

Nucleophilic Substitution Reactions of Aryl Dithiocyclohexanecarboxylates with Anilines in Acetonitrile

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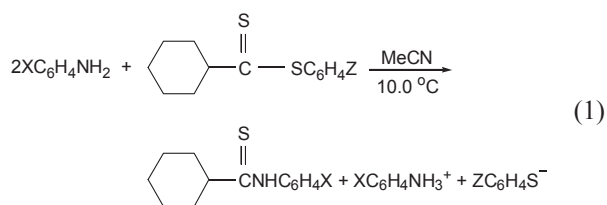
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The mechanisms of the aminolysis of aryl esters and carbonates have been well established.¹ These reactions are known to proceed stepwise through a zwitterionic tetrahedral intermediate, T^\pm . The existence of the intermediate has been deduced from curved Brønsted-type plots. A biphasic dependence of the rate on the amine basicity showing a change of slope from a large ($\beta_{\text{nuc}} \geq 0.8$) to a small ($\beta_{\text{nuc}} \approx 0.1 - 0.3$) value at $\text{p}K_{\text{a}}^0$, where the amine and leaving group have the same expulsion rates from T^\pm , has been attributed to a change in the rate-limiting step from breakdown to formation of a tetrahedral intermediate as the basicity of the amine increases.²⁻⁵

The aminolysis of dithio esters and carbonates has been studied in aqueous and acetonitrile solutions.⁶ An important advantage of using an acetonitrile medium is that there are no complications arising from a kinetically important proton transfer from T^\pm to the amine.⁷ In water, the rate of proton transfer, k_{H} , may be faster than that of expulsion of arenethiolate from T^\pm so that the rate law becomes complex.⁷ This kinetic complexity encountered in the aminolysis of dithiocarboxylates (and also thiono) compounds in water is known to originate from the weak π bond energy of CS (compared to CO) which causes the difficulty in reforming the CS double bond when T^\pm break down expelling either the amine or ArS^- .⁷

In this work, we investigated the kinetics and mechanism of the aminolysis of phenyl dithiocyclohexanecarboxylates with anilines in acetonitrile at 10.0 °C, eq. 1. The objective of the



present work is to elucidate the mechanism by determining β_{X} (β_{nuc}), β_{Z} (β_{lg}) and cross-interaction constant ρ_{XZ} , eq. 2⁸ where X and Z denote substituents in the nucleophile and nucleofuge, respectively.

$$\log(k_{\text{XZ}}/k_{\text{HH}}) = \rho_{\text{X}}\sigma_{\text{X}} + \rho_{\text{Z}}\sigma_{\text{Z}} + \rho_{\text{XZ}}\sigma_{\text{X}}\sigma_{\text{Z}} \quad (2a)$$

$$\rho_{\text{XZ}} = \partial\rho_{\text{Z}}/\partial\sigma_{\text{X}} = \partial\rho_{\text{X}}/\partial\sigma_{\text{Z}} \quad (2b)$$

It has been shown that the ρ_{XZ} is large positive and a higher reactivity is invariably accompanied by a smaller magnitude of selectivity parameters, such as ρ and β , i.e., the reactivity-selectivity principle (RSP)⁹ holds, for the acyl transfer reactions with rate-limiting breakdown of an intermediate, $T^{\pm 10}$.

Results and Discussion

The aminolysis of phenyl dithiocyclohexanecarboxylates with a large excess of anilines in acetonitrile followed the simple kinetic rate law given by eqs. (3) and (4), where P is thiophenolate anion and N represent aniline. The k_{N} values were determined from the slope

$$d[\text{P}]/dt = k_{\text{obs}} [\text{substrate}] \quad (3)$$

$$k_{\text{obs}} = k_{\text{N}} [\text{N}] \quad (4)$$

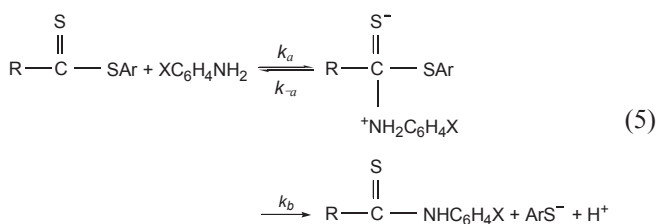
of the linear plot of k_{obs} against $[\text{N}]$. The k_{N} values are summarized in Table 1, where selectivity parameters, i.e., the Hammett (ρ_{X} and ρ_{Z}) and Brønsted (β_{X} and β_{Z}), coefficients, are also shown. The reactions obeyed clean second-order kinetics, eqs. (3) and (4), indicating that there are no complications arising from competition of the fast proton transfer from an intermediate, T^\pm , nor from general base catalysis by the aniline.

Since the reaction were conducted in acetonitrile, reliability of the magnitude β_{X} (β_{nuc}) and β_{Z} (β_{lg}) determined using the $\text{p}K_{\text{a}}$ values in water may be doubted. In this respect, we have recently shown that the β_{X} values determined by correlating the rate constants in acetonitrile with $\text{p}K_{\text{a}}(\text{H}_2\text{O})$ are reliable in spite of the different solvent.¹¹ Theoretical work¹² of the solvent effects on the basicities of pyridines has shown that although the absolute values of $\text{p}K_{\text{a}}(\text{CH}_3\text{CN})$ differ from $\text{p}K_{\text{a}}(\text{H}_2\text{O})$ a constant $\Delta\text{p}K_{\text{a}} [= \text{p}K_{\text{a}}(\text{CH}_3\text{CN}) - \text{p}K_{\text{a}}(\text{H}_2\text{O})] \cong 7.7$ was obtained. The theoretical $\Delta\text{p}K_{\text{a}} = 7.7$ at the MP2/6-31G^{*}/MP2/6-31G^{*} level of theory is in excellent agreement with the experimental $\Delta\text{p}K_{\text{a}} = 7.7 \pm 0.3$.¹³ The $\Delta\text{p}K_{\text{a}} (\cong 7.7)$ value was found to arise solely from the ion solvation energy difference of H^+ ion in water and in acetonitrile, $\delta\Delta G_{\text{s}}^0(\text{H}^+) = 10.5 \text{ kcal mol}^{-1}$, which corresponds to $\Delta\text{p}K_{\text{a}} = 7.7$.¹² Moreover, we are comparing the magnitude of β_{X} and β_{Z} values determined for the reactions carried out under the same reaction condition, i.e. in acetonitrile. The β_{X} values (0.96 ~ 1.21) obtained in this work are larger than those for

Table 1. The second order rate constants, $k_N \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for the reactions of Z-aryl dithiocyclohexanecarboxylates with X-anilines in acetonitrile at 10.0 °C

X	Z				ρ_Z^a	β_Z^b
	<i>p</i> -Me	H	<i>p</i> -Cl	<i>p</i> -Br		
<i>p</i> -OMe	26.1 ± 0.55 ^c	44.8 ± 0.80	161 ± 4.5	289 ± 8.5	2.54 ± 0.13	−1.03 ± 0.08
	17.5 ± 0.14			200 ± 5.5		
	12.1 ± 0.25 ^d			140 ± 3.5		
<i>p</i> -Me	7.45 ± 0.09	21.2 ± 0.4	81.0 ± 1.7	102 ± 2.5	2.73 ± 0.13	−1.11 ± 0.10
H	1.97 ± 0.03	6.26 ± 0.05	28.0 ± 0.6	37.3 ± 1.0	3.05 ± 0.16	−1.23 ± 0.12
<i>p</i> -Cl	0.384 ± 0.009	1.34 ± 0.02	6.96 ± 0.07	9.77 ± 0.10	3.35 ± 0.19	−1.34 ± 0.13
<i>p</i> -Br	0.369 ± 0.004	0.891 ± 0.007	4.79 ± 0.04	10.3 ± 0.10	3.34 ± 0.20	−1.37 ± 0.12
	0.251 ± 0.003			6.92 ± 0.08		
	0.173 ± 0.002			4.77 ± 0.04		
ρ_X^e	−3.50 ± 0.15	−3.24 ± 0.17	−2.89 ± 0.14	−2.77 ± 0.13	$\rho_{XZ}^f = 1.68 \pm 0.14$	
β_X^g	1.21 ± 0.03	1.12 ± 0.02	1.00 ± 0.02	0.96 ± 0.02		

^aThe σ values were taken from ref. 18a. Correlation coefficients were better than 0.996 in all cases. ^bThe pK_a values were taken from ref. 18b. Z = *p*-Br was excluded from the Brønsted plot for β_Z due to an unreliable pK_a values. Correlation coefficients were better than 0.995 in all cases. ^cAt 20 °C. ^dAt 0.0 °C. ^eThe source of σ is the same as for footnote a. Correlation coefficients were better than 0.997 in all cases. ^fCorrelation coefficients was 0.997. ^gThe pK_a values were taken from ref. 18c. Correlation coefficients were better than 0.999 in all cases.



the corresponding reactions with other secondary and tertiary amines ($\beta_X = 0.6 \sim 1.0$) proceeding by rate-limiting breakdown of a zwitterionic tetrahedral intermediate, T^\pm , eq 5. On this account, i.e. large β_X values obtained, the aminolysis of phenyl dithiocyclohexanecarboxylate with anilines in acetonitrile is most likely to occur by the rate-limiting expulsion of thiophenolate ion, ArS^- , from T^\pm , eq. (5), where the proton is consumed by the excess aniline present in the solution in a subsequent rapid step to form anilinium ion. The rate constant, k_N in eq. (3), is therefore a complex quantity represented by eq. (6). The magnitude of β_Z (β_{lg}) values ($\beta_Z = -1.03 \sim -1.37$) is also comparable to similar reaction with rate-limiting expulsion of ArS^- in acetonitrile ($\beta_Z = -1.2 \sim -1.6$).

$$k_N = \frac{k_a}{k_{-a}} \cdot k_b = K \cdot k_b \quad (6)$$

The proposed mechanism is also supported by a large positive cross-interaction constant ($\rho_{XZ} = 1.68$) and adherence to the reactivity-selectivity principle (RSP), which are considered to constitute necessary conditions for the rate-limiting breakdown of T^\pm .^{14,15}

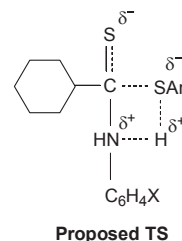
The kinetic isotope effects (Table 2) involving deuterated nucleophile, $\text{XC}_6\text{H}_4\text{ND}_2$, are normal ($k_H/k_D > 1.0$) suggesting a possibility of forming hydrogen-bonded four-center type TS¹⁵ as has often been proposed. Since no base catalysis was found (the rate law is first order with respect to [N], eq.3), the proton transfer occurs concurrently with the rate-limiting expulsion

Table 2. Kinetic isotope effects for the reactions of Z-aryl dithiocyclohexanecarboxylates with deuterated X-anilines in acetonitrile at 10.0 °C

X	Z	$k_H \times 10^3$ ($\text{M}^{-1} \text{s}^{-1}$)	$k_D \times 10^3$ ($\text{M}^{-1} \text{s}^{-1}$)	k_H/k_D
<i>p</i> -OMe	<i>p</i> -Me	$17.5 (\pm 0.14)$	$10.0 (\pm 0.08)$	1.75 ± 0.04^a
<i>p</i> -OMe	H	$44.8 (\pm 0.80)$	$27.6 (\pm 0.35)$	1.62 ± 0.02
<i>p</i> -OMe	<i>p</i> -Cl	$161 (\pm 4.50)$	$108 (\pm 2.60)$	1.48 ± 0.03
<i>p</i> -OMe	<i>p</i> -Br	$200 (\pm 5.55)$	$151 (\pm 4.50)$	1.32 ± 0.03
<i>p</i> -Cl	<i>p</i> -Me	$0.384 (\pm 0.009)$	$0.224 (\pm 0.004)$	1.71 ± 0.02
<i>p</i> -Cl	H	$1.34 (\pm 0.02)$	$0.848 (\pm 0.01)$	1.58 ± 0.02
<i>p</i> -Cl	<i>p</i> -Cl	$6.96 (\pm 0.07)$	$4.93 (\pm 0.06)$	1.41 ± 0.04
<i>p</i> -Cl	<i>p</i> -Br	$9.77 (\pm 0.10)$	$7.51 (\pm 0.07)$	1.30 ± 0.03

^aStandard deviations.

of RS^- in the TS but not catalyzed by aniline. The consumption of proton by the excess aniline should therefore take place in a subsequent rapid step.



The low activation enthalpies, ΔH^\ddagger , and highly negative activation entropies, ΔS^\ddagger , (Table 3) are also in line with the proposed TS. Especially, the ΔH^\ddagger values are somewhat lower and the ΔS^\ddagger values are higher negative values than other aminolysis systems.¹⁴ The expulsion of RS^- anion in the rate determining step (an endoergic process) is assisted by the hydrogen-bonding with

Table 3. Activation parameters^a for the reactions of Z-aryl dithiocyclohexanecarboxylates with X-anilines in acetonitrile

X	Z	$\Delta H^\ddagger/\text{kcal mol}^{-1}$	$-\Delta S^\ddagger/\text{cal mol}^{-1} \text{K}^{-1}$
<i>p</i> -OMe	<i>p</i> -Me	5.5	47
<i>p</i> -OMe	<i>p</i> -Br	5.3	43
<i>p</i> -Br	<i>p</i> -Me	5.5	55
<i>p</i> -Br	<i>p</i> -Br	5.4	49

^aCalculated by the Eyring equation. The maximum errors calculated (by the method of Wiberg, K. B.¹⁹) are $\pm 0.5 \text{ kcal mol}^{-1}$ and $\pm 2 \text{ e.u.}$ for ΔH^\ddagger and ΔS^\ddagger , respectively.

an amino hydrogen of the benzylammonium ion within the intermediate, T^\ddagger . This will lower the ΔH^\ddagger value, but the TS becomes structured and rigid (low entropy process) which should lead to a large negative ΔS^\ddagger value.

In summary the aminolysis of phenyl dithiocyclohexanecarboxylates with anilines in acetonitrile proceeds by rate-limiting breakdown of a tetrahedral intermediate, T^\ddagger . The large β_X (β_{nuc}) values can be accounted for by a strong localized cationic charge on the nitrogen atom of anilines in T^\ddagger , which is lost in the aniline expulsion from T^\ddagger (k_{-a}). The breakdown rate ratio of k_{-a}/k_b is large due to large k_{-a} and relatively small k_b . The proposed mechanism is also supported by a large positive cross-interaction constant, ρ_{XZ} ($= 1.68$), adherence to the RSP, and low activation parameters. The greater than unity k_H/k_D values involving deuterated anilines suggests a four-center type hydrogen-bonded TS.

Experimental Section

Materials. Merck GR acetonitrile was used after three distillations. The aniline nucleophiles, Aldrich GR, were used without further purification. Thiophenols, cyclohexanecarbonyl chloride and Lawesson's reagent were Tokyo Kasei GR grade.

Preparations of thiophenyl cyclohexanecarboxylates. Preparation and analytical data are reported elsewhere.¹⁶

Preparations of phenyl dithiocyclohexanecarboxylates. The thiophenyl cyclohexanecarboxylates prepared as above were dissolved in dry toluene and refluxed with Lawesson's reagent (Aldrich G. R. grade). After extraction of the reaction mixture with dichloromethane, dried and removed solvent by distillation under reduced pressure. Separation by column chromatography gave the products, for which the following analytical data were obtained.

***p*-Tolyl dithiocyclohexanecarboxylate:** Liquid, IR (KBr), 2954 (C-H, aromatic), 2925 (C-H, CH_3), 1705 (C=S), 1512, 1501 (C=C, aromatic); ^1H NMR (400 MHz, CDCl_3), 1.35 ~ 1.83 (10H, m, CH_2), 2.04 (1H, m, CH), 2.42 (3H, s, CH_3), 7.20 (2H, d, $J = 8.78$, meta H), 7.32 (2H, d, $J = 8.78$, ortho H); ^{13}C NMR (100.4 MHz, CDCl_3), 228.2 (C=S), 139.2, 134.4, 129.8, 124.3, 52.3, 29.4, 25.5, 25.4, 21.2. Mass, m/z 250 (M^+). Anal. Calcd. for $\text{C}_{14}\text{H}_{18}\text{OS}_2$: C, 67.1; H, 7.25. Found: C, 67.3; H, 7.23.

Phenyl dithiocyclohexanecarboxylate: Liquid, IR (KBr), 2951 (C-H, aromatic), 1704 (C=S), 1497, 1488 (C=C, aromatic); ^1H NMR (400 MHz, CDCl_3), 1.32 ~ 1.84 (10H, m, CH_2), 2.04 (1H, m, CH), 7.35 ~ 7.41 (5H, m, aromatic ring); ^{13}C NMR

(100.4 MHz, CDCl_3), 227.5 (C=S), 134.4, 130.2, 128.9, 127.8, 52.4, 29.4, 25.5, 25.4. Mass, m/z 236 (M^+). Anal. Calcd. for $\text{C}_{13}\text{H}_{16}\text{S}_2$: C, 66.1; H, 6.82. Found: C, 66.3; H, 6.35.

***p*-Chlorophenyl dithiocyclohexanecarboxylate:** Liquid, IR (KBr), 2956 (C-H, aromatic), 1710 (C=S), 1505, 1494 (C=C, aromatic); ^1H NMR (400 MHz, CDCl_3), 1.34 ~ 1.87 (10H, m, CH_2), 2.03 (1H, m, CH), 7.34 (2H, d, $J = 8.78$ MHz, meta H), 7.39 (2H, d, $J = 8.78$ MHz, ortho H); ^{13}C NMR (100.4 MHz, CDCl_3), 226.1 (C=S), 135.7, 135.4, 129.2, 126.4, 52.4, 39.4, 25.5, 25.3. Mass, m/z 270 (M^+). Anal. Calcd. for $\text{C}_{13}\text{H}_{15}\text{ClS}_2$: C, 57.6; H, 5.58. Found: C, 57.4; H, 5.56.

***p*-Bromophenyl dithiocyclohexanecarboxylate:** mp 49 ~ 51 °C; IR (KBr), 2954 (C-H, aromatic), 1705 (C=S), 1501, 1493 (C=C, aromatic); ^1H NMR (400 MHz, CDCl_3), 1.34 ~ 1.85 (10H, m, CH_2), 2.02 (1H, m, CH), 7.26 (2H, d, $J = 8.78$ MHz, meta H), 7.55 (2H, d, $J = 8.78$ MHz); ^{13}C NMR (100.4 MHz, CDCl_3), 225.3 (C=S), 135.8, 132.6, 126.9, 123.5, 52.3, 29.3, 25.4, 25.2. Mass, m/z 315 (M^+). Anal. Calcd. for $\text{C}_{13}\text{H}_{15}\text{BrS}_2$: C, 49.5; H, 4.80. Found: C, 49.7; H, 4.82.

Kinetic measurement. Rates were measured conductometrically at 10.0 ± 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 Guggenheim method¹⁷ with large excess of aniline. Second-order rate constants, k_N , were obtained from the slope of a plot of k_{obs} vs. aniline with more than five concentrations of more than three runs and were reproducible to within $\pm 3\%$.

Product analysis. Substrate, phenyl dithiocyclohexanecarboxylate (0.05 mole) was reacted with excess aniline (0.5 mole) with stirring for more than 15 half-lives at 10.0 °C in acetonitrile, and the products were isolated by evaporating the solvent under reduced pressure. The product mixture was treated with column chromatography (silica gel, 20% ethylacetate-*n*-hexane). Analysis of the product gave the following results.

Cyclohexyl-C(=S)NHC₆H₄-OCH₃: mp 68 ~ 70 °C; IR (KBr), 3292 (N-H), 2941 (C-H, CH_3), 1705 (C=S), 1597 (C=C, aromatic); ^1H NMR (400 MHz, CDCl_3), 1.01 ~ 1.38 (10H, m, CH_2), 2.11 (1H, m, CH), 4.18 (3H, s, CH_3), 7.36 (2H, d, $J = 8.78$ MHz, meta H), 7.45 (2H, d, $J = 8.78$ MHz, ortho H); ^{13}C NMR (100.4 MHz, CDCl_3), 201.2 (C=S), 135.7, 132.1, 129.3, 121.5, 57.3, 49.5, 32.7, 25.2, 22.6. Mass, m/z 249 (M^+). Anal. Calcd. for $\text{C}_{14}\text{H}_{19}\text{NOS}$: C, 67.4; H, 7.68. Found: C, 67.6; H, 7.66.

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