

Nucleophilic substitution reactions of anilino thioethers with anilines in methanol

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Kinetic studies have been carried out on the solvolysis and aminolysis with anilines of anilino thioethers, *N*-methyl-*N*-[(*Z*-phenylthio)methyl]-*Y*-anilines, YC₆H₄N(CH₃)CH₂SC₆H₄Z, **I**, in methanol at 45.0 °C. In contrast to the iminium cations with significant lifetimes produced in water, the solvolysis proceeds by a direct displacement (S_N2) mechanism in methanol. In the aminolysis, both bond formation and cleavage are well under way in a late S_N2 transition state with high ρ_X (β_X) and ρ_Z (β_Z) values. However, cross interactions between the nucleophile and leaving group are extensive with large negative constants (ρ_{XZ} = −1.7, β_{XZ} = −0.27), which are suggestive of an S_N2 reaction with frontside attack. The inverse secondary kinetic isotope effects involving deuterated anilines (k_H/k_D = 0.84–0.88) along with low Δ*H*[‡] (4.2–5.2 kcal mol^{−1}) and Δ*S*[‡] (−46–−59 e.u.) values are consistent with the proposed mechanism.

The solvolysis of anilino thioethers, ArN(CH₃)CH₂SR, in aqueous solution,¹ and theoretical studies on the gas-phase stabilities and reactivities of iminium ions² have shown that iminium cations are highly unstable in aqueous solution, with a lifetime of 10^{−7}–10^{−8} s, as well as in the gas phase, but the formation of iminium cations is favored by extensive electron donation from the nitrogen to the antibonding orbital of the leaving bond, n_N → σ_{CS}^{*}, by a first-neighbor vicinal charge transfer interaction. In the presence of a strong nucleophilic reagent, a concerted bimolecular nucleophilic substitution (S_N2) mechanism is enforced by the absence of a significant lifetime for an iminium cation that is in contact with nucleophiles.^{1,3}

We report here the results of our detailed examination of the mechanism of the bimolecular nucleophilic substitution reactions of anilino thioethers, YC₆H₄N(CH₃)CH₂SC₆H₄Z, **I**, with anilines, XC₆H₄NH₂, in methanol at 45.0 °C. In particular we have determined cross-interaction constants, ρ_{XY}, ρ_{YZ} and ρ_{XZ}, by subjecting the second-order rate constants, *k*₂ [or *k*_{*ij*} in eqn. (1a)] to multiple regression analysis using eqn. (1a,b), where *i* and *j* represent substituents in the nucleophile (X), substrate (Y) and leaving group (Z):⁴

$$\log(k_{ij}/k_{HH}) = \rho_i \sigma_i + \rho_j \sigma_j + \rho_{ij} \sigma_i \sigma_j \quad (1a)$$

$$\rho_{ij} = \partial \rho_j / \partial \sigma_i = \partial \rho_i / \partial \sigma_j \quad (1b)$$

An especially interesting finding in the present work is that ρ_{XZ} has a large negative value, which has been interpreted to indicate a frontside-attack S_N2 mechanism.⁵

Results and discussion

The pseudo-first-order rate constant observed (*k*_{obs}) for the reactions of anilino thioethers, **I**, with anilines in methanol at 45.0 °C is of the form given by eqn. (2), where *k*_s is the rate constant for substrate solvolysis in the absence of the aniline nucleophile ([Nu] = 0), *k*₂ is the second-order rate constant for nucleophilic attack on the substrate by the substituted

anilines, and [Nu] is the aniline nucleophile concentration, which has been kept in large excess, 10–50 times, to the substrate:

$$k_{\text{obs}} = k_s + k_2[\text{Nu}] \quad (2)$$

The methanolysis rate constants, *k*_s (s^{−1}), and the aminolysis rate constants, *k*₂ (dm³ mol^{−1} s^{−1}), are summarized in Tables 1 and 2.

The linear dependence of the observed pseudo-first-order rate constants (*k*_{obs}) on [Nu] according to eqn. (2) is an indication of the bimolecular nature of the displacement reaction. The solvolysis rate constants, *k*_s, in Table 1 are much smaller than the pseudo-first-order rate constants, *k*_{obs}, for the corresponding aminolysis reactions. We can therefore safely preclude the possibility of an S_N1 mechanism for the aminolysis of the anilino thioethers.⁶

Methanolysis

The methanolysis rates are faster with a stronger nucleofuge (Z = *p*-NO₂) and with a weaker electron acceptor substituent in the substrate (Y = H). The relatively large negative ρ_Y values (ρ_Y = −0.79–−1.15) are indicative of relatively strong positive charge development on the CH₂ carbon in a dissociative transition state (TS). However, in terms of β_{dg} (= 0.22–0.32 in MeOH), which is the slope of the plot of log *k*_s vs. the basicity (p*K*_a) of the nitrogen atom of the dimethylaniline,⁶ positive charge development in the TS is much lower (ca. 1/3) than that in aqueous solution (β_{dg} = 0.79 in water).¹ The Hammett coefficients for the methanolysis with substituent variations in the substrate (ρ_Y = −0.79–−1.15) are also approximately (since we used only two-electron acceptor Y substituents) one-third of (or less than) that for the solvolysis in aqueous solution (ρ_Y = −3.3).¹ It would have been useful to have included a resonance accepting substituent such as NO₂ to investigate the effect of the nitrogen lone pair in the TS. In aqueous solution the Hammett plot has a better correlation with σ[−] than with σ, indicating extensive electron donation by resonance in the TS to assist CH₂–S bond cleavage,

Table 1 Methanolysis rate constants, $k_s \times 10^4 \text{ s}^{-1}$ of Y-anilino Z-thioethers at 45.0 °C

Y	Z						β_Z
	<i>p</i> -Me	H	<i>p</i> -Cl	<i>p</i> -Br	<i>p</i> -NO ₂	ρ_Z^a	
H	4.48	8.08	19.7	23.4	132	1.56 ± 0.07^b	-0.69 ± 0.02
<i>p</i> -Cl	2.73	4.66	13.2	15.9	99.6	1.67 ± 0.09	-0.74 ± 0.02
<i>m</i> -NO ₂	0.654	1.29	3.26	4.37	37.4	1.86 ± 0.07	-0.82 ± 0.03
ρ_Y^a	-1.15 $\pm 0.06^b$	-1.13 ± 0.02	-1.12 ± 0.12	-1.04 ± 0.10	-0.79 ± 0.08		

^a The correlation coefficients are better than 0.995 in all cases. ^b Standard deviations.

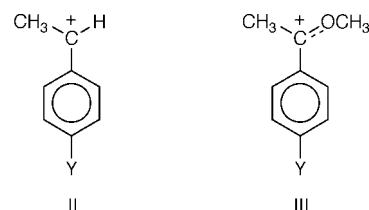
which is again an indication of a high degree of positive charge development that is close to 1.0 in a late TS in water.¹ It is interesting to note here that from the theoretical gas-phase results, at the MP2/6-31G*/RHF/6-31G* level of theory, ρ_Y for iminium ion formation is -4.3 ,² which is slightly more negative than the value in water of $\rho_Y^- = -3.3$. In this respect, it should be noted that two factors cause the observed ρ_Y value to decrease: (i) the N-CH₃ group, which intervenes between the substituent Y and the functional center, C_α, causes a fall-off of the ρ_Y value by a factor of approximately 2.5,^{4b,7} and (ii) the so-called “competing resonance”, in which the lone-pair electron on N (n_N) and the π electron on substituent Y compete for resonance electron donation to the cationic center (C_α⁺), reduces electron demand from the Y-substituted ring.⁸ It is well known that an electron donating α -substituent, such as OCH₃, causes a decrease in, or attenuation of, resonance electron donation from the substituted ring; $\rho_Y^+ = -9.3$ for the equilibrium formation of the 1-phenylethyl cation, **II**, [YC₆H₄CH(CH₃)OH + H⁺ ⇌ YC₆H₄CH⁺CH₃ + H₂O] reduces to $\rho_Y^+ = -2.2$ for the corresponding reaction with a methoxy group on the α -carbon, **III**, [YC₆H₄CCH₃(OCH₃)OH + H⁺ ⇌ YC₆H₄C⁺CH₃(OCH₃) + H₂O] due to delocalization of positive charge onto the oxygen atom of OCH₃ in **III**, causing a large decrease in the charge density on C_α.⁸

In another example, the theoretical ρ_Y^+ values at the MP2/6-31G*/MP2/6-31G* level for the protonation equilibria of 5-membered heteroaromatic aldehydes, have been calculated.

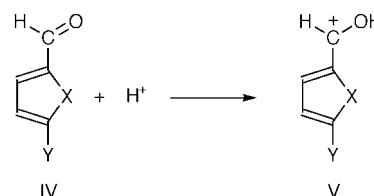
Table 2 The second-order rate constants, $k_N \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for the reactions of Y-anilino Z-thioethers with X-anilines in methanol at 45.0 °C

Y	Z	X			
		<i>p</i> -OMe	<i>p</i> -Me	H	<i>p</i> -Cl
H	<i>p</i> -Me	1.95	1.51	0.933	0.490
		1.45 ^a			0.376 ^a
		1.05 ^b			0.281 ^b
	H	4.27	3.02	1.70	0.891
	<i>p</i> -Cl	16.2	9.77	4.90	2.04
	<i>p</i> -Br	20.9	12.3	6.17	2.57
<i>p</i> -Cl	<i>p</i> -NO ₂	407	186	63.1	16.6
		310 ^a			12.5 ^a
		233 ^b			9.41 ^b
	<i>p</i> -Me	1.35	0.977	0.646	0.309
	H	3.55	2.45	1.41	0.617
	<i>p</i> -Cl	12.9	9.12	4.17	1.55
<i>m</i> -NO ₂	<i>p</i> -Br	17.8	11.2	5.62	1.95
	<i>p</i> -NO ₂	309	138	51.3	12.0
		238 ^a			
		185 ^b			
	<i>p</i> -Me	0.537	0.355	0.204	0.105
	H	1.23	0.794	0.437	0.186
<i>p</i> -Cl	<i>p</i> -Cl	4.68	2.75	1.32	0.468
	<i>p</i> -Br	6.31	3.80	1.70	0.575
	<i>p</i> -NO ₂	123	52.5	17.0	4.27

^a At 35.0 °C. ^b At 25.0 °C.



The magnitude of the ρ_Y^+ value for X = NH is small due to the strong delocalizability of the lone pair on N (n_N) in the protonated form **V**, which leads to reduced positive charge on C_α, which in turn causes a large decrease in the electron demand from the substituted ring.⁹



In the anilino thioethers, **I**, the same effect comes into play leading to a decrease in the resonance electron demand from the Y-substituted ring. The rate dependence on the pK_a of the thiolate leaving group, ($\beta_Z = \beta_{lg}$, ranges from -0.69 to -0.82 ($\rho_Z = 1.56$ – 1.86), which is also smaller than that in aqueous solution ($\beta_Z = \beta_{lg} = -0.93$).¹ Thus, the TS for methanolysis of the anilino thioethers, **I**, is considerably earlier and hence bond cleavage of the leaving group has progressed to a lesser extent with a much smaller amount of positive charge development ($\leq 1/3$) compared with that for the solvolysis in water. These ρ_Z and β_Z values, as well as the ρ_Y and β_{dg} values for the methanolysis, are close to those for the aminolysis with anilines, XC₆H₄NH₂ with X = H–*p*-Cl (*vide infra*). We therefore conclude that the solvolysis of anilino thioether in methanol would produce iminium cation intermediates with a much shorter lifetime than in water, most probably due to capture by MeOH, which is a significantly stronger nucleophile than H₂O (nucleophilicity parameters N are $+0.01$ and -0.26 for MeOH and H₂O, respectively),¹⁰ and consequently leads to enforced concerted bimolecular nucleophilic displacement by methanol.

Aminolysis

The rate constants for aminolysis, k_2 in Table 2, are faster with a stronger nucleofuge and nucleophile, as expected for a typical nucleophilic substitution reaction. The rate decreases with a stronger electron acceptor substituent (Y = *m*-NO₂) in the substrate, indicating that the reaction center carbon becomes more cationic in the TS. This is supported by the negative ρ_Y values shown in Table 3. The magnitude of ρ_Y values (-0.75 – -0.95) and approximate β_{dg} (≈ 0.25) values are slightly smaller than those for the methanolysis ($\rho_Y = -0.79$ – -1.15 and $\beta_{dg} \approx 0.30$), so that bond cleavage is slightly less than, or bond formation is slightly ahead of, that for

Table 3 The Hammett ρ_Y^a coefficients^b for the reactions of Y-anilino Z-thioethers with X-anilines

X/Z	p-Me	H	p-Cl	p-Br	p-NO ₂
p-OMe	-0.80 ± 0.03 ^c	-0.79 ± 0.14	-0.78 ± 0.11	-0.76 ± 0.15	-0.75 ± 0.07
p-Me	-0.89 ± 0.03	-0.85 ± 0.15	-0.82 ± 0.23	-0.76 ± 0.19	-0.79 ± 0.07
H	-0.95 ± 0.08	-0.87 ± 0.17	-0.84 ± 0.17	-0.83 ± 0.22	-0.83 ± 0.14
p-Cl	-0.95 ± 0.02	-0.98 ± 0.09	-0.93 ± 0.13	-0.94 ± 0.14	-0.85 ± 0.07

^a The σ values were taken from J. A. Dean, *Handbook of Organic Chemistry*, McGraw-Hill, New York, 1987, Table 7-1. ^b The correlation coefficients were better than 0.975 in all cases. ^c Standard deviations.

the methanolysis. The theoretical *ab initio* gas phase ρ_Y value obtained for the S_N2 process is -0.8,² which is in good agreement with the results of the present work in methanol. The ρ_X and β_X (β_{nuc}), and ρ_Z and β_Z (β_{lg}) values are summarized in Tables 4 and 5. In general, the magnitudes of β_X and β_Z are large, suggesting a late TS with a high degree of bond formation and cleavage. This is in contrast to an early TS for bond formation by anionic nucleophiles in aqueous solution.⁶ We note that the magnitude of ρ_X (β_X) increases with a stronger nucleofuge and that of ρ_Z (β_Z) increases with a stronger nucleophile. This means that ρ_{XZ} (and β_{XZ}) are negative, according to eqn. (1b), that is, $\delta\rho_Z/\delta\sigma_X = (+)/(-) < 0$ ⁴ (*vide infra*). Furthermore, the magnitude of both ρ_X (β_X) and ρ_Z (β_Z) increases with a stronger electron acceptor substituent (Y) in the substrate; this means that ρ_{XY} is negative while ρ_{YZ} is positive, as normally observed in a concerted nucleophilic displacement (S_N2) reaction.^{4,11} In fact, the ρ_{XY} and ρ_{YZ} values are *ca.* -0.3 and +0.1, respectively. On the other hand, ρ_{XZ} and β_{XZ} have relatively large negative values being -1.70 ± 0.18 ($r = 0.998$) and -0.27 ± 0.03 ($r = 0.998$), respectively. These large and negative ρ_{XZ} and β_{XZ} values are surprising, in view of the high degree of bond cleavage

expected in the TS from the large β_Z (β_{lg}) observed (-0.7 – -1.1) in Table 5; a large magnitude of ρ_{XZ} (β_{XZ}) is normally taken as indicating a tight TS with a low degree of bond cleavage coupled with a high degree of bond formation.⁴ In the typical S_N2 TS involving a primary carbon reaction center, the average ρ_{XZ} and β_{XZ} values are +0.33 and +0.18, respectively,^{5,12} whereas those for a secondary carbon center reduce to approximately one-third ($\rho_{XZ} \approx +0.11$ and $\beta_{XZ} \approx +0.06$).^{5,13,14} For a very loose “exploded” TS the β_{XZ} value decreases to a much lower value of *ca.* 0.01–0.03.^{4b} The negative values of β_{XZ} (and ρ_{XZ}) observed in this work, therefore, precludes the normal (backside attack) S_N2-type mechanism at a primary carbon center. In fact, a large negative β_{XZ} (and ρ_{XZ}) has been interpreted to indicate a frontside attack TS in the concerted nucleophilic substitution reactions, as shown in Table 6. The MO theoretical substrate structures show that the backside approach of the bulky aniline nucleophile to the reaction center carbon is blocked by a benzene ring in the substrate, which almost bisects the reaction center bond angle θ .^{5,15} For example, in the anilinolysis of 1-phenylethyl arene-

**Table 4** The Hammett ρ_X^a and Brønsted β_X^b (values given in parentheses) coefficients^c for the reactions of Y-anilino Z-thioethers with X-anilines

Y/Z	p-Me	H	p-Cl	p-Br	p-NO ₂
H	-1.22 ± 0.01 ^d (0.44 ± 0.01)	-1.37 ± 0.05 (0.50 ± 0.02)	-1.80 ± 0.07 (0.65 ± 0.03)	-1.81 ± 0.08 (0.65 ± 0.04)	-2.77 ± 0.01 (1.00 ± 0.05)
p-Cl	-1.29 ± 0.05 (0.47 ± 0.02)	-1.54 ± 0.04 (0.55 ± 0.02)	-1.88 ± 0.05 (0.68 ± 0.01)	-1.92 ± 0.04 (0.69 ± 0.02)	-2.85 ± 0.08 (1.03 ± 0.04)
m-NO ₂	-1.41 ± 0.07 (0.51 ± 0.03)	-1.64 ± 0.04 (0.59 ± 0.02)	-2.00 ± 0.05 (0.72 ± 0.03)	-2.09 ± 0.02 (0.75 ± 0.02)	-2.91 ± 0.04 (1.05 ± 0.06)

^a The σ values in water were taken from J. A. Dean, *Handbook of Organic Chemistry*, McGraw-Hill, New York, 1987, Table 7-1. The σ_X values are -0.27 (p-OCH₃), -0.17 (p-CH₃) and 0.23 (p-Cl). ^b The pK_a values were taken from A. Streitwieser and C. H. Heathcock, Jr., *Introduction to Organic Chemistry*, Macmillan, New York, 2nd edn., 1981, p. 737. The pK_a values are 5.34 (p-OCH₃), 5.10 (p-CH₃), 4.60 (H) and 3.98 (p-Cl). ^c The correlation coefficients were better than 0.996 in all cases. ^d Standard deviations.

Table 5 The Hammett ρ_Z^a and Brønsted β_Z^b (values given in parentheses) coefficients^c for the reaction of Y-anilino Z-thioethers with X-anilines

Y/X	p-OMe	p-Me	H	p-Cl
H	2.48 ± 0.08 ^d (-1.09 ± 0.03)	2.24 ± 0.07 (-0.99 ± 0.03)	1.96 ± 0.07 (-0.86 ± 0.02)	1.62 ± 0.06 (-0.72 ± 0.02)
p-Cl	2.49 ± 0.09 (-1.10 ± 0.03)	2.27 ± 0.10 (-1.00 ± 0.03)	2.01 ± 0.09 (-0.89 ± 0.03)	1.70 ± 0.08 (-0.74 ± 0.03)
m-NO ₂	2.52 ± 0.08 (-1.11 ± 0.03)	2.31 ± 0.09 (-1.02 ± 0.03)	2.04 ± 0.08 (-0.90 ± 0.02)	1.72 ± 0.06 (-0.76 ± 0.02)

^a The σ values in water were taken from J. A. Dean, *Handbook of Organic Chemistry*, McGraw-Hill, New York, 1987, Table 7-1. The same as in Table 4. The σ values of p-Br and p-NO₂ are 0.23 and 0.78, respectively. ^b The pK_a values in water were taken from *Dictionary of Organic Chemistry*, ed. J. Buckingham, Chapman and Hall, New York, 5th edn., 1982; for Z = p-Br and p-NO₂ pK_a values were extrapolated from the correlation pK_a = -2.26(±0.04) σ + 6.64 (±0.02), $n = 5$, $r = 0.999$. The pK_a values used are 6.82 (p-Me), 6.50 (H), 5.90 (p-Cl) 5.87 (p-Br) and 4.88 (p-NO₂). ^c The correlation coefficients were better than 0.997 in all cases. ^d Standard deviations.

Table 6 Reactions with large negative ρ_{XZ} and β_{XZ} values

Reaction	ρ_{XZ}^a	β_{XZ}^a	Ref.
1. $\text{YC}_6\text{H}_4\text{CH}(\text{CH}_3)\text{OSO}_2\text{C}_6\text{H}_4\text{Z} + \text{XC}_6\text{H}_4\text{NH}_2 \xrightarrow[25\text{ }^\circ\text{C}]{\text{MeOH}}$	−0.56	−0.32	16
2. $\text{YC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OSO}_2\text{C}_6\text{H}_4\text{Z} + \text{XC}_6\text{H}_4\text{NH}_2 \xrightarrow[65\text{ }^\circ\text{C}]{\text{MeOH}}$	−0.45	−0.28	^b
3. $\text{YC}_6\text{H}_4\text{C}(\text{CH}_3)_2\text{OSO}_2\text{C}_6\text{H}_4\text{Z} + \text{XC}_6\text{H}_4\text{NH}_2 \xrightarrow[55\text{ }^\circ\text{C}]{\text{MeCN}}$	−0.75	−0.40	17
4. $2\text{-YC}_6\text{H}_4\text{SCH}_2\text{OSO}_2\text{C}_6\text{H}_4\text{Z} + \text{XC}_6\text{H}_4\text{NH}_2 \xrightarrow[60\text{ }^\circ\text{C}]{\text{MeCN}}$	−0.50	−0.30	15
5. $\text{YC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OSO}_2\text{C}_6\text{H}_4\text{Z} + \text{XC}_6\text{H}_4\text{CH}_2\text{NH}_2 \xrightarrow[65\text{ }^\circ\text{C}]{\text{MeOH}}$	−0.13	−0.21	^c
6. $\text{YC}_6\text{H}_4\text{N}(\text{CH}_3)\text{CH}_2\text{SC}_6\text{H}_4\text{Z} + \text{XC}_6\text{H}_4\text{NH}_2 \xrightarrow[45\text{ }^\circ\text{C}]{\text{MeOH}}$	−1.70	−0.27	This work

^a The magnitude of ρ_{XZ} depends on the fall-off due to intervening groups, such as CH_2 , SO_2 , NCH_3 , *etc.*, between the substituent and reaction center. However, β_{XZ} does not suffer from such an effect, thus it provides a judicious comparison of the magnitude between different reaction series. ^b I. Lee, Y. H. Choi and H. W. Lee, *J. Chem. Soc., Perkin Trans. 2*, 1988, 1537. ^c I. Lee, W. H. Lee and H. W. Lee, *J. Phys. Org. Chem.*, 1990, 3, 545.

sulfonates (entry 1 in Table 6),¹⁶ we obtained large negative values of ρ_{XZ} (−0.56) and β_{XZ} (−0.32). For this reaction, kinetic isotope effects involving deuterated anilines ($\text{XC}_6\text{H}_4\text{ND}_2$) were relatively large, $k_{\text{H}}/k_{\text{D}} = 1.7\text{--}2.6$,⁵ indicating that the amino hydrogens are hydrogen bonded to the negatively charged leaving group oxygen atom in the frontside attack mechanism with a four-center type TS. Similarly, for the anilinolysis of cumyl arenesulfonates (Table 6, entry 3) the large negative ρ_{XZ} (−0.75) and β_{XZ} (−0.40)^{5,17} values are interpreted to indicate a frontside attack $\text{S}_{\text{N}}2$ mechanism. This is again in contrast to the dissociative (“exploded”) TS proposed for the $\text{S}_{\text{N}}2$ reaction of the anilino thioethers with anionic nucleophiles in aqueous solution,⁶ in which there is a relatively weak interaction between the nucleophile and leaving group with a very small positive β_{XZ} value (*i.e.* about 0.01–0.03),^{4b} if it were possible to determine the β_{XZ} value in aqueous solution. The much larger negative ρ_{XZ} value obtained in this work (compared to the other entries in Table

6) is most likely due to the thiophenoxide nucleofuge, since the larger and more polarizable sulfur allows it to interact at greater internuclear distances than does oxygen. This fact provides an alternative interpretation (to frontside attack $\text{S}_{\text{N}}2$) of the large negative ρ_{XZ} obtained, *i.e.* that it is due to this large polarizability of sulfur. In this sense, the magnitude of β_{XZ} (similar to the other entries) should be a more reliable measure of intermolecular interaction.

In view of these results the large negative ρ_{XZ} and β_{XZ} values obtained in the present work are highly suggestive of the involvement of a similar frontside attack $\text{S}_{\text{N}}2$ TS.

We have determined the secondary kinetic isotope effects ($k_{\text{H}}/k_{\text{D}}$) involving deuterated aniline nucleophiles ($\text{XC}_6\text{H}_4\text{ND}_2$), as shown in Table 7. The $k_{\text{H}}/k_{\text{D}}$ values are all substantially less than unity, suggesting that bond formation is relatively well progressed in the TS.⁵ This is consistent with the relatively large ρ_{X} and β_{X} values in Table 4. We note that an electron acceptor substituent on the substrate ($\text{Y} = m\text{-}$

Table 7 The secondary kinetic isotope effects for the reactions of Y-anilino Z-thioethers with deuterated X-anilines in MeOD at 45.0 °C

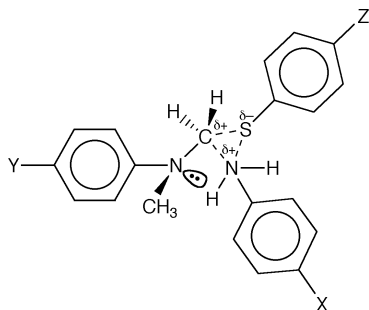
X	Y	Z	$k_{\text{H}} \times 10^3/\text{M}^{-1} \text{ s}^{-1}$	$k_{\text{D}} \times 10^3/\text{M}^{-1} \text{ s}^{-1}$	$k_{\text{H}}/k_{\text{D}}$
<i>p</i> -OMe	H	<i>p</i> -Br	20.9 ± 0.4	24.8 ± 0.5	0.843 ± 0.002^a
<i>p</i> -Cl	H	<i>p</i> -Me	0.490 ± 0.002	0.570 ± 0.003	0.860 ± 0.006
<i>p</i> -OMe	H	<i>p</i> -Me	1.95 ± 0.07	2.24 ± 0.05	0.871 ± 0.004
<i>p</i> -Cl	H	<i>p</i> -Br	2.57 ± 0.02	2.96 ± 0.01	0.867 ± 0.007
<i>p</i> -OMe	<i>m</i> -NO ₂	<i>p</i> -Br	6.31 ± 0.03	7.30 ± 0.02	0.864 ± 0.005
<i>p</i> -Cl	<i>m</i> -NO ₂	<i>p</i> -Me	0.105 ± 0.006	0.120 ± 0.005	0.875 ± 0.006

^a Standard deviations.

Table 8 Activation parameters^a for the reactions of anilino thioethers with anilines in methanol

X	Y	Z	$\Delta H^\ddagger/\text{kcal mol}^{-1}$	$-\Delta S^\ddagger/\text{cal mol}^{-1} \text{ K}^{-1}$
<i>p</i> -OMe	H	<i>p</i> -NO ₂	4.6 ± 0.6	46 ± 1
<i>p</i> -OMe	H	<i>p</i> -Me	5.2 ± 0.6	55 ± 1
<i>p</i> -Cl	H	<i>p</i> -NO ₂	4.7 ± 0.6	52 ± 1
<i>p</i> -Cl	H	<i>p</i> -Me	4.6 ± 0.6	59 ± 2
<i>p</i> -OMe	<i>p</i> -Cl	<i>p</i> -NO ₂	4.2 ± 0.6	48 ± 2

^a Calculated by the Eyring equation. Errors shown are the maximum errors. K. B. Wiberg, *Physical Organic Chemistry*, Wiley, New York, 1964, p. 378.



Scheme 1 Proposed TS structure.

NO_2) leads to a larger $k_{\text{H}}/k_{\text{D}}$ value, indicating a looser bond formation. However, this is in contradiction to the greater magnitude of ρ_{X} (and β_{X}) for a stronger electron acceptor Y, which is normally taken as leading to tighter bond formation. This discrepancy may be resolved by assuming a frontside attack $\text{S}_{\text{N}}2$ TS, in which a stronger electron acceptor Y leads to more extensive bond cleavage (a larger magnitude of ρ_{Z} and β_{Z} in Table 5). In this way the N–H(D) vibrations in the attacking aniline are sterically relieved and as a result a larger $k_{\text{H}}/k_{\text{D}}$ is obtained.⁵ In the present reaction, the amino hydrogens do not form hydrogen bonds to the sulfur atom of the departing thiophenoxide, so that inverse secondary kinetic isotope effects, $k_{\text{H}}/k_{\text{D}} < 1.0$, are observed, in contrast to a four-center type TS, with the primary kinetic isotope effects, observed for the reaction series listed in Table 6.

Finally, we have determined activation parameters, ΔH^\ddagger and ΔS^\ddagger , based on rate data at three temperatures. The results in Table 8 show that both ΔH^\ddagger and ΔS^\ddagger are relatively small with little variation with respect to changes in the substituents X, Y and Z. Strong interaction between the nucleophile and leaving group in a frontside attack $\text{S}_{\text{N}}2$ TS, as indicated by the large negative ρ_{XZ} and β_{XZ} values, will no doubt stabilize the TS electrostatically (Scheme 1) so that both the energy and entropy are lowered. It is also possible that the interaction between leaving group and nucleophile is solvent mediated.

In summary, the solvolysis of anilino thioethers, **I**, in methanol produces iminium ions with much shorter lifetimes than in water, and proceeds by concerted nucleophilic displacement ($\text{S}_{\text{N}}2$ mechanism) by methanol. The aminolysis reactions also proceed through a direct displacement by the nucleophile, aniline, with a rather late TS, in which both bond formation and bond cleavage have progressed to a large extent. The large negative cross-interaction constants obtained ($\rho_{\text{XZ}} \simeq -1.7$, $\beta_{\text{XZ}} = -0.27$), however, suggest a frontside attack $\text{S}_{\text{N}}2$ transition state in which the nucleophile and leaving group are in close proximity and can interact strongly. The inverse secondary kinetic isotope effects involving deuterated aniline nucleophiles and the small activation parameters, ΔH^\ddagger and ΔS^\ddagger , are consistent with the proposed TS structure.

Experimental

Materials

Thiophenol derivatives, *N*-methylaniline, 4-chloro-*N*-methylaniline and 3-nitroaniline, used for the preparation of the substrate, were Aldrich G. R. grade. The nucleophile anilines were Tokyo Kasei G. R. grade. The solvent methanol was G. R. grade. 3-Nitro-*N*-methylaniline was prepared from 3-nitroaniline by the method of Lucier *et al.*¹⁸ in 70% yield.

3-Nitro-*N*-methylaniline. Mp 62–63 °C; ^1H NMR (400 MHz, CDCl_3): δ 2.90 (3H, d, CH_3), 4.13 (1H, br s, NH), 6.85–

7.52 (4H, m, aromatic ring); ^{13}C NMR (100.4 MHz, CDCl_3): δ 149.9, 149.3, 129.5, 118.4, 111.6, 105.6, 30.4.

Preparation of *N*-methyl-*N*-[(aryltio)methyl]anilines

Following the method of Grillot and Schaffrath,¹⁹ thiophenol, *N*-methylaniline and formaldehyde (1 : 1 : 1) were reacted in ethanol at 80 °C. The reaction mixture was extracted with diethyl ether, which was dried over MgSO_4 , and the solvent removed by distillation under reduced pressure. The mixture was purified by column chromatography (silica gel, 10% ethyl acetate–hexane) and the products were identified by IR, ^1H and ^{13}C NMR spectroscopy as follows. The yields ranged from 70 to 95%.

$\text{C}_6\text{H}_5\text{N}(\text{CH}_3)\text{CH}_2\text{SC}_6\text{H}_5$.¹⁹ Mp, 36–38 °C; IR (KBr)/ cm^{-1} : 3060 (C–H), 1598, 1501 (C=C, aromatic), 746 (C–H, aromatic); ^1H NMR (400 MHz, CDCl_3): δ 2.82 (3H, s, CH_3), 4.90 (2H, s, CH_2), 6.74–7.21 (9H, m, aromatic ring); ^{13}C NMR (100.4 MHz, CDCl_3): δ 147.0, 135.6, 129.1, 128.9, 128.7, 127.2, 127.0, 118.1, 113.8, 61.9, 38.4. Calc. for $\text{C}_{14}\text{H}_{15}\text{NS}$: C, 73.3; H, 6.60. Found C, 73.5; H, 6.61%.

$\text{C}_6\text{H}_5\text{N}(\text{CH}_3)\text{CH}_2\text{SC}_6\text{H}_4\text{-4-Cl}$.¹⁹ Mp 44–46 °C; IR (KBr)/ cm^{-1} : 3060 (C–H), 1599, 1503 (C=C, aromatic), 749 (C–H, aromatic); ^1H NMR (400 MHz, CDCl_3): δ 2.89 (3H, s, CH_3), 4.95 (2H, s, CH_2), 6.77–7.41 (9H, m, aromatic ring); ^{13}C NMR (100.4 MHz, CDCl_3): δ 147.0, 134.6, 134.1, 133.4, 129.2, 129.0, 128.9, 118.5, 114.1, 62.5, 38.7. Calc. for $\text{C}_{14}\text{H}_{14}\text{ClNS}$: C, 63.7; H, 5.32. Found C, 63.8; H, 5.31%.

$\text{C}_6\text{H}_5\text{N}(\text{CH}_3)\text{CH}_2\text{SC}_6\text{H}_4\text{-4-CH}_3$. Liquid; IR (KBr)/ cm^{-1} : 3024 (C–H), 1599, 1499 (C=C, aromatic), 749 (C–H, aromatic); ^1H NMR (400 MHz, CDCl_3): δ 2.30 (3H, s, methyl), 2.86 (3H, s, CH_3), 4.90 (2H, s, CH_2), 6.77–7.37 (9H, m, aromatic ring); ^{13}C NMR (100.4 MHz, CDCl_3): δ 147.0, 137.2, 133.7, 131.9, 129.6, 128.9, 128.4, 118.1, 113.8, 62.3, 38.6. Calc. for $\text{C}_{15}\text{H}_{17}\text{NS}$: C, 74.0; H, 7.01. Found C, 74.2; H, 7.02%.

$\text{C}_6\text{H}_5\text{N}(\text{CH}_3)\text{CH}_2\text{SC}_6\text{H}_4\text{-4-Br}$. Mp 55–57 °C; IR (KBr)/ cm^{-1} : 3053 (C–H), 1599, 1501 (C=C, aromatic), 749, 689 (C–H, aromatic); ^1H NMR (400 MHz, CDCl_3): δ 2.87 (3H, s, CH_3), 4.93 (2H, s, CH_2), 6.45–7.40 (9H, m, aromatic ring); ^{13}C NMR (100.4 MHz, CDCl_3): δ 147.0, 134.8, 134.6, 132.1, 131.8, 129.2, 129.0, 121.4, 118.5, 114.0, 62.3, 38.7. Calc. for $\text{C}_{14}\text{H}_{14}\text{BrNS}$: C, 54.6; H, 4.62. Found C, 54.7; H, 4.63%.

$\text{C}_6\text{H}_5\text{N}(\text{CH}_3)\text{CH}_2\text{SC}_6\text{H}_4\text{-4-NO}_2$.¹ Mp 61–63 °C; IR (KBr)/ cm^{-1} : 3368 (C–H), 1519, 1502 (C=C, aromatic), 680 (C–H, aromatic); ^1H NMR (400 MHz, CDCl_3): δ 2.01 (3H, s, CH_3), 4.89 (2H, s, CH_2), 7.01–7.64 (9H, m, aromatic ring); ^{13}C NMR (100.4 MHz, CDCl_3): δ 147.7, 143.9, 126.3, 126.2, 124.3, 124.2, 104.1, 103.9, 103.8, 103.7, 103.6, 64.3, 38.5. Calc. for $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_2\text{S}$: C, 61.3; H, 5.10. Found C, 61.2; H, 5.12%.

4- $\text{ClC}_6\text{H}_4\text{N}(\text{CH}_3)\text{CH}_2\text{SC}_6\text{H}_5$. Mp 47–49 °C; IR (KBr)/ cm^{-1} : 3059 (C–H), 1526, 1622 (C=C, aromatic), 735, 692 (C–H, aromatic); ^1H NMR (400 MHz, CDCl_3): δ 2.82 (3H, s, CH_3), 4.89 (2H, s, CH_2), 7.49–6.64 (9H, m, aromatic ring); ^{13}C NMR (100.4 MHz, CDCl_3): δ 145.8, 136.9, 135.3, 133.4, 130.7, 129.4, 129.3, 129.1, 128.9, 127.4, 115.1, 113.3, 61.9, 38.7. Calc. for $\text{C}_{14}\text{H}_{14}\text{ClNS}$: C, 63.7; H, 5.32. Found C, 63.5; H, 5.32%.

4- $\text{ClC}_6\text{H}_4\text{N}(\text{CH}_3)\text{CH}_2\text{SC}_6\text{H}_4\text{-4-Cl}$. Mp 55–57 °C; IR (KBr)/ cm^{-1} : 3093 (C–H), 1523, 1622 (C=C, aromatic), 689, 735 (C–H, aromatic); ^1H NMR (400 MHz, CDCl_3): δ 2.90 (3H, s, CH_3), 4.89 (2H, s, CH_2), 6.49–7.35 (8H, m, aromatic ring); ^{13}C NMR (100.4 MHz, CDCl_3): δ 147.8, 145.6, 134.7, 133.7, 129.1, 128.9, 123.5, 121.6, 115.4, 113.6, 113.4, 62.3, 38.9.

Calc. for $C_{14}H_{13}Cl_2NS$: C, 56.4; H, 4.41. Found C, 56.7; H, 4.43%.

4-ClC₆H₄N(CH₃)CH₂SC₆H₄-4-CH₃. Mp 40–43 °C; IR (KBr)/cm⁻¹: 3026 (C–H), 1635, 1535 (C=C, aromatic), 729, 688 (C–H, aromatic); ¹H NMR (400 MHz, CDCl₃): δ 2.32 (3H, s, CH₃), 2.84 (3H, s, CH₃), 4.86 (2H, s, CH₂), 6.65–7.34 (8H, m, aromatic ring); ¹³C NMR (100.4 MHz, CDCl₃): δ 145.8, 136.8, 133.9, 133.8, 131.5, 129.8, 129.7, 128.9, 128.8, 123.1, 115.1, 115.0, 62.3, 38.9, 21.2. Calc. for $C_{15}H_{16}ClNS$: C, 64.9; H, 5.81. Found C, 64.7; H, 5.83%.

4-ClC₆H₄N(CH₃)CH₂SC₆H₄-4-Br. Mp 60–63 °C; IR (KBr)/cm⁻¹: 3093 (C–H), 1622, 1523 (C=C, aromatic), 739, 687 (C–H, aromatic); ¹H NMR (400 MHz, CDCl₃): δ 2.85 (3H, s, CH₃), 4.91 (2H, s, CH₂), 6.66–7.39 (8H, m, aromatic ring); ¹³C NMR (100.4 MHz, CDCl₃): δ 145.7, 135.0, 134.9, 134.5, 132.1, 128.9, 123.6, 121.8, 115.2, 62.2, 38.9. Calc. for $C_{14}H_{13}BrClNS$: C, 49.1; H, 3.81. Found C, 49.3; H, 3.82%.

4-ClC₆H₄N(CH₃)CH₂SC₆H₄-4-NO₂. Mp 68–71 °C; IR (KBr)/cm⁻¹: 3367 (C–H), 1518 (C=C, aromatic), 749, 681 (C–H, aromatic); ¹H NMR (400 MHz, CDCl₃): δ 2.90 (3H, s, CH₃), 4.89 (2H, s, CH₂), 7.02–7.62 (8H, m, aromatic ring); ¹³C NMR (100.4 MHz, CDCl₃): δ 147.8, 143.7, 126.3, 126.1, 124.5, 124.1, 104.5, 103.9, 103.9, 103.7, 103.6, 103.4, 64.2, 38.1. Calc. for $C_{14}H_{13}ClN_2O_2S$: C, 54.5; H, 4.21. Found C, 54.7; H, 4.22%.

3-NO₂C₆H₄N(CH₃)CH₂SC₆H₅.¹ Liquid; IR (KBr)/cm⁻¹: 3061 (C–H), 1598, 1526 (C=C, aromatic), 737, 691 (C–H, aromatic); ¹H NMR (400 MHz, CDCl₃): δ 2.90 (3H, s, CH₃), 4.92 (2H, s, CH₂), 6.96–7.55 (9H, m, aromatic ring); ¹³C NMR (100.4 MHz, CDCl₃): δ 148.9, 147.7, 134.1, 133.7, 129.4, 128.9, 127.8, 127.2, 119.0, 112.2, 107.7, 60.9, 38.7. Calc. for $C_{14}H_{14}N_2O_2S$: C, 61.3; H, 5.10. Found C, 61.5; H, 5.12%.

3-NO₂C₆H₄N(CH₃)CH₂SC₆H₄-4-Cl.¹ Liquid; IR (KBr)/cm⁻¹: 3068 (C–H), 1599, 1523 (C=C, aromatic), 690, 738 (C–H, aromatic); ¹H NMR (400 MHz, CDCl₃): δ 2.90 (3H, s, CH₃), 4.93 (2H, s, CH₂), 6.98–7.60 (8H, m, aromatic ring); ¹³C NMR (100.4 MHz, CDCl₃): δ 149.1, 147.8, 135.2, 134.3, 132.8, 129.6, 129.3, 119.2, 112.6, 108.0, 61.4, 38.9. Calc. for $C_{14}H_{13}ClN_2O_2S$: C, 54.5; H, 4.21. Found C, 54.7; H, 4.23%.

3-NO₂C₆H₄N(CH₃)CH₂SC₆H₄-4-CH₃.¹ Liquid; IR (KBr)/cm⁻¹: 3025 (C–H), 1598, 1525 (C=C, aromatic), 740, 691 (C–H, aromatic); ¹H NMR (400 MHz, CDCl₃): δ 2.28 (3H, s, CH₃), 2.88 (3H, s, CH₃), 4.87 (2H, s, CH₂), 6.95–7.54 (8H, m, aromatic ring); ¹³C NMR (100.4 MHz, CDCl₃): δ 149.1, 147.9, 138.2, 134.2, 130.5, 129.9, 129.5, 119.1, 112.2, 107.9, 61.3, 38.9, 21.1. Calc. for $C_{15}H_{16}N_2O_2S$: C, 62.5; H, 5.60. Found C, 62.7; H, 5.62%.

3-NO₂C₆H₄N(CH₃)CH₂SC₆H₄-4-Br. Liquid; IR (KBr)/cm⁻¹: 3089 (C–H), 1598, 1523 (C=C, aromatic), 741, 689 (C–H, aromatic); ¹H NMR (400 MHz, CDCl₃): δ 2.91 (3H, s, CH₃), 4.92 (2H, s, CH₂), 6.96–7.57 (8H, m, aromatic ring); ¹³C NMR (100.4 MHz, CDCl₃): δ 149.0, 137.7, 135.2, 132.1, 131.8, 129.6, 129.5, 129.2, 119.2, 112.5, 107.9, 62.1, 38.9. Calc. for $C_{14}H_{13}BrN_2O_2S$: C, 47.6; H, 3.71. Found C, 47.8; H, 3.73%.

3-NO₂C₆H₄N(CH₃)CH₂SC₆H₄-4-NO₂. Mp 41–43 °C; IR (KBr)/cm⁻¹: 3367 (C–H), 1594, 1525 (C=C, aromatic), 741, 691 (C–H, aromatic); ¹H NMR (400 MHz, CDCl₃): δ 2.91 (3H, s, CH₃), 4.90 (2H, s, CH₂), 7.63–7.01 (8H, m, aromatic ring); ¹³C NMR (100.4 MHz, CDCl₃): δ 147.9, 143.8, 126.5, 126.4, 124.0, 123.9, 104.7, 103.7, 103.5, 103.3, 64.3, 38.7. Calc. for $C_{14}H_{13}N_3O_4S$: C, 52.7; H, 4.11. Found C, 52.5; H, 4.13%.

Kinetic procedures

Rates were measured conductimetrically²⁰ at 45.0 ± 0.05 °C. Pseudo-first-order rate constants, k_{obs} , were determined by the Guggenheim method.²¹ Second-order rate constants were obtained from the slope of a plot of k_{obs} vs. [Nu], eqn. (2). The k_2 values in Tables 1 and 2 are the averages of more than two runs and are reproducible to ± 3%. Nucleophile concentration ranged from 0.20 to 0.40 M.

Product analysis

Products were characterized as anilides and methyl ethers in all cases. For example, *N*-methyl-*N*-[(4-bromophenylthio)methyl]-3-nitroaniline (0.05 mol) and 4-methoxyaniline (0.5 mol) were reacted at 45 °C in methanol for 5 h. The reaction mixture was extracted with ether and the solvent was removed by distillation under reduced pressure. Anilide (yield, 80%) and diethyl ether (yield, 8%) were separated by column chromatography. The spectral data are as follows.

3-NO₂C₆H₄N(CH₃)CH₂NHC₆H₄-4-OMe. Liquid; IR (KBr)/cm⁻¹: 3365 (C–H), 3162 (N–H), 1610, 1475 (C=C, aromatic), 1358 (N=O), 825 (C–H, aromatic); ¹H NMR (400 MHz, CDCl₃): δ 2.95 (3H, s, N–CH₃), 3.78 (3H, s, –OCH₃), 4.13 (1H, br, NH), 7.63–6.99 (8H, m, aromatic ring); ¹³C NMR (100.4 MHz, CDCl₃): δ 149.2, 147.8, 135.4, 133.5, 132.2, 129.7, 122.4, 119.2, 112.7, 108.1, 61.4, 53.5, 39.0.

3-NO₂C₆H₄N(CH₃)CH₂OCH₃. Liquid; IR (KBr)/cm⁻¹: 3345 (C–H), 1530, 1519 (C=C, aromatic), 735, 689 (C–H, aromatic); ¹H NMR (400 MHz, CDCl₃): δ 2.92 (3H, s, N–CH₃), 3.77 (3H, s, –OCH₃), 4.95 (2H, s, CH₂), 7.52–6.85 (4H, m, aromatic ring); ¹³C NMR (100.4 MHz, CDCl₃): δ 149.5, 135.5, 132.0, 129.6, 119.0, 111.2, 105.7, 30.5, 21.1.

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