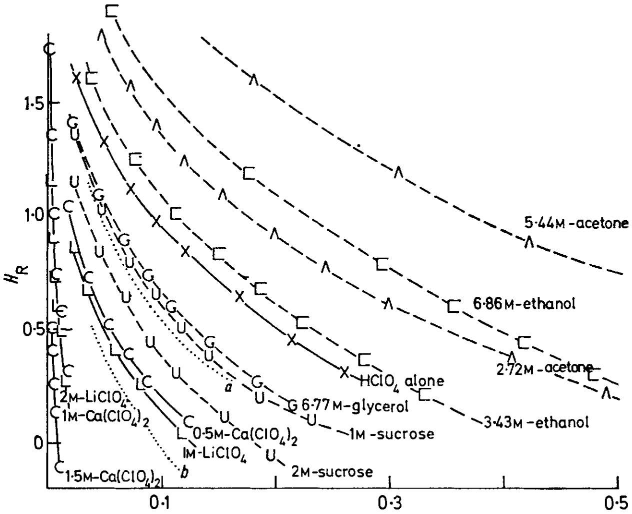

FIGURE 7 Effects of additives upon H_R in $HClO_4$ solutions. × $HClO_4$ alone; other symbols as in Figure 4. The dotted lines show the curves for (*a*) 2M-$LiClO_4$ and (*b*) 1·5M-$Ca(ClO_4)_2$ with the abscissae all multiplied by 10

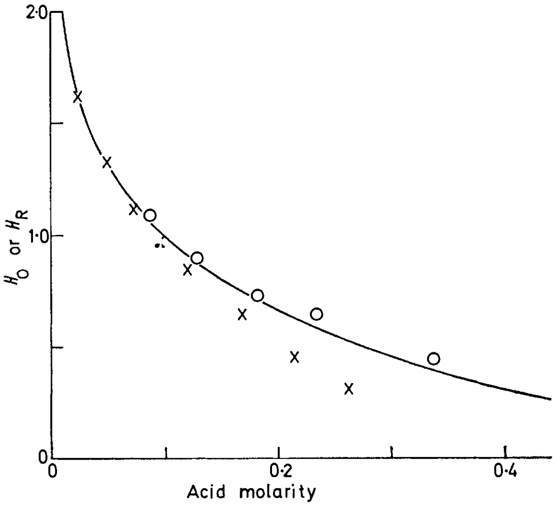

FIGURE 8 Comparison of H_0 and H_R in HCl and $HClO_4$ solutions below 0·5M. The line shows the common curves for H_0 in HCl and $HClO_4$;[7] ○ H_R in HCl, × H_R in $HClO_4$

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[9] N. C. Deno, H. E. Berkheimer, W. L. Evans, and H. J. Patterson, *J. Amer. Chem. Soc.*, 1959, **81**, 2344.

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

of the fact the H_R (unlike H_0 [11]) is not a common function of the water activity for aqueous solutions of the strong acids.[12]

EXPERIMENTAL

Stopped-flow Kinetic Measurements.—The appearance of the coloured R_3C^+ ion was followed spectrophotometrically as described previously,[1] but optical density changes were usually only *ca.* 0·1 and demanded improvements in our apparatus. These included the substitution of a plane mirror for the pivoted concave mirror in the Unicam SP 500 Spectrophotometer to reduce mirror vibration, the use of a high intensity 55 W tungsten–iodine bulb as a source to enable the photomultiplier to be used at low voltages, with consequent reduction in the noise level, and extensive earthing to reduce 50 cycle pick-up. It was not at first easy to arrange that the kinetic runs were carried out at 25°, but the temperature was always recorded and the rate constants for some early runs were corrected to 25° by adding 5% per degree for 1 or 2° below that temperature (corresponding to an energy of activation of *ca.* 40 kJ mol^{-1}).

Solubility Measurements.—Capricious errors gave trouble initially but were eliminated by careful attention to the removal of fine particles before analysis and by devising two special saturators, similar to that of Glew and Hildebrand,[13] one designed for direct immersion in a thermostat and the other for pumping thermostatted water through a surrounding jacket. All operations were also carried out in a room thermostatted at 25 °C. About 0·1 g of pure powdered tris-*p*-methoxyphenylmethanol was added to *ca.* 90 ml of the required solution in the principal chamber of the saturator, and the mixture was rapidly agitated for *ca.* 20 h by a magnetic stirrer. The supernatant liquid was filtered through a fluted Whatman No. 42 paper and an aliquot portion, sufficient to give a final optical density of 0·3, was made up to 10 ml with HCl solution to convert at least 99% of the alcohol into the R_3C^+ ion. Special care was needed in the filtration and the cleaning of pipettes as fine particles and adsorbed films of the alcohol could cause large errors.

H_R Measurements.—The relative concentrations of R_3COH and R_3C^+ in solutions of fixed indicator molarity (2×10^{-5}) were found by estimating $[R_3C^+]$ spectrophotometrically (against an identical reference solution without indicator) in a 1-cm cell on a Unicam SP 500 instrument. The 1-cm cell was connected through a ground joint to a 350 ml glass bulb to facilitate the preparation and sampling of the solutions [10] and the open-cell compartment of the spectrophotometer was always covered with a black cloth during measurements to exclude stray light. Densities were also measured to permit correction of the indicator concentration when additions were made to the 350 ml bulb. The room was thermostatted at 25° ± 1°, but solutions were also equilibrated before use in a bath at 25° ± 0·1°.

The H_R and solubility measurements were fortunately not complicated by medium effects on the extinction coefficient of R_3C^+: $\varepsilon_{\text{max.}}$ was constant at $1{\cdot}01 \times 10^5 \text{M}^{-1} \text{cm}^{-1}$ ($1{\cdot}01 \times 10^4 \text{mol}^{-1} \text{m}^2$), although $\lambda_{\text{max.}}$ did shift slightly from 483 nm in perchlorate and 485 nm in chloride solutions to 487 ± 1 nm in the presence of the nonelectrolytes.

Materials.—Where the inorganic or organic materials were not of analytical reagent grade they were recrystallized from water (KI, KNO_3) or specially prepared in solution (the perchlorates, from standardized acid and weighed carbonate). Triethylamine was distilled before use (b.p. 89—90 °C). Concentrations of acids and chlorides were checked by titration.

Tris-*p*-methoxyphenylmethanol was prepared by reaction of *p*-methoxyphenylmagnesium bromide with diethyl carbonate in dry ether,[14] and purified *via* the picrate, from which the alcohol was obtained by treatment with sodium hydroxide and extraction with benzene. Recrystallization (with difficulty) from aqueous acetone gave colourless crystals, m.p. 80—81° (lit., 81—82 [1] and 83·5—84° [15]). Samples were always freshly purified before use.

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