

# The Effects of Solvation and Polarizability on the Reaction of S-*p*-Nitrophenyl Thiobenzoate with Various Anionic Nucleophiles

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Second-order rate constants have been measured spectrophotometrically for the nucleophilic substitution reactions of S-*p*-nitrophenyl thiobenzoate with various anionic nucleophiles including 6  $\alpha$ -effect nucleophiles. A good Brønsted correlation has been observed for the reactions with 7 aryloxides. However, *p*-chlorothiophenoxide and hydroxide ions exhibit significantly positive and negative deviations, respectively, from the Brønsted plot. The deviations are attributed to the effect of polarizability and solvation rather than a change in the reaction mechanism. The  $\alpha$ -effect nucleophiles except highly basic ones demonstrate remarkably enhanced nucleophilicity. The effects of solvation and/or polarizability are proposed to be important for the cause of the  $\alpha$ -effect.

## Introduction

As many as 17 factors have been suggested to influence nucleophilicity<sup>1</sup>. Among them, basicity has been most commonly used to correlate with nucleophilic reactivity,<sup>2</sup> *i.e.* the basicity of a series of nucleophiles correlates linearly with nucleophilicity for various reactions (Brønsted equation). However, solvation factor has often resulted in curvatures in Brønsted plots for highly basic nucleophiles.<sup>3</sup> Similarly, unusual nucleophilic reactivities have frequently been observed for the reaction of polarizable nucleophiles. Thus, Edwards attempted to correlate nucleophilicity with polarizability and basicity.<sup>4</sup> However, the use of Edwards equation has been restricted to a limited number of reactions.

Abnormally enhanced nucleophilicity has also been observed for the reaction of nucleophiles containing an atom with lone-paired electrons adjacent to the reaction center (the  $\alpha$ -position). Thus, the enhanced nucleophilicity was termed the  $\alpha$ -effect,<sup>5</sup> and many theories have been suggested to explain the unusual reactivity.<sup>6</sup> However, the cause of the  $\alpha$ -effect has not been completely understood. Particularly, effects of solvation and polarizability have been in controversy.<sup>7,8</sup>

We have chosen the following nucleophilic substitution reactions in order to investigate the effect of solvation and polarizability on the  $\alpha$ -effect. Although the structure of the thiol ester **2** is similar to that of the oxygen analogue **1**, the polarizability of the former is considered to be significantly enhanced. Besides, the nucleophiles chosen in the

present study are in a wide range of basicity and polarizability. Therefore, the present system would be proper for a systematic study of solvation and polarizability effects.

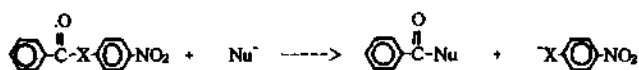
## Experimental

**Materials.** S-*p*-nitrophenyl thiobenzoate, benzohydroxamic acid, acetophenoxime and acetoxime were easily prepared by known procedures<sup>9,10</sup> and their purity was checked by means of their melting point and spectral data such as IR and NMR spectra. Other chemicals used in this study were of the highest quality available from Aldrich and generally recrystallized before use. Doubly glass distilled water was boiled and cooled under a nitrogen atmosphere. All the solutions were freshly prepared just before use. Hamilton gas tight syringes were used to transfer solutions.

**Kinetics.** Kinetic studies were performed with a Hitachi U-2000 Model UV-VIS spectrophotometer equipped with a Neslab RTE-110 Model constant temperature circulating bath to keep the temperature in the UV cell at  $25.0 \pm 0.1^\circ\text{C}$ . The reactions were followed by monitoring the appearance of the leaving group (*p*-nitrothiophenoxide ion) at 410 nm. All the reactions were carried out under pseudo-first order conditions in which the concentration of nucleophiles was generally 100 times greater than that of the substrate. The stock solutions of nucleophiles were made up with NaOH solution and 2 equivalent respective conjugate acid of the nucleophile, except  $\text{N}_3^-$  and  $\text{OH}^-$ , to suppress formation of hydroxide ion by solvolysis as described previously.<sup>20</sup> The stock solution of  $\text{N}_3^-$  was made up with 0.05 M borate buffer solution, and 0.1 M NaOH solution was used as the stock solution of  $\text{OH}^-$ .

## Results

All the reactions studied here obeyed pseudo-first-order kinetics up to over 90% of the total reaction. Pseudo-first-order rate constant ( $K_{obs}$ ) were obtained from the Guggenheim equation,  $\ln(A_\infty - A_t) = -k_{obs} t + c$ . Correlation coefficients of the linear regressions were usually higher than 0.9995. Generally, five different concentrations of nucleophile solution were used to get second-order rate constant ( $k_2$ )



**1**: X = O, *p*-nitrophenyl benzoate

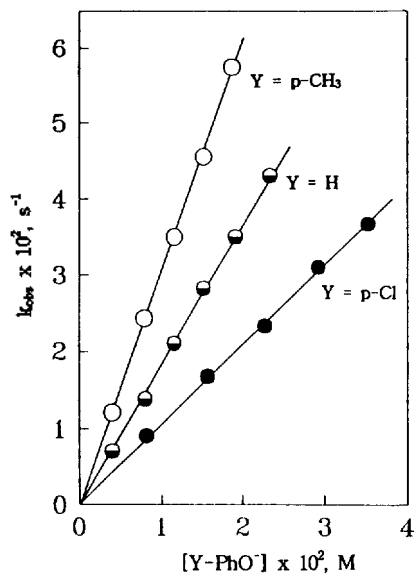
**2**: X = S, S-*p*-nitrophenyl thiobenzoate

Nu<sup>-</sup>: normal nucleophiles:

$\text{Y}-\text{C}_6\text{H}_4\text{O}^-$  (Y = CHO, CN, COCH<sub>3</sub>, Cl, H, CH<sub>3</sub>, OCH<sub>3</sub>),  
*p*-Cl-PhS<sup>-</sup>, HO<sup>-</sup>, CF<sub>3</sub>CH<sub>2</sub>O<sup>-</sup>.

$\alpha$ -effect of nucleophiles:

$\text{N}_3^-$ ,  $\text{SO}_3^{2-}$ , PhC(O)N(H)O<sup>-</sup>, MeC(O)C(Me)=NO<sup>-</sup>, PhC(Me)=NO<sup>-</sup>,  
Me<sub>2</sub>C=NO<sup>-</sup>.



**Figure 1.** Plots of observed rate constant ( $k_{obs}$ ) versus concentration of nucleophile for the reactions of *S-p*-nitrophenyl thiobenzoate with substituted phenoxides ( $Y-PhO^-$ ) in 10 mole% DMSO- $H_2O$  at 25°C.

**Table 1.** Summary of Second-Order Rate Constants ( $k_2$ ) for the Reactions of *S-p*-Nitrophenyl Thiobenzoate with Various Types of Anionic Nucleophiles in 10 mole% DMSO- $H_2O$  at 25°C

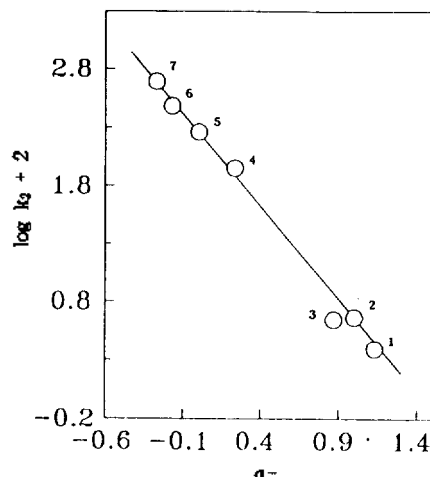
Nu <sup>-</sup>	$pK_a$ (NuH) <sup>a</sup>	$k_2$ , M <sup>-1</sup> s <sup>-1</sup>
1. <i>p</i> -CHOPhO <sup>-</sup>	7.66	0.0249 (0.00180) <sup>b</sup>
2. <i>p</i> -CNPhO <sup>-</sup>	7.73	0.0461 (0.00375)
3. <i>p</i> -CH <sub>3</sub> COPhO <sup>-</sup>	8.05	0.0442 (0.00466)
4. <i>p</i> -ClPhO <sup>-</sup>	9.35	0.893 (0.136)
5. PhO <sup>-</sup>	9.95	1.83 (0.273)
6. <i>p</i> -CH <sub>3</sub> PhO <sup>-</sup>	10.07	3.05 (0.567)
7. <i>p</i> -CH <sub>3</sub> OPhO <sup>-</sup>	10.20	4.94 (0.813)
8. CF <sub>3</sub> CH <sub>2</sub> O <sup>-</sup>	12.37	35.8 (22.9)
9. OH <sup>-</sup>	15.75	4.22 (5.83)
10. <i>p</i> -ClPhS <sup>-</sup>	7.50	53.3 (0.0594)

<sup>a</sup> $pK_a$  data were taken from ref. 26. <sup>b</sup>Figures in parentheses are  $k_2$  values obtained from ref. 24c for the reaction of 1.

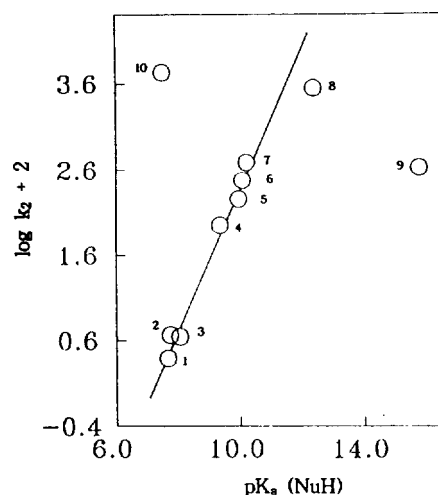
**Table 2.** Summary of Second-Order Rate Constants ( $k_2$ ) for the Reactions of *S-p*-Nitrophenyl thiobenzoate with Various  $\alpha$ -Effect Nucleophiles in 10 mole% DMSO- $H_2O$  at 25°C

Nu <sup>-</sup>	$pK_a$ (NuH) <sup>a</sup>	$k_2$ , M <sup>-1</sup> s <sup>-1</sup>
11. N <sub>3</sub> <sup>-</sup>	4.0	0.238 (0.00290) <sup>b</sup>
12. SO <sub>3</sub> <sup>2-</sup>	7.21	5.33 (0.246)
13. BzH <sup>-</sup> (benzohydroxamate)	8.88	60.2 (7.64)
14. Ox <sup>-</sup> (butane-2,3-dione monoximate)	9.44	37.2 (18.1)
15. APOx <sup>-</sup> (acetophenonoximate)	11.4	22.7 (20.2)
16. AOx <sup>-</sup> (acetonoximate)	12.42	25.2 (19.0)

<sup>a</sup> $pK_a$  data were taken from ref. 26. <sup>b</sup>Figures in parentheses are  $k_2$  values obtained from ref. 24c for the reaction of 1.



**Figure 2.** Hammett plot for the reactions of *S-p*-nitrophenyl thiobenzoate with substituted phenoxides in 10 mole% DMSO- $H_2O$  at 25°C. The numbers refer to the nucleophiles in Table 1.

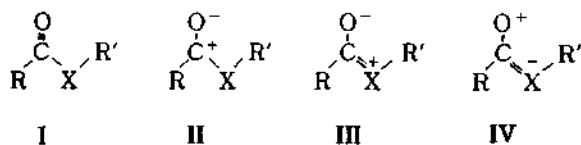


**Figure 3.** Brønsted plot for the reactions of *S-p*-nitrophenyl thiobenzoate with various types of anionic nucleophiles in 10 mole% DMSO- $H_2O$  at 25°C. The numbers refer to the nucleophiles in Table 1.

from the slope of the plot of  $k_{obs}$  versus concentration of nucleophile. In Figure 1 are demonstrated typical plots of  $k_{obs}$  versus concentration of nucleophiles. Standard deviations of the slopes were less than 3%. In Table 1 are summarized second-order rate constants obtained in this way for the reactions *S-p*-nitrophenyl thiobenzoate (2) with 7 aryloxides, *p*-ClPhS<sup>-</sup>, CF<sub>3</sub>CH<sub>2</sub>O<sup>-</sup> and OH<sup>-</sup> ions at 25°C in  $H_2O$  containing 10 mole% dimethyl sulfoxide (DMSO) to eliminate a solubility problem. The kinetic data are demonstrated graphically in Figures 2-3. In Table 2 are summarized second-order rate constants for the reactions of 2 with various  $\alpha$ -effect nucleophiles. In Figure 4 are plotted the kinetic data for the reactions of 2 with all the nucleophiles listed in Tables 1-2.

## Discussion

**The Effect of Polarizability on Rate.** Replacement of ether-like oxygen by sulfur atom in carboxylic esters has often resulted in significant carbonyl shifts to lower frequencies. This was once attributed to contribution of structure IV involving participation of sulfur  $3d$  orbitals.<sup>11</sup> However, considerable evidences are in favor of structure II and III, and the low carbonyl frequency of thiol esters has been attributed to vibrational perturbation due to the mass of the C-S bond.<sup>12</sup> Since the unshared electron pairs on the large sulfur atom are not able to overlap efficiently with the adjacent carbonyl group to form a double bond, structure III has been expected to make little contribution to the structure of a thiol ester. A similar conclusion was drawn by Idoux *et al.* from an intensive NMR study of thiol esters.<sup>13</sup> Therefore, structure II would be more significant for the thiol ester 2 than the oxygen analogue 1.



The carbonyl carbon in a thiol ester would have more enhanced electrophilicity compared to the one in the corresponding oxygen ester due to a difference in contribution of structure II between the two esters. Therefore, the thiol ester 2 is expected to exhibit significantly enhanced reactivity compared to the oxygen analogue 1. In fact, 2 appears to be generally more reactive than 1 as shown in Table 1, *i.e.* the former is 6 to 14 times more reactive than the latter for the reaction with aryloxides. Such reactivity difference is more significant for 4-ClPhS<sup>-</sup>, which exhibits about 90 times higher reactivity toward 2 than 1.

The replacement of oxygen by sulfur atom as in the present system has also been reported to cause significant increase in polarizability of the reaction center.<sup>14</sup> Furthermore, it is evident that a thiophenoxide is more polarizable than a corresponding phenoxide due to the difference in size between S and O. Therefore, the large rate enhancement shown by 4-ClPhS<sup>-</sup> toward polarizable substrate 2 would be attributed to a strong interaction between the polarizable reactants based on the hard-soft acids-bases principle. This argument can be supported from the reaction of N<sub>3</sub><sup>-</sup> and SO<sub>3</sub><sup>2-</sup>. As in Table 2, N<sub>3</sub><sup>-</sup> and SO<sub>3</sub><sup>2-</sup> exhibit about 82 and 52 times higher reactivity toward 2 than 1, respectively. N<sub>3</sub><sup>-</sup> has been reported to have molar refraction of 12.27 which would exert unusually high polarizability.<sup>15</sup> Similarly, the nucleophilic center of SO<sub>3</sub><sup>2-</sup> is known to be polarizable sulfur atom rather than O<sup>-</sup>, when the electrophile is carbonyl carbon.

The significance of polarizability effect on rate is also observed for the OH<sup>-</sup> system. Unlike the thiophenoxide, OH<sup>-</sup> is considered to be nonpolarizable, since its negative charge is mainly localized on the oxygen atom. As shown in Table 1, OH<sup>-</sup> is much less reactive than 4-ClPhS<sup>-</sup> toward 2, although the former is about 8  $pK_a$  units more basic than the latter. Furthermore, OH<sup>-</sup> is less reactive toward 2 than 1, although the leaving group ability of 4-nitrothiophenoxide in 2 would be expected to be much better than that of 4-nitrophenoxide in 1 based on their basicity difference (*e.g.*

the former is about 4  $pK_a$  units less basic than the latter). Therefore, the unusual low reactivity of OH<sup>-</sup> toward 2 would be attributed to a poor interaction between the highly polarizable substrate 2 and nonpolarizable nucleophile OH<sup>-</sup>, at least in part.

**The effect of Solvation on Rate.** In Figure 2 is graphically demonstrated substituent effect on rate for the reaction of 2 with 7 substituted phenoxides. The nucleophilicity of a phenoxide increases with increasing electron donating ability of the substituent on the phenoxide ring. The correlation of logarithmic second-order rate constant ( $\log k_2$ ) with the Hammett  $\sigma^-$  constant results in a good linearity ( $r=0.998$ ) with a large negative Hammett  $\rho^-$  value ( $\rho^- = -1.66$ ). The large  $\rho^-$  value obtained in the present system implies that the attack of the nucleophiles to the carbonyl carbon is definitely involved in the rate-determining step.

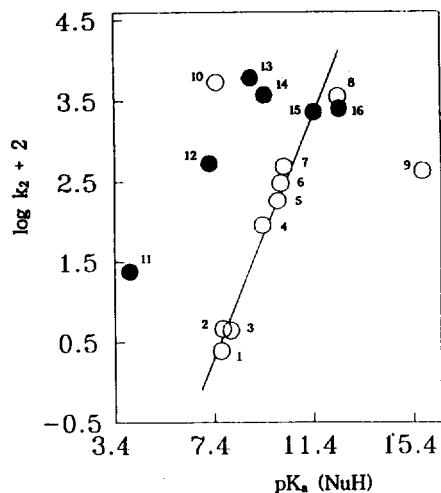
A Brønsted type plot has been constructed to correlate nucleophilicity with the basicity of all the nucleophiles listed in Table 1. As shown in Figure 3, a linear correlation can be seen between nucleophilicity and basicity for the aryloxides. However, 4-ClPhS<sup>-</sup> and OH<sup>-</sup> show significantly positive and negative deviations, respectively, from the linearity.

A linear correlation in a Brønsted plot has generally been suggestive of a common reaction mechanism for a series of reactants.<sup>2,16</sup> On the contrary, a break in a Brønsted plot has been considered to indicate a change in the rate-determining step.<sup>2,16</sup> However, this would be valid only when the reactants in the system are similar in structure. Since 4-ClPhS<sup>-</sup> and OH<sup>-</sup> are structurally different from the aryloxides, the deviations shown by these nucleophiles are not considered due to any mechanistic change.

It has been well known that sulfur does not form a strong H-bonding. It is evident from the fact that sulfur containing compounds are much less soluble in H<sub>2</sub>O than the corresponding oxygen analogue (*e.g.* H<sub>2</sub>S). In fact, PhS<sup>-</sup> has been reported to be less solvated than PhO<sup>-</sup> in H<sub>2</sub>O by 6 kcal/mole,<sup>17</sup> which would account for the high reactivity of the thiophenoxide compared to the phenoxide of a similar basicity. On the other hand, OH<sup>-</sup> has been reported to be 22 and 32 kcal/mole more solvated than CF<sub>3</sub>CH<sub>2</sub>O<sup>-</sup> and PhO<sup>-</sup>, respectively, in H<sub>2</sub>O.<sup>17</sup> Therefore, solvation factor is considered to be also responsible for the unusual reactivities shown by 4-ClPhS<sup>-</sup> and OH<sup>-</sup> in the present system, together with polarizability effect as discussed in the preceding section.

**The Effect of Solvation on the  $\alpha$ -effect.** Many factors have been suggested to influence the magnitude of the  $\alpha$ -effect. Bruice and Dixon demonstrated that the magnitude of the  $\alpha$ -effect correlates  $\beta_{nuc}$  for reactions of 17 substrates with hydrazine as an  $\alpha$ -effect nucleophile and with glycyglycine or glycyamide as the corresponding normal nucleophile.<sup>18</sup> It has also been observed that the magnitude of the  $\alpha$ -effect is substrate dependent. Buncl and his coworkers found that the magnitude of the  $\alpha$ -effect is dependent on structural factors of the substrates, such as hybridization of the reaction center.<sup>19</sup>

In order to examine the magnitude of the  $\alpha$ -effect for the reaction of 2 with various anionic nucleophiles, a Brønsted type plot has been constructed for all the nucleophiles listed in Table 1 and 2. As demonstrated in Figure 4, the low basic  $\alpha$ -effect nucleophiles (*e.g.* N<sub>3</sub><sup>-</sup>, SO<sub>3</sub><sup>2-</sup>, BzH<sup>-</sup> and Ox<sup>-</sup>) show significant  $\alpha$ -effect (positive deviation from the Brønst-



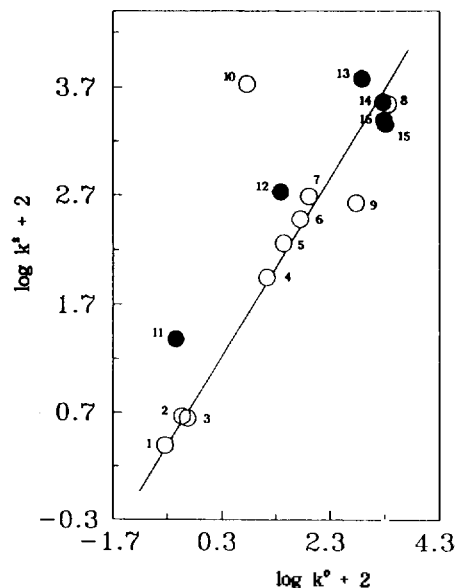
**Figure 4.** Brønsted plot for the reactions of S-p-nitrophenyl thiobenzoate with various types of anionic nucleophiles including  $\alpha$ -effect nucleophiles in 10 mole% DMSO-H<sub>2</sub>O at 25°C. The numbers refer to the nucleophiles in Table 1 and 2.

ed linear line). However, unexpectedly, ApOx<sup>-</sup> shows no  $\alpha$ -effect and the highly basic AOx<sup>-</sup> is even less reactive than the corresponding normal nucleophile (CF<sub>3</sub>CH<sub>2</sub>O<sup>-</sup>). Hudson and his coworkers have observed a similar result in the reaction of 4-nitrophenyl acetate, and attempted to explain the disappearance of the  $\alpha$ -effect for highly basic  $\alpha$ -effect nucleophiles in terms of molecular orbital theory.<sup>20</sup> However, the argument concerning HOMO energies of  $\alpha$ -effect nucleophiles is in controversy.<sup>21</sup>

The negative charge on oxyanionic  $\alpha$ -effect nucleophiles would become more localized on the oxygen atom as their basicity increases. Consequently, it is evident that the degree of solvation of these nucleophiles in H<sub>2</sub>O would increase with increasing their basicity. Since solvation effect on rate is demonstrated to be significant in the present system as discussed in the preceding section, one would ascribe the absence of the  $\alpha$ -effect to a solvation factor for the highly basic  $\alpha$ -effect nucleophiles (ApOx<sup>-</sup> and AOx<sup>-</sup>). This argument might be supported for the Ox<sup>-</sup> system. Ox<sup>-</sup> has been reported to be 4 kcal/mole less solvated than the corresponding normal nucleophile (4-CIPhO<sup>-</sup>) in H<sub>2</sub>O.<sup>22</sup> Thus, one can attribute the large  $\alpha$ -effect shown by Ox<sup>-</sup> to solvation effect. However, BzH<sup>-</sup> shows also significant  $\alpha$ -effect, although it has been reported to be more strongly solvated than the corresponding normal nucleophile.<sup>23</sup> Therefore, solvation factor would be important but cannot be solely responsible for the  $\alpha$ -effect, particularly for the polarizable reaction system as in the present system.

**The effect of Polarizability on the  $\alpha$ -effect.** As demonstrated in Figure 4, N<sub>3</sub><sup>-</sup> and SO<sub>3</sub><sup>2-</sup> show significant positive deviations from the Brønsted linear line (the  $\alpha$ -effect). Since the nucleophilic centers of these  $\alpha$ -effect nucleophiles are different from that of oxyanionic nucleophiles, one might attribute their positive deviations to a difference in reaction mechanism.

It has generally been believed that the reaction of oxygen centered nucleophiles with carboxylic esters would proceed *via* a rate-determining formation of a tetrahedral interme-



**Figure 5.** Plot of logarithmic second-order rate constant for the reaction of 2 with various anionic nucleophiles ( $\log k^2$ ) vs. the corresponding logarithmic second order rate constant for the reaction of 1 ( $\log k^1$ ).

diate,<sup>22a</sup> while break-down of the tetrahedral intermediate has been suggested to be the rate-limiting step for neutral amine nucleophiles.<sup>2b</sup> Although N<sub>3</sub><sup>-</sup> is an anionic nucleophile, it would react in a different manner from the aryloxides and OH<sup>-</sup>. It is because N<sub>3</sub><sup>-</sup> is much less basic than the leaving group (4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>S<sup>-</sup>), and therefore, the former would exert higher nucleofugality than the latter. In fact, Menger *et al.*, have proposed that the rate-determining step for the reaction of N<sub>3</sub><sup>-</sup> with aryl benzoates in CH<sub>3</sub>CN is break-down of a tetrahedral intermediate.<sup>2b</sup> However, the nature of rate-limiting step for N<sub>3</sub><sup>-</sup> in aqueous system is not clear, and remains still in controversy.<sup>2a</sup>

N<sub>3</sub><sup>-</sup> has been known to have abnormally high molar refraction and polarizability like sulfur centered nucleophiles.<sup>15</sup> Therefore, high polarizability of N<sub>3</sub><sup>-</sup> and SO<sub>3</sub><sup>2-</sup> would be considered to be responsible for the large  $\alpha$ -effect shown by these nucleophiles. In order to examine this argument, logarithmic second-order rate constant for the reaction of 2 with all the nucleophiles ( $\log k^2$ ) in Table 1 and 2 is plotted against the corresponding logarithmic second-order rate constant for the reaction of 1 ( $\log k^1$ ). One would expect that nucleophiles having a similar polarizability would result in a linear line in the plot, while more polarizable nucleophiles deviate positively and less polarizable ones do negatively from the line. This is clearly demonstrated in Figure 5, in which the family of aryloxides gives a straight line while highly polarizable 4-CIPhS<sup>-</sup> shows a positive deviation and nonpolarizable OH<sup>-</sup> appears below the linear line. Similarly, the  $\alpha$ -effect nucleophiles such as Ox<sup>-</sup>, ApOx<sup>-</sup> and AOx<sup>-</sup> show negative deviations, indicating that these oximates are less polarizable than ArO<sup>-</sup>. On the contrary, the  $\alpha$ -effect nucleophiles such as N<sub>3</sub><sup>-</sup>, SO<sub>3</sub><sup>2-</sup> and BzH<sup>-</sup> exhibit positive deviations. The positive deviations shown by N<sub>3</sub><sup>-</sup> and SO<sub>3</sub><sup>2-</sup> are considered to originate apparently from their enhanced polarizability, since they exert much higher reactivity toward

the more polarizable substrate **2** than the less polarizable **1**. On the same basis,  $\text{BzH}^-$  is considered to be more polarizable than  $\text{ArO}^-$ , and the  $\alpha$ -effect shown by this would be attributed to a polarizability effect. This is consistent with the preceding proposal that solvent effect is insignificant for the  $\alpha$ -effect observed in the  $\text{BzH}^-$  system.

### Conclusion

The effects of solvation and polarizability appear to be significant on the  $\alpha$ -effect as well as on the reaction rate.

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