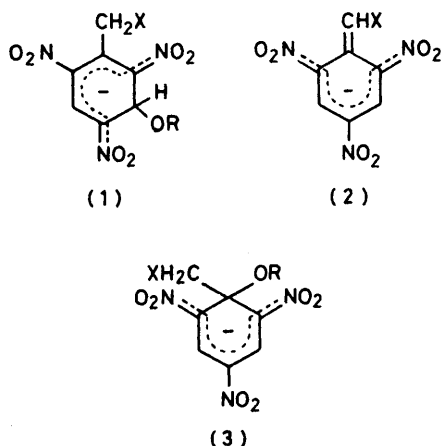


## The Stabilities of Meisenheimer Complexes. Part 29.<sup>1</sup> The Reactions of 2,4,6-Trinitrotoluene and 2,4,6-Trinitrobenzyl Chloride with Aliphatic Amines in Dimethyl Sulphoxide

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Kinetic and spectroscopic studies have been made of the reactions in dimethyl sulphoxide of 2,4,6-trinitrotoluene (TNT) and 2,4,6-trinitrobenzyl chloride (TNBCl) with the amines *n*-butylamine, isopropylamine, benzylamine, piperidine, and 1,4-diazabicyclo[2.2.2]octane. Two processes have been identified,  $\sigma$ -adduct formation and transfer of a side-chain proton. Kinetic and equilibrium data relating to the latter reaction show that the rate of the proton transfer from substrate to amine is relatively insensitive to the nature of the reagents, indicating a reactant-like transition state. The  $\sigma$ -adducts formed from TNBCl and the primary amines are thought to result from attack at the 1-position, while those formed from TNBCl and piperidine or from TNT probably involve attack at the 3-position. Equilibrium constants for these reactions have been determined.

THE reaction of 2,4,6-trinitrotoluene (TNT) with alkoxide ions results<sup>2</sup> in the rapid formation of the adduct (1; X = H) which is followed by the formation of the thermodynamically more stable anion (2; X = H). There have been several studies giving kinetic and equilibrium data for these processes in various alcohols.<sup>3</sup> In the case of 2,4,6-trinitrobenzyl chloride (TNBCl) three processes are observable resulting from 1:1 interaction with alkoxide ions.<sup>4</sup> These are  $\sigma$ -complex formation by



base addition at the 3-position to give (1; X = Cl) or at the 1-position to give (3; X = Cl) or transfer of a side chain proton to give (2; X = Cl). In contrast with the behaviour of TNT the more stable  $\sigma$ -adduct from TNBCl results from addition at the 1-position and has a stability comparable with that of the conjugate base. There has been little work on the reactions of TNT or TNBCl with amines although <sup>1</sup>H n.m.r. spectra of TNT in liquid ammonia indicate the formation of a 1:1 adduct by amide ion addition at an unsubstituted ring position and a 1:2 adduct by addition at the 1- and 3-positions.<sup>5</sup>

We have previously reported equilibrium and kinetic data for  $\sigma$ -complex formation from 1,3,5-trinitrobenzene and some aliphatic amines in dimethyl sulphoxide (DMSO).<sup>6</sup> Measurements have also been reported relating to proton abstraction from 1,5-dimethyl-2,4,8-

trinitronaphthalene by diethylamine and triethylamine in dimethyl sulphoxide and its mixtures with methanol. Here we report rate and equilibrium data for the reactions of TNT and TNBCl with aliphatic amines in dimethyl sulphoxide.

### RESULTS AND DISCUSSION

In the presence of dilute ( $1 \times 10^{-3}$ M) solutions of various aliphatic amines in DMSO, TNT forms a purple species whose spectrum ( $\lambda_{\text{max}}$  377, 530, and 640 nm) is similar to that previously attributed<sup>3</sup> to the conjugate base (2; X = H). In solutions containing higher concentrations of the amines *n*-butylamine, isopropylamine, benzylamine, or piperidine a transient red colour was seen to precede formation of the conjugate base. However at the amine concentrations used ( $<0.1$ M) the visible spectra measured after attainment of equilibrium indicated negligible concentrations of the species responsible. By use of stopped-flow spectrophotometry the visible spectrum of the transient species formed using piperidine was measured (Figure 1). The spectrum shows maxima

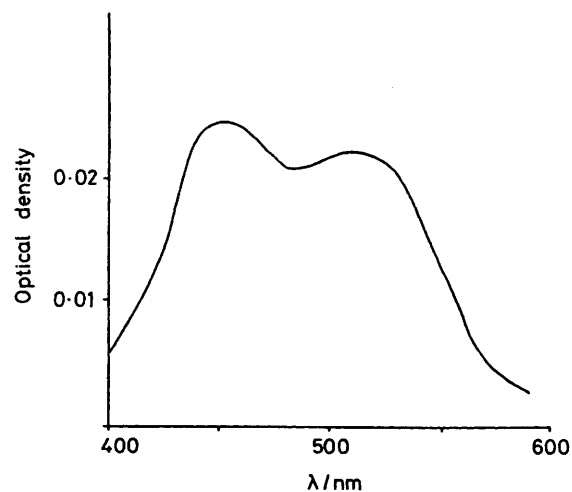


FIGURE 1 Visible spectrum, measured by stopped-flow spectrophotometry, of the  $\sigma$ -adduct rapidly produced from TNT ( $1 \times 10^{-4}$ M) in the presence of piperidine (0.5M) and piperidine hydrochloride (0.1M)

at 450 and 510 nm with intensity ratio 1.1 and is typical of a  $\sigma$ -adduct.<sup>3,4</sup>  $^1\text{H}$  N.m.r. spectra of TNT in  $[\text{D}_6]\text{DMSO}$  containing amines showed bands at  $\delta$  5.54 and 8.2 attributable respectively to side-chain and ring protons of (2;  $\text{X} = \text{H}$ ) but no bands due to  $\sigma$ -adducts were discernible.

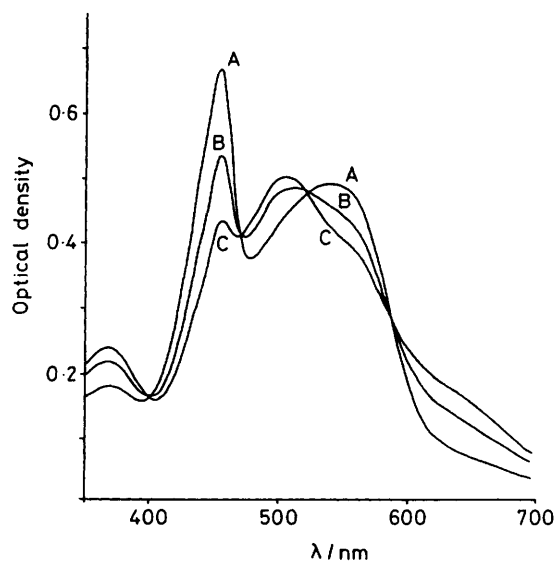
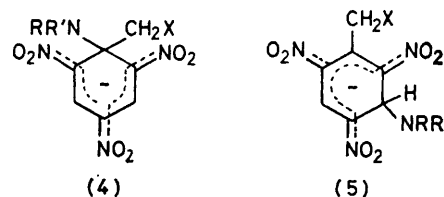


FIGURE 2 Visible spectra of TNBCl ( $4 \times 10^{-5}\text{M}$ ) with isopropylamine (0.2M) and isopropylammonium perchlorate (0.1M) in DMSO recorded at 2 min intervals A—C. These spectra show the initial formation of  $\sigma$ -adduct followed by equilibration with the conjugate base

In DMSO solution reaction of the tertiary amine 1,4-diazabicyclo[2.2.2]octane (DABCO) with TNBCl gives a species whose visible spectrum ( $\lambda_{\text{max}}$  373, 490, and 600 nm) is similar to that previously attributed to the conjugate base<sup>3,4</sup> (2;  $\text{X} = \text{Cl}$ ). With the primary amines *n*-butylamine, isopropylamine, and benzylamine visible spectra indicate the rapid production of  $\sigma$ -complexes with maxima at 452 and 540–550 nm, the ratio of extinction coefficients at these wavelengths being 1.7–1.8. These bands gradually decrease in intensity as new bands attributable to the conjugate base are produced. However in contrast to TNT both  $\sigma$ -adduct and conjugate base are generally present at equilibrium. Representative spectra obtained using isopropylamine are in Figure 2. The behaviour with the secondary amine piperidine is somewhat different in that the visible spectrum of the initially produced  $\sigma$ -adduct shows maxima at 450 and 510 nm (the ratio of  $\epsilon$  values being reduced to 1.1), and that little  $\sigma$ -adduct is present at equilibrium.

The  $^1\text{H}$  n.m.r. spectrum of TNBCl in  $[\text{D}_6]\text{DMSO}$  shows two singlets at  $\delta$  9.1 and 5.0. We have shown previously<sup>4</sup> that the spectrum of the conjugate base (2;  $\text{X} = \text{Cl}$ ) shows doublets at  $\delta$  8.20 and 8.50 due to ring protons and a singlet at  $\delta$  6.90 due to the side-chain proton while the adduct (3;  $\text{X} = \text{Cl}$ ,  $\text{R} = \text{CD}_3$ ) formed by attack at C-1 shows two singlets at  $\delta$  8.70 and 4.70. The spectrum in the presence of 1 mol. equiv. *n*-butylamine shows in addition

to parent bands a singlet at  $\delta$  7.10 attributable to conjugate base. However in the presence of excess of *n*-butylamine (10 equiv.) the spectrum indicates the formation of the adduct (4;  $\text{X} = \text{Cl}$ ,  $\text{R} = \text{H}$ ,  $\text{R}' = \text{Bu}^n$ ) with bands at  $\delta$  8.48 due to ring protons and 4.57 due to side-chain protons. The preference for base addition relative to proton loss at high base concentrations is expected from



the stoichiometries of the reactions. It is known<sup>7</sup> that very clear n.m.r. spectra of amide adducts may be obtained by the generation of amide ions from amines by sodium methoxide in DMSO. Accordingly we find that as *n*-butylamine is added to solutions containing a molar ratio of 1 TNBCl : 1 NaOCD<sub>3</sub> in DMSO the bands at  $\delta$  8.70 and 4.70 due to the methoxide adduct are replaced by bands at  $\delta$  8.48 and 4.57 due to amide adduct. That the bands due to amide adduct are slightly to high field of those due to methoxide adduct is in agreement with previous data relating to adducts of 1,3,5-trinitrobenzene.<sup>7,8</sup>

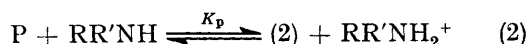
Similarly the spectrum of TNBCl in the presence of a ten-fold excess of isopropylamine shows bands at  $\delta$  8.48 and 4.54 due to adduct (4;  $\text{X} = \text{Cl}$ ,  $\text{R} = \text{H}$ ,  $\text{R}' = \text{Pr}^i$ ). Other bands are formed fairly rapidly at  $\delta$  8.32, 8.03, 7.50, and 5.32 and are probably due to irreversible decomposition products.

Spectra of TNBCl in the presence of piperidine or benzylamine gave less clear results. Bands attributable to the conjugate base were observed at low amine concentrations but no bands definitely attributable to amide adducts were found at high amine concentrations. In solutions containing sodium methoxide and amine only bands resulting from methoxide attack were observed. This probably reflects the lower thermodynamic stabilities of the amide  $\sigma$ -adducts formed from these amines.

**Kinetic and Equilibrium Data.**—Measurements were made with amine concentrations in large excess of parent concentrations, and in the presence of constant concentrations (usually 0.1M) of the corresponding ammonium salt. This allowed data to be obtained at constant ionic strength, buffered the solutions so that the adverse effects of traces of acidic or basic impurities were minimised, and simplified the kinetic analysis.

The equilibria involved are described by equations (1) and (2) in which the parent (P) is converted into  $\sigma$ -adduct ( $\text{P}\cdot\text{NRR}'$ ) or conjugate base (2). The equilibrium constants  $K_c$  and  $K_p$  are defined by equations (3) and (4) from which it is seen that the ratio of concentrations of adduct and conjugate base at equilibrium is given by equation (5). In accord with this expression it

was found experimentally that the fraction of parent present as  $\sigma$ -adduct at equilibrium increased with amine concentration.



$$K_c = \frac{[P \cdot NRR'] [RR'NH_2^+]}{[P] [RR'NH]^2} \quad (3)$$

$$K_p = \frac{[(2)] [RR'NH_2^+]}{[P] [RR'NH]} \quad (4)$$

$$\frac{[P \cdot NRR']}{[(2)]} = \frac{K_c}{K_p} [RR'NH] \quad (5)$$

In all cases formation of the  $\sigma$ -adducts was a much faster process than the transfer of the side-chain proton. We have not in this work examined the kinetics of the reactions forming  $\sigma$ -complexes but note that as in the reactions of 1,3,5-trinitrobenzene with amines<sup>6</sup> a two-step process *via* zwitterionic intermediates is likely. It is readily shown by standard methods<sup>9</sup> that in the presence of  $\sigma$ -adduct the first-order rate coefficient,  $k_{obs.}$ , for formation of the conjugate base is given by equation (6).

$$k_{obs.} = \frac{k_p [RR'NH]}{1 + K_c \frac{[RR'NH]}{[RR'NH_2^+]}} + k_{-p} [RR'NH_2^+] \quad (6)$$

$$k_{obs.} = k_p [RR'NH] + k_{-p} [RR'NH_2^+] \quad (7)$$

This reduces to equation (7) when little  $\sigma$ -adduct is initially formed. It is of interest that equation (6) predicts that the rate of formation of conjugate base should decrease with decreasing concentration of the ammonium salt ( $RR'NH_2^+$ ). Hence visible spectra of TNBCl ( $4 \times 10^{-5}M$ ) in DMSO containing *n*-butylamine, isopropylamine, benzylamine, or piperidine but without the addition of ammonium salt indicate that equilibration between the  $\sigma$ -adduct and conjugate base is a very slow process.

**Data for TNT.** The reaction with the tertiary amine DABCO leads directly to the formation of the conjugate base [equation (2)]. Rate and equilibrium measurements were made by stopped-flow spectrophotometry and are in Table 1. A linear plot of  $k_{obs.}$  versus amine concentration gave values of  $k_p$  20.6 l mol<sup>-1</sup> s<sup>-1</sup> and  $k_{-p}$  230 l mol<sup>-1</sup> s<sup>-1</sup>. Combination of these values gives  $K_p$  ( $8.8 \pm 0.4$ )  $\times 10^{-2}$ , in agreement with values calculated from equilibrium optical densities.

In solutions containing <0.1M-piperidine, with 0.1M-piperidinium chloride, only a single colour-forming reaction was observed giving the conjugate base. At higher base concentrations a second, faster process is observed giving a species whose spectrum corresponds to a  $\sigma$ -complex. Using stopped-flow spectrophotometry, optical density measurements at the completion of the two processes were separately made and rate coefficients of the slower process measured. The data in Table 2 show that the values of  $k_{obs.}$  pass through a maximum value as the piperidine concentration is increased and are

well fitted by equation (6) with  $k_p$  20 l mol<sup>-1</sup> s<sup>-1</sup>,  $k_{-p}$  2.0 l mol<sup>-1</sup> s<sup>-1</sup>, and  $K_c$  3.5 l mol<sup>-1</sup>.

The behaviour of TNT with benzylamine in the presence of 0.1M-benzylammonium perchlorate is similar to

TABLE 1

Rate and equilibrium data for the reaction of TNT with DABCO in DMSO containing 0.05M-DABCOH<sup>+</sup>ClO<sub>4</sub><sup>-</sup> at 25°

[DABCO]/ M	$k_{obs.}/s^{-1}$	O.D. (500 nm) <sup>a</sup>	$K_p$ <sup>b</sup>
0.005	11.6 $\pm 0.2$		
0.010	11.7		
0.020	12.0		
0.040	12.9	0.0143	0.11
0.20	15.9	0.0417	0.08
0.30	18.0	0.0557	0.08
0.40	19.8	0.0722	0.09

<sup>a</sup> Measured at equilibrium with 2 mm cell for  $1 \times 10^{-4}M$  TNT. A Benesi-Hildebrand plot gives a value for complete conversion of 0.174 ( $\epsilon$  8 700 l mol<sup>-1</sup> cm<sup>-1</sup>). <sup>b</sup> Calculated using O.D. (500 nm) [DABCOH<sup>+</sup>]/(0.174 - O.D. (500 nm) [DABCO]).

TABLE 2

Rate and equilibrium data for the reaction of TNT with piperidine in DMSO containing 0.1M-piperidinium chloride at 25°

[Piperidine]/ M	$k_{obs.}/s^{-1}$	$k_{calc.}^a/s^{-1}$	O.D. <sup>b</sup> (525 nm)	$K_c$ <sup>c</sup> / l mol <sup>-1</sup>	O.D. (525 nm)
0.01	0.40	0.40			0.0114
0.02	0.58	0.59			0.0151
0.05	0.97	1.10			0.0178
0.10	1.75	1.70	0.0083	3.7	0.0202
0.20	2.0	1.9	0.0178	3.5	0.0241
0.30	1.8	1.7	0.0240	4.1	0.0250
0.40	1.5	1.4	0.0258	3.4	0.0243
0.50	1.3	1.2	0.0283		0.0255

<sup>a</sup> Calculated from equation (6) with  $k_p$  20 l mol<sup>-1</sup> s<sup>-1</sup>,  $k_{-p}$  2.0 l mol<sup>-1</sup> s<sup>-1</sup>, and  $K_c$  3.5 l mol<sup>-1</sup>. <sup>b</sup> After completion of the rapid reaction forming  $\sigma$ -complex. Measured with 2 mm cells with  $1 \times 10^{-5}M$ -TNT. A Benesi-Hildebrand type plot gives a value for complete conversion of 0.0305 ( $\epsilon$  1.52  $\times 10^4$  l mol<sup>-1</sup> cm<sup>-1</sup>). <sup>c</sup> Calculated using O.D. (525 nm) [pipH<sup>+</sup>]/(0.0305 - O.D. (525 nm) [pip]<sup>2</sup>).

TABLE 3

Rate and equilibrium data for the reaction of TNT with benzylamine in DMSO containing 0.1M-benzylammonium perchlorate at 25°

[Benzylamine]/ M	$k_{obs.}/s^{-1}$	$k_{calc.}^a/s^{-1}$	O.D. <sup>b</sup> (450 nm)	$K_c$ <sup>c</sup> / l mol <sup>-1</sup>	O.D. <sup>d</sup> (640 nm)
0.005	0.11	0.13			
0.010	0.13	0.14			
0.030	0.18	0.17			
0.050	0.20	0.20			0.043
0.070	0.23	0.23	0.0017	0.22	0.053
0.090	0.26	0.26	0.0026	0.20	0.061
0.15	0.35	0.34	0.0070	0.20	0.080
0.20	0.40	0.40	0.011	0.20	0.090
0.30	0.51	0.51	0.022	0.19	0.10
0.40	0.60	0.59	0.036	0.19	0.11
0.50	0.61	0.64	0.048	0.19	0.11
0.70	0.69	0.68	0.069	0.18	0.12

<sup>a</sup> Calculated from equation (6) with  $k_p$  1.5 l mol<sup>-1</sup> s<sup>-1</sup>,  $k_{-p}$  1.2 l mol<sup>-1</sup> s<sup>-1</sup>, and  $K_c$  0.19 l mol<sup>-1</sup>. <sup>b</sup> After completion of the reaction forming  $\sigma$ -complex. Measured with 2 mm cells and  $4 \times 10^{-5}M$ -TNT. A Benesi-Hildebrand plot gives a value for complete conversion of 0.15 ( $\epsilon$  1.9  $\times 10^4$  l mol<sup>-1</sup> cm<sup>-1</sup>). <sup>c</sup> Calculated using O.D. (450 nm) [AmineH<sup>+</sup>]/(0.15 - O.D. (450 nm) [Amine]<sup>2</sup>). <sup>d</sup> After completion of both processes with  $1 \times 10^{-4}M$ -TNT.

that with piperidine. The formation of conjugate base is preceded by  $\sigma$ -adduct formation and measurement of optical densities at 450 nm allows the calculation of a value of  $0.19 \text{ l mol}^{-1}$  for  $K_c$ . The rate data are fitted very well by equation (6) using this value and values of  $k_p$   $1.5 \text{ l mol}^{-1} \text{ s}^{-1}$  and  $k_{-p}$   $1.2 \text{ l mol}^{-1} \text{ s}^{-1}$ . Data are in Table 3.

yielding a value for  $K_p$  of 4.0 in agreement with that obtained from O.D. measurements.

Data obtained with piperidine in solutions containing 0.1M-piperidinium chloride are in Table 7. With amine concentrations in the range  $0.005 < [\text{Amine}] < 0.2\text{M}$  there is virtually complete conversion into conjugate base at equilibrium although initial formation of  $\sigma$ -adduct is

TABLE 4

Rate and equilibrium data for the reaction of TNT with n-butylamine in DMSO in the presence of 0.1M-n-butylammonium perchlorate at 25°

[n-Butylamine]/ M	$k_{\text{obs}}/\text{s}^{-1}$	$k_{\text{calc.}}^a/\text{s}^{-1}$	O.D. <sup>b</sup> (450 nm)	$K_c$ <sup>c</sup> /l mol <sup>-1</sup>	O.D. <sup>d</sup> (650 nm)	$K_p$
0.005	0.082	0.077			0.036	28
0.007	0.092	0.095			0.042	30
0.010	0.120	0.120	0.0026	18	0.045	26
0.020	0.210	0.200	0.013	24	0.050	23
0.050	0.360	0.340	0.050	20	0.058	

<sup>a</sup> Calculated from equation (6) with  $k_p$   $9 \text{ l mol}^{-1} \text{ s}^{-1}$ ,  $k_{-p}$   $0.33 \text{ l mol}^{-1} \text{ s}^{-1}$ , and  $K_c$   $20 \text{ l mol}^{-1}$ . <sup>b</sup> After completion of the fast reaction giving  $\sigma$ -adduct. With  $4 \times 10^{-5}\text{M}$ -TNT and 2 mm pathlength cell. <sup>c</sup> Calculated assuming an extinction coefficient of  $1.9 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$  for the  $\sigma$ -adduct at 450 nm. <sup>d</sup> After completion of both colour-forming reactions. At the base concentrations used little  $\sigma$ -adduct is present at equilibrium. A Benesi-Hildebrand plot gives a value of 0.061 for complete conversion into conjugate base.

Data obtained with n-butylamine in the presence of 0.1M-salt are in Table 4. The rate and equilibrium data are all consistent with values of  $k_p$   $9 \text{ l mol}^{-1} \text{ s}^{-1}$ ,  $k_{-p}$   $0.33 \text{ l mol}^{-1} \text{ s}^{-1}$ ,  $K_p$  27, and  $K_c$   $20 \text{ l mol}^{-1}$ .

With isopropylamine concentrations  $< 0.1\text{M}$  and 0.1M-salt there is little initial formation of  $\sigma$ -adduct. Consequently a linear plot according to equation (7) gave values for  $k_p$   $3.2 \text{ l mol}^{-1} \text{ s}^{-1}$  and  $k_{-p}$   $0.23 \text{ l mol}^{-1} \text{ s}^{-1}$ . These

observed. The optical density data at 450 nm relating to  $\sigma$ -adduct formation lead to a value for  $K_c$  of  $200 \pm 50 \text{ l mol}^{-1}$ . Rate coefficients for formation of the conjugate base pass through a maximum value as the amine

TABLE 5

Rate and equilibrium data for the reaction of TNT with isopropylamine in DMSO with 0.1M-isopropylamine perchlorate at 25°

[Isopropylamine]/ M	$10^3 k_{\text{obs.}}/\text{s}^{-1}$	O.D. <sup>a</sup> (450 nm)	$K_c$ <sup>b</sup> /l mol <sup>-1</sup>	O.D. <sup>c</sup> (650 nm)	$K_p$
0.005	4			0.014	17
	$\pm 0.2$				
0.0075	4.5			0.015	13
0.010	5.5			0.018	15
0.020	8.7			0.023	16
0.050	18.4			0.026	13
0.10	34.3			0.028	14
1.0		0.044	0.13		
1.5		0.055	0.11		
2.0		0.095	0.09		
2.5		0.067	0.12		

<sup>a</sup> After completion of rapid reaction forming  $\sigma$ -adduct with  $2 \times 10^{-5}\text{M}$ -TNT, and using 2 mm cells. <sup>b</sup> Calculated from O.D. (450 nm) data assuming an extinction coefficient of  $19\,000 \text{ l mol}^{-1} \text{ cm}^{-1}$ . <sup>c</sup> At completion of reaction. A Benesi-Hildebrand gives a value for complete conversion into conjugate base of 0.030.

yield a value for  $K_p$  of 14 which is in agreement with that obtained from the equilibrium optical densities at 650 nm. At higher amine concentrations there is evidence for initial formation of  $\sigma$ -adduct and values of O.D. (450 nm) lead to a value for  $K_c$  of  $0.11 \text{ l mol}^{-1}$ . Data are in Table 5.

*Data for TNBCl.* The most straightforward case is reaction with DABCO (Table 6) where the only reaction occurring is formation of the conjugate base and a linear plot of  $k_{\text{obs.}}$  versus amine concentration [equation (7)] gave values of  $k_p$   $16.4 \text{ l mol}^{-1} \text{ s}^{-1}$  and  $k_{-p}$   $4.1 \text{ l mol}^{-1} \text{ s}^{-1}$

TABLE 6

Rate and equilibrium data for reaction of TNBCl with DABCO in DMSO in the presence of 0.05M-DABCO perchlorate at 25°

[DABCO]/ M	$k_{\text{obs.}}/\text{s}^{-1}$	O.D. <sup>a</sup> (500 nm)	$K_p$
0.005	0.30	0.08	3.6
0.010	0.36	0.12	3.6
0.020		0.18	3.8
0.025	0.61		
0.040		0.22	3.5
0.050	1.03		

<sup>a</sup> Measured with [TNBCl]  $1 \times 10^{-4}\text{M}$  using a 2 mm cell. For complete conversion into conjugate base, a Benesi-Hildebrand plot gives a value of 0.295.

concentration is increased. A plot of  $k_{\text{obs.}}$  versus the parameter  $[\text{Am}]/(1 + K_c[\text{Am}]^2[\text{AmH}^+]^{-1})$  was linear and gave a value for  $k_p$  of  $42 \text{ l mol}^{-1} \text{ s}^{-1}$ . However the intercept was too small to allow accurate determination of  $k_{-p}$ . Thus measurements of optical density were made (Table 8) in solutions containing low piperidine concentrations and these gave a value for  $K_p$  of  $420 \pm 40$  allowing calculation of a value for  $k_{-p}$  ( $= k_p/K_p$ ) of  $0.1 \text{ l mol}^{-1} \text{ s}^{-1}$ .

The  $\sigma$ -adduct formed from n-butylamine has high stability and the optical density measurements (Table 9) indicate a value for  $K_c$  of  $(2 \pm 0.2) \times 10^4 \text{ l mol}^{-1}$ . The subsequent isomerisation to give the conjugate base was sufficiently slow to allow measurement with a conventional spectrophotometer (Beckman 25). As the amine concentration is increased  $k_{\text{obs.}}$  decreases, approaching the value of  $k_{-p}[\text{Bu}^n\text{NH}_3^+]$ . The values give a good fit with  $k_p$   $17 \text{ l mol}^{-1} \text{ s}^{-1}$  and  $k_{-p}$   $0.02 \text{ l mol}^{-1} \text{ s}^{-1}$ .

With isopropylamine two processes were observed at



TABLE 7

Rate and equilibrium data for reaction of TNBCl with piperidine in DMSO containing 0.1M-piperidinium chloride at 25°

[Piperidine]/ M	$k_{\text{obs.}}/$ $\text{s}^{-1}$	$k_{\text{calc.}}^a/$ $\text{s}^{-1}$	O.D. <sup>b</sup> (450 nm)	$K_c^c/$ $\text{l mol}^{-1}$	O.D. <sup>d</sup> (600 nm)
0.005	0.21	0.21			0.0089
0.010	0.38	0.36			0.0085
0.015	0.43	0.44			0.0098
0.020	0.50	0.48			0.0091
0.025	0.50	0.48	0.0160	230	0.0102
0.035	0.46	0.44	0.0197	220	0.0108
0.050	0.38	0.36	0.0232	245	0.0106
0.075	0.30	0.27	0.0249	210	0.0097
0.10	0.25	0.21	0.0253		0.0107
0.15	0.19	0.15			0.0100
0.20	0.12	0.12			0.0093

<sup>a</sup> Calculated from equation (6) with  $k_p$  42  $\text{l mol}^{-1} \text{s}^{-1}$ ,  $k_{-p}$  0.1  $\text{l mol}^{-1} \text{s}^{-1}$ , and  $K_c$  200  $\text{l mol}^{-1}$ . <sup>b</sup> After completion of reaction forming  $\sigma$ -adduct with [TNBCl]  $1 \times 10^{-5} \text{M}$  and using 2 mm cells. A Benesi-Hildebrand plot gives a value of 0.027 for complete conversion. <sup>c</sup> The data at 450 nm lead to a value for  $K_c$  of  $225 \pm 30 \text{l mol}^{-1}$ . A second set of data was obtained at 490 nm and yields a value for  $K_c$  of  $170 \pm 30 \text{l mol}^{-1}$ . <sup>d</sup> After completion of reaction forming conjugate base.

TABLE 8

Equilibrium data for proton transfer from TNBCl to piperidine in DMSO containing 0.1M-piperidinium chloride at 25°

[Piperidine]/ M	O.D. <sup>a</sup> (500 nm)	$K_p^b$
0.0005	0.350	460
0.00075	0.382	430
0.0010	0.405	430
0.0020	0.442	380

<sup>a</sup> For [TNBCl]  $4 \times 10^{-5} \text{M}$  with 1 cm cell. <sup>b</sup> Calculated assuming no  $\sigma$ -adduct formation with O.D. 0.50 for complete conversion.

all base concentrations used. Optical density measurements at the completion of the rapid reaction gave a value for  $K_c$  of  $1230 \pm 100 \text{l mol}^{-1}$ . Analysis of the rate data according to equation (6) gave a value of  $k_p$   $9.5 \pm 0.5 \text{l mol}^{-1} \text{s}^{-1}$ . However the contribution to the rate from the term involving  $k_{-p}$  was too small to allow its calculation.

TABLE 11

Equilibrium constants for reaction of TNBCl with isopropylamine <sup>a</sup> in DMSO with 0.1M-isopropylamine perchlorate at 25°

[Isopropylamine]/ M	O.D. (640 nm)	O.D. (450 nm)	[Conjugate base]/M	[ $\sigma$ -Adduct]/M	$K_c K_p^{-1}/$ $\text{l mol}^{-1}$
0.05	0.180	0.316	0.89	0.065	1.4
0.10	0.167	0.335	0.82	0.11	1.3
0.20	0.161	0.400	0.79	0.19	1.2
0.30	0.156	0.470	0.76	0.27	1.2

<sup>a</sup> TNBCl is  $4 \times 10^{-5} \text{M}$ . The values of the extinction coefficient of the conjugate base were determined in the presence of DABCO and were: 640 nm, 5100  $\text{l mol}^{-1} \text{cm}^{-1}$ ; 450 nm, 7400  $\text{l mol}^{-1} \text{cm}^{-1}$ . Values of the extinction coefficients of the  $\sigma$ -adduct were determined in solutions containing no added salt, where isomerisation is slow, and were: 640 nm, 0; 450 nm 22300  $\text{l mol}^{-1} \text{cm}^{-1}$ .

Measurements (Table 11) of equilibrium optical density values at 450 and 640 nm, together with the knowledge of the extinction coefficients of the  $\sigma$ -adduct and conjugate base at these wavelengths, allowed the calculation of the relative concentrations present at equilibrium. Using equation (5) the value of the ratio  $K_c/K_p$  was calculated to be  $1.3 \pm 0.1$ . The knowledge

TABLE 9

Equilibrium and rate data for reaction of TNBCl with n-butylamine in DMSO containing 0.1M-n-butylammonium perchlorate at 25°

[Bu <sup>n</sup> NH <sub>2</sub> ]/ M	O.D. <sup>a</sup> (450 nm)	$10^{-4} K_c/$ $\text{l mol}^{-1}$	$k_{\text{obs.}}/$ $\text{s}^{-1}$	$k_{\text{calc.}}^b/$ $\text{s}^{-1}$
0.002	0.031	2.0		
0.005	0.058	1.9	0.017	0.016
0.0075	0.065	2.1		
0.010			0.0096	0.010
0.020			0.0065	0.0063
0.030			0.0051	0.0050
0.039			0.0041	0.0042
0.049			0.0038	0.0037

<sup>a</sup> For  $2 \times 10^{-5} \text{M}$ -TNBCl, measured with 2 mm cell. After completion of rapid reaction giving  $\sigma$ -adduct. Value for complete conversion is 0.071. <sup>b</sup> Calculated from equation (6) with  $k_p$  17  $\text{l mol}^{-1} \text{s}^{-1}$ ,  $k_{-p}$  0.02  $\text{l mol}^{-1} \text{s}^{-1}$ , and  $K_c$   $2 \times 10^4 \text{l mol}^{-1}$ .

of the value of  $K_c$  then allowed calculation of a value of 950 for  $K_p$  whence  $k_{-p}$  ( $= k_p/K_p$ ) has the value 0.01  $\text{l mol}^{-1} \text{s}^{-1}$ .

Similarly with benzylamine the visible spectra recorded

TABLE 10

Rate and equilibrium data for the reaction of TNBCl with isopropylamine in DMSO with 0.1M-isopropylamine perchlorate at 25°

[Isopropylamine]/ M	O.D. <sup>a</sup> (450 nm)	$K_c/$ $\text{l mol}^{-1}$	$k_{\text{obs.}}/$ $\text{s}^{-1}$	$k_{\text{calc.}}^b/$ $\text{s}^{-1}$
0.005	0.019	1100	0.037	0.037
0.0075	0.038	1300	0.040	0.043
0.010	0.050	1300	0.044	0.044
0.015	0.067	1300	0.035	0.039
0.020	0.074	1200	0.032	0.033
0.050	0.084		0.014	0.016

<sup>a</sup> After completion of rapid colour forming reaction. TNBCl is  $2 \times 10^{-5} \text{M}$ . Measured with 2 mm cell. A Benesi-Hildebrand plot gives value of 0.0893 for complete conversion.

<sup>b</sup> Calculated from equation (6) with  $K_c$  1230  $\text{l mol}^{-1}$ ,  $k_p$  9.5  $\text{l mol}^{-1} \text{s}^{-1}$ , and  $k_{-p}$  negligibly small.

at equilibrium indicated the presence of both conjugate base and  $\sigma$ -adduct. Optical density measurements in Table 12 at 450 and 620 nm allowed the calculation of the values of  $K_p$   $22 \pm 2$  and  $K_c$   $300 \pm 100 \text{l mol}^{-1}$ .

By use of stopped-flow spectrophotometry values of

optical density at the completion of the rapid reaction were measured and yield values of  $K_c$  in reasonable agreement with those in Table 12. Values of the rate coefficients for formation of conjugate base (Table 13) are fitted by equation (6) with values of  $k_p$   $1.25 \text{l mol}^{-1} \text{s}^{-1}$ ,  $k_{-p}$   $0.055 \text{l mol}^{-1} \text{s}^{-1}$ , and  $K_c$  300  $\text{l mol}^{-1}$ .

*Proton Transfer.*—Rate and equilibrium data are

TABLE 12  
Equilibrium constants for reaction of TNBCl<sup>a</sup> with benzylamine in DMSO at 25°

[Benzylamine]/ M	[Benzylammonium perchlorate] <sup>b</sup> / M	O.D. (450 nm)	O.D. (620 nm)	Relative concentrations <sup>c</sup>			$K_p$	$K_c^f$ l mol <sup>-1</sup>
				[Conjugate base]/M	[σ-Adduct]/ M	[Parent]/ M		
0.010	0.10	0.267	0.146	0.62	0.09	0.29	22	310
0.020	0.10	0.361	0.156	0.66	0.18	0.16	21	280
0.005	0.05	0.254	0.155	0.66	0.06	0.28	23	450
0.010	0.05	0.306	0.176	0.75	0.09	0.16	23	280
0.020	0.05	0.379	0.174	0.74	0.17	0.09	21	240

<sup>a</sup> TNBCl  $4 \times 10^{-5}$ M. Measurements made with SP 500 spectrophotometer. <sup>b</sup> Solutions made up to constant ionic strength,  $I$  0.1M, with tetraethylammonium perchlorate. <sup>c</sup> Measurements made with DABCO give values for the extinction coefficients of the conjugate base as 7 400 (450 nm) and 5 900 l mol<sup>-1</sup> cm<sup>-1</sup> (620 nm). Values of the extinction coefficients of the σ-adduct, determined in solutions without added salt where isomerisation is slow, are 23 200 l mol<sup>-1</sup> cm<sup>-1</sup> (450 nm) and 0 (620 nm).

summarised in Table 14. Dimethyl sulphoxide is a solvent with high dielectric constant and shows good solvation properties for polarisable anions. Thus we would not expect extensive ion association of the charged

TABLE 13

Rate and equilibrium data for reaction of TNBCl with benzylamine in DMSO at 25° in the presence of 0.1M-benzylammonium perchlorate

[Benzylamine]/ M	O.D. <sup>a</sup> (450 nm)	$K_c$ / l mol <sup>-1</sup>	$k_{obs.}/$ s <sup>-1</sup>	$k_{calc.}^b/$ s <sup>-1</sup>
0.01	0.0083	340	0.015	0.015
0.02	0.0224	530	0.020	0.017
0.04	0.0284	380	0.012	0.014
0.06	0.0297	250	0.012	0.012
0.10	0.0317	240		

<sup>a</sup> After completion of σ-complex-forming reactions. With  $1 \times 10^{-5}$ M-TNBCl and measured with 2 mm cells. For complete conversion O.D. is 0.033. <sup>b</sup> Calculated from equation (6) with  $k_p$  1.25 l mol<sup>-1</sup> s<sup>-1</sup>,  $k_{-p}$  0.055 l mol<sup>-1</sup> s<sup>-1</sup>, and  $K_c$  300 l mol<sup>-1</sup>.

species present in these systems. Hence the values of  $K_p$  for a given substrate will give a measure of the basicities of the amines used. These values increase in the order DABCO < benzylamine < piperidine < isopropylamine, n-butylamine. This order differs from

In Table 15 we compare values of  $K_p$ ,  $k_p$ , and  $k_{-p}$  for TNBCl with those obtained for TNT using the same amine. As expected<sup>4</sup> the side-chain chlorine in TNBCl has an acid-strengthening effect. It is interesting that the rate constants for proton abstraction from TNBCl or TNT by a given amine have similar values, and that the greater acidity of TNBCl derives almost entirely from the slower rate of protonation of the conjugate base. This may indicate a reactant-like transition state in which proton transfer from the substrate to the amine has not progressed very far. In agreement with this idea the values of  $k_p$  for a given substrate vary much less with the nature of the amine than do values of  $k_{-p}$  (Table 14). Brönsted-type plots further illustrate this point, plots of  $\log k_p$  versus  $\log K_p$  having small slopes with those of  $\log k_{-p}$  versus  $\log K_p$  having slopes close to unity. It was however noticeable that the points for benzylamine, both for  $k_p$  and  $k_{-p}$ , were well below the lines defined by the other amines. This may indicate some unfavourable interaction in the transition state for reaction of the substrates with this amine. An alternative possibility is that the initial and final states, but not the transition state, are stabilised by charge-transfer interaction between the trinitro-substituted and benzylamine aromatic rings.

TABLE 14

Summary of kinetic and equilibrium parameters<sup>a</sup> for reactions of TNT and TNBCl with amines in DMSO at 25°

	$k_p/$ mol <sup>-1</sup> s <sup>-1</sup>	$k_{-p}/$ l mol <sup>-1</sup> s <sup>-1</sup>	$K_p$	$K_c/$ l mol <sup>-1</sup>	$K_c K_p^{-1}/$ l mol <sup>-1</sup>	$pK_a$ (H <sub>2</sub> O) <sup>b</sup>
TNT						
DABCO	20.6	230	0.09			8.8
Piperidine	20	2.0	10	3.5	0.35	11.2
Benzylamine	1.5	1.2	1.25	0.2	0.16	9.4
n-Butylamine	9	0.33	27	20	0.75	10.6
Isopropylamine	3.2	0.23	14	0.1	0.007	10.6
TNBCl						
DABCO	16.4	4.1	4.0			8.8
Piperidine	42	0.1	420	200	0.48	11.2
Benzylamine	1.25	0.055	22	300	13.5	9.4
n-Butylamine	17	0.02	850	20 000	23	10.6
Isopropylamine	9.5	0.01	950	1 230	1.3	10.6

<sup>a</sup> Measurements at ionic strength 0.1M, except data with DABCO which are at  $I$  0.05M. <sup>b</sup> Ref. 11.

the basicity order in water where piperidine is the most basic amine. However it has recently been shown<sup>10</sup> that on transfer from water to DMSO secondary and tertiary amines suffer decreases in basicity while the basicity of primary amines is slightly enhanced, so that our basicity order is reasonable.

**σ-Adduct Formation.**—Steric effects which should be relatively unimportant in the proton-transfer reaction from the side-chain are likely to be much more evident in σ-adduct formation which necessitates covalent bond formation between the amine and a ring-carbon atom.

Addition may occur at the 1-position to give (4) or at

the 3-position to give (5). In the case of TNT n.m.r. data are inconclusive. However it is known that 1:1  $\sigma$ -adducts formed by reaction with alkoxides,<sup>2,3</sup> sulphite,<sup>12</sup> or liquid ammonia<sup>5</sup> all result from attack at the 3-position. Hence a similar position of attack seems probable with the amines used here. Although it is dangerous to draw conclusions from visible spectra<sup>13</sup> there is a very marked similarity between the spectral

TABLE 15

Comparison of equilibrium and rate constants for reaction of TNBCl and TNT with amines in DMSO

	$\frac{K_p(\text{TNBCl})}{K_p(\text{TNT})}$	$\frac{k_p(\text{TNBCl})}{k_p(\text{TNT})}$	$\frac{k_{-p}(\text{TNBCl})}{k_{-p}(\text{TNT})}$
DABCO	45	0.8	0.02
Piperidine	42	2.1	0.05
Benzylamine	18	0.9	0.05
n-Butylamine	31	1.9	0.06
Isopropylamine	66	3.0	0.04

shapes of the piperidine adduct (Figure 1) and the 3-methoxy-adduct which shows<sup>3</sup> maxima at 430 and 495 nm with intensity ratio 1.1. (The shift to longer wavelength on changing from an oxygen to a nitrogen base is expected.<sup>13</sup>) We conclude that it is likely that the adducts from TNT have structure (5; X = H). The values of  $K_e$  in Table 14 decrease in the order n-butylamine > piperidine > benzylamine > isopropylamine. This is the same order, apart from the position of isopropylamine, as for values of  $K_p$  which reflect the basicities of the amines in DMSO. The depressed value of  $K_e$  for isopropylamine may reflect unfavourable steric interaction in the  $\sigma$ -adduct (5; X = H, R = Pr<sup>i</sup>, R' = H). A similar though less severe effect has been noted<sup>6</sup> in the adduct formed from 1,3,5-trinitrobenzene and isopropylamine.

With TNBCl there is definite n.m.r. evidence that with n-butylamine and isopropylamine attack occurs at the 1-position to give adducts of structure (4; X = Cl). In fact the visible spectra of adducts formed with n-butylamine, isopropylamine, and benzylamine have similar characteristics with maxima at 452 and 540–550 nm, the higher-energy band having much the higher intensity. This may indicate that with benzylamine addition also occurs at the 1-position. In contrast the spectrum of the  $\sigma$ -adduct from TNBCl and piperidine has maxima at 450 and 510 nm with similar intensities. It may be that this difference indicates a different mode of interaction so that the piperidine adduct has structure (5; X = Cl). In fact the visible spectrum produced from TNBCl and piperidine is very similar to that produced from TNT and piperidine.

Two factors favouring attack at the 1-position in TNBCl relative to TNT are the inductive withdrawal of the CH<sub>2</sub>Cl group relative to the CH<sub>3</sub> group, and the considerable relief of steric strain which will be felt as the bulky CH<sub>2</sub>Cl group is bent from the ring-plane. These factors account for the high values of  $K_e$ , relative to  $K_p$  values, found with n-butylamine and benzylamine. An unfavourable factor will be steric strain imposed by

the presence of two bulky groups at the 1-position in the adducts (4; X = Cl). (It is noteworthy that attack of the bulky sulphite ion occurs<sup>12</sup> at the 3-position of TNBCl.) This latter factor may reduce the ratio of  $K_e/K_p$  observed with isopropylamine, and inhibit piperidine attack at the 1-position.

## EXPERIMENTAL

2,4,6-Trinitrotoluene, m.p. 82° (lit.,<sup>14</sup> 82°), and 2,4,6-trinitrobenzyl chloride, m.p. 85° (lit.,<sup>15</sup> 85°), were available from previous work,<sup>4</sup> as were the amines.<sup>6</sup> Piperidine hydrochloride was a commercial pure specimen used as supplied. Other salts were prepared as concentrated stock solutions in DMSO from weighed amounts of amine and perchloric acid.

<sup>1</sup>H n.m.r. measurements were made with Bruker HX90E or Varian EM360L instruments using tetramethylsilane as internal reference. [<sup>2</sup>H<sub>6</sub>]Dimethyl sulphoxide was used as solvent with substrate concentration 0.1M. Anionic species were generated from the substrates either by the addition of amines alone, or by the addition of amines to solutions containing substrate and sodium methoxide<sup>7</sup> in a molar ratio of 1:1.

Visible spectral measurements were made with Unicam SP500, Beckman 25, or Canterbury stopped-flow spectrophotometers using freshly prepared solutions of reagents. All rate measurements were made at 25° with amine concentration in large excess of substrate concentration so that first-order kinetics were observed. In most cases rate coefficients are the mean of five separate determinations and are precise to  $\pm 5\%$ .

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