# Kinetics and Mechanism of the Addition of Benzylamines to β-Cyanostilbenes in Acetonitrile

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Nucleophilic addition reactions of benzylamines ($XC_6H_4CH_2NH_2$) to β-cyanostilbenes ($YC_6H_4CH=C(CN)C_6H_4Y'$) have been studied in acetonitrile at 30.0 °C. A greater degree of $N-C_\alpha$ bond formation (larger $\beta_X$) is obtained with a stronger electron-withdrawing substituent in either α- ($\delta\sigma_Y > 0$) or β-ring ($\delta\sigma_{Y'} > 0$). A stronger charge development is observed in the TS on $C_\beta$ ($\rho_{Y'} = 1.06$ for X=Y=H) rather than on $C_\alpha$ ($\rho_Y = 0.62$ for X=Y'=H) indicating the lag in the resonance development into the activating group (CN) on $C_\beta$ in the transition state. Similarly, the magnitude of $\rho_{XY'}$ (−0.72) is greater than $\rho_{XY}$ (−0.66) due to a stronger interaction of the nucleophile with β-ring than α-ring. The positive sign of $\rho_{YY'}$ correctly reflects π bond cleavage between the two rings in the TS. Relatively large kinetic isotope effects ($k_H/k_D \geq 2.0$) involving deuterated nucleophiles ($XC_6H_4CH_2ND_2$) suggest a four-membered cyclic TS in which concurrent $N-C_\alpha$ and $H(D)-C_\beta$ bond formation occurs.

**Key Words :** Nucleophilic addition, β-Cyanostilbene, Cross-interaction constant, Kinetic isotope effects, Concerted mechanism

## Introduction

In nucleophilic additions of amines ($XRNH_2$) to activated olefins ($YC_6H_4CH=CZZ'$), development of resonance and solvation of the incipient carbanion in the TS often lag behind C-N bond formation,[1] an exaggerated form of this can be given as **1** in eq. (1). In aqueous solution,



$$(1)$$
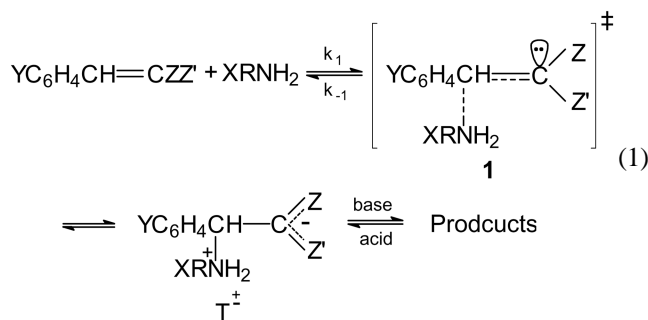
The reaction proceeds through a zwitterionic intermediate,[1] $T^\pm$, (eq. 1) whereas in acetonitrile the adduct was found to form in a single step,[2] **2**. The transition state imbalance, **1**, is far more pronounced for the reactions in aqueous solution than in acetonitrile. Due to weak solvation by MeCN to stabilize the carbanion in $T^\pm$ and hydrogen bonding by N-H proton to negative charge localized on $C_\beta$ in the TS (**2**), the



**2**
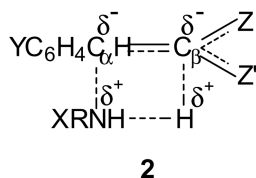
imbalance in the amine additions in acetonitrile becomes very weak. Nevertheless, the localized incipient anionic charge on $C_\beta$ (**1**) due to the imbalance, albeit weak, was found to manifest itself in the strength of hydrogen bonding in the TS (**2**); thus a relatively strong imbalance has led to a stronger kinetic isotope effect ($k_H/k_D > 1.0$) involving deuterated amines ($XRND_2$).[3]

In this work, we carried out kinetic studies of the benzylamine ($XC_6H_4CH_2NH_2$) addition in acetonitrile at 30.0 °C to β-cyanostilbenes (BCS : $YC_6H_4CH=C(CN)C_6H_4Y'$) where both substituents, Y and Y' in α- and β-rings respectively, are varied. By determining various selectivity parameters and the kinetic isotope effects, $k_H/k_D$, for the present reaction we hope to demonstrate that there is TS imbalance in the one step amine additions to olefins in acetonitrile, although it may be weak as noted above.

## Results and Discussion

The kinetic law obeyed in the present reactions is given by eqs. (2) and (3). No catalysis by a second benzylamine (BA) molecule was detected. Plots of $k_{obs}$ against [BA] were linear, and

$$\text{Rate} = k_{obs} [\text{BCS}] \qquad (2)$$

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

the second-order rate constants, $k_2$, determined from the slopes of these plots are summarized in Table 1. The Hammett coefficients, $\rho_X$, $\rho_Y$ and $\rho_{Y'}$, together with Brönsted $\beta_X$ values are shown in Table 2, and cross-interaction constants,[4] $\rho_{ij}$ which are defined as eqs. (4), are given in Table 3, where $i, j = $ X, Y, or Y'.

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**Table 1**. The Second-Order Rate Constants, $k_2 \times 10^4$ dm$^3$ mol$^{-1}$ s$^{-1}$ for the Addition Reactions of $\beta$-Cyanostilbenes with X-Benzylamines in Acetonitrile at 30.0 °C

| Y | Y' | X | | | |
|---|---|---|---|---|---|
| | | *p*-OMe | *p*-Me | H | *p*-Cl |
| *p*-Me | *p*-Me | 1.30 | 1.02 | 0.821 | 0.556 |
| | H | 2.03 | 1.60 | 1.20 | 0.824 |
| | *p*-Cl | 3.87 | 2.79 | 2.09 | 1.20 |
| | *p*-Br | 4.41 | 3.24 | 2.30 | 1.35 |
| | *p*-NO₂ | 18.7 | 12.4 | 8.06 | 3.75 |
| H | *p*-Me | 1.97 | 1.49 | 1.06 | 0.693 |
| | H | 3.27 | 2.40 | 1.57 | 0.973 |
| | *p*-Cl | 6.17 | 4.27 | 2.78 | 1.50 |
| | *p*-Br | 7.07 | 4.83 | 2.91 | 1.66 |
| | *p*-NO₂ | 33.1 | 19.5 | 10.7 | 5.17 |
| *p*-NO₂ | *p*-Me | 7.59 | 5.58 | 3.11 | 1.64 |
| | H | 12.5 | 8.94 | 4.68 | 2.41 |
| | *p*-Cl | 25.5 | 16.1 | 8.71 | 3.72 |
| | *p*-Br | 30.9 | 18.8 | 9.51 | 4.21 |
| | *p*-NO₂ | 177 | 87.9 | 39.4 | 14.2 |

$$\log(k_{ij}/k_{HH}) = \rho_i \sigma_i + \rho_j \sigma_j + \rho_{ij} \sigma_i \sigma_j \quad (4a)$$

$$\rho_{ij} = \partial \rho_i / \partial \sigma_j = \partial \rho_j / \partial \sigma_i \quad (4b)$$

We can get three cross-interaction constants, $\rho_{XY}$, $\rho_{XY'}$, $\rho_{YY'}$. The $\beta_X$ ($\beta_{nuc}$) values were determined by the plots of log $k_2$ (MeCN) versus p$K_a$(H₂O) of benzylamines. This procedure was found to be reliable[5] since the p$K_a$(MeCN) varies in parallel with the p$K_a$(H₂O) with a reasonably constant difference of $\Delta$ p$K_a$ (= p$K_a$ (MeCN)-p$K_a$ (H₂O)) $\cong$ 7.5.

The rates are faster for a stronger nucleophile ($\delta\sigma_X < 0$)

and for the substrate (BCS) with a stronger electron-withdrawing group in both rings ($\delta\sigma_Y > 0$ and $\delta\sigma_{Y'} > 0$) indicating that the reaction is a typical nucleophilic addition. For a given nucleophile, *eg.* X = H, the rate increase is greater for substitution of an electron-withdrawing group (*eg. p*-NO₂) in the $\beta$-ring than in the $\alpha$-ring. This means that the effect of substituents on the rate is greater for the $\beta$- than $\alpha$-ring. This is reflected in the greater magnitude of $\rho_{Y'}$ relative $\rho_Y$ in Table 2. Negative charge development at C$_\alpha$ and C$_\beta$ in the TS leads to positive $\rho_Y$ and $\rho_{Y'}$ values. The fact that $\rho_{Y'}$ is greater than $\rho_Y$ is a clear indication of a stronger anionic charge development at C$_\beta$ rather than at C$_\alpha$ in the TS as a result of the lag (**1**) in the resonance development into the activating group, Z = CN in this case. If there were no lag in the resonance (and solvation) development, charge on C$_\beta$ in the TS should be much smaller than that on C$_\alpha$ and the rate should have been more susceptible to the substituent changes in the $\alpha$-ring rather than the $\beta$-ring, *i.e.*, $\rho_Y > \rho_{Y'}$. In fact when there is another carbon (C$_\beta$) in between the two rings, as in stilbene, the magnitude of $\rho_{Y'}$ for the $\beta$-ring should be attenuated and smaller compared to $\rho_Y$ of the $\alpha$-ring by a fall-off factor of approximately 3.8 (3.5 from bromination),[6] which was experimentally obtained by the ratio of ($\rho_Y/\rho_{Y'}$) = 3.8 from the dehydration of 1,2-diphenylethane.[6] Thus, the difference, $\Delta\rho = \rho_{Y'} - \rho_Y$, obtained in the present work should provide a measure of the imbalance, similarly with I ≡ $\alpha - \beta$ suggested by Bernasconi.[1]

The signs of $\rho_{XY}$ and $\rho_{XY'}$ are negative, as observed in all the bond formation processes in nucleophilic substitution and addition reactions.[1,4] The magnitude of $\rho_{XY'}$ is again greater than that of $\rho_{XY}$ reflecting a stronger interaction of

**Table 2**. The Hammett ($\rho_X$, $\rho_{Y'}$ and $\rho_Y$) and Brönsted ($\beta_X$) Coefficients for the Reactions of $\beta$-Cyanostilbenes with X-Benzylamines

(i) $\rho_X$ and ($\beta_X$) values[a]

| Y/Y' | *p*-Me | H | *p*-Cl | *p*-Br | *p*-NO₂ |
|---|---|---|---|---|---|
| *p*-Me | −0.72 ± 0.05 | −0.78 ± 0.04 | −0.99 ± 0.07 | −1.01 ± 0.05 | −1.37 ± 0.07 |
| *p*-Me | (0.69 ± 0.02) | (0.74 ± 0.02) | (0.94 ± 0.03) | (0.97 ± 0.01) | (1.31 ± 0.03) |
| H | −0.90 ± 0.05 | −1.05 ± 0.06 | −1.21 ± 0.06 | −1.25 ± 0.08 | −1.59 ± 0.12 |
| H | (0.87 ± 0.03) | (1.00 ± 0.05) | (1.16 ± 0.02) | (1.19 ± 0.06) | (1.52 ± 0.08) |
| *p*-NO₂ | −1.35 ± 0.04 | −1.46 ± 0.06 | −1.67 ± 0.05 | −1.73 ± 0.08 | −2.16 ± 0.14 |
| *p*-NO₂ | (1.28 ± 0.06) | (1.38 ± 0.08) | (1.58 ± 0.02) | (1.64 ± 0.06) | (2.06 ± 0.08) |

[a]The correlation coefficients were better than 0.995 in all cases.

(ii) $\rho_{Y'}$ values[b]

| Y/X | *p*-OMe | *p*-Me | H | *p*-Cl |
|---|---|---|---|---|
| *p*-Me | 1.23 ± 0.03 | 1.14 ± 0.04 | 1.05 ± 0.02 | 0.87 ± 0.03 |
| H | 1.29 ± 0.03 | 1.18 ± 0.03 | 1.06 ± 0.01 | 0.92 ± 0.02 |
| *p*-NO₂ | 1.45 ± 0.05 | 1.27 ± 0.04 | 1.17 ± 0.02 | 0.99 ± 0.03 |

[b]The correlation coefficients were better than 0.998 in all cases.

(iii) $\rho_Y$ values[c]

| X/Y' | *p*-Me | H | *p*-Cl | *p*-Br | *p*-NO₂ |
|---|---|---|---|---|---|
| *p*-OMe | 0.79 ± 0.05 | 0.81 ± 0.07 | 0.84 ± 0.06 | 0.87 ± 0.06 | 1.00 ± 0.08 |
| *p*-Me | 0.71 ± 0.03 | 0.77 ± 0.05 | 0.78 ± 0.05 | 0.79 ± 0.04 | 0.88 ± 0.05 |
| H | 0.61 ± 0.01 | 0.62 ± 0.01 | 0.65 ± 0.01 | 0.65 ± 0.01 | 0.73 ± 0.01 |
| *p*-Cl | 0.49 ± 0.01 | 0.50 ± 0.01 | 0.52 ± 0.01 | 0.52 ± 0.01 | 0.60 ± 0.04 |

[c]The correlation coefficients were better than 0.998 in all cases.

**Table 3.** Cross-interaction Constants, $\rho_{XY}$, $\rho_{XY'}$ and $\rho_{YY'}$ for the Reactions of β-Cyanostilbenes with X-Benzylamines in Acetonitrile at 30.0 °C (i) $\rho_{XY}$ values[a]

| Y' | $\rho_{XY}$ |
|---|---|
| *p*-Me | −0.64 ± 0.08 |
| H | −0.66 ± 0.10 |
| *p*-Cl | −0.67 ± 0.10 |
| *p*-Br | −0.71 ± 0.10 |
| *p*-NO₂ | −0.78 ± 0.21 |

[a]The correlation coefficients were better than 0.995 in all cases.

(ii) $\rho_{XY'}$ values[b]

| Y | $\rho_{XY'}$ |
|---|---|
| *p*-Me | −0.71 ± 0.09 |
| H | −0.72 ± 0.10 |
| *p*-NO₂ | −0.87 ± 0.12 |

[b]The correlation coefficients were better than 0.998 in all cases.

(ii) $\rho_{YY'}$ values[c]

| X | $\rho_{YY'}$ |
|---|---|
| *p*-OMe | 0.15 ± 0.01 |
| *p*-Me | 0.10 ± 0.02 |
| H | 0.08 ± 0.01 |
| *p*-Cl | 0.08 ± 0.01 |

[c]The correlation coefficients were better than 0.998 in all cases.

the substituents in the nucleophile with those in the β-ring than in the α-ring. Another important result is that the sign of $\rho_{YY'}$ is positive. The positive $\rho_{ij}$ is normally obtained between substituents *i* and *j* in the bond cleavage process between them.[4] Thus the $\rho_{YZ}$ values are positive for the bond cleavage between the substrate nonleaving (substituent Y) and the leaving group (substituent Z) in the direct displacement (S_N2) reactions.[4,7] For example, in the S_N2 nucleophilic substitution reactions of anilines (XC₆H₄NH₂) with benzyl benzenesulfonates (YC₆H₄CH₂OSO₂C₆H₄Z) in methanol at 35.0 °C,[4a] the cross-interaction constants were : $\rho_{XY} = -0.62$, $\rho_{YZ} = 0.11$ and $\rho_{XZ} = -0.10$. In the present reaction, as the nucleophile (benzylamine) attacks $C_\alpha$, the π-bond between $C_\alpha$ (linked to Y-ring) and $C_\beta$ (linked to Y'-ring) is partially broken in the TS so that the sign of $\rho_{YY'}$ becomes positive. The positive $\rho_{YY'}$ also indicates that a stronger electron acceptor Y ($\delta\sigma_Y > 0$) or Y' ($\delta\sigma_{Y'} > 0$) will result in a greater charge development, $\delta\rho_Y > 0$ or $\delta\rho_{Y'} > 0$, since $\rho_{YY'} = \delta\rho_Y/\delta\sigma_Y = \delta\rho_Y/\delta\sigma_{Y'} > 0$. This is supported by the greater magnitude of $\rho_X$ (and $\beta_X$) for the stronger acceptor Y and Y' as can be seen in Table 2; the greater the

magnitude of $\rho_X$ (and $\beta_X$), the greater is the degree of bond formation and hence the greater becomes the π-bond cleavage in the TS with a stronger anionic charge development on $C_\alpha$ as well as on $C_\beta$ in the TS.

It is interesting to test the reliability of the cross-inter-action constant values ($\rho_{XY}$, $\rho_{XY'}$ and $\rho_{YY'}$) listed in Table 3 by confirming that the third derivative values ($\rho_{XYY'} = \partial\rho_{XY}/\partial\sigma_{Y'} = \partial\rho_{XY'}/\partial\sigma_Y = \partial\rho_{YY'}/\partial\sigma_X$), which can be estimated from Table 3, are indeed constant. The estimated values were −0.10 ± 0.01 (r = 0.970, n = 4), −0.11 ± 0.01 (r = 0.999, n = 3) and −0.12 ± 0.06 (r = 0.810, n = 4) in the order listed, and are reasonably constant as required., although admittedly the last value has a rather large uncertainty.

The kinetic isotope effects involving deuterated benzyl-amine nucleophiles[8] (XC₆H₄CH₂ND₂) are quite large with $k_H/k_D = 1.88$-$2.25$ (Table 4) indicating that strong hydrogen bonding of the N-H(D) proton toward the anionic center, $C_\beta$, in the TS. Thus the reaction proceeds in a single step with concurrent formation of N-$C_\alpha$ and H-$C_\beta$ bonds, **3**.



**3**
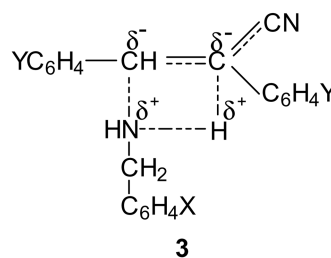
The $k_H/k_D$ values are, however, smaller for Y = *p*-NO₂ than for Y = H, which is rather unexpected since for Y = *p*-NO₂ the degree of bond formation is greater than for Y = H. A greater degree of bond formation should lead to a stronger hydrogen bonding with a larger $k_H/k_D$ value. The reasons for this lower $k_H/k_D$ values with Y = *p*-NO₂ than with Y = H are not clear, but the greater contribution of heavy-atom motion to the reaction coordinate and the nonlinear hydrogen transfer may well be the cause.[9]

The relatively low activation enthalpies, $\Delta H^\neq$, and large negative entropies of activation, $\Delta S^\neq$, in Table 5, are consistent with a four-centered constrained TS structure, **3**, proposed.

## Experimental Section

**Materials.** GR grade acetonitrile was used after three distillations. The benzylamine nucleophiles, GR grade were used after recrystallization. Phenylacetonitrile and benz-aldehydes were commercial reagents.

**Table 4.** Kinetic Isotope Effects on the Second-Order Rate Constants ($k_2$) for the Reactions of β-Cyanostilbenes with Deuterated X-Benzylamines in Acetonitrile at 30.0 °C

| X | Y | Y' | $k_H \times 10^4$ (M⁻¹s⁻¹) | $k_D \times 10^4$ (M⁻¹s⁻¹) | $k_H/k_D$ |
|---|---|---|---|---|---|
| *p*-OMe | H | *p*-Me | 1.97 (± 0.03) | 0.875 (± 0.008) | 2.25 (± 0.04)[a] |
| *p*-Cl | H | *p*-Br | 1.66 (± 0.02) | 0.775 (± 0.007) | 2.14 (± 0.03) |
| *p*-OMe | *p*-NO₂ | *p*-Me | 7.59 (± 0.07) | 3.75 (± 0.03) | 2.02 (± 0.03) |
| *p*-Cl | *p*-NO₂ | *p*-Br | 4.21 (± 0.05) | 2.24 (± 0.02) | 1.88 (± 0.03) |

[a]Standard deviation.

**Table 5**. Activation Parameters[a] for the Reactions of β-Cyano-stilbenes with X-Benzylamines in Acetonitrile

| X | Y | Y' | t (°C) | $k_2 (\times 10^4$ $M^{-1}s^{-1})$ | $\Delta H^{\neq}$ (kcal mol$^{-1}$) | $-\Delta S^{\neq}$ (cal mol$^{-1}$K$^{-1}$) |
|---|---|---|---|---|---|---|
| p-OMe | H | p-Me | 30.0 | 1.97 | 6.3 | 55 |
|  |  |  | 20.0 | 1.33 |  |  |
|  |  |  | 10.0 | 0.878 |  |  |
| p-Cl | H | p-Br | 30.0 | 1.66 | 6.1 | 56 |
|  |  |  | 20.0 | 1.11 |  |  |
|  |  |  | 10.0 | 0.755 |  |  |
| p-OMe | p-NO₂ | p-Me | 30.0 | 7.59 | 6.7 | 51 |
|  |  |  | 20.0 | 5.01 |  |  |
|  |  |  | 10.0 | 3.21 |  |  |
| p-Cl | p-NO₂ | p-Br | 30.0 | 4.21 | 6.3 | 53 |
|  |  |  | 20.0 | 2.86 |  |  |
|  |  |  | 10.0 | 1.89 |  |  |

[a]Calculated by using the Eyring equation. The maximum errors calculated (by the method of K. B. Wiberg, *Physical Organic Chemistry*; Wiley, New York, 1964, p 378) are ± 0.5 kcal mol$^{-1}$ and ± 2 e.u. for $\Delta H^{\neq}$ and $\Delta S^{\neq}$, respectively.

**Preparations of β-Cyanostilbene.** The β-cyanostilbenes were prepared by the literature method of Schonne, Braye and Bruylants.[10] A solution of phenylacetonitrile (10 mmol) and benzaldehyde (10 mmol) in absolute ethanol was treated with a few drops of sodium ethoxide and refluxed for 3 h. The solution was cooled, some of the ethanol was evaporated, and the dark-colored solid was removed by filteration to yield (85%) crude material. This was recrystallized from ethanol. Melting points, IR (Nicolet 5BX FT-IR) and $^1$H and $^{13}$C NMR (JEOL 400 MHz) data were found to agree well with the literature values.[11]

**Kinetic Measurement.** The reaction was followed spectrophotometrically by monitoring the decrease in the concentration of β-cyanostilbenes, [BCS], at $\lambda_{max}$ of the substrate to over 80% completion. The reaction was studied under pseudo-first-order condition, [BCS] = $6.0 \times 10^{-5}$ M and [BA] = $(3.0 \sim 4.5) \times 10^{-1}$ M at 30.0 ± 0.1°C. The pseudo first-order rate constant, $k_{obs}$, was determined from the slope of the plot (r > 0.993) of ln[BCS] vs time. Second-order rate constants, $k_2$, were obtained from the slope of a plot (r > 0.995) of $k_{obs}$ vs [BA] with more than four concentrations of benzylamine, carried out more than three runs, and were reproducible to within ± 3%.

**Product Analysis.** The analysis of final product was difficult due to partial decomposition during product separation and purification. We therefore analysed the reaction mixture by NMR (JEOL 400 MHz) at appropriate intervals under exactly the same reaction conditions as the kinetic measurement in CD$_3$CN at 30.0 °C using larger amount of reactants. Initially we found a peak for CH in the reactant, p-NO$_2$C$_6$H$_4$CH=C(CN)C$_6$H$_4$NO$_2$-p, at 8.04 ppm, which was gradually reduced, and two new peaks for CH-CH in the product, p-NO$_2$C$_6$H$_4$(p-ClC$_6$H$_4$CH$_2$NH)CH-CH(CN)C$_6$H$_4$NO$_2$-p, grew at 3.98 and 4.81 ppm as the reaction proceeded. No other peaks or complications were
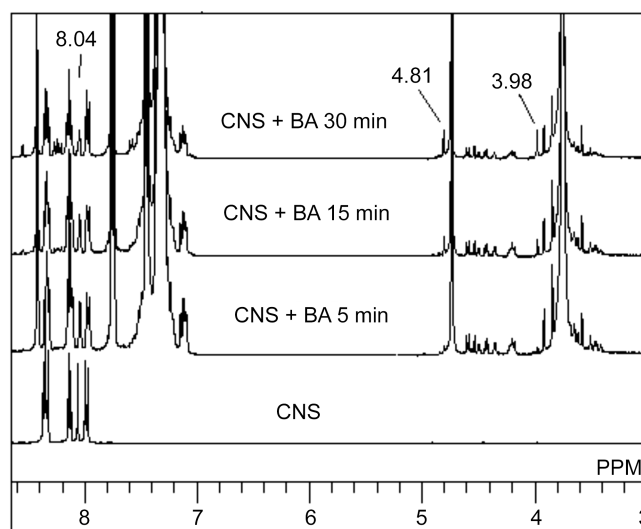


**Figure 1**. $^1$H NMR spectrum for the reaction p-NO$_2$C$_6$H$_4$CH =C(CN)C$_6$H$_4$NO$_2$-p with p-ClC$_6$H$_4$CH$_2$NH$_2$ in CD$_3$CN at 30.0 °C.

found during the reaction except the three peak height changes, indicating that the reaction proceeds with no other side reactions (Figure 1).

**References**

1. Bernasconi, C. F. *Acc. Chem. Res.* **1987**, *20*, 301. (b) Bernasconi, C. F. *Tetrahedron* **1989**, *45*, 4017.
2. (a) Oh, H. K.; Yang, J. H.; Sung, D. D.; Lee, I. *J. Chem. Soc. Perkin Trans. 2* **2000**, 101. (b) Oh, H. K.;Yang, J. H.; Lee, H. W.; Lee, I. *J. Org. Chem.* **2000,** *65*, 2188. (c) Oh, H. K.; Yang, J. H.; Lee, H. W.; Lee, I. *J. Org. Chem.* **2000**, *65*, 5391. Oh, H. K.; Kim, I. K.; Sung, D. D.; Lee, I. *Org. Biomol. Chem.* **2004**, *2*, 1213.
3. (a) Lee, I. *Adv. Phys. Org. Chem.* **1992**, *27*, 57.
4. (a) Lee, I. *Chem. Soc. Rev.* **1990**, *19*, 317. (c) Lee, I.; Lee, H. W. *Collect. Czech. Chem. Commun.* **1999**, *64*, 1529.
5. 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.; Hogan, G.; McGrath, G. P.; King, J.; Brack, C. *J. Chem. Soc. Perkin Trans. 2* **1996**, 2099. (d) Lee, I.; Kim, C. K.; Han, I. S.; Lee, H. W.; Kim, W. K.; Kim, Y. B. *J. Phys. Chem. B* **1999**, *103*, 7302.
6. Ruasse, M.-F. *Adv. Phys. Org. Chem.* **1993**, *28*, 207.
7. Lee, I.; Park, Y. K.; Huh, C.; Lee, H. W. *J. Phys. Org. Chem.* **1994**, *7*, 555.
8. Lee, I. *Chem. Soc. Rev.* **1995**, *24*, 223.
9. (a) Melander, L.; Saunders, W. H. Jr. *Reaction Rates of Isotopic Molecules*; Wiley: New York; 1980; Chapter 5. (b) Oh, H. K.; Park, J. E.; Lee, H. W. *Bull. Korean Chem. Soc.* **2004**, *25*, 1041. (c) Oh, H. K.; Lee, J. M.; Sung, D. D.; Lee, I. *Bull. Korean Chem. Soc.* **2004**, *25*, 557.
10. Schonne, A.; Braye, E.; Braylauts, A. *Bull. Soc. Chim. Belg.* **1953**, *62*, 155.
11. (a) Oh, H. K.; Yang, J. H.; Sung, D. D.; Lee, I. *J. Chem. Soc. Perkin Trans. 2* **2002**, 282. (b) Kroeger, D. J.; Stewart, R. *Can. J. Chem.* **1967**, *45*, 2163.