Kinetics and Mechanism of the Aminolysis of Thiophenyl 2-Thiopheneacetates in Acetonitrile

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Kinetic studies of the reaction of Z-thiophenyl 2-thiopheneacetates with X-benzylamines in acetonitrile at 45.0 °C have been carried out. The reaction proceeds by a stepwise mechanism in which the rate-determining step is the breakdown of the zwitterionic tetrahedral intermediate, $T^{\pm}$, with a hydrogen-bonded four-center type transition state (TS). These mechanistic conclusions are drawn base on (i) the large magnitude of ρ_X and ρ_Z, (ii) the normal kinetic isotope effects ($k_H/k_D > 1.0$) involving deuterated benzylamine nucleophiles, (iii) the positive sign of ρ_{XZ} and the larger magnitude of ρ_{XZ} than that for normal S_N2 processes, and lastly (iv) adherence to the reactivity-selectivity principle (RSP) in all cases.

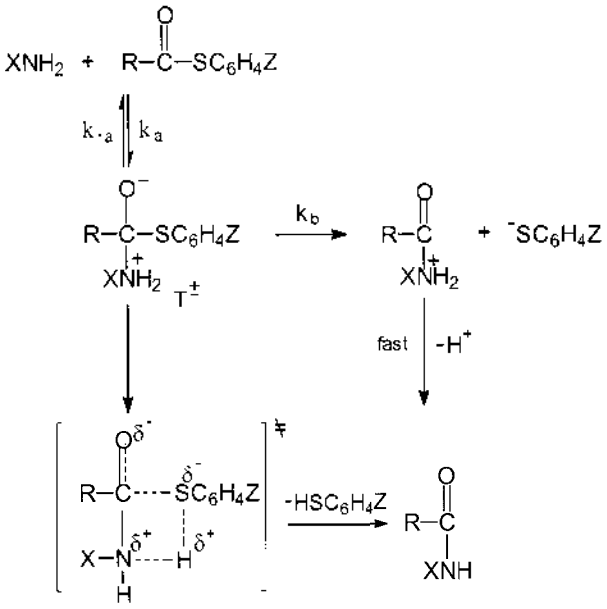
Keywords : Aminolysis, Acyl transfer reaction, Stepwise mechanism.

Introduction

Aminolyses of ester compounds have been the subject of numerous kinetic studies.[1-3] Most of these reactions are nucleophilic and in some of them curved Brönsted-type plots have been found, which have been explained by the existence of at least one tetrahedral intermediate in the reaction path and a change in the rate-determining step.[2]

In contrast to the generally accepted view of the past 20-30 years that nucleophilic substitution reactions at a carbonyl group involve almost invariably the tetrahedral intermediate, it has been shown recently that some acyl transfer reactions can involve a concerted mechanism.[4] Most of these studies are, however, carried out in protic solvents, typically in aqueous solution. Recent results of aminolysis studies of esters[5] and acyl halides[6] have shown that the similar mechanism involving the tetrahedral intermediate also applies in aprotic solvents like acetonitrile.

The following mechanistic criteria are proposed theoretically[7] and found experimentary[1-5] to apply to the stepwise mechanism with rate-limiting expulsion of the leaving group in the aminolysis of esters and carbonates. (i) The magnitudes of the reaction constants ρ_X (ρ_{nuc}) and ρ_Z (ρ_{lg}) [and also the corresponding β_X (β_{nuc}) and β_Z (β_{lg})] values, based on the macroscopic rate constants, $k_b = (k_a/k_{-a})k_b = Kk_b$ for the simplified reaction given by Scheme 1, are large.[1,7] (ii) The sign of cross-interaction constants, ρ_{ij} in Eq. (1),[8] where i and j are the substituents on the nucleophile (X), the substrate (Y) or the leaving group (Z), are opposite ($\rho_{XY} > 0$ and $\rho_{YZ} < 0$)[1,7] to those for normal S_N2 processes or for acyl transfers with rate-limiting formation of the tetrahedral intermediate, $T^{\pm}$ ($\rho_{XY} > 0$ and $\rho_{YZ} < 0$). The sign of ρ_{XZ} is always positive in the stepwise mechanism with rate-limiting decomposition of the tetrahedral intermediate, $T^{\pm}$, (Scheme 1), whereas in the concerted S_N2 reactions it can be either positive or negative.[8] (iii) The magnitudes of ρ_{XY}, ρ_{YZ} and ρ_{XZ} are greater than those for normal S_N2 processes.[1,8] (iv) The deuterium kinetic isotope effects involving deuterated nucleophiles are normal, $k_H/k_D > 1.0$.[1,5,8] (v) The RSP holds, *i.e.* a fast rate is accompanied by a lower selectivity.[9] (vi) There is a small positive enthalpy of activation, $\Delta H^{\neq}$, and a large negative entropy of activation, $\Delta S^{\neq}$.[10]



Scheme 1

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

$$\rho_{XZ} = \partial\rho_Z/\partial\sigma_X = \partial\rho_X/\partial\sigma_Z \quad (1b)$$

Besides a change in the reaction medium from protic to aprotic, a change in the acyl group R to a stronger electron acceptor is also known to favor the stepwise mechanism with rate-limiting decomposition of the terahedral intermediate, $T^{\pm}$ (Scheme 1).[11]

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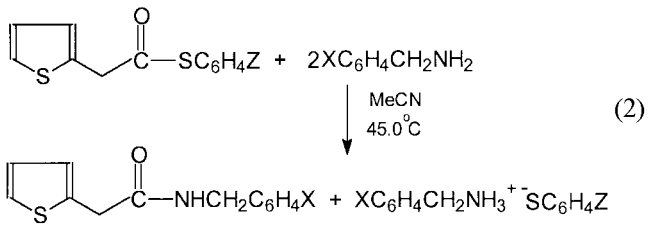
In the present work we carried out a kinetic and mechanistic study of the reactions of thiophenyl 2-thiopheneacetates with benzylamines in acetonitrile at 45.0 °C. We varied the two substituents X and Z on the nucleophile and leaving group, respectively Eq. (2).

Not much is known about the aminolysis of heterocyclic



(2)

ester compounds. Therefore, kinetic studies have been carried out in order to clearfy the mechanism of the reactions of the thiopheneacetate ester compounds. To our knowledge there have been no reports of the kinetics of the aminolysis of thiophenyl 2-thiopheneacetates.

Results and Discussion

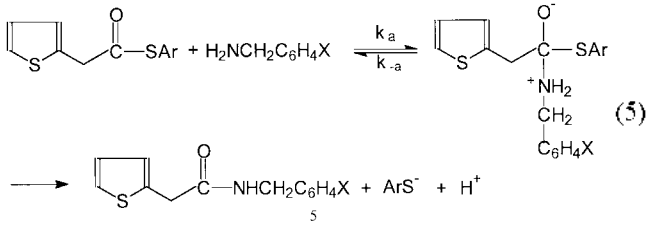
The aminolysis of thiophenyl 2-thiopheneaceates with a large excess of benzylamines in acetonitrile followed the simple kinetic rate law given by Eqs. (2) and (3), where P is thiophenolate anion and N represent benzylamine.

$$d[\mathrm{P}]/dt = k_{obs}\,[\text{substrate}] \tag{3}$$

$$k_{obs} = k_{N}\,[\mathrm{N}] \tag{4}$$

The k_N values were determined from the slope of the linear plot of k_{obs} against [N]. The k_N values are summarized in Table 1, where selectivity parameters, *i.e.*, the Hammett (ρ_X and ρ_Z) and Brönsted (β_X and β_Z), coefficients, are also shown. The reactions obeyed clean second-order kinetics, Eqs. (3) and (4), indicating that there are no complications arising from competition of the fast proton transfer from an intermediate, $T^{\pm}$, nor from general base catalysis by the benzylamine.

Since the reaction were conducted in acetonitrile, reliability of the magnitude $\beta_X(\beta_{nuc})$ and $\beta_Z(\beta_{lg})$ determined using the pK_a values in water may be doubted. In this respect, we have recently shown that the β_X values determined by correlating the rate constants in acetonitrile with p$K_a(H_2O)$ are reliable in spite of the different solvent.[12] Our theoretical work[13] of the solvent effects on the basicities of pyridines has shown that although the absolute values of p$K_a(CH_3CN)$ differ from p$K_a(H_2O)$ a constant ΔpK_a [= p$K_a(CH_3CN)$-p$K_a(H_2O)$] ≅ 7.7 was obtained. The theoretical ΔpK_a = 7.7 at the MP2/6-31G*//MP2/6-31G* level of theory is in excellent agreement with the experimental ΔpK_a = 7.7 ± 0.3.[14] The ΔpK_a(≅ 7.7) value was found to arise solely from the ion solvation energy difference of H^- ion in water and in acetonitrile. $\delta\Delta G_s^{\circ}(H^+)$ = 10.5 kcal mol^{-1}, which corresponds to ΔpK_a = 7.7.[13] Moreover, we are comparing the magnitude of β_X and β_Z values determined for the reactions carried out under the same reaction condition, *i.e.* in acetonitrile. The magnitude of β_X in Table 1 (β_X = 1.07-1.92) is again much



(5)

larger than those for the corresponding reactions with anilines and other secondary and tertiary amines (β_X = 0.6-

Table 1. The Second Order Rate Constants, $k_N \times 10^3$ dm^3 mol^{-1} s^{-1} for the Reactions of Z-Thiophenyl 2-Thiopheneacetates with X-Benzylamines in Acetonitrile at 45.0 °C

X	Z				ρ_Z[a]	β_Z[b]
	p-Me	H	*p*-Cl	*p*-Br		
	13.8			275		
p-OMe	10.1[c]	43.7	234	198	3.19±0.11	-1.32±0.09
	7.27[d]			141		
p-Me	8.71	27.5	170	214	3.40±0.18	-1.39±0.06
H	3.80	14.5	110	138	3.83±0.16	-1.57±0.09
p-Cl	1.48	7.59	63.1	83.2	4.24±0.15	-1.74±0.17
	0.741			52.5		
m-Cl	0.518	3.72	42.7	37.3	4.56±0.16	-1.89±0.11
	0.373			27.2		
ρ_X[e]	-1.97±0.03	-1.59±0.08	-1.13±0.02	-1.10±0.03	ρ_{XZ}[f] =	2.13±0.24
β_X[g]	1.92±0.06	1.56±0.09	1.11±0.02	1.07±0.05		

[a]The σ values were taken from J. A. Dean, *Handbook of organic Chemistry*; McGraw-Hill, New York, 1987, Table 7-1. Correlation coefficients were better than 0.997 in all cases. [b]The p*K*a values were taken from ed., J. Bukingham, *Dictionary of Organic Chemistry*; Chapman and Hall, New York, 1982, 5th, ed. Z=p-Br was excluded from the Brönsted plot for β_Z due to an unreliable p*K*a values. Correlation coefficients were better than 0.995 in all cases. [c]At 35 °C. [d]At 25 °C. [e]The σ values were taken from D. H. McDaniel and H.C. Brown, *J. Org. Chem.*, 1958, **23**, 420. Correlation coefficients were better than 0.997 in all cases. [f]Correlation coefficients was 0.999. [g]The p*K*a values were taken from A. Fischer, W. J. Galloway and J. Vaughan, *J. Chem. Soc.*, 1964, 3588. Correlation coefficients were better than 0.995 in all cases. pK_a= 9.67 was used for X = *p*-CH_3O. (reference H. K. Oh, J. Y. Lee, and I. Lee, *Bull Korean Chem. Soc.*, **1998**, 19, 1198.)

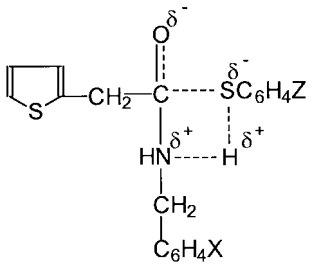
1.0) but similar to those with benzylamines (β_X = 1.4-2.5). All of these latter values are for the thiol ester aminolysis with benzylamines in acetonitrile which are predicted to proceeded by rate-limiting breakdown of a zwitterionic tetrahedral intermediate, $T^{\pm}$. On this account, *i.e.* large β_X values obtained, the aminolysis of thiophenyl 2-thiopheneacetate with benzylamines in acetonitrile is most likely to occur by the rate-limiting expulsion of thiophenolate ion, ArS^-, from $T^{\pm}$, Eq. (4), where the proton is consumed by the excess benzylamine present in the solution in a subsequent rapid step to form benzylammonium ion. The rate constant, k_N in Eq. (3), is therefore a complex quantity represented by Eq. (6).

$$k_N = \frac{k_a}{k_{-a}} \cdot k_b = K \cdot k_b \quad (6)$$

The magnitude of β_Z (β_{lg}) values (β_Z = −1.3 ~ −1.9) is also comparable to or greater than that for the similar reaction with rate-limiting expulsion of ArS^- in acetonitrile (β_Z = −1.2 ~ −1.6).

The proposed mechanism is also supported by a large positive cross-interaction constant (ρ_{XZ} = 2.13) and adherence to the reactivity-selectivity principle (RSP), which are considered to constitute necessary conditions for the rate-limiting breakdown of $T^{\pm}$.[15,16]

The kinetic isotope effects (Table 2) involving deuterated nucleophile, $XC_6H_4CH_2ND_2$, are normal (k_H/k_D > 1.0) suggesting a possibility of forming hydrogen-bonded four-center type TS[16] as has often been proposed. Since no base catalysis was found (the rate law is first order with respect to [N], Eq. 3), the proton transfer occurs concurrently with the rate-limiting expulsion of RS^- in the TS but not catalyzed by



Proposed TS

Table 2. The Secondary Kinetic Isotope Effects for the Reactions of Z-Thiophenyl 2-Thiopheneacetates with Deuterated X-Benzylamines in Acetonitrile at 45.0 °C

X	Z	$k_H \times 10^3$ ($M^{-1}s^{-1}$)	$k_D \times 10^3$ ($M^{-1}s^{-1}$)	k_H/k_D
p-OMe	*p*-Me	13.8(±0.25)	8.57(±0.06)	1.61±0.03[a]
p-OMe	H	43.7(±1.0)	28.5(±0.4)	1.53±0.04
p-OMe	*p*-Cl	234(±5.0)	163(±2.0)	1.44±0.04
P-OMe	*p*-Br	275(±5.5)	203(±2.5)	1.35±0.03
p-Cl	*p*-Me	1.48(±0.01)	0.866(±0.005)	1.71±0.02
p-Cl	H	7.59(±0.07)	4.83(±0.04)	1.57±0.02
p-Cl	*p*-Cl	63.1(±0.9)	42.6(±0.5)	1.48±0.03
p-Cl	*p*-Br	83.2(±1.0)	59.9(±0.8)	1.39±0.03

[a]Standard deviations.

Table 3. Activation Parameters[a] for the Reactions of Z-Thiophenyl 2-Thiopheneacetates 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	5.4	50
p-OMe	*p*-Br	5.7	43
p-Cl	*p*-Me	5.8	55
p-Cl	*p*-Br	5.6	47

[a]Calculated by the Eyring equation. The maximum errors calculated (by the method of K. B. Wiberg, *Physical Organic Chemistry*, Wiley, New York, **1964**, p378) are ±0.6 kcal mol^{-1} and ±2 e.u. for $\Delta H^{\neq}$ and $\Delta S^{\neq}$, respectively.

benzylamine. The consumption of proton by the excess benzylamine should therefore take place in a subsequent rapid step.

The low activation enthalpies, $\Delta H^{\neq}$, and highly negative activation entropies, $\Delta S^{\neq}$, (Table 3) are also in line with the proposed TS. Especially, the $\Delta H^{\neq}$ values are somewhat lower and the $\Delta S^{\neq}$ values are higher negative values than other aminolysis systems[15]. The expulsion of RS^- anion in the rate determining step (an endoergic process) is assisted by the hydrogen-bonding with an amino hydrogen of the benzylammonium ion within the intermediate, $T^{\pm}$. This will lower the $\Delta H^{\neq}$ value, but the TS becomes structured and rigid (low entropy process) which should lead to a large negative $\Delta S^{\neq}$ value.

In summary, the reactions of thiophenyl 2-thiopheneacetates with benzylamines in acetonitrile proceed by a stepwise mechanism in which the rate-determining is the breakdown of the zwitterionic tetrahedral intermediate with a hydrogen-bonded four-center type TS.

These mechanistic conclusions are drawn based on (i) the large magnitude of ρ_X and ρ_Z, (ii) the normal kinetic isotope effects (k_H/k_D > 1.0) involving deuterated benzylamine nucleophiles, (iii) a small positive enthalpy of activation, $\Delta H^{\neq}$, and a large negative entropy of activation, $\Delta S^{\neq}$, (iv) the positive sign of ρ_{XZ} and the larger magnitude of ρ_{XZ} than that for normal S_N2 processes, and lastly (v) adherence to the RSP in all cases.

Experimental Section

Materials. Merk GR acetonitrile was used after three distillations. The benzylamine nucleophiles, Aldrich GR, were used without further purification. Thiophenols and thiopheneacetyl chloride were Tokyo Kasei GR grade.

Preparations of thiophenyl phenylacetates. Thiophenol derivatives and thiopheneacetyl chloride were dissolved in anhydrous ether and added KOH carefully keeping temperature to 0-5 °C. Ice was then added to the reaction mixture and ether layer was separated, dried on $MgSO_4$ and distilled under reduced pressure to remove solvent. The melting point, IR (Nicolet 5BX FT-IR), ^1H and ^{13}C NMR (JEOL 400 MHz), data are as follows:

***p*-Thiotolyl 2-thiopheneacetate**: m.p. 65-67 °C, IR (KBr), 3104 (C-H, thiophene), 1701 (C=O), 1575 (C=C, aromatic), 1473 (C-H, CH_2), 1327 (C-H, CH_3), 695 (C-H,

aromatic): ^{1}H NMR (400 MHz, $CDCl_3$), 4.01 (2H, s, CH_2), 6.96 (2H, m, thiophene), 7.23 (H, dd, thiophene), 7.28 (2H, d, meta aromatic), 7.34 (2H, d, ortho aromatic); ^{13}C NMR (100.4 MHz, $CDCl_3$), 195.1 (C=O), 136.0, 135.5, 133.3, 131.2, 129.3, 129.1, 127.7, 127.2, 125.4, 43.6.

Thiophenyl 2-thiopheneacetate: liquid. IR (KBr), 3087 (C-H, thiophene), 1695 (C=O), 1578 (C=C, aromatic), 1476 (C-H, CH_2), 710 (C-H, aromatic); ^{1}H NMR (400 MHz, $CDCl_3$), 4.03 (2H, s, CH_2), 6.93 (2H, m, thiophene), 7.22 (H, dd, thiophene), 7.24-7.59 (5H, m, aromatic); ^{13}C NMR (100.4 MHz, $CDCl_3$), 194.7, 135.6, 135.4, 133.5, 129.2, 129.0, 127.6, 127.3, 125.7, 43.5.

***p*-Chlorothiophenyl 2-thiopheneacetate**: m.p. 87-89 °C. IR (KBr), 3101 (C-H, thiophene), 1703 (C=O), 1569 (C=C, aromatic), 1475 (C-H, CH_2), 707 (C-H, aromatic); ^{1}H NMR (400 MHz, $CDCl_3$), 4.05 (2H, s, CH_2), 6.94 (2H, m, thiophene), 7.21 (H, dd, thiophene), 7.25 (2H, d, meta aromatic), 7.30 (2H, d, ortho aromatic); ^{13}C NMR (100.4 MHz, $CDCl_3$), 194.0, 135.9, 135.6, 133.7, 129.4, 129.2, 127.9, 127.1, 125.9, 43.8.

***p*-Bromothiophenyl 2-thiopheneacetate**: m.p. 93-95 °C. IR (KBr), 3110 (C-H, thiophene), 1698 (C=O), 1572 (C=C, aromatic), 1470 (C-H, CH_2), 698 (C-H, aromatic); ^{1}H NMR (400 MHz, $CDCl_3$), 4.03 (2H, s, CH_2), 6.97 (2H, m, thiophene), 7.21 (H, dd, thiophene), 7.24 (2H, d, meta aromatic), 7.36 (2H, d, ortho aromatic); ^{13}C NMR (100.4 MHz, $CDCl_3$), 194.5 (C=O), 135.7, 135.6, 133.3, 129.1, 129.0, 127.4, 127.1, 125.5, 43.4.

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_{obs}, were determined by the Guggenheim method[18] with large excess of benzylamine. The k_2 values were reproducible to within ± 3%.

Product analysis. Thiophenyl thiopheneacetates was reacted with excess benzylamine with stirring for more than 15 half-lives at 45.0 °C in acetonitrile, and the products were isolated by evapolating the solvent under pressure. The product mixture was treated with column chromatography (silica gel, 20% ethylacetate-n-hexane). Analysis of the product gave the following results.

$C_5H_3SCH_2C(=O)NHCH_2C_6H_4$: m.p. 67-69 °C, IR (KBr), 3095 (C-H, thiophene), 1695 (C=O), 1591 (N-H), 1579 (C=C, aromatic), 1468 (C-H, CH_2), 672 (C-H, aromatic); ^{1}H NMR (400 MHz, Cl_3), 3.81 (1H, s, NH), 4.35 (2H, s, CH_2), 7.32-7.41 (9H, m, aromatic ring); ^{13}C NMR (100.4 MHz, $CDCl_3$), 200.8 (C=O), 139.3, 134.4, 133.0, 130.2, 129.9, 129.3, 128.9, 128.7, 128.2, 126.9, 126.4, 123.6, 50.1.

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References

1. (a) Oh, H. K.; Shin, C. H.; Lee, I. *J. Chem. Soc., Perkin Trans. 2* **1993**, 2411. (b) Oh, H. K.; Shin, C. H.; Lee, I. *J. Chem. Soc., Perkin Trans. 2* **1995**, 1169. (c) Oh, H. K.; Shin, C. H.; Lee, I. *Bull. Korean Chem. Soc.* **1995**, *16*, 657. (d) Oh, H. K.; Yang, J. H.; Lee, I. *Int. J. Chem. Kinet.* **2000**, *32*, 485. (e) Oh, H. K.; Kim, S. K.; Cho, I. H.; Lee, I. *J. Chem. Soc., Perkin Trans. 2* **2000**, 2306. (f) Oh, H. K.; Kim, S. K; Lee, H. W.; Lee, I. *New J. Chem.* **2001**, *25*, 313.
2. (a) Bond, P. M.; Castro, E. A.; Moodie, R. B. *J. Chem. Soc., Perkin Trans. 2* **1976**, 68. (b) Cresser, J. M.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 6963, 6970. (c) Castro, E. A.; Freudenberg, M. *J. Org. Chem.* **1980**, *45*, 906. (d) Castro, E. A.; Santander, C. L. *J. Org. Chem.* **1985**, *50*, 3595. (e) Castro, E. A.; Ureta, C. L. *J. Org. Chem.* **1990**, *55*, 1676. (f) Castro, E. A.; Salas, M.; Santos, J. G. *J. Org. Chem.* **1994**, *59*, 30. (g) Castro, E. A.; Araneda, C. A. *J. Org. Chem.* **1997**, *62*, 126. (h) Castro, E. A.; Garcia, P.; Leandro, L.; Quesieh, N. *J. Org. Chem.* **2000**, *65*, 9047.
3. (a) Buncel, E.; Um, I. H. *J. Chem. Soc., Chem. Commun.* **1986**, 595. (b) Buncel, E.; Um, I. H.; Hoz, S. *J. Am. Chem. Soc.* **1989**, *111*, 971. (c) Um, I. H.; Lee, G. J.; Yoon, H. W.; Kwon, D. S. *Tetrahedron Lett.* **1992**, *33*, 2023. (d) Um, I. H.; Yoon, H. W.; Lee, J. S.; Moon, H. J.; Kwon, D. S. *J. Org. Chem.* **1997**, *62*, 5939.
4. (a) Williams, A. *Adv. Phys. Org. Chem.* **1992**, *27*, 1. (b) March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley: New york, 1992. (c) Cullum, N. R.; Renfrew, A. H.; Rettura, J. A.; Taylor, J. A.; Whitmore, J. M. J.; Williams, A. *J. Am. Chem. Soc.* **1995**, *117*, 9200.
5. Menger, F. M.; Smith, J. H. *J. Am. Chem. Soc.* **1972**, *94*, 3824.
6. (a) Palling, D. J.; Jencks, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 4869. (b) Jedrzejczak, M.; Motie, R. E.; Satchell, D. P. N.; Satchell, R. S.; Wassef, W. N. *J. Chem. Soc., Perkin Trans. 2* **1994**, 1471. (c) Yew, K. H.; Koh, H. J.; Lee, H. W.; Lee, I. *J. Chem. Soc., Perkin Trans. 2* **1995**, 2263.
7. (a) Lee, I. *Bull. Korean Chem. Soc.* **1994**, *15*, 985. (b) Lee, D.; Kim, C. K. *Bull. Korean Chem. Soc.* **1995**, *16*, 1203. (c) Lee, I.; Lee, D.; Kim, C. K. *J. Phys. Chem. A* **1997**, *101*, 879.
8. Lee, I. *Adv. Phys. Org. Chem.* **1992**, *27*, 57.
9. Lee, I.; Lee, B. S.; Koh, H. J.; Chang, B. D. *Bull. Korean Chem. Soc.* **1995**, *16*, 277.
10. Neuvonen, H. *J. Chem. Soc. Perkin Trans. 2* **1995**, 951.
11. Neuvonen, H. *J. Chem. Soc. Perkin Trans. 2* **1987**, 159.
12. Exner, O. In *Correlation Analysis in Chemistry. Recent Advances*; Chapman, N. B., Shorter, J., Eds.; Plenum Press: New York, 1978; ch. 10.
13. Lee, I.; Han, I. S.; Kim, C. K.; Kim, W. K.; Kim, Y. B. *J. Phys. Chem. A* **2000**, *104*, 6332.
14. The average $\Delta pK_a = 7.7 \pm 0.3$ was obtained from 22 pK_a values for alkyl and alicyclic amines reported in: Coetzee, J. F. *Prog. Phys. Org. Chem.* **1967**, *4*, 45.
15. (a) Oh, H. K.; Woo, S. Y.; Oh, C. H.; Park, Y. S.; Lee, I. *J. Org. Chem.* **1997**, *62*, 5780. (b) Koh, H. J.; Han, K. L.; Lee, I. *J. Org. Chem.* **1999**, *64*, 4783.
16. (a) Pross, A. *Adv. Phys. Org. Chem.* **1997**, *14*, 69. (b) Lee, I.; Lee, H. W. *Collect. Czech. Chem. Commun.* **1999**, *64*, 1529.
17. (a) Lee, I. *Chem. Soc. Rev.* **1994**, *24*, 223. (b) Isaacs, N. S. *Physical Organic Chemistry*, 2nd ed.; Longman Harlow: 1995; p 186.
18. Guggenheim, E. A. *Phil. Mag.* **1926**, *2*, 538.