PERKIN 2

Kinetics and thermodynamics of ionization of 4,4′-dimethoxytrityl alcohol in acetonitrile–aqueous acids: determination of enthalpies and entropies of activation and of reaction

Juan Crugeiras[a] **and Howard Maskill**[b]

[a] *Department of Physical Chemistry, University of Santiago de Compostela, Santiago de Compostela, Spain*
[b] *Chemistry Department, University of Newcastle, Newcastle upon Tyne, UK NE1 7RU*

Received (in Cambridge, UK) 18th November 1999, Accepted 14th December 1999
Published on the Web 10th February 2000

We have studied the equilibration shown in eqn. (2) of 4,4′-dimethoxytrityl alcohol in aqueous perchloric, nitric, and hydrochloric acids containing 20% acetonitrile at different temperatures using stopped-flow kinetics techniques. The observed overall pseudo first-order rate constant for equilibration, k_{obs}, decreases with increasing electrolyte concentrations at constant hydronium ion concentration; k_{obs}, has been resolved into forward and reverse components using the equilibrium UV absorbance and the temperature-independent molar absorptivity of the 4,4′-dimethoxytrityl carbenium ion. The forward reaction (rate constant k_f) is first order in both the alcohol and the acid; the reverse reaction (rate constant k_r) is pseudo first order with respect to the carbocation. At constant hydronium ion concentration, the forward rate constant increases with the concentration of electrolyte whereas the reverse rate constant decreases. Quantitative effects for perchlorate, nitrate, and chloride are different. Results are accommodated by a mechanism which involves pre-equilibrium protonation of the alcohol, heterolysis of the protonated alcohol to give a 4,4′-dimethoxytrityl carbenium ion–water ion–molecule pair, then conversion of this into the dissociated carbenium ion in equilibrium with ion pairs. There are additional parallel reaction channels from the protonated alcohol and electrolyte anions. Some of the elementary rate constants have been evaluated, and enthalpies and entropies of activation have been determined. Correspondingly, some equilibrium constants of the proposed mechanism have been evaluated, and associated enthalpies and entropies of reaction have been determined.

Introduction

The S_N1 reaction mechanism is one of the most widely studied. The theory behind this reaction mechanism, as originally formulated by Hughes and Ingold,[1] has been subject to continuous modification and refinement. An important development was introduced by Winstein *et al.*[2,3] when they recognised that the heterolytic bond breaking should not be considered as a single dissociation leading to the formation of dissociated ions, but the first step of a sequence involving different types of ions and ion pairs, in particular contact ion pairs and solvent-separated ion pairs. Only in the case of stabilised carbenium ions (*e.g.*, trityl) would the sequence lead on to fully dissociated and symmetrically solvated carbocations which may, in extreme cases, actually be the stable end-products of the reaction. Less stable carbenium ions (*e.g.*, simple secondary ones) would be intercepted earlier rather than later in the progression, *i.e.* at the contact ion pair or possibly the solvent-separated ion pair stage.

Wyatt[4–6] and Bunton[7] studied the influence of electrolytes and non-electrolytes upon the equilibration between substituted trityl alcohols and the corresponding carbenium ions under acidic conditions, and found that additives which accelerate the disappearance of the carbenium ion always shift the equilibrium towards the alcohol, whereas those which reduce the rate of disappearance of the carbenium ion shift the equilibrium towards the carbenium ion, *i.e.* effects upon forward and reverse directions are different.

$$Ar_3COH + H_3O^+ \rightleftharpoons Ar_3C^+ + 2\ H_2O$$

They also found that perchlorate ions led to an unexpected extra stability for triarylmethyl carbenium ions in aqueous solution. The study of salt effects upon solvolysis reactions has been used to investigate the role of ion pairs in solvolysis reactions,[8,9] and has led to applications in synthetic chemistry.[10] Also, new techniques have been developed for the study of the dynamics of ion pairs, such as their generation by laser flash photolysis.[11,12]

We have reported previously on the role of ion–molecule pairs in deamination reactions of substituted tritylamines under acidic conditions,[13–15] and more recently on cation–anion pairs in the acid-induced ionization of 4,4′-dimethoxytrityl alcohol (DMTOH) in 2% acetonitrile–water at 25 °C.[16] We now report results obtained for a wider range of electrolytes for the latter system in 20% acetonitrile–water at different temperatures which allow the determination not just of rate and equilibrium constants, but also of enthalpies and entropies both of activation and of overall reactions.

Experimental

Reagents

Aqueous solutions of nitric, hydrochloric, and perchloric acids were prepared from the commercial reagents (Merck 65%, 32%, and 60%, respectively) and glass distilled water, and were titrated against solutions of sodium hydroxide previously standardised using standard solutions of potassium hydrogen phthalate. Electrolyte solutions were made from commercial products of the highest purity available (Merck). 4,4′-Dimethoxytrityl alcohol was available from previous studies at Newcastle.[13–15]

Kinetics experiments

The rates of ionisation of DMTOH were measured using an Applied Photophysics DX.17MV sequential stopped-flow

DOI: 10.1039/a909136j

instrument with an optical path-length of 1 cm. One of the syringes was filled with an aqueous solution of DMTOH (with 40% CH_3CN to avoid solubility problems, especially when using hydrochloric acid and sodium chloride), and the aqueous acid ($HClO_4$, HNO_3, or HCl with an appropriate concentration of $NaClO_4$, $NaNO_3$, or NaCl) was in the other syringe. The temperatures of the solutions in the syringes and the cell of the stopped-flow instrument were kept the same and constant (±0.1 °C) by circulating water from a thermostatted bath.

We have already shown in a previous more limited investigation that ionic strength has a small effect upon the ionization of DMTOH, and that this is not the same as specific effects brought about by particular salts, especially perchlorates.[16] Consequently, in the present study we did not attempt to work at constant ionic strength. We have assumed that activity coefficients are close to unity or that they cancel out, and the thermodynamic equilibrium constants may be replaced by the corresponding practical equilibrium constants in which activities of solutes are replaced by molar concentrations.[17]

The reaction was studied by following the change with time in absorbance at the absorption maximum of the carbocation at 495 nm. The observed pseudo first-order rate constants (k_{obs}) were calculated by fitting the absorbance–time data to the integrated first-order rate equation, eqn. (1), using a

$$A = A_{inf} - \Delta A \exp(-k_{obs}t) \qquad (1)$$

non-linear regression analysis programme supplied by Applied Photophysics. The k_{obs} results are average values of 7–10 kinetic runs and treatment of errors was by standard statistical procedures.[18]

Kinetics analysis

The overall reaction may be described by the equilibrium of eqn. (2) where R stands for 4,4′-dimethoxytrityl, and R^+ does not imply any particular state of solvation or association. The

$$ROH + H_3O^+ \underset{k_r}{\overset{k_f}{\rightleftharpoons}} R^+ + 2\,H_2O \qquad (2)$$

rate equation for equilibration in terms of the changing concentration of carbenium ion is given by eqn. (3).

$$d[R^+]/dt = k_f\,[H_3O^+][ROH] - k_r\,[R^+] \qquad (3)$$

We note that

$$[ROH]_o = [ROH] + [R^+] \qquad (4)$$

where $[ROH]_o$ = the initial concentration of alcohol, and that the only species with significant absorption at 495 nm is the 4,4′-dimethoxytrityl carbenium ion (DMT^+, $A_{495} = [R^+]\varepsilon_{495}$, where A_{495} is the absorbance in the 1 cm cell and ε_{495} is the molar absorptivity of the carbocation at 495 nm). After solving the differential equation obtained by combining eqns. (3) and (4) and comparing the results with the first-order integrated rate equation, we can resolve the overall observed experimental rate constant into forward and reverse components to give eqns. (5) and (6) as demonstrated previously.[16]

$$k_f = \frac{\Delta A k_{obs}}{[H_3O^+][ROH]_o\varepsilon_{495}} \qquad (5)$$

$$k_r = k_{obs} - k_f[H_3O^+] \qquad (6)$$

The value of ε_{495} for DMT^+ was measured in 70% perchloric acid at 15 and 45 °C, and found to be independent of temperature over this range. The average value obtained is 7.0 (±0.1) × 10^4 $dm^3\ mol^{-1}\ cm^{-1}$ and, using this, we were then able to obtain values for k_f and k_r from experimental results for $[ROH]_o$, k_{obs}, $[H_3O^+]$, and ΔA.

Table 1 Influence of total ClO_4^- concentration upon rate constants at $[H_3O^+] = 0.20\ mol\ dm^{-3}$, 20% CH_3CN, between 288 and 318 K[a]

T/K	$[ClO_4^-]_T$/ mol dm^{-3}	ΔA	k_{obs}/s^{-1}	k_f/dm^3 $mol^{-1}\ s^{-1}$	k_r/s^{-1}
288	0.20	0.069	45.0	2.84	44.4
288	0.40	0.111	35.2	3.58	34.5
288	0.70	0.198	27.6	5.00	26.6
288	1.00	0.305	22.3	6.23	21.1
298	0.20	0.101	87.6	8.10	86.0
298	0.40	0.151	72.0	10.0	70.0
298	0.70	0.260	56.4	13.4	53.7
298	1.00	0.385	46.9	16.5	43.6
308	0.20	0.113	168	17.4	165
308	0.40	0.169	143	22.1	139
308	0.70	0.273	112	28.1	107
308	1.00	0.426	92.7	36.2	86
318	0.20	0.147	315	42.4	307
318	0.40	0.218	267	53.3	256
318	0.70	0.347	215	68.3	201
318	1.00	0.509	182	84.8	165

[a] $[DMTOH]_0 = 7.8 \times 10^{-5}\ mol\ dm^{-3}$.

Table 2 Influence of total NO_3^- concentration on rate constants at $[H_3O^+] = 0.20\ mol\ dm^{-3}$, 20% CH_3CN, between 288 and 318 K[a]

T/K	$[NO_3^-]_T$/ mol dm^{-3}	ΔA	k_{obs}/s^{-1}	k_f/dm^3 $mol^{-1}\ s^{-1}$	k_r/s^{-1}
288	0.20	0.048	58.0	2.6	57.5
288	0.40	0.059	53.8	2.9	53.2
288	0.70	0.077	48.9	3.5	48.2
288	1.00	0.097	45.3	4.0	44.5
298	0.20	0.064	113	6.6	112
298	0.40	0.076	105	7.3	104
298	0.70	0.099	96	8.7	94
298	1.00	0.122	88	9.8	86
308	0.20	0.078	211	15.1	208
308	0.40	0.091	204	17	201
308	0.70	0.115	189	19.9	185
308	1.00	0.141	175	22.6	171
318	0.20	0.097	383	34.0	376
318	0.40	0.113	371	38.4	363
318	0.70	0.143	345	45.2	336
318	1.00	0.176	325	52.4	315

[a] $[DMTOH]_0 = 7.8 \times 10^{-5}\ mol\ dm^{-3}$.

Results and discussion

Effect of electrolyte concentrations

The influence of the electrolyte concentration upon the overall reaction rate constant, k_{obs}, was studied at hydronium ion concentration equal to 0.2 mol dm^3 by changing the concentration of the sodium salt of the corresponding acid. These sets of experiments were done at different temperatures, *viz.* 15, 25, 35, and 45 °C, and the results are summarized in Tables 1–3. We observe in these tables, for a constant temperature, appreciable decreases in k_{obs} as the salt concentration increases for all three acids. From the values of k_{obs} and the overall changes in absorbance, ΔA, the values of k_f and k_r were calculated using eqns. (5) and (6). These results are summarized in the last two columns of Tables 1–3 where we see that the forward reaction rate constants, k_f, increase with the increasing electrolyte concentration, whilst the reverse reaction rate constants, k_r, decrease. We have shown in a previous study that the magnitudes of these effects depend upon the nature of the anion, whereas the identity of the cation of the electrolyte seems to be irrelevant.[16]

The mechanism shown in Scheme 1 was proposed to account for our previous results for the perchloric acid-induced reaction of DMTOH.[16]

$$H_3O^+ + ROH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ROH_2^+ + H_2O \qquad \text{(i)}$$

$$ROH_2^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} R^+{\cdot}OH_2 \qquad \text{(ii)}$$

$$R^+{\cdot}OH_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} R^+ + H_2O \qquad \text{(iii)}$$

$$ROH_2^+ + X^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} R^+{\cdot}X^- + H_2O \qquad \text{(iv)}$$

$$R^+ + X^- \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} R^+{\cdot}X^- \qquad \text{(v)}$$

Scheme 1

An additional step, the collapse of the ion pair R^+X^- to form a covalent compound, R–X,[19] was considered but rejected as we could detect no spectroscopic evidence under the conditions of our experiments for the existence of covalent compounds DMT–X where $X = OClO_3$ or Cl.[16]

In order to relate the experimental rate constants k_f and k_r to the elementary rate constants of the mechanism in Scheme 1, we made the following assumptions.

1) Protonation of the alcohol is rapidly reversible, *i.e.* step (i) may be treated as a pre-equilibrium with equilibrium constant K_1 (equal to k_1/k_{-1}).
2) The steady-state approximation may be applied to the ion–molecule pair, $R^+{\cdot}OH_2$, in steps (ii) and (iii).
3) The molar absorptivity of the ion R^+ is the same regardless of its solvolytic environment,[11] *i.e.* ε_{495} for R^+ is equal to ε_{495} for $R^+{\cdot}X^-$ which we denote simply by ε_{495}, and hence $A_{495} = ([R^+] + [R^+{\cdot}X^-])\,\varepsilon_{495}$.
4) Step (v) of Scheme 1 constitutes a post-equilibrium, the equilibrium constant of which is K_5 (equal to k_5/k_{-5}), *i.e.* $[R^+{\cdot}X^-] = K_5[R^+][X^-]$, and that maintenance of this equilibrium does not affect the overall rate of equilibration.[11]
5) Collapse of the ion–molecule pair, $R^+{\cdot}OH_2$, back to the protonated alcohol is much faster than its further conversion to the solvated dissociated carbenium ion, *i.e.* $k_{-2} \gg k_3$, and hence step (ii) may also be treated as a pre-equilibrium with $K_2 = k_2/k_{-2}$.

Table 3 Influence of total Cl^- concentration upon rate constants at $[H_3O^+] = 0.20$ mol dm^{-3}, 20% CH_3CN, between 288 and 318 K[a]

T/K	$[Cl^-]_T$/ mol dm^{-3}	ΔA	k_{obs}/s^{-1}	k_f/dm^3 mol^{-1} s^{-1}	k_r/s^{-1}
288	0.20	0.038	65	2.3	64.5
288	0.40	0.041	63	2.4	62.5
288	0.70	0.050	62	2.8	61.4
288	1.00	0.056	58.6	3.0	58.0
298	0.20	0.051	123	5.8	122
298	0.40	0.059	122	6.6	121
298	0.70	0.070	119	7.6	118
298	1.00	0.084	114	8.8	112
308	0.20	0.059	220	11.9	218
308	0.40	0.068	220	13.7	217
308	0.70	0.081	219	16.2	216
308	1.00	0.099	211	19.1	207
318	0.20	0.076	410	28.5	404
318	0.40	0.087	400	31.9	394
318	0.70	0.101	385	35.6	378
318	1.00	0.119	383	41.7	375

[a] $[DMTOH]_0 = 7.8 \times 10^{-5}$ mol dm^{-3}.

We then obtain the relationships in eqns. (7) and (8) between the equilibrium and rate constants of the elementary steps of the mechanism in Scheme 1 and the forward and reverse rate constants obtained by experiment.[16]

$$k_f = K_1K_2k_3 + K_1k_4[X^-] \qquad (7)$$

$$\frac{1}{k_r} = \frac{1}{k_{-3}} + \frac{K_5}{k_{-3}}[X^-] \qquad (8)$$

Values for $K_1K_2k_3$ and K_1k_4 obtained by linear regression of k_f against $[X^-]$ are summarized in Table 4. The product $K_1K_2k_3$ is, within experimental error, independent of the nature of the electrolyte as required by the mechanism, and as observed previously,[16] so average values only are given in Table 4.

For the reverse rate constants, plotting values of $1/k_r$ against the total concentration of the anion gives straight lines with a common intercept (which gives k_{-3}) but different gradients (different K_5 values according to the nature of X^-). These plots, as before,[16] validate the approximations introduced and allow determination of k_{-3} and K_5 which are also included in Table 4. The result of $K_5 = 1.63$ dm^3 mol^{-1} for $X^- = ClO_4^-$ in 20% (v/v) acetonitrile–water and 25 °C compares very well with the value of 1.3 proposed by Wyatt,[20] the approximate result of 2.5 from our deamination studies,[15] and our value of 1.45 based upon results for barium perchlorate as well as sodium perchlorate at 2% acetonitrile and constant ionic strength.[16] The result of $K_5 = 0.41$ dm^3 mol^{-1} for $X^- = NO_3^-$ is in fair agreement with the result 0.67 dm^3 mol^{-1} at 2% acetonitrile and constant ion strength,[16] and the smaller (and less precise) result of $K_5 = 0.11$ dm^3 mol^{-1} for $X^- = Cl^-$ is new.

According to the proposed mechanism in Scheme 1, $K_{R^+} = k_{-3}/K_1K_2k_3$ where K_{R^+} is the reciprocal of the equilibrium constant for eqn. (2), so we can obtain practical values for the K_{R^+} from values for k_{-3} and $K_1K_2k_3$ already obtained; these results are shown in the last column of Table 4. The value of $K_{R^+} = 22 \pm 1$ ($pK_{R^+} = -1.34$) at zero ionic strength, 25 °C and 20% (v/v) acetonitrile–water is in very good agreement with literature values[21] which adds further support for the mechanism of Scheme 1 and the derivations arising from it.

In step (iv) of Scheme 1, the anion displaces a water molecule from the protonated substituted trityl alcohol to give an ion pair (this may not be a single-step reaction). From the results for K_1k_4 at 25 °C of Table 4, and taking K_1/dm^3 mol^{-1} = 2.5×10^{-3},[22] we calculate the following values for k_4: 4.24×10^3 for perchlorate, 1.64×10^3 for nitrate, and 1.48×10^3 dm^3 mol^{-1} s^{-1} for chloride ion. As seen, perchlorate is more effective than nitrate or chloride, a finding not in general accord with conventional ideas of the relative nucleophilicities of these

Table 4 Influence of temperature upon the rate and equilibrium constants of Scheme 1

		K_1k_4/dm^6 mol^{-2} s^{-1}				K_5/dm^3 mol^{-1}			
T/K	$K_1K_2k_3$/dm^3 mol^{-1} s^{-1}	ClO_4^-	NO_3^-	Cl^-	k_{-3}/s^{-1}	ClO_4^-	NO_3^-	Cl^-	K_{R^+}/ mol dm^{-3}
288	2.1 ± 0.1	4.3 ± 0.1	1.78 ± 0.06	0.9 ± 0.1	63 ± 2	1.88 ± 0.02	0.39 ± 0.01	0.13 ± 0.02	30 ± 2
298	5.6 ± 0.3	10.6 ± 0.2	4.1 ± 0.2	3.7 ± 0.2	121 ± 4	1.63 ± 0.02	0.41 ± 0.01	0.11 ± 0.01	22 ± 1
308	12 ± 1	23 ± 1	9.4 ± 0.1	8.9 ± 0.2	222 ± 3	1.56 ± 0.04	0.30 ± 0.01	0.07 ± 0.02	19 ± 1
318	29 ± 3	52.7 ± 0.7	23.0 ± 0.3	16 ± 1	401 ± 6	1.39 ± 0.02	0.24 ± 0.01	0.10 ± 0.02	14 ± 1

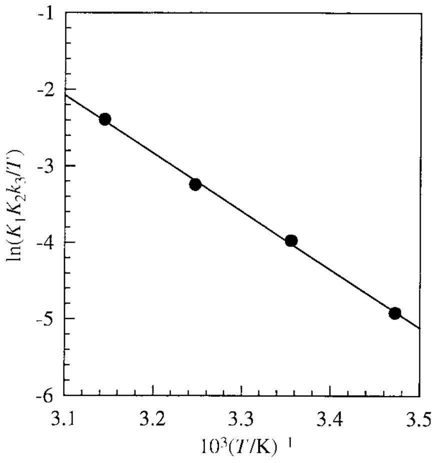

Fig. 1 Plot of ln ($K_1K_2k_3/T$) against $1/T$ for the acid-induced dissociation of 4,4′-dimethoxytrityl alcohol in 20% acetonitrile–water.

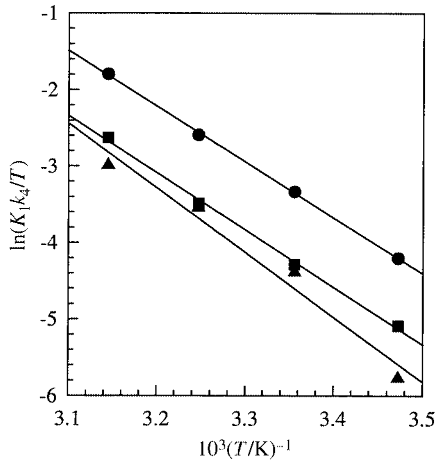

Fig. 2 Plot of ln (K_1k_4/T) against $1/T$ for the acid-induced dissociation of 4,4′-dimethoxytrityl alcohol catalyzed by anions: filled circles for perchlorate, squares for nitrate, and triangles for chloride.

anions with small hard electrophiles. Its peculiar effectiveness in stabilising (developing) delocalized positive charge in an incipient large non-polarising carbocation in the heterolytic transition state has, however, been recognised previously.[4–6,20]

Effect of temperature upon ionization rate constants – determination of enthalpies and entropies of activation

From experiments investigating the influence of electrolyte concentration at temperatures from 15 to 45 °C, we obtained activation parameters for the reactions involving composite rate constants $K_1K_2k_3$ and K_1k_4. The first product of equilibrium and rate constants does not depend on the nature of the electrolyte used, and the Eyring plot using the average values of $K_1K_2k_3$ in Table 4 yields a good straight line (Fig. 1). The second does depend on the nature of the added electrolyte, and we obtain the three linear Eyring plots shown in Fig. 2. Enthalpies of activation were calculated from the gradients of the respective plots in the normal way, and values for the entropies of activation from the intercepts. Results are shown in Table 5 where we see that the values of the enthalpies of activation corresponding to the ionization process catalyzed by perchlorate and nitrate ions are very similar to each other and to the corresponding value for the uncatalyzed reaction (the smaller catalytic effect of chloride led to larger errors; consequently, no results for chloride are included in Table 5). The entropies of activation for the perchlorate and nitrate catalysed routes are also very similar to each other and *numerically* similar to that for the uncatalysed reaction channel. However, since the catalysed and uncatalysed reactions are of different kinetic orders, entropies of activation (unlike enthalpies of activation) cannot properly be directly compared. Nevertheless, the translational aspect of the third-order catalysed reactions should cause them to have appreciably more negative entropies of activation than the second-order uncatalysed reaction, and this is not observed.

Table 5 Activation parameters for the rate constants of Scheme 1

	$K_1K_2k_3$/dm^3 mol^{-1} s^{-1}	K_1k_4/dm^6 mol^{-2} s^{-1}		k_{-3}/s^{-1}
		ClO_4^-	NO_3^-	
$\Delta H^‡$/kJ mol^{-1}	63 ± 1	60.7 ± 0.8	62 ± 1	44.4 ± 0.2
$\Delta S^‡$/J K^{-1} mol^{-1}	−19 ± 5	−22 ± 3	−25 ± 6	−56 ± 1

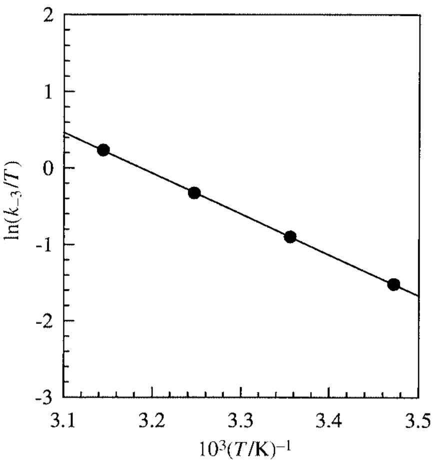

Fig. 3 Eyring plot for the reaction of 4,4′-dimethoxytrityl carbenium ion with water.

The Eyring plot for the elementary rate constant for the reaction of DMT^+ with water, k_{-3}, with no associated equilibrium constant factor, is shown in Fig. 3, and the activation parameters for this reaction are given in the last column of Table 5. They correspond to the conversion of a symmetrically solvated dissociated carbenium ion into an ion–molecule pair. An appreciably negative entropy of activation and a very modest enthalpy of activation are entirely in accord with the developing non-covalent association of the carbenium ion with a single water molecule.

Effect of temperature upon the equilibrium constants K_5 and K_{R^+} – determination of enthalpies and entropies of reaction

We obtained thermodynamic parameters for the equilibria corresponding to K_5 and K_{R^+} from experimental equilibrium constants at different temperatures in the conventional manner. The Van't Hoff plots yielded good straight lines as shown in Fig. 4 for K_5 and Fig. 5 for K_{R^+}; we obtained enthalpies of reaction from the gradients of these plots, and entropies of reaction from the intercepts. The results are summarized in Table 6 and, again, results for chloride are less reliable. We see that ion pair formation corresponding to K_5 is exothermic in all cases but, as anticipated, entropically unfavourable. Quenching of the carbenium ion to generate DMTOH and hydronium ion is exothermic but, almost certainly due to the solvation of the hydronium ion, entropically unfavourable. The standard state for these thermodynamic parameters is unit molarity in 20:80 (v/v) acetonitrile–water and zero ionic strength.

Conclusions

Anions of electrolytes (acids or salts added, for example, to control the ionic strength of the medium) have specific effects on the kinetics of the acid-induced ionization of trityl alcohols

Table 6 Thermodynamic parameters for the equilibrium constants K_5 in Scheme 1 and K_{R^+} for dimethoxytrityl carbenium ion in 20% acetonitrile–water

	K_5/dm^3 mol^{-1}			
	ClO_4^-	NO_3^-	Cl^-	K_{R^+}/mol dm^{-3}
ΔH^0/kJ mol^{-1}	−7.5 ± 0.8	−13 ± 4	−8 ± 8	−18 ± 1
ΔS^0/J K^{-1} mol^{-1}	−20 ± 2	−50 ± 8	−50 ± 24	−36 ± 6

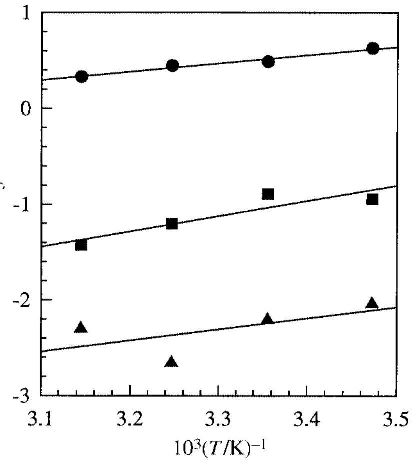

Fig. 4 Van't Hoff plot for the equilibrium formation of ion pairs: filled circles for perchlorate, squares for nitrate, and triangles for chloride.

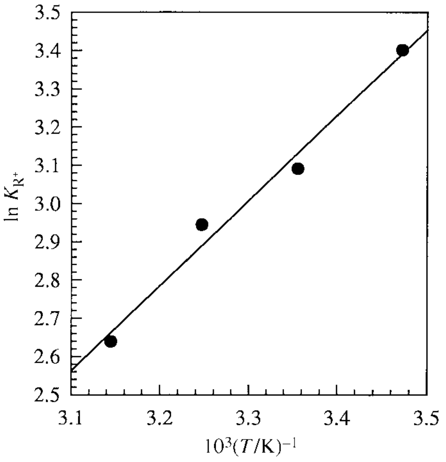

Fig. 5 Van't Hoff plot for the equilibrium constant K_{R^+}.

to give the corresponding carbenium ions; the same is true of the corresponding reactions of tritylammonium ions. These effects may be non-linear at higher concentrations and hence contribute to the non-linearity reported for some Van't Hoff plots;[23] they will be especially important when chloride, which has a small effect, is replaced by perchlorate which has a large effect.

References

1 E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 1935, 244.
2 S. Winstein, E. Clippinger, A. H. Fainberg and G. C. Robinson, *J. Am. Chem. Soc.*, 1954, **76**, 2597.
3 S. Winstein, B. Appel, R. Baker and A. Diaz, "Organic Reaction Mechanisms", *Spec. Publ. Chem. Soc.*, 1965, **19**, 109.
4 H. Nicholson and P. A. H. Wyatt, *J. Chem. Soc. B*, 1968, 198.
5 M. J. Postle and P. A. H. Wyatt, *J. Chem. Soc.*, *Perkin Trans. 2*, 1972, 474.
6 J. N. Ride and P. A. H. Wyatt, *J. Chem. Soc.*, *Perkin Trans. 2*, 1973, 746.
7 C. A. Bunton and S. K. Huang, *J. Am. Chem. Soc.*, 1972, **94**, 3536.
8 J. P. Richard, *J. Org. Chem.*, 1992, **57**, 625.
9 J. P. Richard and P. E. Yeary, *J. Am. Chem. Soc.*, 1993, **115**, 1739.
10 A. Loupy, B. Tchoubar and D. Astruc, *Chem. Rev.*, 1992, **92**, 1141.
11 J. M. Masnovi and J. K. Kochi, *J. Am. Chem. Soc.*, 1985, **107**, 7880.
12 T. M. Bockman and J. K. Kochi, *J. Chem. Soc.*, *Perkin Trans. 2*, 1994, 1901.
13 C. Bleasdale, B. T. Golding, W. H. Lee, H. Maskill, J. Riseborough and E. Smits, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 93.
14 M. C. Lopez, J. C. Martinez, I. Demirtas, H. Maskill and E. Stix, *Org. React.*, 1997, **31**, 71.
15 J. Crugeiras and H. Maskill, *J. Chem. Soc.*, *Perkin Trans. 2*, 1998, 1901.
16 J. Crugeiras and H. Maskill, *Can. J. Chem.*, 1999, **77**, 530.
17 H. Maskill, *The Physical Basis of Organic Chemistry*, Oxford University Press, Oxford, 1985.
18 D. P. Shoemaker, C. W. Garland and J. W. Nibler, *Experiments in Physical Chemistry*, McGraw-Hill, 6th Edition, 1996.
19 N. S. Zefirov, A. S. Koz'min, V. V. Zhdankin, V. N. Kirin, N. M. Yur'eva and V. D. Sorokin, *Chem. Scr.*, 1983, **22**, 195; N. S. Zefirov and A. S. Koz'min, *Acc. Chem. Res.*, 1985, **18**, 154.
20 P. A. H. Wyatt, *J. Chem. Res.* (*S*), 1980, 297.
21 N. C. Deno, J. J. Jaruzelski and A. Schriesheim, *J. Am. Chem. Soc.*, 1955, **77**, 3044; E. M. Arnett and R. D. Bushick, *J. Am. Chem. Soc.*, 1964, **86**, 1564; M. J. Cook, N. L. Dassanayake, C. D. Johnson, A. R. Katritzky and T. W. Toone, *J. Am. Chem. Soc.*, 1975, **97**, 760.
22 N. C. Deno and J. O. Turner, *J. Org. Chem.*, 1966, **31**, 1969; E. M. Arnett, R. P. Quirk and J. J. Burke, *J. Am. Chem. Soc.*, 1970, **92**, 1260.
23 W. H. Lee and H. Maskill, *J. Chem. Soc.*, *Perkin Trans. 2*, 1994, 1463.

Paper a909136j