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Kinetics and Mechanism of the Addition of Benzylamines to Benzylidenediethylmalonates in Acetonitrile

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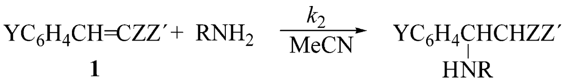
Kinetic studies of the benzylamine additions to benzylidenediethylmalonates (BDM: $YC_6H_4CH{=}C(COOEt)_2$) in acetonitrile at 20.0 °C are reported. The rates in acetonitrile are consistent with that expected from the through-conjugative electron-accepting power of the activating groups, $(COOEt)_2$. The sign and magnitude of the cross-interaction constant, $\rho_{XY} = -0.45$, are in general agreement with those for the single-step amine additions to activated olefins. The kinetic isotope effects ($k_H/k_D > 1.0$) measured with deuterated benzylamines ($XC_6H_4CH_2ND_2$) increase with a stronger electron-acceptor substituent in benzylamines ($\partial\sigma_X > 0$) and a stronger electron donor in the substrate ($\partial\sigma_Y < 0$). These trends are the same as those found for benzylidene-1,3-indandiones but are exactly opposite to those for other activated olefin series, e.g., β-nitrostyrene. It has been shown that the former series are thermodynamically controlled, whereas the latter are intrinsically controlled with a relatively strong transition state imbalance. The activation parameters, $\Delta H^‡$ and $\Delta S^‡$, also support our proposed transition state involving concurrent C_α—N and C_β—H bond formation with a four-membered cyclic structure.

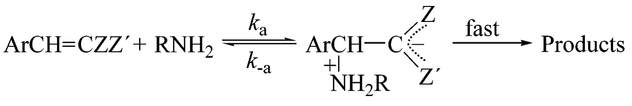
Introduction

Nucleophilic additions of amines (RNH_2) to activated (by Z and/or Z′ groups) olefins **1** in acetonitrile are found to proceed in a single step to neutral products,[1] eq 1. In



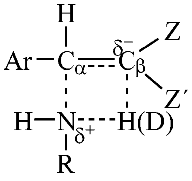
$$\underset{\mathbf{1}}{\mathrm{YC_6H_4CH{=}CZZ'}} + \mathrm{RNH_2} \xrightarrow[\mathrm{MeCN}]{k_2} \mathrm{YC_6H_4}\underset{\mathrm{HNR}}{\underset{|}{\mathrm{C}}}\mathrm{HCHZZ'} \qquad (1)$$

aqueous solution, however, the reactions are reported to occur through a zwitterionic intermediate, $T^{\pm}$, with imbalanced transition states (TSs) in which the development of resonance into the activating groups (Z,Z′) lags behind charge transfer or C−N bond formation,[2] eq 2.



$$\mathrm{ArCH{=}CZZ' + RNH_2} \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} \underset{T^{\pm}}{\mathrm{Ar}\underset{\overset{+|}{\mathrm{NH_2R}}}{\mathrm{CH}}{-}\mathrm{C}\langle^{Z}_{Z'}} \xrightarrow{\text{fast}} \text{Products} \qquad (2)$$

In most cases, in aqueous solution the rapid acid−base equilibria, $T^{\pm} \rightleftharpoons T^{-} + H^{+}$, is established subsequently, and the initial addition, k_a, is the rate determining step.[2] The rates of amine additions in acetonitrile are in general extremely slower than those in aqueous solution ($k_a(\mathrm{aq}) \cong 10^4\ k_2(\mathrm{MeCN})$).[1] In the TS of the one-step addition in acetonitrile, (**2**), hydrogen bonding of the N−H(D) proton to a negative charge developed on C_β was found to result in primary isotope effects, $k_H/k_D > 1.0$.[1] Another interesting observation is that the sign and magnitude ($\rho_{XY} \approx -0.6$ to -0.8) of the cross-interaction constant,[3] ρ_{XY} in eqs 3 where X and Y are substituents in the nucleophile and substrate, are in general agreement with those for bond formation in the concerted nucleophilic substitution (S_N2) reactions.[1,3b]



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$$\log(k_{XY}/k_{HH}) = \rho_X\sigma_X + \rho_Y\sigma_Y + \rho_{XY}\sigma_X\sigma_Y \qquad (3a)$$

$$\rho_{XY} = \partial\rho_X/\partial\sigma_Y = \partial\rho_Y/\partial\sigma_X \qquad (3b)$$

In the present work, we carried out kinetic studies of benzylamine ($XC_6H_4CH_2NH_2$) additions to benzylidene-

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† Chonbuk National University.

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(1) (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. (d) Oh, H. K.; Yang, J. H.; Hwang, Y. H.; Lee, H. W.; Lee, I. *Bull. Korean Chem. Soc.* **2002**, *23*, 221. (e) Oh, H. K.; Kim, T. S.; Lee, H. W.; Lee, I. *J. Chem. Soc., Perkin Trans. 2* **2002**, 282.

(2) (a) Bernasconi, C. F. *Acc. Chem. Res.* **1987**, *20*, 301. (b) Bernasconi, C. F. *Tetrahedron* **1989**, *45*, 4017.

(3) (a) Lee, I. *Chem. Soc. Rev.* **1990**, *19*, 317. (b) Lee, I. *Adv. Phys. Org. Chem.* **1992**, *27*, 57. (c) Lee, I.; Lee, H. W. *Collect. Czech. Chem. Commun.* **1999**, *64*, 1529.

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TABLE 1. The Second-Order Rate Constants, $k_2 \times 10^2$ M^{-1} s^{-1}, and Selectivity Parameters[a] for the Addition Reactions of Y-Benzylidenediethylmalonates with X-Benzylamines in Acetonitrile at 20.0 °C

	Y					
X	*p*-OMe	*p*-Me	H	*p*-Cl	*p*-Br	ρ_Y[f]
p-OMe	3.06[b]	2.86	4.58	7.76	13.9	1.24 ± 0.07
	2.08				9.37	
	1.38[c]				6.16	
p-Me	1.69	2.37	3.70	6.05	7.05	1.15 ± 0.07
H	1.31	1.75	2.48	4.16	4.74	1.05 ± 0.05
	1.28				4.27	
p-Cl	0.850	1.11	1.60	2.56	2.85	1.00 ± 0.04
	0.559				1.86	
ρ_X[d]	−0.77	−0.83	−0.93	−0.97	−1.03	ρ_{XY}[g] = −0.45
	(± 0.03)	(± 0.01)	(± 0.03)	(± 0.02)	(± 0.03)	(± 0.14)
β_X[e]	0.73	0.78	0.88	0.92	0.98	
	(± 0.02)	(± 0.03)	(± 0.04)	(± 0.02)	(± 0.02)	

[a] The σ values were taken from ref 6. The pK_a values were taken from Fischer, A.; Galloway, W. J.; Vaughan, J. *J. Chem. Soc.* **1964**, 3588. pK_a = 9.67 was used for X = *p*-OMe (reference: Oh, H. K.; Lee, J. Y.; Lee, I. *Bull. Korean Chem. Soc.* **1998**, *19*, 1198). [b] At 30.0°C. [c] At 10.0 °C. [d] Correlation coefficients were better than 0.996 in all cases. [e] Correlation coefficient were better than 0.998 in all cases. [f] Correlation coefficients were better than 0.995 in all cases. [g] Correlation coefficient was 0.997.

diethylmalonates (BDM: Z = Z′ = COOEt in **1**) in acetonitrile at 20.0 °C. We aim to further explore the mechanistic differences between amine additions to olefin in aqueous and in acetonitrile solution. We are also interested in the effects of the activating groups, Z,Z′, on the mechanism of the amine addition in MeCN by examining closely the trends of changes in the isotope effects, k_H/k_D, determined using the deuterated benzylamine nucleophiles ($XC_6H_4CH_2ND_2$).[4]

Results and Discussion

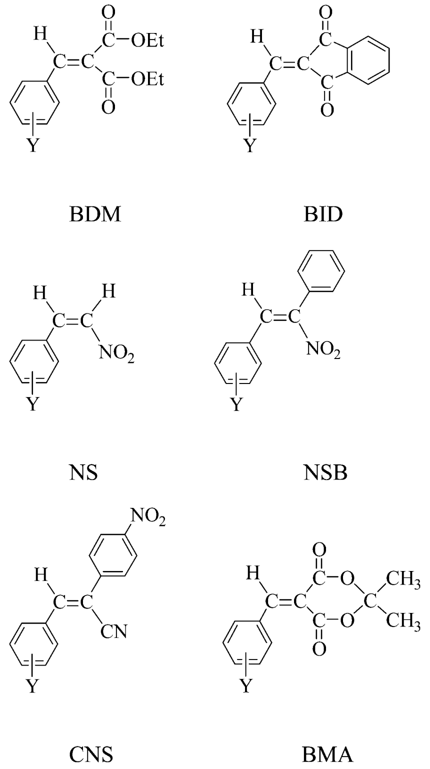
The simple second-order rate law obeyed by all the reactions studied in this work is given by eqs 4 and 5 where [BDM] and [BnA] are concentrations of substrate (**1** with Z = Z′ = COOEt) and benzylamine, respectively.

$$\text{Rate} = k_{\text{obsd}}\,[\text{BDM}] \tag{4}$$

$$k_{\text{obsd}} = k_2\,[\text{BnA}] \tag{5}$$

The second-order rate constants, k_2, were obtained from the slopes of the linear plots of k_{obsd} vs [BnA] and are summarized in Table 1. The Hammett ρ_X and ρ_Y values and the Brönsted β_X values are also shown in Table 1 together with the cross-interaction constant ρ_{XY} (eqs 3). The β_X values are based on the plots of log k_2(MeCN) against the pK_a(H_2O) of benzylamines. This procedure was found to be reliable, since the pK_a(MeCN) varies in parallel with the pK_a(H_2O) with a reasonably constant difference of ΔpK_a (= pK_a(MeCN) − pK_a(H_2O)) ≅ 7.5.[5] In acetonitrile, the rate, k_2, was found to increase with the sum of electron-accepting power of Z,Z′ through π-orbitals,[1c,d] i.e., the sum of through-conjugative electron-accepting power, $\sum\sigma_p^-$ or $\sum R^-$. These values for BDM ($\sum\sigma_p^- = 1.50$ and $\sum R^- = 0.82$)[6] are smaller than those for benzylidenemalononitrile (BMN: Z = Z′ = CN in **1**, with 2.00 and 0.98, respectively)[1b] and benzylidene-1,3-indandione (BID: Z,Z′ = $(CO)_2C_6H_4$, with 2.08 and 1.30, respectively)[1c] but are larger than those for β-nitrostyrene (NS), β-nitrostilbene (NSB), and β-cyano-4′-nitrostilbene (CNS),[1e] Scheme 1. The rate estimated for BDM at 25.0 °C (≅ 3.0×10^{-2} M^{-1} s^{-1}; X = Y = H) fits roughly in the order expected from the order of the direct resonance effect,[1c,d] $\sum\sigma^-$ or $\sum R^-$. The sign of ρ_{XY} (<0) is again negative, which is consistent with the trend found for the bond formation processes.[1,3b] The size of ρ_{XY} (≅ −0.45) is larger than that for BID (−0.33)[1c] but is similar to that for NS (−0.40)[1a] which is also reasonable considering the order expected from $\sum\sigma^-$ or $\sum R^-$.

SCHEME 1



The kinetic isotope effects (KIEs) measured using deuterated benzylamine nucleophiles ($XC_6H_4CH_2ND_2$) are summarized in Table 2. The k_H/k_D values are all greater than 1 indicating N····H(D) bond stretching in the TS. We therefore propose a single-step addition with concurrent C_α−N and C_β−H bond formation in the TS as shown in **2**. We note that the KIEs, k_H/k_D, are smaller ($k_H/k_D \cong 1.5-2.0$) for a stronger nucleophile ($\partial\sigma_X < 0$) than for a weaker nucleophile ($k_H/k_D \cong 1.6-2.1$), albeit the differences are marginal but the trend is clear. Again the KIE is smaller for a stronger electron-acceptor substituent in the substrate ($\partial\sigma_Y > 0$) than for a weaker acceptor: thus $\partial\sigma_X < 0 \rightarrow \partial(k_H/k_D) < 0$ and $\partial\sigma_Y > 0 \rightarrow \partial(k_H/k_D) < 0$. These trends are the same as those found for the benzylamine additions to BID[1c] but are exactly opposite to those found for other corresponding reactions of NS,[1a]

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(4) Lee, I. *Chem. Soc. Rev.* **1995**, *24*, 223.

(5) (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. *Progress in Physical organic Chemistry*; Streitwieser, A., Jr., Taft, R. W., Eds.; Wiley: New York, 1967; Vol. 4, pp 54−92. (c) Spillane, W. J.; Hogan, G.; McGrath, 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) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

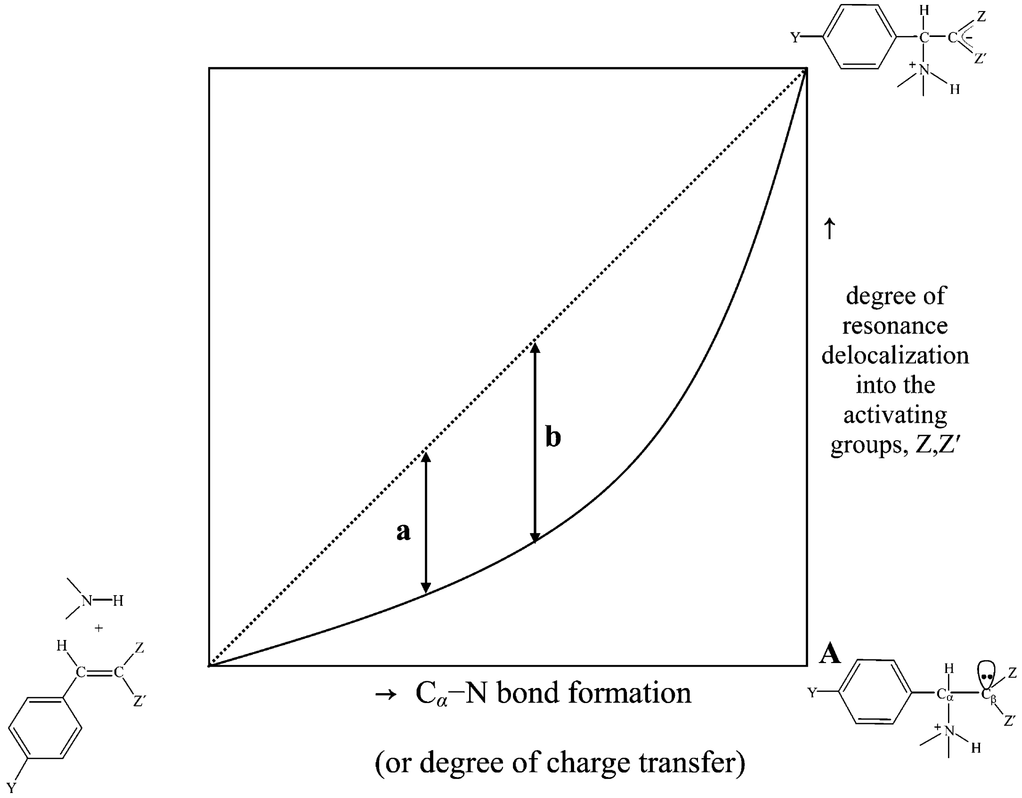

FIGURE 1. More O'Ferrall−Jencks diagram. The **a** and **b** represent the degree of charge imbalance in the TS due to the lag in resonance delocalization.

TABLE 2. Kinetic Isotope Effects on the Second-Order Rate Constants (k_H/k_D) for the Reactions of Y-Benzylidenediethylmalonates with Deuterated X-Benzylamines in Acetonitrile at 20.0 °C

X	Y	$k_H \times 10^2$/M^{-1} s^{-1}	$k_D \times 10^2$/M^{-1} s^{-1}	k_H/k_D
p-OMe	*p*-OMe	2.08 (±0.03)	1.03 (±0.01)	2.02 ± 0.04[a]
p-OMe	*p*-Me	2.86 (±0.04)	1.45 (±0.02)	1.96 ± 0.04
p-OMe	H	4.58 (±0.05)	2.53 (±0.03)	1.81 ± 0.03
p-OMe	*p*-Cl	7.76 (±0.08)	5.11 (±0.06)	1.52 ± 0.02
p-Cl	*p*-OMe	0.850 (±0.005)	0.411 (±0.002)	2.07 ± 0.02
p-Cl	*p*-Me	1.11 (±0.01)	0.552 (±0.003)	2.01 ± 0.02
p-Cl	H	1.60 (±0.02)	0.879 (±0.005)	1.82 ± 0.03
p-Cl	*p*-Cl	2.56 (±0.03)	1.56 (±0.02)	1.64 ± 0.03

[a] Standard deviations.

BMN,[1b] ECC,[1d] NSB, and CNS,[1e] for which $\partial\sigma_X < 0 \rightarrow \partial(k_H/k_D) > 0$ and $\partial\sigma_Y > 0 \rightarrow \partial(k_H/k_D) > 0$ with substantially larger k_H/k_D values ranging from 2.3 to 2.8.[1a,b,d,e] The following is an attempt to rationalize these two opposing trends in the change of k_H/k_D values with substituents in the nucleophile (X) and in the substrate (Y).

(i) First of all, we should recognize that the size of the primary kinetic isotope effects ($k_H/k_D > 1.0$) reflects the extent of N−H(D) bond stretching in the TS, **2**, or alternatively the extent of H−C_β bond formation in the TS.[1c,d,4] The greater the k_H/k_D value, the longer the N−H(D) bond stretch or the greater the C_β−H bond formation. Thus, for the benzylamine addition to BDM and BID,[1c] the greater reactivity by a stronger electron donor X ($\partial\sigma_X < 0$) and by a stronger acceptor Y ($\partial\sigma_Y > 0$) results in a lower selectivity, $\partial(k_H/k_D) < 0$, i.e., a lower extent of N−H(D) bond cleavage or C_β−H bond formation in an *earlier* TS. This is a natural consequence of a thermodynamically controlled reaction series for which the Hammond postulate[7] and Bell−Evans−Polanyi (BEP) principle[7] hold: factors ($\partial\sigma_X < 0$ and $\partial\sigma_Y > 0$) that stabilize products more lead to an earlier TS. This means that the TS structures, or the TS positions along the reaction coordinate, for the benzylamine additions to BDM and BID are largely determined by the product stability, and a greater reactivity is accompanied by a lower selectivity, i.e., the reactivity−selectivity principle (RSP)[8] holds.

(ii) In contrast, for the addition reactions of amine nucleophiles to NS,[1a] BMN,[1b] ECC,[1d] NSB, and CNS,[1e] the same rate enhancing factors, a stronger nucleophile ($\partial\sigma_X < 0$) and a stronger electron acceptor Y ($\partial\sigma_Y > 0$), were found to lead to a greater k_H/k_D value; that is, a faster rate is accompanied by a greater selectivity, i.e., anti-Hammond effect[7] anti-RSP[8] hold. Thus, the effects of substituents X and Y are not thermodynamically controlled but intrinsically controlled. In this case, an electron donor X ($\partial\sigma_X < 0$) and an electron acceptor Y ($\partial\sigma_Y > 0$) stabilize an imbalanced state, **A**, shown in the More O′Ferrall−Jencks diagram,[9] Figure 1.[10] A stronger acceptor Y ($\partial\sigma_Y > 0$) leads to a faster rate of amine addition in response to both the positive charge on the amine nitrogen and negative charge on C_β in **A** as has been pointed out by Bernasconi.[2,11] The curved reaction coordinate in Figure 1 represents a lag in the develop-

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[7] (a) Klumpp, G. W. *Reactivity in Organic Chemistry*; Wiley: New York, 1982; Chapter 5. (b) Pross, A. *Theoretical and Physical Principles of Organic Reactivity*; Wiley: New York, 1995; Chapter 5.

[8] (a) Pross, A. *Adv. Phys. Org. Chem.* **1997**, *14*, 69. (b) Buncel, E.; Wilson, H. *J. Chem. Educ.* **1987**, *64*, 475.

[9] (a) More O'Ferrall, R. A. *J. Chem. Soc. B* **1970**, 274. (b) Jencks, W. P. *Chem. Rev.* **1972**, *72*, 705.

ment of resonance and solvation behind charge transfer (or the C_α−N bond formation). The diagonal straight line (dashed) represents a hypothetical reaction coordinate with no lag. The lag will depend on the degree of C_α−N bond formation, **a** or **b**, in the TS. Since in an imbalanced TS resonance delocalization of the anionic charge developed on C_β into the activation group, Z,Z′, lags behind C_α−N bond formation, the relatively strong incipient localized negative charge, a p-type lone pair orbital, developed on C_β causes a strong C_β−H hydrogen bonding with an enhanced k_H/k_D value, i.e., a greater N−H(D) bond cleavage, and/or C_β−H bond formation, as we found for the reactions of NS,[1a] BMN,[1b] ECC,[1d] NSB, and CNS.[1e] In this case, the faster the rate due to a stronger electron donor X ($\partial\sigma_X < 0$) and/or a stronger electron-withdrawing substituent Y ($\partial\sigma_Y > 0$),[2] the greater the extent of bond formation in the TS and the greater the imbalance, and hence the greater the selectivity, i.e., the greater the k_H/k_D value. This is therefore an anti-Hammond effect[7] and anti-RSP[8] behavior in an intrinsically controlled reaction series.[3b]

(iii) It is therefore clear why we obtained a shift corresponding to an earlier TS for the addition reactions of BDM and BID:[1c] for these the charge imbalance in the TS is practically insignificant and the charge developed on C_β can be efficiently resonance delocalized into the activating groups, Z,Z′, in the TS. This is supported by the very small imbalance[12] found for the addition reactions of amines in *aqueous* solution to benzylidene Meldrum's acid (BMA: Z,Z′ = $(COO)_2C(CH_3)_2$ in **1**), which is also a dicarbonyl compound like the BDM and BID.

(iv) Since an incipient localized charge built up on C_β in the TS causes an enhanced KIE with a N−H(D) bond cleavage that is greater than that expected from a synchronous addition, the TS should have a four-membered hydrogen bonded structure, **2**, rather than a six-membered hydrogen bonded structure, **3**, which may be considered as an alternative possibility.[1] In this structure, **3**, a N−H (D) proton hydrogen bonds to an atom in the activating group. However, the charge on this atom, O in **3**, should be weaker than that on C_β due to the lag in the resonance delocalization of anionic charge into the activating group, NO_2, in the TS[11] and hence should lead to a smaller k_H/k_D value with a lower degree of N−H(D) bond cleavage than that expected from a synchronous addition, not an enhanced k_H/k_D value observed, e.g., for NS.[1a]

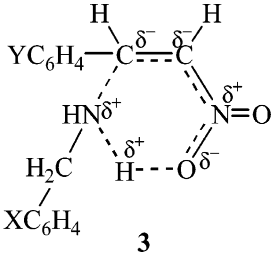

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TABLE 3. Activation Parameters[a] for the Reactions Y-Benzylidenediethylmalonates with X-Benzylamines in Acetonitrile

X	Y	$\Delta H^\ddagger$/kcal mol^{-1}	$-\Delta S^\ddagger$/cal mol^{-1} K^{-1}
p-OMe	*p*-OMe	6.1	50
p-OMe	*p*-Br	6.4	46
p-Cl	*p*-OMe	6.5	50
p-Cl	*p*-Br	6.5	48

[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 ±0.5 kcal mol^{-1} and ±2 eu for $\Delta H^\ddagger$ and $\Delta S^\ddagger$, respectively.

(v) The reasons for the different behavior of the dicarbonyl compounds, BDM and BID, observed in the variations of the KIE (k_H/k_D) with substituents X and Y from other olefins (NS, BMN, NSB, CNS, etc.) are not clear. However, the strong proximate charge transfer of the anionic charge on C_β (a p-type lone pair orbital, n_C) to the π* orbitals of the two carbonyl groups[13] ($n_C \rightarrow p^*_{C=O}$) may contribute to an *efficient* resonance delocalization into the activating groups in the TS. This $n_C \rightarrow p^*_{C=O}$ charge transfer interaction is especially strong due to the relatively low $\pi^*_{C=O}$ level.[13] Another factor could be the weak solvation of the dicarbonyl compounds in acetonitrile requiring little solvent reorganization in the TS. The lag in charge transfer of the developing anionic charge of C_β into the activating groups due to structural and solvent reorganization required in the TS is considered as the principal cause for the TS imbalance.[2]

(vi) The activation parameters, $\Delta H^\ddagger$ and $\Delta S^\ddagger$, are summarized in Table 3. The activation enthalpies, $\Delta H^\ddagger$ = 6.1−6.5 kcal mol^{-1}, are quite similar to those found for the benzylamine additions to BID[1c] in acetonitrile, $\Delta H^\ddagger$ = 6.1−6.4 kcal mol^{-1}. However, these values are somewhat higher than those found for benzylamine additions to the intrinsic control series, NS,[1a] BMN,[1b] NSB,[1e] CNS,[1e] etc.. For example, for the reactions of NS,[1a] the $\Delta H^\ddagger$ values are much lower, $\Delta H^\ddagger = 0.5-1.0$ kcal mol^{-1}. Since the hydrogen bonding in the TS, **2**, constitutes a product stabilizing factor which develops early, it is expected to lower the *intrinsic* reaction barrier,[2] in agreement with the lower energy barrier for the NS reactions which are believed to involve a large TS imbalance.[2,12] The $-\Delta S^\ddagger$ values for the reactions of NS[1a] are a little higher (55−64 eu) than those for BDM (46−50 eu), which is also consistent with the stronger hydrogen bonded (more rigid) structure for the former.

We conclude that in the benzylamine additions to BDM (and also to BID) in acetonitrile there is an insignificant TS imbalance and the structure of the four-membered cyclic TS or the TS position along the reaction coordinate based on the KIE is consistent with that predicted by a model based on the thermodynamic stability of products, i.e., the Hammond postulate, BEP principle, etc.. In contrast, in the corresponding reactions of other olefins, e.g., NS, there is a relatively strong TS imbalance which

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[10] The TS imbalance effect cannot be combined with the thermodynamic effect since the end products in the two are different as has been shown by Bernasconi (refs 2 and 11). Therefore the diagram shows *only* the TS imbalance effect which represents adequately the substituent effects leading to the imbalances; that is, the proposed mechanism is not stepwise involving the zwitterionic intermediate but concerted with a four-membered cyclic structure TS.

[11] Bernasconi, C. F.; Renfrow, R. A. *J. Org. Chem.* **1987**, *52*, 3035.

[12] For BMA, the imbalance parameter, $I = \alpha - \beta \cong 0.1$, while, for NS, $I = 0.26$ (ref 2a).

[13] (a) Li, H. G.; Kim, C. K.; Lee, B.-S.; Kim, C. K.; Rhee, S. K.; Lee, I. *J. Am. Chem. Soc.* **2001**, *123*, 2326. (b) Lee, I. *Int. Rev. Phys. Chem.* **2003**, *22*, 263.

dictates the intrinsic reactivity and the TS structure is determined by intrinsic effects.

Experimental Section

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

Preparations of Benzylidenediethylmalonates. The benzylidenediethylmalonates were prepared by the literature method of Horning et al..[14]

Kinetic Measurement. The reaction was followed spectrophotometrically by monitoring the decrease in the concentration of benzylidenediethylmalonate, [BDM], at λ_{max} of the substrate to over 80% completion. The reaction was studied under pseudo-first-order condition, $[BDM] = 8.0 \times 10^{-5}$ M and $[BnA] = 0.30-0.45$ M at 20.0 ± 0.1 °C. The pseudo-first-order rate constant, k_{obsd}, was determined from the slope of the plot ($r > 0.995$) of log[BDM] vs time. The second-order rate constant, k_2, was obtained from the slope of a plot ($r > 0.993$) of k_{obsd} vs [benzylamine] with more than four concentrations and were reproducible to within ±3%.

Product Analysis. The analysis of the final product was difficult due to partial decomposition during product separation and purification. We therefore analyzed the reaction mixture by NMR (400 MHz) at appropriate intervals under exactly the same reaction conditions as the kinetic measurement in MeCN at 20.0 °C for the reaction of BDM (p-$CH_3OC_6H_4CH{=}C(CO_2C_2H_5)_2$) with p-methoxybenzylamine; initially we found a peak of C*H* in the reactant, p-$CH_3OC_6H_4C\mathit{H}{=}C(CO_2C_2H_5)_2$, at 7.58 ppm, which was gradually reduced, and two new peaks of C*H*—C*H* in the product, p-$CH_3OC_6H_4(p$-$CH_3OC_6H_4CH_2NH)C\mathit{H}{-}C\mathit{H}(CO_2C_2H_5)_2$, grew at 2.35 and 4.78 ppm as the reaction proceeded. No other peaks or complications were found during the reaction except the changes of three peak heights indicating that the reaction proceeded with no other side reactions.

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