# Kinetics and mechanism of the aminolysis of aryl propanedithioates in acetonitrile†

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The kinetics and mechanism of the aminolysis of aryl proanedithioates with benzylamines are investigated in acetonitrile at $-35.0\,^\circ$C. A large magnitude of the Hammett ($\rho_X$ and $\rho_Z$) and Brönsted ($\beta_X$ and $\beta_Z$) coefficients and exceptionally large cross-interaction constant $\rho_{XZ}(=3.5)$ are consistent with a stepwise mechanism in which leaving group expulsion from an intermediate, $T^\pm$, is the rate-determining step. The faster rates observed for dithio esters (**II**) than for thio esters (**I**), and the validity of the reactivity-selectivity principle (RSP) are also in line with the mechanism proposed. The $k_H/k_D$ values ($=1.0$–$1.8$) determined with deuterated benzylamines ($XC_6H_4CH_2ND_2$) and the activation parameters, $\Delta H^\neq(\simeq 8\text{ kcal mol}^{-1})$ and $\Delta S^\neq(=-16\text{ to }-23\text{ e.u.})$, suggest that proton transfer occurs concurrently with leaving group departure in the transition state.

In the aminolysis of thio esters (**I**), it has been shown that replacing them by dithio esters (**II**) [eqn. (1)] results in a weaker push, provided by the $S^-$, to expel the amine, $R_2NH$, from the zwitterionic tetrahedral intermediate, $T^\pm$. This leads to a lowering of $pK_a^o$,[1] where $k_{-a} = k_b$, by decreasing $k_{-a}$ more than $k_b$, thus, decreasing the ratio $k_{-a}/k_b$. This lowering of $pK_a^o$ was found to change the mechanism of the aminolysis of *S*-aryl ethanethioates (**Ia**) with benzylamines ($pK_a \geqslant 9.0$) from a stepwise one with rate-limiting expulsion of the leaving group, $ArS^-$ from $T^\pm$ ($k_b$) with a $\beta_X(=\beta_{nuc})$ of 1.36 to a rate-limiting formation of $T^\pm$ for aryl ethanedithioates (**IIa**) in acetonitrile ($\beta_X = 0.55$), since in the latter case the $pK_a^o$ is lower than the $pK_a$s of the benzylamines used,[2] which may be caused by the destabilization of $T^\pm$ due to the solvent, acetonitrile. It is well-known that a mechanistic change occurs at the $pK_a^o$ where the Brönsted $\beta_{nuc}(\beta_X)$ value changes from a large ($\beta_{nuc} \geqslant 0.8$) to a small ($\beta_{nuc} \leqslant 0.3$) value as the basicity of the amine nucleophile is increased.[3] However, the mechanistic change from a stepwise one for *S*-aryl phenylethanethioates[4] (**Ic**) to a concerted one for aryl phenylethanedithioates[5] (**IIc**) was not observed with benzylamine nucleophiles in acetonitrile. The change of $R = CH_3$ (**a**) to $C_6H_5CH_2$ (**c**) in **I** (and **II**) appears to raise the $pK_a^o$ value due to an electron-withdrawing effect of the phenyl ring in the latter compounds.

In view of the sensitive variation of the aminolysis mechanism depending on the stereoelectronic effects of the R group, we extend our work in this paper to the aminolysis with benzylamines of the dithio series involving $R = CH_3CH_2$ (**IIb**), for which a stepwise mechanism with rate-limiting expulsion of the leaving group ($ArS^-$) has been reported for the *S*-aryl propanethioate analogues, (**Ib**), with $\beta_X = 2.11$ in acetonitrile.[6]

One of the reasons for choosing $R = CH_3CH_2$ (**IIb**) in the present work is that in the aminolysis of the three thio esters (**Ia**–**c**) with benzylamines in acetonitrile,[4,6,7] the magnitudes of $\rho_X(=\rho_{nuc})$, $\beta_X(=\beta_{nuc})$ and $\rho_{XZ}$ were found to be the largest and also the rate $k_N$, [see eqn. (3) below] was the fastest for **Ib** among the three substrates. $\rho_{XZ}$ is defined by eqn. (2)[8] where X and Z are the substituents in the nucleophile ($XC_6H_4CH_2NH_2$) and leaving group ($ZC_6H_4S^-$).

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

$$\rho_{XZ} = \partial \rho_Z / \partial \sigma_X = \partial \rho_X / \partial \sigma_Z \tag{2b}$$
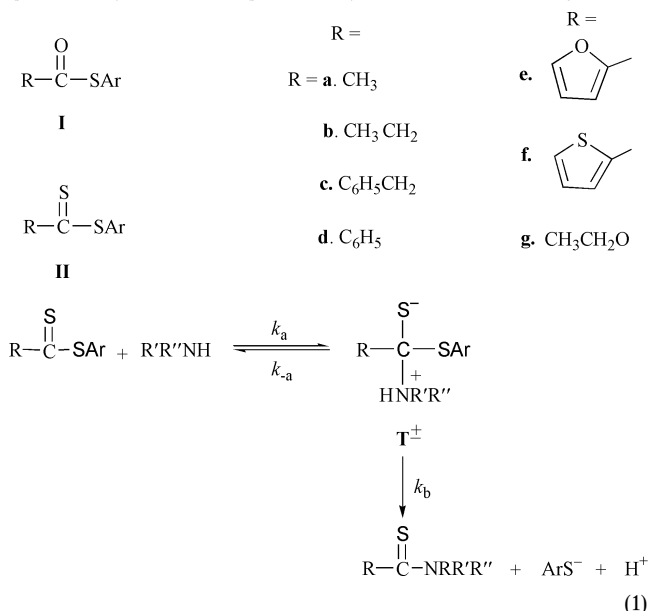
The aminolysis of all three thio esters (**Ia**–**c**) with benzylamines was found to proceed by a stepwise mechanism with rate-limiting expulsion of the leaving group from $T^\pm$, and the rate constants ($k_N$) observed for these reactions can be expressed as:

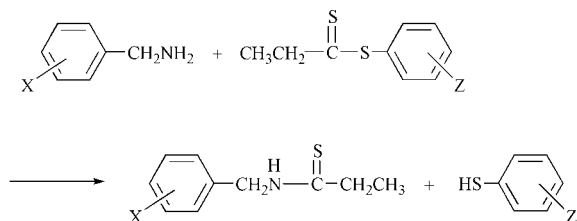$$k_N = (k_a/k_{-a}) \cdot k_b = K \cdot k_b \tag{3}$$

It is therefore of some interest to examine whether the same trends also hold for the dithio esters (**IIa**–**c**) and if so, what could be the causes for this seemingly odd behavior exhibited by the compounds with $R = CH_3CH_2$ in the aminolysis of the two series of esters, **Ia**–**c** and **IIa**–**c**.

## Results and discussion

The aminolysis of aryl propanedithioates (**IIb**) with an excess amount of benzylamines (Scheme 1) in acetonitrile obeyed the

$$\begin{array}{c}
\text{O} \\
\parallel \\
R-C-SAr
\end{array}$$

**I**

$$\begin{array}{c}
\text{S} \\
\parallel \\
R-C-SAr
\end{array}$$

**II**

R =
R = **a**. CH$_3$
**b**. CH$_3$CH$_2$
**c**. C$_6$H$_5$CH$_2$
**d**. C$_6$H$_5$

R =
**e**. (furan)
**f**. (thiophene)
**g**. CH$_3$CH$_2$O

$$\begin{array}{c}
\text{S} \\
\parallel \\
R-C-SAr + R'R''NH
\end{array} \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} \begin{array}{c}
\text{S}^- \\
\mid \\
R-C-SAr \\
\mid + \\
HNR'R''
\end{array}$$

$$T^\pm$$

$$\downarrow k_b$$

$$\begin{array}{c}
\text{S} \\
\parallel \\
R-C-NRR'R'' \ + \ ArS^- \ + \ H^+
\end{array}$$

$$\tag{1}$$

† Non-SI units employed: 1 kcal = 4.184 kJ.

**Scheme 1**

simple rate law given by eqn. (4) and (5), where [S] and [Nu] are the concentrations of substrate (**IIb**) and benzylamine nucleophile, respectively.

$$\text{Rate} = k_{\text{obs}}[\text{S}] \qquad (4)$$

$$k_{\text{obs}} = k_{\text{N}}[\text{Nu}] \qquad (5)$$

The $k_{\text{N}}$ values were determined from the slopes of linear plots of $k_{\text{obs}}$ *vs.* [Nu], eqn. (5) and are summarized in Table 1 together with the Hammett ($\rho_{\text{X}}$ and $\rho_{\text{Z}}$) and Brönsted ($\beta_{\text{X}}$ and $\beta_{\text{Z}}$) coefficients. The rates ($k_{\text{N}}$) and selectivity parameters, including the cross-interaction constants $\rho_{\text{XZ}}$ [eqn. (2)] for the reactions of thio (**I**) and dithio esters (**II**) with benzylamines in acetonitrile are compared together with those for the reactions of other related R groups in Table 2. Surprisingly, the rates are the fastest with R = CH$_3$CH$_2$ among various esters with different R groups in each series of compounds, **Ia–d** and **IIa–f**. For example, for the thio esters, **I**, the rates increase in the order R = C$_6$H$_5$CH$_2$(**c**)[4] < CH$_3$(**a**)[7] < CH$_3$CH$_2$(**b**)[6], and

for the dithio esters, **II**, the rates increase in the order R = CH$_3$(**a**)[2] < C$_6$H$_5$CH$_2$(**c**)[2] < CH$_3$CH$_2$(**b**) (given that at $-25\,^{\circ}$C the rate constant for **IIb** should be more than twice the value at $-35\,^{\circ}$C). It is notable that the rate-limiting formation of T$^{\pm}$ was found only for **IIa** and **d**, and for all other esters (**Ia–d** and **IIb, c, e, f**) the stepwise mechanism with rate-limiting expulsion of the leaving group (LG), ArS$^-$, was found to apply. Furthermore, the rates of reaction of the dithio esters, **II**, are much faster than those of the thio esters, **I**. These trends are in fact in line with the stepwise mechanism, eqn. (1), with rate-limiting expulsion of the leaving group ($k_{\text{b}}$). If the aminolysis mechanism of esters **I** and **II** (excluding **IIa** and **d**) were concerted or stepwise with rate-limiting formation of the intermediate, T$^{\pm}$, the rates of reaction of the thiol esters (**Ia–c**) should have been faster since mixing of the C=O $\pi^*$ orbital and the $\sigma^*$ LUMO of the breaking C–LG bond is stronger due to the narrower energy gap between $\pi^*$ and $\sigma^*$ than the corresponding mixing between $\pi^*_{\text{C=S}}$ and $\sigma^*_{\text{C–LG}}$, which has been shown to lead to a greater possibility of the tetrahedral species becoming a TS rather than a stable adduct[9] for the carbonyl (**I**) than the thiocarbonyl (**II**) esters.

There are examples of aminolysis reactions that are in agreement with these arguments: Castro *et al.*, reported on the aminolyses of *O*-ethyl *S*-aryl thiocarbonates [C$_2$H$_5$OC(=O)SAr; **Ig**][10] and aryl *O*-ethyl dithiocarbonates [C$_2$H$_5$OC(=S)SAr; **IIg**][11] with substituted pyridines (XC$_5$H$_4$N) in aqueous solution. For both dinitrophenyl [Ar = 2,4-(NO$_2$)$_2$C$_6$H$_3$] and trinitrophenyl [Ar = 2,4,6-(NO$_2$)$_3$C$_6$H$_2$] compounds, rates with dithio (**IIg**) esters were faster below the p$K_{\text{a}}^{\text{o}}$ ($\simeq 7$ for DNPDTC and $\simeq 6$ for

**Table 1** The second order rate constants, $k_{\text{N}}$ (M$^{-1}$ s$^{-1}$) for the reactions of aryl propanedithioates [EtC(=S)SC$_6$H$_4$Z] with benzylamines (XC$_6$H$_4$CH$_2$NH$_2$) in acetonitrile at $-35.0\,^{\circ}$C

| X | Z | | | | $\rho_{\text{Z}}{}^{a}$ | $\beta_{\text{Z}}{}^{b}$ |
| | *p*-Me | H | *p*-Cl | *p*-Br | | |
|---|---|---|---|---|---|---|
| *p*-OMe | 23.2 | 42.9 | 111 | 116 | $1.74 \pm 0.05$ | $-0.73 \pm 0.04$ |
| *p*-Me | 9.68 | 20.3 | 70.9 | 84.5 | $2.29 \pm 0.16$ | $-0.93 \pm 0.02$ |
| H | 14.9$^c$ | | | 202$^c$ | | |
| | 7.25$^d$ | | | 98.2$^d$ | | |
| | 3.42 | 9.84 | 39.5 | 47.8 | $2.77 \pm 0.12$ | $-1.14 \pm 0.11$ |
| *p*-Cl | 0.800 | 3.46 | 21.5 | 26.7 | $3.68 \pm 0.14$ | $-1.52 \pm 0.17$ |
| *m*-Cl | 1.45$^c$ | | | 59.1$^c$ | | |
| | 0.698$^d$ | | | 28.9$^d$ | | |
| | 0.310 | 1.31 | 10.2 | 14.1 | $3.99 \pm 0.22$ | $-1.63 \pm 0.12$ |
| $\rho_{\text{X}}{}^{e}$ | $-2.86 \pm 0.07$ | $-2.24 \pm 0.11$ | $-1.53 \pm 0.09$ | $-1.39 \pm 0.06$ | $\left.\right\}\rho_{\text{XZ}}{}^{f} = 3.51 \pm 0.29$ | |
| $\beta_{\text{X}}{}^{g}$ | $2.80 \pm 0.04$ | $2.19 \pm 0.10$ | $1.49 \pm 0.10$ | $1.35 \pm 0.08$ | | |

$^a$ The $\sigma$ values were taken from C. Hansch, A. Leo and R. W. Taft, *Chem. Rev.*, 1991, **91**, 165. Coefficients were better than 0.995 in all cases. $^b$ The p$K_{\text{a}}$ values were taken from J. Buckingham, *Dictionary of Organic Chemistry*, 5th edn., Chapman and Hall, New York, 1982. For Z = *p*-Br, an extrapolated value of 5.87 was used. Correlation coefficients were better than 0.996 in all case. $^c$ At $-15.0\,^{\circ}$C. $^d$ At $-25.0\,^{\circ}$C. $^e$ The source of $\sigma$ is the same as that for footnote *a*. Correlation coefficients were better than 0.994 in all cases. $^f$ Correlation coefficient was 0.995. $^g$ The p$K_{\text{a}}$ values were taken from A. Fischer, W. J. Galloway and J. Vaughan, *J. Chem. Soc.*, 1964, 3588. Correlation coefficients were better than 0.993 in all cases. (For X = *p*-CH$_3$O, p$K_{\text{a}}$ = 9.67 was used; see: H. K. Oh, J. Y. Lee and I. Lee, *Bull. Korean Chem. Soc.*, 1998, **19**, 1198.

**Table 2** Comparison of rate constants $k_{\text{N}}$ and selectivity parameters for the reactions of benzylamines (XC$_6$H$_4$CH$_2$NH$_2$) with thiol [**I**; RC(=O)SC$_6$H$_4$Z] and dithio [**II**; RC(=S)SC$_6$H$_4$Z] esters in acetonitrile

| Ester | $10^3\ k_{\text{N}}$/M$^{-1}$ s$^{-1\,a}$ | $\rho_{\text{X}}{}^{b}$ | $\beta_{\text{X}}{}^{b}$ | $\rho_{\text{Z}}{}^{c}$ | $\beta_{\text{Z}}{}^{c}$ | $\rho_{\text{XZ}}$ | Ref. |
|---|---|---|---|---|---|---|---|
| **Ia** | 3.93(45 °C) | $-1.40$ | 1.36 | 5.32 | $-2.21$ | 0.90 | 7 |
| **Ib** | 7.32(45 °C) | $-2.09$ | 2.11 | 2.74 | $-1.18$ | 2.36 | 6 |
| **Ic** | 3.76(45 °C)$^d$ | $-1.50$ | 1.55 | 1.61 | $-1.66$ | 0.92 | 4 |
| **Id** | 2.51(45 °C) | $-1.88$ | 1.86 | 3.84 | $-1.63$ | 0.27 | 16*b* |
| **IIa** | 699($-20$ °C) | $-0.56$ | 0.55 | 1.19 | $-0.50$ | 0.40$^e$ | 2 |
| **IIb** | 9840($-35$ °C) | $-2.24$ | 2.19 | 2.77 | $-1.15$ | 3.51 | This work |
| **IIc** | 11 600($-25$ °C) | $-2.21$ | 2.03 | 3.51 | $-1.38$ | 2.05 | 5 |
| **IId** | 382(30 °C) | $-0.65$ | 0.24 | 0.56 | $-0.24$ | 0.50$^e$ | 16*d* |
| **IIe** | 34.0(15 °C) | $-1.37$ | 1.40 | 1.85 | $-0.81$ | 0.65 | *f* |
| **IIf** | 25.6(15 °C) | $-1.00$ | 1.02 | 1.26 | $-0.56$ | 0.59 | *f* |

$^a$ For X = Z = H. $^b$ $\rho_{\text{X}}$ and $\beta_{\text{X}}$ values are for Z = H. $^c$ $\rho_{\text{Z}}$ and $\beta_{\text{Z}}$ values are for X = H. $^d$ Extrapolated value. $^e$ Rate-limiting formation of T$^{\pm}$. $^f$ H. K. Oh, S. Y. Woo, C. H. Shin and I. Lee, *Int. J. Chem. Kinet.*, 1998, **30**, 849.

TNPDTC) but they reverse to slower above the $pK_a^o$ than with the corresponding thio (**Ig**) esters. In other words, in the rate-limiting breakdown of $T^\pm$ (below $pK_a^o$) the dithio esters react faster but in the rate-limiting formation of $T^\pm$ (above $pK_a^o$) the thio esters react faster, as shown schematically in Fig. 1.

The faster rates in the rate-limiting expulsion for the dithio esters should be due to the larger $k_b/k_{-a}$ value in the observed rate constants, $k_N$, since the lower ability of the ($\geqslant$C–S$^-$) compared to the ($\geqslant$C–O$^-$) group in $T^\pm$ to form a double bond depresses the rate of amine expulsion ($k_{-a}$) more than that of ArS$^-$ expulsion from $T^\pm$ ($k_b$).[1] Thus, the weaker $\pi$ bond[12] or the lower $\pi$* LUMO level of C=S compared to C=O[13] leads to a more highly stabilized intermediate, $T^\pm$, since the C=S $\pi$ bond is easier to break to form $T^\pm$ but re-formation of the C=S $\pi$ bond from $T^\pm$ is more hindered than with C=O.[12,14]

The higher rates observed with R = CH$_3$CH$_2$ than with R = CH$_3$, as well as with C$_6$H$_5$CH$_2$, for both series of esters **I** and **II** can be explained by the electron-donating effect of the ethyl group in the intermediate, where only the polar effect (but no resonance effect) should be effective (Taft's $\sigma$* values are 0.0, $-0.10$ and $+0.22$ for R = CH$_3$, CH$_3$CH$_2$ and C$_6$H$_5$CH$_2$, respectively).[15]

It has been shown that an electron-donating R group enhances the rate of leaving group expulsion, $k_b$, from the $T^\pm$.[16] We can therefore conclude that the fastest aminolysis rate with R = CH$_3$CH$_2$ among the three esters for both thio (**Ia–c**) and dithio (**IIa–c**) esters and also the faster rates for **IIb** compared to **Ib** are a consequence of the stepwise mechanism with rate-limiting expulsion of the leaving group, ArS$^-$, from $T^\pm$. The proposed mechanism is supported by the large $\rho_X$($-1.4$ to $-2.9$), $\beta_X$(1.4–2.8), $\rho_Z$(1.7–4.0), $\beta_Z$($-0.7$ to $-1.6$) and $\rho_{XZ}$ (3.5) values in Table 1. We have compared these selectivity parameters for different R groups of thio (**I**) and dithio (**II**) esters in Table 2. It should be noted that the reactions proceeding by rate-limiting formation of $T^\pm$(**IIa** and **d**) exhibit much smaller magnitude of $\beta_X$ and $\beta_Z$. Examination of Table 2 shows that for R = CH$_3$CH$_2$ the magnitude of $\beta_X$ is the largest but that of $\beta_Z$ is the smallest among the three R (**a–c**) groups (except for $\beta_Z$ of **IIa**, which reacts by rate-limiting formation of $T^\pm$). Moreover, the $\rho_{XZ}$ value for **IIb** is exceptionally large, suggesting a very strong interaction of nucleophile (XC$_6$H$_5$CH$_2$NH$_2$) and leaving group (ZC$_6$H$_4$S$^-$) in the TS.[8] Although the largest magnitude of $\beta_X$ (tightest bond formation) and smallest $\beta_Z$ (least bond cleavage) suggest a tightest TS[8a–c] for R = CH$_3$CH$_2$ as implied by the largest $\rho_{XZ}$, the reasons for it are not apparent. The steric effect of the extra methylene group in **b** in the TS may provide a clue for this odd behavior, so we are exploring this possibility by conducting *ab initio* geometry optimizations of the ground state and transition state structures involved in the aminolysis of **Ib** and **IIb**. It has been shown that a sterically hindered TS leads to a tighter structure in organic reactions.[8b,17] Since a sterically hindered structure in the expulsion of the LG from the intermediate, $T^\pm$, should lead to a faster rate, the fastest rate observed with R = CH$_3$CH$_2$ supports this argument.

Reference to Table 1 reveals that faster rates are invariably accompanied by smaller magnitudes of selectivity parameters; that is, the reactivity-selectivity principle (RSP)[18] holds in all cases. This is also considered to be consistent with the stepwise mechanism proposed.[19]

The kinetic isotope effects ($k_H/k_D$) for the reaction of aryl propanedithioates (**IIb**) with deuterated benzylamines (XC$_6$H$_4$CH$_2$ND$_2$) in acetonitrile are shown in Table 3. We note that the isotope effects are normal (no inverse secondary effects with $k_H/k_D < 1.0$) with $k_H/k_D = 1.0$–1.8, and the magnitude suggests that proton transfer is involved in the TS,[8b] as has often been observed for a stepwise pathway in which partial proton transfer to the leaving group, ArS$^-$, occurs concurrently with rate-limiting departure of the leaving group from the intermediate, $T^\pm$, forming a four-center type TS,[4–7] as shown in Scheme 2.
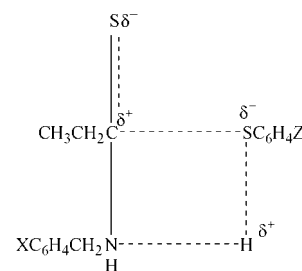


**Scheme 2** Proposed TS structure.

The activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$, determined for the present reaction series using the Eyring equation, are collected in Table 4. The low $\Delta H^{\neq}$ (8–9 kcal mol$^{-1}$) and large negative $\Delta S^{\neq}$($-16$ to $-23$ e.u.) values are consistent with the TS proposed.[4–7] Since rate-limiting expulsion of the leaving group, ArS$^-$, from $T^\pm$ is assisted by a concurrent proton

**Table 3** The kinetic isotope effects for the reactions of aryl propanedithioates with deuterated benzylamines in acetonitrile at $-35.0\,^\circ$C

| X | Z | $k_H$/M$^{-1}$ s$^{-1}$ | $k_D$/M$^{-1}$ s$^{-1}$ | $k_H/k_D$ |
|---|---|---|---|---|
| p-OMe | p-Me | 23.2 ± 0.2[a] | 19.7 ± 0.2[a] | 1.18 ± 0.02[a] |
| p-OMe | H | 42.9 ± 0.8 | 37.9 ± 0.5 | 1.13 ± 0.03 |
| p-OMe | p-Cl | 111 ± 2 | 104 ± 1 | 1.07 ± 0.02 |
| p-OMe | p-Br | 116 ± 2 | 113 ± 2 | 1.03 ± 0.03 |
| p-Cl | p-Me | 0.800 ± 0.007 | 0.442 ± 0.003 | 1.81 ± 0.02 |
| p-Cl | H | 3.46 ± 0.06 | 2.25 ± 0.05 | 1.54 ± 0.04 |
| p-Cl | p-Cl | 21.5 ± 0.2 | 16.5 ± 0.2 | 1.30 ± 0.02 |
| p-Cl | p-Br | 26.7 ± 0.3 | 21.7 ± 0.2 | 1.23 ± 0.02 |

[a] Standard deviations.

**Table 4** Activation parameters[a] for the reactions of aryl propanedithioates with benzylamines in acetonitrile

| X | Z | $\Delta H^{\neq}$/kcal mol$^{-1}$ | $-\Delta S^{\neq}$/kcal mol$^{-1}$ K$^{-1}$ |
|---|---|---|---|
| H | p-Me | 8.5 | 20 |
| H | p-Br | 8.9 | 23 |
| m-Cl | p-Me | 8.3 | 16 |
| m-Cl | p-Br | 8.3 | 18 |

[a] Calculated by the Eyring equation. The maximum errors calculated (K. B. Wiberg, *Physical Organic Chemistry*, Wiley, New York, 1964, p. 378) are +0.6 kcal mol$^{-1}$ and +3 e.u. for $\Delta H^{\neq}$ and $\Delta S^{\neq}$, respectively.
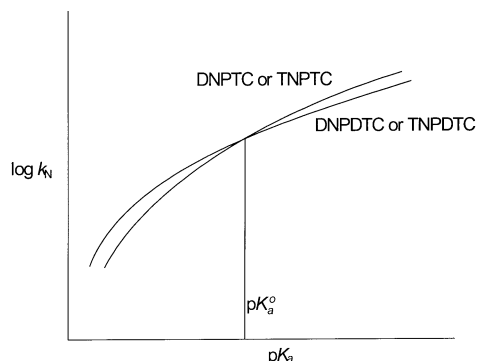


**Fig. 1** Schematic plots of log $k_N$ *vs.* $pK_a$ for the pyridinolysis of dinitro and trinitro thiol (DNPTC and TNPTC)[10] and dithio (DNPDTC and TNPDTC)[11] carbonates in aqueous solution.

transfer, low energy is required to break the C–S bond in the rate-determining step and the strained cyclic structure leads to large negative activation entropies.

## Conclusion

The aminolysis of aryl propanedithioates (**IIb**) with benzyl-amines proceeds by a stepwise mechanism with rate-limiting expulsion of the leaving group, $ArS^-$, from a tetrahedral inter-mediate, $T^\pm$. This conclusion is based on faster rates for dithio (**II**) than for thio (**I**) esters, the large selectivity parameters, $\beta_X$, $\beta_Z$ and $\rho_{XZ}$, and adherence to the reactivity-selectivity prin-ciple (RSP). The kinetic isotope effects involving deuterated benzylamine nucleophiles ($XC_6H_4CH_2ND_2$), giving $k_H/k_D \simeq$ 1.0–1.8, as well as the small $\Delta H^\ne$ ($\sim 8$ kcal $mol^{-1}$) and large negative $\Delta S^\pm$ values ($-16$ to $-23$ e.u.) suggest that proton transfer occurs concurrently with leaving group departure in a four-center type transition state.

## Experimental

### Materials

Merck GR acetonitrile was used after three distillations. Aldrich benzylamines and Tokyo Kasei thiophenols and phenylacetyl chloride were used without further purification.

### Preparation of S-aryl propanethioates

Thiophenol derivatives and propionyl chloride were dissolved in anhydrous ether and KOH added, carefully keeping the temperature at 0–5 °C. Ice was then added to the reaction mixture and the ether layer was separated, dried over $MgSO_4$ and distilled under reduced pressure to remove the solvent. The melting point, IR (Nicolet 5BX FT-IR), $^1H$ and $^{13}C$ NMR (JEOL 400 MHz) data are as follows: A Hewlett-Packard quadrupole mass spectrometer with electron impact ionization mode was used to measure MS data.

*S-p*-**Tolyl propanethioate.** Liquid; IR (KBr): 2979 (C–H, $CH_2$), 2938 (C–H, $CH_3$), 1494, 1459 (C=C, aromatic), 1710 (C=O) $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): 1.61 (3H, t, $CH_3$, $J = 6.35$), 2.31 (3H, s, $CH_3$), 2.60 (2H, q, $CH_2$, $J = 6.35$ Hz), 7.16–7.26 (4H, m, aromatic ring); $^{13}C$ NMR (100.4 MHz, $CDCl_3$): 198.4 (C=O), 139.4, 134.4, 129.9, 124.3, 36.9, 21.2, 9.57.

*S*-**Phenyl propanethioate.** Liquid; IR (KBr): 2993 (C–H, $CH_2$), 2939 (C–H, $CH_3$), 1477, 1440 (C=C, aromatic), 1710 (C=O) $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): 1.19 (3H, t, $CH_3$, $J = 6.35$), 2.63 (3H, q, $CH_2$, $J = 6.44$ Hz), 7.41–7.36 (5H, m, aromatic ring); $^{13}C$ NMR (100.4 MHz, $CDCl_3$): 198.4 (C=O), 134.5, 129.8, 129.3, 129.0, 127.4, 37.1, 9.58.

*S-p*-**Chlorophenyl propanethioate.** Liquid; IR (KBr): 2980 (C–H, $CH_2$), 2946 (C–H, $CH_3$), 1477, 1460 (C=C, aromatic), 1712 (C=O) $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): 1.81 (3H, t, $CH_3$, $J = 7.81$), 2.64 (2H, q, $CH_2$, $J = 7.81$ Hz), 7.28–7.35 (4H, m, aromatic ring); $^{13}C$ NMR (100.4 MHz, $CDCl_3$): 197.5 (C=O), 135.7, 135.6, 126.3, 37.1, 9.51.

*S-p*-**Bromophenyl propanethioate.** Liquid; IR (KBr): 2972 (C–H, $CH_2$), 2932 (C–H, $CH_3$), 1462, 1408 (C=C, aromatic), 1714 (C=O) $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): 1.20 (3H, t, $CH_3$, $J = 7.33$), 2.67 (2H, q, $CH_2$, $J = 7.33$ Hz), 7.27–7.41 (4H, m, aromatic ring); $^{13}C$ NMR (100.4 MHz, $CDCl_3$): 197.2 (C=O), 134.6, 134.2, 132.6, 130.0, 129.5, 37.2, 9.52.

### Preparation of aryl propanedithioates

The *S*-aryl propanethioates, prepared as above, were dissolved in dry toluene and refluxed with Lawesson's reagent.[20] After extraction of the reaction mixture with dichloromethane, it was dried and the solvent removed by distillation under

reduced pressure. Separation by column chromatography gave the products, for which the following analytical data were obtained.

*p*-**Tolyl propanedithioate.** Liquid; IR (KBr): 2975 (C–H, $CH_2$), 2933 (C–H, $CH_3$), 1499, 1487 (C=C, aromatic), 1212 (C=S) $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): 1.41 (3H, t, $CH_3$), 2.41 (3H, s, $CH_3$), 3.08 (2H, q, $CH_2$) 7.01–7.51 (4H, m, aro-matic ring); $^{13}C$ NMR (100.4 MHz, $CDCl_3$): 224.5 (C=S), 134.5, 132.6, 130.3, 129.3, 56.7, 44.4, 15.4; MS: $m/z$ 196 ($M^+$). Anal. calc. for $C_{10}H_{12}S_2$: C, 61.2; H, 6.21%. Found: C, 61.4; H, 6.22%.

**Phenyl propanedithioate.** Liquid; IR (KBr): 2978 (C–H, $CH_2$), 2937 (C–H, $CH_3$), 1501, 1488 (C=C, aromatic), 1218 (C=S) $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): 1.42 (3H, t, $CH_3$), 3.10 (3H, q, $CH_2$), 7.21–7.46 (5H, m, aromatic ring); $^{13}C$ NMR (100.4 MHz, $CDCl_3$): 230.6 (C=S), 136.1, 134.9, 131.5, 129.8, 55.4, 44.5; MS: $m/z$ 182 ($M^+$). Anal. calc. for $C_9H_{10}S_2$: C, 59.3; H, 5.50%. Found: C, 59.4; H, 5.52%.

*p*-**Chlorophenyl propanedithioate.** Liquid; IR (KBr): 2982 (C–H, $CH_2$), 2941 (C–H, $CH_3$), 1502, 1491 (C=C, aromatic), 1211 (C=S) $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): 1.42 (3H, t, $CH_3$), 3.10 (2H, q, $CH_2$), 7.14–7.47 (4H, m, aromatic ring); $^{13}C$ NMR (100.4 MHz, $CDCl_3$): 227.6 (C=S), 134.6, 133.0, 130.5, 130.3, 56.7, 44.5; MS: $m/z$ 217 ($M^+$). Anal. calc. for $C_9H_9ClS_2$: C, 49.9; H, 4.21%. Found: C, 49.8; H, 4.22%.

*p*-**Bromophenyl propanedithioate.** Liquid; IR (KBr): 2981 (C–H, $CH_2$), 2939 (C–H, $CH_3$), 1502, 1490 (C=C, aromatic), 1212 (C=S) $cm^-$; $^1H$ NMR (400 MHz, $CDCl_3$): 1.42 (3H, t, $CH_3$), 3.09 (2H, q, $CH_2$), 7.20–7.49 (4H, m, aromatic ring); $^{13}C$ NMR (100.4 MHz, $CDCl_3$): 224.8 (C=S), 134.8, 132.6, 130.2, 129.3, 57.8, 44.5; MS: $m/z$ 261 ($M^+$). Anal. calc. for $C_9H_9BrS_2$: C, 41.4; H, 3.50%. Found: C, 41.6; H, 3.49%.

### Kinetic measurements

Rates were measured conductometrically in acetonitrile. The conductivity bridge used in this work was a homemade com-puter controlled automatic A/D converter conductivity bridge. Pseudo-first-order rate constants, $k_{obs}$, were deter-mined by the Guggenheim method[21] with a large excess of benzylamine. The $k_N$ values were reproducible to within $\pm 5\%$.

### Product analysis

Phenyl propanedithioate (0.05 mole) was reacted with an excess of *p*-chlorobenzylamine (0.5 mole) with stirring for more than 15 half-lives at $-35.0$ °C in acetonitrile, and the products were isolated by evaporating the solvent under reduced pressure. The product mixture was treated with column chromatography (silica gel, 20% ethyl acetate–*n*-hexane). Analysis of the product gave the following results.

$CH_3CH_2C(=S)NHCH_2C_6H_4Cl$. Liquid; IR (KBr): 2994 (C–H, $CH_2$), 2946 (C–H, $CH_3$), 1606 (N–H), 1504 (C–C, aromatic), 1463 (C=C, aromatic), 1433 (C–H, $CH_2$), 1338 (C–H, $CH_3$), 1277 (C=S), 703 (C–H, aromatic) $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): 2.39 (3H, s, $CH_3$), 2.92 (1H, s, NH), 3.21 (2H, q, $CH_2$), 7.24–7.41 (4H, m, aromatic ring); $^{13}C$ NMR (100.4 MHz, $CDCl_3$): 225.2 (C=S), 136.6, 134.1, 133.2, 132.4, 125.6, 58.0, 47.0; MS: $m/z$ 214 ($M^+$). Anal. calc. for $C_{10}H_{12}ClNS$: C, 56.2; H, 5.70%. Found: C, 56.4; H, 5.71%.

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