Aminolyses of 2,4-Dinitrophenyl and 3,4-Dinitrophenyl 2-Furoates: Effect of *ortho*-Substituent on Reactivity and Mechanism

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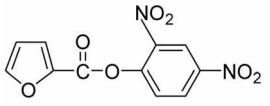
Second-order rate constants (k_N) have been measured spectrophotometrically for reactions of 3,4-dintrophenyl 2-furoate (**2**) with a series of secondary alicyclic amines in 80 mol % H_2O/20 mol % dimethyl sulfoxide (DMSO) at 25.0 °C. The Bronsted-type plot exhibits a downward curvature for the aminolysis of **2**, which is similar to that reported for the corresponding reactions of 2,4-dintrophenyl 2-furoate (**1**). Substrate **2** is less reactive than **1** toward all the amines studied but the reactivity difference becomes smaller as the amine basicity increases. Dissection of the second-order rate constants into the microscopic rate constants has revealed that the reaction of **2** results in a smaller k_2/k_{-1} ratio but slightly larger k_1 value than that of **1**. Steric hindrance has been suggested to be responsible for the smaller k_1 value found for the reactions of **1**, since the *ortho*-substituent of **1** would inhibit the attack of amines (*i.e.*, the k_1 process).

Key Words : Aminolysis, Bronsted-type plot, Steric hindrance, Reaction mechanism, *ortho*-Effect

Introduction

Aminolyses of esters have been intensively investigated including computational studies due to their importance in biological processes as well as in synthetic applications.[1-9] The reactions have generally been understood to proceed through a zwitterionic tetrahedral intermediate ($T^{\pm}$). The rate-determining step (RDS) has been suggested to be dependent on the basicity of the attacking amine and the leaving group, *i.e.*, it changes 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]

Esters with 2,4-dinitrophenoxide as a leaving group (*e.g.*, **1**) have often exhibited a lower reactivity than those with 3,4-dinitrophenoxide (*e.g.*, **2**),[10,11] although 2,4-dinitrophenoxide is expected to be more nucleofugic than 3,4-dinitrophenoxide on the basis of the fact that the former is less basic than the latter. Since the substituent at the *ortho*-position would cause steric hindrance, Jencks *et al.* have suggested that steric effect is responsible for the decreased reactivity shown by esters with a substituent at the *ortho*-position of the leaving group.[11] However, the steric effect has never been investigated in a microscopic rate constant level.



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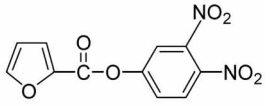
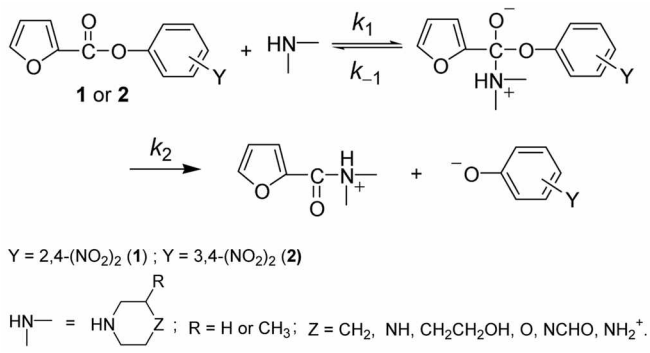


2

We have recently performed a kinetic study on aminolysis of 2,4-dinitrophenyl 2-furoate (**1**) and concluded that the reaction proceeds through a zwitterionic tetrahedral intermediate ($T^{\pm}$) with a change in the RDS on changing the basicity of amines.[12] The kinetic study has now been extended to reactions of 3,4-dinitrophenyl 2-furoate (**2**) with a series of alicyclic secondary amines as shown in Scheme 1. The kinetic data in the current study have been compared with those reported for the corresponding reactions of **1** to investigate the effect of changing the leaving group from 2,4-dinitrophenoxide to 3,4-dinitrophenoxide on reactivity and reaction mechanism (*i.e.*, an *ortho*-substituent effect) in a microscopic rate constant level.



Scheme 1

Results and Discussion

Reactions of **2** with all the amines studied proceeded with quantitative liberation of 3,4-dinitrophenoxide ion. The reactions were followed by monitoring the appearance of the leaving group at 410 nm. Kinetic study was performed under pseudo-first-order conditions, *i.e.*, the concentration of amines was at least 20 times in excess over that of the substrate **2**. All reactions obeyed first-order kinetics. Pseudo-first-order rate constants (k_{obsd}) were determined from the equation, $\ln(A_\infty - A_t) = -k_{obsd}t + C$. The plots of k_{obsd} *vs.* the amine concentration were linear passing through the origin,

Table 1. Summary of Second-order Rate Constants (k_N, $M^{-1}s^{-1}$) for Reactions of 3,4-Dinitrophenyl 2-Furoates (**2**) and 2,4-Dinitrophenyl 2-Furoartes (**1**) with a Series of Secondary Alicyclic Amines in 20 mol % DMSO at 25.0 ± 0.1 °C[a]

Entry	Amines	pK_a	k_N / $M^{-1}s^{-1}$	
			2	**1**
1.	piperidine	11.02	396	427
2.	3-methylpiperidine	10.80	329	402
3.	piperazine	9.85	175	224
4.	morpholine	8.65	30.2	43.5
5.	1-formylpiperazine	7.98	5.75	12.3
6.	piperazinium ion	5.95	0.383	1.47

[a]The data for the reactions of **1** were taken from ref. 12.

indicating that general base catalysis by a second amine molecule is absent and the contribution of OH^- ion from the hydrolysis of amines to k_{obsd} is negligible. Thus, the rate equation can be given as eq. (1). The second-order rate constants (k_N) were determined from the slope of the linear plots of k_{obsd} vs. the amine concentration. Generally five different amine concentrations were used to determine k_N values. It is estimated from replicate runs that the uncertainty in the rate constants is less than 3%. The k_N values determined in this way are summarized in Table 1 together with those reported for the corresponding reactions of **1** for comparison purpose.

$$\text{rate} = k_{obsd}[\mathbf{2}], \text{ where } k_{obsd} = k_N[\text{amine}] \quad (1)$$

Effect of *ortho*-Substituent on Reactivity and Mechanism. As shown in Table 1, the second-order rate constant for the reaction of **2** decreases as the basicity of amines decreases, *i.e.*, k_N decreases from 396 $M^{-1}s^{-1}$ to 30.2 and 0.383 $M^{-1}s^{-1}$ as the pK_a of amines decreases from 11.02 to 8.65 and 5.95, respectively. A similar result is shown for the corresponding reactions of **1**.

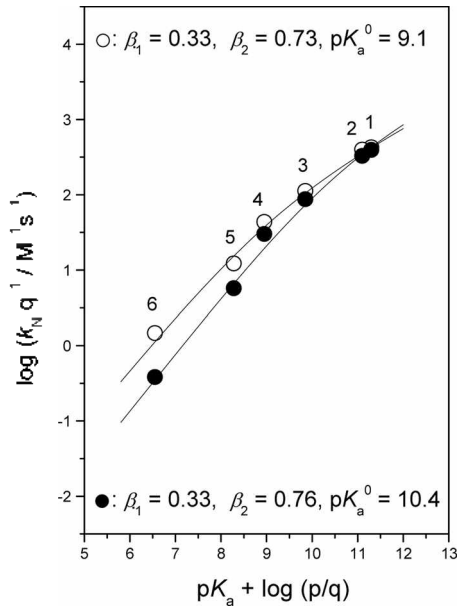


Figure 1. Bronsted-type plots for the reactions of **1** (○) and **2** (●) with secondary alicyclic amines in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C. The identity of points is given in Table 1.

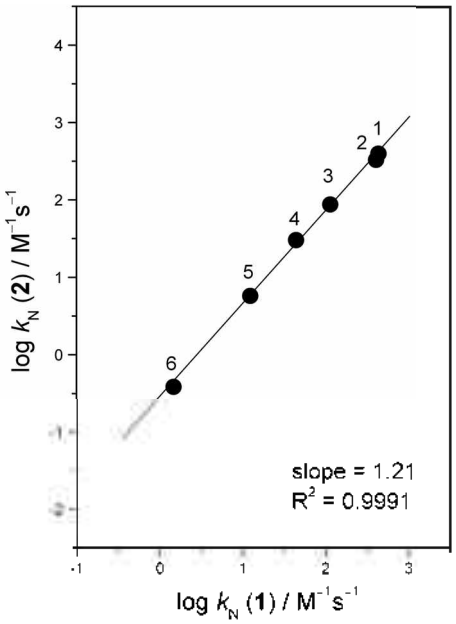


Figure 2. Plot of log k_N for the reactions of **1** *vs.* log k_N for the reactions of **2** in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C.

The effect of amine basicity on reactivity is illustrated in Figure 1. The Bronsted-type plot exhibits a downward curvature for the reactions of **1** and **2**, when k_N and pK_a are statistically corrected using p and q (*i.e.*, p = 2 except p = 4 for piperazinium ion and q = 1 except q = 2 for piperazine).[13] It is also noted that the slope of the Bronsted-type plots is a little larger for the reactions of **2** than for those of **1**.

Figure 1 shows that **2** is less reactive than **1** toward all the amines studied. However, interestingly, the reactivity difference between **1** and **2** becomes smaller as the amine basicity increases. Moreover, **2** would be expected to be more reactive than **1** when the amine basicity increases further (*e.g.*, pK_a > 11.5).

A plot of log k_N for the reactions of **1** *vs.* log k_N for the corresponding reactions of **2** has been constructed to investigate the effect of the *ortho*-NO_2 on reaction mechanism. As shown in Figure 2, an excellent linear correlation is obtained (*e.g.*, R^2 = 0.9991) with a slope of 1.21. Such a good linear plot suggests that the reactions of **1** and **2** proceed through the same mechanism. The slope of 1.21 is consistent with the fact that **2** is more sensitive than **1** toward the amine basicity (see Figure 1). Accordingly, one can suggest that shifting the NO_2 group from the *ortho*-position to the *meta*-position can influence the reactivity but not the reaction mechanism.

The reactions of **1** with the current secondary alicyclic amines have been suggested to proceed through $T^{\pm}$ with a change in the RDS at pK_a = 9.1, which is *ca.* 5 pK_a units more basic than the leaving 2,4-dinitrophenoxide (*i.e.*, pK_a of 2,4-dinitrophenol = 4.11). Thus, one can suggest that the current reactions of **2** proceed also through $T^{\pm}$ with a change in the RDS as shown in Scheme 1 on the basis of the curved Bronsted-type plot in Figure 1 and the linear plot in Figure 2.

Evaluation of Microscopic Rate Constants. The non-linear Bronsted-type plot shown in Figure 1 for the aminolysis of **2** has been analyzed using a semiempirical equation (eq. 2)[11,14] on the basis of the proposed mechanism. The parameters β_1 and β_2 represent the slope of the curved Bronsted plot in Figure 1 for the reactions with strongly basic and weakly basic amines, respectively. Here $k_N°$ refers to the k_N value at $pK_a°$ (*i.e.*, the pK_a at the center of Bronsted curvature where $k_2/k_{-1} = 1$).

$$\log (k_N/k_N°) = \beta_2(pK_a - pK_a°) - \log (1 + \alpha)/2$$
$$\text{where } \log \alpha = (\beta_2 - \beta_1)(pK_a - pK_a°) \quad (2)$$

The parameters determined from the fitting of eq. (2) to the experimental points are $\beta_1 = 0.33$, $\beta_2 = 0.76$, and $pK_a° = 10.4$ for the reactions of **2**. The β_1 value for the reactions of **2** is the same as that reported for the reactions of **1**, while β_2 is slightly larger for the reactions of **2** ($\beta_2 = 0.76$) than for those of **1** ($\beta_2 = 0.73$). The $pK_a°$ value for the reactions of **2** is 10.4, which is *ca.* 5 pK_a units larger than the pK_a of 3,4-dinitrophenol (*i.e.*, 5.42). Thus, the $pK_a°$ value of 10.4 for the reactions of **2** is consistent with the report that a change in the RDS occurs as the attacking amine becomes more basic than the leaving aryloxide by 4 to 5 pK_a units.

The k_N values for the reactions of **2** have been dissected into their microscopic rate constants as shown below. The apparent second-order rate constant k_N can be expressed as eq. (3) by applying the steady-state conditions to the intermediate on the basis of the proposed mechanism.

$$k_N = k_1k_2/(k_{-1} + k_2) \quad (3)$$

The k_2/k_{-1} ratios associated with the aminolysis of **2** have been determined using eqs. (4)-(9). Eq. (3) can be simplified to eq. (4) or (5). Then, β_1 and β_2 can be expressed as eqs. (6) and (7), respectively.

$$k_N = k_1k_2/k_{-1}, \text{ when } k_2 << k_{-1} \quad (4)$$

$$k_N = k_1, \text{ when } k_2 >> k_{-1} \quad (5)$$

$$\beta_1 = d(\log k_1)/d(pK_a) \quad (6)$$

$$\beta_2 = d(\log k_1k_2/k_{-1})/d(pK_a) = \beta_1 + d(\log k_2/k_{-1})/d(pK_a) \quad (7)$$

Eq. (7) can be rearranged as eq. (8). Integral of eq. (8) from $pK_a°$ results in eq. (9). Since $k_2 = k_{-1}$ at $pK_a°$, the term $(\log k_2/k_{-1})_{pK_a°}$ is zero. Therefore, one can calculate the k_2/k_{-1} ratios for the aminolysis of **2** from eq. (9) using $pK_a° = 10.4$, $\beta_1 = 0.33$, and $\beta_2 = 0.76$. The k_1 values have been determined from eq. (10) using the k_N values in Table 1 and the k_2/k_{-1} ratios calculated above. The k_2/k_{-1} ratios and k_1 values are summarized in Table 2.

$$\beta_2 - \beta_1 = d(\log k_2/k_{-1})/d(pK_a) \quad (8)$$

$$(\log k_2/k_{-1})_{pK_a} = (\beta_2 - \beta_1)(pK_a - pK_a°) \quad (9)$$

$$k_N = k_1k_2/(k_{-1} + k_2) = k_1/(k_{-1}/k_2 + 1) \quad (10)$$

Effect of *ortho*-Substituent on Microscopic Rate Constants. It has been suggested that k_2 is independent of the basicity of amines, since the N atom of the aminium moiety of $T^{\pm}$ cannot exert a push to expel the leaving aryloxide from $T^{\pm}$ due to the lack of an electron pair on its nitrogen atom.[11,15] However, the k_{-1} value would decrease as the amine basicity increases. Accordingly, one might expect that the k_2/k_{-1} ratio would increase as the amine basicity increases. In fact, Table 2 shows that the k_2/k_{-1} ratio increases as the amine basicity increases for the aminolyses of **1** and **2**.

Table 2. Summary of Microscopic Rate Constants k_2/k_{-1} Ratios and k_1 values for the Reactions of **2** (and **1**, in parentheses) with a Series of Secondary Alicyclic Amines in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1°C[a]

Entry	Amine	pK_a	k_2/k_{-1}	$k_1/M^{-1}s^{-1}$
1.	piperidine	11.02	2.44 (7.73)	558 (482)
2.	3-methylpiperidine	10.80	2.00 (6.32)	493 (466)
3.	piperazine	9.85	0.580 (2.00)	477 (336)
4.	morpholine	8.65	0.238 (0.872)	157 (93.4)
5.	1-formylpiperazine	7.98	0.123 (0.470)	52.7 (38.5)
6.	piperazinium ion	5.95	0.022 (0.096)	17.7 (16.8)

[a]The data for the reactions of **1** were taken from ref. 12.

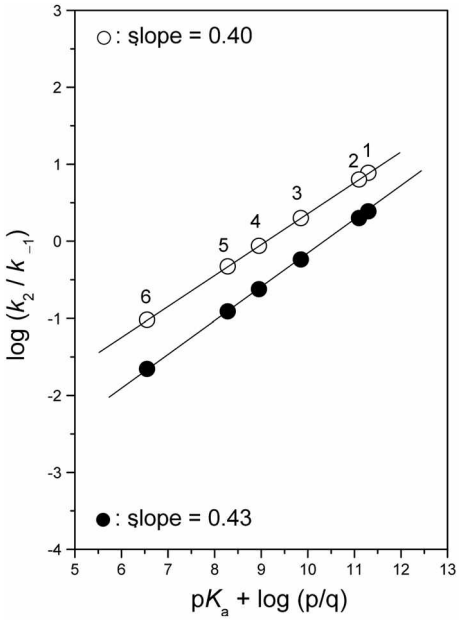


Figure 3. Plots of log k_2/k_{-1} versus pK_a for the reactions of **1** (○) and **2** (●) with a series of secondary alicyclic amines in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C.

The effect of amine basicity on the k_2/k_{-1} ratio is illustrated in Figure 3. The plots of log k_2/k_{-1} *vs.* pK_a are linear for the reactions of **1** and **2**, although the slope of the linear plots is slightly larger for the reactions of **2** (*i.e.*, $\beta_{-1} = 0.43$) than for those of **1** (*i.e.*, $\beta_{-1} = 0.40$). The larger β_{-1} value obtained for the reactions of less reactive **2** appears to be consistent with the so-called reactivity-selectivity principle (RSP).[16]

One might expect that the reactions of **2** would result in a smaller k_2 value than those of **1**, since 3,4-dinitrophenoxide is more basic and a poorer leaving group than 2,4-dinitrophenoxide. However, the k_{-1} value would not be influenced by the basicity of the leaving group. Thus, one might expect

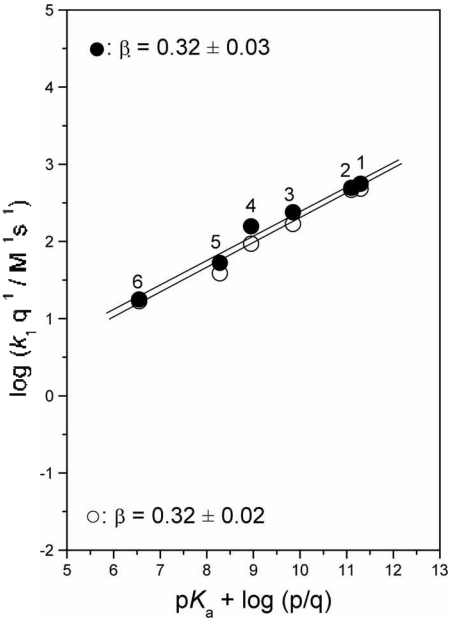


Figure 4. Bronsted-type plots for the reactions of k_1 of **1** (○) and **2** (●) with a series of secondary alicyclic amines in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C. The identity of points is given in Table 2.

that the k_2/k_{-1} ratio is smaller for the reactions of **2** than for those of **1**. In fact, Figure 3 shows that the k_2/k_{-1} ratio is smaller for the reactions of **2** than for those of **1** for a given amine.

As shown in Figure 4, k_1 increases linearly with increasing amine basicity for the reactions of **1** and **2**. However, the k_1 value is slightly larger for the reactions of **2** than for those of **1**, although **2** has a more basic leaving group than **1** (see Table 2). Since the *ortho*-NO_2 in substrate **1** would cause steric hindrance in the k_1 process, one can suggest that steric effect is responsible for the fact that the reaction of **1** results in a smaller k_1 value than that of **2** for a given amine.

Conclusions

The current study has allowed us to conclude the following: (1) Aminolyses of **1** and **2** proceed through $T^{\pm}$ with a change in the RDS. (2) Substrate **2** is less reactive than substrate **1** toward all the secondary amines studied. However, the difference in reactivity becomes smaller as the amine basicity increases. (3) Dissection of k_N into the microscopic rate constants has revealed that aminolysis of **2** results in smaller k_2/k_{-1} ratio but larger k_1 value than that of **1**. (4) Steric hindrance has been suggested to be responsible for the smaller k_1 value obtained from the reactions of **1**.

Experimental Section

Materials. Substrate **2** was readily prepared from the reaction of 3,4-dinitrophenol and 2-furoyl chloride in the presence of triethylamine in anhydrous ether. The purity was confirmed by its melting point and ^{1}H NMR spectrum.[5h] Amines and other chemicals were of the highest quality available and were generally recrystallized or distilled before use. Due to the low solubility of **2** in pure H_2O, 20 mol % DMSO/80 mol % H_2O was used as the reaction medium. Doubly glass distilled water was further boiled and cooled under nitrogen just before use.

Kinetics. The kinetic studies were performed at 25.0 ± 0.1 °C with a Scinco S-3100 UV-Vis spectrophotometer equipped with a constant temperature circulating bath for slow reactions (*e.g.*, $t_{1/2} \geq 10$ s) or with a stopped-flow spectrophotometer for fast reactions (*e.g.*, $t_{1/2} < 10$ s). The reactions were followed by monitoring the appearance of 3,4-dinitrophenoxide ion at 410 nm. All the reactions were carried out under pseudo-first-order conditions in which the amine concentration was at least 20 times greater than that of the substrate.

Products Analysis. 3,4-Dinitrophenoxide ion was 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 samples under the same reaction conditions.

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