# 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 $pK_a \sim 5.2$ ($pK_n^o$). 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, $\rho_{XZ}$, 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, $T^\mp$. This has been attributed to a change in the rate-limiting step from breakdown to formation of $T^\mp$ 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, $T^\mp$, with less basic amines to nucleophilic attack ($k_a$) with more basic amines, eq. (1), where $k_N = (k_a/k_{-a})k_b = Kk_b$.
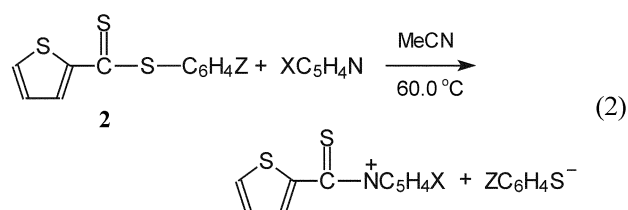
R—C(=Y)—LG + NX ⇌ (k_a / k_{-a}) R—C(LG)(Y⁻)—N⁺X

T⁻

→(k_b) R—C(=Y)—N⁺X + LG⁻    T⁺    (1)
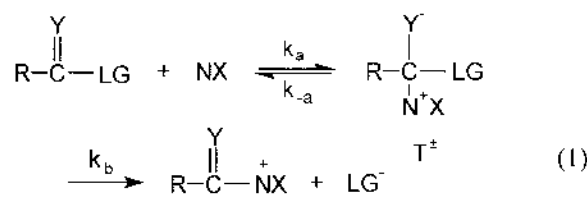
The aminolysis of dithio esters, **1**, has been reported in water[1c,2] and in acetonitrile[3] with various amines, *e.g.*,

benzylamines, anilines, alicyclic secondary amines, pyridines, etc. For example, the aminolysis of dithio esters with

$$R\text{—}\overset{\displaystyle S}{\overset{\|}{C}}\text{—}S\text{—}Ar$$

**1**
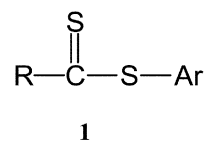
benzylamines[3a,e] in acetonitrile exhibited rather high $pK_a^o$ values ($> 9.0$) whereas that with pyridines[3g-h] gave low $pK_a^o$ values ($\leq 5.0$). On the other hand, our recent results on the pyridinolysis of aryl dithioacetates,[3h] R = Me in **1**, and aryl furan-2-carbodithioates,[3g] R = C₄H₃O 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.

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

$$\text{(thiophene)}\text{—}\overset{\displaystyle S}{\overset{\|}{C}}\text{—}S\text{—}C_6H_4Z + XC_5H_4N \xrightarrow[\text{60.0 °C}]{\text{MeCN}}$$

**2**

$$\text{(thiophene)}\text{—}\overset{\displaystyle S}{\overset{\|}{C}}\text{—}\overset{+}{N}C_5H_4X + ZC_6H_4S^-$$

(2)

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X = 4-NH₂, 4-MeO, 4-Me, 3-Me, 4-C₆H₄CH₂, 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 $pK_a^\circ$ value. As an additional criterion for the elucidation of the mechanism, we determined the cross-interaction constants,[5] $\rho_{XZ}$, 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

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

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

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
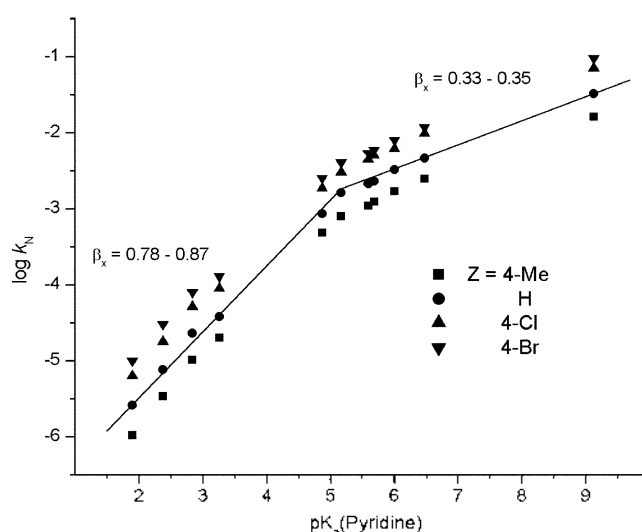


**Figure 1.** Brönsted plot ($\beta_X$) for the reactions of Z-phenyl thiophene-2-carbodithioates with X-pyridines in acetonitrile at 60.0 °C.

the Hammett reaction constants, $\rho_X$ (= $\rho_{nuc}$) and $\rho_Z$ (= $\rho_{lg}$), and the cross-interaction constant, $\rho_{XZ}$, are also presented. We note that the Brönsted plots are biphasic with a change in the slope. For Z = H, the slope changes from $\beta_X = 0.87$ to 0.33 at $pK_a^\circ = 5.2$ 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

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

| X | p$K_a$ | Z | | | | $\rho_Z^h$ |
|---|---|---|---|---|---|---|
| | | 4-CH₃ | H | 4-Cl | 4-Br | |
| 4-NH₂ | 9.12 | 162 | 323 | 700 | 934 | 1.75 ± 0.17 |
| 4-CH₃O | 6.47 | 24.2 | 45.6 | 97.5 | 117 | 1.61 ± 0.10 |
| 4-CH₃ | 6.00 | 16.8 | 32.0 | 61.2 | 79.1 | 1.54 ± 0.16 |
| 3-CH₃ | 5.68 | 12.1 | 22.4 | 49.5 | 58.6 | 1.63 ± 0.10 |
| 4-C₆H₅CH₂ | 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-C₆H₅ | 4.87 | 4.76 | 8.38 | 18.5 | 24.9 | 1.66 ± 0.19 |
| 3-CH₃CO | 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-CH₃CO | 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 | $\rho_{XZ}^{h,i}$ = -0.23 |
| $\beta_X^{b,d}$ | | 0.33 ± 0.01 | 0.33 ± 0.01 | 0.34 ± 0.01 | 0.35 ± 0.01 | |
| $\rho_X^{c,f}$ | | -4.51 ± 0.22 | -4.34 ± 0.21 | -4.22 ± 0.21 | -4.07 ± 0.18 | $\rho_{XZ}^{c,j}$ = +0.92 |
| $\beta_X^{c,g}$ | | 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 p$K_a$ values in H₂O. Justification for this proedure is provided in ref 6. The p$K_a$ 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 p$K_a$ values of X = 3-C₆H₅ and X = 4-CH₃CO were taken from ref 18. [b]For X = 4-NH₂, 4-CH₃O, 4-CH₃, 3-CH₃, 4-C₆H₅CH₂, 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-C₆H₅, 3-CH₃CO, 3-Cl, 4-CH₃CO, 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-dimethyl-anilines at 50.0 °C in acetonitrile gave $\beta_X$ = 0.84 and 0.85 (for Z = H). respectively.[7] The $\beta_X$ values at low p$K_a$ 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 p$K_a$° = 8.6 and 7.3, respectively,[6] and that for 4-nitrophenyl O-ethyl thiolcarbonate in the whole p$K_a$ range (p$K_a$ = 3.43-9.87) was $\beta_X$ = 0.8.[6] Similarly, for the pyridino-lysis of 2.4-dinitrophenyl and 2,4,6-trinitrophenyl thiol-acetates in water, the $\beta_X$ values were 0.85 and 0.80 with p$K_a$° = 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 p$K_a$ values, $k_{-a} \ll k_b$ so that $k_a$ step is the rate-determining step, *i.e.*, $k_N = k_a$. with a smaller Brönsted slope $\beta_X$ (0.33-0.35). On the other hand, at low p$K_a$ values where $k_{-a} \gg k_b$ and $k_N = (k_a/k_{-a})k_b = Kk_b$. the $k_b$ step should be rate limiting with a steeper Brönsted slope $\beta_X$ (0.78-0.87). At the center of the Brönsted curvature, $k_{-a} = k_b$, a pyridine with p$K_a$ = p$K_a$° (5.2) has the same leaving ability from the tetrahedral intermediate. T⁻. as that of the leaving group ArS⁻.

The low p$K_a$° (~5.2) obtained in this work for the dithio compound (Y = S) is in contrast to the much higher p$K_a$° 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⁺. (with $\beta_X$ = 1.3-1.6) can be predicted even at a higher p$K_a$ range (p$K_a$ ≅ 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 p$K_a$° has been reported for Y = S relative to the corresponding Y = O series: for the aminolysis of S-phenyl thioacetate. the estimated p$K_a$° was 12.2, which is larger than that calculated for the same aminolysis of phenyl dithioacetate, p$K_a$° ≅ 10.[10] For the aminolysis of 4-nitrophenyl O-ethyl dithiocarbonate and S-(4-nitrophenyl) O-ethyl thiocarbonates. the p$K_a$° values are 9.6 and 10.7, respectively.[11] Again, for the aminolysis of 4-nitrophenylbenzoate and the corresponding thionobenzoate. the reported values were p$K_a$° > 11 and 9.2 respectively.[12] These examples of lower p$K_a$° values with Y = S than with Y = O clearly support the contention that the tetrahedral intermediate with Y = S. T⁺ (S), is more stable or that $k_{-a}$ and $k_b$ are smaller than those with Y = O. T⁻ (O). The decrease in $k_{-a}$ is, however, greater than that in $k_b$.

The size of $\rho_Z$ in Table 1 also reflects the mechanistic change. The magnitudes of $\rho_Z$ change from larger values. $\rho_Z$ = 1.9-2.2. for less basic pyridines to smaller values, $\rho_Z$ ≅ 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 $\rho_Z$ values from large ($\rho_Z$ = 3.0) to small values ($\rho_Z$ = 2.3) with the mechanistic

**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-CH₃ | 4-CH₃ | 60.0 | 16.8 | 6.1 | 53 |
| | | 50.0 | 12.1 | | |
| | | 40.0 | 8.69 | | |
| 4-CH₃ | 4-Br | 60.0 | 79.1 | 6.1 | 50 |
| | | 50.0 | 57.3 | | |
| | | 40.0 | 41.3 | | |
| 3-Cl | 4-CH₃ | 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.

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 $\beta_Z$ ≅ -0.5 to -0.3 at the breakpoint in agreement with the change in the rate-determining step.

There is a clear-cut change in the $\rho_{XZ}$ value (Table 1) from a large positive value ($\rho_{XZ}$ = +0.92) for the rate-limiting expulsion of the ArS⁻ group from the intermediate, T⁻, with the weakly basic pyridines (X = H−4-CN) to a small negative value ($\rho_{XZ}$ = -0.23) for the rate-limiting formation of T⁺ with the more basic pyridines (4-NH₂−H). Thus, on the basis of the cross-interaction constants. $\rho_{XZ}$. 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-CH₃) 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 $k_N$, $\rho_X$ ($\beta_X$) and $\rho_Z$ 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 $\delta|\rho_{XZ}| < 0$, *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⁺. and provides an additional support for our proposed mechanism.

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

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Brönsted plot changes from a large ($\beta_X = \beta_{nuc} \cong 0.78$-$0.87$) to a small ($\beta_X = 0.33$-$0.35$) value at p$K_a^{\circ} \cong 5.2$ 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 $\rho_{XZ}$ 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 °C in acetonitrile. The salt was filtered and solvent was removed from the precipitate. Analysis of the product gave the following results.

($C_4H_3SC(=S)NC_5H_4$-*p*-$CH_3$)$^{+}$(4-$BrC_6H_4S$)$^{-}$: m.p. 82-84 °C: $^1$H NMR (400 MHz, CDCl$_3$). $\delta$ 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$_3$), $\delta$ 232.8 (C=S), 145.2, 136.5, 135.2, 133.4, 132.2, 129.5, 120.1, 112.8, 22.8 (CH$_3$): $\nu_{max}$ (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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