

Kinetics and Mechanism of the Aminolysis of Aryl *N*-Isopropyl Thiocarbamates in Acetonitrile

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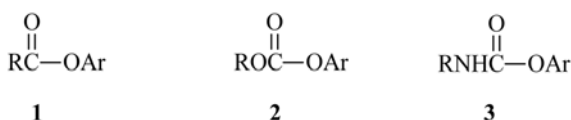
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Aryl esters, **1**, carbonates, **2**, and carbamates, **3**, are three classes of compounds which differ only in the acyl part, R, RO and RNH where R is alkyl or aryl. The aminolysis



mechanism of the carbonates is quite similar to that of esters, **1**, and carbonates, **2**, especially to the latter. For example, the aminolysis of aryl O-ethylcarbonates¹ (**2a**; R=Et) and aryl *N*-phenylcarbamates² (**3a**; R=C₆H₄Y) were found to proceed via two reaction pathway, uncatalyzed and catalyzed, through a zwitterionic tetrahedral intermediate, T[±]. For the two (**2a** and **3a**) aminolysis reactions with benzylamines, the β_X values are large (β_X > 1.0) and the signs of ρ_{XY} (+1.10 for **3a**) and ρ_{XZ} (+0.16 for **2a**) are positive with adherence to the selectivity-reactivity principle (RSP).³

The stepwise aminolysis mechanism of **2a** through a tetrahedral intermediate, however, shifts to a concerted process where the leaving group is changed to a thiophenoxide (**2b**; EtOC(=O)-SAr) instead of a phenoxide (⁻OAr). The push provided by an EtO group to expel ⁻SAr in T[±] is now strong enough to make the intermediate so unstable that the intermediate can not exist. In view of the similar strong push expected from a (CH₃)₂CNH group to expel the ⁻SAr group in T[±], it is of interest to see whether the aminolysis mechanism of the thiol analog of aryl *N*-isopropyl thiocarbamates, (CH₃)₂CHNHC(=O)SC₆H₄Z (**3b**), also shifts to a concerted mechanism or not.

In order to pursue further the mechanistic similarities between carbamates and carbonates, we carried out kinetic studies on the aminolysis of aryl *N*-isopropyl thiocarbamates ((CH₃)₂CHNHC(=O)SC₆H₄Z) with benzylamines in acetonitrile, Eq. (1). The primary purpose of this work is to establish the aminolysis mechanism for Eq. (1) and to ex-

amine the effect of the nonleaving group, (CH₃)₂CHNH-, on the mechanism. We varied substituents in the nucleophile (X) and leaving group (Z) and the rate constants, *k*₂, are subjected to a multiple regression analysis to determine the cross-interaction constant,⁵ ρ_{XZ} in Eq. (2). For a concerted mechanism the sign of ρ_{XZ} was found to be negative⁵ and the reactivity-selectivity principle (RSP) failed.⁶

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

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

Results and Discussion

The reactions of aryl *N*-isopropyl thiocarbamates (AITC: (CH₃)₂CHNHC(=O)SC₆H₄Z) with X-benzylamines (BA) in acetonitrile follow a clear second-order kinetics, Eqs. (3). Unlike in the aminolysis of aryl *N*-phenylcarbamates² (APC: PhNHC(=O)OC₆H₄Z) we found no base

$$\text{rate} = k_{\text{obs}} [\text{AITC}] \quad (3a)$$

$$k_{\text{obs}} = k_2 [\text{BA}] \quad (3b)$$

catalysis by the amine. The rate constants, *k*₂, determined are summarized in Table 1 together with selectivity parameters ρ_X, β_X, ρ_Z, and β_Z. The β_X (β_{nuc}) values are obtained by using the p*K*_a values of benzylamines in water. This procedure was found to be reliable since the p*K*_a values in acetonitrile and in water vary in parallel, although the absolute values are different.⁷ For the β_Z (β_{lg}) values, a factor of 0.62 was multiplied to all the β_Z values determined using the p*K*_a (H₂O) values.⁸

Since strong destabilization of T[±] should be provided by a stronger push to expel the leaving group by the amino nonleaving group, R=NH₂ in **3b**, the aminolysis of AITC (**3b** with R=(CH₃)₂CH-) with benzylamines in acetonitrile is proposed to proceed concertedly. The β_Z values in Table 1 are within the range of values that are expected for a concerted mechanism.⁹ Further supports for the concerted mechanism is provided by a negative ρ_{XZ} (-1.96) obtained, and failure of the reactivity-selectivity principle (RSP).¹⁰ The selectivities (ρ and β values in Table 1) are greater for the faster reactions. This type of *anti*-RSP is considered another criterion for the concerted aminolysis.⁶

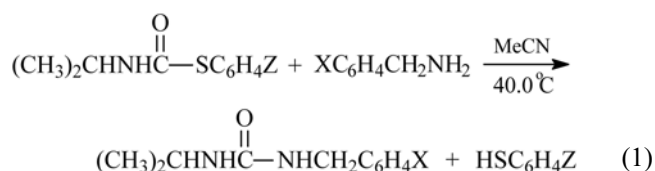


Table 1. The Second Order Rate Constants, k_2 ($10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) for the Reactions of Z-Aryl *N*-Isopropyl Thiocarbamates with X-Benzylamines in Acetonitrile at 40.0 °C

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	1.23	5.06	35.5	45.7	3.80 ± 0.15	-1.58 ± 0.08
<i>p</i> -Me	0.781	2.92	19.5	23.0	3.61 ± 0.10	-1.51 ± 0.06
H	0.411	1.32	7.05	8.42	3.21 ± 0.11	-1.34 ± 0.06
<i>p</i> -Cl	0.176	0.467	2.06	2.54	2.82 ± 0.14	-1.18 ± 0.05
<i>m</i> -Cl	0.0994	0.266	0.975	1.10	2.55 ± 0.06	-1.06 ± 0.06
ρ_X^a	-1.68 ± 0.03	-1.99 ± 0.05	-2.3 ± 0.04	-2.49 ± 0.06	$\rho_{XZ}^c =$	-1.96 ± 0.20
β_X^d	1.65 ± 0.03	1.95 ± 0.03	2.38 ± 0.05	2.43 ± 0.05		

^aThe σ values were taken from C. Hansch, A. Leo and R. W. Taft, *Chem. Rev.* **1991**, 91, 166. Correlation coefficients were better than 0.997 in all cases.

^bThe pK_a values were taken from A. Albert and E. P. Serjeant, "The Determination of Ionization Constants" 3rd Ed., Chapman and Hall, London, p 145. Correlation coefficients were better than 0.997 in all cases. ^cCalculated by a multiple regression analysis using eq (2a). $r = 0.999$, $n = 20$ and $F_{\text{calc}} = 1410$ ($F_{\text{tab}} = 10.66$ at the 99.9% confidence level). ^dThe pK_a values were taken from A. Fischer, W. J. Galloway and J. Vaughan, *J. Chem. Soc.* **1964**, 3588. Correlation coefficients were better than 0.997 in all cases. For X = *p*-CH₃O an extrapolated value of $pK_a = 9.64$ was used.

Reference to Table 1 reveals that the β_X values are 1.65–2.43 which are rather greater than the values normally expected for the concerted aminolysis processes, $\beta_X = 0.4 \sim 0.7$ ¹⁰ However, β_X values smaller than 0.4¹¹ as well as those larger than 0.7¹² have also been observed for the concerted reactions. Especially in solvents less polar than water, larger β_X (1.3–1.6)¹³ are often obtained for the concerted processes. Thus the large β_X values in the present work may be due to the less polar solvent used, acetonitrile. The relatively large β_X values may reflect rather tight bond formation in the TS.

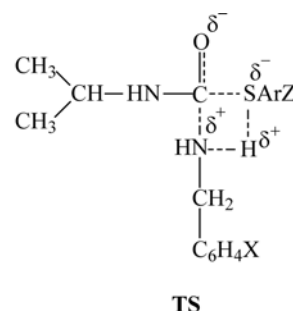
Strong destabilization incurred by powerful nucleofugality of benzylamines from T^\pm is known to cause the aminolysis to proceed by a concerted mechanism.¹⁴ The order of the increasing rate of expulsion of amines from T^\pm is reported as⁶ pyridines < anilines < secondary alicyclic amines < quinuclidines < benzylamines. Moreover, it has been shown that carbonyl (C=O) has a greater proclivity for the concerted mechanism than thiocarbonyl (C=S) group¹⁵ due to a narrower energy gap between π^* and σ^* levels, $\Delta\epsilon = \epsilon(\pi_{\text{C=O}}^*) - \epsilon(\sigma_{\text{C-S}}^*) < \Delta\epsilon = \epsilon(\pi_{\text{C=S}}^*) - \epsilon(\sigma_{\text{C-S}}^*)$, enabling efficient mixing of the two antibonding orbitals.¹⁵ Thus, concerted mechanisms are found for the aminolyses of *S*-(2,4-dinitrophenyl)¹⁵ and *S*-(2,4,6-trinitrophenyl)¹⁷ *O*-ethyl thiocarbonates in contrast to the stepwise mechanisms for the corresponding dithiocarbonates.¹⁸ Less polar solvents are also conducive to a concerted mechanism as observed for the aminolysis of carbonates from stepwise in water to concerted in acetonitrile.¹⁹ For example, the aminolysis of 2,4,6-trinitrophenyl *O*-ethyl dithiocarbonates is stepwise²⁰ (biphasic Brönsted plot) in water, but is concerted ($\beta_X = 0.53$) in a less polar solvent (44 wt % aqueous EtOH).²¹ The change of solvent from water to a less polar solvent such as MeCN destabilizes the zwitterionic intermediate by enhancing the rate of expulsion of the amine from T^\pm , and renders the intermediate, T^\pm , more unstable kinetically so that a concerted mechanism is enforced.²¹

The kinetic isotope effects (k_H/k_D) involving deuterated benzylamines²² (XC₆H₄CH₂ND₂) are presented in Table 2. We note that the isotope effects are normal with $k_H/k_D > 1.0$ suggesting there is a hydrogen bond formed by the amino

Table 2. The Kinetic Isotope Effects for the Reactions of Z-Phenyl *N*-Isopropyl Thiocarbamates with X-Benzylamines in Acetonitrile at 40.0 °C

X	Z	$k_H (\times 10^2 \text{ M}^{-1} \text{ s}^{-1})$	$k_D (\times 10^2 \text{ M}^{-1} \text{ s}^{-1})$	k_H/k_D
<i>p</i> -OMe	<i>p</i> -Me	$1.23(\pm 0.02)$	$0.911(\pm 0.01)$	1.35 ± 0.02^a
<i>p</i> -OMe	H	$5.06(\pm 0.06)$	$3.58(\pm 0.05)$	1.41 ± 0.02
<i>p</i> -OMe	<i>p</i> -Cl	$35.0(\pm 0.7)$	$23.8(\pm 0.4)$	1.47 ± 0.03
<i>p</i> -OMe	<i>p</i> -Br	$45.7(\pm 0.9)$	$29.5(\pm 0.6)$	1.55 ± 0.03
<i>p</i> -Cl	<i>p</i> -Me	$0.176(\pm 0.002)$	$0.127(\pm 0.001)$	1.38 ± 0.03
<i>p</i> -Cl	H	$0.467(\pm 0.003)$	$0.319(\pm 0.003)$	1.46 ± 0.02
<i>p</i> -Cl	<i>p</i> -Cl	$2.06(\pm 0.04)$	$1.34(\pm 0.02)$	1.53 ± 0.02
<i>p</i> -Cl	<i>p</i> -Br	$2.54(\pm 0.05)$	$1.57(\pm 0.03)$	1.61 ± 0.03

^aStandard deviations.



proton (N-H or N-D) in the TS, most probably with the negatively charged S atom in the leaving group. Since the large β_X and β_Z values suggest that the TS is a late type with a large degree of bond formation and bond cleavage the hydrogen bonding seems to be rather strong with relatively large values of $k_H/k_D > 1.0$. This is supported by a larger k_H/k_D value for a stronger nucleophilie ($\delta\sigma_X < 0$) and a stronger nucleofuge ($\delta\sigma_Z > 0$) which will lead to a later TS in accordance with the negative ρ_{XZ} ; a stronger nucleophile, $\delta\sigma_X < 0$, gave a larger ρ_Z value $\delta\rho_Z > 0$ so that $\rho_{XZ} = \delta\rho_Z/\delta\sigma_X < 0$, while a stronger nucleofuge, $\delta\sigma_Z > 0$, gave a larger negative ρ_X value $\delta\sigma_Z > 0$ so that $\rho_{XZ} = \delta\rho_Z/\delta\sigma_X < 0$, while a stronger nucleofuge ($\delta\sigma_Z > 0$) gave a larger negative ρ_X ($\delta\rho_X > 0$) leading to $\rho_{XZ} < 0$.

In summary, we propose a concerted mechanism with a

hydrogen bonded cyclic transition state for the aminolysis of aryl *N*-isopropyl thiocarbamates with benzylamines in acetonitrile based on the negative cross-interaction constant, failure of RSP and the kinetic isotope effects greater than unity. The four conducive factors for the concerted aminolysis mechanism for the present reaction series are: (i) strong (strongest) push provided to expel ArS^- by the nonleaving group, $(\text{CH}_3)_2\text{CHNH}$, (ii) destabilization of the intermediate, T^\pm , by a powerful expulsion rate of the benzylamine from T^\pm , (iii) greater leaving ability of ^-SAr than ^-OAr due to the greater electron acceptor ability of $\sigma_{\text{C-S}}^*$ than $\sigma_{\text{C-O}}^*$ bond orbital, and (iv) instability of the intermediate, T^\pm , in a less polar solvent, MeCN than in water due to the ionic nature of T^\pm .

Experimental Section

Experimental.

Materials: GR grade acetonitrile was used after three distillations. GR grade benzylamine nucleophiles were used after recrystallization.

Substrates.

Phenyl *N*-Isopropyl Thiocarbamate: A solution of thiophenol (0.01 mol) in dry toluene (10 mL) was added to a solution of isopropyl isocyanate (0.01 mol). A catalytic quantity (0.5 mL) of pyridine was added and the solution refluxed for 1 h. On evaporation of the solvent *in vacuo*, the thiocarbamate precipitated and was recrystallized from chloroform-pentane. The other substituted phenyl *N*-isopropyl thiocarbamates were prepared in an analogous manner and recrystallized from chloroform-pentane. The substrates synthesized were confirmed by spectral and elemental analysis as follows.

$(\text{CH}_3)_2\text{CHNHC(=O)SC}_6\text{H}_4\text{-}p\text{-CH}_3$: mp 98-100 °C; ^1H NMR (400 MHz, CDCl_3), δ 1.15 (6H, d, $-(\text{CH}_3)_2$), 1.80 (1H, d, $-\text{CH}-$), 2.41 (3H, d, CH_3), 6.42 (1H, s, NH), 7.19-7.47 (4H, m, C_6H_4); ^{13}C NMR (100.4 MHz, CDCl_3), δ 165.2, 139.5, 135.1, 129.9, 125.0, 43.7, 22.4, 21.2; ν_{max} (KBr), 3301 (NH), 2972 (CH, aliphatic), 2923 (CH, aromatic), 1648 (C=O), 620 (C-S); MS m/z 209 (M^+). Anal. Calcd for $\text{C}_{11}\text{H}_{15}\text{NOS}$: C, 63.1; H, 7.20. Found; C, 63.3; H, 7.21.

$(\text{CH}_3)_2\text{CHNHC(=O)SC}_6\text{H}_5$: mp 102-104 °C; ^1H NMR (400 MHz, CDCl_3), δ 1.21 (6H, d, $-(\text{CH}_3)_2$), 1.66 (1H, d, $-\text{CH}-$), 6.32 (1H, s, NH), 7.37-7.57 (5H, m, C_6H_5); ^{13}C NMR (100.4 MHz, CDCl_3), δ 164.6, 135.1, 129.1, 129.0, 128.5, 43.8, 22.4; ν_{max} (KBr), 3265 (NH), 2970 (CH, aliphatic), 2920 (CH, aromatic), 1662 (C=O), 629 (C-S); MS m/z 195 (M^+). Anal. Calcd for $\text{C}_{10}\text{H}_{13}\text{NOS}$: C, 61.5; H, 6.71. Found; C, 61.3; H, 6.70.

$(\text{CH}_3)_2\text{CHNHC(=O)SC}_6\text{H}_4\text{-}p\text{-Cl}$: mp 150-152 °C; ^1H NMR (400 MHz, CDCl_3), δ 1.27 (6H, d, $-(\text{CH}_3)_2$), 1.62 (1H, d, $-\text{CH}-$), 6.38 (1H, s, NH), 7.34-7.49 (4H, m, C_6H_4); ^{13}C NMR (100.4 MHz, CDCl_3), δ 163.8, 136.3, 135.5, 129.2, 126.9, 44.1, 22.5; ν_{max} (KBr), 3300 (NH), 2974 (CH, aliphatic), 2924 (CH, aromatic), 1649 (C=O), 630 (C-S); MS m/z 229 (M^+). Anal. Calcd for $\text{C}_{10}\text{H}_{12}\text{ClNOS}$: C, 52.3; H, 5.31. Found; C, 52.5; H, 5.32.

$(\text{CH}_3)_2\text{NC(=O)SC}_6\text{H}_4\text{-}p\text{-Br}$: mp 152-154 °C; ^1H NMR (400 MHz, CDCl_3), δ 1.32 (6H, d, $-(\text{CH}_3)_2$), 1.61 (1H, d, $-\text{CH}-$), 6.36 (1H, s, NH), 7.37-7.55 (4H, m, C_6H_4); ^{13}C NMR (100.4 MHz, CDCl_3), δ 163.7, 136.5, 132.1, 127.6, 123.7, 44.1, 22.6; ν_{max} (KBr), 3302 (NH), 2972 (CH, aliphatic), 2916 (CH, aromatic), 1649 (C=O), 625 (C-S); MS m/z 274 (M^+). Anal. Calcd for $\text{C}_{10}\text{H}_{12}\text{BrNOS}$: C, 43.8; H, 4.41. Found; C, 43.9; H, 4.43.

Kinetic Measurement. Rates were measured conductometrically in acetonitrile. The conductivity bridge used in this work was a homemade computer-automatic A/D converter conductivity bridge. Pseudo-first-order rate constants, k_{obsd} , were determined by the Guggenheim method²³ with large excess of pyridine. Second order rate constants, k_2 , were obtained from the slope of a plot of k_{obsd} vs. [BA] with more than five concentrations of benzylamine. The k_2 values in Table 1 are the averages of more than three runs and were reproducible to within $\pm 3\%$.

Product Analysis. The substrate *p*-chlorophenyl *N*-isopropyl thiocarbamate (0.01 mole) was reacted with excess benzylamine (0.1 mole) with stirring for more than 15 half-lives at 40.0 °C in acetonitrile (*ca.* 200 mL) and the products were isolated by evaporating the solvent under reduced pressure. The product mixture was subjected to column chromatography (silica gel, 20% ethyl acetate-*n*-hexane). Analysis of the product gave the following results.

$(\text{CH}_3)_2\text{CHNHC(=O)NHCH}_2\text{C}_6\text{H}_4$: mp 128-130 °C; ^1H NMR (400 MHz, CDCl_3), δ 1.24 (6H, d, $-(\text{CH}_3)_2$), 3.86 (1H, m, $-\text{CH}-$), 4.27 (2H, d, CH_2), 6.32 (1H, s, NH), 7.10-7.37 (5H, m, C_6H_5); ^{13}C NMR (100.4 MHz, CDCl_3), δ 157.9, 139.4, 128.3, 127.2, 126.9, 44.2, 41.9, 23.4; ν_{max} (KBr), 3332 (NH), 2965 (CH, aliphatic), 2922 (CH, aromatic), 1620 (C=O); MS m/z 192 (M^+). Anal. Calcd for $\text{C}_{11}\text{H}_{16}\text{N}_2\text{O}$: C, 68.7; H, 8.41. Found; C, 68.9; H, 8.42.

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