Kinetic Study on Alkaline Hydrolysis of Y-substituted Phenyl X-substituted Benzenesulfonates: Effects of Changing Nucleophile from Azide to Hydroxide Ion on Reactivity and Transition-State Structure

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Second-order rate constants (k_{OH}) for alkaline hydrolysis of 2,4-dinitrophenyl X-substituted benzenesulfonates (**1a–1f**) and Y-substituted phenyl 4-nitrobezenesulfonates (**2a–2g**) have been measured spectrophotometrically. Comparison of k_{OH} with the k_{N3} -values reported previously for the corresponding reactions with N₃- has revealed that OH⁻ is only 10³-fold more reactive than N₃-, although the former is 11 p K_a units more basic than the latter. The Yukawa–Tsuno plot for the reactions of **1a–1f** results in an excellent linear correlation with $\rho_X = 2.09$ and r = 0.41. The Brønsted-type plot for the reactions of **2a–2g** is linear with $\beta_{Ig} = -0.51$, which is typical for reactions reported to proceed through a concerted mechanism. The Yukawa–Tsuno plot for the reactions of **2a–2g** exhibits excellent linearity with $\rho_Y = 1.85$ and r = 0.25, indicating that a partial negative charge develops on the O atom of the leaving group in the transition state. Thus, the alkaline hydrolysis of **1a–1f** and **2a–2g** has been concluded to proceed through a concerted mechanism. Comparison of the ρ_X and β_{Ig} values for the reactions with OH⁻ and N₃- ions suggests that the reactions with hydroxide ion proceed through a tighter transition-state structure than those with azide ion.

Keywords: Aryl benzenesulfonates, Alkaline hydrolysis, Sulfonyl-group transfer, Yukawa–Tsuno plot, Concerted mechanism

Introduction

Acyl-group and phosphoryl-group transfer reactions have been intensively investigated because of their importance in biological processes as well as in synthetic applications.^{1–9} In contrast, sulfonyl-group transfer reactions have received much less attention, although bacteria can use sulfonate esters as sulfur sources when sulfate concentration is low in their environment.¹⁰ Thus, their reaction mechanisms have not been completely understood, *e.g.*, nucleophilic substitution reactions of aryl benzenesulfonates have been reported to proceed through a concerted mechanism or via a stepwise pathway.^{11–17}

Williams and coworkers have reported that reactions of 4nitrophenyl 4-nitrobenzenesulfonate with a series of substituted phenoxides proceed through a concerted mechanism on the basis of a Brønsted-type plot with absence of a break (or curvature) when the pK_a of the aryloxide nucleophile corresponded to that of the leaving 4-nitrophenoxide.¹¹ However, Buncel and coworkers have suggested that reactions of Y-substituted phenyl benzenesulfonates (Y = 4-NO₂, 3-NO₂, 4-CF₃, 3-Br, 4-Cl, and H) with C₂H₅O⁻ proceed through a stepwise mechanism, since the Hammett plot correlated with σ^{o} constants resulted in much better linearity than σ^{-} constants.¹² On the other hand, we have recently reported that alkaline ethanolysis of Y-substituted phenyl benzenesulfonates proceed through a concerted mechanism on the basis of the kinetic result that the Yukawa–Tsuno plot exhibits an excellent linear correlation with $\rho_{\rm Y} = 2.61$ and r = 0.29.¹³

The reaction mechanism for alkaline hydrolysis of aryl benzenesulfonates is also controversial. From a kinetic study, Babtie et al. have concluded that nucleophilic substitution reactions of Y-substituted phenyl benzenesulfonates (Y = 3-F-4-NO₂, 4-NO₂, 4-CN, 3-NO₂, 3-CN, 4-Cl, H, and 3,4-Me₂) with OH⁻ proceed through a stepwise mechanism involving a pentavalent intermediate.¹⁴ The evidence provided for a stepwise mechanism was a biphasic Brønsted-type plot (e.g., $\beta_{1g} = -0.27$ when the leaving group $pK_a < 8.5$ but $\beta_{1g} = -0.97$ when the leaving group $pK_a > 8.5$.¹⁴ The stepwise mechanism has also been supported their quantum/molecular mechanics (OM/MM) calculations.¹⁴ In contrast, Duarte *et al.* have found no computational evidence for a thermodynamically stable intermediate for any of the above sulfonate esters from a detailed computational study using HF/6-31++G^{*}.¹⁵ Furthermore, inclusion of the experimental data for the reactions of 3-pyridyl benzenesulfonate and its N-oxide and N-methylpyridinium derivatives gave a very good Hammett correlation.¹⁵ Thus, the reactions have been concluded to proceed through a concerted mechanism, in which expulsion of the leaving group is advanced only a little in the transition state (TS).15

We have reported that nucleophilic substitution reactions of aryl benzenesulfonates are regioselective, *e.g.*, reactions of 2,4-dinitrophenyl X-substituted benzenesulfonates (**1a–1f**) with primary and cyclic secondary amines proceed through S–O and C–O bond fission competitively.¹⁶ The S–O bond fission, which leads to the formation of 2,4-dinitrophenoxide ion and X-substituted benzenesulfonamides, was found to be the major reaction pathway for the reactions with strongly basic amines (*e.g.*, piperidine or ethylamine) or for those of substrates possessing a strong electron withdrawing group (EWG) in the benzenesulfonates, increased significantly for the reactions with weakly basic amines (*e.g.*, piperazinium ion or 2,2,2-trifluoroethylamine) or for those of substrates bearing a strong electron donating group (EDG) in the benzenesulfonyl moiety.¹⁶



1 or 2

 $\begin{array}{l} \mathsf{Y} = \mathsf{2}, \mathsf{4}\text{-}(\mathsf{NO}_2)_2 \ ; \ \mathsf{X} = \mathsf{4}\text{-}\mathsf{NO}_2(\textbf{1a}), \ \mathsf{3}\text{-}\mathsf{NO}_2(\textbf{1b}), \ \mathsf{3}\text{-}\mathsf{Cl}(\textbf{1c}), \ \mathsf{H}(\textbf{1d}), \\ & \quad \mathsf{4}\text{-}\mathsf{Me}(\textbf{1e}), \ \mathsf{4}\text{-}\mathsf{MeO}(\textbf{1f}) \\ \mathsf{X} = \mathsf{4}\text{-}\mathsf{NO}_2 \ ; \qquad \mathsf{Y} = \mathsf{2}, \mathsf{4}\text{-}(\mathsf{NO}_2)_2(\textbf{2a}), \ \mathsf{4}\text{-}\mathsf{NO}_2(\textbf{2b}), \ \mathsf{4}\text{-}\mathsf{CHO}(\textbf{2c}), \\ & \quad \mathsf{4}\text{-}\mathsf{CN}(\textbf{2d}), \ \mathsf{4}\text{-}\mathsf{COMe}(\textbf{2e}), \ \mathsf{3}\text{-}\mathsf{CHO}(\textbf{2f}), \ \mathsf{4}\text{-}\mathsf{Cl}(\textbf{2g}). \end{array}$

A similar result has been reported for the reactions of **1a–1f** with weakly basic N₃-; *e.g.*, reactions of substrates possessing an EWG produced mainly the S—O bond fission products, while those of substrates bearing an EDG yielded mostly the C—O bond fission products.¹⁷ In contrast, we have previously reported that the corresponding reactions with strongly basic C₂H₅O⁻ in anhydrous ethanol proceed exclusively through the S—O bond fission.¹³ These demonstrate convincingly that the regioselectivity in the nucleophilic substitution reactions of **1a–1f** is governed by the electronic nature of the substituent X in the benzenesulfonyl moiety and by the basicity of the nucleophiles.

Our study has now been extended to alkaline hydrolysis of **1a–1f** and Y-substituted phenyl 4-nitrobenzenesulfonates (**2a–2g**) in 80 mol% H₂O/20 mol% DMSO at 25.0 ± 0.1 °C to obtain further information on the reaction mechanism (Scheme 1). The kinetic results obtained from the current study have been compared with those reported recently¹⁷ for the corresponding reactions with weakly basic N₃⁻ to investigate effects of changing the nucleophile from the azide ion to the hydroxide ion on reactivity and TS structures. Nucleophilic substitution reactions of **1a–1f** and **2a–2g** with strongly basic C₂H₅O⁻ in anhydrous ethanol have previously been carried out to investigate the effects of the alkali metal ions on reactivity (*e.g.*, catalysis or inhibition).¹³ However, the kinetic data obtained previously in anhydrous ethanol



could not be compared with the current data because of the difference in the reaction medium.

Results and Discussion

The kinetic study was carried out under pseudo-firstorder conditions (e.g., the OH⁻ concentration was kept at least 20 times in excess over the substrate concentration) in 80 mol % H₂O/20 mol% DMSO at 25.0 \pm 0.1 °C. All the reactions in this study obeyed pseudo-first-order kinetics with quantitative liberation of 2,4-dinitrophenoxide ion for the reactions of 1a-1f and Y-substituted phenoxide ion for those of 2a-2g. The pseudo-first-order rate constants (k_{obsd}) were calculated from the equation: $\ln (A_{\infty} - A_t) = -k_{obsd}t + C$. The correlation coefficients of the linear regressions were usually higher than 0.9995. Generally, five different OH⁻ concentrations were used to calculate the second-order rate constants (k_{OH}) from the slope of the linear plot of k_{obsd} vs. [OH⁻]. The uncertainty in the k_{OH} values is estimated to be less than $\pm 3\%$ from replicate runs. The k_{OH} values calculated in this way are summarized in Tables 1 and 2 for the reactions of 1a-1f and 2a-2g, respectively. The k_{N3} -values reported previously¹⁷ for the corresponding reactions with weakly basic N₃- are also listed for comparison.

Effect of Substituent X on Reactivity and Reaction Mechanism. As shown in Table 1, reactivity of substrates 1a–1f toward OH⁻ decreases steeply as the substituent X changes from a strong EWG to an EDG; *e.g.*, the k_{OH^-} value decreases from 442 to 7.80 and 1.30 M⁻¹s⁻¹ as the substituent X changes from 4-NO₂ to H and 4-MeO, in turn. A similar result is demonstrated for the corresponding reactions with N₃⁻, although the azide ion is ~10³-fold less reactive than the hydroxide ion. It is noted that N₃⁻ is a weak base since the pK_a of HN₃ is 4.72.¹⁸ Thus, one might suggest that the weak basicity of the azide ion is responsible for the kinetic result that N₃⁻ is less reactive than OH⁻.

However, the difference in their basicity cannot be solely responsible for the kinetic result shown in Table 1, since OH⁻ is only ~10³-fold more reactive than N₃⁻ although the former is ~11 pK_a units more basic than the latter. This appears to be consistent with the report that OH⁻ often deviates

Table 1. Summary of second-order rate constants for the reactions of 2,4-dinitrophenyl X-substituted benzenesulfonates (**1a–1f**) with OH⁻ (k_{OH^-}) and N₃- (k_{N3} -) in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C.^{*a*}

	Х	$k_{\rm OH} - M^{-1} {\rm s}^{-1}$	$10^3 k_{\rm N3}$ -/M ⁻¹ s ⁻¹
1a	4-NO ₂	442	341
1b	3-NO ₂	234	236
1c	4-Cl	22.0	24.7
1d	Н	7.80	12.5
1e	4-Me	3.20	6.67
1f	4-MeO	1.30	3.03

^{*a*} The data for the reactions with N_3^- were taken from Ref. 17.

negatively from linear Brønsted-type plots for nucleophilic substitution reactions of esters with various anionic nucleophiles.¹⁹ Jencks has attributed the negative deviation shown by OH⁻ from the linear Brønsted-type plot to a solvation effect, since OH⁻ is known to be strongly solvated in H₂O through H-bonding interactions.¹⁹ Thus, solvation effects would be also responsible for the kinetic results mentioned above.

The reactions of **1a-1f** with a weakly basic N₃- have been suggested to proceed through the S-O and C-O bond fission competitively.¹⁷ The fraction of the C-O bond fission has been reported to increase significantly as the substituent X in the benzenesulfonyl moiety changes from a strong EWG to an EDG (e.g., the percentage of C-O bond fission increases from 16 to 87% as X changes from 4-NO2 to 4-MeO, respectively).¹⁷ Accordingly, the C-O bond fission becomes the major reaction pathway when the substituent X is an EDG. In contrast, we have previously reported that the reactions of **1a–1f** with strongly basic $C_2H_5O^-$ proceed exclusively through the S-O bond fission on the basis of the product analysis (e.g., the 2,4-dinitrophenoxide ion was found as one of the S-O bond fission products but not 1ethoxy-2,4-dinitrobenzene, one of the C-O bond fission products).¹³ It is noted that the reactions of **1a-1f** with OH⁻ yield the 2,4-dinitrophenoxide ion as one of the reaction products whether or not the reactions proceed through the S-O bond fission or via the C-O bond scission. Accordingly, regioselectivity is not discussed in this study.

The effect of the substituent X on reactivity is shown in Figure 1. The Hammett plot for the reactions of **1a–1f** with OH^- is linear with $\rho_X = 2.27$ and $R^2 = 0.997$. However, a scrutiny of the linear Hammett plot reveals that substrates **1c** and **1f** deviate negatively from the linear plot. It is notable that **1c** and **1f** possess a substituent in the benzenesulfonyl moiety (*i.e.*, 4-Cl and 4-MeO, respectively) that can donate an electron pair through resonance interactions as modeled by the resonance structures $I_R \leftrightarrow II_R$. Since such resonance interactions could stabilize the ground state (GS) of the substrate, one might suggest that the negative deviation shown by **1c** and **1f** from the linear Hammett plot is due to the GS stabilization of substrates **1c** and **1f**.

Table 2. Summary of second-order rate constants for the reactions of Y-substituted phenyl 4-nitrobenzenesulfonates (**2a–2g**) with OH⁻ and N₃- in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C.^{*a*}

Entry	Y	pK_a^{Y-PhOH}	$k_{\rm OH} - M^{-1} {\rm s}^{-1}$	$10^3 k_{\rm N3}$ -/M ⁻¹ s ⁻¹
2a	2,4-(NO ₂) ₂	3.94	442	341
2b	$4-NO_2$	7.79	3.06	0.793
2c	4-CHO	8.45	0.811	0.184
2d	4-CN	8.82	1.67	0.506
2e	4-COMe	8.94	0.610	0.132
2f	3-CHO	10.12	0.299	0.0568
2g	4-Cl	10.63	0.174	-

^{*a*} The k_{N3} -values were taken from Ref. 17.



To examine the validity of the above idea, the Yukawa– Tsuno plot has been constructed in Figure 2. Eq. (1) was originally derived to account for the kinetic results for the solvolysis of benzylic systems in which a positive charge develops partially in the TS.²⁰ We have shown that Eq. (1) is also highly effective in clarifying the ambiguities in reaction mechanisms for nucleophilic substitution reactions of esters with various nucleophiles (*e.g.*, neutral amines as well as anionic nucleophiles such as OH⁻, N₃- and CN⁻).^{6,7,13} As shown in Figure 2, the Yukawa–Tsuno plot for the reactions of **1a–1f** with OH⁻ exhibits excellent linearity ($R^2 = 0.9998$)



Figure 1. Hammett plot for the reactions of 2,4-dinitrophenyl X-substituted benzenesulfonates (**1a–1f**) with OH[–] in 80 mol % H₂O/ 20 mol % DMSO at 25.0 \pm 0.1 °C. The identity of the points is given in Table 1.



Figure 2. Yukawa–Tsuno plot for the reactions of 2,4-dinitrophenyl X-substituted benzenesulfonates (**1a–1f**) with OH^- in 80 mol% H₂O/ 20 mol% DMSO at 25.0 ± 0.1 °C.

with $\rho_{\rm X} = 2.09$ and r = 0.41. A similar linear Yukawa–Tsuno plot has been reported for the corresponding reactions with N₃- (*e.g.*, $R^2 = 0.999$, $\rho_{\rm X} = 1.72$ and r = 0.40).¹⁷

$$\log k^{\mathrm{X}}/k^{\mathrm{H}} = \rho_{\mathrm{X}} \left[\sigma_{\mathrm{X}}^{\mathrm{o}} + r \left(\sigma_{\mathrm{X}}^{+} - \sigma_{\mathrm{X}}^{\mathrm{o}} \right) \right]$$
(1)

The *r* value in Eq. (1) represents the resonance demand of the reaction center or the extent of resonance contribution, while the term $(\sigma_X^+ - \sigma_X^0)$ is the resonance substituent constant that measures the capacity for π -delocalization of the π -electron donor substituent.^{20,21} Thus, the linear Yukawa– Tsuno plot shown in Figure 2 is consistent with the above idea that the negative deviation shown by substrates **1c** and **1f** from the linear Hammett plot (Figure 1) is caused by GS stabilization through resonance interactions, as modeled by the resonance structures $I_R \leftrightarrow II_R$.

Effect of Substituent Y on Reactivity and Reaction Mechanism. The linear Yukawa–Tsuno plot shown in Figure 2 suggests that the reactions of 1a-1f proceed through the same reaction mechanism. However, it does not give any further information on the reaction mechanism. Thus, second-order rate constants for the reactions of Y-substituted phenyl 4nitrobenzenesulfonates (2a-2g) with OH have been measured to obtain more conclusive information on the reaction mechanism. The k_{OH^-} values are summarized in Table 2 together with the k_{N3^-} values reported previously¹⁷ for the corresponding reactions with N₃- for comparison. As shown in Table 2, k_{OH} decreases as the substituent Y in the leaving group becomes a weaker EWG; e.g., it decreases from 442 to 3.06 and 0.174 $M^{-1}s^{-1}$ as the substituent Y changes from 2,4-(NO₂)₂ to 4-NO2 and 4-Cl, in turn. A similar result is demonstrated for the corresponding reactions with N₃-, although the azide ion is $\sim 10^3$ -fold less reactive than the hydroxide ion.

The effect of the substituent Y on the reactivity is illustrated in Figure 3. The Brønsted-type plot for the reactions of **2a–2g** with OH⁻ is linear with $\beta_{lg} = -0.51$, although the correlation



Figure 3. Brønsted-type plot for reactions of Y-substituted phenyl 4nitrobenzenesulfonates (**2a–2g**) with OH⁻ in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C. The identity of the points is given in Table 2.

coefficient for the plot is not excellent (*i.e.*, $R^2 = 0.985$). A similar linear Brønsted-type plot has been reported for the corresponding reactions with N₃- (*e.g.*, $\beta_{lg} = -0.63$ and $R^2 = 0.982$).¹⁷ A β_{lg} value of -0.6 ± 0.1 is typical for reactions reported previously to proceed through a concerted mechanism.^{2–7} In fact, the reactions of **2a–2g** with the azide ion have been reported to proceed through a concerted mechanism on the basis of the β_{lg} value of -0.63.¹⁷ Thus, one might propose that the reactions with OH⁻ also proceed through a concerted mechanism.

Useful information on the reaction mechanism can be obtained from Hammett plots correlated with σ° and σ^{-} constants. If the reactions of **2a–2g** with OH⁻ proceed through a concerted mechanism, a negative charge would develop partially on the O atom of the leaving Y-substituted phenoxide in the TS. Since such a negative charge could be delocalized to the substituent Y through resonance interactions, σ^{-} constants should result in a better Hammett correlation than σ^{o} constants. In contrast, if the current reactions proceed through a stepwise mechanism, expulsion of the leaving group would occur after the rate-determining step (RDS). This is because OH is much more basic and a poorer nucleofuge than aryloxide ions. Accordingly, if the reactions of 2a-2g with OH⁻ proceed through a stepwise mechanism, in which expulsion of the leaving group occurs after the RDS, no negative charge would develop on the O atom of the leaving group in the TS. In this case, σ^{o} constants should exhibit a better linear correlation than σ^- constants.

To examine the above idea, Hammett plots were constructed using σ° and σ^{-} constants. As shown in Figure 4, both Hammett plots exhibit highly scattered points although the plot correlated with σ° constants results in a slightly better correlation ($R^2 = 0.964$) than that with σ^{-} constants ($R^2 = 0.921$). Thus, one cannot obtain any useful information from the poor Hammett plots.

To elucidate the reaction mechanism, Yukawa–Tsuno plots have been constructed for the reactions of 2a-2g with



Figure 4. Hammett plots correlated with $\sigma y^{\circ}(a)$ and $\sigma y^{-}(b)$ constants for reactions of Y-substituted phenyl 4-nitrobenzenesulfonates (**2b–2g**) with OH⁻ in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C. The identity of the points is given in Table 2.

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(a)

OH⁻ and with N₃-. As shown in Figure 5(a), the plot for the reactions of **2a–2g** with OH⁻ exhibits an excellent linear correlation with $\rho_{\rm Y} = 1.85$ and r = 0.25. A similar result is shown for the corresponding reactions with N₃- (*e.g.*, $\rho_{\rm Y} = 2.10$ and r = 0.22). As mentioned above, the *r* value in the Yukawa-Tsuno equation represents the extent of resonance contribution.^{20,21} Thus, the *r* value of 0.25 implies that a negative charge develops partially on the O atom of the leaving group, which can be delocalized to the substituent Y through resonance interactions. This is possible only when the reactions proceed through a concerted mechanism but not possible if the reactions proceed through a stepwise mechanism as discussed earlier. Thus, it is concluded that the alkaline hydrolysis of **2a–2g** proceeds through a concerted mechanism.

Effect of Changing Nucleophile from N₃- to OH⁻ on Reaction Mechanism. It is generally understood that ρ_X and ρ_Y values represents a relative degree of bond formation between the nucleophile and the electrophilic center in the TS and a relative degree of expulsion of the leaving group, respectively. As mentioned earlier, the $\rho_{\rm X}$ value of 2.09 obtained from the reactions with OH⁻ is larger than that reported for the corresponding reactions with N₃- (*i.e.*, $\rho_{\rm X}$ = 1.72). This implies that bond formation in the TS is more advanced for the reactions with OH⁻ than for those with N₃-. In contrast, Figure 5 shows that the $\rho_{\rm Y}$ values are 1.85 and 2.10 for the reactions with OH⁻ and N₃-, respectively, indicating that expulsion of the leaving group is less advanced for the reactions with OH⁻ than for those with N₃-. Thus, one can suggest that the reactions with OH⁻ proceed through a tighter TS than for those with N₃- (*i.e.*, a TS with more bond formation but with less leaving-group expulsion).

Conclusions

The current study has allowed us to conclude the following: (1) Hydroxide ion is only 10^3 -fold more reactive than azide

(b) ⁻²



Figure 5. Yukawa–Tsuno plots for the reactions of Y-substituted phenyl 4-nitrobenzenesulfonates (**2b–2g**) with OH⁻ (a) and N₃- (b) ions in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C. The identity of the points is given in Table 2.

ion toward substrates **1a–1f** and **2a–2g**, although the former is 11 p K_a units more basic than the latter. (2) Substrates **1c** and **1f** deviate negatively from the linear Hammett plot, while the Yukawa–Tsuno plot results in an excellent linear correlation with $\rho_X = 2.09$ and r = 0.41, indicating that GS stabilization of the substrates **1c** and **1f** is responsible for the negative deviation. (3) The Brønsted-type plot for reactions of **2a–2g** with OH⁻ is linear with $\beta_{lg} = -0.51$, a typical value reported for reactions that proceed through a concerted mechanism. (4) The Yukawa–Tsuno plot for the reactions of **2a–2g** with OH⁻ exhibits excellent linearity with $\rho_Y = 1.85$ and r = 0.25, a clear indication that a negative charge develops partially on the O atom of the leaving group. (5) The reactions with OH⁻ proceed through a concerted mechanism with a tighter TS than those with N₃-.

Experimental

Materials. Substrates **1a–1f** and **2a–2g** were readily prepared from reactions of the respective Y-substituted phenol and X-substituted benzenesulfonyl chloride in the presence of triethylamine in anhydrous ether as reported previously.^{13,16} The crude products were purified by recrystallization or column chromatography. DMSO and other chemicals were of the highest quality available. Because of the low solubility of the substrates in pure H₂O, aqueous DMSO was used as the reaction medium (*i.e.*, 20 mol% DMSO/80 mol % H₂O). Double-distilled water was further boiled and cooled under nitrogen just before use. Sodium hydroxide stock solution was titrated using potassium hydrogen phthalate.

Kinetics. The kinetic studies were performed at $25.0 \pm 0.1^{\circ}$ C with a UV-vis spectrophotometer for slow reactions (e.g., $t_{1/2} > 10$ s) or with a stopped-flow spectrophotometer for fast reactions (e.g., $t_{1/2} \le 10$ s) equipped with a constanttemperature circulating bath. The reactions were followed by monitoring the appearance of 2,4-dinitrophenoxide ion for the reactions of 1a-1f (or Y-substituted phenoxide ion for those of 2a-2g). All the reactions were carried out under pseudo-first-order conditions in which the sodium hydroxide concentration was at least 20 times greater than the substrate concentration. Typically, the reaction was initiated by adding $5 \,\mu$ L of $0.02 \,\text{M}$ of a substrate solution in MeCN by a 10-µL syringe into a 10-mm UV cell containing 2.50 mL of the reaction medium and NaOH. All transfers of reaction solutions were carried out by means of gas-tight syringes.

Products Analysis. 2,4-Dinitrophenoxide or Y-substituted phenoxide ion was liberated quantitatively and identified as one of the reaction products after completion of the reaction with that of authentic sample under the same kinetic conditions.

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