The Stabilities of Meisenheimer Complexes. Part 14.[1] Equilibrium and Kinetic Data for Sodium Ethoxide Addition to 2,4-Dinitro-6-X-phenetoles in Ethanol

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Equilibrium and kinetic data are reported for sodium ethoxide addition in ethanol to a series of 2.4-dinitro-6-X-phenetoles (X = NO_2. CO_2Et. Cl. or H) to give 1.1-σ complexes. In the case of 2.4.6-trinitrophenetole data for 1.3-complex formation are also provided. The results are compared with those for methoxide additions and are assessed in terms of the electronic and steric behaviour of the substituents. The 1,1-diethoxy-complexes. but not the 1.3-complex, associate strongly with sodium ions. It is suggested that this association involves interaction of the cation with the oxygen atoms of the alkoxy-groups at C(1) and the *ortho*-substituents.

ONE of the first kinetic studies of σ-complex formation was that of Ainscough and Caldin[2] who measured rates of two reactions of sodium ethoxide and 2,4,6-trinitroanisole at low temperatures. The faster process would in the light of present knowledge[3] be interpreted as giving rise to ethoxide addition at the unsubstituted 3-position and the slower process, which leads to the thermodynamically more stable adduct, to addition at the 1-position. More recently data have been reported for the addition of ethoxide at ring carbon atoms carrying hydrogen in 1,3,5-trinitrobenzene[4,5] and 1-chloro-2,4,6-trinitrobenzene[6] (picryl chloride). The information relating to ethoxide addition is however sparse compared with that available for methoxide addition to ring-activated anisoles.[7]

We report here rate and equilibrium data for sodium ethoxide addition to a series of 2,4-dinitro-6-X-phenetoles (I; R = Et, X = NO_2, CO_2Et, Cl, or H) to give the 1,1-diethoxy-complexes (II; R = Et, X = NO_2, CO_2Et, Cl, or H) and also in the case of 2,4,6-trinitrophenetole the 1,3-adduct (III; R = Et, X = NO_2). The results are assessed in terms of the steric and electronic behaviour of the substituents.

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[1] Part 13, M. R. Crampton and M. J. Willison, *J.C.S. Perkin II*, 1976, 901.

[2] J. B. Ainscough and E. F. Caldin, *J. Chem. Soc.*, 1956, 2528.

[3] For reviews see M. R. Crampton, *Adv. Phys. Org. Chem.*, 1969, **7**, 211; M. J. Strauss, *Chem. Rev.*, 1970, **70**, 667.

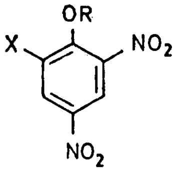
[4] C. F. Bernasconi, *J. Amer. Chem. Soc.*. 1970, **92**, 4682.

[5] L. H. Gan and A. R. Norris, *Canad. J. Chem.*, 1971, **49**, 2490.

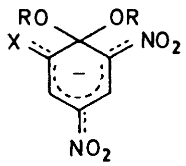
[6] L. H. Gan, *Austral. J. Chem.*, 1975, **28**, 2403.

[7] It is not possible to give a complete literature survey, but see *e.g.* (*a*) V. Gold and C. H. Rochester, *J. Chem. Soc.*, 1964, 1687; (*b*) M. R. Crampton and H. A. Khan, *J.C.S. Perkin II*, 1972, 1173, 1178; (*c*) C. F. Bernasconi, *J. Amer. Chem. Soc.*, 1971, **93**, 6975; (*d*) F. Terrier and F. Millot, *Bull. Soc. chim. France*, 1970, 1743 1974, 1823; (*e*) E. J. Fendler, J. H. Fendler, N. L. Arthur, and C. E. Griffin, *J. Org. Chem.*, 1972, **37**, 812.

In view of our previous evidence[8] for ion-association of 1,1-dimethoxy-complexes with cations we were particularly interested in the possibility of similar association of the 1,1-diethoxy-complexes with cations.



(I)



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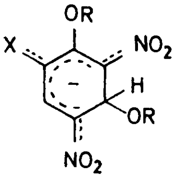

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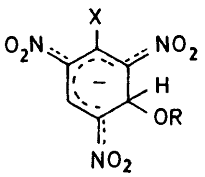


(IV)

EXPERIMENTAL

2,4,6-Trinitrophenetole, m.p. 80° (lit.,[9] 78.5°), 2,4-dinitro-6-ethoxycarbonylphenetole, m.p. 50° (lit.,[10] 49°), 2,4-dinitro-6-chlorophenetole, m.p. 54°, and 2,4-dinitrophenetole, m.p. 87° (lit.,[11] 87°), were prepared by reaction of the corresponding 1-chloro-compounds with one equivalent of sodium ethoxide in ethanol followed by recrystallisation from ethanol. Messrs. B. Eddy and T. Holmes are thanked for these preparations. ^1H N.m.r. spectra showed bands consistent with the required compounds and indicated the absence of impurities. 18-Crown-6 ether was prepared by Mr. J. A. Parkinson by a known method.[12]

Sodium ethoxide solutions were freshly prepared by reaction of clean sodium with absolute ethanol under nitrogen and were titrated with standard acid.

^1H N.m.r. measurements were made with Varian A 56/60 or Bruker HX/90 instruments with tetramethylsilane as internal reference. Visible spectral shapes of stable species were determined with a Unicam SP 8000 instrument. Kinetic measurements, at 25°, were made with a Unicam SP 500 for slow rates and a ' Canterbury ' stopped-flow spectrophotometer for fast rates.

RESULTS

^1H *N.m.r. Spectra.*—Data for the parent compounds in $[^2H_6]$DMSO and for the complexes produced on addition of one equivalent of ethanolic sodium ethoxide are in Table 1. The spectra show that the stable adducts result from ethoxide addition at the 1-position to give 1,1-diethoxy-complexes of structure (II). By analogy with methoxide addition[3,7] transient bands due to base addition at unsubstituted ring-positions would be expected. In the case of 2,4,6-trinitrophenetole such transient bands were observed at δ 8.44 and 6.15 (d, *J* 2 Hz) from the ring protons of the 1,3-adduct (III; R = Et, X = NO_2).

TABLE 1

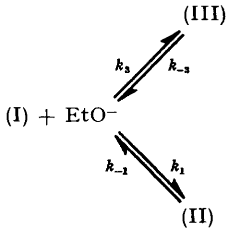
Chemical shifts (δ) for parent molecules and 1,1-diethoxy-complexes in dimethyl sulphoxide

X	R	Ring protons	OCH_2[a]
Structure (I)			
NO_2	Et	9.10 (s)	4.28
CO_2Et	Et	8.94 (d), 8.72 (d, J 3 Hz)	4.41, 4.21
Cl	Et	8.76 (d), 8.69 (d, *J* 2.5 Hz)	4.30
H	Et	8.72 (d, *J* 3 Hz), 8.48 (dd), 7.56 (d, *J* 9 Hz)	4.40
Structure (II)			
NO_2	Et[b]	8.62 (s)	3.20
CO_2Et	Et	8.67 (d), 8.25 (d, *J* 3 Hz)	3.08, 4.15
Cl	Et	8.60 (d), 7.35 (d, *J* 2.5 Hz)	3.08
H	Et[b,c]	8.68 (d, *J* 3 Hz), 7.20 (dd), 5.10 (d, *J* 11 Hz)	3.08

[a] q, *J* 7 Hz. [b] Ref. 13. [c] Ref. 14.

Kinetic and Equilibrium Data.—2,4,6-*Trinitrophenetole.* Examination by stopped-flow spectrophotometry of solutions containing 2,4,6-trinitrophenetole and sodium ethoxide in ethanol shows the presence of two colour forming reactions which are well separated in time. We associate the faster process which gives rise to the less thermodynamically stable adduct with formation of the 1,3-adduct (III; X = NO_2, R = Et) and the slower process with formation of the 1,1-complex (II; X = NO_2, R = Et). Evidence favouring this assignment comes from the ^1H n.m.r. data and the observation[15] that the 1,1-diethoxy-complex can be isolated from such solutions. In these dilute solutions, [NaOEt] < 4 × 10^{-2}M, there was no evidence for formation of complexes of greater than 1 : 1 stoicheiometry.

If we neglect, at present, the effects of ion-association the results are described by Scheme 1. Measurements were carried out in solutions containing a large excess of sodium ethoxide over parent so that first-order kinetics were obtained. Rate coefficients, accurate to 3%, were independent of the wavelength of measurement. Since the



$$K_3 = \frac{k_3}{k_{-3}}$$

$$K_1 = \frac{k_1}{k_{-1}}$$

SCHEME 1

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[8] M. R. Crampton and H. A. Khan, *J.C.S. Perkin II*, 1972, 2286; 1973, 1103; M. R. Crampton, *ibid.*, 1975, 825.

[9] A. Hantzsch and H. Gorke, *Ber.*, 1906, **39**, 1097.

[10] A. Salkowski, *Annalen*, 1974, **173**, 47.

[11] E. Funakubo, M. Imoto, and E. Imoto, *Ber.*, 1938, **71**, 950.

[12] G. W. Gokel, D. J. Cram, C. L. Liotta, H. P. Harris, and F. L. Cook, *J. Org. Chem.*, 1974, **39**, 2445.

[13] R. Foster and C. A. Fyfe, *Rev. Pure Appl. Chem.*, 1966, **16**, 61.

[14] W. E. Byrne, E. J. Fendler, J. H. Fendler, and C. E. Griffin, *J. Org. Chem.*, 1967, **32**, 2506.

[15] R. Destro, C. M. Gramaccioli, and M. Simonetta, *Nature*, 1967, **215**, 389.

timescale of the two processes was well separated equations (1) and (2) apply.

$$k_{\text{fast}} = k_{-3} + k_3[\text{NaOEt}]_{\text{stoich}} \quad (1)$$

$$k_{\text{slow}} = k_{-1} + \frac{k_1[\text{NaOEt}]_{\text{stoich}}}{1 + K_3[\text{NaOEt}]_{\text{stoich}}} \quad (2)$$

A plot (Figure 1) of k_{fast} *versus* the stoicheiometric base concentration showed curvature, the intercept giving a value for k_{-3} of 30 s^{-1} at zero base concentration. However the data at constant ionic strength, I 0.057M, gave a linear plot yielding values of k_{-3}, 30 s^{-1}, and k_3, 1 700 l mol^{-1} s^{-1}. Thus increasing the salt concentration (sodium ion concentration) does not affect the value of k_{-3} but leads to a decrease in value of k_3. The data yield a value at zero ionic strength of 2 100 l mol^{-1} s^{-1} for k_3. Combination of rate coefficients gives values for K_3 of 70 l mol^{-1} at zero base and 57 l mol^{-1} at I 0.057M. An alternative method of calculation of equilibrium constants was afforded by measurement by stopped-flow spectrophotometry of the values of optical density after completion of the fast process. Since, at the base concentrations used only partial conversion of the substrate to (III) was achieved the extinction coefficient of the complex was determined by a Benesi–Hildebrand plot.[16] A plot of the data at constant ionic strength was linear and the intercept yielded a value for ε_{480} of 18 000 l mol^{-1} cm^{-1}. This value was used to calculate the values of K_3 in Table 2 which agree well with those from the kinetic measurements.

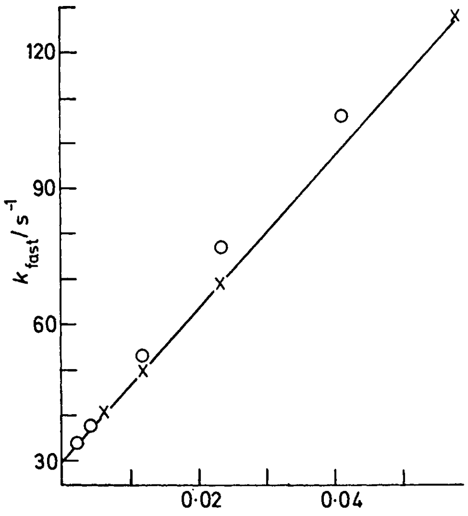

FIGURE 1 Variation of k_{fast} for the reaction of 2,4,6-trinitrophenetole with sodium ethoxide concentration, ○; and at constant ionic strength I 0.057M, ×

The spectrum of the 1,3-complex (III; R = Et, X = NO_2) determined by stopped flow spectrophotometry is shown in Figure 2. The shape was independent of base concentration. Also given in Figure 2 is the spectrum of the 1,1-complex (II; R = Et, X = NO_2). The shape of this latter spectrum depends on the sodium ion concentration, no doubt due to ion-association,[8] and the spectrum shown is that obtained in the presence of 18-crown-6 ether where the concentration of free sodium ions will be reduced to a very low level.

Values of k_1 were obtained from k_{slow} using equation (2). The value of K_1 was sufficiently high that virtually complete conversion to 1,1-complex was achieved at the lowest base concentrations used. Hence K_1 could not be determined directly. However a value for k_{-1} of (6 ± 1) × 10^{-5} s^{-1} was obtained by measuring the initial rate of fading of a solution of the 1,1-complex in ethanol. Combination of this value with the value for k_1 at low base concentration gives a value of K_1, 3 × 10^5 l mol^{-1}. In agreement with this value it is found that in *p*-bromophenol–*p*-bromophenoxide buffers with residual ethoxide concentrations of 6.3 × 10^{-5} and 7.4 × 10^{-6}M conversions of parent to 1,1-complex proceed to 95 and 65% completion respectively.

TABLE 2

Kinetic and equilibrium data for sodium ethoxide addition to 2,4,6-trinitrophenetole in ethanol at 25°

	1,3-Complex			1,1-Complex	
10^3[NaOEt]/ M	k_{fast}/ s^{-1}	O.D. (480 nm) [a]	K_3 [b]/l mol^{-1}	k_{slow}/ s^{-1}	k_1/l mol^{-1} s^{-1}
1.17				0.018	17
1.9	34	0.011	73		
2.1				0.034	18.5
2.1 [c]				0.033	18
3.8	37.5	0.018 5	68		
4.0				0.059	19
5.7	41	0.025	67	0.078	19
11.7	53	0.038	63	0.142	21
23.4	77	0.054	64	0.23	24.5
41	106	0.062	54	0.32	25
57.5	130	0.069	57	0.35	26
5.8 [d]	41	0.022	56	0.113	26
11.7 [d]	50	0.037	59	0.19	27
23.4 [d]	69	0.052	58	0.26	26

[a] For 5 × 10^{-6}M-parent. [b] Using a value for ε_{480} of 18 000 l mol^{-1} cm^{-1}. [c] In the presence of 18-crown-6 ether. [d] Made up to I 0.057M with sodium perchlorate.

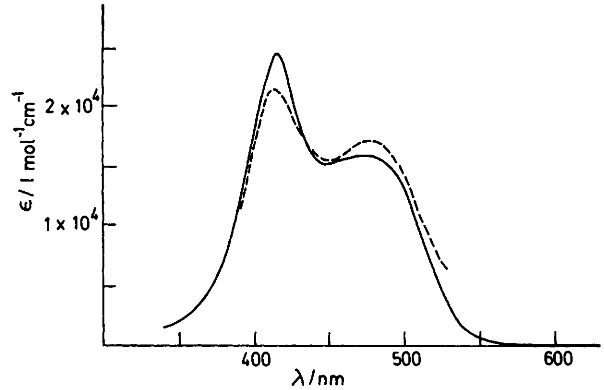

FIGURE 2 Visible spectra in ethanol of complex (II; R = Et, X = NO_2) solid line; and of complex (III; R = Et, X = NO_2) broken line

6-Ethoxycarbonyl-2,4-dinitrophenetole. In the presence of dilute base, [NaOEt] < 4 × 10^{-2}M, only one reaction was observed giving the 1,1-complex (II; X = CO_2Et, R = Et) with $\lambda_{\text{max.}}$ 382 (ε 20 000 l mol^{-1} cm^{-1}) and 475 nm (18 000). Rates of colour formation were measured with an SP 500 spectrophotometer, and values of optical density

[16] H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, 1949, **71**, 2703.

TABLE 3

Rate and equilibrium data for 1,1-complex formation from 2,4-dinitro-6-ethoxycarbonylphenetole in ethanol at 25°

	10^3[NaOEt]/ M	[Crown ether]/M	O.D. (475 nm) [a]	K_1 [b]/ l mol^{-1}	$10^3 k_{obs}$/ s^{-1}	k_1/ l mol^{-1} s^{-1}	$10^3 k_{-1}$/ s^{-1}
1	0.2 [c]			160		0.18	1.1
2	1.15		0.24	440	1.3	0.38	0.86
3	1.9		0.39	640	1.7	0.49	0.77
4	3.8		0.56	980	3.2	0.66	0.68
5	6.1		0.63	1 300	5.5	0.80	0.61
6	10.0		0.67	1 700	10.3	0.97	0.57
7	100		0.71				
8	19 [d]				25	1.3	
9	29 [d]				42	1.4	
10	38 [d]				71	1.9	
11	57 [d]				112	2.0	
12	5.1	0.02	0.23	97	1.95	0.13	1.3
13	10.1	0.04	0.35	97	2.7	0.13	1.3
14	21	0.04	0.49	105	4.6	0.15	1.4
15	31	0.06	0.55	110	6.0	0.15	1.4
16	60	0.08	0.62	115	11.7	0.17	1.5

[a] For 3.9×10^{-5}M-parent. [b] Calculated from O.D. (475 nm)/[0.71 − O.D. (475 nm)][NaOEt]. [c] Excess of parent, see text. [d] Measured with stopped-flow spectrophotometer.

TABLE 4

Rate and equilibrium data for 1,1-complex formation from 2,4-dinitro-6-chlorophenetole in ethanol at 25°

10^3[NaOEt]/ M	[Crown ether]/M	O.D. (495 nm) [a]	K_1 [b]/ l mol^{-1}	$10^3 k_{obs}$/ s^{-1}	k_1/ l mol^{-1} s^{-1}	$10^3 k_{-1}$/ s^{-1}
1.1		0.058	64	2.6	0.15	2.4
1.9		0.106	71	2.6	0.16	2.3
3.7		0.220	88	2.9	0.19	2.2
7.5		0.405	110	4.0	0.24	2.2
11.2		0.510	120	4.7	0.24	2.0
18.5		0.645	140	6.9	0.27	1.9
37		0.78	190	14	0.33	1.7
200		0.89				
1.1	0.02	0.047	51	2.8	0.14	2.6
1.9	0.02	0.077	51	2.8	0.13	2.6
3.7	0.02	0.149	55	3.1	0.14	2.6
11.2	0.05	0.340	55	4.4	0.15	2.7
18.5	0.06	0.47	60	5.7	0.16	2.7
37	0.11	0.63	68	9.0	0.17	2.6

[a] For 3.9×10^{-5}M-parent. [b] Calculated from O.D. (495 nm)/[0.89 − O.D. (495 nm)][NaOEt].

at completion were used to calculate values of K_1, the equilibrium constant for complex formation. In general sodium ethoxide was in excess so that equation (3) applies.

$$k_{obs} = k_{-1} + k_1[\text{NaOEt}] \qquad (3)$$

Since values of $K_1 (= k_1/k_{-1})$ are known, values for the rate coefficients k_1 and k_{-1} could be calculated. Items 2—7 in Table 3 show that with increasing base concentration the value of K_1 increases drastically due to increases in value of k_1 and decreases in value of k_{-1}. This is attributed to association of the Meisenheimer complex with sodium ions.[8] Items 12—16 show that in the presence of 18-crown-6 ether, which will reduce the concentration of free sodium ions to a low level,[17] rate and equilibrium constants are largely independent of base concentration.

We wished to determine values of rate and equilibrium constants at low base concentration, [NaOEt] $< 10^{-3}$M, where reaction of base with carbon dioxide is a problem. Here we used the parent in excess so that equation (4)

$$k_{obs} = k_{-1} + k_1[\text{Parent}] \qquad (4)$$

applies. The sodium ethoxide concentration was nominally 2×10^{-4}M. Linear first-order plots were obtained from

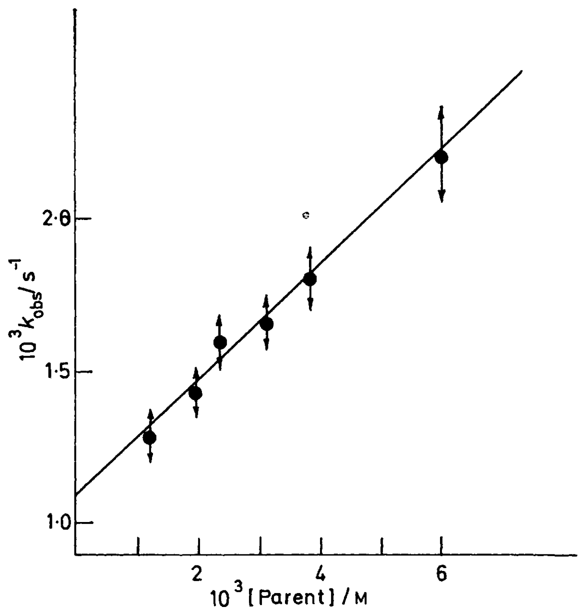

FIGURE 3 Reaction of 6-ethoxycarbonyl-2,4-dinitrophenetole with sodium ethoxide. Plot of data according to equation (4)

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[17] J. J. Christensen, D. J. Eatough, and R. M. Izatt, *Chem. Rev.*, 1974, **74**, 351.

optical density data showing that during the course of a run the sodium ethoxide concentration varied little. Figure 3 shows a plot of k_{obs} *versus* parent concentration which yielded the values given under item 1 of Table 3.

6-*Chloro*-2,4-*dinitrophenetole*. A single colour forming reaction was observed giving the 1,1-complex (II; X = Cl, R = Et) whose visible spectrum showed maxima at 350, 362 (ε 15 000), and 495 nm (ε 23 000). Rate and equilibrium data obtained using sodium ethoxide in excess are in Table 4.

TABLE 5

Equilibrium and kinetic data for 1,1-complex formation from 2,4-dinitrophenetole and sodium ethoxide in ethanol at 25°

10^3[NaOEt]/ M	10^2[Parent]/ M	[Crown ether]/M	O.D. (495 nm) [a]	$10^3 K_1$ [b]/ l mol^{-1}	k_{obs} [c]/ s^{-1}	$10^3 k_1$ [d]/ l mol^{-1} s^{-1}
9.2	9.8		0.052	2.6		
18	9.6		0.122	3.2		
38	9.2		0.303	3.9		
54	8.8		0.475	4.5		
70	8.5		0.65	5.0		
94	4.0		0.44	5.3		
94	8.0		0.92	5.5		
8.4	9.6	0.02	0.026	1.5		
16	9.2	0.03	0.045	1.4		
23	8.9	0.05	0.064	1.4		
30	8.5	0.06	0.086	1.5		
40	8.0	0.08	0.107	1.5		
80	6.0	0.16	0.193	1.8		
10	5.0				3.3	8.9
20	5.0				2.7	8.5
40	5.0				2.2	8.8
94	1.0				1.7	9.2
25	5.0	0.05			7.0	9.8
40	5.0	0.06			7.0	9.8

[a] Corrected for absorption by parent, and by crown ether–Na$^+$ complex. [b] Assuming an extincton coefficient of 22 000.[18] [c] This corresponds to k_{-1}. [d] Calculated from $k_{-1}K_1$.

TABLE 6

Summary of equilibrium and rate data for ethoxide additions at 25°

	Solvent	R	X	K_1/l mol^{-1}	k_1/l mol^{-1} s^{-1}	k_{-1}/s^{-1}	$K_1(EtO^-)/K_1(MeO^-)$
				Structure (II)			
1	Ethanol	Et [a]	NO_2	3×10^5	17	6×10^{-5}	17.5
2	Ethanol	Et [a]	CO_2Et	1×10^2	0.13	1.3×10^{-3}	12.5
3	Ethanol	Et [a]	Cl	5.3×10	0.14	2.6×10^{-3}	17.5
4	Ethanol	Et [a]	H	1.5×10^{-3}	0.010	7.0	30
5	Methanol	Me [b]	NO_2	1.7×10^4	17	1×10^{-3}	
6	Methanol	Me [c]	CO_2Me	8.0	0.20	2.5×10^{-2}	
7	Methanol	Me [c]	Cl	3.0	0.18	6.0×10^{-2}	
8	Methanol	Me [d]	H	5×10^{-5}	2.1×10^{-3}	42	
				Structure (IV)			
				K_3/l mol^{-1}	k_3/l mol^{-1} s^{-1}	k_{-3}/s^{-1}	$K_3(EtO^-)/K_3(MeO^-)$
9	Ethanol	Et [e]	H	$(2 \pm 1) \times 10^3$	4×10^4	20	100
10	Ethanol	Et [a]	OEt	70	2 100	30	26
11	Ethanol	Et [f]	Cl	290	5 800	20	110
12	Methanol	Me [e]	H	20 ± 4	7 300	330	
13	Methanol	Me [g]	OMe	2.7	950	350	
14	Methanol	Me [h]	Cl	2.6	910	300	

[a] Present work. [b] Ref. 20. [c] Ref. 7*b*. [d] Ref. 18. [e] Refs. 4 and 5. Ref. 6. [g] Ref. 7*c*. [h] Ref. 21.

2,4-*Dinitrophenetole*. A single reaction was observable giving the 1,1-complex (II; X = H, R = OEt) whose spectrum showed a maximum at 495 nm. Due to the low stability of the complex it was necessary to use relatively high parent concentrations in order to obtain measurable optical densities. The data in Table 5 show that the value of K_1 increases with base concentration but is independent of parent concentration. However in the presence of crown ether, to complex the sodium ions, K_1 is independent of base concentration.

Because of the low stability of the complex the rate process involving its formation is dominated by the k_{-1} term at the expense of the term involving k_1. Thus rate measurements by stopped flow spectrophotometry yielded values of k_{-1} directly. The decrease in these values with increasing base concentration accounts entirely for the concomitant increase in K_1.

DISCUSSION

The results show clear evidence for ion association. We shall however first consider the values obtained either by extrapolation to very dilute solutions or in the presence of 18-crown-6 ether where such effects are

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[18] C. F. Bernasconi, *J. Amer. Chem. Soc.*, 1968, **90**, 4982.

unimportant. Data for ethoxide addition at unsubstituted ring positions and at ethoxy-substituted positions are in Table 6 where they are compared with data for methoxide additions in methanol. Items 1—4 and 5—8 show that a major factor in determining the stabilities of Meisenheimer complexes is the electron-withdrawing ability of ring substituents. However, as discussed recently,[19] other factors are also important. In brief summary, the high stability of 1,1-dimethoxy-complexes relative to their 1,3-isomers (*cf.* items 5 and 13) has been attributed to the release of steric strain on addition at the 1-position,[3,7a] or alternatively to the stabilising influence of multiple alkoxy-substitution.[4] The slower rate of formation of 1,1-complexes may be due to steric hindrance on approach of the reagent (*F* strain) [7a] or to stabilisation, though resonance interaction between the methoxy-group and nitro-groups, present in the parent and 1,3-complex but not in the 1,1-complex.[4]

Steric effects will not be important in alkoxide additions to 1,3,5-trinitrobenzene so that the ratio of 100 for $K_3(\mathrm{EtO^-})/K_3(\mathrm{MeO^-})$ gives a measure of the enhanced carbon basicity of ethoxide ions in ethanol compared to methoxide ions in methanol. Comparison of the data for 2,4,6-trinitrophenetole with that for 2,4,6-trinitroanisole show that the comparable ratio for addition at C(3) is 26 (items 10 and 13) and for addition at C(1) is 17.5 (items 1 and 5). One possible interpretation of the lower ratios than for 1,3,5-trinitrobenzene would be greater ground state stabilisation in the case of 2,4,6-trinitrophenetole than for 2,4,6-trinitroanisole. However the crystal structure [22] of 2,4,6-trinitrophenetole shows evidence of considerable steric strain. Thus the 2- and 6-nitro-groups are rotated from the ring plane by 32 and 61° respectively. The ethoxy-group is nearly perpendicular to the plane of the benzene ring so that resonance interaction with the nitro-groups is limited. It thus seems unlikely that greater ground state stabilisation of 2,4,6-trinitrophenetole, and the phenetoles in general, is responsible.

If release of steric strain in the parent on alkoxide addition at the 1-position were the major factor contributing to the high stability of 1,1-dialkoxy-complexes it would be expected that the ratio $K_1(\mathrm{EtO^-})/K_1(\mathrm{MeO^-})$ should be >100 for the more strained phenetoles than for the corresponding anisoles. The fact that the ratios are <100 (items 1—4) probably indicates that steric strain in the parent is not as important a factor as multiple alkoxy-substitution which would be expected to operate for both 1,1-dimethoxy- and 1,1-diethoxy-complexes. The lowering of the ratio $K_1(\mathrm{EtO^-})/K_1(\mathrm{MeO^-})$ may well derive from destabilising steric interactions in the 1,1-diethoxy-complexes not present, or present to a smaller extent, in the 1,1-dimethoxy-complexes. Thus Fendler and his co-workers [23] found evidence in the n.m.r. spectrum of a 1,1-diethoxy-complex for restricted rotation about C–O bonds leading to loss of conformational freedom. The greater non-bonded interactions between the ethoxy-groups and the ring may also lead to destabilisation of 1,1-diethoxy-complexes relative to their 1,1-dimethoxy-analogues.

The data for addition at unsubstituted ring-positions shows that the ratio of *ca.* 100 for $K_3(\mathrm{EtO^-})/K_3(\mathrm{MeO^-})$ in the cases of 1,3,5-trinitrobenzene and picryl chloride is reduced to 26 when comparing 2,4,6-trinitrophenetole and 2,4,6-trinitroanisole. This lower ratio probably derives from greater steric strain in complex (III; $X = NO_2$, $R = Et$) than in (III; $X = NO_2$, $R = Me$). Steric strain leading to non-planarity of nitro-groups is likely to be more important in the case of the complexes, where charge delocalisation is very important, than for the parent molecules.

Loss of resonance interaction between alkoxy-groups and ring substituents present in the parent but partially lost in passage to the transition state for 1,1-complex formation has been postulated as the cause of the relatively low rate of formation of such complexes.[4] It might be expected that such through conjugation would be less important in the more strained phenetoles than in the corresponding anisoles, so that the increased stability of 1,1-diethoxy-complexes relative to 1,1-dimethoxy-complexes would be accompanied by an increased rate of formation. However comparison of items 1—3 with 5—7 in Table 6 shows that k_1 values are similar. The alternative explanation of the low rate of formation of 1,1-complexes in terms of *F* strain can better explain these observations. Thus the expected increase in value of k_1 for the 1,1-diethoxy-complexes is not realised because of increased steric hindrance at the reaction centre. The data for the less strained 2,4-dinitro-compounds (items 4 and 8) show that here the increase in stability of the diethoxy-complex is accompanied by an increase in value of k_1.

Ion Association.—The results in Tables 2—5 show large variations with base concentration in the values of rate coefficients and equilibrium constants. However in the presence of 18-crown-6 ether, which will reduce the concentration of free sodium ions to a low level,[17] values are nearly independent of base concentration. Therefore as with methoxide additions,[8] specific ion-pairing effects are deemed to be more important than general medium effects. Ion pairing would be expected between sodium ions and ethoxide ions and between sodium ions and σ-complexes and we discuss the results in terms of Scheme 2 which is a generalisation [24] of our previous treatment.[8]

Let us consider first 1,1-complex formation. Then

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[19] G. Baldini, G. Doddi, G. Illuminati, and F. Stegel, *J. Org. Chem.*, 1976, **41**, 2153; our conclusions regarding the importance of steric and electronic factors are broadly similar to those given in this paper.

[20] J. H. Fendler, E. J. Fendler, and C. E. Griffin, *J. Org. Chem.*, 1969, **34**, 689.

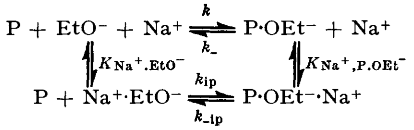
[21] L. H. Gan and A. R. Norris, *Canad. J. Chem.*, 1974, **52**, 18.

[22] C. M. Gramaccioli, R. Destro, and M. Simonetta, *Acta Cryst.*, 1968, **B24**, 129.

[23] J. H. Fendler, E. J. Fendler, W. E. Byrne, and C. E. Griffin, *J. Org. Chem.*, 1968, **33**, 977.

[24] E. Buncel, A. R. Norris, K. E. Russell, P. Sheridan, and H. Wilson, *Canad. J. Chem.*, 1974, **52**, 1750.

the variation with sodium ion concentration of the value of K_1, the measured equilibrium constant, is given by



Scheme 2

equation (5) where $K(= k/k_-)$ is the value of K_1 in the absence of ion pairing. The observed increases in value

$$K_1 = \frac{K(1 + [\mathrm{Na}^+]K_{\mathrm{Na}^+,\mathrm{P.OEt}^-})}{1 + [\mathrm{Na}^+]K_{\mathrm{Na}^+,\mathrm{EtO}^-}} \qquad (5)$$

of K_1 with base concentration (sodium ion concentration) indicate that the 1,1-complexes are better stabilised by association with sodium ions than are ethoxide ions. Taking a value of 50 l mol^{-1} for $K_{\mathrm{Na}^+,\mathrm{EtO}^-}$, the ion-pair association constant of sodium ethoxide,[25] the calculated values of $K_{\mathrm{Na}^+,\mathrm{PO.Et}^-}$ are 3.3×10^3 for 2,4-dinitro-6-ethoxycarbonylphenetole, 270 for 2,4-dinitro-6-chlorophenetole, and 200 l mol^{-1} for 2,4-dinitrophenetole. These are about an order of magnitude higher than corresponding values for association of 1,1-dimethoxy-complexes with sodium ions in methanol.[8]

As shown by Buncel and his co-workers [24] the variations with base concentration in values of the measured rate constants are given by equations (6) and (7), where

$$k_1 = kf + k_{\mathrm{ip}}(1 - f) \qquad (6)$$

$$k_{-1} = \frac{k_- + [\mathrm{Na}^+]k_{-\mathrm{ip}}K_{\mathrm{Na}^+,\mathrm{P.EtO}^-}}{1 + [\mathrm{Na}^+]K_{\mathrm{Na}^+,\mathrm{P.EtO}^-}} \qquad (7)$$

f is the fraction of base dissociated. The values in Table 7 show that for 1,1-complex formation the sodium ethoxide ion pairs show greater reactivity than free ethoxide ions, while the ion-paired σ-complexes revert to reactants less rapidly than their unpaired analogues.

The data in Table 2 show that a very different situation applies in the case of 1,3-addition. The value of K_3 decreases with increasing base concentration showing that the 1,3 σ-complex is less associated with sodium ions than is the ethoxide ion. In terms of Scheme 2, $K_{\mathrm{Na}^+,\mathrm{EtO}^-} > K_{\mathrm{Na}^+,\mathrm{P.EtO}^-}$. Also the observation that the value of k_3 decreases with increasing base concentration indicates that here sodium ethoxide ion pairs are less reactive than the free ethoxide ions.

Table 7

Effects of ion association on 1,1-complex formation of 2,4-dinitro-6-X-phenetoles in ethanol [a]

Substituent X	NO_2	CO_2Et	Cl	H
K [b]/l mol^{-1}	3×10^5	1×10^2	53	1.5×10^{-3}
k [b]/l mol^{-1} s^{-1}	17	0.13	0.14	1×10^{-2}
k_- [b]/s^{-1}	6×10^{-5}	1.3×10^{-3}	2.6×10^{-3}	7.0
$K_{\mathrm{Na}^+,\mathrm{P.OEt}^-}$/l mol^{-1}	[c]	3.3×10^3	2.7×10^2	2.0×10^2
K_{ip}/l mol^{-1}	[c]	6.7×10^3	3×10^2	1×10^{-2}
k_{ip}/l mol^{-1} s^{-1}	30	4	0.5	1×10^{-2}
$k_{-\mathrm{ip}}$/s^{-1}	[c]	6×10^{-4}	1.7×10^{-3}	1.0

[a] Data calculated using a value for $K_{\mathrm{Na}^+,\mathrm{EtO}^-}$ of 50 l mol^{-1}. [b] These are the values of K_1, k_1, and k_{-1} respectively in the absence of ion pairing. [c] No data available.

The general picture from this and previous work [8] is that 1,1-dialkoxy-adducts associate with cations, the strength of the association depending on the nature of the 2- and 6-substituents, while adducts formed by alkoxide addition at ring carbons carrying hydrogen are largely unassociated. We have proposed [8] that association of the 1,1-adduct with cations involves the two oxygen atoms of the alkoxy-groups at C(1) and the oxygen atoms of the *ortho*-substituents.

We thank the S.R.C. for financial support.

[6/2072 *Received*, 10*th November*, 1976]

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[25] J. Barthel, G. Schwitzgebel, and R. Wachter, *Z. Phys. Chem.*, 1967, **55**, 33.