Kinetics and Mechanism of Nucleophilic Displacement Reactions of Y-Substituted Phenyl Benzoates with Z-Substituted Phenoxides

Se-Won Min, Jin-A Seo, and Ik-Hwan Um*

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

Second-order rate constants have been measured for two series of nucleophilic displacement reactions, i.e., reactions of 4-nitrophenyl benzoate with Z-substituted phenoxides and those of Y-substituted phenyl benzoates (**1a-h**) with 4-chlorophenoxide (4-ClPhO⁻) in 80 mol% H_2O/20 mol% DMSO at 25.0 ± 0.1 °C. The Bronsted-type plot for reactions of 4-nitrophenyl benzoate with Z-substituted phenoxides exhibits an excellent linear correlation with $\beta_{nuc} = 0.72$. Reactions of **1a-h** with 4-chlorophenoxide result in also a linear Bronsted-type plot with $\beta_{lg} = -0.62$, a typical β_{lg} value for a concerted mechanism. The Hammett plots correlated with σ° and σ^{-} constants show many scattered points for reactions of **1a-h** with 4-chlorophenoxide. In contrast, the corresponding Yukawa-Tsuno plot exhibits an excellent linear correlation with $\rho_Y = 2.26$ and $r = 0.53$, indicating that expulsion of the leaving group occurs at the rate-determining step (RDS) either in a concerted mechanism or in a stepwise pathway. However, a stepwise mechanism with leaving group departure being the RDS is excluded since the leaving Y-substituted phenoxide is less basic and a better nucleofuge than the incoming 4-ClPhO⁻. Thus, the reactions have been concluded to proceed through a concerted mechanism, in which bond formation between the nucleophile and electrophilic center is more advanced than expulsion of the leaving group in the transition state on the basis of the magnitude of β_{nuc} and β_{lg} values.
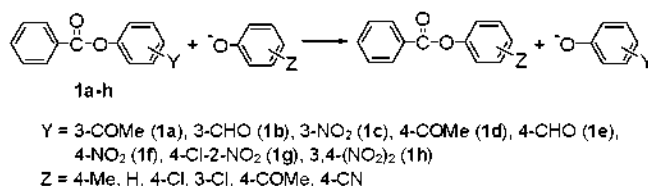
Key Words: Acyl-group transfer, Aryl benzoates, Bronsted-type plot, Concerted mechanism, Yukawa-Tsuno plot

Introduction

Acyl-group transfer reactions have been reported to proceed through a concerted mechanism or through a stepwise mechanism depending on reaction conditions.[1-5] Aminolysis of aryl acetates and benzoates have generally been understood to proceed through a stepwise mechanism with a change in rate-determining step (RDS) on the basis of curved Bronsted-type plots found for reactions of esters with a good leaving group (e.g., 2,4-dinitrophenoxide).[1-5] RDS has been suggested to change at pK_a° defined as the curvature center of a curved Bronsted-type plot, i.e., RDS changes from breakdown of the intermediate to its formation as the incoming amine becomes more basic than the leaving aryloxide by 4 to 5 pK_a units.[1-5]

However, reactions with anionic nucleophiles have not been completely understood. Williams *et al.* have concluded that reactions of 4-nitrophenyl acetate with a series of substituted phenoxides, whose basicity straddles the leaving 4-nitrophenoxide, proceed through a concerted mechanism on the basis of a linear Bronsted-type plot.[6] This is because a curved Bronsted-type plot would be expected if the reaction proceeds through a stepwise mechanism.[6] In contrast, it has been reported that reactions of substituted phenyl acetates with phenoxide proceed through an addition intermediate with its formation being RDS.[7] The evidence provided was that σ^{-} constants result in a poorer Hammett correlation than σ° constants.[7]

We have recently shown that deduction of reaction mechanism based just on Hammett correlations with σ^{-} or σ° constants might be misleading for alkaline hydrolysis and ethanolysis of Y-substituted phenyl diphenylphosphinates and related com-

Y = 3-COMe (**1a**), 3-CHO (**1b**), 3-NO₂ (**1c**), 4-COMe (**1d**), 4-CHO (**1e**), 4-NO₂ (**1f**), 4-Cl-2-NO₂ (**1g**), 3,4-(NO₂)₂ (**1h**)
Z = 4-Me, H, 4-Cl, 3-Cl, 4-COMe, 4-CN

Scheme 1

pounds.[8] It was found that σ° constants result in better Hammett correlation than σ^{-} constants. Traditionally, such a result was taken as evidence for a stepwise mechanism.[9-13] However, we concluded that the reactions proceed through a concerted mechanism since the corresponding Yukawa-Tsuno plot resulted in an excellent linear correlation.[8,14]

To get more information on mechanism for acyl-group transfer reactions, our study has been extended to reactions of 4-nitrophenyl benzoate with a series of Z-substituted phenoxides and those of Y-substituted phenyl benzoates (**1a-h**) with 4-chlorophenoxide (Scheme 1). We have concluded that the reactions proceed through a concerted mechanism on the basis of LFERs (e.g., Bronsted-type plots, Hammett plots, and Yukawa-Tsuno plots).

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. Pseudo-first-order rate constants (k_{obsd}) were calculated

Table 1. Summary of Second-order Rate Constants ($k_{Z\text{-PhO}^-}$) for Reactions of 4-Nitrophenyl Benzoate with Z-Substituted Phenoxides ($Z\text{-}C_6H_4O^-$) in 80 mol% H_2O/20 mol% DMSO at 25.0 ± 0.1 °C.

Entry	Z	$pK_a^{Z\text{-}C_6H_4OH}$	$10^3\ k_{Z\text{-PhO}^-}$/$M^{-1}s^{-1}$
1	4-Me	11.7[a]	925
2	H	11.3[a]	452
3	4-Cl	10.5[a]	185
4	3-Cl	10.2[b]	90.3
5	4-COMe	8.94[b]	8.88
6	4-CN	8.60[a]	5.10

[a]pK_a in 20 mol% DMSO taken from ref. 7(a). [b]pK_a in 20 mol% DMSO calculated from equation. $pK_a^{Z\text{-}C_6H_4OH}$ in 20% DMSO = 1.27 $pK_a^{Z\text{-}C_6H_4OH}$ in H_2O – 1.28.

from the equation $\ln(A_\infty - A_t) = -k_{obsd}t + C$. The plots of k_{obsd} *vs.* nucleophile concentration were linear. Second-order rate constants were determined from the slope of the linear plots and summarized in Tables 1 and 2. It is estimated from replicate runs that the uncertainty in the rate constants is less than ±3 %.

Effect of Basicity of Incoming Aryloxides on Reactivity. As shown in Table 1, the second-order rate constant ($k_{Z\text{-PhO}^-}$) for reactions of 4-nitrophenyl benzoate with Z-substituted phenoxide ($Z\text{-}C_6H_4O^-$) decreases as the basicity of incoming aryloxide decreases. e.g., it decreases from 0.925 $M^{-1}s^{-1}$ to 0.185 and 5.10 × 10^{-3} $M^{-1}s^{-1}$ as the pK_a of the conjugate acid of the aryloxide decreases from 11.7 to 10.5 and 8.6. in turn. The effect of basicity of aryloxides on reactivity is illustrated in Figure 1. The Bronsted-type plot exhibits an excellent linear correlation with β_{nuc} = 0.72.

The magnitude of β_{nuc} values has generally been understood to represent a relative degree of bond formation in the transition state.[15,16] Accordingly, β_{nuc} has been taken as a measure of reaction mechanism. e.g., β_{nuc} = 0.5 ± 0.1 for reactions
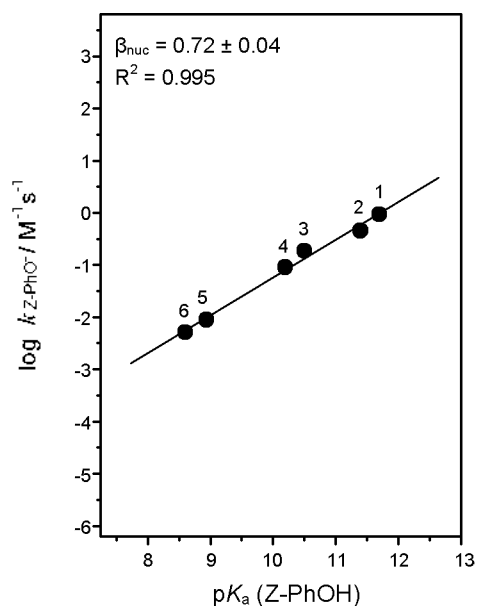
Figure 1. Bronsted-type plot for reactions of 4-nitrophenyl benzoate with Z-substituted phenoxides ($Z\text{-}C_6H_4O^-$) in 80 mol% H_2O/20 mol% DMSO at 25.0 ± 0.1 °C. The identity of points is given in Table 1.

proceeding through a concerted mechanism while β_{nuc} = 0.2 ± 0.1 or 0.9 ± 0.2 for those reported to proceed through a stepwise mechanism depending on the rate-determining step (RDS).[15,16] The current β_{nuc} value of 0.72 implies that the degree of bond formation in the transition state is relatively high. Thus, one might suggest that the current reaction proceeds through intermediate **2**. in which expulsion of 4-nitrophenoxide from **2** occurs in the RDS on the basis of the β_{nuc} value.

2
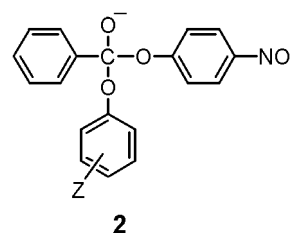
The RDS for a stepwise mechanism would be determined by the basicity of nucleofuges. e.g., 4-nitrophenoxide and Z-substituted phenoxide in this study. One might expect that 4-nitrophenoxide would depart more rapidly than Z-substituted phenoxide. since the former is less basic and a better nucleofuge than the latter. Accordingly, expulsion of 4-nitrophenoxide from **2** is expected to occur after the RDS. Thus, one can suggest that the current reaction proceeds through a concerted mechanism and the β_{nuc} value of 0.72 found in this study would be an upper limit for a concerted mechanism (i.e., a large bond formation in the transition state).

Effect of Leaving-Group Basicity on Reactivity. To examine the above argument. second-order rate constants ($k_{4\text{-ClPhO}^-}$) have been measured for reactions of Y-substituted phenyl benzoates (**1a-h**) with 4-chlorophenoxide (4-ClPhO⁻). As shown in Table 2. $k_{4\text{-ClPhO}^-}$ increases as the leaving aryloxide becomes less basic. e.g., it increases from 3.45 × 10^{-3} $M^{-1}s^{-1}$ to 5.52 × 10^{-2} and 7.19 $M^{-1}s^{-1}$ as the pK_a of the conjugate acid of the leaving aryloxide decreases from 10.4 to 8.45 and 5.60. in turn.

The effect of leaving group basicity on reactivity is illustrated in Figure 2. The Bronsted-type plot is linear with β_{lg} = −0.62. which is a typical β_{lg} value for reactions reported to proceed

Table 2. Summary of Second-order Rate Constants for Reactions of Y-Substituted Phenyl Benzoates (**1a-h**) with 4-Chlorophenoxide (4-ClPhO⁻) in 80 mol% H_2O/20 mol% DMSO at 25.0 ± 0.1 °C.[a]

	Y	$pK_a^{Y\text{-PhOH}}$	$k_{4\text{-ClPhO}^-}$/$M^{-1}s^{-1}$
1a	3-COCH₃	10.4	3.45 × 10^{-3}
1b	3-CHO	10.1	6.10 × 10^{-3}
1c	3-NO₂	9.32	4.16 × 10^{-2}
1d	4-COCH₃	8.94	2.36 × 10^{-2}
1e	4-CHO	8.45	5.52 × 10^{-2}
1f	4-NO₂	7.79	1.85 × 10^{-1}
1g	4-Cl-2-NO₂	6.92	2.15 × 10^{-1}
1h	3,4-(NO₂)₂	5.60	7.19

[a]pK_a in 20 mol% DMSO calculated from equation. $pK_a^{Z\text{-}C_6H_4OH}$ in 20% DMSO = 1.27$pK_a^{Z\text{-}C_6H_4OH}$ in H_2O −1.28.
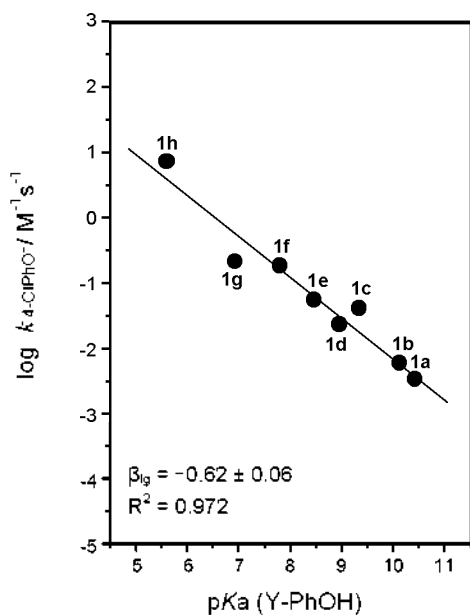
Figure 2. Bronsted-type plot for reactions of Y-substituted phenyl benzoates (1a-h) with 4-ClPhO⁻ in 80 mol% H₂O/20 mol% DMSO at 25.0 ± 0.1 °C. The identity of points is given in Table 2.

Figure 3. Hammett correlations with σ⁰ (A) and σ⁻ (B) for reactions of Y-substituted phenyl benzoates (1a-h) with 4-ClPhO⁻ in 80 mol% H₂O/20 mol% DMSO at 25.0 ± 0.1 °C. The identity of points is given in Table 2.

Figure 4. Yukawa-Tsuno plot for reactions of Y-substituted phenyl benzoates (1a-h) with 4-ClPhO⁻ in 80 mol% H₂O/20 mol% DMSO at 25.0 ± 0.1 °C. The identity of points is given in Table 2.

through a concerted mechanism.[8,17-20] However. one cannot obtain conclusive information on mechanism for the current reactions since the plots exhibit many scattered points.

To get more conclusive information on the reaction mechanism, Hammett plots have been constructed using σ^0 and σ^- constants in Figures 3A and 3B. One might expect that σ^0 constants would result in a better Hammett correlation than σ^-, if the leaving group departure is not advanced at RDS. In contrast. σ^- constants would give a better correlation than σ^0, if the leaving group departure occurs in RDS either in a stepwise mechanism or in a concerted pathway. This is because a partial negative charge, which can be delocalized on the substituent Y through resonance. would develop on the oxygen atom of the leaving aryloxide when the leaving group departure occurs in RDS. As shown in Figures 3A and 3B. σ^- constants result in a slightly better Hammett correlation than σ^0 constants. but both plots exhibit highly scattered points. Thus. these Hammett plots cannot provide definitive information on reaction mechanism.

We have recently shown that deduction of reaction mechanism based just on a linear or nonlinear Hammett plot can be misleading for reactions of 2,4-dinitrophenyl X-substituted benzoates and related compounds with amines as well as with anionic nucleophiles such as OH⁻, CN⁻, and N₃⁻.[5,14,21,22] Instead. Yukawa-Tsuno plots have been found to be highly effective to elucidate reaction mechanism.[5,14,21,22] Thus. a Yukawa-Tsuno plot has been constructed using the current kinetic results to deduce reaction mechanism. As shown in Figure 4, the Yukawa-Tsuno plot results in an excellent linear correlation with ρ_Y = 2.26 and r = 0.53. The r value in the Yukawa-Tsuno equation (eq 2) represents the extent of resonance contribution between the reaction site and substituent Y.[23] Since eq (2) becomes the Hammett equation when r = 0 or 1, the fact that r is neither 0 nor 1 is consistent with the poor Hammett correlations with σ^0
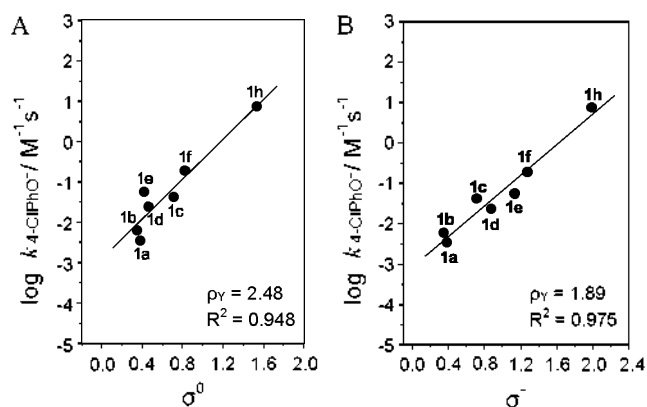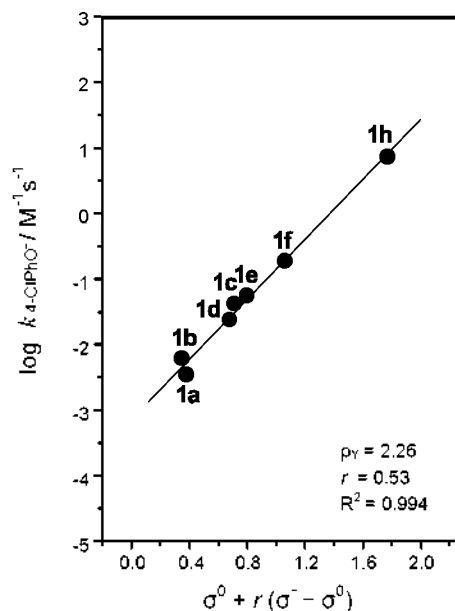
or σ^- constants shown in Figure 3.

$$\log k^Y/k^H = \rho \, (\sigma^0 + r(\sigma^- - \sigma^0)) \qquad (2)$$

The r value of 0.53 indicates that a negative charge develops partially on the oxygen atom of the leaving aryloxide. Since such a negative charge can be delocalized onto the substituent Y through resonance interaction, two different mechanisms are possible, i.e.. a concerted mechanism and a stepwise process in which expulsion of the leaving group occurs in the RDS. However, one can exclude the latter mechanism as mentioned above, since expulsion of the leaving group is expected to occur rapidly after the RDS on the basis of the fact that 4-ClPhO⁻ is more basic and a poorer nucleofuge than all the Y-substituted phenoxides employed in this study. Thus. one can conclude that the reactions of aryl benzoates **1a-h**

with 4-ClPhO⁻ proceed through a concerted mechanism, in which bond formation between the nucleophile and the electrophilic center is expected to be more advanced than expulsion of the leaving group.

Summary

(1) The Bronsted-type plot for reactions of 4-nitrophenyl benzoate with Z-substituted phenoxides exhibits an excellent linear correlation with $\beta_{nuc} = 0.72$.

(2) Reactions of Y-substituted phenyl benzoates (**1a-h**) with 4-ClPhO⁻ result in a linear Bronsted-type plot with $\beta_{lg} = -0.62$, a typical β_{lg} value for a concerted reaction.

(3) Hammett plots correlated with σ^o and σ^- constants exhibit highly scattered points for the reactions of **1a-h** with 4-ClPhO⁻, while the corresponding Yukawa-Tsuno plot results in an excellent linearity with $\rho_Y = 2.26$ and $r = 0.53$, indicating that expulsion of the leaving group occurs at the RDS.

(4) A stepwise mechanism with leaving group departure being the RDS is excluded since the nucleophile is more basic and a poorer nucleofuge than the leaving Y-substituted phenoxides.

(5) The current reaction proceeds through a concerted mechanism, in which bond formation is expected to be more advanced than expulsion of the leaving group on the basis of the magnitude of β_{nuc} and β_{lg} values.

Experimental Section

Materials. Y-Substituted phenyl benzoates (**1a-h**) were readily prepared from the reactions of Y-substituted phenol and benzoyl chloride in anhydrous ether in the presence of triethylamine. Their purity was checked by their melting points and ^{1}H NMR spectra. Phenols were generally recrystallized before use. DMSO and other chemicals were of the highest quality available. Doubly glass-distilled water was further boiled and cooled under nitrogen just before use.

Kinetics. The kinetic study was performed using a UV-Vis spectrophotometer equipped with a constant temperature circulating bath. The reactions were followed by monitoring the appearance of Y-substituted phenoxide at a fixed wavelength corresponding the maximum absorption. Due to low solubility of substrates **1a-h** in pure water, kinetics were performed in 80 mol% H₂O/20 mol% DMSO. Typically, the reaction was initiated by adding 5 μL of a 0.02 M of substrate stock solution in MeCN by a 10 μL syringe to a 10 mm UV cell containing 2.50 mL of the reaction medium and nucleophile. The nucleophile stock solution of *ca.* 0.2 M was prepared in 25.0 mL volumetric flask under nitrogen by adding 2 equiv. of Z-substituted phenol to 1 equiv. of standardized NaOH solution to obtain a self-buffered solution. Transfers of solutions were carried out by means of gas-tight syringes. All reactions were carried out under pseudo-first-order conditions in which nucleophile concentrations were at least 20 times greater than the substrate concentration.

Product Analysis. Y-Substituted phenoxide was identified as one of the products by comparison of the UV-Vis spectra at the end of the reactions with the authentic samples under the same reaction conditions.

References

1. (a) Jencks, W. P. *Catalysis in Chemistry and Enzymology*; McGraw-Hill: New York, U. S. A., 1969; p 480-483. (b) Jencks, W. P. *Chem. Soc. Rev.* **1981**, *10*, 345-375. (c) Jencks, W. P.; Gilchrist, M. *J. Am. Chem. Soc.* **1968**, *90*, 2622-2637. (d) Gresser, M. J.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 6963-6970.
2. (a) Page, M.; Williams, A. *Organic and Bio-organic Mechanisms*; Longman: Harlow, U. K., 1997; Chapter 7. (b) Williams, A. *Adv. Phys. Org. Chem.* **1992**, *27*, 1-55. (c) Chrystiuk, E.; Williams, A. *J. Am. Chem. Soc.* **1987**, *109*, 3040-3046.
3. (a) Castro, E. A. *Chem. Rev.* **1999**, *99*, 3505-3524. (b) Castro, E. A.; Echevarria, G. R.; Opazo, A.; Robert, P. S.; Santos, J. G. *J. Phys. Org. Chem.* **2008**, *21*, 62-67. (c) Castro, E. A.; Aguayo, R.; Bessolo, J.; Santos, J. G. *J. Phys. Org. Chem.* **2006**, *19*, 555-561. (d) Castro, E. A.; Echevarria, G. R.; Opazo, A.; Robert, P. S.; Santos, J. G. *J. Phys. Org. Chem.* **2006**, *19*, 129-135. (e) Castro, E. A.; Aguayo, R.; Bessolo, J.; Santos, J. G. *J. Org. Chem.* **2005**, *70*, 7788-7791. (f) Castro, E. A.; Aguayo, R.; Bessolo, J.; Santos, J. G. *J. Org. Chem.* **2005**, *70*, 3530-3536. (g) Castro, E. A.; Vivanco, M.; Aguayo, R.; Santos, J. G. *J. Org. Chem.* **2004**, *69*, 5399-5404. (h) Castro, E. A.; Bessolo, J.; Aguayo, R.; Santos, J. G. *J. Org. Chem.* **2003**, *68*, 8157-8161.
4. (a) Sung, D. D.; Koo, I. S.; Yang, K.; Lee, I. *Chem. Phys. Lett.* **2006**, *432*, 426-430. (b) Sung, D. D.; Koo, I. S.; Yang, K.; Lee, I. *Chem. Phys. Lett.* **2006**, *426*, 280-284. (c) Oh, H. K.; Oh, J. Y.; Sung, D. D.; Lee, I. *J. Org. Chem.* **2005**, *70*, 5624-5629. (d) Oh, H. K.; Park, J. E.; Sung, D. D.; Lee, I. *J. Org. Chem.* **2004**, *69*, 3150-3153.
5. (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.; Shin, Y. H.; Han, J. Y.; Mishima, M. *J. Org. Chem.* **2006**, *71*, 7715-7720. (d) Um, I. H.; Lee, J. Y.; Fujio, M.; Tsuno, Y. *Org. Biomol. Chem.* **2006**, *4*, 2979-2985. (e) Um, I. H.; Lee, J. Y.; Ko, S. H.; Bae, S. K. *J. Org. Chem.* **2006**, *71*, 5800-5803. (f) Um, I. H.; Jeon, S. E.; Seok, J. A. *Chem. Eur. J.* **2006**, *12*, 1237-1243.
6. (a) Williams, A. *Acc. Chem. Res.* **1989**, *22*, 387-392. (b) Ba-Saif, S.; Luthra, A. K.; Williams, A. *J. Am. Chem. Soc.* **1989**, *111*, 2647-2652. (c) Ba-Saif, S.; Luthra, A. K.; Williams, A. *J. Am. Chem. Soc.* **1987**, *109*, 6362-6368.
7. (a) Buncel, E.; Um, I. H.; Hoz, S. *J. Am. Chem. Soc.* **1989**, *111*, 971-975. (b) Um, I. H.; Hwang, S. J.; Buncel, E. *J. Org. Chem.* **2006**, *71*, 915-920.
8. (a) Um, I. H.; Han, J. Y.; Hwang, S. J. *Chem. Eur. J.* **2008**, *14*, 7324-7330. (b) Um, I. H.; Park, J. E.; Shin, Y. H. *Org. Biomol. Chem.* **2007**, *5*, 3539-3543.
9. (a) Jencks, W. P. *Chem. Rev.* **1985**, *85*, 511-527. (b) Grunwald, E. *J. Am. Chem. Soc.* **1985**, *107*, 125-133. (c) Grunwald, E. *J. Am. Chem. Soc.* **1985**, *107*, 4710-4715.
10. (a) Williams, A. *Free Energy Relationships in Organic and Bio-Organic Chemistry*. Royal Society of Chemistry: Cambridge, U. K., 2003; p 297. (b) Leffler, J. E.; Grunwald, E. *Extrathermo-dynamic Free Energy Relationships, Rates and Equilibria of Organic Reactions*; Wiley: New York, U. S. A., 1963; Chapter 7.
11. (a) Jencks, W. P. *Catalysis in Chemistry and Enzymology*; McGraw-Hill: New York, U. S. A., 1969; p 193-199. (b) Anslyn, E. V.; Dougherty, D. A. *Modern Physical Organic Chemistry*;

University Science Books: Sausalito, California, U. S. A., 2006; p 410.

12. (a) Ul Hoque, M. E.; Dey, S.; Guha, A. K.; Kim, C. K.; Lee, B. S.; Lee, H. W. *J. Org. Chem.* **2007**, *72*, 5493-5499. (b) Guha, A. K.; Lee, H. W.; Lee, I. *J. Org. Chem.* **2000**, *65*, 12-15. (c) Guha, A. K.; Lee, H. W.; Lee, I. *J. Chem. Soc., Perkin Trans. 2* **1999**, 765-770.

13. (a) Buncel, E.; Albright, K. G.; Onyido, I. *Org. Biomol. Chem.* **2004**, *2*, 601-610. (b) Cook, R. D.; Rahhal-Arabi, L. *Tetrahedron Lett.* **1985**, *26*, 3147-3150. (c) Cook, R. D.; Daouk, W. A.; Hajj, A. N.; Kabbani, A.; Kurku, A.; Samaha, M.; Shayban, F.; Tanielianm, O. V. *Can. J. Chem.* **1986**, *64*, 213-219. (d) Haake, P.; McCoy, D. R.; Okamura, W.; Alpha, S. R.; Wong, S. Y.; Tyssee, D. A.; McNeal, J. P.; Cook, R. D. *Tetrahedron Lett.* **1968**, *9*, 5243-5246. (e) Wallerberg, G.; Haake, P. *J. Org. Chem.* **1981**, *46*, 43-46.

14. (a) Um, I. H.; Han, J. Y.; Shin, Y. H. *J. Org. Chem.* **2009**, *74*, 3073-3078. (b) Im, L. R.; Park, Y. M.; Um, I. H. *Bull. Korean Chem. Soc.* **2008**, *29*, 2477-2481.

15. (a) Carrol, F. A. *Perspectives in Structures and Mechanism in Organic Chemistry*; Brook/Cole: New York, 1998; p 371-380. (b) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd Ed.; Harper Collins Publishers: New

York, 1987; p 143-151.

16. (a) *Advances in Linear Free-Energy Relationships*; Chapman, N. B., Ed.; Plenum: London, 1972. (b) *Techniques of Organic Chemistry*, Vol. 6, 3rd Ed.; Lewis, E. S., Ed.; Wiley: New York, 1974; Part 1. (c) *Techniques of Organic Chemistry*, Vol. 6, 4th Ed.; Bernasconi, C. F., Ed.; Wiley: New York, 1986.

17. Onyido, I.; Swierczek, K.; Purcell, J.; Hengge, A. C. *J. Am. Chem. Soc.* **2005**, *127*, 7703-7711.

18. (a) Bourne, N.; Chrystiuk, E.; Davis, A. M.; Williams, A. *J. Am. Chem. Soc.* **1988**, *110*, 1890-1895. (b) Douglas, K. T.; Williams, A. *J. Chem. Soc., Perkin Trans. 2* **1976**, 513-515.

19. Younker, J. M.; Hengge, A. C. *J. Org. Chem.* **2004**, *69*, 9043-9048.

20. Oh, H. K.; Jin, Y. C.; Sung, D. D.; Lee, I. *Org. Biomol. Chem.* **2005**, *3*, 1240-1244.

21. (a) Um, I. H.; Han, H. J.; Baek, M. H.; Bae, S. Y. *J. Org. Chem.* **2004**, *69*, 6365-6370. (b) Um, I. H.; Kim, K. H.; Park, H. R.; Fujio, M.; Tsuno, Y. *J. Org. Chem.* **2004**, *69*, 3937-3942. (c) Um, I. H.; Min, J. S.; Lee, H. W. *Can. J. Chem.* **1999**, *77*, 659-666.

22. Um, I. H.; Han, H. J.; Ahn, J. A.; Kang, S.; Buncel, E. *J. Org. Chem.* **2002**, *67*, 8475-8480.

23. (a) Tsuno, Y.; Fujio, M. *Adv. Phy. 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.