Nucleophilic Substitution Reactions of Aryl Thiophene-2-carbodithioates with Pyridines in Acetonitrile

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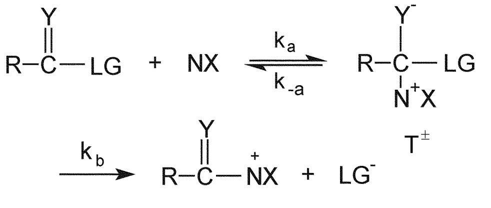
The kinetics of reactions between Z-aryl thiophene-2-carbodithioates and X-pyridines in acetonitrile at 60.0 °C have been investigated. The Brönsted plots obtained for the pyridinolysis of aryl thiophene-2-carbodithioates are curved, with the center of curvature at pK_a ~ 5.2 (pK_a^o). The Brönsted plots for these nucleophilic reactions show a change in slope from a large ($\beta_X \cong 0.78$-0.87) to a small ($\beta_X \cong 0.33$-0.35) value, which can be attributed to a change in the rate-determining step from breakdown to formation of a zwitterionic tetrahedral intermediate in the reaction path as the basicity of the pyridine nucleophile increases. A clear-cut change in the cross-interaction constants, ρ_{XZ}, from +0.92 to -0.23 supports the proposed mechanistic change. The breakpoint at pK_a = 5.2 for R = thiophene ring in the present work is in agreement with those for the pyridinolysis of R = Me and 2-furyl, and attests to the insignificant effects of acyl group, R, on the breakpoint.

Key Words : Nucleophilic substitution reaction, Pyridinolysis, Cross-interaction constant, Zwitterionic tetrahedral intermediate, Stepwise mechanism

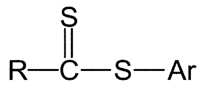
Introduction

The aminolysis of carbonyl and thiocarbonyl esters has been a subject of considerable interest in mechanistic as well as synthetic organic chemistry.[1] The rate- determining step and transition state (TS) structure of acyl transfer reactions in general have been found to depend on the nucleophile, leaving and nonleaving group, and solvent.[1] In the aminolysis of aryl esters and carbonates, a biphasic dependence of the rate on the amine basicity is often observed showing a change of slope from a large ($\beta_{nuc} \geq 0.8$) to a small ($\beta_{nuc} \cong$ 0.1-0.3) value at pK_a^o, where the amine (XN) and leaving group (LG^-) have the same expulsion rates from a zwitterionic tetrahedral intermediate, $T^\pm$. This has been attributed to a change in the rate-limiting step from breakdown to formation of $T^\pm$ as the basicity of the amine increases. The break at pK_a^o has been interpreted as a consequence of a change in the rate-limiting step from leaving group expulsion (k_b) from a tetrahedral intermediate, $T^\pm$, with less basic amines to nucleophilic attack (k_a) with more basic amines, eq. (1), where $k_N = (k_a/k_{-a})k_b = Kk_b$.



(1)

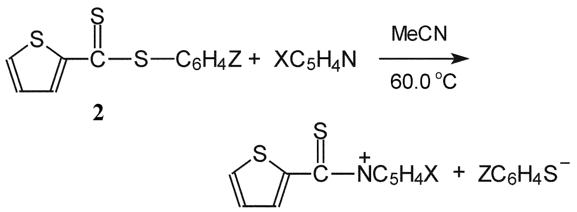
The aminolysis of dithio esters, **1**, has been reported in water[1c,2] and in acetonitrile[3] with various amines, *e.g.*, benzylamines, anilines, alicyclic secondary amines, pyridines, etc. For example, the aminolysis of dithio esters with benzylamines[3ce] in acetonitrile exhibited rather high pK_a^o values (> 9.0) whereas that with pyridines[3g-h] gave low pK_a^o values (≤ 5.0). On the other hand, our recent results on the pyridinolysis of aryl dithioacetates,[3h] R = Me in **1**, and aryl furan-2-carbodithioates,[3g] R = C_4H_4O in **1**, in acetonitrile at 60.0 °C indicated that the effect of the acyl group, R, on the pK_a^o value is insignificant with a similar pK_a^o value of 5.2. This means that in the acyl group transfer reactions, the breakpoint, pK_a^o, in a biphasic plot of the rate vs. basicity of amine depends on the nucleophile and leaving group, but seems practically independent of the acyl group. This is quite plausible since pK_a^o depends on the pK_a values of the nucleophile (amine) and leaving group but should be independent of the acyl group.



$$R-\overset{S}{\overset{\|}{C}}-S-Ar$$

1

In the present work, we report the result of kinetic studies on the pyridinolysis of aryl thiophene-2-carbodithioates in acetonitrile at 60.0 °C, eq. (2). The aim is to complete



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(2)

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X = 4-NH_2, 4-MeO, 4-Me, 3-Me, 4-$C_6H_4CH_2$, H, 3-Ph,
3-MeCO, 3-Cl, 4-MeCO and 4-CN
Z = 4-Me, H, 4-Cl and 4-Br

the previous studies[4] on the aminolysis mechanism of **2** and to further clarify the influence of the amine nature on the pK_a^o value. As an additional criterion for the elucidation of the mechanism, we determined the cross-interaction constants,[5] ρ_{XZ}, in eqs 3 where X and Z denote substituents in the pyridine nucleophile and the leaving group, respectively.

$$\log(k_{XZ}/k_{HH}) = \rho_X\sigma_X + \rho_Z\sigma_Z + \rho_{XZ}\sigma_X\sigma_Z \qquad (3a)$$

$$\rho_{XZ} = \partial\rho_Z/\partial\sigma_X = \partial\rho_X/\partial\sigma_Z \qquad (3b)$$

Results and Discussion

The reactions in the present work followed the rate law given by eqs. (4) and (5), where S and Py represent the substrate and pyridine nucleophile, respectively. The reactions

$$\text{Rate} = k_{obsd}\,[S] \qquad (4)$$

$$k_{obsd} = k_N\,[Py] \qquad (5)$$

were run under pseudo-first-order condition with a large excess of pyridine nucleophiles. The values of second-order rate constant, k_N, were obtained as the slopes of plots of k_{obsd} against [Py], and are summarized in Table 1

Using the k_N and pK_a values in Table 1, the Brönsted plots for the reactions under study were obtained as shown in Figure 1. The slopes ($\beta_X = \beta_{nuc}$) are shown in Table 1, where the Hammett reaction constants, ρ_X (= ρ_{nuc}) and ρ_Z (= ρ_{lg}), and the cross-interaction constant, ρ_{XZ}, are also presented. We note that the Brönsted plots are biphasic with a change in the slope. For Z = H, the slope changes from β_X = 0.87 to 0.33 at pK_a^o = 5.2 as the basicity of pyridine increases (see Figure 1). This breakpoint agrees with that calculated by means of a semiempirical equation derived by Castro *et al.*[6] The values of b_X are in accord with the corresponding values

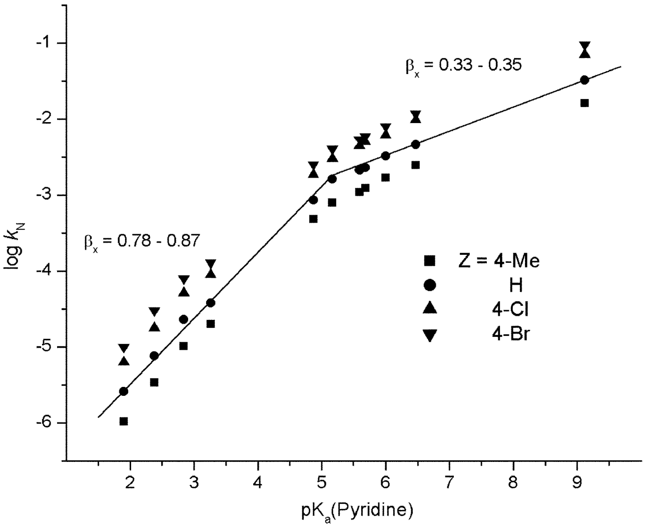

Figure 1. Brönsted plot (β_X) for the reactions of Z-phenyl thiophene-2-carbodithioates with X-pyridines in acetonitrile at 60.0 °C.

Table 1. The Second Order Rate Constants, k_N ($\times 10^4$ M^{-1} s^{-1}), and Selectivity Parameters,[a] ρ_X, ρ_Z, ρ_{XZ}, β_X, for the Reaction of Z-Phenyl Thiophene-2-carbodithioates with X-Pyridines in Acetonitrile at 60.0 °C

X	pK_a	Z				ρ_Z^h
		4-CH_3	H	4-Cl	4-Br	
4-NH_2	9.12	162	323	700	934	1.75 ± 0.17
4-CH_3O	6.47	24.2	45.6	97.5	117	1.61 ± 0.10
4-CH_3	6.00	16.8	32.0	61.2	79.1	1.54 ± 0.16
3-CH_3	5.68	12.1	22.4	49.5	58.6	1.63 ± 0.10
4-$C_6H_5CH_2$	5.59	10.9	21.2	43.9	53.5	1.62 ± 0.12
H	5.17	7.83	16.0	30.0	39.9	1.60 ± 0.18
3-C_6H_5	4.87	4.76	8.38	18.5	24.9	1.66 ± 0.19
3-CH_3CO	3.26	0.195	0.372	0.875	1.27	1.86 ± 0.23
3-Cl	2.84	0.102	0.228	0.512	0.793	1.99 ± 0.27
4-CH_3CO	2.38	0.0335	0.0752	0.176	0.297	2.10 ± 0.32
4-CN	1.90	0.0103	0.0255	0.0617	0.0983	2.19 ± 0.29
$\rho_X^{b,c}$		-1.96 ± 0.07	-1.97 ± 0.08	-2.03 ± 0.10	-2.06 ± 0.10	$\rho_{XZ}^{b,i}$ = -0.23
$\beta_X^{b,d}$		0.33 ± 0.01	0.33 ± 0.01	0.34 ± 0.01	0.35 ± 0.01	
$\rho_X^{e,f}$		-4.51 ± 0.22	-4.34 ± 0.21	-4.22 ± 0.21	-4.07 ± 0.18	$\rho_{XZ}^{e,j}$ = +0.92
$\beta_X^{e,g}$		0.87 ± 0.02	0.84 ± 0.04	0.81 ± 0.02	0.78 ± 0.02	

[a]The values were taken from C. Hansch, A. Leo, and R. W. Taft, *Chem. Rev.* **1991**, *91*, 165. The b_X value were determining using pK_a values in H_2O. Justification for this proedure is provided in ref 6. The pK_a values of pyridine in water at 25 °C were taken from: (a) Albert, A.; Serjeant, E. P. *The determination of Ionization Constants*; 3nd ed.; Chapman and Hall: New York, 1984; pp 154-155. (b) Dean, J. A. *Handbook of Organic Chemistry*; McGraw-Hill: New York, 1987; Chapter 8. (c) Fischer, A.; Galloway, J. A.; Vaughan, J. *J. Chem. Soc.* **1964**, 3591. (d) The pk_a values of X = 3-C_6H_5 and X = 4-CH_3CO were taken from ref 18. [b]For X = 4-NH_2, 4-CH_3O, 4-CH_3, 3-CH_3, 4-$C_6H_5CH_2$, H. [c]Correlation coefficients are better than 0.996 in all cases. [d]Correlation coefficients are better than 0.998 in all cases. [e]For [c]X = H, 3-C_6H_5, 3-CH_3CO, 3-Cl, 4-CH_3CO, 4-CN. [f]Correlation coefficients are better than 0.995 in all cases. [g]Correlation coefficients are better than 0.997 in all cases. [h]Correlation coefficients are better than 0.977 in all cases. [i]Correlation coefficient is 0.991. [j]Corelation coefficient is 0.994.

found in other similar aminolysis reactions: the aminolysis of aryl dithioacetates with anilines and with N,N-dimethylanilines at 50.0 °C in acetonitrile gave β_X = 0.84 and 0.85 (for Z = H), respectively.[7] The β_X values at low pK_a values for the pyridinolysis of 2,4-dinitrophenyl and 2,4,6-trinitrophenyl O-ethyl thiolcarbonates in water were 0.9 and 0.8 with pK_a^o = 8.6 and 7.3, respectively,[6] and that for 4-nitrophenyl O-ethyl thiolcarbonate in the whole pK_a range (pK_a = 3.43-9.87) was β_X = 0.8.[6] Similarly, for the pyridinolysis of 2,4-dinitrophenyl and 2,4,6-trinitrophenyl thiolacetates in water, the β_X values were 0.85 and 0.80 with pK_a^o = 6.6 and 4.9, respectively, at 25 °C.[8]

On the basis of the biphasic Brönsted plots and the rate law obtained in the present work, we propose the reaction shown in eq. (1), where R = thiophene ring, Y = S, and amine = pyridine, as the most probable mechanism for the present reactions.

In this mechanism for pyridines of high pK_a values, $k_{-a} << k_b$ so that k_a step is the rate-determining step, *i.e.*, $k_N = k_a$, with a smaller Brönsted slope β_X (0.33-0.35). On the other hand, at low pK_a values where $k_{-a} >> k_b$ and $k_N = (k_a/k_{-a})k_b = Kk_b$, the k_b step should be rate limiting with a steeper Brönsted slope β_X (0.78-0.87). At the center of the Brönsted curvature, $k_{-a} = k_b$, a pyridine with pK_a = pK_a^o (5.2) has the same leaving ability from the tetrahedral intermediate, $T^{\pm}$, as that of the leaving group ArS^-.

The low pK_a^o (~5.2) obtained in this work for the dithio compound (Y = S) is in contrast to the much higher pK_a^o value (>9.6) observed for the corresponding thiol series (Y = O),[9] for which the rate-limiting expulsion of ArS^- from the tetrahedral intermediate, $T^{\pm}$, (with β_X = 1.3-1.6) can be predicted even at a higher pK_a range (p$K_a \cong$ 9.1-9.6). This may be due to the greater nucleofugality of benzylamines relative to pyridines and also partly due to the change of Y = S to Y = O. Similarly, the depression of pK_a^o has been reported for Y = S relative to the corresponding Y = O series: for the aminolysis of S-phenyl thioacetate, the estimated pK_a^o was 12.2, which is larger than that calculated for the same aminolysis of phenyl dithioacetate, p$K_a^o \cong$ 10.[10] For the aminolysis of 4-nitrophenyl O-ethyl dithiocarbonate and S-(4-nitrophenyl) O-ethyl thiocarbonates, the pK_a^o values are 9.6 and 10.7, respectively.[11] Again, for the aminolysis of 4-nitrophenylbenzoate and the corresponding thionobenzoate, the reported values were pK_a^o > 11 and 9.2 respectively.[12] These examples of lower pK_a^o values with Y = S than with Y = O clearly support the contention that the tetrahedral intermediate with Y = S, $T^{\pm}$ (S), is more stable or that k_{-a} and k_b are smaller than those with Y = O, $T^{\pm}$ (O). The decrease in k_{-a} is, however, greater than that in k_b.

The size of ρ_Z in Table 1 also reflects the mechanistic change. The magnitudes of ρ_Z change from larger values, ρ_Z = 1.9-2.2, for less basic pyridines to smaller values, $\rho_Z \cong$ 1.6 for more basic pyridines, which is in agreement with the decrease in bond cleavage a the rate-determining step switches from breakdown to formation of the intermediate. Such decrease in the magnitude of the ρ_Z values from large (ρ_Z = 3.0) to small values (ρ_Z = 2.3) with the mechanistic change is also reported in the pyridinolysis of aryl dithioacetates.[13] A rough estimate[13] of the $\beta_Z(=\beta_{lg})$ values shows a decrease from $\beta_Z \cong$ -0.5 to -0.3 at the breakpoint in agreement with the change in the rate-determining step.

Table 2. Activation Parameters[a] for the Reactions of Z-Phenyl Thiophene-2-carbodithioates with X-Pyridines in Acetonitrile

X	Z	t (°C)	k_N ($\times 10^4$ M^{-1} s^{-1})	$\Delta H^{\neq}$ (kcal mol^{-1})	$-\Delta S^{\neq}$ (cal mol^{-1} K^{-1})
4-CH_3	4-CH_3	60.0	16.8	6.1	53
		50.0	12.1		
		40.0	8.69		
4-CH_3	4-Br	60.0	79.1	6.1	50
		50.0	57.3		
		40.0	41.3		
3-Cl	4-CH_3	60.0	0.102	6.3	62
		50.0	0.0729		
		40.0	0.0520		
3-Cl	4-Br	60.0	0.793	6.4	68
		50.0	0.568		
		40.0	0.403		

[a] Calculated by the Eyring equation. The maximum errors calculated (by the method of K. B. Wiberg, Physical Organic Chemistry, Wiley, New York, 1964, p 378.) are ± 0.6 kcal mol^{-1} and ± 2 e.u. for $\Delta H^{\neq}$ and $\Delta S^{\neq}$, respectively.

There is a clear-cut change in the ρ_{XZ} value (Table 1) from a large positive value (ρ_{XZ} = +0.92) for the rate-limiting expulsion of the ArS^- group from the intermediate, $T^{\pm}$, with the weakly basic pyridines (X = H–4-CN) to a small negative value (ρ_{XZ} = -0.23) for the rate-limiting formation of $T^{\pm}$ with the more basic pyridines (4-NH_2–H). Thus, on the basis of the cross-interaction constants, ρ_{XZ}, the mechanistic change is more clearly defined.[14] Similar changes in the cross-interaction constants accompanying mechanistic changes have been observed within a series of nucleophiles used, especially pyridines[15] since a biphasic dependence of the rate upon the basicity of pyridines is often obtained.

The activation parameters, $\Delta H^{\neq}$ and $-\Delta S^{\neq}$, for the pyridinolysis of **2** are shown in Table 2. Both the $\Delta H^{\neq}$ and -$\Delta S^{\neq}$ values are rather smaller for more basic pyridine (X = 4-CH_3) than less basic pyridine (X = 3-Cl), albeit the differences are small but significant enough to be over the error limits. These trends are in accord with the breakdown step (for X = 3-Cl) requiring larger energy and lower (more negative) entropy in the transition state due to bond cleavage to the two ionic products, eq. (2).

Lastly, examination of the trends of changes in k_N, ρ_X (β_X) and ρ_Z in Table 1 shows that the fast rate ($\delta k_N > 0$) is invariably accompanied by a smaller magnitude of selectivity parameters, $\delta\beta_X < 0$, $\delta\rho_Z < 0$ and $\delta\,|\rho_X| < 0$, *i.e.*, the reactivity-selectivity principle (RSP)[16] holds. The adherence of the rate data to the RSP constitutes another mechanistic criterion for the stepwise mechanism with rate-limiting breakdown of the intermediate,[17] $T^{\pm}$, and provides an additional support for our proposed mechanism.

In summary, the rates of the pyridinolysis of aryl dithiomethylacetates in acetonitrile show a biphasic dependence on the basicity of the pyridine nucleophiles. The slope of the

Brönsted plot changes from a large ($\beta_X = \beta_{nuc} \cong 0.78\text{-}0.87$) to a small ($\beta_X = 0.33\text{-}0.35$) value at $pK_a^o \cong 5.2$ as the basicity of pyridine increases. This change is accompanied not only by a decrease in the magnitude of the Hammett reaction constant from $\rho_X = \rho_{nuc} = -4.1$ to -4.5 to $\rho_X = -2.0$ to -2.1 but also by a change of the cross-interaction constant ρ_{XZ} from a large positive (=0.92) to a small negative (=-0.23) value. These results are consistent with a change in the rate-determining step from breakdown to formation of a tetrahedral intermediate. This mechanistic change is also supported by a change from adherence to failure of the RSP as the basicity of the pyridine nucleophile increases.

Experimental Section

Materials. GR acetonitrile was used after three distillations. The pyridine nucleophiles, GR, were used without further purification.

Substrates. Preparations and analytical data are reported elsewhere.[3a]

Kinetic Measurement. Rates were measured conductometrically in acetonitrile. The conductivity bridge used in this work was a homemade computer-automatic A/D converter conductivity bridge. Pseudo-first-order rate constants, k_{obsd}, were determined by the Guggenheim method with large excess of pyridine. Second order rate constants, k_N, were obtained from the slope of a plot of k_{obsd} vs. [Py] with more than five concentrations of pyridine. The k_N values in Table 1 are the averages of more than three runs and were reproducible to within ± 3%.

Product Analysis. The substrate *p*-bromophenyl thiophene-2-carbodithioate (0.05 mole) was reacted with excess picoline (0.5 mole) with stirring for more than 15 half-lives at 60.0 ^oC in acetonitrile. The salt was filtered and solvent was removed from the precipitate. Analysis of the product gave the following results.

$(C_4H_3SC(=S)NC_5H_4\text{-}p\text{-}CH_3)^+(4\text{-}BrC_6H_4S)^-$: m.p. 82-84 ^oC; ^1H NMR (400 MHz, $CDCl_3$), δ 2.18 (3H, s, CH_3), 6.38-7.25 (3H, m, thiophene), 7.30 (2H, dd, phenyl), 7.41 (2H, d, pyridine), 7.58 (2H, dd, phenyl), 8.47 (2H, d, pyridine); ^{13}C NMR (100.4 MHz, $CDCl_3$), δ 232.8 (C=S), 145.2, 136.5, 135.2, 133.4, 132.2, 129.5, 120.1, 112.8, 22.8 (CH_3); ν_{max} (KBr), 1205 (C=S), 813 (C-H, pyridine), 808 (C-H, phenol), 1558, 1442 (C=C, phenyl), MS *m*/z 406 (M^+). Anal. Calcd for $C_{17}H_{14}BrNS_3$: C, 50.0: 3.50. Found; 50.2; H, 3.52.

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