Kinetics and Mechanism of Pyridinolysis of Aryl Dithiocyclopentanecarboxylates in Acetonitrile

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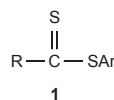
Kinetic studies on the pyridinolysis of aryl dithiocyclopentanecarboxyaltes **2** were carried out at 60.0 $^{\circ}$C in acetonitrile. In the aminolysis of **2**, the β_X values were 0.5 - 0.8 with anilines, and there was no breakpoint. However, in the pyridinolysis of **2**, biphasic Brönsted plots were obtained, with a change in slope from a large value ($\beta_X \cong 0.7$) to a small value ($\beta_X \cong 0.4$) at $pK_a^0 = 5.2$. This was attributed to a change in the rate-limiting step from breakdown to the formation of a zwitterionic tetrahedral intermediate, $T^{\pm}$, in the reaction path, with an increase in the basicity of the pyridine nucleophile. An obvious change in the cross-interaction constant ρ_{XZ} from a large positive ($\rho_{XZ} = +1.02$) value to a small negative value ($\rho_{XZ} = -0.17$) supports the proposed mechanistic change.

Key Words: Nucleophilic substitution reaction, Pyridinolysis, Cross-interaction constant, Zwitterionic tetrahedral intermediate, Stepwise mechanism

Introduction

The transfer of a carbonyl (or thiocarbonyl) group among nucleophiles is one of the most extensively investigated subjects in mechanistic organic chemistry.[1] The rate-determining step and transition state (TS) structure of acyl transfer reactions have been found to depend on the nucleophile, leaving and non-leaving groups, and solvent.[1] In the aminolysis of aryl esters and carbonates, a biphasic dependence of the rate on amine basicity is often observed, with the slope changing from a large value ($\beta_{nuc} \geq 0.8$) to a small value ($\beta_{nuc} \cong 0.1 - 0.3$) at pK_a^0, where the amine and leaving group have the same expulsion rates from a zwitterionic tetrahedral intermediate, $T^{\pm}$. This has been attributed to a change in the rate-limiting step from the breakdown to the formation of $T^{\pm}$ with an increase in the basicity of the amine.

The aminolysis of dithio esters **1** has been reported in water[1c,2] and in acetonitrile[3] with various amines, e.g., benzylamines, anilines, alicyclic secondary amines, pyridines, *etc*. For example, the aminolysis of dithio esters with benzylamines[3c-d] in acetonitrile exhibited rather

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high pK_a^0 values (> 9.0), whereas that with pyridines[3f-g] gave low pK_a^0 values (≤ 5.0). On the other hand, our recent results on the pyridinolysis of aryl dithioacetates[3g] (R = Me in **1**) and aryl furan-2-carbodithioates[3e] (R = C$_4$H$_4$O in **1**) in acetonitrile at 60.0 $^{\circ}$C indicated that the effect of the acyl group (R) on the pK_a^0 value is insignificant with a similar pK_a^0 value of 5.2. This means that in acyl group transfer reactions, the breakpoint pK_a^0 in a biphasic plot of rate *vs.* basicity of amine depends on the nucleophile and leaving group, but seems practically independent of the acyl group. This is quite plausible because

pK_a^0 depends on the pK_a values of the nucleophile (amine) and leaving group, but should be independent of the acyl group.

In this work, we report the results of kinetic studies on the pyridinolysis of aryl dithiocyclopentanecarboxylates **2** in acetonitrile at 60.0 $^{\circ}$C (eq. 1). The aim was to complete the

$$\text{(1)}$$
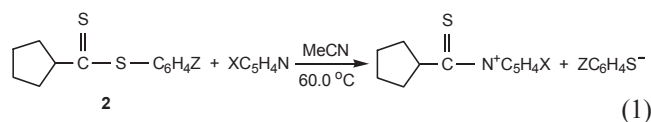
X = 4-MeO, 4-Me, 3-Me, 4-C$_6$H$_4$CH$_2$, H, 3-Ph, 3-MeCO, 3-Cl, and 4-MeCO
Z = 4-Me, H, 4-Cl, and 4-Br

previous studies[4] on the aminolysis of **2** and to further clarify the influence of the amine nature on the pK_a^0 value. We especially wanted to demonstrate that the breakpoint pK_a^0 in biphasic Brönsted plots has a much lower pK_a value than the corresponding point for carbonyl esters. As an additional investigation to elucidate the mechanism, we determined the cross-interaction constant[5] ρ_{XZ} in eqs. 2a and 2b, where X and Z represent the substituents in the nucleophile and leaving group, respectively.

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

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

Results and Discussion

The reactions obeyed the simple kinetic law given by eqs. 3 and 4, where ArS$^-$ is a thiophenoxide ion and Py is pyridine. The plots of k_{obs} *vs.* [Py] were linear, and the second-order rate constants (k_N) were obtained from the slopes of these plots. The k_N values are summarized in Table 1.

$$d[ArS^-]/dt = k_{obs} [\text{Substrate}] \qquad (3)$$

Table 1. Second-order rate constants k_N ($\times 10^3$ M^{-1} s^{-1}) and selectivity parameters[a] ρ_X, ρ_Z, ρ_{XZ}, and β_X, for reaction of Z-phenyl dithio-cyclopentanecarboxylates with X-pyridines in acetonitrile at 60.0 ^{o}C

X	pK_a^f	Z				ρ_Z^h
		4-CH$_3$	H	4-Cl	4-Br	
4-CH$_3$O	6.47	9.49	13.7	22.9	25.5	1.03 ± 0.02
4-CH$_3$	6.00	6.56	9.59	15.9	17.8	1.02 ± 0.02
3-CH$_3$	5.68	4.79	6.92	11.4	12.8	1.01 ± 0.02
4-C$_6$H$_5$CH$_2$	5.59	4.46	6.31	10.5	11.5	0.99 ± 0.02
H	5.17	3.47	4.89	8.13	8.89	0.98 ± 0.02
3-C$_6$H$_5$	4.87	2.32	3.37	5.49	6.02	0.99 ± 0.02
3-CH$_3$CO	3.26	0.118	0.192	0.358	0.407	1.27 ± 0.03
3-Cl	2.84	0.102	0.164	0.330	0.373	1.35 ± 0.03
4-CH$_3$CO	2.38	0.0338	0.0552	0.122	0.141	1.49 ± 0.03
$\rho_X^{b,c}$		−1.58 ± 0.01	−1.61 ± 0.02	−1.63 ± 0.02	−1.66 ± 0.02	$\rho_{XZ}^{b,i}$ = −0.17
$\beta_X^{b,d}$		0.34 ± 0.02	0.35 ± 0.02	0.36 ± 0.02	0.36 ± 0.02	
$\rho_X^{e,f}$		−4.39 ± 0.07	−4.15 ± 0.06	−3.94 ± 0.06	−3.92 ± 0.06	$\rho_{XZ}^{e,j}$ = +1.02
$\beta_X^{e,g}$		0.71 ± 0.10	0.69 ± 0.10	0.65 ± 0.10	0.64 ± 0.10	

[a]The values were taken from Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165. The β_X values were determined using pK_a values in H$_2$O. Justification for this procedure is provided in ref. 6. The pK_a values of pyridine in water at 25°C were taken from ref. 15. The pK_a values of X = 3-C$_6$H$_5$ and X = 4-CH$_3$CO were taken from ref. 16. [b]For X = 4-CH$_3$O, 4-CH$_3$, 3-CH$_3$, 4-C$_6$H$_5$CH$_2$, H. [c]Correlation coefficients are better than 0.998 in all cases. [d]Correlation coefficients are better than 0.995 in all cases. [e]For X = H, 3-C$_6$H$_5$, 3-CH$_3$CO, 3-Cl, 4-CH$_3$CO. [f]Correlation coefficients are better than 0.995 in all cases. [g]Correlation coefficients are better than 0.995 in all cases. [h]Correlation coefficients are better than 0.996 in all cases. [i]Correlation coefficient is 0.997. [j]Correlation coefficient is 0.993.

Figure 1. Brönsted plots for reactions of Z-aryl dithiocyclopentane-carboxylates with X-pyridines in acetonitrile at 60.0 ^{o}C.

$$k_{obs} = k_N [\text{Py}] \tag{4}$$

The rates of pyridine nucleophiles ($k_N = 4.89 \times 10^{-3}$ M^{-1}s^{-1} at 60.0 ^{o}C with Z = H) are slower than those of aniline ($k_N = 4.35 \times 10^{-3}$ M^{-1}s^{-1} at 10.0 ^{o}C with Z = H).[4] The Brönsted plots that use the k_N and pK_a values given in Table 1 are presented in Figure 1. The slopes are listed in Table 1, which also contains Hammett coefficients ρ_X ($= \rho_{nuc}$) and ρ_Z ($= \rho_{lg}$) and cross-interaction constant ρ_{XZ}. Although the β_X values are based on the plots of log k_N(MeCN) *vs.* pK_a(H$_2$O), they can provide reasonable insights because a near constant ΔpK_a ($= pK_a$(MeCN) − pK_a(H$_2$O) $\cong$ 7.5) was found experimentally,[6] as well as theoretically,[7] and the slopes remain practically the same irrespective of whether pK_a(H$_2$O) or pK_a(MeCN) is used in the Brönsted correlation. It should be noted that the Brönsted plots in Figure 1 are biphasic,

with a change in the slope. For Z = H, the slope changes from $\beta_X = 0.69$ to $\beta_X = 0.35$ at breakpoint ($pK_a^0 = 5.2$) with an increase in the basicity of pyridine. The magnitude of β_X is somewhat smaller than those normally obtained ($\beta_X \geq 0.8$),[8] but it is well within the range ($\beta_X \geq 0.7$ - 0.8 in water[9] and $\beta_X \geq 0.6$ - 0.7 in acetonitrile[10]) of the corresponding values for stepwise reactions with rate-limiting expulsions of the leaving group. For example, in the aminolysis of ethyl S-aryl thiolcarbonates with secondary alicyclic amines in water, the slopes were $\beta x = 0.7$ - 0.8,[9] whereas in the pyridinolysis of S-phenyl 4-nitrobenzoates in acetonitrile, the slopes were $\beta x = 0.6$ - 0.7,[10] both of which were consistent with those stepwise mechanisms where the breakdown of a zwitterionic tetrahedral intermediate T$^\pm$ determines the rate. The value of 0.35 obtained for the more basic pyridines, as listed in Table 1, is also consistent with those obtained for stepwise mechanisms in which the formation of T$^\pm$ limits the rate.[11] In the pyridinolysis of aryl dithioacetates CH$_3$C(=S)SC$_6$H$_4$Z, a biphasic plot with a slope change from $\beta x \cong 0.9$ to a small value of $\beta x \cong 0.4$ was observed with a breakpoint at $pK_a^0 = 5.2$.[3g]

$$\tag{5}$$

In this mechanism for pyridines with a high pK_a value, $k_{-a} \ll k_b$; therefore, the k_a step is the rate-determining step, i.e., $k_N = k_a$, with a smaller Brönsted slope β_X ($= 0.34 \sim 0.36$). On the other hand, at low pK_a values, where $k_{-a} \gg k_b$ and $k_N = (k_a/k_{-a}) k_b = Kk_b$, the k_b step should be rate-limiting, with a steeper Brönsted slope, β_X ($= 0.64 \sim 0.71$). At the center of the Brön-

Table 2. Second-order rate constants k_N Based on various temperatures and activation parameters[a] for reactions of Z-phenyl dithiocyclopentanecarboxylates with X-pyridines in acetonitrile.

X	Z	t (°C)	k_N ($\times 10^3$ M^{-1} s^{-1})	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$-\Delta S^{\ddagger}$ (cal mol^{-1} K^{-1})
4-CH$_3$O	4-CH$_3$	60.0	9.49		
		50.0	7.11	5.5	51
		40.0	5.26		
4-CH$_3$O	4-Br	60.0	25.5		
		50.0	18.8	5.5	49
		40.0	14.1		
3-Cl	4-CH$_3$	60.0	0.102		
		50.0	0.0734	5.7	59
		40.0	0.0535		
3-Cl	4-Br	60.0	0.373		
		50.0	0.272	5.7	56
		40.0	0.195		

[a]Calculated using the Eyring equation. The maximum errors calculated (by the method of K. B. Wiberg[17]) are ±0.6 kcal mol^{-1} and ±2 e.u. for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, respectively.

sted curvature, $k_{-a} = k_b$, a pyridine with pK_a = pK_a^{0} (= 5.2) has the same leaving ability from tetrahedral intermediate T$^{\pm}$ as the leaving group ArS^{-}.

In the reactions of **2**, the β_X values were 0.5 - 0.8 with anilines (at 10.0 °C)[4] and no breakpoints were observed. This means that p$K_a^{0} \geq 5.4$ (the highest pK_a used; 4-methoxyaniline) for the reactions with anilines. The decreasing pK_a^{0} value is related to a decrease in the k_{-a}/k_b ratio, with the value for aniline (≥ 5.4) greater than that for pyridine (= 5.2). This decreasing value is also consistent with the general sequence for the amine expulsion (k_{-a}) rates from the tetrahedral intermediate: primary amines > secondary alicyclic amines > anilines > pyridines.[12] In the aminolysis of **2**, the breakpoint pK_a^{0} (= 5.2), can be experimentally observed only in the reactions with pyridines because the pK_a^{0} value is higher than the basicities of the amines used in the reactions with anilines. This is why biphasic plots with a clear-cut breakpoint pK_a^{0} are often observed in the aminolysis with pyridine nucleophiles, as in the pyridinolysis of aryl dithioacetates[13] and aryl dithiocyclopentanecarboxylates in this work, both of which had pK_a^{0} values of 5.2. The other reasons for the relatively low pK_a^{0} value (= 5.2) for the pyridinolysis of two compounds of the dithio series: (i) Using the thiono (S^{-}) series rather than the carbonyl (O^{-}) series leads to a lower pK_a^{0} caused by a decrease in the k_{-a}/k_b ratio. This is because, in T$^{\pm}$, the lower proclivity of S^{-} to form a double bond and expel a leaving group, compared to O^{-}, leads to an amine expulsion from T$^{\pm}$ that is slower (smaller k_{-a}) than ArS^{-} leaving (k_b).[1] (ii) The thiophenoxide leaving groups (ZC$_6$H$_4$S^{-}) that are used have lower basicities than the phenoxide leaving groups (ZC$_6$H$_4$O^{-}) for the same Z. Hence, k_b should be greater (with a decrease in k_{-a}/k_b), leading to a lower pK_a^{0} than the corresponding esters with a phenoxide leaving group.

The size of ρ_Z in Table 1 also reflects the mechanistic change. The magnitudes of ρ_Z change from large values (ρ_Z = 1.5) for the less basic pyridines to smaller values ($\rho_Z \cong 1.0$) for the more basic pyridines; this is in agreement with the decrease in bond

cleavage because the rate-determining step switches from the breakdown to the formation of the intermediate. Such a decrease in the magnitude of the ρ_Z values from large (ρ_Z = 2.4 - 3.2) to small values ($\rho_Z \cong 2.3$) with the mechanistic change has also been reported in the pyridinolysis of aryl dithioacetates.[13] Rough estimates of the β_Z (=β_{lg}) values indicate a decrease from $\beta_Z \cong -0.5$ to $\beta_Z \cong -0.3$ at the breakpoint, which agrees with the change in the rate-determining step.

A clear-cut change in the cross-interaction constant is another important result supporting the mechanistic change at pK_a^{0} = 5.2 from the breakdown to the formation of T$^{\pm}$ as the basicity of pyridine is increased. The cross-interaction constant changes from a relatively large *positive* value (ρ_{XZ} = +1.02) to a small *negative* value (ρ_{XZ} = −0.17) at the breakpoint. Similar changes in ρ_{XZ} values have been reported for the pyridinolysis of S-phenyl 4-nitrobenzoates[10] (4-NO$_2$C$_6$H$_4$C(=O)SC$_6$H$_4$Z) and aryl dithioacetates[13] (CH$_3$C(=S)SC$_6$H$_4$Z). In the former, the ρ_{XZ} value changed from +1.41 to −0.32 at p$K_a^{0} \cong 4.2$, and in the latter, it changed from +1.34 to −0.15 at pK_a^{0} = 5.2, as the basicity of pyridine was increased. These are interpreted to indicate mechanistic changes from the breakdown to the formation of T$^{\pm}$. These changes in the ρ_{XZ} values with changes in the reaction mechanism give further credence to the use of the cross-interaction constant as a useful mechanistic criterion.

Table 2 lists the activation parameters $\Delta H^{\ddagger}$ and $-\Delta S^{\ddagger}$ for the pyridinolysis of **2**. The values of $\Delta H^{\ddagger}$ and $-\Delta S^{\ddagger}$ are smaller for a more basic pyridine (X = 4-OCH$_3$) than for a less basic pyridine (X = 3-Cl). Although the differences are small, they are significant enough to be over the error limits. These trends are in accordance with the breakdown step (for X = 3-Cl) requiring higher energy and lower (more negative) entropy in the TS due to bond cleavage to two ionic products (eq. 2).

In summary, kinetic studies on the pyridinolysis of aryl dithiocyclopentanecarboxylates **2** were carried out at 60.0 °C in acetonitrile. In the aminolysis of **2**, the β_X values were 0.5 - 0.8 with anilines, and there was no breakpoint. However, in the pyridinolysis of **2**, biphasic Brönsted plots were obtained, with a slope change from a large value ($\beta_X \cong 0.7$) to a small value ($\beta_X \cong 0.4$) at pK_a^{0} = 5.2. This slope change was attributed to a change in the rate-limiting step from the breakdown to the formation of a zwitterionic tetrahedral intermediate T$^{\pm}$ in the reaction path with an increase in the basicity of the pyridine nucleophile. A clear-cut change in the cross-interaction constant ρ_{XZ} from a large positive value (ρ_{XZ} = +1.02) to a small negative value (ρ_{XZ} = −0.17) supports the proposed mechanistic change. Other selectivity parameters (ρ_X and ρ_Z) and activation parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) are also consistent with the proposed mechanism, as is the adherence to the reactivity selectivity principle (RSP).

Experimental Section

Materials. Acetonitrile (Merk, GR grade) was used after three distillations. The pyridine nucleophiles (Aldrich, GR grade) were used without further purification. The preparation and analytical data are reported elsewhere.[12]

Kinetic measurement. The rates were measured conductometrically in acetonitrile. The conductivity bridge used in this

work was a homemade computer-automated A/D converter conductivity bridge. Pseudo first-order rate constants k_{obs} were determined by the Guggenheim method[14] with a large excess of pyridine (Py). Second-order rate constants k_2 were obtained from the slope of a plot of k_{obs} *vs.* [Py] with more than five concentrations of pyridine. The k_2 values in Table 1 are the averages of more than three runs, and were reproducible to within ±3%.

Product analysis. The substrate, *p*-bromophenyl dithiocyclopentanecarboxylate (0.05 mole), was reacted with excess 4-picoline (0.5 mole) with stirring for more than 15 half-lives at 60.0 °C in acetonitrile. The salt was filtered, and the solvent was removed from the precipitate. An analysis of the product gave the following results.

c-C$_5$H$_9$C(=S)N$^+$C$_5$H$_4$-*p*-CH$_3$$^-SC_6H_4$-4-Br: mp 65 - 67 °C, ^{1}H NMR (400 MHz, CDCl$_3$), 1.38 (8H, m, CH$_2$), 1.48 (3H, s, CH$_3$), 2.37 (1H, m, CH), 7.26-7.30 (2H, dd, pyridine), 7.32-7.36 (9H, m, phenyl), 7.36-7.39 (2H, d, pyridine); ^{13}C NMR (100.4 MHz, CDCl$_3$), 230.1(C=S), 135.8, 135.3, 132.3, 132.1, 132.0, 129.8, 129.5, 52.7, 30.5, 27.2, 25.1 (CH$_3$); ν$_{max}$ (KBr), 1567, 1456 (C=C, phenyl), 1230 (C=S), 857 (C-H, pyridine), 802 (C-H, phenyl); mass, *m/z* 394 (M$^+$). Anal. Calcd for C$_{18}$H$_{20}$Br-NS$_2$; C, 54.8; H, 5.11. Found C, 54.6; H. 5.13.

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