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Kinetics and Mechanism of the Aminolysis of Phenyl Dithioacetates in Acetonitrile

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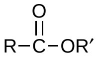
The aminolysis reactions of phenyl dithioacetates with anilines (AN), *N*,*N*-dimethylanilines (DMA), and benzylamines (BA) in acetonitrile are investigated. The mechanism is relatively simple, involving a zwitterionic tetrahedral intermediate, $T^{\pm}$, and is uncomplicated by the fast proton transfer step which may become rate limiting in the aminolysis of thiono and dithio esters and carbonates with poor leaving groups in water. The mechanism changes from rate-limiting expulsion of the leaving group with $\beta_X = 0.80-0.86$ and $\beta_Z = -0.71$ to -0.84 for ANs and DMAs to rate-limiting attack by the nucleophile with much smaller magnitudes of β_X and β_Z for BAs. The relatively large β_{XZ} values for the former series and a smaller β_{XZ} for the latter series support the proposed mechanistic change.

Introduction

The mechanism of aminolysis of oxyesters, **IE**, and oxycarbonates, **IC**, has been extensively studied and is relatively well established.[1,2] In contrast only a few works devoted to the investigation of the mechanism of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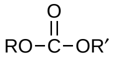
IE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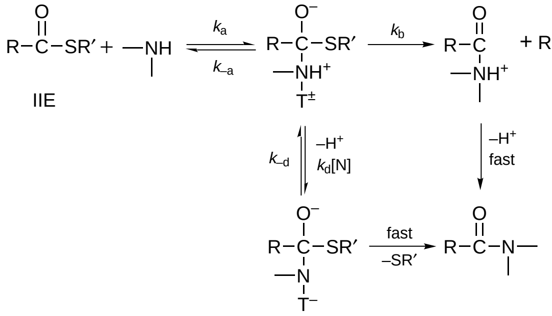
IC

the aminolysis of their thio analogues, thiol (−SR′),[1c,3] **IIE** and **IIC**, thiono[4] (−C(=S)−), **IIIE** and **IIIC**, and dithio[5] (−C(=S)SR′), **IVE** and **IVC**, compounds, have been reported lately. The aminolysis reactions of thiol esters (RCOSR′, **IIE**) and carbonates (ROCOSR′, **IIC**) have been found to proceed according to eq 1 with rate-limiting expulsion of the leaving group, $R'S^-$, for weakly basic nucleophiles and basic leaving groups, with large values of β_{nuc} (0.8−1.4) and β_{lg} (*ca.* 1.0), and rate-limiting attack of the nucleophile for basic nucleophiles and good leaving group with small values of β_{nuc} (0.1−0.7) and β_{lg} (*ca.* 0.3).[1c,3] In this mechanism, the deprotonation of $T^{\pm}$ (k_d[N]) is slow and negligible compared to k_b. Thus, the aminolysis mechanism of the thiol derivatives is in general similar to that of their oxy analogues, **IE** and **IC**.[1,2]



(1)

However, the mechanistic behavior for the aminolysis of thiono analogues, **IIIE** and **IIIC**, has been found to deviate from that of oxy and thiol derivatives when the reactions are conducted *in water* involving substrates with a *poor leaving group*.[4c,d] In these latter reactions, the k_b becomes sufficiently lower to enable a competition between the expulsion of the leaving group (OR′) from the zwitterionic tetrahedral intermediate, $T^{\pm}$, and the deprotonation of $T^{\pm}$ by the amine, k_d[N], leading to T^-, *i.e.*, $k_b \cong k_d$[N]. The importance of the deprotonation step

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was also found in the aminolysis of dithio derivatives, **IVE** and **IVC.**[5a,b,c,e] For example, Castro et al. reported in the aminolysis of phenyl dithioacetate,[5b] $CH_3C(=S)SC_6H_5$, and phenyl *O*-ethyl dithiocarbonates,[5a] $EtOC(=S)SC_6H_5$, in water at 25.0 °C a general reaction scheme, eq 1 (where $-C(=O)-$ is replaced by $-C(=S)-$ and $R = CH_3$ and EtO, respectively, with $R' = C_6H_5$), with $T^{\pm}$ and T^{-}. Depending on the basicities of the amine, the relative importance of the three competing steps of $T^{\pm}$ decomposition, k_{-1}, k_b, and $k_d[N]$, varies and different rate equations hold. When the amine is strongly basic ($pK_a = 11.24$), a simple expression, eq 2, was obtained,

$$k_{obs} = k_a[N] \tag{2}$$

whereas when the nucleofugality of the leaving group, SR′, is sufficiently strong, first-order dependence of k_{obs} on the nucleophile (amine) concentration [N], eq 3, where

$$k_N = \frac{k_a}{k_{-a}} k_b = Kk_b$$

was observed. In other reactions,[5a,b,c,e] however, the competition of the deprotonation step, $k_d[N]$, with the leaving group expulsion, k_b, becomes possible since the

$$k_{obs} = k_0 + k_N[N] \tag{3}$$

mobility of the proton in water is anomalously high, $k_d \cong 10^{10}$ dm^3 mol^{-1} s^{-1}.[6a] Due to the involvement of the proton transfer step in the rate expression, the original simple dependence of k_{obs} on [N], eq 3, disappears and the simple biphasic dependence of log k_{obs} vs pK_a of the amine basicity, *i.e.*, either k_b or k_a as rate-limiting, no longer holds. One way of circumventing the complication incurred by the competition of the fast proton transfer step may be to use an aprotic solvent instead of water as a reaction medium.[5f,g] It is expected that the mobility of the proton will be reduced greatly in aprotic media, and we can disregard the $k_d[N]$ term. We therefore conducted studies on the aminolysis mechanism of phenyl dithioacetates in acetonitrile varying both the leaving group, $-SC_6H_4Z$, and the nucleophiles, $XC_6H_4NH_2$ (AN), $XC_6H_4N(CH_3)_2$ (DMA), and $XC_6H_4CH_2NH_2$ (BA), eq 4.

$$\begin{gathered} 2XC_6H_4NH_2 + CH_3C(=S)SC_6H_4Z \xrightarrow{MeCN} \\ \text{also with } XC_6H_4N(CH_3)_2 \\ \text{and } XC_6H_4CH_2NH_2 \\ CH_3C(=S)NHC_6H_4X + {}^{+}NH_3C_6H_4X + {}^{-}SC_6H_4Z \quad (4) \end{gathered}$$

$$X = p\text{-OMe}, p\text{-Me}, H, \text{ or } p\text{-Cl}$$

$$Z = p\text{-Me}, H, p\text{-Cl}, \text{ or } p\text{-Br}$$

The object of this work is to shed more light on the mechanism of the aminolysis of dithioacetates by investigating the effects of substitutents in the nucleophile and leaving group and the nature of the amine (primary vs tertiary) on the mechanism. It is also of interest to examine whether the use of an aprotic solvent really results in a simple reaction scheme with negligible contribution of the deprotonation step, $k_d[N]$, in the rate-determining step. In addition, we have determined and compared the cross-interaction constants, ρ_{XZ} and β_{XZ} in eqs 5 and 6,[7] where X and Z refer to the substituents in the nucleophile and leaving group, respectively, and $\Delta pK_i = pK_i - pK_H$. Previous works in our laboratories have

$$\log(k_{XZ}/k_{HH}) = \rho_X\sigma_X + \rho_Z\sigma_Z + \rho_{XZ}\sigma_X\sigma_Z \tag{5}$$

$$\log(k_{XZ}/k_{HH}) = \beta_X\,\Delta pK_X + \beta_Z\,\Delta pK_Z + \beta_{XZ}\,\Delta pK_X\,\Delta pK_Z \tag{6}$$

indicated that the ρ_{XZ} and β_{XZ} are both positive and the magnitude is relatively large for the stepwise mechanism of acyl transfer reactions involving rate-limiting breakdown of the zwitterionic tetrahedral intermediate compared to that for rate-limiting formation of $T^{\pm}$.[1i,5f,g,8] Furthermore, by varying substitutents in both the nucleophile and leaving group, it will be possible to examine the effects of nucleophilicity on the magnitude of β_{lg} (or β_Z in eq 6) and of nucleofugality on the β_{nuc} (or β_X in eq 6) value.

Table 1. Second-Order Rate Constants, k_2 ($\times 10^4$ dm^3 mol^{-1} s^{-1}), for the Reactions of Z-Substituted Phenyl Dithioacetates with X-Substituted Anilines and *N*,*N*-Dimethylanilines in Acetonitrile at 50.0 °C

		Z			
Nu	X	*p*-Me	H	*p*-Cl	*p*-Br
AN	*p*-OMe	33.8	64.8	153	159
	p-Me	14.7	30.9	74.6	75.9
	H	4.99	9.46	27.4	28.4
	p-Cl	0.923	1.97	6.42	5.65
DMA	*p*-OMe	57.4	118	279	284
	p-Me	27.6	56.9	146	149
	H	7.83	16.0	45.8	47.9
	p-Cl	1.55	3.47	9.65	10.4
BA[a]	*p*-OMe	1.03	1.50	2.72	2.81
	p-Me	0.898	1.33	2.45	2.54
	H	0.699	1.06	2.03	2.12
	p-Cl	0.503	0.795	1.58	1.66

[a] At −20.0 °C.

Results and Discussion

All reactions studied obeyed the kinetic law shown in eqs 7 and 8, where [N] is amine concentration. Plots of

$$\frac{d[P]}{dt} = k_{obs}[\text{Substrate}] \tag{7}$$

$$k_{obs} = k_N[N] \tag{8}$$

k_{obs} vs [N] were linear, and the k_N values were obtained from the slopes of these plots. The k_N values determined are summarized in Table 1. The rates are faster with DMAs than with the corresponding ANs, and also are faster with a stronger nucleophile (X = *p*-OMe) and a better nucleofuge (Z = *p*-Br). These trends are in accord with those for typical nucleophilic substitution reactions. The Hammett ρ_X and ρ_Z and the Brönsted β_X and β_Z values are shown in Table 2. Here, ρ_X and β_X correspond to ρ_{nuc} and β_{nuc}, and ρ_Z and β_Z to ρ_{lg} and β_{lg}. First of all, we note that the correlation is good for all the linear plots

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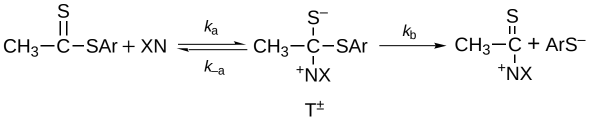
Table 2. Hammett (ρ_X and ρ_Z)[a] and Brönsted (β_X and β_Z)[a] Coefficients for the Reactions of Phenyl Dithioacetates with Anilines and *N,N*-Dimethylanilines in Acetonitrile at 50.0 °C

Nu	Z	ρ_X	β_X	X	ρ_Z	β_Z
AN	*p*-Me	−3.11	0.85	*p*-OMe	1.66	−0.71
	H	−3.05	0.84	*p*-Me	1.76	−0.76
	p-Cl	−2.90	0.80	H	1.90	−0.81
	p-Br	−2.89	0.79	*p*-Cl	1.95	−0.82
DMA	*p*-Me	−3.17	0.87	*p*-OMe	1.73	−0.73
	H	−3.09	0.85	*p*-Me	1.82	−0.77
	p-Cl	−2.96	0.82	H	1.94	−0.82
	p-Br	−2.90	0.80	*p*-Cl	2.00	−0.84
BA[b]	*p*-Me	−0.63	0.63	*p*-OMe	1.09	−0.45
	H	−0.56	0.55	*p*-Me	1.12	−0.47
	p-Cl	−0.48	0.48	H	1.19	−0.50
	p-Br	−0.46	0.46	*p*-Cl	1.28	−0.55

[a] Correlation coefficents > 0.995 in all cases. [b] At −20.0 °C, correlation coefficents > 0.998 in all cases.

(not shown) both for the AN and DMA nucleophiles. The straight line for DMA is parallel to that for AN and shows a higher intercept, *i.e.*, the tertiary amines react faster than the primary amines toward aryl dithioacetates. These types of behavior are well-known.[1d,g,3b,f] The β_X values range from 0.80 to 0.86, and the β_Z values vary from −0.71 to −0.84. The magnitudes of β_X and β_Z are large and are similar to those obtained for the rate-limiting expulsion of the leaving group from $T^{\pm}$ in the aminolysis of phenyl dithiobenzoates (**IVE** with $R = C_6H_5$ and $R' = ZC_6H_4$) in MeCN[5f] ($\beta_X = 1.0$, $\beta_Z = -0.8$), *O*-ethyl *S*-aryl dithiocarbonates (**IVC** with R = Et and $R' = 2,4\text{-}(NO_2)_2C_6H_3$ and $R' = 2,4,6\text{-}(NO_2)_3C_6H_2$) in water ($\beta_X = 0.9-1.0$)[5h] and other reactive acetates (**IE**−**IIIE**)[1a−g] and carbonates (**IC**−**IIIC**).[2a−c] For these series of reactions with AN and DMA, there are no complications arising from competition of the fast proton transfer from $T^{\pm}$ leading to T^-, $k_d[N]$ in eq 1, in the rate-determining step, and the mechanism of the reactions can be described completely by eq 9, where $Ar = C_6H_4Z$ and XN represents amines with substitutent X. The rate-determining step is the breakdown of $T^{\pm}$, k_b, and hence k_N in eq 8 is a complex quantity with

$$k_N = \frac{k_a}{k_{-a}}k_b = Kk_b$$



$$CH_3-\overset{\overset{S}{\|}}{C}-SAr + XN \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} \underset{T^{\pm}}{CH_3-\underset{{}^+NX}{\overset{S^-}{C}}-SAr} \xrightarrow{k_b} CH_3-\underset{{}^+NX}{\overset{S}{\overset{\|}{C}}} + ArS^- \quad (9)$$

This conclusion is based on the following. (i) A simple rate law, eq 8, is obeyed in all cases. (ii) The two classes of amines, primary (AN) and tertiary (DMA), exhibit the same behavior. If the deprotonation step, $k_d[N]$ in eq 1, were important in the rate-determining step, the primary amines (AN) would have followed different kinetic law from that of the tertiary (DMA) since the latter bases cannot form an acidic $T^{\pm}$, and therefore there is no deprotonation step for their reactions. (iii) The large magnitudes of both β_X and β_Z.

The rate-limiting breakdown mechanism proposed above for the aminolysis of phenyl dithioacetates in MeCN is in sharp contrast to the complex mechanism involving the rate-limiting deprotonation step, $k_d[N]$ in eq 1, proposed for the aminolysis of the same substrates in water.[5b,c] This difference in the mechanism, one with and the other without the deprotonation step, clearly shows that in aprotic solvent, MeCN, the mechanism becomes simple with no complications arising from participation of the rate-limiting deprotonation step.[5f,g] The complex mechanism found in water is indeed due to the anomalously fast rate of proton transfer (k_d) in water.[6] Another notable aspect concerning the magnitudes of β_X and β_Z found in this work is that the use of the pK_a values determined in water instead of in MeCN[9] seems to have little effect on the magnitudes, since in our plots we used the rate data in MeCN but the pK_a values in water. This suggests that although the absolute values may differ[9] the relative values remain constant in H_2O and CH_3CN. Such a constant ΔpK_a ($= pK_{CH_3CN} - pK_{H_2O} \cong 7.5$) was indeed found for various amines.[9b−d] The values of β_Z may be significantly smaller than the values reported on the basis of on aqueous acidities. However, we are comparing the β_Z values determined under similar conditions.[5f,g] Overall, variations in the magnitudes of both ρ and β (Table 2) with substituents show that a stronger nucleophile ($\delta\sigma_X < 0$) and/or nucleofuge ($\delta\sigma_Z > 0$) lead to a decrease in the magnitude.[1k,l] This trend is in accord with that observed for the aminolyses of *O*-ethyl *S*-aryl dithiocarbonates[5h] (**IVC** with R = Et and R′ = Ar) and other aryl acetates[3b] and carbonates.[3c,e,4d] In the former reaction series for 2,4-dinitro (DN) and 2,4,6-trinitro (TN) substituents in the *S*-aryl leaving group, the observed β_X values were 1.0 and 0.9, respectively.[5h] In the aminolysis of $CH_3C(=O)SAr$ with Ar = 4-nitro; 2,4-dinitro, and 2,4,6-trinitrophenyl, the β_X values observed were 0.86, 0.85, and 0.80, respectively,[3b] and in the aminolysis of $EtOC(=S)OAr$ with Ar = 2,4-dinitro- and 2,4,6-trinitrophenyl, the β_X obtained were 0.9 and 0.8, respectively.[3f] There are also some examples in the literature of a stronger nucleophile leading to a smaller magnitude of β_Z.[2b,3a,b]

For the reactions with BAs, we were unable to measure rates at the same temperature of 50.0 °C used in the reactions with ANs and DMAs. Since the reaction temperature was -20.0 °C, there is 70.0° temperature difference between the two reaction series. The magnitudes of ρ_X (β_X) and ρ_Z (β_Z) in Table 2 are smaller than those with the ANs and DMAs; the size should be in fact much smaller than those at −20.0 °C if we compare them at the same temperature of 50.0 °C, since numerical values of all susceptibility factors decrease with increasing temperature.[10] Thus, the much smaller sizes of β_X and β_Z suggest that the reactions with BAs proceed by rate-limiting attack of the nucleophile, the step represented by k_a in eqs 1 and 9, or by a concerted S_N2 type mechanism. This is reasonable since the basicities of the BAs (for X = H, $pK_a = 9.35$ in water) are much stronger than those of the ANs (for X = H, $pK_a = 4.60$ in water) and DMAs (for X = H, $pK_a = 5.07$ in water), $\Delta pK > 4$. A rough estimate of temperature dependence indicated that at the same temperature of 50 °C β_X and β_Z should be *ca.* 0.1−0.3 and −0.2 to −0.3, respectively.[11] These values are well within the range of values reported for

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Table 3. Secondary Kinetic Isotope Effects for the Reactions of Phenyl Dithioacetates with Deuterated Anilines ($XC_6H_4ND_2$) at 50.0 °C and Benzylamines ($XC_6H_4CH_2ND_2$) at −20.0 °C in Acetonitrile

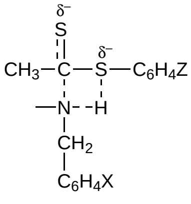
Nu	X	Z	k_H ($dm^3\ mol^{-1}\ s^{-1}$)	k_D ($dm^3\ mol^{-1}\ s^{-1}$)	k_H/k_D
AN	*p*-OMe	*p*-Me	$(3.38 \pm 0.21^{a}) \times 10^{-3}$	$(3.21 \pm 0.21) \times 10^{-3}$	1.05 ± 0.09^{b}
	p-Cl	*p*-Me	$(9.23 \pm 0.25) \times 10^{-5}$	$(8.55 \pm 0.24) \times 10^{-5}$	1.08 ± 0.04
	p-OMe	*p*-Br	$(1.59 \pm 0.06) \times 10^{-2}$	$(1.45 \pm 0.06) \times 10^{-2}$	1.10 ± 0.06
	p-Cl	*p*-Br	$(5.65 \pm 0.41) \times 10^{-4}$	$(4.96 \pm 0.49) \times 10^{-4}$	1.14 ± 0.14
BA	*p*-OMe	*p*-Me	1.03 ± 0.02	0.93 ± 0.02	1.11 ± 0.03
	p-Cl	*p*-Me	$(5.03 \pm 0.04) \times 10^{-1}$	$(4.20 \pm 0.03) \times 10^{-1}$	1.20 ± 0.01
	p-OMe	*p*-Br	2.81 ± 0.02	2.14 ± 0.03	1.31 ± 0.02
	p-Cl	*p*-Br	1.66 ± 0.02	1.22 ± 0.02	1.36 ± 0.03

[a] Standard deviation. [b] Standard error.

such mechanism, *i.e.*, the rate-limiting attack in the stepwise mechanism or concerted.[1h−m]

We therefore conclude that the aminolysis of phenyl dithioacetes with anilines and *N*,*N*-dimethylanilines in acetonitrile at 50.0 °C proceed by a stepwise mechanism involving rate-limiting breakdown of the zwitterionic intermediate, $T^{\pm}$, whereas that with benzylamines in acetonitrile changes to a mechanism with rate-limiting attack of the substrate. This mechanistic changeover is quite similar to the corresponding mechanistic change observed with phenyl dithiobenzoates in acetonitrile; for the aminolysis with ANs, the magnitudes of β_X (0.8−1.1) and β_Z (−0.5 to −0.8) were large[5f] and with BAs they were smaller with $\beta_X = 0.5{-}0.7$ and $\beta_Z = -0.2$ to -0.3.[5g] Thus substitution of methyl for phenyl group in dithio compounds does not cause any change in the aminolysis mechanism. This is also true for the aminolysis of other esters and carbonates. However, it is well-known that substitution of ethoxy for methyl can sometimes cause change of the aminolysis mechanism to a concerted reaction which is enforced by the high instability caused to $T^{\pm}$ by ethoxy (or methoxy) group.[3c,e]

The cross-interaction constants, ρ_{XZ} and β_{XZ}, calculated by subjecting the rate data in Table 1 to multiple regression analysis using eqs 5 and 6 gave ρ_{XZ} (β_{XZ}) of 0.58 (0.13) and 0.61 (0.10) for the AN and DMA series, respectively. For the BA series the values are smaller with 0.40 (0.08) at −20.0 °C; as noted above these values are expected to decrease to much smaller values at 50.0 °C. The larger β_{XZ} (and ρ_{XZ}) for the rate-limiting expulsion of the leaving group (^{-}SAr) compared to the β_{XZ} (and ρ_{XZ}) for the rate-limiting attack of the nucleophile is consistent with our earlier results.[1i,5f,g,8] Finally we have determined the secondary kinetic isotope effects with deuterated nucleophiles, $XC_6H_4ND_2$, and $XC_6H_4CH_2ND_2$, and the results are shown in Table 3. The k_H/k_D values (1.05−1.14) for the reactions with deuterated ANs are consistent with the mechanism proposed.[1h,i,5f,12] We note that for the reactions with deuterated BAs the k_H/k_D values are somewhat larger than those for the reactions with ANs. Since in the rate-determing step the benzylamine approaches to the substrate and vibrational frequencies are expected to increase due to steric crowding in the TS, the secondary kinetic isotope effect should be of inverse type, $k_H/k_D < 1.0$,[5g,7b,13] rather than the normal effect ($k_H/k_D > 1.0$) observed. It may be possible that the TS in the rate-limiting attack by BA involves a four-center type hydrogen bond strucutre, **V**, in which



V

partial proton transfer takes place leading to a relatively large normal primary kinetic isotope effect, $k_H/k_D > 1.0$.[7b,14] It is well-known that formation of the double C═S bond in **V** to expel the nucleofuge is more difficult compared to the formation of the C═O double bond due to a weaker π-bonding energy of the thiocarbonyl (a $d\pi{-}p\pi$ bond) compared to the carbonyl group (a $p\pi$-$p\pi$ bond).[4d,15] As a result, the zwitterionic tetrahedral intermediate, $T^{\pm}$, becomes relatively more stable and causes a lowering of the nucleofugality of the leaving group. This is why there is a mechanistic change for the aminolysis of thiono and dithio derivatives to a competitive proton transfer from $T^{\pm}$, *i.e.*, $k_d[N] \geq k_b$. Thus, in the bond-making step in **V**, extra push is provided by the BA to expel the leaving group. This is supported by the larger k_H/k_D values for an acceptor X (facile deprotonation) and a stronger nucleofuge (greater negative charge on S) in Table 3.

Conclusion

In summary, the mechanism of aminolysis of phenyl dithioacetates in acetonitrile is relatively simple, involving only one tetrahedral intermediate, $T^{\pm}$, and being uncomplicated by the fast proton transfer step which may become rate determining in the aminolysis of thiono and dithio esters and carbonates with poorer leaving groups, and especially when the reactions are conducted in aqueous solution. The mechanism changes from rate-limiting expulsion of the leaving group for anilines and *N*,*N*-dimethylanilines to a rate-limiting attack by the nucleophile or concerted for the more basic nucleophiles (benzylamines).

In the stepwise (or less likely concerted) process of the reactions with benzylamine, a four-center type TS involving a hydrogen-bonded bridged structure is suggested in view of the relatively large deuterium kinetic isotope effects observed with deuterated amines, $XC_6H_4CH_2ND_2$.

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(11) Temperature coefficient of ρ_X obtained for 10° was calculated to be *ca.* 0.20 (Lee, B. C.; Yoon, J. H.; Lee, C. G.; Lee, I. *J. Phys. Org. Chem.* **1994**, *7*, 273−279). Since the β_X values are *ca.* 1/3 to 1/4 of ρ_X, $\Delta\beta_X/\Delta T \cong 0.05$ for $\Delta T = 10°$.

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Experimental Section

Materials. Anilines were Tokyo Kasei G. R. grade, and *N*,*N*-dimethylanilines were prepared and purified by the known method.[16] Benzylamines, thiophenol, acetyl chloride, and the Lawesson's reagent[17] used for the preparation of substrates were Aldrich G. R. grade. Merck G. R. grade acetonitrile was distilled three times before use. *S*-Phenyl thioacetates were prepared by reacting corresponding thiophenols with acetyl chloride in ether at 0−5 °C. The products were confirmed by NMR analysis. *S*-Phenyl thioacetates were dissolved in toluene and refluxed with the Lawesson's reagent.[17] The mixture was extracted with dichloromethane and distilled under reduced pressure after drying. The products were identified by their ^{1}H NMR, ^{13}C NMR, and IR spectra as follows.[5b,c]

$CH_3C(=S)SC_6H_5$: as reported in the literature.[5b]

$CH_3C(=S)SC_6H_4$-*p*-CH_3: liquid; IR (cm^{-1}, KBr), 1196 (S=O), 1098 (CO−S), 1012 (CH_3), 853 (phenyl); δ_H ($CDCl_3$), 2.41 (3H, s, CH_3), 2.86 (3H, s, CH_3), 7.28−7.33 (4H, m, aromatic ring); δ_C 21.42, 38.79, 128.48, 130.36, 134.51, 140.71, 234.86.

$CH_3C(=S)SC_6H_4$-*p*-Cl: liquid; IR (cm^{-1}, KBr), 1209 (S=O), 1087(CO−S), 852 (phenyl); δ_H ($CDCl_3$), 2.88 (3H, s, CH_3), 7.33 (2H, d, J = 8.06 Hz), 7.45 (2H, d, J = 8.79H Hz); δ_C 38.77, 129.86, 132.37, 136.05, 136.78, 232.94.

$CH_3C(=S)SC_6H_4$-*p*-Br: mp 49−50 °C; IR (cm^{-1}, KBr), 1209 (S=O), 1071 (CO−S), 852 (phenyl); δ_H ($CDCl_3$) 2.879 (3H, s, CH_3), 7.26 (2H, d, J = 8.06 Hz), 7.61 (2H, d, J = 8.79 Hz); δ_C 38.86, 125.19, 130.66, 132.84, 136.26, 232.85.

Kinetic Measurements. The reactions were followed conductometrically under pseudo-first-order condition with excess amounts of amine, [S] ≅ 10^{-3} M, and [N] ≅ 0.02−0.45 M. The rate constants, k_N in eq 8, were obtained as described previously.[5f,g] The rate constants reported were averages of more than two determinations and were reproducible to ±5%.

Product Analysis. Phenyl dithioacetate (0.05 mol) was reacted with aniline (0.5 M) in acetonitrile at 50.0 °C for more than 15 half-lives. After the solvent was evaporated under reduced pressure, anilides were separated by column chromatography (hexane:ethyl acetate = 10:1). Products for the reactions with benzylamine were similarly obtained. Analytical data are as follows.

$CH_3C(=S)NHC_6H_5$: liquid; δ_H ($CDCl_3$) 2.33 (3H, s, CH_3), 7.11−7.62 (5H, m, aromatic ring); δ_C 31.04, 128.50, 129.16, 133.15, 195.73.

$CH_3C(=S)NHCH_2C_6H_5$: liquid; δ_H ($CDCl_3$) 2.55 (3H, s, CH_3), 3.62 (1H, br, NH), 6.00 (2H, d, CH_2, J = 5.13 Hz) 7.15−7.65 (5H, m, aromatic ring); δ_C 21.35, 51.05, 127.10, 127.44, 129.05, 137.00, 198.89.

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