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Kinetic Studies on Nucleophilic Substitution Reactions of *O*-Aryl Thionobenzoates with Azide, Cyanide, and Hydroxide: Contrasting Reactivity and Mechanism

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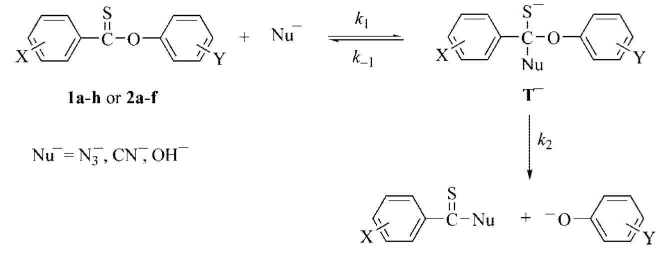

A kinetic study is reported for nucleophilic substitution reactions of *O*-Y-substituted phenyl thionobenzoates (**1a−h**) and *O*-4-nitrophenyl X-substituted thionobenzoates (**2a−f**) with N_3^- and CN^- in 80 mol % H_2O−20 mol % DMSO at 25.0 ± 0.1 °C. The Brønsted-type plot for the reactions of **1a−h** with N_3^- exhibits a downward curvature, i.e., the slope (β_{lg}) changes from −1.10 to −0.33 as the leaving group basicity decreases, indicating that the reactions proceed through a stepwise mechanism with a change in rate-determining step (RDS). In contrast, the Brønsted-type plot for the corresponding reactions with CN^- is linear with a β_{lg} value of −0.33. This value is similar to that found previously for the reactions of **1a−h** with OH^- (−0.35). Besides, σ^o constants result in much better Hammett correlation than σ^- constants. Thus, the reactions with CN^- and OH^- have been concluded to proceed through a stepwise mechanism in which departure of the leaving group occurs after RDS. Reactions of **2a−f** with N_3^- and CN^- result in nonlinear Hammett plots. However, the Yukawa−Tsuno plots for the same reactions exhibit excellent linearity with $r = 0.5 \pm 0.1$, indicating that the nonlinear Hammett plots are not due to a change in RDS but are caused by ground state stabilization through resonance interactions between the electron-donating substituent and the thio carbonyl functionality. Calculation of the k_1 values (nucleophile attack as RDS) for the reactions of **1a−h** with N_3^- indicates that azide ion is more reactive than OH^- toward the thione esters, although the former is over 11 pK_a units less basic than the latter. The high polarizability of N_3^- has been suggested to be responsible for its great affinity for the polarizable thione esters **1a−h** and **2a−f**.

Introduction

Acyl-group transfer reactions have been the subject of intensive experimental and theoretical studies due to their importance in biological processes as well as synthetic applications.[1−16] Reactions of acid chlorides or anhydrides have been suggested to proceed through a concerted mechanism.[2−7] However, reactions of carboxylic esters have been reported to proceed through a concerted or stepwise mechanism depending

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on the nature of nucleophiles (e.g., neutral amines and anionic nucleophiles).[8−16]

Reactions of esters with amines have generally been reported to proceed through an addition−elimination mechanism, in which the rate-determining step (RDS) is dependent on the basicity of the entering amine and the leaving group.[12−15] Evidence provided is nonlinear Brønsted-type plots that have often been observed for reactions of esters possessing a weakly basic aryloxide (e.g., 2,4-dinitrophenoxide).[12−15] Theoretical studies have also favored a stepwise mechanism although the difference in activation energies between the two pathways was calculated to be insignificant.[16]

However, reactions of carboxylic esters with anionic nucleophiles have not been completely understood. Williams et al. have concluded that nucleophilic substitution reactions of 4-nitrophenyl acetate with a series of aryloxides proceed through a concerted mechanism. The evidence consisted mainly of the absence of a break (or curvature) in the Brønsted-type plot when the pK_a of the incoming aryloxide corresponded to that of the leaving 4-nitrophenoxide.[10] The concerted mechanism has been supported by Hengge et al. from heavy atom kinetic isotope effects (KIEs)[11] and by Xie et al. from computational studies.[9a] On the contrary, we have concluded that reactions of phenoxide with a series of substituted phenyl acetates proceed through a stepwise mechanism on the basis of the kinetic results that σ^o constants exhibit better Hammett correlation than σ^- constants.[17] A similar conclusion has been drawn from kinetic studies of alkaline hydrolysis of aryl benzoates[18] as well as from theoretical analysis of the free energy profile in alkaline hydrolysis of methyl formate.[19]

It has been reported that the effect of replacing the O atom of the C=O bond in 4-nitrophenyl benzoate (PNPB) by polarizable S on reactivity and reaction mechanism is significant.[20−25] We have shown that *O*-4-nitrophenyl thionobenzoate (PNPTB) is 1.4×10^4 times more reactive than PNPB toward 4-chlorothiophenoxide.[20] In contrast, Campbell et al. have reported that PNPTB is 8 times less reactive than PNPB toward OH^-.[21] The effect of changing the electrophilic center from C=O to C=S on reaction mechanism has also been investigated. We have found that reactions of PNPTB with a series of alicyclic secondary amines proceed through two intermediates, a zwitterionic tetrahedral intermediate $T^{\pm}$ and its deprotonated form T^-, while the corresponding reactions of its oxygen analogue PNPB proceed without the deprotonation process from $T^{\pm}$.[22] Similar results have been reported for aminolyses of aryl carbonates and thionocarbonates.[23,24]

Recently, we performed a systematic study for alkaline hydrolysis of *O*-Y-substituted phenyl thionobenzoates (**1a−h**) and *O*-4-nitrophenyl X-substituted thionobenzoates (**2a−f**). The reactions were concluded to proceed through an anionic tetrahedral intermediate T^-, in which departure of the leaving group from T^- occurs after the RDS.[25] To get more information on reactivity and mechanism, our kinetic study has been extended to reactions of **1a−h** and **2a−f** with N_3^- and CN^- (i.e., representing an anionic nitrogen and carbon nucleophile, respectively). The kinetic results obtained from the current reactions with N_3^- and CN^- have been compared with those reported previously for the corresponding reactions with OH^- to investigate the effect of the nucleophile nature on reactivity and mechanism.

Results and Discussion

The kinetic study was performed under pseudo-first-order conditions with the concentration of nucleophile in excess over the substrate concentration. All reactions obeyed first-order kinetics with quantitative liberation of Y-substituted phenoxide ion and/or its conjugate acid. Pseudo-first-order rate constants (k_{obsd}) were calculated from the equation $\ln(A_\infty - A_t) = -k_{obsd}t + C$. The plots of k_{obsd} vs nucleophile concentration were linear passing through the origin. Thus, the rate equation can be given as eq 1. Second-order rate constants (k_{Nu}) have been determined from the slope of the linear plots and summarized in Table 1 for reactions of **1a−h** and in Table 3 for those of **2a−f**. It is

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TABLE 1. Summary of Second-Order Rate Constants for Reactions of *O*-Y-Substituted Phenyl Thionobenzoates (1a−h) with N_3^-, CN^-, and OH^- in 80 mol % H_2O−20 mol % DMSO at 25.0 ± 0.1 °C[a]

Y	$pK_a^{Y\text{-}C_6H_4OH}$	$10^2k_{N_3^-}$/ M^{-1} s^{-1}	$10^2k_{CN^-}$/ M^{-1} s^{-1}	k_{OH^-}/ M^{-1} s^{-1}
1a: 4-MeO	10.20	0.544(±0.045)	2.13(±0.02)	0.172
1b: 4-Me	10.19	0.509(±0.010)	1.89(±0.04)	0.161
1c: H	9.95	1.22(±0.01)	2.75(±0.03)	0.210
1d: 3-COMe	9.19		5.52(±0.08)	0.489
1e: 4-COMe	8.05	139(±1)	7.88(±0.04)	0.650
1f: 4-CHO	7.66	250(±1)	9.26(±0.09)	0.846
1g: 4-NO_2	7.14	1100(±10)	19.7(±0.2)	1.87
1h: 3,4-$(NO_2)_2$	5.42	18300(±200)	93.5(±0.5)	10.5

[a] pK_a of phenols and the k_{Nu} values for reactions of **1a−h** with OH^- were taken from ref 25.

TABLE 2. Summary of Microscopic Rate Constants for Reactions of *O*-Y-Substituted Phenyl Thionobenzoates (1a−h) with N_3^- in 80 mol % H_2O− 0 mol % DMSO at 25.0 ± 0.1°C

Y	$pK_a^{Y\text{-}C_6H_4OH}$	k_1/M^{-1} s^{-1}	k_2/k_{-1}
1a: 4-MeO	10.20	5.48	9.93×10^{-4}
1b: 4-Me	10.19	5.84	0.00101
1c: H	9.95	7.90	0.00155
1d: 3-COMe	9.19		
1e: 4-COMe	8.05	32.3	0.0449
1f: 4-CHO	7.66	30.4	0.0897
1g: 4-NO_2	7.14	59.8	0.226
1h: 3,4-$(NO_2)_2$	5.42	221	4.76

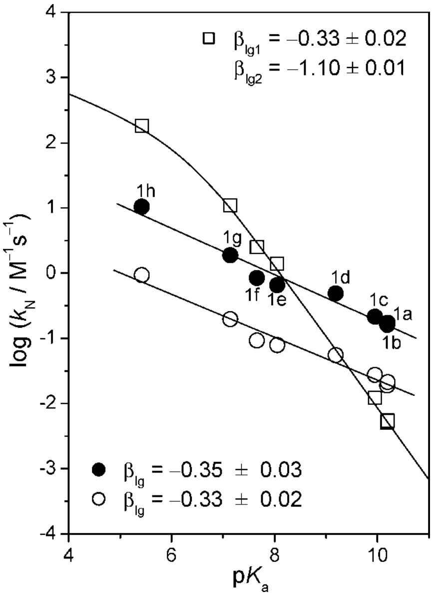


FIGURE 1. Brønsted-type plots for reactions of *O*-Y-substituted phenyl thionobenzoates (**1a−h**) with N_3^- (□), CN^- (○), and OH^- (●)[25] in 80 mol % H_2O−20 mol % DMSO at 25.0 ± 0.1 °C. The identity of numbers is given in Table 1.

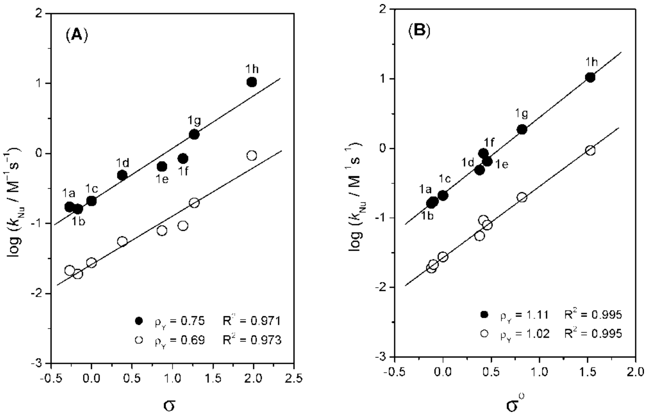


FIGURE 2. Hammett correlations with σ^- (A) and σ^o (B) constants for reactions of *O*-Y-substituted phenyl thionobenzoates (**1a−h**) with OH^- (●) and CN^- (○) in 80 mol % H_2O−20 mol % DMSO at 25.0 ± 0.1 °C. The identity of numbers is given in Table 1.

estimated from replicate runs that the uncertainty in the rate constants is less than ±3%.

$$\text{rate} = k_{obsd}[\text{substrate}], \quad \text{where } k_{obsd} = k_{Nu}[Nu^-] \qquad (1)$$

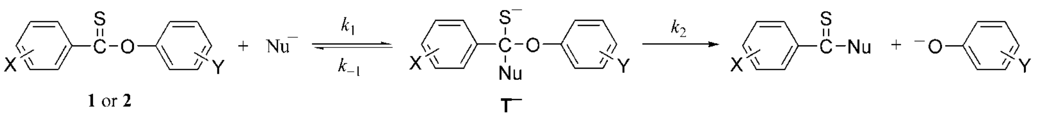
Effect of Leaving-Group Substituent Y on Reaction Mechanism. As shown in Table 1, the second-order rate constant (k_{Nu}) increases as the substituent Y in the leaving group changes from an electron-donating substituent (EDS) to a strong electron-withdrawing substituent (EWS). It is noted that the effect of substituent on reactivity is more significant for the reactions with N_3^- than for those with CN^- and OH^-, e.g., as the substituent Y changes from 4-MeO to 3,4-$(NO_2)_2$, the k_{Nu} value for reactions with N_3^- increases from 5.44×10^{-3} to 183 M^{-1} s^{-1}, over a 10^4-fold increase in reactivity. In contrast, the k_{Nu} value increases from 0.0213 to 0.935 M^{-1} s^{-1} for the reactions with CN^- and from 0.172 to 10.5 M^{-1} s^{-1} for the reactions with OH^-, only a 40- to 60-fold increase in reactivity as the substituent Y changes from 4-MeO to 3,4-$(NO_2)_2$. More interestingly, Table 1 shows that N_3^- is more reactive than OH^- toward **1e−h**, although the former is over 11 pK_a units less basic than the latter.

The effect of leaving-group basicity on reactivity is illustrated in Figure 1. The Brønsted-type plot for the reactions with N_3^- exhibits a downward curvature, i.e., the slope (β_{lg}) changes from −1.10 to −0.33 as the leaving-group basicity decreases. Such a curved Brønsted-type plot has often been reported for reactions which proceed through a stepwise mechanism with a change in the RDS (e.g., aminolysis of esters possessing a good nucleofuge).[12−15] Thus, one can suggest that the reactions of **1a−h** with N_3^- proceed through a stepwise mechanism with a change in the RDS upon changing the leaving-group basicity as shown in Scheme 1.

On the other hand, the Brønsted-type plots for the reactions with OH^- and CN^- are linear with β_{lg} values of −0.35 and −0.33, respectively. Such linear Brønsted-type plots are typical for reactions that proceed through a stepwise mechanism with formation of an intermediate being the RDS.[12−15] Thus, one can suggest that the reactions of **1a−h** with OH^- and CN^- proceed through a stepwise mechanism, in which leaving-group departure occurs after the RDS.

To examine the above argument, Hammett plots have been constructed with use of σ^- and σ^o constants. If the leaving-group departure occurs at the RDS, a partial negative charge would develop on the oxygen atom of the leaving aryloxide. Such a partial negative charge can be delocalized on the substituent Y through resonance. Thus, one can expect that σ^- constants should result in a good Hammett correlation if the leaving group departs at the RDS. As shown in Figure 2A, the Hammett correlation with σ^- constants exhibits many scattered points for reactions with both OH^- and CN^-. On the contrary, σ^o constants result in excellent linear correlations (Figure 2B), indicating that no negative charge is developing on the oxygen atom of the leaving aryloxides at the rate-determining transition state. Thus, one can conclude that the reactions of **1a−h** with

SCHEME 1



X = H; Y = 4-MeO(**1a**), 4-Me(**1b**), H(**1c**), 3-COMe(**1d**), 4-COMe(**1e**), 4-CHO(**1f**), 4-NO_2(**1g**), 3,4-$(NO_2)_2$(**1h**)

Y = 4-NO_2; X = 4-NMe_2(**2a**), 4-MeO(**2b**), 4-Me(**2c**), H(**2d**), 3-MeO(**2e**), 3-Cl(**2f**)

$Nu^- = N_3^-$, CN^-, OH^-

TABLE 3. Summary of Second-Order Rate Constants for Reactions of *O*-4-Nitrophenyl X-Substituted Thionobenzoates (2a−f) with N_3^-, CN^-, and OH^- in 80 mol % H_2O−20 mol % DMSO at 25.0 ± 0.1 °C

X	$k_{N_3^-}$/M^{-1} s^{-1}	$10^3k_{CN^-}$/M^{-1} s^{-1}	$10^2k_{OH^-}$/M^{-1} s^{-1}
2a: 4-NMe_2	0.0460	1.30	1.44
2b: 4-MeO	1.78	36.4	40.8[a]
2c: 4-Me	4.77	88.0	83.0[a]
2d: H	11.0	197	187[a]
2e: 3-MeO	17.3	262	271[a]
2f: 3-Cl	81.6	822	797[a]

[a] The k_{OH^-} values for reactions of **2b-f** were taken from ref 25.

OH^- and CN^- proceed through a stepwise mechanism, in which leaving group departure occurs rapidly after the RDS (i.e., $k_{Nu} = k_1$).

Dissection of Macroscopic Rate Constants into Microscopic Rate Constants. The nonlinear Brønsted-type plot shown in Figure 1 for the reactions of **1a−h** with N_3^- has been analyzed by using a semiempirical equation (eq 2)[27] on the basis of the proposed mechanism. In eq 2, β_{lg1} and β_{lg2} represent the slope of the Brønsted-type plots for the weakly basic and strongly basic leaving groups, respectively. The pK_a at the curvature center of the nonlinear Brønsted-type plot has been defined as pK_a^o, where a change in RDS occurs (i.e., $k_{-1} = k_2$ at pK_a^o).[27] The k_{Nu}^o refers to the k_{Nu} value at pK_a^o. The parameters determined from the fitting of eq 2 to the experimental points are $\beta_{lg1} = -0.33$, $\beta_{lg2} = -1.10$, $k_{Nu}^o = 50.1$, and $pK_a^o = 6.3$.

$$\log(k_{Nu}/k_{Nu}^{o}) = \beta_{lg1}(pK_a - pK_a^{o}) - \log[(1+\alpha)/2],$$
$$\text{where } \log\alpha = (\beta_{lg1} - \beta_{lg2})(pK_a - pK_a^{o}) \quad (2)$$

To get further information on reaction mechanism, the macroscopic rate constants (k_{Nu}) have been dissected into the microscopic rate constants (i.e., k_1 and k_2/k_{-1} ratios) associated with the reactions of **1a−h** with N_3^-. The k_2/k_{-1} ratios have been calculated from eq 3,[27c] using β_{lg1}, β_{lg2}, and pK_a^o values obtained above. The k_1 values have been calculated from eq 4,[27c] using the k_{Nu} values in Table 1 and the k_2/k_{-1} ratios calculated above, and summarized in Table 2.

$$(\log k_2/k_{-1}) = (\beta_{lg2} - \beta_{lg1})(pK_a - pK_a^{o}) \quad (3)$$

$$k_{Nu} = k_1k_2/(k_{-1} + k_2) = k_1/(k_{-1}/k_2 + 1) \quad (4)$$

As shown in Table 2, k_1 and k_2/k_{-1} ratios increase as the substituent Y in the leaving group changes from an EDS to a strong EWS, e.g., as the substituent Y in the leaving group changes from 4-MeO to 3,4-$(NO_2)_2$, the k_1 value and k_2/k_{-1} ratio increase from 5.48 to 221 M^{-1} s^{-1} and from 9.93×10^{-4} to 4.76, respectively. The k_1 value increases only ca. 40-fold while the k_2/k_{-1} ratio increases ca. (5×10^3)-fold, indicating that the effect of leaving group substituent is more significant on the k_2/k_{-1} ratios than on the k_1 values. It is noted that the k_2/k_{-1} ratio is 4.76 for the reaction of **1h** with N_3^-, indicating that N_3^- is a poorer nucleofuge than 3,4-dinitrophenoxide although the former is less basic than the latter. Thus, one can suggest that N_3^- has greater affinity than an isobasic aryloxide for the thio carbonyl carbon. This is in contrast to what is found in aminolysis: amines leave the zwitterionic tetrahedral intermediate faster than an isobasic aryloxide.[13] This must be due to the fact that N_3^- in the anionic tetrahedral intermediate can exert its push and enforce its bond to the central C, whereas the cationic amino moiety in the zwitterionic tetrahedral intermediate cannot.

The effect of leaving-group basicity on k_1 is illustrated in Figure 3 together with the Brønsted-type plots for the reactions with OH^- and CN^- for comparison purposes. The plot of log k_1 vs pK_a for the reactions of **1a−h** with N_3^- exhibits an excellent linearity with $\beta_{lg1} = -0.33$. It is noted that the β_{lg1} value for the reactions with N_3^- is practically identical with the β_{lg} values for the corresponding reactions with OH^- and CN^-, although the k_1 values for reactions with N_3^- and the macroscopic rate constant k_{Nu} values for reactions with OH^- and CN^- are employed to construct the Brønsted-type plots. This result is consistent with the preceding conclusion that $k_{Nu} = k_1$ for the reactions of **1a−h** with OH^- and CN^-.

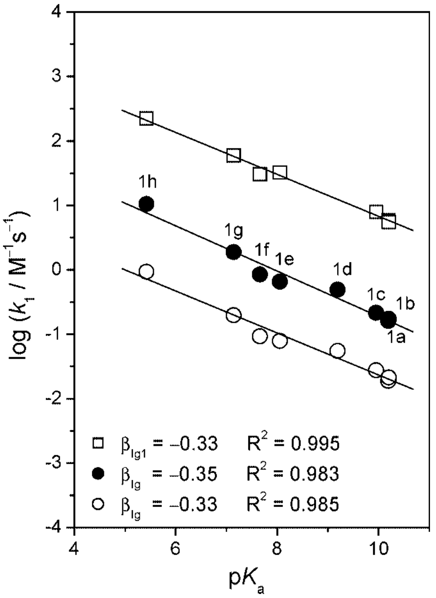


FIGURE 3. Plots of log k_1 (or log k_{Nu}) vs $pK_a^{Y\text{-}C_6H_4OH}$ for reactions of *O*-Y-substituted phenyl thionobenzoates (**1a−h**) with N_3^- (□), CN^- (○), and OH^- (●) in 80 mol % H_2O−20 mol % DMSO at 25.0 ± 0.1 °C. The identity of numbers is given in Tables 1 and 2.

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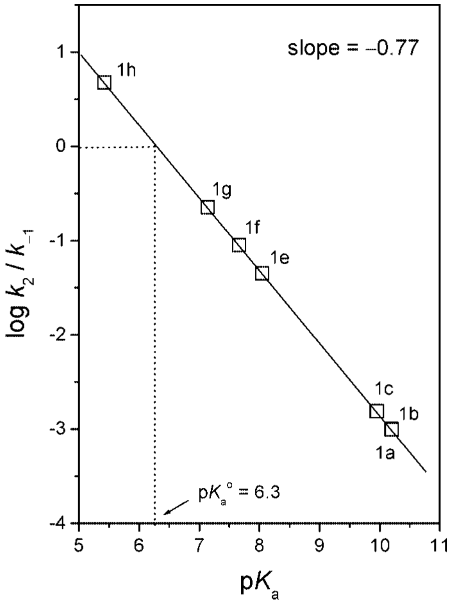


FIGURE 4. Plot of log k_2/k_{-1} vs p$K_a^{\text{Y-C}_6\text{H}_4\text{OH}}$ for reactions of *O*-Y-substituted phenyl thionobenzoates (**1a−h**) with N_3^- in 80 mol % H_2O−20 mol % DMSO at 25.0 ± 0.1 °C. The identity of numbers is given in Table 2.

The effect of leaving-group basicity on the k_2/k_{-1} ratios is illustrated in Figure 4 for the reactions of **1a−h** with N_3^-. The plot exhibits an excellent linearity with a slope of −0.77, which is much steeper than those shown in Figure 3. However, such a large negative slope is not unexpected for reactions which proceed through a stepwise mechanism. This is because the k_2 value increases significantly as the leaving group becomes less basic. On the contrary, the k_{-1} value would decrease as the substituent Y in the leaving aryloxide becomes a stronger EWS, although the effect of the substituent Y on the k_{-1} value would not be significant due to the long distance between the reaction center and the substituent. Thus, one can expect a large slope in the plot of log k_2/k_{-1} vs leaving group basicity due to the contrasting substituent effect on the k_2 and k_{-1} values.

Effect of Nonleaving-Group Substituent X on Reactivity and Mechanism. To investigate the effect of nonleaving-group substituent on mechanism, we have performed reactions of *O*-4-nitrophenyl X-substituted thionobenzoates (**2a−f**) with N_3^- and CN^-. The second-order rate constants, together with those for the reactions with OH^-,[25] are summarized in Table 3. It is seen that the k_{Nu} value increases as the substituent X changes from a strong EDS to an EWS.

The effect of substituent X on reactivity is illustrated in Figure 5. Each Hammett plot consists of two intersecting straight lines. Such a nonlinear Hammett plot has traditionally been interpreted as a change in RDS.[28] Thus, at a first sight, one might suggest that a change in RDS occurs as the substituent X changes from EDSs to EWSs. However, we propose that the nonlinear Hammett plots are not due to a change in RDS on the basis of the following argument. The RDS is determined by the k_2/k_{-1} ratio. Since the leaving aryloxide and nucleophile leave from the anionic intermediate T^- with the bonding electron pair, both k_2 and k_{-1} processes would be accelerated by an EDS in the thionobenzoyl moiety but retarded by an EWS. Thus, the k_2/k_{-1} ratio should be independent of the electronic nature of substituent X in the nonleaving group.

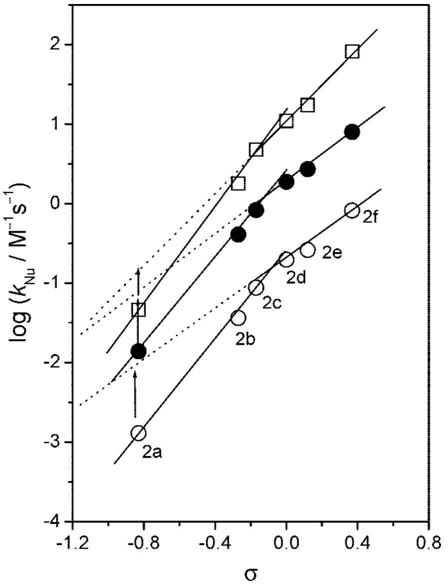
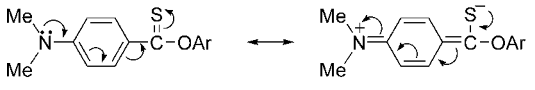


FIGURE 5. Hammett plots for reactions of *O*-4-nitrophenyl X-substituted thionobenzoates (**2a−f**) with N_3^- (□), CN^- (○), and OH^- (●) in 80 mol % H_2O−20 mol % DMSO at 25.0 ± 0.1 °C. The identity of numbers is given in Table 3.

A careful examination of Figure 5 reveals that the substrates with an EDS exhibit negative deviations from the Hammett plots and the degree of deviation is more significant for the substrate with a stronger EDS, e.g., X = 4-NMe_2 (**2a**). Thus, one can suggest that the origin of the nonlinear Hammett plots is stabilization of the ground state (GS) through resonance interaction between the EDS on the thionobenzoyl moiety and the thio carbonyl functionality as illustrated by resonance structures I and II.



I II

To confirm the above argument, Yukawa−Tsuno plots have been constructed in Figure 6. The *r* value in the Yukawa−Tsuno equation (eq 5) represents the resonance demand of the reaction center or the extent of resonance contribution, while the term ($\sigma^+ - \sigma^o$) is the resonance substituent constant that measures the capacity for π-delocalization of the π-electron donor substituent.[29]

$$\log(k^X/k^H) = \rho[\sigma^o + r(\sigma^+ - \sigma^o)] \qquad (5)$$

As shown in Figure 6, the Yukawa−Tsuno plots exhibit excellent linear correlations with *r* values of 0.46, 0.56, and 0.62 for the reactions with N_3^-, OH^-, and CN^-, in turn. Since the *r* value is neither 0 nor 1, the Yukawa−Tsuno plots result in much better linear correlations than the Hammett plot using σ or σ^+ constants alone. It is apparent that the nonlinear Hammett plots shown in Figure 5 are not due to a change in

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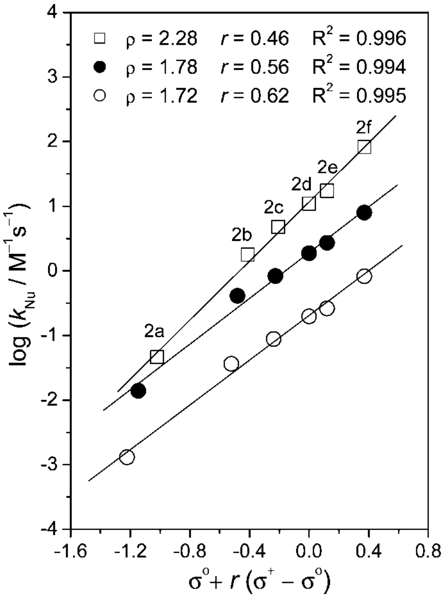

FIGURE 6. Yukawa−Tsuno plots for reactions of *O*-4-nitrophenyl X-substituted thionobenzoates (**2a−f**) with N_3^- (□), CN^- (○), and OH^- (●) in 80 mol % H_2O−20 mol % DMSO at 25.0 ± 0.1 °C. The identity of numbers is given in Table 3.

RDS but are caused by the GS stabilization through resonance interactions as mentioned above. Thus, one can conclude that the nature of substituent X in the nonleaving group does not influence the reaction mechanism in the current system.

Figure 6 shows that N_3^- is more reactive than OH^- toward thione esters **2a−f**, although the former is over 11 pK_a units less basic than the latter. A similar result is demonstrated in Figure 3, i.e., N_3^- exhibits larger k_1 values than OH^- in the reactions of **1a−h**. It is apparent that the current results are in accordance with the hard−soft acid and base principle, since OH^- is a typical hard base while N_3^- has been suggested to be a highly polarizable nucleophile.[30] Thus, one can suggest that the high polarizability of N_3^- is responsible for the great affinity of N_3^- for the polarizable thione esters.

Conclusions

The present study has allowed us to conclude the following: (1) The reactions of **1a−h** with N_3^- proceed through a stepwise mechanism with a change in RDS at pK_a^o = 6.3. (2) The corresponding reactions with OH^- and CN^- proceed also through a stepwise mechanism in which departure of the leaving group occurs after RDS regardless of the leaving-group basicity. (3) Dissection of the macroscopic rate constants (k_{Nu}) into the microscopic rate constants for the reactions of **1a−h** has revealed that N_3^- exhibits larger k_1 values than OH^-, although the former is over 11 pK_a units less basic than the latter. The high polarizability of N_3^- is responsible for the great affinity of N_3^- for the polarizable thione esters. (4) The reactions of **2a−f** with N_3^-, CN^-, and OH^- result in nonlinear Hammett plots. In contrast, the Yukawa−Tsuno plots for the same reactions are linear with $r = 0.5 \pm 0.1$, indicating that the nonlinear Hammett plots are not due to a change in RDS but are caused by GS stabilization through resonance interactions between the EDS in the thionobenzoyl moiety and the thio carbonyl functionality.

Experimental Section

Materials. Compounds **1a−h** and **2a−f** were prepared as reported previously.[22a,25] Other chemicals used were of the highest quality available. The reaction medium was H_2O containing 20 mol % DMSO due to low solubility of the substrates in pure H_2O. Doubly glass distilled water was further boiled and cooled under nitrogen just before use.

Kinetics. The kinetic study was performed with a UV−vis spectrophotometer for slow reactions ($t_{1/2} \geq 10$ s) or with a stopped-flow spectrophotometer for fast reactions ($t_{1/2} < 10$ s) equipped with a constant temperature circulating bath to maintain the temperature in the reaction cell at 25.0 ± 0.1 °C. The reaction was followed by monitoring the appearance of the leaving Y-substituted phenoxide ion or its conjugate acid. All the reactions were carried out under pseudo-first-order conditions in which nucleophile concentrations were at least 20 times greater than the substrate concentration. All solutions were prepared freshly just before use under nitrogen, and transferred by gas-tight syringes. Typically, reactions were initiated by adding 5 μL of a 0.02 M solution of the substrate in CH_3CN by a 10 μL syringe to a 10 mm quartz UV cell containing 2.50 mL of the thermostated reaction mixture made up of solvent and an aliquot of the nucleophile stock solution.

Product Analysis. Y-Substituted phenoxide (and/or its conjugate acid) was liberated quantitatively and identified as one of the products by comparison of the UV−vis spectrum at the end of reaction with that of the authentic sample under the experimental condition.

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Supporting Information Available: Kinetic conditions and results for the reactions of **1a−h** with N_3^- and CN^- and for those of **2a−f** with N_3^-, CN^-, and OH^- in 80 mol % DMSO−20 mol % DMSO at 25.0 ± 0.1 °C. This material is available free of charge via the Internet at http://pubs.acs.org.

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