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Nucleophilic Substitution Reactions of *O*-Aryl *N*-phenyl Thioncarbamates with Benzylamines in Acetonitrile

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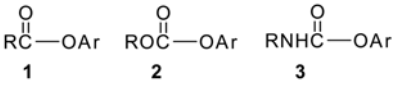
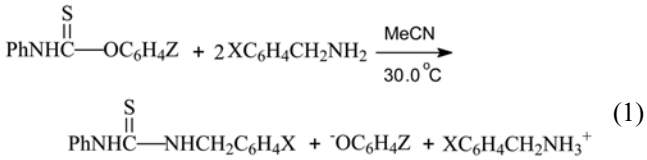
Although there is abundant literature on the kinetics and mechanism of the aminolysis of aryl carbonates[1] and esters,[2] the aminolysis reactions of aryl carbamates[3] have been less studied in terms of kinetics. The mechanism of the aminolysis of substituted diphenyl carbonates has been studied, and structure-reactivity relationships for those reactions have also been examined in detail by Gresser and Jencks.[1a] Castro and co-workers have reported a number of mechanistic studies on the aminolysis of aryl carbonates[1e-f] and esters.[2f-j] These and other studies showed that most of the aminolysis of aryl carbonates and esters proceed by either a stepwise mechanism through a zwitterionic tetrahedral intermediate, $T^{\pm}$, or a concert mechanism depending on the amine, substrate, and solvent involved.

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 carbamates is expected to be similar to the relatively well known aminolysis mechanism of the esters **1**



and carbonates **2**. Shawali *et al*.[3] proposed a stepwise mechanism with rate-limiting breakdown of a tetrahedral intermediate, $T^{\pm}$, for the reactions of aryl *N*-arylcarbamates, R=Ar in **3**, with *n*-butylamine in dioxane. Aminolysis reactions of thionesters showed extensive mechanistic similarity to the corresponding reactions of oxygen esters, but with differences which lend insight into the role of the carbonyl heteroatom in acyl transfer and thionacyl transfer reaction.[4]

We extend here our series of kinetic studies on the effect of thionacyl group on the mechanism of the aminolysis of carbonyl compounds to the reactions of aryl *N*-phenyl thioncarbamates with benzylamines in acetonitrile, Eq. (1).



(1)

X = *p*-OMe, *p*-Me, H, *p*-Cl, *m*-Cl
Z = *p*-OMe, *p*-Me, H, *p*-Cl

In this work, we invoke the mechanistic criteria based on the sign of cross-interaction constants, ρ_{XZ} (eqs. 2) where X and Z are the substituents in the nucleophile and leaving group, respectively; for a stepwise mechanism the sign of ρ_{XZ} was invariably positive and the reactivity-selectivity principle (RSP) was found to hold.[5]

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

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

Results and Discussion

The reactions of aryl *N*-phenylthioncarbamates [**3b**; $C_6H_5NHC(=S)OC_6H_4Z$] with benzylamines (BnA) follow a clean second-order kinetics, Eq. (3). Unlike in the aminolysis

$$\text{Rate} = k_{obs}\,[\text{Substrate}] \quad (3a)$$

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

of aryl *N*-phenylcarbamate (**3a**),[6] no base catalysis by the amine was noted. The rate constants, k_2, determined are summarized in Table 1 together with the selectivity parameters, ρ_X, β_X, β_Z and ρ_Z. We note in Table 1 that the rates are substantially faster than those for the corresponding aminolysis of thionester [RC(=S)OAr] which are reported to be 1.86 M^{-1} s^{-1} at 25 °C for R = Ph.[4] This rate enhancement by substitution of R=PhNH for R=Ph is no doubt due to a stronger push provided by the PhNH group to expel the leaving group, $^{-}$OAr, as a result of the vicinal charge transfer interaction of the lone-pair electron on the nitrogen atom (η_N) with the σ^* orbital of the C-O bond ($\sigma^*_{C\text{-}O}$), $\eta_N \rightarrow \sigma^*_{C\text{-}O}$ interaction.[7] This is evident by comparing the rates of the aminolysis of **3a** (k_2= 0.655 M^{-1} s^{-1} at 25.0 °C with X=H, Y=H and Z=*p*-NO_2) with aryl *N*-phenyl thioncarbamate (k_2= 5.39 M^{-1} s^{-1} at 30.0 °C with X=H, Y=H and Z=H). The lone-pair electrons on N can also delocalize into the π^* orbital of the thiocarbonyl group by an $\eta_N \rightarrow \pi^*_{C=S}$ interaction. This will facilitate the formation of a tetrahedral structure, which can be a transition state in the concerted reaction, or an

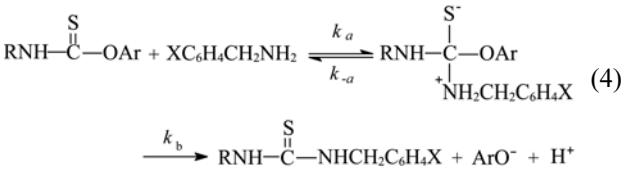
Table 1. The Second Order Rate Constants, k_2 (dm^3 mol^{-1} s^{-1}) for the Reactions of *O*-(Z)Aryl *N*-Phenyl Thioncarbamates with X-Benzylamines in Acetonitrile at 30.0 °C

X	Z				ρ_Z[a]	β_Z[b]
	p-OMe	Me	H	*p*-Cl		
	5.13			24.9		
p-OMe	3.64[c]	7.23	10.9	19.6[c]	1.36 ± 0.03	−0.63 ± 0.01
	2.54[d]			15.2[d]		
p-Me	3.44	5.21	8.18	19.5	1.48 ± 0.03	−0.67 ± 0.01
H	1.95	3.19	5.39	14.3	1.69 ± 0.04	−0.76 ± 0.01
	0.978			8.07		
p-Cl	0.675[c]	1.60	2.95[c]	5.72[c]	1.82 ± 0.02	−0.82 ± 0.03
	0.473[d]			4.00[d]		
m-Cl	0.641	1.01	1.95	5.57	1.86 ± 0.03	−0.83 ± 0.03
ρ_X[a]	−1.39 ± 0.02	−1.29 ± 0.01	−1.15 ± 0.01	−1.00 ± 0.02	ρ_{XZ}[e] =	0.83 ± 0.03
β_X[f]	1.41 ± 0.02	1.31 ± 0.01	1.16 ± 0.01	1.01 ± 0.02		

[a]The s values were taken from C. Hansch, A. Leo and R. W. Taft, *Chem. Rev.* 1991, 91, 166. Correlation coefficients were better than 0.996 in all cases. [b]The 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. [c]At 20 °C. [d]At 10 °C. [e]Calculated by a multiple regression analysis using Eq. (2a). r = 0.998, n = 20 and F_{calc} = 1410 (F_{tab} = 10.66 at the 99.9% confidence level). [f]The pK_a values were taken from A. Fischer, W. J. Galloway and J. Vaughan, *J. Chem. Soc*., 1964, 3588. Correlation coefficients were better than 0.998 in all cases. For X=*p*-CH_3O an extrapolated value of pK_a=9.64 was used.

intermediate in the stepwise reaction. The most striking feature of the aminolysis reaction is that aryl *N*-phenylthioncarbamate (**3b**) is more reactive than aryl *N*-phenylcarbamate (**3a**). This is not unreasonable if different steps of the mechanism are rate determining in the reactions of different nucleophile. In aminolysis the observed rate will depend on both the stability of the intermediate and the ability of $–O^-$ and $–S^-$ to expel the leaving group. The unshared electrons on sulfur can provide a significantly greater driving force for the expulsion of phenoxide than can those on oxygen.[4]

The Hammett (ρ_X and ρ_Z) and Brönsted (β_X and β_Z) coefficient determined are given in Table 1 for the k_2 step. The exceptionally large magnitudes of these selectivity parameters are consistent with stepwise mechanism with rate-limiting breakdown of $T^{\pm}$; both ρ_X and ρ_Z should be compared with other corresponding values after taking into account of a non-conjugating intervening group, CH_2 and NH, present in the benzylamine nucleophile and in the aryl *N*-phenyl thioncarbamate substrate respectively, which are known to reduce the ρ values by a factor of *ca*. 2.8.[8] The large β_X values are also in line with the proposed mechanism, but they are less reliable since the pK_a values used are those in water, not in acetonitrile. However, it is well known that although the absolute pK_a values are different in H_2O and MeCN, the $\Delta pK_a = (pK_a)_{MeCN} - (pK_a)_{H_2O}$ values for the structurally similar amines are nearly the same.[9] Thus the β_X values should be nearly the same in both H_2O and MeCN.[9] The β_X values (1.0-1.4) obtained in this work are considerably larger than those for the corresponding reactions (**1** and **2**) with anilines[10] and other secondary and tertiary amines (β_X = 0.6-1.0) proceeding by rate-limiting breakdown of a zwitterionic tetrahedral intermediate, $T^{\pm}$, Eq. (3b). On this account, *i.e*., large β_X values obtained, the aminolysis of phenyl *N*-phenylthioncarbamates with benzylamines in acetonitrile is most likely to occur by rate-limiting expulsion of phenolate ion, ArO^-, from $T^{\pm}$ (k_b step). The large β_X values observed with benzylamine nucleophile in the present work are considered to represent a very sensitive change in the benzylamine expulsion rate (k_{-a}) with substituent (X) variation due to the loss of a strong localized charge on the nitrogen atom of the benzylammonium ion in the $T^{\pm}$.



(4)

$$k_2 = \frac{k_a}{k_{-a}}k_b = Kk_b \quad (5)$$

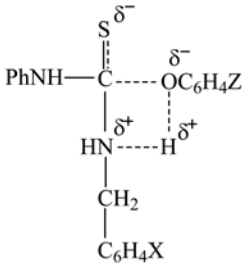
The proposed mechanism is also supported by a large positive cross-interaction constant (ρ_{XZ} = 0.83) and adherence to the reactivity-selectivity principle (RSP), which are considered to constitute necessary conditions for the rate-limiting breakdown of $T^{\pm}$.[11]

Table 2. The Kinetic Isotope Effects for the Reactions of *O*-(Z)Aryl *N*-Phenyl Thioncarbamates with X-Benzylamines in Acetonitrile at 30.0 °C

X	Z	k_H ($M^{-1}s^{-1}$)	k_D ($M^{-1}s^{-1}$)	k_H/k_D
p-OMe	*p*-OMe	5.13(±0.05)	3.37(±0.03)	1.52 ± 0.03[a]
p-OMe	*p*-Me	7.23(±0.06)	4.57(±0.04)	1.58 ± 0.03
p-OMe	H	10.9(±0.09)	6.56(±0.07)	1.66 ± 0.02
P-OMe	*p*-Cl	24.9(±0.52)	14.4(±0.35)	1.72 ± 0.03
p-Cl	*p*-OMe	0.978(±0.002)	0.635(±0.001)	1.54 ± 0.02
p-Cl	*p*-Me	1.60(±0.02)	0.993(±0.01)	1.61 ± 0.03
p-Cl	H	2.95(±0.03)	1.71(±0.03)	1.72 ± 0.03
p-Cl	*p*-Cl	8.07(±0.08)	4.48(±0.05)	1.80 ± 0.04

[a]Standard deviations.

The kinetic isotope effects (k_H/k_D) in Table 2 involving deuterated benzylamine ($XC_6H_4CH_2ND_2$) nucleophiles in acetonitrile are greater than unity (k_H/k_D = 1.5-1.8), indicating that the N-H proton transfer takes place in the rate determining step[12] so that a four-center type TS is involved.[12] In this type of TS, hydrogen bonding of an amine hydrogen atom to the departing phenoxide facilitates the rate-limiting bond cleavage step, forming a rather constrained four membered ring.



Proposed TS

The low activation enthalpies, $\Delta H^{\neq}$, and highly negative activation entropies, $\Delta S^{\neq}$, (Table 3) are also in line with the proposed TS. Especially, the $\Delta H^{\neq}$ values are somewhat lower and the $\Delta S^{\neq}$ values are higher negative values than other aminolysis systems.[11] The expulsion of RO^- anion in the rate determining step (an endoergic process) is assisted by the hydrogen-bonding with an amino hydrogen of the benzylammonium ion within the intermediate, $T^{\pm}$. This will lower the $\Delta H^{\neq}$ value, but the TS becomes structured and rigid (low entropy process) which should lead to a large negative $\Delta S^{\neq}$ value.

In summary the aminolysis of *O*-aryl *N*-phenyl thioncarbamates with benzylamines in acetonitrile proceeds by rate-limiting breakdown of a tetrahedral intermediate, $T^{\pm}$. The unusually large β_X (β_{nuc}) values can be accounted for by a strong localized cationic charge on the nitrogen atom of benzylamines in $T^{\pm}$, which is lost in the benzylamine expulsion from $T^{\pm}$ (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} (= 0.83), adherence to the RSP, and low activation parameters. The greater than unity k_H/k_D values involving deuterated benzylamines suggests a four-center type hydrogen-bonded TS.

Table 3. Activation Parameters[a] for the Reactions of *O*-(Z)Aryl *N*-Phenyl Thioncarbamates with X-Benzylamines in Acetonitrile

X	Z	$\Delta H^{\neq}$/kcal mol^{-1}	$-\Delta S^{\neq}$/cal mol^{-1} K^{-1}
p-OMe	*p*-OMe	5.3	38
p-OMe	*p*-Cl	4.0	40
p-Cl	*p*-OMe	5.6	40
p-Cl	*p*-Cl	4.6	37

[a]Calculated by the Eyring equation. The maximum errors calculated (by the method of K. B. Wiberg, *Physical Organic Chemistry*; Wiley: New York, 1964; p 378) are ± 0.5 kcal mol^{-1} and ± 2 e.u. for $\Delta H^{\neq}$ and $\Delta S^{\neq}$, respectively.

Experimental Section

Materials. Acetonitrile (Merck, GR) was used after three-time distillations. The benzylamine nucleophiles, Aldrich GR, were used after recrystallization.

Substrates.

Phenyl *N*-Phenyl Thioncarbamate: Phenyl *N*-phenyl thioncarbamate was prepared by adding aniline (16 mmol) dissolved in carbon tetrachloride (2.5 mL) to a stirred, cooled solution of phenyl chlorothioformate (1.65 g, 5 mmol) in carbon tetrachloride (25 mL). The mixture was stirred at room temperature for 24 h and filtered. The filtrate was evaporated to dryness, and the residual solid was recrystallized from toluene to provide the desired thioncarbamate. The other substituted phenyl *N*-phenyl thioncarbamates were prepared in an analogous manner and recrystallized from toluene. The substrates synthesized were confirmed by spectral and elemental analysis as follows.

$C_6H_5NHC(=S)OC_6H_5$-*p*-OMe: mp 124-126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.86 (3H, s, CH_3), 6.34 (1H, s, NH), 6.79-7.75 (9H, m, C_6H_4, C_6H_5); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 188.2, 157.5, 146.8, 136.7, 129.0, 125.7, 122.9, 121.8, 114.1, 55.1; ν_{max} (KBr), 3254 (NH), 3052 (CH, aromatic), 1179 (C=S), 1167 (C-O); MS *m*/z 308 (M^+). Anal. Calcd for $C_{14}H_{13}NO_2S$: C, 64.8; H, 5.10. Found; C, 564.6; H, 5.12.

$C_6H_5NHC(=S)OC_6H_5$-*p*-CH_3: mp 164-166 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46 (3H, s, CH_3), 6.31 (1H, s, NH), 6.93-7.80 (9H, m, C_6H_4, C_6H_5); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 188.0, 151.1, 136.1, 129.7, 129.0, 125.7, 123.0, 122.2, 121.8, 21.1; ν_{max} (KBr), 3232 (NH), 3203 (CH), 2925 (CH, aromatic), 1286 (C=S), 1166 (C-O); MS *m*/z 243 (M^+). Anal. Calcd for $C_{14}H_{13}NOS$: C, 69.1; H, 5.41. Found; C, 69.3; H, 5.38.

$C_6H_5NHC(=S)OC_6H_5$: mp 154-156 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.35 (1H, s, NH), 7.18-7.77 (10H, m, C_6H_5, C_6H_5); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 187.8, 153.2, 136.7, 129.2, 126.4, 125.8, 122.8, 122.3, 121.8; ν_{max} (KBr), 3236 (NH), 3049 (CH, aromatic), 1199 (C=S), 1144 (C-O); MS *m*/z 229 (M^+). Anal. Calcd for $C_{13}H_{11}NOS$: C, 68.1; H, 4.81. Found; C, 68.3; H, 4.83.

$C_6H_5NHC(=S)OC_6H_5$-*p*-Cl: mp 176-178 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.31 (1H, s, NH), 7.06-7.74 (9H, m, C_6H_4, C_6H_5); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 187.5, 157.5, 136.5, 129.3, 129.2, 128.9, 124.2, 123.7, 122.0; ν_{max} (KBr), 3235 (NH), 3083 (CH, aromatic), 1205 (C=S), 1158 (C-O); MS *m*/z 263 (M^+). Anal. Calcd for $C_{13}H_{10}ClNOS$: C, 59.2; H, 3.80. Found; C, 59.4; H, 3.82.

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 method[12] with large excess of benzylamine[BnA]; [substrate] = 2.0×10^{-4} M and [BnA] = 5×10^{-2} to 8×10^{-1} M. Second order rate constants, k_2, were obtained from the slope of a plot of k_{obsd} *vs*. [BnA] with more than five concentrations of benzyl-

amine. 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 phenyl *N*-phenyl thioncarbamate (1.0×10^{-3} mole) was reacted with excess benzylamine (1.0×10^{-2} mole) with stirring for more than 15 half-lives at 30.0 °C in 200 mL acetonitrile 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*-hexene). Analysis of the product gave the following results.

$C_6H_5NHC(=S)NHCH_2C_6H_5$: mp 148-150 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.95 (2H, d, CH_2), 7.16-7.44 (10H, m, C_6H_5, C_6H_5); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 180.8, 137.1, 135.7, 130.2, 128.7, 127.7, 127.5, 127.4, 125.3, 49.5; ν_{max} (KBr), 3197 (NH), 3177 (CH), 3091 (CH, aromatic), 1179 (C=S); MS *m*/z 242 (M^+). Anal. Calcd for $C_{14}H_{14}N_2S$: C, 69.4; H, 5.81. Found; C, 69.6; H, 5.82.

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