monitoring the photoracemization of (*S*)-(+)-MDB as a function of conversion. The small experimental value of $P_r \approx 0.04$ means that only about 4% of initially formed triplet RPs which go on to products eventually recombine by any mechanism to reform starting ketone. In order to estimate the contribution of geminate pairs and free pairs to P_r, the photolysis of (*S*)-(+)-MDB in benzene was carried out in the presence of radical scavengers. Photoracemization of the starting ketone is completely suppressed even at a modest concentration of dodecanethiol. This result shows that even the small observed value of $P_r \approx 0.04$, obtained under the absence of scavengers, corresponds to the recombination of RP which have undergone extensive diffusive walks, i.e., have become random radicals. We thus conclude that triplet geminate recombination is negligable in nonviscous homogeneous solution.

In support of this conclusion, the ^{1}H CIDNP of the starting ketone and other products of the triplet benzoyl/*sec*-phenethyl RP observed under photolysis of MDB in benzene is completely suppressed by the addition of modest concentrations of dodecanethiol. This means that all the nuclear spin selective recombination of the radicals is taking place after diffusive walks by FRP and that there is no geminate cage recombination of triplet GRP.

In contrast to the difficulty in distinguishing between the various stages of combination reactions in solution, such experimental discrimination has recently been reported for the restricted reaction space of a zeolite[34] and a micelle.[35]

Acknowledgment. The authors thank Prof. F. D. Lewis for stimulating discussions and advice. The authors at Columbia thank the AFOSR, NSF, and DOE for their generous support of this research.

Registry No. (*S*)-(+)-MDB, 951-85-9; TEMPO, 2564-83-2; $CH_3(CH_2)_{11}SH$, 112-55-0; PhCHO, 100-52-7; PhCH=CH$_2$, 100-42-5.

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Kinetics and Mechanism of the Aminolysis of 4-Nitrophenyl Dithioacetate

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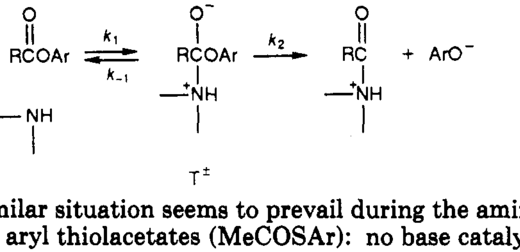
The reaction of the title substrate with a series of secondary alicylic amines has been the subject of a kinetic study in aqueous solution, 25 °C, ionic strength 0.2 M (KCl). With the amine in excess, pseudo-first-order rate constants (k_{obsd}) are observed. The order in amine varies from 1 to 2 depending on the basicity of the amine and the reaction conditions. A reaction scheme is deduced on the basis of the existence of zwitterionic ($T^\pm$) and anionic (T^-) tetrahedral intermediates. Proton transfer from $T^\pm$ to an amine or base (to yield T^-) seems to compete with 4-nitrothiophenoxide (NPS$^-$) expulsion from $T^\pm$. The pK_a of $T^\pm$ and all the rate microconstants of the scheme are estimated. The rates of expulsion of NPS$^-$ and amine from $T^\pm$ are smaller than those from analogous $T^\pm$ formed in the aminolyses of *O*-ethyl *S*-(4-nitrophenyl) dithiocarbonate and 4-nitrophenyl thiolacetate. It is claimed that substitution of Me by RO (R = alkyl) or S$^-$ by O$^-$ in $T^\pm$ destablizes this intermediate.

Introduction

The mechanism of the aminolysis of reactive oxyesters is well established.[1] In the reactions of secondary and primary amines with substrates with good leaving groups the rate of expulsion of the nucleofuge (k_2 of eq 1) from the zwitterionic tetrahedral intermediate ($T^\pm$) found in most of these reactions is fast, precluding therefore the occurrence of acid-base catalysis involving $T^\pm$.[1,2]



$$\mathrm{RCOAr}\ (\mathrm{C{=}O}) + \mathrm{{-}NH} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{RC(O^-)(OAr)(\overset{+}{N}H{-})}\ (T^\pm) \xrightarrow{k_2} \mathrm{RC({=}O)(\overset{+}{N}H{-})} + \mathrm{ArO^-} \qquad (1)$$

A similar situation seems to prevail during the aminolysis of aryl thiolacetates (MeCOSAr): no base catalysis was found in the reactions of secondary alicyclic amines with phenyl,[3] 4-nitrophenyl,[3] 2,4-dinitrophenyl,[4] and 2,4,6-trinitrophenyl thiolacetates.[4] This was attributed to instability of $T^\pm$ due to the fast nucleofugality rate from this intermediate of the arenethiolate anion which prevents deprotonation of $T^\pm$ by a base to give an anionic intermediate.[3,4]

In contrast to the above findings, base catalysis by amine was observed in the reactions of secondary alicyclic amines with phenyl dithioacetate (eq 2).[5] This was explained by the relatively slow leaving of thiophenoxide anion from $T^\pm$ (small k_2) due to the weaker "push" exerted by S$^-$ in $T^\pm$ (relative to O$^-$ in the similar $T^\pm$ formed with phenyl thiolacetate), which increases the lifetime of the dithio intermediate and allows time for proton removal from $T^\pm$ by the amine to yield T^- (eq 2).[5]

As a continuation of our studies on the aminolysis of thioesters we now examine the reactions of secondary alicyclic amines with 4-nitrophenyl dithioacetate. It was of particular interest to compare the results from this study with those of phenyl dithioacetate[5] in order to investigate whether there is still base catalysis involving the presumably more unstable $T^\pm$ formed in the present reactions (due to an expected larger k_2).

It was also of interest to compare the present reactions with the aminolyses of 4-nitrophenyl thiolacetate[3] and

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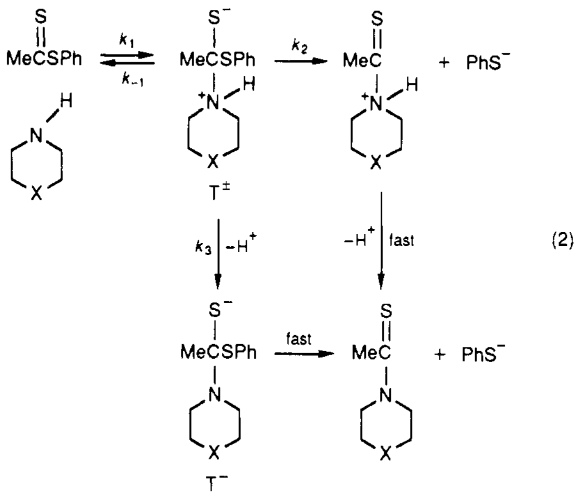

(2)

O-ethyl *S*-(4-nitrophenyl) dithiocarbonate,[6] in order to evaluate the influence of the thiocarbonyl and "acyl" groups of the substrate on the mechanism of these reactions and on the leaving abilities of amines and arenethiolates from T±.

Experimental Section

Materials. The secondary alicylic amines were purified as reported.[3] The buffers used and other materials were as described.[5]

To our knowledge 4-nitrophenyl dithioacetate (NPDTA) has not been previously prepared. The compound was synthesized by a modification of a method used to prepare phenyl dithioacetate:[7] Lawesson's reagent[7,8] (2.6 g) and 4-nitrophenyl thiolacetate[3] (1.3 g) in dry toluene (10 mL) were refluxed under nitrogen for 18 h. The mixture was filtered and toluene was removed by evaporation. The residue was dissolved in chloroform, placed on a silica gel column, and eluted with hexane:benzene (3:1). NPDTA was obtained from the second fraction and purified by TLC in hexane:benzene (4:1). The pure solid was red, mp 73–74 °C and was identified by ^{1}H NMR, ^{13}C NMR, and IR analyses: ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.93 (s, 3 H), 7.60 (d, 2 H, J = 6.9 Hz), 8.32 (d, 2 H, J = 6.9 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 39.08 (CH_3), 124.42 (C-3/5), 135.88 (C-2/6), 139.05 (C-1), 148.79 (C-4), 219.75 (C=S); IR (KBr) 1600 (C=C), 1397 and 1562 (CNO_2), 1229 (C=S), 830 (CH, arom) cm^{-1}.

Kinetic Methods. The appearance of 4-nitrothiophenoxide ion (NPS$^-$) was followed spectrophotometrically at 412 nm in aqueous solution at 25.0 ± 0.1 °C and at an ionic strength of 0.2 M (KCl).[5] The initial NPDTA concentration was (2–3) $\times 10^{-5}$ M in the kinetic runs. The amine was in excess throughout and pseudo-first-order rate constants (k_{obsd}) were found in all reactions. The experimental conditions of the kinetics and the k_{obsd} values are shown in Table I.

Product Studies. NPS$^-$ was identified as one of the final products in the reaction of NPDTA with piperidine in 0.02 M borate buffer under similar conditions as those described in Table I. The identification was achieved by comparison of the UV spectrum at the end of the reaction with that of an authentic sample of NPSH at the same experimental conditions (NPSH, with a pK_a of 4.6,[3] is fully dissociated at the pH of concern).

Results and Discussion

In the reactions of the substrate with piperidine and morpholine the plots of k_{obsd} vs [N] at constant pH (N is the free amine) were linear with slopes independent of pH.

Table I. Experimental Conditions and k_{obsd} Values for the Aminolysis of NPDTA[a]

amine	$10^3[N]_{tot}$,[b] M	pH	$10^3 k_{obsd}$, s^{-1}	n[c]
piperidine[d]	0.07–0.50	8.7	5.3–33	4
	0.05–0.50	9.0	6.6–66	5
	0.03–0.25	9.3	6.7–61	5
piperazine[d]	0.96–4.8	8.4	4.9–28	4
	0.64–6.4	8.7	7.1–84	5
	0.48–4.8	9.0	13–136	5
1-(β-hydroxyethyl)piperazine[e]	5.0–50	6.7	2.8–23	5
	2.5–25	7.0	2.0–19	5
	1.3–13	7.3	1.8–15	5
	1.3–13	7.5	3.0–24	5
morpholine[e]	5.1–51	6.7	3.8–37	5
	3.4–34	7.0	5.4–50	5
	1.7–17	7.3	5.1–51	5
1-formylpiperazine	0.6–24	7.7	0.9–95	7
	0.3–30	7.8	0.4–184	12
	0.6–18	8.0	0.9–118	7
	0.6–12	8.3	0.5–94	7
piperazinium ion	1.0–77	5.5	0.3–24	10
	4.5–90	5.8	1.4–51	6
	2.5–113	6.1	1.1–134	17
1-(β-hydroxyethyl)piperazinium ion[f]	7.0–95	4.6	0.3–2.7	11

[a] In aqueous solution at 25 °C, ionic strength 0.2 M (KCl). [b] Concentration of total amine (free base plus protonated forms). [c] Number of runs. [d] In the presence of 0.02 M borate buffer. [e] In the presence of 0.02 M phosphate buffer. [f] This is species 2. Four more reactions were carried out at pH 4.2 and 4.4 and $[N]_{tot}$ = (3.5 − 7.0) $\times 10^{-2}$ M. The k_{obsd} values obtained were well correlated with those found at pH 4.6 from a k_{obsd} vs [N] plot.

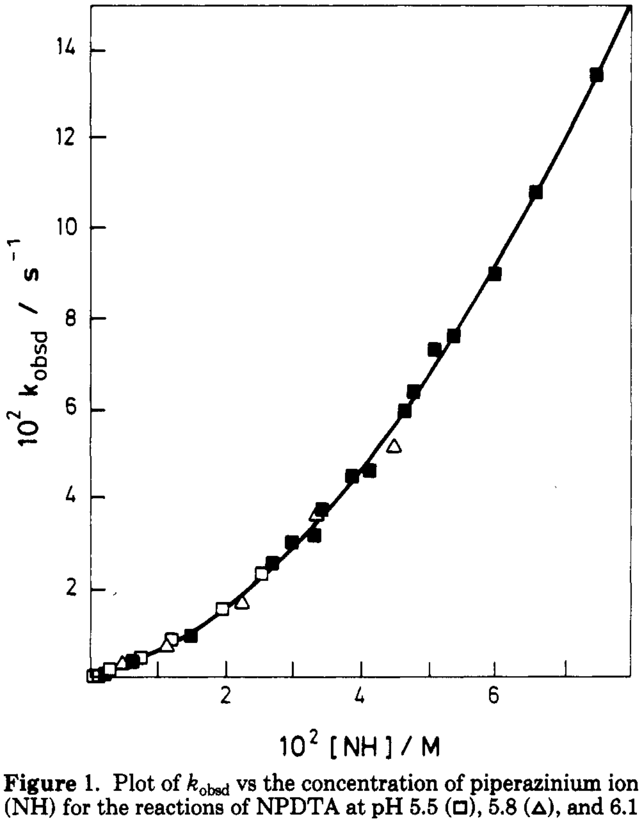

Figure 1. Plot of k_{obsd} vs the concentration of piperazinium ion (NH) for the reactions of NPDTA at pH 5.5 (□), 5.8 (△), and 6.1 (■). The solid line was calculated by means of eq 4 with k_0 = 5.4 $\times 10^{-4}$ s^{-1}, m_3 = 0.38 s^{-1} M^{-1}, and m_4 = 18.7 s^{-1} M^{-2}. The points are experimental.

In the reactions of NPDTA with piperazine and 1-(β-hydroxyethyl)piperazine (BHPA) at high pH values (8.4–9.0 and 6.7–7.5), the plots of k_{obsd} vs [N] at constant pH were also linear but the slopes were pH dependent.

The reactions of the former amine are in accord with eq 3, where m_1 and m_2 are constants and F_B is the free base fraction of the borate buffer. A straight line was obtained when the reciprocal of the slopes of the plots of k_{obsv} vs

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$$k_{obsd} = \frac{m_1F_B}{1 + m_2F_B}[N] \qquad (3)$$

[N] were plotted against $1/F_B$. The values of m_1 and m_2 were obtained from the slope and intercept, respectively, of the latter plot.

At lower pH values (pH 5.5–6.1) and without external buffer the above reaction obeys eq 4, where k_0 is the rate

$$k_{obsd} = k_0 + m_3[NH] + m_4[NH]^2 \qquad (4)$$

of hydrolysis of NPDTA, the m's are constants, and NH represents the piperazinium ion (monocation). The values of k_0, m_3, and m_4 were found by nonlinear least-squares fitting. The theoretical curve and the experimental points are shown in Figure 1.

In the case of the reactions with BHPA at pH 6.7–7.5, the slopes of the k_{obsd} vs [N] plots were linearly correlated with F_{BH}, where F_{BH} is the free-acid fraction ($H_2PO_4^-$) of the phosphate buffer used. When this reaction was carried out at a lower pH, 4.6, and with no external buffer, eq 4 was followed. In this case, NH represents the conjugate acid of the amine protonated at the 1-nitrogen atom.

In the reactions of NPDTA with 1-formylpiperazine the plot of k_{obsd} against [N] was nonlinear and was pH-independent; the form of k_{obsd} is similar to that of eq 4, except that NH is replaced by N and k_0 is negligible compared to the other terms.

A general mechanism for the present reactions which accounts for the experimental results obtained is that shown in eq 2 (for NPDTA). The k_3 step could in principle be catalyzed by the solvent, OH^-, the external buffer free base, or the amine. However, in the conditions of the reactions the former two species seemed to have negligible effect as compared to the free base and the amine. Applying the steady-state treatment to the tetrahedral intermediates in eq 2 (for NPDTA), a general rate expression can be derived for the present reactions (eq 5).

$$k_{obsd} = \frac{k_1(k_2 + \sum k_3[\text{Base}])[N]}{k_{-1} + k_2 + \sum k_3[\text{Base}]} \qquad (5)$$

For the reactions of the substrate with piperidine and morpholine, $k_2 + \sum k_3[\text{Base}] \gg k_{-1}$, during the experimental conditions. (This inequality together with others below will be justified later.) Therefore, eq 5 reduces to $k_{obsd} = k_1[N]$, which explains the rate law found for these reactions. the value of k_1 for each reaction was obtained as the slope of the corresponding k_{obsd} vs [N] plot.

In the reaction of NPDTA with piperazine at high pH, $\sum k_3[\text{Base}] = k_3^B[B] > k_2$, where B refers to $H_2BO_3^-$. When expressing [B] as $[B]_{tot}F_B$, where F_B is the base fraction of the buffer, eq 5 reduces to eq 6, which has the same form

$$k_{obsd} = \frac{k_1k_3^B[B]_{tot}F_B}{k_{-1} + k_3^B[B]_{tot}F_B}[N] \qquad (6)$$

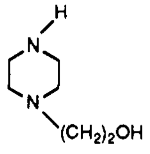
as the experimental one, eq 3. In agreement with eq 6 the plots of k_{obsd} vs [N] at constant pH were linear, with the slopes (m) pH-dependent. From the linear plot of $1/m$ vs $1/F_B$, the values of k_1 and k_{-1} were obtained (the value of k_3^B is known, see below).

In the above reaction at lower pH values (5.5–6.1) and without external buffer the concentration of the piperazinium monocation (NH) is significantly larger than that of piperazine (N). According to the rate law obtained only the former species was found to be responsible for the attack on the substrate and the deprotonation of the intermediate. Under the reaction conditions $\sum k_3[\text{Base}] = k_3^{NH}[NH]$ and $k_{-1} \gg k_2 + k_3^{NH}[NH]$; eq 5 reduces to eq 7

$$k_{obsd} = k_0 + K_1k_2[NH] + K_1k_3^{NH}[NH]^2 \qquad (7)$$

(replacing N of eq 5 by NH and introducing k_0), where K_1 ($=k_1/k_{-1}$) is the equilibrium constant for the first step of eq 2. Equation 7 is analogous to the experimental eq 4. From the values of m_3 and m_4 (Figure 1) and that of k_2 (see below) the values of K_1 and k_3^{NH} were found.

In the reactions of the substrate with BHPA at pH 6.7–7.5 and with phosphate buffer, the simultaneous attack on NPDTA by the free amine (1) and its conjugate acid protonated at the 1-position (2) was observed.[4] In this case the mechanism is more complex than that of eq 2 and the rate law has two terms, each of the form of eq 5. Under the reaction conditions, $k_1^1 \ll k_2 + \sum k_3[\text{Base}]$, $k_1^2 \gg k_2 + k_3^B[B]$, and $k_3^B[B] \gg k_2$, where k_3^B is the rate constant for deprotonation by HPO_2^{2-} of the tetrahedral intermediate formed by the attack of 2 on the substrate (the other bases had a negligible contribution). Taking into account these inequalities the general rate law reduces to $k_{obsd} = k_1^1[1] + K_1^2k_3^B[B]\ [2]$, where $K_1^2 = k_1^2/k_{-1}^2$. Replacing $[B] = K_a^{BH}[B]_{tot}F_{BH}/[H^+]$ and $[2] = [1][H^+]/K_a^2$, where the K_as are the dissociation constants and F_{BH} is the fraction of $H_2PO_4^-$, eq 8 results. Since $[B]_{tot}$ is constant (see Table I) eq 8 accounts for the experimental results.



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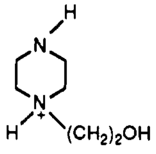
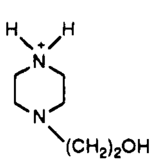


2

$$k_{obsd} = \left(k_1^1 + \frac{K_1^2K_a^{BH}}{K_a^2}\,k_3^B[B]_{tot}F_{BH}\right)[1] \qquad (8)$$

Since in this case the proton transfer is thermodynamically favorable and involves a dianion base and a monocation intermediate, we can assume $k_3^B = 5 \times 10^{10}\ s^{-1}\ M^{-1}$.[9] From a plot of the slope of eq 8 vs F_{BH} the values of k_1^1 and K_1^2 were found. The latter value is in accord (within an error of 1 order of magnitude) with the value found by extrapolation of a Brönsted plot for K_1 (see below).

The rate law obtained in the latter reaction at pH 4.6 without external buffer (eq 4) can be explained by the attack of 2 on the substrate and rate-determining deprotonation by 2 and 3 of the resulting cation intermediate (4, X = $NH^+ - (CH_2)_2OH$). Attack of 3 on NPDTA can be discarded for steric reasons and by the fact that 3 is less basic than 2.[4] Although the rate constant for deprotonation of 4 (with X = $NH^+(CH_2)_2OH$) by 2 (k_3^2) should be larger than that by 3 (k_3^3), the latter process cannot be ruled out in view of the larger concentration of 3 compared to 2 at pH 4.6 (ca. 22 fold).[4] Since at the reaction conditions, $k_{-1} \gg k_2 + k_3^2[2] + k_3^3[3]$ and $[3] = 22[2]$, the general rate law reduces to eq 9, which accounts for the



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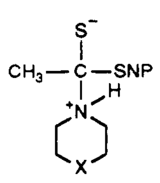

4

$$k_{obsd} = k_0 + K_1k_2[2] + K_1(k_3^2 + 22k_3^3\ )[2]^2 \qquad (9)$$

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[9] Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 1.

Table II. Values of the Microconstants Involved in the Present Reactions

amine	pK_a[a]	k_1, s^{-1} M^{-1}	10^6K_1, M^{-1}	$10^{-7}k_{-1}$,[b] s^{-1}	$10^{-10}k_3^B$, s^{-1} M^{-1}
piperidine	11.24	221	200	0.11	1[e]
piperazine	9.94	312	11[d]	1.4	1[e]
1-(β-hydroxyethyl)-piperazine	9.38	117	5.3	2.2	0.5[f]
morpholine	8.78	92	1.7	5.4	1[f]
1-formyl-piperazine	7.98	76[c]	0.1[d]	76	
piperazinium ion	5.81	40[c]	0.012[d]	330	
1-(β-hydroxyethyl)-piperazinium ion	5.9	37[c]	0.006	630	5[g]

other microconstants

$k_2 = 3 \times 10^7$ s^{-1} [h]

$k_3^{NH} = 2 \times 10^9$ s^{-1} M^{-1} [i]

$k_3^N = 1 \times 10^{10}$ s^{-1} M^{-1} [j]

[a] Values taken from ref 4 at the same experimental conditions of the reactions. [b] Values obtained as k_1/K_1. [c] Values found by extrapolation of the Brönsted plot (statistically corrected) for k_1. [d] With these three experimental values the Brönsted equation (statistically corrected) for K_1 was plotted. The K_1 values for the other amines were obtained from the Brönsted line. [e] In these cases B = $H_2BO_3^-$ and the rate constant is for deprotonation of 4. [f] In these cases B = HPO_4^{2-} and the rate constants refer to deprotonation of 4. [g] In this case B = HPO_4^{2-} and the rate constant refers to deprotonation of species 4 (with X = $NH^+(CH_2)_2OH$). [h] This value should be independent of the amine basicity.[11] [i] This rate constant refers to deprotonation of the cationic tetrahedral intermediate 4 (with X = NH_2^+) by piperazinium ion. [j] This is the rate constant for deprotonation of 4 by the corresponding free amine.

experimental rate law (eq 4 with NH = 2). Since the k_2 value is known (see below), K_1 can be obtained by nonlinear least-squares fitting. The obtained values, $(2 \pm 1) \times 10^{-8}$ M^{-1}, agrees within experimental error with the one obtained at higher pH values and also with that found by extrapolation of the Brönsted plot for K_1.

For the reaction of the substrate with 1-formylpiperazine (without external buffer) k_{-1} will be much larger than $k_2 + k_3^N[N]$. Thus, the general rate law (eq 5) simplifies to eq 10, which agrees with the experimental rate equation.

$$k_{obsd} = K_1k_2[N] + K_1k_3^N[N]^2 \qquad (10)$$

With the values of the macrocoefficients and that of $k_3^N = 10^{10}$ s^{-1} M^{-1} (see below), the magnitudes of K_1 and k_2 were determined.

The values of all the microconstants involved in the present reactions are shown in Table II.

In order to justify the inequalities stated above we must first estimate the pK_a of the T$^\pm$ formed in the present reactions (4). It is known that the pK_a of the analogous thiol derivative (O$^-$ instead of S$^-$ in 4) is 0.5 pK_a unit lower than that of the parent aminium ion.[3] Since $\sigma_I(O^-) = -0.26$ and $\sigma_I(S^-) = 0.03$[12] and $\rho = -7.3$ for the pK_a of XCH_2N-morpholinium ions,[13] it follows by Jenck's procedure[13] that the pK_a change when going from the thiol intermediate to 4 is $\Delta pK_a = -7.3(0.03 - (0.26))$ = ca. -2. Therefore, the pK_a of 4 is ca. 2.5 pK_a units lower than that of the parent aminium ion. It follows that the proton transfer from 4 to the corresponding amine is thermodynamically favorable, i.e., k_3^N is ca. 10^{10} s^{-1} M^{-1}.[9] In the reactions of the substrate with the two aminium cations included in this study it is expected that proton transfers from the cationic intermediates (e.g., 4 with X = NH_2^+) to the corresponding aminium ions will be slower since the same charges are involved. One of these rate constants was determined and is in fact smaller than 10^{10} s^{-1} M^{-1} (see Table II).

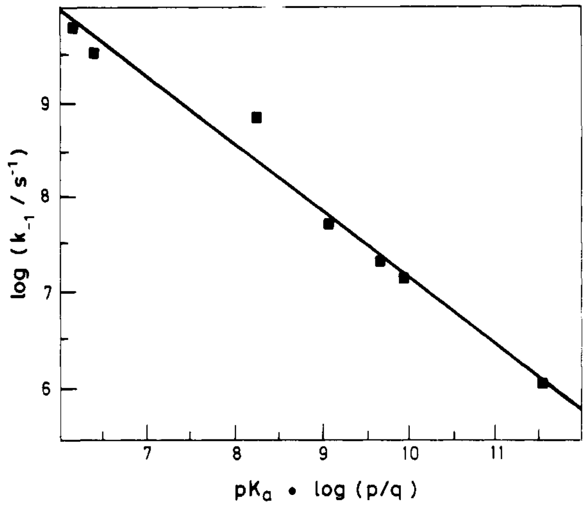

Figure 2. Brönsted-type plot (pK_a (pK_a values statistically corrected) for k_{-1}, obtained in the present reactions. The slope is -0.7.

From the knowlege of the pK_a of 4 and of those of the acid forms of the external buffers used, the rate constant for proton transfer from 4 to the basic form of the external buffer, $H_2BO_3^-$ or HPO_4^{2-}, can be determined. Since these transfers are thermodynamically favorable in the reactions with piperidine, piperazine, and morpholine, we can estimate k_3^B to be approximately 10^{10} s^{-1} M^{-1} in these cases.[9] The intermediate 4 formed with BHPA has a pK_a similar to that of $H_2PO_4^-$; therefore k_3^B can be estimated to be ca. 5×10^9 s^{-1} M^{-1}.[9] In the case of the attack of 2 on the substrate, the rate constant for proton transfer from the cation 4 (X = $NH^+(CH_2)_2OH$) to HPO_4^{2-} should be larger than 10^{10} s^{-1} M^{-1} for electrostatic reasons; by a rough estimate k_3^B will be $\sim 5 \times 10^{10}$ s^{-1} M^{1-}.[9]

All the inequalities stated and the assumptions made above seem reasonable in terms of the concentrations of the amines and buffers used (Table I) and the values of the microconstants involved in the mechanism (Table II).

Based upon the data of Table II the Brönsted-type plots for k_1 (4 points) and K_1 (3 points) were obtained. These were statistically corrected with $q = 2$ for piperazine and $p = 2$ for the protonated amines, except $p = 4$ for the piperazinium dication.[4,5,14] The values of the Brönsted slopes, $\beta_N = 0.15$ and 0.83, respectively, satisfactorily agree with the ones found in the aminolyses of aryl thiolacetates,[4] aryl acetates,[1,2,11] and *O*-ethyl *S*-aryl dithiocarbonates.[6] From the former values, it can be deduced that for k_{-1}, $\beta_N = 0.15 - 0.83 = -0.68$, in good accord with the values obtained in the above aminolyses.[1,2,4,6,11] Figure 2 shows the statistically corrected Brönsted plot for k_{-1} (k_{-1} determined as k_1/K_1), the slope of which is $\beta_N = -0.7$.

The β_N value for k_1 found in this work is also in agreement with that reported in the aminolysis of phenyl dithioacetate (PDTA, $\beta_N = 0.2$).[5] However, the Brönsted sensitivities for K_1 and k_{-1} reported for PDTA are larger ($\beta_N = 1.2$ and -1.0, respectively) than those obtained in the present work.

The values of k_1 for the NPDTA reactions (Table II) are larger than those for the reactions of the same amines with PDTA[5] and *O*-ethyl *S*-(4-nitrophenyl) dithiocarbonate (NPDTC).[6] The former can be explained by the larger

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(10) The pK_a values of BH and 2 are 6.7 and 8.04,[4] respectively.

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electron withdrawal of the NPS group in NPDTA compared to PhS in PDTA, which renders the thiocarbonyl carbon of NPDTA more electrophilic. The larger k_1 value for the aminolysis of NPDTA relative to NPDTC is in line with the general lower reactivity of carbonates than acetates, which is attributed to electron donation from the "acyl" alkoxy (or aryloxy) group of the carbonate to the carbonyl carbon.[11,15]

The rate constant for expulsion of NPS^- from the $T^{\pm}$ formed in the aminolysis of NPDTC has been estimated to be ca. 3×10^8 s^{-1}.[16] This value is larger than that found in the present work (k_2 ca. 3×10^7 s^{-1}). With the former value the magnitudes of k_{-1} for the NPDTC reactions can be determined;[6,17] these values are also larger than those obtained here (Table II).

These findings are in line with the results obtained in the aminolysis of monothio derivatives. A destabilization of the corresponding $T^{\pm}$ is produced when replacing Me by EtO. In fact a concerted process was found in the aminolysis of *O*-ethyl *S*-(2,4-dinitrophenyl) thiocarbonate,[15] whereas a stepwise mechanism occurs in the same reactions with 2,4-dinitrophenyl thiolacetate.[4,15] The higher instability of the former "intermediate" was attributed to electron donation from EtO in $T^{\pm}$ which enhances the nucleofugality of both the amine and ArS^-.[4] Similar destabilization of $T^{\pm}$, by substitution of Me by MeO, can be deduced from the aminolyses of 2,4-dinitrophenyl acetate and methyl carbonate,[18] 2,4,6-trinitrophenyl acetate and methyl carbonate,[19] and acetylpyridinium and (methoxycarbonyl)pyridinium ions.[20]

The nucleofugality of NPS^- from 4 (k_2 of Table II) is greater than that of PhS^- from the corresponding $T^{\pm}$ [5] in agreement with the lower basicity of the former anion (pK_a of NPSH and PhSH are 4.6 and 6.5, respectively, under the reaction conditions).[3]

The rate of departure of NPS^- from the $T^{\pm}$ formed in the aminolysis of 4-nitrophenyl thiolacetate (NPTA) can be determined from the empirical equation for thiolacetates;[4] the value ($k_2 = 1 \times 10^9$ s^{-1}) is much larger than the one observed in the present study (Table II). It can also be deduced[4] that the nucleofugality of a given alicyclic amine (k_{-1}) from the $T^{\pm}$ formed in the NPTA reactions is greater than that from 4 (Table II).

This indicates that $T^{\pm}$ is also destabilized by substitution of S^- by O^-. The same effect was found in the aminolysis of thiocarbonates: a curved Brönsted plot was obtained in the reactions of alicyclic amines with *O*-ethyl *S*-(2,4-dinitrophenyl) dithiocarbonate[21] whereas the same plot is linear with $\beta = 0.56$ in the reactions of the same amines with *O*-ethyl *S*-(2,4-dinitrophenyl) thiocarbonate.[15] The plots were interpreted in terms of a stepwise and a concerted mechanism, respectively, which means that the change of S^- by O^- destabilizes $T^{\pm}$.

The same effect is found from a comparison of the aminolysis of PDTA[5] and phenyl thiolacetate.[3] Both k_2 and k_{-1} are larger in the latter reaction.[5] This effect was attributed to the known C^+–S^- character of the thione "double" bond, which effectively makes more difficult the formation of the C=S bond from $T^{\pm}$ as compared to the C=O bond from the analogous $T^{\pm}$ and, therefore, retards the expulsion of both the amine and leaving group from the zwitterionic intermediate.[5,22]

In conclusion, we have found that the substitution of 4-H by 4-NO_2 at the nucleofuge of the substrate gives the following effects on the aminolysis reactions: (i) a faster attack of the amine on NPDTA, (ii) a faster nucleofugality of NPS^- from $T^{\pm}$, (iii) a lower sensitivity of both the equilibrium constant for formation of $T^{\pm}$ and the rate constant for the amine expulsion from $T^{\pm}$ on the amine basicity, (iv) observance of base catalysis by amine in the NPDTA reactions in spite of the larger nucleofugality of NPS^- from $T^{\pm}$ (relative to PhS^-).

Comparison of the present reactions with those of similar 4-nitrophenyl derivatives indicates that the changes of S^- by O^- and Me by EtO in $T^{\pm}$ destabilizes this intermediate.

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