Aminolysis of Aryl Dithio-2-Thiophenates and Dithio-2-Furoates in Acetonitrile

HYUCK KEUN OH,[1] SO YOUNG WOO,[1] CHUL HO SHIN,[1] IKCHOON LEE[2]

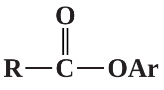
[1]*Department of Chemistry, Chonbuk National University, Chonju 560-756, Korea*
[2]*Department of Chemistry, Inha University, Inchon 402-751, Korea*

Received 25 February 1998; accepted 19 May 1998

ABSTRACT: The aminolyses of the title substrates with anilines and benzylamines are investigated in acetonitrile. A clean second-order kinetics is obtained with a first-order rate law in the amine concentration, which is uncomplicated by the fast proton transfer step. The large magnitude of ρ_Z (ρ_{1g}) as well as ρ_X (ρ_{nuc}) together with relatively large positive ρ_{XZ} values is consistent with a stepwise mechanism in which thiophenolate ion expulsion from the intermediate is rate limiting. For the reactions of aryl dithio-2-thiophenates with benzylamines the magnitude of ρ_X and ρ_Z values is relatively smaller suggesting that both the addition and expulsion of thiophenolate are partially rate determining. Relatively large secondary kinetic isotope effects, $k_H/k_D \geq 1.7$, with deuterated nucleophiles, support involvement a concurrent proton transfer to the departing thiophenolate ion in the transition state. © 1998 John Wiley & Sons, Inc. Int J Chem Kinet 30: 849–857, 1998

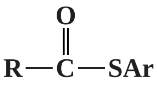
INTRODUCTION

In the acyl transfer reactions, one of the factors that favors the stepwise mechanism involving a tetrahedral addition intermediate is the presence of a strong electron acceptor acyl group [1], R, in **a–d.** It has been shown that a phenyl group, R = C_6H_5, exhibits a relatively strong accepting power leading to the stepwise mechanism with rate-limiting breakdown of a zwitterionic tetrahedral intermediate, $T^{\pm}$, in the aminolysis with relatively basic amines, benzylamines (p$K_a \geq 8.5$), as well as with weakly basic amines, anilines for both aryl benzoates [2], **Ia,** and S-aryl thiolbenzoates [3], **Ib,** in acetonitrile. However, in the aminolysis of dithio analogs, **Id,** and **IId,** a mechanistic changeover from a stepwise mechanism with rate-limiting leaving group departure for weakly basic amines, anilines [4], to that of rate-limiting attack (or concerted mechanism) for basic amines, benzylamines [5,4(b)], was observed in acetonitrile solvent; thus, for **I** (R = C_6H_5) with aniline nucleophiles ($XC_6H_5NH_2$) the magnitudes of β_X (β_{nuc}) and β_Z (β_{1g}, for Ar =



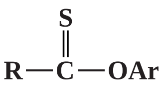
$R-\overset{\displaystyle O}{\overset{\|}{C}}-OAr$

a



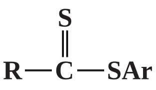
$R-\overset{\displaystyle O}{\overset{\|}{C}}-SAr$

b



$R-\overset{\displaystyle S}{\overset{\|}{C}}-OAr$

c

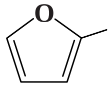


$R-\overset{\displaystyle S}{\overset{\|}{C}}-SAr$

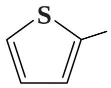
d

R
I : C_6H_5
II : CH_3

III :



IV :



Correspondence to: I. Lee

Contract grant Sponsor: Ministry of Education of Korea
Contract grant number: Basic Science Research Grant (BSRI-97-3431)

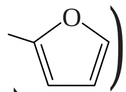
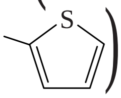
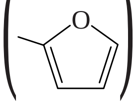
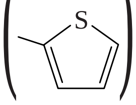
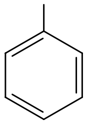
Table I Second-Order Rate Constants, k_N ($\times 10^3$ M^{-1} s^{-1}), for the Reactions of Phenyl Dithio-2-Furoates with Anilines in Acetonitrile at 40.0°C

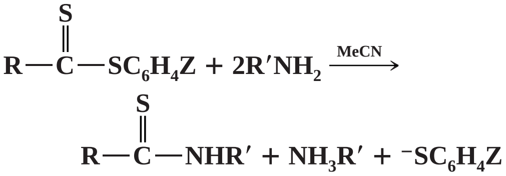
X\Z	*p*-Me	H	*p*-Cl	*p*-Br	ρ_Z[a]	β_Z[a]
p-OMe	12.3	18.5	32.7	35.3	1.05 ± 0.02	-0.46 ± 0.02
p-Me	6.53	10.2	19.3	21.2	1.17 ± 0.03	-0.52 ± 0.02
H	2.70	4.35	8.94	10.1	1.31 ± 0.04	-0.58 ± 0.03
p-Cl	0.829	1.41	2.99	3.43	1.40 ± 0.05	-0.62 ± 0.03
m-Cl	0.341	0.621	1.41	1.62	1.54 ± 0.04	-0.68 ± 0.04
ρ_X[a]	-2.36 ± 0.07	-2.24 ± 0.06	-2.09 ± 0.05	-2.05 ± 0.05		
β_X[a]	0.84 ± 0.02	0.80 ± 0.02	0.74 ± 0.01	0.73 ± 0.01		

[a] Correlation Coeff.: r ≥ 0.997. Errors shown are standard deviations.

C_6H_4Z in **I**) were large, 1.03 and −0.76, respectively, at 55.0°C in acetonitrile [4a] whereas, they were much smaller with $\beta_X = 0.24$ and $\beta_Z = -0.24$ with benzylamines at 30.0°C in acetonitrile [5]. This mechanistic changeover was supported by a change of normal ($k_H/k_D > 1.0$) to inverse ($k_H/k_D < 1.0$) secondary kinetic isotope effect (SKIE) involving deuterated amine nucleophiles [6].

A similar mechanistic change was also observed for aryl dithioacetates, R = CH_3 in **IId** [4(b)].

In this work, we examine the influence of the electron donating ability of the acyl group, R, on the mechanism of the aminolysis of the dithio analogs using 2-furan (R = ), **(IIId),** and 2-thiophene (R = ), **(IVd),** groups. Our high level ab initio MO theoretical studies have shown that the relative delocalizability of lone pair π electrons is in the order **III** () > **IV** () > **I** () [7]. Especially, we are interested to see if there is any mechanistic change of the kind encountered in the aminolysis of benzoates (R = C_6H_5) as we vary amines from weakly basic, anilines, to basic, benzylamines, eq. (1), where R = 2-furan or 2-thiophene, R′ = XC_6H_4, or $XC_6H_4CH_2$ with X = *p*-OMe,



$$\mathrm{R{-}\overset{\overset{\large S}{\|}}{C}{-}SC_6H_4Z + 2R'NH_2 \xrightarrow{MeCN} R{-}\overset{\overset{\large S}{\|}}{C}{-}NHR' + NH_3R' + {}^{-}SC_6H_4Z} \qquad (1)$$

p-Me, H, *p*-Cl, or *m*-Cl and Z = *p*-CH_3, H, *p*-Cl, or *p*-Br. Acetonitrile was used as a reaction medium in order to avoid complexities arising from the fast proton transfer step in aqueous solution [3–5,8]. In this work, we adopt a convention of labeling substituents in the nucleophile (anilines), substrate, and departing group as X, Y, and Z, respectively.

RESULTS AND DISCUSSION

Under the reaction conditions (see Tables I–IV) all reactions obeyed the simple kinetic law given by eqs.

Table II Second-Order Rate Constants, k_N ($\times 10^2$ M^{-1} s^{-1}), for the Reactions of Phenyl Dithio-2-Furoates with Benzylamines in Acetonitrile at 15.0°C

X\Z	*p*-Me	H	*p*-Cl	*p*-Br	ρ_Z[a]	β_Z[a]
p-OMe	4.70	8.63	19.6	22.5	1.55 ± 0.04	-0.68 ± 0.04
p-Me	3.14	5.98	15.3	17.4	1.71 ± 0.03	-0.75 ± 0.03
H	1.67	3.40	9.19	10.7	1.85 ± 0.04	-0.81 ± 0.04
p-Cl	0.831	1.71	4.79	5.64	1.90 ± 0.05	-0.84 ± 0.04
ρ_X[a]	-1.47 ± 0.08	-1.37 ± 0.05	-1.21 ± 0.02	-1.18 ± 0.01		
β_X[a]	1.50 ± 0.09	1.40 ± 0.06	1.24 ± 0.03	1.21 ± 0.02		

[a] Correlation Coeff.: r ≥ 0.997. Errors shown are standard deviations.

Table III Second-Order Rate Constants, k_N ($\times 10^4$ M^{-1} s^{-1}), for the Reactions of Phenyl Dithio-2-Thiophenates with Anilines in Acetonitrile at 40.0°C

X\Z	*p*-Me	H	*p*-Cl	*p*-Br	ρ_Z[a]	β_Z[a]
p-OMe	8.02	15.9	42.2	44.5	1.74 ± 0.02	−0.77 ± 0.03
p-Me	4.45	9.15	25.6	26.5	1.82 ± 0.03	−0.80 ± 0.04
H	1.70	3.76	10.7	11.0	1.90 ± 0.05	−0.84 ± 0.05
p-Cl	0.412	0.955	3.03	3.27	2.10 ± 0.02	−0.92 ± 0.05
m-Cl	0.184	0.428	1.43	1.56	2.17 ± 0.01	−0.95 ± 0.04
ρ_X[a]	−2.55 ± 0.02	−2.44 ± 0.04	−2.29 ± 0.03	−2.26 ± 0.02		
β_X[a]	0.91 ± 0.02	0.87 ± 0.02	0.81 ± 0.02	0.80 ± 0.02		

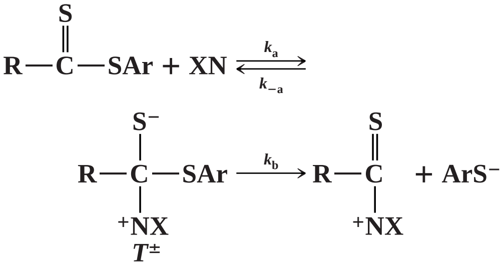
[a] Correlation Coeff.: r ≥ 0.996. Errors shown are standard deviations.

(2) and (3), where P is thiophenolate anion and N is amine. Plots of k_{obs} vs. [N] were linear, and

$$d[P]/dt = k_{obs}[\text{Substrate}] \qquad (2)$$

$$k_{obs} = k_N[N] \qquad (3)$$

the k_N values were obtained from the slopes of these plots. The k_N values determined are summarized in Tables I–IV. The rates are faster with benzylamines than with anilines, and, also, are faster with a stronger nucleophile (X = *p*-OMe) and a stronger nucleofuge (Z = *p*-Br). These trends are in accord with those for typical nucleophilic substitution reactions. For these series of reactions with benzylamines as well as anilines, clean second-order kinetics, eqs. (2) and (3), were obtained and, hence, there were no complications arising from competition of the fast proton transfer from $T^{\pm}$, nor from general base catalysis by the amines [8]. The mechanism of the reactions can, therefore, be described completely by eq. (4), where Ar = C_6H_4Z, XN represents amines with substituent X, and R is 2-furan or 2-thiophene. Thus k_N in eq. (3) is a complex quantity given by eq. (5).



(4)

$$kN = \frac{k_a}{k_{-a}} \cdot k_b = Kk_b \qquad (5)$$

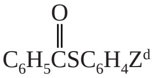
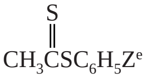
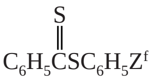
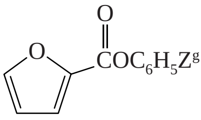
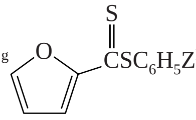
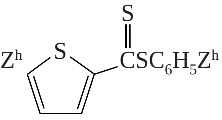
The Hammett ρ and Brønsted β values are summarized in Tables I–IV. Since the reactions were conducted in acetonitrile, the magnitude of β_X (β_{nuc}) and β_Z (β_{1g}) determined using the pK_a values in water may not be reliable. However, as we have pointed out previously the β_X values can provide reasonable guides [4b], since although the absolute values of pK_a in MeCN differ from those in water a constant ΔpK_a ($= pK_{CH_3CN_3} - pK_{a\ H_2O_2} \cong 7.5$) was experimentally found [9]. The values of β_z may be significantly smaller than the values reported on the basis of

Table IV Second-Order Rate Constants, k_N ($\times 10^2$ M^{-1} s^{-1}), for the Reactions of Phenyl Dithio-2-Thiophenates with Benzylamines in Acetonitrile at 15.0°C

X\Z	*p*-Me	H	*p*-Cl	*p*-Br	ρ_Z[a]	β_Z[a]
p-OMe	3.24	4.84	9.00	9.46	1.09 ± 0.02	−0.48 ± 0.01
p-Me	2.37	3.72	7.33	7.73	1.20 ± 0.01	−0.53 ± 0.01
H	1.61	2.56	5.28	5.57	1.26 ± 0.02	−0.56 ± 0.02
p-Cl	0.885	1.48	3.31	3.52	1.41 ± 0.02	−0.62 ± 0.02
ρ_X[a]	−1.09 ± 0.04	−1.00 ± 0.02	−0.85 ± 0.01	−0.84 ± 0.01		
β_X[a]	1.11 ± 0.03	1.02 ± 0.02	0.87 ± 0.01	0.86 ± 0.01		

[a] Correlation Coeff.: r ≥ 0.999. Errors shown are standard deviations.

Table V Comparison of ρ_X, ρ_Z, and ρ_{XZ} Values for the Aminolysis of Various Aryl Thiol and Dithio Compounds in Acetonitrile

		 $C_6H_5\overset{\overset{O}{\|}}{C}SC_6H_4Z$[d] (Ib)	 $CH_3\overset{\overset{S}{\|}}{C}SC_6H_5Z$[e] (IId)	 $C_6H_5\overset{\overset{S}{\|}}{C}SC_6H_5Z$[f] (Id)	 [g] (IIIa)	 [h] (IIId)	 [h] (IVd)
ρ_X	AN[a]		-2.86–-3.11	-2.23–-2.96		-2.05–-2.36	-2.26–-2.55
	BA	-1.41–-2.06	-0.46–-0.63	-0.51–-0.73	-1.05–-1.92	-1.18–-1.47	-0.84–-1.09
ρ_Z	AN		1.66–1.95	1.46–2.33		1.05–1.54	1.74–2.17
	BA	3.22–4.07	1.09–1.28	0.43–0.69	1.76–2.53	1.55–1.90	1.09–1.41
ρ_{XZ}	AN		0.58(50°)	0.60(55°)		0.75 ± 0.05(40°)[i] (0.998)[j]	0.68 ± 0.07(40°)[i] (0.999)[j]
	BA	0.27(55°)[c]	0.61(−20°)	0.50(30°)	1.19(55°)	0.65 ± 0.14(15°) (0.999)	0.59 ± 0.06(15°) (0.999)
RDS[b]	AN		Ex.	Ex.		Ex.	Ex.
	BA	Ex.	Ad.	Ad.	Ex.	Ex.	Ad-Ex.

[a] Nucleophiles: AN = aniline, BA = benzylamine.

[b] RDS: rate-determining step: Either expulsion of leaving group (Ex.) or addition (Ad.) step.

[c] Temperature in °C.

[d] Ref. [3].

[e] Ref. [4(b)].

[f] Ref. [4(a), 5].

[g] H. J. Koh, J-W Lee, H. W. Lee, and I. Lee, *New J. Chem.*, **21,** 447, 1997.

[h] This work.

[i] Standard deviation.

[j] Correlation coefficient.

aqueous acidities. In Table V, we compared ρ_X (ρ_{nuc}), ρ_Z (ρ_{1g}), and ρ_{XZ} (defined in eqs. (6)) [10] values for the aminolysis of various aryl thiol and dithio derivatives in acetonitrile. It has been shown that the magnitudes of ρ_X and ρ_Z are

$$\log(k_{XZ}/k_{HH}) = \rho_X\sigma_X + \rho_Z\sigma_Z + \rho_{XZ}\sigma_X\sigma_Z \tag{6a}$$

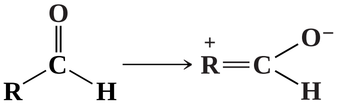
$$\rho_{XZ} = \frac{\partial\rho_Z}{\partial\sigma_X} = \frac{\partial\rho_X}{\partial\sigma_Z} \tag{6b}$$

considerably larger for the rate-limiting leaving group departure (k_b) than those for the corresponding values of the rate-limiting addition (k_a) [4(a),5,11], and the cross-interaction constants ρ_{XZ} are relatively large positive value for the rate-determining expulsion of leaving group from $T^{\pm}$ [4(a),5,11].

Reference to Table V reveals that for rate-limiting leaving group departure in the aminolysis of **Ib** and **IIIa** with benzylamines the magnitudes of ρ_X and ρ_Z values are indeed much greater than those corresponding reactions of **Id** and **IId** with benzylamines for which the rate-determining step is the addition of benzylamines. Comparison of the reactions of **Ib** and **Id** with benzylamines (p$K_a \geq 9$) shows that the change of O^- **(Ib)** to S^- **(Id)** in $T^{\pm}$ favors arylthiolate ion expulsion suggesting the change of the k_{-a}/k_b ratio from >1.0 for **Ib** to $\ll 1.0$ for **Id.** In contrast, the aminolysis of **Id** with anilines (p$K_a < 5$) leads to rate-limiting addition, i. e., to the k_{-a}/k_b ratio of >1.0. These are in line with the results of Castro et. al., for the aminolysis of **IId** with secondary alicyclic amines in aqueous solution [8(a)].

Relatively large magnitudes of ρ_X and ρ_Z values for the aminolysis of **IIId** and **IVd** seem to support a stepwise mechanism with rate-limiting expulsion of the arylthiolate group. Consideration of temperature effect on the relatively smaller magnitude of ρ_X and ρ_Z values [12] for the reactions of **IVd** with benzylamines (15°C), however, raises some doubt about this conclusion. We note that the magnitudes of ρ_X and ρ_Z values for **IVd** with benzylamines are smaller than those for **Ib** and **IIIa** (which are believed to proceed by rate-limiting leaving group departure) but are greater than those for **Id** and **IId** (for which rate-limiting addition is predicted). Thus, based on these comparisons, we may conclude that both steps are partially rate determining in the reactions of **IVd** with benzylamines. It is also notable that the magnitude of β_X (0.86–1.11) as well as β_Z (-0.48–-0.62) for the reactions of **IVd** with benzylamines in acetonitrile is also in between those reported for the rate-limiting attack (β_X = 0.2–0.7, $\beta_Z = -0.3$–-0.4) and rate-limiting expulsion of phenolate or thiophenolate ion (β_X = 0.8–1.4, $\beta_Z = -1.0$–-1.5) in aqueous solution [13]. Relatively large positive ρ_{XZ} values for both **IIId** and **IVd** are also in line with the proposed mechanism [11].

Our ab initio computations at the MP2/6-31G*//MP2/6-31G* level [14] have shown that the delocalizability of ring electrons (R) to the carbonyl group, eq. (7), i.e., the stability of RCOH, is in the order R = **III** > **IV** > **I** [7].



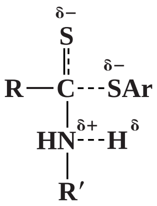
(7)

Accordingly, the natural bond orbital (NBO) positive charge on the carbonyl carbon has been found to be in the reverse order **III** (0.328) < **IV** (0.351) < **I** (0.376). This analysis suggests that if the initial state stability and the positive charge on the carbonyl carbon were important, i.e., if all the reactions proceeded by rate-limiting attack, the aminolysis rate should be the least with **IIId** and the fastest with **Id.** Examination of the rate constants in Table VI, however, shows that this expectation is not fulfilled. In fact, there is a change in the rate determining step from addition of amine to expulsion of thiophenolate as we vary R from **I** through **IV** to **III** so that direct comparison of the rate is meaningless. For example, the reactions of **Ia**–**Ic** with benzylamines are reported to proceed by rate-limiting departure of the leaving group. Roughly, change of OAr **(Ia)** to SAr **(Ib)** (for Ar = $C_6H_4 \cdot$ p-NO_2) brings a rate increase of ca. 10^2, while change of —C(=O)—**(Ia)** to —C(=S)—**(Ic)** leads to a rate increase of ca. 20. Thus, there is a ca. 10^3 times rate increase from **Ia** to **Ic.** However, no such large rate increase is expected when the rate with benzylamine of **Ia** is compared with that of **Id;** although a direct comparison is difficult due to the different reaction temperature, rough estimate gives a rate ratio that is an order of magnitude lower, $k_{(Id)}/k_{(Ia)} \approx 10^2$. This may be due to the mechanistic difference in the reactions of the two, **Ia** (ex.) vs. **Id** (ad.). Similarly, comparison of rates between the reactions of **IIIa** and **IIId** leads to ca. 10^3 considering the temperature difference of 40° [12] between the two rate constants listed in Table VI. Since the mechanism of the two reactions is rate-limiting expulsion of the thiophenolate ion, the approximate agreement with the rate increase accompanied in the change of **Ia** → **Ib** → **Ic** is satisfactory.

We note that a change of phenolate (OAr) to thiophenolate (SAr) results in a large rate increase, ca. 10^2 times, but a change of —C(=O)— to —C(=S)— only leads to a moderate rate increase, ca. 20 times. This seems to contradict the results of Castro et. al., who reported a decrease of rate with change of —C(=O)— to —C(=S)— [8], but discrepancy may result from the different medium, i. e., aprotic vs. aqueous solution.

In summary, the reactions of **Id**–**IVd** with anilines proceed by a stepwise mechanism with rate-limiting departure of the thiophenolate ion from the zwitterionic tetrahedral intermediate, $T^{\pm}$. In contrast, for the corresponding reactions with the more basic amines, benzylamine, the rate determining step changes from the rate-limiting departure for a stronger inductive electron acceptor acyl group, R = **III,** to the rate-limiting addition for a weaker acceptor acyl group, R = **I.** For R = **IV,** which has an intermediate acceptor ability [16], both steps are partially rate determining.

Finally, we have determined secondary kinetic isotope effects involving deuterated aniline and benzylamine nucleophiles. The k_H/k_D values are substantially greater than 1.0 ranging from 1.7–1.9, Table VII. Since the rates were first-order with respect to amine concentration, eq. (3), general base catalysis by the amine can be safely precluded. Thus, the relatively large k_H/k_D values in Table VII seem to reflect a four-center type transition state, **V,** where R′ = C_6H_4X or $C_6H_4CH_2X$.



V

This type of four-centered transition state in which there is concurrent thiophenolate ion departure and proton transfer has also been proposed previously for the aminolysis of phenyl dithioacetates **(IId)** [4(b)], ethyl aryl carbonates [17] (EtO—C(=O)—OAr) and O-ethyl S-aryl dithiocarbonates [18] (EtO—C(=S)—SAr) in acetonitrile.

Table VI Rate Constants, k_N (M^{-1} s^{-1}), for Acyl Transfer Reactions between Amines and Phenolates or Thiophenolates in Acetonitrile[a]

Nucleophile	$C_6H_5\overset{O}{\overset{\|}{C}}OAr^{c,e}$ Ia	$C_6H_5\overset{O}{\overset{\|}{C}}SAr^{d}$ Ib	$C_6H_5\overset{S}{\overset{\|}{C}}OAr^{e}$ Ic	$C_6H_5\overset{S}{\overset{\|}{C}}SAr^{f}$ Id	$C_4H_3O\overset{O}{\overset{\|}{C}}OAr^{g}$ IIIa	$C_4H_3O\overset{S}{\overset{\|}{C}}SAr^{h}$ IIId	$C_4H_3S\overset{S}{\overset{\|}{C}}SAr^{h}$ IVd
Aniline				2.85×10^{-3}(55°)		4.35×10^{-3}(40°)	3.76×10^{-4}(40°)
Benzylamine	2.29×10^{-2}(55°)*[b]	2.51×10^{-3}(55°)	1.86 (25°)* (20%MeCN)	3.82×10^{-1}(30°)	5.01×10^{-2}(55°)*	3.40×10^{-2}(15°)	2.56×10^{-2}(15°)
	9.65×10^{-2}(25°)* (20%MeCN)	2.50(55°)*		1.05(30°)*		1.13(15°)*	

[a] Unless otherwise noted, acetonitrile is used.

[b] Temperature (°C). Starred for $Z = p\text{-}NO_2$ in $Ar = C_6H_4Z$ and unstarred for Z = H. Some k_N values for $Z = p\text{-}NO_2$ are estimated using $\rho\sigma$ relations.

[c] H. J. Koh, H. C. Lee, H. W. Lee, and I. Lee, *Bull. Korean Chem. Soc.*, **16,** 839 (1995).

[d] Same as in Table V.

[e] Ref. [2(b)].

[f–h] Same as in Table V.

Table VII Secondary Kinetic Isotope Effects for the Reactions of Phenyl Dithio-2-Furoates (IIId) with Deuterated Anilines at 40.0°C and Phenyl Dithio-2-thiophenates (IVd) with Deuterated Benzylamines in Acetonitrile at 15.0°C

Nucleophile	X	Z	k_H (dm^3 mol^{-1} s^{-1})	k_D (dm^3 mol^{-1} s^{-1})	k_H/k_D
AN	*p*-OMe	*p*-Me	(12.3 ± 0.13[a]) × 10^{-3}	(7.02 ± 0.12) × 10^{-3}	1.75 ± 0.04[a]
	p-Cl	*p*-Me	(8.29 ± 0.02) × 10^{-3}	(4.53 ± 0.02) × 10^{-3}	1.83 ± 0.01
	p-OMe	*p*-Br	(35.3 ± 0.21) × 10^{-3}	(19.9 ± 0.23) × 10^{-3}	1.78 ± 0.02
	p-Cl	*p*-Br	(3.43 ± 0.05) × 10^{-3}	(1.86 ± 0.05) × 10^{-3}	1.84 ± 0.06
BA	*p*-OMe	*p*-Me	(32.4 ± 0.24[a]) × 10^{-3}	(18.8 ± 0.25) × 10^{-3}	1.72 ± 0.03[a]
	p-Cl	*p*-Me	(8.85 ± 0.16) × 10^{-3}	(4.97 ± 0.16) × 10^{-3}	1.78 ± 0.07
	p-OMe	*p*-Br	(94.6 ± 0.45) × 10^{-3}	(52.3 ± 0.47) × 10^{-3}	1.81 ± 0.02
	p-Cl	*p*-Br	(35.2 ± 0.22) × 10^{-3}	(18.6 ± 0.21) × 10^{-3}	1.89 ± 0.02

[a] Standard deviation.

EXPERIMENTAL

Materials

Solvent, acetonitrile, was Merck G. R. grade, which was used after three distillations. Anilines and benzylamines were Tokyo Kasei G. R. grade.

a. Preparation of S-phenyl thio-2-thiophenecarboxylates (and thio-2-furancarboxylates). Thiophenol derivatives (Aldrich G. R. grade) and 2-thiophenecarbonyl chloride (Aldrich G. R. grade) were dissolved in dry ether kept at 0 ca. 5°C, and a small amount of KOH was added successively. Adding ice to the reaction mixture, ether layer was separated and extracted twice. After drying with MgSO$_4$, solvent was removed by distillation under reduced pressure. Melting points, IR, proton, and carbon ^{13}NMR analytical data are as follows.

S-phenyl thio-2-thiophenate: m. p. 62–63°C, IR (KBr), 3082 (C—H, thiophene), 1658 (C═O), 1553, 1465 (C═C, aromatic), 803 (C—H, aromatic); δ_H (CDCl$_3$), 7.96 (1H, dd, J = 3.66, 1.47Hz, thiophene), 7.71 (1H, dd, J = 5.13, 1.46Hz, thiophene), 7.48–7.59 (5H, m, phenyl ring), 7.20 (1H, dd, J = 5.13, 4.40Hz, thiophene); δ_C 181.0 (C═O), 141.4, 135.1, 133.2, 131.6, 129.3, 128.0, 127.0.

S-p-methylphenyl thio-2-thiophenate: m. p. 68–69°C, IR (KBr), 3104 (C—H, thiophene), 1659 (C═O), 1552, 1478 (C═C, aromatic), 804 (C—H, aromatic); δ_H (CDCl$_3$), 7.89 (1H, dd, J = 3.66Hz, thiophene), 7.65 (1H, d, J = 4.39Hz, thiophene), 7.39 (2H, d, phenyl ring), 7.25 (1H, d, J = 8.06Hz, phenyl ring), 7.15 (1H, t, J = 4.40Hz), 2.43 (3H, s, methyl); δ_C 182.5 (C═O), 140.0, 135.0, 133.0, 131.5, 130.0, 127.9, 123.4 (methyl).

S-p-chlorophenyl thio-2-thiophenate: m. p. 85–86°C, IR (KBr), 3122 (C—H, thiophene), 1658 (C═O), 1556, 1478 (C═C, aromatic), 809 (C—H, aromatic); δ_H (CDCl$_3$), 7.89 (1H, dd, J = 3.66, 1.47Hz, thiophene), 7.67 (1H, dd, J = 4.39, 1.46Hz, thiophene), 7.45 (2H, dd, 8.80, 2.20Hz, phenyl ring), 7.41 (2H, dd, J = 8.80, 2.20Hz, phenyl ring), 7.16 (1H, dd, J = 5.14, 4.40Hz, thiophene); δ_C 181.5 (C═O), 141.0, 136.3, 136.1, 133.5, 131.8, 129.5, 128.1, 125.4.

S-p-bromophenyl thio-2-thiophenate: m. p. 90–91°C, IR (KBr), 3110 (C—H, thiophene), 1658 (C═O), 1557, 1462 (C═C, aromatic), 810 (C—H, aromatic); δ_H (CDCl$_3$), 7.96 (1H, d, J = 2.93Hz, thiophene), 7.68 (1H, dd, J = 5.13, 1.47Hz, thiophene), 7.57 (2H, dt, 8.80, 2.20Hz, phenyl ring), 7.38 (2H, dt, J = 8.80, 2.20Hz, phenyl ring), 7.16 (1H, dd, J = 5.13, 4.40Hz, thiophene); δ_C 181.3 (C═O), 141.0, 136.4, 133.5, 132.5, 131.8, 128.1, 126.1, 124.4.

S-phenyl thio-2-furoate: m. p. 54–55°C, IR (KBr), 3033 (C—H, furan), 1662 (C═O), 1565, 1464 (C═C, aromatic), 751 (C—H, aromatic); δ_H (CDCl$_3$), 7.61 (1H, s, furan), 7.43–7.51 (5H, m, phenyl), 7.25 (1H, d, J = 3.42Hz, furan), 6.59 (1H, dd, J = 3.42, 1.47Hz, furan); δ_C 178.4 (C═O), 150.1, 146.3, 134.9, 129.5, 129.1, 126.0, 116.1, 112.4.

S-p-methylphenyl thio-2-furoate: m. p. 77–78°C, IR (KBr), 3124 (C—H, furan), 1661 (C═O), 1561, 1459 (C═C, aromatic), 768 (C—H, aromatic); δ_H (CDCl$_3$), 7.61 (1H, s, furan), 7.38 (2H, d, J = 7.81Hz, phenyl ring), 7.25 (2H, d, 8.30Hz, phenyl ring), 7.23 (1H, d, J = 3.42Hz, furan), 6.56 (1H, dd, J = 3.42, 1.47Hz, furan), 2.39 (3H, s, methyl); δ_C 177.7 (C═O), 150.3, 141.1, 139.8, 134.9, 129.9, 122.4, 116.0, 112.2, 21.3 (methyl).

S-p-chlorophenyl thio-2-furoate: m. p. 102–103°C, IR (KBr), 3122 (C—H, furan), 1665 (C═O), 1556, 1468 (C═C, aromatic), 767 (C—H, aromatic); δ_H (CDCl$_3$), 7.63 (1H, s, furan), 7.39–7.43 (4H, m, phenyl ring), 7.27 (1H, d, J = 3.42Hz, furan), 6.59

(1H, dd, J = 3.42, 1.47Hz, furan); δ_C 177.0 (C═O), 149.9, 146.5, 136.2, 136.0, 129.4, 124.5, 116.4, 112.4.

S-p-bromophenyl thio-2-furoate: m. p. 138–139°C, IR (KBr), 3105 (C—H, furan), 1662 (C═O), 1561, 1470 (C═C, aromatic), 766 (C—H, aromatic); δ_H ($CDCl_3$), 7.63 (1H, s, furan), 7.57 (2H, d, J = 8.30Hz, phenyl ring), 7.36 (2H, d, J = 8.30Hz, phenyl ring), 7.27 (1H, d, J = 3.91Hz, furan), 6.59 (1H, dd, J = 3.42, 1.47Hz, furan); δ_C 177.7 (C═O), 149.9, 146.5, 136.4, 132.3, 125.2, 124.2, 116.4, 112.4.

b. Preparation of Phenyl Dithio-2-thiophenecarboxylates (and Phenyl Dithio-2-furan-carboxylates). The S-phenyl thio-2-thiophenecarboxylates prepared as above were dissolved in dry toluene and refluxed with Lawesson's reagent (Aldrich G. R. grade). After extraction of the reaction mixture with dichloromethane, dried and removed solvent by distillation under reduced pressure. Separation by column chromatography gave the products, for which the following analytical data were obtained.

phenyl dithio-2-thiophenate: m. p. 52–53°C, IR (KBr), 3081 (C—H, thiophene), 1562, 1471 (C═C, aromatic), 1054 (C═S), 783 (C—H, aromatic); δ_H ($CDCl_3$), 7.96 (1H, d, J = 3.91Hz, thiophene), 7.67 (1H, d, J = 4.88Hz, thiophene), 7.47–7.50 (5H, m, phenyl ring), 7.15 (1H, t, J = 4.40Hz, thiophene); δ_C 213.8 (C═S), 151.2, 135.8, 135.5, 133.1, 130.4, 129.5, 128.6, 127.0.

p-methylphenyl dithio-2-thiophenate: m. p. 58–59°C, IR (KBr), 3075 (C—H, thiophene), 1594, 1496 (C═C, aromatic), 1050 (C═S), 777 (C—H, aromatic); δ_H ($CDCl_3$), 7.95 (1H, d, J = 3.90Hz, thiophene), 7.66 (1H, d, J = 4.89Hz, thiophene), 7.36 (2H, d, J = 7.82Hz, phenyl ring), 7.29 (2H, d, J = 7.82Hz, phenyl ring), 7.15 (1H, t, J = 4.40Hz, thiophene), 2.42 (3H, s, methyl); δ_C 214.4 (C═S), 21.58 (methyl), 151.2, 140.9, 135.6, 135.3, 130.8, 130.4, 128.6, 127.0.

p-chlorophenyl dithio-2-thiophenate: m. p. 67–68°C, IR (KBr), 3075 (C—H, thiophene), 1572, 1473 (C═C, aromatic), 1049 (C═S), 774 (C—H, aromatic); δ_H ($CDCl_3$), 7.94 (1H, dd, J = 5.14, 1.47Hz, thiophene), 7.68 (1H, dd, J = 5.13, 1.47Hz, thiophene), 7.47 (2H, d, J = 8.79Hz, phenyl ring), 7.40 (2H, d, J = 8.79Hz, phenyl ring), 7.16 (1H, dd, J = 5.13, 4.40Hz, thiophene); δ_C 212.9 (C═S), 151.0, 137.0, 136.9, 135.8, 129.8, 128.7, 128.6, 127.2.

p-bromophenyl dithio-2-thiophenate: m. p. 77–78°C, IR (KBr), 3075 (C—H, thiophene), 1565, 1473 (C═C, aromatic), 1049 (C═S), 775 (C—H, aromatic); δ_H ($CDCl_3$), 7.94 (1H, d, J = 3.91Hz, thiophene), 7.68 (1H, d, J = 4.89Hz, thiophene), 7.62 (2H, d, J = 7.81Hz, phenyl ring), 7.32 (2H, d, J = 7.81Hz, phenyl ring), 7.16 (1H, t, J = 4.40Hz, thiophene); δ_C 212.7 (C═S), 151.0, 137.3, 135.8, 132.8, 129.4, 128.7, 127.3, 125.4.

phenyl dithio-2-furoate: m. p. 54–55°C, IR (KBr), 3105 (C—H, furan), 1550, 1448 (C═C, aromatic), 1055 (C═S), 600 (C—H, aromatic); δ_H ($CDCl_3$), 7.69 (1H, s, furan), 7.46–7.51 (5H, m, phenyl), 7.44 (1H, d, J = 3.91Hz, furan), 6.57 (1H, dd, J = 3.42, 1.47Hz, furan); δ_C 206.6 (C═S), 157.3, 146.6, 135.8, 130.2, 129.3, 129.1, 116.0, 113.4.

p-methylphenyl dithio-2-furoate: m. p. 79–80°C, IR (KBr), 3125 (C—H, furan), 1561, 1451 (C═C, aromatic), 1058 (C═S), 804 (C—H, aromatic); δ_H ($CDCl_3$), 7.68 (1H, s, furan), 7.44 (2H, d, J = 3.42Hz, furan), 7.36 (2H, d, J = 8.30Hz, phenyl ring), 7.31 (2H, d, J = 8.30Hz, phenyl ring), 6.54 (1H, dd, J = 3.42, 1.47Hz, furan), 2.43 (3H, s, methyl); δ_C 205.5 (C═S), 157.4, 146.6, 140.7, 135.6, 130.3, 125.6, 115.9, 113.5, 21.6 (methyl).

p-chlorophenyl dithio-2-furoate: m. p. 83–84°C, IR (KBr), 3138 (C—H, furan), 1552, 1451 (C═C, aromatic), 1056 (C═S), 803 (C—H, aromatic); δ_H ($CDCl_3$), 7.70 (1H, s, furan), 7.47 (2H, d, J = 8.79Hz, phenyl ring), 7.44 (1H, s, furan), 7.38 (2H, d, J = 8.79Hz, phenyl ring), 6.58 (1H, dd, J = 3.42, 1.47Hz, furan); δ_C 205.8 (C═S), 157.3, 146.8, 137.2, 136.9, 129.8, 127.6, 116.4, 113.6.

p-bromophenyl dithio-2-furoate: m. p. 86–87°C, IR (KBr), 3128 (C—H, furan), 1554, 1452 (C═C, aromatic), 1058 (C═S), 804 (C—H, aromatic); δ_H ($CDCl_3$), 7.70 (1H, s, furan), 7.62 (2H, d, J = 8.30Hz, phenyl ring), 7.45 (1H, d, J = 3.91Hz, furan), 7.31 (1H, d, J = 8.79Hz, phenyl ring), 6.58 (1H, dd, J = 3.42, 1.47Hz, furan); δ_C 205.6 (C═S), 157.3, 146.8, 137.3, 132.7, 128.1, 125.2, 116.4, 113.6.

Kinetic Procedure

The reactions were followed conductimetrically under pseudo-first-order condition with excess amount of amine, [substrate] $\cong 10^{-3}$M and [N] $\cong$ 0.03–0.5M. The rate constants, k_N in eq. (3), were obtained as described previously [3,19]. The rate constants reported were averages of more than two determinations and were reproducible to ±5%.

Product Analysis

Substrate, phenyl dithio-2-thiophenate (dithio-2-furoate) (0.05 mole) and aniline (0.5 mole) were added to acetonitrile and reacted at 40.0°C under the same condition as the kinetic measurements. After more than 15 half-lives, solvent was removed under reduced pressure and anilide was separated by column chromatography. Analytical data are as follows.

$C_4H_3SC({=}S)NHCH_2C_6H_5$: m. p. 85–87°C, IR (KBr), 3073 (thiophene, C—H), 1120 (C═S), 811 (aromatic, C—H); δ_{H} ($CDCl_3$), 8.55 (1H, br.s, NH), 6.98–7.56 (8H, m, phenyl, and thiophene), 4.53 (2H, s, CH_3), δ_{C} 170.9, 137.9, 135.5, 132.0, 130.0, 128.4, 128.2, 127.6, 127.2, 43.8.

$C_4H_3SC({=}S)NHC_6H_5$: m. p. 74–76°C, IR (KBr), 2927 (thiophene, C—H), 1122 (C═S), 818 (aromatic, C—H); δ_{H} ($CDCl_3$), 8.62 (1H, br.s, NH), 6.98–7.76 (8H, m, aromatic, and thiophene), δ_{C} 182.0, 139.2, 135.4, 131.9, 129.1, 128.6, 128.5, 127.6, 124.2.

$C_4H_3OC({=}S)NHCH_2C_6H_5$: m. p. 81–83°C, IR (KBr), 3374 (furan, C—H), 1070 (C═S), 811 (aromatic, C—H); δ_{H} ($CDCl_3$), 8.18 (1H, br.s, NH), 6.44–7.47 (8H, m, phenyl, and furan), 4.97 (2H, d, J = 5.37Hz, CH_2), δ_{C} 182.0, 151.9, 143.6, 136.1, 128.7, 128.1, 127.8, 117.9, 113.0, 48.9.

$C_4H_3OC({=}S)NHC_6H_5$: m. p. 65–67°C, IR (KBr), 3356 (furan, C—H), 1072 (C═S), 811 (aromatic, C—H); δ_{H} ($CDCl_3$), 8.11 (1H, br.s, NH), 6.52–7.81 (8H, m, aromatic, and furan), δ_{C} 180.3, 152.7, 143.6, 137.8, 128.8, 126.7, 123.5, 118.5, 113.5.

We thank the Ministry of Education of Korea for a Basic Science Research Grant (BSRI-97-3431) for this work, and, also, Inha University for the continued support.

BIBLIOGRAPHY

1. I. Lee, D. Lee, and C. K. Kim, *J. Phys. Chem. (A),* **101,** 879 (1997).
2. (a) F. M. Menger and J. H. Smith, *J. Am. Chem. Soc.,* **94,** 3824 (1972); (b) P. Campbell and B. A. Lapinskas, *J. Am. Chem. Soc.,* **99,** 5378 (1977).
3. I. Lee, and H. J. Koh, *New. J. Chem.,* **20,** 131 (1996).
4. (a) H. K. Oh, C. H. Shin, and I. Lee, *J. Chem. Soc., Perkin Trans.* **2,** (1995), 1169; (b) H. K. Oh, S. Y. Woo, C. H. Shin, Y. S. Park, and I. Lee, *J. Org. Chem.,* **62,** 5780 (1997).
5. H. K. Oh, C. H. Shin, and I. Lee, *Bull. Korean Chem. Soc.,* **16,** 657 (1995).
6. I. Lee, *Chem. Soc. Rev.,* **24,** 223 (1995).
7. I. Lee, C. K. Kim, and B. S. Lee, *J. Phys. Chem.,* submitted.
8. (a) E. A. Castro, F. Ibàñez, J. G. Santos, and C. Ureta, *J. Chem. Soc., Perkin Trans. 2,* 1991, 1919; (b) E. A. Castro, M. Cubillos, and J. G. Santos, *J. Org. Chem.,* **61,** 3501 (1996).
9. (a) C. D. Ritchie in *Solute-Solvent Interactions*, J. F. Coetzee and C. D. Ritchie, Eds., Marcel Dekker, New York, 1969, Chap. 4; (b) J. F. Coetzee, *Prog. Phys. Org. Chem.,* **4,** 54 (1967); (c) W. J. Spillane, G. Hogan, P. McGrath, J. King, and C. Brack, *J. Chem. Soc., Perkin Trans.* **2,** 2099, (1996).
10. (a) I. Lee, *Chem. Soc. Rev.,* **19,** 317 (1990); (b) I. Lee, *Adv. Phys. Org. Chem.,* **27,** 57 (1992).
11. (a) I. Lee, *Bull. Korean Chem. Soc.,* **15,** 985 (1994); (b) D. Lee, C. K. Kim, B. S. Lee, and I. Lee, *Bull. Korean Chem. Soc.,* **16,** 1203 (1995).
12. G. W. Klumpp, *Numerical Values of all Susceptibility Factors Decrease with Increasing Temperature, Reactivity in Organic Chemistry* Wiley, New York, p.224, (1982).
13. D. J. Hupe, and W. P. Jencks, *J. Am. Chem. Soc.,* **99,** 451 (1977).
14. W. J. Hehre, L. Radom, P. v. R. Schleyer, and J. A. Pople, *"Ab Initio Molecular Orbital Theory"* Wiley, New York, Chapter 4, (1986).
15. (a) T. K. Brunck, and F. Weinhold, *J. Am. Chem. Soc.,* **101,** 1700 (1979); (b) A. E. Reed, L. A. Curtiss, and F. Weinhold, *Chem. Rev.,* **88,** 899 (1988).
16. The *average aryl substituent constants* are 0.57, 0.50, and 0 for III, IV, and I, respectively. O. Exner, in *"Correlation Analysis in Chemistry"* ed. by N. Chapman, and J. Shorter, Plenum, New York, Chapter 10, (1978).
17. H. J. Koh, J-W. Lee, H. W. Lee, and I. Lee, Submitted.
18. H. K. Oh, J. Y. Lee, J. H. Yun, Y. S. Park, and I. Lee, *Int. J. Chem. Kinet.,* In press.
19. (a) I. Lee, H. K. Kang, and H. W. Lee, *J. Am. Chem. Soc.,* **107,** 7472 (1987); (b) I. Lee, W. H. Lee, H. W. Lee, *J. Org. Chem.,* **56,** 4682 (1991).