Aminolysis of 3,4-Dinitrophenyl Cinnamate and Benzoate 2: Activation Parameters and Transition-State Structures

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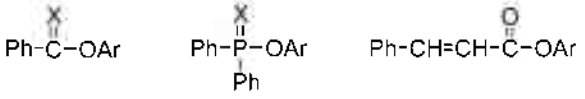
The apparent second-order rate constants (k_N) have been dissected into the microscopic rate constants (*i.e.*, k_1 and k_2/k_{-1}) associated with the reactions of Y-substituted phenyl cinnamates (**5a-g**) with piperidine and morpholine on the assumption that the reactions proceed through a stepwise mechanism with a change in the rate-determining step (RDS). The k_1 value is larger for the reactions with the more basic piperidine, and increases with decreasing the basicity of the leaving aryloxides. However, the k_2/k_{-1} ratio is almost the same for the reaction of 3,4-dinitrophenyl cinnamate (**5a**) with piperidine and for that with morpholine, which is not possible if the reactions proceed through a stepwise mechanism. Thus, the aminolysis of **5a-g** has been proposed to proceed through a concerted mechanism. The activation parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) have been measured for the reactions of 3,4-dinitrophenyl benzoate (**1a**) and cinnamate (**5a**) with morpholine from the kinetic study performed at 5 different temperatures in 80 mol % H_2O/20 mol % DMSO. The reaction of **5a** results in a lager enthalpy of activation ($\Delta H^{\ddagger}$) but a less negative entropy of activation ($\Delta S^{\ddagger}$) than that of **1a**.

Key Words : Bronsted-type plot, Concerted mechanism, Enthalpy of activation, Entropy of activation, Transition state

Introduction

Aminolyses of esters have been suggested to proceed through a concerted or a stepwise mechanism depending on the reaction condition and the nature of reactants.[1-12] Reactions of aryl benzoates (**1**) with a series of alicyclic secondary amines have been reported to proceed through a stepwise mechanism with a change in the rate-determining step (RDS) in water containing ethanol[4] or DMSO.[5] However, we have shown that aminolysis of **1** proceeds through a concerted mechanism in MeCN.[6]



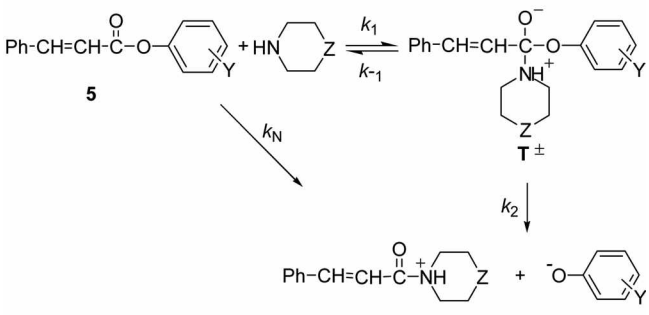
X = O(**1**), S(**2**) X = O(**3**), S(**4**) **5**

The nature of reactants has been suggested to be also significant to determine reaction mechanism.[7-12] We have reported that reactions of *O*-4-nitrophenyl thionobenzoate (**2**) with secondary amines proceed through two intermediates, a zwitterionic tetrahedral intermediate ($T^{\pm}$) and its deprotonated form (T^{-}) both in H_2O and MeCN,[7] while the corresponding reactions with primary amines proceed through only $T^{\pm}$.[8] A similar result has been reported for aminolysis of aryl phenyl carbonates and their thiono analogues.[9,10]

The effect of modification of the electrophilic center has been reported to be less significant for reactions of aryl diphenylphosphinates (**3**) and diphenylphosphinothioates (**4**).[11-14] We have shown that both reactions of **3** and **4** with alicyclic secondary amines proceed through a concerted mechanism, although **3** exhibits slightly higher reactivity than **4** toward amines.[11a]

We have also been investigating the effect of modification of nonleaving group on reactivity and reaction mechanism.[15,16] We have recently found that reactions of aryl cinnamates (**5**) with secondary amines result in curved Bronsted-type plots, *i.e.*, the slope of the Bronsted-type plot decreases as the basicity of amines increases or the leaving aryloxide becomes weakly basic.[16a] Traditionally, such a curved Bronsted-type plot has been interpreted as a change in the RDS of a stepwise mechanism.[1-5] However, we have proposed that the curved Bronsted-type plots are not due to a change in the RDS but due to a normal Hammond effect.[16a]

To get further information on the reaction mechanism, we have dissected the second-order rate constants (k_N) into the microscopic rate constants (*i.e.*, k_1 and k_2/k_{-1}) for the reactions of Y-substituted phenyl cinnamates (**5a-g**) with



Y = 3,4-$(NO_2)_2$ (**a**), 4-NO_2 (**b**), 4-CHO (**c**), 4-COMe(**d**), 4-COOEt (**e**), 3-Cl (**f**), 3-COMe (**g**).

Z = CH_2 and O

Scheme 1

piperidine and morpholine on the assumption that the reactions proceed through a stepwise mechanism with a change in the RDS. We have also measured activation parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) for the reactions of 3,4-dinitrophenyl benzoate (**1a**) and cinnamate (**5a**) with morpholine to investigate the transition-state (TS) structures.

Results and Discussion

All reactions in this study obeyed pseudo-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 correlation coefficients for the linear regressions were usually higher than 0.9995. The plots of k_{obsd} *vs.* morpholine concentration were linear passing through the origin, indicating that general base catalysis is absent and the contribution of H_2O and/or OH^- from hydrolysis of amine to the k_{obsd} is negligible. The second-order rate constants (k_N) were determined from the slope of the linear plots of k_{obsd} *vs.* amine concentration. The uncertainty in the rate constants is estimated to be less than 3% from replicate runs. The activation parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) were calculated from the Arrhenius equation.[17] The plots for the reactions of **1a** and **5a** with morpholine performed at five different temperatures resulted in good linear correlations.

Evaluation of Microscopic Rate Constants. As shown in Figure 1, the Bronsted-type plots for reactions of Y-substituted phenyl benzoates (**1a-e**) with morpholine (■) is linear, while those for the reactions of Y-substituted phenyl cinnamates (**5a-g**) with piperidine (●) and morpholine (○) are curved. One might attribute the curved Bronsted-type plots to a change in the RDS. Thus, the curved Bronsted-type plots for the reactions of **5a-g** have been analyzed using a semiempirical equation (eq. 1)[18] on the assumption that the reaction proceeds through a stepwise mechanism with a change in the RDS.

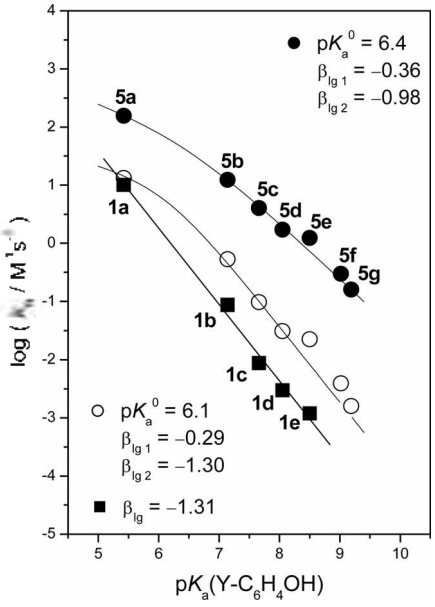


Figure 1. Bronsted-type plots for reactions of Y-substituted phenyl benzoates (**1a-e**) with morpholine (■), and Y-substituted phenyl cinnamates (**5a-g**) with piperidine (●) and morpholine (○) in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C. The kinetic data were taken from ref. 16a.

In eq. (1), β_{lg1} and β_{lg2} represent the slope of the curved Bronsted-type plots in Figure 1 for the reactions with weakly basic and strongly basic leaving groups, respectively. The k_N° refers to the k_N value at pK_a°, the curvature center of the curved Bronsted-type plot, where $k_2/k_{-1} = 1$. The pK_a°, β_{lg1} and β_{lg2} determined are 6.4, –0.26 and –1.00, in turn for the reactions of **5a-g** with piperidine, while 6.1, –0.35 and –1.24, respectively for those with morpholine.

$$\log (k_N/k_N^\circ) = \beta_{lg1}(pK_a - pK_a^\circ) - \log [(1 + \alpha)/2]$$

$$\text{where } \log \alpha = (\beta_{lg1} - \beta_{lg2})(pK_a - pK_a^\circ) \quad (1)$$

The microscopic rate constants (*i.e.*, k_1 and k_2/k_{-1} ratios) associated with the reactions of **5a-g** with piperidine and morpholine have been calculated using the following method. The rate equation and the apparent second-order rate constant (k_N) can be expressed as eqs. (2) and (3) on the assumption that the reactions proceed through a zwitterionic tetrahedral intermediate $T^{\pm}$. Eq (3) can be simplified to eq. (4) or (5). Then, β_{lg1} and β_{lg2} can be expressed as eqs. (6) and (7), respectively.

$$\text{Rate} = k_N[\text{substrate}][\text{amine}] \quad (2)$$

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

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

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

$$\beta_{lg1} = d(\log k_1)/d(pK_a) \quad (6)$$

$$\beta_{lg2} = d(\log k_1k_2/k_{-1})/d(pK_a) = \beta_{lg1} + d(\log k_2/k_{-1})/d(pK_a) \quad (7)$$

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 $(\log k_2/k_{-1})_{pKa}^\circ$ is zero. Therefore, one can calculate the k_2/k_{-1} ratios for the reactions of **5a-g** from eq. (9) using pK_a° = 6.4, β_{lg1} = –0.26 and β_{lg2} = –1.00 for the reactions with piperidine, and pK_a° = 6.1, β_{lg1} = –0.35 and β_{lg2} = –1.24 for those with morpholine.

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

$$(\log k_2/k_{-1})_{pKa} = (\beta_{lg2} - \beta_{lg1})(pK_a - pK_a^\circ) \quad (9)$$

The k_1 values have been determined from eq. (10) using the k_N values reported previously 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.

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

Reaction Mechanism. As shown in Table 1, k_1 increases as the pK_a of the conjugate acid of the leaving aryloxides decreases. The effect of leaving group basicity on k_1 is illustrated in Figure 2. Linear Bronsted-type plots are

Table 1. Summary of Microscopic Rate Constants Associated with Reactions of Y-Substituted Phenyl Cinnamates (**5a-g**) with Piperidine and Morpholine in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C

	Y	$k_1/M^{-1}s^{-1}$		$10^2\ k_2/k_{-1}$	
		piperidine	morpholine	piperidine	morpholine
5a	Y = 3,4-$(NO_2)_2$	185	16.5	319	403
5b	Y = 4-NO_2	55.7	5.00	17.0	11.9
5c	Y = 4-CHO	38.5	2.47	7.01	0.409
5d	Y = 4-COMe	30.2	1.64	3.61	1.84
5e	Y = 4-CO_2Et	45.6	3.11	1.68	0.731
5f	Y = 3-Cl	26.1	1.57	0.691	0.252
5g	Y = 3-$COCH_3$	18.7	0.902	0.517	0.178

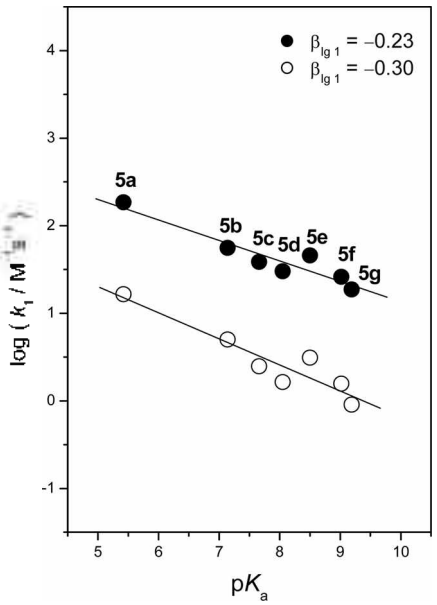


Figure 2. Bronsted-type plots for reactions of Y-substituted phenyl cinnamates (**5a-g**) with piperidine (●) and morpholine (○) in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C.

obtained with β_{lg1} values of –0.23 and –0.30 for the reactions with piperidine and morpholine, respectively. The β_{lg1} value of 0.2 ± 0.1 is typical for reactions which proceed through formation of $T^{\pm}$ in the RDS.[1-5] Besides, the k_1 value is larger for the reaction with piperidine than for the corresponding reaction with morpholine as expected. Thus, one might attribute the curved Bronsted-type plots in Figure 1 to a change in the RDS.

The k_2 value has been suggested to be independent of the basicity of amines,[1,19] but would increase as the basicity of the leaving aryloxide decreases. On the other hand, k_{-1} would be larger for the reaction with morpholine than that with piperidine, since the former is less basic than the latter. Accordingly, one might expect that the k_2/k_{-1} ratio would be larger for the reaction with piperidine and would increase as the basicity of the leaving aryloxide decreases. In fact, as shown in Figure 3, the k_2/k_{-1} ratio is larger for the reaction with more basic piperidine and increases linearly as the

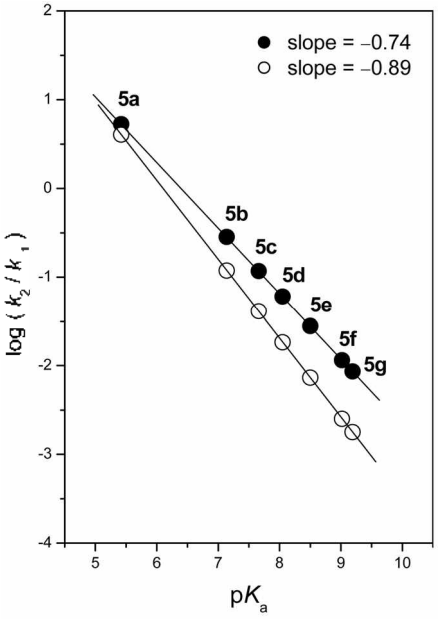


Figure 3. Plots of log k_2/k_{-1} *vs.* pK_a of the conjugate acids of leaving aryloxides for reactions of Y-substituted phenyl cinnamates (**5a-g**) with piperidine (●) and morpholine (○) in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C.

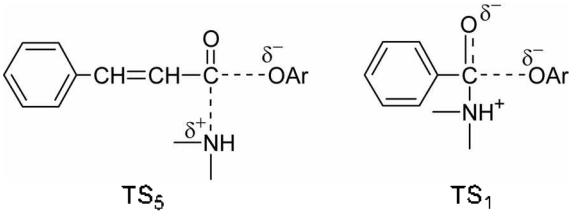
basicity of the leaving aryloxide decreases. However, the difference in the k_2/k_{-1} ratio between the two series of reactions becomes smaller as the leaving group basicity decreases. Consequently, the k_2/k_{-1} ratio is almost the same for the reaction of **5a** with piperidine and with morpholine, although the former is *ca.* 2.4 pK_a units more basic than the latter.

The above result is not possible if the reactions proceed through a stepwise mechanism with a change in the RDS. Thus, one can suggest that the curved Bronsted-type plots in Figure 1 are not due to a change in the RDS of a stepwise mechanism. This argument is consistent with our previous proposal[16a] that the curved Bronsted-type plots are due to a normal Hammond effect[20] of a concerted mechanism (*i.e.*, earlier TS with decreasing the basicity of the leaving group).

TS Structures and Activation Parameters. Two transition-state (TS) structures are proposed for the reactions of 3,4-dinitrophenyl cinnamate (**5a**) and benzoate (**1a**) with morpholine (*i.e.*, TS_5 and TS_1). One can suggest TS_5 as the TS structure for the reaction of **5a** on the basis of the mechanism proposed in the preceding section (*i.e.*, a concerted mechanism). In TS_5, both the attack of the nucleophile and the departure of the leaving group are partially advanced. On the other hand, the reaction of **1a** with morpholine has been suggested to proceed through a zwitterionic tetrahedral intermediate $T^{\pm}$ with its breakdown being the RDS.[16a] The fact that the Bronsted-type plot for the reactions of **1a-e** with morpholine is linear with β_{lg} = –1.30 (Figure 1) is consistent with the suggested mechanism. Thus, one can consider TS_1 as the TS structure for the reaction of **1a**.

Table 2. Summary of Second-Order Rate Constants and Activation Parameters for Reactions of 3,4-Dinitrophenyl Cinnamate (**5a**) and Benzoate (**1a**) with Morpholine in 80 mol % H_2O/20 mol % DMSO at 15.0, 20.0, 25.0, 35.0, and 45.0 ± 0.1°C

	k_N / $M^{-1}s^{-1}$					$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/eu
	15.0 °C	20.0 °C	25.0 °C	35.0 °C	45.0 °C		
5a	8.58	10.0	13.2	22.3	36.3	8.33 ± 0.40	–25.1 ± 1.4
1a	6.13	7.42	10.1	15.1	21.7	7.14 ± 0.20	–29.8 ± 1.0



TS_5 TS_1

A common feature of TS_1 and TS_5 is that departure of the leaving group is partially advanced, while the major structural difference between the two TS's is the degree of bond formation between the amine nucleophile and the carbonyl carbon (*i.e.*, bond formation is advanced partially in TS_5 but fully in TS_1). Thus, one might suggest that TS_5 is less ordered than TS_1.

To examine the above argument, activation parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) have been measured for the reactions of 3,4-dinitrophenyl benzoate (**1a**) and cinnamate (**5a**) with morpholine from the kinetic study performed at five different temperatures. We have chosen the reactions of **1a** and **5a** with morpholine since their reactivities are almost the same (Figure 1). The kinetic data and activation parameters obtained are summarized in Table 2.

The Arrhenius plots in Figure 4 exhibit good linear correlations for both systems, indicating that the activation parameters calculated from the slope and intercept are accurate. Table 2 shows that the reaction of **5a** results in ca. 1.2 kcal/mol higher $\Delta H^{\ddagger}$ than that of **1a** although **5a** is slightly more reactive than **1a** toward morpholine. However, this is not unexpected on the basis of the structural difference between TS_5 and TS_1. One might expect that the energy released by formation of the C-N bond is smaller for the reaction of **5a** than for that of **1a**, while the energy required to break the C-OAr bond in the two TS is almost the same. This seems to account for the fact that the former reaction exhibits larger enthalpy of activation than the latter reaction.

It is also noted that the reactions of **5a** exhibits 4.7 eu less negative $\Delta S^{\ddagger}$ than those of **1a**, which is in accord with the above argument that TS_5 is less ordered than TS_1. The $\Delta S^{\ddagger}$ difference of 4.7 eu is equivalent to $T\Delta S^{\ddagger}$ of *ca.* 1.4 kcal/mol at 25 °C, which overcomes the unfavorable $\Delta H^{\ddagger}$ of 1.2 kcal/mol for the reaction of **5a**. Thus, the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values determined in this study also support the proposed mechanism and TS structures.

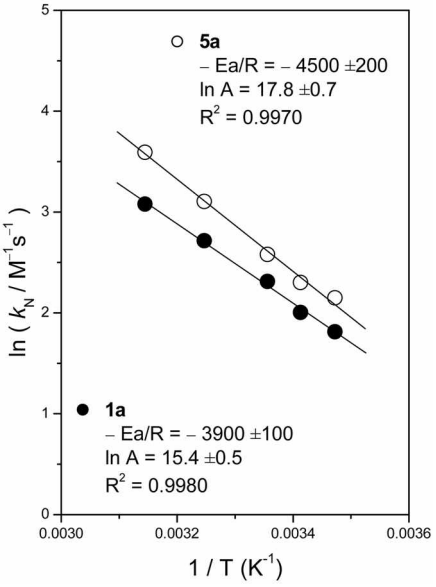


Figure 4. Arrhenius plots for reactions of 3,4-dinitrophenyl cinnamate (**5a**, ○) and benzoate (**1a**, ●) with morpholine at 15.0, 20.0, 25.0, 35.0, and 45.0 ± 0.1 °C in 80 mol % H_2O/20 mol % DMSO.

Conclusions

The current study has allowed us to conclude the following: (1) The k_2/k_{-1} ratio is almost the same for the reaction of 3,4-dinitrophenyl cinnamate (**5a**) with piperidine and for that with morpholine, which is not possible if the reactions proceed through a stepwise mechanism. (2) The reactions of **5a-g** proceed through a concerted mechanism and the curved Bronsted-type plots for the reactions of **5a-g** with piperidine and morpholine are not due to a change in the RDS. (3) The reaction of **5a** with morpholine results in *ca.* 1.2 kcal/mol higher enthalpy of activation ($\Delta H^{\ddagger}$) but 4.7 eu less negative entropy of activation ($\Delta S^{\ddagger}$) than that of **1a**, which is also consistent with the proposed mechanism and the TS structures.

Experimental Section

Materials. 3,4-Dinitrophenyl benzoate and cinnamate were readily prepared as reported previously from the reactions of 3,4-dinitrophenol with benzoyl chloride and cinnamoyl chloride under the presence of triethylamine in anhydrous ether and purified by column chromatography.[16a,21] 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 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 3,4-dinitrophenoxide. 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 morpholine. 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 morpholine stock solution. The stock solution (*ca.* 0.2 M) was prepared in a 25.0 mL volumetric flask under nitrogen by adding 2 equiv of morpholine and 1 equiv of standardized HCl solution to obtain a self-buffered solution.

Products Analysis. 3,4-Dinitrophenoxide 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 sample under the same reaction conditions.

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