Studies on Nitroaromatic Compounds. Part 8.† A Kinetic and Spectroscopic Study of the Reaction of Di- and Tri-ethylamine with 1,5-Dimethyl-2,4,8-trinitronaphthalene

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The reaction of 1,5-dimethyl-2,4,8-trinitronaphthalene with diethylamine and triethylamine in DMSO and in DMSO–MeOH solvent systems has been studied. ^{1}H N.m.r. investigations have shown that a benzyl type anion is formed due to hydrogen abstraction from the 1-methyl group of the nitroaromatic compound. Kinetic and thermodynamic data for the systems have been determined. The results are explained in terms of the difference in solvation of the two amines and the charged products and the difference in solvating ability of the solvent media used. The effect of added triethylammoniun chloride on the reaction of 1,5-dimethyl-2,4,8-trinitronaphthalene with triethylamine in DMSO has been studied and the change in kinetics is attributed to ion association between the added salt and the charged products.

KINETIC, thermodynamic, and structural investigations of the reaction of bases with nitroaromatic compounds have received considerable attention and a variety of products have been proposed including Meisenheimer complexes, radical ions, and carbanions.[1-6]

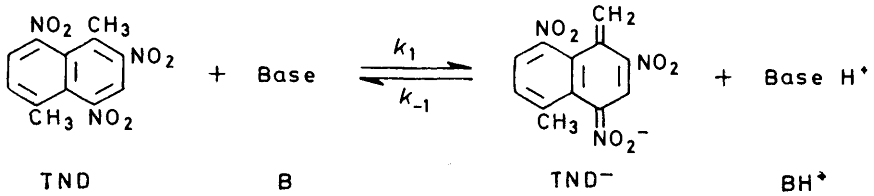
The kinetics of the reaction of 2,4,6-trinitrotoluene with base to give the 2,4,6-trinitrobenzyl anion has been investigated by various workers,[7-11] but only recently has there been a successful n.m.r. investigation of the formation of this anion in flow and static systems.[12] N.m.r. spectroscopy has also been used to show the formation of a benzyl type anion in the reaction of 1,5-dimethyl-2,4,8-trinitronaphthalene with methoxide ion.[13] As far as is known, no other evidence for the formation of benzyl type anions from alkylpolynitronaphthalenes has been reported.

Previous studies of the reaction of amines with nitroaromatic compounds have indicated the formation of the zwitterionic form of a Meisenheimer complex and the conjugate base of this complex. For example, primary and secondary amines react with 2,4,6-trinitro-benzene and -anisole in DMSO to give a Meisenheimer complex with addition at C-1.[14-17] The reaction of butylamines with ethyl 2,4-dinitro-1-naphthyl ether in DMSO proceeds through an intermediate zwitterionic Meisenheimer complex by addition at C-1. The complex then loses a proton to the base to give the conjugate base of the neutral zwitterionic form.[18] Recently a flow n.m.r. study of this system confirmed the presence of the intermediate complexes.[19]

The present paper reports on the formation of a benzyl type anion in the reaction of diethylamine and triethylamine with 1,5-dimethyl-2,4,8-trinitronaphthalene (TND) in DMSO and DMSO–MeOH solvent systems.

RESULTS

Spectroscopy.—The ^{1}H n.m.r. spectrum of a mixture of TND and one equivalent of triethylamine in [$^2H_6$]dimethyl sulphoxide exhibited a set of product peaks which were assigned to the benzyl type anion, TND$^-$, shown in the Scheme. No peaks attributable to products other than those of the Scheme were observed in the spectrum. A similar ^{1}H n.m.r., spectrum was obtained for the product formed when diethylamine was added to TND in [$^2H_6$]-dimethyl sulphoxide. The product resonances in these spectra were in similar positions to those reported for the product formed on reaction of TND with methoxide ion.[13]



SCHEME

^{1}H N.m.r. spectroscopy showed that the reactions did not go to completion when methanol was present in the solvent system. Thus, the ^{1}H n.m.r. spectrum of a reaction system containing TND and three equivalents of triethylamine in a 3 : 1 mixture of [$^2H_6$]dimethyl sulphoxide–[$^2H_4$]methanol exhibited peaks due to both TND and TND$^-$. Addition of further [$^2H_4$]methanol to the system shifted the equilibrium position as evidenced by an increase in the relative intensity of the peaks due to TND and a concomitant decrease in intensity of the peaks due to TND$^-$. That is, the equilibrium constant for the system shown in the Scheme decreases as the methanol content of the solvent increases.

Visible absorption spectra of mixtures of TND and either di- or tri-ethylamine are typified by that shown in Figure 1. Since neither the reactants or the BH$^+$ species absorb in the visible region, the band with $\lambda_{max.}$ at 560 nm can be assigned to the TND$^-$ anion. The values obtained for the molar decadic absorptivity, ε, of this species at 560 nm by reacting TND with excess of diethylamine and substituting the final absorbance (Abs) into the expression (Abs) = $\varepsilon[\text{TND}]_0 l$ are 1 970, 1 960, and 1 940 m^2 mol^{-1} at 303.5, 314.0, and

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† Part 7 is ref. 13.

324.5 K, respectively. There is good agreement between these values and the respective values of 2 000, 1 970, and 1 940 m^2 mol^{-1}, determined at the same temperatures, from Benesi–Hildebrand type plots on the results of the reaction of TND with an excess of triethylamine. A point of note is that the values for ε decrease with increase in temperature, a trend which has previously been reported for the values of ε for the charge-transfer complex formed between hexamethylbenzene and tetracyanoethylene.[20]

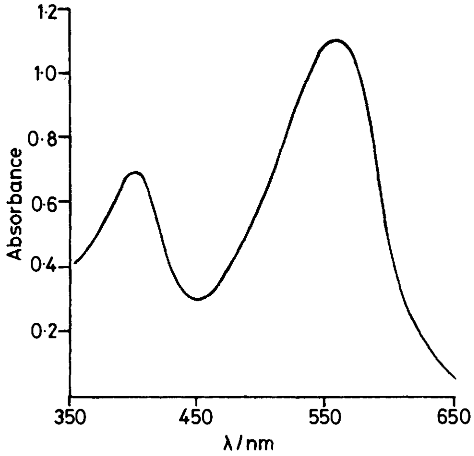


FIGURE 1 Absorption spectrum of a solution containing TND (6.8×10^{-5}M) and 800 equiv. of diethylamine in DMSO–MeOH (2 : 1). Cell path length l = 10 mm

Kinetics.—Kinetic results were obtained by monitoring the change with time of the absorbance due to the TND^- anion at 560 nm. Kinetic analyses were then carried out using the appropriate equations given in the Experimental section. In the majority of cases the initial concentration of base was in excess, usually between 100 and 1 600 times the initial concentration of TND, so that pseudo-first-order kinetics applied to the forward reaction and second-order kinetics to the reverse reaction of the Scheme. For this situation, the pseudo-first-order rate constant, k_{obs}, for the forward reaction was evaluated using either equations (1) or (2). The values of k_{obs} for the reaction of TND with diethylamine and with triethylamine in different solvent systems are listed in Tables 1 and 2 respectively.

The second-order rate constant, k_1, for the forward reaction is related to k_{obs} by the expression $k_{obs} = k_1$[Base], and the values for k_1 listed in Tables 1 and 2 were obtained from the slope of the straight line plots of k_{obs} *versus* [Base].

Values for the equilibrium constant, K for the reaction of TND with base under various conditions are also listed in Tables 1 and 2. These values were derived using equations (3) or (4), or, in the case of solvent containing 67% DMSO, from the ratio of k_1/k_{-1}. Typical plots according to equation (4) are shown in Figure 2. The values for the second-order reverse rate constant, k_{-1}, given in Tables 1 and 2 were derived in most cases from the relationship $k_{-1} = k_1/K$. In

TABLE 1

Kinetic data for reaction of TND with diethylamine

t °C	% DMSO by vol. in solvent	10^5[TND]/M	$10^3[HNEt_2]$/M	$10^3k_{obs}/s^{-1}$	$k_1/dm^3\ mol^{-1}\ s^{-1}$	$k_{-1}/dm^3\ mol^{-1}\ s^{-1}$	K
21.4	100	5.11	5.11	1.93	0.37	0.45	0.82 [a]
		5.11	10.22	3.81			
		5.11	15.30	5.62			
30.5	100	5.11	5.11	3.01	0.59	0.89	0.65 [a]
		5.11	5.11	3.12			
		5.11	5.11	3.13			
		5.11	10.22	5.93			
		5.11	15.30	9.33			
41.4	100	5.11	5.11	5.38	0.97	1.67	0.59 [a]
		5.11	5.11	5.50			
		5.11	10.22	10.30			
		5.11	10.22	10.23			
		5.11	15.30	15.10			
		5.11	15.30	14.50			
31.5	67	6.82	6.82	0.792	0.112	0.86 [b]	0.130 [c]
		6.81	13.60	1.44			
		6.80	34.00	4.00			
		6.78	54.30	5.99			
41.0	67	6.82	3.41	0.588	0.210	2.35 [b]	0.089 [c]
		6.82	6.82	1.16			
		6.81	13.60	2.89			
		6.78	54.30	11.00			
51.5	67	3.41	3.41	1.14	0.36	5.99 [b]	0.060 [c]
		6.81	13.60	4.83			
		6.80	34.00	12.26			
30.5	50	5.11	10.22	0.567	0.06	0.50	0.12
		5.11	15.30	0.882			
		5.09	50.90	3.02			
		5.09	50.90	3.10			
41.0	50	5.11	5.11	0.405	0.088	3.14	0.028
		5.11	10.20	0.784			
		5.11	15.30	1.26			
		5.10	30.60	2.66			
		5.09	50.90	4.11			
52.3	50	5.11	10.22	1.97	0.213	10.00	0.021
		5.11	15.30	2.98			
		5.09	50.90	10.82			

[a] Value determined using low base concentrations. [b] Value determined using equation (5). [c] Value determined from k_1/k_{-1}.

TABLE 2

Kinetic data for the reaction of TND with triethylamine

t/°C	% DMSO by vol. in solvent	10^5[TND]/M	10^3[NEt$_3$]/M	10^3k_{obs}/s^{-1}	k_1/dm^3 mol^{-1} s^{-1}	k_{-1}/dm^3 mol^{-1} s^{-1}	K
30.0	100	5.11	5.11	0.441	0.081	0.64	0.126
		5.11	10.22	0.862			
		5.09	40.07	3.34			
		5.06	80.93	6.53			
40.8	100	5.11	5.11	0.854	0.133	1.13	0.118
		5.11	10.22	1.62			
		5.11	10.22	1.63			
		5.10	20.40	3.05			
		5.09	40.70	6.12			
		5.06	80.93	10.20			
		5.06	80.93	11.05			
51.3	100	5.11	2.56	0.684	0.268	3.01	0.089
		5.11	3.83	1.08			
		5.11	5.11	1.41			
		5.11	10.22	2.82			
		5.11	10.22	2.80			
		5.10	25.50	6.82			
60.3	100	5.11	2.56	1.19	0.449	4.93	0.091
		5.11	5.11	2.18			
		5.11	5.11	2.41			
		5.11	10.22	4.59			
31.3	90	4.60	4.60	0.275	0.068	0.51	0.134
		4.60	9.20	0.621			
		4.60	10.50	0.782			
		4.59	23.00	1.59			
		4.58	36.70	2.42			
		4.57	54.80	3.77			
		4.56	72.90	4.96			
41.0	90	4.60	4.60	0.507	0.113	1.40	0.081
		4.60	11.49	1.28			
		4.58	36.70	4.14			
52.0	90	4.60	4.60	0.877	0.201	4.18	0.048
		4.60	11.49	2.41			
		4.58	36.70	7.91			
		4.56	72.90	14.40			
31.6	80	5.11	5.11	0.241	0.049	0.702	0.070
		5.11	10.22	0.453			
		5.10	20.40	1.09			
		5.09	40.70	2.07			
		5.07	60.90	3.02			
		5.06	81.00	3.94			
31.5	67	6.82	5.11	0.176	0.038	2.28 [a]	0.0167 [b]
		6.81	6.81	0.201			
		6.81	10.22	0.273			
		6.79	27.20	0.827			
		6.78	40.70	1.52			
		6.77	54.20	2.07			
41.0	67	6.82	5.11	0.216	0.070	6.84 [a]	0.0079 [b]
		6.81	10.22	0.497			
		5.10	20.40	1.09			
		5.07	60.90	3.28			
51.5	67	6.82	5.11	0.383	0.117	17.8 [a]	0.0066 [b]
		6.81	10.22	0.815			
		6.79	27.20	2.47			
		5.09	40.70	3.68			
		5.07	60.90	5.62			
60.3	67	6.82	6.82			32.3 [a]	
32.0	50	5.11	10.22	0.182	0.021	4.88	0.0043
		5.11	15.30	0.300			
		5.10	20.40	0.455			
		5.09	30.60	0.611			
		5.08	50.80	1.06			
41.0	50	5.11	10.22	0.217	0.027	15.9	0.0017
		5.09	30.60	0.868			
		5.08	50.80	1.33			
52.3	50	5.11	10.22	0.635	0.070	25.9	0.0027
		5.09	30.60	2.17			
		5.68	50.80	3.50			

[a] Value determined using equation (5). [b] Value determined from k_1/k_{-1}.

those systems where the solvent contained 67% DMSO, values for k_{-1} were determined using equation (5).

Arrhenius plots for the change with temperature of k_1 and k_{-1} in different solvent mixtures gave good straight lines. Values for the enthalpy of activation, $\Delta H^{\ddagger}$, and entropy of activation, $\Delta S^{\ddagger}$, calculated from such plots are listed in Table 3. Also listed in certain cases are the calculated values for the overall enthalpy change, ΔH, and the overall entropy change ΔS, for the two reaction systems.

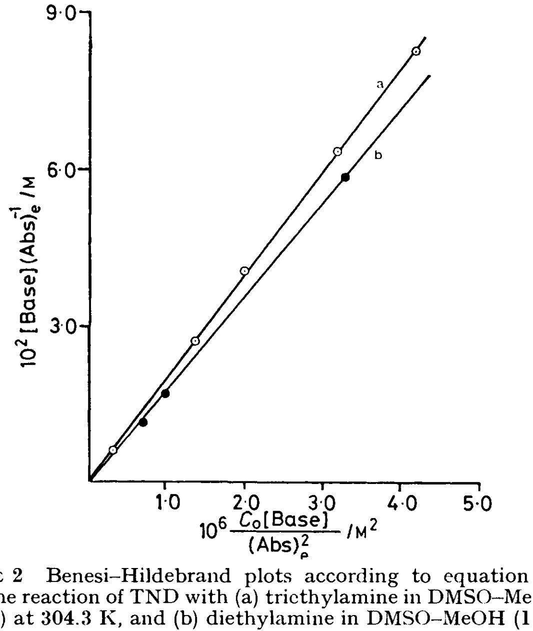


FIGURE 2 Benesi–Hildebrand plots according to equation (4) for the reaction of TND with (a) triethylamine in DMSO–MeOH (9 : 1) at 304.3 K, and (b) diethylamine in DMSO–MeOH (1 : 1) at 303.5 K

TABLE 3

Thermodynamic parameters for the reaction of TND with di- and tri-ethylamine in DMSO–MeOH at 298 K

Base	% DMSO	$\Delta H_1^{\ddagger}$/ kJ mol^{-1}	$\Delta H_{-1}^{\ddagger}$/ kJ mol^{-1}	ΔH/ kJ mol^{-1}	$\Delta S_1^{\ddagger}$/ J K^{-1} mol^{-1}	$\Delta S_{-1}^{\ddagger}$/ J K^{-1} mol^{-1}	ΔS/ J K^{-1} mol^{-1}.
Et_2NH	100	34.9 ± 3.0	48.4 ± 4.0	−13.5 ± 5.0	−135 ± 6	−87 ± 8	−48 ± 10
	67	45.6 ± 3.0	76.0 ± 3.5	−30.4 ± 4.6	−113 ± 6	3 ± 7	−117 ± 9
	50	45.2 ± 4.5			−120 ± 10		
Et_3N	100	45.9 ± 3.0	56.4 ± 4.0	−10.5 ± 5.0	−115 ± 6	−63 ± 8	−52 ± 10
	90	40.4 ± 4.0	82.3 ± 4.0	−41.9 ± 5.7	−135 ± 8	12 ± 8	−147 ± 11
	67	43.7 ± 3.0	81.0 ± 3.5	−37.3 ± 4.6	−129 ± 6	28 ± 7	−157 ± 9
	50	47.0 ± 4.5			−124 ± 10		

The standard state in $\Delta S^{\ddagger}$ calculations taken as 1 mol dm^{-3}.

Kinetic data for the reaction of TND with triethylamine in the presence of triethylammonium chloride are given in Table 4.

TABLE 4

Kinetic data for the reaction of TND (5.12×10^{-5}M) with triethylamine in DMSO at 313.4 K in the presence of triethylammonium chloride (5.12×10^{-3}M)

$10^2[Et_3N]$/M	10^3k_{obs}/s^{-1}	k_1 [a]/dm^3 mol^{-1} s^{-1}	k_{-1}/dm^3 mol^{-1} s^{-1}
0.512	0.661	0.129	0.076,[b] 0.067 [c]
1.024	1.350	0.132	
8.190	9.910	0.121	

[a] Derived from expression $k_f = k_{obs}/[\text{Base}]$. [b] Derived from expression $k_{-1} = k_1/K$ where the value of K as determined experimentally using equation (7) is 1.67. [c] Determined by addition of triethylammonium chloride (5.12×10^{-3}M) to a previously equilibriated mixture of TND (5.12×10^{-5}M) and triethylamine (1.02×10^{-3}M) followed by analysis using equation (9).

DISCUSSION

Tables 1 and 2 show that the rate constants, k_1, for the forward reaction increase as the percentage of DMSO in the solvent system increases, whilst Figure 3 shows that a reasonably linear relationship is observed when log k_1 is plotted against % DMSO. The rate constants, k_{-1}, for the reverse reaction decrease as the percentage of DMSO is increased although the results for the composition range 90—100% DMSO are not entirely consistent with this behaviour.

Generally in the formation of Meisenheimer complexes from lyate ions and nitroaromatic compounds in DMSO–ROH solvent mixtures, the increase in the forward rate constant as the amount of DMSO is increased is attributed to the enhanced nucleophilicity of the lyate ion which results from the lower solvation of the ion as the percentage of DMSO increases,[3,5,6] whilst the decrease in the reverse rate constant is attributed to the enhanced solvation of the Meisenheimer complex in solvents containing a high percentage of DMSO.[5] Normally when anions react with aromatic molecules in Meisenheimer complex formation or in nucleophilic displacement reactions, $\Delta H^{\ddagger}$ decreases and $\Delta S^{\ddagger}$ often increases as the percentage of DMSO in the solvent increases.[21,22] However the opposite trend in $\Delta H^{\ddagger}$ was observed for the reaction between hydroxide ion and 2,4-dinitrophenyl 3-nitrophenyl ether.[23]

In the present study of hydrogen abstraction by a neutral base from a nitroaromatic compound, the increase in k_1 with increase in the DMSO content of the solvent for the reaction of TND with triethylamine appears to be due to an increase in $\Delta S_1^{\ddagger}$, as indicated by the trend in $\Delta H_1^{\ddagger}$ values (see Table 3). However, for the reaction with diethylamine the corresponding increase in k_1 appears to be due to a decrease in $\Delta H_1^{\ddagger}$. For both reactions the decrease in k_{-1} as the percentage of DMSO increases is due to a large decrease in $\Delta S_{-1}^{\ddagger}$ compensating for a decrease in $\Delta H_{-1}^{\ddagger}$.

An interesting feature of the results given in Table 3 is that for the reaction of TND with both di- and triethylamine the overall enthalpy change, ΔH, is more exothermic in mixed solvent than in 100% DMSO. This can be explained on the basis that there is a greater degree of solvation of products in the mixed solvent than in 100% DMSO, with the greater solvation arising because of hydrogen bonding between methanol in the mixed solvent and nitro-groups carrying a partial negative charge in the product species.[23,24] Thus, the greater release of energy arises because hydrogen bonding stabilises the system relative to the situation where hydrogen bonding does not occur. The fact that the overall entropy change, ΔS, for the two reactions are much more negative in mixed solvent than in 100% DMSO is consistent with the foregoing in that there will be a lesser degree of freedom for product molecules and a more ordered system produced in the mixed solvent.

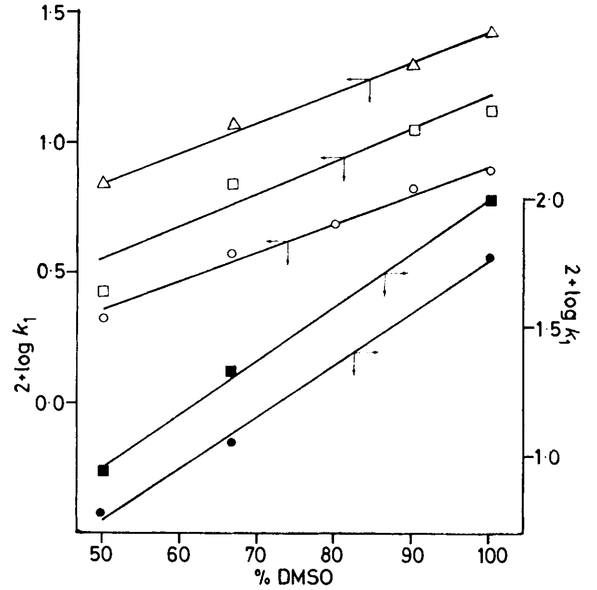


FIGURE 3 Plots of log k_1 against % DMSO in solvent for reaction of TND with (a) diethylamine at 303.5 (●) and 314 K (■), and (b) triethylamine at 304.5 (○), 314 (□), and 325 K (△)

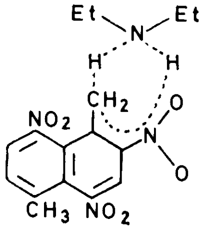
It is noteworthy that in 67% DMSO the overall entropy change is less negative for the reaction with diethylamine than for that with triethylamine. The most likely explanation is that in the former reaction system hydrogen bonding occurs between the amine hydrogen of diethylamine and the methanol in the mixed solvent [25] and, as a consequence, diethylamine is solvated to a greater extent than triethylamine. This would lead to a smaller decrease in entropy on forming products from the TND–diethylamine system than from the TND–triethylamine system.

The large negative values for the entropy of activation, $\Delta S^{\ddagger}$, for the forward step in the reaction of TND with both of the amines in the different solvent systems indicates that the activated complex is more highly ordered than the reactants. It is of interest that the values for the entropy of activation given in Table 3 are similar to the value of -134 J K^{-1} mol^{-1} determined for the reaction of n-butylamine with ethyl 2,4-dinitro-1-naphthyl ether in DMSO to form a zwitterionic Meisenheimer complex by addition at C-1.[18]

The value of $\Delta S_1^{\ddagger}$ for the reaction of TND with diethylamine in 100% DMSO is more negative than the corresponding value for the reaction with triethylamine. Since solvation of the reactants in the two systems will be similar in 100% DMSO, this result implies that there is a greater restriction imposed on the activated complex in the former situation. This could arise by the formation of the complex (X) which contains an eight-membered ring in which bonding occurs to the hydrogen atom of diethylamine. This conclusion supports the postulate previously put forward of involvement of an eight-membered cyclic transition state in hydrogen abstraction from 2,4,6-trinitrotoluene by sodium isopropoxide.[26]

The entropy of activation, $\Delta S_{-1}^{\ddagger}$, for the reverse reaction has positive values for the reactions carried out in mixed solvent and negative values for the reactions carried out in 100% DMSO (see Table 4). This is consistent with the expected large increase in entropy when during the course of the reverse reaction in mixed solvent, the activated complex is formed from the two highly solvated charged species TND$^-$ and BH$^+$.

Comparison of the results presented in Table 4 for the reaction of TND with triethylamine in DMSO at 313.4 K in the presence of triethylammonium chloride with the corresponding results at 314.0 K in the absence of triethylammonium chloride (Table 2) shows that the effect of the added salt is to decrease the value of the reverse rate constant, k_{-1}, from 1.130 to 0.076 dm^3 mol^{-1} s^{-1} and to increase the value of the equilibrium constant from 0.12 to 1.67. These results parallel the observations of previous workers [6] who noted that in the formation of a Meisenheimer complex by addition of methoxide ion to substituted dinitro-anisoles the value of K increased markedly with increase in concentration of sodium methoxide owing to an apparent decrease in k_{-1} values. Both sets of results are explainable in terms of the charged product, benzyl-type ion or Meisenheimer complex, being stabilised by ion association.



(X)

EXPERIMENTAL

1,5-Dimethyl-2,4,8-trinitronaphthalene (TND) was prepared and purified as previously described.[27] Reagent grade di- and tri-ethylamine were distilled using a Fischer Spaltrohr 60 theoretical plate column, the middle fractions being selected. Dimethyl sulphoxide (reagent grade), [$^2H_6$]dimethyl sulphoxide, AnalaR methanol, and [$^2H_4$]-methanol were dried over molecular sieve prior to use. Triethylammonium chloride was prepared by addition of concentrated hydrochloric acid to stirred triethylamine at 0 °C; the crystals formed on neutralisation were filtered off, twice recrystallised from absolute ethanol, and dried in *vacuo*.

90-MHz ^{1}H Continuous-wave n.m.r. spectra were recorded at 31 °C on a Perkin-Elmer R32 spectrometer, whilst 90-MHz ^{1}H Fourier-transform n.m.r. spectra were recorded on the same instrument fitted with a Nicolet TT4 Fourier transform unit. 220-MHz ^{1}H continuous-wave n.m.r. spectra were recorded at PCMU, Harwell. Chemical shifts were measured relative to internal tetramethylsilane as reference. Dissolution of TND (0.021 g) in [$^2H_6$]dimethyl sulphoxide (0.5 cm^3) followed by addition of triethylamine (0.01 cm^3) and recording of the 220 MHz spectrum within 5 min gave the following spectrum for the benzyl type anion: τ 1.35 (1 H, s), 2.54 and 2.72 (2 H, ABq, J_{AB} 8 Hz), 4.09 (1 H, s), 5.12 (1 H, s), and 7.86 (3 H, s).

U.v.–visible absorption spectra were recorded on a Perkin-Elmer SP 1700 spectrophotometer using 10 mm matched silica cells in a thermostatted cell compartment maintained at ±0.1 °C. Reaction mixtures were prepared by mixing thermostatted solutions of TND with the appropriate amine in a cell capped with a PTFE stopper. To check that evaporation of the amine did not occur, the PTFE stopper was replaced by a silica-seal rubber cap in some runs and the amine injected through the cap by syringe. Identical results were obtained by each method. Reversal of the reaction was achieved by letting the reaction reach the equilibrium position, removing one-third of the solution from the cell, replacing with the same volume of methanol at the same temperature, the cell being rapidly shaken and replaced in the spectrophotometer. Reversal of the reaction was also achieved by adding 0.5 cm^3 of triethylammonium chloride (3.07×10^{-2}M) in DMSO to 2.5 cm^3 of an equilibrated mixture of TND (5.12×10^{-5}M) and triethylamine (1.023×10^{-3}M) in DMSO.

Treatment of Experimental Data.—In cases where pseudo-first-order kinetics applied to the forward reaction and second-order kinetics to the reverse reaction of the Scheme values for the pseudo-first-order rate constant, k_{obs}, were obtained from plots according to equation (1) where C_o

$$\ln\left[\frac{C_oC^-{}_e + C^-(C_o - C^-{}_e)}{C_o(C_e^- - C^-)}\right] = \frac{(2C_o - C^-{}_e)}{C_e^-}\,k_{obs}t \qquad (1)$$

represents the initial concentration of TND, and C^- and C_e^- represent the respective concentrations of TND$^-$ at time *t* and at equilibrium. The reaction between TND and excess of diethylamine in DMSO proceeded virtually to completion and for this system equation (1) could be used in the simplified form (2).

$$-\ln(C_e^- - C^-) = k_{obs}t + \text{constant} \qquad (2)$$

The concentration of TND$^-$ during a run was determined by monitoring the absorbance, (Abs), at 560 nm and substituting the absorbance values into the Beer–Lambert relationship $C^- = (\text{Abs})/\varepsilon l$. The molar absorptivity, ε, of the TND$^-$ anion was determined from Benesi–Hildebrand type plots, according to either equations (3) or (4), with the latter equation being used in the majority of cases. The equilibrium constant, *K*, was also determined from these plots.

$$\frac{C_o}{(\text{Abs})_e} = \frac{(\text{Abs})_e}{[\text{Base}]\,K(\varepsilon l)^2} + \frac{1}{\varepsilon l} \qquad (3)$$

$$\frac{[\text{Base}]}{(\text{Abs})_e} = \frac{C_o[\text{Base}]\varepsilon l}{(\text{Abs})_e^2} + \frac{1}{\varepsilon l K} \qquad (4)$$

Since the reaction of TND with excess of diethylamine in DMSO proceeded to virtual completion under the conditions used for kinetic runs, the molar absorptivity, ε, could be obtained directly from the expression $C_o = (\text{Abs})_e/\varepsilon l$. However the equilibrium constant, *K*, had to be determined using lower base concentrations than those used in the kinetic runs. Typically a ratio of [Base]/C_o of *ca.* 10 used, and the values of *K* were obtained by substitution of the measured value of $(\text{Abs})_e$ into equation (3) or (4).

In a number of runs, reaction mixtures in DMSO were allowed to reach equilibrium and sufficient methanol was then added to give a final solvent composition containing 67% DMSO. Addition of the methanol resulted in a reversal of the forward reaction of the Scheme, and the resultant decrease in absorbance at 560 nm was followed with time. The kinetic expression applicable in these cases is given in equation (5) where C_o is the concentration

$$\ln\left[\left\{\frac{C^- + C_eC_o/(C_o - C_e^-)}{C^- - C_e^-}\right\}\left\{\frac{C_o^- - C_e^-}{C_o^- + C_e^-C_o/(C_o^- - C_e^-)}\right\}\right] = \frac{C_o - C_e^-}{C_e^-(2C_o - C_e^-)}\,k_{-1}t \qquad (5)$$

of TND in the original DMSO solvent multiplied by a dilution factor of 2/3, C_o^- and C^- are the respective concentrations of TND$^-$ immediately after the addition of methanol and after time *t* and C_e^- is the concentration of TND$^-$ at the *final* equilibrium position. Values of k_{-1} were determined by plotting the left-hand side of equation (5) against *t*.

The reaction of TND with excess triethylamine in DMSO in the presence of triethylammonium chloride was investigated in a number of runs and was found to obey pseudo-first-order forward and first-order reverse kinetics. Plots based on equation (6) were used to derive values for the pseudo-first-order rate constant k_{obs} from which values for the rate constant k_1 were determined using the expression $k_{obs} = k_1[\text{Base}]$. The values of ε and *K* for these systems

$$-\frac{C_e^-}{C_o}\ln\left[1 - \frac{C^-}{C_e^-}\right] = k_{obs}t \qquad (6)$$

were determined from Benesi–Hildebrand type plots according to equation (7) where [BH$^+$] represents the concentration of triethylammonium chloride.

$$\frac{C_o}{(\text{Abs})_e} = \frac{[\text{BH}^+]}{K\varepsilon l[\text{Base}]} + \frac{1}{\varepsilon l} \qquad (7)$$

Addition of triethylammonium chloride to a previously equilibrated mixture of TND and triethylamine in DMSO causes reversal of the forward reaction of the Scheme and a consequent decrease in the absorbance at 560 nm due to the TND$^-$ anion. The kinetic expression (8) applies to the approach to the new equilibrium position where C_0 is the

$$-\ln\left[\frac{C^- - C_e^-}{C_o^- - C_e^-}\right] = [\text{BH}^+]\left[1 + \frac{C_e^-}{C_o - C_e^-}\right]k_{-1}t \qquad (8)$$

initial concentration of TND corrected for dilution caused by addition of the solution of triethylammonium chloride in DMSO, C_o^- is the concentration of TND$^-$ at the first equilibrium position, and C^- and C_e^- are the respective concentrations of TND$^-$ at time *t* after the addition of triethylammonium chloride and at the *final* equilibrium position. The second-order rate constant, k_{-1}, for the reverse reaction was determined by monitoring the decrease in absorbance at 560 nm with time after the addition of triethylammonium chloride and plotting the results according to the following modified form of equation (8)

$$-\ln(C^- - C_e^-) = ak_{-1}t + b \qquad (9)$$

where a and b are constants.

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