

Metal-Ion Catalysis in Alkaline Ethanolysis of 2-Pyridyl Thionobenzoate: Effects of Modification of Electrophilic Center from C=O to C=S

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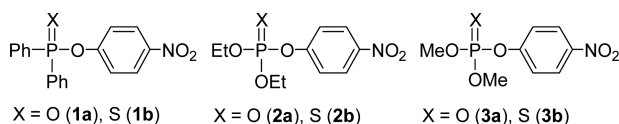
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Pseudo-first-order rate constants (k_{obsd}) have been measured spectrophotometrically for the nucleophilic substitution reactions of 2-pyridyl thionobenzoate (**5b**) with alkali-metal ethoxides (EtOM, $M^+ = \text{Li}^+, \text{Na}^+, \text{K}^+$, and 18-crown-6-ether complexed K^+) in anhydrous ethanol at 25.0 ± 0.1 °C. The plots of k_{obsd} vs. $[\text{EtOM}]_0$ curve upward regardless of the nature of the M^+ ions, while those of $k_{\text{obsd}}/[\text{EtO}^-]_{\text{eq}}$ vs. $[\text{EtO}^-]_{\text{eq}}$ are linear with a positive intercept. Dissection of k_{obsd} into k_{EtO^-} and k_{EtOM} (*i.e.*, the second-order rate constants for the reactions with the dissociated EtO^- and ion-paired EtOM, respectively) has revealed that the ion-paired EtOM is more reactive than the dissociated EtO^- , and M^+ ions catalyze the reactions in the order $\text{K}^+ < \text{Na}^+ < \text{Li}^+ < 18\text{C}6\text{-complexed } \text{K}^+$. The plot of $\log k_{\text{EtOM}}$ vs. $1/r_{\text{Stokes}}$ results in an excellent linear correlation, indicating that the reactions are catalyzed by the solvated M^+ ions but not by the bare M^+ ions. The reactions of **5b** with EtOM have been concluded to proceed through a six-membered cyclic TS, in which the solvated M^+ ions increase the electrophilicity of the reaction center and the nucleofugality of the leaving group.

Key Words : Alkali metal ion, Solvent-separated ion-pair, Transition state, Electrophilicity, Nucleofugality

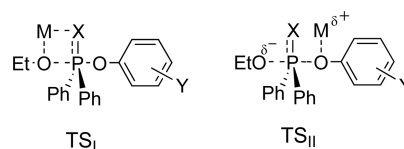
Introduction

Alkali metal ions are ubiquitous in nature and are known to play important roles in biological processes, *e.g.*, the Na^+/K^+ pump to maintain high K^+ and low Na^+ concentration in mammalian cells.¹ Moreover, alkali metal ions have often been reported to catalyze acyl-group transfer reactions as a Lewis acid catalyst.²⁻¹¹ The first systematic study has been carried out by Buncler *et al.* on nucleophilic substitution reactions of 4-nitrophenyl diphenylphosphinate (**1a**) with alkali metal ethoxides (EtOM, $M^+ = \text{Li}^+, \text{Na}^+$ and K^+) in anhydrous ethanol to investigate the effect of alkali metal ions on the phosphinyl transfer reaction.^{5a} They have found that the M^+ ions catalyze the reactions and the catalytic effect increases as the size of M^+ ions decreases, *i.e.*, $\text{K}^+ < \text{Na}^+ < \text{Li}^+$.^{5a} However, the catalytic effect has been shown to disappear in the presence of complexing agents, *e.g.*, 18-crown-6-ether for K^+ (18C6), 15-crown-5-ether (15C5) for Na^+ , and 2,1,1-cryptand for Li^+ .^{5a}



Recently, a contrasting M^+ ion effect has been reported for the corresponding reactions of 4-nitrophenyl diphenylphosphinothioate (**1b**), *i.e.*, Li^+ ion inhibits the reaction while the other M^+ ions including the K^+ ion complexed by 18C6 behave as a catalyst in the order $\text{Na}^+ < \text{K}^+ < \text{K}^+/18\text{C}6$,⁸ indicating that the effect of M^+ ions is strongly dependent of the nature of the electrophilic centers (*i.e.*, P=O vs. P=S). Similar results have been observed for the corresponding

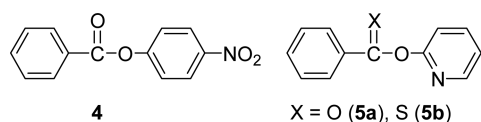
reactions of the insecticides paraoxon (**2a**), parathion (**2b**), methylparaoxon (**3a**), and methylparathion (**3b**).⁹ The reactions of the P=O centered electrophiles (*i.e.*, **2a** and **3a**) were catalyzed by M^+ ions in the order $\text{K}^+ < \text{Na}^+ < \text{Li}^+$.⁹ In contrast, the reactions of the P=S centered electrophiles (*i.e.*, **2b** and **3b**) were inhibited by Li^+ ion but were catalyzed by the K^+ ion complexed by 18C6.⁹



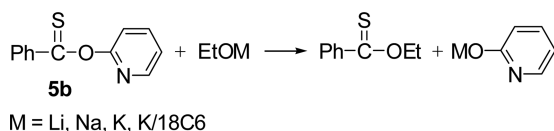
One might suggest that M^+ ions catalyze the reactions either by increasing the electrophilicity of the reaction center through TS_I or by enhancing the nucleofugality of the leaving group through TS_{II} . If the enhanced nucleofugality through TS_{II} is responsible for the metal ion catalysis, the effect of M^+ ions should be similar for the reactions of the P=O and P=S centered electrophiles, since their leaving groups are identical. However, the effects of M^+ ions have been found to be strongly dependent on the nature of the electrophilic centers (*i.e.*, P=O vs. P=S) as mentioned above.^{8,9} Accordingly, it has been concluded that M^+ ions catalyze the reaction by increasing the electrophilicity through TS_I .^{8,9} This idea has been further supported by the kinetic result that the catalytic effect shown by K^+ ion is independent of the electronic nature of the substituent Y in the leaving group of Y-substituted phenyl diphenylphosphinothioates (*i.e.*, **1b** and its derivatives)⁸ and related compounds.¹⁰

The effect of M^+ ions on benzoyl transfer reactions has also been studied for the reactions of 4-nitrophenyl benzoate

(4) and 2-pyridyl benzoate (5a) with EtOM in anhydrous ethanol.¹¹ The effect of M⁺ ions on reaction rates has been reported to be insignificant for the reactions of 4, while the reaction of 5a has been demonstrated to be strongly catalyzed by the M⁺ ions in the order K⁺ < Na⁺ < Li⁺.¹¹



Our study has now been extended to the reactions of 2-pyridyl thionobenzoate (5b) with EtOM in anhydrous ethanol to get further information on the role of the M⁺ ions in the acyl-group transfer reactions (Scheme 1). The kinetic results obtained in this study have been compared with those reported previously for the corresponding reactions of 5a¹¹ to investigate the effect of modification of the electrophilic center from C=O to C=S.



Scheme 1

Results and Discussion

The kinetic study was performed spectrophotometrically under pseudo-first-order conditions, *i.e.*, [EtOM] ≫ [5b]. All reactions in the current study obeyed pseudo-first-order kinetics. Pseudo-first-order rate constants (k_{obsd}) were obtained from the slope of linear plots of $\ln A_t$ vs. t . The correlation coefficients of the linear plots are usually higher than 0.9995. The uncertainty in the k_{obsd} values is estimated to be less than ± 3% from replicate runs. The kinetic conditions and results are summarized in Table 1.

Effect of M⁺ Ions on Reactivity. Figure 1(b) demonstrates that the plots of k_{obsd} vs. [EtOM]₀ for the reactions of 5b with EtOM curve upward as the concentration of EtOM increases. The upward curvature is most significant for the reaction with EtOLi but is insignificant for that with EtOK. The corresponding reactions of 5a have resulted in similarly curved plots with the same reactivity order (*i.e.*, EtOLi > EtONa > EtOK) when the complexing agent 18C6 is absent (Figure 1(a)). However, in the presence of 18C6, the reactivity of EtOK exhibits quite different patterns for the

Table 1. Summary of Kinetic Data for the Reactions of 2-Pyridyl Thionobenzoate (5b) with EtOM in Anhydrous Ethanol at 25.0 ± 0.1 °C^a

EtOM	10 ³ [EtOM]/M	10 ³ k_{obsd}/s^{-1}	No. of runs
EtOLi	4.04-55.2	1.33-24.6	12
EtONa	9.35-56.1	2.42-17.7	10
EtOK	4.38-51.2	0.900-12.3	10
EtOK/18C6	4.33-50.6	0.941-18.4	10

^a[5b] = 8 × 10⁻⁵ M.

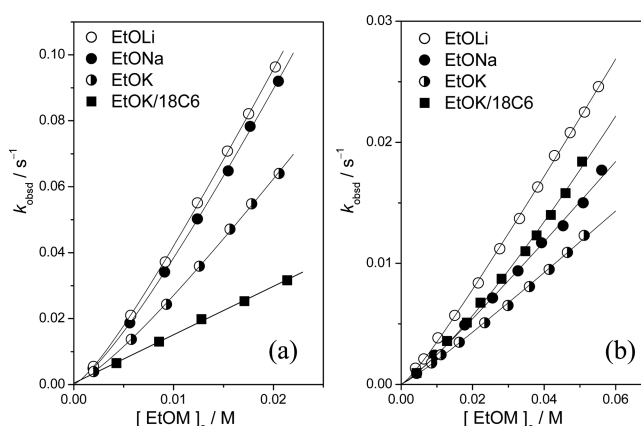


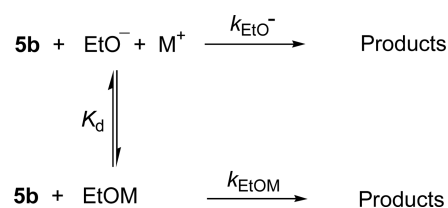
Figure 1. Plots of k_{obsd} vs. [EtOM]₀ for the reactions of 2-pyridyl benzoate 5a (a) and 2-pyridyl thionobenzoate 5b (b) with EtOM in anhydrous ethanol at 25.0 ± 0.1 °C. [18C6]/[EtOK] = 2.0. The kinetic data for the reactions of 5a were taken from ref. 11b.

reactions of 5a and 5b, *i.e.*, the plot of k_{obsd} vs. [EtOK] is linear with decreased k_{obsd} values for the reaction of 5a (Figure 1(a)) but curves upward with enhanced k_{obsd} values for the reactions of 5b (Figure 1(b)). It is also noted that 5b is much less reactive than 5a. Thus, the current study demonstrates convincingly that the effects of modification of the electrophilic center from C=O to C=S on reactivity and the role of M⁺ ions are significant.

The upward curvature shown in Figure 1(a) and 1(b) for the plot of k_{obsd} vs. [EtOM] is typical of reactions in which M⁺ ions have been reported to behave as a Lewis acid catalyst.⁵⁻¹¹ In fact, it has been concluded that the M⁺ ions catalyze the reactions of 5a with EtOM.^{11b} Thus, one can suggest that the M⁺ ions including the 18C6 complexed K⁺ ion catalyze the reactions of 5b as a Lewis acid catalyst.

Dissection of k_{obsd} into k_{EtOM} and k_{EtO^-} . To examine the above idea, k_{obsd} has been dissected into k_{EtO^-} and k_{EtOM} , the second-order rate constant for the reaction with the dissociated EtO⁻ and ion-paired EtOM, respectively. EtOM in anhydrous ethanol was previously reported to exist mainly as the dissociated EtO⁻ and ion-paired EtOM when [EtOM] < 0.1 M.¹² Since the concentration of EtOM in this study is much lower than 0.1 M (Table 1 and Figure 1(b)), one might expect that EtOM would exist as the dissociated EtO⁻ and ion-paired EtOM. Accordingly, 5b would react with the dissociated EtO⁻ and ion-paired EtOM with the rate constants k_{EtO^-} and k_{EtOM} , respectively, as shown in Scheme 2.

One can derive a rate equation as shown in Eq. (1) on the basis of the reactions proposed in Scheme 2. Under pseudo-first-order kinetic conditions, k_{obsd} can be expressed as Eq.



Scheme 2

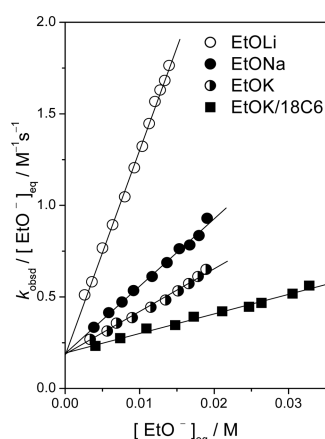


Figure 2. Plots illustrating dissection of k_{obsd} into k_{EtO^-} and k_{EtOM} for the reactions of 2-pyridyl thionobenzoate **5b** with EtOM in anhydrous ethanol at 25.0 ± 0.1 °C.

(2). Since the dissociation constant $K_d = [\text{EtO}^-]_{\text{eq}}[\text{M}^+]_{\text{eq}} / [\text{EtOM}]_{\text{eq}}$, and $[\text{EtO}^-]_{\text{eq}} = [\text{M}^+]_{\text{eq}}$ at equilibrium, Eq. (2) becomes Eq. (3). Thus, the concentrations of $[\text{EtO}^-]_{\text{eq}}$ and $[\text{EtOM}]_{\text{eq}}$ can be calculated from the reported K_d value¹³ and the initial concentration of EtOM (*i.e.*, $[\text{EtOM}]_0$) using Eqs. (4) and (5).

$$\text{Rate} = k_{\text{EtO}^-} [\text{EtO}^-]_{\text{eq}} [\mathbf{5b}] + k_{\text{EtOM}} [\text{EtOM}]_{\text{eq}} [\mathbf{5b}] \quad (1)$$

$$k_{\text{obsd}} = k_{\text{EtO}^-} [\text{EtO}^-]_{\text{eq}} + k_{\text{EtOM}} [\text{EtOM}]_{\text{eq}} \quad (2)$$

$$k_{\text{obsd}} / [\text{EtO}^-]_{\text{eq}} = k_{\text{EtO}^-} + k_{\text{EtOM}} [\text{EtO}^-]_{\text{eq}} / K_d \quad (3)$$

$$[\text{EtOM}]_0 = [\text{EtO}^-]_{\text{eq}} + [\text{EtOM}]_{\text{eq}} \quad (4)$$

$$[\text{EtO}^-]_{\text{eq}} = [-K_d + (K_d^2 + 4K_d[\text{EtOM}]_0)^{1/2}] / 2 \quad (5)$$

One might expect that the plot of $k_{\text{obsd}} / [\text{EtO}^-]_{\text{eq}}$ vs. $[\text{EtO}^-]_{\text{eq}}$ is linear with a positive intercept, if the reaction proceeds as suggested in Scheme 2. In fact, the plots shown in Figure 2 for the reactions of **5b** with EtOM are linear with a positive intercept in all cases, indicating that the above equations derived from the reactions proposed in Scheme 2 are correct.

Accordingly, one can calculate the k_{EtO^-} and k_{EtOM}/K_d values from the intercept and the slope of the linear plots, respectively. The k_{EtOM} value can be calculated from the k_{EtOM}/K_d ratios determined above and the K_d value reported previously (*i.e.*, $K_d = 4.72 \times 10^{-3}$, 9.80×10^{-3} , 1.11×10^{-2} , and 6.02×10^{-2} M for EtOLi, EtONa, EtOK, and EtOK/18C6, in turn).^{11d,13} The calculated k_{EtO^-} and k_{EtOM} values in this way are summarized in Table 2.

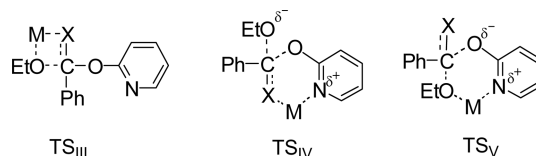
As shown in Table 2, the k_{EtO^-} value for the reactions of **5b** is almost identical within the experimental error range. This

Table 2. Summary of the Second-Order Rate Constants k_{EtO^-} , k_{EtOM} and the Ratios of $k_{\text{EtOM}}/k_{\text{EtO}^-}$ for the Reactions of 2-Pyridyl Thionobenzoate (**5b**) with EtOM in Anhydrous Ethanol at 25.0 °C

EtOM	$k_{\text{EtO}^-} / \text{M}^{-1} \text{s}^{-1}$	$k_{\text{EtOM}} / \text{M}^{-1} \text{s}^{-1}$	$k_{\text{EtOM}} / k_{\text{EtO}^-}$
EtOLi	0.189 ± 0.017	0.528 ± 0.008	2.79
EtONa	0.191 ± 0.024	0.361 ± 0.016	1.89
EtOK	0.179 ± 0.010	0.266 ± 0.008	1.49
EtOK/18C6	0.195 ± 0.010	0.645 ± 0.030	3.31

is consistent with the result illustrated in Figure 2, in which the plots result in a common intercept regardless of the nature of M^+ ions. The k_{EtOM} value is larger than the k_{EtO^-} value, indicating that the ion-paired EtOM is more reactive than the dissociated EtO^- in the reactions of **5b**. Besides, the k_{EtOM} value is dependent on the nature of the M^+ ions, *i.e.*, it increases in the order $k_{\text{EtOK}} < k_{\text{EtONa}} < k_{\text{EtOLi}} < k_{\text{EtOK/18C6}}$. Interestingly, the 18C6-complexed K^+ ion exerts the largest catalytic effect (*i.e.*, the $k_{\text{EtOM}}/k_{\text{EtO}^-}$ ratio) among the M^+ ions studied. This is contrasting to the result reported previously for the corresponding reaction of **5a**,^{11a} *i.e.*, the catalytic effect shown by K^+ ion disappears in the presence of 18C6 (Figure 1(a), the linear plot with significantly decreased k_{obsd} value for the reaction **5a** with EtOK in the presence of 18C6). To account for the contrasting metal ion effects found in the reactions of **5a** and **5b**, the TS structures are depicted in the following section.

TS Structures and Role of M^+ Ions. Three different TS structures are plausible for the reactions of **5a** and **5b** with EtOM, *i.e.*, TS_{III}, TS_{IV} and TS_V. The reactions could be catalyzed by increasing the electrophilicity of the reaction center through TS_{III}. However, the four-membered cyclic TS is expected to be less favorable than the six-membered cyclic TSs due to large ring strain. Accordingly, one can suggest that the reactions would proceed either through TS_{IV} which increases both the electrophilicity of the reaction center and the nucleofugality of the leaving group, or *via* TS_V that enhances the nucleofugality of the leaving group.



If the reactions of **5a** and **5b** proceed through TS_V, one might expect that the M^+ effect should be similar for the reactions of the C=O and C=S centered electrophiles (*i.e.*, **5a** and **5b**, respectively). This is because the X (*i.e.*, O or S) of the C=X moiety of TS_V is not involved in the ring member. In contrast, the C=X moiety of TS_{IV} is involved in the six-membered ring. Thus, if the reactions proceed through TS_{IV}, the effect of M^+ ions would be dependent on the nature of the electrophilic centers (*i.e.*, C=O vs. C=S). In fact, as mentioned above, the 18C6-complexed K^+ ion exerts no catalytic effect in the reaction of **5a** but exhibits the largest catalytic effect in the reaction of **5b**. Thus, one can suggest that the reactions proceed through TS_{IV}, in which M^+ ions increase both the electrophilicity of the reaction center and the nucleofugality of the leaving group.

It is apparent that the C=O bond in **5a** is a hard electrophilic center while the C=S bond in **5b** is a soft one. Similarly, the O and S atoms in the C=X moiety of TS_{IV} could behave as a hard base and a soft base, respectively, while Li^+ ion and the 18C6-complexed K^+ ion are a hard acid and a soft acid, respectively. Thus, one might expect that the O atom of the C=O moiety in TS_{IV} would interact strongly with Li^+ ion but weakly with the 18C6-complexed K^+ ion on

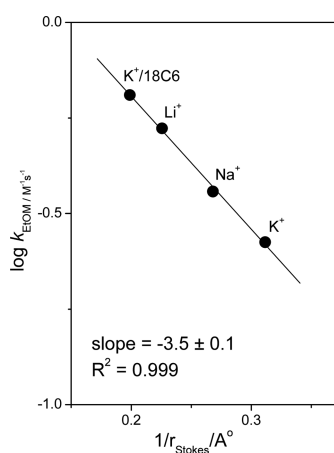


Figure 3. Plot of $\log k_{\text{EtOM}}$ vs. the reciprocal of the Stokes radius of M^+ ions ($1/r_{\text{Stokes}}$) for the reactions of **5b** with EtOM in anhydrous ethanol at 25.0 °C.

the basis of the hard and soft acids and bases (HSAB) principle.¹⁴ This idea is consistent with the kinetic results shown in Figure 1(a), in which the reactivity of EtOM toward **5a** increases as the size of M^+ ions decreases, *i.e.*, EtOK/18C6 < EtOK < EtONa < EtOLi.

In contrast, one might expect that EtOK/18C6 is the most reactive species toward **5b** while EtOLi is the least reactive on the basis of the HSAB principle. In fact, the 18C6-complexed K^+ ion exhibits the largest catalytic effect in the reactions of **5b** (Table 2). However, interestingly the reactivity of the other EtOM is opposite to the expectation since it increases as the radius of the bare M^+ ions decreases, *i.e.*, EtOK < EtONa < EtOLi.

EtOM can form solvent separated ion-pairs in ethanol. The radius of solvated M^+ ions (*i.e.*, the Stokes radius) in anhydrous ethanol was reported to decrease as the size of the bare-metal ions increases, *i.e.*, 4.43, 3.73, and 3.21 Å for Li^+ , Na^+ , and K^+ , respectively.¹⁵ It is noted that the order of reactivity of EtOM shown in Table 2 increases as the radius of solvated M^+ ions (*i.e.*, the Stokes radius) increases. Thus, one can suggest that the M^+ ions in TS_{IV} for the reactions of **5b** are not the bare-metal ions but the solvated-metal ions from the solvent separated ion-pair. This idea is also consistent with the Eisenmann's theory of ion-exchange selectivity patterns,¹⁶ since the polarizable S atom in TS_{IV} would interact weakly with the bare M^+ ions but strongly with the solvated-metal ions.

To examine the above idea, a plot of $\log k_{\text{EtOM}}$ vs. the reciprocal of the Stokes radius of M^+ ions has been constructed for the reactions of **5b** with EtOM. As shown in Figure 3, the plot exhibits an excellent linear correlation with a slope of -3.5 . The Stokes radius of 18C6-complexed K^+ ion is not available but is estimated to be 5.03 Å from the linear plot. Such a good linear plot with a large slope supports clearly that the M^+ ions in TS_{IV} are the solvated species.

Conclusions

The current reactions of **5b** with EtOM have allowed us to

conclude the following: (1) The ion-paired EtOM is more reactive than the dissociated EtO^- . (2) M^+ ions catalyze the reactions of **5b** and the catalytic effect increases in the order $K^+ < Na^+ < Li^+ < K^+/18C6$. (3) Substrate **5b** is less reactive than **5a**. Furthermore, 18C6-complexed K^+ ion, which exerts no catalytic effect for the reaction of **5a**, strongly catalyzes the reaction of **5b**, indicating that the effects of modification of the electrophilic center from C=O to C=S on the reactivity and the role of M^+ ions are significant. (4) The reactions of **5b** with EtOM proceed through TS_{IV} , in which M^+ ions increase the electrophilicity of the reaction center and the nucleofugality of the leaving group. (5) The plot of $\log k_{\text{EtOM}}$ vs. $1/r_{\text{Stokes}}$ results in an excellent linear correlation, indicating that the reactions of **5b** are catalyzed by the solvated M^+ ions rather than by the bare M^+ ions.

Experimental Section

Materials. Compound **5b** was readily prepared from the reaction of dithiobenzoic acid and di-2-pyridyl carbonate (2-DPC) in the presence of 0.1 equiv. of 4-(dimethylamino)-pyridine in methylene chloride at room temperature. The crude compound **5b** was purified by short pathway silica gel column chromatography and subsequent recrystallization. The purity was confirmed by the melting point (43–45 °C) and 1H and ^{13}C NMR spectra (Supporting Information). The solutions of EtOM were prepared by dissolving the respective alkali metal in anhydrous ethanol under N_2 and stored in the refrigerator. The concentrations of EtOM stock solutions were measured by titration with mono potassium phthalate. 18-Crown-6-ether was recrystallized from acetonitrile and dried under vacuum. The anhydrous ethanol was further dried over magnesium and distilled under N_2 just before use.

Kinetics. Kinetic study was performed using a UV-Vis spectrophotometer equipped with a constant-temperature circulating bath. The reactions were followed by monitoring the disappearance of the substrate. Reactions were followed generally for 9–10 half-lives and k_{obsd} values were calculated using the equation, $\ln A_t = -k_{\text{obsd}}t + c$.

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Supporting Information. 1H and ^{13}C NMR spectra for 2-pyridyl thionobenzoate **5b**.

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