Kinetic and equilibrium studies of σ-adduct formation and nucleophilic substitution in the reactions of trinitro-activated benzenes with aliphatic amines in acetonitrile

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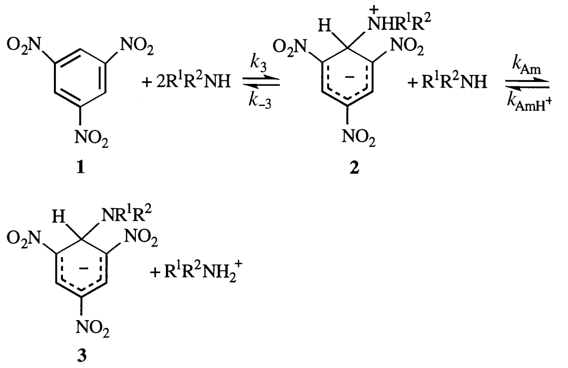
Rate and equilibrium constants are reported for reactions in acetonitrile of butylamine, pyrrolidine and piperidine with 1,3,5-trinitrobenzene, 1, and with ethyl 2,4,6-trinitrophenyl ether, 4a, and phenyl 2,4,6-trinitrophenyl ether, 4b. Rapid nucleophilic attack at unsubstituted ring-positions may yield anionic σ-adducts *via* zwitterionic intermediates, while slower attack at the 1-position of 4a and 4b may lead to substitution to give 2,4,6-trinitroaniline derivatives. Base catalysis in the substitution reaction reflects rate-limiting proton transfer which may be from the zwitterionic intermediates to amine in the case of 4b, or from a substituted ammonium ion to the ethoxy leaving group in the case of 4a.

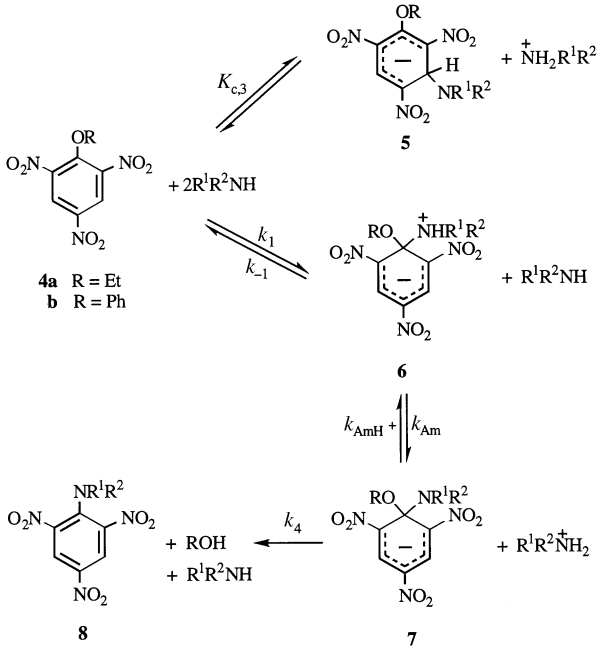
Comparisons with values in DMSO indicate that values of overall equilibrium constants for adduct formation are *ca.* 10^4 lower in acetonitrile, while rate constants for proton transfer are *ca.* 10^4 higher. These differences may reflect strong hydrogen-bonding between DMSO and $-NH^+$ protons in ammonium ions and in zwitterions. In acetonitrile homoconjugation of substituted ammonium ions with free amine is an important factor.

The reaction of 1,3,5-trinitrobenzene **1**, with aliphatic amines in dipolar aprotic solvents yields[1–3] anionic σ-adduct by the processes shown in Scheme 1. Kinetic studies of these reactions have shown that in dimethyl sulfoxide[4,5] (DMSO) and in mixed aqueous solvents[6] the proton transfer step may be rate-determining. In DMSO the value of k_{Am} is *ca.* 10^7 dm^3 mol^{-1} s^{-1} for reaction with butylamine, 10^6 for pyrrolidine and 10^5 for piperidine. These values are considerably lower than that expected for diffusion controlled reaction even though the proton transfers from the zwitterions, **2**, to amines are thermodynamically downhill. The greater acidity of compounds **2** than of the parent ammonium ions is due to the electron withdrawing effect of the trinitro-aromatic moiety.[7,8]



Scheme 1

The observation of general base catalysis in nucleophilic substitution reactions is also indicative of rate-determining proton transfer. Several detailed studies have been reported[2,3] in DMSO solvent and the overall mechanism is shown in Scheme 2. The base-catalysed pathway may, in an analogous fashion to that shown in Scheme 1, involve rate-limiting proton transfer from the zwitterionic intermediate, **6**, to base (the k_{Am} step), or it may involve general acid catalysis of leaving group departure (the k_4 step). The latter, the SB-GA mechanism has been shown to apply for substrates, such as alkyl ethers, carrying poor leaving groups.[9–12] However, there is now strong evidence that for substrates carrying good leaving groups, such as phenyl ethers and phenyl sulfides, base catalysis results from rate-limiting proton transfer from zwitterions to base.[13,14] Reaction at the 1-position leading to substitution may be preceded by rapid reversible reaction at the unsubstituted 3-position leading to adducts **5**.



Scheme 2

We report here kinetic and equilibrium results for reactions in acetonitrile corresponding to those shown in Scheme 1 with trinitrobenzene, and in Scheme 2 with ethyl, **4a**, and phenyl, **4b**, ethers. The amines used were butylamine, pyrrolidine and piperidine. Although acetonitrile has been widely used as a solvent for the examination of base catalysis in substitution reactions,[15–18] the substrates previously studied have been less activated than the trinitroaryl ethers, **4**, so that intermediates

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Table 1 Equilibrium data for formation of **3** from **1**[a] and pyrrolidine in acetonitrile at 25 °C

[Pyrrolidine]/ mol dm^{-3}	[Pyrrolidinium perchlorate]/mol dm^{-3}	A (445 nm)	$K_{c,3}$ [b]/dm^3 mol^{-1}	$K_{c,3}$ [c]
0.01	0.001	0.028	0.26	0.25
0.02	0.001	0.120	0.31	0.31
0.03	0.001	0.267	0.36	0.36
0.04	0.001	0.46	0.46	0.42
0.06	0.001	0.71	0.52	0.52
0.08	0.001	0.88	0.65	0.63
0.10	0.001	0.96	0.74	0.74
0.10	—	1.08	—	
0.20	—	1.09	—	
0.03	0.002	0.153	0.36	0.37
0.03	0.004	0.087	0.38	0.37

[a] Concentration is 4 × 10^{-5} mol dm^{-3}. [b] Calculated as $(A/1.09 - A)\,(R^1R^2NH_2^+)_{stoich}/(R^1R^2NH)^2$. [c] Calculated from eqn. (4) with $K^0_{c,3}$ 0.20 dm^3 mol^{-1} and K_h 27 dm^3 mol^{-1}.

were not observed. Our aims were: (i) to determine rate constants for proton transfer reactions in acetonitrile and compare these with corresponding values in DMSO, and (ii) to examine the detailed mechanism of base catalysis in acetonitrile and identify the nature of the rate determining step.

The relative permittivity of acetonitrile is comparable with that of DMSO; the values are 36 and 46.6, respectively. However acetonitrile is a much less basic solvent and pK_a values for aliphatic ammonium ions are *ca.* 8 units larger than in DMSO.[19,20] Nevertheless extensive studies of acid–base behaviour have been made in acetonitrile and the solvent is sufficiently basic to completely dissociate perchloric acid.[21] For this reason we have used perchlorate salt in our studies. It is also known[22] that association of aliphatic ammonium ions with the parent amines produces homoconjugates [eqn. (1)]; values of the equilibrium

$$R^1R^2\overset{+}{N}H_2 + R^1R^2NH \rightleftharpoons R^1R^2\overset{+}{N}H_2\cdots NHR^1R^2 \quad (1)$$

constant K_h are *ca.* 30 dm^3 mol^{-1}. A further important difference between the solvents is that DMSO is known to be a strong hydrogen-bond acceptor while acetonitrile shows weak hydrogen-bonding properties.[23] Acetonitrile has previously been used as a solvent for obtaining NMR spectra of σ-adducts.[24–27] However, the only previous quantitative measurement in this solvent was a determination of the equilibrium constant for adduct formation between **1** and piperidine.[28]

Experimental

1,3,5-Trinitrobenzene, ethyl 2,4,6-trinitrophenyl ether[11] and phenyl 2,4,6-trinitrophenyl ether[13] were available from previous work. Amines and acetonitrile were the purest available commercial specimens. Solutions of amine perchlorates were prepared by neutralisation of perchloric acid in acetonitrile with the appropriate amine. UV–VIS spectra and kinetic measurements were made with Perkin-Elmer Lambda 2, or Hi-Tech SF 3L or Applied Photophysics SX-17 MV stopped flow spectrophotometers at 25 °C. Reported rate coefficients are the means of several determinations and are precise to ±5%. Rate constants were measured under first-order conditions; hence for reactions in buffers (amine plus amine perchlorate) the buffer components were in large excess of the substrate concentration (1–5 × 10^{-5} mol dm^{-3}).

Results and discussion

Reaction with 1,3,5-trinitrobenzene, 1

Reaction of **1** with aliphatic amines in acetonitrile resulted in the rapid formation of a species having absorption maxima at *ca.* 450 and 530 nm, characteristic of the σ-adducts **3**. In the absence of added salt virtually complete conversion to **3** could be obtained at high amine concentrations, allowing the determination of the values of the extinction coefficients (see Table 3).

Measurement of absorbance values in solutions containing 0.001 mol dm^{-3} amine perchlorate and varying concentrations of amine allowed the calculation of values of $K_{c,3}$ defined in eqn. (2). Data are given in Table 1 for reaction with pyrrolidine

$$K_{c,3} = \frac{[\mathbf{3}]}{[\mathbf{1}]}\,\frac{[R^1R^2NH_2^+]_{Stoich}}{[R^1R^2NH]^2} \quad (2)$$

and show that values of $K_{c,3}$ increase with increasing amine concentration. This is attributed to stabilisation, eqn. (1), of the pyrrolidinium cations by association with pyrrolidine, which is in large excess. We define $K^0_{c,3}$ in terms of the free, unassociated cations, eqn. (3), and note that $K_{c,3}$ will approach the value of

$$K^0_{c,3} = \frac{k_3}{k_{-3}}\,\frac{k_{Am}}{k_{AmH^+}} = \frac{[\mathbf{3}]}{[\mathbf{1}]}\,\frac{[R^1R^2NH_2^+]_{Free}}{[R^1R^2NH]^2} \quad (3)$$

$K^0_{c,3}$ as the amine concentration tends to zero. $K_{c,3}$ and $K^0_{c,3}$ are related to the equilibrium constant, K_h, for homoconjugation by eqn. (4). A plot, not shown, of $K_{c,3}$ *vs.* pyrrolidine concentration gave values for $K^0_{c,3}$ 0.20 dm^3 mol^{-1} and K_h 27 dm^3 mol^{-1}.

$$K_{c,3} = K^0_{c,3}(1 + K_h[R^1R^2NH]) \quad (4)$$

The data in Table 1 show that, as expected, values of $K_{c,3}$ are virtually independent of the cation concentration in the presence of a large excess of amine. Data equivalent to that in Table 1 for reactions with butylamine and with piperidine are reported as supplementary information in Tables 11 and 12.†

Kinetic measurements were made by stopped-flow spectrophotometry with amine in large excess of parent, **1**. The equilibration of **1** and **3** will, in the absence of added ammonium salt, give rise to complex kinetics[4] since it represents mixed first-order (forward) and second-order (reverse) reactions. If sufficient amine is used to ensure virtually complete conversion to product then the forward rate term dominates and first-order kinetics are predicted. However, with this condition rate constants were too rapid for measurement. We overcame this problem for the pyrrolidine and piperidine reactions by measuring the reverse reaction. Thus, pre-formed solutions of the adduct were reacted with the appropriate ammonium salt and the rate constants of the fading reactions were measured. Assuming that the zwitterions **2** may be treated as steady-state intermediates[4] the general rate expression for the equilibration process is eqn. (5). If conditions are chosen so that >90% reversion of adduct to parent is achieved, then the reverse reaction domin-

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† Tables 11–13 have been deposited as supplementary data at the British Library; Suppl. No. 57173 (4 pp). For details of the British Library Supplementary Publications scheme, see 'Instructions for Authors (1997)', *J. Chem. Soc., Perkin Trans. 2*, 1997, issue 1.

$$k_{\mathrm{obs}} = \frac{k_3 k_{\mathrm{Am}}[\mathrm{Am}]^2}{k_{-3} + k_{\mathrm{Am}}[\mathrm{Am}]} + \frac{k_{-3} k_{\mathrm{AmH^+}}[\mathrm{AmH^+}]_{\mathrm{stoich}}}{(k_{-3} + k_{\mathrm{Am}}[\mathrm{Am}])(1 + K_{\mathrm{h}}[\mathrm{Am}])} \quad (5)$$

ates [this is represented by the final term in eqn. (5)]. The results in Table 2 relate to low amine concentrations where the condition $1 \gg K_{\mathrm{h}}[\mathrm{Am}]$ applies. They show that rate constants for the fading reactions depend directly on the concentration of the ammonium salt but are independent of the amine concentration. This indicates that $k_{-3} \gg k_{\mathrm{Am}}[\mathrm{Am}]$ so that eqn. (6) applies.

$$k_{\mathrm{obs}} = k_{\mathrm{AmH^+}}[\mathrm{AmH^+}] \quad (6)$$

Hence, at the low amine concentrations used, the proton transfer step is rate determining in the equilibration of **1** and **3**. We obtain values for $k_{\mathrm{AmH^+}}$ of 9×10^6 dm^3 mol^{-1} s^{-1} for the pyrrolidine reaction and 2.5×10^6 dm^3 mol^{-1} s^{-1} for the piperidine reaction. We note that these values are *ca.* 10^4 times larger than the corresponding values for reaction in DMSO.[4,5] Since values of $K^0_{\mathrm{c,3}}$ are known from the equilibrium measurements, values of $k_3 k_{\mathrm{Am}}/k_{-3}$ ($\equiv k_{\mathrm{AmH^+}} K^0_{\mathrm{c,3}}$) were calculated and are given in Table 3.

In the case of the adduct formed with butylamine, rate constants for both forming and fading reactions were too fast for measurement.

Reaction with ethyl 2,4,6-trinitrophenyl ether, 4a

The reactions with pyrrolidine, piperidine and butylamine in acetonitrile were qualitatively similar to the corresponding reactions in DMSO reported previously,[11,29] and shown in Scheme 2. With each amine a very rapid reaction with low amplitude was observed, attributed to equilibration of the parent with **5**, the adduct at the 3-position. In acetonitrile the rate of this process was too rapid for measurement by the stopped-flow method. With each amine this was followed by a fast but measurable reaction giving rise to species with λ_{max} 430, 500 nm; this is attributed to equilibration with the adducts, **7**, on the substitution pathways. The general rate expression[11] for this process is eqn. (7), where $K_1 \equiv k_1/k_{-1}$ and where $K_{\mathrm{c,3}}$ is the equilibrium

$$k_{\mathrm{fast}} = \frac{K_1 k_{\mathrm{Am}}[\mathrm{Am}]^2}{\left(1 + \dfrac{k_{\mathrm{Am}}[\mathrm{Am}]}{k_{-1}}\right)\left(1 + \dfrac{K_{\mathrm{c,3}}[\mathrm{Am}]^2}{[\mathrm{AmH^+}]_{\mathrm{stoich}}}\right)} + \frac{k_{\mathrm{AmH^+}}[\mathrm{AmH^+}]_{\mathrm{stoich}}}{\left(1 + \dfrac{k_{\mathrm{Am}}[\mathrm{Am}]}{k_{-1}}\right)(1 + K_{\mathrm{h}}[\mathrm{Am}])} \quad (7)$$

constant for formation of **5** from **4**. The value of $K_{\mathrm{c,3}}$ is expected to show a dependence on amine concentration as indicated in eqn. (4). Our results are only compatible with the assumption that only free ammonium ions are active in reprotonating the anions **7**; the relation between concentrations of free and total ammonium ions is eqn. (8). If the condition $k_{\mathrm{Am}}[\mathrm{Am}] \gg k_{-1}$

$$[\mathrm{AmH^+}]_{\mathrm{Free}} = [\mathrm{AmH^+}]_{\mathrm{stoich}}/(1 + K_{\mathrm{h}}[\mathrm{Am}]) \quad (8)$$

applies, so that the proton transfer equilibrium between **6** and **7** is rapid, then eqn. (7) reduces to eqn. (9).

$$k_{\mathrm{fast}} = \frac{k_1[\mathrm{Am}]}{1 + \dfrac{K_{\mathrm{c,3}}[\mathrm{Am}]^2}{[\mathrm{AmH^+}]_{\mathrm{stoich}}}} + \frac{k_{-1} k_{\mathrm{AmH^+}}[\mathrm{AmH^+}]_{\mathrm{stoich}}}{k_{\mathrm{Am}}[\mathrm{Am}](1 + K_{\mathrm{h}}[\mathrm{Am}])} \quad (9)$$

In the reactions with pyrrolidine and butylamine a third reaction, k_{slow}, was observed leading to the substitution product **8**. The spectral maxima were at 362 nm in the pyrrolidine reaction

Table 2 Rate data for the fading reactions[a] of adducts **3**, from pyrrolidine or piperidine, with appropriate ammonium salt at 25 °C

[Pyrrolidine]/mol dm^{-3}	[Pyrrolidinium perchlorate]/10^{-5} mol dm^{-3}	k_{obs}/s^{-1}	$k_{\mathrm{AmH^+}}$/10^6 dm^3 mol^{-1} s^{-1}
0.001	2	160 ± 20	8
0.001	3	260 ± 20	9
0.001	4	330 ± 40	8
0.002	2	175 ± 15	9
0.002	3	255 ± 20	9

[Piperidine]/mol dm^{-3}	[Piperidinium perchlorate]/10^{-5} mol dm^{-3}	k_{obs}/s^{-1}	$k_{\mathrm{AmH^+}}$/10^6 dm^3 mol^{-1} s^{-1}
0.001	2	52 ± 2	2.6
0.001	3	75	2.5
0.001	4	110	2.7
0.001	5	130	2.6
0.001	8	200 ± 10	2.5
0.002	2	55 ± 2	2.7
0.002	3	73	2.4
0.002	4	105	2.6
0.002	5	125	2.5
0.002	8	200 ± 10	2.5

[a] The concentration of **1** is 1×10^{-4} mol dm^{-3}. The estimated concentration of adduct, **3**, before reaction with salt is $\leqslant 5 \times 10^{-6}$ mol dm^{-3}.

Table 3 Summary of data for reaction of **1** with amines in acetonitrile at 25 °C

Amine	**3**, λ_{max}[a]/nm	$K^0_{\mathrm{c,3}}$/dm^3 mol^{-1}	K_{h}/dm^3 mol^{-1}	$k_{\mathrm{AmH^+}}$/dm^3 mol^{-1} s^{-1}	$K_3 k_{\mathrm{Am}}$/dm^6 mol^{-2} s^{-1}
Butylamine	450 (2.8×10^4) 534 (1.6×10^4)	0.0025	20	—	—
Pyrrolidine	445 (2.7×10^4) 524 (1.6×10^4)	0.20	27	9×10^6	2×10^6
Piperidine[b]	446 (2.8×10^4) 524 (1.6×10^4)	0.055	25	2.5×10^6	1.4×10^5

[a] ε/dm^3 mol^{-1} cm^{-1} in parentheses. [b] Previous values[28] were $K^0_{\mathrm{c,3}}$ 0.058, K_{h} 24 at 20 °C.

and 340 nm in the butylamine reaction. At high amine concentrations the product spectra were shifted to longer wavelengths consistent with the known formation,[30] in rapid equilibria, of anions by adduct formation at the 3-position and/or by loss of a side-chain proton. At all concentrations the final spectra were identical to those of authentic samples of product in the same reaction medium. The rate expression for product formation is eqn. (10), where $K^{0}_{c,1}$ is defined in eqn. (11). Our results are

$$k_{\mathrm{slow}} = \frac{k_4 K^{0}_{c,1}[\mathrm{Am}]^2[\mathrm{AmH}^+]_{\mathrm{stoich}}}{K^{0}_{c,1}[\mathrm{Am}]^2(1 + K_{\mathrm{h}}[\mathrm{Am}]) + [\mathrm{AmH}^+]_{\mathrm{stoich}}} \qquad (10)$$

$$K^{0}_{c,1} = \frac{[\mathbf{7}]}{[\mathbf{6}]}\,\frac{[\mathrm{AmH}^+]_{\mathrm{Free}}}{[\mathrm{Am}]^2} = \frac{k_1 k_{\mathrm{Am}}}{k_{-1} k_{\mathrm{AmH}^+}} \qquad (11)$$

compatible only with the assumption, used in the derivation of eqn. (10), that only free (non-homoconjugated) ammonium ions are effective in the acid catalysed expulsion of the ethoxy leaving group from **7**.

Although reaction of **4a** with piperidine leads to the formation of the adduct **7**, the subsequent reaction was very slow and did not lead to the expected substitution product **8**. This slow reaction was not investigated further.

Results for reaction with pyrrolidine are in Table 4. The absorbance values at completion of the reaction forming adduct **7** allow the calculation of values of $K_{c,1}$ and lead to a value for $K^{0}_{c,1}$ of 0.3 dm^3 mol^{-1}. Values of k_{fast} decrease with increasing amine concentration before rising to a maximum and then falling. This behaviour is predicted by eqn. (7) and the results are accommodated with values of $K_1 k_{\mathrm{Am}}$ (1 ± 0.2) × 10^5 dm^6 mol^{-2} s^{-1}, k_{Am}/k_{-1} 80 ± 20 dm^3 mol^{-1}, k_{AmH^+} (4 ± 1) × 10^5 dm^3 mol^{-1} s^{-1}, K_{h} 23 dm^3 mol^{-1} and with $K^{0}_{c,3}$ 0.01 ± 0.002 dm^3 mol^{-1}. The data allow the calculation of a value for k_1 ($\equiv K_1 k_{\mathrm{Am}} k_{-1}/k_{\mathrm{Am}}$) of 1250 dm^3 mol^{-1} s^{-1}. Values of k_{slow}, the product forming reaction, go through a maximum with increasing amine concentration. Use of eqn. (10) using the known values of $K^{0}_{c,1}$ 0.3 dm^3 mol^{-1}, and K_{h} 23 dm^3 mol^{-1} yields a value for k_4 of 190 ± 20 dm^3 mol^{-1} s^{-1}.

The data for reaction with piperidine in Table 5 give a nice fit with eqn. (7) with the values given in the footnotes. They yield a value for k_1 of 780 dm^3 mol^{-1} s^{-1}. The value of 0.025 dm^3 mol^{-1} obtained for $K^{0}_{c,1}$ from absorbance data is in good accord with that obtained, eqn. (11), by combination of values for $K_1 k_{\mathrm{Am}}$ and k_{AmH^+}.

The data in Table 6 for reaction with butylamine indicate that, at the amine concentrations used, the condition $k_{\mathrm{Am}}[\mathrm{Am}] \gg k_{-1}$ applies. Hence eqn. (9) is applicable and a good fit is achieved with values of k_1 130 dm^3 mol^{-1} s^{-1} and $k_{-1}k_{\mathrm{AmH}^+}/k_{\mathrm{Am}}$ 360 s^{-1}. Combination of these values yields [eqn. (11)] a value for $K^{0}_{c,1}$ of 0.36 dm^3 mol^{-1}. Using this value and the known value for K_{h} we obtain using eqn. (10) a value of (8.5 ± 1) × 10^3 dm^3 mol^{-1} s^{-1} for k_4. We estimate that $k_{\mathrm{Am}}/k_{-1} > 500$ dm^3 mol^{-1}, so that $k_{\mathrm{AmH}^+} > 1.8 \times 10^5$ dm^3 mol^{-1} s^{-1}.

Reaction with phenyl 2,4,6-trinitrophenyl ether, 4b

In the reactions with amines of the phenyl ether only two time dependent processes were observed. These were an initial rapid colour forming reaction attributed to equilibration with the 3-adducts **5b** and a slower reaction yielding the substitution product **8**. The UV–VIS spectra at completion of these reactions were identical to those of authentic samples of the corresponding *N*-substituted 2,4,6-trinitroanilines in the same reaction medium. ^{1}H NMR spectroscopy was also used to confirm the identities of the reaction products. Data are given as

Table 4 Kinetic and equilibrium results[a] for reaction of **4a** with pyrrolidine in acetonitrile containing 0.001 mol dm^{-3} pyrrolidinium perchlorate at 25 °C

[Pyrrolidine]/ mol dm^{-3}	$k_{\mathrm{fast}}{}^{b}$/s^{-1}	$k_{\mathrm{calc}}{}^{c}$/s^{-1}	A^{d} (430)	$K_{c,1}{}^{e}$/dm^3 mol^{-1}	$k_{\mathrm{slow}}{}^{f}$/10^{-2} s^{-1}	$k_4{}^{g}$/dm^3 mol^{-1} s^{-1}
0.004	—	—	—	—	0.082	180
0.005	—	—	—	—	0.13	190
0.006	—	—	—	—	0.20	200
0.008	—	—	—	—	0.35	200
0.010	—	—	—	—	0.55	200
0.020	120	110	0.027	0.39	2.0	210
0.030	90	87	0.054	0.41	3.9	220
0.050	78	81	0.125	0.67	6.0	230
0.070	85	87	0.162	0.87	6.2	200
0.10	95	97	0.183	1.08	5.2	210
0.15	95	94	0.195	—	3.9	200
0.20	80	77	0.198	—	2.9	190

[a] Concentration of **4a** is 4 × 10^{-5} mol dm^{-3}. [b] Measured as a colour forming reaction; identical values were obtained at 430 and at 500 nm. [c] Calculated from eqn. (7) with $K_1 k_{\mathrm{Am}}$ 1.1 × 10^5 dm^6 mol^{-2} s^{-1}, k_{Am}/k_{-1} 86 dm^3 mol^{-1}, k_{AmH^+} 3.9 × 10^5 dm^3 mol^{-1} s^{-1}, K_{h} 27 dm^3 mol^{-1} and with $K_{c,3} = 0.009\,(1 + 27\,[\mathrm{Am}])$. [d] At completion of reaction forming the adduct **7**. [e] Calculated as $A/(0.20 - A)\,[\mathrm{AmH}^+]/[\mathrm{Am}]^2$. The data fit the expression $K_{c,1} = 0.28\,(1 + 27[\mathrm{Am}])$. [f] Identical results were obtained from measurements of colour forming reaction at 430 nm or fading reaction at 500 nm. [g] Calculated from eqn. (10) with $K^{0}_{c,1}$ 0.3 dm^3 mol^{-1}, and K_{h} 23 dm^3 mol^{-1}.

Table 5 Kinetic and equilibrium results[a] for reaction of **4a** with piperidine in acetonitrile containing 0.001 mol dm^{-3} piperidinium perchlorate at 25 °C

[Piperidine]/mol dm^{-3}	$k_{\mathrm{fast}}{}^{b}$/s^{-1}	$k_{\mathrm{calc}}{}^{c}$/s^{-1}	A^{d} (430 nm)	$K_{c,1}{}^{e}$/dm^3 mol^{-1}
0.030	106	114	—	—
0.050	90	89	0.0239	0.056
0.070	77	75	0.0478	0.067
0.10	70	70	0.0902	0.087
0.15	75	77	0.141	0.12
0.20	84	85	0.169	0.17
0.25	87	88	0.183	—
0.30	85	85	0.189	—
0.40	69	69	0.194	—

[a] Concentration of **4a** is 4 × 10^{-5} mol dm^{-3}. [b] Fast reaction forming **7** measured at 430 nm. [c] Calculated from eqn. (7) with $K_1 k_{\mathrm{Am}}$ 6200 dm^6 mol^{-2} s^{-1}, k_{Am}/k_{-1} 8 dm^3 mol^{-1}, k_{AmH^+} 2.4 × 10^5 dm^3 mol^{-1} s^{-1}, K_{h} 25 dm^3 mol^{-1} and with $K_{c,3}$ 0.0015 (1 + 25[Am]). [d] At completion of reaction forming adduct **7**. [e] Calculated as $A/(0.194 - A)/[\mathrm{AmH}^+]/[\mathrm{Am}]^2$. The data fit the expression $K_{c,1} = 0.025\,(1 + 25[\mathrm{Am}])$.

Table 6 Rate data for reaction of **4a** with butylamine in acetonitrile containing 0.001 mol dm^{-3} butylammonium perchlorate at 25 °C

[Butylamine]/mol dm^{-3}	$k_{fast}{}^{a}$/s^{-1}	$k_{calc}{}^{b}$/s^{-1}	$k_{slow}{}^{c}$/s^{-1}	$k_4{}^{d}$/10^3 dm^3 mol^{-1} s^{-1}
0.02	14	15	1.1	9.2
0.03	12	11	1.8	8.7
0.05	11	10	2.8	8.7
0.07	11	11	3.1	9.3
0.10	14	14	2.8	9.3
0.15	18	18	2.1	8.8
0.20	23	24	1.7	8.3
0.25	28	28	1.4	8.1
0.30	32	31	1.1	8.0

[a] Colour forming reaction at 430 nm. [b] Calculated from eqn. (9) with k_1 130 dm^3 mol^{-1} s^{-1}, $k_{-1}k_{AmH^+}/k_{Am}$ 360 s^{-1}, $K_{c,3} = 0.0004\,(1 + 20[\mathrm{Am}])$ and K_h 20 dm^3 mol^{-1}. [c] Identical values were obtained at 340 and at 430 nm. [d] Calculated from eqn. (10) with $K^0_{c,1}$ 0.36 dm^3 mol^{-1} and K_h 20 dm^3 mol^{-1}.

Table 7 Kinetic and equilibrium results[a] for reaction of **4b** with pyrrolidine in acetonitrile containing 0.001 mol dm^{-3} pyrrolidinium perchlorate at 25 °C

[Pyrrolidine]/mol dm^{-3}	A^{b} (415 nm)	$K_{c,3}{}^{c}$/dm^3 mol^{-1}	$k_{sub}{}^{d}$/s^{-1}	$k_{calc}{}^{e}$/s^{-1}
0.004	—	—	1.72	1.70
0.005	—	—	2.56	2.54
0.006	—	—	3.52	3.50
0.008	—	—	5.89	5.72
0.010	—	—	8.29	8.23
0.020	—	—	22.5	22.6
0.030	—	—	35.6	35.3
0.050	0.064	0.36	46.4	45.5
0.070	0.090	0.41	42.0	41.1
0.100	0.115	0.58	28.7	29.6

[a] Concentration of **4b** is 4 × 10^{-5} mol dm^{-3}. [b] At completion of reaction forming **5b**. Measurements in the absence of added pyrrolidinium perchlorate give a value of 0.135 for complete conversion. Final values at completion of the substitution reaction are 0.056. [c] Calculate $A/(0.135 - A)$-$[\mathrm{AmH^+}]/[\mathrm{Am}]^2$. [d] Measured at 415 nm. Colour forming reaction when [pyrrolidine] ≤ 0.030 mol dm^{-3}, fading when [pyrrolidine] > 0.030 mol dm^{-3}. [e] Calculated from eqn. (12) with K_1k_{Am} 1.3 × 10^5 dm^6 mol^{-2} s^{-1}, k_{Am}/k_{-1} 55 dm^3 mol^{-1} and $K_{c,3}$ 0.155 (1 + 27[Am]) dm^3 mol^{-1}.

supplementary information in Table 13.† Failure to observe the intermediates, **7b**, on the reaction pathway is attributed to their rapid cleavage by loss of phenoxide. It is known that phenoxide ions are considerably better leaving groups than alkoxide ions,[31] explaining the contrast in behaviour with the ethyl ether **4a**. A similar difference has been observed in DMSO as solvent.[13] Hence in the substitution pathway, shown in Scheme 2, formation of the adducts **7b** becomes rate determining with $k_4 \gg k_{AmH^+}$. The rate expression for substitution is eqn. (12).

$$k_{sub} = \frac{K_1k_{Am}[\mathrm{Am}]^2}{\left(1 + \dfrac{k_{Am}[\mathrm{Am}]}{k_{-1}}\right)\left(1 + \dfrac{K_{c,3}[\mathrm{Am}]^2}{[\mathrm{AmH^+}]_{stoich}}\right)} \tag{12}$$

$$k_{sub} = \frac{k_1[\mathrm{Am}]}{\left(1 + \dfrac{K_{c,3}[\mathrm{Am}]^2}{[\mathrm{AmH^+}]_{stoich}}\right)} \tag{13}$$

Our results indicate that for reactions with pyrrolidine and piperidine proton transfer is partially rate limiting in the formation of **7b**, and hence in the substitution pathway. However with butylamine nucleophilic attack is the slow step $k_{Am}[\mathrm{Am}] \gg k_{-1}$, so that eqn. (12) reduces to eqn. (13).

Data for reaction with pyrrolidine in the presence of pyrrolidinium perchlorate are in Table 7. At the highest amine concentrations used there was appreciable initial conversion to the 3-adduct, **5b**, allowing calculation of values of $K_{c,3}$. Rate constants for the substitution reaction give an excellent fit with eqn. (12) with K_1k_{Am} 1.3 × 10^5 dm^6 mol^{-2} s^{-1} and k_{Am}/k_{-1} 55 dm^3 mol^{-1}. Combination of these values yields k_1 2400 dm^3 mol^{-1} s^{-1}.

The results for reaction with piperidine are in Table 8. The presence of piperidinium perchlorate largely inhibited the formation of the 3-adduct, **5b**. Absorbance measurements in the absence of added salt allowed the estimation of values of $K_{c,3}$ although these are subject to error since the solutions are not buffered. Fitting of the rate constants for the substitution reaction with eqn. (12) yielded values of K_1k_{Am} 5200 dm^6 mol^{-2} s^{-1}, k_{Am}/k_{-1} 8 dm^3 mol^{-1}, and hence k_1 650 dm^3 mol^{-1} s^{-1}.

Data in Table 9 for reaction with butylamine in the absence of added salt yielded values of $K_{c,3}$. Rate constants for the substitution reaction give a good fit with eqn. (13) with k_1 183 dm^3 mol^{-1} s^{-1}.

Comparison of rate and equilibrium data

The results are summarised in Table 10 where they are compared with corresponding values in DMSO.

Comparison of substrates

With each amine the most rapid reaction observed in acetonitrile is attack at an unsubstituted ring position to give the corresponding 3-adduct. Values of $K^0_{c,3}$ decrease with substrate in the order **1** > **4b** > **4a**. There is evidence that the presence of a bulky 1-substituent forces the nitro-groups at the 2- and 6-positions from the ring-plane,[2,32] thus reducing their electron withdrawing capacity, and hence decreasing the value of the equilibrium constant. This is counterbalanced to some extent by the favourable electronic effects of the phenoxy and ethoxy substituents for which the σ_{meta} values are 0.25 and 0.10, respectively.[33] Important factors influencing the values of k_1 for *ipso*-attack are expected[34,35] to be the electronegativity of the 1-substituent and also its steric bulk which will affect the *F* strain associated with approach of the amine. Comparisons of **4a** and **4b** give ratios close to unity; 0.6 for pyrrolidine, 0.7 for butylamine and 1.2 for piperidine. Hence these factors are evenly balanced.

Comparison of amines

The pK_a values in acetonitrile[20,22] are butylamine 18.26, piperidine 18.92 and pyrrolidine 19.58. There is little steric hindrance to attack at the 3-position and values of $K^0_{c,3}$ reflect the basicities of the amines; values are between four and ten times larger for

Table 8 Kinetic and equilibrium data for reaction of **4b** with piperidine in acetonitrile at 25 °C

[Piperidine]/ mol dm^{-3}	[Piperidinium perchlorate]/mol dm^{-3}	A[a] (430 nm)	$K_{c,3}$[b]/dm^3 mol^{-1}	k_{sub}[c]/s^{-1}	k_{calc}[d]/s^{-1}
0.020	—	0.069	0.024	—	—
0.030	—	0.096	0.027	—	—
0.050	—	0.132	0.032	—	—
0.070	—	0.152	0.038	—	—
0.10	—	0.17	—	—	—
0.01	0.001	—	—	0.47	0.48
0.0125	0.001	—	—	0.73	0.74
0.015	0.001	—	—	1.03	1.04
0.0175	0.001	—	—	1.40	1.39
0.020	0.001	—	—	1.78	1.77
0.030	0.001	—	—	3.81	3.69
0.050	0.001	—	—	9.20	8.60
0.07	0.001	—	—	14.4	13.8
0.10	0.001	—	—	19.0	19.5

[a] At completion of reaction forming **5b**. [b] Calculated as $A/(0.18 - A)[\mathrm{AmH}^+]/[\mathrm{Am}]^2$, where $[\mathrm{AmH}^+] = [\mathbf{5b}]$. [c] Colour forming reaction at 353 nm. [d] Calculated from eqn. (12) with K_1k_{Am} 5200 dm^6 mol^{-2} s^{-1}, k_{Am}/k_{-1} 8 dm^3 mol^{-1} and $K_{c,3}$ 0.016 (1 + 25 [Am]) dm^3 mol^{-1}.

Table 9 Kinetic and equilibrium results[a] for reaction of **4b** with butylamine in acetonitrile at 25 °C

[Butylamine]/ mol dm^{-3}	[Butylammonium perchlorate]/mol dm^{-3}	A[b] (430 nm)	$K_{c,3}$[c]/10^{-3} dm^3 mol^{-1}	k_{sub}[d]/s^{-1}	k_{calc}[e]/s^{-1}
0.02	—	0.019	1.2	—	—
0.04	—	0.044	2.0	—	—
0.07	—	0.109	2.8	—	—
0.50	—	0.181	—	—	—
0.01	0.001	—	—	1.81	1.83
0.02	0.001	—	—	3.65	3.66
0.05	0.001	—	—	9.20	9.10
0.07	0.001	—	—	12.7	12.6
0.10	0.001	—	—	17.5	17.6

[a] Concentration of **4b** is 4×10^{-5} mol dm^{-3}. [b] At completion of reaction forming **5b**. [c] Calculated as $A/(0.18 - A)[\mathrm{AmH}^+]/[\mathrm{Am}]^2$, where $[\mathrm{AmH}^+] = [\mathbf{5b}]$. [d] Colour forming reaction at 418 nm. [e] Calculated from eqn. (13) with k_1 183 dm^3 mol^{-1} s^{-1} and $K_{c,3}$ 9.4×10^{-4} (1 + 20[Am]) dm^3 mol^{-1}.

reaction with pyrrolidine than with piperidine, and between four and twenty times larger for reaction with piperidine than with butylamines. Values of k_1 also reflect the basicities of the amines. However amine basicity is not the major factor in determining values of $K^0_{c,1}$ which decrease in the order butylamine > pyrrolidine > piperidine. This order is likely to reflect the increasing steric congestion in the 1-adducts, **7a**, which contain two bulky groups at the 1-position. It is however noteworthy that for each amine values of $K^0_{c,1}$ are larger than values of $K^0_{c,3}$; the ratios are 900 for butylamine, 31 for pyrrolidine and 17 for piperidine. The thermodynamic preference for the 1-adducts can be attributed to the polar effect of the alkoxy group and to the relief of strain present in the parent when the alkoxy group is twisted from the ring-plane. The kinetic preference for attack at the 3-position and thermodynamic preference for the 1-adducts may be described as K3T1 in Buncel's nomenclature.[36]

Mechanism of substitution

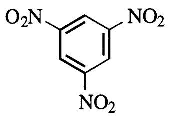
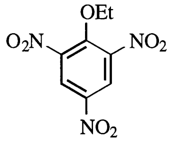
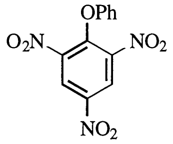
In the reactions of the ethyl ether, **4a**, the intermediates, **7a**, on the substitution pathway are spectroscopically observable. Reprotonation of the intermediates is more rapid than leaving group departure, $k_{\mathrm{AmH}^+} > k_4$, so that general acid catalysed loss of the ethoxy group becomes rate determining. The substitution conforms to the SB-GA mechanism.[2,9] The results in Table 10 show that k_4(butylamine) > (pyrrolidine) reflecting the greater acidity of the butylammonium ion. Steric factors are also likely to be important so that the approach of the butylammonium ion to **7a** is less hindered than approach of the pyrrolidinium ion. In fact the k_4 step involving the piperidinium ion is so slow that alternative reaction pathways dominate.

By contrast in reactions of the phenyl ether, **4b**, there was no evidence for the accumulation of intermediates, **7b**, on the substitution pathway. The situation is qualitatively similar to that observed[13] in DMSO. The phenoxide ion is a much better leaving group than ethoxide[31] so that $k_4 > k_{\mathrm{AmH}^+}$ and formation of the intermediates **7b** becomes rate determining in the substitution process. The reaction with butylamine is first order in amine indicating that nucleophilic attack is rate limiting, $k_{Am}[\mathrm{Am}] \gg k_{-1}$. However the reactions with pyrrolidine and piperidine show base catalysis, so that proton transfer (from zwitterions **6b** to amine) is rate-limiting or partially so, $k_{-1} \geqslant k_{Am}[\mathrm{Am}]$. This is probably due to the lower values of k_{Am} expected for reaction with the secondary amines resulting from steric hindrance to proton transfer. Values of k_{-1} for the secondary amines are also likely to be higher due to steric strain in the zwitterions **6b**. An analogous situation is observed in the formation of the adducts **7a** from the ethyl ether; the rate-limiting step changes from nucleophilic attack to proton transfer as the amine is changed from primary to secondary.

Solvent effects

It is particularly interesting to compare data in acetonitrile with those observed in DMSO (Table 10). Values of the overall equilibrium constants for adduct formation, $K^0_{c,3}$ and $K^0_{c,1}$, are considerably higher in DMSO than in acetonitrile. The major factor here is probably the greater ability of DMSO than acetonitrile to solvate charged species.[19,20] The ratios of values in the two solvents are *ca.* 10^5 for reactions involving butylamine, *ca.* 3×10^4 with piperidine and *ca.* 10^4 with pyrrolidine. DMSO is known to be a particularly good hydrogen-bond acceptor[23] and this trend may reflect the greater relative stabilisation, through hydrogen-bonding interactions, of the primary ammonium ions than of the secondary ammonium ions in this solvent. The need for stabilisation of the substituted ammonium ions in acetonitrile is evidenced by the observation of their homoconjugation with the parent amines. This interaction is not observed in DMSO.

Table 10 Summary of kinetic and equilibrium data in acetonitrile[a] (MeCN) and comparison with values in DMSO

						
	1		**4a**		**4b**	
Reaction with butylamine	MeCN	DMSO	MeCN	DMSO	MeCN	DMSO
$K^0_{c,3}$/dm^3 mol^{-1}	0.0025	1000	0.0004	15	0.00094	210
$K^0_{c,1}$/dm^3 mol^{-1}			0.36	5×10^4		
k_1/dm^3 mol^{-1} s^{-1}			130	250	183	410
$k_{AmH^+}{}^{b}$/dm^3 mol^{-1} s^{-1}			$>1.8 \times 10^5$	>50		
k_4/dm^3 mol^{-1} s^{-1}			8500	8.3		
Reaction with pyrrolidine						
$K^0_{c,3}$/dm^3 mol^{-1}	0.20	3500	0.009	70	0.155	1300
K_3k_{Am}/dm^6 mol^{-2} s^{-1}	2×10^6	1×10^7				
$k_{AmH^+}{}^{c}$/dm^3 mol^{-1} s^{-1}	9×10^6	3000				
$K^0_{c,1}$/dm^3 mol^{-1}			0.28	2000		
k_1/dm^3 mol^{-1} s^{-1}			1300	4000	2400	10000
k_{Am}/k_{-1} dm^3 mol^{-1}			86	30	55	20
$k_{AmH^+}{}^{b}$/dm^3 mol^{-1} s^{-1}			3.9×10^5	60		
k_4/dm^3 mol^{-1} s^{-1}			200	0.25		
Reaction with piperidine						
$K^0_{c,3}$/dm^3 mol^{-1}	0.055	2140	0.0015	27	0.016	400
K_3k_{Am}/dm^6 mol^{-2} s^{-1}	1.4×10^5	6×10^5				
$k_{AmH^+}{}^{c}$/dm^3 mol^{-1} s^{-1}	2.5×10^6	280				
$K^0_{c,1}$/dm^3 mol^{-1}			0.025	600		
k_1/dm^3 mol^{-1} s^{-1}			780	1800	650	5000
k_{Am}/k_{-1} dm^3 mol^{-1}			8	3	8	0.6
$k_{AmH^+}{}^{b}$/dm^3 mol^{-1} s^{-1}			2.4×10^5	9		

[a] All values are at 25 °C. Data in DMSO are from refs. 4, 5, 11, 13, 29. The subscript 3 indicates reaction at an unsubstituted ring position, and the subscript 1 reaction at the 1-position of **4a** or **4b**. Statistical corrections have not been applied. [b] For reaction at the 1-position, see Scheme 2. [c] For reaction at the unsubstituted 3-position, see Scheme 1.

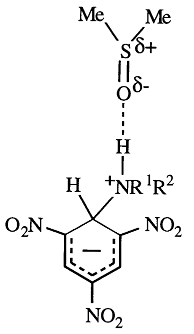
The results in acetonitrile lead to the direct determination of values of k_{AmH^+}, the rate constants for protonation of anionic adducts by substituted ammonium ions. The values are *ca.* 10^4 larger in acetonitrile than in DMSO, when reaction is both at an unsubstituted and at a substituted ring position. There are however no major differences between the two solvents in values of k_1, the rate constant for nucleophilic attack by the amine at the 1-position, or in values of the ratio k_{Am}/k_{-1}. The former values are lower by a factor of *ca.* 2–4 in acetonitrile, while the latter ratios are larger by a factor of *ca.* 3–10. Although comparisons are not possible from experimental data we would, similarly, not expect large differences between the two solvents in values of k_3 or of the ratio k_{Am}/k_{-3} involving reaction at unsubstituted ring positions.

The decrease in values of $K^0_{c,1}$ ($\equiv k_1k_{Am}/k_{-1}k_{AmH^+}$) and $K^0_{c,3}$ ($\equiv k_3k_{Am}/k_{-3}k_{AmH^+}$) on transfer from DMSO to acetonitrile are largely explicable in terms of corresponding increases in values of k_{AmH^+}. However, it is interesting to speculate on the solvent dependence of k_{Am}, the rate constant for proton transfer from zwitterionic adducts to amine. It has been shown that ratios k_{Am}/k_{-1} (and k_{Am}/k_{-3}) have little solvent dependence. Nevertheless, values of both k_{Am} and k_{-1} (k_{Am} and k_{-3}) may be much larger in acetonitrile than in DMSO.

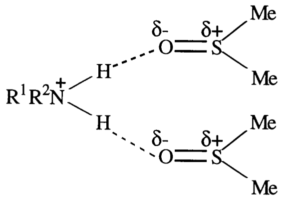
The first step in adduct formation, Scheme 1, is zwitterion formation and this involves production of charges. Hence it is reasonable to expect that the equilibrium constant, K_1 ($\equiv k_1/k_{-1}$), for this process should be strongly solvent dependent, whereas the equilibrium constant for the second step ($\equiv k_{Am}/k_{AmH^+}$) should show little dependence on solvent. It has been argued previously[4,6] that in DMSO the ratio k_{Am}/k_{AmH^+} has a value of *ca.* 500 reflecting the greater acidity of the zwitterions than of the parent ammonium ions. Since values of k_{AmH^+} are much larger in acetonitrile than in DMSO, this implies that values of k_{Am} will also be much larger in acetonitrile. Using the factor of 500 for k_{Am}/k_{AmH^+} in acetonitrile yields values for k_{Am} of (1 to *ca.* 5) × 10^9 dm^3 mol^{-1} s^{-1} for reaction at an unsubstituted ring position and (1 to *ca.* 2) × 10^8 dm^3 mol^{-1} s^{-1} when reaction is at a substituted ring position. The former value approaches the diffusion limit (2×10^{10} dm^3 mol^{-1} s^{-1}) which is consistent with proton transfers that are in the thermodynamically favoured direction. There is likely to be some steric hindrance when reaction involves attack at a 1-substituted position, accounting for the somewhat lower values observed in formation of **7a**.

In fact, the value of 500 for k_{Am}/k_{AmH^+} may be somewhat too large in acetonitrile, since the reaction involves formation of a free substituted ammonium ion from a zwitterion. Nevertheless the conclusion is that both values of k_{AmH^+} and k_{Am} are considerably lower in DMSO than in acetonitrile. It has previously been reported that values of rate constants for thermodynamically favourable proton transfers in DMSO are often well below that expected for diffusion-controlled reaction. Steric hindrance is thought to be an important factor contributing to this reduction.[6,37–39] However, this factor should similarly apply to reactions in acetonitrile. The lower values for rate constants for proton transfer observed in DMSO probably reflect the strong hydrogen-bonding between DMSO and the proton to be transferred.[40] Hydrogen bonding in the zwitterions, depicted by **9**, reduces values of k_{Am} and in the ammonium ions, depicted by **10**, reduces values of k_{AmH^+}.

It is worth noting that solvent effects on rate constants for proton transfer from phenols to the anthracene radical anion have been reported.[41,42] It was suggested that only the free phenol, in equilibrium with phenol hydrogen-bonded to the solvent, is able to effect proton transfer. Faster reaction in acetonitrile than in DMSO reflects the weaker interaction with the former solvent. A similar situation may apply in our systems with proton transfer occurring only from non hydrogen-bonded ammonium ions and zwitterions.



9



10

Since ratios k_{Am}/k_{-1} are only slightly higher in acetonitrile than in DMSO, the implication of higher k_{Am} values is that k_{-1} values are also higher in acetonitrile. Hence the expected reduction in values of K_1 reflects slightly smaller values of k_1 with much higher values of k_{-1}. The ratio k_{Am}/k_{-1} affects the susceptibility of substitution reaction to base catalysis. The similar values obtained for this ratio in acetonitrile and in DMSO imply that, as observed,[15–18] reactions should generally show a rather similar susceptibility to base catalysis in the two solvents.

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References

1 M. R. Crampton and V. Gold, *Chem. Commun.*, 1965, 549; *J. Chem. Soc. B*, 1967, 23.
2 F. Terrier, *Nucleophilic Aromatic Displacement*, VCH, New York, 1991.
3 E. Buncel, M. R. Crampton, M. J. Strauss and F. Terrier, *Electron Deficient Aromatic- and Heteroaromatic-base Interactions*, Elsevier, Amsterdam, 1984.
4 M. R. Crampton and B. Gibson, *J. Chem. Soc., Perkin Trans. 2*, 1981, 533.
5 M. R. Crampton and C. Greenhalgh, *J. Chem. Soc., Perkin Trans. 2*, 1983, 1175.
6 C. F. Bernasconi, M. C. Muller and P. Schmid, *J. Org. Chem.*, 1979, **44**, 3189.
7 M. R. Crampton, *J. Chem. Soc.*, 1971, 2112.
8 E. Buncel and J. G. K. Webb, *Can. J. Chem.*, 1974, **52**, 630.
9 J. A. Orvik and J. F. Bunnett, *J. Am. Chem. Soc.*, 1970, **92**, 2417.
10 J. F. Bunnett, S. Sekiguchi and L. A. Smith, *J. Am. Chem. Soc.*, 1981, **103**, 4865.
11 M. R. Crampton and P. Routledge, *J. Chem. Soc., Perkin Trans. 2*, 1984, 573.
12 Y. Hasegawa, *J. Chem. Soc., Perkin Trans. 2*, 1985, 87.
13 R. Chamberlin and M. R. Crampton, *J. Chem. Soc., Perkin Trans. 2*, 1995, 1831.
14 R. Chamberlin and M. R. Crampton, *J. Chem. Soc., Perkin Trans. 2*, 1994, 425.
15 D. Ayediran, T. O. Bamkole, J. Hirst and I. Onyido, *J. Chem. Soc., Perkin Trans. 2*, 1977, 597; 1977, 1580.
16 T. O. Bamkole, J. Hirst and I. Onyido, *J. Chem. Soc., Perkin Trans. 2*, 1979, 1317.
17 T. A. Emokpae, P. U. Uwakwe and J. Hirst, *J. Chem. Soc., Perkin Trans. 2*, 1993, 125.
18 T. O. Bamkole, J. Hirst and I. Onyido, *J. Chem. Soc., Perkin Trans. 2*, 1982, 889.
19 J. F. Coetzee and C. D. Ritchie, *Solute Solvent Interactions*, Marcel Dekker, New York, 1969.
20 J. F. Coetzee, *Progr. Phys. Org. Chem.*, 1967, **4**, 45.
21 I. M. Kolthoff, S. Bruckenstein and M. K. Chantooni, *J. Am. Chem. Soc.*, 1961, **83**, 3927; J. M. Kolthoff and M. K. Chantooni, 1965, **87**, 4428.
22 J. F. Coetzee and G. R. Padmanabhan, *J. Am. Chem. Soc.*, 1965, **87**, 5005.
23 M. J. Kamlet and R. W. Taft, *J. Am. Chem. Soc.*, 1976, **98**, 377; L. Joris, J. Mitsky and R. W. Taft, *J. Am. Chem. Soc.*, 1972, **94**, 3438.
24 M. R. Crampton and V. Gold, *J. Chem. Soc.*, 1964, 4293.
25 R. Foster and R. K. Mackie, *Tetrahedron*, 1965, **21**, 3363.
26 P. Caveng and H. Zollinger, *Helv. Chim. Acta*, 1967, **50**, 861.
27 E. Buncel and R. A. Manderville, *J. Am. Chem. Soc.*, 1993, **115**, 8985; E. Buncel and R. A. Manderville, *J. Phys. Org. Chem.*, 1993, **6**, 71.
28 G. Briegleb, W. Liptay and M. Cantner, *Az. Phys. Chem. N.F.*, 1960, **26**, 55.
29 R. Chamberlin, M. R. Crampton and I. Robotham, *J. Chem. Res.* (*S*), 1994, 408; (*M*), 1994, 2232.
30 R. Chamberlin and M. R. Crampton, *J. Chem. Res.* (*S*), 1993 106; (*M*), 1993, 811.
31 C. F. Bernasconi and M. C. Muller, *J. Am. Chem. Soc.*, 1978, **100**, 5536.
32 C. Grammacioli, R. Destro and M. J. Simonetta, *J. Chem. Soc., Chem. Commun.*, 1967, 331; *Acta Crystallogr., Sect. B*, 1968, **24**, 129.
33 D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420.
34 G. Baldini, G. Doddi, G. Illuminati and F. Stegel, *J. Org. Chem.*, 1976, **41**, 2153.
35 R. Chamberlin, M. R. Crampton and R. L. Knight, *J. Chem. Res.* (*S*), 1993, 444; (*M*), 1993, 2986.
36 E. Buncel, J. M. Dust, A. Jonczyk, R. A. Manderville and I. Onyido, *J. Am. Chem. Soc.*, 1992, **114**, 5610; R. A. Manderville and E. Buncel, *J. Am. Chem. Soc.*, 1993, **115**, 8985.
37 C. F. Bernasconi and D. J. Carre, *J. Am. Chem. Soc.*, 1979, **101**, 2698.
38 C. F. Bernasconi, J. P. Fox and S. Fornarini, *J. Am. Chem. Soc.*, 1980, **102**, 2810.
39 C. D. Ritchie, *J. Am. Chem. Soc.*, 1983, **105**, 3573.
40 C. D. Ritchie and S. Lu, *J. Am. Chem. Soc.*, 1989, **111**, 8542.
41 M. F. Nielsen, *Acta Chem. Scand.*, 1992, **46**, 533.
42 M. F. Nielsen and O. Hammerich, *Acta Chem. Scand.*, 1992, **46**, 883.

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