Kinetics and Mechanism of the Pyridinolysis of Aryl Cyclopropanecarboxylates in Acetonitrile

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Kinetic studies of the reaction of Z-aryl cyclopropanecarboxylates 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.

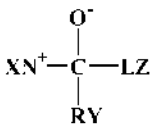
Key Words : Aryl cyclopropanecarboxylates, Stepwise mechanism, Zwitterionic tetrahedral intermediate, Cross interaction constant, Reactivity-selectivity principle

Introduction

Although the kinetics and mechanisms of the acetate[1] and benzoate[2] esters, and diaryl[3] and alkyl aryl carbonates[4] are well documented, only few reports have delt with the kinetics of the same reactions 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 the rate-limiting expulsion of a leaving group (aryl oxides) from a tetrahedral intermediate, $T^{\pm}$, with a hydrogen-bonded, four-center transition state.

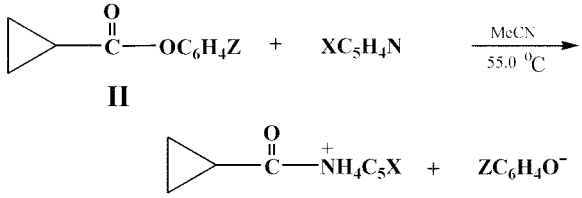
The Brønsted type plots for the aminolysis of carbonyl compounds are often curved with a change in slope from a large ($\beta_{nuc} \geq 0.8$) to a small ($\beta_{nuc} \leq 0.3$) value, which can be attributed to a change in the rate determining step from breakdown to formation of a tetrahedral zwitterionic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



I

(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 of the mechanism of the reaction of a cyclopropane group, RY = cyclo – C_3H_5, with benzylamines in acetonitrile[5] and found that the cyclopropyl group leads to stepwise aminolysis with the rate-limiting breakdown of the intermediate, $T^{\pm}$. In this paper, we extend our work to the pyridinolysis of aryl cyclopropanecarboxylates, II, with pyridines (Py) in acetonitrile eq. 1.



II

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 (1)

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 cyclopropanecarboxylates 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 constant,[10] ρ_{XZ} in eqns. 2a and 2b, where X and Z are the substituents

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

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

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 rate law obtained in the present reactions is given by eqns. 3 and 4, where ArO^- is the leaving group, k_{obs} is the pseudo-first-order rate constant, k_o and k_N are the rate constants for solvolysis and pyridinolysis of the substrate, respectively, and [Py] and [S] represent the pyridine and substrate concentrations, respectively. The value of k_o was negligible in acetonitrile, $k_o \cong 0$. The second-order rate constants for pyridinolysis (k_N) were obtained as the slopes of plots of eq. 4. These values, together with those of the p*K*a of the conjugate acids of the pyridines, are summarized in Table 1.

$$d[ArO^-]/dt = k_{obs}[S] \quad (3)$$

$$k_{obs} = k_0 + k_N[Py] \quad (4)$$

No third-order or higher-order terms were detected, and no complications arising from side reaction were found in the determination of k_{obs} and also in the linear plots of eq. 4. This suggests that the overall reaction follows cleanly the route given by eq. 1.

The p*K*a values of pyridines (Table 1) used in the Brϕnsted plots were determined in water. Thus the Brϕnsted 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 Brϕnsted coefficients determined by the plot of log k_N(MeCN) against p*K*a(H_2O) should be almost the same as those against p*K*a (MeCN).[12]

A similar invariance of Brϕnsted coefficient for the reactions of para-nitrophenylsulfonate in chloroform with eight pyridines has been reported using p*K*a(H_2O) and p*K*a(CH_3CN) values with β = 0.31±0.02(r =0.985) and β = 0.30±0.02(r = 0.994), respectively.[12] Moreover, the plots of pKa(ε) (in five 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. 5 with correlation coefficient of 0.999 (n = 5).[11] 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 = 78.3[13](water) and = 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.

$$\rho_s = 14.6\left[\frac{\varepsilon - 1}{2\varepsilon + 1}\right] - 16.1 \quad (5)$$

Using the k_N and p*K*a values in Table 1, the Bronsted plots for the reactions under study were obtained as shown in Figure 1. The excellent linearities found in the Brϕnsted plots using ten nucleophiles ($r \geq 0.997$), standard devation ≤ 0.02) in Figure 1 lend more credence to our procedure. In figure 1 is demonstrated a Brϕnsted-type plot for the reaction of aryl cyclopropanecarboxylates with pyridines run in acetonitrile.

The linear Brϕnsted-type slope should correspond to

Table 1. Rate constants, k_N (× 10^4 M^{-1}s^{-1}), for the reactions of Z-aryl cyclopropanecarboxylates 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	18.6	34.7	120	204	–	2.67	−1.79
p-CH_3	6.03	6.17	10.5	50.1	91.2	447	2.72	−1.31
m-CH_3	5.67	4.07	6.31	28.8	47.9	240	2.76	−1.25
H	5.21	1.55	1.74	15.5	24.5	174	3.06	−1.49
m-C_6H_5	4.92	0.933	0.955	7.94	13.2	117	3.11	−1.81
m-CH_3CO	3.17	0.0178	0.0550	0.417	1.01	12.9	3.80	−1.84
m-Br	2.85	–	0.0275	0.269	0.834	8.32	3.87	−1.71
p-CH_3CO	2.38	–	–	0.141	0.347	4.07	3.82	−1.72
p-CN	1.86	–	–	0.0562	0.162	2.45	4.14	−1.43
m-CN	1.35	–	–	0.0251	0.0776	1.26	4.29	−1.47
ρ_X[d]		−4.63	−4.04	−3.80	−3.48	−2.97	ρ_{XZ}[f] = 2.00	
β_X[e]		0.89	0.73	0.71	0.65	0.54		

[a]The p*K*a values of pyridines water at 25.0 °C were taken from: 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 0.993 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 0.993 in all cases. [e]Correlation coefficients are better than 0.997 in all cases. [f]Correlation coefficient is better than 0.991.

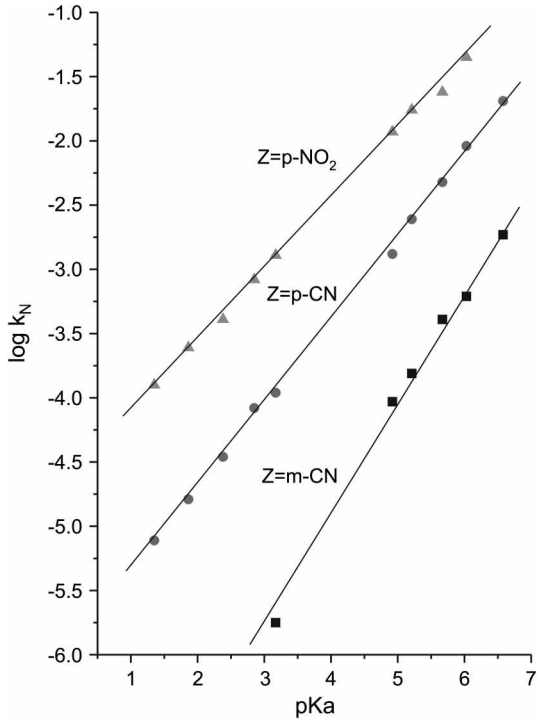


Figure 1. Bronsted plots (β_X) for the pyridinolysis of Z-aryl cyclopropanecarboxylates with X-pyridines in MeCN at 55.0 °C

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 coefficients, $\rho_X(=\rho_{nuc})$ and $\rho_{\bar{Z}}(=\rho_{lg}^{-})$ (Figures 2 and 3), and the cross-interaction constant, ρ_{XZ}, is also presented.

The activation parameters, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ (Table 2), were determined based on the k_N values at three temperatures, 35.

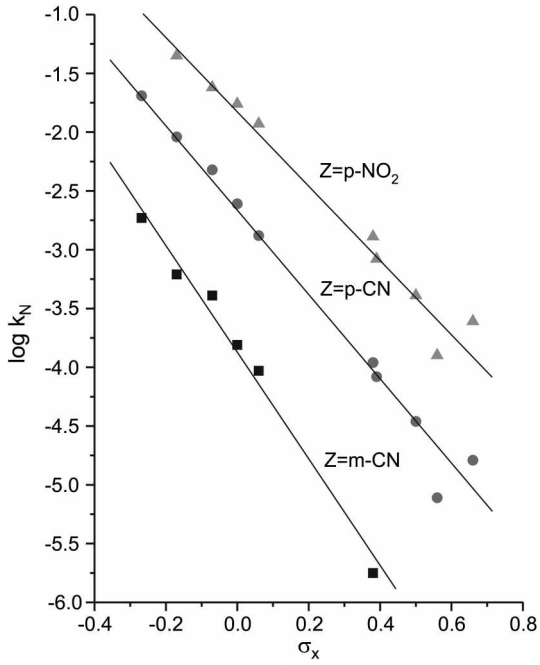


Figure 2. Hammett plots (ρ_X) for the pyridinolysis of Z-aryl cyclopropanecarboxylates with X-pyridines in MeCN at 55.0 °C.

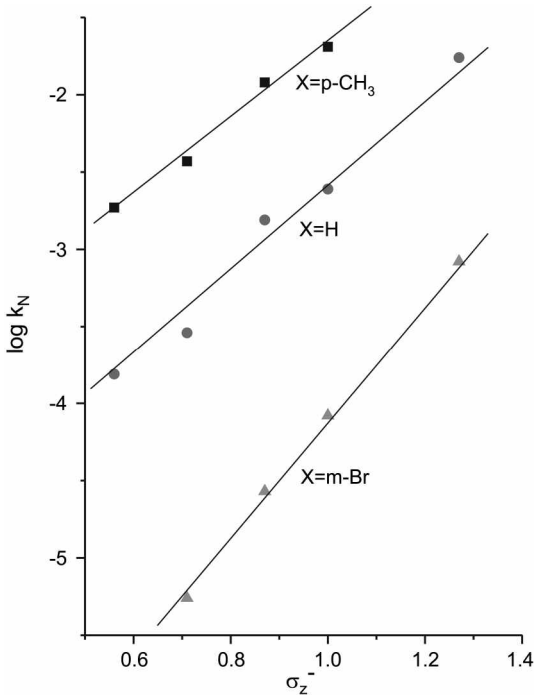


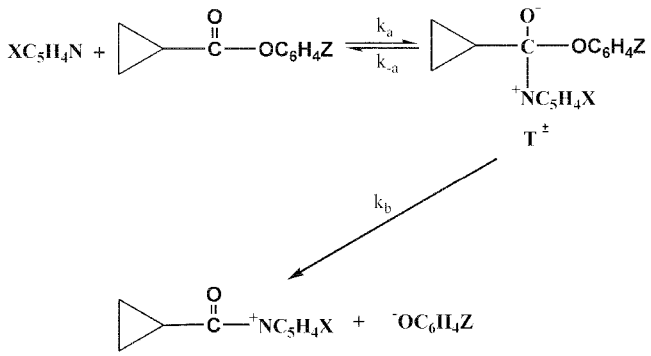
Figure 3. Bronsted plots ($\rho_{\bar{Z}}$) for the pyridinolysis of Z-aryl cyclopropanecarboxylates with X-pyridines in MeCN at 55.0 °C

45, and 55.0 °C. These are comparable to those corresponding values for the reactions of aryl cyclopropanecarboxylates with benzylamines in acetonitrile.[5]

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 ~2-9 times slower than those for benzylamines[5] under the same reaction conditions. 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 –2.97 to –4.63 (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 $\beta_X(\beta_{nuc})$ is also reflected in the similarly large magnitude of $\beta_X(\beta_{nuc})$ = 0.54-0.89 (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),[9e] and 1.33-2.09 (aryl cylopropanecarboxylates + benzylamines),[5] 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, σ_Z ($\sigma_{\bar{Z}}$). The importance of the leaving group departure in the rate-determining step is reflected in the better Hammett correlations with $\sigma_{\bar{Z}}$ than with σ_Z and large magnitude of $\rho_{\bar{Z}}$ (= 2.67-4.29) suggesting a strong negative charge development in the aryl oxide



Scheme 1

leaving group with a relatively large extent of bond cleavage in the TS (β_Z = −1.25-1.84). Also these large ρ_Z^- (β_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] For rate-limiting formation of the tetrahedral intermediate, β_Z values of between 0 and −0.5 were obtained for the aminolysis of the aryl esters and carbonates and ethyl S-aryl dithiocarbonates.[1,3] On the other hand, for the concerted aminolysis reactions of O-ethyl S-aryl thiocarbonates, the β_Z values of −0.2 is reported in water.[17a]

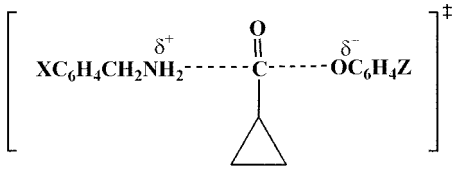
The rate constants (k_N = k_{NZ}) in Table 1 are subjected to multiple regression analysis using eq. 2. We note that the correlation is satisfactory with the cross-interaction constant, ρ_{XZ}, of +2.00. This values is also similar to that for the reactions of aryl cyclopropanecarboxylates with benzylamines (ρ_{XZ} = +1.06),[5] 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_N2 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.[5,9] The cross-interaction constant ρ_{XZ} obtained was positive and large at +2.00. This provides further strong support for the proposed mechanism comes from a large positive cross-interaction constant ρ_{XZ}.[5,6,9,17] 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 positive, eq. 2b.[5,6,9,17]

Also, the size of ρ_{XZ} is considered to represent the intensity of interaction in the TS[10] between the two substituents in the nucleophile (*X*) and the leaving group (*Z*), and hence the larger the ρ_{XZ}, the stronger is the interaction, *i.e.*, the closer are the two fragments, the nucleophile and leaving group, in the TS.

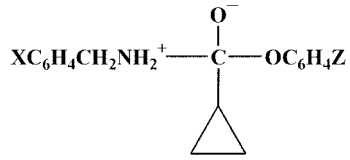
We also note in Table 1 that the rate increase is invariably accompanied by a decrease in the selectivities, ρ(ρ_X or ρ_Z^-), and hence the reactivity-selectivity principle (RSP) holds.[14e,18] This adherence to the RSP is considered another necessary condition for a stepwise acyl transfer reaction with rate-limiting expulsion of the leaving group (aryl oxides).[14e,18]

We have recently studied the kinetic isotope effects (k_H/k_D) in acetonitrile for the reactions of Z-aryl cyclopropanecarboxylates with X-benzylamies deuterated on the nitrogen ($XC_6H_4CH_2ND_2$).[5] 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 tetrahedral intermediate



TS 1

(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 = 1.21-1.38,[5] 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, 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

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

X	Z	Temp (°C)	k_N ($\times10^4$ $M^{-1}s^{-1}$)	$\Delta H^{\neq}$ (kcal · mol^{-1})	$-\Delta S^{\neq}$ (cal · $mol^{-1}K^{-1}$)
p-CH_3	*m*-CN	35	2.27	4.77	55
		45	2.95		
		55	3.89		
p-CH_3	*p*-NO_2	35	211	5.23	45
		45	282		
		55	379		
m-Br	*m*-CN	35	0.00429	5.09	67
		45	0.00571		
		55	0.00759		
m-Br	*p*-NO_2	35	1.48	5.84	53
		45	2.04		
		55	2.82		

[a]Calculated by the Eyring equation. Maximum errors calculated (by the method of Wiberg, K. B. Physical Organic Chemistry; Wiley: New York, 1964; p. 378) are ±0.7 kcal · mol^{-1} and ±2 cal·$mol^{-1}K^{-1}$ for $\Delta H^{\neq}$ and $\Delta S^{\neq}$, respectively.

Activation parameters for the reactions of aryl cyclopropanecarboxylates with pyridines are shown in Table 2. The values of H, and S were obtained from the slope and intercept, respectively, of Eyring plots, by least-squares analysis. Although the relatively low positive H and large negative S values are in line with the stepwise mechanism,[4c,9g,19] they can also be interpreted as supportive of a concerted mechanism.

Castro *et al.*[20] 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.[16,20] (Scheme 1). Thus a concerted mechanism is enforced.[16,20] However, for the reaction systems investigated in this work, the cyclopropane group has a relatively low resonance donor effect (σ_R = −0.15 *vs.* −0.44 for C_2H_5O group)[21] so that the T intermediate seems to be stable enough to lead to the proposed stepwise mechanism.

In summary, the reactions of aryl cyclopropanecarboxylates 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 σx and σz, (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 were purchased from Aldrich. The substituted phenols (Aldrich) were purified either by distillation or recrystallization. Reacting phenols with cyclopropanecarbonyl chloride prepared aryl cyclopropanecarboxylates. The substrates synthesized were confirmed by spectral analyses as follows.

***p*-Cyanoaryl cyclopropanecarboxylate**: Mp 41-42 °C, δ_H (400 MHz, $CDCl_3$), 7.68 (2H, d, m-H, J = 8.79), 7.24 (2H, d, o-H, J = 8.80), 1.82-1.89 (1H, m, CH), 1.05-1.21 (4H, m, $2CH_2$); ν_{max} (KBr)/cm 2900 (CH, aromatic), 2300 (CN), 1720 (C=O); m/z = 187 (M^-) (Calc. for $C_{11}H_9NO_2$: C, 65.8; H, 4.80. Found: C, 65.7; H, 4.81%).

***m*-Cyanoaryl cyclopropanecarboxylate**: Mp. 41-42 °C δ_H (400 MHz, $CDCl_3$), 7.69 (1H, d, p-H, J = 8.70), 7.60 (1H, t, o-H, J = 2.20), 7.29 (1H, t, m-H, J = 8.06), 7.20 (1H, d, o-H, J = 5.86), 1.82-1.89 (1H, m, CH), 1.05-1.21 (4H, m, $2CH_2$); ν_{max} (KBr)/cm 2900 (CH, aromatic), 2300 (CN), 1720 (C=O); m/z = 187 (M^-) (Calc. for $C_{11}H_9NO_2$: C, 65.8; H, 4.80. Found: C, 65.7; H, 4.79%).

***p*-Nitroaryl cyclopropanecarboxylate**: Mp 102-103 °C, δ_H (400 MHz, $CDCl_3$), 7.68 (2H, d, m-H, J 8.79), 7.24 (2H, d, o-H, J = 8.80), 1.83-1.89 (1H, m, CH), 1.04-1.22 (4H, m, $2CH_2$); ν_{max} (KBr)/cm 2900 (CH, aromatic), 1720 (C=O); m/z = 207 (M^+) (Calc. for $C_{10}H_9NO_4$: C, 58.0; H, 4.35. Found: C, 57.1; H, 4.36%).

***m*-Nitroaryl cyclopropanecarboxylate**: Mp 52-53 °C, δ_H (400 MHz, $CDCl_3$), 8.10 (1H, d, p-H, J = 8.06), 8.01 (1H, o-H, J = 2.20), 7.55 (1H, t, m-H, J = 8.06), 7.46 (1H, d, o-H, J = 5.86), 1.83-1.89 (1H, m, CH), 1.04-1.22 (4H, m, $2CH_2$); ν_{max} (KBr)/cm 2900 (CH, aromatic), 1720(C=O); m/z = 207 (M^-) (Calc. for $C_{10}H_9NO_4$: C, 58.0; H, 4.35. Found: C, 57.1; H, 4.36%).

***p*-Acetylaryl cyclopropanecarboxylate**: Mp 91-92 °C, δ_H (400 MHz, $CDCl_3$), 7.98 (2H, d, m-H, J = 8.06), 7.20 (2H, d, o-H, J = 8.79), 2.60 (3H, s, CH_3), 1.83-1.88 (1H, m, CH), 1.03-1.21 (4H, m, $2CH_2$); ν_{max} (KBr)/cm 2900 (CH, aromatic), 1720 (C=O); m/z = 204 (M^+) (Calc. for $C_{12}H_{12}O_3$: C, 70.6; H, 5.88. Found: C, 70.7; H, 5.86%).

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 cyclopropanecarboxylate] $\simeq 1 \times 10^{-3}$ 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. 4, and Figure 4. The k_N values in Table 1 are the averages of more than three runs and were reproducible to within 3%.

Product Analysis. *p*-Nitroaryl cyclopropanecarboxylate was refluxed with excess *p*-methylpyridine for more than 15

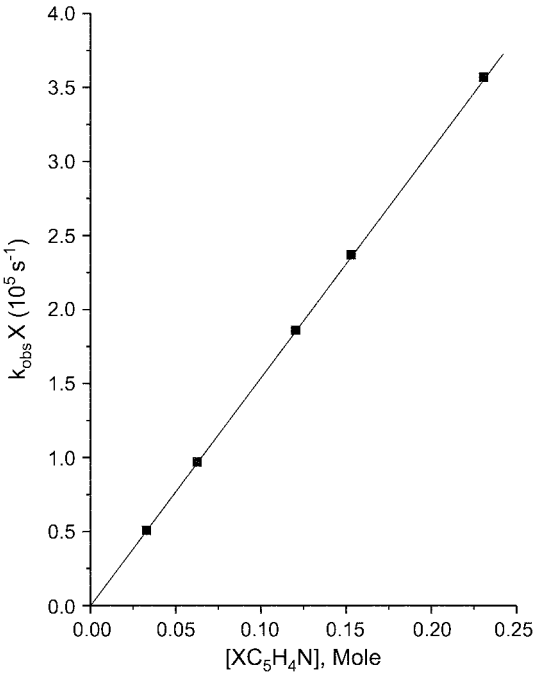


Figure 4. Plots of pseudo-first order rate constants (k_{obs}) *vs.* nucleophile concentration, [XC_5H_4N], for reaction of m-cyanoaryl cyclopropanecarboxylate with X-pyridine (X=H) in acetonitrile at 55.0 °C.

half-lives at 55.0 in acetonitrile. Acetonitrile was evaporated under reduced pressure, and the product mixture was treated with ether and water for workup; during workup, dilute hydrochloric acid was treated to remove excess *p*-methylpyridine and after workup dried over anhydrous $MgSO_4$. The product was isolated by evaporating the solvent under reduced pressure after filtration. The physical constants after column chromatography (silica gel/ethyl acetate + *n*-hexane) were as follows.

Cyclopropyl-C(=O)N$^+$C$_5$H$_4$-*p*-CH$_3$: Mp 138-140 °C, δ_H (400 MHz, $CDCl_3$), 7.13-7.18 (4H, m, aromatic), 2.33 (3H, s, CH_3), 1.65-1.69 (1H, m, CH), 0.73-1.32 (4H, m, $2CH_2$); ν_{max} (KBr)/cm 2900(CH, aromatic), 1720 (C=O); m/z = 162 (M^+). (Calc. for $C_{10}H_{12}NO$; C, 74.1; H, 7.41. Found: C, 74.0; H, 7.42%).

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