KINETIC AND EQUILIBRIUM STUDY OF THE INTERACTION OF N-(1-ETHYLPROPYL)-3,4-DIMETHYL-2,6-DINITROANILINE WITH HYDROXIDE ION

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The reversible interaction of N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitroaniline (1) with HO^- is characterized by several kinetic processes. The relaxation times of two of them were measured. It is suggested that the faster one is related to the protonation–deprotonation of the 3-methyl group and the value of the protonation rate is $0 \cdot 19 \ s^{-1}$. The slowest process leads to the dianionic species with maximum absorption at 340 nm where one HO^- group adds to the unsubstituted ring position of an anion derived from 1 by deprotonation of either the NH or the 3-methyl group. The rate and equilibrium constants for the formation of this species are reported.

INTRODUCTION

Dinitroanilines with substituents on the aromatic ring and on the nitrogen are commonly used as pesticides, but little is known about their mechanism of action.[1] Since di- and tri-nitroanilines add nucleophiles to the aromatic ring to form Meisenheimer complexes,[2] it was suggested that the biological activity of these herbicides might be due to this property[3] since they might react with the nucleophilic part of proteins and act as inhibitors of mytosis.

We have previously studied the interaction of the widely used herbicide trifluralin [N,N-di-n-propyl-2,6-dinitro-4-(trifluoromethyl)aniline] with different nucleophiles and found that it reacts with HO^-[4] and several amines and amino acids[5] to form σ-complexes. Therefore, we consider it of interest to determine whether there is any relationship between the biological

and chemical reactivity of this family of herbicides. We report here results regarding the interaction of hydroxide ions with N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitroaniline (1), known as pendimethalin, in dimethyl sulphoxide (DMSO)–water mixtures. Compound 1 is intrinsically interesting because it has several possibilities of 1:1 and 1:2 interaction with HO^- and several of them have been identified in this study.

RESULTS

Spectroscopic studies and equilibrium determinations

The spectrum of 1 in DMSO–water mixtures (30–80%, v/v) shows an absorption band at 440 nm. The addition of NaOH, KOH or tetramethylammonium hydroxide (TMAOH) to a solution of 1 results instantly in the development of a violet colour that slowly turns to yellow. The spectrum of the final solution in 30–50% DMSO–water shows a maximum at 340 nm and a shoulder at 550 nm. The absorption at 340 nm increases in intensity with increasing hydroxide concentration whereas that at 550 nm decreases. In 30% DMSO–water, the spectra of 1 were recorded after the violet colour had disappeared in solutions containing different HO^- concentrations and at each concentration as a function of time until the final equilibrium was reached. In both cases a good isosbestic point was obtained at 394 nm (Figure 1 is
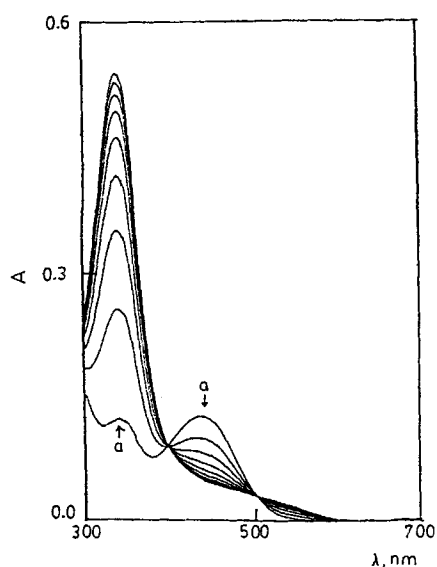

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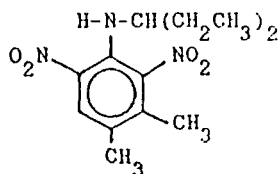
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Figure 1. Change in the spectrum of 1 with time in 30% DMSO. $[1]_0 = 4 \times 10^{-5}$ M; $[KOH]_0 = 0\cdot3$ M; $T = 25\,°$C. (a) Immediately after mixing. Intervals between cycles: 32 s

Table 1. Equilibrium data for the interaction of 1 with HO^- in 30% DMSO–water at 25 °C[a]

$[HO^-]$ (M)	ΔA[b]	ΔA[c]	ΔA[d]
0·044		0·067	
0·05	0·080		0·197
0·088		0·158	
0·10	0·172		0·359
0·132		0·280	
0·15	0·283		0·452
0·176		0·331	
0·20	0·377		0·501
0·220		0·395	
0·25	0·473		0·548
0·264		0·436	
0·30	0·535		0·576
0·309		0·498	
0·35	0·585		
0·353		0·503	
0·40	0·628		0·609
0·397		0·547	
0·441		0·542	
0·45	0·643		0·617
0·50	0·684		0·651

[a] Constant ionic strength 1 M; the compensating electrolyte is indicated in parentheses in footnotes b, c and d. Absorbances measured at 340 nm. $[1]_0 = 3 \times 10^{-5}$ M.
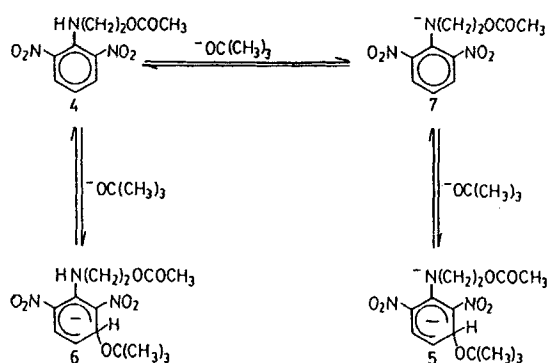[b] NaOH (NaCl).
[c] KOH (KCl).
[d] Tetramethylammonium hydroxide (tetramethylammonium chloride).

representative). The species formed immediately after mixing has an absorption band at 650 nm.

The addition of acid to the final solution reverts the spectrum to that of the starting material under the same conditions, indicating that the reactions are reversible.

The absorbance at 340 nm was measured as a function of HO^- concentration for KOH, NaOH and TMAOH. In all cases the dependence of the absorbance with the HO^- concentration shows that the absorbing species comes from the interaction of 1 with two equivalents of HO^-. The observed change in absorbance (ΔA) with HO^- concentration should follow an equation of the form $\Delta A = C_1[HO^-]/(1 + C_2[HO^-])$, where C_1 and C_2 are constants if the species responsible for the change comes from a 1:1 interaction of the substrate with HO^-; our data could not be correlated in that way but they could be correlated by an equation of the type $\Delta A = C_1'[HO^-]^2/(1 + C_2'[HO^-]^2)$, indicating that the interaction involves two equivalents of HO^- for each substrate. The absorbances vs HO^- concentration are collected in Table 1.

The reaction of N-n-butyl-2,6-dinitroaniline (2) with HO^- under the same conditions as those used for 1 was studied for comparative purposes. In addition, a separate study is being carried out on the interaction of 2,4-dinitrotoluene (3) with HO^-, which will be reported elsewhere.

The spectrum of 2 in 30% DMSO–water shows an absorption band at 440 nm. The addition of increasing amounts of KOH $(0\cdot1–0\cdot5$ M) to a solution of 2 leads to the appearance of an absorption band at 370 nm.

The spectrum of solutions as a function of time displays a good isosbestic point at 410 nm. There is also an isosbestic point at 410 nm for equilibrated solutions at different HO^- concentrations and the absorbance shows a similar HO^- dependence to that of 1.

In 90% DMSO–water, the spectrum of 2 is the same as that in 30% DMSO, but the addition of KOH results in the development of two bands, one at 580 nm and the other at 390 nm, and the disappearance of the original band. The band at 580 nm decreases with time whereas the other increases, showing a good isosbestic point at 470 nm.

The spectrum of 3 in 30% DMSO–water shows an absorption band at 250 nm. After the addition of KOH the solution became blue greenish, then it changed to colourless and finally to yellow. The spectrum of the final solution shows a maximum at 420 nm and a shoulder at 320 nm. This process is reversible. The spectrum of solutions of 3 at different HO^- concentrations shows an isosbestic point at 280 nm.

The ^1H NMR spectrum of 1 in 30% DMSO–water shows a single absorption in the aromatic region at δ 7·75. After the addition of 2 equivalents of KOH (fully deuterated solvents were used), two new peaks appear after 13 min at δ 6·54 and 5·92, each of which integrated for one proton. The spectrum of 2 in DMSO shows bands at δ 7·02 and 8·38 due to the ring protons

HN(CH₂)₂OCOCH₃

O₂N— —NO₂ ⁻OC(CH₃)₃

4

⁻OC(CH₃)₃

HN(CH₂)₂OCOCH₃

O₂N— —NO₂
—H
6 OC(CH₃)₃

⁻N(CH₂)₂OCOCH₃

O₂N— —NO₂

7

⁻OC(CH₃)₃

⁻N(CH₂)₂OCOCH₃

O₂N— —NO₂
—H
5 OC(CH₃)₃

Scheme 1

and a broad band at δ 7·94 due to the amino proton. On addition of 2 equivalents of KOH and of enough water to make the composition of the solvent 30% in DMSO, the amine proton signal disappeared instantly and H3,5 and H4 signals shifted upfield (δ 8·38 → 8·30; 7·02 → 6·92) owing to the formation of the conjugate base of **2**. After 9 min, collapsed doublets appeared at δ 8·11, 6·88, 7·38 and 8·34. Similar behaviour was observed in the reaction of *N*-(2-acetoxyethyl)-2,6-dinitroaniline (**4**) with KOC(CH₃)₃ in DMSO when studied by NMR,[6] and it was suggested that final equilibrium of the system could be represented as shown in Scheme 1. It was also shown that on addition of base to **4** the solution instantly became purple and then the colour slowly faded away. The solution has bands at 320, 368 and 585 nm. Together with the NMR spectral evidence, these bands were attributed to **5, 6** and **7**, respectively.

Kinetic studies

The changes in colour observed when HO⁻ is added to

a solution of **1** indicate that there are several kinetic processes taking place. The slowest of these processes leads to the formation of the species with maximum absorption at 340 nm, whereas the faster gives rise to a species with a broad band centred at 660 nm.

We are able to measure the rate of two of these processes. The fastest one (τ_f^{-1}) was determined by measuring the decrease in absorbance at 660 and 550 nm and as a function of KOH concentration in the range 0·1–0·5 M. The rate of this process was independent of the wavelength and of the HO⁻ concentration.

The reciprocal relaxation time of the slowest process (τ_s^{-1}) was determined from the change in absorbance with time at 340 nm and was measured as a function of NaOH, KOH and TMAOH concentration and at constant ionic strength. All experiments were performed with HO⁻ in large excess over **1**. The values of τ_s^{-1} are collected in Table 2.

It can be seen that the values of τ_s^{-1} in the presence of TMAOH are larger than with KOH and NaOH, despite the fact that the ionic strength was constant and that the compensating electrolyte used had the same cation as the hydroxide. This specific salt effect is commonly observed in reactions of nitro compounds with nucleophiles.[7,8]

In the interaction of **2** with HO⁻, we found two kinetic processes well separated in time. We considered that the fastest of these processes, which is too fast for our experimental techniques, corresponds to the deprotonation of the amino group from comparison of our results with others reported for similar systems.[9] The slowest process occurs in the same time range as that of **1** and the values of the measured relaxation time as a function of HO⁻ concentration are summarized in Table 3. When **3** reacts with HO⁻ there are several kinetic processes, the slowest taking place on the same time scale as those measured with **1** and **2** as substrates.

Table 2. Reciprocal relaxation times for the slowest process (τ_s^{-1}) in the reaction of **1** with HO⁻ in 30% DMSO–water at 25 °C[a]

[KOH] (M)	$10^3\tau_s^{-1}$ (s⁻¹)	[NaOH] (M)	$10^3\tau_s^{-1}$ (s⁻¹)	[TMAOH] (M)	$10^3\tau_s^{-1}$ (s⁻¹)
0·05	2·7 ± 0·1	0·06	2·6 ± 0·1	0·05	4·0 ± 0·1
0·10	3·12 ± 0·05	0·10	2·23 ± 0·05	0·07	4·2 ± 0·1
0·20	3·4 ± 0·1	0·21	2·50 ± 0·05	0·10	4·7 ± 0·1
0·30	4·5 ± 0·1	0·32	3·18 ± 0·05	0·20	8·8 ± 0·1
0·40	5·9 ± 0·1	0·42	3·54 ± 0·05	0·30	14·3 ± 0·1
0·50	6·4 ± 0·1	0·53	4·42 ± 0·05	0·45	23·3 ± 0·1
		0·63	4·8 ± 0·1		
		0·70	6·4 ± 0·1		
		0·80	9·3 ± 0·1		
		0·90	12·1 ± 0·1		

[a] Deviations reported are mean values of three determinations.

Table 3. Reciprocal relaxation times (τ^{-1}) for the slowest process in the reaction of **2** with HO^- in 30% DMSO–water at 25 °C[a]

| [KOH] (M)	$10^3\tau_s^{-1}(s^{-1})$
0·15	0·12 ± 0·02
0·25	0·90 ± 0·01
0·30	1·16 ± 0·02
0·35	2·1 ± 0·1
0·45	3·51 ± 0·01
0·5	4·2 ± 0·2

[a] Deviations reported are mean values of three determinations.

DISCUSSION

The interaction of HO^- with **2** can be described as shown in Scheme 2. Although there are other possibilities for reversible 1 : 1 and 1 : 2 interactions of nitro compounds with bases, such as addition of the nucleophile to the carbon bearing the nitrogen [10] and to an unsubstituted ring position, in previous studies it was shown that the addition of nucleophiles to nitroaromatic amines occurs preferentially at an unsubstituted ring position.[2,11] The ionization of the HO^- group in **8** and **9** might also take place, but we have no evidence.[12]

For a reaction of this type, three relaxation times are expected.[13] The faster should be related to the proton transfer equilibria $\mathbf{2} \rightleftharpoons \mathbf{10}$, the second pertains to the addition of HO^- to an unsubstituted ring position forming **9** and the slowest to the addition of HO^- to position 3 in the anion **10** with the other two species in fast equilibrium. We think that the process that we measured pertains to the third and slowest relaxation time, and it is given by the equation

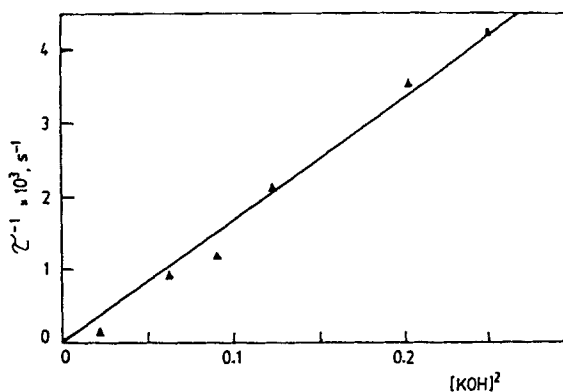$$\tau^{-1} = \frac{k_3 K_1 [HO^-]^2}{1 + (K_1 + K_2)[HO^-]} + k_{-3} \qquad (1)$$
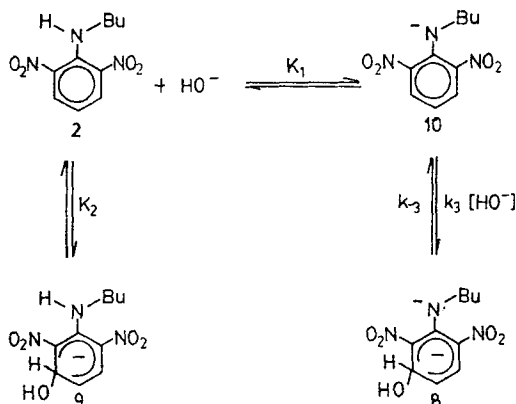
Scheme 2

Figure 2. Reciprocal relaxation time for the interaction of **2** with HO^- as a function of $[KOH]^2$. $[\mathbf{2}]_0 = 7 \times 10^{-5}$ M; ionic strength = 1 M; $T = 25$ °C

Since K_1 is estimated to be smaller than $0\cdot1$ M^{-1} (Ref. 9) and K_2 is also probably smaller than 1 [the equilibrium constant for the addition of MeO^- to an unsubstituted position of n-butylpicramide is 22 (see Ref. 11), similar to the value for trinitrobenzene, namely 23 (see Ref. 14); the equilibrium constant for the addition of HO^- to trinitrobenzene is $3\cdot7$ (see Ref. 14), and reducing the activation by one nitro group should reduce the equilibrium constant by about three orders of magnitude (see Ref. 15)], then in the denominator of equation (1) $(K_1 + K_2)[HO^-] < 1$. A plot of τ^{-1} vs $[HO^-]^2$ is linear (Figure 2) with a very small intercept. From the slope of this line the value of $k_3 K_1$ reported in Table 4 is calculated. The measured absorbances after the final equilibrium is reached are related to the equilibrium constants by equation (2), which was derived assuming that **2** and **8** are the major species present at equilibrium; this assumption is justified because a very good isosbestic point is observed.

Table 4. Calculated equilibrium and rate constants for the interaction of **1** and **2** with HO^- in 30% DMSO–water

Compound	Constant	KOH	NaOH	TMAOH
1[a]	$k_5 \times 10^{-3}(M^{-1}s^{-1})$	21	6·9	130
	$k_{-5} \times 10^{-3}(s^{-1})$	2·5	2·1	4·2
	$K_2(M^{-1})$	1·4	0·7	1·1
	$K_2 K_5{}^b(M^{-2})$	12·3	2·3	33·6
	$K_2 K_5{}^c(M^{-2})$	45·6	28·4	93
2[d]	$K_1 k_3 \times 10^{-3}(M^{-2}s^{-1})$	1·2		
	$K_1 K_3{}^e(M^{-2})$	41		

[a] Rate and equilibrium constants as indicated in Scheme 3.
[b] Values from kinetic data.
[c] Values calculated from equations (7) and (8)
[d] Rate and equilibrium constants as indicated in Scheme 2.
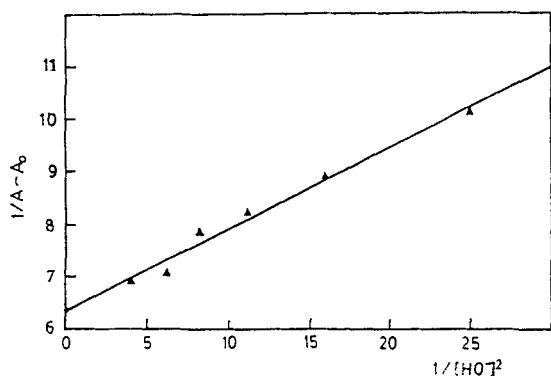[e] Obtained from equation (2).

Figure 3. Plot of the change in absorbance with KOH concentration from solutions of 2 in 30% DMSO, according to the reciprocal of equation (2). $[2]_0 = 6 \times 10^{-5}$ M; $T = 25\,°C$. Slope and intercept of the regression line are $0\cdot154$ and $6\cdot33$, respectively

$$A - A_0 = \frac{(\varepsilon_8 - \varepsilon_2)[2]_0 K_1 K_3 [HO^-]^2}{1 + K_1 K_3 [HO^-]^2} \qquad (2)$$

A plot of $(A - A_0)^{-1}$ vs $1/[HO^-]^2$ (Figure 3) is linear and from the ratio of the slope and intercept $K_1 K_3$ is calculated (Table 4).

Considering the structure of pendimethalin, the results obtained with 2 and 3 and reports in the literature with regard to the interaction of nitroaromatic compounds with nucleophiles,[10] we suggest that the interaction of 1 with HO$^-$ can be described by Scheme 3. There are other possibilities such as deprotonation of the other methyl group or electron transfer forming a radical anion. However, the acidity of a methyl group in a compound having nitro groups in 3- and 5-positions is expected to be lower than that which has the electron-withdrawing substituents in 2- and 4-positions,[16] and therefore its contribution might be only minor, if any. The formation of radical anions cannot be discarded with the data available but they cannot be the major species which represent the kinetic process measured, since the formation and decomposition of radical anions are expected to occur on a shorter time scale than accessible to our experimental technique.[17] In addition, the formation of radical anions in reactions of nitroaromatics with bases is more important when the base is present at a lower concentration than the nitroaromatic compound.[18] Therefore, we shall not discuss the latter two possibilities further.

From Scheme 3, five relaxation times are expected.[13] The first should be associated with the proton transfer equilibria of the NH group, $1 \rightleftharpoons 13$. The second should be related to the addition of the HO$^-$ group to an unsubstituted position of the substrate forming the σ-complex 11. It is expected that this process is faster than that related to the proton transfer to form 12 since in
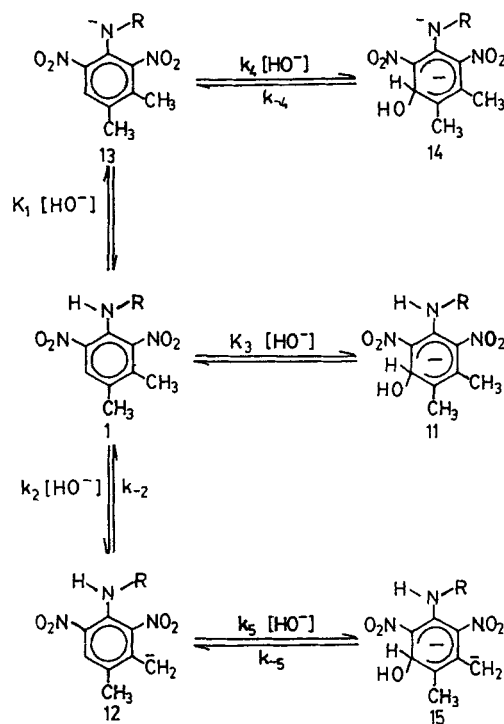
Scheme 3

the reaction of trinitrotoluene with bases the addition of HO$^-$ to the aromatic ring was shown to be faster than proton transfer to form the carbanion[19,20] and the decrease in activation of the aromatic ring is not expected to change the relative rates of these two reactions. The two processes associated with the first and second relaxation times are too fast for our techniques. The third relaxation corresponds to the deprotonation of 1 to form 12. We think that the faster kinetic process that we were able to measure corresponds to this process and its expression as derived from standard procedures[13] is given by

$$\tau_f^{-1} = \frac{k_2 [HO^-]}{1 + (K_1 + K_3)[HO^-]} + k_{-2} \qquad (3)$$

In this process a species with a UV spectrum similar to that of the 2,4-dinitrotoluene anion is formed.[21] Since τ_f^{-1} is independent of the HO$^-$ concentration, either the first term of equation (3) is smaller than k_{-2} or $(K_1 + K_3)[HO^-] > 1$. We think that the first alternative holds because the value of K_1 should be lower than the corresponding value for N-n-butyl-2,6-dinitroaniline. Further, K_3 should also be <1, considering the values for the addition of HO$^-$ to dinitro compounds[10] and the results obtained with N-n-butyl-2,6-dinitroaniline. Additional evidence comes from the fact that only very little 12 is formed since the total

absorbance change during this process is $0\cdot020$. We conclude that $\tau_f^{-1} = k_{-2} = 0\cdot12$ s^{-1}. This value compares well with the corresponding value for the protonation of the 2,4-dinitrotoluene anion measured in our laboratory, namely $0\cdot19$ s^{-1}, and with the value extrapolated from published data,[22] namely $0\cdot1$ s^{-1} for the same reaction in a solvent of higher DMSO content.

The fourth and fifth relaxation times should be associated with the formation of **14** and **15** with the other species in fast equilibrium. The values of k_4 and k_{-4} are probably very similar to those of k_5 and k_{-5} since in both reactions the HO^- group adds to the same position, and in both cases the substrate (**13** and **12**, respectively) bears a negative charge. Assuming that $k_4 = k_5$ and $k_{-4} = k_{-5}$, the two relaxation times are given by the equations[23]

$$\tau_4^{-1} = \frac{k_5(K_1 + K_2)[HO^-]^2}{1 + (K_1 + K_2)[HO^-]} + k_{-5} \qquad (4)$$

$$\tau_5^{-1} = k_{-5} \qquad (5)$$

As mentioned above, K_1 is estimated to be smaller than $0\cdot1$ M^{-1}. The value of K_2 should be similar to the corresponding value for the ionization of 2,4-dinitrotoluene in the same solvent, namely 2,[22] then equation (4) can be simplified to

$$\tau_4^{-1} = \frac{k_5 K_2[HO^-]^2}{1 + K_2[HO^-]} + k_{-5} = \tau_5^{-1} \qquad (6)$$

This relaxation time is identified with the slow process that we measured. The fifth relaxation time was not detected, probably owing to its small amplitude because **14** and **15** are formed in their equilibrium concentrations.[13] By non-linear adjustment of the values of τ_s^{-1} vs HO^- we calculated the values of K_2, k_5 and k_{-5} reported in Table 4. The value estimated for K_2 is similar to that of the ionization of 2,4-dinitrotoluene, as expected considering that the ionization of **1** is mainly determined by the two nitro groups.

The equilibrium absorbances reported in Table 1 are related to the equilibrium constants of Scheme 3 by equation (7), which can be rearranged to equation (8).

$$\Delta A = A - A_0 =$$

$$\frac{[(\varepsilon_{14} - \varepsilon_1)K_1K_4 + (\varepsilon_{15} - \varepsilon_1)K_2K_5] [1]_0[HO^-]^2}{1 + (K_1K_4 + K_2K_5)[HO^-]^2} \qquad (7)$$

$$\frac{[HO^-]^2}{\Delta A} = \frac{1}{D[1]_0} + \frac{K_1K_4 + K_2K_5}{D[1]_0}[HO^-]^2 \qquad (8)$$

where $D = [(\varepsilon_{14} - \varepsilon_1)K_1K_4 + (\varepsilon_{15} - \varepsilon_1)K_2K_5]$.

A plot of the left-hand side of equation (8) vs $[HO^-]^2$ is linear (Figure 4) and from the ratio of the slope and the intercept, $K_1K_4 + K_2K_5$ is calculated. Since $K_4 = K_5$ and $K_1 < K_2$, the calculated equilibrium constant should be K_2K_5. The values for the three hydroxides are reported in Table 4. The fact that the
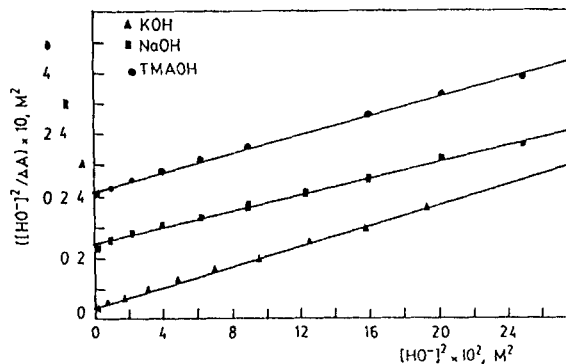

Figure 4. Plot of the change in absorbance of solutions of **1** in 30% DMSO with the concentration of HO^- according to equation (8). (▲) KOH, slope $= 1\cdot66 \pm 0\cdot035$, intercept $= (3\cdot64 \pm 0\cdot35) \times 10^{-2}$ M^2, $r^2 = 0\cdot9964$; (■) NaOH, slope $= 1\cdot30 \pm 0\cdot03$, intercept $= (4\cdot57 \pm 0\cdot39) \times 10^{-2}$ M^2, $r^2 = 0\cdot9956$; (●) TMAOH, slope $= 1\cdot5 \pm 0\cdot02$, intercept $= (1\cdot61 \pm 0\cdot3) \times 10^{-2}$ M^2, $r^2 = 0\cdot9984$

spectrophotometrically determined equilibrium constant does not agree with the kinetic value may be attributed to the specific salt effect which manifests itself in a different form in the kinetic and equilibrium studies. The fact that the specific salt effect is playing a role in this reaction is evident from the different rates obtained at the same hydroxide concentration but with different cations. An important salt effect is expected considering the highly charged species formed. The effect of the salt is more important for k_5 than for k_{-5}; similar effects have been observed with other dianion complexes.[24] The kinetic data are treated according to equation (6) whereas the equilibrium determinations are treated by equations (7) and (8). Since these two equations are of different form, τ^{-1} and A are expected to respond differently to the differential salt effect and K_2K_5 determined by the two methods should be different. Further, both equations imply a series of assumptions which might not be completely valid.

To derive equation (6) it is assumed that $k_4 = k_5$ and $k_{-4} = k_{-5}$; this may not be exactly true and so the rate coefficients calculated may have some errors. On the other hand, to derive equation (7) it is assumed that species **11**, **12** and **13** are present in very low concentrations, which also may introduce some errors in the calculated values of the equilibrium constants; therefore, the values reported in Table 4 should be taken only as approximate but it does not invalidate the general conclusions.

It is remarkable that the thermodynamic stability of the dianionic σ-complexes is higher than that of mono-anions. The formation of highly charged σ-complexes seems to be favoured at high base concentrations and in aqueous solutions,[25] but the tendency to form these highly charged complexes seems to be even more

marked in the reactions of aromatic amines. For instance, K_1/K_2 for the addition of HO$^-$ to trinitrobenzene is 14·8,[23,26] whereas the ratio of the equilibrium constants for the addition of one and two HO$^-$ groups to picrylpiperidine[27] is $2·6 \times 10^{-2}$.

Further, the ratio between the equilibrium constants for the formation of **17a** and **17b** from **16a** and **16b**, respectively, is 10^7, whereas the ratio for the formation of **18a** and **18b** from **17a** and **17b**, respectively, is 0·2.[28] These results indicate that the effect of the third nitro group in the nucleus is more important for the formation of the monoanion than for the formation of the dianion, and this may be a consequence of the very high stability of trinitro-substituted compounds.

16   17   18

a Z = NO₂   b Z = H
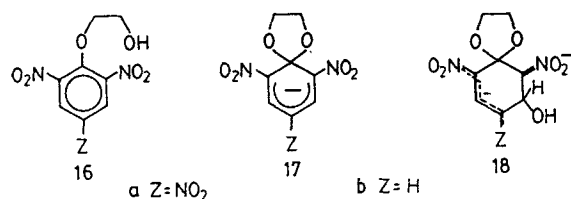
EXPERIMENTAL

Pendimethalin was obtained from a commercial sample of Herbadox (Cyanamid) and purified by recrystallization from ethanol–water (50 : 50); m.p. = 56–57 °C (lit.[29] m.p. = 56–57 °C). 2,4-Dinitrotoluene was obtained from a commercial sample and purified by recrystallization from methanol; m.p. = 70–71 °C (lit.[30] m.p. = 71 °C).

N-n-Butyl-2,6-dinitroaniline was prepared by reaction of 1-chloro-2,6-dinitrobenzene (1 mmol) and n-butylamine in 1 ml of N,N-dimethylformamide. After 2 h at room temperature in the dark, the solution was poured into ice–water, filtered and recrystallized from ethanol; m.p. = 41–42 °C (lit.[31] m.p. = 41 °C). DMSO was dried on 5 Å type molecular sieves and vacuum distilled.

Absorbance measurements were made by using a Shimadzu UV 260 or a Bechman 24 spectrophotometer with a thermostated cell compartment. The faster reactions were studied by using a Rapid Kinetic Accessory HI-TECH Scientific Model SFA-11.

^{1}H NMR studies were carried out on a Bruker 80-MHz instrument at the probe temperature (28 °C) and the absorption is reported in δ values relative to tetramethylsilane.

Reactions were initiated by adding substrate dissolved in DMSO to a solution containing all the other constituents. The total DMSO concentration was 30%. The observed rate constants were determined by following the appearance of the species formed at 340 nm (slow process) and 550 nm (fast process) for **1** and at 370 nm for **2**. The ionic strength was kept constant at 1 M by adding NaCl, KCl or tetramethylammonium

chloride to solutions containing NaOH, KOH and TMAOH, respectively. All kinetic runs were carried out under pseudo-first-order conditions at 25 °C.

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