

The Stabilities of Meisenheimer Complexes. Part 37.¹ Kinetic and Equilibrium Studies of the Reactions of 2,2',4,4',6,6'-Hexanitrobibenzyl with Aliphatic Amines in Dimethyl Sulphoxide

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Kinetic and equilibrium data are reported for the reversible reactions of 2,2',4,4',6,6'-hexanitrobibenzyl (HNBB) with aliphatic amines in dimethyl sulphoxide, leading either to σ -adduct formation or to transfer of methylene protons to the base. The most rapid reaction observed with the primary amines n-butylamine and benzylamine and with the secondary amines piperidine and pyrrolidine is attack at the 3(3')-positions of the substrate. With the primary, but not the secondary amines, this is followed by isomerisation to the thermodynamically preferred 1(1')-adducts. Slow formation of the blue dianion (7) is observed with the primary and secondary amines and with DABCO. Analysis of the kinetic data indicates that two pathways for the production of (7) involve rate-determining attack of amine on the parent, or on the σ -adducts (2) or (4).

Several studies have been reported of the reversible reactions of aromatic nitro-compounds with aliphatic amines in dimethyl sulphoxide (DMSO). The modes of interaction depend on the substrate and include (i) σ -adduct formation, observed for example with 1,3,5-trinitrobenzene²⁻⁵ (TNB), 2,4,6-trinitrobenzyl chloride (TNBCl)^{6,7} and 2,4,6-trinitrotoluene (TNT)⁶ and (ii) transfer of a side-chain proton,^{6,7} observed with TNBCl and TNT. The reactions of ring-activated alkyl aryl ethers with amines may result in irreversible substitution of the alkoxy substituent *via* observable σ -adduct intermediates.⁸⁻¹²

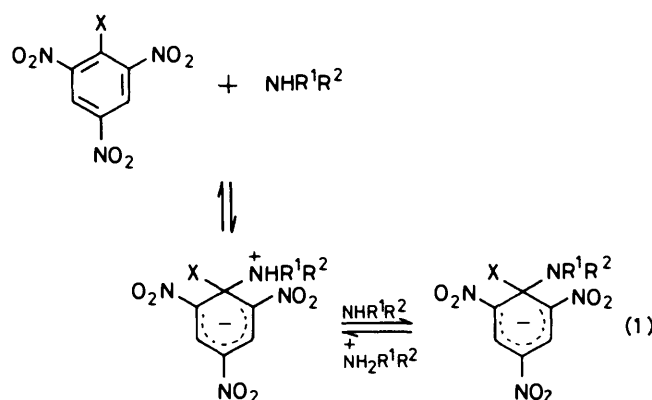
σ -Adduct formation occurs [equation (1)] *via* zwitterionic intermediates and kinetic studies have shown that proton transfer from the zwitterion to amine may be rate determining.³⁻⁵ Reduction of the values of rate constants for proton transfer below those expected for diffusion-controlled reaction has been attributed to steric effects which are particularly severe for reactions involving secondary amines and/or when X is a bulky substituent.^{3,7,12}

Here we report kinetic and equilibrium data for reactions of 2,2',4,4',6,6'-hexanitrobibenzyl (HNBB) (1) with the amines DABCO, piperidine, pyrrolidine, n-butylamine, and benzylamine in DMSO. The reaction has practical significance in that dehydrogenation of HNBB in basic DMSO leads to the commercially important product 2,2',4,4',6,6'-hexanitrostilbene (HNS).^{13,14} The presence of two trinitro-activated rings encourages the formation of dianionic species and we shall interpret our data according to the Scheme in which we have not, for compactness, included the free amine molecules, ammonium ions, or zwitterionic intermediates. This Scheme is clearly a simplification in that we have not included mixed diadducts formed by attack at the 1- and 3'-positions. It does, however, represent the major pathways we have observed. We shall draw attention to an additional pathway for formation of the deprotonated species (7) involving rate-limiting attack of amine on the σ -adducts (2) or (4).

Experimental

HNBB, m.p. 218–220 °C (lit.,¹⁵ 218–220 °C) was provided by the Ministry of Defence. Amines, amine salts, and DMSO were prepared and/or purified as before.^{7,12} ¹H N.m.r. measurements were made with a Varian EM 360L instrument using tetramethylsilane as internal reference.

Kinetic and equilibrium measurements were made with

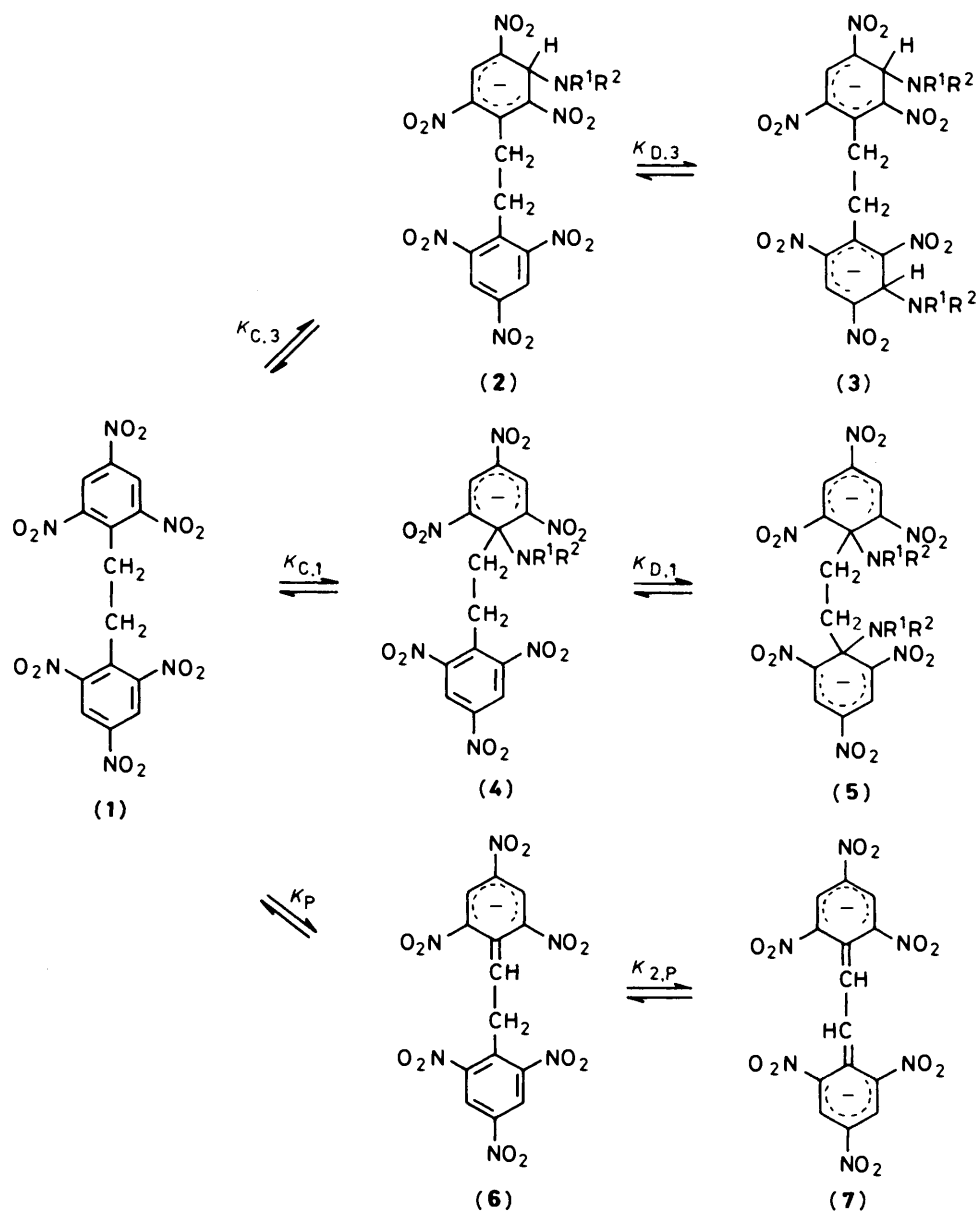


freshly prepared solutions of reagents by using a Hi-Tech SF3L stopped-flow spectrophotometer or a Pye-Unican SP8-100 recording spectrometer. All rate measurements were made under first-order conditions. For reactions of HNBB with amines sufficient excess of amine was used so that >95% conversion into product was achieved at equilibrium. For reactions with buffers (amine plus amine salt) the buffer components were in large excess of the HNBB concentration. In Tables 1–15 the stated concentrations of amines and ammonium salts are accurate to $\pm 2\%$, the rate coefficients which are the mean of five separate determinations are precise to $\pm 5\%$, and the optical densities are precise to $\pm 2\%$. Calculated values, where given, are quoted with the same precision as the observed values with which they are compared.

Results

Different types of behaviour were observed with tertiary, secondary, and primary amines so that we shall consider them separately.

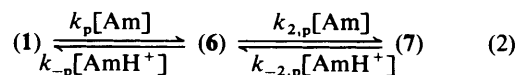
Reaction with DABCO.—The most straightforward case is with the tertiary amine where σ -adduct formation is unlikely.^{2,6} A blue species is produced with maxima in the visible region at 380 (ϵ 1.3×10^4 l mol⁻¹ cm⁻¹) and 620 nm (4.2×10^4). Evidence based on conductance and ¹H n.m.r. measurements has been presented separately¹⁶ showing that this is the dianion



Scheme.

(7) formed by transfer of two side-chain protons. Although reaction is likely to proceed through the monoanion (6), as shown in equation (2), there is no evidence from stopped-flow

kinetic expression given by equation (3) which simplifies to equation (4) when the condition $k_{2,p}[\text{Am}] \gg k_{-p}[\text{AmH}^+]$ applies.



$$k_{\text{obs}} = \frac{k_p k_{2,p} [\text{Am}]^2 + k_{-p} k_{-2,p} [\text{AmH}^+]^2}{k_{2,p} [\text{Am}] + k_{-p} [\text{AmH}^+]} \quad (3)$$

$$k_{\text{obs}} = k_p [\text{Am}] + \frac{k_{-p}}{K_{2,p}} \frac{[\text{AmH}^+]^2}{[\text{Am}]} \quad (4)$$

$$K_p \cdot K_{2,p} = \frac{[(7)] [\text{AmH}^+]^2}{[(1)] [\text{Am}]^2} \quad (5)$$

measurements for a build-up in concentration of this species. Treatment of (6) as a steady-state intermediate leads to the

The rate data in Table 1 are well fitted by equation (4) with the values k_p 1.1 ± 0.1 l mol⁻¹ s⁻¹ and $k_{-p}/K_{2,p}$ 0.01 ± 0.002 l mol⁻¹ s⁻¹. Combination of these values gives a value of 110 for the equilibrium constant, $K_p \cdot K_{2,p}$, for overall conversion of parent dianion as defined by equation (5).

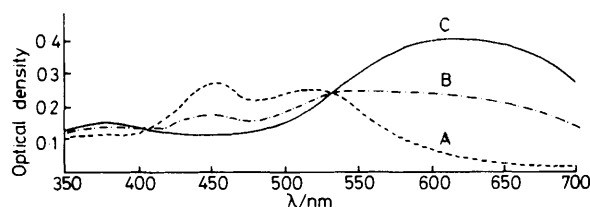
It has been found¹⁷ that the presence of oxygen may accelerate the fading of the blue colour formed in these solutions. However, our measurements using de-gassed solvent and under nitrogen showed that the rates of equilibration of parent and blue species were identical, within experimental error, to those obtained in the presence of air. E.s.r. measurements* on the intensely blue solutions indicated the absence of free radicals from these solutions.

* We thank Dr. B. C. Gilbert, University of York, for these measurements.

Table 1. Rate data for the reaction of HNBB (5×10^{-6} M) with DABCO in DMSO at 25 °C

| [DABCO]/M | [DABCOH ⁺ ·ClO ₄ ⁻]/M | k_{obs}^a/s^{-1} | k_{calc}^b |
|-----------|---|---------------------------|---------------------|
| 0.01 | | 0.011 | 0.011 |
| 0.02 | | 0.021 | 0.022 |
| 0.04 | | 0.042 | 0.044 |
| 0.06 | | 0.064 | 0.066 |
| 0.08 | | 0.082 | 0.088 |
| 0.10 | | 0.100 | 0.11 |
| 0.01 | 0.1 | 0.025 | 0.021 |
| 0.02 | 0.1 | 0.026 | 0.027 |
| 0.04 | 0.1 | 0.044 | 0.046 |
| 0.06 | 0.1 | 0.063 | 0.067 |
| 0.08 | 0.1 | 0.089 | 0.089 |
| 0.10 | 0.1 | 0.110 | 0.11 |
| 0.02 | 0.2 | 0.042 | 0.042 |
| 0.04 | 0.2 | 0.063 | 0.054 |
| 0.06 | 0.2 | 0.079 | 0.073 |
| 0.08 | 0.2 | 0.093 | 0.093 |
| 0.10 | 0.2 | 0.118 | 0.114 |

^a Measured at 600 nm using stopped-flow spectrophotometry. Rates were unaffected by the exclusion of oxygen. ^b Calculated from equation (4) with k_p 1.1 l mol⁻¹ s⁻¹, and $k_{-p}/K_{2,p}$ 0.01 l mol⁻¹ s⁻¹.

Visible spectra of HNBB (1×10^{-5} M) and piperidine (0.05 M) in DMSO after A, 1 min; B, 3 min; C, 7 min

Reaction with Piperidine.—The visible spectra of HNBB in solutions containing piperidine (0.005–0.1 M) show the initial formation of a red species, λ_{max} 450 and 515 nm, followed by conversion into a blue species with maxima 380 and 620 nm, identical to those observed for the product of reaction with DABCO. Spectra are shown in the Figure. With time the blue species fades irreversibly. We interpret these results as σ -adduct formation followed by formation of the dianion (7).¹⁶ Examination of the σ -adduct-forming reaction by stopped-flow spectrophotometry showed that with [piperidine] ≤ 0.01 M a single colour-forming reaction was observed. The extinction coefficient at 450 nm of the species produced was 2.1×10^4 l mol⁻¹ cm⁻¹ which is in the range expected^{2,6} for adducts of

Table 2. Rate and equilibrium data for σ -adduct formation from HNBB (2×10^{-5} M) and piperidine in DMSO at 25 °C

| [Piperidine]/M | [PipH ⁺ ClO ₄ ⁻]/M | [PipH ⁺ Cl ⁻]/M | k_{obs}/s^{-1} | k_{calc}^a | OD ^b | $K_{c,3}/l \text{ mol}^{-1}$ |
|----------------|--|--|-------------------------|---------------------|-----------------|------------------------------|
| 0.006 | | | 0.38 | 0.40 | 0.087 | |
| 0.008 | | | 0.62 | 0.70 | 0.086 | |
| 0.01 | | | 0.94 | 1.1 | 0.088 | |
| 0.02 | | | 4.7 | 4.4 | 0.082 | |
| 0.04 | | | 19 | 18 | 0.082 | |
| 0.06 | | | 41 | 40 | 0.082 | |
| 0.08 | | | 70 | 70 | 0.084 | |
| 0.01 | 0.1 | | 42 | 43 | | |
| 0.02 | 0.1 | | 45 | 46 | 0.009 | 30 |
| 0.03 | 0.1 | | 54 | 52 | 0.018 | 30 |
| 0.04 | 0.1 | | 62 | 60 | 0.027 | 30 |
| 0.05 | 0.1 | | 78 | 70 | 0.034 | 27 |
| 0.06 | 0.1 | | 85 | 82 | 0.043 | 29 |
| 0.01 | | 0.1 | 20 | 20 | 0.005 | 64 |
| 0.02 | | 0.1 | 24 | 23 | 0.017 | 63 |
| 0.03 | | 0.1 | 29 | 29 | 0.032 | 68 |
| 0.04 | | 0.1 | 35 | 36 | 0.044 | 69 |
| 0.05 | | 0.1 | 46 | 46 | 0.050 | 59 |
| 0.06 | | 0.1 | 57 | 59 | 0.056 | 56 |

^a Calculated from equation (8) with $K_3 k_{\text{Am}}$ 1.1×10^4 l² mol⁻² s⁻¹, k_{AmH} 420 l mol⁻¹ s⁻¹ (perchlorate salt), and k_{AmH} 190 l mol⁻¹ s⁻¹ (chloride salt). ^b Measured at 450 nm at completion of the rapid colour-forming reaction with a cell of 2 mm pathlength. ^c Calculated as OD [AmH⁺]/(0.084 - OD)[Am]².

Table 3. Rate data for formation of the blue dianion (7) from HNBB and piperidine in DMSO containing 0.1 M-piperidinium chloride at 25 °C

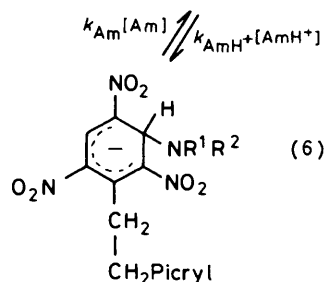
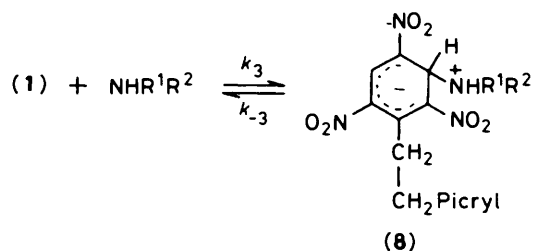
| [Piperidine]/M | $10^2 k_{\text{obs}}/s^{-1}$ | $10^2 k_{\text{calc}}^a$ | $10^2 k_{\text{calc}}^b$ | OD (640 nm) ^c |
|----------------|------------------------------|--------------------------|--------------------------|--------------------------|
| 0.005 | 0.97 | 0.90 | 0.90 | 0.035 |
| 0.01 | 1.75 | 1.70 | 1.71 | 0.035 |
| 0.02 | 2.72 | 2.92 | 2.98 | 0.037 |
| 0.04 | 3.98 | 3.70 | 4.02 | 0.037 |
| 0.06 | 4.08 | 3.50 | 4.14 | 0.038 |
| 0.08 | 3.99 | 3.06 | 4.06 | 0.036 |
| 0.10 | 4.24 | 2.65 | 4.01 | 0.037 |
| 0.15 | 4.43 | 1.92 | 4.16 | 0.037 |
| 0.20 | 4.68 | 1.49 | 4.61 | 0.037 |

^a Calculated from equation (10) with k_p 1.8 l mol⁻¹ s⁻¹, $K_{c,3}$ 58 l mol⁻¹, and $k_{-p}/K_{2,p}$ 0. ^b Calculated from equation (11) with k_p 1.8 l mol⁻¹ s⁻¹, k_p' 0.16 l mol⁻¹ s⁻¹, and $K_{c,3}$ 58 l mol⁻¹. ^c For 5×10^{-6} M-substrate, measured with a 2 mm pathlength cell.

1:1 stoichiometry. At higher piperidine concentrations a slower colour-forming reaction (450 nm) was observed, which we attribute to formation of an adduct with 1:2 stoichiometry. In the presence of added piperidinium salts, which inhibit adduct formation, only the faster process was observed at all piperidine concentrations used.

The 1:1 adduct formed will have either structure (2; NR¹R² = NC₅H₁₀) or (4; NR¹R² = NC₅H₁₀). Unfortunately, n.m.r. measurements were inconclusive. However, we will show later that our kinetic and equilibrium data accord with attack at the 3-position to give an adduct of type (2) and will proceed on that basis.

The general kinetic expression relating to the reactions of equation (6) is given^{3,7} by equation (7). When the proton-transfer step is rate limiting ($k_{-3} \gg k_{\text{Am}}[\text{Am}]$) then we obtain equation (8). The overall equilibrium constant for formation of the adduct (2) is defined by equation (9).



$$k_{\text{obs}} = \frac{k_3 k_{\text{Am}} [\text{Am}]^2 + k_{-3} k_{\text{AmH}^+} [\text{AmH}^+]}{k_{\text{Am}} [\text{Am}] + k_{-3}} \quad (7)$$

$$k_{\text{obs}} = K_3 k_{\text{Am}} [\text{Am}]^2 + k_{\text{AmH}^+} [\text{AmH}^+] \quad (8)$$

$$K_{\text{c},3} = \frac{k_3 \cdot k_{\text{Am}}}{k_{-3} \cdot k_{\text{AmH}^+}} = \frac{[(2)] [\text{AmH}^+]}{[(1)] [\text{Am}]^2} \quad (9)$$

The data in Table 2 are in accord with equation (8). Plots, at constant concentration of amine salt, of k_{obs} versus $[\text{Am}]^2$ are linear with slope ($=K_3 k_{\text{Am}}$) $1.1 \times 10^4 \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$. The intercepts give values for k_{AmH^+} of 420 $\text{l mol}^{-1} \text{ s}^{-1}$ in the presence of the perchlorate salt and 190 $\text{l mol}^{-1} \text{ s}^{-1}$ in the presence of the chloride salt. Combination of the values of these parameters gives values for $K_{\text{c},3}$ of 26 (perchlorate) and 58 l mol^{-1} (chloride), in good agreement with those obtained from equilibrium optical densities. The diversity with respect to the nature of the counterion has been noted in related work^{7,18} and has been attributed to stabilisation of substituted ammonium ions by association with chloride ions, $\text{R}^1\text{R}^2\text{NH}_2^+ \cdots \text{Cl}^-$. The observed approximate doubling of the value of $K_{\text{c},3}$ in the presence of 0.1M-chloride ions is as expected from previous work.⁷

We also made rate measurements of the formation of the blue dianion (7). These provide evidence for production of (7) not only by rate-limiting attack of piperidine on the substrate (1) but also by attack of piperidine on the σ -adduct (2; $\text{NR}^1\text{R}^2 = \text{NC}_5\text{H}_{10}$): Measurements were made by stopped-flow spectrophotometry at 640 nm and are reported in Table 3. The reaction was characterised by a single relaxation time and the optical density values at completion show virtually complete conversion into product at all amine concentrations used.

If we assume that reaction may occur only by attack of piperidine on the parent we obtain the rate expression (10). This is related to equation (4) used with DABCO but takes account of the preliminary rapid formation of the σ -adduct (2). Since conversion into dianion is nearly complete in all solutions used it follows that the second term involving k_{-p} is vanishingly small. Equation (10) fits the data reasonably well up to an amine concentration of 0.04M but then observed values become progressively larger than calculated values. If we allow an additional pathway involving formation of the dianion by rate-limiting amine attack on the adduct (2) we obtain equation (11). Here the final term is the product of k_p' , the rate constant for

Table 4. Kinetic and equilibrium data for σ -adduct formation from HNBB ($2 \times 10^{-5}\text{M}$) and pyrrolidine in DMSO at 25 °C

| [Pyrrolidine]/M | [PyrH ⁺ ClO ₄ ⁻]/ ^a M | $k_{\text{obs}}/$ s ⁻¹ | k_{calc}^b | OD ^c | $K_{\text{c},3}^d/$ l mol ⁻¹ |
|-----------------|--|--------------------------------------|---------------------|-----------------|--|
| 0.008 | | 15.5 | 15.1 | 0.084 | |
| 0.009 | | 18.3 | 18.5 | 0.082 | |
| 0.010 | | 21 | 22 | 0.084 | |
| 0.015 | | 43 | 43 | 0.080 | |
| 0.020 | | 70 | 69 | 0.084 | |
| 0.004 | 0.01 | | | 0.009 | 75 |
| 0.006 | 0.01 | 39 | 40 | 0.017 | 70 |
| 0.008 | 0.01 | 45 | 45 | 0.027 | 74 |
| 0.010 | 0.01 | 50 | 50 | 0.032 | 62 |
| 0.012 | 0.01 | 57 | 57 | 0.043 | 73 |
| 0.015 | 0.01 | 67 | 68 | 0.053 | 76 |
| 0.01 | 0.001 | 23 | 25 | 0.071 | 55 |
| 0.01 | 0.002 | 27 | 28 | 0.066 | 73 |
| 0.01 | 0.004 | 32 | 33 | 0.056 | 80 |
| 0.01 | 0.007 | 41 | 41 | 0.044 | 77 |
| 0.01 | 0.010 | 50 | 50 | 0.034 | 68 |
| 0.01 | 0.020 | 75 | 78 | 0.022 | 71 |

^a Solutions made up to constant ionic strength, $I = 0.1\text{M}$, with tetraethylammonium perchlorate. ^b Calculated from equation (12) with $K_3 k_{\text{Am}} 3.1 \times 10^5 \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$, $k_{\text{Am}}/k_{-3} 40 \text{ l mol}^{-1}$, and $k_{\text{AmH}^+} 3 900 \text{ l mol}^{-1} \text{ s}^{-1}$. ^c Measured at completion of the fast colour-forming reaction at 450 nm with cells of 2 mm pathlength. ^d Calculated from $\text{OD} \cdot [\text{AmH}^+] / (0.084 - \text{OD}) [\text{Am}]^2$.

piperidine attack on (2), and the fractionation of substrate to adduct.

$$k_{\text{obs}} = \frac{k_p [\text{Am}]}{1 + K_{\text{c},3} [\text{Am}]^2 / [\text{AmH}^+]} + \frac{k_{-p} [\text{AmH}^+]^2}{K_{2,p} [\text{Am}]} \quad (10)$$

$$k_{\text{obs}} = \frac{k_p [\text{Am}]}{1 + K_{\text{c},3} [\text{Am}]^2 / [\text{AmH}^+]} + \frac{k_p' K_{\text{c},3} [\text{Am}]^3}{[\text{AmH}^+] (1 + K_{\text{c},3} [\text{Am}]^2 / [\text{AmH}^+])} \quad (11)$$

Our data are fitted well by equation (11) with values of $k_p 1.8 \text{ l mol}^{-1} \text{ s}^{-1}$ and $k_p' 0.16 \text{ l mol}^{-1} \text{ s}^{-1}$.

Reaction with Pyrrolidine.—The visible spectra of HNBB ($2 \times 10^{-5}\text{M}$) and pyrrolidine (0.001–0.5M) in DMSO were quite similar to those observed with piperidine. With pyrrolidine concentrations $< 0.1\text{M}$ a red species with maxima 450 and 530 nm was initially formed ($\epsilon 2.1 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 450 nm), typical of 1:1 adducts. At higher pyrrolidine concentrations the maxima shifted to 455 and 520 nm and the extinction coefficient at 455 nm increased to $4 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ indicating formation of an adduct with 1:2 stoichiometry. At all base concentrations used these initial σ -adduct-forming reactions were followed by conversion into the blue dianion (7) with maxima at 380 and 620 nm.

We limited kinetic measurements to dilute pyrrolidine solutions where the major product initially produced was the 1:1 σ -adduct. As we shall show later our data are in better accord with formation of the adduct (2; $\text{NR}^1\text{R}^2 = \text{NC}_4\text{H}_8$) by attack at the 3-position than with attack at the 1-position to give (4; $\text{NR}^1\text{R}^2 = \text{NC}_4\text{H}_8$). Hence equation (7) will apply to our data. As has been observed in related systems^{4,7} the ratio k_{Am}/k_{-3} has a higher value for reaction with pyrrolidine than for reactions with piperidine so that the condition $k_{-3} \gg k_{\text{Am}} [\text{Am}]$, which leads to equation (8), does not apply. However, our data in

Table 5. Rate data for formation of the blue dianion (7) from HNBB and pyrrolidine in DMSO containing 0.1M-pyrrolidinium perchlorate at 25 °C

| [Pyrrolidine]/ M | $10^2 k_{\text{obs}}/\text{s}^{-1}$ | $10^2 k_{\text{calc}}^a$ | $10^2 k_{\text{calc}}^b$ | OD ^c (640 nm) |
|---------------------|-------------------------------------|--------------------------|--------------------------|-----------------------------|
| 0.005 | 4.0 | 4.1 | 4.1 | 0.024 |
| 0.008 | 4.6 | 5.1 | 5.1 | 0.032 |
| 0.01 | 6.1 | 5.8 | 5.8 | 0.032 |
| 0.02 | 8.5 | 8.7 | 8.8 | 0.036 |
| 0.04 | 10.2 | 10.2 | 11.0 | 0.038 |
| 0.06 | 9.2 | 9.1 | 10.9 | 0.039 |
| 0.08 | 10.7 | 7.7 | 10.3 | 0.033 |
| 0.10 | 10.0 | 6.6 | 10.1 | 0.037 |
| 0.15 | 11.5 | 4.7 | 10.4 | 0.036 |
| 0.20 | 11.7 | 3.5 | 11.2 | 0.036 |

^a Calculated from equation (10) with k_p $5.5 \text{ l mol}^{-1} \text{ s}^{-1}$, $k_{-p}/K_{2,p}$ $0.007 \text{ l mol}^{-1} \text{ s}^{-1}$, and $K_{c,3}$ 75 l mol^{-1} . ^b Calculated from equation (11) with k_p $5.5 \text{ l mol}^{-1} \text{ s}^{-1}$, $k_{-p}/K_{2,p}$ $0.007 \text{ l mol}^{-1} \text{ s}^{-1}$, k_p' $0.4 \text{ l mol}^{-1} \text{ s}^{-1}$, and $K_{c,3}$ 75 l mol^{-1} . ^c For $5 \times 10^6 \text{ M}$ -substrate measured with a 2 mm pathlength cell.

Table 4 are well fitted by equation (12), which follows directly from equation (7), with the values $K_3 k_{\text{Am}}$ $3.1 \times 10^5 \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$, k_{AmH^+} $3900 \text{ l mol}^{-1} \text{ s}^{-1}$, and k_{Am}/k_{-3} 40 l mol^{-1} . Combination of these values leads to a value of $K_{c,3}$ of 79 l mol^{-1} , in good agreement with that obtained from equilibrium optical densities.

$$k_{\text{obs}} = \frac{K_3 k_{\text{Am}} [\text{Am}]^2 + k_{\text{AmH}^+} [\text{AmH}^+]}{1 + k_{\text{Am}} [\text{Am}]/k_{-3}} \quad (12)$$

Data for formation of the blue dianion are in Table 5. With $[\text{pyrrolidine}] < 0.08 \text{ M}$ a good fit is obtained by using equation (10) with the values k_p $5.5 \text{ l mol}^{-1} \text{ s}^{-1}$ and $k_{-p}/K_{2,p}$ $0.007 \text{ l mol}^{-1} \text{ s}^{-1}$. Combination of these quantities gives a value for the equilibrium constant $K_p \cdot K_{2,p}$, defined in equation (5), of 800. As observed in the similar reaction with piperidine the rate data at higher amine concentrations require the use of equation (11) which includes a term involving k_p' . Hence with pyrrolidine, also, there is evidence for formation of the deprotonated species by a pathway involving amine attack on the adduct (2).

Reaction with *n*-Butylamine.—Here there is evidence for all three pathways shown in the Scheme. Visible spectra recorded with a conventional spectrophotometer showed maxima at 460 and 520–530 nm typical of σ -adducts. Conversion into the blue species was slow, especially in the absence of added butylammonium salts, and a ¹H n.m.r. spectrum recorded soon after mixing showed bands of equal intensity at δ 8.38 and 2.33 attributed respectively to the ring and methylene protons of the 1,1'-diadduct (5; $R^1 = \text{H}$, $R^2 = \text{Bu}^n$). Visible spectra were sufficiently stable to allow the measurement of optical densities corresponding to σ -adduct formation. The extinction coefficient at 460 nm of $6 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ corresponds to formation of the diadduct (5). The optical density data reported in Table 6 correspond to step-wise formation of 1:1 and 1:2 adducts and allow the calculation of values for $K_{c,1}$ and $K_{D,1}$ as defined in equations (13) and (14). Values obtained in the presence of 0.1M-

$$K_{c,1} = \frac{[(4)] [\text{AmH}^+]}{[(1)] [\text{Am}]^2} \quad (13)$$

$$K_{D,1} = \frac{[(5)] [\text{AmH}^+]}{[(4)] [\text{Am}]^2} \quad (14)$$

n-butylammonium perchlorate are 1150 and 17 l mol^{-1} , respectively. As found in related work^{4,7,18} specific effects due to chloride ions are present; so that with 0.02M-butylammonium

Table 6. Equilibrium data for σ -adduct formation from HNBB ($2 \times 10^{-5} \text{ M}$) and *n*-butylamine in DMSO containing *n*-butylammonium perchlorate (0.1M) at 25 °C

| [<i>n</i> -Butylamine]/M | OD (460 nm) | OD ^a (calc.) |
|---------------------------|-------------|-------------------------|
| 0.000 97 | 0.010 | 0.007 |
| 0.001 92 | 0.026 | 0.024 |
| 0.003 95 | 0.100 | 0.090 |
| 0.005 90 | 0.164 | 0.172 |
| 0.007 99 | 0.263 | 0.248 |
| 0.009 80 | 0.334 | 0.323 |
| 0.0194 | 0.515 | 0.519 |
| 0.0381 | 0.628 | 0.680 |
| 0.0594 | 0.813 | 0.806 |
| 0.0792 | 0.891 | 0.901 |
| 0.0990 | 0.954 | 0.964 |
| 0.198 | 1.13 | 1.11 |
| 0.396 | 1.16 | 1.17 |
| 0.594 | 1.17 | 1.18 |
| 1.16 | 1.19 | 1.19 |

^a Calculated with values of $K_{c,1}$ 1150 l mol^{-1} , $K_{D,1}$ 17 l mol^{-1} , and with optical densities for complete conversion into 1:1 adduct of 0.595 and into 1:2 adduct of 1.19.

chloride plus 0.08M-tetraethylammonium perchlorate the value of $K_{c,1}$ is increased to 1500 l mol^{-1} , and with 0.1M-butylammonium chloride $K_{c,1}$ has the value 2500 l mol^{-1} .

We limited kinetic measurements to low butylamine concentrations where only adducts of 1:1 stoichiometry were present. Examination by stopped-flow spectrophotometry indicated two processes which we take to be rapid attack at the 3-position to give (2; $R^1 = \text{H}$, $R^2 = \text{Bu}^n$) and attack at the 1-position to give (4; $R^1 = \text{H}$, $R^2 = \text{Bu}^n$). Rate data for the faster process, obtained in solutions without added butylammonium ions, are in Table 7. The equations relevant to this reaction are (6) and (7). Our data correspond to equation (15) which is a limiting form of equation (7) when $k_{\text{Am}} [\text{Am}] \gg k_{-3}$ and when $[\text{AmH}^+]$ is small. We obtain a value for k_3 of $1700 \text{ l mol}^{-1} \text{ s}^{-1}$.

$$k_{\text{obs}} = k_3 [\text{Am}] \quad (15)$$

In the presence of 0.1M-butylammonium perchlorate formation of the adduct (4; $R^1 = \text{H}$, $R^2 = \text{Bu}^n$) were measured. flow methods but the optical density data, in Table 8, give a value for the equilibrium constant $K_{c,3}$ of 25 l mol^{-1} . Rates of formation of the adduct (4; $R^1 = \text{H}$, $R^2 = \text{Bu}^n$) were measured. Treatment of the zwitterionic intermediate in equation (16) as a

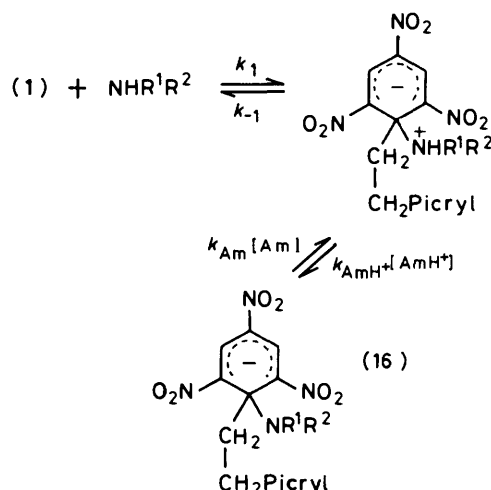


Table 7. Rate data for formation of (2; R¹ = H, R² = Buⁿ) from HNBB (5 × 10⁻⁶M) and n-butylamine in DMSO at 25 °C

| [n-Butylamine]/M | k _{obs} /s ⁻¹ | k _{obs} /[Amine] ^a (l mol ⁻¹ s ⁻¹) | OD (460 nm) |
|------------------|-----------------------------------|--|-------------|
| 0.01 | 17.4 | 1 740 | 0.019 |
| 0.015 | 27 | 1 800 | 0.019 |
| 0.02 | 31 | 1 550 | 0.019 |
| 0.025 | 37 | 1 480 | 0.020 |
| 0.04 | 69 | 1 720 | 0.020 |

^a This corresponds to the value of k₃.**Table 8.** Kinetic and equilibrium data for σ-adduct formation from HNBB (1 × 10⁻⁵M) and n-butylamine in DMSO containing 0.1M-n-butylammonium perchlorate at 25 °C

| [n-Butylamine]/M | OD (460) ^a | K _{c,3} ^b /l mol ⁻¹ | k _{obs} /s ⁻¹ | k _{calc} ^c | OD ^d (460) |
|------------------|-----------------------|--|-----------------------------------|--------------------------------|-----------------------|
| 0.002 | | | 6.7 | 7.3 | 0.0024 |
| 0.004 | | | 4.2 | 4.1 | 0.0071 |
| 0.006 | | | 3.2 | 3.2 | 0.0146 |
| 0.008 | | | 3.0 | 3.0 | 0.0205 |
| 0.010 | | | 2.9 | 2.9 | 0.0255 |
| 0.015 | | | 3.1 | 3.1 | 0.0353 |
| 0.020 | 0.0042 | 29 | 3.5 | 3.4 | 0.0414 |
| 0.030 | 0.0081 | 28 | | | 0.0526 |
| 0.040 | 0.0110 | 23 | 4.8 | 4.7 | 0.0575 |
| 0.060 | 0.0173 | 21 | | | 0.0716 |
| 0.080 | 0.0232 | 22 | | | 0.0800 |

^a At completion of the rapid colour-forming reaction. Value for complete conversion into adduct (2) is 0.040 as determined in a solution containing no added butylammonium perchlorate. ^b Calculated as OD·[AmH⁺]/(0.040 - OD) [Am]². ^c Calculated from equation (18) with k₁ 150 l mol⁻¹ s⁻¹, K_{c,3} 25 l mol⁻¹, and k₋₁k_{AmH}⁺/k_{Am} 0.14 s⁻¹. ^d At completion of the slower colour-forming reaction, giving (4).

steady-state intermediate leads, as shown previously,⁷ to the kinetic expression of equation (17). If k_{Am}[Am] ≫ k₋₁ this reduces to equation (18).

$$k_{\text{obs}} = \frac{k_1 k_{\text{Am}} [\text{Am}]^2}{\left(k_{-1} + k_{\text{Am}} [\text{Am}] \right) \left(1 + K_{c,3} \frac{[\text{Am}]^2}{[\text{AmH}^+]} \right)} + \frac{k_{-1} k_{\text{AmH}^+} [\text{AmH}^+]}{k_{-1} + k_{\text{Am}} [\text{Am}]} \quad (17)$$

$$k_{\text{obs}} = \frac{k_1 [\text{Am}]}{1 + K_{c,3} \frac{[\text{Am}]^2}{[\text{AmH}^+]}} + \frac{k_{-1} k_{\text{AmH}^+} [\text{AmH}^+]}{k_{\text{Am}} [\text{Am}]} \quad (18)$$

The rate data in Table 8 conform to equation (18) with values of K_{c,3} 25 l mol⁻¹, k₁ 150 l mol⁻¹ s⁻¹, and k₋₁k_{AmH}⁺/k_{Am} 0.14 s⁻¹. Combination of the latter two quantities gives a value for K_{c,1} of 1 100 l mol⁻¹ in good agreement with that obtained from optical density measurements in Table 6. Our data require that k_{Am}/k₋₁ ≳ 5 000 l mol⁻¹.

Rate data for the slower σ-adduct-forming reaction in the presence of 0.1M-butylammonium chloride were also measured and are given in Table 9. They give a good fit with equation (18) with the values k₁ 150 l mol⁻¹ s⁻¹, k₋₁k_{AmH}⁺/k_{Am} 0.06 s⁻¹, and K_{c,3} 50 l mol⁻¹. The variation in values of the parameters with chloride ion concentration is as expected from previous work.^{4,7} Thus values of equilibrium constants approximately

Table 9. Kinetic data for σ-adduct formation from HNBB (1 × 10⁻⁵M) and n-butylamine in DMSO containing 0.1M-n-butylammonium chloride at 25 °C

| [n-Butylamine]/M | k _{obs} /s ⁻¹ | k _{calc} ^a |
|------------------|-----------------------------------|--------------------------------|
| 0.002 | 3.1 | 3.3 |
| 0.003 | 2.5 | 2.5 |
| 0.005 | 2.1 | 2.0 |
| 0.0075 | 2.0 | 1.9 |
| 0.010 | 2.1 | 2.0 |
| 0.015 | 2.5 | 2.4 |
| 0.020 | 3.0 | 2.8 |
| 0.040 | 3.5 | 3.5 |

^a Calculated from equation (18) with k₁ 150 l mol⁻¹ s⁻¹, K_{c,3} 50 l mol⁻¹, and k₋₁k_{AmH}⁺/k_{Am} 0.06 s⁻¹.**Table 10.** Rate data for formation of the blue dianion from HNBB (2 × 10⁻⁵M) and n-butylamine in DMSO containing n-butylammonium chloride (0.1M) at 25 °C

| [n-Butylamine]/M | 10 ³ k _{obs} ^a /s ⁻¹ | 10 ³ k _{calc} ^b | 10 ³ k _{calc} ^c |
|------------------|--|--|--|
| 0.001 | 1.9 | 1.8 | 1.8 |
| 0.002 | 2.0 | 2.0 | 2.0 |
| 0.003 | 2.4 | 2.3 | 2.3 |
| 0.004 | 2.6 | 2.6 | 2.6 |
| 0.006 | 2.7 | 2.7 | 2.7 |
| 0.008 | 2.9 | 2.6 | 2.7 |
| 0.010 | 2.9 | 2.9 | 2.6 |
| 0.015 | 2.2 | 1.8 | 2.2 |
| 0.020 | 2.0 | 1.4 | 2.0 |
| 0.040 | 2.0 | 0.8 | 2.0 |

^a Measured at 640 nm with a conventional spectrophotometer. ^b Calculated from equation (19) with k_p 0.8 l mol⁻¹ s⁻¹, k_{-p}/K_{2,p} 1 × 10⁻⁴ l mol⁻¹ s⁻¹, and K_{c,1} 2 500 l mol⁻¹. ^c Calculated from equation (20) with the parameters given above and with k_p' 0.03 l mol⁻¹ s⁻¹.

double with 0.1M-chloride and the value of k_{AmH}⁺ is reduced by about one half.

Rate data for the slow reaction forming the blue species are in Table 10. With concentrations of n-butylamine ≤ 0.01M the data correspond well with equation (19) which allows for prior equilibration with the σ-adduct but assumes that only the parent reacts with amine to give the blue dianion. At the higher base concentrations a significantly better fit is achieved with equation (20) which allows for an additional pathway involving

$$k_{\text{obs}} = \frac{k_p [\text{Am}]}{1 + K_{c,1} \frac{[\text{Am}]^2}{[\text{AmH}^+]}} + \frac{k_{-p} [\text{AmH}^+]^2}{K_{2,p} [\text{Am}]} \quad (19)$$

$$k_{\text{obs}} = \frac{k_p [\text{Am}] + k_p' K_{c,1} [\text{Am}]^3 / [\text{AmH}^+]}{1 + K_{c,1} \frac{[\text{Am}]^2}{[\text{AmH}^+]}} + \frac{k_{-p} [\text{AmH}^+]}{K_{2,p} [\text{Am}]} \quad (20)$$

proton transfer from a methylene group of the σ-adduct (4). Values are k_p 0.8 l mol⁻¹ s⁻¹, k_{-p}/K_{2,p} 1 × 10⁻⁴ l mol⁻¹ s⁻¹, and k_p' 0.03 l mol⁻¹ s⁻¹. Combination of the former two quantities gives a value for K_p·K_{2,p} of 8 000. The blue species slowly fades irreversibly.

Reaction with Benzylamine.—The behaviour here is qualitatively similar to that observed with n-butylamine. Optical

Table 11. Equilibrium data for σ -adduct formation from HNBB (2×10^{-5} M) and benzylamine in DMSO containing benzylammonium chloride (0.1M) at 25 °C

| [Benzylamine]/M | OD (460 nm) | OD ^a (calc) |
|-----------------|-------------|------------------------|
| 0.001 96 | 0.006 | 0.003 |
| 0.003 99 | 0.017 | 0.013 |
| 0.005 97 | 0.029 | 0.027 |
| 0.007 95 | 0.051 | 0.046 |
| 0.009 92 | 0.066 | 0.068 |
| 0.0148 | 0.137 | 0.134 |
| 0.0196 | 0.182 | 0.200 |
| 0.0292 | 0.308 | 0.314 |
| 0.0385 | 0.372 | 0.393 |
| 0.0607 | 0.491 | 0.498 |
| 0.0890 | 0.549 | 0.551 |
| 0.101 | 0.595 | 0.589 |
| 0.202 | 0.720 | 0.737 |
| 0.404 | 0.920 | 0.934 |
| 0.606 | 1.06 | 1.02 |
| 0.809 | 1.08 | 1.07 |

^a Calculated with values of $K_{c,1}$ 140 l mol⁻¹, $K_{D,1}$ 1.1 l mol⁻¹, and with optical densities for complete conversion into 1:1 adduct of 0.57 and into 1:2 adduct of 1.14.

Table 12. Rate data for formation of (2; R¹ = H, R² = benzyl) from HNBB (5×10^{-6} M) and benzylamine in DMSO at 25 °C

| [Benzylamine]/M | k_{obs}/s^{-1} | $k_{obs}^a/[Amine]$ (l mol ⁻¹ s ⁻¹) | OD (460) |
|-----------------|------------------|---|----------|
| 0.04 | 20.4 | 510 | 0.017 |
| 0.06 | 32 | 540 | 0.021 |
| 0.07 | 37 | 530 | 0.021 |
| 0.08 | 42 | 530 | 0.022 |
| 0.10 | 57 | 570 | 0.022 |

^a This corresponds to the value of k_3 [equation (15)].

Table 13. Kinetic and equilibrium data for σ -adduct formation from HNBB (1×10^{-5} M) and benzylamine in DMSO containing 0.1M-benzylammonium perchlorate at 25 °C

| [Benzylamine]/M | OD (460) ^a | $K_{c,3}^b/l mol^{-1}$ | k_{obs}/s^{-1} | k_{calc}^c | OD ^d (460) |
|-----------------|-----------------------|------------------------|------------------|--------------|-----------------------|
| 0.006 | | | 13.6 | 13.7 | 0.0011 |
| 0.008 | | | 10.5 | 10.5 | 0.0020 |
| 0.010 | | | 8.8 | 8.6 | 0.0031 |
| 0.020 | | | 5.9 | 5.2 | 0.0102 |
| 0.040 | | | 4.9 | 4.4 | 0.0236 |
| 0.060 | | | 5.0 | 4.9 | 0.0306 |
| 0.080 | | | 5.5 | 5.5 | 0.0372 |
| 0.100 | | | 6.2 | 6.1 | 0.0400 |
| 0.150 | | | 7.4 | 7.5 | 0.0477 |
| 0.200 | 0.012 | 1.25 | 8.1 | 8.4 | 0.0545 |
| 0.300 | 0.019 | 1.25 | | | |
| 0.400 | 0.024 | 1.25 | | | |
| 0.600 | 0.030 | 1.4 | | | |

^a At completion of rapid colour-forming reaction. Value for complete conversion into adduct (2) is 0.036. ^b Calculated as $OD \cdot [AmH^+]/(0.036 - OD) [Am]^2$. ^c Calculated from equation (18) with k_1 60 l mol⁻¹ s⁻¹, $K_{c,3}$ 1.25 l mol⁻¹, and $k_{-1}k_{AmH^+}/k_{Am}$ 0.8 s⁻¹. ^d At completion of the slower colour-forming reaction giving (4).

density data (Table 11) measured at completion of the σ -adduct-forming reactions give values in the presence of 0.1M-benzylammonium chloride of $K_{c,1}$ 140 l mol⁻¹ and $K_{D,1}$ 1.1 l mol⁻¹.

We again limited kinetic studies to the formation of adducts

Table 14. Kinetic and equilibrium data for σ -adduct formation from HNBB (1×10^{-5} M) and benzylamine in DMSO containing 0.1M-benzylammonium chloride at 25 °C

| [Benzylamine]/M | OD (460) ^a | $K_{c,3}^b/l mol^{-1}$ | k_{obs}/s^{-1} | k_{calc}^c | OD ^d (460) |
|-----------------|-----------------------|------------------------|------------------|--------------|-----------------------|
| 0.006 | | | 6.8 | 7.0 | 0.0026 |
| 0.008 | | | 5.5 | 5.5 | 0.0040 |
| 0.010 | | | 4.6 | 4.6 | 0.0053 |
| 0.020 | | | 3.3 | 3.2 | 0.0159 |
| 0.040 | | | 3.4 | 3.4 | 0.0311 |
| 0.060 | | | 4.0 | 3.9 | 0.0381 |
| 0.080 | | | 4.6 | 4.7 | 0.0429 |
| 0.100 | 0.0083 | 2.4 | 5.2 | 5.3 | 0.0458 |
| 0.200 | 0.021 | 2.5 | | | |
| 0.300 | 0.028 | 2.2 | | | |
| 0.400 | 0.031 | 1.8 | | | |
| 0.600 | 0.037 | 2.1 | | | |

^a At completion of rapid colour-forming reaction. Value for complete conversion into adduct (2) is 0.042. ^b Calculated as $OD \cdot [AmH^+]/(0.042 - OD) [Am]^2$. ^c Calculated from equation (18) with k_1 60 l mol⁻¹ s⁻¹, $K_{c,3}$ 2.2 l mol⁻¹, and $k_{-1}k_{AmH^+}/k_{Am}$ 0.4 s⁻¹. ^d At completion of the slower reaction giving (4).

Table 15. Rate data for formation of the blue dianion from HNBB (2×10^{-5} M) and benzylamine in DMSO containing benzylammonium chloride (0.1M) at 25 °C

| [Benzylamine]/M | $10^3 k_{obs}^a/s^{-1}$ | $10^3 k_{calc}^b$ | $10^3 k_{calc}^c$ |
|-----------------|-------------------------|-------------------|-------------------|
| 0.005 | 4.7 | 5.1 | 5.1 |
| 0.0075 | 4.2 | 4.3 | 4.3 |
| 0.010 | 4.0 | 4.1 | 4.1 |
| 0.020 | 4.1 | 4.1 | 4.1 |
| 0.040 | 3.3 | 3.5 | 3.6 |
| 0.060 | 2.9 | 3.0 | 3.2 |
| 0.080 | 2.7 | 2.2 | 2.6 |
| 0.100 | 2.6 | 1.8 | 2.5 |
| 0.200 | 2.4 | 1.0 | 2.4 |

^a Measured at 620 nm with a conventional spectrophotometer.

^b Calculated from equation (19) with k_p 0.24 l mol⁻¹ s⁻¹, $k_{-p}/K_{2,p}$ 0.002 l mol⁻¹ s⁻¹, and $K_{c,1}$ 140 l mol⁻¹. ^c Calculated from equation (20) with the parameters given above and with k_p' 0.007 l mol⁻¹ s⁻¹.

of 1:1 stoichiometry. Rate data for the faster process are in Table 12; they conform to equation (15) with a value for k_3 of 550 l mol⁻¹ s⁻¹.

Data obtained in the presence of 0.1M-benzylammonium perchlorate are in Table 13. Optical densities measured at the completion of the faster colour forming reaction give a value for $K_{c,3}$ of 1.25 l mol⁻¹. Rate data for the slower reaction adhere to equation (18) with values of k_1 60 l mol⁻¹ s⁻¹ and $k_{-1}k_{AmH^+}/k_{Am}$ 0.8 s⁻¹. Combination of these values gives $K_{c,1}$ 75 l mol⁻¹. Similar data measured with 0.1M-benzylammonium chloride (Table 14) gives values of k_1 60 l mol⁻¹ s⁻¹, $k_{-1}k_{AmH^+}/k_{Am}$ 0.4 s⁻¹, and $K_{c,3}$ 2.2 l mol⁻¹.

Rate data for the slow deprotonation reaction yielding (7) measured in the presence of 0.1M-benzylammonium chloride are in Table 15. The values accord with equation (20) with the values k_p 0.24 l mol⁻¹ s⁻¹, k_p' 0.007 l mol⁻¹ s⁻¹, $k_{-p}/K_{2,p}$ 0.002 l mol⁻¹ s⁻¹, and $K_{c,1}$ 140 l mol⁻¹. Combination of the former two quantities gives a value for $K_p \cdot K_{2,p}$ of 120.

Discussion

Our results relate to ionic strength 0.1M. In agreement with previous work involving related compounds^{4,7,18} we find that differential effects are observed when using perchlorate and

Table 16. Comparison of kinetic and equilibrium data for reaction at unsubstituted position of HNBB, TNBCl,^a and TNB^b

| | Benzylamine | n-Butylamine | Pyrrolidine | Piperidine | |
|--|-------------|--------------|-------------|-------------------|-------------------|
| $k_3/l \text{ mol}^{-1} \text{ s}^{-1}$ | HNBB | 550 | 1 700 | 8 000 | > 5 000 |
| | TNBCl | 1 000 | 3 000 | 17 000 | > 13 000 |
| | TNB | 13 000 | 45 000 | 750 000 | > 200 000 |
| $K_3/l \text{ mol}^{-1}$ | HNBB | 1.25 | 25 | 79 | 26 |
| | TNBCl | 5 | 73 | 240 | 93 |
| | TNB | 105 | 1 000 | 3 500 | 2 140 |
| $K_3 k_{Am}/l^2 \text{ mol}^{-2} \text{ s}^{-1}$ | HNBB | | | 3.1×10^5 | 1.1×10^4 |
| | TNBCl | | | 5.8×10^5 | 2.6×10^4 |
| | TNB | | | 1.0×10^7 | 6×10^5 |
| $k_{Am}/k_{-3} (l \text{ mol}^{-1})$ | HNBB | | | 40 | < 2 |
| | TNBCl | | | 34 | < 2 |
| | TNB | | | 14 | < 10 |
| $k_{AmH^+}/l \text{ mol}^{-1} \text{ s}^{-1}$ | HNBB | | | 3 900 | 420 |
| | TNBCl | | | 2 400 | 280 |
| | TNB | | | 3 000 | 280 |
| $k_{-3} k_{AmH^+}/k_{Am} (s^{-1})$ | HNBB | 450 | 70 | 100 | > 200 |
| | TNBCl | 200 | 41 | 70 | > 140 |
| | TNB | 125 | 45 | 210 | > 90 |

^a Data for TNBCl from ref. 7. ^b Data for TNB from refs. 3 and 4.

chloride salts. These effects have been attributed to stabilising association of the substituted ammonium ions with the chloride ions.^{4,7,18} The presence of 0.1M-chloride ions has the effect of increasing the values observed for equilibrium constants $K_{c,1}$ and $K_{c,3}$ by a factor of *ca.* 2 and of decreasing values of k_{AmH^+} by a similar factor. In the subsequent discussion we shall, unless otherwise stated, use data obtained in the presence of perchlorate salts.

Attack at Unsubstituted Ring Positions.—Kinetic and equilibrium data for σ -adduct formation at the 3-position of the substrate are collected in Table 16, where they are compared with corresponding data for reaction of 2,4,6-trinitrobenzyl chloride (TNBCl) and 1,3,5-trinitrobenzene (TNB). The data for HNBB have not been statistically corrected. We shall see that the data for reaction of HNBB with piperidine and pyrrolidine fit precisely into the pattern expected for attack at an unsubstituted ring position of the substrate, thus justifying our initial assumption.

Values of the equilibrium constant $K_{c,3}$ fall, for a given amine, along the series TNB, TNBCl, HNBB. Comparing TNB and HNBB, ratios vary from 40 to 80 depending on the amine, and comparing TNBCl and HNBB ratios are between 3 and 4. Both the $\text{CH}_2\text{CH}_2\text{Picryl}$ substituent and the CH_2Cl substituent are electron withdrawing relative to hydrogen¹⁹ and should therefore encourage amine attack at the 3-position. The observed lowering in values of $K_{c,3}$ indicates that the steric effect of the bulky substituents at the 1-position is dominant. Thus the nitro-groups at the 2- and 6-positions will be forced from the ring-plane in HNBB and TNBCl so that they cannot exert their maximum electron-withdrawing influence. The lower values observed for $K_{c,3}$ with HNBB than with TNBCl may derive from the larger steric effect of $\text{CH}_2\text{CH}_2\text{Picryl}$ relative to that of CH_2Cl and/or the larger inductive relay of the latter substituent to the 3-position. Values of k_3 , the rate coefficient for amine attack at the 3-position, similarly fall in the order $\text{TNB} > \text{TNBCl} > \text{HNBB}$ and largely account for variations in values of $K_{c,3}$. For a given nitro-compound values of $K_{c,3}$ and k_3 fall in the order pyrrolidine > piperidine > n-butylamine > benzylamine reflecting the basicity order of the amines.²⁰⁻²²

For reactions with piperidine and pyrrolidine we were able to

Table 17. Comparison of kinetic and equilibrium data for reaction at the 1-position of HNBB and TNBCl^a

| | Benzylamine | n-Butylamine | |
|---|-------------|--------------|--------|
| $K_{c,1}/l \text{ mol}^{-1}$ | HNBB | 75 | 1 150 |
| | TNBCl | 1 000 | 23 000 |
| $K_{D,1}/l \text{ mol}^{-1}$ | HNBB | 0.6 | 17 |
| | TNBCl | 60 | 150 |
| $k_1/l \text{ mol}^{-1} \text{ s}^{-1}$ | HNBB | 230 | 630 |
| | TNBCl | 0.8 | 0.14 |
| $k_{-1} k_{AmH^+}/k_{Am} (s^{-1})$ | HNBB | 0.23 | 0.028 |
| | TNBCl | | |

^a Data for TNBCl from ref. 7.

measure values for k_{AmH^+} , the rate coefficient for proton transfer from substituted ammonium ion to anionic adduct [equation (6)]. The values obtained are similar to those for the corresponding reactions involving TNBCl and TNB and may be considered typical for reaction at unsubstituted ring-positions in trinitro-activated substrates. It is known^{7,12} that when reaction occurs at a substituted ring-position steric effects cause large reductions in rate coefficients for proton transfer.

Attack at the 1- and 1'-Positions.—With the primary amines we also observe attack at the 1-position to give adducts of structure (4). Data are collected in Table 17. Values of the equilibrium constant $K_{c,1}$ are larger than those of $K_{c,3}$, for the corresponding amine, by factors of 60 (benzylamine) and 46 (n-butylamine). The thermodynamic preference for attack at the 1-position may be attributed to steric relief as the bulky 1-substituent is rotated from the ring plane, thus allowing the nitro-groups at the 2- and 6-positions to achieve coplanarity with the ring with a consequent increase in their electron-withdrawing ability. An additional factor may be the inductive withdrawal of the $\text{CH}_2\text{CH}_2\text{Picryl}$ substituent. That values of k_1 for attack at the 1-position are lower than those of k_3 for attack at the 3-position may be attributed to steric hindrance to the approach of the amine (*F* strain).²³ We may obtain an estimate of the relative values of k_{-1} and k_{-3} by comparison of the data in the final rows of Tables 16 and 17. We expect that the ratio k_{Am}/k_{AmH^+} , which measures the acidity of the zwitterionic intermediate relative to that of the corresponding substituted ammonium ion, will not vary greatly with the position of

Table 18. Summary of rate data for transfer of methylene protons

| | | Benzylamine | n-Butylamine | Pyrrolidine | Piperidine | Dabco |
|--|--|------------------|-----------------|------------------|-----------------|-------------------|
| $k_p/l \text{ mol}^{-1} \text{ s}^{-1}$ | $\left\{ \begin{array}{l} \text{HNBB} \\ \text{TNBCl} \end{array} \right.$ | 0.24 | 0.8 | 5.5 | 1.8 | 1.1 |
| | | 3.4 ^a | 17 ^b | 140 ^a | 42 ^b | 16.4 ^b |
| $k_p'/l \text{ mol}^{-1} \text{ s}^{-1}$ | HNBB | 0.007 | 0.03 | 0.4 | 0.16 | |

^a Data from ref. 7. ^b Data from ref. 6.

attack.⁷ Thus comparison of the data for benzylamine and for n-butylamine gives ratios of k_{-3}/k_{-1} of ca. 500, indicating the very much slower expulsion of amine from the 1-position than from the 3-position.

The failure to observe attack at the 1-position in reaction with the secondary amines is probably due to the large steric requirements of such amines.^{10,24} Thus the presence of two very bulky groups at the 1-position would create such a sterically crowded environment as to render production of such an adduct kinetically and/or thermodynamically unfavourable.

The values of $K_{D,1}$ for conversion of the 1:1 adducts into 1:2 adducts are lower than the $K_{c,1}$ values by factors of 120 for benzylamine and 70 for n-butylamine. The corresponding factor for reaction with ethoxide ions¹⁹ is 40. Even allowing for the statistical correction which will reduce these ratios by a factor of two, these results show that although the picryl rings are separated by two methylene groups σ -adduct formation in one ring inhibits reaction of the second ring.

Proton Transfer from Methylene Groups.—In contrast to the behaviour in σ -adduct formation, proton transfer from the methylene groups results, as shown previously,¹⁶ in the formation of the blue dianion (7) without an appreciable build-up in concentration of the monoanion (6). Our kinetic results indicate rate-determining proton transfer from the substrate to the amine [equation (2)] followed by rapid conversion into the dianion. The results taken together imply greater acidity for the monoanion (6) than for the parent (1).

The relatively high acidity of (6) invites discussion. The ready formation of dianions from 2,2'-bi-indenyl and 9,9'-bifluorenyl has been rationalised²⁵ by coulombic stabilisation of anions by simultaneous interaction with two cations. However, in our systems, using alkylammonium cations in DMSO, ion-association is unlikely, as evidenced by conductance measurements.¹⁶ Hence we do not think this will be an important factor. We have previously¹⁶ suggested two possible factors for the low stability of (6) relative to (7). The first is the steric strain in (6) due to the close proximity of the CH_2 Picryl group and an *o*-nitro group. Models show that this may be partially removed during the formation of (7) by ionization of one of the CH_2 Picryl hydrogens. The second factor is the extended delocalisation available in (7). A further factor, related to the latter, involves consideration of the electronic effects in (1) and in (6). In (1) the CH_2 protons are activated by a picryl ring and by a picryl ring attenuated by the second CH_2 group. In (6) activation is again by a picryl ring and also by a $\text{C}_6\text{H}_2(\text{NO}_2)_3^-$ group coupled through a double bond. It is known^{26,27} that the $\text{C}_6\text{H}_2(\text{NO}_2)_3^-$ group, despite being negatively charged, is electron withdrawing relative to hydrogen. We suggest that the electronic influence of this group in (6) relayed through a double bond may be greater than that of the picryl ring in (1) relayed through the methylene group.

Values of the rate coefficient, k_p , for proton transfer are summarised in Table 18. The order with respect to amine is pyrrolidine > piperidine > n-butylamine, DABCO > benzylamine and is similar to that observed for σ -adduct formation. Values are between 14 and 23 times smaller than those for reaction of TNBCl with the corresponding amines. Our results

also require that an additional pathway exists involving rate-limiting deprotonation of σ -adducts. Values of k_p' representing this process are also in Table 18. With benzylamine and n-butylamine reaction will involve the 1-adducts of structure type (4) and ratios of k_p/k_p' have values of 34 and 27, respectively. With pyrrolidine and piperidine k_p' represents transfer of methylene proton from adducts of type (2) and here the values of the ratio are reduced to 14 and 11, respectively. Formation of the dianion (7) will involve subsequent loss of a second methylene proton and reversal of the σ -adduct forming reaction, but our data do not provide information regarding the relative timing of these processes.

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