# Kinetics and Mechanism of the Aminolysis of Aryl *N,N*-Dimethyl Thiocarbamates in Acetonitrile

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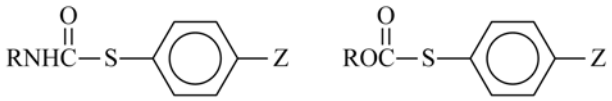
The kinetics and mechanisms of the aminolysis of aryl esters and carbonates have been widely investigated.[1,2] For example there is abundant literature on the mechanistic studies of the aminolysis of aryl thiocarbonates,[3] **2a**, with R



**1a** **2a**

**1.** Carbamate : Leaving group : **a.** $^{-}SC_6H_4Z$

**2.** Carbonate : **b.** $^{-}OC_6H_4Z$

= alkyl or aryl group. Kinetic studies on the aminolysis mechanisms of aryl carbamates, **1**, are however relatively scarce,[4] albeit they (**1**) are structurally similar to the corresponding esters and carbonates. Recent works on the aminolysis of aryl thiocarbamates, **1a**, with R = Et[4e] and Ph[4d] have indicated that the aminolysis rates with benzylamines in acetonitrile are more than 3 times faster with R = Et than with R = Ph in concerted processes. This rate enhancement with R = Et relative to R = Ph has been attributed mainly to a stronger push to expel the thiophenoxide leaving group by EtNH than by PhNH in the tetrahedral transition state.

It is, however, not well understood that (i) exactly what type of electronic effect is responsible for this push, *e.g.* is it a polar or a charge transfer effect?[2] and (ii) whether there is a steric inhibition effect operative with a bulkier phenyl group relative to an ethyl group or not. In order to shed more light on the aminolysis mechanism of aryl *N,N*-dimethyl thiocarbamates by elucidating effects of the nonleaving (RNH) group in **1a**, we carried out kinetic studies on the aminolysis of aryl *N,N*-dimethyl thiocarbamates (ADTC; RH = $(CH_3)_2$ in **1a**) with benzylamines in acetonitrile, eq. (1). We varied

$$2XC_6H_4CH_2NH_2 + (CH_3)_2NC(=O)-SC_6H_4Z \xrightarrow[40.0\ ^{\circ}C]{MeCN} (CH_3)_2NC(=O)-NHCH_2C_6H_4X + {}^{-}SC_6H_4Z + XC_6H_4CH_2NH_3^{+} \quad (1)$$

substitutents in the nucleophile (X) and leaving group (Z), and subjected the second-order rate constants ($k_2$) to multiple regression analysis and determined the cross-interaction constant,[5] $\rho_{XZ}$, as defined by eqs. (2), (2a) and (2b).

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

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

## Experimental Section

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

**Substrates. Phenyl *N,N*-dimethyl thiocarbamate:** A solution of thiophenol 1.02 mL (10 mmol) in dry toluene (20 mL) was added to a solution of dimethylcarbamyl chloride 0.92 mL (10 mmol). A catalytic quantity of KOH was added and the solution refluxed for 3 h. On evapolation of the solvent *in vacuo*, the phenyl *N,N*-dimethyl thiocarbamate precipitated and was recrystalized from ethanol. The other substituted phenyl *N,N*-dimethyl thiocarbamates were prepared in an analogous manner and recrystallized from petroleum ether. The substrates synthesized were confirmed by spectral and elemental analysis as follows.

**$(CH_3)_2NC(=O)SC_6H_4$-*p*-$CH_3$:** m.p. 40-42 °C; $^1$H NMR (400 MHz, $CDCl_3$), $\delta$ 2.24 (3H, d, $CH_3$), 2.84 (6H, d, $(CH_3)_2$), 7.07-7.46 (4H, m, $C_6H_4$); $^{13}$C NMR (100.4 MHz, $CDCl_3$), $\delta$ 166.2, 138.5, 134.9, 129.1, 124.7, 36.1, 20.8; $\nu_{max}$ (KBr), 3079 (CH, aliphatic), 2923 (CH, aromatic), 1653 (C=O), 619 (C-S); MS *m*/z 195 ($M^+$). Anal. Calcd for $C_{10}H_{13}NOS$: C, 61.5; H, 6.71. Found; C, 61.3; H, 6.72.

**$(CH_3)_2NC(=O)SC_6H_5$:** m.p. 56-58 °C; $^1$H NMR (400 MHz, $CDCl_3$), $\delta$ 2.73 (6H, d, $(CH_3)_2$), 7.27-7.60 (5H, m, $C_6H_5$); $^{13}$C NMR (100.4 MHz, $CDCl_3$), $\delta$ 166.3, 135.2, 128.6, 128.5, 128.4, 36.6; $\nu_{max}$ (KBr), 3055 (CH, aliphatic), 2920 (CH, aromatic), 1668 (C=O), 628 (C-S); MS *m*/z 181 ($M^+$). Anal. Calcd $C_9H_{11}NOS$: C, 59.6; H, 6.11. Found; C, 59.7; H, 6.13.

**$(CH_3)_2NC(=O)SC_6H_4$-*p*-Cl:** m.p. 90-92 °C; $^1$H NMR (400 MHz, $CDCl_3$), $\delta$ 2.91 (6H, d, $(CH_3)_2$), 7.31-7.48 (4H, m, $C_6H_4$); $^{13}$C NMR (100.4 MHz, $CDCl_3$), $\delta$ 165.9, 136.6, 135.2, 128.8, 127.1, 36.8; $\nu_{max}$ (KBr), 3071 (CH, aliphatic), 2925 (CH, aromatic), 1653 (C=O), 616 (C-O); MS *m*/z 215 ($M^+$). Anal. Calcd $C_9H_{10}ClNOS$: C, 50.1; H, 4.71. Found; C,

50.2; H, 4.73.

**$(CH_3)_2NC(=O)SC_6H_4$-*p*-Br:** m.p. 116-118 °C; $^1$H NMR (400 MHz, $CDCl_3$), $\delta$ 2.91 (6H, d, $(CH_3)_2$), 7.28-7.54 (4H, m, $C_6H_4$); $^{13}$C NMR (100.4 MHz, $CDCl_3$), $\delta$ 165.3, 136.6, 131.7, 128.7, 123.1, 36.5; $\nu_{max}$ (KBr), 3073 (CH, aliphatic), 2917 (CH, aromatic), 1668 (C=O), 684 (C-O); MS *m*/z 260 ($M^+$). Anal. Calcd $C_9H_{10}BrNOS$: C, 41.6; H, 3.90. Found; C, 41.8; H, 3.91.

**Kinetic measurement.** Rates were measured conductometrically in acetonitrile. The conductivity bridge used in this work was a homemade computer-automatic A/D converter conductivity bridge. Pseudo-first-order rate constants, $k_{obsd}$, were determined by the Guggenheim method[6] with large excess of benzylamine. Second order rate constants, $k_2$, were obtained from the slope of a plot of $k_{obsd}$ *vs.* [BA] with more than five concentrations of benzylamine. The $k_2$ values in Table 1 are the averages of more than three runs and were reproducible to within ± 3%.

**Product analysis.** The substrate *p*-tolyl *N*,*N*-dimethyl thiocabamate (0.01 mole) was reacted with excess *p*-chlorobenzylamine (0.1 mole) with stirring for more than 15 half-lives at 40.0 °C in acetonitrile (*ca*. 200 mL) and the products were isolated by evaporating the solvent under reduced pressure. The product mixture was subjected to column chromatography (silica gel, 20% ethyl acetate-*n*-hexane). Analysis of the product gave the following results.

**$(CH_3)_2NC(=O)NHCH_2C_6H_4$-Cl:** m.p. 113-115 °C; $^1$H NMR (400 MHz, $CDCl_3$), $\delta$ 2.83 (6H, d, $(CH_3)_2$), 5.31 (2H, d, $CH_2$), 6.31 (1H, s, NH), 7.08-7.33 (4H, m, $C_6H_4$); $^{13}$C NMR (100.4 MHz, $CDCl_3$), $\delta$ 167.6, 139.3, 135.5, 130.2, 126.2, 103.7, 36.2; $\nu_{max}$ (KBr), 3322 (NH), 3018 (CH, aliphatic), 2925 (CH, aromatic), 1665 (C=O); MS *m*/z 211 ($M^+$). Anal. Calcd for $C_{10}H_{12}ClN_2O$: C, 56.7; H, 5.70. Found; C, 56.9; H, 5.71.

## Results and Discussion

The reactions of Z-phenyl *N*,*N*-dimethyl thiocarbamates with X-benzylamines in acetonitrile at 40.0 °C obey a clean second-order rate law, eqs. 3 and 4, where [ADTC] and [BA] are the concentration of aryl *N*,*N*-dimethyl thiocarbamate

$$\text{rate} = k_{obs}\,[\text{ADTC}] \tag{3}$$

$$k_{obs} = k_2\,[\text{BA}] \tag{4}$$

and benzylamine, respectively. The second-order rate constants, $k_2$, summarized in Table 1 are obtained from a straight line plot of $k_{obs}$ *vs* [BA]. The rates are substantially faster than the corresponding aminolysis values for the aryl *N*-phenylthiocarbamates (APTC).[4d] This rate enhancement found with *N*,*N*-dimethyl (ADTC) relative to *N*-phenyl (APTC) analog can be attributed to the stronger push provided by the dimethylamino ($Me_2N$) than phenylamino (PhNH) group to expel the leaving group from a tetrahedral structure[8] which may be either an intermediate $T^{\pm}$ or a transition state, $T^{\pm}$ (TS). Electron donor abilities ($\sigma < 0$) of the RO and RNH groups are compared in Table 2. Since the lone pair electrons on O ($n_O$) and N ($n_N$) atoms are donated to the lowest unoccupied MO (LUMO) of the C-S bond orbital ($\sigma^*_{C\text{-}S}$) by an $n_O \rightarrow \sigma^*_{C\text{-}S}$ and $n_N \rightarrow s^*_{C\text{-}S}$ type vicinal charge transfer interaction within the $T^{\pm}$ structures,[7,10] the higher the nonbonding orbital ($\varepsilon_{nO} < \varepsilon_{nN}$) (and the lower the $\sigma^*_{C\text{-}S}$ level) the stronger is the charge transfer interaction, ΔE in eq. 5 where $\Delta\varepsilon = \varepsilon_{\sigma^*} - \varepsilon_n$ and $F_{n\sigma^*}$ is the Fock matrix element, and hence the stronger will become the push provide by the RNH than the RO group to expel the leaving group. The resonance electron donor ability ($\sigma_p^+$) listed[9] in

$$\Delta E = -\frac{2F^2_{n^*_\sigma}}{\Delta\varepsilon} \tag{5}$$

Table 2 should roughly parallel with Δ*E* in eq. 5, since the lone pair electrons on N or O are delocalized through $\pi^*$ orbital of the benzene ring by $n \rightarrow \pi^*$ interaction to the electron deficient functional center in the $\sigma_p^+$ scale.[10] We note that in general RNH groups are stronger electron

**Table 1**. The Second Order Rate Constants, $k_N$ ($10^2$ dm$^3$ mol$^{-1}$ s$^{-1}$) for the Reactions of Z-Aryl *N*,*N*-Dimethyl Thiocarbamates with X-Benzylamines in Acetonitrile at 40.0 °C

| X | Z | | | | $\rho_Z$[a] | $\beta_Z$[b] |
|---|---|---|---|---|---|---|
| | *p*-Me | H | *p*-Cl | *p*-Br | | |
| *p*-OMe | 2.88 | 5.26 | 12.2 | 13.3 | 1.63 ± 0.02 | −0.67±0.03 |
| | 2.07[c] | | | 9.57[c] | | |
| | 1.46[d] | 4.36 | 10.1 | 6.98[d] | | |
| *p*-Me | 2.59 | | | 10.4 | 1.59 ± 0.02 | −0.64 ± 0.02 |
| H | 1.82 | 3.19 | 7.15 | 7.51 | 1.52 ± 0.01 | −0.64 ± 0.03 |
| *p*-Cl | 1.16 | 1.96 | 4.28 | 4.43 | 1.45 ± 0.01 | −0.61 ± 0.02 |
| | 0.823[c] | | | 3.14[c] | | |
| | 0.576[d] | | | 2.19[d] | | |
| *m*-Cl | 0.910 | 1.54 | 3.18 | 3.35 | 1.39 ± 0.01 | −0.58 ± 0.03 |
| $\rho_X$[a] | −0.81 ± 0.02 | −0.84 ± 0.01 | −0.92 ± 0.01 | −0.93 ± 0.01 | $\rho_{XZ}$[e] = −0.31 ± 0.01 | |
| $\beta_X$[f] | 0.81 ± 0.02 | 0.85 ± 0.01 | 0.93 ± 0.01 | 0.94 ± 0.01 | | |

[a]The $\sigma$ values were taken from C. Hansch, A. Leo and R. W. Taft, *Chem. Rev.* 1991, 91, 166. Correlation coefficients were better than 0.998 in all cases. [b]The pKa values were taken from A. Albert and E. P. Serjeant, "*The Determination of Ionization Constants*" 3rd Ed., Chapman and Hall, London, p 145. Correlation coefficients were better than 0.997 in all cases. [c]At 30 °C. [d]At 20 °C. [e]Calculated by a multiple regression analysis using eq 2a. r = 0.999, n = 20 and $F_{calc}$ = 1410 ($F_{tab}$ = 10.66 at the 99.9% confidence level). [f]The pKa values were taken from A. Fischer, W. J. Galloway and J. Vaughan, *J. Chem. Soc*., 1964, 3588. Correlation coefficients were better than 0.998 in all cases. For X = *p*-$CH_3O$ an extrapolated value of p$K_a$ = 9.64 was used.

**Table 2**. Substituent Costnants for RO and RNH Group[7,9]

| | $\sigma_m$ | $\sigma_p$ | $\sigma_p^+$ |
|---|---|---|---|
| EtO | 0.10 | −0.24 | −0.81 |
| PhO | 0.25 | −0.03 | −0.50 |
| $Me_2N$ | −0.16 | −0.83 | −1.70 |
| EtNH | −0.24 | −0.61 | −1.80 |
| PhNH | −0.02 | −0.56 | −1.40 |

donors than the corresponding RO groups, and the two alkyl groups (R = $Me_2$ and Et) have similar electron releasing effect, which is stronger than that for phenyl (R = Ph) group. The order of increasing electron donor ability can be given as shown in eq. 6. The stronger electron donor ability of the $Me_2N$ than PhNH group is thus reflected in the faster

$$PhO < EtO << PhNH < Me_2N \cong EtNH \quad (6)$$

aminolysis rates for ADTC than for the corresponding reactions of APTC. Again, the order expected from the steric substituent constant, $E_S$,[11] NHPh > NHEt > $N(CH_3)_2$ is consistent with the observed rate order (NHPh < NHEt < $N(CH_3)_2$). This comparisons clearly show that the polar and steric effects of the amino non-leaving group (RNH) on the rates of aminolysis are significant.

Note that the sign of $\rho_{XZ}$ is invariably positive for stepwise but is negative for concerted reactions.[7] The definition of $\rho_{XZ}$ requires that a stronger nucleophile ($\delta\sigma_X < 0$) should lead to a greater degree of bond cleavage ($\delta\rho_Z > 0$) when $\rho_{XZ}$ is negative. This trend is exactly opposite to a greater bond cleavage observed with a weaker nucleophile when $\rho_{XZ}$ is positive. Since the aminolysis of *N,N*-dimethyl arylthiocarbamates involves a still stronger electron donor (PhNH < $Me_2N$ in Table 2) than in the corresponding concerted aminolysis reactions of *N*-phenyl arylthiocarbamates, it is reasonable to expect a concerted mechanism for the present series of reactions. Further support for the concerted mechanism is provided by a negative $\rho_{XZ}$ (−0.31) obtained,[5,7] and failure of the reactivity-selectivity principle (RSP).[4] This type of anti-RSP is considered another criterion for the concerted aminolysis.[4] It is also notable that the magnitude of $\rho_{XZ}$ (−0.31) value for ADTC is smaller than those for APTC (−0.63)[4d] and AETC (−0.86).[4e] This is consistent with somewhat lower degree of C-S bond cleavage in the TS for ADTC than those for APTC and AETC. Examination of Table 1 shows that the $\beta_X$ values are 0.8-0.9 which are rather larger than the values normally expected for the concerted aminolysis reactions, $\beta_X$ = 0.4-0.7.[12] However, $\beta_X$ values smaller than 0.4[13] and larger than 0.7[14] have also been obtained for the concerted aminolysis reactions. Especially in solvents less polar than water, larger $\beta_X$ values (1.3-1.6) are often obtained for the concerted processes.[15] Thus the large $\beta_X$ values in the present work may be due to the less polar solvent used, MeCN. The relatively large $\beta_X$ values are however consistent with the rather tight TS structure with a tighter bond formation. The $\beta_Z$ values in Table 1 are within the range of values that are expected for a concerted aminolysis reaction.[16]

**Table 3**. The Secondary Kinetic Isotope Effects for the Reactions of Z-Aryl *N,N*-Dimethyl Thiocarbamates with X-Benzylamines in Acetonitrile at 40.0 °C

| X | Z | $k_H$ ($\times 10^2$ $M^{-1}s^{-1}$) | $k_D$($\times 10^2$ $M^{-1}s^{-1}$) | $k_H/k_D$ |
|---|---|---|---|---|
| *p*-OMe | *p*-Me | 2.88(± 0.05) | 1.97(± 0.03) | 1.46 ± 0.03[a] |
| *p*-OMe | H | 5.26(± 0.06) | 3.48(± 0.04) | 1.51 ± 0.02 |
| *p*-OMe | *p*-Cl | 12.2(± 0.09) | 7.82(± 0.06) | 1.56 ± 0.03 |
| *p*-OMe | *p*-Br | 13.3(± 0.10) | 8.20(± 0.06) | 1.62 ± 0.04 |
| *p*-Cl | *p*-Me | 1.16(± 0.02) | 0.778(± 0.01) | 1.49 ± 0.01 |
| *p*-Cl | H | 1.96(± 0.03) | 1.26(± 0.02) | 1.55 ± 0.01 |
| *p*-Cl | *p*-Cl | 4.28(± 0.05) | 2.67(± 0.03) | 1.60 ± 0.02 |
| *p*-Cl | *p*-Br | 4.43(± 0.05) | 2.70(± 0.03) | 1.65 ± 0.02 |

[a]Standard deviations.

**Table 4**. Activation Parameters[a] for the Reactions of Z-Aryl *N,N*-Dimethyl Thiocarbamates with X-Benzylamines in Acetonitrile

| X | Z | $\Delta H^{\neq}$/kcal $mol^{-1}$ | $\Delta S^{\neq}$/cal $mol^{-1}$ $K^{-1}$ |
|---|---|---|---|
| *p*-OMe | *p*-Me | 5.6 | 48 |
| *p*-OMe | *p*-Br | 5.2 | 46 |
| *p*-Cl | *p*-Me | 5.6 | 49 |
| *p*-Cl | *p*-Br | 4.6 | 46 |

[a]Calculated by the Eyring equation. The maximum errors calculated (by the method of K. B. Wiberg, *Physical Organic Chemistry*; Wiley, New York, **1964**, p 378) are ± 1.0 kcal $mol^{-1}$ and ± 4 e.u. for $\Delta H^{\neq}$ and $\Delta S^{\neq}$, respectively.

The kinetic isotope effects ($k_H/k_D$) involving deuterated benzylamines[17] ($XC_6H_4CH_2ND_2$) are presented in Table 3. We note that the isotope effects are normal with $k_H/k_D > 1.0$ suggesting there is a hydrogen bond formed by the amino proton (N-H or N-D) in the TS, most probably with the negatively charged S atom in the leaving group. Since the large $\beta_X$ and $\beta_Z$ values suggest that the TS is a late type with a large degree of bond formation and bond cleavage the hydrogen bonding seems to be rather strong with relatively large values of $k_H/k_D > 1.0$. This is supported by a larger $k_H/k_D$ value for a stronger nucleophilie ($\delta\sigma_X < 0$) and a stronger nucleofuge ($\delta\sigma_Z > 0$) which will lead to a later TS in accordance with the negative $\rho_{XZ}$; a stronger nucleophile, $\delta\sigma_X < 0$, gave a larger $\rho_Z$ value $\delta\rho_Z > 0$ so that $\rho_{XZ} = \delta\rho_Z/\delta\sigma_X < 0$, while a stronger nucleofuge, $\delta\sigma_Z > 0$, gave a larger negative $\rho_X$ value $\delta\sigma_Z > 0$ so that $\rho_{XZ} = \delta\rho_Z/\delta\sigma_X < 0$, while a stronger nucleofuge ($\delta\sigma_Z > 0$) gave a larger negative $\rho_X$ ($\delta\rho_X > 0$) leading to $\rho_{XZ} < 0$.

The activation parameters determined with the rate data at three temperatures are summarized in Table 4. The values are well within the ranges obtained for the concerted reactions. However, it is difficult to distinguish by the magnitude of the activation parameters a stepwise from a concerted process.

In summary, we propose a concerted mechanism with a hydrogen bonded cyclic transition state for the aminolysis of aryl *N,N*-dimethyl thiocarbamates with benzylamines in acetonitrile based on the negative cross-interaction constant, failure of RSP, a strong push provided to expel $ArS^-$ by the nonleaving group, $Me_2N$, the kinetic isotope effects greater

than unity and relatively low $\Delta H^{\neq}$ with large negative $\Delta S^{\neq}$ values.

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