Amines as leaving groups in nucleophilic aromatic substitution reactions. Part 4.[1] σ-Adduct formation in the hydrolysis of 1-amino-2,4,6-trinitrobenzenes

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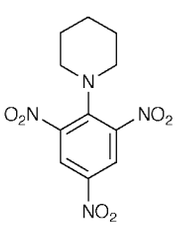
The kinetic study of the reaction of 2,4,6-trinitro-1-pyrrolidinobenzene **3**, 2,4,6-trinitro-1-piperidinobenzene **1** and 1-morpholino-2,4,6-trinitrobenzene **2** was made in 1,4-dioxane–water mixtures at 25 °C. In all cases, several processes were observed, the slowest of them leading to the formation of picrate ion. The fastest processes involved the formation of σ complexes by addition of one or two HO^- to unsubstituted ring positions and the ionisation of the 1 : 1 complex. Besides, for compounds **1** and **3**, *cis–trans* isomerisation of 1 : 2 complexes was kinetically detected. Substitution occurred by displacement of the amino group on the substrate and the 1 : 1 complex. The reaction pathway for the formation of phenol which involves the formation of these complexes has lower energy than that which results from addition to the 1 position of the substrate.

Introduction

We have demonstrated that cyclic amines like pyrrolidine, piperidine and morpholine can act as leaving groups in aromatic nucleophilic substitution reactions of 1-amino-2,4-dinitrobenzenes, and proposed a mechanism involving the formation of σ complexes by addition of HO^- or the amine to the unsubstituted positions of the aromatic ring.[1]

The substitution of amines by nucleophiles from several 1-amino-2,4,6-trinitrobenzenes has previously been studied and different mechanisms for its occurrence were observed. For instance, the hydrolysis of 1-imidazolyl-2,4,6-trinitrobenzene is general-base catalysed from pH 0.47 to 10.6 and the hydroxide ion catalysed rate of hydrolysis is 20 times the rate of hydrolysis of 1-chloro-2,4,6-trinitrobenzene.[2] A concerted general-base catalysis of water addition to the aromatic ring was suggested for this reaction.[2] The reaction of 1-imidazolyl-2,4,6-trinitrobenzene with n-butylamine to give *N*-n-butyl-2,4,6-trinitroaniline is pH dependent and has a mechanism involving acid catalysed leaving group departure.[3] In the hydrolysis reactions of 2,4,6-trinitro-1-piperidinobenzene **1** and 1-morpholino-2,4,6-trinitrobenzene **2**, σ complexes of 1 : 1 and 1 : 2 stoichiometry were formed by addition of one and two HO^- to unsubstituted ring positions. From the data available we suggested that picrate ion was formed from the attack of HO^- on the substrate and the two σ complexes.[4]

We report here our results regarding the reaction of 2,4,6-trinitro-1-pyrrolidinobenzene **3** with NaOH in water at 25 °C together with complementary results for the reactions of **1** and **2**.



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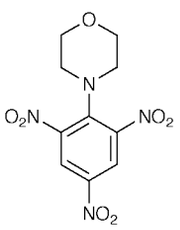

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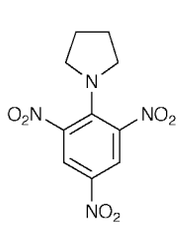

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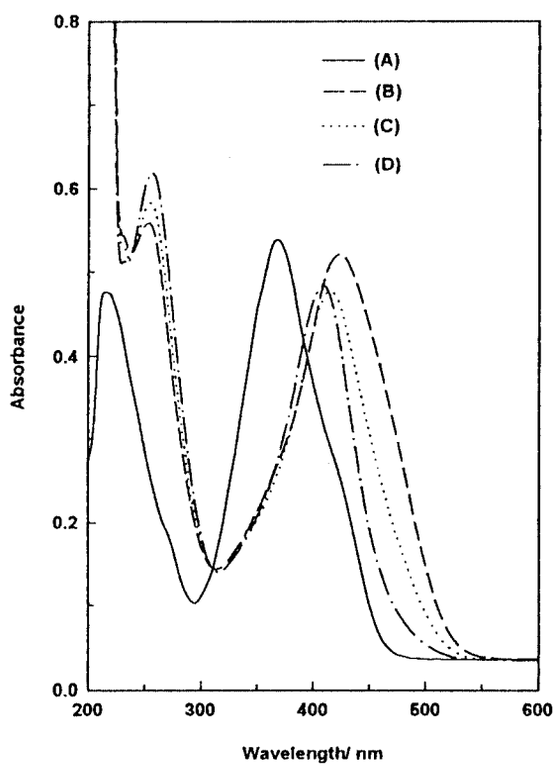

Fig. 1 Absorbance of **3** (2.6×10^{-5} M) in 20% 1,4-dioxane–water at 6 °C (A) and in the presence of 0.457 M NaOH at different reaction times: (B) $t = 10$ s; (C) $t = 1$ min; (D) $t = 9$ min.

Results

2,4,6-Trinitro-1-pyrrolidinobenzene 3

The spectrum of **3** in 20% 1,4-dioxane–water shows an absorption band at 364 nm (Fig. 1). The addition of NaOH > 0.05 M at 25 °C results instantly in the development of a spectrum with maxima at 424 and 253 nm which changes, to maxima at 414.5 and 254 nm and to maxima at 407.5 and 256 nm. The spectra of

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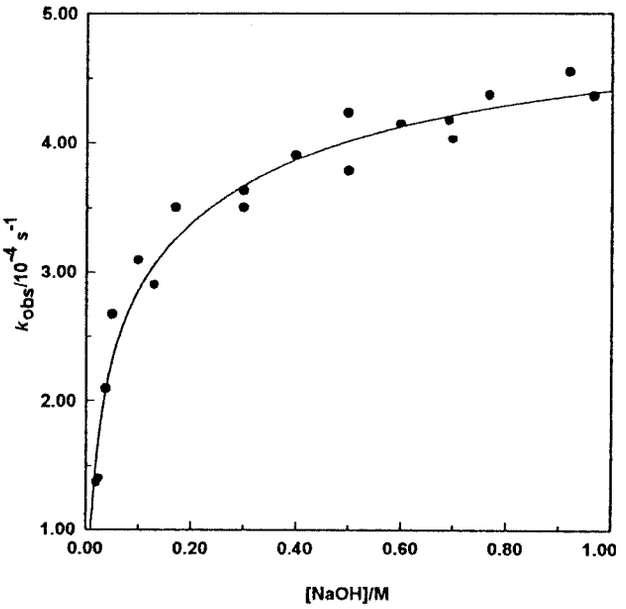


Fig. 2 Plot of k_{obs} *vs.* [NaOH] for the formation of picrate anion from **3** at 25 °C. $[\mathbf{3}]_0 = 2.24 \times 10^{-5}$ M. Solvent 20% 1,4-dioxane–water. The line was drawn using eqn. (4) and the values of rate and equilibrium constants reported in Table 7.

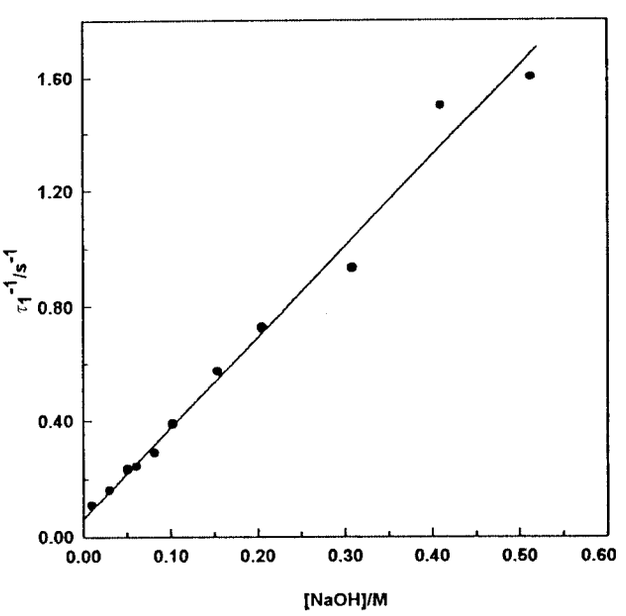


Fig. 3 Plot of τ_1^{-1} *vs.* [NaOH] for the reaction of **3** at 25 °C. $[\mathbf{3}]_0 = 2.24 \times 10^{-5}$ M. The line was drawn using eqn. (1) and the values of rate and equilibrium constants reported in Table 7.

the species formed in this process taken with a conventional spectrophotometer at 6 °C are shown in Fig. 1. Addition of acid after the formation of any of these species reverts the reaction to starting materials; at longer time these species are transformed quantitatively into picrate ion with a good isosbestic point at 377 nm.

The kinetic measurements for all the processes observed were made at 25 °C. The rate of formation of picrate ion was measured by following the decrease in absorbance at 410 nm with 1 > [NaOH] > 0.020 M (Table 1). There is a non-linear dependence of the observed rate constants with HO^- concentration (Fig. 2).

The fastest processes were followed in a stopped-flow spectrophotometer and three relaxation times were measured. Kinetic measurements of the first relaxation time (τ_1) were made by following the absorbance at 460 nm (Table 2, Fig. 3), while the second (τ_2) and third (τ_3) relaxation times were followed at 455 nm (Table 2). The observed reciprocal relaxation times $1/\tau_2$ and $1/\tau_3$ are independent of [HO^-] with mean values of 0.15 ± 0.02 and 0.035 ± 0.006 s^{-1} respectively.

Table 1 Observed rate constants for the formation of picrate ion in the hydrolysis of 2,4,6-trinitro-1-pyrrolidinobenzene **3** in water at 25 °C[a]

[NaOH/M	$k_{obs}/10^{-4}$ s^{-1}
0.020	1.37 ± 0.04
0.025	1.4 ± 0.1
0.038	2.09 ± 0.03
0.050	2.67 ± 0.08
0.099	3.09 ± 0.09
0.129	2.9 ± 0.2
0.170	3.5 ± 0.1
0.299	3.63 ± 0.04
0.299	3.5 ± 0.1
0.398	3.9 ± 0.1
0.498	4.23 ± 0.06
0.499	3.78 ± 0.04
0.598	4.15 ± 0.07
0.690	4.17 ± 0.05
0.697	4.03 ± 0.07
0.767	4.37 ± 0.08
0.920	4.55 ± 0.08
0.966	4.36 ± 0.07

[a] Solvent contains 20% 1,4-dioxane; ionic strength $I = 1$ M (NaCl); $[\mathbf{3}]_0 = 2.24 \times 10^{-5}$ M.

Table 2 Observed reciprocal relaxation times $1/\tau_1$, $1/\tau_2$ and $1/\tau_3$ in the hydrolysis of 2,4,6-trinitro-1-pyrrolidinobenzene **3** in water at 25 °C[a]

[NaOH]/M	τ_1^{-1}/s^{-1}	τ_2^{-1}/s^{-1}	τ_3^{-1}/s^{-1}
0.0102	0.108 ± 0.001		
0.0304	0.162 ± 0.004		
0.0513	0.233 ± 0.004		
0.0615	0.243 ± 0.006		
0.0820	0.29 ± 0.01		
0.103	0.388 ± 0.004		
0.154	0.574 ± 0.006		
0.198		0.14 ± 0.02	0.040 ± 0.001
0.205	0.725 ± 0.007		
0.298		0.12 ± 0.02	0.031 ± 0.004
0.308	0.93 ± 0.01		
0.395		0.17 ± 0.05	0.04 ± 0.01
0.410	1.50 ± 0.06		
0.499		0.16 ± 0.01	0.038 ± 0.002
0.513	1.6 ± 0.1		
0.593		0.16 ± 0.02	0.034 ± 0.003
0.705		0.149 ± 0.007	0.024 ± 0.001
0.791		0.17 ± 0.04	

[a] Solvent contains 20% 1,4-dioxane; ionic strength $I = 1$ M (NaCl); $[\mathbf{3}]_0 = 2.24 \times 10^{-5}$ M. The errors shown are deviations from the mean value.

2,4,6-Trinitro-1-piperidinobenzene 1

The spectrum of **1** in 10% 1,4-dioxane–water shows an absorption band at 397 nm. The addition of NaOH > 0.19 M produces the consecutive formation of three species: the first one with maxima at 417 and 257 nm, the second with maxima at 411.5 and 259 nm and the third with maxima at 409 and 260 nm. Acidification of the reaction solution after the formation of any of the three species gives quantitatively substrate. In a slower process these species lead to the formation of picrate ion. In Table 3 and Fig. 4 are collected the data for the formation of this ion.

The kinetic measurements at 25 °C of the fastest processes were made in a stopped-flow spectrophotometer following the change in absorbance at 409, 460 and 510 nm with [NaOH] from 0.04 to 1 M. The results are shown in Table 4 and Figs. 5 and 6. The observed reciprocal relaxation time $1/\tau_3$ is independent of [HO^-] with a mean value of 0.023 ± 0.007 s^{-1}.

Table 3 Observed rate constants for the formation of picrate ion in the hydrolysis of 2,4,6-trinitro-1-piperidinobenzene **1** in water at 25 °C[a]

[NaOH]/M	$k_{obs}/10^{-4}$ s^{-1}
0.020[b]	0.477
0.030[b]	0.566
0.040[b]	0.734
0.050[b]	0.802
0.075[b]	1.04
0.100[b]	1.32
0.125[b]	1.62
0.175[b]	2.08
0.200[b]	2.20
0.200[b]	2.21
0.200	2.24 ± 0.03
0.304	2.85 ± 0.05
0.401	3.44 ± 0.08
0.499	4.88 ± 0.05
0.499	4.69 ± 0.08
0.596	5.37 ± 0.08
0.705	5.80 ± 0.07
0.802	6.45 ± 0.08
0.900	7.11 ± 0.08
0.997	7.45 ± 0.08

[a] Solvent contains 2% 1,4-dioxane; ionic strength $I = 1$ M (NaCl); $[\mathbf{1}]_0 = 3.60 \times 10^{-5}$ M. [b] Data from ref. 4.

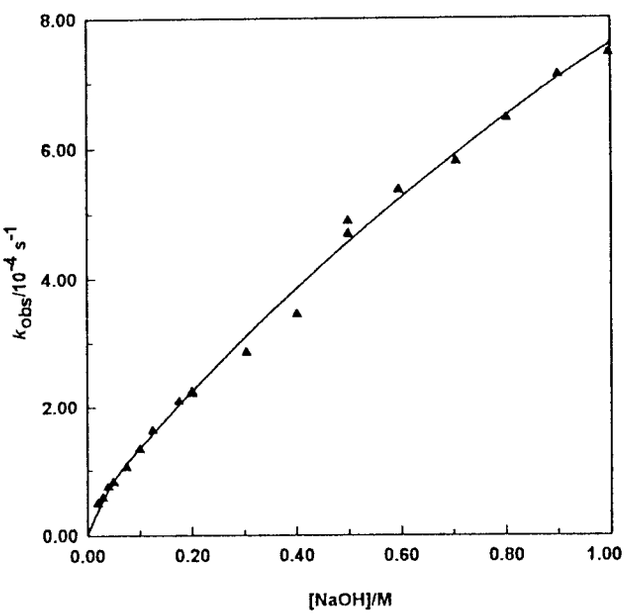


Fig. 4 Plot of k_{obs} *vs.* [NaOH] for the formation of picrate anion from **1** at 25 °C. $[\mathbf{1}]_0 = 3.60 \times 10^{-5}$ M. Solvent 10% 1,4-dioxane–water. The line was drawn using eqn. (4) and the values of rate and equilibrium constants reported in Table 7.

1-Morpholino-2,4,6-trinitrobenzene 2

The spectrum of **2** in 10% 1,4-dioxane–water has an absorption band at 378 nm. The addition of NaOH > 0.05 M produces instantly the appearance of a species with maxima at 418.5 and 261 nm. This species is rapidly transformed into another with maxima at 419.5 and 260.5 nm. Acidification of the reaction solution after the formation of these two species leads to substrate. Careful search for formation of a third species was made but we could not detect it under any condition. In a slower process these species lead to picrate ion; the results are shown in Table 5 and Fig. 7.

The fastest processes were followed in a stopped-flow spectrophotometer at 409, 418, 470 and 485 nm varying the HO^- concentration between 0.05 and 0.6 M. The first process is completed in 5 s while the second ends before 5 min. The observed reciprocal relaxation times for these processes are collected in Table 6.

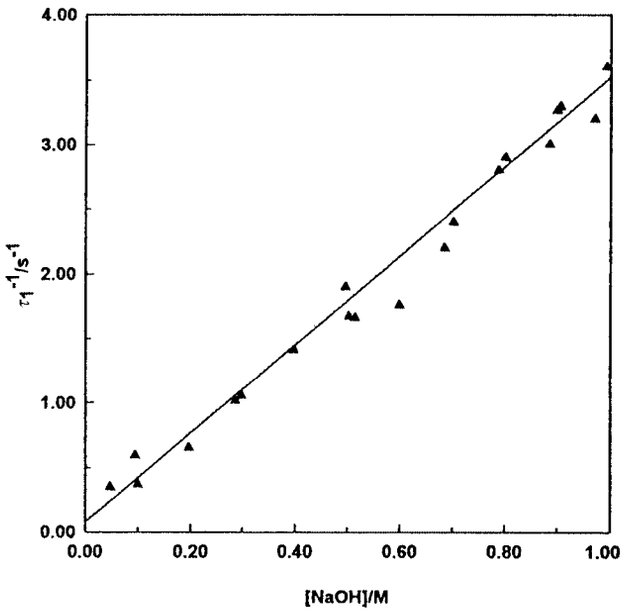


Fig. 5 Plot of τ_1^{-1} *vs.* [NaOH] for the reaction of **1** at 25 °C. $[\mathbf{1}]_0 = 4.09 \times 10^{-5}$ M. The line was drawn using eqn. (1) and the values of rate and equilibrium constants reported in Table 7.

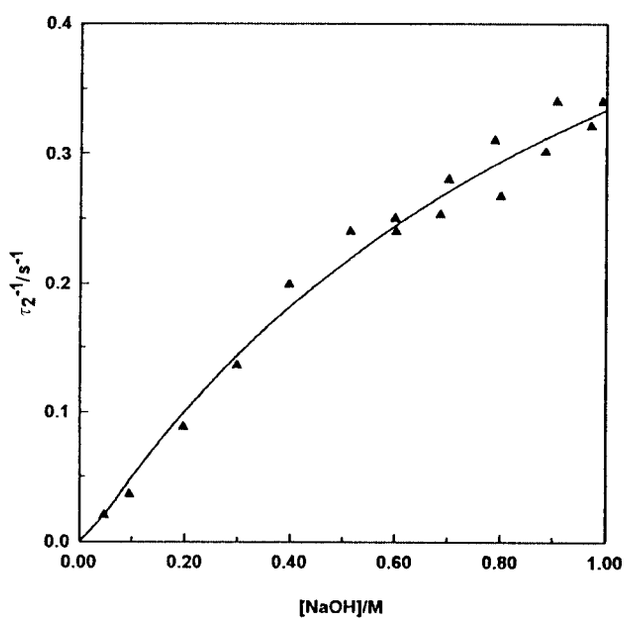


Fig. 6 Plot of τ_2^{-1} *vs.* [NaOH] for the reaction of **1** at 25 °C. $[\mathbf{1}]_0 = 4.09 \times 10^{-5}$ M. The line was drawn using eqn. (2) and the values of rate and equilibrium constants reported in Table 7.

Discussion

We reported previously data for the kinetics of the hydrolysis of substrates **1** and **2** measured at concentrations lower than 0.2 M and proposed the mechanism shown in Scheme 1.[4] This mechanism involves the formation of two σ complexes, which yield picrate ion upon attack of HO^-.

The spectral changes observed with substrates **1** and **3** indicate that more than two intermediates are formed. These intermediates must be σ complexes because their spectra are similar to those of other σ complexes.[5] It should be noticed that all the steps that lead to product in Scheme 1 are not elementary steps and must involve the attack of HO^- on the carbon bearing the amine with formation of intermediates **6**, **7**, and **8**. The fact that the substrate is quantitatively obtained upon acidification of the reaction solution after the formation of each species

Table 4 Observed reciprocal relaxation times $1/\tau_1$, $1/\tau_2$ and $1/\tau_3$ in the hydrolysis of 2,4,6-trinitro-1-piperidinobenzene **1** in water at 25 °C[a]

[NaOH]/M	τ_1^{-1}/s^{-1} [b]	τ_2^{-1}/s^{-1} [b]	τ_3^{-1}/s^{-1} [b]
0.047	0.349 ± 0.006	0.021 ± 0.002	
0.095	0.59 ± 0.03	0.036 ± 0.001	
0.0995	0.366 ± 0.003		0.016 ± 0.001
0.197	0.65 ± 0.06	0.09 ± 0.01	0.015 ± 0.004
0.197			0.012 ± 0.003
0.286	1.01 ± 0.02		0.018 ± 0.004
0.298	1.05 ± 0.04		0.015 ± 0.002
0.299		0.14 ± 0.01	0.014 ± 0.002
0.398	1.41 ± 0.04	0.20 ± 0.03	0.015 ± 0.002
0.398			0.021 ± 0.003
0.496	1.9 ± 0.2		
0.502	1.67 ± 0.02		0.026 ± 0.003
0.512			0.020 ± 0.007
0.514	1.66 ± 0.04	0.24 ± 0.02	0.03 ± 0.01
0.599	1.76 ± 0.03	0.25 ± 0.04	0.024 ± 0.007
0.601		0.24 ± 0.02	0.024 ± 0.004
0.685	2.20 ± 0.04	0.253 ± 0.002	0.03 ± 0.01
0.701		0.28 ± 0.02	0.027 ± 0.006
0.702	2.40 ± 0.1		0.030 ± 0.009
0.788	2.8 ± 0.3	0.31 ± 0.01	0.030 ± 0.003
0.801	2.9 ± 0.1	0.27 ± 0.02	0.030 ± 0.004
0.885	3.0 ± 0.2	0.301 ± 0.009	
0.900	3.27 ± 0.03		0.029 ± 0.008
0.906	3.3 ± 0.2	0.34 ± 0.02	0.039 ± 0.005
0.971	3.2 ± 0.2	0.321 ± 0.006	
0.993	3.6 ± 0.4	0.34 ± 0.02	

[a] Solvent contains 10% 1,4-dioxane; ionic strength $I = 1$ M (NaCl); $[\mathbf{1}]_0 = 4.09 \times 10^{-5}$ M. [b] Values reported are mean values of determinations at λ 510, 460 and 409 nm. The errors shown are deviations from the mean value.

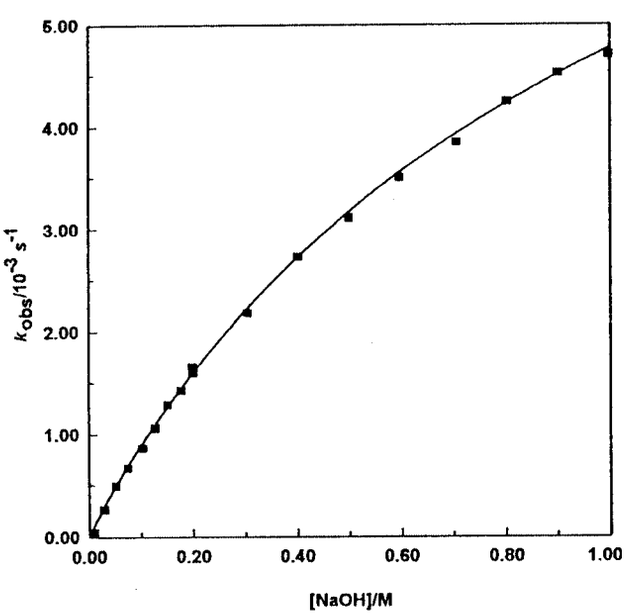
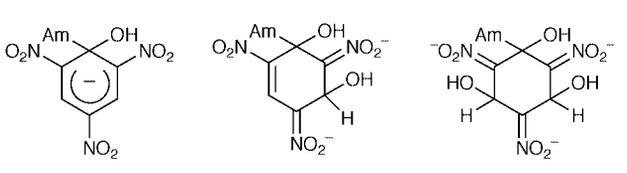


Fig. 7 Plot of k_{obs} *vs.* [NaOH] for the formation of picrate anion from **2** at 25 °C. $[\mathbf{2}]_0 = 5.58 \times 10^{-5}$ M. Solvent 10% 1,4-dioxane–water. The line was drawn using eqn. (4) and the values of rate and equilibrium constants reported in Table 7.



6 **7** **8**

indicates that **6**, **7** or **8** cannot be responsible for the spectra observed, since in acidic solution the amine should leave faster than HO^- leading to the formation of picric acid.[6]

Table 5 Observed rate constants for the formation of picrate ion in the hydrolysis of 1-morpholino-2,4,6-trinitrobenzene **2** in water at 25 °C[a]

[NaOH]/M	$k_{obs}/10^{-3}$ s^{-1}
0.010[b]	0.0437
0.029[b]	0.266
0.051[b]	0.493
0.074[b]	0.673
0.102[b]	0.867
0.127[b]	1.06
0.150[b]	1.29
0.176[b]	1.43
0.198	1.65 ± 0.02
0.199[b]	1.60
0.199[b]	1.62
0.304	2.18 ± 0.01
0.401	2.73 ± 0.01
0.499	3.11 ± 0.03
0.596	3.50 ± 0.04
0.705	3.85 ± 0.04
0.802	4.25 ± 0.02
0.900	4.52 ± 0.07
0.997	4.7 ± 0.1

[a] Solvent contains 2% 1,4-dioxane; ionic strength $I = 1$ M (NaCl); $[\mathbf{2}]_0 = 5.58 \times 10^{-5}$ M. [b] Data from ref. 4.

Table 6 Observed reciprocal relaxation times for the first and second processes observed in the hydrolysis of 1-morpholino-2,4,6-trinitrobenzene **2** in water at 25 °C[a]

[NaOH]/M	τ_1^{-1}/s^{-1} [b]	τ_2^{-1}/s^{-1} [b]
0.048	0.55 ± 0.08	0.018 ± 0.002
0.202	1.4 ± 0.3	0.14 ± 0.02
0.398	2.1 ± 0.1	0.23 ± 0.02
0.598	3.3 ± 0.2	0.36 ± 0.01

[a] Solvent contains 10% 1,4-dioxane; ionic strength $I = 1$ M (NaCl); $[\mathbf{2}]_0 = 4.08 \times 10^{-5}$ M. [b] Values reported are mean values of determinations at λ 409, 418, 470 and 485 nm. The errors shown are deviations from the mean value.

Another possibility is the ionisation of complex **4**, as was reported previously in different cases,[7–9] and the formation of the *cis* and *trans* isomer of complex **5** as was reported for sulfite complexes of 1,3,5-trinitrobenzene[10] (Scheme 2).

The expressions for the relaxation times for the mechanism shown in Scheme 2 can be derived by standard procedures[11] and assuming that $k_1[HO^-] + k_{-1} \gg k_2[HO^-] + k_{-2} \gg k_3[HO^-] + k_{-3}$, they are given by eqns. (1), (2) and (3).

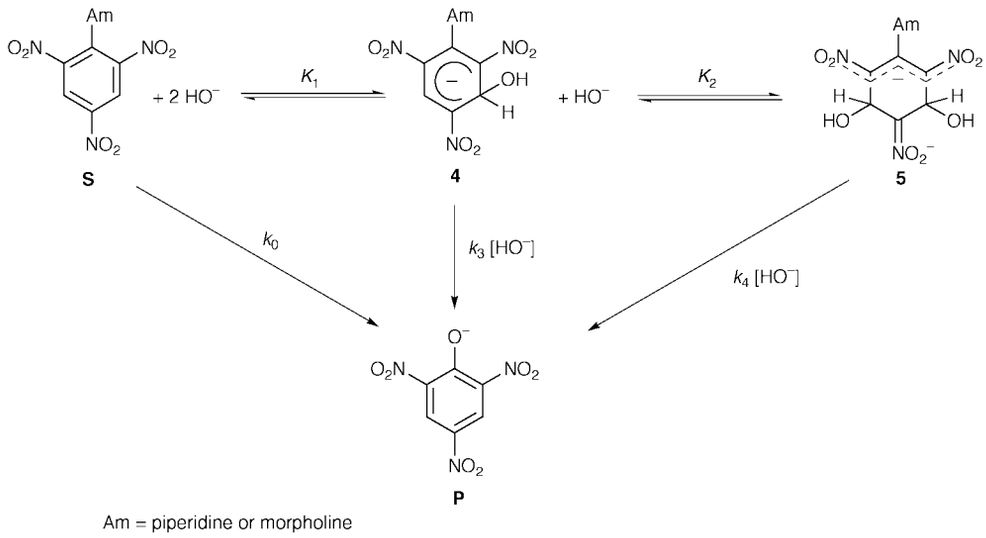
$$\frac{1}{\tau_1} = k_1[HO^-] + \frac{k_{-1}}{1 + K[HO^-]} \quad (1)$$

$$\frac{1}{\tau_2} = \frac{k_2K_1[HO^-]^2}{1 + K_1[HO^-] + KK_1[HO^-]} + k_{-2} \quad (2)$$

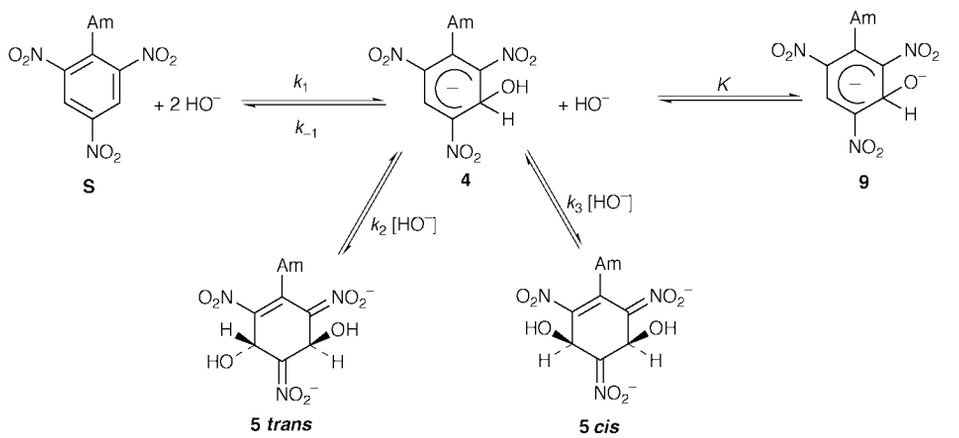
$$\frac{1}{\tau_3} = \frac{k_3K_1[HO^-]^2}{1 + K_1[HO^-] + K_1(K + K_2)[HO^-]^2} + k_{-3} \quad (3)$$

The fact that we did not detect a third relaxation time in the reaction of **2** does not necessarily mean that there is no *trans–cis* isomerism. This isomerism may not be observed when one or more of the following situations hold: a) the UV-visible spectra of the *cis* and *trans* isomers are very similar; b) the formation of one of them is thermodynamically and kinetically favoured over the other; c) both isomers have the same stability and are formed and decomposed at equal rates.[12] So we believe that one of these possibilities is taking place with substrate **2**.

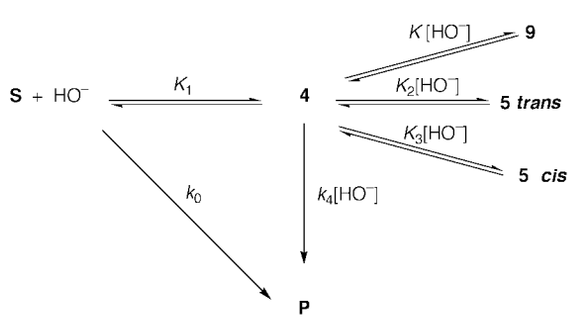
For the formation of picrate ion we propose the mechanism depicted in Scheme 3.[13]



Scheme 1



Scheme 2



Scheme 3

Nucleophilic displacement of the leaving group by hydroxide within 3-nucleophile σ complexes was previously proposed.[1,9]

The rate law for the mechanism of Scheme 3 is given by eqn. (4). The calculated equilibrium and rate constants for the

$$k_{obs} = \frac{k_0[HO^-] + k_4K_1[HO^-]^2}{1 + K_1[HO^-] + K_1(K + K_2 + K_3)[HO^-]^2} \quad (4)$$

mechanism proposed are collected in Table 7 and were calculated as follows.

For compound **3** a good fit by eqn. (1) of the data from $1/\tau_1$ was obtained with a value of $K = 1$ M^{-1} (Fig. 3). The data for $1/\tau_2$ and $1/\tau_3$ are independent of [HO^-] with mean values of

Table 7 Calculated rate and equilibrium constants for the hydrolysis of **1**, **2** and **3** in water at 25 °C

Compound	**3**	**1**	**2**
k_0/s^{-1}	0.015 ± 0.002	0.0031 ± 0.0005	0.0106 ± 0.0009
K/M^{-1}	1	0.9 ± 0.4	1.0 ± 0.3
k_1/M^{-1} s^{-1}	3.2 ± 0.1	3.48 ± 0.05	5.05 ± 0.03
k_{-1}/s^{-1}	0.06 ± 0.02	0.08 ± 0.02	0.28 ± 0.06
K_1/M^{-1}	53 ± 19	45 ± 10	18 ± 4
k_2/M^{-1} s^{-1}		0.6 ± 0.2	1.0 ± 0.3
k_{-2}/s^{-1}	0.17 ± 0.03		
k_{-3}/s^{-1}	0.04 ± 0.01	0.023 ± 0.007	
k_4/M^{-1} s^{-1}	0.0013 ± 0.0005	0.0010 ± 0.0003	0.009 ± 0.002
$K + K_2 + K_3$	3 ± 1	0.4 ± 0.2	0.9 ± 0.3

0.17 ± 0.03 and 0.04 ± 0.01 s^{-1} respectively. Considering the [HO^-] used in these measurements, the mean value of $1/\tau_2$ could be attributed to $k_2 + k_{-2}$. An acceptable fit of k_{obs} by eqn. (4) was obtained with $K_1 = 53$ M^{-1} (Fig. 2).

For compound **1** the plot of $1/\tau_1$ *vs.* [HO^-] (Fig. 5) has a small intercept which did not allow an accurate determination of k_{-1} and only k_1 could be calculated. An acceptable fit of the data for the slow process by eqn. (4) (Fig. 4) gives a value of K_1 of 45 ± 10 M^{-1} which leads to a value for k_{-1} of 0.08 ± 0.02 s^{-1}. The plot of $1/\tau_2$ *vs.* [HO^-] (Fig. 6) fits well the first term of eqn. (2) with $K_1 = 45$ M^{-1}. From this plot we could calculate k_2 and K. The line in Fig. 5 was drawn with the rate and equilibrium

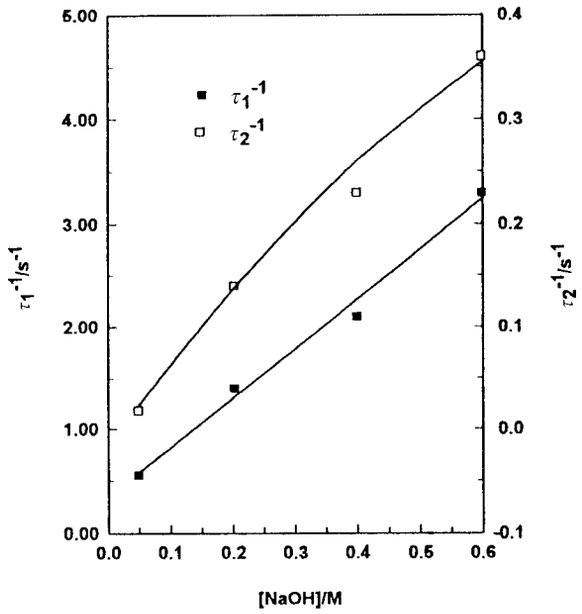


Fig. 8 Plots of τ_1^{-1} and τ_2^{-1} *vs.* [NaOH] for the reaction of **2** at 25 °C. $[\mathbf{2}]_0 = 4.08 \times 10^{-5}$ M. The lines were drawn using eqns. (1) and (2) respectively and the values of rate and equilibrium constants reported in Table 7.

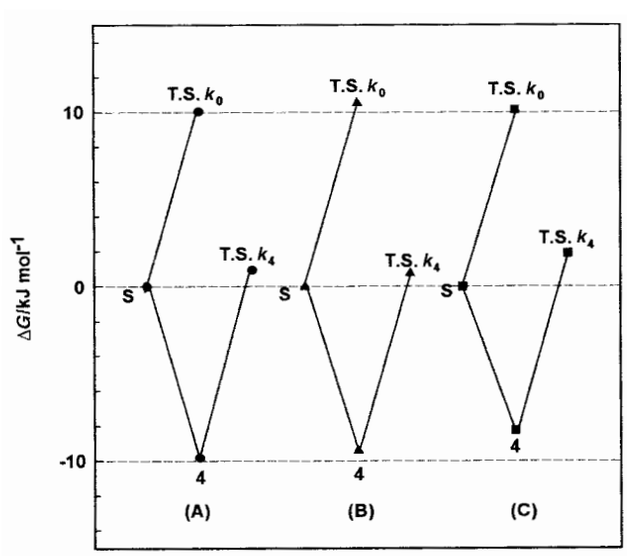


Fig. 9 Suggested schematic free energy profile for the hydrolysis of (A) compound **3**; (B) compound **1** and (C) compound **2**.

constants calculated and eqn. (1). Data for $1/\tau_3$ are independent of $[HO^-]$ and k_{-3} was calculated as the mean value.

In the case of compound **2** only two relaxation times were observed. The first one gives a good fit using eqn. (1) with $K = 1$ M^{-1} (Fig. 8). The second relaxation time gives a good fit using the first term of eqn. (2) with K_1 calculated with eqn. (4) (Figs. 8 and 7, respectively).

From the values of k_0 and k_4 it can be seen that the pyrrolidine derivative of S and **4** is the most reactive at position 1 while from k_1 we can infer that this derivative is the less reactive at position 3 (Table 7).

The equilibrium constant for deprotonation of **4** is the same for all the derivatives as was observed previously with various picryl thioethers.[8a] Though the equilibrium constant for the formation of **4** is greater for the pyrrolidine derivative than for the others, they are all of the same order of magnitude.

From the values of k_0, K_1 and k_4, we can estimate the free energy of activation for the substitution on the substrate, the change in free energy for the formation of **4** and the free energy of activation for the substitution on **4**. These values are plotted in Fig. 9 where we can see that the formation of **4** provides a reaction pathway with lower energetic requirements for the substitution of the amino group.

The low reactivity of nitroaromatic amines towards substitution of the amino group is considered to be a consequence of the interaction of the nitrogen lone pair of electrons with the π system that stabilises the ground state of the substrate. We suggest that the addition of a nucleophile to an unsubstituted position of the aromatic ring favours the displacement due to rotation of the amine group from the mean plane to enable delocalisation of the negative charge. This effect was observed before in the hydrolysis reaction of 1-amino-2,4-dinitrobenzenes.[1] The catalytic effect of formation of σ complexes was greater with 2,4-dinitrobenzene derivatives than with compounds **1**, **2** and **3**. Structural investigation of compounds **1**, **2** and **3** in the solid state and in solution indicates that the *ortho*-nitro groups and the amino group are rotated out of the aromatic plane.[14] Although rotation of the *ortho*-nitro group and the amino group was also observed in 1-amino-2,4-dinitrobenzenes,[16] the corresponding trinitro derivatives are less planar than these compounds so the change in rotation of the amine upon formation of the complex is less significant.

Conclusions

1-Amino-2,4,6-trinitrobenzenes form σ complexes by addition of nucleophiles to non-substituted ring positions of the aromatic ring. The formation of these complexes facilitates the substitution of the amino group. Rotation of the amino group out of the aromatic plane favours substitution.

Experimental

Materials

2,4,6-Trinitro-1-pyrrolidinobenzene, mp 194–196 °C (Lit.[16] 189.5–191 °C), was prepared by the method used previously for 1-imidazolyl-2,4,6-trinitrobenzene, **1** and **2**,[2] and used without further purification. The identity of **3** was confirmed by ^{1}H NMR (200 MHz, Cl_4C, δ 1.10 (s, 4H), 1.26 (s, 4H), 8.7 (s, 2H)) and ^{13}C NMR (200 MHz, $CDCl_3$, δ 25.10, 53.99, 125.25, 131.88, 137.3, 141.3). Substrates **1** and **2** were available from previous work.[4] 1,4-Dioxane was purified as described previously.[2] Water purified in a Millipore Milli-Q apparatus was used throughout. All of the inorganic reagents were of analytical-reagent grade used without further purification.

UV spectra and kinetic measurements were recorded on a Shimadzu UV-2101PC spectrophotometer. An Applied Photophysics SF 17MV stopped-flow spectrofluorimeter was used to measure rate coefficients and to determine spectral shapes of species present after short reaction times. The spectra of these species between 200 and 600 nm were obtained by plotting the absorbance of the reaction mixture after 10 s of reaction ($[HO^-]$ 0.5 M) as a function of the wavelength, each point being the mean value of at least 5 runs.

Kinetic procedures

The total 1,4-dioxane concentration was 20% v/v for the reactions of **3** and 10% v/v for the other substrates; the temperature was 25 °C and the ionic strength 1 M. NaCl was used as compensating electrolyte. All kinetic runs were carried out under pseudo-first-order conditions, with substrate concentrations of about $(2–5) \times 10^{-5}$ M. In a typical stopped-flow experiment, two solutions in 20 or 10% 1,4-dioxane–water of two times the concentration required for the final solution were prepared; one of them contained the substrate and the other the nucleophile and NaCl. The reaction was initiated by mixing equal volumes of both solutions. All relaxation times represent average values from five to fifteen determinations.

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References

1 Part 3. E. Buján de Vargas, M. V. Remedi and R. H. de Rossi, *J. Phys. Org. Chem.*, 1995, **8**, 113.
2 R. H. de Rossi and E. B. de Vargas, *J. Am. Chem. Soc.*, 1981, **103**, 1533.
3 E. B. de Vargas and R. H. de Rossi, *Tetrahedron Lett.*, 1982, **23**, 4423.
4 E. B. de Vargas and R. H. de Rossi, *J. Phys. Org. Chem.*, 1989, **2**, 507.
5 J. J. K. Boulton and N. R. MacFarlane, *J. Chem. Soc. B*, 1971, 925, 928; M. R. Crampton and V. Gold, *J. Chem. Soc. B*, 1967, 23; V. Gold and C. H. Rochester, *J. Chem. Soc. B*, 1964, 1727; E. Buncel, A. R. Norris, K. E. Russell and P. J. Sheridan, *Can. J. Chem.*, 1974, **52**, 25.
6 C. F. Bernasconi, R. H. de Rossi and G. L. Gehriger, *J. Org. Chem.*, 1973, **38**, 2838.
7 E. A. Castro, M. Cubillos, J. G. Santos, E. I. Buján, M. V. Remedi, M. A. Fernández and R. H. de Rossi, *J. Chem. Soc.*, *Perkin Trans. 2*, 1999, 2603.
8 (*a*) R. Chamberlin, M. R. Crampton and R. L. Knight, *J. Chem. Res.* (*S*), 1993, 444; (*b*) M. R. Crampton, A. B. Davis, C. Greenhalgh and J. A. Stevens, *J. Chem. Soc.*, *Perkin Trans. 2*, 1989, 675.
9 B. Gibson and M. R. Crampton, *J. Chem. Soc.*, *Perkin Trans. 2*, 1979, 648.
10 C. F. Bernasconi and R. G. Bergstrom, *J. Am. Chem. Soc.*, 1973, **95**, 3603; M. R. Crampton and M. J. Willison, *J. Chem. Soc.*, *Chem. Commun.*, 1973, 215; M. J. Strauss and S. P. B. Taylor, *J. Am. Chem. Soc.*, 1973, **95**, 3813.
11 C. F. Bernasconi, *Relaxation Kinetics*, Academic Press, New York, 1976.
12 C. F. Bernasconi and H.-Ch. Wang, *J. Chem. Kin.*, 1979, **XI**, 375.
13 It should be noticed that the experimental data reported in ref. 4 were nicely reproduced but using the complete set of data we cannot detect the formation of picrate ion from the complexes having 1 : 2 stoichiometry.
14 R. Baggio, M. V. Remedi, M. T. Garland and E. I. Buján, *J. Chem. Crystallogr.*, 1997, **27**, 499.
15 J. Ellena, G. Punte, B. E. Rivero, M. V. Remedi, E. B. de Vargas and R. H. de Rossi, *J. Chem. Crystallogr.*, 1995, **25**, 801; M. V. Remedi, E. I. Buján, R. Baggio and M. T. Garland, *J. Phys. Org. Chem.*, 1998, **11**, 895.
16 S. Sekiguchi, H. Ishikura, Y. Hirosawa and N. Ono, *Tetrahedron*, 1990, **46**, 5567.