Kinetics and Mechanism of the Pyridinolysis of Aryl Cyclobutanecarboxylates in Acetonitrile

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Received February 20, 2002

Kinetic studies of the reaction of Z-aryl cyclobutanecarboxylates with X-pyridines in acetonitrile at 55.0 °C have been carried out. The reaction proceeds by a stepwise mechanism in which the rate-determining step is the breakdown of the zwitterionic tetrahedral intermediate, $T^{\pm}$. These mechanistic conclusions are drawn based on (i) the large magnitude of ρ_X and ρ_Z, (ii) the positive sign of ρ_{XZ} and the larger magnitude of ρ_{XZ} than normal S_N2 processes, (iii) a small positive enthalpy of activation, $\Delta H^{\neq}$, and a large negative, $\Delta S^{\neq}$, and lastly (iv) adherence to the reactivity-selectivity principle (RSP) in all cases.

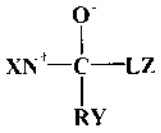
Keywords : Aryl cyclobutanecarboxylates, Stepwise mechanism, Zwitterionic tetrahedral intermediate, Cross-interaction constant.

Introduction

Although the mechanisms of aminolyses of acetate[1] and benzoate[2] esters, and diaryl[3] and alkyl aryl carbonates[4] are well understood, much less is known about the aminolysis of small ring cyclo ester compounds.

We have recently studied the kinetics of the aminolysis of aryl cyclopropanecarboxylates,[5] and aryl cyclobutanecarboxylates.[6] We have found that the reactions of aryl cyclopropancarboxylates[5] and the aryl cyclobutanecarboxylates[6] proceed through a stepwise mechanism with late-limiting expulsion of a leaving group (aryl oxides) from a tetrahedral intermediate, $T^{\pm}$, with a hydrogen-bonded, four-center transition state.

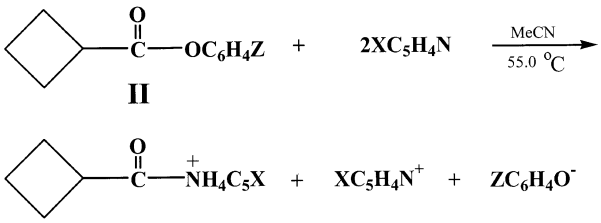
The Bronsted plots for the aminolysis of carbonyl compounds are often curved with a change in slope from a large ($\beta_{nuc} \geq 0.8$) to a small ($\beta_{nuc} \leq 0.3$) value, which can be attributed to a change in the rate determining step from breakdown to formation of a tetrahedral zwitterionic intermediate ($T^{\pm}$) in the reaction path as the amine basicity is increased.[7] The stepwise mechanism with rate-limiting expulsion of leaving group (LZ) from $T^{\pm}$ (I) is more likely to be observed



I

in the aminolysis of a carbonyl compound with (i) a stronger electron acceptor acyl group, RY,[8] (ii) a poor leaving group, LZ,[8] and (iii) a more weakly basic (or nucleophilic) amine (XN).[8b,c] However, the effect of the acyl group, RY, on the mechanism is subtle and is not quite straight-forward, since the effect can be both on the substrate and the intermediate, $T^{\pm}$, and the electronic effect can be either inductive or resonance delocalized, or both. This is the reason why it is rather difficult to predict the mechanism simply by taking account of the stereoelectronic effect of the acyl group, RY.

In view of the importance of predicting the effects of the acyl group on the mechanism of aminolysis of carbonyl compounds, we have used many different acyl groups in our studies of the aminolysis mechanism.[5,6,8b,9] In previous work, we investigated the effect on the mechanism of the reaction of a cyclobutane group, RY = cyclo-C_4H_7, with benzylamines in acetonitrile[6] and found that the cyclobutyl group leads to stepwise aminolysis with rate-limiting breakdown of the intermediate, $T^{\pm}$. In this paper, we extend our work to the pyridinolysis of aryl cyclobutanecarboxylates, II, with pyridines (Py) in acetonitrile (eq. 1).



II

(1)

X = *p*-CH_3O, *p*-CH_3, *m*-CH_3, H, *m*-C_6H_5, *m*-CH_3CO, *m*-Br, *p*-CH_3CO, *p*-CN or *m*-CN
Z = *m*-CN, *m*-NO_2, *p*-CH_3CO, *p*-CN or *p*-NO_2

The purpose of the present work is to further explore the effect of the acyl group on the pyridinolysis mechanism by investigating the structure-reactivity behavior of aryl cyclobutanecarboxylates in acetonitrile. We are interested in the effects of the small ring acyl group on the mechanism, especially on the sign and magnitude of the cross-interaction

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$$\log(k_{XZ}/k_{HH}) = \rho_X\sigma_X + \rho_Z\sigma_Z + \rho_{XZ}\sigma_X\sigma_Z \quad (2a)$$

$$\rho_{XZ} = \partial\rho_Z / \partial\sigma_X = \partial\rho_X / \partial\sigma_Z \quad (2b)$$

constant.[10] ρ_{XZ} in eqns. (2a) and (2b), where X and Z are the substituents in the nucleophile, pyridine, and leaving group, aryl oxide, respectively. Furthermore, the activation parameters, $\Delta H^{\neq}$ and $\Delta S^{\neq}$, are also determined since they can provide valuable information regarding the transition state (TS) structure.

Results and Discussion

The pseudo-first-order rate constants observed (k_{obs}) for all the reactions obeyed eq. 3 with negligible k_0 ($\cong$0) in acetonitrile. The second-order rate constants, $k_N(M^{-1}s^{-1})$ summarized in Table 1, were determined using eq. 3 with at least five

$$k_{obs} = k_0 + k_N[Py] \quad (3)$$

pyridine concentrations, [Py]. No third-order or higher-order terms were detected, and no complications were found in the determination of k_{obs} and also in the linear plots of eq. 3. This suggests that there are no base-catalysis or noticeable side reactions and the overall reaction follows the route given by eq. 1.

The p*K*a values of pyridines (Table 1) used in the Bronsted plots were those determined in water. Thus the Bronsted coefficients in Table 1 ($\beta_{X(nuc)}$) could be in error since the rate data in Table 1 (in acetonitrile) should be plotted using p*K*a values measured in acetonitrile. However our recent theoretical studies of solvent effects on the basicity of substituted pyridines at the IPCM/B3LYP/6-31G* level[11] have shown that there is a constant pKa difference of ΔpKa = p*K*a(MeCN)−p*K*a(H_2O) = 7.7 due mainly to the H^+ ion solvation free energy difference of 10.5 kcal·mol^{-1} between acetonitrile and water. The plot of p*K*a(MeCN) *vs* p*K*a(H_2O) exhibited a straight line of near unity (1.02) slope so that the Bronsted coefficients determined by the plot of log *k*(MeCN) against p*K*a(H_2O) should be almost the same as those against p*K*a(MeCN).[12] Moreover, the plots of p*K*a(ε) (in 5 solvents including water) *vs* σ gave the slopes, $\rho_s(\varepsilon)$, which is linear with the Onsager dielectric function, $(\varepsilon - 1)/(2\varepsilon + 1)$, eq. 4 with correlation coefficient of 0.999 (n = 5). This means that the specific hydrogen-bonding solvation component is not important in the solvation effect on the ionization equilibria of pyridinum ions in water. The slope, ρ_s, is thus solely dependent on the bulk solvent effect(ε) and for $\varepsilon = 78.3$[13] (water) and $\varepsilon = 37.9$[13] (acetonitrile) the ρ_s values are quite similar being -8.9 and -9.1, respectively. This provides evidence in support of correlating the rate data determined in acetonitrile with the p*K*a values measured in water.

$$\rho s = 14.6\left[\frac{\varepsilon - 1}{2\varepsilon + 1}\right] - 16.1 \quad (4)$$

The excellent linearities found in the Bronsted plots using ten nucleophiles ($r \geq 0.998$, standard devation ≤ 0.01) in Figure 1 lend more credence to our procedure. In Figure 1 is demonstrated a Bronsted-type plot for the reaction of aryl cyclobutanecarboxylates with pyridines run in acetonitrile. The linear Bronsted-type slope should correspond to the mechanism change does not occur in the present pyridinolysis.[2,4,9,15] We therefore think that our $\beta_{X(nuc)}$ values in Table 1 represent reasonable and meaningful values. The Hammett [$\rho_X(\rho_{nuc})$ and $\rho_Z{}^-(\rho_{lg}{}^-)$] values (Figures 2 and 3) coefficients, are also shown in Table 1.

The activation parameters, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ (Table 2), were determined based on the k_N values at three temperatures, 35, 45, and 55.0 °C. These are comparable to those corresponding values for the reactions of aryl cyclobutanecarboxylates with bezylamines in acetonitrile.[6]

Rates are faster with a stronger nucleophile ($\delta\sigma_X < 0$) and nucleofuge ($\delta\sigma_Z > 0$) as is expected from a typical nucleophilic substitution reaction. The rates are ~1.3 times slower than those for benzylamines[6] under the same reaction condi-

Table 1. Rate constants, k_N ($\times 10^3$ $M^{-1}s^{-1}$), for the reactions of Z-aryl cyclobutanecarboxylates with X-pyridines in acetonitrile at 55.0 °C

X	p*K*a[a]	Z = *m*-CN	*m*-NO_2	*p*-CH_3CO	*p*-CN	*p*-NO_2	ρ_Z[b]	β_Z[c]
p-CH_3O	6.58	20.1	33.1	97.7	177	833	2.33	-1.14
p-CH_3	6.03	3.89	11.5	31.6	81.3	379	2.81	-1.35
m-CH_3	5.67	2.95	5.13	16.2	51.3	224	2.77	-1.33
H	5.21	1.05	2.51	6.46	15.8	72.4	2.61	-1.26
m-C_6H_5	4.92	0.490	1.51	3.31	9.77	49.0	2.80	-1.35
m-CH_3CO	3.17	0.0126	0.0589	0.162	0.630	4.17	3.52	-1.69
m-Br	2.85	0.00759	0.0347	0.0977	0.309	2.82	3.56	-1.72
p-CH_3CO	2.38	–	–	0.0417	0.166	1.23	3.61	-1.06
p-CN	1.86	–	–	–	0.0813	0.630	3.30	-1.09
m-CN	1.35	–	–	–	0.0331	0.269	3.37	-1.11
ρ_X[d]		-5.10	-4.47	-4.45	-3.88	-3.55	ρ_{XZ}[f]=2.05	
β_X[e]		0.91	0.79	0.79	0.72	0.66		

[a]In water at 25.0 °C. Fischer, A.; Galloway, W. J.; Vaughan, J. *J. Chem. Soc.* **1964**, 3591. Hong, S. W.; Koh, H. J.; Lee, I. *J. Phys. Org. Chem.* **1999**, *12*, 425. [b]Sigma (σ and σ^-) values were taken from: Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165. Correlation coefficients are better than 0.994 in all cases. [c]The p*K*a values are taken from: Albert, A.; Serjeant, E. P. The Determination of Ionization Constants, 3rd ed., Chapman and Hall, London, **1984**, p. 45. Z = *p*-CH_3CO is excluded. [d]The source of σ is the same as for footnote b. X = *m*-CN is excluded. Correlation coefficients are better than 0.994 in all cases. [e]Correlation coefficients are better than 0.998 in all cases. [f]Correlation coefficient is better than 0.997.

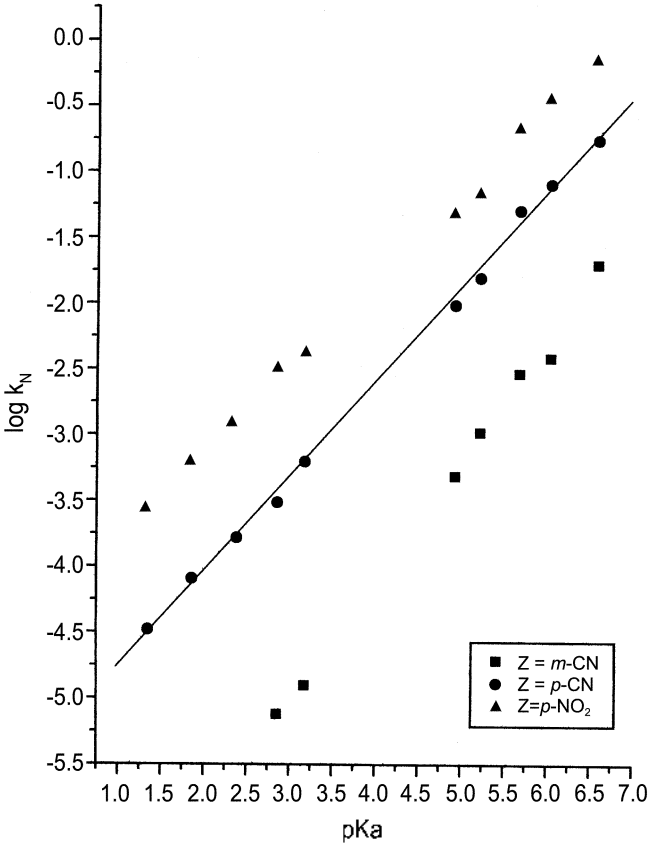


Figure 1. Brønsted plots (β_X) for the pyridinolysis of *Z*-aryl cyclobutanecarboxylates with X-pyridines (XC_5H_4N) in MeCN at 55.0 °C.

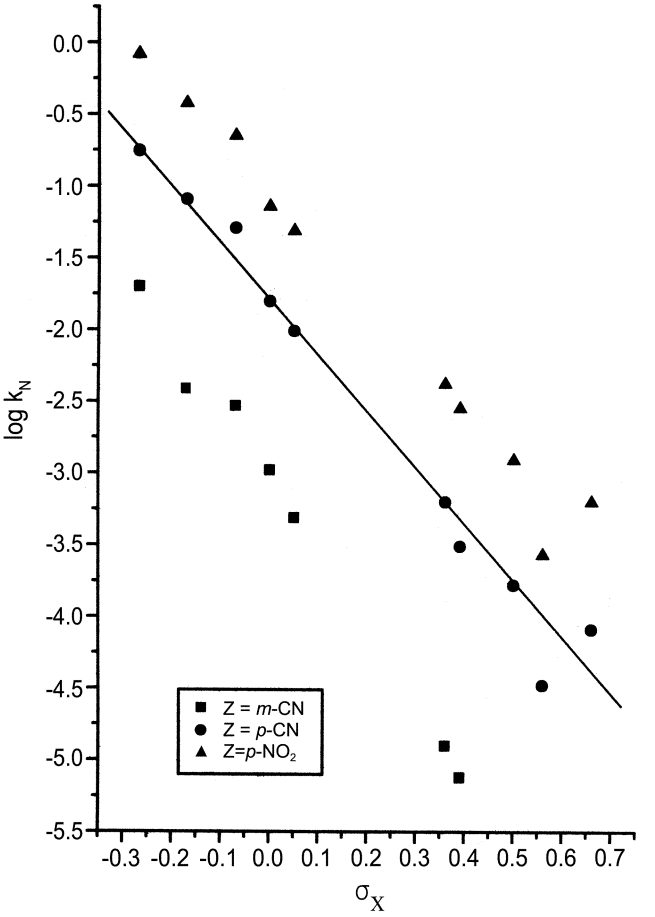


Figure 2. Hammett plots (ρ_X) for the pyridinolysis of *Z*-aryl cyclobutanecarboxylates with X-pyridines (XC_5H_4N) in MeCN at 55.0 °C.

tions. This could be due to a larger basicity of the benzylamine (p*K*a = 9.38) relative to that of the pyridine (p*K*a = 5.21) in the nucleophiles.

The results in Table 1 reveal that the magnitude of ρ_X is quite large; it ranges from -3.55 to -5.10 (the corresponding values are -0.76 to -1.90 (phenyl benzoates − benzylamines)),[2a] -2.85 to -4.83 (phenyl carbonates + benzylamines)[9c] after allowing for a fall-off factor of 2.8[14] for the non-conjugating intervening group CH_2 in benzylamine(relative to pyridine). This large magnitude of $\rho_X(\rho_{nuc})$ is also reflected in the similarly large magnitude of $\beta_X(\beta_{nuc})$ = 0.66-0.91 (the corresponding values are 0.25-0.70 (phenyl benzoates + benzylamines)[2a]), 1.08-1.17 (phenyl carbonates + benzylamines)[9c] and 1.06-1.83 (phenyl furoates + benzylamines),[9c] and 1.33-2.09 (aryl cyclobutanecarboxylates + benzylamines).[6] These large magnitudes of ρ_X and β_X are indicative of a stepwise mechanism with a rate-limiting breakdown of a zwitterionnic tetrahedral intermediate, $T^{\pm}$ [2,4,9,15] (Scheme 1).

Figure 3 shows the Hammett plots for variations of substituent in the leaving group, $\sigma_Z(\sigma_Z^-)$. The importance of the leaving group departure in the rate-determining step in reflected in the better Hammett correlations with σ_Z^- than with σ_Z and large magnitude of ρ_Z^- (=2.33-3.61) suggesting a strong negative charge development in the aryl oxide leaving group with a relatively large extent of bond cleavage in the TS (β_Z = -1.06 ~ -1.72). Also these large ρ_Z^- values are again indicative of the stepwise mechanism with a rate-limiting breakdown of a zwitterionic tetrahedral intermediate, $T^{\pm}$ (Scheme 1).[2,4,9,15]

The 52 rate constants ($k_N = k_{XZ}$), in Table 1 are subjected to multiple regression analysis using eq. 2. We note that the correlation is quite satisfactory with the cross-interaction constant, ρ_{XZ}, of +2.05. This values is also similar to that for the reactions of aryl cyclobutanecarboxylates with benzylamines (ρ_{XZ} = +1.02),[6] under the same reaction conditions. The cross-interaction between the substituents X in the nucleophile and Z in the substrate is reduced by a factor of two due to an intervening non-conjugative CH_2 group in benzylamines, albeit transition state may be similar for the two series.[14]

Previously we have shown that in the S_NAr process or in the rate-limiting formation of an intermediate the ρ_{XZ} is negative, but in a stepwise mechanism with a rate-limiting breakdown of the tetrahedral intermediate it is large positive.[6,9] The cross-interaction constant ρ_{XZ} obtained was positive and large at +2.05. This provides further strong support for the proposed mechanism comes from a large positive cross-interaction constant ρ_{XZ}.[5,6,9,16] Since an electron acceptor in the nucleophile, $\delta\sigma_X > 0$ (in the nucleofuge, $\delta\sigma_Z > 0$) leads to an increase in ρ_Z, $\delta\rho_Z > 0$ ($\delta\rho_X > 0$), ρ_{XZ} is

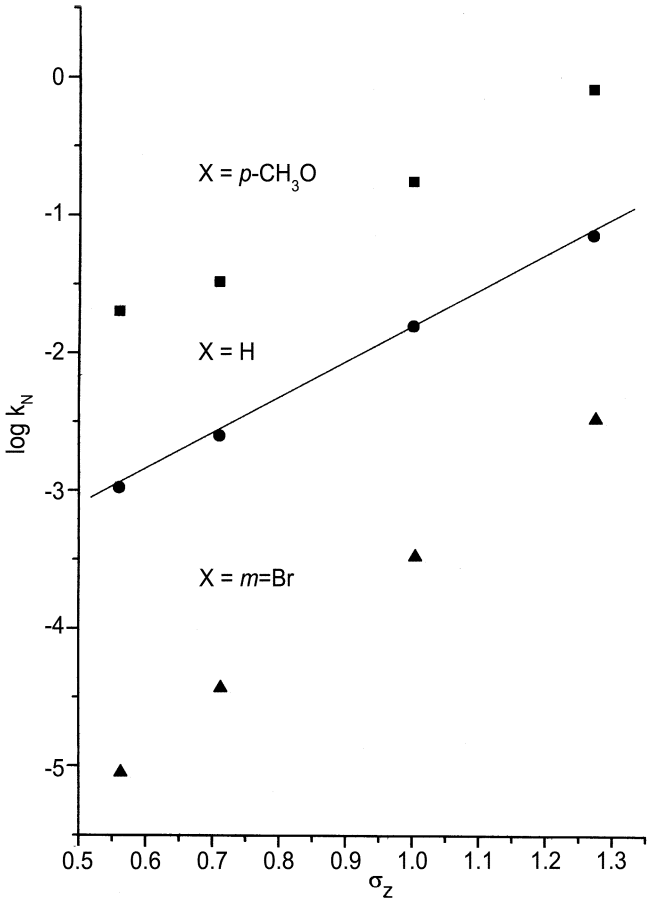


Figure 3. Hammett plots (ρ_Z) for the pyridinolysis of Z-aryl cyclobutanecarboxylates with X-pyridines (XC_5H_4N) in MeCN at 55.0 °C.

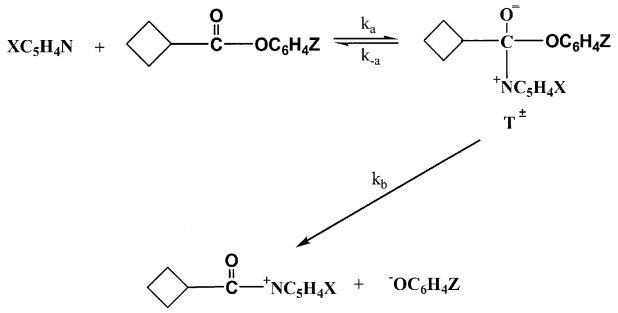
Table 2. Activation parameters[a] for the reactions of Z-aryl cyclobutanecarboxylates with X-pyridines in acetonitrile

X	Z	Temp /°C	k_N ($\times 10^3$ $M^{-1}s^{-1}$)	$\Delta H^{\neq}$ /kcal·mol^{-1}	$-\Delta S^{\neq}$ /cal·mol^{-1}K^{-1}
p-CH_3	*m*-CN	35	2.27	4.77 ± 0.04	55 ± 2
		45	2.95		
		55	3.89		
p-CH_3	*p*-NO_2	35	211	5.23 ± 0.05	45 ± 1
		45	282		
		55	379		
m-Br	*m*-CN	35	0.00429	5.09 ± 0.05	67 ± 2
		45	0.00571		
		55	0.00759		
m-Br	*p*-NO_2	35	1.48	5.84 ± 0.06	53 ± 1
		45	2.04		
		55	2.82		

[a]Calculated by the Eyring equation. Errors shown are standard deviations.

positive, eq. (2b).[5,6,9,16]

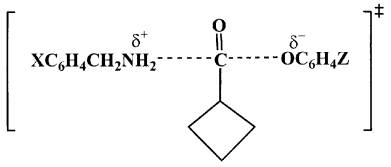
We also note in Table 1 that the rate increase is invariably accompanied by a decrease in the selectivities, ρ (ρ_X or ρ_Z), and hence the reactivity-selectivity principle (RSP) holds.[14c,17] Adherence to the RSP is considered another criterion for the stepwise mechanism with rate-limiting expulsion of the



Scheme 1

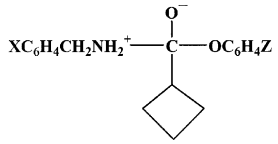
leaving group (aryl oxides).[14c,17]

We have recently studied the kinetic isotope effects (k_H/k_D) in acetonitrile for the reactions of Z-aryl cyclobutanecarboxylates with X-benzylamies deuterated on the nitrogen ($XC_6H_4CH_2ND_2$).[6] We noted that the k_H/k_D values were all greater than one $k_H/k_D > 1.0$, indicating that the rate-determining step was not a simple concerted S_N2 process (TS1), or a stepwise mechanism with a rate-limiting formation of a



TS 1

tetrahedral intermediate (TS2) since in such cases inverse kinetic isotope effect, k_H/k_D, were expected due to an increase in the N-H vibrational frequency as a result of steric congestion of the N-H moiety in the bond making step. The kinetic isotope effects observed, $k_H/k_D = 1.19$-1.46,[6] were larger than those expected from a stepwise acyl transfer mechanism, but were smaller than normal primary kinetic isotope effects.[10b] The k_H/k_D values were smaller for a stronger nucleophile and nucleofuge. Since in the intermediate, $T^{\pm}$, both a stronger nucleophile and nucleofuge facilitate the leaving group departure, less assistance was needed in the rate-limiting leaving group departure by the hydrogen bonding of the amine hydrogen.[9a,b,15j]



TS 2

Activation parameters for the reactions of aryl cyclobutanecarboxylates with pyridines are shown in Table 2. The values of $\Delta H^{\neq}$, and $\Delta S^{\neq}$ were obtained from the slope and intercept, respectively, of Eyring plots, by least-squares analysis. Although the relatively low positive $\Delta H^{\neq}$ and large negative $\Delta S^{\neq}$ values are in line with the stepwise mechanism,[4c,9g,18] they can also be interpreted as supportive of a

concerted mechanism.

Castro *et al.*[19] have argued and Lee *et al.*[16c] have shown theoretically that a tetrahedral intermediate cannot be formed for a substrate with a strong electron donor acyl group, *i.e.* C_2H_5O, due to the kinetic instability brought about by the large values of k_a and k_b,[19,20] (Scheme 1). Thus a concerted mechanism is enforced.[19,20] However, for the reaction systems investigated in this work, the cyclobutane group has a relatively low resonance donor effect (σ_R = -0.12 *vs.* -0.44 for C_2H_5O group)[21] so that the $T^{\pm}$ intermediate seems to be stable enough to lead to the proposed stepwise mechanism.

In summary, the reactions of aryl cyclobutanecarboxylates with pyridines in acetonitrile proceed by a stepwise mechanism in which the rate-determining step is the breakdown of the zwitterionic tetrahedral intermediate.

These mechanistic conclusions are drawn based on (i) the large magnitude of ρx and ρz, (ii) the positive sign of ρxz and the larger magnitude of ρxz than that for normal S_N2 processes, (iii) a small positive enthalpy of activation, $\Delta H^{\neq}$, and a large negative entropy of activation, $\Delta S^{\neq}$, and lastly (iv) adherence to the reactivity-selectivity principle (RSP) in all cases.

Experimental Section

Materials. Merck GR acetonitrile was used after three distillations. The pyridine nucleophiles, Aldrich GR, were used without further purification. Reacting phenols with cyclobutanecarbonyl chloride prepared Aryl cyclobutanecarboxylates. The substrates synthesized were confirmed by spectral analyses as follows.

***p*-Cyanoaryl cyclobutanecarboxylate.** δ_H (250 MHz, $CDCl_3$) 7.25-7.70 (4H, m, C_6H_4), 3.5-3.6 (1H, m, CH), 2.3-2.5 (4H, m, $2CH_2$), 1.9-2.1 (2H, m, CH_2); ν_{max}(neat)/cm^{-1} 2900 (CH), 2300 (CN), 1730 (C=O); m/z = 201 (M^-) (Calc. for $C_{12}H_{11}NO_2$; C, 71.6; H, 5.47. Found: C, 71.7; H, 5.46%).

***m*-Cyanoaryl cyclobutanecarboxylate.** δ_H (250 MHz, $CDCl_3$) 7.25-7.70 (4H, m, C_6H_4), 3.5-3.6 (1H, m, CH), 2.3-2.5 (4H, m, $2CH_2$), 1.9-2.1 (2H, m, CH_2); ν_{max}(neat)/cm^{-1} 2900 (CH), 2300 (CN), 1730 (C=O); m/z = 201 (M^-) (Calc. for $C_{12}H_{11}NO_2$; C, 71.6; H, 5.47. Found: C, 71.7; H, 5.46%).

***p*-Nitroaryl cyclobutanecarboxylate.** Mp 60-62 °C; δ_H (250 MHz, $CDCl_3$) 7.24-7.80 (4H, m, C_6H_4), 3.4-3.6 (1H, m, CH), 2.3-2.6 (4H, m, $2CH_2$), 2.0-2.2 (2H, m, CH_2); ν_{max} (KBr)/cm^{-1} 2900 (CH), 1730 (C=O); m/z = 221 (M^-) (Calc. for $C_{11}H_{11}NO_4$; C, 59.7; H, 4.98. Found: C, 59.8; H, 4.99%).

***m*-Nitroaryl cyclobutanecarboxylate.** δ_H (250 MHz, $CDCl_3$) 7.24-7.80 (4H, m, C_6H_4), 3.4-3.6 (1H, m, CH), 2.3-2.6 (4H, m, $2CH_2$), 2.0-2.2 (2H, m, CH_2); ν_{max}(neat)/cm^{-1} 2900 (CH), 1730 (C=O); m/z = 221 (M^-) (Calc. for $C_{11}H_{11}NO_4$; C, 59.7; H, 4.98. Found: C, 59.8; H, 4.99%).

***p*-Acetylaryl cyclobutanecarboxylate.** δ_H (250 MHz, $CDCl_3$) 7.25-7.70 (4H, m, C_6H_4), 3.5-3.6 (1H, m, CH), 2.3-2.5 (4H, m, $2CH_2$), 1.9-2.1 (2H, m, CH_2); ν_{max}(neat)/cm^{-1} 2900 (CH), 1730 (C=O); m/z = 218 (M^+) (Calc. for $C_{13}H_{14}O_3$; C, 71.6; H, 6.42. Found: C, 71.6; H, 6.43%).

Rate constants. Rates were measured conductimetrically at 55.0±0.05 °C. The conductivity bridge used in this work was a self-made computer automatic A/D converter conductivity bridge. Pseudo-first-order rate constants, k_{obs}, were determined by the curve fitting analysis of the computer data with a modified version of the Origin program, which fits conductance *vs.* time data to the equation $A = A_\infty + (A_o - A_\infty)\exp(-k_{obs} \times t)$, where A is the observed conductivity and A_∞, $A_o - A_\infty$, and k_{obs} are iteratively optimized to achieve the best possible least-squares fit with a large excess of pyridine (Py); [aryl cyclobutanecarboxylate] ≈1×10^{-3} M and [Py] = 0.03-0.24 M. Second-order rate constants, k_N, were obtained from the slope of a plot of k_{obs} *vs.* [Py] with more than five concentrations of pyridine, eq. 3, and Figure 4. The k_N values in Table 1 are the averages of more than three runs and were reproducible to within ±3%.

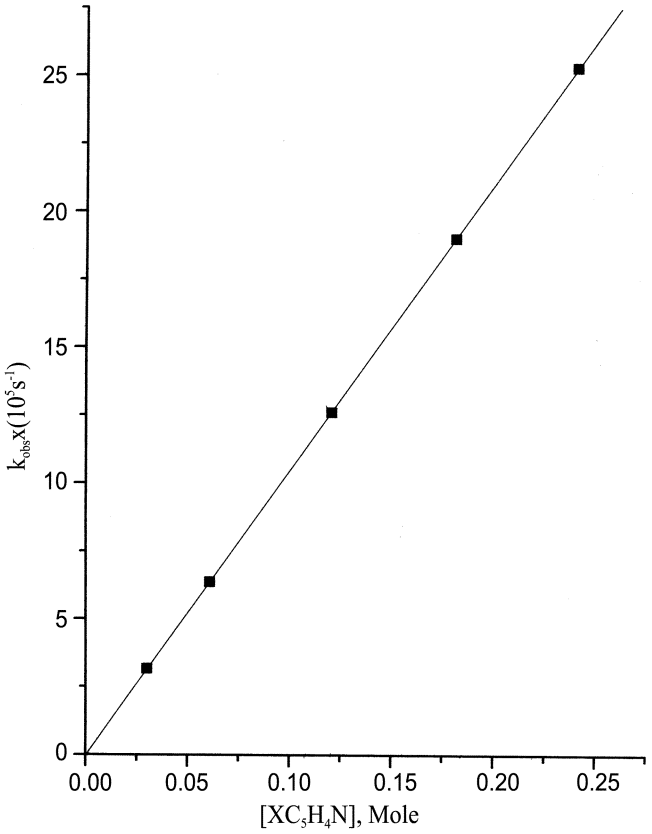


Figure 4. Plots of pseudo-first order rate constants (k_{obs}) *vs.* nucleophile concentration, [XC_5H_4N], for reactions of *m*-cyanoaryl cyclobutanecarboxylate with X-pyridine (X H) in acetonitrile at 55.0 °C.

Product analysis. *p*-Nitroaryl cyclobutanecarboxylate was reacted with excess *p*-methylpyridine with stirring for more than 15 half-lives at 55.0 °C in acetonitrile, and the products were isolated by evaporating the solvent under reduced pressure. The product mixture was separated by column chromatography (silica gel, 20% ethyl acetate-*n*-hexane). Analysis of the products gave the following results.

Cyclobutyl-C(=O)N$^+$C$_5$H$_4$-*p*-CH$_3$. δ_H (250 MHz, $CDCl_3$), 3.4-3.6 (1H, m, CH), 2.5-2.8 (4H, m, $2CH_2$), 2.3 (3H, m, CH_3), 2.0-2.1 (2H, m, CH_2); $\nu_{max(neat)}$/cm^{-1} 2900 (CH), 1730 (C=O); m/z = 176 (M^-). (Calc. for $C_{11}H_{14}NO$; C, 75; H,

7.95. Found : C, 74.9; H. 7.96%).

Acknowledgment. We thank the Korean Chemical Society and the Korean Science and Engineering Foundation (KCS-KOSEF-2001-01) for support of this work.

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