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Effect of Changing Electrophilic Center from C═O to C═S on Rates and Mechanism: Pyridinolyses of *O*-2,4-Dinitrophenyl Thionobenzoate and Its Oxygen Analogue

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Received May 10, 2004

Second-order rate constants have been measured spectrophotometrically for the reactions of *O*-2,4-dinitrophenyl thionobenzoate (**1**) and 2,4-dinitrophenyl benzoate (**2**) with a series of substituted pyridines in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C. The Brønsted-type plots obtained are nonlinear with $\beta_1 = 0.26$, $\beta_2 = 1.07$, and $pK_a^\circ = 7.5$ for the reactions of **1** and $\beta_1 = 0.40$, $\beta_2 = 0.90$, and $pK_a^\circ = 9.5$ for the reactions of **2**, suggesting that the pyridinolyses of **1** and **2** proceed through a zwiterionic tetrahedral intermediate $T^\pm$ with a change in the rate-determining step at $pK_a^\circ =$ 7.5 and 9.5, respectively. The thiono ester **1** is more reactive than its oxygen analogue **2** except for the reaction with the strongest basic pyridine studied ($pK_a = 11.30$). The k_1 value is larger for the reactions of **1** than for those of **2** in the low pK_a region, but the difference in the k_1 value becomes negligible with increasing the basicity of pyridines. On the other hand, **1** exhibits slightly larger k_2/k_{-1} ratio than **2** in the low pK_a region but the difference in the k_2/k_{-1} ratio becomes more significant with increasing the basicity of pyridines. Pyridines are more reactive than alicyclic secondary amines of similar basicity toward **2** in the pK_a above ca. 7.2 but less reactive in the pK_a below ca. 7.2. The k_1 value is slightly larger, but the k_2/k_{-1} ratio is much smaller for the reactions of **2** with pyridines than with isobasic secondary amines in the low pK_a region, which is responsible for the fact that the weakly basic pyridines are less reactive than isobasic secondary amines.

Introduction

Nucleophilic substitution reactions of carbonyl derivatives have recently received intensive attention due to the importance in chemical and biological processes.[1−5] The reactions of carboxylic esters with amines have generally been understood to proceed through a zwitterionic tetrahedral intermediate $T^\pm$, in which the rate-determining step (RDS) is dependent on the basicity of the attacking amine and the leaving group.[1−5]

However, reactions of thiocarbonyl derivatives have been much less investigated, and their reaction mechanisms are not completely understood.[6−12] Castro et al. have shown that aminolysis of thiono esters such as

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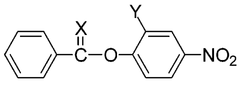
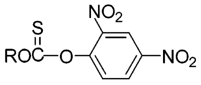
10.1021/jo0492160 CCC: $27.50

O-phenyl thionoacetate, *O*-aryl *O*-4-nitrophenyl thionocarbonates, and *O*-methyl *O*-4-nitrophenyl thionocarbonates proceeds through $T^{\pm}$ and its deprotonated T^{-} when the attacking amines are weakly basic (e.g., piperazinium ion and *N*-formylpiperazine) but without the deprotonation process for the reaction with strongly basic piperazine and piperidine.[6,7] Thus, the basicity of amines has been suggested to be an important factor to determine the presence or absence of the deprotonation process from the zwitterionic $T^{\pm}$.[6,7] Lee et al. have suggested that the nature of the reaction medium is also an important factor to determine the reaction mechanism, since the deprotonation process from $T^{\pm}$ to T^{-}, which has often been observed as the RDS for the reactions performed in H_2O, is absent for aminolyses of aryl dithioacetates and their related esters in MeCN.[8] On the contrary, we have recently shown that the reaction of *O*-4-nitrophenyl thionobenzoate (**3**) with a series of secondary amines proceeds through the two intermediates ($T^{\pm}$ and T^{-}) regardless of amine basicity and the nature of reaction medium.[9] However, the corresponding reaction with primary amines has been found to proceed without the deprotonation process, indicating that the nature of amine also influences the mechanism for aminolyses of **3**.[10]



1 ; X = S, Y = NO_2
2 ; X = O, Y = NO_2
3 ; X = S, Y = H
4 ; X = O, Y = H



5 ; R = Me
6 ; R = Et
7 ; R = Ph

Another interesting argument is about the effect of nonleaving group on the reaction mechanism. Castro et al. have reported that the reactions of substituted phenoxide anions with *O*-ethyl *O*-2,4-dinitrophenyl thionocarbonate (**6**) proceed concertedly, while the corresponding reactions with *O*-methyl and *O*-phenyl *O*-2,4-dinitrophenyl thionocarbonates (**5** and **7**, respectively) proceed through an addition intermediate, indicating that the nature of the nonleaving group affects the reaction mechanism.[11] However, we have recently shown that the nature of the nonleaving group substituents does not influence the reaction mechanism significantly for hydrolysis and aminolysis of thiocarbonyl[12] as well as carbonyl[4a−d] and sulfonyl esters.[13a,b]

We have extended our kinetic study to pyridinolyses of *O*-2,4-dinitrophenyl thionobenzoate (**1**) and its oxygen analogue, 2,4-dinitrophenyl benzoate (**2**). The aim is to investigate (i) the effect of changing the electrophilic center from a C=O to a C=S bond on the reaction rate and mechanism and (ii) the effect of amine nature on the reaction rate by comparing the kinetic data obtained in this study with those reported for the reactions of **2** with primary and secondary amines.[4a,d]

Results and Discussion

TABLE 1. Summary of Second-Order Rate Constants (k_N) for the Reactions of 1 and 2 with Z-Substituted Pyridines in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C

		$k_N/M^{-1}s^{-1}$	
Z-pyridine, Z =	pK_a	**1**	**2**
H	4.73^a	0.0537 ± 0.0004	0.00861 ± 0.00005
3-Me	5.09^a	0.106 ± 0.002	0.0167 ± 0.0002
4-Me	5.53^a	0.389 ± 0.001	0.0469 ± 0.0007
3,4-Me_2	5.78^a	0.727 ± 0.011	0.0725 ± 0.0004
4-NH_2	8.93^a	107 ± 2	32.0 ± 0.5
4-NMe_2	9.12^a	122 ± 2	43.0 ± 0.3
4-O^-	11.30^b	450 ± 8	822 ± 7

[a] The pK_a data in 80 mol % H_2O/20 mol % DMSO were taken from ref 26. [b] Determined in this study by using the method shown in ref 26.

Reactions of **1** and **2** with pyridines proceeded with quantitative liberation of 2,4-dinitrophenoxide. All the reactions obeyed first-order kinetics over 90% of the reaction. Pseudo-first-order rate constants (k_{obsd}) were determined from the slope of the linear plots of $\ln(A_\infty - A_t)$ vs time. The kinetic results obeyed the simple kinetic law given by eqs 1 and 2.

$$d[ArO^-]/dt = k_{obsd}[\mathbf{1} \text{ or } \mathbf{2}] \qquad (1)$$

$$k_{obsd} = k_N[\text{pyridine}]$$

where

$$k_N = k_1k_2/(k_{-1} + k_2) \qquad (2)$$

Generally, five different pyridine concentrations were used to determine the second-order rate constant (k_N) from the slope of the linear plots of k_{obsd} vs pyridine concentration. Correlation coefficients of the plots were usually higher than 0.9995. It is estimated from replicate runs that the uncertainty in the rate constants is less than ±3%. The second-order rate constants determined in this way are summarized in Table 1.

The initial product (e.g., 1-thionobenzoyl-4-dimethylaminopyridinium ion or its oxygen analogue) was detected as explained in the Experimental Section but hydrolyzed to yield thiobenzoate (or benzoate for the reaction of **2**) as shown in Scheme 1. Similar intermediates have been reported for the pyridinolyses of **5**, **6**, **7**,[14a] methyl chloroformate,[14b−d] and acetic anhydride.[14e] Since the intermediate does not absorb at 420 nm where the reactions were monitored, the k_N values obtained are the macroscopic rate constants for the formation of the intermediate and 2,4-dinitrophenoxide ion.

Effect of Changing C=O to C=S on Reaction Mechanism. As shown in Table 1, the second-order rate constant (k_N) increases as the basicity of pyridines increases for the reactions of **1**; i.e., k_N increases from 0.0537 to 0.727 and 450 M^{-1} s^{-1} as the pK_a of pyridines increases from 4.73 to 5.78 and 11.30, respectively. A similar result can be seen for the reactions of **2**. The effect of pyridine basicity on reactivity has been illustrated in

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SCHEME 1

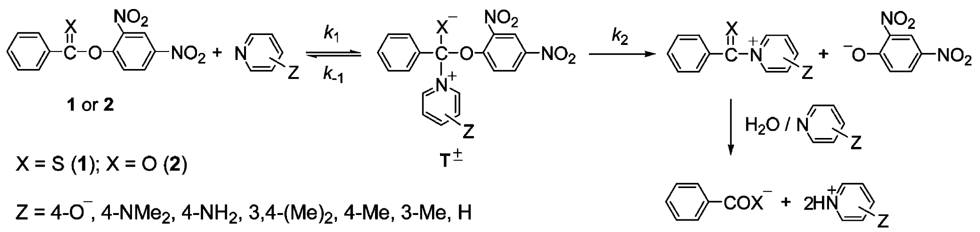

Figure 1. The Brønsted-type plot exhibits a downward curvature for the reactions of **1**. The corresponding plot for the reaction of **2** is also nonlinear, although the curvature is not significant. Such a nonlinear Brønsted-type plot has often been observed for aminolyses of esters with a good leaving group and interpreted as a change in the RDS.[1–6] Thus, one can suggest that the reactions of **1** and **2** with pyridines proceed through $T^{\pm}$ with a change in the RDS from the breakdown of $T^{\pm}$ to its formation as the basicity of pyridines increases.

The nonlinear Brønsted-type plots shown in Figure 1 have been analyzed using a semiempirical equation (eq 3)[2a,4a,15] in which β_1 and β_2 represent the slope of the Brønsted-type plot at the high and the low pK_a region, respectively. The $k_N°$ refers to the k_N value at p$K_a°$, the center of the curvature on the Brønsted-type plot, where $k_{-1} = k_2$. The parameters determined from the fitting of eq 3 to the experimental points are $\beta_1 = 0.26$, $\beta_2 = 1.07$, and p$K_a° = 7.5$ for the reactions of **1** and $\beta_1 = 0.40$, $\beta_2 = 0.90$, and p$K_a°= 9.5$ for the reactions of **2**.

$$\log(k_N/k_N°) = \beta_2(\mathrm{p}K_a - \mathrm{p}K_a°) - \log[(1 + a/2)]$$

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

The β_1 and β_2 values for the reactions of **1** and **2** are comparable to those obtained for the pyridinolyses of various thionocarbonates, which have been suggested to proceed in a stepwise manner (e.g., $\beta_1 = 0.3 \pm 0.1$ and $\beta_2 = 0.9 \pm 0.2$ for reactions of *O*-phenyl *O*-2,4-dinitrophenyl thionocarbonate (**7**),[16a] *O*-4-methylphenyl *O*-4-nitrophenyl thionocarbonates,[7d] and bis (*O*-4-nitrophenyl) thionocarbonate[16b]). Thus, one can suggest that the pyridinolyses of **1** and **2** proceed through a tetrahedral intermediate $T^{\pm}$ with a change in the RDS on the basis of the magnitude of β_1 and β_2 values.

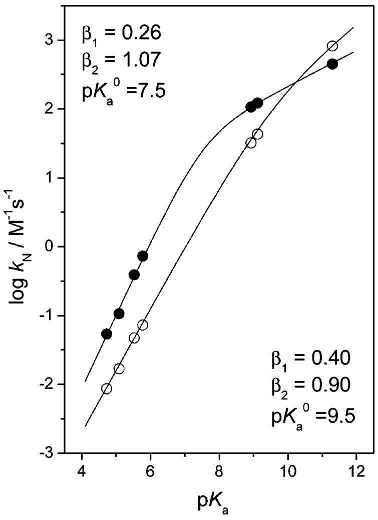

FIGURE 1. Brønsted-type plots for the pyridinolyses of **1** (●) and **2** (○) in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C.

Since $k_2 = k_{-1}$ at p$K_a°$, the basicity of the leaving group and nucleophiles would be the most important factor to determine the p$K_a°$ value. In fact, the p$K_a°$ value has generally been reported to be ca. 4−5 pK_a units higher than the pK_a of the conjugate acid of the leaving aryloxide for aminolyses of various oxygen esters.[1–5] The pK_a of 2,4-dinitrophenol was estimated to be ca. 5 in 80 mol % H_2O/20 mol % DMSO.[17] Thus, one can expect that the p$K_a°$ would be in a pK_a range 9−10 for the reactions of **2**, which is consistent with the result that p$K_a° = 9.5$ for the reaction of **2** in present study.

On the other hand, the p$K_a°$ value has often been reported to be smaller for the reactions of thiocarbonyl compounds compared to the corresponding carbonyl compounds.[10a,18–20] We have recently shown that p$K_a° = 8.8$ for the reaction of **3** with a series of primary amines in 80 mol % H_2O/20 mol % DMSO, while p$K_a° > 11.2$ for the corresponding reaction of **4**.[10a] A similar result has been reported by Campbell et al. for the same reactions run in 80% H_2O/20% CH_3CN; i.e., the Brønsted-type plot has been found to be nonlinear with p$K_a° = 9.2$ for the reactions of **3** but linear (p$K_a° > 11$) for the reactions of **4** with primary amines.[18] More significant decreases in the p$K_a°$ value have been reported for pyridinolyses of dithio compounds, i.e., p$K_a° = 5.2$ for reactions of aryl furan 2-carbodithioates and aryl dithioacetates in MeCN[19] and p$K_a° = 6.9$ for reactions of *O*-ethyl 2,4-dinitrophenyl dithiocarbonate in H_2O.[20] Thus, the present result is consistent with the report that replacing the C=O in a carboxylic or carbonate ester by a C=S bond causes the RDS change to occur at a lower p$K_a°$.

Effect of Changing C=O to C=S on Rates. Figure 1 demonstrates that the thiono ester **1** is more reactive than its oxygen analogue **2** except for the reaction with the strongest basic pyridine studied. However, a contrasting reactivity order has been reported; i.e., **3** is less reactive than **4** toward anionic nucleophiles such as OH^- and EtO^- ions.[18,21] Similarily, Castro et al. have shown

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TABLE 2. Summary of the Microscopic Rate Constants (k_1 and k_2/k_{-1}) for the Reactions of 1 and 2 with Z-Substituted Pyridines in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C

		k_1/M^{-1}s^{-1}		k_2/k_{-1}	
Z-pyridine, Z =	pK_a	**1**	**2**	**1**	**2**
H	4.73	8.34	2.10	0.00648	0.00412
3-Me	5.09	8.60	2.70	0.0125	0.00624
4-Me	5.53	14.4	4.58	0.0278	0.0104
3,4-Me$_2$	5.78	17.3	5.32	0.0438	0.0138
4-NH$_2$	8.93	114	93.7	13.5	0.519
4-NMe$_2$	9.12	128	109	19.0	0.646
4-O$^-$	11.30	450	925	1120	7.94

that 4-nitrophenyl chlorothionoformate and bis(4-nitrophenyl) thionocarbonate are less reactive than their oxygen analogues toward phenoxide anions[22a] and alicyclic secondary amines,[22b,c] respectively. The contrasting reactivity order might be explained by the hard and soft acids and bases (HSAB) principle;[23] i.e., the soft thiocarbonyl group relative to carbonyl would exhibit higher reactivity toward relatively soft pyridines of low basicity (pK_a ≤ 9.12), while the harder nature of the carbonyl group would prefer to bind hard oxyanionic nucleophiles (e.g., OH$^-$, EtO$^-$ and phenoxide anions) and relatively hard alicyclic secondary amines.[23] However, the qualitative HSAB principle cannot explain the finding that **3** is more reactive than **4** toward relatively hard primary amines,[10,18] while **6** is less reactive than its oxygen analogue toward relatively soft pyridines.[14a]

Since a larger k_N value can be obtained by increasing k_1 and/or the k_2/k_{-1} ratio, dissection of the apparent second-order rate constant (k_N) to its microscopic rate constants would allow one to understand the reactivity order more quantitatively. Thus, we have determined the microscopic rate constants associated with the pyridinolyses of **1** and **2** as shown below.

Equation 2 can be simplified to eqs 4 and 5 depending on the RDS. Accordingly, β_1 and β_2 can be expressed as eqs 6 and 7, respectively.

$$k_N = k_1k_2/k_{-1}, \text{ when } k_2 \ll k_{-1} \tag{4}$$

$$k_N = k_1, \text{ when } k_2 \gg k_{-1} \tag{5}$$

$$\beta_1 = \mathrm{d}(\log k_1)/\mathrm{d}(\mathrm{p}K_a) \tag{6}$$

$$\begin{aligned}\beta_2 &= \mathrm{d}(\log k_1k_2/k_{-1})/\mathrm{d}(\mathrm{p}K_a)\\ &= \beta_1 + \mathrm{d}(\log k_2/k_{-1})/\mathrm{d}(\mathrm{p}K_a)\end{aligned} \tag{7}$$

Equation 7 can be rearranged as eq 8. The integral of eq 8 from pK_a° results in eq 9. Since $k_2 = k_{-1}$ at pK_a°, the term $(\log k_2/k_{-1})_{\mathrm{p}K_a°}$ is zero. Therefore, one can calculate the k_2/k_{-1} ratio from eq 9 using $\beta_1 = 0.26$, $\beta_2 = 1.07$, and pK_a° = 7.5 for the reactions of **1** and $\beta_1 = 0.40$, $\beta_2 = 0.90$,and pK_a° = 9.5 for the reactions of **2**. The k_2/k_{-1} ratios determined by this method are summarized in Table 2.

$$\beta_2 - \beta_1 = \mathrm{d}(\log k_2/k_{-1})/\mathrm{d}(\mathrm{p}K_a) \tag{8}$$

$$(\log k_2/k_{-1})_{\mathrm{p}K\mathrm{a}} = (\beta_2 - \beta_1)(\mathrm{p}K_a - \mathrm{p}K_a°) \tag{9}$$

Since eq 2 can be rearranged to eq 10, one can calculate the k_1 values using the k_2/k_{-1} ratios in Table 2 and the k_N values in Table 1. The k_1 values determined are summarized in Table 2.

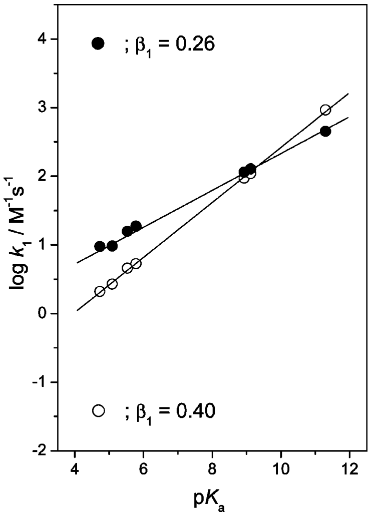

FIGURE 2. Plots of log k_1 vs pK_a for the pyridinolyses of **1** (●) and **2** (○) in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C.

$$k_N = k_1/(k_{-1}/k_2 + 1) \tag{10}$$

As shown in Table 2, **1** exhibits larger k_1 values than **2** except for the reaction with the strongest basic pyridine studied. The effect of the pyridine basicity on the k_1 value has been illustrated in Figure 2. The Brønsted-type plots exhibit that the k_1 value increases linearly with increasing the basicity of pyridines for both reactions of **1** and **2** although **1** exhibits smaller slope than **2**. It is also noted that the k_1 and the apparent second-order rate constant (k_N) for the reactions of **1** and **2** are in the same order.

As shown in Table 2, the k_2/k_{-1} ratio increases as the basicity of pyridine increases for the reactions of **1** and **2**. The effect of pyridine basicity on the k_2/k_{-1} ratio has been illustrated in Figure 3. The Brønsted-type plots are linear with $-\beta_{-1}$ values of 0.81 and 0.50 for the reactions of **1** and **2**, respectively. The k_2/k_{-1} ratio is slightly larger for the reactions of **1** than for those of **2** when the pyridine is weakly basic, but **1** exhibits much larger k_2/k_{-1} ratio than **2** as the basicity of pyridines increases.

Effect of Amine Nature on Rate. Tertiary amines have generally been reported to be more reactive than secondary and primary amines of similar basicity for ester aminolyses[4a,7e,13,14a,24] as well as for deprotonations of various carbon acids (e.g., phenylnitromethane,[25a]

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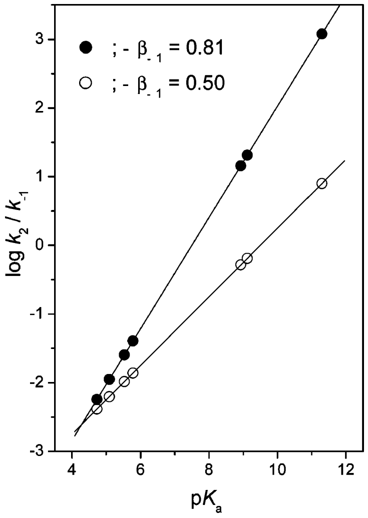

FIGURE 3. Plots of log k_2/k_{-1} vs pK_a for the pyridinolyses of **1** (●) and **2** (○) in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C.

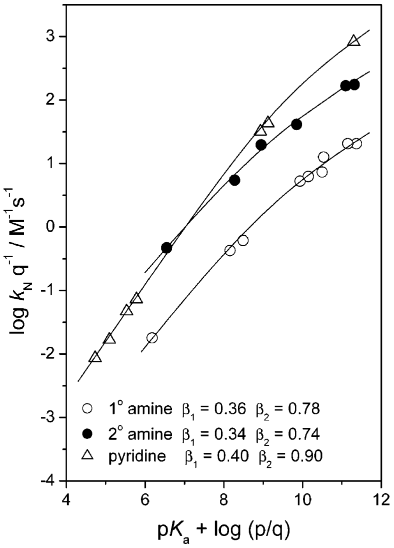

FIGURE 4. Brønsted-type plots for the reactions of **2** with pyridines (△), alicyclic secondary amines (●), and primary amines (○) in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C. The data for the reactions of **2** with primary and secondary amines were taken from ref 4a.

4-nitrophenylacetonitrile,[25b] and 9-carbomethoxyfluorene[25c]) and additions to activated ethylenes (e.g., benzylidene Meldrum's acid[25d] and β-methoxy-α-nitrostylbene[25e]). Since solvation energy has been reported to decrease in the order $RNH_3^+ > R_2NH_2^+ > R_3NH^+$, solvent effect has been suggested to be responsible for the reactivity order.[25]

As shown in Figure 4, pyridines are more reactive than isobasic secondary amines in the high pK_a region (e.g., pK_a > ca. 7.2) but less reactive in the low pK_a region (e.g., pK_a < ca. 7.2). This is an interesting result since pyridines have often been reported to be more reactive than isobasic secondary amines toward various esters (e.g., 4-methylphenyl 4-nitrophenyl thionocarbonate,[7d] *O*-ethyl aryl dithiocarbonates,[25a] *O*-methyl *O*-4-nitrophenyl thionocarbonate,[7e] ethyl *S*-aryl carbonates,[25b] and *O*-ethyl *O*-4-nitrophenyl thionocarbonate[14a]).

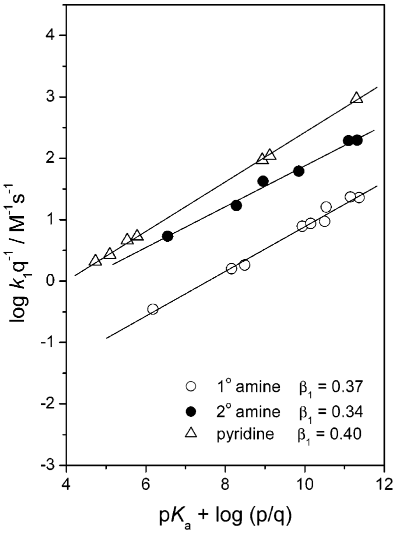

FIGURE 5. Plots of log k_1 vs pK_a for the reactions of **2** with pyridines (△), alicyclic secondary amines (●), and primary amines (○) in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C. The data for the reactions of **2** with primary and secondary amines were taken from ref 4a.

The reactivity of **2** toward pyridines and amines has been compared in the microscopic rate constant level. Figure 5 shows that log k_1 increases linearly with increasing the pK_a of the conjugate acid of pyridines and amines. Interestingly, all the pyridines studied exhibit larger k_1 values than primary and secondary amines of similar basicity, although pyridines are less reactive than isobasic secondary amines in the low pK_a region (e.g., pK_a < ca. 7.2). This result clearly suggests that the reactivity order shown in Figure 4 is not due to the k_1 value.

Gresser and Jencks have suggested that k_{-1} would be smaller for the reactions with pyridines than for those with other amines of similar basicity.[15] The poor nucleofugality of pyridines from the tetrahedral intermediate $T^{\pm}$ has been attributed to a significant contribution of resonance stabilization by electron donation from the pyridine to the carbonyl group of the product and to the oxygen leaving group in the transition-state for the breakdown of the tetrahedral intermediate.[15] Since k_2 has been suggested to be independent of the nature of amines,[2–4,8–12] one can expect that the k_2/k_{-1} ratio would be larger for the reactions with pyridines than for those with primary and secondary amines of similar basicity. However, the result shown in Figure 6 is contrary to the expectation; i.e., the k_2/k_{-1} ratio is smaller for the reactions with pyridines (except for the reaction with the strongest basic pyridine studied) than for those with primary and secondary amines of similar basicity. The difference in the k_2/k_{-1} ratio is negligible for highly basic pyridines but it becomes significant as the pK_a decreases. This result can account for the fact that pyridine becomes less reactive than isobasic secondary amine as the basicity of pyridines decreases, although the former exhibits slightly larger k_1 values than the latter in the low pK_a region.

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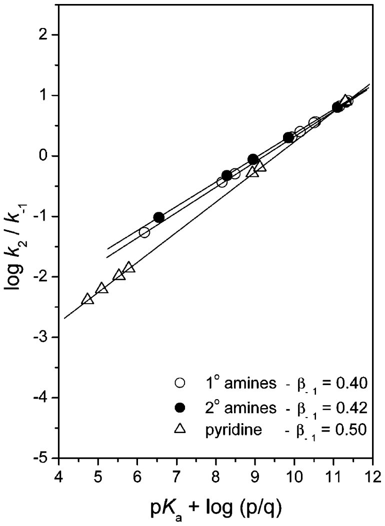

FIGURE 6. Plots of log k_2/k_{-1} vs pK_a for the reactions of **2** with pyridines (△), alicyclic secondary amines (●), and primary amines (○) in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C. The data for the reactions of **2** with primary and secondary amines were taken from ref 4a.

Conclusions

The present study has allowed us to conclude the following: (1) The pyridinolyses of **1** and **2** proceed through an addition intermediate $T^{\pm}$ in which a change in the RDS occurs at pK_a° 7.5 and 9.5, respectively. (2) The thiono ester **1** is more reactive than its oxygen analogue **2** except for the reaction with the strongest basic pyridine studied (pK_a = 11.30). The higher reactivity shown by **1** compared to **2** in the low pK_a region has been attributed to the fact that the former exhibits much larger k_1 for the reactions with weakly basic pyridines. (3) Pyridines are more reactive than alicyclic secondary amines of similar basicity toward **2** in the pK_a above ca. 7.2 but become less reactive in the pK_a below ca. 7.2. Pyridines exhibit slightly larger k_1 values but much smaller k_2/k_{-1} ratios than isobasic secondary amines in the low pK_a region, which accounts for the lower reactivity shown by the weakly basic pyridines toward **2**.

Experimental Section

Materials. Compound **1** was prepared by treating thionobenzoyl chloride and 2,4-dinitrophenol under the presence of triethylamine in anhydrous ether.[9,10,18] The structure and purity of **1** were checked by mp (113−113.5 °C), ^{1}H NMR spectroscopy, and elemental analysis: ^{1}H NMR ($CDCl_3$) δ 7.52 (m, 3H), 7.69 (t, J = 8 Hz, 1H), 8.33 (d, J = 8 Hz, 2H), 8.59 (m, 1H), 9.06 (s, 1H). The ^{1}H NMR spectrum of **1** is also shown in the Supporting Information. Anal. Calcd for $C_{13}N_2O_5S$: C, 51.31; H, 2.65; N, 9.21; O, 26.29; S, 10.54. Found: C, 51.46; H, 2.62; N, 9.18; S, 10.32.

Kinetics. The kinetic study was performed with a UV−vis spectrophotometer for slow reactions ($t_{1/2} \geq$ 10s) or with a stopped-flow spectrophotometer for fast reactions ($t_{1/2}$ < 10s) equipped with a constant temperature circulating bath at 25.0 ± 0.1 °C. All the solutions were transferred by gastight syringes. The reactions were followed by monitoring the appearance of the leaving 2,4-dinitrophenoxide ion at 420 nm. All the reactions were carried out under pseudo-first-order conditions in which pyridine concentrations were at least 50 times greater than the substrate concentration.

Typically, a reaction was initiated by adding 5 μL of a 0.01 M solution of *O*-2,4-dinitrophenyl thionobenzoate (**1**) in acetonitrile by syringe to a 10-mm quartz UV cell containing 2.50 mL of the thermostated reaction mixture made up of solvent and aliquot of the pyridine stock solution. The pyridine stock solution of ca. 0.2 M was prepared by dissolving 2 equiv of pyridine and 1 equiv of standardized HCl solution to keep the pH constant by making a self-buffered solution. Generally, the pyridine concentration was varied over the range (1−100) × 10^{-3} M, while the substrate concentration was 2 × 10^{-5} M. Pseudo-first-order rate constants (k_{obsd}) were calculated from the equation, $\ln(A_\infty - A_t) = -k_{obsd}t + c$. The plots of $\ln(A_\infty - A_t)$ vs time were linear over ca. 90% reaction. Usually, five different pyridine concentrations were employed and replicate values of k_{obsd} were determined to obtain the second-order rate constants (k_N) from the slope of linear plots of k_{obsd} vs pyridine concentrations. Detailed kinetic conditions and results for the reactions of **1** and **2** with pyridines are summarized in the Supporting Information.

Products Analysis. 2,4-dinitrophenoxide was liberated quantitatively and identified as one of the products in the pyridinolyses of **1** and **2** by comparison of the UV−vis spectra after completion of the reactions with those of authentic samples under the same reaction conditions. The formation and later decomposition of the initial product (e.g., 1-thionobenzoyl-4-dimethylaminopyridinium ion, λ_{max} = 360 nm) was detected spectrophotometrically during the reactions.

Acknowledgment. This work was supported by a grant from KOSEF of Korea (R01-1999-00047).

Supporting Information Available: ^{1}H NMR spectrum for **1** and detailed kinetic conditions and results (Tables S1−S14). This material is available free of charge via the Internet at http://pubs.acs.org.

JO0492160