9f (77%), and unchanged starting material **4f** (10%), mp 181 °C (mixture melting point).

Irradiation of 4g. A solution of **4g** (475 mmol) in benzene (175 mL) was irradiated for 12 h and worked up to give 20 mg (6%) of **10**, mp 130 °C (mixture melting point) (elution with a 1:4 mixture of benzene and petroleum ether), 215 mg (46%) of 4,5-dibenzoyl-3-(*p*-(dimethylamino)phenyl)-1-phenylpyrazole (**9g**), mp 156 °C (elution with a 1:4 mixture of benzene and petroleum ether and recrystallization from a 1:1 mixture of benzene and petroleum ether), and 145 mg (31%) of unchanged starting material **4g**, mp 234 °C (mixture melting point) (elution with a 9:1 mixture of benzene and ethyl acetate).

In a repeat run, irradiation of a methanol solution of **4g**, under analogous conditions, gave a mixture of **10** (6%), **9g** (47%), and unchanged starting material **4g** (32%).

Attempted Thermal Transformations of 4a–g in Benzene and Methanol (Blank Runs). Blank runs were carried out by stirring solutions of **4a–g** in benzene and methanol (4 mmol) around 30 °C for 5–15 h. Workup in the usual manner gave back the starting material (**4a–g**), in each case, in nearly quantitative yield.

Attempted Thermal Transformation of 4a in Refluxing Benzene. A solution of **4a** in benzene (430 mg, 1 mmol in 175 mL) was refluxed in the dark for 5 h. Workup of the mixture of the usual manner resulted in the recovery of 410 mg (95%) of the unchanged starting material **4a**, mp 206–207 °C (mixture melting point).

Thermal Transformation of 4a (Neat Heating at 215 °C). A sample of **4a** (860 mg, 2 mmol) was heated around 215 °C in a sealed tube for 1 h. The reaction mixture, on cooling, was chromatographed over silica gel. Elution with a mixture (1:4) of benzene and petroleum ether gave 35 mg (5%) of **10**, mp 130 °C (mixture melting point). Further elution and petroleum ether gave 695 mg (82%) of **9a**, mp 136 °C (mixture melting point).

Thermal Transformation of 4c (Neat Heating at 215 °C). A sample of **4c** (460 mg, 1 mmol) was heated around 215 °C in a sealed tube for 1 h. The reaction mixture was chromatographed on silica gel, and elution with a mixture (1:4) of benzene and petroleum ether gave 15 mg (5%) of **10**, mp 130 °C (mixture melting point). Further elution with a mixture (3:2) of benzene and petroleum ether yielded 382 mg (83%) of **9c**, mp 133 °C (mixture melting point).

Laser Flash Photolysis. The laser flash photolysis experiments were carried out in a computer-controlled setup by using pulse excitation at 337.1 nm (Molectron UV-400 nitrogen, 2–3 mJ, ~8 ns) or 355 nm (Quanta-Ray DCR-1 Nd-YAG, ≤ 10 mJ, ~6 ns). Details of the apparatus and procedures are described elsewhere.[28-30]

Acknowledgment. We thank the Department of Science and Technology, Government of India, Indian Institute of Technology, Kanpur, and the Office of Basic Energy Sciences of U.S. Department for financial support of this work.

Registry No. **1a**, 588-64-7; **1b**, 2829-25-6; **1c**, 622-73-1; **1d**, 100726-23-6; **1e**, 101773-48-2; **1f**, 87829-01-4; **1g**, 2829-28-9; **2**, 1087-09-8; **4a**, 101773-49-3; **4b**, 101773-50-6; **4c**, 101773-51-7; **4d**, 101773-52-8; **4e**, 101773-53-9; **4f**, 101773-54-0; **4g**, 101773-55-1; **9a**, 78830-57-6; **9b**, 101773-56-2; **9c**, 101773-57-3; **9d**, 101773-58-4; **9e**, 101773-59-5; **9f**, 101773-60-8; **9g**, 101773-61-9; **10**, 29954-08-3.

(28) Small, R. D., Jr. Scaiano, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 6965–6970, and references cited therein.
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(30) Nagarajan, V.; Fessenden, R. W. *J. Phys. Chem.* **1985**, *89*, 2330–2335.

Amines as Leaving Groups in Nucleophilic Aromatic Substitution Reactions

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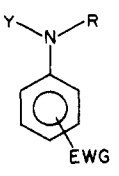
Received September 19, 1985

The hydrolysis reactions of *N*-(2,4-dinitrophenyl)piperidine (**7**) and *N*-(2,4-dinitrophenyl)morpholine (**8**) were studied. Both reactions lead quantitatively to the formation of 2,4-dinitrophenol. They are second order toward the HO^- concentration and are strongly catalyzed by the amine leaving group. The catalysis is interpreted in terms of the formation of 1,3-σ complexes with the amine or the HO^-, which then react with another hydroxide ion to give the final product. The reactivity of the 1,3-σ complexes toward HO^- is higher than that of the substrates themselves.

Aromatic amines with general structure **1** are quite resistant to elimination of the amino group.



1

In the presence of bases, compounds of type **1** can react in several forms.[1,2] In Scheme I they are summarized for the case of a trinitro substituted compound, reacting with a base Z^-.

The formation of intermediate **3** eventually leads to the replacement of the amino group,[3] but this reaction has only been studied in a few instances as a primary reaction. Most rate data regarding reactions where an amino group in an aromatic ring is displaced by a nucleophile were obtained as secondary reactions in other studies.[4]

The low reactivity of compounds of the type **2** toward attack at carbon 1 is considered to be a consequence of the interaction of the lone pair of electrons on the nitrogen

(1) Boulton, J. J. K.; McFarlane, N. R. *J. Chem. Soc. B* **1971**, 925, 928. Grudtsyn, J. D.; Gitis, S. S. *J. Org. Chem. USSR (Engl. Transl.)* **1975**, *11*, 2616.
(2) Buncel, E.; Norris, A. R.; Russell, K. E.; Sheridan, P. J. *Can. J. Chem.* **1974**, *52*, 25. Buncel, E.; Hamaguchi, M.; Norris, A. R. *Can. J. Chem.* **1980**, *58*, 1615.
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(4) (a) Bernasconi, C. F.; Schmid, P. *J. Am. Chem. Soc.* **1967**, *32*, 2953. (b) Bunnett, J. F.; Garst, R. H. *J. Org. Chem.* **1968**, *33*, 2320.

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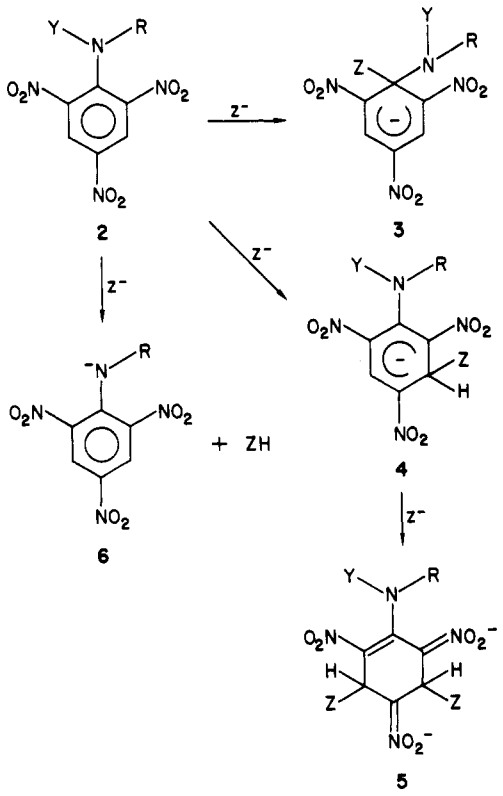
Scheme I

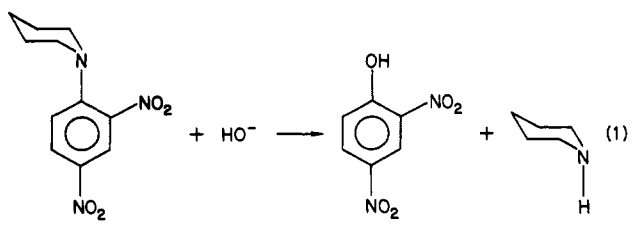


with the π system. When this interaction is decreased for some reason, carbon 1 is attacked as readily as when substituted by other groups, and the amine is displaced; this is, for instance, the case with *N*-(2,4,6-trinitrophenyl)imidazole, which hydrolyzes at a rate 20 times as high as that of 2,4,6-trinitrochlorobenzene.[5]

In the course of our studies of the aminolysis of *N*-(2,4-dinitrophenyl)imidazole,[6] we found that the product *N*-(2,4-dinitrophenyl)piperidine was hydrolyzed at a rate which was dependent on the piperidine concentration. Thus, it was of interest to conduct a comprehensive study of the hydrolysis of compounds with amines as leaving group. We report here our results on the hydrolysis of *N*-(2,4-dinitrophenyl)piperidine and *N*-(2,4-dinitrophenyl)morpholine which are catalyzed by hydroxide ions and the respective amine.

Results

***N*-(2,4-Dinitrophenyl)piperidine (7).** The reaction of **7** in water at various HO^- concentrations in the presence or absence of piperidine leads quantitatively to the formation of 2,4-dinitrophenol as evidenced by comparison of the product with a mock solution of 2,4-dinitrophenol (eq 1). A good isosbestic point is obtained when the spectra of the solution is taken at different reaction times (Figure 1).



(1)

(5) de Rossi, R. H.; de Vargas, E. B. *J. Org. Chem.* **1979**, *44*, 4100. de Rossi, R. H.; de Vargas, E. B. *J. Am. Chem. Soc.* **1981**, *103*, 1533.
(6) de Vargas, E. B.; de Rossi, R. H. *J. Org. Chem.* **1984**, *49*, 3978.

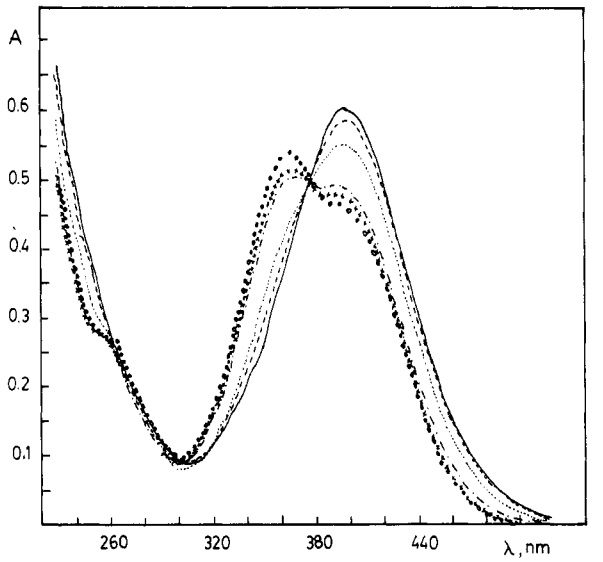


Figure 1. Absorbance of **7** in the presence of 0.4 M NaOH at different reaction times: $[7]_0 = 4.02 \times 10^{-5}$ M; (—) 1 min; (- - -) 156 min; (···) 312 min; (-·-·-) 426 min; (+++) 1398 min; (∞) 1686 min.

Table I. Observed Rate Constants for the Hydrolysis of *N*-(2,4-Dinitrophenyl)piperidine and *N*-(2,4-Dinitrophenyl)morpholine in Water at 25 °C: Dependence on Hydroxide Ion Concentration[a]

$[N_2OH]$, M	$10^6 k_{obsd}$, s^{-1}
N-(2,4-Dinitrophenyl)piperidine[b]	
0.049	0.447
0.151	2.28
0.198	3.92
0.250	5.42
0.330	9.39
0.440	13.3
N-(2,4-Dinitrophenyl)morpholine[c]	
0.050	0.790
0.100	1.81
0.150	3.14
0.200	4.86
0.250	6.68
0.301	9.73
0.350	12.4
0.401	16.1

[a] Solvent contains 2% dioxane; ionic strength 1 M (NaCl). [b] $[7]_0 = 4.02 \times 10^{-5}$ M. [c] $[8]_0 = 4.74 \times 10^{-5}$ M.

The observed rate constant depends on the HO^- concentration in a nonlinear fashion (Table I). When the observed rate constant is divided by the HO^- concentration and plotted vs. the HO^- concentration (Figure 2) a good linear plot is obtained ($r = 0.997$).

At constant HO^- concentrations the reaction is linearly dependent on the piperidine concentration (Table II). Besides, at constant piperidine concentration and variable HO^- concentration a linear plot (not shown) is obtained when k_{obsd}/HO^- is plotted vs. HO^- concentration.

In order to determine whether there were radicals or radical anions involved as intermediates, the reactions were carried out under N_2 and, in other experiments, in the presence of *m*-dinitrobenzene. Neither O_2 nor dinitrobenzene affect the observed rate or the product formed. On the other hand, there is no catalysis by diazabicyclo-[2.2.2]octane (Dabco).

The observed rate constant may be represented by eq 2.

$$k_{obsd} = k_1[HO^-] + k_2[HO^-]^2 + k_3[Pip][HO^-]^2 \quad (2)$$

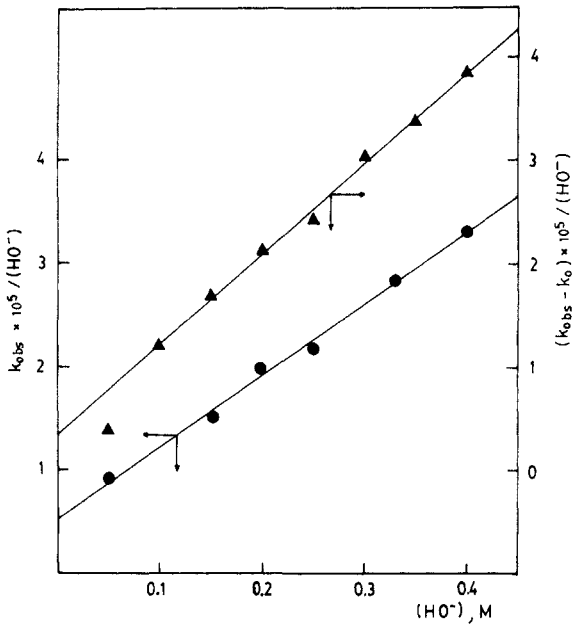


Figure 2. Plot of $k_{obsd}/[HO^-]$ vs. $[HO^-]$ for the reaction of *N*-(2,4-dinitrophenyl)piperidine with NaOH in water at 25 °C [data from Table I (●)] and of $(k_{obsd} - k_o)/[HO^-]$ vs. $[HO^-]$ for the reaction of *N*-(2,4-dinitrophenyl)morpholine with NaOH in water at 25 °C [data from Table I (▲)].

Then, from the slope and intercept of Figure 2, $k_1 = (5.3 \pm 0.8) \times 10^{-6}$ M^{-1} s^{-1} and $k_2 = 6.92 \times 10^{-5}$ M^{-2} s^{-1} are calculated.

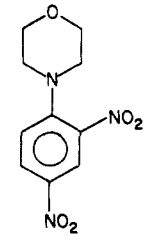
Equation 2 can be rearranged to eq 3; then from the slope of a plot according to eq 3, $(k_2 + k_3[Pip]) = 1.84 \times 10^{-3}$ M^{-2} s^{-1} is obtained.

$$k_{obsd}/[HO^-] = k_1 + (k_2 + k_3[Pip])[HO^-] \quad (3)$$

The value of k_1 could, in principle, be calculated from the intercept of this plot, but it has a large error because it is very small compared with the slope. Combining the value of the slope with k_2 calculated above, $k_3 = 9.13 \times 10^{-3}$ M^{-3} s^{-1} is obtained.

From the slope of a plot of k_{obsd} vs. piperidine concentration drawn with the data at constant HO^- concentrations, $k_3 = 8.8 \times 10^{-3}$ M^{-3} s^{-1} is obtained, which is in good agreement with the value obtained above.

***N*-(2,4-Dinitrophenyl)morpholine (8).** The hydrolysis of this compound leads quantitatively to the formation of 2,4-dinitrophenol. Similarly as in the reaction of 7, the observed rate constant depends on the second-order concentration of HO^- and on the first-order concentration of morpholine (Tables I and II).



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From the dependence of the observed pseudo-first-order rate constant with the HO^- and morpholine concentration, the value of k_{obsd} can be represented as in eq 4. Equation

$$k_{obsd} = k_o + k_1[HO^-] + k_2[HO^-]^2 + k_3[Mor][HO^-]^2 \quad (4)$$

4 is similar to eq 2 but has an additional term, k_o, whose mechanistic significance is not clear to us; thus we will not discuss it further.

The value of k_o was obtained from the intercept of a plot of k_{obsd} vs. $[HO^-]$ (not shown) and is equal to 6×10^{-7} s^{-1}. Equation 4 can be arranged to eq 5.

$$\frac{k_{obsd} - k_o}{[HO^-]} = k_1 + (k_2 + k_3[Mor])[HO^-] \quad (5)$$

Then, plotting the data obtained in the absence of morpholine according to eq 5 we obtained $k_1 = 3.6 \pm 0.6 \times 10^{-6}$ M^{-1} s^{-1} and $k_2 = 8.68 \times 10^{-5}$ M^{-2} s^{-1} (Figure 2).

From the reactions carried out in the presence of constant morpholine concentration we obtained $(k_2 + k_3[Mor]) = 2.18 \times 10^{-3}$ M^{-2} s^{-1}, which combined with the value of k_2 yields $k_3 = 1.07 \times 10^{-2}$ M^{-3} s^{-1}.

The value of k_3 can also be obtained from the slope of the plot of k_{obsd} vs. morpholine concentration at constant HO^- concentration. This value is 8.32×10^{-3} M^{-3} s^{-1} and agrees very well with the one obtained using the other set of data.

In Table III the values of k_o, k_1, k_2, and k_3 calculated for compounds 7 and 8 are collected.

Table II. Observed Rate Constants for the Hydrolysis of *N*-(2,4-Dinitrophenyl)piperidine and *N*-(2,4-Dinitrophenyl)morpholine in Water at 25 °C: Dependence on Hydroxide Ion Concentration and on Amine Concentration[a]

$[N_2OH]$, M	[amine], M	$10^5 k_{obsd}$, s^{-1}
N-(2,4-Dinitrophenyl)piperidine[b]		
0.010	0.196	0.206
0.050	0.196	0.675
0.069	0.193	1.03
0.100	0.193	2.32
0.140	0.193	3.98
0.149	0.193	4.25
0.199	0.193	8.16
0.298	0.196	16.4
0.300	0.193	18.5
0.397	0.196	31.4
0.400	0.193	33.4
0.199	0.097	4.27
0.199	0.146	6.43
0.199	0.195	7.65
0.200[c]	0.050	4.12
0.200[c]	0.100	4.36
0.200[c]	0.150	4.04
0.200[c]	0.200	5.04
N-(2,4-Dinitrophenyl)morpholine[d]		
0.020	0.196	0.090
0.039	0.196	0.310
0.059	0.196	0.631
0.079	0.196	1.12
0.100	0.195	1.71
0.200	0.195	7.87
0.299	0.195	17.9
0.400	0.195	34.4
0.394[e]	0.196	32.9
0.394[f]	0.196	31.1
0.197	0.050	2.15
0.197	0.100	4.16
0.197	0.150	5.81
0.197	0.200	6.99

[a] Solvents contains 2% dioxane; ionic strength 1 M (NaCl). [b] Amine is piperidine unless otherwise stated. $[7]_0 = (4\text{–}4.5) \times 10^{-5}$ M. [c] Amine = Dabco. [d] Amine = morpholine. $[8]_0 = (4\text{–}4.6) \times 10^{-5}$ M unless otherwise stated. [e] $[8]_0 = 6.06 \times 10^{-5}$ M. [f] $[8]_0 = 2.42 \times 10^{-5}$ M.

Discussion

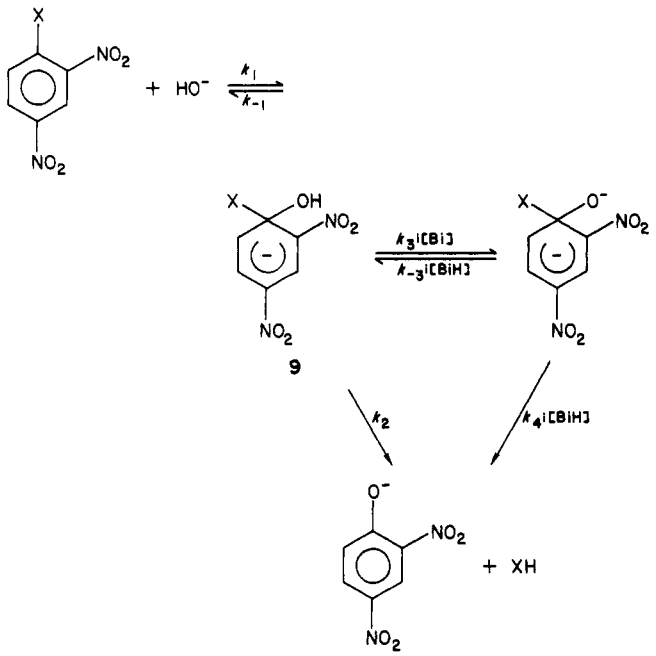
The mechanism of hydrolysis of aromatic substrates in

Table III. Calculated Rate Constants for the Hydrolysis of *N*-(2,4-Dinitrophenyl)piperidine and *N*-(2,4-Dinitrophenyl)morpholine

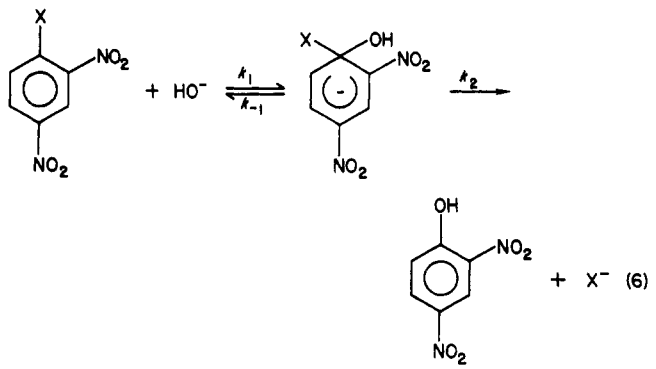
substrate	10^7k_0, s^{-1}	10^6k_1, M^{-1} s^{-1}	10^5k_2, M^{-2} s^{-1}	10^3k_3, M^{-3} s^{-1}
7		5.3[a]	6.92[a]	9.13[b]
8	6[c]	3.6[d]	8.68[d]	10.7[e]

[a] Obtained from the intercept and slope of Figure 2 lower line (data from Table I). [b] Obtained from the slope of a plot according to eq 3 (see text) (data from Table II). [c] Obtained from the intercept of a plot of k_{obsd} vs. [HO^-] in the absence of amine (data from Table I). [d] Obtained from the intercept and slope of Figure 2 upper line (data from Table I). [e] Obtained from the slope of a plot according to eq 5 (see text) (data from Table II).

Scheme II



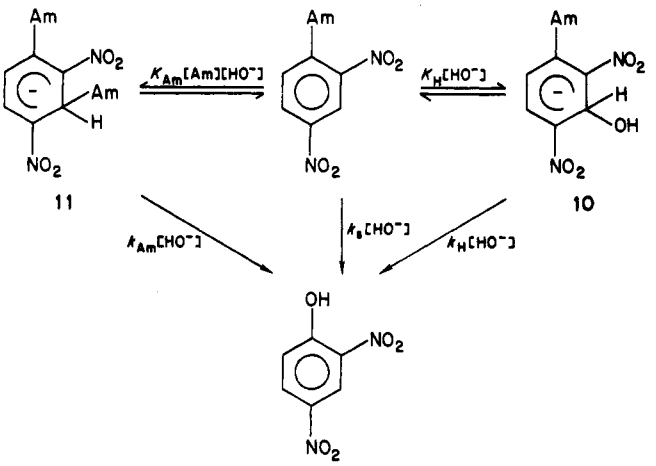
basic solutions can be described in general terms as in eq 6.



The hydroxide ion is a very poor leaving group;[7] thus for leaving groups such as alkoxide, phenoxide, or halogen anions $k_2 \gg k_{-1}$ and the addition of the nucleophile to the aromatic ring is the rate-determining step. In the reactions reported here the leaving group is an amine anion, which is highly basic; thus it is likely that the second step, namely, leaving group expulsion, is rate determining. Then, eq 6 can be written as in Scheme II where proton transfers are indicated and might be partially rate determining, which accounts for the catalysis observed by HO^- and the amines.

(7) Bernasconi, C. F. *J. Am. Chem. Soc.* **1970**, *92*, 4682.

Scheme III



The mechanism described in Scheme II is analogous to that of aromatic nucleophilic substitution by amines.[8] When the k_4^i step is rate determining and general acid catalyzed ($k_4^i \ll k_{-3}^i$), the observed rate constant is given by eq 7.[9]

$$k_{obsd} = \frac{k_1[OH][\sum k_4^i K_3^i[Bi] + k_2]}{k_{-1} + k_2 + \sum k_4^i K_3^i[Bi]} \quad (7)$$

For the particular case where Bi is HO^- and amine (Am) and k_{-1} predominates in the denominator, eq 7 can be simplified to eq 8. This equation predicts that a plot of k_{obsd} =

$$k_1[OH^-]\left(\frac{k_2}{k_{-1}} + \frac{k_4^{OH}}{k_{-1}}K_3^{OH}[HO^-] + \frac{k_4^{Am}}{k_{-1}}K_3^{Am}[Am]\right) \quad (8)$$

k_{obsd}/HO^- vs. HO^- should have the same slope whether or not amine is present, and thus it is not in agreement with our experimental results. This mechanism cannot be kinetically distinguished from that where the rate of proton transfer from the anionic intermediate **9** to the base (k_3^i) is rate determining. Besides, this mechanism predicts that there should be general base catalysis, and thus the reaction of *N*-(2,4-dinitrophenyl)piperidine should be catalyzed by Dabco as well as by piperidine, since Dabco has been shown to act as catalyst in other nucleophilic aromatic substitution reactions where there is general base catalysis.

We suggest that the mechanism of the hydrolysis of the (2,4-dinitrophenyl)amines studied here, **7** and **8**, can be represented as in Scheme III.

This mechanism takes account of the possibility of substitution of the amine (Am) within the 3-hydroxy σ complex **10** and the 3-amine σ complex **11**.[11] Kinetic evidence of the substitution of the leaving group (NO_2, MeO, and Cl) within 1,3-σ complexes was previously reported.[12]

The observed rate constant for Scheme III is given by eq 9.[13]

(8) Bernasconi, C. F. *MTP Int. Rev. Sci.: Org. Chem., Ser. One*, **1973**, *3*, 33.

(9) Equation 7 is equivalent to eq 11 in ref 10. K_3^i is the ratio of the acid dissociation constants of the anionic intermediate **9** and the general acid BiH.

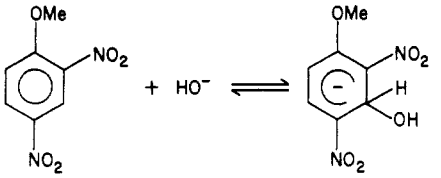
(10) Bernasconi, C. F.; de Rossi, R. H.; Schmid, P. *J. Am. Chem. Soc.* **1977**, *99*, 4090.

(11) The addition of the nucleophile, amine or hydroxyde ion, may occur at the 3 or 5 position of 1-X-2,4-dinitrophenyl ring, but the overall kinetic behavior of the system is the same if either one or both of the σ complexes are formed.

(12) Gibson, B.; Crampton, M. R. *J. Chem. Soc., Perkin Trans. 2*, **1979**, 648.

$$k_{obsd} = \frac{k_s[HO^-] + k_H K_H (HO^-)^2 + k_{Am} K_{Am} [HO^-]^2 [Am]}{1 + K_H[HO^-] + K_{Am}[HO^-][Am]} \quad (9)$$

The equilibrium constant for addition to the position 3 of 2,4-dinitroanisole has been measured in 60% Me_2SO/H_2O, and it is 1.3×10^{-3} M^{-1} (eq 10).[14]



(10)

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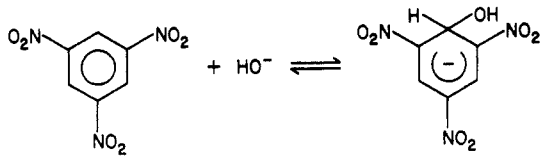
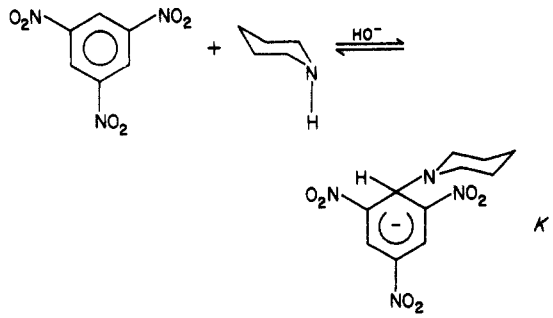
To estimate the effect of the change of a methoxy group by an amine on the equilibrium constant for eq 10 we compared the ratio of the equilibrium constant for the addition of a nucleophile to C3 of 2,4,6-trinitroanisole and *N,N*-dimethyl-2,4,6-trinitroaniline, i.e., 2.1×10^2.[15] Thus the expected value of K_H should be in the order of 0.3 M^{-1}. On the other hand, from the ratio of the equilibrium constant for reactions 11[16] and 12,[17] we can estimate the value of K_{Am} as ~45 M^{-2}. Since the highest value of [Am]



(11)



(12)

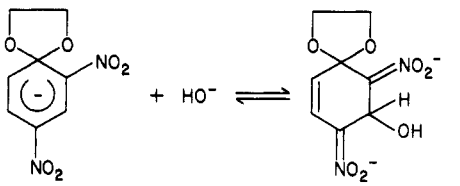
was 0.2 M and that of [HO^-] was 0.4 M, we see that the situation $K_H[HO^-] + K_{Am}[HO^-][Am] < 1$ applies under all our reaction conditions; thus eq 9 can be simplified to eq 13, which has the same form of the experimentally determined observed rate constant with $k_s = k_1$, $k_H K_H = k_2$,

$$k_{obsd} = k_s[HO^-] + k_H K_H [HO^-]^2 + k_{Am} K_{Am} [HO^-]^2 [Am] \quad (13)$$

and $k_{Am}K_{Am} = k_3$. Since $k_2/k_1 = 13$ and 24 for piperidine and morpholine, respectively, and the estimated value of K_H is 0.3 M^{-1}, this means that the reactivity of the 1,3-σ complex toward HO^- is about 40 times higher than the reactivity of the substrate itself.

On the other hand, the ratio k_3/k_1 is 2.8×10^3 and 3×10^3 for piperidine and morpholine, respectively. These values divided by K_{Am} estimated above give 62 and 67 for k_{Am}/k_s for piperidine and morpholine, respectively. The fact that the calculated ratios k_H/k_s and k_{Am}/k_s are almost the same indicates that the activation of the position 1 due to the formation of 1,3-σ complex is almost independent of the nucleophile bonded to carbon 3. We cannot say from our data whether k_s, k_H, and k_{Am} represent the rate of addition of HO^- to the substrate and complexes **10** and **11**, respectively, or whether the leaving group expulsion is rate determining in these steps, but the fact that the values of k_1, k_2, and k_3 for both substrates (Table III) are so similar may indicate that the former situation holds.

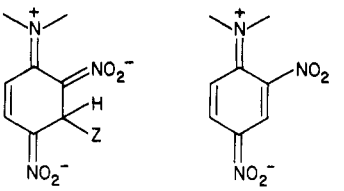
The increase in reactivity of complexes **10** and **11** compared with the unsubstituted substrate appears unexpected. However, we found that the addition of HO^- to the spirocyclic Meisenheimer complex **13** (eq 14) to form the dianionic Meisenheimer complex **14** is 0.5 M^{-1} s^{-1} in water,[18] whereas in 60% Me_2SO/H_2O the rate of formation of **12** is 1.3×10^{-2} M^{-1} s^{-1}.[14]



(14)

13 14

We suggest that the increase in rate of addition of HO^- to the 1,3-σ complex as compared with the rate of addition of HO^- to carbon 1 of the substrate may be due to the fact that in 1,3-σ complexes like **10** or **11** the nitrogen of the amino group is rotated out of plane to favor the planarity of two nitro groups with the cyclohexadienyl ring. If this rotation occurs, structures of the type **15** do not contribute



15 16

to the ground state of the 1,3-σ complex. On the other hand, the contribution of structures of type **16** is significant for the stabilization of the ground state of the substrate, thus decreasing very much the reactivity of this type of compounds compared with others where this interaction is less important.

Experimental Section

Materials. *N*-(2,4-Dinitrophenyl)piperidine, mp 92–93 °C (lit.[19] mp 92–93 °C) was prepared and purified by standard methods. *N*-(2,4-Dinitrophenyl)morpholine was prepared by the same method used for *N*-(2,4-dinitrophenyl)imidazole.[6] The product, mp 117–118 °C (lit.[4a] mp 118 °C) was used without further purification. 2,4-Dinitrophenol was purified by sublimation, mp 111.5–113 °C (lit.[20] mp 118 °C). Dioxane was purified as described previously.[5]

Piperidine was refluxed 12 h over Na and distilled. Morpholine was purified by the method described by Perrin.[21] Twice distilled water in a glass apparatus was used throughout.

All of the inorganic reagents were of reagent grade and were used without further purification.

UV spectra were recorded on a Beckman 24 spectrophotometer and the change in optical density during a kinetic run was measured on the same instrument.

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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 observed rate constants, k_{obsd}, were determined by following the disappearance of the substrate at 25 °C and ionic strength 1 M. All kinetic runs were carried out under pseudo-first-order conditions with substrate concentrations of 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.

Aliquots of the reaction mixture were taken at a number of times and made acidic with 3.7 M H_2SO_4 in 50% ethanol–water. The concentration of substrate was then determined by reading the absorbance at the wavelength maximum of the particular substrate, namely, 400 nm for *N*-(2,4-dinitrophenyl)piperidine and 378 nm for *N*-(2,4-dinitrophenyl)morpholine.

The pseudo-first-order coefficient for the disappearance of the substrate, k_{obsd}, was determined from the slope of the plot of ln A_t vs. time.

Acknowledgment. INFIQC is jointly sponsored by the Consejo Nacional de Investigaciones Científicas y Técnicas and the Universidad Nacional de Córdoba. A.V.V. is a grateful recipient of a fellowship from the Consejo Nacional de Investigaciones Científicas y Técnicas. Research support in part by the Consejo Provincial of Investigaciones Científicas y Tecnológicas of Córdoba.

Registry No. 7, 839-93-0; 8, 39242-76-7.

Kinetics and Mechanism of the Addition of Sulfite to *p*-Benzoquinone

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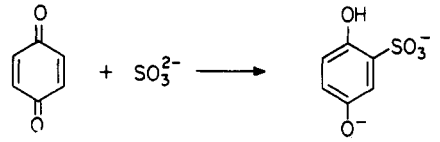
Received July 19, 1985

The 1,4-addition of sulfite to *p*-benzoquinone (BZQ) forming hydroquinone monosulfonate (HQMS) occurs rapidly in neutral solution. From pH 4.5 to 8.0 HQMS is the sole product, and the reaction kinetics are cleanly first order in the quinone. The rapid reversible formation of intermediate carbonyl bisulfite adducts, which precedes irreversible sulfite attack, leads to a complex kinetic dependence on total sulfite concentration and pH (Scheme I and eq 3). The rate constant for the reaction of sulfite with free benzoquinone to form HQMS is 7.7×10^4 M^{-1} s^{-1} (T = 25 °C, μ = 0.1). The carbonyl bisulfite adduct is also attacked by sulfite to form HQMS with a rate constant of 1.7×10^4 M^{-1} s^{-1} (T = 25 °C, μ = 0.1).

The irreversible 1,4-addition of sulfite to *p*-benzoquinone (eq 1) has long been a reaction of practical importance in photographic science.[1] During photographic processing



(1)

with hydroquinone developers, sulfite scavenges *p*-benzoquinone, which is the oxidation product of development. By preventing accumulation of the quinone at the silver halide development site, this scavenging reaction maintains the driving force for the reduction of silver halide by hydroquinone. Also, sulfite eliminates the undesired color associated with alkaline solutions of *p*-benzoquinone.

A number of fundamental studies have characterized the reactions of sulfite with various quinones.[2-12] In neutral solution carbonyl bisulfite adducts can form rapidly and reversibly, and their formation may precede other irreversible reactions such as displacement of labile substituents[5,11] or reductive 1,4-addition.[4,11,12] In acidic solution quinones react with sulfite in a simple redox reaction to yield hydroquinone and sulfate.[4,11] According to Arai, the nature of the reaction of quinones with sulfite depends strongly upon pH and upon the relative half-cell potentials of the sulfite/sulfate (E_S) couple and the hydroquinone/quinone couple (E_Q).[11] Thus, for large values of $E_Q - E_S$, simple redox reactions are dominant, whereas for smaller values 1,4-addition becomes more prominent. When $E_Q - E_S$ is negative, the reactions are likely to be limited to reversible carbonyl addition.

Of particular relevance to the reaction of sulfite with *p*-benzoquinone are papers by LuValle[4] and Arai,[11] which examined how the reaction products differ at various pHs. Below pH 4, a mixture of hydroquinone and hydroquinone monosulfonate is formed, reflecting competition between redox and reductive 1,4-addition. Between pH 4 and 8, reductive 1,4-addition completely dominates, and the yield of hydroquinone monosulfonate is virtually quantitative.[4,11] At pH >8, the yield of hydroquinone monosulfonate decreases with increasing pH, and hydroquinone disulfonate and unidentified products are formed.[4]

Although several of the papers cited above deal with rates of 1,4-addition of sulfite to quinones, there have been

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