The Stabilities of Meisenheimer Complexes. Part 38.[1] Kinetic and Equilibrium Studies of the Reactions of 2,2',4,4',6,6'-Hexanitrostilbene with Aliphatic Amines in Dimethyl Sulphoxide

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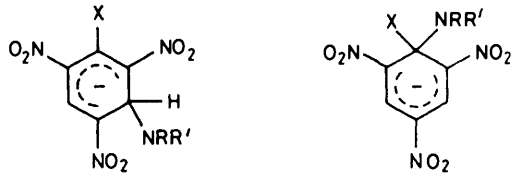
Kinetic and equilibrium data are reported for the reactions of 2,2',4,4',6,6'-hexanitrostilbene (HNS) with four aliphatic amines in dimethyl sulphoxide, and are compared with those for related aromatic nitro-compounds. With each amine the most rapid reaction involves σ-adduct formation by attack at the 3(3')-positions. With the primary amines, n-butylamine and benzylamine, isomerisation to the thermodynamically more stable 1(1')-adducts occurs. However, with the secondary amines piperidine and pyrrolidine, attack at the 1(1')-positions is not observed, and this is attributed to their high steric requirements. It is shown that the formation of σ-adducts may involve rate-limiting proton transfer from zwitterionic intermediates to amine. A slow reaction is observed between HNS and each amine and is likely to involve amine attack at the olefinic bond.

The reactions of 1-substituted 2,4,6-trinitrobenzenes with aliphatic amines in dimethyl sulphoxide (DMSO) may result in the reversible formation of the isomeric σ-adducts[2] (1) and (2). Studies with compounds containing the substituents X = H,[3-6] CH_2Cl,[7] CH_2CH_2picryl,[1] and OEt[8] have shown that attack at the unsubstituted position to give (1) is kinetically favoured. With primary amines isomerisation to the thermodynamically more stable adducts of structure (2) follows. However, when X is a sufficiently bulky group[1,7] (CH_2Cl, CH_2CH_2picryl) adducts of structure type (2) are not observed with the secondary amines piperidine and pyrrolidine; this has been attributed to the steric congestion that would result from the presence of two large groups at the 1-position. Nucleofugic X groups, such as OEt, may be expelled to yield the products of nucleophilic substitution.[8-11]

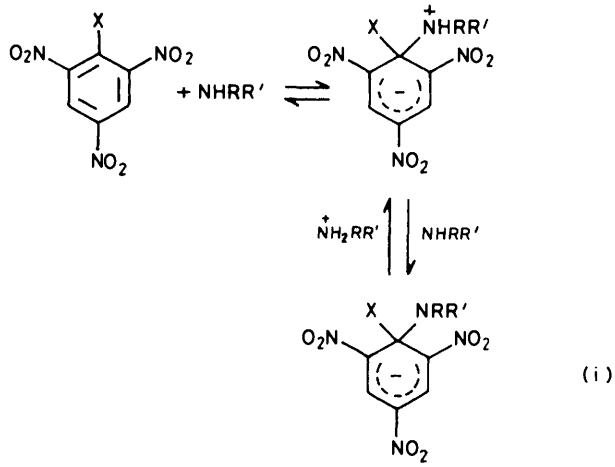
The mechanism of σ-adduct formation involves[3-6] a zwitterionic intermediate that may transfer a proton to a second amine molecule, equation (i). Kinetic studies in DMSO have shown that this proton-transfer step may be rate determining. Reduction of the values of rate constants for proton transfer below those expected for diffusion-controlled reaction has been attributed to steric effects which are particularly large when reaction involves secondary amines and/or when X is a bulky substituent.[5-8]

We report here a continuation of our studies involving the reactions of 2,2',4,4',6,6'-hexanitrostilbene (HNS) with amines in DMSO. Our interest derives from the commercial importance of HNS as a thermally stable explosive,[12] and from one method of its preparation involving reaction of 2,2',4,4',6,6'-hexanitrobibenzyl with amines.[9,13]

The presence in HNS of two picryl rings allows the ready formation of di-adducts and we have identified the major pathways shown in the Scheme. These involve reaction at unsubstituted ring positions, substituted ring positions, and at the olefinic bond. For simplicity we have not included in this Scheme the free amine molecules, ammonium ions, or zwitterionic intermediates.



(1) (2)

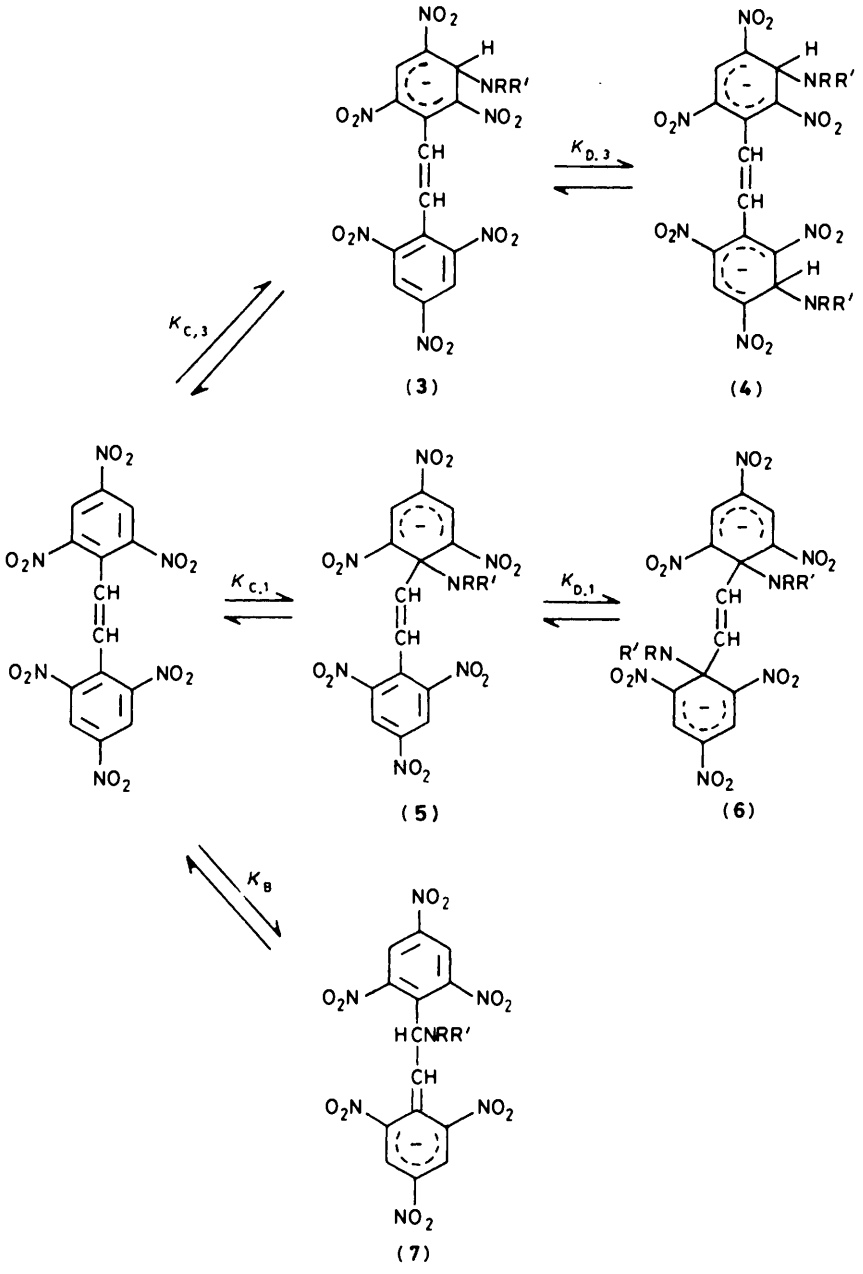


(i)

Experimental

HNS, m.p. 324 °C, was supplied by the Ministry of Defence; this is the *trans*-isomer. Amines, amine salts, and DMSO were prepared and/or purified as described previously.[7,8] ^{1}H N.m.r. spectra were recorded with a Varian EM 360L instrument using tetramethylsilane as the internal reference.

Kinetic and equilibrium measurements were made with freshly prepared solutions of reagents using a Hi-Tech SF 3L stopped-flow spectrophotometer or a Pye Unicam SP8-100 recording spectrophotometer. All rate measurements were made under first-order conditions. For reactions of HNS with amines in the absence of added salts a sufficient excess of amine was used to ensure >95% conversion into the product at equilibrium. For reactions with buffers (amine plus amine salt) the buffer components were in a large excess over the HNS concentration. Rate coefficients at 25 °C are the mean of five separate determinations and are precise to ±5%.



Scheme.

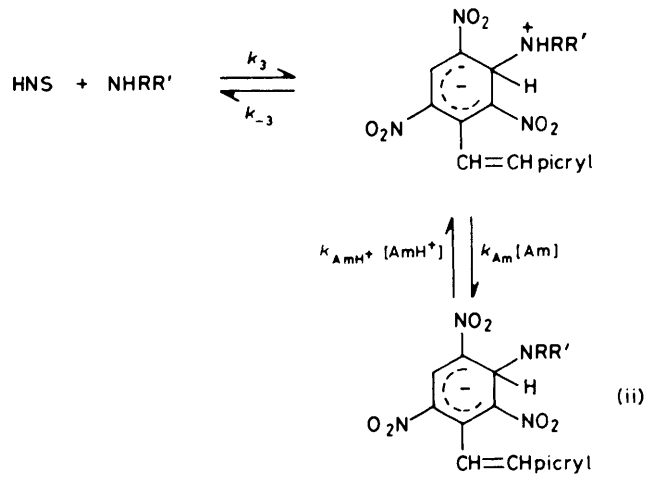
Results

Reactions with Pyrrolidine.—The visible spectra of HNS (2×10^{-5}M) in DMSO containing pyrrolidine indicate the rapid formation of σ-adducts. At amine concentrations <0.01M maxima are at 450 and 530 nm and the molar absorptivity, 2×10^4 l mol^{-1} cm^{-1} at 450 nm, is that expected [1,3] for an adduct of 1:1 stoicheiometry. At higher amine concentrations there is evidence for further interaction to give the di-adduct. Thus with 0.1M pyrrolidine the maxima have shifted to 455 and 515 nm and the molar absorptivity, at 455 nm, has increased to *ca.* 4×10^4 l mol^{-1} cm^{-1}. There is a slow increase in absorption at 650 nm, which may indicate slow formation of the di-anion of HNS by two-electron transfer from the amine or from the σ-adduct.[1,14]

Spectra were also recorded with amine in the presence of 0.1M pyrrolidinium perchlorate. The presence of the salt inhibits σ-adduct formation, *cf.* equation (ii), and here there is slow reversible formation of a species having a single broad absorption with a maximum at 500 nm. By analogy with the reaction of HNS with alkoxides,[15] this is reasonably attributed to attack at the olefinic bond to give (7; NRR′ = NC_4H_8).

Kinetic measurements were made of the σ-adduct-forming reaction and of attack at the double bond. We limited measurements of the former reaction to solutions where the major product was the 1:1 adduct and there was little 1:2 adduct formed. In the discussion we shall show that our data accord better with attack at the 3-position to give (3; NRR′ = NC_4H_8) than with formation of (5; NRR′ = NC_4H_8).

The general kinetic expression relating to the reactions of equation (ii) is given [1,5] by equation (iii). Division by k_{-3} gives equation (iv). The equilibrium constant $K_{C,3}$ is defined by equation (v).



$$k_{obs} = \frac{k_3 k^{A}_{m}[Am]^2 + k_{-3}k_{AmH^+}[AmH^+]}{k_{-3} + k_{Am}[Am]} \quad \text{(iii)}$$

$$k_{obs} = \frac{K_3 k_{Am}[Am]^2 + k_{AmH^+}[AmH^+]}{1 + k_{Am}[Am]/k_{-3}} \quad \text{(iv)}$$

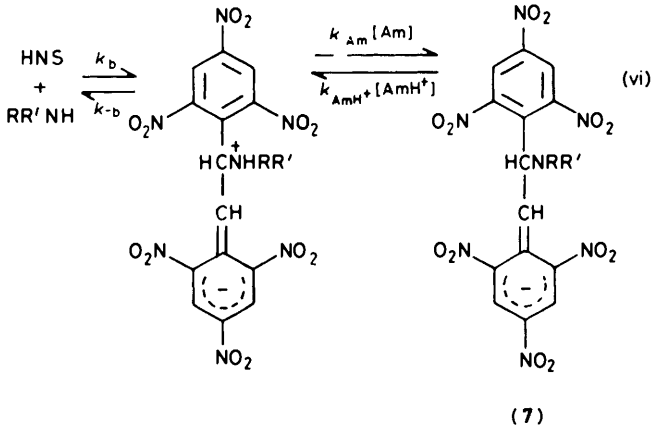
$$K_{C,3} = \frac{k_3}{k_{-3}}\frac{k_{Am}}{k_{AmH^+}} = \frac{[(3)]\ [AmH^+]}{[HNS]\ [Am]^2} \quad \text{(v)}$$

The data in Table 1 accord with equation (iv) with the parameters K_3k_{Am} 7.5 × 10^5 l^2 mol^{-2} s^{-1}, k_{AmH^+} 2 100 l mol^{-1} s^{-1}, and k_{Am}/k_{-3} 21 l mol^{-1}. Combination of the former two values gives a value for $K_{C,3}$ of 360 l mol^{-1} in good agreement with that obtained from equilibrium absorbances.

We assume that (7) will be formed, as shown in equation (vi), by attack of amine at the double bond followed by transfer of the excess proton. The rate expression for this reaction, after allowing for the prior formation of the 3-adduct (3), is given by equation (vii). When $k_{Am}[Am] \gg k_{-b}$ this reduces to equation (viii), and if the reverse reaction is very slow compared with the forward reaction we obtain equation (ix).

The data in Table 2, measured using a conventional spectrophotometer, accord with equation (ix). This indicates that under the conditions used, attack of amine at the double bond is rate limiting, and the proton-transfer step is not kinetically significant. The absorbances at completion of all runs in Table 2 were almost identical. The implication is that virtually complete conversion into (7) is achieved in each case, indicating a high value for K_B. In agreement with this, our data indicate that the rate of the reverse reaction is negligibly small.

Reaction with Piperidine.—The visible spectra obtained in the presence of piperidine show features basically similar to those observed with pyrrolidine. However, formation of (7; NRR' = NC_5H_{10}) was inconveniently slow and was accompanied by irreversible processes. Hence we limited kinetic measurements to the initial rapid reaction giving a σ-adduct with maxima at 450 and 520—530 nm. As with the reaction involving pyrrolidine the data accord better with attack at the 3-position than at the 1-position. Results are given in Table 3 for reaction with piperidine alone and with piperidine in the presence of piperidinium perchlorate. Work with related compounds[1,7] has shown that the proton-transfer step in equation (ii) is slower with piperidine than pyrrolidine. When $k_{-3} \gg k_{Am}[Am]$ the rate expression of equation (iii) reduces to equation (x). Data in Table 3 can be interpreted by equation (x) with values for K_3k_{Am}



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

$$k_{obs} = \frac{k_b[Am]}{1 + K_{C,3}\frac{[Am]^2}{[AmH^+]}} + \frac{k_{-b}k_{AmH^+}[AmH^+]}{k_{Am}[Am]} \quad \text{(viii)}$$

$$k_{obs} = \frac{k_b[Am]}{1 + K_{C,3}\frac{[Am]^2}{[AmH^+]}} \quad \text{(ix)}$$

$$k_{obs} = K_3k_{Am}[Am]^2 + k_{AmH^+}[AmH^+] \quad \text{(x)}$$

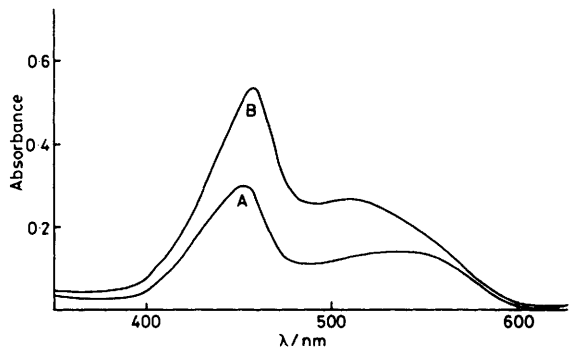


Figure. Visible spectra of HNS (1 × 10^{-5}M) in DMSO containing 0.1M n-butylammonium chloride and, (A) 0.005M n-butylamine and (B) 0.1M n-butylamine

of 4 × 10^4 l^2 mol^{-2} s^{-1} and k_{AmH^+} 270 l mol^{-1} s^{-1}. Combination of these values gives $K_{C,3}$ 150 l mol^{-1}, in good agreement with values obtained from equilbrium absorbances. Our data allow a maximum limit of 5 to be set for the ratio k_{Am}/k_{-3}.

Reaction with n-Butylamine.—The visible spectra shown in the Figure indicate the formation of σ-adducts. At low amine concentrations (0.001M) maxima are at 452 and 530 nm. With increasing amine concentrations the maxima shift to 460 and 510 nm and the molar absorptivity increases to *ca.* 6 × 10^4 l mol^{-1} cm^{-1}. This high value indicates formation of a di-adduct.[1,3] The ^{1}H n.m.r. spectra are in accord with the

Table 1. Kinetic and equilibrium data for σ-adduct formation from HNS and pyrrolidine in DMSO at 25 °C

[Pyrrolidine]/M	[Pyrrolidinium perchlorate][a]/M	k_{obs}/s^{-1}	k_{calc}[b]	Absorbance (450 nm)[c]	$K_{C,3}$[d]/l mol^{-1}
0.004	0	11.5	11.1	0.042	
0.005	0	18.6	17.0	0.042	
0.006	0	24	24	0.043	
0.008	0	40	41	0.042	
0.010	0	60	62	0.042	
0.006	0.002	27	28	0.034	240
0.006	0.004	31	31	0.031	320
0.006	0.007	37	37	0.024	260
0.006	0.010	43	43	0.022	300
0.006	0.020	59	61	0.016	330
0.001	0.01	21	21	0.002	
0.002	0.01	22	23	0.004	300
0.004	0.01	29	30	0.014	310
0.006	0.01	43	43	0.022	300
0.008	0.01	58	59	0.028	310
0.010	0.01	80	79	0.032	320
0.001	0.02	41	42		
0.002	0.02	42	43		
0.004	0.02	52	50	0.009	350
0.008	0.02	76	77	0.022	360
0.01	0.02	102	97	0.027	360

[a] Ionic strength, 0.1M, with tetraethylammonium perchlorate. [b] Calculated from equation (iv) with K_3k_{Am} 7.5 × 10^5 l^2 mol^{-2} s^{-1}, k_{AmH^+} 2 100 l mol^{-1} s^{-1}, and k_{Am}/k_{-3} 21 l mol^{-1}. [c] Measured at the completion of the rapid colour-forming reaction. [d] Calculated as $A_{450}[AmH^+]/(0.042 - A_{450})[Am]^2$, A = absorbance.

Table 2. Kinetic data for slow addition of pyrrolidine to the olefinic bond of HNS to give (7). All solutions contain 0.1M pyrrolidinium perchlorate

[Pyrrolidine]/M	10^4k_{obs}/s^{-1}	10^4k_{calc}[a]
0.0005	2.5	2.6
0.001	6.2	5.3
0.002	12	10
0.003	12	15
0.004	16	20
0.006	30	28
0.008	30	34
0.010	38	38
0.020	46	43

[a] Calculated from equation (ix) with k_b 0.52 l mol^{-1} s^{-1} and $K_{C,3}$ 360 l mol^{-1}.

formation of adducts by attack at the 1(1′)-positions. The spectrum of HNS (0.02M) in [$^2H_6$]DMSO shows two bands with intensity ratio 2:1 at δ 9.13 (ring protons) and δ 7.15 (olefinic protons). In the presence of two molecular equivalents of amine, three bands of equal intensity are observed at δ 9.00, 8.50, and 6.63 attributed to (**5**; R = H, R′ = n-butyl). With excess of amine two bands are observed at δ 8.37 (ring protons) and δ 6.60 (olefinic protons) indicating the formation of (**6**; R = H, R′ = n-butyl).

Values of the equilibrium constants $K_{C,1}$ and $K_{D,1}$, defined by equations (xi) and (xii), were determined to be 4 500 and 65 l mol^{-1}, respectively, using the absorbances (455 nm) in Table 4.

$$K_{C,1} = \frac{[5][AmH^+]}{[HNS][Am]^2} \quad (xi)$$

$$K_{D,1} = \frac{[6][AmH^+]}{[5][Am]^2} \quad (xii)$$

$$[HNS]_{stoich} = [HNS] + [5] + [6] \quad (xiii)$$

Our calculation uses the condition of material balance, equation (xiii), and assumes that at 455 nm the molar absorptivity of the 1:1 adduct is half that of the 1:2 adduct.

Kinetic measurements were limited to low n-butylamine concentrations where only adducts of 1:1 stoicheiometry were observed. Two fast processes were observed on the stopped-flow time-scale. These are taken to be rapid attack at the 3-position to give (**3**; R = H, R′ = n-butyl) followed by isomerisation to (**5**; R = H, R′ = n-butyl). The general rate expression for reaction at the 3-position is given by equation (iii). In the absence of added n-butylammonium salt values of k_{obs} increase linearly with amine concentration. This indicates that the condition $k_{Am}[Am] \gg k_{-3}$ applies so that equation (iii) contracts to equation (xiv). The value obtained for k_3 is

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

5 300 ± 300 l mol^{-1} s^{-1}. In solutions containing 0.1M n-butylammonium perchlorate the formation of the 3-adduct is too rapid for rate measurements, but the absorbances at completion of this process give (Table 5) a value for $K_{C,3}$ of 145 l mol^{-1}. The rate expression[1] for the slower reaction leading to (**5**; R = H, R′ = n-butyl) is equation (xv); this takes account of

$$k_{obs} = \frac{K_1k_{Am}[Am]^2}{\left(1 + \frac{k_{Am}[Am]}{k_{-1}}\right)\left(1 + K_{C,3}\frac{[Am]^2}{[AmH^+]}\right)} + \frac{k_{AmH^+}[AmH^+]}{\left(1 + \frac{k_{Am}[Am]}{k_{-1}}\right)} \quad (xv)$$

the prior equilibrium forming the 3-adduct. The data in Table 5 allow calculation of values k_1 840 l mol^{-1} s^{-1}, k_{Am}/k_{-1}, 1 600 l mol^{-1}, and k_{AmH^+} 320 l mol^{-1} s^{-1}. Combination of these values gives $K_{C,1}$ 4 200 l mol^{-1}, in good agreement with the value quoted previously.

Visible spectra indicated a very slow process giving a new

Table 3. Kinetic and equilibrium data for σ-adduct formation from HNS and piperidine in DMSO at 25 °C

[Piperidine]/M	[Piperidinium perchlorate]/M	k_{obs}/s^{-1}	k_{calc}[a]	Absorbance[b] (450 nm)	$K_{C,3}$/l mol^{-1}
0.004		0.74	0.64	0.042	
0.006		1.7	1.5	0.042	
0.008		2.8	2.6	0.042	
0.010		3.8	4.0	0.042	
0.020		16	16	0.042	
0.030		33	36	0.042	
0.010	0.10	31	31	0.006	168
0.015	0.10	33	36	0.010	140
0.020	0.10	43	43	0.015	138
0.025	0.10	52	52	0.019	135
0.030	0.10	60	63	0.024	152
0.040	0.10	86	91	0.029	138

[a] Calculated from equation (x) with K_3k_{Am} 4 × 10^4 l^2 mol^{-2} s^{-1}, k_{AmH}, 270 l mol^{-1} s^{-1}. [b] With HNS 1 × 10^{-5}M, measured with 2 mm pathlength cell.

Table 4. Equilibrium data for reaction at the 1(1′)-positions with n-butylamine in DMSO containing 0.1M n-butylammonium perchlorate at 25 °C

[n-Butylamine]/M	Absorbance[a] (455 nm)	Calculated absorbance[b]
0.001	0.0018	0.0020
0.002	0.0066	0.0071
0.004	0.0205	0.0197
0.006	0.0317	0.0295
0.008	0.0373	0.0361
0.01	0.0410	0.0406
0.015	0.0490	0.0480
0.020	0.0516	0.0535
0.030	0.0615	0.0623
0.040	0.0675	0.0694
0.050	0.0757	0.0747
0.060	0.0799	0.0786
0.080	0.0836	0.0836

[a] Measured with stopped-flow spectrophotometer with 2 mm pathlength cell. [b] Calculated from equations (xi)—(xiii) with $K_{C,1}$ 4 500 l mol^{-1}, $K_{D,1}$ 65 l mol^{-1}. Absorbance for complete conversion into di-adduct is 0.0926.

Table 5. Kinetic and equilibrium data for σ-adduct formation from HNS and n-butylamine in DMSO in the presence of 0.1M n-butylammonium perchlorate

[n-Butylamine]/M	Absorbance[a] (455 nm)	$K_{C,3}$/ l mol^{-1}	k_{obs}[c]/s^{-1}	k_{calc}[d]
0.001			13.2	12.9
0.002			9.3	9.0
0.004			7.1	7.2
0.006			7.3	7.4
0.008			7.9	8.0
0.010			8.6	8.8
0.015	0.0092	149	10.2	10.4
0.020			11.8	11.3
0.030	0.0205	141		
0.040	0.0259	151		
0.050	0.0287	145		
0.060	0.0306	142		
0.080	0.0362			

[a] Measured at completion of the rapid colour-forming reaction. Value for complete conversion into the 3-adduct is 0.0366 (Benesi–Hildebrand plot). [b] Calculated as $A_{455}[Am^+]/(0.0366 - A_{455})[Am]^2$. [c] For the slower reaction giving the 1-adduct. [d] Calculated from equation (xv) with k_1 840 l mol^{-1} s^{-1}, k_{Am}/k_{-1} 1 600 l mol^{-1} k_{AmH}, 320 l mol^{-1} s^{-1}, and $K_{C,3}$ 145 l mol^{-1}.

band at *ca.* 500 nm. We take this to be formation of the species (7; R = H, R′ = n-butyl). The rate of this reaction was inconveniently slow for measurement.

Reaction with Benzylamine.—The behaviour observed with benzylamine is qualitatively similar to that found with n-butylamine. Absorbance values (not shown) at completion of the slower adduct-forming reaction lead to values for $K_{C,1}$ of 190 l mol^{-1} and $K_{D,1}$ 0.8 l mol^{-1}.

Again two processes were observed leading to adducts with 1:1 stoicheiometry. Kinetic data for the more rapid reaction measured without added benzylammonium salts accord with equation (xiv) with a value for k_3 of 1 200 ± 200 l mol^{-1} s^{-1}. Data obtained in the presence of benzylammonium perchlorate are given in Table 6. The absorbance values at the completion of the more rapid value give $K_{C,3}$ 7.3 l mol^{-1}; the rate data for the slower reaction leading to the adduct (5; R = H, R′ = benzyl) are fitted by equation (xv) with values for K_1k_{Am} 6.8 × 10^4 l^2 mol^{-2} s^{-1}, k_{AmH}, 310 l mol^{-1} s^{-1}, and k_{Am}/k_{-1} 245 l mol^{-1}.

Discussion

We interpret our data in terms of the Scheme. In the case of reaction with n-butylamine there is n.m.r. evidence that the more stable σ-adducts result from attack at the 1(1′)-positions. The two processes of 1:1 stoicheiometry observed on the stopped-flow time-scale may then be attributed to rapid attack at the 3-position followed by isomerisation to the 1-adduct. By analogy, reaction with the other primary amine, benzylamine, will proceed similarly. With the secondary amines, piperidine and pyrrolidine, n.m.r. measurements were inconclusive. This is possibly due to the presence of traces of free radicals, which broaden the spectrum. With the secondary amines isomerisation of the initially formed adducts was not observed. Our data might, therefore, refer to attack at the 3-position or, alternatively, at the 1-position. Comparison, in Table 7, with data for attack at unsubstituted ring positions clearly indicates the former process. Thus, rate and equilibrium data for reaction of HNS with piperidine and pyrrolidine fit regularly into the pattern for reaction at unsubstituted positions. In particular, values of k_{AmH}, are those expected for attack at the 3-position.[5–7]

After statistical correction, values of the equilibrium constant, $K_{C,3}$, increase in the order HNBB < HNS, TNBCl < TNB for each amine used. The main factor responsible for the lower values, relative to TNB, of the

substituted compounds is probably steric in origin. Bulky substituents at the 1-position will force the nitro-groups at the 2- and 6-positions from the ring-plane, thus reducing their electron-withdrawing capability. Values of k_3, the rate coefficient for amine attack at the 3-position, follow the same order as values of $K_{C,3}$ while values of the ratio $k_3k_{AmH^+}/k_{Am}$ show relatively small changes with substrate. Since the ratio k_{AmH^+}/k_{Am}, which reflects the acidity of the zwitterionic intermediate relative to the acidity of the corresponding substituted ammonium ion, is not likely to show a large variation with the nature of the substrate[5-7] this implies that values of k_{-3} are insensitive to substrate structure. Similarly values of k_{-3} do not vary very much with the nature of the amine, while values of $K_{C,3}$ and also k_3 decrease in the order pyrrolidine > piperidine, n-butylamine > benzylamine. This may indicate that the transition states for amine attack at the 3-position in these compounds are 'product-like.'

Table 6. Kinetic and equilibrium data for σ-adduct formation from HNS and benzylamine in the presence of benzylammonium perchlorate at 25 °C

[Benzylamine]/M	[Benzylammonium perchlorate]/M	Absorbance[a] (450 nm)	$K_{C,3}$[b]	k_{obs}[c]/s^{-1}	k_{calc}
0.004	0.1			17.7	16.2
0.006	0.1			13.3	13.5
0.008	0.1			12.9	11.9
0.01	0.1			11.2	10.9
0.02	0.1			10.2	9.7
0.04	0.1			11.7	11.9
0.06	0.1			14.5	14.3
0.08	0.1			17.0	16.0
0.10	0.1	0.0177	7.3		
0.15	0.1	0.0259	7.2		
0.20	0.1	0.0315	7.5		
0.25	0.1	0.0343	7.1		
0.01	0.01			2.8	2.7
0.01	0.02			3.7	3.7
0.01	0.04			5.5	5.5
0.01	0.06			7.4	7.3
0.01	0.08			8.9	9.1
0.006	0.01			2.2	2.2
0.006	0.02			3.4	3.5
0.006	0.04			5.9	6.0
0.006	0.06			8.6	8.5
0.006	0.08			10.9	11.0

[a] Measured at completion of the rapid colour-forming reaction. Value for complete conversion into 3-adduct is 0.042 (Benesi–Hildebrand plot). [b] Calculated as $A[AmH^+]/(0.042 - A)[Am]^2$. [c] For the slower reaction giving the 1-adduct. [d] Calculated from equation (xv) with K_1k_{Am} 6.8 × 10^4 l^2 mol^{-2} s^{-1}, k_{AmH^+} 310 l mol^{-1} s^{-1}, k_{Am}/k_{-1} 245 l mol^{-1}, and $K_{C,3}$ 7.3 l mol^{-1}.

For reactions with the secondary amines it is possible to measure values for k_{AmH^+}, the rate constant relating to proton transfer between anionic adduct and zwitterion [equation (ii)]. Previously a value of 500 has been justified[4,5] for the ratio k_{Am}/k_{AmH^+}. Hence values of k_{Am} are *ca.* 10^6 l mol^{-1} s^{-1} for reactions involving pyrrolidine and *ca.* 10^5 l mol^{-1} s^{-1} for reactions involving piperidine. That these values are much below those expected for diffusion-controlled reaction has been attributed to the steric difficulty, particularly severe with piperidine, of approach of a bulky amine to the zwitterionic reaction centre.[5-7]

Attack at the 1(1′) *Positions.*—With the primary amines, adducts are observed by attack at the 1(1′)-positions. The values of the equilibrium constant $K_{C,1}$ are higher than the values of $K_{C,3}$, for attack at the 3-position, by factors of 29 for butylamine and 26 for benzylamine. The inductive withdrawal of the CH=CHpicryl substituent at the reaction centre may be partially responsible. However, another factor is likely to be the relief, on attack at the 1-position of steric compression between this substituent and the adjacent nitro-groups. That attack at the 1-position is slower than at the 3-position may be attributed

Table 7. Comparison of kinetic and equilibrium data (statistically corrected) for reaction at unsubstituted ring-positions[a] in DMSO at 25 °C

		Benzylamine	n-Butylamine	Pyrrolidine	Piperidine
k_3/l mol^{-1} s^{-1}	HNBB	275	850	4 000	>2 500
	HNS	600	2 700	18 000	>4 000
	TNBCl	1 000	3 000	17 000	>13 000
	TNB	13 000	45 000	75 000	>2 × 10^5
$K_{C,3}$/l mol^{-1}	HNBB	0.6	13	40	13
	HNS	3.7	73	180	75
	TNBCl	5	73	240	93
	TNB	105	1 000	3 500	2 140
K_3k_{Am}/l^2 mol^{-2} s^{-1}	HNBB			1.5 × 10^5	6 000
	HNS			3.7 × 10^5	20 000
	TNBCl			5.8 × 10^5	26 000
	TNB			1.0 × 10^7	6 × 10^5
(k_{Am}/k_{-3}) (l mol^{-1})	HNBB			40	<2
	HNS			21	<5
	TNBCl			34	<2
	TNB			14	<10
k_{AmH^+}/l mol^{-1} s^{-1}	HNBB			3 900	420
	HNS			2 100	270
	TNBCl			2 400	280
	TNB			3 000	280
($k_{-3}k_{AmH^+}/k_{Am}$) s^{-1}	HNBB	450	70	100	>200
	HNS	160	37	97	>55
	TNBCl	200	41	70	>140
	TNB	125	45	210	>90

[a] Data for HNBB (2,2′,4,4′,6,6′-hexanitrobibenzyl) from ref. 1; for TNBCl (2,4,6-trinitrobenzyl chloride) from ref. 7; and for TNB (1,3,5-trinitrobenzene) from refs. 5 and 6. The measured values for HNBB and HNS have been statistically corrected to allow for the presence, in these compounds, of two picryl rings. Measured values of k_3, $K_{C,3}$, and K_3k_{Am} have been divided by two.

Table 8. Comparison of kinetic and equilibrium data (statistically corrected) for reaction at substituted ring positions[a] in DMSO at 25 °C

		Benzylamine	n-Butylamine
$K_{C,1}$/l mol^{-1}	HNBB	37	580
	HNS	95	2 100
	TNBCl	1 000	23 000
	TNP	4 700	50 000
$K_{D,1}$/l mol^{-1}	HNBB	0.6	17
	HNS	0.8	65
k_1/l mol^{-1} s^{-1}	HNBB	30	75
	HNS	140	420
	TNBCl	230	630
	TNP	95	250
$(k_{-1}k_{AmH\cdot}/k_{Am})$s^{-1}	HNBB	0.8	0.14
	HNS	1.5	0.20
	TNBCl	0.23	0.028
	TNP	0.02	0.005
(k_{Am}/k_{-1}) l mol^{-1}	HNBB	> 1 000	> 5 000
	HNS	245	1 600
	TNBCl	200	2 000
	TNP	> 3 000	> 10 000
$k_{AmH\cdot}$/l mol^{-1} s^{-1}	HNBB	> 800	> 700
	HNS	310	320
	TNBCl	46	55
	TNP	> 60	> 50

[a] Data for HNBB (2,2',4,4',6,6'-hexanitrobibenzyl) from ref. 1; for TNBCl (2,4,6-trinitrobenzyl chloride) from ref. 7; and for TNP (2,4,6-trinitrophenetole) from ref. 8. The measured values of $K_{C,1}$ and k_1 for HNBB and HNS have been divided by two, to allow for the presence of two picryl rings (statistical correction).

to the *F*-strain associated with reaction at the substituted position.[16]

Values of $K_{D,1}$ for formation of di-adducts of structure (**6**) are much smaller than the corresponding values of $K_{C,1}$, showing that even though the picryl rings are separated by two carbon atoms attack on one ring inhibits attack on the second.

Our failure to observe attack at the 1(1')-positions with the secondary amines is likely to be due to steric factors. It is known that secondary amines, particularly piperidine,[10] have high steric requirements so that their attack at the 1-position, which already carries a bulky substituent, is rendered kinetically and/or thermodynamically unfavourable.

In Table 8 we compare equilibrium and kinetic data for reaction of benzylamine and n-butylamine with four substrates. Values of $K_{C,1}$ increase in the order HNBB < HNS < TNBCl < TNP (2,4,6-trinitrophenetole). If the substrates are regarded as 1-substituted 2,4,6-trinitrobenzenes then this order reflects the inductive electron-withdrawal of the 1-substituent, with the ethoxy-group being the most powerful.[17] However, steric effects will also be important since there will be an energy gain as the bulky 1-substituent is rotated from the ring plane. It is not however possible to quantify these factors. It is worth noting that the values observed for attack at an unsubstituted ring position in TNB ($K_{C,3}$ values in Table 7) are similar, for a given amine, to those observed for $K_{C,1}$ for HNS and are larger than $K_{C,1}$ values for HNBB. The implication is that the adducts formed by attack at the 1-positions of HNS and HNBB are still subject to steric strain so that the 2- (and 6-) nitro-groups have not achieved co-planarity with the ring. The failure to observe 1-adducts with the more sterically demanding secondary amines has been mentioned previously.

Values of k_1 for HNBB, HNS, and TNBCl increase in the same order as do values for $K_{C,1}$. However, the value of k_1 for TNP is lower than expected on this basis. Electrostatic repulsion between the electronegative entering group and the ethoxy-substituent may be responsible.[18] Values of k_1 show a rather smaller variation, both with change in substrate and with amine, than do values of the ratio $k_{-1}k_{AmH\cdot}/k_{Am}$. As before, values of the ratio $k_{Am}/k_{AmH\cdot}$ are not expected to vary widely, so that the latter ratios give a measure of k_{-1} values. These values necessarily affect the k_{Am}/k_{-1} ratios, which measure the susceptibility of adduct formation to base catalysis. Relatively low values are observed for HNS and TNBCl, indicating a high susceptibility to catalysis. Values of $k_{AmH\cdot}$ are in Table 8. We expect that values of k_{Am} will be *ca.* 500 times larger.[5-7] Nevertheless, the values will be several orders of magnitude lower than those expected for diffusion-controlled reaction. This may be attributed to the steric difficulty of the approach of the amine molecule to take off the excess of proton from the zwitterionic intermediate. There are several other examples in the literature of slow proton transfers involving nitrogen centres.[19]

Attack at the Olefinic Bond.—Following σ-adduct formation there is observed with each amine a very slow reversible reaction giving rise to species with maxima at *ca.* 500 nm. It seems very likely[15,20-22] that, by analogy with related systems, this involves attack at the double bond to give (**7**) by the mechanism of equation (vi). Kinetic data were obtained for reaction with pyrrolidine and indicate that the rate-limiting step is reaction of substrate with amine with a rate constant of 0.52 l mol^{-1} s^{-1}.

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