

A Mechanistic Study on Alkaline Hydrolysis of Y-Substituted Phenyl Benzenesulfonates

Li-Ra Im, Youn-Min Park, and Ik-Hwan Um*

Department of Chemistry and Nano Science, Ewha Womans University, Seoul 120-750, Korea. *E-mail: ihum@ewha.ac.kr
Received October 1, 2008

Second-order rate constants (k_{OH^-}) have been measured spectrophotometrically for reactions of Y-substituted phenyl benzenesulfonates (**1a-h**) with OH^- in H_2O containing 20 mol % DMSO at 25.0 ± 0.1 °C. The Brønsted-type plot is linear with $\beta_{\text{g}} = -0.55$ including the points for the reactions of 2,4-dinitrophenyl benzenesulfonate (**1a**) and 4-chloro-2-nitrophenyl benzenesulfonate (**1c**), indicating that the *ortho*-nitro group on the leaving aryloxy does not exert steric hindrance in the current reactions. The Hammett plot correlated with σ° constants exhibits highly scattered points, while the Hammett correlation with σ^- constants results in a slightly better correlation but still many points deviate from the linearity. In contrast, the Yukawa-Tsuno plot shows an excellent linear correlation with $r = 0.52$, implying that leaving-group departure occurs at the RDS either in a stepwise mechanism or in a concerted pathway. However, the stepwise mechanism in which the leaving group departs in the RDS is excluded since the incoming OH^- is much more basic and a poorer nucleofuge than the leaving aryloxy. Thus, the alkaline hydrolysis of **1a-h** has been concluded to proceed through a concerted mechanism.

Key Words : Alkaline hydrolysis, Rate-determining step, Concerted mechanism, Transition state, Yukawa-Tsuno equation

Introduction

Nucleophilic substitution reactions of carbon and phosphorus centered esters have been intensively investigated due to the importance in biological processes as well as synthetic applications.¹⁻⁷ However, the corresponding reactions of sulfur centered esters have much less been studied.⁸⁻¹³ Reactions of aryl benzenesulfonates possessing a weakly basic aryloxy (e.g., 2,4-dinitrophenoxide) have been reported to proceed through competitive S–O and C–O bond fission pathways (Scheme 1). The regioselectivity has been reported to be influenced strongly by solvents, polarizability of nucleophiles, steric hindrance, etc.⁸⁻¹⁰

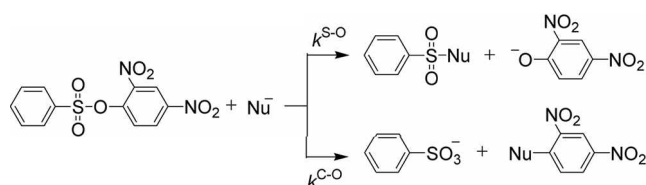
The reactions which result in a C–O bond fission have been suggested to proceed through a Meisenheimer complex (MC). The rate-determining step (RDS) has been reported to be formation of the MC on the basis of the fact that the reactivity is independent of the substituent in the sulfonyl moiety.⁹

On the other hand, the reactions which yield the S–O bond-fission products have been reported to proceed through either a concerted mechanism or a stepwise pathway depending on reaction conditions.⁹⁻¹³ Williams and his co-workers have concluded that reactions of 4-nitrophenyl 4-

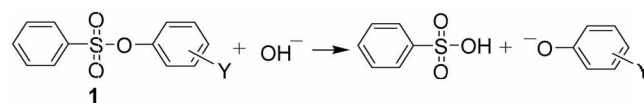
nitrobenzenesulfonate with a series of anionic nucleophiles, whose basicity straddles the leaving 4-nitrophenoxide, proceed through a concerted mechanism on the basis of the linear Brønsted-type plot obtained.¹¹ In contrast, Bunce and his coworkers have shown that alkaline ethanolysis of aryl benzenesulfonates proceed through a stepwise mechanism.¹² The evidence provided was that σ° constants result in better correlation than σ^- constants in the Hammett treatment of the leaving-group effects.¹² A similar conclusion has been drawn from reactions of aryl benzenesulfonates with aryloxides in anhydrous ethanol.¹³

We have recently performed reactions of 2,4-dinitrophenyl X-substituted benzenesulfonates with a series of aliphatic primary and secondary amines in H_2O containing 20 mol % DMSO.^{9a,b} It has been shown that the regioselectivity is influenced by the basicity of amine (i.e., the more S–O bond fission for the more basic amine) and the nature of substituent X in the sulfonyl moiety (i.e., the more S–O bond fission for the stronger electron withdrawing substituent).^{9a,b}

We have now extended our study to reactions of Y-substituted phenyl benzenesulfonates (**1a-h**) with OH^- in H_2O containing 20 mol % DMSO (Scheme 2). We have measured second-order rate constant (k_{OH^-}) and analyzed the kinetic data using Linear Free Energy Relationships such as



Scheme 1



Y = 2,4-(NO₂)₂ (**a**), 3,4-(NO₂)₂ (**b**), 4-Cl-2-NO₂ (**c**), 4-NO₂ (**d**), 4-CHO (**e**), 4-COMe (**f**), 3-COMe (**g**), 4-Cl (**h**).

Scheme 2

Brønsted, Hammett and Yukawa-Tsuno equations to investigate reaction mechanism.

Results and Discussion

All reactions obeyed first-order kinetics with quantitative liberation of Y-substituted phenoxide ion. Pseudo-first-order rate constants (k_{obsd}) were calculated from the equation $\ln(A_0 - A_t) = -k_{\text{obsd}}t + C$. The plots of k_{obsd} vs. hydroxide concentration are linear passing through the origin. Thus, the rate equation can be given as eq. (1) and the second-order rate constants (k_{OH^-}) have been determined from the slope of the linear plots. The kinetic conditions and results are shown in Table 1 and the k_{OH^-} values determined are summarized in Table 2. It is estimated from replicate runs that the uncertainty in the rate constants is less than $\pm 3\%$.

$$\text{Rate} = k_{\text{obsd}}[\text{substrate}], \text{ where } k_{\text{obsd}} = k_{\text{OH}^-}[\text{OH}^-] \quad (1)$$

Examination of Steric Hindrance from Brønsted-type Analysis. As shown in Table 2, the second-order rate constant decreases as the substituent Y in the leaving aryloxide becomes weakly electron withdrawing, *i.e.*, k_{N} decreases from $7.80 \text{ M}^{-1}\text{s}^{-1}$ to 0.0491 and $0.00207 \text{ M}^{-1}\text{s}^{-1}$ as Y changes from 2,4-(NO₂)₂ to 4-NO₂ and 4-Cl, respectively. The effect of substituent Y on reactivity is illustrated in Figure 1 as a function of $\text{p}K_{\text{a}}$ of the conjugate acid of the leaving aryl-

Table 1. Kinetic Conditions and Results for Reactions of Y-Substituted Phenyl Benzenesulfonates (1a-h) with OH⁻ in 80 mol % H₂O/20 mol % DMSO at 25.0 \pm 0.1 °C

entry	Y	[OH ⁻]/mM	10 ³ $k_{\text{obsd}}/\text{s}^{-1}$	n ^a
1a	2,4-(NO ₂) ₂	3.78-17.5	29.8-138	10
1b	3,4-(NO ₂) ₂	17.5-64.3	22.6-82.9	10
1c	4-Cl-2-NO ₂	17.5-64.3	11.2-41.1	15
1d	4-NO ₂	17.5-64.3	0.886-3.12	10
1e	4-CHO	38.6-154	0.662-2.71	12
1f	4-COMe	17.5-64.3	0.305-1.22	10
1g	3-COMe	99.0-198	0.327-0.674	10
1h	4-Cl	99.0-198	0.209-0.414	10

^aNumber of runs.

Table 2. Summary of Second-Order Rate Constants (k_{OH^-}) for Reactions of Y-Substituted Phenyl Benzenesulfonates (1a-h) with OH⁻ in 80 mol % H₂O/20 mol % DMSO at 25.0 \pm 0.1 °C.

entry	Y	$\text{p}K_{\text{a}}^{\text{Y-C}_6\text{H}_4\text{OH}^-}$	10 ² $k_{\text{OH}^-}/\text{M}^{-1}\text{s}^{-1}$
1a	2,4-(NO ₂) ₂	3.94	780
1b	3,4-(NO ₂) ₂	5.60	129
1c	4-Cl-2-NO ₂	6.92	62.2
1d	4-NO ₂	7.79	4.91
1e	4-CHO	8.45	1.73
1f	4-COMe	8.94	1.94
1g	3-COMe	10.39	0.350
1h	4-Cl	10.63	0.207

^aThe $\text{p}K_{\text{a}}$ value of phenols in 20 mol % DMSO was calculated from the equation $\text{p}K_{\text{a}}^{20\% \text{ DMSO}} = 1.27\text{p}K_{\text{a}}^{\text{H}_2\text{O}} - 1.28$ with the known $\text{p}K_{\text{a}}$ values of phenols in H₂O (see ref. 14).

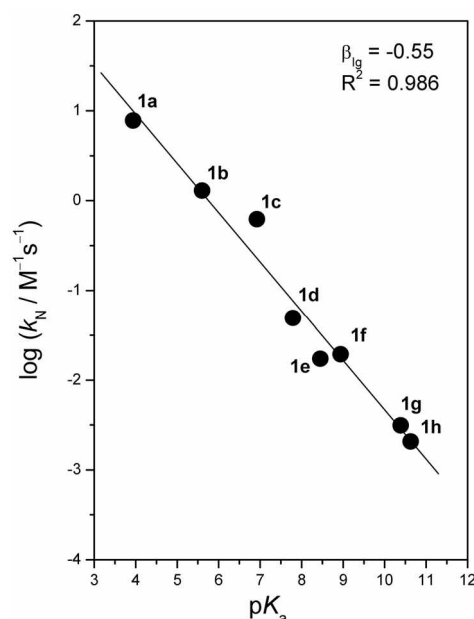


Figure 1. Brønsted-type plot for reactions of Y-substituted phenyl benzenesulfonates (1a-h) with OH⁻ in 80 mol % H₂O/20 mol % DMSO at 25.0 \pm 0.1 °C. The identity of the numbers is given in Table 2.

oxide. The Brønsted-type plot for the reactions of 1a-h is linear with $\beta_{\text{lg}} = -0.55$. It is noted that 1a and 1c do not exhibit negative deviations from the linearity although they have a nitro group on the *ortho*-position of the leaving phenoxide.

It has often been reported that carboxylic esters possessing an *ortho*-nitrophenoxide as a leaving group (*e.g.*, 2,4-dinitrophenyl acetate, benzoate, 2-furoate, and thiophene-2-carboxylate) exhibit negative deviations from Brønsted-type plots.^{15,16} Steric hindrance exerted by the *ortho*-nitro group has been suggested to be responsible for the negative deviation, since the *ortho*-nitro group on the leaving aryloxide would cause steric hindrance.^{15,16} The fact that 1a and 1c do not exhibit negative deviations suggests that the steric hindrance is absent in the current sulfonate system. A similar result has been reported for nucleophilic substitution reactions of Y-substituted phenyl diphenylphosphinates including 2,4-dinitrophenyl diphenylphosphinates with piperidine, OH⁻, and ethoxide ion, indicating that steric hindrance is also absent for the reactions of the phosphorus esters.^{7a-d}

One can suggest that at least two factors are responsible for the absence of the steric hindrance in the reactions of the sulfur and phosphorus centered esters, *i.e.*, the size and hybridization type of the electrophilic centers. The size of the electrophilic center of the sulfonate (*i.e.*, O=S=O) and phosphinate esters (*i.e.*, P=O) is much larger than that of the carboxylate esters (*i.e.*, C=O). One might expect that steric hindrance would not be significant for the reaction of substrates possessing a large electrophilic center. The type of hybridization of the electrophilic center is also considered to be responsible for the absence of steric hindrance in the phosphorus and sulfur centered electrophiles. The hybridization of the carboxylic esters in the ground state (GS) is sp^2

which becomes sp^3 in the transition state (TS). Accordingly, the TS for the reactions of carboxylic esters becomes more crowded than the GS. In contrast, the hybridization of sulfur and phosphorus centered esters changes from tetrahedral in the GS to trigonal bipyramidal in the TS. Accordingly, the TS for the reactions of the current benzenesulfonate system becomes less crowded than the GS. This argument is consistent with the fact that **1a** and **1c** do not exhibit a negative deviation from the linear Brønsted-type plot.

Determination of Reaction Mechanism. The second-order rate constant k_{OH^-} can be expressed as eq. (2) under the assumption of steady-state approximation for reactions which proceed through a stepwise mechanism with an intermediate. Then, eq. (2) becomes eq. (3) or eq. (4) depending on the RDS.

$$k_{OH^-} = k_1 k_2 / (k_{-1} + k_2) \quad (2)$$

$$k_{OH^-} = k_1 k_2 / k_{-1}, \text{ when } k_{-1} \gg k_2 \quad (3)$$

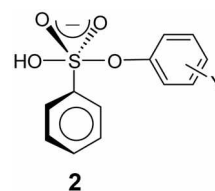
$$k_{OH^-} = k_1, \text{ when } k_{-1} \ll k_2 \quad (4)$$

It is apparent that the electronic nature of the substituent *Y* in the leaving group influences the microscopic rate constants k_1 , k_2 , and k_{-1} , *i.e.*, the k_1 and k_2 values would increase, while the k_{-1} value would decrease as substituent *Y* becomes a stronger electron withdrawing group (EWG). However, the effect of leaving-group substituent *Y* on k_2 would be more significant than on k_1 and k_{-1} , since *Y* is located directly on the leaving aryloxyde. Accordingly, one might expect a large negative β_g value for reactions in which k_2 is the RDS but a small one for those in which $k_1 = \text{RDS}$. Thus, the magnitude of β_g values has been taken as a measure of reaction mechanism, *e.g.*, β_g is *ca.* -0.8 or larger for reactions whose RDS is the k_2 step but *ca.* -0.4 or smaller for reactions in which $k_1 = \text{RDS}$.¹⁴ The β_g value of -0.55 is typical for reactions which proceed through a concerted mechanism.¹⁻⁷ In fact, we have recently reported that β_g values of -0.6 ± 0.1 for reactions which proceed concertedly (*e.g.*, nucleophilic substitution reactions of *Y*-substituted phenyl diphenylphosphinates and diphenylphosphinothioates with amines and anionic nucleophiles such as OH^- and ethoxide ion),⁷ while β_g values of -1.2 or larger for reactions in which $k_2 = \text{RDS}$ (*e.g.*, aminolysis of *Y*-substituted phenyl benzoates).⁴

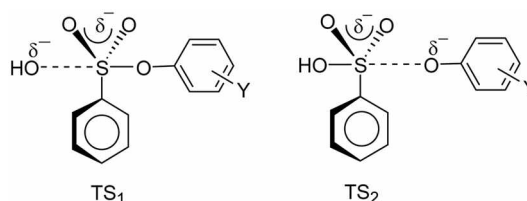
As shown in Figure 1, the β_g value for the reactions of **1a-h** is -0.55 . Thus, one can propose that the current reactions of *Y*-substituted phenyl benzenesulfonates with OH^- proceed through a concerted mechanism. To support our proposal, Hammett plots have been constructed using σ^o and σ^- constants as in the following section. It is noted that the points for the reactions of **1a** and **1c** are excluded in the Hammett plots, since they have an *ortho*-substituent whose σ^- or σ^o values are not known.

Hammett Correlations with σ^o and σ^- Constants. If the current reaction proceeds through a stepwise mechanism instead of a concerted pathway, the structure of the intermediate should be similar to **2** as illustrated below. It is noted that the incoming hydroxide and leaving aryloxyde

occupy the apical positions of the trigonal bipyramidal intermediate **2**.



Then the reaction would proceed through either TS_1 or TS_2 depending on the RDS. TS_1 represents the TS structure when formation of intermediate **2** is the RDS, while TS_2 applies to the TS structure when breakdown of **2** occurs in the RDS.



In TS_1 , the negative charge is delocalized on the incoming hydroxide and the two oxygen atoms of the sulfonyl moiety, but clearly not on the oxygen atom of the leaving ArO^- since leaving-group departure is not advanced at all. In this case, one might expect a good Hammett correlation with σ^o constants. As shown in Figure 2, the Hammett plot correlated with σ^o constants demonstrates highly scattered points, indicating that the current reaction does not proceed through TS_1 .

If the current reactions proceed through a stepwise mechanism with TS_2 , a partial negative charge develops on the oxygen atom of the leaving aryloxyde. Since such a negative

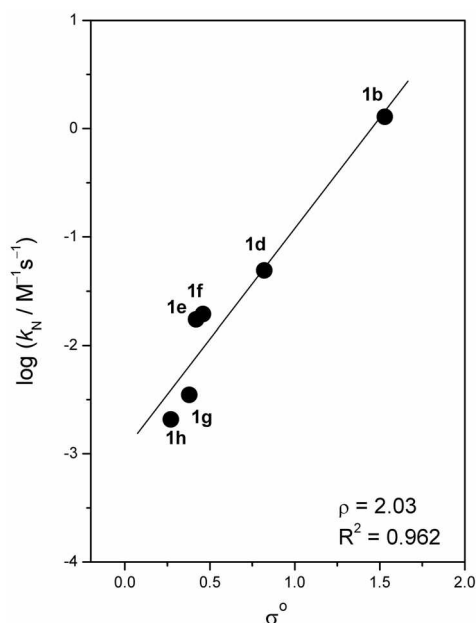


Figure 2. Hammett plot correlated with σ^o constants for reactions of *Y*-substituted phenyl benzenesulfonates (**1b** and **1d-h**) with OH^- in 80 mol % H_2O /20 mol % DMSO at 25.0 ± 0.1 °C. The identity of the numbers is given in Table 2.

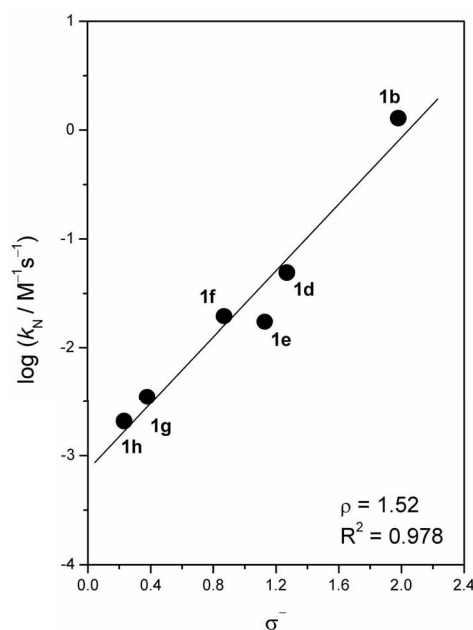


Figure 3. Hammett correlation with σ^- constants for reactions of Y-substituted phenyl benzenesulfonates (**1b** and **1d-h**) with OH^- in 80 mol % H_2O /20 mol % DMSO at 25.0 ± 0.1 °C. The identity of the numbers is given in Table 2.

charge can be delocalized on the substituent Y through resonance interaction, one can expect that σ^- constants should result in a good Hammett correlation. As shown in Figure 3, the Hammett plot correlated with σ^- constants results in only a slightly better correlation than that with σ^0 constants (e.g., $R^2 = 0.979$ in Figure 3 vs. $R^2 = 0.961$ in Figure 2). However, the Hammett plot also exhibits scattered points, indicating that the reactions do not proceed through TS_2 either. Accordingly, one can also exclude TS_2 in which the RDS is departure of the leaving aryloxide. This idea can be further supported by the fact that OH^- is much more basic and a poorer nucleofuge than the leaving aryloxide.

Yukawa-Tsuno plot and TS structure. We have recently shown that the Yukawa-Tsuno equation (eq. 5) is highly informative to investigate reaction mechanisms.^{4,7} The magnitude of the r value in eq. (5) represents the resonance demand of the reaction center or the extent of resonance contribution while the term $(\sigma^- - \sigma^0)$ is the resonance substituent constant that measures the capacity for π -delocalization.¹⁷

$$\log k^{\text{X}}/k^{\text{H}} = \rho [\sigma^0 + r(\sigma^- - \sigma^0)] \quad (5)$$

Thus, Yukawa-Tsuno plot has been constructed for the reactions of **1b** and **1d-h** with OH^- . As shown in Figure 4, the Yukawa-Tsuno plot exhibits an excellent linear correlation ($R^2 = 0.994$) with $r = 0.52$. The best correlation would be obtained with σ^- constants when $r = 1$ or with σ^0 constants when $r = 0$. Since the r value determined in this study is neither 0 nor 1, the Yukawa-Tsuno plot exhibits the best linear correlation.

The r value of 0.52 clearly indicates that a partial negative charge develops on the oxygen atom of the leaving aryl-

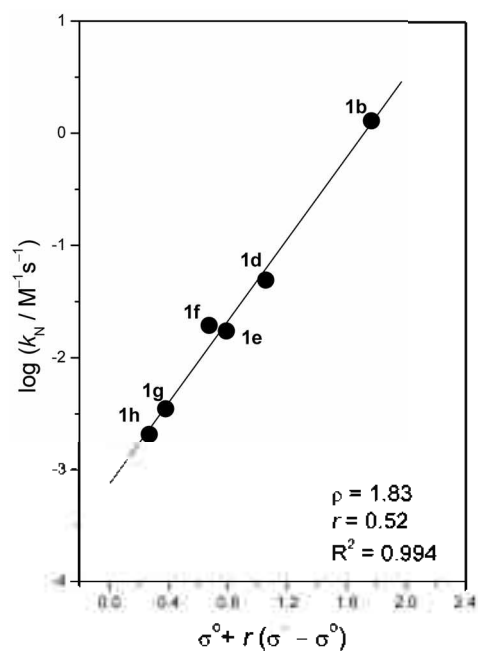
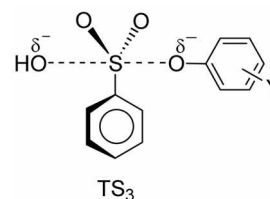


Figure 4. Yukawa-Tsuno plot for reactions of Y-substituted phenyl benzenesulfonates (**1b** and **1d-h**) with OH^- in 80 mol % H_2O / 20 mol % DMSO at 25.0 ± 0.1 °C. The identity of the numbers is given in Table 2.

oxide. Thus, one can suggest that the reaction proceeds either through TS_2 or TS_3 . However, TS_2 has already been excluded as a TS structure in the current reactions on the basis of the fact that OH^- is much more basic and a poorer nucleofuge than the leaving aryloxide. Accordingly, one can conclude that the current reactions proceed through a concerted mechanism with a TS structure similar to TS_3 , in which the partial negative charge on the oxygen atom of the leaving aryloxide can be delocalized on the substituent Y through resonance interaction. This is consistent with the preceding proposal that the reactions of **1a-h** with OH^- proceed through a concerted mechanism on the basis of the β_{lg} value of -0.55 .



Conclusions

The current study has allowed us to conclude the following: (1) The Brønsted-type plot for the alkaline hydrolysis of **1a-h** is linear with $\beta_{\text{lg}} = -0.55$ including the points for the reactions of **1a** and **1c** which possess an *ortho*-nitro group on the leaving aryloxide, indicating that steric hindrance is absent in the current reactions. (2) The linear Brønsted-type plot with $\beta_{\text{lg}} = -0.55$ has been taken as evidence for a concerted mechanism. (3) The Hammett plot correlated with σ^0 constants exhibits highly scattered points, while the

Hammett correlation with σ^- constants results in only a slightly better correlation. (4) In contrast, the Yukawa-Tsuno plot shows an excellent linear correlation, implying that the leaving group departs in the RDS either in a stepwise mechanism or in a concerted pathway. (5) However, the stepwise mechanism in which the leaving group departs in the RDS has been excluded since the incoming OH^- is much more basic and a poorer nucleofuge than the leaving aryloxy. Thus, the alkaline hydrolysis of **1a-h** has been concluded to proceed through a concerted mechanism.

Experimental Section

Materials. Compounds **1a-h** were readily prepared from reactions of benzenesulfonyl chloride with Y-substituted phenols in the presence of triethylamine as a base catalyst in anhydrous ether as reported previously.⁹ Other chemicals used were of the highest quality available. The reaction medium was H_2O containing 20 mol % DMSO due to low solubility of **1a-h** 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 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. All the reactions were carried out under pseudo-first-order conditions in which hydroxide concentrations were at least 20 times greater than the substrate concentration. All solutions were prepared freshly just before use under nitrogen, and transferred by using 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 thermostatted reaction mixture made up of solvent and aliquot of NaOH stock solution.

Product Analysis. Y-Substituted phenoxide was liberated quantitatively and identified as one of the products by comparison of the UV-vis spectrum at the end of reaction with the authentic sample under the experimental condition. Our previous study has shown that alkaline ethanolysis of Y-substituted phenyl benzenesulfonates including $\text{Y} = 2,4\text{-(NO}_2)_2$ proceeds exclusively through the S-O bond fission.^{9c,13} Accordingly, it is assumed that the current alkaline hydrolysis also proceeds through the S-O bond fission exclusively since both C-O and S-O bond fissions result in the same products.

Acknowledgments. This work was supported by a grant from Korea Research Foundation (KRF-2005-015-C00256). L. R. Im and Y. M. Park are also grateful for the BK 21 Scholarship.

References

- (a) Gresser, M. J.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 6963-6970. (b) Gresser, M. J.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 6970-6980.
- (a) Castro, E. A.; Campodonico, P. R.; Contreras, R.; Fuentealba, P.; Santos, J. G.; Leis, J. R.; Garcia-Rio, L.; Saez, J. A.; Domingo, L. R. *Tetrahedron* **2006**, *62*, 2555-2562. (b) Castro, E. A.; Gazitua, M.; Santos, J. G. *J. Org. Chem.* **2005**, *70*, 8088-8092.
- (a) Hoque, M. E. U.; Dey, S.; Guha, A. K.; Kim, C. K.; Lee, B. S.; Lee, H. W. *J. Org. Chem.* **2007**, *72*, 5493-5499. (b) Oh, H. K.; Oh, J. Y.; Sung, D. D.; Lee, I. *J. Org. Chem.* **2005**, *70*, 5624-5629. (c) Lee, H. W.; Guha, A. K.; Kim, C. K.; Lee, I. *J. Org. Chem.* **2002**, *67*, 2215-2222. (d) Hoque, M. E. U.; Dey, N. K.; Guha, A. K.; Kim, C. K.; Lee, B. S.; Lee, H. W. *Bull. Korean Chem. Soc.* **2007**, *28*, 1797-1802. (e) Hoque, M. E. U.; Lee, H. W. *Bull. Korean Chem. Soc.* **2007**, *28*, 936-940.
- (a) Um, I. H.; Park, Y. M.; Fujio, M.; Mishima, M.; Tsuno, Y. *J. Org. Chem.* **2007**, *72*, 4816-4821. (b) Um, I. H.; Hwang, S. J.; Baek, M. H.; Park, E. J. *J. Org. Chem.* **2006**, *71*, 9191-9197. (c) Um, I. H.; Ko, S. H.; Bae, S. K. *J. Org. Chem.* **2006**, *71*, 5800-5803. (d) Um, I. H.; Lee, H. W.; Nagano, Y.; Fujio, M.; Tsuno, Y. *J. Org. Chem.* **2005**, *70*, 4980-4987.
- (a) Han, X.; Balakrishnan, V. K.; Buncel, E. *Langmuir* **2007**, *23*, 6519-6525. (b) Han, X.; Balakrishnan, V. K.; van Loon, G. W.; Buncel, E. *Langmuir* **2006**, *22*, 9009-9017. (c) Cheung, J. C. F.; Park, Y. S.; Smith, V. H.; van Loon, G.; Buncel, E.; Churchill, D. *Can. J. Chem.* **2006**, *84*, 926. (d) Churchill, D.; Cheung, J. C. F.; Park, Y. S.; Smith, V. H.; van Loon, G.; Buncel, E. *Can. J. Chem.* **2006**, *84*, 702-708.
- (a) Cleland, W. W.; Hengge, A. C. *Chem. Rev.* **2006**, *106*, 3252-3278. (b) Hengge, A. C. *Adv. Phys. Org. Chem.* **2005**, *40*, 49-108. (c) Catrina, I.; O'Brien, P. J.; Purcell, J.; Nikolic-Hughes, I.; Zalatan, J. G.; Hengge, A. C.; Herschlag, D. *J. Am. Chem. Soc.* **2007**, *129*, 5760-5765. (d) Rawlings, J.; Cleland, W. W.; Hengge, A. C. *J. Am. Chem. Soc.* **2006**, *128*, 17120-17125. (e) Hengge, A. C.; Onyido, I. *Curr. Org. Chem.* **2005**, *9*, 61-74. (f) Sorensen-Stowell, K.; Hengge, A. C. *J. Org. Chem.* **2005**, *70*, 8303-8308. (g) Sorensen-Stowell, K.; Hengge, A. C. *J. Org. Chem.* **2005**, *70*, 4805-4809.
- (a) Um, I. H.; Han, J. Y.; Hwang, S. J. *Chem. Eur. J.* **2008**, *14*, 7324-7330. (b) Um, I. H.; Shin, Y. H.; Lee, S. E.; Yang, K.; Buncel, E. *J. Org. Chem.* **2008**, *73*, 923-920. (c) Um, I. H.; Akhtar, K.; Shin, Y. H.; Han, J. Y. *J. Org. Chem.* **2007**, *72*, 3823-3829. (d) Um, I. H.; Park, J. E.; Shin, Y. H. *Org. Biomol. Chem.* **2007**, *5*, 3539-3543.
- Choi, J. H.; Lee, B. C.; Lee, H. W.; Lee, I. *J. Org. Chem.* **2002**, *67*, 1277-1282.
- (a) Um, I. H.; Hong, J. Y.; Kim, J. J.; Chae, O. M.; Bae, S. K. *J. Org. Chem.* **2003**, *68*, 5180-5185. (b) Um, I. H.; Chun, S. M.; Chae, O. M.; Fujio, M.; Tsuno, Y. *J. Org. Chem.* **2004**, *69*, 3166-3172. (c) Um, I. H.; Kim, J. J.; Kim, M. J.; Kwon, D. S. *Bull. Korean Chem. Soc.* **1996**, *17*, 353-357.
- (a) Tagaki, W.; Kurusu, T.; Oae, S. *B. Chem. Soc. Jpn.* **1969**, *42*, 2894-2898. (b) Oae, S.; Kiritani, R. *B. Chem. Soc. Jpn.* **1965**, *38*, 765-770.
- (a) Williams, A. *Acc. Chem. Res.* **1989**, *22*, 387-392. (b) D'Rozario, P.; Smyth, R. L.; Williams, A. *J. Am. Chem. Soc.* **1984**, *106*, 5027-5028.
- (a) Pregel, M. J.; Dunn, E. J.; Buncel, E. *J. Am. Chem. Soc.* **1991**, *113*, 3545-3550. (b) Pregel, M. J.; Dunn, E. J.; Buncel, E. *Can. J. Chem.* **1990**, *68*, 1846-1858.
- Um, I. H.; Lee, S. J.; Kim, J. J.; Kwon, D. S. *Bull. Korean Chem. Soc.* **1994**, *15*, 473-477.
- Buncel, E.; Um, I. H.; Hoz, S. *J. Am. Chem. Soc.* **1989**, *111*, 971-975.
- (a) Gresser, M. J.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 6963-6970. (b) Gresser, M. J.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 6970-6980.
- (a) Um, I. H.; Seo, J. A.; Lee, H. M. *Bull. Korean Chem. Soc.* **2008**, *29*, 1915-1919. (b) Um, I. H.; Seo, J. A.; Chun, S. M. *Bull. Korean Chem. Soc.* **2008**, *29*, 1459-1463. (c) Um, I. H.; Akhtar, K. *Bull. Korean Chem. Soc.* **2008**, *29*, 772-776.
- (a) Tsuno, Y.; Fujio, M. *Adv. Phys. Org. Chem.* **1999**, *32*, 267-385. (b) Tsuno, Y.; Fujio, M. *Chem. Soc. Rev.* **1996**, *25*, 129-139. (c) Yukawa, Y.; Tsuno, Y. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 965-970.