Molar Absorptivity and pK_{R^+} of the 4,4′-Dimethoxytrityl Carbenium Ion in Methanolic Water, and its Equilibrium with Chloride Ion†

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The 4,4′-dimethoxytrityl carbenium ion has been generated in 80:20 (v/v) water–methanol containing perchloric acid in a rapid reaction from 4,4′-dimethoxytrityl alcohol and in a slower reaction from 4,4′-dimethoxytritylamine. The pK_{R^+} (-0.95; $K_{R^+} = 8.98$) and molar absorptivity ($\varepsilon_{R^+} = 297\,000$) of the cation have been measured directly under equilibrium conditions in this highly aqueous medium at ionic strength = 1.0 mol dm^{-3} by a convenient spectrophotometric method at 25 °C. In addition, the pK_{R^+} has been measured at other temperatures, which allows the determination of the standard enthalpy ($\Delta H^{\circ} = -11.4$ kJ mol^{-1}) and entropy ($\Delta S^{\circ} = -20$ J K^{-1} mol^{-1}) of the reaction of the cation with the solvent, and at other ionic strengths. The equilibrium constant for the formation of 4,4′-dimethoxytrityl chloride from the cation and chloride has also been measured in the same medium ($K_{RCl} = 8.20$ at 25.0 °C, ionic strength = 1.0 mol dm^{-3}) by generating the cation from the alcohol and perchloric acid in the presence of 0.10 mol dm^{-3} sodium chloride.

Carbocations react with water in aqueous solution according to eqn. (1) thereby generating alcohols and hydronium ion, and acidity dissociation constants for these equilibria (K_{R^+}) may be formulated in the conventional manner according to eqn. (2).

$$R^+ + 2H_2O \rightleftharpoons ROH + H_3O^+ \qquad (1)$$

$$K_{R^+} = \frac{[ROH][H_3O^+]}{[R^+]} \qquad (2)$$

The equilibrium constant is usually expressed as its pK_{R^+}, and is generally determined by measurements of the equilibrium concentrations of the species present in solutions of known acidity. For less stable carbocations, more acidic conditions are required, and acidity functions are then usually employed to express the acidity of the medium; eqn. (1) has in fact been used as the basis of one of the better known acidity functions, H_R.[1,2]

We are presently investigating quantitative aspects of the deamination of substituted tritylamines[3]—reactions by which substituted trityl cations are also generated—and we need the UV molar absorptivity (ε_{R^+}) of the cations produced under the methanolic aqueous acidic conditions of our reactions. We have developed a simple and convenient method for the direct determination of the ε_{R^+} of the 4,4′-dimethoxytrityl cation even when formed incompletely under only mildly acidic conditions from the corresponding alcohol or amine. This method which we now report also yields the equilibrium constants for the reactions of the cation with the solvent (leading to the pK_{R^+}) and with a nucleophilic solute, chloride, and may be more widely applicable.

Experimental

Glass distilled water and HPLC grade methanol were used throughout, perchloric acid was BDH Aristar grade, and acid concentrations were determined by titration with standard aqueous sodium hydroxide. 4,4′-Dimethoxytrityl alcohol and the corresponding amine were kindly supplied as pure crystalline compounds by Miss Jane Riseborough of this Department.[4] All other compounds used were of commercial reagent grade. Aqueous methanol mixtures were made by mixing volumes of methanol and water (or the appropriate aqueous solution) measured by pipette or Gilson ‘Pipetman’. Reactions were initiated by the addition of the organic substrate (amine or alcohol) as a standard solution in pure methanol by microlitre syringe to a measured volume of the methanolic aqueous electrolyte solution of known concentration in a UV cell. All volumes were delivered such that the final compositions were accurately methanol–water = 20:80 by volume. Reactions were usually carried out at constant ionic strength (using sodium perchlorate where necessary) in the thermostatted cell block of a Cecil Instruments CE5502 double beam spectrophotometer interfaced to an Elonex PC433 microcomputer. Spectra were occasionally recorded but, more usually, the absorbance at the maximum due to the 4,4′-dimethoxytrityl carbenium ion (498 nm) was monitored at predetermined time intervals until equilibrium was established. This required minutes for reactions starting from the alcohol and hours for reactions from the amine. For other reasons,[3] the rates of the reactions starting from the amine were invariably measured.

Results

Scheme 1 establishes the relationship in eqn. (5) between the hydronium ion concentration ([H_3O^+]), the initial concentration of the substituted trityl alcohol ([ROH]$_0$), and the spectrophotometric absorbance at equilibrium (A_e) at the wavelength where the molar absorptivity of the carbenium ion is ε_{R^+}; no other species in the reaction has a significant absorption at this wavelength. The data in Table 1 led to entries 1 and 15 in Table 2 for K_{R^+} and ε_{R^+}, respectively, *via* the plot of $(A_e)^{-1}$ against $[H_3O^+]^{-1}$ at constant ionic strength shown in Fig. 1. The origin of the species present at equilibrium in the chemical system described by eqn. (1) is, of course, of no consequence, and we have already demonstrated that deamination of the corresponding tritylamine under acidic conditions also leads to the same equilibrium.[3,4] As a further check upon the present method of determining K_{R^+} and ε_{R^+} and additional

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$[ROH]_0$ = Initial concentration of alcohol used

$$[ROH]_0 = [R^+]_e + [ROH]_e \qquad (3)$$

where $[\ ]_e$ represents concentrations at equilibrium and A_e = spectrophotometric absorbance at equilibrium at a wavelength where only the carbenium ion absorbs.

Using a 1 cm pathlength cell

$$A_e = \varepsilon_{R^+} \times [R^+]_e \qquad (4)$$

From eqns. (2) and (3)

$$K_{R^+} = \frac{([ROH]_0 - [R^+]_e) \times [H_3O^+]}{[R^+]_e}$$

Using eqn. (4)

$$K_{R^+} = \frac{([ROH]_0 - A_e/\varepsilon_{R^+}) \times [H_3O^+]}{A_e/\varepsilon_{R^+}}$$

or

$$\frac{K_{R^+}}{[H_3O^+]} = \frac{[ROH]_0 \times \varepsilon_{R^+}}{A_e} - 1$$

Therefore

$$\frac{[ROH]_0}{A_e} = \frac{K_{R^+}}{\varepsilon_{R^+}} \times \frac{1}{[H_3O^+]} + \frac{1}{\varepsilon_{R^+}} \qquad (5)$$

and a graph of

$$\frac{1}{A_e}\ vs.\ \frac{1}{[H_3O^+]}$$

gives a linear plot with

$$\text{intercept} = \frac{1}{\varepsilon_{R^+} \times [ROH]_0}$$

and

$$\text{gradient} = \frac{K_{R^+}}{\varepsilon_{R^+} \times [ROH]_0}$$

Scheme 1

Table 1 Equilibrium absorbances for the reaction of 4,4'-dimethoxytrityl alcohol in 20:80 (v/v) methanol–water containing perchloric acid and sodium perchlorate at 25 °C[a]

$[HClO_4]$/mol dm^{-3}	$[NaClO_4]$/mol dm^{-3}	A_e
1.00	0	1.826
0.80	0.20	1.533
0.65	0.35	1.290
0.50	0.50	1.012
0.35	0.65	0.740
0.20	0.80	0.411

[a] Initial 4,4'-dimethoxytrityl alcohol concentration, $[ROH]_0 = 6.41 \times 10^{-5}$ mol dm^{-3} in all reactions.

confirmation of the identity of the final reaction mixtures in the two reactions, we also obtained entries 2 and 16 in Table 2 from the data in Table 3 obtained by duplicate measurements at just three acid concentrations for reactions starting from the amine.

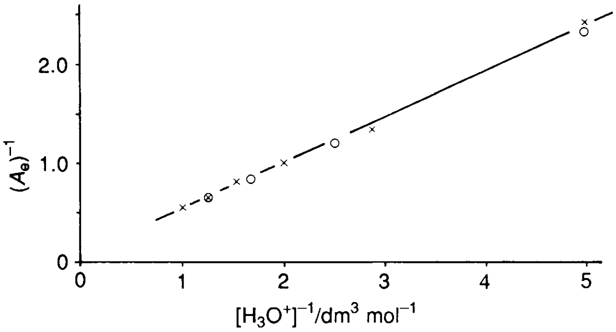

Fig. 1 Plot of $(A_e)^{-1}$ against $[H_3O^+]^{-1}$ for the reaction of 4,4'-dimethoxytrityl alcohol at 25 °C in 80:20 water–methanol, ionic strength = 1 mol dm^{-3} {×, in absence of chloride, and ○, in the presence of 0.1 mol dm^{-3} chloride}

Table 2 Results for 4,4'-dimethoxytrityl carbenium ion in 20:80 (v/v) methanol–water

Parameter	Entry	Value[a]	T/°C	Footnote
K_{R^+} (pK_{R^+})	1	8.98 (−0.95)	25.0	*b*
	2	7.47	25.0	*c*
	3	7.10	25.0	*d*
	4	10.7	25.0	*e*
	5	28.4	25.0	*f*
	6	40	25.0	*g*
	7	9.18	18.0	*h*
	8	8.44	25.0	*h*
	9	6.78	40.0	*h*
	10	5.42	55.0	*h*
	11	(−0.89)	25.0	*i*
	12	(−1.02)	25.0	*j*
	13	(−1.16)	25.0	*k*
	14	(−1.14)	25.0	*l*
ε_{R^+} (log ε_{R^+})	15	297 000 (5.47)	25.0	*b,m*
	16	275 000	25.0	*c,m*
	17	(5.47)	25.0	*l*
K_{RCl}	18	4.60	18.0	*h*
	19	8.20	25.0	*h*
	20	17.2	40.0	*h*
	21	22.2	55.0	*h*
ΔH°/kJ mol^{-1}	22	−11.4		*h*
	23	−23.8		*i*
	24	−26.0		*j*
	25	−25.9		*k*
ΔS°/J K^{-1} mol^{-1}	26	−20		*h*
	27	−62.6		*i*
	28	−67		*j*
	29	−64.8		*k*

[a] This work at ionic strength = 1.0 mol dm^{-3} ($NaClO_4$) unless otherwise stated. [b] Calculated using data in Table 1 from experiments starting with the alcohol and based upon measurements at six perchloric acid concentrations; estimated possible error = 5% in K_{R^+} and 3% in ε_{R^+}. [c] Calculated using data in Table 3 from experiments with $[RNH_2]_0 = 6.41 \times 10^{-5}$ mol dm^{-3} at three acid concentrations. [d] Calculated using data in Table 3 from a single determination with $[RNH_2]_0 = 6.37 \times 10^{-5}$ mol dm^{-3}. [e] Calculated using data in Table 3 from a single determination with $[RNH_2]_0 = 6.37 \times 10^{-5}$ mol dm^{-3} and ionic strength = 0.70 mol dm^{-3}. [f] Calculated using data in Table 3 from a single determination with $[RNH_2]_0 = 6.37 \times 10^{-5}$ mol dm^{-3} and ionic strength = 0.20 mol dm^{-3}. [g] Value (± 5) at zero ionic strength in 80:20 (v/v) water–methanol estimated from data in Table 3 (see the Results section). [h] Calculated using data in Table 4 from experiments starting with the alcohol and based upon measurements at four perchloric acid concentrations, 0.1 mol dm^{-3} sodium chloride, ionic strength = 1.00 mol dm^{-3}, and assuming ε_{R^+} = 297,000; estimated errors = ±2 kJ mol^{-1} and ±8 J K^{-1} mol^{-1}. [i] Ref. 8 relating to a standard state of pure water. [j] Ref. 5 relating to a standard state of pure water; ΔS° is wrongly given as +67 J K^{-1} mol^{-1} in the original publication (C. D. Johnson, personal communication). [k] Ref. 9 relating to a standard state of pure water. [l] Ref. 1. [m] Rounded off to three significant figures and reliable to ± 5 in the 3rd figure.

Table 3 Equilibrium absorbances for the reaction of 4,4′-dimethoxytritylamine in 20:80 (v/v) methanol–water containing perchloric acid and sodium perchlorate at 25 °C

$[HClO_4]$/mol dm^{-3}	$[NaClO_4]$/mol dm^{-3}	A_e
1.00	0	2.013[a]
0.50	0.50	1.133[a]
0.20	0.80	0.458(5)[a]
0.20	0	0.1321[b]
0.20	0.50	0.3467[b]
0.20	0.80	0.5181[b]

[a] Initial 4,4′-dimethoxytritylamine concentration, $[RNH_2]_0 = 6.41 \times 10^{-5}$ mol dm^{-3}; results are means of duplicate determinations and lead to entries 2 and 16 in Table 2. [b] Initial 4,4′-dimethoxytritylamine concentration, $[RNH_2]_0 = 6.37 \times 10^{-5}$ mol dm^{-3}, single determinations leading to entries 3–5 in Table 2.

Table 4 Equilibrium absorbances for the reactions of 4,4′-dimethoxytrityl alcohol[a] in 20:80 (v/v) methanol–water containing perchloric acid, sodium perchlorate and 0.10 mol dm^{-3} sodium chloride (total ionic strength = 1.00 mol dm^{-3}) at 18–55 °C

$[HClO_4]$/mol dm^{-3}	$[NaClO_4]$/mol dm^{-3}	T/°C	A_e
0.20	0.70	18.0	0.399[b]
0.20	0.70	25.0	0.429[c]
0.20	0.70	40.0	0.516[c]
0.20	0.70	55.0	0.623[b]
0.40	0.50	18.0	0.783[b]
0.40	0.50	25.0	0.831[c]
0.40	0.50	40.0	0.968[c]
0.40	0.50	55.0	1.144[b]
0.60	0.30	18.0	1.124[b]
0.60	0.30	25.0	1.189[c]
0.60	0.30	40.0	1.343[c]
0.60	0.30	55.0	1.534[b]
0.80	0.10	18.0	1.450[b]
0.80	0.10	25.0	1.514[c]
0.80	0.10	40.0	1.683[c]
0.80	0.10	55.0	1.878[b]

[a] Initial 4,4′-dimethoxytrityl alcohol concentration, $[ROH]_0 = 6.37 \times 10^{-5}$ mol dm^{-3}. [b] Mean of three results. [c] Mean of five, six or seven results.

Table 5 Equilibrium absorbances for the reactions of 4,4′-dimethoxytrityl alcohol[a] in 20:80 (v/v) methanol–water containing perchloric and hydrochloric acids at 25 and 40 °C

$[HCl]$/mol dm^{-3}	$[HClO_4]$/mol dm^{-3}	T/°C	A_e[b]
1.00	0	25.0	0.684[c]
0.80	0.20	25.0	0.925
0.60	0.40	25.0	1.147
0.40	0.60	25.0	1.400
0.20	0.80	25.0	1.631
0	1.00	25.0	1.818
1.00	0	40.0	0.818[d]
0.80	0.20	40.0	1.055[d]
0.60	0.40	40.0	1.330[d]
0.40	0.60	40.0	1.574[d]
0.20	0.80	40.0	1.816[d]
0	1.00	40.0	2.030[d]

[a] Initial 4,4′-dimethoxytrityl alcohol concentration, $[ROH]_0 = 6.37 \times 10^{-5}$ mol dm^{-3}. [b] Mean of three results except where otherwise stated. [c] Mean of two results. [d] Single measurements.

We regard these results as in satisfactory agreement with those obtained from the alcohol (entries 1 and 15), though less accurate being based upon a more limited set of experimental data.

$$R^+ + Cl^- \rightleftharpoons RCl \qquad (6)$$

$$K_{RCl} = \frac{[RCl]}{[R^+][Cl^-]} \qquad (7)$$

$$\frac{[ROH]_0 \times \varepsilon_{R^+}}{A_e} = 1 + \frac{K_{R^+}}{[H_3O^+]} + K_{RCl} \times [Cl^-] \qquad (8)$$

Scheme 2

Also included in Table 2 are K_{R^+} results from the amine calculated non-graphically from data in Table 4 obtained in single determinations at $[H_3O^+] = 0.20$ mol dm^{-3} but at different ionic strengths and using the value of $\varepsilon_{R^+} = 297\,000$ (entries 3–5). From an empirical linear correlation of pK_{R^+} against the ionic strength ($R > 0.99$), we estimate a value of p$K_{R^+} = -1.6$ ($K_{R^+} = 40$) at zero ionic strength (entry 6).

If the reaction of eqn. (1) is carried out in the presence of a nucleophilic solute, then another equilibrium with its own equilibrium constant will be superimposed upon that described by eqn. (2). Chloride is just such an anion and will combine with the substituted trityl cation as described by eqns. (6) and (7) to give an equilibrium concentration of the substituted trityl chloride, RCl, as shown in Scheme 2. Neglect of this equilibrium may be a cause of inaccuracy in acidity function work based upon eqn. (1) in media containing significant concentrations of chloride.[5]

By the same sort of analysis as that in Scheme 1, it is readily shown that eqn. (8) in Scheme 2 describes the extended relationship between the total substituted trityl concentration (equal to the initial alcohol concentration, $[ROH]_0$), the equilibrium absorbance (A_e), the concentrations of hydronium and chloride ions ($[H_3O^+]$ and $[Cl^-]$), and the two equilibrium constants (K_{R^+} and K_{RCl}). If we assume a value for ε_{R^+}, this equation (in principle) allows the determination of both equilibrium constants by plotting $(A_e)^{-1}$ either against $[H_3O^+]^{-1}$ (as before) at constant $[Cl^-]$, or against $[Cl^-]$ at constant $[H_3O^+]$. Fig. 1 includes also the points ($R = 0.999$) obtained from the data in Table 4 by the former method, and the resultant value for K_{R^+} (Table 2, entry 8) is in good agreement with the value obtained in the absence of Cl^-, entry 1. The data shown in Table 5 obtained by varying $[Cl^-]$ at constant $[H_3O^+]$ led to non-linear plots at 25 and at 40 °C. We had already established that the reaction is sensitive to the ionic strength of the medium (see above), but that substituting lithium or ammonium for sodium has no appreciable effect. Consequently, we conclude that the non-linearity in the above mentioned plots as ClO_4^- is replaced by Cl^- is due to specific anionic effects; rate manifestations of such effects have been reported previously.[6]

We also investigated the equilibria at constant chloride concentration at other temperatures (Table 4) and obtained the equilibrium constants also shown in Table 2 (entries 7, 9 and 10). The gradient of the graph of $\ln(K_{R^+})$ *vs.* $(T/K)^{-1}$ shown in Fig. 2 ($R = 0.998$) leads to the standard enthalpy of the reaction of eqn. (1), $\Delta H^\ominus = -11.4$ kJ mol^{-1} (entry 20), and the computed intercept gives the standard entropy, $\Delta S^\ominus = -21$ J K^{-1} mol^{-1} (entry 26), the standard state being unit molarity in 20:80 (v/v) methanol–water containing 0.10 mol dm^{-3} sodium chloride and total ionic strength = 1.0 mol dm^{-3}. In contrast, the corresponding plot for K_{RCl}, also included in Fig. 2, is not linear.

Discussion

Scheme 1 ignores the minor equilibrium formation of the methyl ether from the low concentration of methanol or, rather, it assumes that the small extent of the reaction of the cation with methanol parallels the reaction with water so, strictly, the K_{R^+} parameter includes reaction of the cation with both components

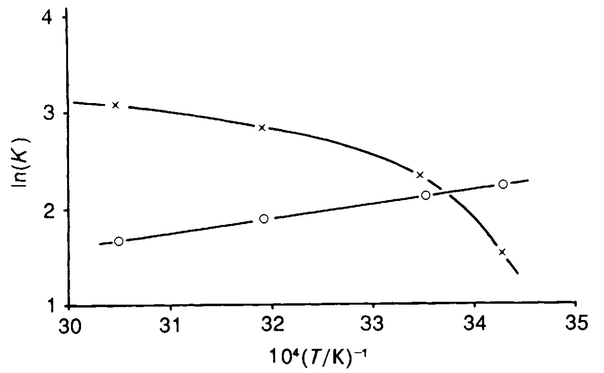

Fig. 2 Plot of ln (K) against $(T/\mathrm{K})^{-1}$ for the reaction of 4,4′-dimethoxytrityl alcohol in 80:20 water–methanol at $[\mathrm{Cl}^-] = 0.1$ mol dm^{-3}, total ionic strength = 1 mol dm^{-3} [○, $K = K_{\mathrm{R}^+}$ of the text; ×, $K = K_{\mathrm{RCl}}$ of the text]

of the solvent. Deno's result[1] of log ($\varepsilon_{\mathrm{R}^+}$) = 5.47, which was determined in sulfuric acid (it should not be appreciably affected by the different solvent), is also included in Table 2, entry 17. The agreement between this and our result of entry 15 is very satisfactory and indicates the reliability of this simple and convenient method.

The similarity between our value for the pK_{R^+} (entry 1) and others obtained by acidity function methods relating to a standard state of pure water (entries 11–14) is unexpectedly close considering the difference between the media and the earlier findings by Wyatt on the effect of additives;[7] addition of a modest proportion of methanol to water would be expected to increase the equilibrium constant of the reaction of eqn. (1). However, we had found that increasing the ionic strength decreased K_{R^+} in line with the findings of Bunton and Huang[6] who had analysed the effect in terms of separate kinetic salt effects upon the forward and reverse directions of reactions such as that of eqn. (1). Evidently, the enhancing effect upon K_{R^+} of the 20% methanol as cosolvent, compared with the result in pure water, is just about balanced by the depressing effect of a total electrolyte concentration of 1.0 mol dm^{-3} in the methanolic water that we used.

The enthalpy and entropy results for the reaction of eqn. (1) in aqueous methanol are in qualitative agreement with, though numerically smaller than, earlier results in pure water, also shown in Table 2, determined from acidity function measurements[5,8] (entries 23, 24, 27 and 28) and the excess acidity method[9] (entries 25 and 29) in aqueous sulfuric acid. Failure to obtain a linear Van't Hoff plot for the reaction of the cation with chloride indicates that the enthalpy of this reaction (at least) is not temperature-independent; in this respect, it is comparable to other ionogenic reactions.[10] Qualitatively, however, it appears that the enthalpy and entropy of the reaction as written in eqn. (6) have opposite signs to those of the reaction in eqn. (1), and are numerically appreciably larger.* This is reasonable since eqn. (6), unlike eqn. (1), involves the cancellation of charges so progress of the reaction from left to right will lead to a substantial release of solvating molecules with an associated increase in entropy, but an endothermic contribution to the overall enthalpy term.

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* From an estimate of the gradient at 25 °C, we calculate $\Delta H^{\circ}_{298\mathrm{K}} = 52.3$ kJ mol^{-1} which, when combined with $\Delta G^{\circ}_{298\mathrm{K}} = -5.22$ kJ mol^{-1} calculated from the equilibrium constant (8.20 at 25 °C), gives $\Delta S^{\circ}_{298\mathrm{K}} = 193$ K^{-1} mol^{-1}, but we regard these results as approximate.