The Stabilities of Meisenheimer Complexes. Part 16.[1] Kinetic and Equilibrium Data for Sodium Isopropoxide Addition to Some Aromatic Nitro Compounds in Propan-2-ol

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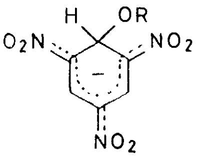
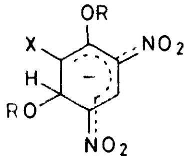
Equilibrium and kinetic data are reported for reaction of sodium isopropoxide in propan-2-ol with 1,3,5-trinitrobenzene and a series of 1-isopropoxy-2,4-dinitro-6-X-benzenes (X = NO_2, Cl, CO_2Pr^i, or H). Three types of reaction can be distinguished: addition of base at unsubstituted ring positions, addition at alkoxy-substituted positions, and S_N2 dealkylation. Complexes formed by base addition at unsubstituted ring positions show little tendency to associate with sodium ions and the rate constants for isopropoxide addition are considerably reduced by ion-pairing. However, the 1,1-di-isopropoxy complexes and the transition states leading to them are strongly stabilised by association with sodium ions.

MUCH quantitative information is now available relating to the addition of methoxide and ethoxide ions to aromatic nitro-compounds to give σ-complexes.[2,3] 1,3,5-Trinitrobenzene gives the complex (I). In the case of 1-alkoxy-2,4-dinitro-6-X-benzenes addition at unsubstituted ring positions, to give for example (II), is kinetically favoured while isomeric addition at the 1-position gives the thermodynamically more stable products (III). There is evidence[4] for strong association of the 1,1-dialkoxy complexes with cations such as Na^+, K^+, Ba^{2+}, and Ca^{2+}. This association almost certainly involves interaction of the cations with the oxygen atoms of the alkoxy groups at C-1 and with the electronegative atoms of the *ortho*-substituents and is reminiscent of reaction of cations with crown ethers.


(I)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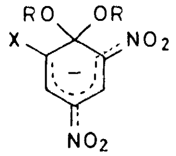

(III)

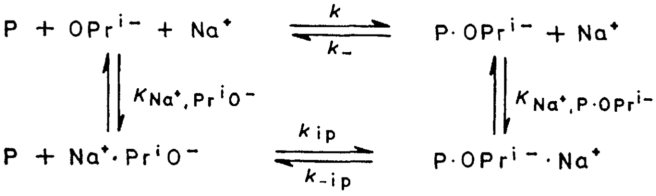
We report here rate and equilibrium data for reaction of sodium isopropoxide with several nitro-compounds. Three types of reaction were detected: (a) addition at unsubstituted ring positions, (b) addition at alkoxy-substituted positions, and (c) dealkylation to give substituted phenoxide ions.

In view of the high association constant[5] of sodium isopropoxide in propan-2-ol (K_{Na^+,PrO^-}, 1.9×10^4 l mol^{-1}) ion-pairing is important and the data allow comparison of the reactivities of free and paired isopropoxide ions in these reactions.

In previous work Gan and Norris[6] measured the rate of addition of sodium isopropoxide to 1,3,5-trinitrobenzene and found no evidence of ion-association. However, Buncel *et al.*[7] found that the value of the equilibrium constant for isopropoxide addition to the 3-position of 2,4,6-trinitro[$^2H_3$]toluene is reduced by added sodium perchlorate or sodium tetraphenylborate.

RESULTS

Data are interpreted[2,7] in terms of Scheme 1, which takes account of association of sodium ions with isopropoxide ions and with complex. Values of the equilibrium constants K_c were determined from spectrophotometric data using equation (1). Their variation with sodium ion concentration is given by equation (2) where K ($=k/k_-$) is the equilibrium constant for reaction of free isopropoxide ions.



SCHEME 1

$$K_c = \frac{[P{\cdot}OPr^{i-}] + [P{\cdot}OPr^{i-}{\cdot}Na^+]}{[P]([OPr^{i-}] + [Na^+{\cdot}Pr^iO^-])} \qquad (1)$$

$$K_c = \frac{K(1 + [Na^+]K_{Na^+,P\cdot OPr^{i-}})}{1 + [Na^+]K_{Na^+,Pr^iO^-}} \qquad (2)$$

Rate coefficients were determined with base as the excess component. The variations with base concentration of the forward, k_f, and reverse, k_r, rate coefficients are given by equations (3) and (4) where f is the fraction of base dissociated.

$$k_f = kf + k_{ip}(1 - f) \qquad (3)$$

$$k_r = \frac{k_- + [Na^+]k_{-ip}K_{Na^+,P\cdot OPr^{i-}}}{1 + [Na^+]K_{Na^+,P\cdot OPr^{i-}}} \qquad (4)$$

1,3,5-*Trinitrobenzene*.—In agreement with Gan and Norris[6] we find that in very dilute base solutions conversion into complex (I), $\lambda_{max.}$ 425 (ε 2.65×10^4 l mol^{-1} cm^{-1} and 500 nm (1.85×10^4), is largely complete. Thus with 1×10^{-4}M-sodium isopropoxide *ca.* 97% conversion is achieved. Because of the very low base concentrations required a spectrophotometric determination of K_c is unlikely to be of high accuracy. Our results indicate a value of $\geqslant 3 \times 10^5$ l mol^{-1} which compares with the previous value of 2×10^5.

Measurements were made of the rates of complex formation by stopped-flow spectrophotometry. With base as the excess component the measured rate coefficient, $k_{obs.}$ is related by equation (5) to the forward rate coefficient,

$$k_{obs.} = k_f[NaOPr^i] + k_r \qquad (5)$$

k_f, the reverse rate coefficient, k_r, and the stoicheiometric base concentration, $[NaOPr^i]$. However, because of the high value of K_c (= k_f/k_r) the reverse rate will be negligible (<1 s^{-1}) under our conditions.

TABLE 1

Rate and equilibrium data for 1,1-complex formation from 6-chloro-1-isopropoxy-2,4-dinitrobenzene in propan-2-ol at 25°

	10^3[NaOPr^i]/M	10^3[NaClO$_4$]/M	[Crown ether]/M	OD (500 nm) [a]	K_c[b]/l mol^{-1}	$10^3k_{obs.}$/s^{-1}	k_f/l mol^{-1} s^{-1}	10^3k_r/s^{-1}
1	0.45			0.220	750	1.95	1.1	1.5
2	0.67			0.294	750	2.55	1.2	1.6
3	0.89			0.365	790	3.1	1.4	1.8
4	1.34			0.43	710	4.3	1.6	2.2
5	2.2			0.54	690	6.2	1.7	2.5
6	4.3			0.66	670	11.5	2.0	3.0
7	6.8			0.71	580	13.8	1.6	2.8
8	11.3			0.765	540			
9	57			0.89				
10	115			0.89				
11	0.67	9.7		0.193	420	4.45	1.5	3.6
12	1.34	9.7		0.36	500	6.0	1.8	3.6
13	2.2	7.7		0.46	490	7.7	1.8	3.6
14	4.3	5.6		0.60	480	11.6	1.8	3.7
15	0.67		0.01		1 000 [c]		0.10 [c]	0.10 [c]
16	1.34		0.01		1 100		0.09	0.08
17	2.2		0.01		900		0.10	0.11
18	3.3		0.01		1 100		0.10	0.09
19	4.3		0.01		1 100		0.10	0.09

[a] For 4 × 10^{-5}M-substrate. [b] Calculated from OD(500 nm)/[0.89 − OD (500 nm)] [NaOPr^i]. [c] See Experimental section for method of calculation.

Figure 1 shows the results in the presence of sodium isopropoxide (crosses). Rates of reaction are considerably reduced in the presence of 10^{-2}M-sodium perchlorate (line B) where reaction will occur very largely *via* sodium isopropoxide ion pairs. Rates were also measured in the presence of 18-crown-6 polyether which is known to efficiently complex sodium ions. These data (line A) represent reaction *via* free isopropoxide ions. The bulky tetramethylammonium ion will not be expected to associate strongly with anions in dilute solution and the data obtained using tetramethylammonium isopropoxide also conform to line A.

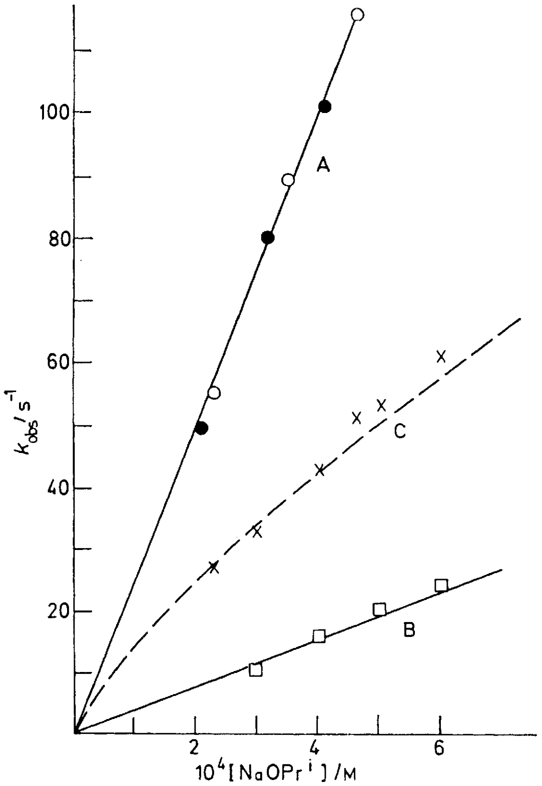


FIGURE 1 Rate data for reaction at 25° of 1,3,5-trinitrobenzene with sodium isopropoxide (×); with sodium isopropoxide and 10^{-2}M-sodium perchlorate (□); with sodium isopropoxide and crown ether (○); and with tetramethylammonium isopropoxide (●). The broken line, C, is that calculated from equation (3) with k 26 × 10^4, k_{ip} 4 × 10^4 l mol^{-1} s^{-1}

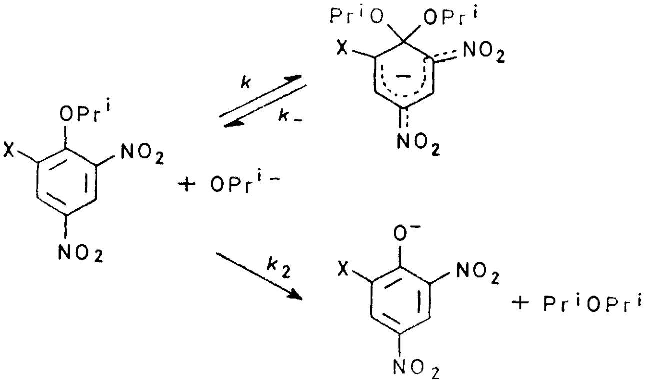
These results show that the reactivity of isopropoxide ions is considerably reduced by ion-pairing. The data obtained with sodium isopropoxide alone are well correlated (line C) by equation (3) with the values k 26 × 10^4 and k_{ip} 4 × 10^4 l mol^{-1} s^{-1}.

6-Chloro-1-isopropoxy-2,4-dinitro-benzene.—In the presence of dilute sodium isopropoxide in propan-2-ol a single colour forming reaction was observed giving the 1,1-complex (III; X = Cl, R = Pr^i) whose visible spectrum showed maxima at 350, 364 (ε 15 000 l mol^{-1} cm^{-1}), and 500 nm (22 000). The solutions were stable for some time after completion of the reaction. Rate and equilibrium data are in Table 1. Items 1—8 show that the value of K_c decreases somewhat with increasing base concentration, while values of k_f and k_r increase. In the presence of added sodium ions in the form of sodium perchlorate the base will be very largely ion-paired so that items 11—14 yield values for K_{ip}, k_{ip}, and k_{-ip} (Scheme 1).

In the presence of added crown ether where reaction will occur *via* free isopropoxide ions there is a really dramatic decrease in the rate of complex formation. Also in addition to 1,1-complex formation there is evidence for a concurrent reaction which gives increased absorption below 420 nm. We take this second reaction to be formation of 6-chloro-2,4-dinitrophenol which has $\lambda_{max.}$ 360 (ε 17 500) and 400 nm (13 000). These results are accommodated by Scheme 2. A kinetic analysis outlined in the Experimental section yielded the values given in items 15—19 and a value of 0.03 ± 0.01 l mol^{-1} s^{-1} for k_2.

The small decrease in the value of the equilibrium constant, K_c, in the presence of increasing sodium ion concentration indicates that the 1,1-complex is less well stabilised by ion-association than is the isopropoxide ion. The equilibrium and rate constants in items 1—7 are fitted well by equations (2)—(4) with a value of $K_{\mathrm{Na^+,P\cdot OPr^{i-}}}$ of 1×10^4 l mol^{-1}.

1-*Isopropoxy*-6-*isopropoxycarbonyl*-2,4-*dinitrobenzene*.— In the presence of dilute base the 1,1-dialkoxy complex (III; X = CO_2Pr^i, R = Pr^i) is formed. Visible spectra are in Figure 2 and rate and equilibrium data in Table 2. As with the 6-chloro compound the rate of Meisenheimer complex formation is greatly reduced in the presence of crown ether where there is evidence for the concurrent



SCHEME 2

formation of 6-isopropoxycarbonyl-2,4-dinitrophenol which has $\lambda_{\text{max.}}$ 365 nm (ε 8 000). The data in the presence of crown ether are in accord with Scheme 2 and give a value for k_2 of 0.04 ± 0.02 l mol^{-1} s^{-1}.

TABLE 2

Rate and equilibrium data for 1,1-complex formation from 1-isopropoxy-6-isopropoxycarbonyl-2,4-dinitrobenzene in propan-2-ol at 25°

	10^4[NaOPr^i]/M	[NaClO$_4$]/M	[Crown ether]/M	OD(483) nm [a]	K_c[b]/l mol^{-1}	$10^3k_{\text{obs.}}$/s^{-1}	k_f/l mol^{-1} s^{-1}	10^3k_r/s^{-1}
1	2.65			0.40	8 600	2.48	7.0	0.80
2	4.38			0.46	8 600	4.0	7.2	0.85
3	6.08			0.50	9 500	6.3	8.8	0.95
4	8.59			0.525	9 500	8.5	8.9	0.95
5	17.6			0.56	10 700	19.6	10.6	1.0
6	223			0.59				
7	446			0.59				
8	2.65	0.01		0.43	11 000	3.4	10	0.90
9	4.38	0.01		0.48	10 400	5.4	10	0.95
10	6.08	0.01		0.495	9 000	7.4	10	1.1
11	8.6	0.01		0.53	10 600	11.0	11.5	1.1
12	4.4		0.01		1 400 [c]		0.10 [c]	0.07 [c]
13	6.1		0.01		1 400		0.10	0.07
14	8.6		0.01		1 600		0.10	0.06
15	17.6		0.01		1 500		0.12	0.08
16	43		0.01		1 500		0.13	0.09

[a] For 3×10^{-5}M-parent. [b] Calculated from OD(483 nm)/[0.59 — OD(483 nm)][NaOPr^i]. [c] See Experimental section for method of calculation.

The increase in value of K_c in the presence of sodium ions shows that the complex is more stabilised by ion association than is the isopropoxide ion. In terms of Scheme 1, $K_{\mathrm{Na^+,P\cdot OPr^{i-}}} > K_{\mathrm{Na^+,OPr^{i-}}}$ and the equilibrium and rate data yield a value for $K_{\mathrm{Na^+,P\cdot OPr^{i-}}}$ of 1.3×10^5 l mol^{-1}. The rather small variation in values of rate and equilibrium constants in solutions of varying sodium isopropoxide concentration (items 1—5) is a consequence of the fact that even in the most dilute solutions used the base will be largely (>65%) ion paired.

1-*Isopropoxy*-2,4-*dinitrobenzene*.—There is a fast reaction producing the 1,1-complex (III; X = H, R = Pr^i) with $\lambda_{\text{max.}}$ 500 nm. A much slower reaction yields 2,4-dinitrophenol. Due to the rather low stability of the complex it was necessary to use relatively high concentrations of parent to obtain measurable optical densities. The data in Table 3 show that values of K_c are independent of substrate concentration but decrease with increasing base concentration, indicating that the complex is less stabilised by sodium ions than is the isopropoxide ion. The data correspond to equation (2) with K 0.08 l mol^{-1} and $K_{\mathrm{Na^+,P\cdot OPr^{i-}}}$ 6×10^3 l mol^{-1}.

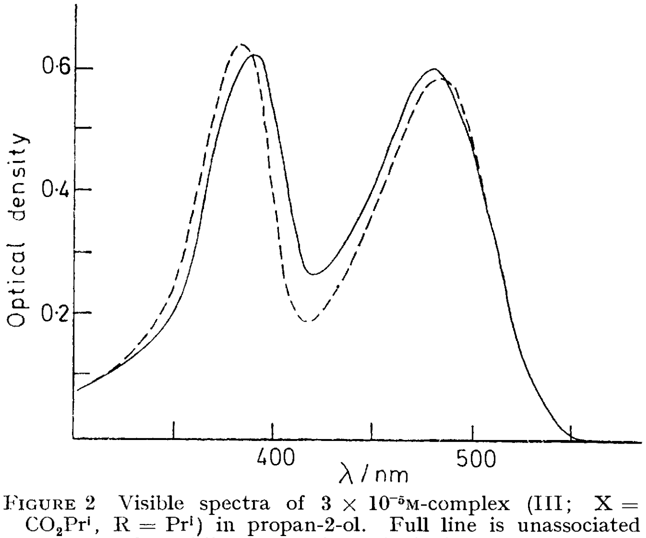
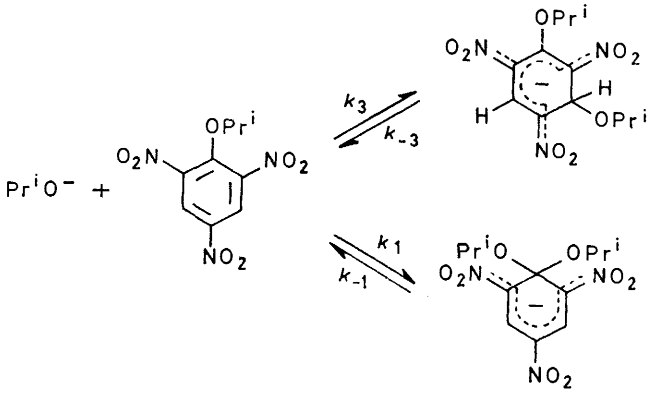


FIGURE 2 Visible spectra of 3×10^{-5}M-complex (III; X = CO_2Pr^i, R = Pr^i) in propan-2-ol. Full line is unassociated complex; dashed line is complex paired with sodium ions

Because of the low stability of the complex the rate process involving its formation is dominated by the k_r term [equation (5)]. Thus measurements by the stopped-flow method yielded values of k_r. The values in the presence of sodium ions are *ca.* 3 times higher than those obtained with crown ether present. This increase largely accounts for the lowering of K_c values in the presence of sodium ions. Hence values of k_f are similar with or without sodium ions.

1-Isopropoxy-2,4,6-trinitrobenzene.—In this case two isomeric complexes are formed whose structures were determined by ^{1}H n.m.r. spectroscopy. The fast formation of the 1,3-complex was followed by slow conversion to the 1,1-complex. The results are described by Scheme 3.



SCHEME 3

Since the time-scale of the two processes was well separated equations (6) and (7) will apply where the subscripts denote the position of addition. In the presence of sodium ions, ion-pairing will modify the constants to $k_{3,\mathrm{ip}}$, $k_{-3,\mathrm{ip}}$, $k_{1,\mathrm{ip}}$, and $k_{-1,\mathrm{ip}}$.

TABLE 3

Equilibrium and rate data for 1,1-complex formation from 1-isopropoxy-2,4-dinitrobenzene in propan-2-ol at 25°

10^3 [NaOPr^i]/ M	10^2 [Parent]/ M	[Crown ether]/ M	OD (500 nm) [a]	K_c [b]/ l mol^{-1}	$k_{\mathrm{obs.}}$ [c]/ s^{-1}
5.7	1.9		0.095	0.040	
5.7	4.7		0.24	0.041	
5.7	9.4		0.50	0.043	
10	2.0		0.14	0.032	0.39
10	5.0		0.35	0.032	
20	2.0		0.22	0.025	0.38
40	1.0		0.21	0.024	
50	0.3				0.36
90	1.0		0.45	0.023	
5.0	5.0	0.1	0.43	0.078	
10	2.25	0.1	0.40	0.081	0.12
20	0.4	0.05			0.12
40	1.0	0.1	0.64	0.073	
80	0.4	0.2	0.62	0.088	

[a] Corrected for absorption by parent. [b] Assuming an extinction coefficient of 22,000.[8] [c] This corresponds to k_r.

$$k_{\mathrm{fast}} = k_{-3} + k_3\,[\mathrm{Pr^iO^-}] \qquad (6)$$

$$k_{\mathrm{slow}} = k_{-1} + k_1[\mathrm{Pr^iO^-}]/(1 + K_3[\mathrm{Pr^iO^-}]) \qquad (7)$$

Rate data obtained by the stopped-flow method for addition at the 3-position are in Table 4. In the presence of added sodium perchlorate the isopropoxide will be very largely ion-paired and a plot of items 8—12 was linear giving values for $k_{3,\mathrm{ip}}$ 2 400 l mol^{-1} s^{-1} and $k_{-3,\mathrm{ip}}$ 0.6 s^{-1}. Combination of these values gives $K_{3,\mathrm{ip}}$ 4 × 10^3 l mol^{-1}. The values obtained with tetramethylammonium isopropoxide (items 13—16) where ion-pairing will be unimportant gave a linear plot with small intercept which yielded a value for k_3 of 8 000 l mol^{-1} s^{-1}. The situation here is similar to 1,3,5-trinitrobenzene in that addition occurs at a ring carbon carrying hydrogen and again the reactivity of sodium isopropoxide ions is considerably less than that of free isopropoxide ions. The kinetic data indicate that the value of k_{-3} is lower than that of $k_{-3,\mathrm{ip}}$ but do not allow its determination. Measurement of equilibrium optical densities by the stopped-flow method indicated that >95% conversion to 1,3-complex occurred in solutions containing 2 × 10^{-4}M-tetramethylammonium isopropoxide. Hence $K_3 \geqslant 1 \times 10^5$ l mol^{-1}.

TABLE 4

Rate data for isopropoxide addition to 1-isopropoxy-2,4,6-trinitrobenzene in propan-2-ol at 25°

	10^3[NaOPr^i]/ M	10^3[NaClO$_4$]/ M	k_{fast}/ s^{-1}	k_{fast} [a]/s^{-1} (calculated)	$10^3 k_{\mathrm{slow}}$/ s^{-1}
1	0.30		1.12	1.3	
2	0.59		2.05	2.2	
3	1.18		3.80	4	
4	3.0		8.5	9	
5	5.9		16	17	
6	10		26	28	
7	20		53	53	
8	0.30	9.7	1.33		8.5
9	0.59	9.4	1.93		17
10	1.18	8.8	3.33		22
11	3.0	7.1	7.3		24
12	5.9	4.1	14.3		28
	10^3[NMe$_4$OPr^i]/ M				
13	0.40		2.8		0.5
14	0.80		5.5		0.45
15	1.6		12.7		
16	2.0		16		

[a] Calculated from equation (3) with k_3 8 000 and $k_{3,\mathrm{ip}}$ 2 400 l mol^{-1} s^{-1}.

The isomerisation of the 1,3-complex to its 1,1-isomer was accompanied by a small decrease in absorption at 480 nm and an increase in absorption at 420 nm. The 1,1-complex will be expected to have high stability and the value of k_{-1} in equation (7) will be small compared to the value of the term involving k_1. The rate of isomerisation was measured in solutions containing added sodium perchlorate (items 8—12) and yielded a value of 100 ± 20 l mol^{-1} s^{-1} for $k_{1,\mathrm{ip}}$. The rate of isomerisation with tetramethylammonium isopropoxide (items 13 and 14) was considerably reduced and was independent of base concentration. Since $K_3 \geqslant 10^5$ equation (7) will reduce to $k_{\mathrm{slow}} = k_1/K_3$ explaining the invariance of the rate and leading to a value for k_1 of $\geqslant$50 l mol^{-1} s^{-1}.

DISCUSSION

Ion Association.—There is a clear distinction between addition at unsubstituted ring positions and at alkoxy-substituted positions. The complexes formed by addition to 1,3,5-trinitrobenzene or the 3-position of 1-isopropoxy-2,4,6-trinitrobenzene show little tendency to associate with sodium ions and rate constants for isopropoxide addition are considerably reduced by ion-pairing. However the 1,1-di-isopropoxy complexes show considerable stabilisation by sodium ions. Values are collected in Table 5 and show that for (III; X = CO$_2$Pr^i, R = Pr^i) $K_{\mathrm{ip}} > K$ indicating that the complex is better stabilised by association with sodium ions than are isopropoxide ions. In terms of Scheme 1 $K_{\mathrm{Na^+,P\cdot OPr^{i-}}} > K_{\mathrm{Na^+,OPr^{i-}}}$. For (III; X = Cl and H) $K > K_{\mathrm{ip}}$ showing that although the complexes are still strongly stabilised by sodium ions $K_{\mathrm{Na^+,OPr^{i-}}} > K_{\mathrm{Na^+,P\cdot OPr^{i-}}}$. It is likely that in the complex the cation is held by the oxygen atoms of the two isopropyl groups at C-1 and by the electronegative atoms of the *ortho*-substituents (IV). The large increase in value of both forward and reverse rates of complex formation in the presence of sodium ions indicates very strong interaction of the cation with the transition state. This is not unreasonable since in the transition state more negative charge will reside around the reaction centre than in the complex where negative charge will be more dispersed.

TABLE 5

Effects of ion-association on 1,1-complex formation of 1-isopropoxy-2,4-dinitro-6-X-benzenes in propan-2-ol at 25°

Substituent	NO_2	CO_2Pr^i	Cl	H
K/mol^{-1} l		1 500	1 100	0.08
k/mol^{-1} l s^{-1}	$\geqslant 50$	0.11	0.10	0.01
k_-/s^{-1}		7×10^{-5}	1×10^{-4}	0.12
K_{ip}/l mol^{-1}		10 000	500	0.024
k_{ip}/mol^{-1} l s^{-1}	100	10	1.8	0.009
k_{-ip}/s^{-1}		1×10^{-3}	3.6×10^{-3}	0.36

TABLE 6

Association constants of sodium ions with alkoxide ions ($K_{\mathrm{Na^+.OR^-}}$) and with 1,1-dialkoxy complexes ($K_{\mathrm{Na^+.P\cdot OR^-}}$)

Solvent	R	Na^+OR^-	(III; X = CO_2R)	(III; X = Cl)	(III; X = NO_2)	(III; X = H)
Methanol	Me	4.9 [a]	160 [b]	25 [b]	70 [b]	
Ethanol [c]	Et	49 [a]	3.3×10^3	2.7×10^2		2×10^2
Propan-2-ol [d]	Pr^i	1.9×10^4	1.3×10^5	1×10^4		6×10^3

[a] Ref. 5. [b] Ref. 4. [c] Ref. 2. [d] Present work.

TABLE 7

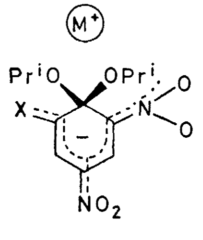
Comparison of equilibrium and rate data for alkoxide additions

	Structure (III)					
Solvent	R	X	K/l mol^{-1}	k/l mol^{-1} s^{-1}	k_-/s^{-1}	$K(Pr^iO^-)/K(MeO^-)$
Propan-2-ol	Pr^i	CO_2Pr^i	1 500	0.11	7×10^{-5}	200
Propan-2-ol	Pr^i	Cl	1 100	0.10	1×10^{-4}	400
Propan-2-ol	Pr^i	H	0.08	0.01	0.12	1 600
Methanol	Me	CO_2Me	8.0	0.20	2.5×10^{-2}	
Methanol [a]	Me	Cl	3.0	0.18	6×10^{-2}	
Methanol [a]	Me	H	5×10^{-5}	2.1×10^{-3}	42	
			Structure (I)			
Propan-2-ol	Pr^i		$>3 \times 10^5$	2.6×10^5	$\leqslant 1$	$\geqslant 1.5 \times 10^4$
Methanol [b]	Me		20	7 300	330	
			Structure (II)			
Propan-2-ol	Pr^i	NO_2	$\geqslant 1 \times 10^5$	8 000	$\leqslant 0.1$	$\geqslant 3 \times 10^4$
Methanol [c]	Me	NO_2	2.7	950	350	

[a] Ref. 4. [b] Ref. 10. [c] Ref. 13.

In Table 6 are tabulated values of the association constants of sodium ions with alkoxide ions and with various 1,1-dialkoxy complexes in methanol, ethanol, and propan-2-ol. As might be expected the values increase with decreasing dielectric constant of the solvent. The increase on going from ethanol to propan-2-ol is somewhat greater in the case of the sodium alkoxides where both anion and cation carry localised negative charges than for the 1,1-dialkoxy complexes where the negative charge is delocalised.

1,3- versus 1,1-*Addition*.—The greater thermodynamic stability of 1,1-complexes relative to their 1,3-isomers has been attributed to release of steric strain on addition at the 1-position,[9] or alternatively to the stabilising influence of multiple alkoxy substitution.[10] Illuminati and his co-workers [11] have concluded from studies of methoxide addition to thiophens that the latter factor is the more important. Nevertheless the observation that the stable adduct derived from 2-methoxy-3,5-dinitropyridine results from addition at the unsubstituted 6-position shows that when steric strain around the methoxy substituent is reduced the stability of geminal dimethoxy complexes decreases.[12]



(IV)

In the present case isopropoxide ions are similar to methoxide and ethoxide ions in that addition to alkoxy-substituted positions gives thermodynamically more stable adducts than addition to unsubstituted ring positions. Thus the 1,3-complex formed under kinetic control from 1-isopropoxy-2,4,6-trinitrobenzene isomerises to the 1,1-adduct. One important factor which favours the 1,1-complexes in sodium isopropoxide solutions is their greater stabilisation by association with the sodium ions present. However, even in the absence of ion-pairing the 1,1-adducts have greater thermodynamic stabilities than their isomers.

It is of interest to compare the values of equilibrium constants for isopropoxide addition in propan-2-ol $K(\mathrm{Pr^iO^-})$ with those for methoxide addition in methanol $K(\mathrm{MeO^-})$ under conditions when ion-pairing is not present. The data in Table 7 show that for addition at unsubstituted ring positions $K(\mathrm{Pr^iO^-})/K(\mathrm{MeO^-}) > 10^4$, giving a measure of the enhanced carbon basicity of isopropoxide ions relative to methoxide ions. The corresponding ratios for addition at alkoxy-substituted positions range from 200 for (III; $X = CO_2R$) to 1 600 for (III; X = H). Hence there is a smaller difference between the stabilities of 1,1- and 1,3-complexes in the isopropoxy series than in the methoxy series. It could be argued that if relief of steric strain in the parent compounds was of prime importance then since the isopropoxy group is sterically more demanding than the methoxy group there would be greater steric relief on isopropoxide addition of the 1-position of 1-isopropoxy-2,4-dinitro-6-X-benzenes than on methoxide addition to the 1-position of the corresponding anisoles. Since the $K(\mathrm{Pr^iO^-})/K(\mathrm{MeO^-})$ ratios do not bear out this interpretation stabilisation due to multiple alkoxy substitution may be the more important factor here. The argument is probably overstated in that it does not take account of possible destabilising steric interactions in the 1,1-dialkoxy complexes themselves. Thus non-bonded interactions between the alkoxy groups and the ring may lead to increased destabilisation in di-isopropoxy complexes compared to di-methoxy complexes.

Dealkylation.—There have been relatively few reports of the occurrence of dealkylation during reactions of nitro-activated anisoles with methoxide in methanol. However, the S_N2 demethylation of 2,4-dinitroanisole [8,14] and 2-methoxy-3,5-dinitropyridine [12,15] are known. Our results show that with isopropoxide ions in propan-2-ol dealkylation is important and can compete with base addition at ring positions (Scheme 2). Increased steric hindrance to attack at the crowded 1-position of the ring is probably an important factor here. In the case of 6-chloro-1-isoproxy-2,4-dinitrobenzene the rate constants for attack of free isoproxide ions at the 1-position of the ring and at the alkyl carbon have values of 0.10 and 0.03 l mol^{-1} s^{-1} respectively. The reactivities are similar for 1-isopropoxy-6-isopropoxycarbonyl-2,4-dinitrobenzene, 0.11 and 0.04 l mol^{-1} s^{-1}.

Nevertheless in the presence of sodium ions dealkylation is unimportant. This is a consequence of the dramatic enhancement of the rate of 1,1-complex formation when the isopropoxide ions are paired with sodium ions. It implies that in the dealkylation reaction ion-pairing does not similarly enhance the reactivity of isopropoxide ions.

EXPERIMENTAL

1-Isopropoxy-2,4,6-trinitrobenzene, m.p. 95° (lit.,[16] 95°), 1-isopropoxy-2,4-dinitrobenzene, m.p. 53° (lit.,[17] 53°), 6-chloro-1-isopropoxy-2,4-dinitrobenzene, m.p. 64°, and 1-isopropoxy-6-isopropoxycarbonyl-2,4-dinitrobenzene, m.p. 87°, were prepared by reaction of the corresponding 1-chloro compounds with one equivalent of sodium isopropoxide in propan-2-ol and were recrystallised from propan-2-ol. 18-Crown-6 polyether was prepared by a standard method.[18] Messrs. T. Holmes, J. Parkinson, and R. Plumb are thanked for these preparations. ^{1}H N.m.r. spectra of the nitro-compounds showed bands consistent with the required compounds and indicated the absence of impurities.

Sodium isopropoxide solutions were freshly prepared by reaction of clean sodium with AnalaR propan-2-ol under nitrogen and were titrated with standard acid. Dilute solutions of tetramethylammonium isopropoxide in propan-2-ol were prepared by dilution of concentrated tetramethylammonium hydroxide solution in water. The maximum amount of water added in this way was 0.2 g l^{-1} which was judged to be negligible.

Visible spectral shapes of stable species were determined with a Unicam SP 8000 instrument. Kinetic measurements at 25° were made with Unicam SP 500 or Beckman S25 instruments for slow rates and a Canterbury stopped-flow spectrophotometer for fast rates. The rate constants of first-order reactions were calculated by standard methods and were reproducible within 3%.

In the presence of crown ether the reaction of isopropoxide ions with 6-chloro-1-isopropoxy-2,4-dinitrobenzene involves two simultaneous reactions (Scheme 2). Measurements of optical density were made at various times at two wavelengths, 400 and 500 nm, where the extinction coefficients of both products are known (the reactants have negligible absorption at these wavelengths). The relative concentrations of parent, Meisenheimer complex and phenol were then calculated throughout the course of the reaction. The concentration of complex was found to reach a maximum value and then very slowly decrease. Values of the equilibrium constant were calculated from the concentrations at the maximum and rate constants were found from the differential forms of the rate equations (8) and (9). Values so calculated did not vary during the course of the

$$\mathrm{d[complex]}/\mathrm{d}t = k_f[\mathrm{P}][\mathrm{NaOPr^i}] - k_r[\mathrm{complex}] \quad (8)$$

$$\mathrm{d[phenol]}/\mathrm{d}t = k_2[\mathrm{P}][\mathrm{NaOPr^i}] \quad (9)$$

reaction. ^{1}H N.m.r. spectra were measured with a Bruker 90 MHz instrument using tetramethylsilane as internal reference. The spectral data for the parent compounds in [$^2H_6$]DMSO are in Table 8.

TABLE 8

^{1}H N.m.r. parameters [a] for parent molecules in [$^2H_6$]DMSO

	Ring	Isopropyl	
1-Isopropoxy-2,4,6-trinitrobenzene	9.2	4.58 (h)	1.27 (d)
1-Isopropoxy-6-isopropoxycarbonyl-2,4-dinitrobenzene	9.05 (d) 8.75 (d)	4.56 (h) 5.30 (h)	1.23 (d) 1.38 (d)
6-Chloro-1-isopropoxy-2,4-dinitrobenzene	8.94 (d) 8.80 (d)	4.8 (h)	1.3 (d)
1-Isopropoxy-2,4-dinitrobenzene	8.84 (d) 8.56 (dd) 7.71 (d)	5.08 (d)	1.35 (d)

[a] d = doublet, h = heptet.

Spectra of the complexes produced on the addition of 1 mol. equiv. of sodium isopropoxide in propan-2-ol were recorded in media containing various ratios of DMSO: propan-2-ol. In media rich in propan-2-ol the spectra indicated the formation of the 1,1-adducts (III) which were stable with time. Data are in Table 9. In media rich in DMSO transient bands were observed due to addition at unsubstituted ring positions. In the case of 1-isopropoxy-2,4,6-trinitrobenzene bands at δ 8.57 and 6.41 were observed due to the 1,3-complex. Isomerisation to the 1,1-complex was very slow (hours) in media rich in DMSO.

TABLE 9

^{1}H N.m.r. data for 1,1-complexes in propan-2-ol–DMSO

Structure (III)		
X	R	Ring protons
NO_2	Pr^i [a]	8.92
CO_2Pr^i	Pr^i [b]	8.83 (d), 8.40 (d)
Cl	Pr^i [a]	8.85 (d), 7.57 (d)
H	Pr^i [b]	8.77 (d), 7.17 (dd), 5.2 (d)

[a] Solvent is 90 : 10 (v/v) propan-2-ol–DMSO. [b] Solvent is 50 : 50 (v/v) propan-2-ol–DMSO.

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Note added in proof: We have written the dealkylation reaction (Scheme 2 and text) as a substitution. We have, however no evidence that di-isopropyl ether is produced. In fact, the reaction giving the substituted phenoxide ion may well involve, elimination or free-radical pathways rather than substitution.