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AMINES AS LEAVING GROUPS IN NUCLEOPHILIC AROMATIC SUBSTITUTION REACTIONS. II.* HYDROLYSIS OF *N*-(2,4,6-TRINITROPHENYL)AMINES

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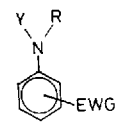
ABSTRACT

The hydrolysis reactions of *N*-(2,4,6-trinitrophenyl)piperidine (**2**) and *N*-(2,4,6-trinitrophenyl)-morpholine (**3**) were studied. Two kinetic processes well separated in time are observed in both reactions. The fastest process, which is reversible, leads to the formation of a species of λ_{max} 260 and 410 nm and is attributed to the formation of a σ complex of stoichiometry 1 : 2 due to the addition of a second HO^- to the σ complex of 1 : 1 stoichiometry. The slowest process leads quantitatively to picrate ion. The equilibrium constants for the formation of the σ complexes of 1 : 1 and 1 : 2 stoichiometries and the rate of formation and decomposition of the latter complex were determined. The kinetic data for the slow process lead to the conclusion that the picrate ion is formed from the attack of HO^- on the two σ complexes, confirming previous findings. There are some differences in the calculated rates for **2** and **3** which may be an indication that the elimination of the amine is partially rate determining.

INTRODUCTION

Despite the fact that aromatic amines with general structure **1** are resistant to elimination of the amino group, we have already demonstrated that in some special cases the substitution of the amino group by a nucleophile is possible.[1,2] The requirement for having substitution of the amino group seems to be a low interaction of the nitrogen lone pair of electrons with the π system.



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We report here our results regarding the reaction of *N*-(2,4,6-trinitrophenyl)piperidine and *N*-(2,4,6-trinitrophenyl)morpholine with hydroxide ion in water solution and we show that

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substitution takes place on σ complexes where one and two HO^- groups are added to the unsubstituted ring carbons of the substrate. These results confirm our previously reported finding that the addition of a nucleophile (HO^- or an amine) to C-3 of *N*-(2,4-dinitrophenyl)-piperidine or *N*-(2,4-dinitrophenyl)morpholine activates the substitution of the amine.

RESULTS

When *N*-(2,4,6-trinitrophenyl)piperidine (**2**) or *N*-(2,4,6-trinitrophenyl)morpholine (**3**) is added to a basic aqueous solution, two kinetic processes, well separated in time, are observed. In both cases the slowest process leads quantitatively to the formation of picrate ion.

The fastest process is characterized by the formation of a species with λ_{max} at 260 and 410 nm. Good isosbestic points are obtained when the spectrum of the solution is taken at different reaction times (Figure 1). This species is then slowly transformed into picrate ion and also a good isosbestic point is obtained (Figure 2).

Fast process

The observed rate constant for this process, k_f, was obtained for **2** and **3** by measuring the increase in absorbance at 260 nm. In all cases good pseudo-first-order kinetic plots were obtained up to 80% conversion of the substrate. The values of k_f as a function of HO^-

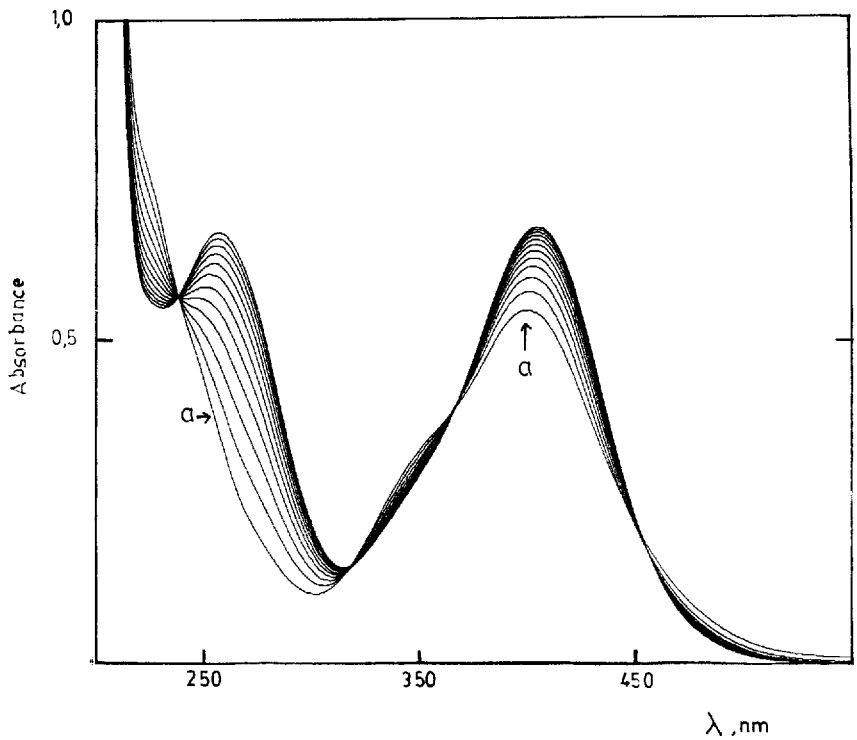


Figure 1. Absorbance of **2** in the presence of 0·01 M NaOH at different reaction times; fast process. $[2]_0 = 4{\cdot}38 \times 10^{-5}$ M. First cycle (a) = 1 min. Intervals between cycles: 83 s

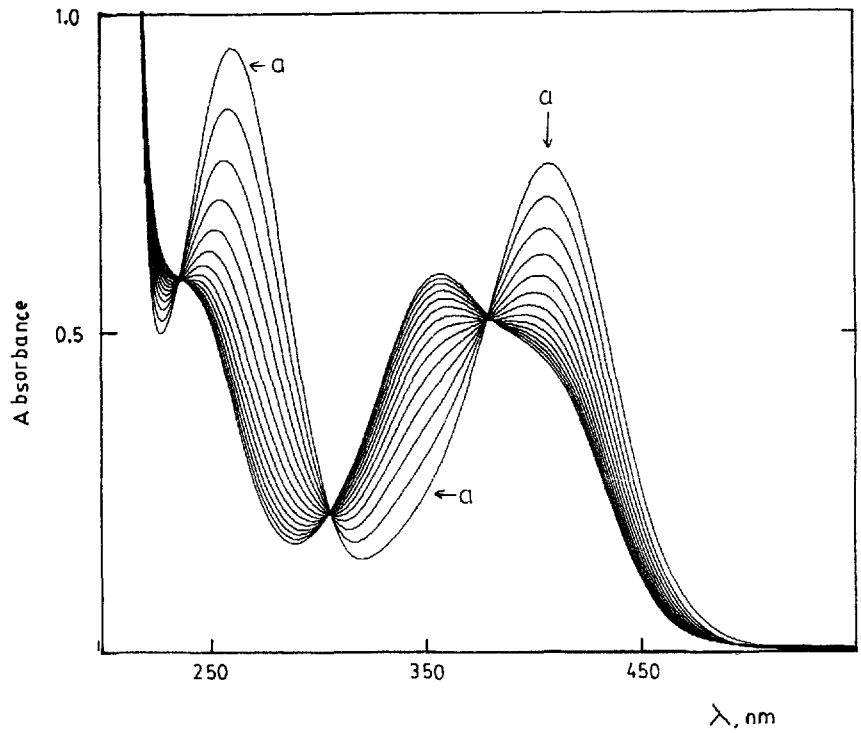


Figure 2. Absorbance of **2** in the presence of 0·2 M NaOH at different reaction times; slow process. $[\mathbf{2}]_0 = 4{\cdot}38 \times 10^{-5}$ M. First cycle (a) 1 min. Intervals between cycles: 13 min

concentration are summarized on Table 1. The plot of k_f vs HO^- concentration (not shown) is non-linear and the whole set of data for each individual substrate can be fitted into an equation of the form

$$k_f = \frac{k_I[HO^-]^2}{1 + k_{II}[HO^-]} + k_{III} \quad (1)$$

Slow process

The observed rate constant for this process, k_s, was determined at different HO^- concentrations by measuring the increase in absorbance at 358 nm for substrates **2** and **3**. These values are summarized in Table 2.

For the reaction of **2** the plot of k_s vs HO^- is linear with slope $(9{\cdot}72 \pm 0{\cdot}4) \times 10^{-4}$ l mol^{-1} s^{-1} and intercept $(3{\cdot}2 \pm 0{\cdot}4) \times 10^{-5}$ s^{-1} ($r = 0{\cdot}997$) (Figure 3, upper line).

In the case of **3**, the plot is also linear at $[HO^-] > 0{\cdot}05$ M but the points at the lower concentration of HO^- deviate slightly from the line (Figure 3, lower line). Neglecting the two values at low concentration (see below), the slope is $(7{\cdot}55 \pm 0{\cdot}2) \times 10^{-3}$ l mol^{-1} s^{-1} and the intercept is $(1 \cdot 1 \pm 0{\cdot}2) \times 10^{-4}$ s^{-1}. It should be noted that these values are almost one order of magnitude higher than the corresponding values for **2**.

Table 1. Observed rate constants for the fast process in the hydrolysis of *N*-(2,4,6-trinitrophenyl)piperidine and *N*-(2,4,6-trinitrophenyl)morpholine in water at 25 °C[a]

Compound	[NaOH] (M)	$10^2 k_f$ (s^{-1})
N-(2,4,6-Trinitrophenyl)piperidine	0·010	0·205 ± 0·005
	0·020	0·487 ± 0·008
	0·030	0·800 ± 0·005
	0·040	1·31 ± 0·005
	0·050	1·81 ± 0·04
	0·075	3·49 ± 0·2
	0·100	4·70 ± 0·3
	0·125	6·43 ± 0·03
	0·150	8·14 ± 0·3
	0·175	10·2 ± 0·6
	0·200	11·2 ± 1·1
N-(2,4,6-Trinitrophenyl)morpholine	0·010	0·302 ± 0·06
	0·020	0·740 ± 0·05
	0·030	1·38 ± 0·03
	0·039	2·06 ± 0·06
	0·051	3·04 ± 0·08
	0·060	4·03 ± 0·1
	0·070	5·24 ± 0·07
	0·075	5·97 ± 0·1
	0·080	5·77 ± 0·05
	0·090	7·15 ± 0·08
	0·101	9·22 ± 0·3

[a] Solvent contains 2% dioxane; ionic strength 1 M (NaCl). $[\text{Substrate}]_0 = (4–5) \times 10^{-5}$ M. Error limits represent the mean deviation of three or four determinations.

Table 2. Observed rate constants for the slow process in the hydrolysis of *N*-(2,4,6-trinitrophenyl)piperidine and *N*-(2,4,6-trinitrophenyl)morpholine)[a]

Compound	[NaOH] (M)	$10^4 k_s$ (s^{-1})
N-(2,4,6-Trinitrophenyl)piperidine[b]	0·020	0·477
	0·030	0·566
	0·040	0·734
	0·050	0·802
	0·075	1·04
	0·100	1·32
	0·125	1·62
	0·175	2·08
	0·200	2·20
	0·200	2·21
N-(2,4,6-Trinitrophenyl)morpholine[c]	0·010	0·437
	0·029	2·66
	0·051	4·93
	0·074	6·73
	0·102	8·67
	0·127	10·6
	0·150	12·9
	0·176	14·3
	0·199	16·0
	0·199	16·2

[a] Solvent contains 2% dioxane ionic strength 1 M (NaCl).
[b] $[\mathbf{2}]_0 = 3·60 \times 10^{-5}$ M.
[c] $[\mathbf{3}]_0 = 4 \times 10^{-5}$ M.

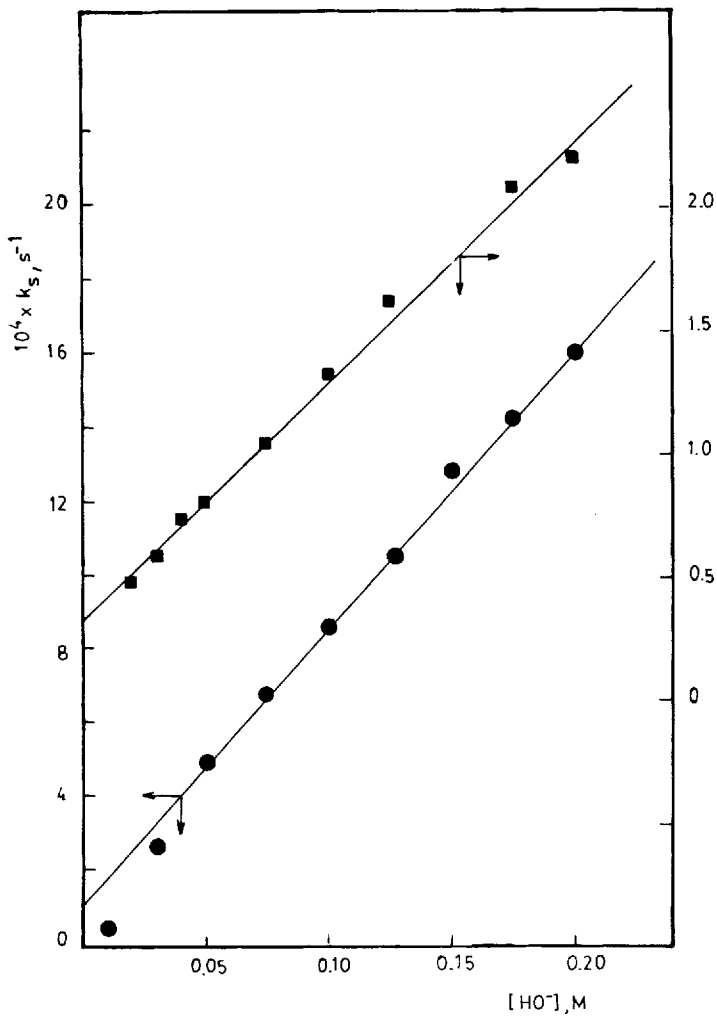


Figure 3. Plot of k_s vs $[HO^-]$ for the formation of picric acid from *N*-(2,4,6-trinitrophenyl)piperidine (■) and *N*-(2,4,6-trinitrophenyl)morpholine (•) in water at 25 °C (data from Table 2)

Equilibrium constant determinations

The reversibility of the fast process was established by taking samples of solutions of **2** in 0·01 M HO^- at 5, 10 and 15 min (where the maximum of the absorbance at 260 nm was reached) and making them acidic. The spectra of the resulting solutions were almost the same as those of **2** under similar conditions. There was only a small difference in absorption at 290 and 350 nm, from which we calculated that less than 10% of picrate ion was formed. Similar results were obtained with **3**.

The absorption of solutions of **2** and **3** at 260 nm was measured as a function of the HO^- concentration at the end of the fast process. From these data the stoichiometry of the interaction between **2** or **3** and HO^- was determined [equation (2)] and also the corresponding equilibrium constants.[3] These values are collected in Table 3.

$$\mathbf{2}(\text{or } \mathbf{3}) + 2HO^- \underset{}{\overset{K_1K_2}{\rightleftharpoons}} \mathbf{2}(\text{or } \mathbf{3})(HO^-)_2 \qquad (2)$$

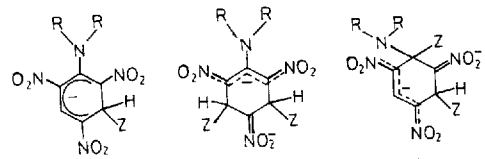
Table 3. Calculated rate and equilibrium constans for the hydrolysis of **2** and **3**

Substrate	K_1 ($l\,mol^{-1}$)	$K_2 \times 10^{-2}$ ($l\,mol^{-1}$)	k_2 ($l\,mol^{-1}\,s^{-1}$)	k_{-2} ($l\,mol^{-1}\,s^{-1}$)	$K_1K_2 \times 10^{-4}$ ($l^{-2}\,mol^{-2}$)	$k_4 \times 10^4$ ($l\,mol^{-2}\,s^{-1}$)	$k_3 \times 10^2$ ($l\,mol^{-1}\,s^{-1}$)
2	19·6[a]	7·5	0·72[b]	10^{-3}[c]	1·47[d](1·24)[e]	9·72[f]	2·3[g]
3	16·7[h]	13·5	1·37[i]	10^{-3}[c]	2·29[d](2·07)[e]	75·5[j]	15·1[k]

[a] Obtained from the ratio of the slope and intercept of Figure 4 (upper line).
[b] Obtained from the intercept of Figure 4 (upper line).
[c] Obtained from intercept of a plot of k_f vs HO^- concentration.
[d] Values from the kinetic data.
[e] Values from spectrophotometric data.
[f] Obtained from the slope of Figure 3 (upper line).
[g] Obtained from the intercept of Figure 3 (upper line) and K_2.
[h] Same as footnote a, but from Figure 4, lower line.
[i] Same as footnote b, but from Figure 4, lower line.
[j] Same as footnote f, but from Figure 3, lower line.
[k] Same as footnote g, but from Figure 3, lower line.

DISCUSSION

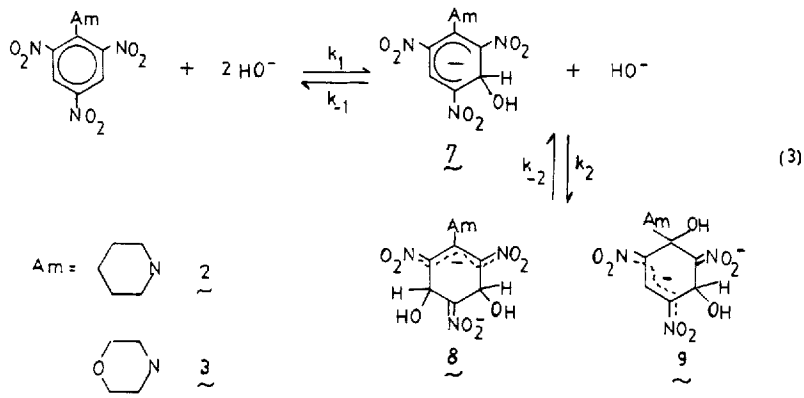
The interaction of picramides with nucleophiles Z ($Z = SO_3^{2-}$,[4-6] HO^-[7,8] or MeO^-[9,10]) in water, dimethylsulfoxide (DMSO)–water or DMSO–MeOH mixtures leads to two types of σ complexes, namely **4** and **5**.



4 **5** **6**

The ratio of the two species formed depends on the solvent and on Z. In protic solvents and particularly in water **5** is favored over **4**.[5,11] In no instance was there evidence for the formation of a 1 : 2 σ complex involving the addition of the nucleophile at both C-1 and C-3 positions so as to yield complex **6**, although kinetic evidence of the substitution of the leaving group (NO_2, MeO and Cl) within 1,3-σ complexes has been reported.[12] We have reported the substitution of piperidine and morpholine within the 1,3-σ complex of *N*-(2,4-dinitrophenyl)piperidine and *N*-(2,4-dinitrophenyl)morpholine with HO^-.[1]

In the reactions of **2** and **3** with HO^-, the change in the spectrum observed during the fast process may be attributed to the formation of the 1 : 2 σ complex **8** and/or **9** through equation (3). The fact that more than 90% of the starting substrate is obtained on acidification of basic solutions of **2** and **3** indicates that less than 10% of **9** is formed, since in acidic solution the amine should leave faster than HO^-, leading to the formation of picric acid.[13] Hence in the discussion that follows we shall consider that only **8** is formed



(3)

Since during the fast process a good isosbestic point is observed, the 1,3-σ complex **7** must be at very low concentration at all times. If we consider **7** as a steady-state intermediate, the observed rate constant k_f is given by equation (4),[14] which is different from the experimentally determined equation, namely equation (1).

$$k_f = \frac{k_1 k_2 [HO^-]^2}{k_{-1} + k_2 [HO^-]} + \frac{k_{-1} k_{-2}}{k_{-1} + k_2 [HO^-]} \tag{4}$$

Another possibility is the fast equilibration of **7** with **2** (or **3**) and rate-limiting formation of

8. In this case the pseudo-first-order rate constant is given by equation (5), which has the same mathematical form as equation (1) with $k_I = K_1 k_2$, $K_{II} = K_1$ and $k_{III} = k_{-2}$.

$$k_f = \frac{K_1 k_2 [HO^-]^2}{1 + K_1 [HO^-]} + k_{-2} \tag{5}$$

Since the equilibrium constant for the process described by equation (3) is high (see $K_1 K_2$ in Table 3), the main contribution to the observed rate constant comes from the forward rate constant, i.e. the first term of the right-hand side of equation (5). Therefore, it can be simplified and rearranged into equation (6).

$$\frac{[HO^-]}{k_f} = \frac{1}{k_2} + \frac{1}{K_1 k_2 [HO^-]} \tag{6}$$

From a plot of the left hand side of equation (6) vs $[HO^-]^{-1}$ (Figure 4) we calculated k_2

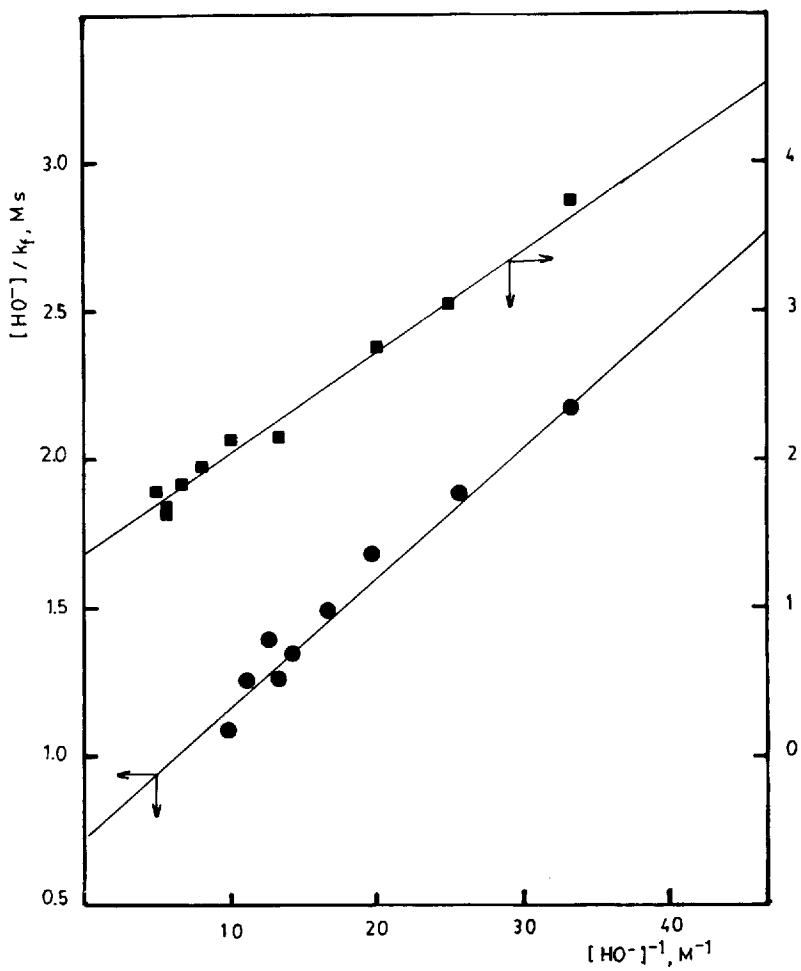
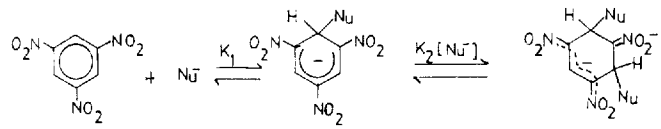


Figure 4. Plot of $[HO^-]/k_f$ vs $[HO^-]$ for the fast process in the hydrolysis of *N*-(2,4,6-trinitrophenyl)piperidine (■) and *N*-(2,4,6-trinitrophenyl)morpholine (•) in water at 25 °C (data from Table 1)

and K_1 for **2** and **3**. We could estimate k_{-2} from the intercept of a plot (not shown) of k_f vs $[HO^-]$. Combining these values we can calculate K_1K_2 which is in good agreement with the value obtained spectrophotometricaly (Table 3). (We also calculated K_1, k_2 and k_{-2} using a non-linear least-squares program for fitting an arbitrary function which was generously provided by Dr Robin A. Cox, University of Toronto, Canada. The calculated rate and equilibrium constants were the same within experimental error.) In addition, the values of K_1K_2 are similar to that reported[7] for the formation of a σ complex of stoichiometry 1 : 2 in the reaction of HO^- with *N*,*N*-dimethylpicramide, i.e. $1{\cdot}88 \times 10^4\ l^{-1}\,mol^{-2}$. Further, from the kinetic data reported in the same paper,[7] we could estimate $K_1 = 15\ l\,mol^{-1}$ and $k_2 = 1{\cdot}2\ s^{-1}$ for the latter compound. The similarity between the values of the equilibrium and rate constants for the three picramides is reasonable since piperidine, morpholine and dimethylamine are all secondary amines and they affect those values through their inductive effect. Comparing the statistically corrected values for the addition of HO^- to 1,3,5-trinitrobenzene [equation (7), $Nu^- = HO^-$] which is $1{\cdot}24\ l\,mol^{-1}$,[15] with $K_1/2$ for the picramides, we see that the amines stabilize the σ complex by a factor of 6–8. The stabilization is stronger for the complex of 1 : 2 stoichiometry.



(7)

The statistically corrected value of K_2 for 1,3,5-trinitrobenzene [equation (7), $Nu^- = HO^-$] is 0·4,[16] which is 750 and 3400 times smaller than the corresponding values for **2** and **3**, respectively. More significant is the increase in the stability of the σ complexes of picramides compared with those of trinitrobenzene when sulphite is the nucleophile. The ratio of K_1 for 2,4,6-dimethylpicramide and 1,3,5-trinitrobenzene is 156, and that of K_2 is 10^4.[6]

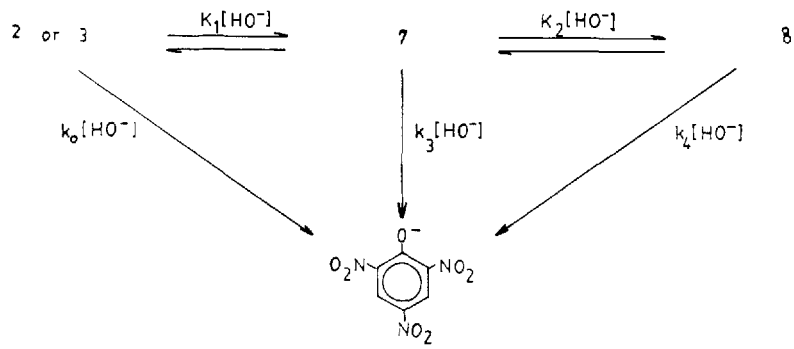
These differences in equilibrium constants when hydrogen and secondary amines are compared as substituents of trinitrobenzene are mainly due to differences in the rates of decomposition of the complexes.[17] This effect is very remarkable for the σ complexes with the highest electron density, namely those formed with sulphite as nucleophile. Part of the observed stabilization may be attributed to the inductive effect of the amino group and to solvation effects. We have previously suggested that in the 1 : 1 and 1 : 2 σ complexes the amine is rotated out of the plane to allow coplanarity of the nitro groups in order to delocalize the negative charge. If this rotation occurs, the electron pair of the nitrogen of the amine does not interact with the ring but with the solvent through hydrogen bonding, thus providing some of the extra stabilization. The importance of water in stabilizing complexes of 1 : 2 stoichiometry is well known.[18] In addition, if the amino group is rotated, it can exert its full inductive effect which is not counterbalanced by the mesomeric effect.

The mechanism of the formation of picrate ion may be described as in Scheme 1. It should be noted that **9** must be an intermediate in the pathway from **7** to picrate ion.

The observed rate constant for Scheme 1, considering that the substrate is in fast equilibrium with **7** and **8**, is given by

$$k_s = \frac{k_o[HO^-] + k_3K_1[HO^-]^2 + k_4K_1K_2[HO^-]^3}{1 + K_1[HO^-] + K_1K_2[HO^-]^2} \tag{8}$$

Since under most of our experimental conditions $K_1K_2[HO^-]^2 > 1 + K_1[HO^-]$, equation (8) simplifies into equation (9). Considering that the first term of the right-hand side of this



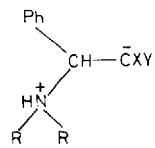
Scheme 1

equation is negligible, it predicts a linear dependence of k_s on the HO^- concentration which is consistent with the experimental results (see Figure 3). The deviation of the points at $HO^- < 0{\cdot}05$ M for the reactions of **3** (see Results) can be attributed to the fact that under these conditions, the requirements for linearization of equation (8) are not fulfilled.

$$k_s = \frac{k_0}{K_1 K_2 [HO^-]} + \frac{k_3}{K_2} + k_4 [HO^-] \tag{9}$$

From the slopes and intercepts of the linear plots for **2** and **3** we can calculate k_4 and k_3. These values are given in Table 3.

The calculated rate constants k_4 and k_3 for **3** are 7·8 and 6·6 times greater than the corresponding values for **2**. This might indicate that in the mechanism of these steps the expulsion of the amine is partially rate determining. These values can be compared with the relative leaving ability of morpholine and piperidine from compounds of the type **10**, which is 14–18.[19-20] We found no evidence of a rate-determining leaving group in the reactions of *N*-(2,4-dinitrophenyl)piperidine and *N*-(2,4-dinitrophenyl)morpholine. Thus, if in the present case the amines were partially rate determining, this would imply that the extra nitro group in the picryl system affects differently the rates of breakdown of the amine and of the HO^-. A knowledge of the rate-determining steps in these reactions awaits further studies.



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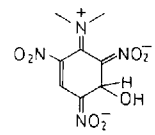
CONCLUSIONS

The hydrolysis of 1-X-2,4,6-trinitrobenzene (X = piperidine or morpholine) involves the formation of σ complexes of 1 : 1 and 1 : 2 stoichiometry (**7** and **8**), where the nucleophile HO^- adds to one and two of the unsubstituted ring positions of the substrate, respectively. Formation of the hydrolysis product, 2,4,6-trinitrophenol, requires the replacement of the amine group by a hydroxide group and this reaction occurs on the two types of σ complexes.

From the kinetic data we can estimate that the rate of the overall reaction of **7** is more than ten times faster than the corresponding rate of the substrate itself. This result confirms previous findings regarding the hydrolysis of 1-X-2,4-dinitrobenzene (X = piperidine and morpholine) where it was also found that the reactivity of HO^- with the 1,3 σ complex is higher than with the substrate. This behavior indicates that the unfavorable electrostatic repulsion of a negative nucleophile approaching a negatively charged substrate is counterbalanced by other favorable factors. We suggest that the increase in the rate of addition of HO^- to the 1,3-σ complex compared with the rate of addition of HO^- to C-1 of the substrate may be due to the fact that in these complexes the nitrogen of the amino group is rotated out of plane to favor the planarity of the nitro groups with the cyclohexadienyl ring.

If this rotation occurs, structures of the type **11** do not contribute to the ground state of the 1,3-σ complex. On the other hand, the contribution of structures such as **12** is significant for the stabilization of the ground state of the substrate, thus decreasing the reactivity of this type of compounds compared with others where this interaction is less important.



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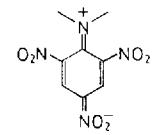

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EXPERIMENTAL

Materials

N-(2,4,6-Trinitrophenyl)piperidine, m.p. 102–103 °C (lit[21] 104–106 °C), and *N*-(2,4,6-trinitrophenyl)morpholine, m.p. 163·5–164·5 °C (lit.[22] 166–166·5 °C) were prepared by the method used for *N*-(2,4,6-trinitrophenyl)imidazole.[2a] Both products were used without further purification. Dioxane was purified as described previously.[2] Doubly glass-distilled water was used throughout. All of the inorganic reagents were of analytical-reagent grade and were used without further purification.

UV spectra were recorded on a Shimadzu UV 260 spectrophotometer and the change in absorbance during a kinetic run was measured with a Beckman 24 spectrophotometer.

Kinetic procedures

Reactions were initiated by adding the substrate dissolved in dioxane to a solution containing all the other constituents. The total dioxane concentration was 2% in all reactions, the temperature was 25 °C and the ionic strength was 1 M. NaCl was used as compensating electrolyte.

The kinetic measurements for the fast process were made by rapidly injecting about 10 μl of the substrate solution in dioxane into the thermostated cell of the spectrophotometer and recording the increase in absorbance at 265 nm. The temperature inside the cell was maintained at 25 ± 0·5 °C.

The rate of the slow process was determined by measuring the appearance of picrate ion at its maximum absorption, 358 nm.

All kinetic runs were carried out under pseudo-first-order conditions with substrate

concentrations about 4×10^{-5} M. In all cases the reactions were followed up to 90% conversion and good pseudo-first-order kinetic plots were obtained.

ACKNOWLEDGEMENT

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