Kinetics and Mechanism of the Pyridinolysis of 2,4-Dinitrophenyl and 2,4,6-Trinitrophenyl *O*-Ethyl Dithiocarbonates

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The title reactions are subjected to a kinetic study in water, 25.0 °C, ionic strength 0.2 M (KCl). Under amine excess, pseudo-first-order rate coefficients are found, which are linearly related to the free amine concentration. No dependence of the slopes of these plots (k_N) on the pH values was observed. The Brönsted-type plots (log k_N vs pK_a of the pyridines) are biphasic with slopes $\beta_1 = 0.2$ (high pK_a) for both reaction series and $\beta_2 = 1.0$ and 0.9 (low pK_a) for the dinitro and the trinitro derivatives, respectively, and with the curvature center at pK_a = pK_a^0 = 6.9 and 5.6 for the dinitro and the trinitro compounds, respectively. These results can be explained by the formation of a zwitterionic tetrahedral intermediate ($T^{\pm}$) in a stepwise reaction. Comparison of these Brönsted-type plots with those in the reactions of the same substrates with secondary alicyclic amines shows that the latter amines are better nucleofuges from $T^{\pm}$ than isobasic pyridines. Comparison of the Brönsted-type plots for the dinitro and trinitro derivatives obtained in this work with those for the pyridinolysis of *S*-(2,4-dinitrophenyl) and *S*-(2,4,6-trinitrophenyl) *O*-ethyl thiocarbonates indicates that substitution of S^- by O^- in $T^{\pm}$ increases the amine/ArS^- nucleofugality ratio from $T^{\pm}$.

Introduction

Although the kinetics of the aminolysis of aryl esters and carbonates have been extensively studied and their mechanisms are well established,[1−4] those of the thioanalogues have been given less attention. Among the latter there are in the literature some mechanistic studies on the aminolysis of 4-nitrophenyl thionobenzoate,[5] *S*-(4-nitrophenyl) thioacetate,[6] and *S*-phenyl thiobenzoates and phenyl dithiobenzoates.[7]

We have recently investigated the mechanism of the reactions of secondary alicyclic amines with *S*-aryl dithioacetates[8] and *O*-ethyl *S*-aryl dithiocarbonates.[9,10] We have also kinetically studied the pyridinolysis of *S*-(2,4-dinitrophenyl) and *S*-(2,4,6-trinitrophenyl) *O*-ethyl thiocarbonates (or thiolcarbonates).[11] In some of these reactions the existence of a tetrahedral addition intermediate ($T^{\pm}$) was deduced from the biphasic Brönsted-type plots obtained.[9−11]

The object of this work is to shed more light into the mechanism of the aminolysis of dithiocarbonates and to investigate the influence of the nature of the amine on the mechanism and stability of $T^{\pm}$, by comparing the present reactions with those of the same substrates with secondary alicyclic amines.[10] Also of interest is to examine the influence of S^- in $T^{\pm}$ by comparison of the reactions of this work with the pyridinolysis of the corresponding dinitrophenyl and trinitrophenyl thiolcarbonates.[11]

Experimental Section

Materials. The substituted pyridines were purified as described,[12] and the substrates, *O*-ethyl 2,4-dinitrophenyl dithiocarbonate (DNPDTC) and *O*-ethyl 2,4,6-trinitrophenyl dithiocarbonate (TNPDTC), were prepared as reported.[10]

Kinetic Measurements. These were performed spectrophotometrically by following the substituted benzenethiolate anion release at 400 nm in a Perkin-Elmer Lambda 3 instrument. The reactions were started by addition of a stock solution (7−10 μL) of the substrate in acetonitrile into to 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 substrate concentration was $(4-6) \times 10^{-5}$ M.

All reactions were carried out under amine excess over the substrate. Pseudo-first-order rate constants (k_{obsd}) were found throughout from $\ln(A_\infty - A)$ vs time plots, where A_∞ and A are the absorbances at "infinity" and at variable times, respectively. The reactions of each amine were measured at three pH values, maintained constant during the reactions by partial acidification of the amine (in most cases) or by addition of an external buffer. The experimental conditions of the reactions and the values of k_{obsd} are shown in Tables 1 and 2.

Product Studies. The presence of 2,4-dinitro- or 2,4,6-trinitrobenzenethiolate anions as one of the products of the

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[1] Satterthwait, A. C.; Jencks, W. P. *J. Am. Chem. Soc.* **1974**, *96*, 7018.

[2] Gresser, M. J.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 6963, 6970.

[3] Fife, T. H.; Hutchins, J. E. C. *J. Am. Chem. Soc.* **1981**, *103*, 4194. Brunelle, D. J. *Tetrahedron Lett.* **1982**, *23*, 1739. Castro, E. A.; Gil, F. J. *J. Am. Chem. Soc.* **1977**, *99*, 7611. Castro, E. A.; Ibañez, F.; Lagos, S.; Schick, M.; Santos, J. G. *J. Org. Chem.* **1992**, *57*, 2691.

[4] Kovach, I. M.; Belz, M.; Larson, M.; Rousy, S.; Schowen, R. L. *J. Am. Chem. Soc.* **1985**, *107*, 7360. Neuvonen, H. *J. Chem. Soc., Perkin Trans. 2* **1987**, 159. Yoh, S.-D.; Kang, J.-K.; Kim, S.-H. *Tetrahedron* **1988**, *44*, 2167. Knowlton, R. C.; Byers, L. D. *J. Org. Chem.* **1988**, *53*, 3862. Castro, E. A.; Ureta, C. *J. Org. Chem.* **1990**, *55*, 1676. Koh, H. J.; Lee, H. C.; Lee, H. W.; Lee, I. *Bull. Korean Chem. Soc.* **1995**, *16*, 839.

[5] Campbell, P.; Lapinskas, B. A. *J. Am. Chem. Soc.* **1977**, *99*, 5378. Um, I.-H.; Kwon, H.-J.; Kwon, D.-S.; Park, J.-Y. *J. Chem. Res., Synop.* **1995**, 301.

[6] Um, I. H.; Choi, K. E.; Kwon, D. S. *Bull. Korean Chem. Soc.* **1990**, *11*, 362.

[7] Lee, I.; Shim, C. S.; Lee, H. W. *J. Chem. Res., Synop.* **1992**, 90. Oh, H. K.; Shin, C. H.; Lee, I. *Bull. Korean Chem. Soc.* **1995**, *16*, 657. Oh, H. K.; Shin, C. H.; Lee, I. *J. Chem. Soc., Perkin Trans. 2* **1995**, 1169.

[8] (a) Castro, E. A.; Ibáñez, F.; Santos, J. G.; Ureta, C. *J. Chem. Soc., Perkin Trans. 2* **1991**, 1919. (b) Castro, E. A.; Ibáñez, F.; Santos, J. G.; Ureta, C. *J. Org. Chem.* **1992**, *57*, 7024.

[9] Cabrera, M.; Castro, E. A.; Salas, M.; Santos, J. G.; Sepúlveda, P. *J. Org. Chem.* **1991**, *56*, 5324.

[10] Castro, E. A.; Ibáñez, F.; Salas, M.; Santos, J. G.; Sepúlveda, P. *J. Org. Chem.* **1993**, *58*, 459.

[11] Castro, E. A.; Pizarro, M. I.; Santos, J. G. *J. Org. Chem.* **1996**, *61*, 5982.

[12] Bond, P. M.; Castro, E. A.; Moodie, R. B. *J. Chem. Soc., Perkin Trans. 2* **1976**, 68.

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Table 1. Experimental Conditions and k_{obsd} Values for the Pyridinolysis of DNPDTC[a]

pyridine substituent	pH	F_N[b]	$10^2[N]_{tot}$/M[c]	$10^3\ k_{obsd}/s^{-1}$	no. of runs
4-dimethylamino	9.58	0.33	0.06–0.90	2.9–40	7
	9.88	0.50	0.05–0.50	3.6–33	5
	10.18	0.67	0.10–0.50	6.8–42	5
4-amino	9.07	0.33	0.12–0.85	2.2–15	5
	9.37	0.50	0.70–1.3	17–38	5
	9.67	0.67	0.55–1.5	22–45	5
3,4-dimethyl[d]	8.20	0.96	2.0–18	32–173	8
	8.50	0.98	3.0–17	38–183	7
	8.80	0.99	2.0–16	23–171	7
4-methyl	5.95	0.33	3.0–30	4.8–62	6
	6.25	0.50	3.0–30	15–95	7
	6.55	0.67	7.0–21	27–78	6
3-methyl	5.56	0.33	4.0–20	13–33	4
	5.86	0.50	5.0–30	16–53	4
	6.16	0.67	4.0–40	24–92	5
none[e]	7.00	0.98	25–75	53–85	6
	7.50	0.99	25–75	49–80	6
	8.00	1.00	20–70	36–66	6
3-carbamoyl[e]	7.00	1.00	20–70	1.2–1.5	6
	7.50	1.00	20–80	0.56–0.82	6
	8.00	1.00	20–80	0.37–0.57	6

[a] In aqueous solution at 25.0 °C, ionic strength 0.2 M (KCl). [b] Fraction of amine free base. [c] Concentration of total amine (free base plus protonated forms). [d] In the presence of borate buffer 5 × 10^{-3} M. [e] In the presence of phosphate buffer 5 × 10^{-3} M.

Table 2. Experimental Conditions and k_{obsd} Values for the Pyridinolysis of TNPDTC[a]

pyridine substituent	pH	F_N	$10^2[N]_{tot}$/M	$10^3\ k_{obsd}/s^{-1}$	no. of runs
4-dimethylamino	9.58	0.33	0.10–0.35	7.9–19	6
	9.88	0.50	0.10–0.60	8.5–46	6
	10.18	0.67	0.06–0.42	7.6–39	7
4-amino	9.07	0.33	0.15–0.65	2.9–13	6
	9.37	0.50	0.10–0.60	2.4–17	6
	9.67	0.67	0.15–0.65	4.7–24	4
3,4-dimethyl	6.47	0.33	0.10–1.3	1.4–14	6
	6.77	0.50	0.20–1.5	3.0–23	6
	7.07	0.67	0.68–1.1	13–22	6
4-methyl	5.95	0.33	2.0–20	7.2–72	6
	6.25	0.50	3.0–30	18–162	7
	6.55	0.67	7.0–21	46–151	7
3-methyl	5.56	0.33	3.0–30	8.7–79	7
	5.86	0.50	5.0–40	21–156	6
	6.16	0.67	4.0–40	25–217	7
none	5.67	0.67	2.5–15	6.9–31	5
	5.97	0.80	2.5–25	8.4–67	7
	6.32	0.90	2.5–25	9.1–83	7
3-carbamoyl[b]	4.90	0.97	2.5–25	1.1–4.2	6
	5.10	0.98	2.6–26	1.0–4.5	7
	5.30	0.99	2.5–25	1.1–4.3	5
3-chloro[c]	7.00	1.00	3.0–8.0	0.47–0.73	5
	7.50	1.00	3.0–8.0	0.36–0.73	6
	8.00	1.00	3.0–8.0	0.33–0.64	6

[a] Experimental conditions and symbols as in Table 1. [b] In the presence of acetate buffer 5 × 10^{-3} M. [c] In the presence of phosphate buffer 5 × 10^{-3} M.

reactions of DNPDTC and TNPDTC, respectively, was deduced by comparison of the UV–vis spectra at the end of some reactions with those of authentic samples of the substituted benzenethiols under the same experimental conditions.

The accumulation and later decomposition of an intermediate was observed in the reactions of DNPDTC with pyridine and nicotinamide. This was achieved by HPLC at 254 nm, using as eluant a solution of acetate buffer in methanol at pH 4.9. This intermediate could not be identified, but it is presumably 1-(ethoxythiocarbonyl)piridinium ion (reaction with pyridine) and 1-(ethoxythiocarbonyl)-3-carbamoylpyridinium ion (reaction with nicotinamide). A similar intermediate, 1-(methoxycarbonyl)pyridinium ion, was detected by UV spectrophotometry in the reaction of methyl chloroformate with pyridine.[12]

Table 3. Values of pK_a for Substituted Pyridinium Ions and k_N for the Pyridinolysis of DNPDTC and TNPDTC[a]

pyridine substituent	pK_a[b]	$k_N/s^{-1}\ M^{-1}$[c]	
		DNPDTC	TNPDTC
4-N(CH$_3$)$_2$	9.87	13	13
4-NH$_2$	9.37	4.8	5.5
3,4-(CH$_3$)$_2$	6.77	1.0	2.9
4-CH$_3$	6.25	0.55	1.1
3-CH$_3$	5.86	0.30	0.79
none	5.37	0.062	0.32
3-CONH$_2$	3.43	4.7 × 10^{-4}	0.014
3-Cl	2.97		0.006

[a] Both the pK_a and k_N values were obtained in aqueous solution at 25.0 °C, ionic strength 0.2 M (KCl). [b] Values taken from ref 13. [c] These values are subject to a standard deviation of ca. 10%.

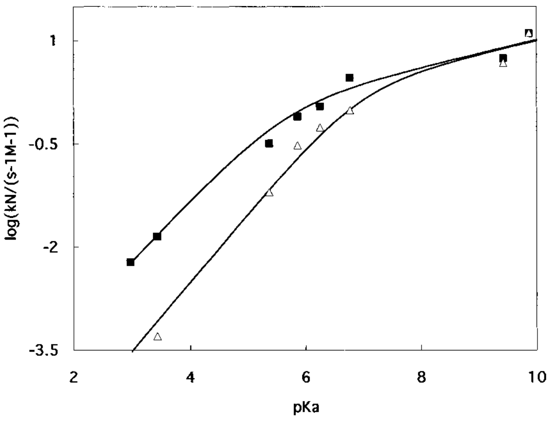

Figure 1. Brönsted-type plots obtained in the pyridinolysis of DNPDTC (△) and TNPDTC (■) in water, 25.0 °C, ionic strength 0.2 M (KCl).

Results and Discussion

The kinetic law obtained in the present reactions is given by eqs 1 and 2, where ArS$^-$ is the leaving group (2,4-dinitrobenzenethiolate or 2,4,6-trinitrobenzenethiolate anions), k_{obsd} is the pseudo-first-order rate constant, k_0 and k_N are the rate constants for hydrolysis and aminolysis of the substrate, respectively, and N and S represent the free amine and the substrate, respectively.

$$\frac{d[ArS^-]}{dt} = k_{obsd}[S] \qquad (1)$$

$$k_{obsd} = k_0 + k_N[N] \qquad (2)$$

The value of k_0 was negligible compared to that of k_N[N], except for the reactions of TNPDTC with 3-chloropyridine and those of DNPDTC with pyridine and nicotinamide.

The values of k_N were obtained as the slopes of plots of eq 2, i.e., k_{obsd} vs [N] at constant pH. The k_N values were independent of pH for all the reactions. These values are shown in Table 3, together with the pK_a values of the conjugate acids of the amines under the same experimental conditions of the kinetic measurements.[13]

With the k_N and pK_a values of Table 3, the Brönsted-type equation for the reactions under study was plotted (Figure 1). The lines in the plots were calculated by means of a semiempirical equation (eq 3, see derivation in the Appendix) based on the existence of a zwitterionic tetrahedral addition intermediate (T$^\pm$) on the reaction

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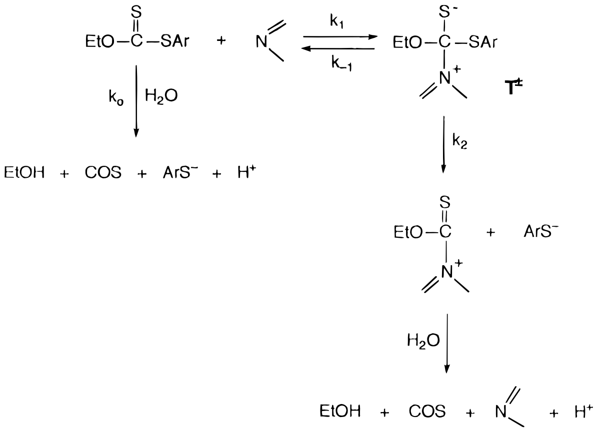
(13) Castro, E. A.; Ureta, C. *J. Chem. Soc., Perkin Trans. 2* **1991**, 63.

Scheme 1



path and a change in the rate-determining step from its decomposition to its formation as the basicity of the nucleophile (amine) increases.[1,2,9–13] In eq 3, β_1 and β_2

$$\log (k_N/k_N{}^0) = \beta_2(\mathrm{p}K_a - \mathrm{p}K_a{}^0) - \log \frac{1+a}{2}$$

$$\log a = (\beta_2 - \beta_1)(\mathrm{p}K_a - \mathrm{p}K_a{}^0) \qquad (3)$$

are the slopes at high and low pK_a values, respectively, and p$K_a{}^0$ and $k_N{}^0$ are the corresponding values for an amine at the center of the curvature. The Brönsted lines were calculated with the following parameters: $\beta_1 = 0.2$ for the reactions of both substrates, $\beta_2 = 1.0$ and 0.9 for DNPDTC and TNPDTC, respectively, log $k_N{}^0 = 0.078$ and p$K_a{}^0 = 6.9$ for the reactions of DNPDTC, and log $k_N{}^0 = -0.17$ and p$K_a{}^0 = 5.6$ for the pyridinolysis of TNPDTC.

The values of β_1 and β_2 are in accord to the corresponding values found in other similar aminolyses: the reactions of primary amines with aryl acetates,[1] quinuclidines with diaryl carbonates,[2] secondary alicyclic amines with 4-nitrophenyl, 2,4-dinitrophenyl and 2,4,6-trinitrophenyl *O*-ethyl dithiocarbonates,[9,10] pyridines with methyl chloroformate,[12] and pyridines and secondary alicyclic amines with 2,4-dinitrophenyl and 2,4,6-trinitrophenyl thiolacetates.[13]

According to the rate law and the Brönsted-type plots obtained in the present work, and the intermediate and product studies, we propose Scheme 1 as the most probable mechanism for the present reactions, where Ar is 2,4-dinitrophenyl or 2,4,6-trinitrophenyl, and $-\mathrm{N}=$ represents the substituted pyridine.

In Scheme 1, the k_1 step should be rate determining at high pK_a values, i.e., for amines such that $k_{-1} \ll k_2$. In this case $k_N = k_1$ and the Brönsted slope is β_1. On the other hand, the k_2 step should be rate limiting at low pK_a values where $k_{-1} \gg k_2$, and $k_N = K_1k_2$ ($K_1 = k_1/k_{-1}$). In this case the Brönsted slope is β_2. Near the center of the Brönsted curvature there is no clear rate-determining step and $k_N = k_1k_2/(k_{-1} + k_2)$. A nonlinear Brönsted-type relationship should occur in this pK_a region due to the sum of terms in the denominator of the k_N equation. At the very center of the Brönsted curvature, $k_{-1} = k_2$, i.e., a pyridine of pK_a = p$K_a{}^0$ should leave the tetrahedral intermediate at a rate equal to that of ArS$^-$.[2,9–13]

It can be seen in Figure 1 that the k_N values for the reactions of both substrates with the two most basic pyridines are very similar. This fact can be explained by steric hindrance of the second *o*-nitro group of TNPDTC to the rate-determining attack of these pyridines. This steric hindrance must be compensated by a larger electron withdrawal effect from the trinitrophenylthio group of TNPDTC relative to the dinitro analogue in DNPDTC. A similar situation occurs in the reactions of the same substrates with secondary alicyclic amines, where the steric hindrance of the reactions of the trinitro derivative is such that the k_N values are slightly smaller for TNPDTC compared to the dinitro derivative, when amine attack is rate determining.[10] Also, the rate constant for attack (k_1) of substituted quinuclidines on 2,4-dinitrophenyl phenyl carbonate is smaller than that of the same amines on 3,4-dinitrophenyl phenyl carbonate,[2] and this has been attributed to a steric effect by the *o*-nitro in the former substrate.[2]

Figure 1 shows that the reactivity of TNPDTC is higher than that of DNPDTC when the k_2 step of Scheme 1 is rate determining. In this case $k_N = K_1k_2$ (see above). This higher reactivity of TNPDTC should be due to a much larger k_2 value and a similar K_1 ($=k_1/k_{-1}$) value for both reactions; this can be explained as follows. A much larger k_2 is expected for TNPS$^-$ leaving relative to DNPS$^-$ from T$^\pm$ of Scheme 1, due to the much lower basicity of the former anion (pK_a of TNPSH and DNPSH are 1.4 and 3.4, respectively).[13] A similar K_1 is reasonable for both reactions since the k_1 values are similar (see above), and the values of k_{-1} for both reactions should be alike in view that the higher basicity of DNPS$^-$ (stronger electronic push) compared to TNPS$^-$ should be compensated by a stronger steric push by TNPS, resulting in a similar push from both groups in T$^\pm$ to expel the amine.[2]

The fact that the p$K_a{}^0$ value is lower for the TNPDTC reactions compared to DNPDTC (Figure 1) is in agreement with the hypothesis of the tetrahedral intermediate. The stepwise reactions exhibit a decrease of p$K_a{}^0$ as the leaving group of the substrate decreases its basicity.[1,2,9,10,13–15] This is due to the larger k_2 for the less basic nucleofuge which needs a less basic amine (lower pK_a) to satisfy the relation $k_2 = k_{-1}$.[2]

Nonlinear Brönsted-type plots were also found in the reactions of DNPDTC and TNPDTC with secondary alicyclic amines in water.[10] These were explained through the presence of a zwitterionic tetrahedral intermediate on the reaction pathway and a change in the rate-determining step.[10] The p$K_a{}^0$ values are 9.2 and 8.4 for the aminolysis of DNPDTC and TNPDTC, respectively.[10]

According to the hypothesis of the tetrahedral intermediate it can be shown that the value of p$K_a{}^0$ is linearly related to the log of the k_{-1}/k_2 ratio, through eq 4.[14,16]

$$\log(k_{-1}/k_2) = (\beta_2 - \beta_1)\,(\mathrm{p}K_a{}^0 - \mathrm{p}K_a) \qquad (4)$$

Since for the reactions of DNPDTC and TNPDTC with secondary alicyclic amines, the values of β_2 and β_1 are 0.8 and 0.2, respectively,[10] very similar to those for the pyridinolysis of these substrates, the value of p$K_a{}^0$ in eq 4 is decisive in assessing the relative magnitude of the k_{-1}/k_2 ratios when comparing the reactions of a given substrate with pyridines and alicyclic amines. Since the p$K_a{}^0$ values for the aminolyses of DNPDTC and TNPDTC are greater than those for the corresponding pyridinolyses, it follows from eq 4 that for a given secondary

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

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

(16) According to ref 14, d[log(k_2/k_{-1})] = ($\beta_2 - \beta_1$) d(pK_a). Integrating this expression between $k_2/k_{-1} = 1$ at the corresponding pK_a = p$K_a{}^0$, and k_2/k_{-1} at the corresponding pK_a, one gets log(k_2/k_{-1}) = ($\beta_2 - \beta_1$)(pK_a − p$K_a{}^0$). Multiplying this by −1, one obtains eq 4.

alicyclic amine the k_{-1}/k_2 ratio is greater compared to that of an isobasic pyridine.

It is known that the value of the rate constant for expulsion of the nucleofuge from a zwitterionic tetrahedral intermediate (k_2) is not significantly dependent on the basicity or nature of the amino moiety.[1,2] This is due to the lack of an electron pair on the nitrogen atom of the cationic amino group in the zwitterionic intermediate ($T^{\pm}$), which prevents a "push" from this moiety to expel the leaving group.[1,2]

Since the k_{-1}/k_2 ratio is larger for a secondary alicyclic amine relative to an isobasic pyridine and since k_2 is independent of the amine nature it follows that k_{-1} is larger for the former amine, i.e., the secondary alicyclic amines are better nucleofuges from $T^{\pm}$ than isobasic pyridines.

The above is in agreement with the results of Gresser and Jencks on the aminolysis of diaryl carbonates: quinuclidines are better nucleofuges from $T^{\pm}$ than isobasic pyridines.[2] Also in accord is the finding that the pK_a^0 values for the reactions of 2,4-dinitrophenyl and 2,4,6-trinitrophenyl thiolacetates with secondary alicyclic amines are larger than those for the corresponding reactions of pyridines with the same substrates;[13] i.e., the former amines are expelled faster than isobasic pyridines from the tetrahedral intermediate formed in these reactions.[13]

In the pyridinolysis of *S*-(2,4-dinitrophenyl) and *S*-(2,4,6-trinitrophenyl) *O*-ethyl thiocarbonates (DNPTC and TNPTC, respectively), biphasic Brönsted-type plots were found with the center of curvature at $pK_a = pK_a^0 = 8.6$ and 7.3, respectively.[11] Comparison of these values with those obtained in this work for DNPDTC and TNPDTC, respectively, indicates that, according to eq 4, the k_{-1}/k_2 ratio for a given pyridine is larger for a thiolcarbonate relative to the corresponding dithiocarbonate. In other words, substitution of S^- by O^- in $T^{\pm}$ increases the k_{-1}/k_2 ratio for a given pyridine. Since it has been found in similar reactions that the above substitution enlarges both k_{-1} and k_2,[8,17] it means that the larger k_{-1}/k_2 ratio for thiolcarbonates relative to that for dithiocarbonates is due to a larger k_{-1} and less large k_2 for the former substrate. That is, the greater ability of O^- in $T^{\pm}$, compared to S^-, to form a double bond and expel a leaving group[18] favors amine expulsion from $T^{\pm}$ relative to $DNPS^-$ or $TNPS^-$ leaving.

In the aminolysis (secondary alicyclic amines) of 4-nitrophenyl dithioacetate a pK_a^0 value of ca. 9 can be calculated on the basis of the k_{-1} values and the k_2 value found.[8b,19] The experimental pK_a^0 value is 10.5 for the biphasic Brönsted-type plot obtained in the same aminolysis of *S*-(4-nitrophenyl) thioacetate.[14] The larger pK_a^0 for the reactions of the carbonyl derivative is in line with our results. Similarly, the linear Brönsted-type plot found in the aminolysis of *S*-phenyl thioacetate,[14] with an estimated $pK_a^0 = 12.2$,[13] shows a larger pK_a^0 than that calculated for the same aminolysis of phenyl dithioacetate, pK_a^0 ca. 10. [8a] Also, the biphasic Brönsted-type plots obtained in the reactions of secondary alicyclic amines with *O*-ethyl 4-nitrophenyl dithiocarbonate[9] and *O*-ethyl *S*-(4-nitrophenyl) thiocarbonate[20] show the same feature, the latter exhibiting a larger pK_a^0 (=10.7) than the former ($pK_a^0 = 9.6$). A last example is the linear Brönsted-type plot found in the aminolysis of 4-nitrophenyl benzoate ($pK_a^0 > 11$) compared to the biphasic plot obtained in the same reactions of 4-nitrophenyl thionobenzoate, with pK_a^0 ca. 9.2.[5]

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Appendix

Equation 3 was deduced as follows: Applying the steady state condition to $T^{\pm}$ in Scheme 1, eq 1a results.

$$k_N = k_1k_2/(k_{-1} + k_2) \qquad (1a)$$

At the center of the Brönsted curvature $k_{-1} = k_2$; therefore, $k_N^0 = k_1^0/2$ is obtained, where the 0 superscripts denote the k values which correspond to a pyridine of $pK_a = pK_a^0$. At the center of the Brönsted plot the straight lines at low and high pK_a intercept, therefore $k_1^0k_2^0/\,k_{-1}^0 = k_1^0$, which together with the latter equation yields eq 2a.

$$k_1^0k_2^0/k_{-1}^0 = k_1^0 = 2k_N^0 \qquad (2a)$$

Rearranging and applying logarithms to eq 1a, eq 3a results.

$$\log k_N = \log (k_1\, k_2\, /\, k_{-1}) - \log ((k_2\, /\, k_{-1}) + 1) \qquad (3a)$$

On the other hand,

$$d[\log(k_1k_2/k_{-1})] = \beta_2\ d(pK_a) \qquad (4a)$$

Integrating this expression between $k_1^0k_2^0/k_{-1}^0$ and k_1k_2/k_{-1}, and between the corresponding pK_a^0 and pK_a, and taking into account eq 2a, the following equation is obtained:

$$\log(k_1k_2/k_{-1}) = \log k_N^0 + \beta_2(pK_a - pK_a^0) + \log 2 \qquad (5a)$$

From eq 4a, and knowing that $d(\log k_1)/d(pK_a) = \beta_1$, one gets the expression $d[\log(k_2/k_{-1})] = (\beta_2 - \beta_1)\ d(pK_a)$. Integrating this from 1 to k_2/k_{-1} and from pK_a^0 to pK_a eq 6a is obtained.

$$k_2/k_{-1} = 10^{(\beta 2-\beta 1)(pK_a - pK_a^0)} \qquad (6a)$$

By replacing eqs 5a and 6a in eq 3a, the final equation (eq 3 of the text) results.

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(17) Castro, E. A.; Ibáñez, F.; Santos, J. G.; Ureta, C. *J. Org. Chem.* **1993**, *58*, 4908.

(18) 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.

(19) From Table II of ref 8b, the value of k_{-1} which equals k_2 ($=3 \times 10^7\ s^{-1}$) is for an amine (hypothetical) of pK_a ca. 9.2.

(20) Castro, E. A.; Cubillos, M.; Santos, J. G. *J. Org. Chem.* **1994**, *59*, 3572.