The Stabilities of Meisenheimer Complexes. Part 34.[1] Kinetic Studies of σ-Adduct Formation and Nucleophilic Substitution in the Reactions of 2,4,6-Trinitrophenetole with Aliphatic Amines in Dimethyl Sulphoxide

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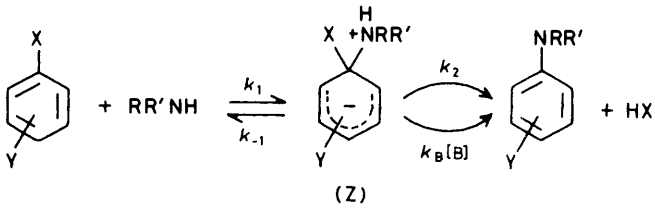
The reaction of 2,4,6-trinitrophenetole with aliphatic amines in dimethyl sulphoxide results in the formation of anionic σ-adducts *via* zwitterionic intermediates. Rapid attack at the 3-position is followed by attack at the ethoxy-substituted 1-position. The 1-adducts formed by reaction with n-butylamine and benzylamine undergo acid-catalysed expulsion of ethoxide to yield *N*-substituted picramides; that formed by reaction with piperidine is relatively stable. Rate and equilibrium data for these reactions have been determined and compared with data for reactions of related compounds. Increased steric crowding at the reaction centre caused by a change from primary amines to piperidine results in reductions in the rate of proton transfer from zwitterionic intermediates to amine catalyst and in the rate of leaving-group expulsion.

Important evidence for the S_NAr mechanism of aromatic substitution has come from studies of base catalysis of reactions with amine nucleophiles.[2-4] The base catalysed step (k_B[B] in Scheme 1) may involve rate-limiting proton transfer [5,6] from the zwitterionic intermediate (Z), or rapid conversion of (Z) into its deprotonated form followed by general acid-catalysed leaving group departure (SB–GA mechanism).[7,8] The latter mechanism is likely to hold in dipolar aprotic solvents such as dimethyl sulphoxide (DMSO) where leaving group expulsion is difficult.[9] Thus in an elegant kinetic study of the reactions of 1-ethoxy-2,4-dinitronaphthalene with n-butylamine and t-butylamine in DMSO Orvik and Bunnett [10] were able to observe in separate steps formation of intermediates of structure (1) and their acid-catalysed conversion into substitution products. Structure (1; R = Bu^n) has since been confirmed by flow-n.m.r. spectroscopy.[11] Adducts (2; R = Bu^n or Me) have also been observed by n.m.r. as transient intermediates during reactions of 2,4,6-trinitroanisole with primary aliphatic amines.[12,13] When reaction involves secondary amines the anionic adducts, such as (3) formed from 2,4,6-trinitroanisole and piperidine, may have long lifetimes and in some cases do not yield the expected substitution products.[14,15]

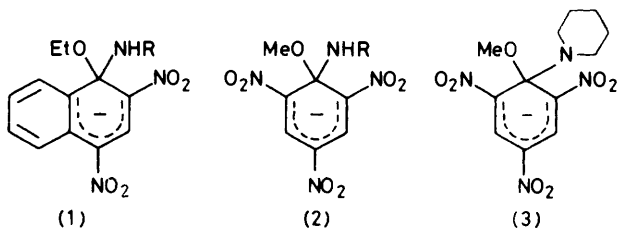
Previously the kinetics of reaction of 1,3,5-trinitrobenzene (TNB) [16-18] and 2,4,6-trinitrobenzyl chloride [1] (TNBCl) with primary and secondary aliphatic amines have been examined. Here relatively stable σ-adducts are formed by attack at ring-carbon atoms carrying hydrogen or, in the case of TNBCl, CH_2Cl groups, and nucleophilic substitution is not observed. It has been shown that in these reactions proton transfer from zwitterionic adducts to amines may be rate-limiting. Reduction below the values expected for diffusion-controlled reaction of the rates of proton transfer were attributed to steric effects, which are particularly severe (i) when reaction involves secondary amines or (ii) when the bulky CH_2Cl group is at the reaction site.

In the present work we have examined reactions of 2,4,6-trinitrophenetole (1-ethoxy-2,4,6-trinitrobenzene) (TNP) with n-butylamine, benzylamine, and piperidine in DMSO. Our results provide evidence for three types of process as shown in Scheme 2. These are the reversible formation of σ-adducts by attack at the 3-positon or the 1-position and, in the case of reaction with the primary amines, acid-catalysed expulsion of ethoxide to yield *N*-substituted pictamides. It is known that the reaction products may undergo further reaction with an excess of amine either by proton transfer [10] or by base addition,[12,13,19] but we have not studied these reactions.

Our results allow comparison of the effects of H, CH_2Cl, and OEt ring substituents on rates and equilibria for reaction with amines, and also comparison of the 2,4,6-trinitrophenetole system with the 1-ethoxy-2,4-dinitronaphthalene system.



Scheme 1



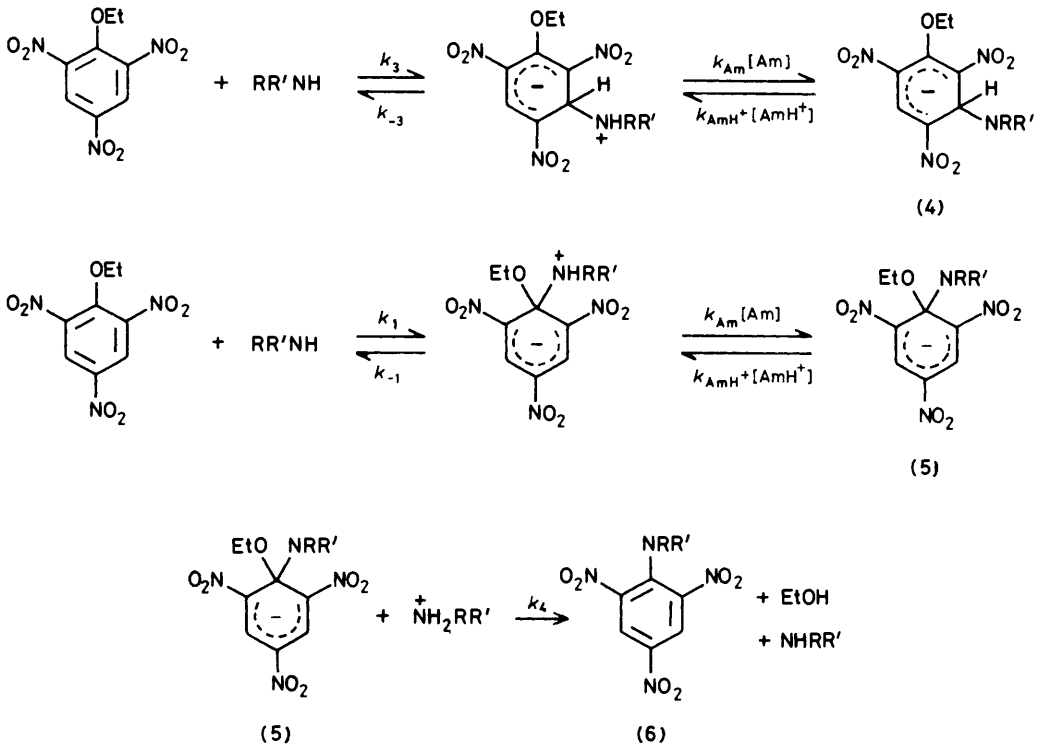
Experimental

2,4,6-Trinitrophenetole, m.p. 80 °C (lit.,[20] 78.5 °C) was prepared by reaction of picryl chloride with 1 equiv. of sodium ethoxide in ethanol. Solvent, amines, and amine salts were prepared and purified as described previously.[1,17]

^{1}H N.m.r. measurements were made on 0.1M-solutions of the substrate in [$^2H_6$]dimethyl sulphoxide using a Varian EM 360L instrument. Chemical shifts were measured relative to internal tetramethylsilane. Visible spectra measurements were made with a Unicam SP 8000, a Pye Unicam SP8-100, or a Hi-Tech SF3L stopped-flow spectrophotometer. Kinetic and equilibrium measurements were made at 25 °C using freshly prepared solutions of reagents. Reported rate coefficients are the mean values of five separate determinations and are precise to within ±5%.

Results

The visible spectra, recorded 1 min after mixing, of solutions of TNP (2×10^{-5}M) in DMSO containing n-butylamine (0.001—0.1M) show maxima at 435 (ε 2.7×10^4 l mol^{-1} cm^{-1})



Scheme 2

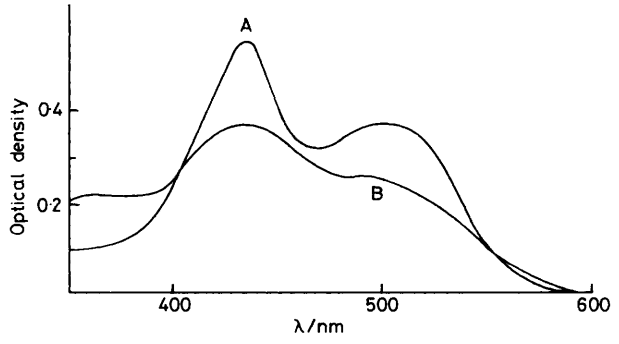


Figure. Visible spectra of TNP (2×10^{-5}M) in DMSO containing (A) 0.01M-butylamine and (B) 0.01M-butylamine and 0.01M-butylammonium perchlorate; spectra recorded 2 min after mixing and correspond to (A) the adduct (5; R = H, R′ = Bu), and (B) the reaction product (6; R = H, R′ = Bu)

and 505 nm (ε 1.8×10^4 l mol^{-1} cm^{-1}). The spectra are typical [21,22] of 1 : 1 σ-adducts. Very similar spectra were observed for TNP in the presence of benzylamine ($\lambda_{max.}$ 435 and 505 nm) and piperidine (435 and 495 nm). Stopped-flow spectrophotometry showed that for each amine there were two distinct colour-forming reactions whose rate coefficients were separated by at least an order of magnitude. We interpret this (Scheme 2) as fast formation of the 3-adducts followed by conversion into the 1-adducts. The spectra recorded 1 min after mixing will correspond to the thermodynamically more stable (but more slowly formed) 1-adducts. The justification for this interpretation is (i) that nucleophilic attack at unsubstituted ring positions is almost always faster than at substituted positions; [22,23] (ii) that the rate parameters calculated for the faster process correlate well with those determined [17] for attack at an unsubstituted ring position in TNB; and (iii) that in the case of piperidine the ^{1}H n.m.r. spectrum of the thermodynamically more stable adduct indicates attack at the 1-position.

With n-butylamine and benzylamine the visible absorption ($\lambda_{max.}$ 435 and 505 nm) gradually fades and a new band is formed at *ca.* 360 nm. This change, whose rate is greatly enhanced by the addition of ammonium salts, is attributed to the acid-catalysed departure of ethoxide (k_4 in Scheme 2). Spectra are shown in the Figure. With piperidine the adduct formed is very stable and fading is very slow even in the presence of added piperidinium ions.

The ^{1}H n.m.r. spectrum of TNP in [$^2H_6$]DMSO shows bands at δ 9.2 (ring protons), 4.3 (q, *J* 7 Hz, OCH_2), and 1.35 (t, CH_3). The spectrum of (5; NRR′ = NC_5H_{10}) obtained in the presence of 2 equiv. of piperidine has bands at δ 8.53 (ring), 3.05 (OCH_2), and 1.07 (CH_3). This spectrum is unchanged after several hours. In the case of reaction with n-butylamine conversion into the product, *N*-butyl-2,4,6-trinitroaniline, is relatively fast and the spectrum obtained in the presence of 1 equiv. of base shows a singlet at δ 8.95 due to ring protons of the product and bands due to liberated ethanol.

Kinetic Analysis.—Rates of reaction were measured under first-order conditions. For reactions with buffers (amine plus amine salt) the buffer components were in large excess of the TNP concentration, which was usually 1×10^{-5}M. For reactions with amines in the absence of added amine salts sufficient excess of amine was used that >95% conversion into adduct was achieved at equilibrium. Under these conditions equation (i) applies. [17]

$$\ln\left(\frac{OD_\infty}{OD_\infty - OD}\right) = k_{obs} \cdot t \qquad \text{(i)}$$

We assume that the zwitterionic forms may be treated as steady-state intermediates, so that the general rate expres-

sion [17] for reaction at the unsubstituted 3-position is given by equation (ii). When $k_{-3} \gg k_{Am}[Am]$ this simplifies to equation (iii). If $k_{Am}[Am] \gg k_{-3}$ and when no added salt, AmH^+, is initially present equation (ii) becomes equation (iv).

$$k_{obs} = \frac{k_3 k_{Am}[Am]^2 + k_{-3}k_{AmH^+}[AmH^+]}{k_{-3} + k_{Am}[Am]} \quad (ii)$$

$$k_{obs} = K_3 k_{Am}[Am]^2 + k_{AmH^+}[AmH^+] \quad (iii)$$

$$k_{obs} = k_3[Am] \quad (iv)$$

The reactions yielding 1-adducts were, for each amine, considerably slower than those giving the 3-adducts, so that rates could be measured consecutively. Also the formation of the 3-adducts may be treated as a mobile equilibrium [24] as compared with attack at the 1-position. We can express, by equation (v), the rate of reaction in terms of coefficients for the forward and the reverse reactions. Using standard methods [1,24] it can be shown that the general rate expression for reaction at the 1-position is given by equation (vi). If the condition $k_{Am}[Am] \gg k_{-1}$ applies then we obtain equation (vii). It is also convenient to use expression (viii), which applies in the absence of added amine salt, where k_r will be negligible, and where the fractionation of parent and 3-adduct is expressed in terms of $(OD)_3$, the absorption observed for the 3-adduct, and $(OD_\infty)_3$, the absorption for complete conversion of parent into 3-adduct.

$$k_{obs} = k_f + k_r \quad (v)$$

$$k_{obs} = \frac{k_1 k_{Am}[Am]^2}{(k_{-1} + k_{Am}[Am])\left(1 + K_{c,3}\frac{[Am^2]}{[AmH^+]}\right)} + \frac{k_{-1}k_{AmH^+}[AmH^+]}{k_{-1} + k_{Am}[Am]} \quad (vi)$$

$$k_{obs} = \frac{k_1[Am]}{\left(1 + K_{c,3}\frac{[Am]^2}{[AmH^+]}\right)} + \frac{k_{-1}k_{AmH^+}[AmH^+]}{k_{Am}[Am]} \quad (vii)$$

$$k_{obs} = \frac{k_1[Am]}{\left(1 + \frac{(OD)_3}{(OD_\infty)_3 - (OD)_3}\right)} \quad (viii)$$

The rate expression appropriate to the conversion of adducts (5) into products (6) catalysed by substituted ammonium salts has been derived previously and is given by equation (ix). When the equilibrium between parent and adduct (5) is almost entirely in favour of the adduct, equation (ix) simplifies to equation (x).

$$k_{obs} = \frac{k_4 K_{c,1}[Am]^2[AmH^+]}{K_{c,1}[Am]^2 + [AmH^+]} \quad (ix)$$

$$k_{obs} = k_4[AmH^+] \quad (x)$$

Equilibrium Constants.—We define by equation (xi) an equilibrium constant $K_{c,3}$ for the overall conversion of TNP into its 3-adduct (4). This constant $K_{c,3}$ is related by equation (xii) to K_3 $(=k_3/k_{-3})$ and to the acid dissociation constants of the zwitterion, K_a^z, and protonated amine, $K_a^{AmH^+}$. Equation (xiii) relates $K_{c,3}$ to the rate coefficients associated with formation of the 3-adduct.

$$K_{c,3} = \frac{[4][AmH^+]}{[TNP][Am]^2} \quad (xi)$$

$$K_{c,3} = \frac{K_3 K_a^z}{K_a^{AmH^+}} \quad (xii)$$

$$K_{c,3} = \frac{k_3}{k_{-3}}\frac{k_{Am}}{k_{AmH^+}} \quad (xiii)$$

Expressions exactly analogous to (xi)—(xiii) apply to $K_{c,1}$, the equilibrium constant for formation of the 1-adduct (5).

Table 1. Kinetic data for reactions of TNP with n-butylamine in DMSO at 25 °C giving 3-adduct and 1-adduct

$[BuNH_2]$/M	k_{fast}/s^{-1}	k_3 [a]/l mol^{-1} s^{-1}	$(OD)_3$ [b]	k_{slow}/s^{-1}	k_1 [c]/l mol^{-1} s^{-1}
0.0005			0.0017	0.10	210
0.00075			0.0040	0.14	220
0.001			0.0057	0.19	230
0.002			0.014	0.27	210
0.003			0.022	0.28	220
0.004			0.025	0.27	200
0.006	21.5	3 600	0.035		
0.008	26	3 200	0.037		
0.010	31	3 100	0.038		
0.015	48	3 200	0.038		

[a] Calculated from equation (iv). [b] Optical density, 435 nm, at completion of the faster colour-forming reaction. [c] Calculated from equation (viii).

Table 2. Kinetic and equilibrium data for the σ-adduct-forming reactions of TNP with n-butylamine in DMSO containing 0.01M-n-butylammonium perchlorate at 25 °C

$[BuNH_2]$/M	$(OD)_3$ [a]	$K_{c,3}$/l mol^{-1}	k_{obs} [b]/s^{-1}	k_{calc} [c]	$(OD)_1$ [d]	$K_{c,1}$/l mol^{-1}
0.0006			0.22	0.23	0.029	53 000
0.0008			0.26	0.26	0.033	47 000
0.001			0.30	0.30	0.036	45 000
0.002			0.53	0.53	0.042	
0.006			1.44	1.44		
0.008	0.0042	16	1.80	1.83		
0.01	0.0055	15	2.20	2.2	0.044	
0.02	0.016	14	3.3	3.1	0.044	
0.03	0.026	16				
0.04	0.031	15	3.0	3.0	0.044	
0.05	0.034	14				

[a] Optical density, 435 nm, at completion of the reaction forming the 3-adduct. A Benesi–Hildebrand type plot gives a value for complete conversion $(OD_\infty)_3$ of 0.044. [b] For attack at the 1-position. [c] Calculated from equation (vii) with k_1 250 l mol^{-1} s^{-1}, $K_{c,3}$ 15 l mol^{-1}, and $k_{-1}k_{AmH^+}/k_{Am}$ 0.005 s^{-1}. [d] Optical density, 435 nm, at completion of the slower adduct-forming reaction.

Reaction with n-Butylamine.—Data for the reaction in the absence of added butylammonium ions are in Table 1. The rate data for the more rapid reaction giving the 3-adduct conform to equation (iv), and yield a value for k_3 of 3 200 l mol^{-1} s^{-1}. The invariance with base concentration of the calculated values of k_3 allow us to estimate that $k_{Am}/k_{-3} > 200$ l mol^{-1}.

Table 3. Rate data for formation of *N*-(n-butyl)picramide from TNP and butylamine containing n-butylammonium perchlorate (0.01M) in DMSO at 25 °C

[BuNH$_2$]/M	k_{obs} [a]/s^{-1}	k_{calc} [b]
0.0002	0.015	0.014
0.0004	0.038	0.037
0.0006	0.053	0.053
0.0008	0.057	0.063
0.001	0.071	0.069
0.002	0.075	0.078
0.01	0.083	0.083
0.02	0.081	0.083
0.04	0.083	0.083
0.05	0.084	0.083
0.06	0.086	0.083

[a] Measured with Pye Unicam spectrophotometer at 360 nm. [b] Calculated from equation (ix) with k_4 8.3 l mol^{-1} s^{-1}, $K_{c,1}$ 50 000 l mol^{-1}.

The data for the slower reaction giving the 1-adduct yield, *via* equation (viii), a value for k_1 of 220 l mol^{-1} s^{-1} and allow us to estimate a lower limit for the ratio k_{Am}/k_{-1} of 10 000 l mol^{-1}.

Measurements were also made (Table 2) in the presence of varying concentrations of amine and with 0.01M-butylammonium perchlorate. The reaction at the 3-position was too rapid to allow rate measurements but optical density measurements at the completion of this reaction gave a value for $K_{c,3}$ of 15 ± 1 l mol^{-1}. The rate of reaction at the 1-position was measureable and the results show that $k_{Am}[Am] \gg k_{-1}$ so that equation (vii) applies. At amine concentrations >0.002 the second term in equation (vii) (the k_r term) will be negligibly small; hence knowing the value of $K_{c,3}$ we were able to calculate a value of k_1 of 250 l mol^{-1} s^{-1}. This is quite close to the value obtained in the absence of salt. We were then able to calculate values for the first term of equation (vii) (the k_f term) for the four lowest amine concentrations and hence determine values, by difference, for the k_r term. These give a value for $k_{-1}k_{AmH^+}/k_{Am}$ of 0.005 ± 0.001 s^{-1}. Combination of this value with the value of k_{-1} gives a value for $K_{c,1}$ (= $k_1k_{Am}/k_{-1}k_{AmH^+}$) of 50 000 l mol^{-1}, in agreement with that obtained from the equilibrium optical density data.

The product-forming reaction was measured at 360 nm using a conventional spectrophotometer; the data (Table 3) accord well with equation (ix) with k_4 8.3 l mol^{-1} s^{-1} and $K_{c,1}$ 50 000 l mol^{-1}.

Table 4. Kinetic data for reaction of TNP with benzylamine in DMSO at 25 °C giving 3-adduct and 1-adduct

[PhCH$_2$NH$_2$]/M	k_{fast}/s^{-1}	k_3 [a]/l mol^{-1} s^{-1}	$(OD)_3$ [b]	k_{slow}/s^{-1}	k_1 [c]/l mol^{-1} s^{-1}
0.0010				0.093	93
0.0016			0.0015	0.143	93
0.0020			0.0023	0.183	97
0.0040			0.0083	0.345	108
0.0060			0.0141	0.437	109
0.0080			0.0186	0.487	100
0.010			0.0259		
0.020	18	900	0.0357		
0.040	32	800	0.0400		
0.050	44	900	0.0419		
0.060	52	900	0.0410		
0.070	65	900	0.0419		
0.080	72	900	0.0429		

[a] Calculated from equation (iv). [b] Optical density, 434 nm, at completion of the faster colour-forming reaction. [c] Calculated from equation (viii).

Table 5. Kinetic and equilibrium data for the σ-adduct-forming reactions of TNP with benzylamine in DMSO containing 0.01M-benzylammonium perchlorate at 25 °C

[PhCH$_2$NH$_2$]/M	$(OD)_3$ [a]	$K_{c,3}$/l mol^{-1}	k_{obs} [b]/s^{-1}	k_{calc} [c]	$(OD)_1$ [d]	$K_{c,1}$/l mol^{-1}
0.001			0.26	0.29	0.017	5 700
0.0015					0.023	4 400
0.002			0.31	0.29	0.031	5 000
0.003					0.037	4 400
0.004			0.42	0.43	0.040	3 900
0.006			0.57	0.60	0.044	
0.008			0.79	0.78	0.047	
0.01			0.92	0.95	0.046	
0.02			2.0	1.9	0.046	
0.04			3.5	3.4	0.047	
0.06	0.0088	0.75			0.046	
0.08	0.0150	0.87			0.047	
0.10	0.0195	0.87			0.047	
0.15	0.0278	0.87			0.046	
0.20	0.0334	0.97			0.047	

[a] Optical density, 434 nm, at completion of the reaction forming the 3-adduct. A Benesi–Hildebrand type plot gives a value for complete conversion, $(OD_\infty)_3$ of 0.042. [b] For attack at the 1-position. [c] Calculated from equation (vii) with k_1 95 l mol^{-1} s^{-1}, $K_{c,3}$ 0.87 l mol^{-1}, and $k_{-1}k_{AmH^+}/k_{Am}$ 0.02 s^{-1}. [d] Optical density, 434 nm, at completion of the slower colour-forming reaction.

Table 6. Kinetic and equilibrium data for the σ-adduct forming reaction of TNP with benzylamine in DMSO containing 0.01M-benzylammonium chloride at 25 °C

$[PhCH_2NH_2]$/M	$(OD)_3$ [a]	$K_{c,3}$/l mol^{-1}	k_{obs} [b]/s^{-1}	k_{calc} [c]	$(OD)_1$ [d]	$K_{c,1}$/l mol^{-1}
0.0008					0.012	5 500
0.001			0.28	0.28	0.018	6 300
0.0015					0.026	5 600
0.002			0.29	0.28	0.033	6 100
0.003					0.038	5 000
0.004			0.43	0.42	0.042	5 800
0.006			0.59	0.60	0.046	
0.008			0.77	0.78	0.047	
0.01			0.94	0.95	0.047	
0.02			1.80	1.8	0.046	
0.04	0.0062	1.08	3.50	3.3	0.047	
0.05	0.0092	1.12			0.047	
0.06	0.0114	1.03			0.046	
0.08	0.0164	1.00			0.046	
0.10	0.0214	1.04			0.047	

[a] Optical density, 435 nm, at completion of the reaction forming the 3-adduct. A Benesi–Hildebrand type plot gives a value for complete conversion, $(OD_\infty)_3$, of 0.042. [b] For attack at the 1-position. [c] Calculated from equation (vii) with k_1 95 l mol^{-1} s^{-1}, $K_{c,3}$ 1.05 l mol^{-1}, and $k_{-1}k_{AmH^+}/k_{Am}$ 0.018 s^{-1}. [d] Optical density, 435 nm, at completion of the slower colour-forming reaction.

Table 7. Rate data for formation of *N*-benzylpicramide from TNP and benzylamine containing benzylammonium salts (0.01M) in DMSO at 25 °C

$[PhCH_2NH_2]$/M	$[PhCH_2NH_3^+ClO_4^-]$/M	$[PhCH_2NH_3^+Cl^-]$/M	k_{obs} [a]/s^{-1}	k_4 [b]/l mol^{-1} s^{-1}
0.0008		0.01	0.0055	2.2
0.0009		0.01	0.0065	2.2
0.001		0.01	0.0077	2.2
0.0015		0.01	0.012	2.2
0.002		0.01	0.015	2.2
0.003		0.01	0.020	2.4
0.004		0.01	0.020	2.2
0.005		0.01	0.022	2.4
0.01		0.01	0.023	2.3
0.02		0.01	0.022	2.2
0.04		0.01	0.025	2.5
0.06		0.01	0.022	2.2
0.08		0.01	0.021	2.1
0.10		0.01	0.021	2.1
0.01	0.01		0.026	2.6
0.02	0.01		0.026	2.6
0.04	0.01		0.026	2.6
0.06	0.01		0.026	2.6
0.08	0.01		0.025	2.5
0.10	0.01		0.025	2.5

[a] Measured at 380 nm using a Pye Unicam 8-100 instrument. [b] Calculated from equations (ix) and (x) using a value for $K_{c,1}$ of 5 300 l mol^{-1} (chloride salt).

Reaction with Benzylamine.—The behaviour and treatment of data are very similar to those with n-butylamine. The data in Table 4 obtained in the absence of added salt give values for k_3 of 900 ± 100 l mol^{-1} s^{-1} and k_1 of 100 ± 10 l mol^{-1} s^{-1}. At the benzylamine concentrations used, the proton-transfer steps are not rate-limiting in the formation of either 3-adduct or 1-adduct, and we can estimate that $k_{Am}/k_{-3} > 100$ l mol^{-1} and $k_{Am}/k_{-1} > 3000$ l mol^{-1}.

Measurements were also made in solutions containing 0.01M-benzylammonium perchlorate or benzylammonium chloride. It has been shown previously that the anion present may affect the values of rate and equilibrium constants obtained.[1,18,25] However at the low salt concentration used here the effects are not large. The data in Tables 5 and 6 were treated independently using the approach outlined for the n-butylamine data. The rate data yield a value for k_1 of 95 ± 5 l mol^{-1} s^{-1} and values for $k_{-1}k_{AmH^+}/k_{Am}$ of 0.02 s^{-1} in the presence of perchlorate and 0.018 s^{-1} with the chloride salt. The values of $K_{c,1}$ obtained from combination of these values, 4 700 l mol^{-1} (perchlorate) and 5 300 l mol^{-1} (chloride), are in good agreement with those determined independently from equilibrium optical densities.

Rate data for the formation of the product *N*-benzylpicramide were measured at 380 nm and are in Table 7. They yield values for k_4 of 2.6 l mol^{-1} s^{-1} in the presence of 0.01M-perchlorate and 2.2 l mol^{-1} s^{-1} with the chloride salt.

Reaction with Piperidine.—Examination by stopped-flow spectrophotometry of the reactions of TNP with piperidine (0.008—0.04M) without added salts indicated two processes. The more rapid was colour-forming and resulted in nearly complete conversion of TNP into adduct at all amine concentrations used. We take this to be formation of the 3-adduct (4; NRR′ = NC_5H_{10}). A much slower reaction, representing isomerisation to the 1-adduct (5; NRR′=NC_5H_{10}), gave in-

conveniently small changes in optical density. Data for the faster process, giving the 3-adduct, are in Table 8. Since no added piperidinium ions are present the term in equations (ii) and (iii) involving $[AmH^+]$ will be negligibly small. These data, in contrast to those observed with the primary amines, conform to the case where $k_{-3} \gg k_{Am}[Am]$ and yield a value for K_3k_{Am} of 44 000 ± 3 000 l² mol⁻² s⁻¹. Our results allow us to set a limit of $k_{Am}/k_{-3} < 5$.

Data obtained in the presence of 0.01M-piperidinium salts are in Tables 9 and 10. Here two processes were measurable giving rise to 3-adduct and 1-adduct, respectively. The rate data for the faster reaction lead to values for $K_{c,3}$ (= K_3k_{Am}/k_{AmH^+}) of 27 ± 5 l mol⁻¹ with perchlorate salt and 30 ± 5 l mol⁻¹ with chloride salt. These values are in good agreement with those obtained from equilibrium optical densities.

The interpretation of the rate data for isomerisation to the 1-adduct requires the use of the complete rate expression, equation (vi). However at sufficiently low amine concentrations the condition $k_{-1} \gg k_{Am}[Am]$ applies so that we obtain equation (xiv). Plots of the left hand side of this equation

$$k_{obs}(1 + K_{c,3}[Am]^2/[AmH^+])] = K_1k_{Am}[Am]^2 + k_{AmH^+}[AmH^+](1 + K_{c,3}[Am]^2/[AmH^+]) \quad (xiv)$$

versus $[Am]^2$ were linear at low amine concentrations. For the data measured with the perchlorate salt, the slope gave a value for K_1k_{Am} of (5.6 ± 0.2) × 10³ l² mol⁻² s⁻¹ and the intercept a value for k_{AmH^+} of 10 ± 2 l mol⁻¹ s⁻¹. An alternative method for calculating k_{AmH^+} is to combine the value of $K_{c,1}$ (600 l mol⁻¹) obtained from equilibrium optical densities with the value for K_1k_{Am}; this gives k_{AmH^+} 9 l mol⁻¹ s⁻¹. Using the known values for these parameters, k_{Am}/k_{-1} was calculated for each experimental value using equation (vi). The value obtained was 3 ± 1 l mol⁻¹. The rate coefficients calculated with these parameters agree with the experimental values over the whole concentration range. The value for k_1 (= $K_1k_{Am}k_{-1}/k_{Am}$) is calculated to be 1 800 l mol⁻¹ s⁻¹. Similar treatment for the run containing the chloride salt yielded values for K_1k_{Am} of 5.6 × 10³ l² mol⁻² s⁻¹, k_{AmH^+} 7 l mol⁻¹ s⁻¹, and k_{Am}/k_{-1} 4 l mol⁻¹.

We should point out that whereas the values obtained for K_1k_{Am} and k_{AmH^+} have relatively low error limits, the values for the ratio k_{Am}/k_{-1} and hence also k_1 depend critically on the value used for $K_{c,3}$. The foregoing values represent the 'best' values; however for the data in Table 10 k_{Am}/k_{-1} is calculated to be 10 l mol⁻¹ for $K_{c,3}$ = 25 instead of 30 l mol⁻¹, and 0 for $K_{c,3}$ = 35 l mol⁻¹.

The visible and ¹H n.m.r. spectra indicate that the 1-adduct

Table 8. Rate data for formation of the 3-adduct from TNP and piperidine in DMSO at 25 °C

[piperidine]/M	k_{obs}/s⁻¹	k_{obs} [a]/[piperidine]²
0.008	3.0	47 000
0.01	4.8	48 000
0.015	10.3	46 000
0.02	17.5	44 000
0.025	27.2	43 000
0.03	37.7	42 000
0.035	52.2	43 000
0.04	67.8	42 000

[a] This column gives values for K_3k_{Am}/l² mol⁻² s⁻¹.

Table 9. Kinetic and equilibrium data for adduct formation from TNP and piperidine in DMSO containing 0.01M-piperidinium perchlorate at 25 °C

[piperidine]/M	k_{fast} [a]/s⁻¹	k_{calc} [b]	$(OD)_3$ [c]	$K_{c,3}$/l mol⁻¹	k_{slow} [d]/s⁻¹	k_{calc} [e]	$(OD)_1$ [f]	$K_{c,1}$/l mol⁻¹
0.006					0.27	0.27	0.032	610
0.008					0.38	0.38	0.037	610
0.010	20	20	0.0072	21	0.50	0.51	0.040	610
0.015	25	26	0.0141	23			0.043	560
0.020	32	33	0.0205	24	1.12	1.10	0.046	
0.025	44	44	0.0259	26			0.046	
0.030	52	55	0.0297	27	1.43	1.43	0.047	
0.040					1.62	1.59	0.047	
0.060					1.66	1.67	0.046	

[a] Represents attack at the 3-position. [b] Calculated from equation (iii) with K_3k_{Am} 44 000 l² mol⁻¹ s⁻², k_{AmH^+} 1 600 l mol⁻¹ s⁻¹. [c] Optical density, 434 nm, at completion of rapid colour-forming reaction. Value for complete conversion $(OD_\infty)_3$ is 0.042. [d] Represents attack at the 1-position. [e] Calculated from equation (vi) with K_1k_{Am} 5.6 × 10³ l² mol⁻² s⁻¹, k_{AmH^+} 9 l mol⁻¹ s⁻¹, $K_{c,3}$ 27 l mol⁻¹, k_{Am}/k_{-1} 3 l mol⁻¹. [f] Optical density, 434 nm, at completion of slower colour-forming reaction. Value for (OD_∞) is 0.0465.

Table 10. Kinetic and equilibrium data for adduct formation from TNP and piperidine in DMSO containing 0.01M-piperidinium chloride at 25 °C

[piperidine]/M	k_{fast} [a]/s⁻¹	k_{calc} [b]	$(OD)_3$ [c]	$K_{c,3}$/l mol⁻¹	k_{slow} [d]/s⁻¹	k_{calc} [e]	$(OD)_1$ [f]	$K_{c,1}$/l mol⁻¹
0.004							0.027	720
0.006					0.25	0.25	0.035	630
0.008					0.35	0.36	0.040	600
0.010	16	18	0.011	31	0.48	0.48	0.049	
0.015	23	24	0.018	30	0.79	0.77	0.050	
0.020	31	31	0.025	31	1.02	1.01	0.050	
0.025	43	42	0.030	30	1.18	1.17	0.051	
0.030	55	53	0.033	30	1.29	1.29	0.051	
0.040			0.038	32	1.36	1.40	0.050	

[a] Represents attack at the 3-position. [b] Calculated from equation (iii) with K_3k_{Am} 44 000 l² mol⁻² s⁻¹, k_{AmH^+} 1 400 l mol⁻¹ s⁻¹. [c] Optical density, 434 nm, at completion of rapid colour-forming reaction. Value for complete conversion $(OD_\infty)_3$ is 0.0455. [d] Attack at 1-position. [e] Calculated from equation (vi) with K_1k_{Am} 5.6 × 10³ l² mol⁻² s⁻¹, k_{AmH^+} 7 l mol⁻¹ s⁻¹, $K_{c,3}$ 30 l mol⁻¹, and k_{Am}/k_{-1} 4 l mol⁻¹. [f] Optical density, 434 nm, at completion of slower colour-forming reaction. Value for $(OD_\infty)_1$ is 0.0505.

Table 11. Effects of chloride ions on equilibrium and rate constants

	$K_{c,3}$/ l mol^{-1}	$K_{c,1}$/ l mol^{-1}	k_1/ l mol^{-1} s^{-1}	$(k_{-1}k_{AmH^+}/k_{Am})$/s^{-1}	k_{AmH^+}/ l mol^{-1} s^{-1}
Benzylammonium perchlorate	0.87	4 700	95	0.020	
Benzylammonium chloride	1.05	5 300	95	0.018	
Piperidine perchlorate	27	600			9
Piperidine chloride	30	650			7

Table 12. Comparison of kinetic and equilibrium data for reaction at unsubstituted ring positions of 2,4,6-trinitrophenetole (TNP),[a] 2,4,6-trinitrobenzyl chloride (TNBCl),[b] and 1,3,5-trinitrobenzene (TNB) [c]

		n-Butylamine	Benzylamine	Piperidine
k_3/l mol^{-1} s^{-1}	TNP	3 200	900	>9 000
	TNBCl	3 000	1 000	>13 000
	TNB	45 000	13 000	>2 × 10^5
$K_{c,3}$/l mol^{-1}	TNP	15	0.87	27
	TNBCl	73	5	93
	TNB	1 000	105	2 140
$\left(\frac{k_{-3}k_{AmH^+}}{k_{Am}}\right)$/s^{-1}	TNP	210	1 000	>320
	TNBCl	41	200	>140
	TNB	45	120	>900
(k_{Am}/k_{-3})/l mol^{-1}	TNP	>200	>100	<5
	TNBCl	>1 000	>140	<2
	TNB	1 200	120	<10
k_{AmH^+}/l mol^{-1} s^{-1}	TNP	>4.2 × 10^4	>10^5	1 600
	TNBCl	>4 × 10^4	3 × 10^4	280
	TNB	6 × 10^4	1.5 × 10^4	280

[a] Data for TNP measured with 0.01M-salt. [b] Data for TNBCl, measured with 0.1M-salt, from ref. 1. [c] Data for TNB, measured with 0.1M-salt, from refs. 17 and 18.

(5; NRR′ = NC_5H_{10}) is stable in solution for several hours. Hence conversion into the product of nucleophilic substitution is very slow even in the presence of piperidinium ions.

Discussion

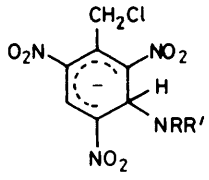
In the present work we have used a salt concentration of 0.01M (either perchlorate or chloride anion). Comparisons of values obtained with benzylammonium and piperidinium salts are in Table 11. The data show that values of the equilibrium constants $K_{c,1}$ and $K_{c,3}$ are significantly higher when measured in the presence of chloride ions. A similar effect has been noted previously in related work [1,18,25] and has been attributed to association of the chloride ions with substituted ammonium ions as shown in Scheme 3. The effects observed

$$\mathrm{TNP} + 2\mathrm{RR'NH} + \mathrm{Cl^-} \overset{K_c}{\rightleftharpoons} (\mathrm{TNP{\cdot}NRR'})^- + \mathrm{RR'NH_2^+} + \mathrm{Cl^-}$$

$$(\mathrm{TNP{\cdot}NRR'})^- + \mathrm{RR'NH_2^+} + \mathrm{Cl^-} \overset{K_{Cl^-}}{\rightleftharpoons} \mathrm{RR'NH_2^+ \cdots Cl^-}$$

Scheme 3.

here are smaller than those observed with the substrate 2,4,6-trinitrobenzyl chloride,[1] where 0.1M-chloride ion was used. The value for K_{Cl^-} of *ca.* 10 l mol^{-1} obtained previously [1] would with a chloride concentration of 0.01M give rise to a 10% increase in values of $K_{c,1}$ and $K_{c,3}$. This is in line with the increases observed in Table 11. The main effect of chloride ions on rate coefficients is to lower the values for the rate coefficients, k_{AmH^+}, for reaction of substituted ammonium ions with anionic adducts. In the following discussion we shall use values obtained using perchlorate salts.



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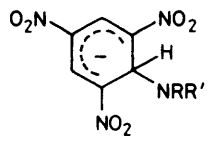


(8)

Reaction at Unsubstituted Ring Positions.—In Table 12 we compare data for formation of adducts of structure (4) with those for formation of adducts (7) and (8) respectively from 2,4,6-trinitrobenzyl chloride and 1,3,5-trinitrobenzene. Since reaction occurs in each case at an unsubstituted ring position steric factors *at the reaction centre* should be similar for the three substrates. Thus values of k_3 measuring the rate of amine attack and values of $K_{c,3}$ measuring the stabilities of the adducts decrease in the order piperidine > n-butylamine > benzylamine, which is that expected from the relative basicities of the amines.[26-29] Before a comparison of the value of these parameters for the three different nitro-compounds is made, it must be stated that the data for TNP refer to an ionic strength of 0.01M whereas those for TNB and TNBCl were measured with 0.1M-salt. Values of k_3 are not expected to vary with ionic strength,[1,17,18] but the values of $K_{c,3}$, which relate to the formation of ionic products from neutral reagents, will increase with increasing ionic strength. We estimate that if activity coefficients follow Debye–Hückel theory, changing the salt concentration from 0.01 to 0.1M will increase K_c values by a factor of 2. Values of k_{Am} will be increased and values of k_{AmH^+} reduced as the ionic strength is increased.

Table 13. Summary of kinetic and equilibrium data for amine attack at the 1-position of 2,4,6-trinitrophenetole in DMSO at 25 °C

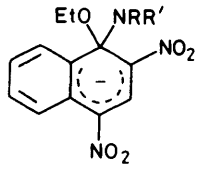
	n-Butylamine	Benzylamine	Piperidine [a]
k_1/l mol^{-1} s^{-1}	250	95	(1 800)
$K_{c,1}$/l mol^{-1}	50 000	4 700	600
$(k_{-1}k_{AmH^+}/k_{Am})$/s^{-1}	0.005 [b]	0.020 [b]	(3) [b]
k_{AmH^+}/l mol^{-1} s^{-1}	>50	>60	9
K_1k_{Am}/l^2 mol^{-2} s^{-1}	>2.5 × 10^6	>3 × 10^5	5 600
(k_{Am}/k_{-1})/l mol^{-1}	>10 000	>3 000	(3)
k_4/l mol^{-1} s^{-1}	8.3	2.6	Very slow reaction

[a] Values in parentheses depend critically on value taken for $K_{c,3}$, and should be regarded only as 'best estimates'. [b] Since values of k_{AmH^+}/k_{Am} will not vary greatly with the nature of the amine (ref. 17) these values give approximately the ratios of k_{-1} values for the three amines.

If allowance is made for ionic strength effects, values of k_3 and $K_{c,3}$ are, for a given amine, very similar for TNP and TNBCl. Both sets of values are lower by at least an order of magnitude than corresponding values for reaction with TNB. The inductive electron withdrawal of the OEt group (or CH_2Cl group) might be expected to enhance the stabilities of the 3-adducts formed from TNP (or TNBCl) relative to TNB. However the steric effect of the substituent is probably the major factor. Thus the crystal structure [30] of TNP shows that the 2- and 6-nitro-groups are rotated from the ring plane by 32 and 61°, respectively, so that they cannot exert their maximum electron-withdrawing influence.

Comparison, for a given amine, of the values (or inequalities) of k_{AmH^+} and k_{Am}/k_{-3} show that there is not a wide variation with the nature of the nitro compound. This probably results from the fact that in each case addition is occurring at an unsubstituted ring position. Nevertheless, the values of these parameters are considerably smaller for reaction of the secondary amine piperidine than for reaction of the primary amines. Thus values of k_{AmH^+} are *ca.* two orders of magnitude smaller for the reactions involving piperidine. This is attributable [17] to the greater steric bulk of piperidine which reduces the rate of proton transfer from the piperidinium ion to the anionic adduct. Similarly values of k_{Am} for proton transfer from the zwitterionic intermediate to amine will be reduced when reaction involves the secondary amine. This is a major factor in producing the lower values of k_{Am}/k_{-3} observed for piperidine relative to the primary amines, and accounts for the observation that in the overall equilibrium the proton-transfer step remains rate-determining at much higher base concentrations for secondary than for primary amines.

Reaction at the 1-*Position.*—In Table 13 we summarise the values of parameters for reaction at the ethoxy-substituted ring position. For a given amine the value of the equilibrium constant $K_{c,1}$ is considerably higher than the value of $K_{c,3}$. The values of $K_{c,1}/K_{c,3}$ are 3 300 for n-butylamine, 5 500 for benzylamine, and 22 for piperidine. The polar effect of the ethoxy group at the reaction centre is expected to increase the value of K_1 relative to K_3 and there may also be a small increase in $K_a^z/K_a^{AmH^+}$, the ratio of acidities of zwitterion and substituted ammonium ion. However the major factor is likely to be the relief of steric strain present in the parent [30] when the ethoxy group is twisted from the ring plane during formation of the 1-adducts. This will manifest itself in a large value for K_1/K_3. That the value of this ratio is much lower for reaction with the secondary amine piperidine than for reaction with the primary amines probably indicates that the adduct (5; NRR′ = NC_5H_{10}), where two bulky groups are at C-1, is itself subject to steric strain. It is noteworthy that in the reaction of 2,4,6-trinitrobenzyl chloride with piperidine we were unable to observe attack at the 1-position [1] presumably because of steric strain.



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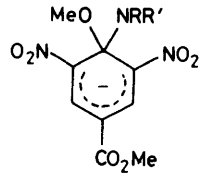

(10)

As has been noted in related systems [1,22,23] rate coefficients, k_1, for attack at the 1-position are considerably lower than corresponding values of k_3 for attack at the unsubstituted 3-position. Since values of K_1/K_3 are large this indicates that for a given amine values of k_{-1} will be several orders of magnitude smaller than values of k_{-3}.

The susceptibility of adduct formation to base catalysis depends on the value of k_{Am}/k_{-1}. If at a given amine concentration $k_{Am}[Am] \gg k_{-1}$ then base catalysis is not observed. This is the situation which applies to our measurements with the primary amines n-butylamine and benzylamine and may be attributed to the low values of k_{-1}. Nevertheless with piperidine our results indicate that formation of the 1-adduct is subject to catalysis by piperidine and we estimate that k_{Am}/k_{-1} is reduced to *ca.* 3. The data of row 3 of Table 13 indicate that k_{-1} for reaction with piperidine will be much greater than for reaction with the primary amines, the bulky piperidine being expelled more rapidly. There is evidence also that the proton transfer between zwitterion and amine, k_{Am}, is considerably reduced for reaction with the secondary amine. Thus we were able to determine a value of 9 l mol^{-1} s^{-1} for k_{AmH^+}, the rate coefficient for protonation of (5; NRR′ = NC_5H_{10}) by piperidinium ions. This very low value, *ca.* 20 times smaller than the corresponding value for reaction at the unsubstituted position (Table 12), results from the severe steric congestion around the 1-position. The value is lower than those for reaction involving primary amines. Hence, since the value of $K_a^z/K_a^{AmH^+}$ is not expected to show large variations with the nature of the amine,[17] the value of k_{Am} ($=k_{AmH^+}K_a^z/k_a^{AmH^+}$) will be smaller for the reaction with piperidine than with primary amines.

As has been observed in related systems [8,10,31] the value of k_4, the rate coefficient for acid-catalysed expulsion of the leaving group, is much lower for reaction with piperidine than for reaction with the primary amines. The result is that the adduct (5; NRR′ = NC_5H_{10}) remains in solution for several hours with little decomposition. The reason for this increased stability is almost certainly steric in origin. The k_4 step involves proton transfer to the ethoxy group of the anionic intermediate coupled with rotation of the piperidine moiety into the ring plane. The rate of proton transfer will be reduced by steric congestion and there is evidence [8,19] for unfavourable stereoelectronic/conformational effects when the transition state contains the piperidine group.

Comparison with Related Reactions.—In Table 14 we compare our data with those for reaction with amines of 1-ethoxy-2,4-dinitronaphthalene [8] and methyl 4-methoxy-3,5-dinitrobenzoate.[31] In each case nucleophilic substitution of the alkoxy group proceeds through detectable intermediates whose structures are respectively (5), (9), and (10). The values of the equilibrium constant $K_{c,1}$ decrease in the order (5) > (9) > (10), largely reflecting the electron-withdrawing ability of the ring substituents.[22] Values of k_1 decrease in the same order and it is expected that k_{-1} values will increase in this

Table 14. Comparison of data for attack at the 1-position of 2,4,6-trinitrophenetole, 1-ethoxy-2,4-dinitronaphthalene, and methyl 4-methoxy-3,5-dinitrobenzoate

		Adduct (5)	Adduct (9) [a]	Adduct (10) [b]
k_1/l mol^{-1} s^{-1}	n-Butylamine	250	31.8	
	Piperidine	1 800	240	100
$K_{c.1}$/l mol^{-1}	n-Butylamine	50 000	540	
	Piperidine	600	1.55	0.083
$(k_{-1}k_{AmH^+}/k_{Am})$/s^{-1}	n-Butylamine	0.005	0.059	
	Piperidine	3	154	1 200
(k_{Am}/k_{-1})/l mol^{-1}	n-Butylamine	>10 000		
	Piperidine	3	>20 [c]	0.28

[a] From refs. 8 and 10. [b] From ref. 31. [c] Estimated from ref. 8.

order. The value of k_{Am}/k_{AmH^+} ($\equiv K_a^z/K_a^{AmH^+}$) reflects the acidity of the zwitterionic intermediates relative to that of the corresponding substituted ammonium ions and will also depend on the electron-withdrawing ability of ring substituents. We have previously estimated a value of 500 for this quantity in a trinitro-activated compound,[17] and lower values are expected in the formation of (9) and (10). These changes coupled with the increases expected in values of k_{-1} are reflected in the increases in $k_{-1}k_{AmH^+}/k_{Am}$ along the series (5), (9), (10).

Values of k_{Am}/k_{-1} are lower in the formation of (5) and (10) than in the formation of (9). A major factor here is likely to be a reduction in k_{Am} as the reaction centre becomes increasingly sterically crowded.[1,31] The consequence is that the formation of (5) and (10) is more susceptible to base catalysis than is the formation of (9).

In conclusion, our results indicate that increased steric crowding at the reaction centre, engendered for example by a change from primary amines to piperidine, results in (i) a reduction in the rate of proton transfer from zwitterionic intermediates to amine catalyst; and (ii) slower leaving group departure. There is evidence [18] that the first of these factors may be less severe in aqueous or partially aqueous media where proton transfer may proceed *via* interstitial water molecules. However both these factors will increase the probability of the observation of base catalysis during nucleophilic substitution reactions.

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