The 4,4′-dimethoxytrityl carbenium ion by ionization of 4,4′-dimethoxytrityl alcohol in acetonitrile – aqueous perchloric and nitric acids containing electrolytes: kinetics, equilibria, and ion-pair formation

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Abstract: We have studied the equilibration shown in eq. [3] of 4,4′-dimethoxytrityl alcohol in aqueous perchloric and nitric acids containing low proportions of acetonitrile using stopped-flow kinetics techniques. The rate constants for the overall progress to equilibrium, k_{obs}, have been resolved into forward and reverse components using the equilibrium UV absorbance and a value for the molar absorptivity of the 4,4′-dimethoxytrityl carbenium ion determined in concentrated aqueous perchloric acid. The forward reaction (rate constant k_f) is first order in both the alcohol and the acid concentrations; 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 linearly with the concentration of electrolyte, whereas the reverse rate constant decreases. These effects depend upon the nature of the anion, but not the cation, and are not ionic strength effects. At constant anion concentrations, k_f in both acids, and k_r in perchloric acid, are independent of hydronium ion concentration; however, k_r decreases with increasing hydronium ion concentration at constant nitrate concentration. At nonconstant ionic strength, changes in k_f and k_r observed in increasing concentrations of perchloric acid are attributable wholly to changes in perchlorate concentration. A mechanism is proposed 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 a dissociated carbenium ion in equilibrium with ion pairs. To account for the strong effects of perchlorate and nitrate upon the forward rate constants, it is proposed that these anions provide additional reaction channels from the ion–molecule pair. However, we find no evidence of acid catalysis in the reaction of the ion–molecule pair (in contrast to our finding for the reaction of the corresponding ion–molecule pair formed from dimethoxytritylamine in acidic media). Some of the elementary rate and equilibrium constants of the proposed mechanism have been evaluated.

Key words: trityl, carbenium ion, stopped-flow, ion pair, ion–molecule pair.

Résumé : Faisant appel à des techniques de cinétique à flux stoppé, on a étudié l’équilibre (représenté par l’équation 3) de l’alcool 4,4′-diméthoxytritylique dans les acides perchlorique et nitrique contenant de faibles quantités d’acétonitrile. Utilisant l’absorbance UV à l’équilibre et une valeur pour l’absorptivité molaire de l’ion 4,4′-diméthoxytritylcarbénium déterminé en solution aqueuse concentrée d’acide perchlorique, on a résolu les constantes de vitesse globales de réaction pour le déplacement vers l’équilibre, k_{obs}, en deux composantes, l’une pour réaction vers l’avant et l’autre pour l’inverse. La réaction vers l’avant (constante de vitesse k_a) est du premier ordre en concentrations tant d’alcool que d’acide; la réaction inverse (constante de vitesse k_i) est de pseudo premier ordre par rapport au carbocation. À concentration d’ion hydronium constante, la constante de vitesse vers l’avant augmente d’une façon linéaire avec la concentration de l’électrolyte alors que la constante de vitesse inverse diminue. Ces effets dépendent de la nature de l’anion, mais pas de celle du cation, et elles ne sont pas des effets de la force ionique. À des concentrations d’anion constantes, les valeurs de k_a dans les deux acides et les valeurs de k_i dans l’acide perchlorique sont indépendantes de la concentration en ion hydronium; toutefois, à concentration constante de nitrate, la valeur de k_i diminue avec une augmentation de la concentration en ion hydronium. À des forces ioniques qui ne sont pas constantes, on observe des changements dans les valeurs de k_a et de k_i lorsqu’on augmente la concentration de l’acide perchlorique; ces changements sont entièrement attribués à des changements dans la concentration du

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This paper is dedicated to Jerry Kresge in recognition of his many achievements in chemistry.

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perchlorate. On propose un mécanisme qui implique un prééquilibre, protonation de l'alcool, une hétérolyse de l'alcool protoné pour donner une paire d'ion 4,4′-diméthytritycarbénium – molécule d'eau et finalement une transformation de celle-ci en un ion carbénium dissocié en équilibre avec des paires d'ions. Afin d'expliquer les effets importants des ions perchlorate et nitrate sur les constantes de vitesse vers l'avant, on suggère que ces anions fournissent des moyens additionnels de réaction pour la paire ion–molécule. Toutefois, on n'a pas mis en évidence de catalyse acide dans la réaction de la paire ion–molécule (en opposition avec les résultats que nous avons obtenus antérieurement pour la réaction de la paire ion-molécule correspondante formée à partir de la diméthoxytritylamine en milieu acide). On a évalué quelques-unes des constantes de vitesse élémentaire et d'équilibre du mécanisme proposé.

Mots clés : trityle, ion carbénium, flux stoppé, paire d'ion, paire ion–molécule.

[Traduit par la Rédaction]

Introduction

The kinetics and equilibria of ionization of substituted triphenylmethanols (substituted trityl alcohols) have been extensively studied, partly in connection with the development of the H_R acidity function (1, 2), and partly due to the importance of substituted trityl as a protecting group in organic synthesis (3). The H_R acidity function is based on the ionization equilibria of triarylmethanols, eq. [1], and equilibrium constants, K_{R^+}, for these reactions are given by eq. [2].

$$[1] \qquad Ar_3C^+ + H_2O \leftrightarrow Ar_3COH + H^+$$

$$[2] \qquad K_{R^+} = \frac{a_{Ar_3COH}\,a_{H^+}}{a_{Ar_3C^+}\,a_{H_2O}}$$

In a kinetic study of the ionization reaction of 4,4′,4′′-trimethoxytrityl alcohol (TMTOH) under acidic conditions, Postle and Wyatt (4) found that the addition of salts and nonelectrolytes has appreciable effects upon the forward and reverse rate constants of the reaction in eq. [1]. These effects were explained qualitatively in terms of the change in the activity of the water, changes in the activity coefficients of the different solutes involved in the equilibrium, and the formation of ion pairs. The effects are especially large in the case of perchlorate, an electrolyte regarded as inert in many contexts, but with an appreciable effect upon the ionization of neutral substrates where a delocalized positive charge is developed in a carbon residue in the transition state (5). Wyatt (6) proposed a value of 1.3 dm^3 mol^{-1} for the equilibrium constant for the formation of the ion pair $TMT^+ClO_4^-$ from dissociated ions in aqueous solution in order to bring the derived H_R values for aqueous perchloric acid onto the same water activity scale as that for aqueous sulfuric acid.

In other contexts, the formation of covalent organic perchlorates has been proposed in some reactions with carbocation intermediates (7). However, triarylmethyl perchlorates are fully ionic in the crystalline state and in solution in solvents of even low dielectric constant such as chloroform or dichloromethane (8).

In the investigation reported here, we have measured the overall rates of equilibration of 4,4′-dimethoxytrityl alcohol (DMTOH) in aqueous perchloric and aqueous nitric acid. From these rate constants and UV measurements at equilibrium, we have obtained experimental values for forward and reverse rate constants for the equilibrium reaction expressed as eq. [3].

$$[3] \qquad ROH + H_3O^+ \underset{k_r}{\overset{k_f}{\leftrightarrow}} R^+ + 2H_2O$$

Under the dilute acidic conditions of our investigations using the 4,4′-dimethoxytrityl system, activity coefficient effects are expected to be small and to cancel out. Consequently, thermodynamic equilibrium constants may be replaced by practical versions (9) in which activities of dilute solutes are replaced by molar concentrations, and water is referred to the mole fraction activity scale and given the value of unity.

This investigation is closely related to our prior study of the dimethoxytrityl carbenium ion generated by deamination of dimethoxytritylamine (10). In that study, we identified specific acid catalysis in the reaction of the substituted tritylammonium cation, and invoked the dimethoxytrityl carbenium ion – ammonia ion–molecule pair as a kinetically significant intermediate.

Experimental

Reagents

Aqueous solutions of nitric and perchloric acid were prepared from the commercial reagents (Merck 65 and 60%, respectively) and glass distilled water, and were titrated against solutions of sodium hydroxide previously standardized using standard solutions of potassium hydrogen phthalate. Electrolyte solutions were made from the commercial products of the highest purity available (Merck). 4,4′-Dimethoxytrityl alcohol was available from previous studies at Newcastle (10, 11).

Kinetics experiments

The rates of ionization of DMTOH were measured using an Applied Photophysics DX.17MV sequential stopped-flow spectrofluorimeter with an optical path length of 1 cm. One of the syringes of the stopped-flow device was filled with an aqueous solution of DMTOH (with 4% of CH_3CN to avoid solubility problems), and the aqueous acid ($HClO_4$ or HNO_3 with an appropriate concentration of $NaClO_4$, $Ba(ClO_4)_2$, or $NaNO_3$) was in the other syringe. The temperature of the solutions in the syringes and cell of the stopped-flow instrument was kept constant (25.0 ± 0.1°C) by circulating water from a thermostatted bath.

Spectra in Fig. 1 of the reaction mixture recorded at different times show the appearance of two absorption bands corresponding to the 4,4′-dimethoxytrityl carbocation. 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 law using a nonlinear regression analysis program 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 (12).

Results

Influence of electrolyte concentration

The influence of the electrolyte concentration upon the overall reaction rate constant (k_{obs}) was studied at 0.2 mol dm^{-3} perchloric acid by changing the concentration of sodium perchlorate, and at 0.2 mol dm^{-3} nitric acid by changing the concentration of sodium nitrate, but keeping the other reaction conditions constant in each series. We observe in Table 1 appreciable decreases in k_{obs} as the salt concentration increases for both acids. To study the effect of the charge on the cation of the electrolyte on the reaction rate, the influence of barium perchlorate concentration in perchloric acid was also investigated. These results are also included in Table 1 and show the same effect.

Influence of hydronium ion concentration

The effect of hydronium ion concentration upon the overall reaction rate constant (k_{obs}) was studied at a constant ionic strength of 1.0 mol dm^{-3} by changing the concentration of both perchloric acid (using sodium perchlorate to maintain constant ionic strength) and nitric acid (using sodium nitrate). The results obtained in these experiments are shown in Table 2. There is a distinct increase in k_{obs} with increasing perchloric acid concentration, but only a small increase for nitric acid. Analogous experiments were carried out using perchloric acid at nonconstant ionic strength; an appreciable decrease in k_{obs} with increasing acid concentration is now evident from the results in Table 3.

Kinetic analysis

The overall reaction may be described by the equilibrium in eq. [3] above where R stands for 4,4′-dimethoxytrityl, and R^+ does not imply any particular state of solvation or association. The rate equation for equilibration in terms of the changing concentration of carbenium ion is given in eq. [4].

$$[4] \qquad d[R^+]/dt = k_f[H_3O^+][ROH] - k_r[R^+]$$

Taking into account that

$$[ROH]_0 = [ROH] + [R^+]$$

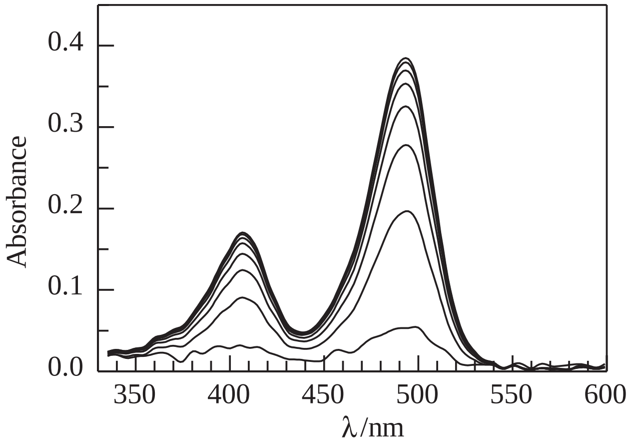
where $[ROH]_0$ = the initial concentration of alcohol, and assuming that the only species absorbing at 495 nm is the carbocation ($A_{495} = [R^+]\varepsilon_{495}$ where A_{495} is the absorbance in the 1 cm cell and ε_{495} is the molar absorptivity (extinction coefficient) of the carbocation at 495 nm), then

$$dA_{495}/dt = \varepsilon_{495} d[R^+]/dt$$

hence,

$$[5] \qquad dA_{495}/dt = k_f[H_3O^+][ROH]_0\varepsilon_{495} - (k_f[H_3O^+] + k_r)A_{495}$$

Fig. 1. Spectra of the reaction mixture at different times. $[DMTOH]_0 = 3.3 \times 10^{-5}$ mol dm^{-3}, $[HClO_4] = 0.5$ mol dm^{-3}, ionic strength = 1.0 mol dm^{-3} ($NaClO_4$), 25°C, time intervals = 0.01 s.



Solution of this differential equation gives eq. [6]:

$$[6] \qquad A_{495} = \frac{k_f[H_3O^+][ROH]_0\varepsilon_{495}}{k_f[H_3O^+]+k_r}[1-e^{-(k_f[H_3O^+]+k_r)t}]$$

Comparison of eq. [6] with eq. [7], the integrated first-order rate equation used to fit the experimental absorbance–time data,

$$[7] \qquad A_{495} = A_\infty - \Delta A e^{-k_{obs}t}$$

in which $\Delta A = A_\infty - A_0$, A_∞ is the absorbance at time = infinity, and A_0 (the absorbance at time = 0) is generally zero, leads to the relationships in eqs. [8] and [9] between the single experimental rate constant for equilibration, k_{obs}, the observed overall change in absorbance associated with the attainment of equilibrium, ΔA, and the attributed forward and reverse rate constants of eq. [3].

$$[8] \qquad k_f = \frac{\Delta A k_{obs}}{[H_3O^+][ROH]_0\varepsilon_{495nm}}$$

$$[9] \qquad k_r = k_{obs} - k_f[H_3O^+]$$

Taking the value for ε_{495} of DMT^+ in 70% perchloric acid obtained in this work (10) of 7×10^4 dm^3 mol^{-1} cm^{-1}, we obtain the results for k_f and k_r at different electrolyte concentrations summarized in Table 4. Clearly, the forward reaction rate constants, k_f, increase with the increasing electrolyte concentration, whilst the reverse reaction rate constants, k_r, decrease. However, the magnitudes of these effects depend upon the nature of the anion, whereas the identity of the cation in perchloric acid seems to be irrelevant.

The influence of perchloric and nitric acid concentrations on the forward and reverse rate constants k_f and k_r at constant ionic strength (1.0 mol dm^{-3}) were also investigated using eqs. [8] and [9], and results are shown in Table 5. We observe that, within experimental error, k_f remains constant with increasing concentrations of both acids, as does k_r for perchloric acid. In contrast, k_r decreases appreciably with increasing concentrations of nitric acid. Results for perchloric acid at nonconstant ionic strength are shown in Table 6, and we observe a modest increase in k_f and a pronounced decrease in k_r as the acid concentration increases.

Table 1. Influence of concentration of electrolytes NaX and BaX_2 on the observed reaction rate constant at $[H_3O^+] = 0.20$ mol dm^{-3}, 2% CH_3CN, 25°C.[a]

Acid	Salt	$[X^-]_T$/M	μ[b]	ΔA	k_{obs}/s^{-1}
$HClO_4$	$NaClO_4$	0.20	0.20	0.051 ± 0.002	93 ± 1
		0.40	0.40	0.071 ± 0.005	76.5 ± 0.5
		0.70	0.70	0.107 ± 0.003	60.35 ± 0.05
		1.00	1.00	0.160 ± 0.010	49.9 ± 0.3
$HClO_4$	$Ba(ClO_4)_2$	0.20	0.20	0.051 ± 0.002	93 ± 1
		0.40	0.50	0.069 ± 0.001	77.9 ± 0.9
		0.70	0.95	0.103 ± 0.005	64 ± 1
		1.00	1.40	0.148 ± 0.006	53.3 ± 0.4
HNO_3	$NaNO_3$	0.20	0.20	0.040 ± 0.001	107 ± 3
		0.40	0.40	0.0496 ± 0.0001	93 ± 1
		0.70	0.70	0.0674 ± 0.0003	81 ± 1
		1.00	1.00	0.087 ± 0.002	73.4 ± 0.4

[a] $[DMTOH]_0 = 3.3 \times 10^{-5}$ mol dm^{-3}.

[b] Ionic strength (mol dm^{-3}).

Table 2. Influence of acid concentration upon the observed reaction rate constant; ionic strength = 1.0 mol dm^{-3} ($NaClO_4$ or $NaNO_3$), 2% CH_3CN, 25°C.[a]

Acid	Salt	$[H_3O^+]$/M	ΔA	k_{obs}/s^{-1}
$HClO_4$	$NaClO_4$	0.20	0.160 ± 0.010	49.9 ± 0.3
		0.40	0.318 ± 0.001	51.4 ± 0.4
		0.70	0.487 ± 0.001	55.2 ± 0.3
		1.00	0.633 ± 0.009	60.3 ± 0.2
HNO_3	$NaNO_3$	0.20	0.087 ± 0.002	73.4 ± 0.4
		0.40	0.1815 ± 0.0005	73.1 ± 0.3
		0.70	0.313 ± 0.001	74.4 ± 0.6
		1.00	0.417 ± 0.001	76.2 ± 0.2

[a] $[DMTOH]_0 = 3.3 \times 10^{-5}$ mol dm^{-3}.

Table 3. Influence of acid concentration upon the observed reaction rate constant; ionic strength not constant, 2% CH_3CN, 25°C.[a]

$[HClO_4]$/mol dm^{-3}	ΔA	k_{obs}/s^{-1}
0.20	0.051 ± 0.002	93 ± 1
0.40	0.139 ± 0.001	74.8 ± 0.3
0.70	0.351 ± 0.001	62.8 ± 0.3
1.00	0.633 ± 0.009	60.3 ± 0.2

[a] $[DMTOH]_0 = 3.3 \times 10^{-5}$ mol dm^{-3}.

Table 4. Influence of concentration of electrolytes NaX and BaX_2 on forward and reverse rate constants, k_f and k_r; $[H_3O^+] = 0.20$ mol dm^{-3}, 2% CH_3CN, 25°C.[a]

Acid	Salt	$[X^-]_T$ /M	μ[b]	k_f /M^{-1}s^{-1}	k_r /s^{-1}
$HClO_4$	$NaClO_4$	0.20	0.20	10.2 ± 0.4	91 ± 1
		0.40	0.40	11.8 ± 0.8	74.1 ± 0.5
		0.70	0.70	14.0 ± 0.4	57.6 ± 0.1
		1.00	1.00	17 ± 1	46.4 ± 0.4
$HClO_4$	$Ba(ClO_4)_2$	0.20	0.20	10.2 ± 0.4	91 ± 1
		0.40	0.50	11.6 ± 0.2	75.6 ± 0.9
		0.70	0.95	14.3 ± 0.7	61 ± 1
		1.00	1.40	17.1 ± 0.7	49.8 ± 0.4
HNO_3	$NaNO_3$	0.20	0.20	9.3 ± 0.3	105 ± 3
		0.40	0.40	10.0 ± 0.1	91 ± 1
		0.70	0.70	11.8 ± 0.2	79 ± 1
		1.00	1.00	13.8 ± 0.3	70.6 ± 0.4

[a] $[DMTOH]_0 = 3.3 \times 10^{-5}$ mol dm^{-3}.

[b] Ionic strength (mol dm^{-3}).

Table 5. Influence of acid concentration upon forward and reverse rate constants, k_f and k_r; ionic strength = 1.0 mol dm^{-3} ($NaClO_4$ or $NaNO_3$), 2% CH_3CN, 25°C.[a]

Acid	Salt	$[H_3O^+]$/M	k_f /M^{-1}s^{-1}	k_r /s^{-1}
$HClO_4$	$NaClO_4$	0.20	17.5 ± 0.2	46.4 ± 0.4
		0.40	17.7 ± 0.1	44.3 ± 0.4
		0.70	16.6 ± 0.1	43.6 ± 0.3
		1.00	16.5 ± 0.2	43.8 ± 0.3
HNO_3	$NaNO_3$	0.20	13.8 ± 0.1	70.6 ± 0.4
		0.40	14.4 ± 0.1	67.4 ± 0.3
		0.70	14.4 ± 0.1	64.3 ± 0.6
		1.00	13.8 ± 0.1	62.4 ± 0.2

[a] $[DMTOH]_0 = 3.3 \times 10^{-5}$ mol dm^{-3}.

Discussion

By analogy with the mechanism proposed for the deamination of 4,4′-dimethoxytritylammonium ions (10, 11), we propose the mechanism shown in Scheme 1 for the reaction of DMT alcohol.

In this mechanism, step (*i*) is the reversible protonation of the alcohol. The protonated alcohol then undergoes heterolysis in step (*ii*) to yield an ion–molecule pair, i.e., a discrete intermediate comprising a carbenium ion which has a special relationship with a single water molecule. Since the single water molecule of this ion–molecule pair is identical with the water molecules of the solvent (except regarding its unique relationship with the carbenium ion), this intermediate is intrinsically different from that implicated in the corresponding deamination reaction (10). In the latter, the molecule of the ion–molecule pair (NH_3) is different from the solvent molecules. Thus, the ion–molecule pair in deamination can undergo a diffusional separation, which is followed

Table 6. Influence of perchloric acid concentration upon forward and reverse rate constants, k_f and k_r; 2% CH_3CN, 25°C (ionic strength not constant).[a]

$[HClO_4]$/mol dm^{-3}	k_f /$M^{-1}s^{-1}$	k_r /s^{-1}
0.20	10.2 ± 0.3	91 ± 1
0.40	11.3 ± 0.1	70.3 ± 0.3
0.70	13.6 ± 0.1	53.3 ± 0.3
1.00	16.5 ± 0.2	43.8 ± 0.3

[a] $[DMTOH]_0 = 3.3 \times 10^{-5}$ mol dm^{-3}.

by protonation of the ammonia under the acidic conditions, and full solvation of both cations by water molecules. In the corresponding reaction of the ion–molecule pair in Scheme 1, i.e., step (*iii*), the change is in the number of water molecules immediately around the carbenium ion and in the nature of the relationship of each of them with the carbenium ion. This step, therefore, rather than being a dissociation or diffusion apart, will involve the loosening of one water and the addition of further loosely held solvating water molecules around the cation. Two additional steps are included in Scheme 1 to accommodate the salt effects observed experimentally. Step (*iv*) is the formation of an ion pair from the protonated alcohol and the common anion of the acid and the salt present (we denote all types of ion pairs by $R^+\|X^-$), and step (*v*) is the equilibrium formation of ion pairs from dissociated anion and carbenium ion regardless of their provenance. In principle, an additional step to include collapse of the ion pair to form a covalent compound, R-X, could be added to Scheme 1 (7). However, trityl perchlorate is fully ionic in the crystal state and in solvents of low dielectric constant such as chloroform or dichloromethane (8), and we found no spectroscopic evidence (^{13}C and ^{35}Cl NMR, IR, and UV-vis) for the existence of covalent compounds DMT-X when X = $OClO_3$ or Cl (using hydrochloric acid). Consequently, we omit this extra step.

Several approximations are now required in order to relate the experimental rate constants k_f and k_r to the elementary rate constants of the mechanism in Scheme 1. First, we assume that 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}). Secondly, we assume that the steady-state approximation may be applied to the ion–molecule pair, $R^+\cdot OH_2$, in steps (*ii*) and (*iii*). Thirdly, we assume that the molar absorptivity of the ion R^+ is the same regardless of its solvolytic environment (13), i.e., ε_{495} for R^+ = ε_{495} for $R^+\|X^-$, which we denote simply by ε_{495}, and hence $A_{495} = ([R^+] + [R^+\|X^-])\varepsilon_{495}$. (Although in some cases there are appreciable changes in the spectra of carbocations on increasing the concentrations of added perchlorate (14), in our reactions the position of the main absorption maximum in spectra of solutions of the carbocation is essentially the same on changing the concentration of electrolyte from 0.5 to 3.5 mol dm^{-3}.) Finally, we assume that step (*v*) of Scheme 1 constitutes a postequilibrium with equilibrium constant K_5 (equal to k_5/k_{-5}), i.e., $[R^+\|X^-] = K_5[R^+][X^-]$ and that maintenance of this equilibrium does not affect the overall rate of equilibration (13). With no further assumptions, these approximations allow derivation of the following equation:

Scheme 1.

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

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

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

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

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

$$\frac{dA_{495}}{dt} = \frac{K_1(k_2k_3 + (k_{-2} + k_3)k_4[X^-])\varepsilon_{495}[ROH]_0[H_3O^+]}{(k_{-2} + k_3)(1 + K_1[H_3O^+])} - \left[\frac{K_1(k_2k_3 + (k_{-2} + k_3)k_4[X^-])[H_3O^+]}{(k_{-2} + k_3)(1 + K_1[H_3O^+])} + \frac{(k_{-2} + k_3)k_{-4}K_5[X^-] + k_{-2}k_{-3}}{(k_{-2} + k_3)(1 + K_5[X^-])}\right]A_{495}$$

Noting that $K_1/dm^3\ mol^{-1}$ will be less than 10^{-2} and possibly as low as 10^{-5} (15), $(1 + K_1[H_3O^+])$ will be approximately unity at the hydronium ion concentrations involved, so the above may be rewritten as eq. [10].

$$[10]\quad \frac{dA_{495}}{dt} = \frac{K_1(k_2k_3 + (k_{-2} + k_3)k_4[X^-])\varepsilon_{495}[ROH]_0[H_3O^+]}{(k_{-2} + k_3)} - \left[\frac{K_1(k_2k_3 + (k_{-2} + k_3)k_4[X^-])[H_3O^+]}{(k_{-2} + k_3)} + \frac{(k_{-2} + k_3)k_{-4}K_5[X^-] + k_{-2}k_{-3}}{(k_{-2} + k_3)(1 + K_5[X^-])}\right]A_{495}$$

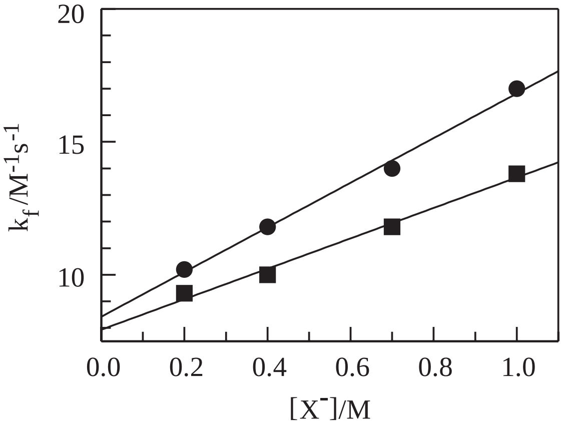
Comparison of eq. [10] with eq. [5] now leads to eqs. [11] and [12] as the relationships for k_f and k_r in terms of the elementary rate constants in the mechanism of Scheme 1.

$$[11]\quad k_f = \frac{K_1k_2k_{-3}}{(k_{-2} + k_3)} + K_1k_4[X^-]$$

$$[12]\quad k_r = \frac{k_{-2}k_{-3}}{(k_{-2} + k_3)(1 + K_5[X^-])} + \frac{k_{-4}K_5[X^-]}{(1 + K_5[X^-])}$$

The linearity and finite intercept in the plot of k_f against $[X^-]$ shown in Fig. 2, using data from Table 4, provide experimental support for the validity of the mechanism in Scheme 1 and the derivations based upon it. Assuming that the 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., $k_{-2} >> k_3$,

Fig. 2. Influence of anion concentration upon the forward reaction rate constant k_f at constant acid concentration (closed circles for perchlorate and closed squares for nitrate).



eq. [11] gives eq. [13] where $K_2 = k_2/k_{-2}$ and values for $K_1K_2k_3$ and K_1k_4 obtained by linear regression of k_f against

$$[13] \quad k_f = K_1K_2k_3 + K_1k_4[X^-]$$

$[X^-]$ using the data of Table 4 are summarized in the columns 2 and 3 of Table 7. From column 2, we see that the product $K_1K_2k_3$ is, within experimental error, independent of the nature of the electrolyte as required by the mechanism. Furthermore, since virtually identical correlations are obtained for sodium and barium perchlorate, we conclude that k_f in these solutions is principally dependent upon concentration of perchlorate and not the ionic strength.

The same approximation ($k_{-2} >> k_3$,) applied to eq. [12] for the reverse rate constant, k_r, yields eq. [14].

$$[14] \quad k_r = \frac{k_{-3} + k_{-4}K_5[X^-]}{(1 + K_5[X^-])}$$

Nonlinear regression analysis of k_r against $[X^-]$ using eq. [14] shows that $k_{-4}K_5$ is very much smaller than k_{-3}, so the second term of the numerator in eq. [14] may be neglected. By rearranging the simplified eq. [14], we obtain the linear relationship between $1/k_r$ and $[X^-]$ shown in eq. [15].

$$[15] \quad \frac{1}{k_r} = \frac{1}{k_{-3}} + \frac{K_5}{k_{-3}}[X^-]$$

By plotting values of $1/k_r$ against the total concentration of the anion using data from Table 4, we get straight lines shown in Fig. 3 with a common intercept (same value of k_{-3}) but different gradients (different K_5 values according to the nature of X^-). These plots validate the approximations introduced and allow determination of k_{-3} and K_5, which are included in columns 4 and 5 of Table 7. The average value of $k_{-3} = 118$ s^{-1} compares with earlier results for the *overall reverse* rate constant k_r of eq. [3], i.e., the *overall forward* rate constant of eq. [1] when electrolyte effects are absent of 95 s^{-1} for reaction in water at 25°C (16), and 86 s^{-1} for reaction in 2:1 aqueous acetonitrile at 20°C (17). The average result of $K_5 = 1.45$ dm^3 mol^{-1} for $X^- = ClO_4^-$ in aqueous solution compares very well with the value of 1.3 proposed by Wyatt (6) and the approximate result of 2.5 from our deamination studies (10). As expected, it is much smaller than the value of 795 dm^3 mol^{-1} reported for unsubstituted trityl perchlorate in the less polar 1,2-dichloroethane (8). The smaller value of $K_5 = 0.67$ dm^3 mol^{-1} for $X^- = NO_3^-$ in water has not previously been measured as far as we are aware.

As we now have values for k_{-3} and $K_1K_2k_3$ (see Table 7), and noting that, according to the proposed mechanism of Scheme 1, $K_{R^+} = k_{-3}/K_1K_2k_3$, we can obtain practical values for the equilibrium constant K_{R^+}, which are shown in the penultimate column of Table 7. The average value of $K_{R^+} = 14.4 \pm 0.4$ (p$K_{R^+} = -1.16$) is in good agreement with literature results (1), which adds further support for the mechanism of Scheme 1 and the derivations arising from it.

Step (*iv*) of Scheme 1 could be considered either in terms of a nucleophilic attack by perchlorate anion on the protonated alcohol, water being the nucleofuge, or as a stabilization by the anion of the positive charge of the incipient carbocation in the heterolytic transition state. Sodium perchlorate is an electrolyte that has been used in kinetics and electrochemistry to control ionic strength. The term "inert electrolyte" has been used in many cases for this and other compounds used to keep ionic strength constant. But despite its low reactivity in general, there are isolated examples in the literature where perchlorate reacts with electrophiles faster than nucleophiles such as chloride (7). In such cases, and in our proposed mechanism, perchlorate acts by stabilizing the developing positive charge of nascent large nonpolarizing cations, especially those in which the positive charge is highly delocalized. From the results in column 3 of Table 7, and taking K_1/dm^3 mol^{-1} = 2.5×10^{-3} (15), we calculate the values for k_4 shown in the final column of Table 7; perchlorate is more effective than nitrate. However, in spite of serious efforts, we found no spectroscopic evidence for the formation of fully covalent $DMTClO_4$ (see above).

Influence of hydronium ion concentration

As seen in Table 5, k_f is independent of the acid concentration as required by the mechanism in Scheme 1, which does not include a channel involving acid-catalyzed forward reaction of the ion–molecule pair. In this respect, therefore, the reaction of DMT alcohol is significantly different from the reaction of DMT amine (10); the latter includes a reaction channel involving acid-catalyzed separation of the cation–molecule pair. The average results obtained from Table 5 ($k_f = 17.1$ dm^3 mol^{-1} s^{-1} for perchloric acid and 14.1 for nitric) at total electrolyte concentrations of 1 mol dm^{-3} are in excellent agreement with the ones obtained from the study of the influence of electrolyte concentration for total electrolyte concentration equal to 1.0 mol dm^{-3} and constant hydronium ion concentration (17.1 and 13.8 dm^3 mol^{-1} s^{-1}, respectively) shown in Table 4.

The results of Table 5 also show that the concentration of perchloric acid has no effect upon k_r again as required by the mechanism. However, there is a noticeable decrease in k_r with increasing nitric acid concentration at constant total nitrate. We have no mechanistic explanation of this finding and assume, for the present, that under the particular experimental conditions of the reactions in nitric acid plus sodium nitrate, our total neglect of activity coefficient considerations is not justified.

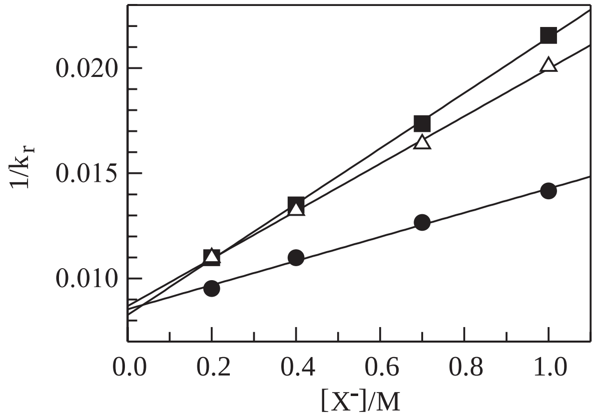
Table 7. Derived rate and equilibrium parameters using data from Table 4 for the mechanism proposed in Scheme 1; 25°C.

Electrolyte	$K_1K_2k_3$/M^{-1} s^{-1}	K_1k_4/M^{-2} s^{-1}	k_{-3}/s^{-1}	K_5/M^{-1}	K_{R^+}/M[a]	k_4/M^{-1} s^{-1}[b]
$NaClO_4$	8.4 ± 0.3	8.4 ± 0.4	121 ± 2	1.60 ± 0.04	14.4 ± 0.6	3.4×10^3
$Ba(ClO_4)_2$	8.3 ± 0.2	8.7 ± 0.3	115 ± 2	1.30 ± 0.04	13.9 ± 0.4	3.5×10^3
$NaNO_3$	7.9 ± 0.3	5.7 ± 0.4	117 ± 3	0.67 ± 0.04	14.8 ± 0.6	2.3×10^3

[a] From the mechanism, $K_{R^+} = k_{-3}/K_1K_2k_3$.

[b] From results in column 3 using $K_1 = 2.5 \times 10^{-3}$ dm^3 mol^{-1} (see text).

Fig. 3. Plot of the inverse of k_r against the total anion concentration (closed squares for sodium perchlorate, triangles for barium perchlorate, and closed circles for sodium nitrate).



From the results for the influence of perchloric acid on the reaction parameters at nonconstant ionic strength (Table 6), we obtain the following using eq. [13] (linear regression of k_f against $[ClO_4^-]$) and eq. [15] (linear regression of $1/k_r$ against $[ClO_4^-]$): $K_1K_2k_3 = 8.3 \pm 0.4$ dm^3 mol^{-1} s^{-1}, $K_1k_4 = 7.9 \pm 0.6$ dm^6 mol^{-2} s^{-1}, $k_{-3} = 122 \pm 3$ s^{-1}, $K_5 = 1.80 \pm 0.07$ dm^3 mol^{-1}, $K_{R^+} = 14.7 \pm 0.8$ mol dm^{-3}, and $k_4 = 3200$ dm^3 mol^{-1} s^{-1}. These results are in good agreement with the ones obtained under conditions of constant hydronium ion concentration and varying perchlorate shown in Table 7.

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