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Curved Hammett Plot in Alkaline Hydrolysis of *O*-Aryl Thionobenzoates: Change in Rate-Determining Step versus Ground-State Stabilization

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Second-order rate constants have been measured for alkaline hydrolysis of *O*-aryl thionobenzoates (X-C_6H_4-CS-OC_6H_4-Y) in 80 mol % H_2O−20 mol % DMSO at 25.0 ± 0.1 °C. The Hammett plot for the reaction of *O*-4-nitrophenyl X-substituted thionobenzoates (X-C_6H_4-CS-OC_6H_4-NO_2, **1a**−**e**) exhibits a downward curvature. However, a possible traditional explanation in terms of a change in the rate-determining step (RDS) has been considered but rejected. The proposed explanation involves stabilization of the ground-state (GS) through-resonance interaction between the electron-donating substituent X and the thionocarbonyl functionality on the basis of the linear Yukawa−Tsuno plot obtained for the same reaction. The Brønsted-type plot for the reaction of *O*-aryl thionobenzoates (C_6H_5-CS-OC_6H_4-Y, **2a**−**i**) is linear but exhibits many scattered points with a small β_{lg} (−0.35). The Hammett plot for the same reaction shows rather poor correlation with σ^- constants but much better correlation with σ° constants. The alkaline hydrolysis of *O*-aryl thionobenzoates (**1a**−**e** and **2a**−**i**) has been proposed to proceed through an addition intermediate in which bond formation is the RDS.

Introduction

Nucleophilic substitution reactions of thionocarbonyl derivatives (e.g., R-CS-OR′, R-CS-SR′, RO-CS-OR′, RO-CS-SR′ etc.) have intensively been investigated in recent years.[1−5] Reactions of thionocarbonyl compounds with amine nucleophiles have generally been understood to proceed in a stepwise manner with one or two intermediates.[1−7] Castro et al. have reported that the reaction of aryl 4-nitrophenyl thionocarbonates with weakly basic amines (e.g., piperazinium ion and 1-formylpiperazine) proceeds through two intermediates (e.g., a zwiterionic $T^\pm$ and its deprotonated anionic T^-), while the corresponding reaction with strongly basic amines (e.g., piperidine and piperazine) proceeds through one intermediate ($T^\pm$).[1,2] Lee et al. have suggested that the nature of 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 rate-determinining step for the reaction in H_2O, is absent for aminolysis of aryl dithioacetates and their related esters in MeCN.[3a] However, we have recently reported that the reaction of *O*-4-nitrophenyl thionobenzoate with alicyclic secondary amines proceeds through two intermediates regardless of amine basicity and the nature of the reaction medium.[4a]

On the other hand, the reactions of thionocarbonyl derivatives with anionic nucleophiles have been suggested to proceed either in a stepwise manner with one intermediate or in a concerted manner without an intermediate.[8,9] Castro et al. have proposed that the reactions of bis(4-nitrophenyl) and methyl 4-nitrophenyl thionocarbonates with substituted phenoxides proceed in a stepwise manner with a change in the rate-determining

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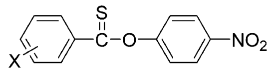
step (RDS) from breakdown of an addition intermediate to its formation upon increasing the basicity of the attacking phenoxides on the basis of biphasic Brønsted-type plots, e.g., $\beta_{\text{nuc}} = 1.25$ and 1.60, respectively, at pK_a < 7.1 and $\beta_{\text{nuc}} = 0.30$ and 0.44, respectively, at pK_a > 7.1.[8a] In contrast, the reactions of thiol or dithiocarbonate esters with substituted phenoxides and thiophenoxides have been suggested to proceed through a concerted mechanism on the basis of linear Brønsted-type plots with a β_{nuc} value ca. 0.65.[8b−e] Similarly, the absence of a break in the Brønsted-type plot for the reaction of 4-nitrophenyl acetate and related esters with substituted phenoxides has been proposed as evidence of a concerted mechanism by Williams et al.[10] In contrast, Buncel et al. have argued against a concerted mechanism for the reaction of substituted phenyl acetates and diphenylphosphinates with phenoxide, on the basis of the Hammett plot exhibiting rather poor correlation with σ^- but significantly better correlation with σ^{o} constants.[11]

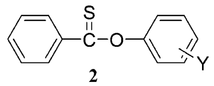
One of the most common criteria used to determine reaction mechanism is the presence or absence of a break in a Hammett- or Brønsted-type plot.[12] However, the controversy concerning the reaction mechanism arises mainly from the Hammett- or Brønsted-type investigation.[10,11] The study performed by changing the substituent only in the nucleophile or in the leaving group appears to be inconclusive. We believe that properly balanced information of substituent effects is necessary to determine the reaction mechanism more conclusively.

Thus, we have synthesized two series of *O*-aryl thionobenzoates (**1a**−**e** and **2a**−**i**) and investigated the effect of substituents in the nonleaving and leaving groups on reaction rates and mechanism for their alkaline hydrolyses. We report that deduction of a reaction mechanism based just on a linear or a nonlinear Hammett or Brønsted-type plot can be misleading.



1

X= 4-MeO(**1a**), 4-Me(**1b**), H(**1c**), 3-MeO(**1d**), 3-Cl(**1e**)



2

Y= 4-MeO(**2a**), 4-Me(**2b**), H(**2c**), 3-COMe(**2d**), 3-NO$_2$(**2e**), 4-COMe(**2f**), 4-CHO(**2g**), 4-NO$_2$(**2h**), 3,4-(NO$_2$)$_2$(**2i**)

Results

All the reactions in the present study obeyed pseudo-first-order kinetics. Pseudo-first-order rate constants (k_{obs}) were measured spectrophotometrically for the alkaline hydrolyses of *O*-4-nitrophenyl X-substituted thionobenzoates (**1a**−**e**) and *O*-Y-substituted phenyl thionobenzoates (**2a**−**i**) in 80 mol % H$_2$O−20 mol % DMSO at 25.0 ± 0.1°C. The k_{obs} values were determined from the slope of linear plots of ln($A_\infty - A_t$) vs time. Generally five different OH$^-$ concentrations were used to determine the second-order rate constants (k_{OH^-}) from the slope of the linear plots of k_{obs} vs OH$^-$ 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 Tables 1 and 2.

TABLE 1. Summary of Second-Order Rate Constants for Reactions of *O*-4-Nitrophenyl Thionobenzoates (X-C$_6$H$_4$-CS-OC$_6$H$_4$-4-NO$_2$, 1a−e) with OH$^-$ in 80 mol % H$_2$O−20 mol % DMSO at 25.0 ± 0.1 °C

X	k_{OH^-}/M^{-1} s^{-1}
1a, 4-OCH$_3$	0.408 ± 0.001
1b, 4-CH$_3$	0.830 ± 0.003
1c, H	1.87 ± 0.03
1d, 3-OCH$_3$	2.71 ± 0.02
1e, 3-Cl	7.97 ± 0.07

TABLE 2. Summary of Second-Order Rate Constants for Reactions of *O*-Y-Substituted Phenyl Thionobenzoates (C$_6$H$_5$-CS-OC$_6$H$_4$-Y, 2a−i) with OH$^-$ in 80 mol % H$_2$O−20 mol % DMSO at 25.0 ± 0.1 °C

Y	pK_a (Y-C$_6$H$_5$OH)^a	k_{OH^-}/M^{-1}s^{-1}
2a, 4-OCH$_3$	10.20	0.172 ± 0.003
2b, 4-CH$_3$	10.19	0.161 ± 0.007
2c, H	9.95	0.210 ± 0.004
2d, 3-COCH$_3$	9.19	0.489 ± 0.006
2e, 3-NO$_2$	8.35	1.46 ± 0.01
2f, 4-COCH$_3$	8.05	0.650 ± 0.004
2g, 4-CHO	7.66	0.846 ± 0.007
2h, 4-NO$_2$	7.14	1.87 ± 0.03
2i, 3,4-(NO$_2$)$_2$	5.42	10.5 ± 0.1

^{a} pK_a data taken from: Jencks, W. P.; Regenstein, J. In *Handbook of Biochemistry*, 2nd ed.; Sober, H. A., Ed.; Chemical Rubber Publishing Co.: Cleveland, OH, 1970; p J-195.

Discussion

Effect of Nonleaving Group Substituent on Rate and Mechanism. As shown in Table 1, the second-order rate constant (k_{OH^-}) increases as the substituent X in the thionobenzoyl moiety changes from an electron-donating group (EDG) to an electron-withdrawing group (EWG) for the reaction of **1a**−**e** with OH$^-$. The effect of the substituent X on the reactivity is illustrated in Figure 1. The Hammett plot exhibits distinct curvature with two intersecting linear portions. Such a curved Hammett plot has traditionally been interpreted as a change in the RDS for a reaction proceeding through a stepwise mechanism.[12,13] In fact, a change in the RDS has been

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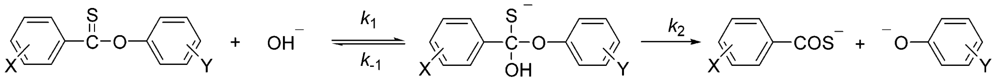
SCHEME 1



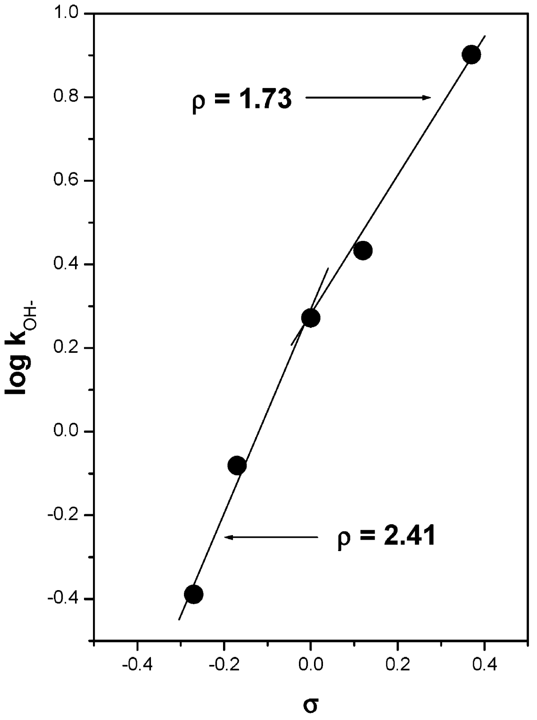


FIGURE 1. Hammett plot for alkaline hydrolysis of *O*-4-nitrophenyl X-substituted thionobenzoates (**1a**−**e**) in 80 mol % H_2O−20 mol % DMSO at 25.0 ± 0.1 °C. $\rho = 2.41$ ($\sigma \leq 0$) and 1.73 ($\sigma \geq 0$). The same type of Hammett plot was found in the reactions of 2,4-dinitrophenyl substituted benzoates with OH^-, CN^-, and N_3^- in the same reaction medium.[19c]

suggested to be responsible for the curved Hammett plot obtained for the reaction of substituted benzaldehydes with semicarbazide in weakly acidic solution (pH = 3.9), i.e., from a large positive ρ to a small one upon changing the substituent in the phenyl ring of benzaldehyde from electron-donating to electron-withdrawing.[13]

Since the electrophilicity of the thionocarbonyl carbon atom of **1a**−**e** would be increased by an EWG in the nonleaving thionobenzoyl moiety but decreased by an EDG, one might expect a large ρ value for the reaction in which the nucleophilic attack by OH^- occurs in the RDS of a stepwise reaction. In contrast, the nucleofugality of the negatively charged leaving group, 4-nitrophenoxide, would be decreased by an EWG but increased by an EDG in the nonleaving thionobenzoyl moiety. Thus, due to the opposite substituent effect, one might expect a small ρ value for the reaction in which the leaving group departure is involved in the RDS, whether the reaction proceeds concertedly or stepwisely. As shown in Figure 1, the Hammett ρ value has been determined to decrease from 2.41 to 1.73 as the substituent X changes from EDG to EWG. Thus, one might suggest that the RDS of the present reaction changes from the breakdown of the addition intermediate (the k_2 step in Scheme 1) to its formation (the k_1 step in Scheme 1) upon changing the substituent X in the nonleaving group from EWG to EDG.

The above argument appears to be consistent with the proposal that the electronic nature of the substituent in the nonleaving group influences the $pK_a°$, the center of the curvature on a curved Brønsted-type plot (log k_{Nuc} vs pK_a of the conjugate acid of nucleophile), where a change in the RDS of a stepwise reaction occurs.[2a,14,15] Castro et al. have suggested that the $pK_a°$ value increases as the substituent in the nonleaving group becomes a stronger EWG, i.e., pyridinolysis of 2,4-dinitrophenyl X-substituted benzoates in 44% aqueous EtOH results in a curved Brønsted-type plot when X = H ($pK_a° = 9.5$) but linear plots when X = 4-Cl and 4-NO_2 ($pK_a° > 9.5$).[14a−c] More recently, the $pK_a°$ for the reaction of *S*-4-nitrophenyl X-substituted thiobenzoates with a series of secondary alicyclic amines in the same medium has been found to increase from 10.0 to 10.4 and > 10.8 as the substituent X changes from H to 4-Cl and 4-NO_2, respectively.[2a] Gresser and Jencks have also found a similar result for the reaction of aryl 3,4-dinitrophenyl carbonates with quinuclidines.[15]

Origin of the Curved Hammett Plot. However, one can propose a different explanation for the curved Hammett plot, other than due to a change in the RDS, on the basis of the following argument. First, the RDS cannot be determined by the magnitude of the k_1 and k_2 values. Because a direct comparison of the k_1 with the k_2 value is not possible due to the difference in their units, e.g., the first-order (k_2) vs second-order rate constant (k_1). Thus, the RDS should be determined by the ratio of the nucleofugality of the leaving group and that of the nucleophile from the addition intermediate, k_2/k_{-1}. As mentioned in the preceding section, the magnitude of k_2 and k_{-1} would be increased by an EDG but decreased by an EWG in the nonleaving thionobenzoyl moiety. Therefore, the ratio of k_2/k_{-1} would not be significantly influenced by the electronic nature of the substituent in the nonleaving group. In fact, we have recently shown that the k_2/k_{-1} ratio is nearly constant upon changing the substituent in the nonleaving group for aminolysis of 2,4-dinitrophenyl substituted benzoates.[16] Second, OH^- ion would be always a poorer leaving group than 4-nitrophenoxide anion due to the large difference in the basicity of the two anions. Accordingly, nucleophilic attack by OH^- ion to form an addition intermediate is expected to be always the RDS and a change in the RDS would not occur

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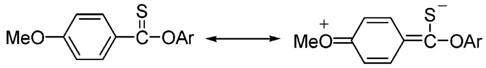
upon changing the substituent X in the thionobenzoyl moiety.



I II

Therefore, we propose that the origin of the curved Hammett plot in Figure 1 is stabilization of the GS through resonance between the electron donating substituent and the thionocarbonyl group as illustrated by resonance structures I and II. The presence of such a resonance structure stabilizes the GS of the substrate (but not the TS) and would cause a decrease in reactivity. The decrease in the reactivity of the substrates by the contribution of the resonance structure II would be more significant for the substrate with a stronger EDG. This argument is consistent with the result that the points for **1a** and **1b** deviate negatively from the Hammett plot in Figure 1 and the degree of negative deviation is more significant for the reaction of **1a** (X = 4-MeO) than for the reaction of **1b** (X = 4-Me). A similar explanation has recently been advanced by Neuvonen et al.[17] A kinetic study together with spectroscopic measurements of ^{13}C NMR chemical shifts and $\upsilon(C{=}O)$ frequencies has shown that presence of an EWG in the nonleaving (or leaving) group of esters increases the reactivity toward imidazole and results in an upfield shift of the carbonyl carbon resonance.[17] Neuvonen et al. have attributed the enhanced reactivity of esters with an EWG in the nonleaving (or leaving) group to a decrease in the resonance stabilization of the GS of esters.[17]

$$\log k^{X}/k^{H} = \rho[\sigma^{\circ} + r(\sigma^{+} - \sigma^{\circ})] \qquad (1)$$

To ascertain the validity of our proposal, the kinetic data in Table 1 have been treated by the Yukawa–Tsuno equation (eq 1).[18] The term $(\sigma^{+} - \sigma^{\circ})$ is the resonance substituent constant measuring the capability for π-delocalization of the π-electron donor substituent, while the r value is a parameter characteristic of the given reaction, representing the extent of resonance contribution.[18] As illustrated in Figure 2, the Yukawa–Tsuno plot exhibits a good linearity for the reaction of **1a**–**e** with OH^-. Such a good linear Yukawa–Tsuno plot clearly indicates that the downward curvature in Figure 1 is not due to a change in the RDS but due to stabilization of the GS of the substrate through resonance structure II. Thus, the present study suggests that deduction of a reaction mechanism based just on a linear or a nonlinear Hammett- or Brønsted-type plot can be misleading, as reported previously for aminolyses of 4-nitrophenyl-substituted benzoates[19a] and 2,4-dinitrophenyl-substituted benzensulfonates[19b] as well as alkaline hydrolysis of 2,4-dinitrophenyl-substituted benzoates.[19c]

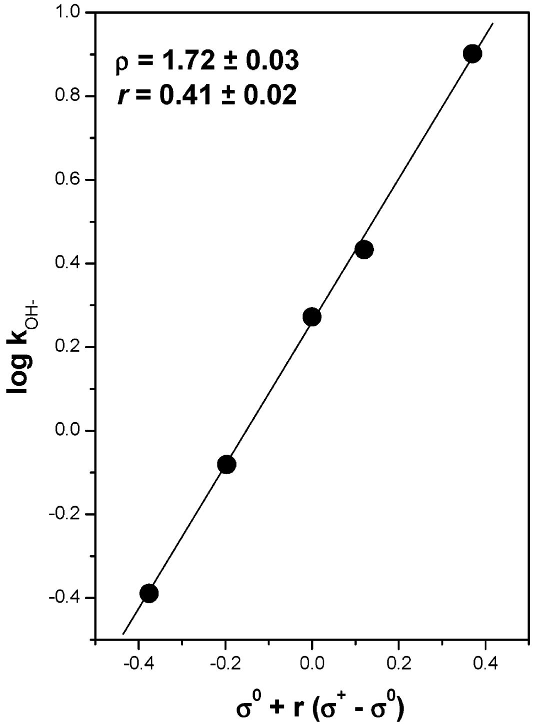
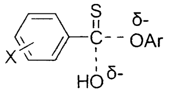


FIGURE 2. Yukawa–Tsuno plot for alkaline hydrolysis of *O*-4-nitrophenyl X-substituted thionobenzoates (**1a**–**e**) in 80 mol % H_2O–20 mol % DMSO at 25.0 ± 0.1 °C. The same type of Hammett plot was found in the reactions of 2,4-dinitrophenyl-substituted benzoates with OH^-, CN^-, and N_3^- in the same reaction medium.[19c]

The ρ value in the present system has been determined to be 1.72. A similar ρ value has been reported for the reaction of 4-nitrophenyl-substituted benzoates with OH^- performed in 33% MeCN.[20] One would not expect such a large ρ value for a reaction in which the leaving group departure is involved in the RDS of a stepwise reaction due to the opposite substituent effect as mentioned above. Similarly, if the reaction of **1a**–**e** with OH^- were a direct S_N2-type displacement with a TS illustrated as TS1, the ρ value would not be so large because little charge would develop on the thionobenzoyl moiety. In fact, the ρ values (either positive or negative) have been reported to be small in S_N2 reactions, e.g., $\rho = -0.3$ and $+0.8$ for S_N2 reactions of benzyl chlorides with OH^- in H_2O and with I^- in acetone, respectively.[12a] Thus, the large positive ρ value obtained in the present system is consistent with the argument that the reaction of **1a**–**e** with OH^- proceeds through an addition intermediate in which formation of the intermediate is the RDS.



TS1

Effect of Leaving Group Substituent on Rate and Reaction Mechanism. As a test of the preceding

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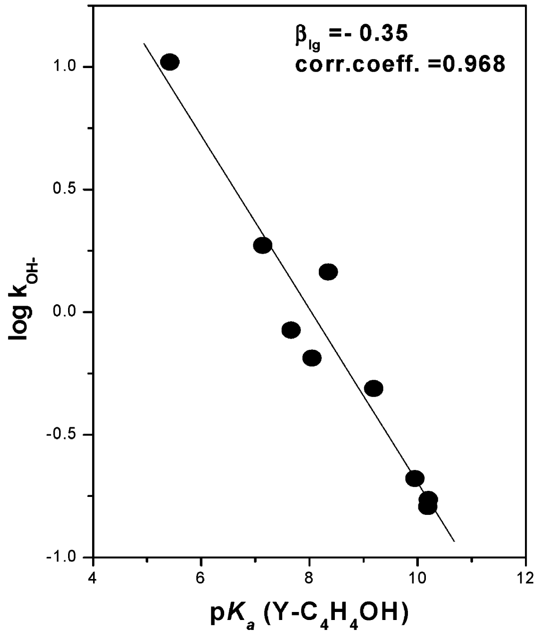

FIGURE 3. Brønsted-type plot for alkaline hydrolysis of *O*-Y-substituted phenyl thionobenzoates (**2a**−**i**) in 80 mol % H_2O−20 mol % DMSO at 25.0 ± 0.1 °C.

argument, the study has been extended to the alkaline hydrolysis of **2a**−**i**. The second-order rate constants for alkaline hydrolysis of **2a**−**i** are summarized in Table 2. It is shown that the k_{OH^-} value increases as the basicity of the leaving group decreases except $3\text{-}NO_2C_6H_4O^-$. The effect of the leaving group basicity on the reactivity is illustrated in Figure 3. The Brønsted-type plot is linear but involves many scattered points. Besides, the β_{lg} value has been determined to be rather a small value ($\beta_{lg} = -0.35$). Such a small β_{lg} value has often been reported for reactions which proceed through rate-determining formation of an addition intermediate, e.g., $\beta_{lg} = -0.3 \pm 0.1$ for alkaline hydrolysis of aryl acetates,[21a,b] and cinnamates,[21c] and for aminolyses of aryl acetates, carbonates, and their thio analogues.[2,22] However, significantly large β_{lg} values have been reported for reactions involving leaving group departure as the RDS, e.g., reactions of aryl cinnamates with N_3^- ion ($\beta_{lg} = -0.95$) and aminolysis of aryl acetates and benzoates with a poor leaving group ($\beta_{lg} = -1.4$).[21c,22]

The magnitude of β_{lg} value has been understood as a measure of the extent of leaving group departure in the rate-determining TS. Thus, one can suggest that the leaving group departure is not advanced in the TS of the RDS on the basis of the small β_{lg} obtained in the present system.

To obtain further information on the TS structure, Hammett plots are constructed for the reaction of **2a**−**i** with OH^-. As shown in Figure 4, the Hammett plot exhibits good correlation when $\sigma°$ constants are used ($r^2 = 0.996$). However, much poorer correlation is obtained when σ^- constants are used ($r^2 = 0.956$, the inset of Figure 4).

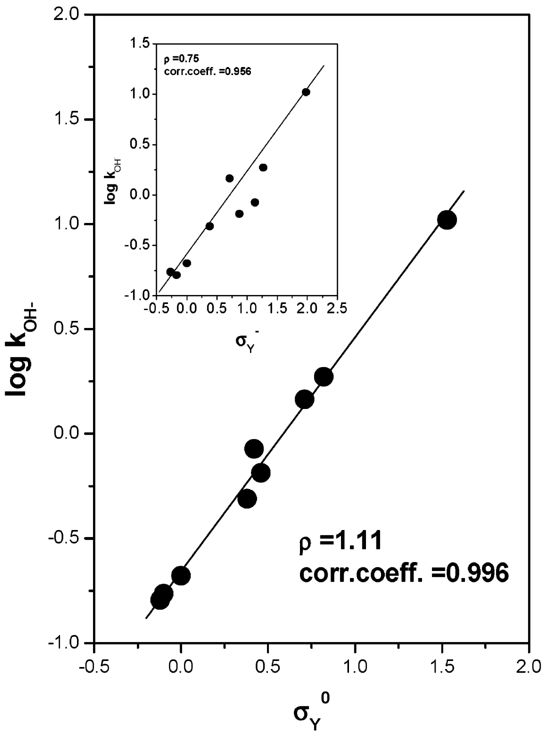

FIGURE 4. Hammett plots for alkaline hydrolysis of *O*-Y-substituted phenyl thionobenzoates (**2a**−**i**) in 80 mol % H_2O−20 mol % DMSO at 25.0 ± 0.1 °C.

If the leaving group departure occurs in the RDS (either in a concerted or stepwise mechanism), a partial negative charge would develop on the O atom of the leaving aryl oxides. Thus, one might expect good correlation with σ^- constants for the reaction in which the leaving group departure is involved in the RDS. In fact, σ^- constants have often reported to give the best correlation with a large ρ value for ester aminolysis in which the RDS was suggested to be the leaving group departure from an addition intermediate.[22] The fact that $\sigma°$ constants give much better correlation than σ^- constants (Figure 4) suggests that no negative charge develops on the O atom of the leaving aryl oxides in the rate-determining TS. Thus, one can propose that the alkaline hydrolysis in this study proceeds through an addition intermediate in which its formation is the RDS.

Conclusions

The present study has allowed us to conclude the following. (1) The nonlinear Hammett plot obtained from the reaction of **1a**−**e** with OH^- is not due to a change in the RDS since the Yukawa−Tsuno plot is linear. Thus, determination of the reaction mechanism based just on a nonlinear Hammett plot can be misleading. (2) The origin of the curved Hammett plot is GS stabilization through resonance between the electron donating substituent and the thionocarbonyl group as illustrated by the resonance structures I and II. (3) The alkaline hydrolysis of **1a**−**e** and **2a**−**i** proceeds through an addi-

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tion intermediate in which formation of the intermediate is the RDS.

Experimental Section

Materials. Compound *O*-4-nitrophenyl thionobenzoate (**1c** and **2h**) was prepared as reported previously.[6] Other compounds (**1a**,**b**,**d**,**e** and **2a**−**g**,**i**) were synthesized easily by a similar method used for preparing **1c** (e.g., by treating the respective substituted thionobenzoyl chloride and the substituted phenol under the presence of triethylamine in anhydrous ether). The structure and purity of **1a**−**e** and **2a**−**i** were checked by their melting points, ^{1}H NMR spectra, and elemental analyses. The analytical data are summarized in the Supporting Information.

Kinetics. The kinetic study was performed with a UV−vis spectrophotometer equipped with a constant temperature circulating bath at 25.0 ± 0.1°C. All the solutions were transferred by Hamilton gastight syringes. The reactions were followed by monitoring the appearance of the leaving aryl oxide. All the reactions were carried out under pseudo-first-order conditions in which NaOH concentrations were at least 100 times greater than the substrate concentration.

Typically, a reaction was initiated by adding 5 μL of a 0.01 M solution of *O*-4-nitrophenyl thionobenzoate 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 an aliquot of the NaOH stock solution. Generally, the base concentration was varied over the range (5−100) × 10^{-3} M, while the substrate concentration was 2 × 10^{-5} M. Pseudo-first-order rate constants (k_{obs}) were calculated from the well-known equation, $\ln(A_\infty - A_t) = -k_{obs}t + c$. The plots of $\ln(A_\infty - A_t)$ vs time were linear over ca. 90% reaction. Usually, five different OH^- concentrations were employed and replicate values of k_{obs} were determined to obtain the second-order rate constants (k_{OH^-}) from the slope of linear plots of k_{obs} versus NaOH concentrations.

Product Analysis. Y-substituted phenoxide was liberated quantitatively and identified as one of the products in the hydrolysis of **1a**−**e** and **2a**−**i** by comparison of the UV−vis spectra after completion of the reactions with those of authentic samples under the same reaction conditions.

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Supporting Information Available: Tables S1−S14 for the kinetic results for the reactions of **1a**−**e** and **2a**−**i** with OH^- in 80 mol % H_2O−20 mol % DMSO at 25.0 ± 0.1 °C. The melting points of compounds **1a**−**e** and **2a**−**i** together with their IR and ^{1}H NMR spectra and elemental analyses data. This material is available free of charge via the Internet at http://pubs.acs.org.

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