Research Article

Journal of Physical Organic Chemistry

Received: 15 December 2007, Revised: 10 May 2008, Accepted: 5 June 2008, Published online in Wiley InterScience: 10 July 2008

(www.interscience.wiley.com) DOI 10.1002/poc.1418

# Kinetics and mechanism of the anilinolysis of *S*-aryl *N*-arylthiocarbamates in acetonitrile

**Dae Dong Sung[a]*, Hee Man Jang[a], Dae Il Jung[a] and Ikchoon Lee[b]**

**The aminolysis reactions of *S*-aryl *N*-arylthiocarbamates ($YC_6H_4NH—C(=O)—SC_6H_4Z$, 1) with anilines in acetonitrile are studied. The reaction rates are more influenced by the nucleophilicity of the nucleophile than the nucleofugality of the leaving group, but the change in the effective charge from reactants to the TS for formation of the tetrahedral intermediate is slightly greater in the leaving group ($\beta_Z$ from −0.07 to −0.14) than in the nucleophile ($\beta_X = 0.04–0.12$). The magnitude of the Brönsted coefficients are in the range of values that are consistent for a stepwise mechanism with rate-limiting formation of the zwitterionic tetrahedral intermediate. Signs of cross-interaction constants, $\rho_{XY}$ (>0), $\rho_{XZ}$ (>0) and $\rho_{YZ}$ (<0), are all consistent with a stepwise mechanism. It is concluded that the change of the amine from benzylamines to anilines causes a shift of the aminolysis mechanism from a concerted to a stepwise process.**


*Supporting information may be found in the online version of this article.*

**Keywords:** *S*-aryl *N*-arylthiocarbamate; cross-interaction constant; stepwise mechanism; zwitterionic intermediate; kinetic isotope effect

## INTRODUCTION

Although the mechanisms of the aminolysis of esters and carbonates have been extensively studied, relatively less attention has been given to those for carbamates. In our recent experimental[1–3] and theoretical[4] works, the aminolyses of carbamates have been shown to proceed by a direct displacement, concerted mechanism, in contrast to a stepwise mechanism involving zwitterionic tetrahedral intermediates for the aminolysis of esters[5–9] and carbonates.[10–13] According to natural bond orbital (NBO)[4,14,15] analyses, the major cause of this mechanistic variation for the carbamates is a considerable charge transfer of nonbonding orbital electrons on the amino nitrogen, $n_N$, to the carbonyl $\pi^*_{CO}$ orbital, a vicinal $\underline{n}_N \rightarrow \pi^*_{CO}$ charge transfer interaction,[4,14–17] which in effect enhances the leaving ability of the phenolate or thiolate group. In the esters there is no vicinal nonbonding orbital and hence this type of vicinal charge transfer is lacking, whereas in the carbonates the charge transfer of the vicinal nonbonding orbital, $n_O$, of the methoxy oxygen to $\pi^*_{CO}$ is not strong enough to sufficiently weaken the carbonyl-leaving group bond to induce a concerted process.

In the present work, we have investigated the anilinolysis of *S*-aryl *N*-arylthiocarbamates, $Y—C_6H_4—NHC(=O)—SC_6H_4Z$, **1**, where Y and Z are substituents on the nonleaving and leaving groups, respectively, in acetonitrile, eqn (1). We have used anilines, $XC_6H_4NH_2$ with X = *p*-OMe, *p*-Me, H, *p*-Cl, or *p*-$NO_2$, instead of benzylamines which were used in the previous kinetic studies of the carbamate aminolysis.[1–3]

$$2XC_6H_4NH_2 + \underset{\mathbf{1}}{YC_6H_4NH - C(=O) - SC_6H_4Z} \rightarrow YC_6H_4NH - C(=O) - NHC_6H_4X + XC_6H_4NH_3^+ + ZC_6H_4S^- \quad (1)$$

The object of this work is to shed more light into the mechanism of the aminolysis of carbamates, and to investigate the influence of the amine nature on the mechanism and transition state structure by comparing the present reaction with the aminolysis results for benzylamines. In this work, we determined cross-interaction constants,[18,19] $\rho_{ij}$ (eqn (2)) where *i* and *j* are substituents X, Y, or Z in eqn (1), in order to shed more light on the mechanism.

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

## RESULTS AND DISCUSSION

Reactions (1), carried out with excess aniline ($[S] = 5 \times 10^{-5}$ M and $[An] = 3–5 \times 10^{-1}$ M) in acetonitrile followed clean, pseudo-first-order kinetics given by the following eqns (3) and (4), where S and An denote the substrate and the aniline, respectively.

$$\text{rate} = k_{obs}[S] \quad (3)$$

$$k_{obs} = k_2[An] \quad (4)$$

* *Correspondence to: D. D. Sung, Department of Chemistry, Dong-A University, Busan, 604-714, Korea.*
*E-mail: ddsung@dau.ac.kr*

a *D. D. Sung, H. M. Jang, D. I. Jung, I. Lee*
*Department of Chemistry, Dong-A University, Busan 604-714, Korea*

b *I. Lee*
*Department of Chemistry, Inha University, Inchon 402-751, Korea*

The second-order rate constants, $k_2$, obtained are summarized in Table 1. The Hammett ($\rho_X$, $\rho_Y$, and $\rho_Z$) and Brönsted [$\beta_X$ ($\beta_{nuc}$) and $\beta_Z$ ($\beta_{lg}$)] coefficients are collected in Table 2. In the determination of $\beta_X$, we found that the values obtained with p$K_a$s in water are 1.25-fold uniformly greater than those determined with p$K_a$s in acetonitrile.[20] The magnitude of $\rho_X$ (−0.60 for Y = Z = H) is in general larger than that of $\rho_Z$ (0.31 for Y = X = H) indicating that the positive charge development on the nitrogen atom of aniline is greater than the negative charge developed on the sulfur atom of the leaving group in the TS. In contrast, the magnitude of βz (for Y = Br, average $\beta_Z = -0.10$ with p$K_a$s in water)[21] is somewhat larger than that of $\beta_X$ (for Y = Br, average of $\beta_X = 0.07$ with p$K_a$s in water) which implies that the change in effective charge at the TS is somewhat greater in the leaving group than that in the nucleophile. This is further supported by the negative sign of $\rho_Y$ values in Table 2. We note, however, that the magnitude of both $\beta_X$ (0.04–0.12) and $\beta_Z$ (from −0.07 to −0.18) is rather small, which is in the range of values ($\beta_X = -\beta_Z = 0$–0.4) normally found for a stepwise mechanism where the formation of a zwitterionic tetrahedral intermediate is the rate-determining step.[5,22–29] It has been shown that the $\beta_X$ values are normally greater than *ca.* 0.8 for a stepwise mechanism with rate-limiting breakdown of the intermediate,[5–13] while they are in the range of 0.4–0.6 for a concerted aminolysis process.[1–3,22–31] Based on the magnitude of Brönsted coefficients therefore, we propose that reaction (1), proceeds through a zwitterionic tetrahedral intermediate, $T^{\pm}$, **2**, the formation of which is rate determining.

**Table 1.** The second-order rate constants, $k_2$ ($\times 10^3\ M^{-1}\ s^{-1}$)*, for the reactions of *S*-aryl *N*-arylthiocarbamates ($YC_6H_4NH$-C(=O)-$SC_6H_4Z$) with anilines ($XC_6H_4NH_2$) in acetonitrile at 25.0 °C

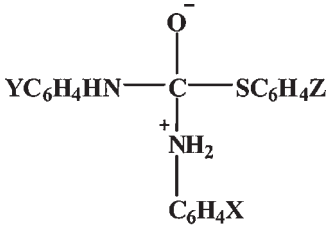
| | | X | | | | |
|---|---|---|---|---|---|---|
| Y | Z | *p*-OMe | *p*-Me | H | *p*-Cl | *p*-$NO_2$ |
| H | *p*-OMe | 7.01 | 6.11 | 4.73 | 3.29 | 1.47 |
| | *p*-Me | 7.48 | 6.52 | 5.11 | 3.59 | 1.65 |
| | H | 8.36 | 7.28 | 5.75 | 4.10 | 1.93 |
| | *p*-Cl | 9.75 | 8.55 | 6.79 | 4.95 | 2.43 |
| | *p*-$NO_2$ | 14.0 | 12.5 | 10.1 | 7.71 | 4.05 |
| *p*-Cl | *p*-OMe | 2.10 | 1.93 | 1.67 | 1.38 | 0.867 |
| | *p*-Me | 2.18 | 2.02 | 1.76 | 1.46 | 0.937 |
| | H | 2.33 | 2.17 | 1.90 | 1.60 | 1.06 |
| | *p*-Cl | 2.55 | 2.40 | 2.12 | 1.81 | 1.25 |
| | *p*-$NO_2$ | 3.16 | 3.06 | 2.77 | 2.46 | 1.87 |
| *p*-Br | *p*-OMe | 2.03 | 1.86 | 1.64 | 1.35 | 0.857 |
| | *p*-Me | 2.12 | 1.94 | 1.71 | 1.43 | 0.920 |
| | H | 2.27 | 2.08 | 1.85 | 1.56 | 1.04 |
| | *p*-Cl | 2.48 | 2.29 | 2.04 | 1.78 | 1.23 |
| | *p*-$NO_2$ | 3.06 | 2.90 | 2.64 | 2.40 | 1.83 |

*The $k_2$ values are averages of more than three kinetic runs and were reproducible to within ± 3%.

**Table 2.** Hammett ($\rho_x$, $\rho_y$, and $\rho_z$) and Brőnsted (in parentheses) coefficients for the reactions of *S*-aryl *N*-arylthiocarbamates with anilines in acetonitrile at 25.0 °C

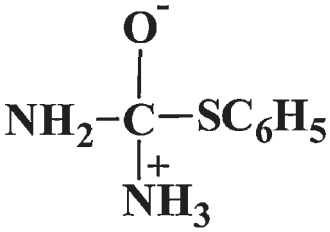
| Y/Z | *p*-OMe | *p*-Me | H | *p*-Cl | *p*-$NO_2$ |
|---|---|---|---|---|---|
| | | | $\rho_X$ and ($\beta_X$) values[a] | | |
| H | −0.65 (0.12) | −0.63 (0.11) | −0.60 (0.10) | −0.58 (0.11) | −0.51 (0.09) |
| *p*-Cl | −0.37 (0.07) | −0.35 (0.06) | −0.33 (0.06) | −0.30 (0.05) | −0.22 (0.04) |
| *p*-Br | −0.36 (0.07) | −0.34 (0.06) | −0.32 (0.06) | −0.29 (0.05) | −0.21 (0.04) |
| Y/X | *p*-OMe | *p*-Me | H | *p*-Cl | *p*-$NO_2$ |
| | | | $\rho_Z$ and ($\beta_Z$) values[b] | | |
| H | 0.29 (−0.13) | 0.30 (−0.13) | 0.31 (−0.14) | 0.35 (−0.15) | 0.42 (−0.18) |
| *p*-Cl | 0.17 (−0.07) | 0.19 (−0.08) | 0.21 (−0.09) | 0.24 (−0.10) | 0.32 (−0.14) |
| *p*-Br | 0.17 (−0.07) | 0.18 (−0.08) | 0.20 (−0.09) | 0.24 (−0.10) | 0.31 (−0.14) |
| X/Z | *p*-OMe | *p*-Me | H | *p*-Cl | *p*-$NO_2$ |
| | | | $\rho_Y$ values[c] | | |
| *p*-OMe | −2.26 | −2.30 | −2.38 | −2.50 | −2.77 |
| *p*-Me | −2.16 | −2.20 | −2.27 | −2.39 | −2.65 |
| H | −1.94 | −2.00 | −2.07 | −2.19 | −2.43 |
| *p*-Cl | −1.63 | −1.68 | −1.76 | −1.87 | −2.13 |
| *p*-$NO_2$ | −0.99 | −1.06 | −1.12 | −1.24 | −1.45 |

[a] The correlation coefficients were better than 0.991, and standard deviations were less than 0.01 (with an average value of 0.006) in all cases. $\beta_X$ values were determined with p$K_a$s in acetonitrile[8a].
[b] The correlation coefficients were better than 0.996, and standard deviations were less than 0.01.in all cases. $\beta_Z$ values were determined with p$K_a$s in water[8b] at 25 °C.
[c] The correlation coefficients were better than 0.999, and standard deviations were less than 0.05 in all cases.



**2**

In this type of TS, the changes in effective charge from reactants to the TS for formation of the tetrahedral intermediate, $\beta_X$ ($\beta_{nuc}$) and $-\beta_Z$ ($-\beta_{lg}$), are small ranging from 0 to 0.4, and in some cases the $-\beta_Z$ values become greater than the $\beta_X$ values. Such examples are found in the work of Castro group on the aminolysis of 2,4-dinitrophenyl and 2,4,6-trinitrophenyl thiolacetates ($\beta_X = 0.2$ and $\beta_Z = -0.3$),[24] and in the work of Jencks group on the acyl transfer reactions between sulfur and oxygen nucleophiles ($\beta_X = 0.2$ and $\beta_Z = -0.3$).[9] Thus, in the stepwise reactions with rate-limiting bond formation, changes in the effective charge on the nitrogen of the aniline nucleophile and on the sulfur of the leaving group are small, but the latter can be larger. This does not mean that the reaction proceeds concertedly[24,26] since the effective charge change is involved in the process of formation of the zwitterionic tetrahedral intermediate. According to our DFT calculations at the B3LYP/6-31G** level of theory[4,32] in the gas phase, the C—S bond stretches from 1.839 to 1.844 Å while the Mulliken charge of the carbonyl carbon increases from +0.4131 to +0.4183 in going from the reactants to the TS for formation of the tetrahedral intermediate **3**, which is formed from *S*-phenyl thiocarbamate ($NH_2$—(C═O)—SPh) and ammonia. In general, charged species are more stabilized in solvents than in the gas phase so that this gas-phase results can serve as an indication that the effective charge development for rate-limiting formation can be larger in the leaving group than in the nucleophile.



**3**

The cross-interaction constants, $\rho_{XY}$, $\rho_{XZ}$, and $\rho_{YZ}$, determined by multiple regression using eqn (2) are shown in Table 3. The signs of these constants, $\rho_{XY} > 0$, $\rho_{XZ} > 0$, and $\rho_{YZ} < 0$, are indeed consistent with our proposed mechanism of the stepwise process.[19,34,35] It has been shown that in a concerted aminolysis, the signs of these constants are all reversed to $\rho_{XY} < 0$, $\rho_{XZ} < 0$ ,and $\rho_{YZ} > 0$.[19,34,35] The variations of these constants with substituents are negligible, i.e.,the values of $\rho_{XYZ}$, are very small (~0) in all cases. For example, $\rho_{XY}$ varies from 1.23 for Z = *p*-OMe to 1.27 for Z = *p*-$NO_2$ so that $\rho_{XYZ} \sim 0.04$. This is an indication of a loose C-nucleophile bond in the TS, as we have proposed above based on the small magnitude of the Brönsted $\beta_X$ coefficients.

**Table 3.** Cross-interaction constants, $\rho_{xy}$, $\rho_{xz}$, and $\rho_{yz}$, for the reactions of *S*-aryl *N*-aryl thiocarbamates with anilines in acetonitrile at 25.0 °C

| Z | $\rho_{XY}$ |
|---|---|
| $\rho_{XY}$ values[a] | |
| *p*-OMe | 1.23 ± 0.03 |
| *p*-Me | 1.20 ± 0.02 |
| H | 1.21 ± 0.03 |
| *p*-Cl | 1.21 ± 0.03 |
| *p*-$NO_2$ | 1.27 ± 0.03 |
| **Y** | **$\rho_{XZ}$** |
| $\rho_{XZ}$ values[a] | |
| H | 0.13 ± 0.01 |
| *p*-Cl | 0.14 ± 0.02 |
| *p*-Br | 0.14 ± 0.01 |
| **X** | **$\rho_{YZ}$** |
| $\rho_{YZ}$ values[a] | |
| *p*-OMe | −0.50 ± 0.04 |
| *p*-Me | −0.47 ± 0.01 |
| H | −0.47 ± 0.02 |
| *p*-Cl | −0.48 ± 0.03 |
| *p*-$NO_2$ | −0.43 ± 0.02 |

[a] The $R^2$ values were greater than 0.9997 in all cases, and Fischer's *F*-tests at the 99.9% confidence level by comparing the calculated *F*-values ($F_{calc}$) with the tabulated *F*-value ($F_{tab} = 999.5$)[33] indicated that the results of the multiple regressions are highly significant ($F_{cal} >> F_{tab}$).

Amine nature is one of the key factors that influences the mechanism of the aminolysis reactions of esters, carbonates, and carbamates.[2,13,35] The rate of amine expulsion from $T^{\pm}$ increases in the order pyridines < anilines < secondary alicyclic amines < quinuclidines < benzylamines and the stability of the zwitterionic intermediate, $T^{\pm}$, increases in the reverse order.[13,34,35] Thus, pyridine nucleophiles are most likely to lead the aminolysis to a stepwise reaction with a stable intermediate, whereas benzylamines are known to strongly destabilize $T^{\pm}$ so that the intermediate cannot exist and as a result the aminolysis reactions are likely to proceed by a

$NH_2-C(=O)-SAr$ **4** $\qquad$ $EtNH-C(=O)-SAr$ **5**

$YC_6H_4NH-C(=O)-OC_6H_4-p-NO_2$ **6**

concerted pathway.[34,35] For example, aminolyses of *S*-aryl-,[1] **4**, *S*-aryl *N*-ethyl-,[2] **5**, and *p*-nitrophenyl *N*-aryl carbamates,[3] **1**, with benzylamines in acetonitrile were found to proceed by a concerted mechanism, while pyridinolyses of many aryl esters and carbonates are reported to proceed by a stepwise mechanism through a zwitterionic tetrahedral intermediate.[36–43]

Anilines destabilize the tetrahedral intermediate relative to pyridines but stabilize it compared with benzylamines. The nucleofugality of anilines from $T^{\pm}$ being intermediate between the two extremes, mechanistic changes can occur readily when

other factors are varied. For example, the aminolyses of *S*-aryl *O*-ethyl thiocarbonates [EtO–C(=O)–$SC_6H_4Z$] with anilines are reported to shift from stepwise for a poorer leaving group [Z = 2,4-$(NO_2)_2$] to concerted manner for a better leaving group [Z = 2,4,6-$(NO_2)_3$].[44] This means that the nucleofugality of the leaving group from $T^{\pm}$ is also a key factor influencing the aminolysis mechanism of carbonates and carbamates. For example, the aminolysis of *p*-nitrophenyl *N-ary*carbamates, **6**, with benzylamines is stepwise[45] in acetonitrile due to the low nucleofugality of phenolate ($OPh^-$) relative to thiolate ($SPh^-$) in **1** despite the strong leaving ability of benzylamines from $T^{\pm}$. The stepwise mechanism proposed for the present *anilinolysis* reactions of *S*-aryl *N*-aryl*thio*carbamates is therefore reasonable in view of the possible mechanistic shift to a stepwise process by changing the amine to aniline from benzylamine,[3] for which a concerted process was observed.

The solvent change from water to a less polar solvent, MeCN, can cause a mechanistic stepwise change in water to a concerted change in acetonitrile, mainly due to a decrease in the stability of zwitterionic intermediates in MeCN.[46] The higher expulsion rate of the amine from $T^{\pm}$ in a less polar solvent leads to a lower stability of $T^{\pm}$. However, in many cases due to other stronger effects, mechanistic changes are not observed and the same mechanism is observed in both water and in MeCN.[34,35]

The kinetic isotope effects, $k_H/k_D$, involving deuterated anilines[47] ($XC_6H_4ND_2$) are normal but negligible as shown in Table 4 (Supporting Information). This is in line with the proposed mechanism since the TS is very loose in the process involving the formation of the tetrahedral intermediate. The activation parameters, $\Delta H^{\neq}$ and $\Delta S^{\neq}$, in Table 5 (Supporting Information) are also consistent with our proposed mechanism. The activation enthalpies (*ca.* 10 kcal/mol) are lower than those for the stepwise process with rate-limiting breakdown of the intermediate (*ca.* 14 kcal/mol for **6** with benzylamines)[45] but are higher than those for the H-bonded cyclic TS in the concerted processes (*ca.* 8 kcal/mol for **4** with benzylamines).[1] The entropies of activations (*ca.* −35 e.u.) are also intermediate between the two (−13 for **6**, and −37 e.u. for **4** with benzylamines).[1,45]

## EXPERIMENTAL

### Materials

*General procedure*

GR grade acetonitrile was purchased from Aldrich and used after re-distillation. The aniline nucleophilesof GR grade from Aldrich were used after re-crystallization or re-distillation. FT-IR spectra were taken using a Bruker IFS 55 spectrophotometer. $^1$H NMR spectra were recorded on a Bruker DPX 300 MHz-NMR instrument using $CD_3CN$ and $CDCl_3$ as solvents with TMS as an internal standard.

Preparation of *S-p*-substituted phenyl *N-p*-substituted phenylcarbamates. These were prepared by the literature method of Velikorodov,[48] Moseley,[49] and Knapton.[50] To a solution of 0.1 mol of thiophenol and phenyl isocyanate in 20 ml of toluene, 10 ml of pyridine was added and purged with argon into the solution. The reaction mixture was stirred for 2 h at 25 °C. When the reaction was completed, the solid was filtered under reduced pressure. The solid was added to the solvent mixture of chloroform and *n*-pentane (2:1 v/v%) and filtered under reduced pressure. The product was separated by column chromatography on aluminum oxide (neutral $Al_2O_3$ grade 90, 63–200 μm) eluted with diethyl ether (10%)-*n*-hexane.

*S*-Phenyl *N*-phenylthiocarbamate. IR (KBr ($cm^{-1}$)), N—H; 3257.3, C=O; 1670, C—S; 1010.5, C=C (Ar); 1486.9,1596.8, Ar—H; (3182.1, 3108.8, 3043.3, 2923.7, 2852.3), $^1$H-NMR (350 MHz, acetonitrile-$d_3$) δ 7.19–7.29 (4H, m, aromatic), 7.39–7.47 (2H, t, aromatic), 7.56–7.72 (4H, m, aromatic), 8.27 (1H, s, NH).

*S-p*-Nitrophenyl *N*-phenylthiocarbamate. IR (KBr ($cm^{-1}$)), N—H; 3257.3, C=O; 1670, C—$NO_2$; 1107, Ar—$NO_2$; 885, C—S; 1010.5, C=C (Ar); 1486.9, 1596.8, Ar—H; (3182.1, 3108.8, 3043.3, 2923.7, 2852.3), $^1$H-NMR (350 MHz acetonitrile-$d_3$) δ 7.15–7.24 (1H, m, aromatic), 7.40–7.47 (2H, t, aromatic), 7.61–7.72 (4H, m, aromatic), 8.00 (1H, s, NH), 8.12–8.20 (2H, d, aromatic).

*S-p*-Methylphenyl *N*-phenylthiocarbamate. IR (KBr ($cm^{-1}$)), N—H; 3257.3, C=O; 1670, C—S; 1010.5, C=C (Ar); 1486.9, 1596.8, $CH_3$; 2950.8, 1480.4 Ar—H; (3182.1, 3108.8, 3043.3, 2923.7, 2852.3), $^1$H-NMR; (350 MHz acetonitrile-$d_3$) δ 2.17 (3H, s, $CH_3$), 6.82–6.89 (2H, d, aromatic), 7.06–7.15 (2H, d, aromatic), 7.19–7.28 (1H, m, aromatic), 7.40–7.48 (2H, m, aromatic), 7.52–7.63 (2H, d, aromatic), 8.90 (1H, s, NH).

*S-p*-Methoxyphenyl *N*-phenylthiocarbamate. IR (KBr ($cm^{-1}$)), N—H; 3257.3, C=O; 1670, C—S; 1010.5, C=C (Ar); 1486.9, 1596.8, OCH3; 1000, 1250, 2940, Ar—H; (3182.1, 3108.8, 3043.3, 2923.7, 2852.3), $^1$H-NMR (350 MHz, acetonitrile-$d_3$) δ 3.83 (3H, s, $OCH_3$),7.19–7.28 (1H, m, aromatic), 7.40–7.51 (6H, m, aromatic), 7.60–7.65 (2H, d, aromatic), 8.36 (1H, s, NH).

*S-p*-Chlorophenyl *N*-phenylthiocarbamate. IR (KBr ($cm^{-1}$)), N—H; 3257.3, C=O; 1670, C—S; 1010.5, C=C (Ar); 1486.9, 1596.8, Ar—H; (3182.1, 3108.8, 3043.3, 2923.7, 2852.3), $^1$H-NMR (350 MHz acetonitrile-$d_3$) δ 7.01–7.05 (1H, m, aromatic), 7.36 (4H, s, aromatic), 7.42–7.47 (2H, m, aromatic), 7.61–7.65 (2H, d, aromatic), 8.36 (1H, s, NH).

*S-p*-Chlorophenyl *N-p*-chlorophenylthiocarbamate. IR (KBr ($cm^{-1}$)), N—H; 3257.3, C=O; 1670, C—S; 1010.5, C=C (Ar); 1486.9, 1596.8, Ar—H; (3182.1, 3108.8, 3043.3, 2923.7, 2852.3), $^1$H-NMR (350 MHz acetonitrile-$d_3$) δ 7.28–7.33 (4H, s, aromatic), 7.43–7.49 (2H, d, aromatic), 7.69–7.76 (2H, d, aromatic), 8.58 (1H, s, NH).

*S-p*-Nitrophenyl *N-p*-chlorophenylthiocarbamate. IR (KBr ($cm^{-1}$)), N—H; 3257.3, C=O; 1670, C—S; 1010.5, Ar-$NO_2$; 885, C=C (Ar); 1486.9, 1596.8, Ar—H; (3182.1, 3108.8, 3043.3, 2923.7, 2852.3), 1H-NMR (350 MHz acetonitrile-$d_3$) δ 7.15–7.19 (2H, d, aromatic), 7.64–7.69 (2H, d, aromatic), 7.70–7.76 (2H, d, aromatic), 8.06 (1H, s, NH), 8.59–8.62 (2H, d, aromatic).

*S-p*-Methylphenyl *N-p*-chlorophenylthiocarbamate. IR (KBr ($cm^{-1}$)), N—H; 3257.3, C=O; 1670, C—S; 1010.5, $CH_3$; 2950.8, 1480.4, C=C (Ar); 1486.9, 1596.8, Ar—H; (3182.1, 3108.8, 3043.3, 2923.7, 2852.3), $^1$H-NMR (350 MHz acetonitrile-$d_3$) δ 3.85 (3H, s, $CH_3$), 6.86–6.92 (2H, d, aromatic), 7.04–7.09 (2H, d, aromatic), 7.43–7.48 (2H, d, aromatic), 7.71–7.75 (2H, d, aromatic), 8.73 (1H, s, NH).

*S-p*-Methoxyphenyl *N-p*-chlorophenylthiocarbamate. IR (KBr ($cm^{-1}$)), N—H; 3257.3, C=O; 1670, C—S; 1010.5, C=C (Ar); 1486.9, 1596.8, $OCH_3$; 1000, 1250, 2940, Ar—H; (3182.1, 3108.8, 3043.3, 2923.7, 2852.3), $^1$H-NMR (350 MHz acetonitrile-$d_3$) δ 3.81 (3H, s, $OCH_3$), 7.13–7.47 (6H, m, aromatic), 7.73–7.78 (2H, d, aromatic), 8.80 (1H, s, NH).

*S*-Phenyl *N-p*-chlorophenylthiocarbamate. IR (KBr ($cm^{-1}$)), N—H; 3257.3, C=O; 1670, C—S; 1010.5, C=C (Ar); 1486.9, 1596.8, Ar—H; (3182.1, 3108.8, 3043.3, 2923.7, 2852.3), $^1$H-NMR (350 MHz acetonitrile-$d_3$) δ 7.19–7.29 (3H, m, aromatic), 7.41–7.47

(2H, d, aromatic), 7.53–7.58 (2H, d, aromatic), 7.72–7.77 (2H, d, aromatic), 8.60 (1H, s, NH).

*S-p*-Nitrophenyl *N-p*-bromophenylthiocarbamate. IR (KBr ($cm^{-1}$)), N—H; 3257.3, Ar—Br; 1070.3, Ar—$NO_2$; 885, C═O; 1670, C—S; 1010.5, C═C (Ar); 1486.9, 1596.8, Ar—H; (3182.1, 3108.8, 3043.3, 2923.7, 2852.3), $^1$H-NMR (350 MHz acetonitrile-$d_3$) $\delta$ 7.49–7.74 (6H, m, aromatic), 8.27 (1H, s, NH), 8.71–8.75 (2H, d, aromatic).

*S*-Phenyl *N-p*-bromophenythiocarbamate. IR (KBr ($cm^{-1}$)), N—H; 3257.3, Ar—Br; 1070.3, C═O; 1670, C—S; 1010.5, C═C (Ar); 1486.9, 1596.8, Ar—H; (3182.1, 3108.8, 3043.3, 2923.7, 2852.3), $^1$H-NMR (350 MHz acetonitrile-$d_3$) $\delta$ 7.11–7.29 (3H, m, aromatic), 7.53–7.58 (4H, t, aromatic), 7.67–7.74 (2H, d, aromatic), 8.40 (1H, s, NH).

*S-p*-Methylphenyl *N-p*-bromophenylthiocarbamate. IR (KBr ($cm^{-1}$)), N—H; 3257.3, Ar—Br; 1070.3, C═O; 1670, C—S; 1010.5, $CH_3$; 2950.8, 1480.4, C═C (Ar); 1486.9, 1596.8, Ar—H; (3182.1, 3108.8, 3043.3, 2923.7, 2852.3), $^1$H-NMR (350 MHz acetonitrile-$d_3$) $\delta$ 2.37 (3H, s, $CH_3$), 6.84–6.89 (2H, d, aromatic), 7.07–7.11 (2H, d, aromatic), 7.53–7.58 (2H, d, aromatic), 7.65–7.70 (2H, d, aromatic), 8.74 (1H, s, NH).

*S-p*-Methoxyphenyl *N-p*-bromophenylthiocarbamate. IR (KBr ($cm^{-1}$)), N—H; 3257.3, Ar—Br; 1070.3, C═O; 1670, C—S; 1010.5, C═C (Ar); 1486.9, 1596.8, $OCH_3$; 1000, 1250, 2940, Ar—H; (3182.1, 3108.8, 3043.3, 2923.7, 2852.3),$^1$H-NMR (350 MHz acetonitrile-$d_3$) $\delta$ 3.83 (3H, s, $OCH_3$), 7.42–7.51 (4H, m, aromatic), 7.55–7.60 (2H, d, aromatic), 7.71–7.75 (2H, d, aromatic), 8.34 (1H, s, NH).

*S-p*-Chlorophenyl *N-p*-bromophenylthiocarbamate. IR (KBr ($cm^{-1}$)), N—H; 3257.3, Ar—Br; 1070.3, C═O; 1670, C—S; 1010.5, C═C (Ar); 1486.9, 1596.8, Ar—H; (3182.1, 3108.8, 3043.3, 2923.7, 2852.3),$^1$H-NMR (350 MHz, acetonitrile-$d_3$) $\delta$ 7.33 (4H, s, aromatic), 7.52–7.58 (2H, d, aromatic), 7.64–7.70 (2H, d, aromatic), 8.59 (1H, s, NH).

### *Kinetic measurements*

Rates were measured conductometrically in acetonitrile. The conductivity bridge used in this study was WTW LF330 conductivity meter. Pseudo-first-order rate constants, $k_{obs}$, were determined by the Guggenheim method[51] with a large excess of aniline, $[S] = 5 \times 10^{-5}$ M and $[An] = 3–5 \times 10^{-1}$ M. Second-order rate constants, $k_2$, were obtained from the slope of a plot of $k_{obs}$ *versus* [An] with more than five concentrations of aniline. The $k_2$ values are summarized in Table 1.

### *Product analysis*

The substrate, 4-methoxy-*S*-phenyl thio-4-bromo-*N*-phenyl-carbamate (0.1 mol) was reacted with excess aniline (0.3 mol) and stirred for 24 h at 25 °C in acetonitrile and the product was isolated by evaporating the solvent under reduced pressure. The product was collected by column chromatography on aluminum oxide (neutral $Al_2O_3$ grade 90, 63–200 μm) eluted with diethyl ether (10%)-*n*-hexane. Analysis of the product gave the following results:

4-MeO-$C_6H_4NHCONHC_6H_4Br$. Colorless oily liquid; $^1$H NMR (350 MHz, acetonitrile-$d_3$) $\delta$ 3.74 (3H, s, $CH_3$), 6.0 (2H, s, NH), 6.75–6.77 (2H, d, aromatic), 7.41–7.44 (2H, d, aromatic), 7.53–7.57 (4H, m, aromatic); $^{13}$C NMR (100.4 MHz, acetonitrile-$d_3$) $\delta$ 156.4, 151.9, 135.0, 132.2, 122.8, 123.9, 114.8, 55.9; $\nu_{max}$ (KBr) 3350 (NH), 3057 (CH, aromatic), 2837 (CH, $CH_3$), 1598 (C═C, aromatic), 1690 (C═O), 576 (C—Br); MS *m/z* 321 ($M^+$). Anal. Calcd for $C_{14}H_{13}N_2O_2Br$: C, 52.4; H, 4.10; N, 8.73. Found; C, 52.5; H, 4.11; N,8.74.

## Acknowledgements

This work was supported by a Korea Research Foundation Grant funded by the Korean Government (MOEHRD)(KRF-2006-042-C00074).

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