Kinetics and Mechanism of the Aminolysis of Phenyl Thionoacetate in Aqueous Solution

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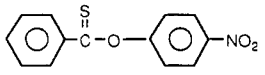
The reactions of a series of secondary alicyclic amines with the title substrate have been subjected to a kinetic study in water at 25 °C, ionic strength 0.2 M. Pseudo-first-order rate coefficients (k_{obsd}) are found throughout, under amine excess. The order in amine varies from 1 to 2 according to its basicity and the reaction conditions. A reaction mechanism consisting of a zwiterionic ($T^{\pm}$) and an anionic (T^-) tetrahedral intermediate is proposed to account for the results. Base catalysis by OH^- and the amine is observed for conversion of $T^{\pm}$ to T^-. The microscopic rate coefficients involved in the reaction scheme are either estimated or determined. The Brönsted slopes for formation of $T^{\pm}$ and for its back step are $\beta_N = 0.16$ and -0.82, respectively. The rate coefficients for formation of $T^{\pm}$ (k_1) and that for expulsion of PhO^- from $T^{\pm}$ (k_2) are smaller than those in the phenyl acetate (PA) and phenyl dithioacetate (PDTA) reactions. The rate coefficient for amine expulsion from $T^{\pm}$ (k_{-1}) is smaller than that in the PA reactions, but it is similar to that in the aminolysis of PDTA and 4-nitrophenyl dithioacetate. It is claimed that there is little sensitivity of k_{-1} to the leaving group (ArO or ArS) basicity when the C–S^- bond is involved in $T^{\pm}$, and reasons for this are given.

Introduction

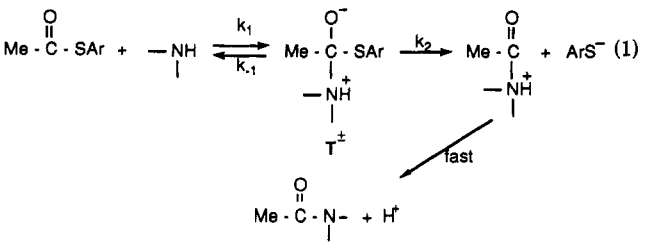
The chemistry of thionoesters (*O*-alkyl or *O*-aryl thioesters, R^1CSOR^2) has not been extensively studied.[1] Some of these investigations have dealt with the hydrolysis, solvolysis, and desulfurization of the above compounds.[1] Only a few works devoted to the subject have appeared lately,[2] dealing with the synthesis and properties of thionoesters[2a] and their influence on the degree of polymerization of styrene and related compounds.[2b] Also, the rate constants for the reactions of alkali metal ethoxides with *O*-(4-nitrophenyl) thionobenzoate (NPTB) have been



NPTB

measured in ethanol at 25 °C.[2c] Concerning the mechanistic study of the aminolysis of thionoesters we have found only one report: the reaction of NPTB with primary and secondary amines.[3] In that work the existence of a zwitterionic tetrahedral intermediate in the reaction pathway was inferred from the nonlinear Brönsted-type plot found.[3]

We have investigated the mechanisms of the aminolyses (secondary alicyclic amines) of *S*-aryl thioacetates (aryl thiolacetates)[4,5] and dithioacetates[6,7] and *O*-ethyl *S*-aryl dithiocarbonates.[8] We have found that the reactions of thioacetates proceed according to eq 1 where NH represents a secondary alicyclic amine.[4,5] Nevertheless, in the aminolyses of phenyl dithioacetate (PDTA)[6] and *O*-ethyl *S*-phenyl dithiocarbonate (PDTC)[8a] we observed base catalysis of $T^{\pm}$ by the amine to yield an anionic tetrahedral intermediate (T^-). The fact that no base catalysis was found in the aminolysis of *S*-phenyl thioacetate (PTA)[4] was attributed to the higher instability (larger k_{-1} and k_2 in eq 1) of the $T^{\pm}$ formed in this reaction compared to the corresponding intermediates formed in the aminolyses of PDTA and PDTC.[6] The lower k_2 in the latter reactions makes possible a competition between the expulsion of PhS^- from the zwitterionic tetrahedral intermediate and the deprotonation of this species by the amine.[6]



In order to extend our studies to thionoesters we report in this work the reactions of secondary alicyclic amines with phenyl thionoacetate (*O*-phenyl thioacetate). The aim is to compare this mechanism with the ones found for the aminolysis of thioacetates, dithioacetates, and *O*-alkyl dithiocarbonates. In particular it is of interest to compare the present study with the aminolysis of PDTA and phenyl acetate[9,10] in order to assess the influence of the leaving and thiocarbonyl groups of the substrate on these mechanisms.

Experimental Section

Materials. The amines were purified as reported.[4] Phenyl thionoacetate (PTOA) has not been synthesized previously, to our knowledge. We prepared it the following way: Lawesson's

(1) Janssen, M. J. In *Chemistry of Carboxylic Acids and Esters*; Patai, S., Ed.; Wiley-Interscience: London, 1969; p 705. Bradshaw, J. S.; Jones, B. A.; Gebhard, J. S. *J. Org. Chem.* **1983**, *48*, 1127. Storer, A. C.; Angas, R. H.; Carey, P. R. *Biochemistry* **1988**, *27*, 264.

(2) (a) Hartke, K. *Phosph. Sulfur, Silicon* **1991**, *58*, 223. (b) Meijs, G. F.; Rizzardo, E.; Le, T. P. T.; Chen, Y. C. *Makrom. Chem.* **1992**, *193*, 369. (c) Kwon, D. S.; Park, H. S.; Um, I.-H. *Bull. Korean Chem. Soc.* **1991**, *12*, 93.

(3) Campbell, P.; Lapinskas, B. A. *J. Am. Chem. Soc.* **1977**, *99*, 5378.

(4) Castro, E. A.; Ureta, C. *J. Org. Chem.* **1989**, *54*, 2153.

(5) Castro, E. A.; Ureta, C. *J. Chem. Soc., Perkin Trans. 2* **1991**, 63.

(6) Castro, E. A.; Ibáñez, F.; Santos, J. G.; Ureta, C. *J. Chem. Soc., Perkin Trans. 2* **1991**, 1919.

(7) Castro, E. A.; Ibáñez, F.; Santos, J. G.; Ureta, C. *J. Org. Chem.* **1992**, *57*, 7024.

(8) (a) Cabrera, M.; Castro, E. A.; Salas, M.; Santos, J. G.; Sepúlveda, P. *J. Org. Chem.* **1991**, *56*, 5224. (b) Castro, E. A.; Ibáñez, F.; Salas, M.; Santos, J. G.; Sepúlveda, P. *J. Org. Chem.* **1993**, *58*, 459.

(9) Jencks, W. P.; Gilchrist, M. *J. Am. Chem. Soc.* **1968**, *90*, 2622.

(10) Satterthwait, A. C.; Jencks, W. P. *J. Am. Chem. Soc.* **1974**, *96*, 7018.

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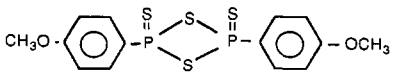
Table I. Experimental Conditions and k_{obsd} Values for the Aminolysis of Phenyl Thionoacetate (PTOA)[a]

amine	$10^3[N]_{tot}$,[b] M	pH	F_N[c]	10^3k_{obsd}, s^{-1}	n[d]
piperidine[e]	1.5–60	8.9–9.5	0.0044–0.017	2.4–26	15
piperazine	0.3–6.0	9.4–10.2	0.22–0.67	2.6–140	18
1-(2-hydroxyethyl)-piperazine	0.4–8.0	9.0–9.6	0.29–0.62	3.2–87	15
morpholine	0.4–12	8.2–8.8	0.21–0.50	0.9–76	15
1-formylpiperazine	1.4–30	7.7–8.3	0.33–0.67	0.6–50	16
piperazinium ion	9.0–90	5.5–6.1	0.33–0.67	0.4–24	18

[a] In aqueous solution at 25.0 °C, ionic strength 0.2 M (KCl). [b] Concentration of total amine (free amine plus protonated forms). [c] Free amine fraction of the total amine. [d] Number of runs. [e] In the presence of borate buffer 0.02 M.

reagent (LR)[11] (5.8 g) and phenyl acetate (1.3 mL) in dry *p*-xylene



LR

(10 mL) were refluxed under nitrogen for 20 h. Once cool the mixture was filtered and *p*-xylene was removed by evaporation. The residue was dissolved in chloroform, placed on a silice gel column, and eluted with petroleum ether. The yield was 24%. PTOA is an orange liquid and was identified by ^1H NMR, ^{13}C NMR, and IR analyses: ^1H NMR (200 MHz, $CDCl_3$) δ 2.83 (s, 3H), 7.04 (d, 2H, J = 7.0 Hz), 7.30 (t, 1H, J = 7.0 Hz), 7.45 (t, 2H, J = 7.0 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 34.47 (CH_3), 124.64 (C-2/6), 126.05 (C-4), 126.76 (C-3/5), 154.67 (C-1), 219.70 (C=S); IR (KBr) 1600 (C=C), 1350 and 1480 (CH_3), 1250 (C=S), 1190 (CO), 690–820 (CH, arom) cm^{-1}.

Kinetic Measurements. These were performed by means of a Perkin-Elmer Lambda 3 spectrophotometer, following the release of phenol and/or phenoxide ion at 269 nm. The reactions were started by addition of a solution (ca. 10 μL) of the substrate in acetonitrile into the kinetic solutions (2.5 mL) contained in 1-cm cells placed in the thermostated compartment (25.0 ± 0.1 °C) of the spectrophotometer. The initial concentration of the substrate was $[PTOA]_o = (4–5) \times 10^{-5}$ M, and the amine was at least in 10-fold excess over PTOA. Pseudo-first-order rate coefficients (k_{obsd}) were found in all cases from log ($A_\infty - A$) vs time plots, where A_∞ and A are the absorbances at the end of the reaction and at any time, respectively. The runs showing correlation coefficients worse than 0.999 were discarded. The experimental conditions of the reactions and the values of k_{obsd} are shown in Table I.

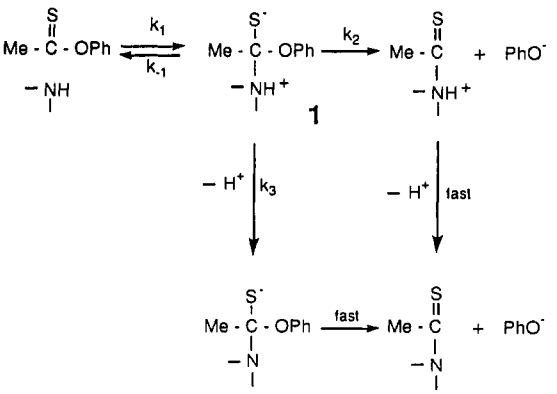
Product Studies. Phenol and/or its conjugate base was found as one of the products of the reactions by comparison of the UV–vis spectra at the end of some reactions with that of phenol under the same experimental conditions.

Results and Discussion

The plots of k_{obsd} vs [N] (where N is the free amine) at constant pH (range of data in Table I) were linear for the reactions of PTOA with piperidine, with both the intercept and slope independent of pH (plots not shown).

The reactions of the substrate with piperazine showed a linear k_{obsd} vs [N] plot at pH 10.2 and nonlinear (upward curvature) and pH-dependent ones at lower pH values. In the reactions of PTOA with all the other amines the above plots were nonlinear (upwards) and pH-independent.

These results are compatible with the mechanism shown in eq 2. Applying the steady-state treatment to the tetrahedral intermediates 1 and 2 the general expression for k_{obsd}, shown in eq 3, can be derived. In this equation



1

2

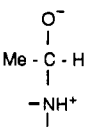
(2)

$$k_{obsd} = \frac{k_1(k_2 + k_3^{OH}[OH^-] + k_3^N[N])[N]}{k_{-1} + k_2 + k_3^{OH}[OH^-] + k_3^N[N]} \quad (3)$$

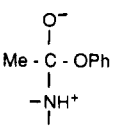
k_3^{OH} and k_3^N are rate coefficients for proton transfer from 1 to OH^- and the amine. In the reactions with piperidine borate was used as external buffer; therefore, in this case the term $k_3^{H_2BO_3}[H_2BO_3^-]$ should be added to both the numerator and denominator of eq 3.

The values of the rate constants for proton transfer from 1 to various bases (k_3^{OH}, k_3^N, and $k_3^{H_2BO_3}$) can be estimated by knowledge of the pK_a values of 1 and those of the conjugate acids of the bases.

By following Jencks procedure (see below) the pK_a of 3 has been estimated as 2.2 pK_a units higher than that of the parent aminium ion.[4] Jencks has satisfactorily esti-



3



4

mated the pK_a values of tetrahedral intermediates similar to 3 by using $\rho_I = -7.3$ for the pK_a of α-substituted aminium ions.[12] We have used Jencks' procedure to obtain the pK_a of several intermediates.[4–8] Since σ_I of PhO is +0.40,[13] addition of PhO to 3 should change the latter pK_a by $-7.3 \times 0.40 = -2.9$ pK_a units, yielding a pK_a for 4 of 0.7 pK_a unit lower than that of the parent aminium ion. Substitution of O^- by S^- in 4 should vary the pK_a by $-7.3 \times (0.03 - (-0.26)) = -2.1$ pK_a units (σ_I for S^- and O^- are 0.03 and −0.26, respectively[14]); therefore, the pK_a of 1 should be ca. 2.8 pK_a units lower than that of the parent aminium ion.

Since 1 is much more acidic than the parent aminium ion it follows that the proton transfer from 1 to the corresponding amine is thermodynamically favorable. By following the Eigen procedure[15] we can estimate that k_3^N is ca. 10^{10} s^{-1} M^{-1}.[5–8,10,12,15] In the particular case of the reaction of the substrate with the piperazinium monocation, it is expected that this proton transfer be slower in view that the same charges are involved in the tetrahedral intermediate and the base. In this case it could be estimated that k_3^N is ca. 10^9 s^{-1} M^{-1}.[7,15] It also follows from

(11) Pedersen, B. S.; Scheibye, S.; Clausen, K.; Lawesson, S. O. *Bull. Soc. Chim. Belg.* **1978**, *87*, 293.

(12) Sayer, J. M.; Jencks, W. P. *J. Am. Chem. Soc.* **1973**, *95*, 5637. Fox, J. P.; Jencks, W. P. *J. Am. Chem. Soc.* **1974**, *96*, 1436.

(13) Charton, M. *Prog. Phys. Org. Chem.* **1987**, *16*, 287.

(14) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

(15) Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 1.

Table II. Values of Equilibrium and Rate Microcoefficients Involved in the Reactions of Phenyl Thionoacetate (PTOA) with Secondary Alicyclic Amines[a]

amine	pK_a[b]	k_1,[c] s^{-1} M^{-1}	10^{-7} k_{-1},[d] s^{-1}	10^7K_1,[e] M^{-1}
piperidine	11.24	95	0.04[f]	2400
piperazine	9.94	122	0.6	200
1-(2-hydroxyethyl)piperazine	9.38	48	1.0	48
morpholine	8.78	36	4.0	9.0
1-formylpiperazine	7.98	29	50	0.6
piperazinium ion	5.81	14	400	0.035
other rate microcoefficients				
$k_2 = 1 \times 10^6$ s^{-1}[g]				
$k_3^{OH} = 5 \times 10^{10}$ s^{-1} M^{-1}[h]				
$k_3^{N} = 1 \times 10^{10}$ s^{-1} M^{-1}[i]				
$k_3^{NH} = 2 \times 10^9$ s^{-1} M^{-1}[j]				

[a] In aqueous solution at 25.0 °C, ionic strength 0.2 M (KCl). [b] Values taken from ref 4. [c] Values obtained as slopes of linear k_{obsd} vs [N] plots (piperidine and piperazine) and by nonlinear least-squares fitting to eq 3 (the other amines). [d] Values obtained by nonlinear least-squares fitting to eq 3, except the value for piperidine. [e] Equilibrium constant for the first step of eq 2, calculated as k_1/k_{-1}. [f] Value obtained by extrapolation of the Brönsted plot for k_{-1}. [g] Rate coefficient for expulsion of PhO^- from 1, obtained by nonlinear least-squares fitting to eq 3, except in the reactions of piperidine, piperazine at pH 10.2, and piperazinium ion. [h] Rate coefficient for deprotonation of 1 by OH^-, estimated from the corresponding pK_a values and ref 15. [i] Rate coefficient for deprotonation of 1 by the corresponding amine, estimated as in *h*. [j] Rate coefficient for deprotonation of 1 (formed with piperazinium ion) by piperazinium ion, estimated as in *h*.

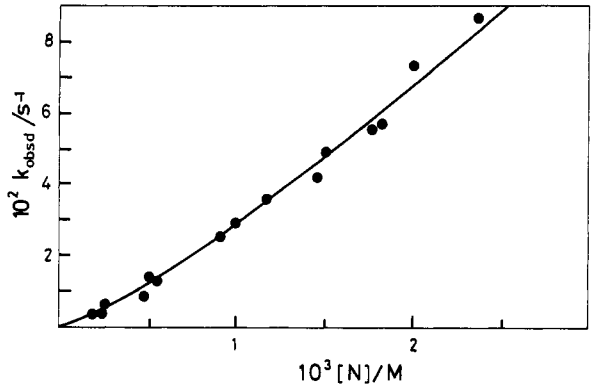


Figure 1. Plot of k_{obsd} vs free amine concentration for the reaction of PTOA with 1-(2-hydroxyethyl)piperazine at pH 9.0, 9.3, and 9.6, at 25.0 °C, ionic strength 0.2 M. The curve was calculated by means of eq 3 and the microcoefficients shown in Table II. The points are experimental.

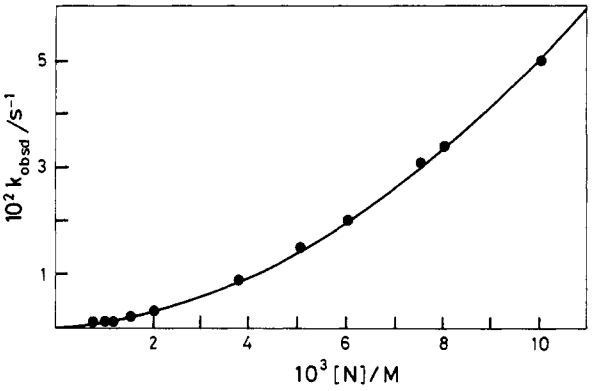


Figure 2. Plot of k_{obsd} vs free amine concentration for the reaction of PTOA with 1-formylpiperazine at pH 7.7, 8.0, and 8.3, at 25.0 °C, ionic strength 0.2 M. The curve was calculated by means of eq 3 and the microcoefficients of Table II. The points are experimental.

the value of the pK_a of 1 that the proton transfer from 1 (with any of the amine moieties) to OH^- is also thermodynamically favorable, and an estimation of k_3^{OH} would be 5×10^{10} s^{-1} M^{-1}.[6,15] In the reaction of the substrate with piperidine borate buffer was used. The pK_a of 1 in this case is 11.2 - 2.8 = 8.4 and since $pK_a(H_3BO_3)$ = 9.2, it follows that the proton transfer from 1 (with piperidine as moiety) to $H_2BO_3^-$ is also thermodynamically favorable, and we can assume $k_3^{H_2BO_3} = 10^{10}$ s^{-1} M^{-1}.[6,7,15]

The values of k_1 for the reactions of PTOA with piperidine and that for piperazine at pH 10.2 were obtained as the slopes of linear k_{obsd} vs [N] plots. The values of the other rate microconstants involved in eq 3 were obtained by nonlinear least-squares fitting of eq 3 to the experimental k_{obsd} vs [N] data, as described.[7] Values for the microconstants are shown in Table II; a description of their source is located in the footnotes of the table. Figures 1 and 2 are examples of the fits to eq 3, using the values of the microconstants of Table II, for the reactions of PTOA with 1-(2-hydroxyethyl)piperazine and 1-formylpiperazine, respectively.

The value of k_2 was independent of the amine basicity (within an experimental error of 30%), as expected,[4-6,16] since there is little or no electron donation from the cationic amine moiety of 1 to exert the push to expel the leaving phenoxide ion.[16] The errors involved in the estimated rate microcoefficients of Table II (k_3^{OH}, k_3^{N}, and k_3^{NH}) are ca. 50%, and those of k_1 and k_{-1} are ca. 10%.

With the data of Table II, the Brönsted plots, statistically corrected,[17] of log (k_1/q), log k_{-1}, and log (K_1/q) against pK_a + log (p/q) were obtained (see Figures 3-5).[7] The plots exhibit the following slopes (β) and correlation coefficients (R): $\beta = 0.16 \pm 0.03$ and $R = 0.994$ for k_1, $\beta = -0.82 \pm 0.1$ and $R = 0.977$ for k_{-1}, and $\beta = 1.0 \pm 0.1$ and $R = 0.992$ for K_1.

These β values agree with the ones found in the aminolysis of aryl thioacetates,[5] aryl acetates,[10,16] and *O*-ethyl *S*-aryl dithiocarbonates.[8] The β value for k_1 also agrees with the corresponding values obtained in the aminolyses of phenyl and *p*-nitrophenyl dithioacetates (PDTA and NPDTA, respectively);[6,7] nevertheless, the β value for K_1 of the present reactions is intermediate between those found in the latter reactions (β = 1.2 and 0.83 for PDTA and NPDTA, respectively). This indicates an intermediate charge development on the nitrogen atom of the amine in going from the amine reactant to 1 in eq 2, relative to the same charge development in the reactions of PDTA and NPDTA.[16] This means that the value of the positive charge on the aminic moiety of the zwitterionic tetrahedral intermediate formed in these reactions follows the sequence: PDTA > PTOA > NPDTA.

(16) Gresser, M. J.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 6963.

(17) Bell, R. P. *The Proton in Chemistry*; Methuen: London, 1959; p 159.

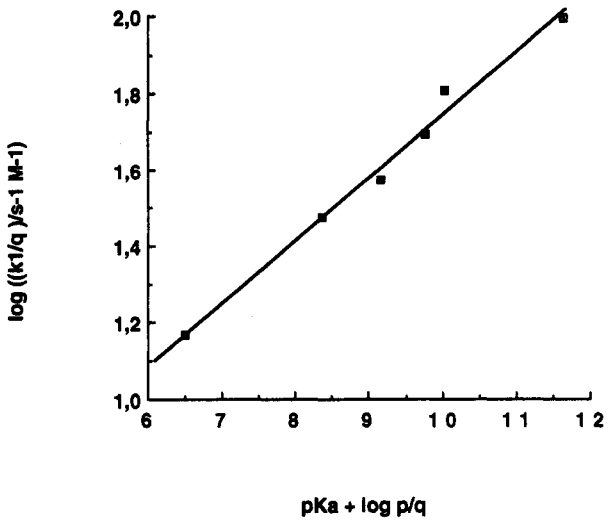


Figure 3. Brönsted-type plot (statistically corrected) obtained in this work for k_1 of eq 2. The slope is 0.16.

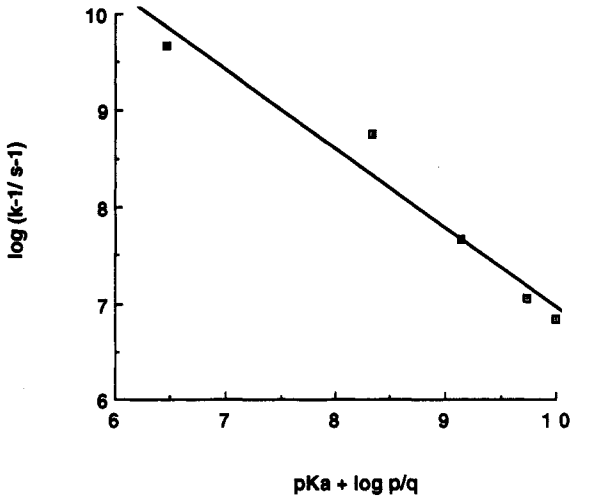


Figure 4. Brönsted-type plot (pK_a statistically corrected) obtained in this work for k_{-1} of eq 2. The slope is −0.82.

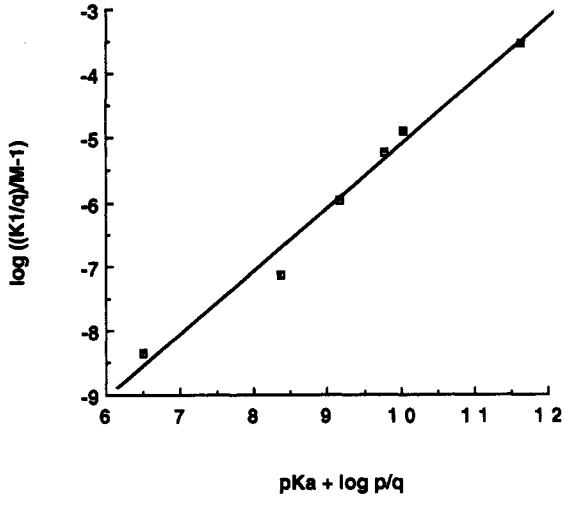


Figure 5. Brönsted-type plot (statistically corrected) obtained in this work for K_1 ($=k_1/k_{-1}$) of eq 2. The slope is 1.0.

The values of k_1 for the aminolysis of PTOA (Table II) are smaller than those for the same reactions with PDTA.[6] This should be due to the fact that the PhO group of the substrate is more electron donating than PhS (as determined for instance by the pK_a values of 10.0 and 6.5 for PhOH and PhSH at 25 °C, respectively,[18] and the σ_R values of −0.40 and −0.23, respectively)[14] leaving the thiocarbonyl carbon of PTOA less susceptible to nucleophilic attack by the amine.

The values of k_1 for the reaction of phenyl acetate (PA) with piperidine, piperazine, morpholine, and piperazinium ion can be calculated with th values of k_N when expulsion of PhO^- from the zwitterionic tetrahedral intermediate ($T^{\pm}$) is rate determining[9] and the k_{-1} and k_2 values. In this case, $k_N = k_1k_2/k_{-1}$.[10] The k_{-1} and k_2 values can be determined from the corresponding equations described.[19] The values of k_1 calculated in this manner for the reactions of PA (e.g., 610 and 230 s^{-1} M^{-1} for piperidine and morpholine, respectively) are larger than those for the corresponding reactions of PTOA (Table II). This is in line with the rather hard character of the alicyclic amines which preferentially will bind to a harder center such as the carbonyl group compared to a softer one such as thiocarbonyl.[20]

The calculated value of k_2 for the aminolysis of PA ($k_2 = 3 \times 10^6$ s^{-1})[9,19] is apparently larger than that found in the present reactions ($k_2 = 1 \times 10^6$ s^{-1}, Table II). This is in accord with the results obtained in the aminolysis of 4-nitrophenyl thioacetate (NPTA)[4] and 4-nitrophenyl dithioacetate (NPDTA):[7] the substitution of S^- by O^- in $T^{\pm}$ enhances the k_2 value; i.e., 4-nitrobenzenethiolate ion expulsion is faster from the $T^{\pm}$ formed in the NPTA reactions.[7] The same effect was found in the aminolyses of *O*-ethyl *S*-(2,4-dinitrophenyl) dithiocarbonate[8b] and *O*-ethyl *S*-(2,4-dinitrophenyl) thiocarbonate.[21] Substitution of S^- by O^- in $T^{\pm}$ favors the expulsion of 2,4-dinitrobenzenethiolate ion in such a manner that the "intermediate" no longer exists in the latter reaction.[21] This effect was attributed to the higher polarizability of the C=S bond compared to C=O, which hinders the formation of the C=S bond from $T^{\pm}$ compared to the C=O bond from the analogous transition state, thus decreasing the rate of expulsion of the nucleofuge from the transition state.[6,7,22]

The value of k_2 found in the aminolysis of PDTA is larger than that obtained in the present reactions.[6,23] This can be ascribed to the lower basicity of PhS^- compared to PhO^-, which makes the former a better nucleofuge from $T^{\pm}$ compared to the latter, in spite of a greater intrinsic nucleofugality of RO^- compared to an isobasic $R'S^-$.[24]

The calculated values of k_{-1} (eq 2) for the reactions of PA with secondary alicyclic amines[19] (e.g., $k_{-1} = 3 \times 10^{10}$, 2×10^{11}, and 10^{12} s^{-1} for piperidine, piperazine, and morpholine, respectively[19]) are larger than those obtained in the present reactions (Table II). This result is in line with those found in the aminolyses of PDTA[6] and *S*-phenyl thioacetate (PTA)[5] and in the aminolyses of NPDTA[7] and

(18) Albert, A.; Serjeant, E. P. *The Determination of Ionization Constants*; Chapman and Hall: London, 1971.
(19) Castro, E. A.; Ureta, C. *J. Org. Chem.* **1990**, *55*, 1676.
(20) Pearson, R. G. *J. Chem. Educ.* **1968**, *45*, 581. Pearson, R. G. *J. Org. Chem.* **1989**, *54*, 1423.
(21) Castro, E. A.; Ibáñez, F.; Salas, M.; Santos, J. G. *J. Org. Chem.* **1991**, *56*, 4819.
(22) Hill, S. V.; Thea, S.; Williams, A. *J. Chem. Soc., Perkin Trans. 2* **1983**, 437. Cottrell, T. L. *The Strengths of Chemical Bonds*, 2nd ed.; Butterworth: London, 1959, pp 275–276. Kwon, D. S.; Park, H. S.; Um, I. H. *Bull. Korean Chem. Soc.* **1991**, *12*, 93.
(23) Although the value reported for k_2 in the aminolysis of PDTA is uncertain (10^6–10^7 s^{-1}),[6] the actual value is probably larger than that reported for the reaction of PTOA (Table II).
(24) Jensen, J. L.; Jencks, W. P. *J. Am. Chem. Soc.* **1979**, *101*, 1476. Douglas, K. T. *Acc. Chem. Res.* **1986**, *19*, 186.

NPTA;[5] i.e., the change of S^- by O^- in $T^{\pm}$ also enhances the nucleofugality of the amine from $T^{\pm}$. This can be explained by the same argument given above in relation to the expulsion of the leaving group of the substrate from $T^{\pm}$.[6,7]

The values of k_{-1} obtained in this study are similar to those in the same aminolysis of PDTA.[6] This is in contrast with the results obtained in the aminolyses of PA and PTA. The k_{-1} values determined from the coresponding empirical equations,[5,19] are larger for PA; i.e., the push provided by PhO in $T^{\pm}$ to expel a given amine is stronger than that exerted by PhS in the analogous $T^{\pm}$. Even for isobasic ArO and ArS groups the value of k_{-1} is larger for ArO.[5] These results indicate that the push provided by ArO or ArS from $T^{\pm}$ to expel an amine is much hindered when O^- is changed by S^- in $T^{\pm}$. This could be due to the fact that electron donation from ArO or ArS in the latter $T^{\pm}$ is delocalized significantly toward S^- instead of aiding the amine expulsion. This explanation is reasonable in view of the polarizability of the C–S^- bond discussed earlier.[22]

The above results indicate that the sensitivity of k_{-1} to the basicity of the leaving group, ArS or ArO, (β_{1g}) is nill or very small when the C–S^- bond is involved in $T^{\pm}$. This is confirmed by the similar k_{-1} values obtained in the aminolysis of PDTA[6] and NPDTA.[7] In contrast, a value of $\beta_{1g} = +0.4$ for k_{-1} has been reported in the aminolyses of oxyesters,[10] diaryl carbonates,[16] and *S*-aryl thioesters.[5]

Conclusions

(1) The same mechanism is observed in the aminolysis of PA, PDTA, and PTOA (described in eq 2 for PTOA); i.e., there is no change in mechanism when C=O of PA is replaced by C=S (in PTOA) or when PhS of PDTA is substituted by PhO (in PTOA).

(2) The values of both k_1 and k_2 (eq 2) for the reactions of secondary alicyclic amines with PTOA are smaller than those obtained in the same aminolysis of PA and PDTA. The value of k_{-1} for a given amine (eq 2) for the reactions of secondary alicyclic amines with PTOA is smaller than that obtained in the same aminolysis of PA, but it is similar to that found in the same aminolysis of PDTA.

(3) The Brönsted sensitivity of k_1 to the amine basicity, β_1(N), is similar for the aminolysis of PTOA, PA, and PDTA. The corresponding value for k_{-1}, β_{-1}(N), follows the sequence NPDTA < PA ≈ PTOA < PDTA. The Brönsted sensitivity of k_{-1} to the leaving group basicity, β_{-1}(lg), is very small (near zero) when the C=S group is present in the substrate. This is evidenced by the similar k_{-1} values obtained (for a given amine) in the aminolysis of PTOA, PDTA, and NPDTA. This is in contrast to the value $\beta_{-1}(lg) = +0.4$ found in the aminolysis of aryl acetates and aryl thioacetates, where the C=O group is involved in the substrate.

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