

Kinetics and mechanism of the aminolysis of phenyl dithiobenzoates

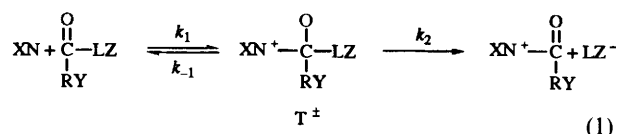
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The kinetics and mechanism of the reactions of phenyl dithiobenzoates with anilines in acetonitrile at 55.0 °C have been studied. The large magnitude of $\beta_X(\beta_{\text{nuc}})$ and the signs of cross-interaction constants, $\rho_{XY}^* > 0$, $\rho_{YZ} < 0$ and $\rho_{XZ} > 0$, are all consistent with the carbonyl addition mechanism in which the breakdown of the tetrahedral intermediate, T^\pm , is rate limiting. The thiocarbonyl group ($>C=S$) is found to favour amine expulsion in contrast to the carbonyl group ($>C=O$) which favours the S-bonded nucleofuge expulsion from T^\pm . The signs of cross-interaction constants, ρ_{XY} , ρ_{YZ} and/or ρ_{XZ} , are shown to provide useful mechanistic criteria for distinguishing, especially, the carbonyl addition mechanism involving the rate-limiting breakdown of the tetrahedral intermediate (T^\pm) from the concerted S_N2 mechanism.

The aminolysis reaction of carbonyl compounds is one of the most extensively investigated subjects in mechanistic organic chemistry. In this type of reaction, a non-linear Brønsted-type plot showing a break from a large ($\beta = 0.8-1.0$) to a small ($\beta \approx 0.1-0.3$) rate dependence on basicity of the attacking amine is often obtained at pK_0 as the basicity of nucleophile is increased.¹⁻⁸ The break at pK_0 where $k_{-1} = k_2$ has been attributed to a change in the rate-determining step from breakdown (k_2) to formation (k_1) of a tetrahedral intermediate, T^\pm , in the reaction path,¹⁻⁸ eqn. (1), where X, Y



and Z are the substituents in the nucleophile, substrate and leaving group, respectively. Such rate-limiting breakdown of T^\pm has been reported, for example, in the reactions of methyl chloroformate with pyridines,¹ substituted diphenyl carbonates with quinuclidines,² 2,4-dinitrophenyl acetate and methyl carbonate with pyridines,³ acetic anhydride with pyridines,⁴ 2,4-dinitrophenyl benzoate and *p*-nitrobenzoate with pyridines,⁵ phenyl and *p*-nitrophenyl thioacetates with amines,⁶ 2,4-dinitrophenyl and 2,4,6-trinitrophenyl thioacetates with amines⁷ and 2,4-dinitrophenyl methyl carbonate with secondary alicyclic amines.⁸

For a doubly substituted reaction system, a Taylor expansion of $\log k_{ij}$ around $\sigma_i = \sigma_j = 0$ neglecting pure second order (ρ_{ii} and ρ_{jj}) and higher order terms has been shown to give eqn. (2a); the cross-interaction constant ρ_{ij} can then be alternatively defined as eqn. (2b).⁹

Based on the results of these experimental studies, we were able to determine the signs of the cross-interaction constants, ρ_{ij} in eqns. (2)⁹ where $i, j = X, Y$ or Z in eqn. (1), for the

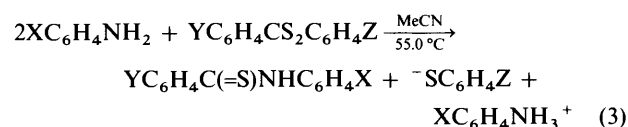
$$\log(k_{ij}/k_{\text{HH}}) = \rho_i\sigma_i + \rho_j\sigma_j + \rho_{ij}\sigma_i\sigma_j \quad (2a)$$

$$\rho_{ij} = \frac{\partial \rho_j}{\partial \sigma_i} = \frac{\partial \rho_i}{\partial \sigma_j} \quad (2b)$$

rate-limiting breakdown mechanism of the zwitterionic tetrahedral intermediate, T^\pm .¹⁰ For this type of mechanism, it was found that in the rate-limiting breakdown step, k_2 , the sign of ρ_{YZ} is negative while for equilibrium $K = k_1/k_{-1}$ the sign of

ρ_{XY} is positive, which are in quite contrast to those ($\rho_{YZ} > 0$ and $\rho_{XY} < 0$)⁹ for a normal concerted bimolecular nucleophilic displacement, S_N2 mechanism. On the other hand, the sign of ρ_{XZ} is always positive,⁹ whereas in the concerted S_N2 reactions it can be either positive or negative.¹⁰

In this work, we report the results of kinetic studies on the aminolysis of phenyl dithiobenzoates in acetonitrile at 55.0 °C, eqn. (3). We have applied the mechanistic criteria involving the



signs of ρ_{YZ} , ρ_{XY}^* and ρ_{XZ} to the reaction and concluded that the reaction conforms to the mechanistic criteria for the rate-limiting breakdown of the tetrahedral intermediate, T^\pm .

Results and discussion

The second-order rate constants, k_N , for the reactions under study [eqn. (3)] were obtained from k_{obsd} vs. aniline concentration, $[\text{AN}]$, plots, eqn. (4), where the intercepts, k_0 , were

$$k_{\text{obsd}} = k_0 + k_N[\text{AN}] \quad (4)$$

zero in all cases. No third order kinetics were observed implying that there is no general base catalysis by aniline. The k_N values are summarized in Table 1. Considering the kinetic results and product studies (*vide infra*) the general mechanism for the aminolysis of phenyl dithiobenzoate under the reaction conditions can be given by eqn. (3). The ion pair formed, $\text{SC}_6\text{H}_4\text{Z}^-$ and $\text{XC}_6\text{H}_4\text{NH}_3^+$, enables us to follow the reaction by an increase in conductivity of the reaction mixture. The Brønsted as well as the Hammett type plot obtained in the aminolysis exhibited a good straight line (Table 2). A non-linear Brønsted plot showing a break from a large to a small $\beta_X(\beta_{\text{nuc}})$ at pK_0 is expected if there is a mechanistic change from breakdown (k_2) to formation (k_1) of a tetrahedral intermediate, T^\pm , in the reaction path (Scheme 1). Although we did not obtain such a break in the Brønsted-type plot,¹⁻⁸ most probably due to the narrow range of basicity of anilines used, *i.e.*, pK_a values of the aniline nucleophiles used are all lower than those of the thiophenolate leaving groups (*e.g.* pK_a of PhNH_3^+ and PhSH

are 4.60 and 7.80, respectively)¹¹ the existence of a tetrahedral intermediate in the reaction pathway (T^\ddagger in Scheme 1) cannot be precluded. Since in this work, large excess of aniline concentrations ($[\text{substrate}] \cong 10^{-3}$ and $[\text{aniline}] \geq 0.03 \text{ mol dm}^{-3}$) were used in all cases the deprotonation process after the rate determining step, k_2 , should be fast and the reverse process, k_{-2} , is not likely to occur. Application of the steady-state treatment to T^\ddagger results in $k_N = k_1 k_2 / (k_{-1} + k_2)$, where k_N is the macroscopic rate constant defined in eqn. (4).

Three mechanisms are conceivable. (i) The normal concerted S_N2 mechanism, e.g. in the reactions of anilines with benzyl and benzoyl chlorides,⁹ for which the signs of cross-interaction constants are expected to be $\rho_{XY} < 0$, $\rho_{YZ} > 0$ and $\rho_{XZ} > 0$.^{9,10} (ii) The carbonyl addition mechanism, Scheme 1, with a rate-limiting formation of the tetrahedral intermediate (T^\ddagger) with a small β_X (0.1–0.3). In this case, $k_{-1} \ll k_2$ with $k_N = k_1$ and the sign of cross-interaction constants is predicted to be $\rho_{XY} < 0$, $\rho_{YZ} \cong 0$ and $\rho_{XZ} > 0$.^{9,10} (iii) Lastly the carbonyl addition mechanism, Scheme 1, with a rate-limiting breakdown of the leaving group with a large β_X (0.8–1.0). In this case, $k_{-1} \gg k_2$ so that $k_N = (k_1/k_{-1})k_2 = Kk_2$ and hence,

Table 1 Second-order rate constants, $k_N \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, for the reactions of phenyl dithiobenzoates with anilines in acetonitrile at 55.0 °C^a

Y	Z	X			
		<i>p</i> -OMe	<i>p</i> -Me	H	<i>p</i> -Cl
H	<i>p</i> -Me	6.71	3.29	1.17	0.222
	H	15.3	8.43	2.85	0.589
	<i>p</i> -Cl	41.9	24.6	9.04	1.86
<i>p</i> -Cl	<i>p</i> -Br	43.0	25.6	9.61	1.98
	<i>p</i> -Me	9.98	5.20	1.99	0.423
	H	23.6	13.2	4.63	1.08
<i>p</i> -NO ₂	<i>p</i> -Cl	57.8	33.3	13.9	3.07
	<i>p</i> -Br	58.8	34.5	14.8	3.20
	<i>p</i> -Me	24.6	14.3	6.73	1.55
<i>p</i> -Cl	H	50.3	30.7	12.7	3.45
	<i>p</i> -Cl	96.9	63.0	29.8	7.55
	<i>p</i> -Br	98.1	64.3	30.7	7.71

^a From at least four aniline concentrations and reproducible to within 3%.

Table 2 Hammett (ρ_X , ρ_Y and ρ_Z) and Brønsted (β_X and β_Z) coefficients for reactions of Z-phenyl Y-dithiobenzoates with X-anilines

(i) ρ_X and (β_X) values ^a					
Y/Z	<i>p</i> -Me	H	<i>p</i> -Cl	<i>p</i> -Br	
H	-2.96 (1.07)	-2.86 (1.03)	-2.74 (0.99)	-2.71 (0.98)	
<i>p</i> -Cl	-2.75 (0.99)	-2.71 (0.98)	-2.56 (0.92)	-2.54 (0.91)	
<i>p</i> -NO ₂	-2.39 (0.86)	-2.35 (0.85)	-2.23 (0.81)	-2.23 (0.80)	
(ii) ρ_Z and (β_Z) values ^b					
Y/X	<i>p</i> -OMe	<i>p</i> -Me	H	<i>p</i> -Cl	
H	1.99 (-0.67)	2.19 (-0.73)	2.26 (-0.76)	2.33 (-0.78)	
<i>p</i> -Cl	1.89 (-0.63)	2.00 (-0.67)	2.14 (-0.72)	2.15 (-0.72)	
<i>p</i> -NO ₂	1.46 (-0.49)	1.59 (-0.53)	1.64 (-0.55)	1.70 (-0.57)	
(iii) ρ_Y values ^a					
X/Z	<i>p</i> -Me	H	<i>p</i> -Cl	<i>p</i> -Br	
<i>p</i> -OMe	0.72	0.65	0.46	0.45	
<i>p</i> -Me	0.82	0.71	0.52	0.51	
H	0.98	0.83	0.65	0.64	
<i>p</i> -Cl	1.07	0.97	0.77	0.74	

^a The correlation coefficients were better than 0.995 in all cases. ^b The correlation coefficients were better than 0.992 in all cases.

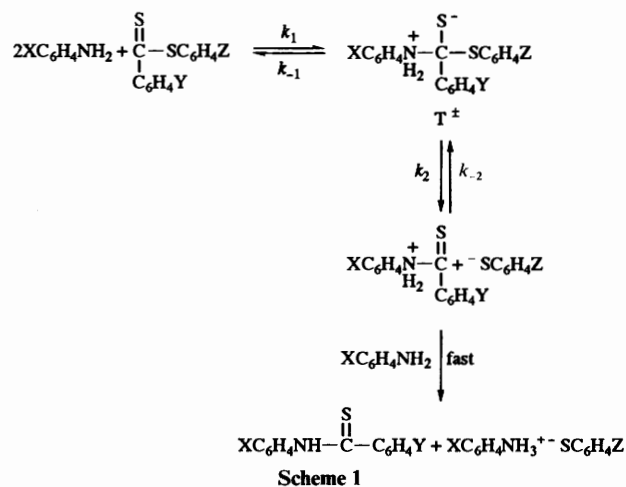
These simplifications apply because in the rate-determining step, k_2 , the change in the intensity of the interaction between X and Y is insignificant [*i.e.*, the second term of eqn. (5) is zero],¹²

$$\left(\frac{\partial^2 \log k_N}{\partial \sigma_X \times \partial \sigma_Y} \right)_Z = \left(\frac{\partial^2 \log K}{\partial \sigma_X \times \partial \sigma_Y} \right)_Z + \left(\frac{\partial^2 \log k_2}{\partial \sigma_X \times \partial \sigma_Y} \right)_Z = \rho_{XY}^{\ddagger} > 0 \quad (5)$$

whereas in the adduct formation equilibrium, K , the intensity of interaction between Y and Z stays practically constant [*i.e.*, the first term in eqn. (6) is zero].¹² Likewise it has been shown that

$$\left(\frac{\partial^2 \log k_N}{\partial \sigma_Y \times \partial \sigma_Z} \right)_X = \left(\frac{\partial^2 \log K}{\partial \sigma_Y \times \partial \sigma_Z} \right)_X + \left(\frac{\partial^2 \log k_2}{\partial \sigma_Y \times \partial \sigma_Z} \right)_X = \rho_{YZ} < 0 \quad (6)$$

the sign of ρ_{XZ} is always positive in this type of mechanism.¹⁰ The signs of ρ_{XY}^{\ddagger} (> 0), ρ_{YZ} (< 0) and ρ_{XZ} (> 0) were determined by analysing effects of various groups, X, Y and Z in eqn. (1), on the favoured partitioning of the tetrahedral intermediate (T^\ddagger)



in the reactions for which such rate-limiting breakdown (of T^\ddagger) mechanism are reported to apply.¹⁰

We have subjected the k_N values in Table 1 to the multiple regression analysis using eqn. (2), where $k_{ij} = k_N$ and $i, j = X, Y$ or Z , and determined the three cross-interaction constants, ρ_{XY}, ρ_{YZ} and ρ_{XZ} , as shown in Table 3. We note that the signs, $\rho_{XY} > 0, \rho_{YZ} < 0$ and $\rho_{XZ} > 0$, are all consistent with the mechanism (iii) above, i.e., the rate-limiting breakdown of T^\ddagger in Scheme 1. These signs are also readily obtainable by the change in ρ_X, ρ_Y and ρ_Z in Table 2 with substituents, X, Y or Z. For example, the ρ_X value becomes less negative ($\delta\rho_X > 0$) uniformly as the substituent in the substrate, Y, is changed to a more electron-withdrawing one ($\delta\sigma_Y > 0$), i.e., $\partial\rho_X/\partial\sigma_Y = \rho_{XY} > 0$. This is in line with the experimental evidence reported¹⁻⁸ for the type (iii) mechanism that the partitioning of T^\ddagger favours amine expulsion as the group that remains behind becomes more electron-withdrawing. Likewise, as Z becomes a stronger electron-withdrawing group ($\delta\sigma_Z > 0$), the ρ_Y value decreases, ($\delta\rho_Y < 0$), i.e., $\partial\rho_Y/\partial\sigma_Z = \rho_{YZ} < 0$. This is again consistent with the experimental evidence reported¹⁻⁸ that the amine expulsion from T^\ddagger is favoured by electron withdrawing substituents in the leaving group. It can be shown similarly that the sign of ρ_{XZ} is positive. Since the signs of ρ_{XY} and ρ_{YZ} are distinctly different, i.e., opposite, from those of the other two mechanisms, (i) and (ii) above, we can conclude that the reaction under study proceeds *via* the mechanism in which the breakdown of T^\ddagger (k_2) in Scheme 1 is the rate-determining step.

Table 3 Cross-interaction constants, ρ_{XY}, ρ_{YZ} and ρ_{XZ} (β_{XZ}) values for the reactions Z-phenyl dithiobenzoates with X-anilines in acetonitrile at 55.0 °C

(i) ρ_{XY} values ^a		
Z	ρ_{XY}	
<i>p</i> -Me	0.71	
H	0.66	
<i>p</i> -Cl	0.64	
<i>p</i> -Br	0.61	
(ii) ρ_{YZ} values ^a		
X	ρ_{YZ}	
<i>p</i> -OMe	-0.70	
<i>p</i> -Me	-0.77	
H	-0.81	
<i>p</i> -Br	-0.81	
(iii) ρ_{XZ} and β_{XZ} values ^a		
Y	ρ_{XZ}	β_{XZ}
H	0.60	0.07
<i>p</i> -Cl	0.52	0.06
<i>p</i> -NO ₂	0.43	0.05

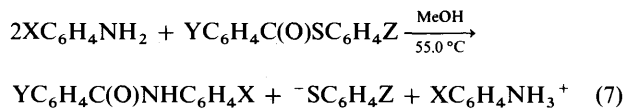
^a The correlation coefficients were better than 0.997 with 99% confidence limit in all cases.

The large magnitude of β_X (β_{nuc}) (0.80–1.07) obtained in Table 2 also supports the mechanism (iii).¹⁻⁸

Secondary kinetic isotope effects (SKIE) were determined using deuterated aniline nucleophiles, $XC_6H_4ND_2$. The results are summarized in Table 4. Reference to this Table reveals that the magnitude of k_H/k_D is close to unity, and hence the SKIE is small. If in the rate-determining step an attack of the thiocarbonyl centre by the aniline molecule was involved i.e., mechanisms (i) and/or (ii) apply, k_H/k_D would have been less than unity, $k_H/k_D < 1.0$, as has been reported for the typical S_N2 reactions.¹³

The k_H/k_D values of slightly greater than unity observed in Table 4, however, are consistent with the mechanism (iii), since in this case the observed SKIE corresponds to a β -deuterium isotope effect. The β isotope effects for solvolytic reactions of primary alkyl tosylates and halides in water are reported to be small with the k_H/k_D values of 1.02–1.04 at 60–80 °C.^{14,15} The β isotope effect is known to become stronger and hence the k_H/k_D value becomes greater, when a p orbital developed on the α -carbon centre becomes more electron deficient, i.e., the extent of bond cleavage becomes greater, in the TS.¹⁵ The lowest and highest k_H/k_D values observed for the (X, Y, Z) sets of (*p*-MeO, *p*-NO₂, *p*-Br) and (*p*-Cl, H, *p*-Me), respectively, are consistent with the lowest and highest degree of leaving group expulsion expected from T^\ddagger in the TS (*vide infra*) in view of an earlier TS predicted by $\rho_{XZ} > 0$ for a stronger nucleophile and nucleofuge.

The magnitude of ρ_{XY} and ρ_{YZ} are significantly smaller than those ($\rho_{XY} = 1.48$ vs. 0.66 and $\rho_{YZ} = -1.38$ vs. -0.81 for Z = H and X = Z)¹⁶ for the aminolysis of phenyl thiobenzoates with anilines in methanol at 55.0 °C, eqn. (7).¹⁶



This means that in the reaction of dithiobenzoates, eqn. (3), the amines are somewhat loosely bound in T^\ddagger and the extent of bond cleavage of the leaving group from T^\ddagger is rather low. The difference in the magnitude, i.e., a greater decrease in ρ_{XY} (55%) than in ρ_{YZ} (41%) reflects that under similar conditions the $>C=S$ group favours N-bonded nucleofuge expulsion in contrast to the $>C=O$ group which favours the S-bonded nucleofuge ($^-SC_6H_4Z$) expulsion.

We conclude, based on the signs of the cross-interaction constants, $\rho_{XY} > 0, \rho_{YZ} < 0$ and $\rho_{XZ} > 0$, that the reactions of phenyl dithiobenzoates with anilines in acetonitrile at 55.0 °C proceed by a carbonyl addition mechanism in which the breakdown of the tetrahedral intermediate is the rate-determining step. This mechanism is also supported by the large magnitude of β_X (β_{nuc}), 0.80–1.07. The thiocarbonyl group favours N-bonded nucleofuge expulsion in contrast to the carbonyl group which favours the S-bonded nucleofuge expulsion from the tetrahedral intermediate, T^\ddagger . Now that we have established the signs of cross-interaction constants, ρ_{XY}, ρ_{YZ} and ρ_{XZ} , applicable for different mechanisms, the signs of ρ_{ij} as well as β_{ij} (which are the same as those for ρ_{ij})

Table 4 Secondary kinetic isotope effects for the reactions of phenyl dithiobenzoates with deuterated anilines in acetonitrile at 55.0 °C

X	Y	Z	k_H/s^{-1}	$k_D/dm^3 mol^{-1} s^{-1}$	k_H/k_D
<i>p</i> -OMe	H	<i>p</i> -Br	$(4.30 \pm 0.02_2) \times 10^{-2}$	$(4.25 \pm 0.00_5) \times 10^{-2}$	$1.012 \pm 0.00_6^b$
<i>p</i> -Cl	H	<i>p</i> -Me	$(2.22 \pm 0.00_3) \times 10^{-4}$	$(2.18 \pm 0.01_5) \times 10^{-4}$	$1.018 \pm 0.00_7$
<i>p</i> -OMe	<i>p</i> -NO ₂	<i>p</i> -Br	$(9.81 \pm 0.02_4) \times 10^{-2}$	$(9.76 \pm 0.01_7) \times 10^{-2}$	$1.005 \pm 0.00_6$
<i>p</i> -Cl	<i>p</i> -NO ₂	<i>p</i> -Me	$(1.55 \pm 0.01_3) \times 10^{-3}$	$(1.53 \pm 0.02_4) \times 10^{-3}$	$1.013 \pm 0.00_5$

^a Standard deviation. ^b Standard error.¹⁸

should provide a useful mechanistic criteria for distinguishing especially the carbonyl addition mechanism from the concerted S_N2 mechanism.

Experimental

Materials

Merck GR acetonitrile was used after three distillations. The aniline nucleophiles, Tokyo Kasei GR, were redistilled or recrystallized before use. Preparation of deuteriated anilines were as described previously.¹³ The analysis (NMR spectroscopy) of the deuteriated anilines showed more than 99% deuterium content, so no corrections to kinetic isotope effects for incomplete deuterium were made.

S-phenyl thiobenzoates. These were prepared by reacting Tokyo Kasei GR thiophenols with benzoyl chlorides.¹⁷ Final products were recrystallized twice from isopropyl alcohol-acetic acid. The S-phenyl thiobenzoates were confirmed by spectral analyses as follows.

S-Phenyl thiobenzoate, PhCOSPh. Mp 53–54 °C; $\nu(\text{KBr})/\text{cm}^{-1}$ 1675 (C=O), 1202, 1175 (CO-S) and 755 (mono subst, phenyl); δ_{H} (400 MHz; CDCl_3) 7.4–8.1 (10 H, Ph); δ_{C} 100.4 MHz, CDCl_3) 189.9 (C=O), 136.4 (C-1), 135.0 (C-2*/6*), 133.6 (C-4), 129.7 (C-3*/5*), 128.9 (C-3*/5*), 128.5 (C-3/5) 127.3 (C-2/6) and 127.2 (C-1*).

PhCOS $_6$ H $_4$ -p-Me. Mp 60–61 °C; ν/cm^{-1} 1690 (C=O), 1300 (CH $_3$), 1210, 1170 (CO-S), 890 and 735 (Ph); δ_{H} 7.2–8.2 (9 H, m, Ph) and 2.4 (3 H, s, Me); δ_{C} 190.6 (C=O), 139.8 (C-4*), 136.6 (C-1), 134.9 (C-2*/6*), 133.4 (C-4), 129.9 (C-3*/5*), 128.6 (C-3/5), 127.2 (C-2/6), 123.7 (C-1*) and 21.4 (Me).

PhCOS $_6$ H $_4$ -p-Cl. Mp 75–76 °C; ν/cm^{-1} 1675 (C=O), 1225 (CO-S) and 815 (Ph); δ_{H} 7.3–7.9 (9 H, m, Ph); δ_{C} 189.6 (C=O), 138.2 (C-4*), 136.2 (C-1), 136.1 (C-2*/6*), 133.5 (C-4), 129.4 (C-3*/5*), 128.7 (C-3/5), 127.5 (C-2/6) and 125.8 (C-1*).

PhCOS $_6$ H $_4$ -p-Br. Mp 61–62 °C; ν/cm^{-1} 1680 (C=O), 1205, 1175 (CO-S), 900 (Ph); δ_{H} 7.5–8.3 (9 H, m, Ph); δ_{C} 188.0 (C=O), 136.1 (C-1), 135.4 (C-2*/6*), 134.3 (C-4), 132.9 (C-3*/5*), 128.9 (C-3/5), 127.6 (C-2/6) and 124.4 (C-4*).

p-ClC $_6$ H $_4$ COSPh. Mp 59–60 °C; ν/cm^{-1} 1685 (C=O), 1225 (CO-S) and 900 (Ph); δ_{H} 7.4–8.0 (9 H, m, phenyl ring); δ_{C} 189.0 (C=O), 140.0 (C-4), 135.0 (C-2*/6*), 134.9 (C-1), 129.7 (C-4*), 129.3 (C-3/5), 129.1 (C-3*/5*), 128.8 (C-2/6) and 126.9 (C-1*).

p-ClC $_6$ H $_4$ COSC $_6$ H $_4$ -p-Me. Mp 86–87 °C; ν/cm^{-1} 1690 (C=O), 1330 (Me), 1250 (CO-S) and 815 (Ph); δ_{H} 7.2–8.0 (8 H, m, Ph) and 2.4 (3 H, s, Me); δ_{C} 189.5 (C=O), 140.0 (C-4), 139.9 (C-4*), 134.9 (C-2*/6*), 134.8 (C-1), 130.2 (C-3*/5*), 129.0 (C-3/5), 128.8 (C-2/6), 123.3 (C-1*) and 21.4 (Me).

p-ClC $_6$ H $_4$ COSC $_6$ H $_4$ -p-Cl. Mp 132–133 °C; ν/cm^{-1} 1670 (C=O), 1255, 1225 (CO-S), 810 (Ph); δ_{H} 7.4–8.0 (8 H, m, Ph); δ_{C} 188.5 (C=O), 140.3 (C-4), 136.3 (C-2*/6*), 136.2 (C-4*), 134.6 (C-1), 129.6 (C-3*/5*), 129.1 (C-3/5), 128.8 (C-2/6) and 125.3 (C-1*).

p-ClC $_6$ H $_4$ COSC $_6$ H $_4$ -p-Br. Mp 138–139 °C; ν/cm^{-1} 1680 (C=O), 1205, 1170 (CO-S), 910 (Ph); δ_{H} 7.3–8.0 (8 H, m, Ph); δ_{C} 188.4 (C=O), 140.3 (C-4), 136.5 (C-2*/6*), 134.6 (C-1), 132.5 (C-3*/5*), 129.1 (C-3/5), 128.8 (C-2/6), 126.0 (C-1*) and 124.5 (C-4*).

p-NO $_2$ C $_6$ H $_4$ COSPh. Mp 155–156 °C; ν/cm^{-1} 1650 (C=O), 1200, 1170 (CO-S), 845, 775 (Ph); δ_{H} 7.5–8.4 (9 H, m, Ph); δ_{C} 188.8 (C=O), 150.6 (C-4), 141.3 (C-1), 134.9 (C-2*/6*), 130.0 (C-4*), 129.5 (C-3*/5*), 128.5 (C-2/6), 126.1 (C-1*) and 124.0 (C-3/5).

p-NO $_2$ C $_6$ H $_4$ COSC $_6$ H $_4$ -p-Me. Mp 106–107 °C; ν/cm^{-1} 1630 (C=O), 1330 (Me), 1200, 1175 (CO-S) and 855 (Ph); δ_{H} 7.3–8.4 (8 H, m, Ph) and 2.4 (3 H, s, Me); δ_{C} 189.3 (C=O), 150.6 (C-4), 141.3 (C-1), 140.4 (C-4*), 134.8 (C-2*/6*), 130.3 (C-3*/5*), 128.4 (C-2/6), 123.9 (C-3/5), 122.5 (C-1*) and 21.4 (Me).

p-NO $_2$ C $_6$ H $_4$ COSC $_6$ H $_4$ -p-Cl. Mp 141–142 °C; ν/cm^{-1} 1670 (C=O), 1205, 1175 (CO-S) and 850 (Ph); δ_{H} 7.3–8.4 (8 H, m, Ph); δ_{C} 188.4 (C=O), 150.7 (C-4), 140.9 (C-1), 136.6 (C-4*), 136.1 (C-2*/6*), 129.8 (C-3*/5*), 128.5 (C-2/6), 124.6 (C-1*) and 124.1 (C-3/5).

p-NO $_2$ C $_6$ H $_4$ COSC $_6$ H $_4$ -p-Br. Mp 155–156 °C; ν/cm^{-1} 1670 (C=O), 1200, 1170 (CO-S) and 845 (Ph); δ_{H} 7.7–8.4 (8 H, m, Ph); δ_{C} 186.3 (C=O), 150.8 (C-4), 140.8 (C-1), 135.4 (C-2*/6*), 134.8 (C-3*/5*), 128.7 (C-2/6), 126.4 (C-1*), 124.5 (C-4*) and 124.3 (C-3/5).

Phenyl dithiobenzoates. These were prepared by reacting S-phenyl thiobenzoates with Aldrich GR Lawesson reagent with stirring at reflux in toluene. The organic layer was separated and the aqueous layer was extracted with methylene chloride (10 cm^3). The solution was dried briefly over magnesium sulfate, and the products in pure form were isolated by evaporating the solvent under reduced pressure. Other substrates were prepared by a similar method, as above. The mixture was treated with column chromatography (silica gel, 10% ethyl acetate-hexane). The substrates synthesized were confirmed (without recrystallization) by identifying peaks at correct mass positions in the MS analysis and also by spectral and elemental analyses as follows.

Phenyl dithiobenzoate, PhCS $_2$ Ph. Mp 58–59 °C; $\nu(\text{KBr})/\text{cm}^{-1}$ 1230 (C=S), 1040 (C-S) and 860 (CH-aromatic); δ_{H} 400 MHz; CDCl_3) 7.4–8.2 (10 H, m, Ph); δ_{C} (100.4 MHz; CDCl_3) 228.4 (C=S), 144.5 (C-1), 135.4 (C-2*/6*), 132.6 (C-4), 131.3 (C-1*), 130.3 (C-4*), 129.6 (C-C3*/5*), 128.4 (C-3/5) and 127.0 (C-2/6); GC-MS 230 (M^+) (Found: C, 67.7; H, 4.7; S, 27.6. Calc. for $\text{C}_{13}\text{H}_{10}\text{S}_2$: C, 67.8; H, 4.7; S, 27.7%).

PhCS $_2$ C $_6$ H $_4$ -p-Me. Mp 64–65 °C; ν/cm^{-1} 1230 (C=S), 1050 (C-S), 870 (CH-aromatic); δ_{H} 2.4 (3 H, s, Me) and 7.2–8.2 (9 H, m, Ph); δ_{C} 228.7 (C=S), 144.3 (C-1), 140.7 (C-4*), 134.9 (C-2*/6*), 132.4 (C-4), 130.3 (C-3*/5*), 128.2 (C-3/5), 127.6 (C-1*), 126.8 (C-2/6), 21.9 (CH $_3$); GC-MS m/z 244 (M^+) (Found: C, 68.8; H, 5.0; S, 26.2. Calc. for $\text{C}_{14}\text{H}_{12}\text{S}_2$: C, 68.9; H, 4.9; S, 26.3%).

PhCS $_2$ C $_6$ H $_4$ -p-Cl. Mp 77–78 °C; ν/cm^{-1} 1230 (C=S) and 1040 (C-S), 860 (CH-aromatic); δ_{H} 7.4–8.2 (9 H, m, Ph); δ_{C} 227.4 (C=S), 144.2 (C-1), 136.8 (C-4*), 136.6 (C-2*/6*), 132.7 (C-4), 129.9 (C-3*/5*), 129.6 (C-1*), 128.4 (C-3/5) and 126.9 (C-2/6); GC-MS m/z 265 (M^+) (Found: C, 59.0; H, 3.4; S, 24.2. Calc. for $\text{C}_{13}\text{H}_9\text{ClS}_2$: C, 59.0; H, 3.5; S, 24.3%).

PhCS $_2$ C $_6$ H $_4$ -p-Br. Mp 64–65 °C; ν/cm^{-1} 1230 (C=S), 1050 (C-S) and 860 (CH-aromatic); δ_{H} 7.3–8.1 (9 H, m, Ph); δ_{C} 227.1 (C=S), 144.2 (C-1), 136.8 (C-2*/6*), 132.8 (C-3*/5*), 132.7 (C-4), 130.2 (C-1*), 128.4 (C-3/5), 126.9 (C-2/6) and 125.2 (C-4*); GC-MS m/z 309 (M^+) (Found: C, 50.5; H, 2.8; S, 20.6. Calc. for $\text{C}_{13}\text{H}_9\text{S}_2\text{Br}$: C, 50.5; H, 2.9; S, 20.7%).

p-ClC $_6$ H $_4$ CS $_2$ Ph. Mp 79–80 °C; ν/cm^{-1} 1230 (C=S), 1040 (C-S) and 870 (CH-aromatic); δ_{H} 7.4–8.1 (9 H, m, Ph); δ_{C} 226.3 (C=S), 142.6 (C-1), 139.0 (C-4), 135.3 (C-4*), 131.0 (C-1*), 130.4 (C-2*/6*), 129.7 (C-3*/5*), 128.5 (C-2/6) and 128.2 (C-3/5); GC-MS m/z 265 (M^+) (Found: C, 59.0; H, 3.4; S, 24.2. Calc. for $\text{C}_{13}\text{H}_9\text{ClS}_2$: C, 59.0; H, 3.5; S, 24.3%).

p-ClC $_6$ H $_4$ CS $_2$ C $_6$ H $_4$ -p-Me. Mp 89–90 °C; ν/cm^{-1} 1235 (C=S), 1055 (C-S), 895 (CH-aromatic); δ_{H} 7.3–8.1 (8 H, m, Ph) and 2.5 (3 H, s, Me); δ_{C} 226.9 (C=S), 142.8 (C-1), 140.6 (C-4*), 139.2 (C-4), 134.8 (C-2*/6*), 130.7 (C-3*/5*), 128.4 (C-3/5), 128.3 (C-2/6), 127.7 (C-1*) and 22.2 (CH $_3$); GC-MS m/z 279 (M^+) (Found: C, 60.2; H, 4.0; S, 22.9. Calc. for $\text{C}_{13}\text{H}_{11}\text{ClS}_2$: C, 60.3; H, 4.0; S, 22.9%).

p-ClC $_6$ H $_4$ CS $_2$ C $_6$ H $_4$ -p-Cl. Mp 139–140 °C; ν/cm^{-1} 1230 (C=S), 1055 (C-S) and 865 (CH-aromatic); δ_{H} 7.4–8.1 (8 H, m, phenyl ring); δ_{C} 225.4 (C=S), 142.3 (C-1), 139.3 (C-4), 137.0 (C-4*), 136.6 (C-2*/6*), 130.0 (C-3*/5*), 129.3 (C-1*), 128.6 (C-3/5) and 128.2 (C-2/6); GC-MS m/z 299 (M^+) (Found: C, 52.2; H, 2.7; S, 21.4. Calc. for $\text{C}_{13}\text{H}_8\text{S}_2\text{Cl}_2$: C, 52.2; H, 2.7; S, 21.4%).

p-ClC₆H₄CS₂C₆H₄-*p*-Br. Mp 141–142 °C; ν/cm^{-1} 1230 (C=S), 1060 (C-S) and 860 (CH-aromatic); δ_{H} 7.3–8.0 (8 H, m, Ph); δ_{C} 225.2 (C=S), 142.4 (C-1), 139.3 (C-4), 136.8 (C-2*/6*), 132.9 (C-3*/5*), 129.9 (C-1*), 128.6 (C-3/5), 128.2 (C-2/6) and 125.4 (C-4*); GC-MS 344 (M⁺) (Found: C, 45.5; H, 2.4; S, 18.6. Calc. for C₁₃H₈BrClS₂: C, 45.4; H, 2.4; S, 18.6%).

p-NO₂C₆H₄CS₂Ph. Mp 111–112 °C; ν/cm^{-1} 1240 (C=S), 1055 (C-S) and 840 (CH-aromatic); δ_{H} 7.4–8.3 (9 H, m, phenyl ring); δ_{C} 225.6 (C=S), 149.6 (C-4), 148.8 (C-1), 135.1 (C-2*/6*), 130.8 (C-4*), 130.4 (C-1*), 129.9 (C-3*/5*), 127.8 (C-2/6) and 123.6 (C-3/5); GC-MS *m/z* 275 (M⁺) (Found: C, 56.7; H, 2.4; S, 23.3. Calc. for C₁₃H₉NO₂S₂: C, 56.7; H, 2.4; S, 23.3%).

p-NO₂C₆H₄CS₂C₆H₄-*p*-Me. Mp 97–98 °C; ν/cm^{-1} 1240 (C=S), 1060 (C-S) and 815 (CH-aromatic); δ_{H} 7.4–8.3 (8 H, m, Ph) and 2.4 (3 H, s, Me); δ_{C} 226.1 (C=S), 179.6 (C-4), 148.8 (C-1), 141.3 (C-4*), 134.8 (C-2*/6*), 130.7 (C-3*/5*), 127.8 (C-2/6), 127.0 (C-1*), 123.5 (C-3/5) and 21.5 (Me); *m/z* 289 (M⁺) (Found: C, 58.0; H, 3.8; S, 22.3. Calc. for C₁₄H₁₁NO₂S₂: C, 58.2; H, 3.8; S, 22.2%).

p-NO₂C₆H₄CS₂C₆H₄-*p*-Cl. Mp 142–143 °C; ν/cm^{-1} 1235 (C=S), 1060 (C-S) and 815 (CH-aromatic); δ_{H} 7.4–8.3 (8 H, m, Ph); δ_{C} 224.8 (C=S), 149.8 (C-4), 148.5 (C-1), 137.4 (C-4*), 136.4 (C-2*/6*), 130.3 (C-3*/5*), 129.6 (C-1*), 127.8 (C-2/6) and 123.7 (C-3/5); GC-MS *m/z* 310 (M⁺) (Found: C, 50.3; H, 2.6; S, 20.7. Calc. for C₁₃H₈ClNO₂S₂: C, 50.4; H, 2.6; S, 20.7%).

p-NO₂C₆H₄CS₂C₆H₄-*p*-Br. Mp 162–163 °C; ν/cm^{-1} 1240 (C=S), 1060 (C-S) and 820 (CH-aromatic); δ_{H} 7.3–8.3 (8 H, m, Ph); δ_{C} 224.6 (C=S), 149.8 (C-4), 148.5 (C-1), 136.6 (C-2*/6*), 133.3 (C-3*/5*), 129.3 (C-1*), 127.8 (C-2/6), 125.8 (C-4*) and 123.7 (C-3/5); GC-MS *m/z* 354 (M⁺) (Found: C, 44.1; H, 2.3; S, 18.2. Calc. for C₁₃H₈BrNO₂S₂: C, 44.2; H, 2.3; S, 18.1%).

Kinetic procedure

Rates were measured conductimetrically at 55.0 ± 0.05 °C in acetonitrile. Good linearities were found between conductance ($\Lambda = 506\text{--}2511$) and concentration (0.05–0.25 mol dm⁻³) of product ions (PhNH₃⁺ SPh⁻, eqn. (3)). The k_{N} values were determined [eqn. (4)] with at least four aniline concentrations [AN] using the procedure described previously.¹⁶ The k_{N} values were reproducible to within 3%.

Product analysis

Z-chlorophenyl dithiobenzoate reacted with excess aniline with stirring for more than 15 half-lives at 55.0 °C in acetonitrile, and the products were isolated by evaporating the solvent under reduced pressure. The TLC analysis of the product mixture gave three spots (silica gel, glass plate, 10% ethyl acetate–hexane) R_{f} 5.5 (*p*-Cl-C₆H₄SH), 0.38 [PhC(=S)NHC₆H₄-*p*-Me] and 0.10 (*p*-MeC₆H₄NH₂). The product mixture was treated with column chromatography (silica gel, 10% ethyl acetate–

hexane). Analysis of the product, PhC(=S)NHC₆H₄-*p*-Me, gave the following results.

N-*p*-Tolyl thiobenzamide, PhC(=S)NHC₆H₄-*p*-Me. Mp 104–105 °C; $\nu(\text{KBr})/\text{cm}^{-1}$ 3160 (NH), 1240 (C=S), 815 (CH-aromatic); δ_{H} (400 MHz; CDCl₃), 8.98 (1 H, s, NH), 7.23–7.86 (9 H, m, Ph) and 2.38 (3 H, s, Me); δ_{C} (100.4 MHz; CDCl₃) 198.3 (C=S), 143.1 (C-1), 135.5 (C-1*), 133.3 (C-4*), 131.2 (C-4), 129.4 (C-3*/5*), 128.6 (C-3/5), 126.6 (C-2/6), 120.4 (C-2*/6*) and 21.2 (Me); GC-MS *m/z* 227 (M⁺) (Found: C, 73.9; H, 5.7; S, 14.2. Calc. for C₁₄H₁₃S: C, 74.0; H, 5.7; S, 14.1%).

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