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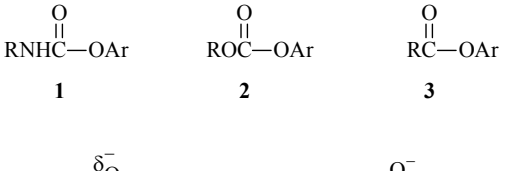
# Kinetics and Mechanism of the Aminolysis of Aryl *N*-Allyl Thiocarbamates in Acetonitrile

**Hanna Lee and Hyuck Keun Oh***

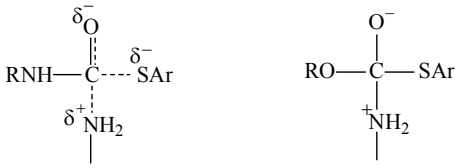
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The aminolysis mechanism of aryl carbamates, **1**, is quite similar to that of aryl carbonates, **2**, and aryl esters, **3**.[1-3] A change in the mechanism of the aminolysis with benzylamines in acetonitrile has been observed from stepwise through a tetrahedral intermediate, $T^{\pm}$, to concerted for the carbamates[1] (**1** with R = Ph) as well as for the carbonates[2] (**2** with R = Et) when leaving group is changed from phenoxides (**a** : $^{-}$OAr) to thiophenoxides (**b** : $^{-}$SAr). This suggests that the strength of push provided to expel the leaving group from $T^{\pm}$ by PhNH is similar to that by EtO, and the destabilization of $T^{\pm}$ due to this push is strong enough for $^{-}$SAr but is too weak for $^{-}$OAr to lead the aminolysis to a concerted process.

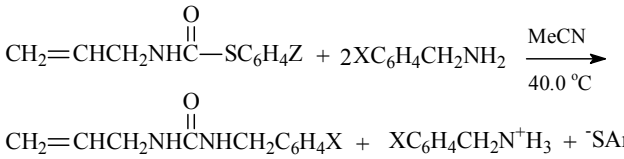


**1** **2** **3**



TS : for **1b** $T^{\pm}$ : intermediate for **2b**

In this work, we carried out kinetic studies on the aminolysis of aryl *N*-allyl thiocarbamates (**1b : AATC**) with benzylamines in acetonitrile at 40.0 °C, eq 1. The first purpose of the present work is to establish the aminolysis reaction mechanism for eq. 1 and to see whether the mechanistic change from a stepwise to a concerted by the change **2a** → **2b** is also carried on to the change **1a** → **1b** or not. In this work, we varied substituents in the nucleophile (X) and leaving group (Z) and the rate constants, $k_2$, are subjected to a multiple regression analysis to determine the cross-interaction constant,[4] $\rho_{XZ}$ in eqs 2. For a concerted mechanism the sign of $\rho_{XZ}$ was found to be negative[4] and the reactivity-selectivity principle (RSP) failed.[5]



(1)

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

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

## Results and Discussion

The reactions of aryl *N*-allyl thiocarbamates (AATC : $CH_2$=$CHCH_2HNC(=O)SC_6H_4Z$) with X-benzylamines (BA) in acetonitrile follow a clear second-order kinetics, eqs. 3. Unlike in the aminolysis of aryl *N*-phenylcarbamates[1] (APC : $PhNHC(=O)OC_6H_4Z$) we found no base catalysis by the amine. The rate constants, $k_2$, determined are summarized in Table 1 together with selectivity parameters $\rho_X$, $\beta_X$, $\rho_Z$, and $\beta_Z$. The $\beta_X$ ($\beta_{nuc}$) values are obtained by using the p$K_a$ values of benzylamines in water. This procedure was found to be reliable since the p$K_a$ values in acetonitrile and in water vary in parallel, although the absolute values are different.[6] For the $\beta_Z$ ($\beta_{lg}$) values, a factor of 0.62 was multiplied to all the $\beta_Z$ values determined using the p$K_a$ ($H_2O$) values.[7]

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

$$k_{obs} = k_2[\text{BA}] \quad (3b)$$

Since strong destabilization of $T^{\pm}$ should be provided by a stronger push to expel the leaving group by the amino nonleaving group, R = $NH_2$ in **1b**, the aminolysis of AATC (**1b** with R = $CH_2$=$CHCH_2$-) with benzylamines in acetonitrile is proposed to proceed by a concerted mechanism. The $\beta_Z$ values in Table 1 are within the range of values that are expected for a concerted mechanism.[8] Further supports for the concerted mechanism is provided by a negative $\rho_{XZ}$ (−0.43) values, and failure of the reactivity-selectivity principle (RSP).[9] The selectivities ($\rho$ and $\beta$ values in Table 1) are greater for the faster reactions. This type of anti-RSP is considered another criterion for the concerted aminolysis.[5]

Reference to Table 1 reveals that the $\beta_X$ values are 1.42 ~ 1.60 which are rather greater than the values normally expected for the concerted aminolysis processes, $\beta_X$ = 0.4 ~ 0.7[9] However, $\beta_X$ values smaller than 0.4[10]as well as those larger than 0.7[11] have also been observed for the concerted reactions. Especially in solvents less polar than water, larger $\beta_X$ (1.3 ~ 1.6)[12] are often obtained for the concerted processes. Thus the

**Table 1.** The Second Order Rate Constants, $k_2$ ($10^2$ dm$^3$ mol$^{-1}$ s$^{-1}$) for the Reactions of *Z*-Aryl *N*-Allyl 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 | 1.14<br>0.764[c]<br>0.519[d] | 2.74 | 9.55 | 10.7<br>7.28[c]<br>5.02[d] | 2.39 ± 0.02 | −0.99 ± 0.05 |
| *p*-Me | 0.757 | 1.79 | 6.30 | 6.98 | 2.37 ± 0.02 | −0.98 ± 0.04 |
| H | 0.440 | 0.988 | 3.32 | 3.76 | 2.29 ± 0.03 | −0.94 ± 0.04 |
| *p*-Cl | 0.225<br>0.153[c]<br>0.103[d] | 0.501 | 1.56 | 1.67<br>1.10[c]<br>0.737[d] | 2.15 ± 0.01 | −0.90 ± 0.04 |
| *m*-Cl | 0.135 | 0.285 | 0.893 | 1.00 | 2.13 ± 0.03 | −0.88 ± 0.03 |
| $\rho_X$[a] | −1.41 ± 0.04 | −1.49 ± 0.02 | −1.58 ± 0.02 | −1.59 ± 0.01 | $\rho_{XZ}$[e] = −0.43 ± 0.13 | |
| $\beta_X$[f] | 1.42 ± 0.03 | 1.50 ± 0.03 | 1.59 ± 0.03 | 1.60 ± 0.02 | | |

[a]The σ values were taken from Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev*. **1991**, *91*, 166. Correlation coefficients were better than 0.998 in all cases. [b]The p$K_a$ values were taken from Albert, A.; Serjeant, E. P. *The Determination of Ionization Constants*; 3rd ed., Chapman and Hall: London, p145. 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 p$K_a$ values were taken from Fischer, A.; Galloway, W. J.; Vaughan, J. *J. Chem. Soc*. **1964**, 3588. Correlation coefficients were better than 0.997 in all cases. For X = *p*-$CH_3O$ an extrapolated value of p$K_a$ = 9.64 was used.

**Table 2.** The Kinetic Isotope Effects for the Reactions of Z-Phenyl *N*-Allyl Thiocarbamates with X-Benzylamines in Acetonitrile at 40.0 °C

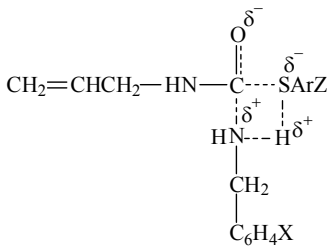
| X | Z | $k_H$ (×$10^2$ M$^{-1}$s$^{-1}$) | $k_D$ (×$10^2$ M$^{-1}$s$^{-1}$) | $k_H/k_D$ |
|---|---|---|---|---|
| *p*-OMe | *p*-Me | 1.14 (±0.02) | 0.844 (±0.008) | 1.35 ± 0.02[a] |
| *p*-OMe | H | 2.74 (±0.04) | 1.94 (±0.03) | 1.41 ± 0.02 |
| *p*-OMe | *p*-Cl | 9.55 (±0.08) | 6.49 (±0.06) | 1.47 ± 0.03 |
| *p*-OMe | *p*-Br | 10.7 (±0.10) | 6.90 (±0.07) | 1.55 ± 0.03 |
| *p*-Cl | *p*-Me | 0.225 (±0.002) | 0.163 (±0.001) | 1.38 ± 0.03 |
| *p*-Cl | H | 0.501 (±0.003) | 0.343 (±0.003) | 1.46 ± 0.02 |
| *p*-Cl | *p*-Cl | 1.56 (±0.01) | 1.01 (±0.01) | 1.53 ± 0.02 |
| *p*-Cl | *p*-Br | 1.67 (±0.02) | 1.03 (±0.01) | 1.61 ± 0.03 |

[a]Standard deviations.

large $\beta_X$ values in the present work may be due to the less polar solvent used, acetonitrile. The relatively large $\beta_X$ values may reflect rather tight bond formation in the TS.

Strong destabilization incurred by powerful nucleofugality of benzylamines from $T^{\pm}$ is known to cause the aminolysis to proceed by a concerted mechanism.[13] The order of the increasing rate of expulsion of amines from $T^{\pm}$ is reported as [5] pyridines < anilines < secondary alicyclic amines < quinuclidines < benzylamines. Moreover, it has been shown that carbonyl (C=O) has a greater proclivity for the concerted mechanism than thiocarbonyl (C=S) group[14] due to a narrower energy gap between π* and σ* levels, $\Delta\varepsilon = \varepsilon(\pi^*_{C=O}) - \varepsilon(\sigma^*_{C-S}) < \Delta\varepsilon = \varepsilon(\pi^*_{C=S}) - \varepsilon(\sigma^*_{C-S})$, enabling efficient mixing of the two antibonding orbitals.[15] Thus, concerted mechanisms are found for the aminolyses of *S*-(2,4-dinitrophenyl)[14] and *S*-(2,4,6-trinitrophenyl)[3b] *O*-ethyl thiocarbonates in contrast to the stepwise mechanisms for the corresponding dithiocarbonates.[16] Less polar solvents are also conductive to a concerted mechanism as observed for the aminolysis of carbonates from stepwise in water to concerted in acetonitrile.[17] For example, the aminolysis of 2,4,6-trinitrophenyl *O*-ethyl dithiocarbonates is stepwise[18] (biphasic Brönsted plot) in water, but is concerted ($\beta_X$ = 0.53) in a less polar solvent (44 wt % aqueous EtOH).[19] The change of solvent from water to a less polar solvent such as MeCN destabilizes the zwitterionic intermediate by enhancing the rate of expulsion of the amine from $T^{\pm}$, and renders the intermediate, $T^{\pm}$, more unstable kinetically so that a concerted mechanism is enforced.[19]

The kinetic isotope effects, $k_H/k_D$, involving deuterated benzylamines ($XC_6H_4CH_2ND_2$)[20] in Table 2 are larger than unity (1.35 ~ 1.61) indicating that a proton transfer is involved in the TS, which in turn suggests that a hydrogen bonded cyclic TS. The relatively low $\Delta H^{\neq}$ with large negative $\Delta S^{\neq}$ values in




**TS**

Table 3 are consistent with this proposed TS structure. The $\Delta H^{\neq}$ values are small due to a large energy gain in C-N bond formation relative to energy loss in C-S bond cleavage in the TS and also the assistance in the C-S bond cleavage by the hydrogen bonding, and the $\Delta S^{\neq}$ values are large negative due to the strained cyclic four-membered TS structure.

In summary, we propose a concerted mechanism with a hydrogen bonded cyclic transition state for the aminolysis of aryl *N*-allyl thiocarbamates with benzylamines in acetonitrile based on the negative cross-interaction constant, failure of RSP,

**Table 3.** Activation Parameters[a] for the Reactions of Z-Phenyl *N*-Allyl 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 | 6.6 | 46 |
| *p*-OMe | *p*-Br | 6.2 | 43 |
| *p*-Cl | *p*-Me | 6.4 | 50 |
| *p*-Cl | *p*-Br | 6.6 | 46 |

[a]Calculated by the Eyring equation. The maximum errors calculated (by the method of Wiberg, K. B. *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 greater than unity and relatively low $\Delta H^{\neq}$ with large negative $\Delta S^{\neq}$ values.

## Experimental Section

**Materials.** GR grade acetonitrile was used after three distillations. GR grade benzylamine nucleophiles were used after recrystallization.

**Substrates.**

**Phenyl *N*-allyl thiocarbamate.** A solution of thiophenol (0.01 mol) in dry toluene (10 mL) was added to a solution of allyl isocyanate (0.01 mol). A catalytic quantity (0.5 mL) of pyridine was added and the solution refluxed for 2 h. On evaporation of the solvent *in vacuo*, the thiocarbamate precipitated and was recrystallized from chloroform-pentane. The other substituted phenyl *N*-allyl thiocarbamates were prepared in an analogous manner and recrystallized from chloroform-pentane. The substrates synthesized were confirmed by spectral and elemental analysis as follows.

**$CH_2$=CH$CH_2$-NHC(=O)S$C_6H_4$-*p*-$CH_3$:** mp 80 - 82 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 2.31 (3H, s, $CH_3$), 3.78 (2H, t, $CH_2$), 5.01 (2H, t, =$CH_2$), 5.70 (1H, m, =CH). 6.22 (1H, s, NH), 7.20-7.52 (4H, m, $C_6H_4$); $^{13}$C NMR (100.4 MHz, $CDCl_3$) δ 166.5, 140.1, 135.0, 130.3, 124.8, 133.4, 116.5, 43.6, 21.3; $\nu_{max}$ (KBr), 3307 (NH), 2834 (CH, aromatic), 1651 (C=O), 598 (C-S); MS *m*/z 207 ($M^+$). Anal. Calcd for $C_{11}H_{13}NOS$ : C, 63.7; H, 6.31. Found; C, 63.9; H, 6.32.

**$CH_2$=CH$CH_2$-NHC(=O)S$C_6H_5$:** mp 65 - 67 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 3.71 (2H. t, $CH_2$), 4.91 (2H, t, =$CH_2$), 5.61 (1H, m, =CH). 6.25 (1H, s, NH), 7.29-7.65 (4H, m, $C_6H_4$); $^{13}$C NMR (100.4 MHz, $CDCl_3$) δ 165.8, 135.1, 133.2, 129.2, 129.0, 128.1, 116.2, 43.4; $\nu_{max}$ (KBr), 3306 (NH), 2835 (CH, aromatic), 1681 (C=O), 595 (C-S); MS *m*/z 193 ($M^+$). Anal. Calcd $C_{10}H_{11}NOS$ : C, 62.1; H, 5.70. Found; C, 62.3; H, 5.72.

**$CH_2$=CH$CH_2$-NHC(=O)S$C_6H_4$-*p*-Cl:** mp 114 - 116 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 3.84 (2H. t, $CH_2$), 5.09 (2H, t, =$CH_2$), 5.74 (1H, m, =CH). 6.21 (1H, s, NH), 7.34-7.52 (4H, m, $C_6H_4$); $^{13}$C NMR (100.4 MHz, $CDCl_3$) δ 165.1, 136.4, 135.8, 133.1, 129.4, 126.6, 116.9, 43.8; $\nu_{max}$ (KBr), 3304 (NH), 2832 (CH, aromatic), 1656 (C=O), 601 (C-S); MS *m*/z 227 ($M^+$). Anal. Calcd $C_{10}H_{10}ClNOS$ : C, 52.7; H, 4.41. Found; C, 52.9; H, 4.42.

**$CH_2$=CH$CH_2$-NHC(=O)S$C_6H_4$-*p*-Br:** mp 120 - 122 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 3.86 (2H. t, $CH_2$), 5.05 (2H, t, =$CH_2$), 5.75 (1H, m, =CH). 6.28 (1H, s, NH), 7.38-7.59 (4H, m, $C_6H_4$); $^{13}$C NMR (100.4 MHz, $CDCl_3$) δ 165.0, 136.7, 133.2, 132.4, 127.3, 124.2, 117.0, 43.9; $\nu_{max}$ (KBr), 3306 (NH), 2833 (CH, aromatic), 1657 (C=O), 595 (C-S); MS *m*/z 272 ($M^+$). Anal. Calcd $C_{10}H_{10}BrNOS$ : C, 44.1; H, 3.70. Found; C,44.3; H, 3.71.

**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[21] with large excess of pyridine. 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 phenyl *N*-allyl thiocabamate (0.01 mol) was reacted with excess benzylamine (0.1 mol) 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.

**$CH_2$=CH$CH_2$-NHC(=O)NH$CH_2C_6H_5$:** mp 89 - 91 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 3.52 (2H. t, $CH_2$), 4.05 (2H, d, $CH_2$), 4.90 (2H, m, =$CH_2$), 5.88 (1H, m, =CH). 6.19 (1H, s, NH), 7.05-7.35 (5H, m, $C_6H_5$); $^{13}$C NMR (100.4 MHz, $CDCl_3$) δ 147.3, 127.9, 123.8, 116.8, 115.5, 115.3, 103.4, 32.4, 31.0; $\nu_{max}$ (KBr), 3322 (NH), 2837 (CH, aromatic), 1622 (C=O), 1247 (C-N); MS *m*/z 188 ($M^+$). Anal. Calcd for $C_{11}H_{12}N_2O$ : C, 70.2; H, 6.41. Found; C, 70.4; H, 6.42.

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## References

1. Koh, H. J.; Kim, O. K.; Lee, H. W.; Lee, I. *J. Phys. Org. Chem.* **1997**, *10*, 725.
2. (a) Satterthwait, A. C.; Jencks, W. P. *J. Am. Chem. Soc.* **1974**, *96*, 7018. (b) Castro, E. A.; Ureta, C. *J. Chem. Soc. Perkin Trans 2* **1991**, 63. (c) Oh, H. K.; Shin, C. H.; Lee, I. *Bull. Korean Chem. Soc.* **1995**, *16*, 657. (d) Oh, H. K.; Woo, S. Y.; Shin, C. H.; Park, Y. S.; Lee, I. *J. Org. Chem.* **1997**, *62*, 5780. (e) Um, I-H.; Kwon, H-J.; Kwon, D-S.; Park, J-Y. *J. Chem. Res.* **1995**, *(S) 301*, (M) 1801.
3. (a) Gresser, M. J.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 6970. (b) Castro, E. A.; Cubillos, M.; Santos, J. G. *J. Org. Chem.* **2001**, *66*, 6000. (c) Bond, P. M.; Moodie, R. B. *J. Chem. Soc. Perkin Trans. 2* **1976**, 679.
4. (a) Lee, I. *Chem. Soc. Rev.* **1990**, *19*, 317. (b) Lee, I. *Adv. Phys. Org. Chem.* **1992**, *27*, 57.
5. Lee, I.; Sung, D. D. *Curr. Org. Chem.* **2004**, *8*, 557.
6. (a) Ritchie, C. D. In *Solute-Solvent Interactions*; Coetzee, J. F., Ritchie, C. D., Eds.; Marcel Dekker : New York, 1969; Chapter 4. (b) Coetzee, J. F. *Prog. Phys. Org. Chem.* **1967**, *4*, 54. (c) Spillane, W. J.; Hagan, G.; McGrath, P.; King, J.; Brack, C. *J. Chem. Soc. Perkin Trans. 2* **1996**, 2099.
7. Oh, H. K.; Ku, M. H.; Lee, H. W.; Lee, I. *J. Org. Chem.* **2002**, *67*, 3874.
8. (a) Castro, E. A.; Pavez, P.; Santos, J. G. *J. Org. Chem.* **2001**, *66*, 3129. (b) Stefanidas, D.; Cho, S.; Dhe-Paganon, S.; Jencks, W. P. *J. Am. Chem. Soc.* **1993**, *115*, 1650.
9. Skoog, M. T.; Jencks, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 7597.
10. (a) Ba-Saif, S.; Luthra, A. K.; Williams, A. *J. Am. Chem. Soc.* **1989**, *111*, 2647. (b) Colthurst, M. J.; Nanni, M.; Williams, A. *J.*

*Chem. Soc. Perkin Trans. 2* **1996**, 2285.
11. (a) Maude, A. B.; Williams, A. *J. Chem. Soc. Perkin Trans. 2* **1997**, 179. (b) Castro, E. A.; Cubillos, M.; Santos, J. G. *J. Org. Chem*. **1998**, *63*, 6820.
12. Castro, E. A. *Chem. Rev.* **1991**, *99*, 3505.
13. (a) Yamabe, S.; Minato, T. *J. Org. Chem*. **1983**, *48*, 2972. (b) Lee, I.; Lee, D.; Kim, C. K. *J. Phys. Chem. A* **1997**, *101*, 879. (c) Lee, I.; Kim, C. K.; Li, H. G.; Sohn, C. K.; Kim, C. K.; Lee, H. W.; Lee, B-S. *J. Am. Chem. Soc.* **2000**, *122*, 11162. (d) Lee, I. *Int. Rev. Phys. Chem.* **2003**, *22*, 263.
14. Castro, E. A.; Ibanez, F.; Salas, M.; Santos, J. G.; Sepulveda, P. *J. Org. Chem*. **1993**, *58*, 459.
15. (a) Castro, E. A.; Ruiz, M. G.; Santos, J. G. *Int. J. Chem. Kinet*. **2001**, *33*, 281. (b) Yew, K. H.; Koh, H. J.; Lee, H. W.; Lee, I. *J. Chem. Soc. Perkin Trans. 2* **1995**, 2263. (c) Castro, E. A.; Ruiz, M. G.; Salinas, S.; Santos, J. G. *J. Org. Chem*. **1999**, *64*, 4817.
16. Oh, H. K.; Lee, J-Y.; Park, Y. S.; Lee, I. *Int. J. Chem. Kinet*. **1998**, *30*, 419.
17. Castro, E. A.; Cubillas, M.; Munoz, G.; Santos, J. G. *Int. J. Chem. Kinet*. **1994**, *26*, 571.
18. Dewar, M. J. S.; Dougherty, R. C. *The PMO Theory of Organic Chemistry*; Plenum: New York, 1975; Chapter 5.
19. Lee, I. *Chem. Soc. Rev*. **1995**, *24*, 571.
20. Lee, I.; Shin, C. S.; Chung, S. Y.; Kim, H. Y.; Lee, H. W. *J. Chem. Soc. Perkin Trans. 2* **1988**, 1919.
21. (a) Guggenheim, E. A. *Philos. Mag*. **1926**, *2*, 538. (b) Oh, H. K.; Hong, S. K. *Bull. Korean Chem. Soc*. **2009**, *30*, 2453. (c) Jeong, K. S.; Oh, H. K. *Bull. Korean Chem. Soc*. **2008**, *29*, 1621.