

# Origin of the $\alpha$ -Effect in Nucleophilic Substitution Reactions of Y-Substituted Phenyl Benzoates with Butane-2,3-dione Monoximate and Z-Substituted Phenoxides: Ground-State Destabilization vs. Transition-State Stabilization

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Second-order rate constants ( $k_{\text{Nu}}$ ) have been measured for nucleophilic substitution reactions of Y-substituted phenyl benzoates (**1a-i**) with butane-2,3-dione monoximate ( $\text{Ox}^-$ , an  $\alpha$ -nucleophile) and Z-substituted phenoxides in 80 mol%  $\text{H}_2\text{O}/20$  mol% DMSO at  $25.0 \pm 0.1$  °C. Hammett plots correlated with  $\sigma^0$  and  $\sigma^-$  constants for reactions of **1a-h** with  $\text{Ox}^-$  exhibit many scattered points. In contrast, the Yukawa-Tsuno plot results in a good linear correlation with  $\rho_Y = 2.20$  and  $r = 0.45$ , indicating that expulsion of the leaving group occurs in the rate-determining step (RDS). A stepwise mechanism with expulsion of the leaving-group being the RDS has been excluded, since Y-substituted phenoxides are less basic and better nucleofuges than  $\text{Ox}^-$ . Thus, the reactions have been concluded to proceed through a concerted mechanism.  $\text{Ox}^-$  is over  $10^2$  times more reactive than its reference nucleophile, 4-chlorophenoxide ( $4\text{-ClPhO}^-$ ). One might suggest that stabilization of the transition-state (TS) through intramolecular general acid/base catalysis is responsible for the  $\alpha$ -effect since such general acid/base catalysis is not possible for the corresponding reactions with  $4\text{-ClPhO}^-$ . However, destabilization of the ground-state (GS) of  $\text{Ox}^-$  has been concluded to be mainly responsible for the  $\alpha$ -effect found in this study on the basis of the fact that the magnitude of the  $\alpha$ -effect is independent of the nature of the substituent Y.

**Key Words:** The  $\alpha$ -effect, Concerted mechanism, Ground-state destabilization, Solvent effect, Transition-state stabilization

## Introduction

Nucleophiles possessing one or more nonbonding electron pairs on the atom  $\alpha$  to the nucleophilic site have often been reported to exhibit abnormally enhanced reactivity than would be expected from their basicity.<sup>1-19</sup> Thus, the enhanced reactivity shown by these nucleophiles was termed the  $\alpha$ -effect.<sup>1</sup> Numerous studies have been performed to investigate the cause of the  $\alpha$ -effect.<sup>2-19</sup> Many theories have been advanced to explain the  $\alpha$ -effect, e.g., destabilization of the ground state (GS) due to electronic repulsion between the nonbonding electron pairs, transition state (TS) stabilization including general acid/base catalysis, thermodynamic stability of products, solvent effects.<sup>2-19</sup> However, none of these theories is conclusive. Particularly, solvent effect on the  $\alpha$ -effect remains controversial.<sup>8-19</sup>

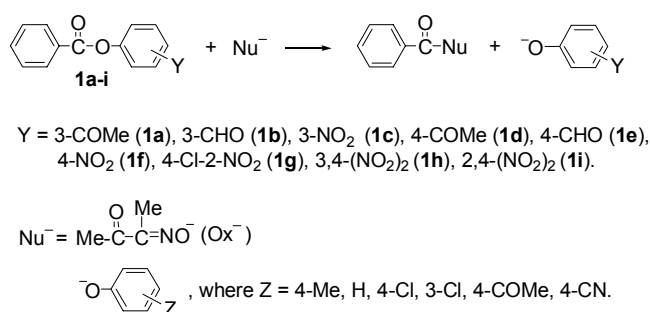
Solvent effect was suggested to be unimportant since the magnitude of the  $\alpha$ -effects was found to be similar for reactions performed in  $\text{H}_2\text{O}$  and in organic solvents such as MeCN and toluene.<sup>8</sup> Besides, it has been reported that  $\alpha$ -nucleophiles are intrinsically more reactive than normal nucleophiles of similar basicity in gas-phase reactions.<sup>9,10</sup> High-level theoretical calculations have also shown that  $\alpha$ -nucleophiles (e.g.,  $\text{HOO}^-$ ,  $\text{H}_2\text{NO}^-$ ,  $\text{FO}^-$  and  $\text{ClO}^-$ ) exhibit lower activation energies than normal nucleophiles of similar basicity in gas-phase  $\text{S}_{\text{N}}2$  reactions.<sup>11</sup> Accordingly, solvent effect on the  $\alpha$ -effect has been concluded to be unimportant.<sup>8-11</sup> In contrast, DePuy *et al.* concluded that solvent effect is responsible for the  $\alpha$ -effect shown by  $\text{HOO}^-$  in  $\text{H}_2\text{O}$ , since the  $\alpha$ -nucleophile did not exhibit the  $\alpha$ -effect in the gas-phase reaction with methyl formate.<sup>12</sup> Furthermore, from recent gas-phase ion-molecule studies, Bierbaum *et al.* have found that  $\alpha$ -nucleophiles such as  $\text{HOO}^-$ ,  $\text{BrO}^-$  and  $\text{ClO}^-$  do not exhibit enhanced reactivity in gas-phase reactions

with alkyl chlorides.<sup>13</sup> Accordingly, they have concluded that the  $\alpha$ -effect is due to solvent effect but not due to an intrinsic property.<sup>12,13</sup>

We have initiated a systematic study to investigate the effect of solvent on the  $\alpha$ -effect.<sup>14</sup> Our study has shown that solvent effect on the  $\alpha$ -effect is remarkable for nucleophilic substitution reactions of 4-nitrophenyl acetate (PNPA) with butane-2,3-dione monoximate ( $\text{Ox}^-$ , an  $\alpha$ -nucleophile) and 4-chlorophenoxide ( $4\text{-ClPhO}^-$ , a reference nucleophile) in DMSO- $\text{H}_2\text{O}$  mixtures of varying compositions.<sup>14</sup> It has been found that the  $\alpha$ -effect (i.e.,  $k_{\text{Ox}^-} / k_{4\text{-ClPhO}^-}$ ) increases as the DMSO content in the medium increases up to ca. 50 mol% DMSO and then decreases thereafter, resulting in a bell-shaped  $\alpha$ -effect profile.<sup>14</sup> Similar bell-shaped  $\alpha$ -effect profiles have been obtained for the corresponding reactions of aryl acetates, 4-nitrophenyl benzoate, thionobenzoate, benzenesulfonate, and diphenylphosphinate, although the magnitude of the  $\alpha$ -effect is highly dependent on the nature of the electrophilic center.<sup>15-19</sup>

Our calorimetric study has revealed that  $\text{Ox}^-$  is ca. 4 kcal/mol less solvated than  $4\text{-ClPhO}^-$  in  $\text{H}_2\text{O}$ .<sup>14b</sup> Furthermore, it has been found that  $\text{Ox}^-$  becomes more destabilized than  $4\text{-ClPhO}^-$  as the DMSO content in the medium increases up to ca. 50 mol% DMSO, and then the difference in their solvation energies remains nearly constant upon further addition of DMSO.<sup>14b</sup> Dissection of the  $\alpha$ -effect found in the reactions of PNPA into TS and GS contributions through combination of the kinetic data with calorimetric data has led us to conclude that destabilization of the  $\alpha$ -nucleophile (i.e.,  $\text{Ox}^-$ ) is mainly responsible for the increasing  $\alpha$ -effect up to 50 mol% DMSO (i.e., GS effect) while differential stabilization of TS contributes to the decreasing  $\alpha$ -effect beyond 50 mol% DMSO.<sup>14b</sup>

Our study has been extended to reactions of Y-substituted



Scheme 1

phenyl benzoates (**1a-i**) with Ox<sup>-</sup> and Z-substituted phenoxides (Scheme 1) to investigate the origin of the  $\alpha$ -effect. Comparison of the results obtained in the current study with those reported previously for the corresponding reactions with hydrazine and glycylglycine has shown that destabilization of Ox<sup>-</sup> is more important than stabilization of TS for the  $\alpha$ -effect in the current system.

## Results and Discussion

Reactions were 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 ( $k_{\text{obsd}}$ ) were calculated from the equation  $\ln(A_{\infty} - A_t) = -k_{\text{obsd}}t + C$ . The plots of  $k_{\text{obsd}}$  vs. nucleophile concentration were linear with positive intercepts. Thus, the rate law is given as eq (1), in which  $k_0$  represents the contribution of H<sub>2</sub>O and/or OH<sup>-</sup> from hydrolysis of the anionic nucleophiles to the  $k_{\text{obsd}}$  values. Accordingly, second-order rate constants ( $k_{\text{Nu}^-}$ ) 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  $\pm 3\%$ .

$$\text{Rate} = k_{\text{obsd}} [\text{substrate}], \text{ where } k_{\text{obsd}} = k_{\text{Nu}^-} [\text{nucleophile}] + k_0 \quad (1)$$

**Reaction Mechanism.** As shown in Table 1, second-order rate constant for reactions with Ox<sup>-</sup>, an  $\alpha$ -nucleophile, increases as

the leaving-group basicity decreases, e.g.,  $k_{\text{Ox}^-}$  increases from 0.703 M<sup>-1</sup>s<sup>-1</sup> to 34.2 and 961 M<sup>-1</sup>s<sup>-1</sup> as the pK<sub>a</sub> of the conjugate acid of the leaving group decreases from 10.4 to 7.79 and 5.60, in turn. A similar result is shown for the corresponding reactions with 4-ClPhO<sup>-</sup> (a reference nucleophile), although it is much less reactive than Ox<sup>-</sup>. The  $\alpha$ -effect shown by Ox<sup>-</sup> will be discussed in the following section.

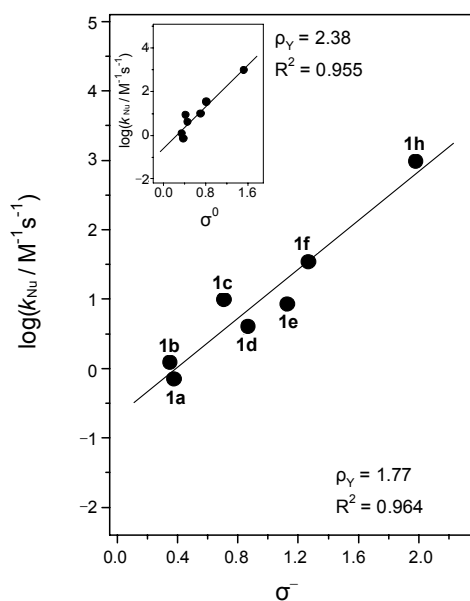
One might expect that a partial negative charge develops on the oxygen atom of the leaving aryloxy when expulsion of the leaving group occurs either in a concerted or stepwise mechanism. Such negative charge can be delocalized on the substituent Y through resonance interactions. Thus,  $\sigma^-$  constants would exhibit a good Hammett correlation if expulsion of the leaving group occurs at rate-determining step (RDS). In contrast,  $\sigma^0$  constants would result in a better Hammett correlation than  $\sigma^-$  constants if expulsion of the leaving group occurs after RDS. Thus, Hammett plots have been constructed for reactions of Y-substituted phenyl benzoates (**1a-h**) with Ox<sup>-</sup> using  $\sigma^-$  and  $\sigma^0$  constants to deduce the reaction mechanism. As shown in Figure 1, the Hammett plot correlated with  $\sigma^-$  constants exhibits a slightly better correlation coefficient than that correlated with  $\sigma^0$  constants (inset). However, both Hammett plots show many scattered points. Accordingly, one cannot get any conclusive information from these plots.

Yukawa-Tsuno plots have been reported to be highly informative to clarify ambiguities in reaction mechanism for nucleophilic substitution reactions of various esters (e.g., aryl benzoates, thionobenzoates, and diphenylphosphinates).<sup>21-23</sup> Thus, a Yukawa-Tsuno plot has been constructed for reactions of **1a-h** with Ox<sup>-</sup> in Figure 2. One can see that the Yukawa-Tsuno plots exhibit a good linear correlation with  $\rho_Y = 2.20$  and  $r = 0.45$ . The  $r$  value in the Yukawa-Tsuno equation (eq 2) represents the extent of resonance contribution between the reaction site and substituent Y.<sup>24,25</sup> Thus, the  $r$  value of 0.45 indicates that a negative charge develops partially on the oxygen atom of the leaving aryloxy. Thus, one might suggest two different mechanisms to account for the result, i.e., a concerted mechanism and a stepwise pathway in which departure of the leaving group occurs in the RDS. However, one can exclude the latter mechanism since the leaving Y-substituted phenoxides are less basic and better nucleofuges than the incoming Ox<sup>-</sup>. Accordingly, one can conclude that the current reactions proceed through a concerted mechanism.

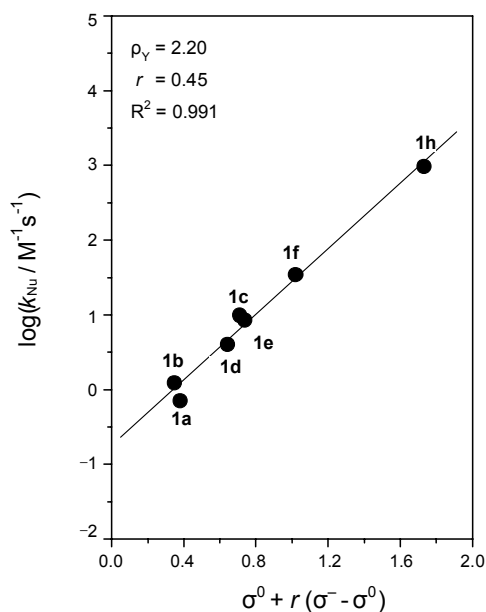
**Table 1.** Summary of Second-order Rate Constants for Reactions of Y-Substituted Phenyl Benzoates (**1a-i**) with Butane-2,3-dione Monoximate (Ox<sup>-</sup>) and 4-Chlorophenoxide (4-ClPhO<sup>-</sup>) in 80 mol% H<sub>2</sub>O / 20 mol% DMSO at 25.0  $\pm$  0.1 °C.<sup>a</sup>

	Y	pK <sub>a</sub> <sup>Y-PhOH</sup>	$k_{\text{Ox}^-}/\text{M}^{-1}\text{s}^{-1}$	$k_{4\text{-ClPhO}^-}/\text{M}^{-1}\text{s}^{-1}$	$k_{\text{Ox}^-}/k_{4\text{-ClPhO}^-}$
<b>1a</b>	3-COMe	10.4	0.703	$3.45 \times 10^{-3}$	204
<b>1b</b>	3-CHO	10.1	1.22	$6.10 \times 10^{-3}$	200
<b>1c</b>	3-NO <sub>2</sub>	9.32	9.78	$4.16 \times 10^{-2}$	235
<b>1d</b>	4-COMe	8.94	4.01	$2.36 \times 10^{-2}$	170
<b>1e</b>	4-CHO	8.45	8.39	$5.52 \times 10^{-2}$	152
<b>1f</b>	4-NO <sub>2</sub>	7.79	34.2	$1.85 \times 10^{-1}$	185
<b>1g</b>	4-Cl-2-NO <sub>2</sub>	6.92	47.1	$2.15 \times 10^{-1}$	219
<b>1h</b>	3,4-(NO <sub>2</sub> ) <sub>2</sub>	5.60	961	7.19	134
<b>1i</b>	2,4-(NO <sub>2</sub> ) <sub>2</sub>	4.11	-	6.50	-

<sup>a</sup>The pK<sub>a</sub> values in 20 mol% DMSO and kinetic data for reactions with 4-ClPhO<sup>-</sup> were taken from ref. 20.



**Figure 1.** Hammett plots correlated with  $\sigma^-$  and  $\sigma^0$  (inset) for reactions of Y-substituted phenyl benzoates (**1a-h**) with  $\text{Ox}^-$  in 80 mol%  $\text{H}_2\text{O}$  / 20 mol% DMSO at  $25.0 \pm 0.1$  °C. The identity of points is given in Table 1.



**Figure 2.** Yukawa-Tsuno plots for reactions of Y-substituted phenyl benzoates (**1a-h**) with  $\text{Ox}^-$  in 80 mol%  $\text{H}_2\text{O}$  / 20 mol% DMSO at  $25.0 \pm 0.1$  °C. The identity of points is given in Table 1.

$$\log k^Y/k^H = \rho_Y (\sigma^0 + r(\sigma^- - \sigma^0)) \quad (2)$$

**Origin of the  $\alpha$ -Effect: GS Destabilization vs. TS Stabilization.** As mentioned in the preceding section,  $\text{Ox}^-$  is over  $10^2$  times more reactive than its reference nucleophile, 4-ClPhO $^-$ , although the basicity of the two nucleophiles is known to be similar (e.g., the  $\text{pK}_a$  values of the conjugate acids of  $\text{Ox}^-$  and 4-ClPhO $^-$  in 20 mol% DMSO were reported to be 10.68 and 10.58, respectively).<sup>16</sup> Interestingly, Table 1 shows that the mag-

**Table 2.** Summary of Second-order Rate Constants ( $k_{\text{Z-PhO}^-}$ ) for Reactions of Y-Substituted Phenyl Benzoates (Y = 4-NO $_2$ , **1f**; Y = 4-Cl-2-NO $_2$ , **1g**; Y = 3,4-(NO $_2$ ) $_2$ , **1h**; Y = 2,4-(NO $_2$ ) $_2$ , **1i**) with Z-Substituted Phenoxides in 80 mol%  $\text{H}_2\text{O}$  / 20 mol% DMSO at  $25.0 \pm 0.1$  °C.<sup>a</sup>

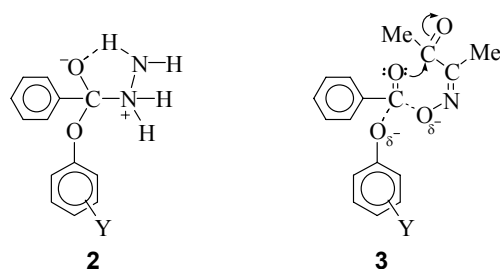
Entry	Z	$\text{pK}_a^{\text{Z-PhOH}}$	$10^2 k_{\text{Z-PhO}^-} / \text{M}^{-1} \text{s}^{-1}$			
			<b>1f</b>	<b>1g</b>	<b>1h</b>	<b>1i</b>
1	4-Me	11.7	92.5	84.1	2080	2170
2	H	11.3	45.2	35.5	1580	1160
3	4-Cl	10.5	18.5	21.5	719	650
4	3-Cl	10.2	9.03	11.2	424	397
5	4-COMe	8.94	0.888	0.945	36.0	36.8
6	4-CN	8.60	0.510	0.656	18.6	29.4

<sup>a</sup>The  $\text{pK}_a$  values in 20 mol% DMSO and kinetic data for the reactions of 4-nitrophenyl benzoate (**1f**) were taken from ref. 20.

nitude of the  $\alpha$ -effect is independent of the electronic nature of the substituent Y in the leaving group. This is in contrast to our previous report that the  $\alpha$ -effect increases linearly with increasing the basicity of the leaving group for reactions of Y-substituted phenyl benzoates with hydrazine (an  $\alpha$ -nucleophile) and glycylglycine (a reference nucleophile).<sup>26</sup>

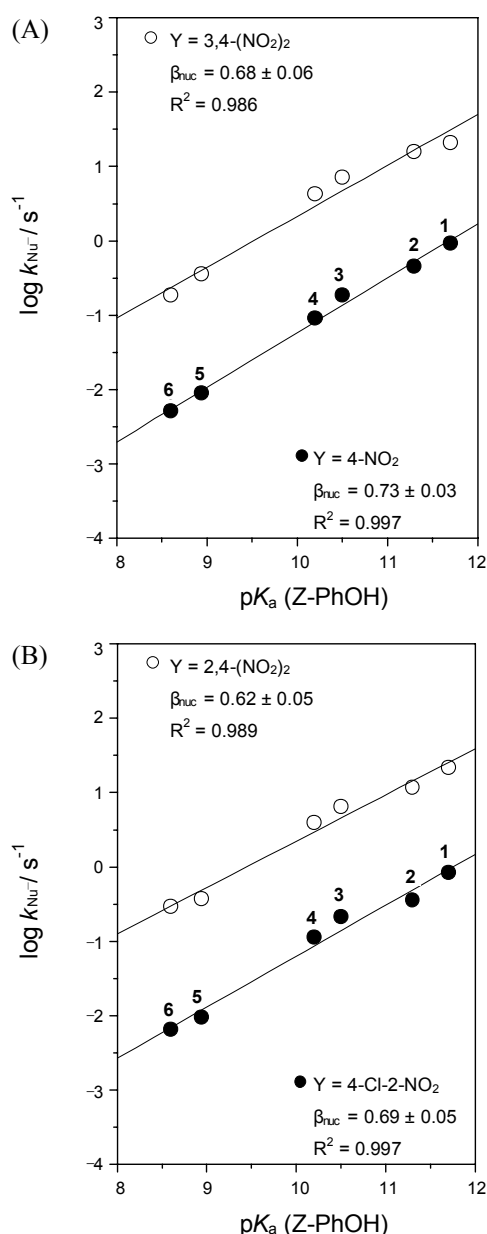
Stabilization of transition state (TS) through intramolecular H-bonding as modeled by **2** has been suggested to be responsible for the substituent dependent  $\alpha$ -effect for the reactions with hydrazine, since such 5-membered H-bonding interaction is not possible for the corresponding reactions with glycylglycine.<sup>26</sup> One might draw a similar conclusion that TS stabilization is responsible for the  $\alpha$ -effect shown by  $\text{Ox}^-$  in the current study. This is because TS stabilization through intramolecular general acid/base catalysis as modeled by **3** is possible for the reactions with  $\text{Ox}^-$ , while such general acid/base catalysis is impossible for the reactions with 4-ClPhO $^-$ .

If TS stabilization through **3** is responsible for the enhanced reactivity shown by  $\text{Ox}^-$ , the  $\alpha$ -effect should be dependent on the nature of the substituent Y in the leaving group as reported previously for the reactions with hydrazine and glycylglycine.<sup>26</sup>



However, in fact, the magnitude of the  $\alpha$ -effect is independent of the substituent Y (see Table 1), indicating that TS stabilization through general acid/base catalysis is not responsible for the  $\alpha$ -effect found in this study.

$\text{Ox}^-$  has been reported to be 5.7 kcal/mol less solvated than 4-ClPhO $^-$  in 20 mol% DMSO,<sup>14b</sup> which is the reaction medium in this study. Since  $\text{Ox}^-$  and 4-ClPhO $^-$  have been employed as a pair of nucleophiles throughout the reactions of **1a-i**, the difference in the GS solvation energy of the two nucleophiles remains constant at 5.7 kcal/mol. Accordingly, if the difference



**Figure 3.** Brønsted-type plots for reactions of Y-substituted phenyl benzoates with Z-substituted phenoxides in 80 mol% H<sub>2</sub>O / 20 mol% DMSO at 25.0 ± 0.1 °C. **A:** Y = 4-NO<sub>2</sub> (**1f**) and 3,4-(NO<sub>2</sub>)<sub>2</sub> (**1h**); **B:** Y = 4-Cl-2-NO<sub>2</sub> (**1g**) and 2,4-(NO<sub>2</sub>)<sub>2</sub> (**1i**). The identity of points is given in Table 2.

in the GS solvation energies of the two nucleophiles is mainly responsible for the  $\alpha$ -effect, one can expect that the magnitude of the  $\alpha$ -effect remains nearly constant upon changing the substituent Y in the leaving group. In fact, the  $\alpha$ -effect is independent of the nature of Y. Thus, one can suggest that the  $\alpha$ -effect found in this study is mainly due to destabilization of Ox<sup>−</sup> in the GS.

To examine the above idea, second-order rate constants ( $k_{\text{Z-PhO}^-}$ ) have been measured for reactions of 4 different Y-substituted phenyl benzoates with 6 different Z-substituted phenoxides (Z-PhO<sup>−</sup>). The  $k_{\text{Z-PhO}^-}$  values are summarized in Table 2 and illustrated graphically in Figures 3A and 3B. Table 2 shows that  $k_{\text{Z-PhO}^-}$  decreases as the basicity of Z-PhO<sup>−</sup> decreases in all

cases. It is also noted that the  $k_{\text{Z-PhO}^-}$  values for the reactions of **1i** are not always larger than those for the corresponding reactions of **1h**, although 2,4-dinitrophenoxide in **1i** is less basic than 3,4-dinitrophenoxide in **1h**. Similarly, **1g** is not always more reactive than **1f**, although the former possesses a much less basic leaving group (i.e., 4-chloro-2-nitrophenoxide) than the latter does (i.e., 4-nitrophenoxide). One might suggest that steric hindrance caused by the substituent on the 2-position of **1i** and **1g** is responsible for the unusual reactivity order.<sup>27</sup>

The effect of basicity of Z-PhO<sup>−</sup> on reactivity is illustrated in Figures 3A and 3B. The Brønsted-type plots are linear with  $\beta_{\text{nuc}}$  values varying from 0.73 to 0.69, 0.68 and 0.62 as the substituent Y changes from 4-NO<sub>2</sub> to 4-Cl-2-NO<sub>2</sub>, 3,4-(NO<sub>2</sub>)<sub>2</sub>, and 2,4-(NO<sub>2</sub>)<sub>2</sub> in turn, which is in accordance to reactivity-selectivity principle.<sup>28</sup>

It is well known that the magnitude of the  $\alpha$ -effect increases with increasing  $\beta_{\text{nuc}}$  values when TS stabilization is responsible for the  $\alpha$ -effect.<sup>2,5-8</sup> The  $\beta_{\text{nuc}}$  values determined in this study exhibit a linear correlation with the basicity of the leaving Y-substituted phenoxides (Figure not shown). Thus, one might expect that the  $\alpha$ -effect increases with increasing the leaving-group basicity, if TS stabilization (through general acid/base catalysis as modeled by **3**) contributes to the current  $\alpha$ -effect. However, in fact, the  $\alpha$ -effect is independent of the leaving-group basicity, indicating that stabilization of TS is not responsible for the  $\alpha$ -effect. This is consistent with the preceding argument that the  $\alpha$ -effect found in current study is mainly due to GS destabilization.

## Conclusions

The current study has allowed us to conclude the following: (1) The Yukawa-Tsuno plot for the reactions of Y-substituted phenyl benzoates (**1a-h**) with Ox<sup>−</sup> exhibits good linearity with  $\rho_Y = 2.20$  and  $r = 0.45$ , indicating that expulsion of the leaving group occurs in RDS. (2) A concerted mechanism or a stepwise pathway, in which expulsion of the leaving-group occurs in RDS, can account for the results. However, the latter mechanism has been excluded since Y-substituted phenoxides are less basic and better nucleofuges than the incoming Ox<sup>−</sup> ion. (3) Ox<sup>−</sup> is over 10<sup>2</sup> times more reactive than 4-ClPhO<sup>−</sup> toward **1a-h** (i.e., the  $\alpha$ -effect). (4) TS stabilization through intramolecular general acid/base catalysis has been ruled out as the origin of the  $\alpha$ -effect found in the current reactions, since the magnitude of the  $\alpha$ -effect is independent of the nature of substituent Y and of  $\beta_{\text{nuc}}$  values. (5) Since Ox<sup>−</sup> has been reported to be 5.7 kcal/mol less solvated than 4-ClPhO<sup>−</sup> in 20 mol% DMSO, GS destabilization of Ox<sup>−</sup> has been concluded to be mainly responsible for the  $\alpha$ -effect found in this study.

## Experimental Section

**Materials.** Y-Substituted phenyl benzoates were readily prepared from reactions of benzoyl chloride with Y-substituted phenol in anhydrous ether under the presence of triethylamine. The crude products were purified through column chromatography. Other chemicals including butane-2,3-dione monoxime

and phenols were of the highest quality available. Doubly glass-distilled water was further boiled and cooled under nitrogen just before use to exclude dissolved  $\text{CO}_2$ . Since solubility of the substrates is low in pure water, 80 mol%  $\text{H}_2\text{O}$ /20 mol% DMSO was used as the reaction medium.

**Kinetics.** The kinetic study was performed using a UV-Vis spectrophotometer for slow reactions ( $t_{1/2} > 10$  s) or a stopped-flow spectrophotometer for fast reactions ( $t_{1/2} \leq 10$  s) 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.

Typically, the reaction was initiated by adding 5  $\mu\text{L}$  of a 0.02 M substrate stock solution in MeCN by a 10  $\mu\text{L}$  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 for the reactions was prepared in 25.0 mL volumetric flask under nitrogen by adding 2 equiv. of butan-2,3-dione monoxime (or 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 (and/or its conjugate acid) was identified as one of the products by comparison of the UV-Vis spectra at the end of reactions with the authentic sample.

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