Aminolyses of 2,4-Dinitrophenyl 2-Furoate and Benzoate: Effect of Nonleaving Group on Reactivity and Mechanism

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Second-order rate constants (k_N) have been determined spectrophotometrically for reactions of 2,4-dintrophenyl 2-furoate (2) with a series of alicyclic secondary amines in 80 mol % H_2O/20 mol % dimethyl sulfoxide (DMSO) at 25.0 °C. The furoate 2 is more reactive than 2,4-dintrophenyl benzoate (1) toward all the amines studied. The higher acidity of 2-furoic acid (pK_a = 3.16) compared with benzoic acid (pK_a = 4.20) has been suggested to be responsible for the reactivity order, at least in part. The Bronsted-type plots for the reactions of 1 and 2 are curved downwardly, indicating that the aminolyses of both 1 and 2 proceed through a zwitterionic tetrahedral intermediate ($T^\pm$) with a change in the rate-determining step on changing the amine basicity. Dissection of the k_N values into their microscopic rate constants has revealed that the pK_a^o and k_2/k_{-1} ratios for the reactions of 1 and 2 are identical, indicating that the nature of the nonleaving group (*i.e.*, benzoyl and 2-furoyl) does not affect the reaction mechanism. The k_1 values have been found to be larger for the reactions of 2 than for those of 1, which is fully responsible for the fact that the former is more reactive than the latter.

**Key Words :** Aminolysis, Nonleaving group, Yukawa-Tsuno plot, Rate-determining step, Reaction mechanism

Introduction

Aminolysis of esters with a good leaving group has often resulted in a curved Bronsted-type plot, *i.e.*, a large slope (β_2 = 0.8 ± 0.2) for reactions with weakly basic amines but a small one (β_1 = 0.3 ± 0.1) for reactions with strongly basic amines.[1-11] Accordingly, aminolyses of esters have generally been understood to proceed through a zwitterionic tetrahedral intermediate ($T^\pm$) with a change in the rate-determining step (RDS).[1-11]

It has been reported that the RDS changes at pK_a^o (*i.e.*, the curvature center of the curved Bronsted-type plot) 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.[6-11] Gresser and Jencks have found that the pK_a^o value increases as the substituent in the nonleaving group becomes a stronger electron withdrawing group (EWG) for quinuclidinolysis of diaryl carbonates in water.[6] This result has been explained through the argument that an EWG in the nonleaving group favors the departure of amine from $T^\pm$ (k_{-1}) than that of the leaving group (k_2) as the electron withdrawing ability of the substituent in the nonleaving group increases.[6] Castro et al. have obtained a similar result for pyridinolysis of 2,4-dinitrophenyl X-substituted benzoates (*i.e.*, pK_a^o = 9.5 when X = H but pK_a^o > 9.5 when X = Cl, CN, or NO_2)[7] and S-2,4-dinitrophenyl X-substituted thiobenzoates (*i.e.*, pK_a^o increases from 8.5 to 8.9 and 9.9 as substituent X changes from 4-Me to H and 4-NO_2, respectively)[8] in aqueous ethanol. Thus, it has been concluded that an EWG in the nonleaving group increases the pK_a^o value by increasing the k_2/k_{-1} ratio.[6-8]

In contrast, we have recently shown that the pK_a^o value and the k_2/k_{-1} ratio are not influenced by the electronic nature of the substituent X in the nonleaving group for aminolyses of 2,4-dinitrophenyl X-substituted benzoates and benzenesulfonates.[9-11] We have argued that an electron donating group (EDG) in the nonleaving group would increase k_2 and k_{-1}, while an EWG would decrease k_2 and k_{-1}, since both the leaving group and amine depart from $T^\pm$ with the bonding electrons. Thus, it has been concluded that the k_2/k_{-1} ratio is independent of the electronic nature of the substituent X in the nonleaving group.

We have extended our kinetic study to reactions of 2,4-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 for the corresponding reactions of 2,4-dinitrophenyl benzoate (1) to

1 ; X = HC=CH (2,4-dinitrophenyl bezoate)
2 ; X = O (2,4-dinitrophenyl 2-furoate)

HN— = HN⟨Z⟩ ; R = H or CH_3; Z = CH_2, NH, O, NCHO, NH_2^+
         R
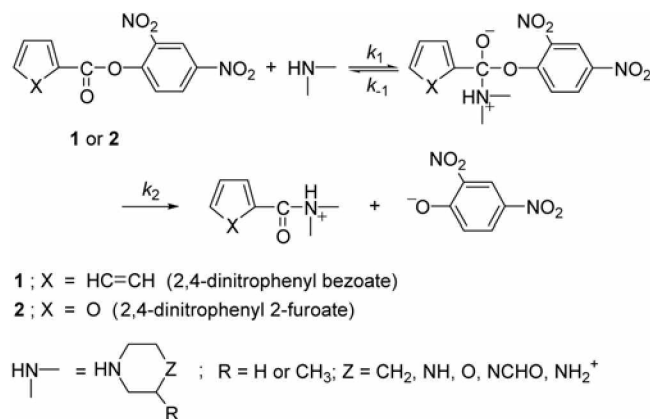
Scheme 1

investigate the effect of changing the nonleaving group from benzoyl to 2-furoyl on reactivity and reaction mechanism, particularly on pK_a^0 and k_2/k_{-1} ratio.

Results and Discussion

Reactions of **2** with all the amines studied proceeded with quantitative liberation of 2,4-dinitrophenoxide ion. The reactions were followed by monitoring the appearance of 2,4-dinitrophenoxide ion at 400 nm. Kinetic study was performed under pseudo-first-order conditions; the amine concentration was always in excess over that of the substrate **2**. All reactions obeyed first-order kinetics over 90% of the total reaction. 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, 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 expressed as eq (1). The second-order rate constants (k_N) were determined from the slope of these linear plots. 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.

$$\text{rate} = k_N[\mathbf{2}][\text{amine}] \tag{1}$$

Effect of Nonleaving Group on Reactivity. As shown in Table 1, the k_N value for the reaction of **2** decreases as the basicity of amines decreases, *i.e.*, it decreases from 427 $M^{-1}s^{-1}$ to 43.5 and 1.47 $M^{-1}s^{-1}$ 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**. However, the furoate **2** is more reactive than the benzoate **1** for all the amines studied.

We have recently shown that the effect of substituent in the nonleaving group on reactivity is significant for nucleophilic substitution reactions of aryl X-substituted benzoates and benzensulfonates with primary and secondary amines[9-11] as well as with anionic nucleophiles such as OH^-, CN^-, and N_3^-.[12] In all cases, the reactivity of these esters increased as

Table 1. Summary of Second-order Rate Constants (k_N, $M^{-1}s^{-1}$) for the Reactions of 2,4-Dinitrophenyl Benzoate (**1**) and 2-Furoate (**2**) with Alicyclic Secondary Amines in 80 mol % $H_2O/20$ mol % DMSO at 25.0 ± 0.1 °C

No.	Amines	pK_a	$k_N/M^{-1}s^{-1}$	
			1	**2**
1	piperidine	11.02	174[a]	427
2	3-methyl piperidine	10.80	167[a]	402
3	piperazine	9.85	82.1[a]	224
4	morpholine	8.65	19.6[a]	43.5
5	1-formyl piperazine	7.98	5.43[a]	12.3
6	piperazinium ion	5.95	0.467[a]	1.47

[a]Data taken from ref. 9b.

the substituent X in the benzoyl or the sulfonyl moiety becomes a stronger EWG.[9-12] We have found that the Yukawa-Tsuno plots for these reactions are linear with r values ranging from 0.4 to 1.6.[9-12] Since the r value in the Yukawa-Tsuno plot represents a relative extent of resonance contribution between the electron donating substituent (*e.g.*, 4-MeO) and the reaction center (*e.g.*, the carbonyl or sulfonyl group),[13,14] the ground state has been suggested to be stabilized through resonance as illustrated by resonance structures I ↔ II.
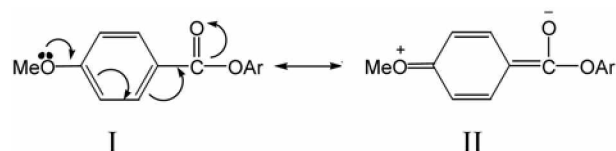
The effect of delocalizability of ring electrons to the carbonyl group (*i.e.*, resonance structures III ↔ IV, where R = benzoyl, 2-furoyl, and 2-thiophenecarboxyl) has also been studied theoretically.[15] Lee *et al.* have reported that the delocalizability of ring electrons decreases in the order 2-furoyl > 2-thiophenecarboxyl > benzoyl on the basis of the ab initio calculations at the MP2/6-31G*//MP2/6-31G* level.[15] Furthermore, the natural bond orbital (NBO) positive charge on the carbonyl carbon has been computed to be in the reverse order, *i.e.*, 2-furoyl (0.328) < 2-thiophenecarboxyl (0.351) < benzoyl (0.376),[15] indicating that the benzoate **1** is more electrophilic than the furoate **2**. Accordingly, one might expect that **1** is more reactive than **2**. However, Table 1 shows that **2** is more reactive than **1** toward all the amines studied. Thus, one can suggest that the delocalizability of ring electron (or the NBO positive charge) cannot determine the reactivity of **1** and **2** toward the amines in the current study.

2-Furoic acid ($pK_a = 3.16$) is 1.04 pK_a units more acidic than benzoic acid ($pK_a = 4.20$).[16] Thus, one might suggest that the high acidity of 2-furoic acid is responsible, at least in part, for the fact that **2** is more reactive than **1**. This argument is consistent with our recent reports that an acid strengthening substituent X in the benzoyl or benzenesulfonyl moiety increases the reactivity of aryl X-substituted benzoates or benzenesulfonates toward various nucleophiles.[9-12]
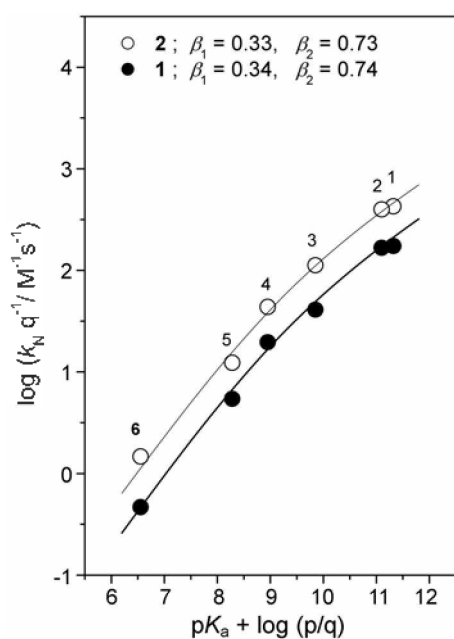
Effect of Nonleaving Group on Reaction Mechanism. In Figure 1 is demonstrated the effect of amine basicity on reactivity. The Bronsted-type plots exhibit downward curvature for reactions of **1** and **2**. Such a nonlinear Bronsted-type plot has often been found for aminolysis of esters with a good leaving group and suggested as evidence of a stepwise mechanism with a change in the RDS. In fact, we have
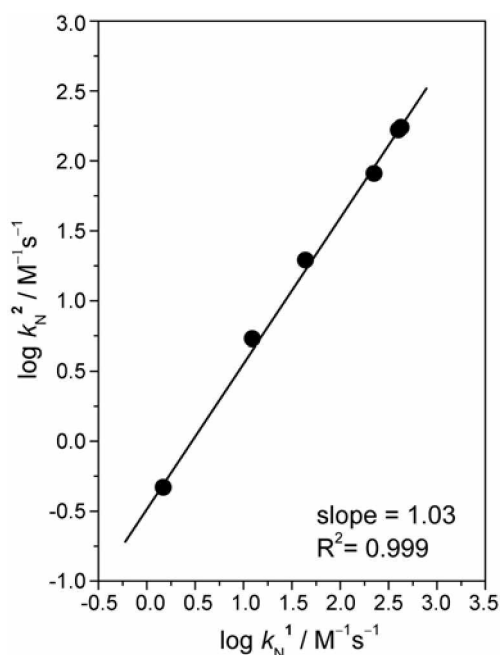
Figure 1. Bronsted-type plots for the reactions of **1** (●) and **2** (○) with alicyclic secondary amines in 80 mol % $H_2O/20$ mol % DMSO at 25.0 ± 0.1 °C. The identity of points is given in Table 1.

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

recently reported that the reactions of **1** with all the amines employed in this study proceed through $T^{\mp}$ with a change in the RDS from the breakdown of $T^{\pm}$ to its formation as the amine becomes more basic than the leaving 2,4-dinitrophenoxide ion by *ca.* 5 pK_a units.[5a,9a] Thus, one can suggest that the aminolysis of **2** proceeds also through $T^{\pm}$ on the basis of the nonlinear Bronsted-type plot as shown in Figure 1. This argument can be supported from the linear correlation between the logarithmic second-order rate constants

for the reactions of **1** and **2**. As shown in Figure 2, the log k_N for the reactions of **2** exhibits a good linear correlation with that for the corresponding reactions of **1** with a slope close to unity.

The nonlinear Bronsted-type plot shown in Figure 1 for the aminolysis of **2** has been analyzed using a semiempirical equation (eq 2)[6,17] on the basis of the proposed mechanism shown in Scheme 1. The parameters β_1 and β_2 represent the slope of the curved Bronsted plots in Figure 1 for the reactions with strongly basic and weakly basic amines, respectively. Here k_N^o refers to the k_N value at pK_a^o where $k_2/k_{-1} = 1$. The parameters determined from the fitting of eq (2) to the experimental points are $\beta_1 = 0.33$, $\beta_2 = 0.73$, and $pK_a^o = 9.1$. Although the β_1 and β_2 values are slightly smaller for the reactions of **2** than for those of **1** (*i.e.*, $\beta_1 = 0.34$ and $\beta_2 = 0.74$), the pK_a^o value is the same, *i.e.*, $pK_a^o = 9.1$ for both reactions of **1** and **2**. This result is consistent with our previous conclusion that the nature of the nonleaving group does not influence the pK_a^o value.[5,9-11]

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

The k_N values for the reactions of **2** have been dissected into their microscopic rate constants to obtain further information about the reaction mechanism. 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.

$$k_N = k_1 k_2 / (k_{-1} + k_2) \quad (3)$$

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.

$$k_N = k_1 k_2 / k_{-1}, \text{ when } k_2 \ll k_{-1} \quad (4)$$

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

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

$$\beta_2 = d(\log k_1 k_2 / k_{-1}) / d(pK_a)$$
$$= \beta_1 + d(\log k_2 / k_{-1}) / d(pK_a) \quad (7)$$

Eq (7) can be rearranged as eq (8). Integral of eq (8) from pK_a^o results in eq (9). Since $k_2 = k_{-1}$ at pK_a^o, the term $(\log k_2 / k_{-1})_{pK_a^o}$ is zero. Therefore, one can calculate the k_2/k_{-1} ratios for the aminolysis of **2** from eq (9) using $pK_a^o = 9.1$, $\beta_1 = 0.33$, and $\beta_2 = 0.73$.

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

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

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.

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

The k_2 value has been suggested to be independent of the

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

No.	Amines	pK_a	$k_1 \cdot M^{-1} s^{-1}$	k_2/k_{-1}
1	piperidine	11.02	482 (197)[a]	7.73 (7.73)[a]
2	3-methyl piperidine	10.80	466 (193)[a]	6.32 (6.32)[a]
3	piperazine	9.85	336 (123)[a]	2.00 (2.00)[a]
4	morpholine	8.65	93.4 (42.1)[a]	0.872 (0.872)[a]
5	1-formyl piperazine	7.98	38.5 (17.0)[a]	0.470 (0.470)[a]
6	piperazinium ion	5.95	16.8 (5.36)[a]	0.096 (0.096)[a]

[a]Data in the parentheses are for the reactions of **1** taken from ref. 9b.
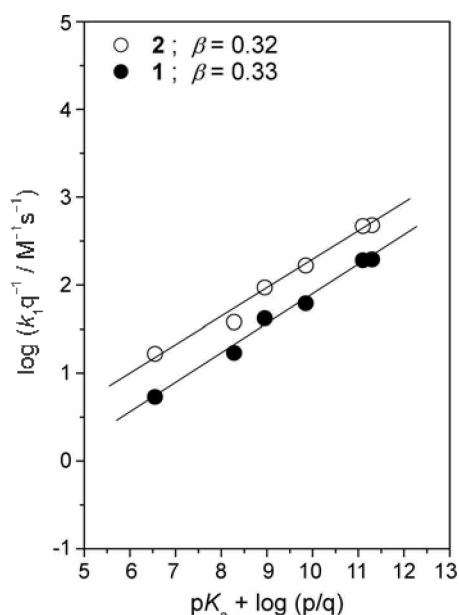
Figure 3. Bronsted-type plots for k_1 for the reactions of **1** (●) and **2** (○) with alicyclic secondary amines in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C.

basicity of amines. while k_{-1} would decrease as the amine basicity increases.[6-11] Accordingly. one might expect that the k_2/k_{-1} ratio would increase as the amine basicity increases. Table 2 shows that the k_2/k_{-1} ratio increases as the amine basicity increases. which is consistent with the expectation. Table 2 also shows that the k_2/k_{-1} ratios for the reactions of **2** are the same as those for the reactions of **1**. This result supports our previous conclusion that the electronic nature of substituent X in the benzoyl or benzenesulfonyl moiety does not affect the k_2/k_{-1} ratio.[9-11]

As shown in Table 2. k_1 increases with increasing amine basicity for both reactions of **1** and **2**. The effect of amine basicity on k_1 is illustrated in Figure 3. Both Bronsted-type plots are linear with almost the same slope. It is noted that the k_1 value is larger for the reactions of **2** than for those of **1** for a given amine. which is fully responsible for the fact that the former exhibits higher reactivity than the latter.

Conclusions

The current study has allowed us the following conclu-

sions: (i) The furoate **2** is more reactive than the benzoate **1**. The higher acidity of 2-furoic acid compared with benzoic acid is responsible. at least in part. for the higher reactivity of **2**. (ii) The aminolysis of **2** has been suggested to proceed through $T^{\pm}$ with a change in the RDS on the basis of the nonlinear Bronsted-type plot. (iii) The pK_a° and k_2/k_{-1} ratios for the reactions of **1** and **2** are identical. indicating that the nature of the nonleaving group (*i.e.*, benzoyl and 2-furoyl) does not affect the reaction mechanism. (iv) The k_1 value is larger for the reactions of **2** than for those of **1**. which is fully responsible for the fact that the former is more reactive than the latter.

Experimental Section

Materials. Substrate **2** was readily prepared from the reaction of 2,4-dinitrophenol and 2-furoyl chloride in the presence of triethylamine in anhydrous ether. The purity was confirmed by its melting point and ^1H NMR spectrum. 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. aqueous DMSO was used as the reaction medium (*i.e.*, 20 mol % DMSO/80 mol % H_2O). 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 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 2,4-dinitrophenoxide ion at 400 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.

Typically. reaction was initiated by adding 5 μL of 0.02 M of a substrate solution in MeCN by a 10 μL syringe into a 10 mm UV cell containing 2.50 mL of the reaction medium and the amine. The amine stock solution of *ca*. 0.2 M was prepared in a 25.0 mL volumetric flask under nitrogen by adding 2 equiv of amine to 1 equiv of standardized HCl solution in order to obtain a self-buffered solution. All the transfers of reaction solutions were carried out by means of gas-tight syringes.

Products Analysis. The amount of 2,4-dinitrophenoxide ion was determined quantitatively 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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