Kinetics and Mechanism of Azidolysis of Y-Substituted Phenyl Benzoates

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Second-order rate constants (k_N) have been measured spectrophotometrically for reactions of Y-substituted phenyl benzoates (**1a-h**) with azide ion (N_3^-) in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C. The Brønsted-type plot for the azidolysis exhibits a downward curvature, *i.e.*, the slope (β_{lg}) changes from –0.97 to –0.20 as the basicity of the leaving group decreases. The pK_a^o (defined as the pK_a at the center of the Brønsted curvature) is 4.8, which is practically identical to the pK_a of the conjugate acid of N_3^- ion (4.73). Hammett plots correlated with σ^o and σ^- constants exhibit highly scattered points for the azidolysis. On the contrary, the corresponding Yukawa-Tsuno plot results in an excellent linear correlation with ρ = 2.45 and r = 0.40, indicating that the leaving group departs in the rate-determining step. The curved Brønsted-type plot has been interpreted as a change in the rate-determining step in a stepwise mechanism. The microscopic rate constants (k_1 and k_2/k_{-1} ratio) have been calculated for the azidolysis and found to be consistent with the proposed mechanism.

Key Words : Acyl-transfer reaction, Azidolysis, Brønsted-type plot, Hammett plot, Yukawa-Tsuno plot

Introduction

Nucleophilic substitution reactions of carbonyl,[1-5] sulfonyl,[6] and phosphyl derivatives[7,8] have been intensively investigated due to the importance in biological processes as well as in synthetic applications. Reactions of carboxylic esters with neutral nucleophiles (*e.g.*, amines and pyridines) are now firmly understood to proceed through a zwitterionic tetrahedral intermediate $T^{\pm}$ with a change in the rate-determining step (RDS) on the basis of curved Brønsted-type plots found for reactions of esters with a good leaving group.[1-5] The RDS has generally been suggested to change from breakdown of $T^{\pm}$ to its formation as the attacking amine becomes more basic than the leaving group by 4 to 5 pK_a units.[1-5]

However, reactions with anionic nucleophiles (*e.g.*, OH^- and aryloxides) have not been clearly understood. In a series of important studies, Williams and coworkers have concluded that reactions of 4-nitrophenyl acetate with substituted phenoxides proceed through a concerted mechanism.[9] The evidence consisted mainly of the absence of a break or curvature in the Brønsted-type plot when the pK_a of the aryloxides corresponded to that of the leaving 4-nitrophenoxide.[9] The concerted mechanism has further been supported through structure-reactivity correlations reported by Jencks,[10] Rossi,[11] and Castro,[12] as well as the study of kinetic isotope effect by Hengge[13] and Marcus analysis by Guthrie.[14]

On the contrary, Buncel *et al.* have concluded that acyl-transfer to aryloxides occurs through a stepwise mechanism with formation of an addition intermediate being the RDS on the basis of Hammett plots exhibiting rather poor correlation with σ^- constants but better correlation with σ^o constants.[15] A similar result has been reported for reactions of aryl diphenylphosphinates with OH^- and for those of aryl dimethylphosphinates with ethoxide ion.[16,17] Furthermore, we have presented the first spectroscopic evidence, along with kinetic evidence, for an addition intermediate in the reaction of a cyclic sulfinate ester with sodium ethoxide in anhydrous ethanol.[18]

We have recently performed nucleophilic substitution reactions of aryl benzoates and thionobenzoates with OH^- and CN^- ions and reported that the reactions proceed through a stepwise mechanism.[19] We have extended our study to reactions of Y-substituted phenyl benzoates (**1a-h**) with N_3^- ion to get further information on the reaction mechanism involving anionic nucleophiles.

Results and Discussion

Reactions of **1a-h** with N_3^- ion proceeded with quantitative liberation of Y-substituted phenoxide ion and/or its conjugate acid. The kinetic study was performed under pseudo-first-order conditions, *e.g.*, the N_3^- ion concentration in excess over the substrate concentration. All the reactions obeyed first-order kinetics. Pseudo-first-order rate constants (k_{obsd}) were calculated from the equation $\ln (A_\infty - A_t) = -k_{obsd} t + C$. The plots of k_{obsd} *vs.* N_3^- ion concentration are linear. Thus, the apparent second-order rate constants (k_N) were determined from the slope of the linear plots of k_{obsd} *vs* [N_3^-], and summarized in Table 1.

Brønsted-type Correlation. Table 1 shows that the apparent second-order rate constant (k_N) is significantly dependent on the leaving group basicity, *e.g.*, the k_N value decreases from 0.224 $M^{-1}s^{-1}$ to 2.34×10^{-3} and 6.42×10^{-5} $M^{-1}s^{-1}$ as the pK_a of the conjugate acid of the leaving aryloxide increases from 4.11 to 7.14 and 8.98, respectively.

The effect of leaving group basicity on reactivity is illustrated in Figure 1. Esters with 2,4-dinitrophenoxide as a

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Table 1. Summary of Apparent Second-order and Microscopic Rate Constants for Reactions of Y-Substituted Phenyl Benzoates (**1a-h**) with N_3^- in 20 mol % DMSO/80 mol % H_2O at 25.0 ± 0.1 °C

Y	pK_a (Y-PhOH)	$10^3\,k_N/M^{-1}s^{-1}$	$10^3\,k_1/M^{-1}s^{-1}$	$10^2\,k_2/k_{-1}$
1a, 2,4-$(NO_2)_2$	4.11	224 ± 3	383	340
1b, 3,4-$(NO_2)_2$	5.42	124 ± 11	496	33.3
1c, 4-NO_2	7.14	2.34 ± 0.09	151	1.58
1d, 4-CHO	7.66	0.479 ± 0.049	76.8	0.628
1e, 4-CN	7.95	0.993 ± 0.062	266	0.375
1f, 4-$COCH_3$	8.05	0.232 ± 0.040	74.0	0.314
1g, 4-COOEt	8.50	0.151 ± 0.006	107	0.142
1h, 3-CHO	8.98	0.064 ± 0.012	106	0.0605

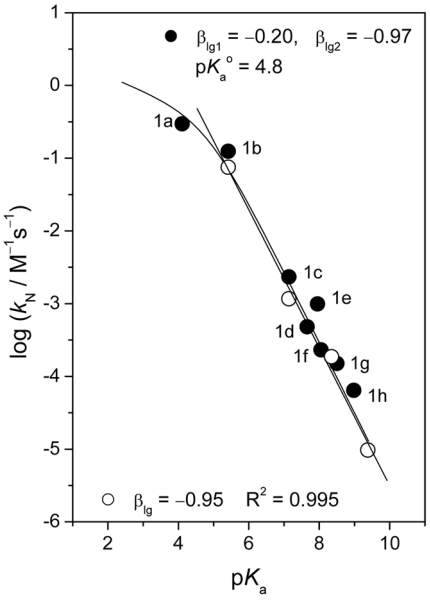
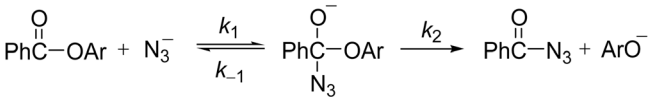


Figure 1. Brønsted-type plots for azidolysis of Y-substituted phenyl benzoates (●, **1a-h**) and cinnamates (○) at 25.0 ± 0.1 °C. The identity of the points is given in Table 1. The data for the azidolysis of aryl cinnamates were taken from ref. 20.

leaving group (*e.g.*, **1a**) have often exhibited a negative deviation from Brønsted-type plot.[1c,7a] Jencks *et al.* have attributed such negative deviation to steric hindrance caused by the presence of a NO_2 group at the 2-position of the leaving aryloxide.[1c] The effect of steric hindrance has been suggested to be 0.12 log units. Thus, the point for the reaction of **1a** in Figure 1 has been corrected by 0.12 log units.[1c]

As shown in Figure 1, the Brønsted-type plot for the azidolysis of **1a-h** exhibits a downward curvature. The current Brønsted-type plot can be compared with the one reported for azidolysis of Y-substituted phenyl cinnamates (Y = 3,4-$(NO_2)_2$, 4-NO_2, 3-NO_2, and 4-Cl).[20] Suh *et al.* have reported a linear Brønsted-type plot with $\beta_{lg} = -0.95$ for the reactions of aryl cinnamates with N_3^-, and concluded that the reactions proceed through a stepwise mechanism with the second step being the RDS on the basis of the magnitude of the β_{lg} value.[20] The Brønsted-type plot shown in Figure 1 is



Scheme 1

almost identical to the one reported by Suh *et al.* when the point for the reaction of **1a** is excluded (see the open circles in Figure 1). Thus, one can suggest that the current azidolysis proceeds through a stepwise mechanism as shown in Scheme 1, and a change in the RDS is responsible for the curved Brønsted-type plot.

Hammett Correlations. To examine the above argument, Hammett plots have been constructed using the kinetic data in Table 1. Hammett correlations with σ^o and σ^- constants have often been found to be useful to determine reaction mechanisms, especially to get information on the RDS.[15-17] For example, one might expect a better Hammett correlation with σ^- than σ^o constants if the departure of the leaving group occurs in the RDS, or σ^o constants would result in a better linear correlation than σ^- constants if the leaving group departs after the RDS.

As shown in Figures 2A and 2B, σ^o constants result in only slightly better correlation than σ^- constants (*i.e.*, R^2 = 0.979 for σ^o and R^2 = 0.971 for σ^- constants). Besides, both Hammett plots exhibit highly scattered points. Thus, one cannot obtain any conclusive information on the reaction mechanism from these Hammett plots.

Yukawa-Tsuno Correlation. We have recently shown that the dual-parameter Yukawa-Tsuno equation (eq. 1) is highly effective to elucidate ambiguities in the reaction mechanism of benzoyl-,[5] sulfonyl-,[6] and phosphinyl-transfer reactions.[7,21] Thus, a Yukawa-Tsuno plot has been constructed for the reactions of **1b-h** with N_3^-. As shown in Figure 3, the Yukawa-Tsuno plot exhibits an excellent linear correlation (*i.e.*, R^2 = 0.999) with ρ = 2.45 and r = 0.40.

$$\log k^Y/k^H = \rho\,[\sigma^o + r(\sigma^- - \sigma^o)] \qquad (1)$$

The r value in the Yukawa-Tsuno equation represents the resonance demand of the reaction center or the extent of

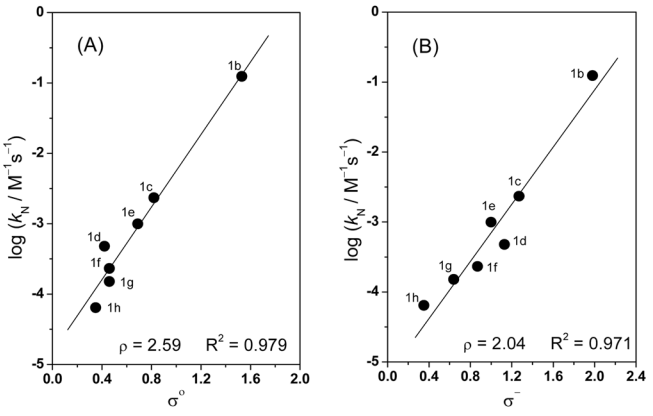


Figure 2. Hammett plots correlated with σ^o (A) and σ^- (B) constants for reactions of Y-substituted phenyl benzoates (**1b-h**) with N_3^- in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1°C.

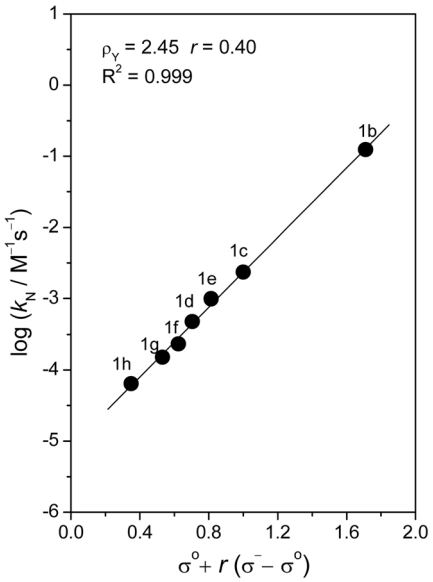
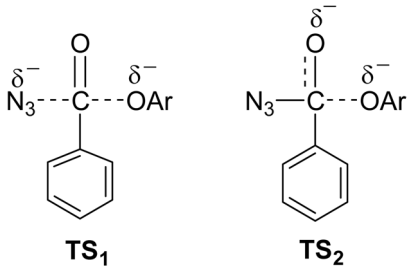


Figure 3. Yukawa-Tsuno plot for reactions of Y-substituted phenyl benzoates (**1b-h**) with N_3^- in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C.

resonance contribution.[22] The fact that r = 0.40 in the current azidolysis indicates that a partial negative charge develops on the O atom of the leaving aryloxide in the rate-determining transition state, which can be delocalized on the substituent Y through resonance interaction. Thus, the linear Yukawa-Tsuno plot with r = 0.40 indicates clearly that departure of the leaving group occurs in the RDS for the azidolysis of **1b-h**.



One can suggest two transition-state (TS) structures, TS_1 and TS_2. TS_1 represents the TS for a concerted mechanism, in which the N-C bond formation and C-OAr bond rupture occur at the same time. TS_2 corresponds to the TS for a stepwise mechanism, where the N-C bond formation is complete and the leaving group departs partially in the TS of the RDS. Departure of the leaving group is advanced partially for both TS_1 and TS_2. However, the ρ value of 2.45 in Figure 3 is typical for reactions which proceed through rate-determining breakdown of an intermediate. Thus, one can suggest that the azidolysis of **1b-h** proceeds through TS_2.

Dissection of k_N into k_1 and k_2/k_{-1} Ratio. The nonlinear Brønsted-type plot shown in Figure 1 can be analyzed using a semiempirical equation (eq. 2),[23] in which β_{lg1} and β_{lg2} represent the slope of the Brønsted-type plot at the low and the high pK_a region, respectively. The curvature center of the curved Brønsted-type plot has been defined as pK_a^o (*i.e.*, the pK_a where the RDS changes).[24] The k_N^o refers the k_N value at pK_a^o. The parameters determined from the fitting of eq. 2 to the experimental points are β_{lg1} = –0.20, β_{lg2} = –0.97, and pK_a^o = 4.8 for the reactions of **1a-h** with N_3^-.

$$\log (k_N/k_N^o) = \beta_{lg1}(pK_a - pK_a^o) - \log [(1 + \alpha)/2],$$
$$\text{where } \log \alpha = (\beta_{lg1} - \beta_{lg2})(pK_a - pK_a^o) \quad (2)$$

The pK_a^o of 4.8 is practically identical to the pK_a of the conjugate acid of N_3^- (4.73). This indicates that the nucleofugality of azide is similar to that of the isobasic aryloxide. This is contrasting to the report by Suh *et al.*[20] They performed azidolysis of aryl cinnamates and concluded that azide is a better nucleofuge than the aryloxides employed in their study.[20] Such conclusion was possible since N_3^- is *ca.* 0.7 pK_a units less basic than the least basic leaving aryloxide (*i.e.*, 3,4-dinitrophenoxide).

The microscopic rate constants (*i.e.*, k_1 and k_2/k_{-1} ratios) associated with the reactions of **1a-h** with N_3^- have been calculated using the method reported by Castro *et al.*[24] on the assumption that the reactions proceed through a stepwise mechanism as shown in Scheme 1. The rate equation and the apparent second-order rate constant (k_N) for the current reactions can be expressed as eqs. (3) and (4). Eq. (4) can be simplified to eq. (5) or (6). Then, β_{lg1} and β_{lg2} can be expressed as eqs. (7) and (8), respectively.

$$\text{Rate} = k_N[\text{substrate}][N_3^-] \quad (3)$$

$$k_N = k_1k_2/(k_{-1} + k_2) \quad (4)$$

$$k_N = k_1k_2/k_{-1}, \text{ when } k_2 << k_{-1} \quad (5)$$

$$k_N = k_1, \text{ when } k_2 >> k_{-1} \quad (6)$$

$$\beta_{lg1} = d(\log k_1)/d(pK_a) \quad (7)$$

$$\beta_{lg2} = d(\log k_1k_2/k_{-1})/d(pK_a) = \beta_{lg1} + d(\log k_2/k_{-1})/d(pK_a) \quad (8)$$

Eq. (8) can be rearranged as eq. (9). Integral of eq. (9) from pK_a^o results in eq. (10). Since $k_2 = k_{-1}$ at pK_a^o, the term $(\log k_2/k_{-1})_{pKa^o}$ is zero. Therefore, one can calculate the k_2/k_{-1} ratios for the reactions of **1a-h** from eq. (10) using pK_a^o = 4.8, β_{lg1} = –0.20 and β_{lg2} = –0.97.

$$\beta_{lg2} - \beta_{lg1} = d(\log k_2/k_{-1})/d(pK_a) \quad (9)$$

$$(\log k_2/k_{-1})_{pKa} = (\beta_{lg2} - \beta_{lg1})(pK_a - pK_a^o) \quad (10)$$

The k_1 values have been determined from eq. (11) using the k_N values in Table 1 and the k_2/k_{-1} ratios calculated above. The k_1 and k_2/k_{-1} ratios obtained in this way are summarized in Table 1 and illustrated graphically in Figure 4.

$$k_N = k_1k_2/(k_{-1} + k_2) = k_1/(k_{-1}/k_2 + 1) \quad (11)$$

Table 1 shows that $k_2/k_{-1} > 1$ for the reaction of **1a** but $k_2/k_{-1} < 1$ for the reactions of **1b-h**. This result is consistent with the preceding proposal that the azidolysis of **1a-h** proceeds through a stepwise mechanism with a change in the RDS, *i.e.*, the RDS is breakdown of the addition intermediate for the azidolysis of **1b-h**, but its formation for the

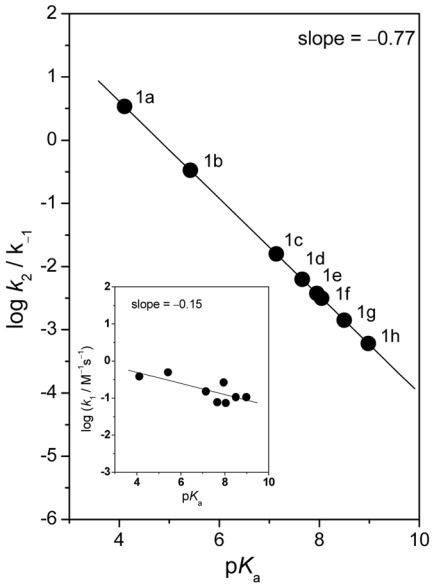


Figure 4. Plots of log k_2/k_{-1} *vs* pK_a (and log k_1 *vs* pK_a, inset) for azidolysis of Y-substituted phenyl benzoates (**1a-h**) in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C.

reaction of **1a**.

As shown in the inset of Figure 4, the Brønsted-type plot for the k_1 values results in a poor correlation with β_{lg1} = –0.15, indicating that the effect of leaving group basicity on k_1 is insignificant for the current azidolysis. On the contrary, one might expect that the effect of leaving group basicity is significant for the k_2/k_{-1} ratio, since k_2 would be strongly dependent on the leaving group basicity while k_{-1} for N_3^- ion would remain nearly constant. In fact, as shown in Figure 4, the plot of log k_2/k_{-1} *vs* pK_a results in a large negative slope (–0.77). Thus, the microscopic rate constants are also consistent with the proposal that the current azidolysis proceeds through a stepwise mechanism with a change in the RDS.

Conclusions

The current study has allowed us to conclude the following: (1) The Brønsted-type plot for the azidolysis of **1a-h** exhibits a downward curvature, *i.e.*, β_{lg1} = –0.20 and β_{lg2} = –0.97. (2) The Hammett plots correlated with σ^o or σ^- constants for the reactions of **1b-h** do not give any conclusive information on the reaction mechanism, since both plots show highly scattered points. (3) The corresponding Yukawa-Tsuno plot results in excellent linearity with ρ = 2.45 and r = 0.40, indicating that the leaving group departure occurs in the RDS. (4) The current azidolysis proceeds through a stepwise mechanism with a change in the RDS. (5) The microscopic rate constants (k_1 and k_2/k_{-1} ratio) calculated are consistent with the proposed mechanism.

Experimental Section

Materials. Y-Substituted phenyl benzoates (**1a-h**) were readily prepared as reported previously[19] from the reactions of Y-substituted phenol with benzoyl chloride under the presence of triethylamine in anhydrous ether and purified by column chromatography. The purity was checked by their mp's and spectral data such as ^{1}H NMR and IR spectra.

Kinetics. The kinetic study was performed with a Scinco S-3100 Model UV-vis spectrophotometer equipped with a constant temperature circulating bath. The reactions were followed by monitoring the appearance of Y-substituted phenoxide. Due to the low solubility of the substrates in pure water, aqueous DMSO (80 mol % H_2O/20 mol % DMSO) was used as the reaction medium. Doubly glass distilled water was further boiled and cooled under nitrogen just before use.

All the reactions were carried out under pseudo-first-order conditions in the presence of excess azide ion. Typically, the reaction was initiated by adding 5 μL of a 0.01 M of substrate solution in MeCN by a 10 μL gastight syringe to a 10 mm quarts UV cell containing 2.50 mL of the thermostated reaction mixture made up of solvent and an aliquot of the NaN_3 stock solution. The stock solution of NaN_3 was prepared in 0.1 M triethyl amine buffer solution (pH = 10.72).

Products Analysis. Y-Substituted phenoxides (and/or the conjugate acids) were liberated quantitatively and identified as one of the reaction products by comparison of the UV-vis spectra after the completion of the reactions with those of the authentic sample under the same reaction conditions.

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