Kinetics and mechanism of the addition of benzylamines to β-nitrostilbenes and β-cyano-4′-nitrostilbenes

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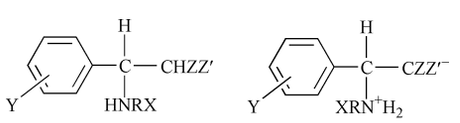
Nucleophilic addition reactions of benzylamines (BA) to β-nitrostilbenes (NSB) and β-cyano-4′-nitrostilbenes (CNS) have been studied in acetonitrile at 25.0 and 30.0 °C, respectively. The rate is first order with respect to BA and substrate. The rate of reaction with CNS is much lower than that expected from the rate sequence observed in aqueous solution indicating that the mechanisms of BA addition in acetonitrile and in water are different. The major factor determining reactivity of the amine addition in acetonitrile is the direct resonance effect (σ^- or R^-) while that in aqueous solution is the polar electron-withdrawing effect (σ) of the activating groups. Due to steric inhibition the β-phenyl rings in NSB and CNS are prevented from π-overlap with the anionic center in the TS so that the reduced resonance effect leads to unduly low addition rates. The kinetic isotope effects and activation parameters are in line with the one step addition mechanism in which N–C_α and H–C_β bonds are formed concurrently with a hydrogen bonded four-center cyclic transition state. The cross-interaction constant ρ_{XY} is negative and the magnitude is somewhat larger than those for other similar addition reactions.

Introduction

Addition of amines ($XRNH_2$) to olefins ($YC_6H_4CH{=}CZZ'$) is known to proceed in acetonitrile by concerted formation of the C_α–N and C_β–H bonds in a single-step process leading to a neutral product,[1] **I**. This is, however, quite in contrast to the mechanism in aqueous solution, which occurs through a zwitterionic intermediate, **II** (**T**$^\pm$), with imbalanced transition states (TSs) in which the development of resonance into the activating (electron-acceptor) group (Z,Z′) lags behind charge transfer or bond formation.[2] The rates of amine additions in acetonirile are in general much slower than in aqueous solution (k_2(aq) ≈ $10^4 \times k_2$(MeCN)), but the relative order depending on the Z,Z′ group was found to remain the same.[1] The mechanistic difference found between amine additions to the activated olefins in aqueous and acetonitrile solutions has been attributed to[1] (i) weak solvation by MeCN to stabilize the carbanion in the putative intermediate (**T**$^\pm$), and (ii) hydrogen bonding to negative charge localized on C_β in the TS due partly to the well known "imbalance", which causes a lag in charge delocalization into the activating groups (Z,Z′) behind C–N bond formation.[2] Another interesting point is that the sign and magnitude ($\rho_{XY} \approx -0.6$ to -0.8) of the cross-interaction constant (CIC) [ρ_{XY} in eqn. (1)[3] where X and Y are substituents in the nucleophile and substrate for the one-step amine additions] are in general agreement with those for the bond formation in the concerted nucleophilic substitution (S_N2) reactions.[3]



I **II** (T$^\pm$)

$$\log (k_{XY}/k_{HH}) = \rho_X\sigma_X + \rho_Y\sigma_Y + \rho_{XY}\sigma_X\sigma_Y \quad (1a)$$

$$\rho_{XY} = \partial\rho_X/\partial\sigma_Y = \partial\rho_Y/\partial\sigma_X \quad (1b)$$

In this work we carried out kinetic studies of the benzylamine ($XC_6H_4CH_2NH_2$) additions to β-nitrostilbenes (NSB; Z,Z = NO_2, C_6H_5) and β-cyano-4′-nitrostilbenes (CNS; Z,Z′ = CN, p-$NO_2C_6H_4$) in acetonitrile at 25.0 and 30.0 °C, respectively, eqn. (2).

$$XC_6H_4CH_2NH_2 + YC_6H_4CH{=}CZZ' \xrightarrow{MeCN} YC_6H_4CHCHZZ' \quad (2)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad NHCH_2C_6H_4X$$

where (Z, Z′) = (NO_2, C_6H_5) and (CN, p-$NO_2C_6H_4$).

The objective of this work is to further explore the mechanistic differences between amine addition to olefin in aqueous solution and in acetonitrile by examining the structure–reactivity behavior of olefins and amines. It is also of interest to examine the effects of the activating groups, Z,Z′, on the rate and mechanism of the amine addition in dipolar aprotic solvent.

Results and discussion

The reactions investigated in the present work obeyed a simple kinetic law given by eqns. (3) and (4) where k_2 is the second-

$$-d[S]/dt = k_{obs}[S] \quad (3)$$

$$k_{obs} = k_2[BA] \quad (4)$$

order rate constant for the benzylamine (BA) addition to the substrate (S), *i.e.*, NSB and CNS.

In contrast to the benzylamine catalysis observed in the additions to β-nitrostyrene (NS),[1a] no catalysis was detected by a second BA molecule in the present studies. Plots of k_{obs} against [BA] were linear with a *ca.* 10-fold increase in [BA]. The k_2 values obtained from the slopes of these plots are summarized in Tables 1 and 2. The Hammett ρ_X and ρ_Y values are also shown in the tables together with the cross-interaction

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Table 1 The second order rate constants, $k_2 \times 10^2$ M^{-1} s^{-1}, for the addition of X-benzylamines to β-nitrostilbenes in acetonitrile at 25 °C

	Y					
X	*p*-OMe	*p*-Me	H	*p*-Cl	*p*-Br	ρ_Y [a]
p-OMe	1.90	2.79	4.49	9.39	11.3	1.46 ± 0.08
	1.47 [b]				8.72	
	1.12 [c]				6.64	
p-Me	1.72	2.18	3.89	7.24	8.71	1.36 ± 0.07
H	1.28	1.78	2.69	5.14	6.09	1.27 ± 0.07
p-Cl	0.890	1.15	1.78	3.24	3.69	1.19 ± 0.05
	0.638				2.71	
	0.461				1.96	
ρ_X [d]	−0.68	−0.75	−0.82	−0.92	−0.97	
	(±0.03)	(±0.06)	(±0.03)	(±0.03)	(±0.02)	ρ_{XY} [e] = −0.52
β_X [f]	0.68	0.71	0.78	0.88	0.92	(±0.16)
	(±0.03)	(±0.03)	(±0.05)	(±0.01)	(±0.01)	

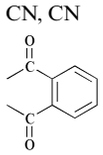
[a] The σ values were taken from ref. 5. Correlation coefficients were better than 0.996 in all cases. [b] At 15.0 °C. [c] At 5.0 °C. [d] The source of σ is the same as for footnote *a*. Correlation coefficients were better than 0.994 in all cases. [e] Correlation coefficient was 0.997. [f] Brønsted coefficient. The pK_a values were taken from ref. 7. Correlation coefficients were better than 0.993 in all cases. pK_a = 9.67 was used for X = *p*-CH_3O (ref. 8).

Table 2 The second order rate constants, $k_2 \times 10^3$ M^{-1} s^{-1} for the addition of X-benzylamines to β-cyano-4′-nitrostilbenes in acetonitrile at 30.0 °C

	Y					
X	*p*-OMe	*p*-Me	H	*p*-Cl	*p*-Br	ρ_Y [a]
p-OMe	1.17	1.56	2.52	4.50	4.74	1.19 ± 0.02
	0.751 [b]				3.08	
	0.479 [c]				1.98	
p-Me	0.951	1.23	1.95	3.38	3.63	1.14 ± 0.02
H	0.619	0.839	1.26	2.17	2.31	1.10 ± 0.03
p-Cl	0.399	0.490	0.681	1.05	1.07	0.84 ± 0.01
	0.257				0.671	
	0.165				0.422	
ρ_X [d]	−0.95	−1.01	−1.15	−1.27	−1.30	
	(±0.04)	(±0.01)	(±0.01)	(±0.04)	(±0.06)	ρ_{XY} [e] = −0.67
β_X [f]	0.90	0.96	1.09	1.20	1.24	(±0.08)
	(±0.05)	(±0.03)	(±0.04)	(±0.05)	(±0.08)	

[a] The σ values were taken from ref. 5. Correlation coefficients were better than 0.996 in all cases. [b] At 20.0 °C. [c] At 10.0 °C. [d] The source of σ is the same as for footnote *a*. Correlation coefficients were better than 0.994 in all cases. [e] Correlation coefficients was 0.997. [f] The pK_a values were taken from ref. 7. Correlation coefficients were better than 0.993 in all cases. pK_a = 9.67 was used for X = *p*-CH_3O (ref. 8).

Table 3 Reactivity parameters for the amine addition reactions, $YC_6H_4CH{=}CZZ' + XC_6H_4CH_2NH_2$, in acetonitrile at 25 °C

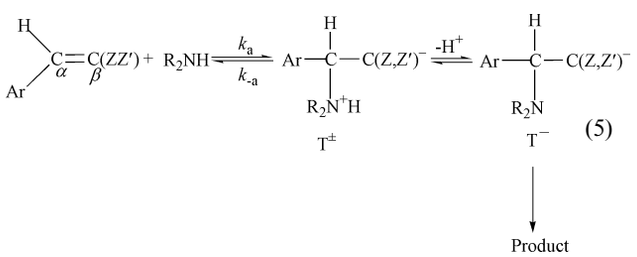
Entry	Z,Z′	k_2 [a]/M^{-1} s^{-1}	log k_0 [b]	ρ_X [d]	ρ_Y [d]	ρ_{XY} [e]	$\Sigma\sigma$ [f]	$\Sigma\sigma^-$ [g]	ΣR^- [h]
1 (BMN)	CN, CN	1.48 [i]	4.94 (≈7.0) [c]	−1.62	−0.55	−0.31	1.32	2.00	0.98
2 (BID)		1.48	(3.13) [c]	−1.10	0.41	−0.33	0.83	2.08	1.30
3 (NS)	NO_2, H	2.63×10^{-2}	2.55 (0.73) [c]	−1.22	1.73	−0.40	0.78	1.27	0.62
4 (NSB)	NO_2, C_6H_5	2.69×10^{-2}	1.42 (−0.25) [c]	−0.82	1.27	−0.52	0.77	1.29 (1.27)	0.52 (0.62)
5 (CNS)	CN, *p*-$NO_2C_6H_4$	1.02×10^{-3} [i]	3.35 (3.95) [c]	−1.15	1.10	−0.67	0.92	1.31 (1.00)	0.54 (0.49)

[a] For X = Y = H. [b] Intrinsic rate constants for carbanion forming reactions of ArCH=CZZ′ in 50% Me_2SO–50% water at 20 °C with amines. [c] The same as *b* but for $CH_2ZZ' + R_2NH$. [d] For Y = H or X = H. [e] Correlation coefficients are better than 0.997 in all cases. [f] Normal Hammett substituent constants (σ_p). [g] Exalted substituent constants (σ_p^-) for direct conjugation with anionic functional center. [h] Swain–Lupton resonance constants.[5] [i] Extrapolated values of amine additions (BA) in MeCN at 25 °C.

constants, ρ_{XY} [eqn. (1)]. Comparison of the rates with those in aqueous solution[4] shows that the rate constants in acetonitrile are lower by more than 10^2-fold as we found for other susbstrates, *e.g.*, benzylidenemalononitrile (BMN),[1b] 2-benzylideneindan-1,3-dione (BID)[1c] and nitrostyrene (NS);[1a] for NSB, the rate constant for the addition step is 11.7 with piperidine in 50% Me_2SO–50% water at 20 °C[4a] and 2.69×10^{-2} with BA in acetonitrile at 25 °C. We have collected reactivity parameters for various activating groups, Z,Z′, in Table 3. An essential difference between the reactivity in aqueous solution and that in acetonitrile solution is that the former increases with the (polar) electron-withdrawing power (normal substituent constant σ) of the activating groups, Z,Z′ (8th column in Table 3), whereas the latter depends on the through conjugative electron-withdrawing strength (σ^- or R^-)[5] of the Z,Z′ groups. For example in aqueous solution the intrinsic rate constant (log k_0), which represents a pure kinetic rate under thermoneutral conditions,[2] increases in the order NSB < NS < BID < CNS < BMN. In

contrast the rates in acetonitrile are in the order CNS < NS ≈ NSB < BID ≈ BMN, which is roughly the order of the direct resonance effect, $\Sigma\sigma^-$ or ΣR^-. Note that we summed the substituent constants of Z,Z′, and for BID this summation procedure may not be correct, especially for the direct resonance constants. So the exact correspondence of the reactivity with $\Sigma\sigma^-$ (or ΣR^-) cannot be expected, but it is certain that the reactivities of BMN and BID are larger than those of the rest: NS, NSB and CNS. Previous works indicate that there is steric inhibition of resonance for the β-phenyl rings in NSB[4a] and CNS[4a,6] so that the resonance effect of the β-phenyl rings in these compounds is nonexistent. Eliminating the resonance effect of the β-phenyl rings in these compounds changes the $\Sigma\sigma^-$ and ΣR^- values in the order CNS < NSB ≈ NS as shown in the parentheses under the $\Sigma\sigma^-$ and ΣR^- columns in Table 3. Thus if we take into account the approximate nature of the $\Sigma\sigma^-$ value for BID, the rates in acetonitrile increase in the order of direct resonance electron-withdrawing strength, the order being CNS < NSB ≈ NS < BID < BMN.

In summary, the rates in aqueous solution are dependent on the polar electron-withdrawing effect (σ) of Z,Z′, while those in acetonitrile are determined by the direct resonance electron-withdrawing strength of the activating groups (σ^- or R^-), Z,Z′. This difference is of course originated by the difference in the amine addition mechanisms in the two different media. It has been well established that the amine addition reactions of activated olefins in aqueous solution proceed by the initial rate-limiting addition of the amine to form a zwitterionic intermediate, $\mathbf{T}^{\pm}$, which is deprotonated to an anionic intermediate ($\mathbf{T}^-$) in a later fast step and then on a longer time scale $\mathbf{T}^-$ eventually decomposes [eqn. (5)].[2] In the rate-limiting



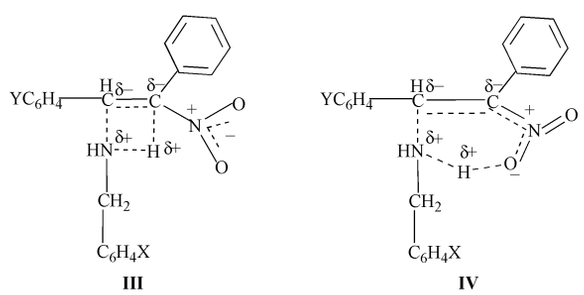
(5)

addition step, k_a, the positive charge on C_α is important, which is determined by the electron-withdrawing polar effect of Z,Z′. The development of negative charge on Z,Z′ lags behind bond making of the N···C_α bond in water to some extent depending on the Z,Z′ groups.[2] Thus the ease of the initial attack by amines on C_α and hence the polar electron-withdrawing effect of Z,Z′ is the rate determining factor for the reaction in aqueous solution as evidenced by the rate sequence of the intrinsic rate constant with $\Sigma\sigma$ in Table 3. In contrast, however, the same reactions in a dipolar aprotic solvent, acetonitrile, proceed in a single step by concurrent formation of N···C_α and H···C_β bonds to a saturated product.[1] In this concerted addition in acetonitrile there is no transition state (TS) imbalance due to the lag in the negative charge delocalization within the Z,Z′ groups, and the direct resonance, or through conjugation, of the incipient anionic charge on C_α toward the Z,Z′ groups is the most important TS stabilization which determines the reactivity. Thus for the reactions in acetonitrile the reactivity depends primarily on the resonance electron-withdrawing effect of the Z,Z′ groups. Since in such resonance stabilized TS the two large activating groups, *e.g.*, Z,Z′ = NO_2 and phenyl groups, interfere sterically,[2a,6] the resonance effect of the phenyl group becomes negligible since steric hindrance prevents π-overlap with the phenyl group. This is why the two compounds, NSB (Z,Z′ = NO_2, C_6H_5) and NS (Z,Z′ = NO_2, H), have almost the same reactivity (Table 3), *i.e.*, the resonance effect of the C_6H_5 group becomes nearly zero.

Furthermore, the reactivity of CNS (Z = CN, Z′ = *p*-NO_2-C_6H_4) becomes the lowest due to the negligible resonance effect of Z′ = *p*-$NO_2C_6H_4$. For this compound, the resonance effect is the lowest since it is only due to a CN group, which leads to the lowest rate in acetonitrile. This is in contrast to a much faster intrinsic rate (second among those listed in Table 3) observed in aqueous solution.

We note in Table 3 that the sign of ρ_{XY} is negative in all cases as expected from a bond formation process,[3] and the magnitude of ρ_{XY} is larger for NSB and CNS than for other substrates[1] (entries 1–3) suggesting a stronger interaction between substituents in the approaching nucleophile (X) and in the ring (Y) through the reaction center, C_α. This could be due (i) to the larger negative charge on C_α as a result of the weaker resonance electron-withdrawing effect from the Z,Z′ groups and (ii) to the greater degree of bond making with closer N and C_α in the TS.

The kinetic isotope effects, k_H/k_D (Tables 4 and 5), involving deuterated benzylamine nucleophiles ($XC_6H_4CH_2ND_2$) are greater than one, k_H/k_D = 2.4–2.7 (NSB) and 2.2–2.6 (CNS), indicating a possibility of hydrogen-bond formation[10] (**III**) as has been proposed for the benzylamine addition to BMN, BID and NS in acetonitrile.[1] The hydrogen bonding of a N–H proton toward a hydrogen atom of the β-nitro group, **IV**, may be a possibility, but involves too long a hydrogen-bond since the lone pair on N (n_N) of benzylamine approaches the C_α–C_β π-bond almost vertically from above (or below) the molecular plane of NSB. The situation is similar in the hydrogen-bonded structure with the CN group in CNS. The k_H/k_D values increase with an electron acceptor Y and an electron donor X for both NSB and CNS. This is in line with the tightly formed C_α–N bond in the TS with a greater degree of bond making by a stronger electron-donor X, $\partial\sigma_X < 0$, (with a larger positive ρ_Y, $\partial\rho_Y > 0$) and by a stronger electron-acceptor, $\partial\sigma_Y > 0$, (with a larger negative ρ_X, $\partial\rho_X < 0$) leading to a negative cross-interaction constant ρ_{XY}, eqn. (1c).[3] The greater negative charge on C_α in the TS due to a weaker resonance electron-withdrawing effect of Z,Z′ (as a result of the out-of-plane phenyl ring) may contribute to the relatively strong susceptibility of the Hammett (ρ) constant to the substituent (σ) changes in eqn. (1c) with a relatively large magnitude of ρ_{XY}.



$$\rho_{XY} = \partial\rho_Y/\partial\sigma_X = \partial\rho_X/\partial\sigma_Y < 0 \qquad (1c)$$

The activation parameters, $\Delta H^{\neq}$ and $\Delta S^{\neq}$, for the benzylamine additions to NSB and CNS in Table 6 are quite similar to those for the reactions of BMN and BID with low $\Delta H^{\neq}$ and large negative $\Delta S^{\neq}$ values. These are consistent with the concurrent bond formation of N–C_α and H–C_β in the TS, **III**. Since exclusion repulsion energy in the N–C_α bond making is partially offset by the bond energy of the bond formation and also by the proton transfer from N to C_β in the H–C_β bond formation, the barrier to bond formation is normally low showing little variation with substituents X and Y. This is because the higher barrier for a weaker nucleophile ($\partial\sigma_X > 0$) is partially offset by a stronger acidity of the N–H proton in the hydrogen bond formation. Slightly greater $\Delta H^{\neq}$ values for the reactions of CNS than NSB reflect somewhat weaker TS stabilization due to the weaker resonance electron accepting power of CN than

Table 4 Kinetic isotope effects on the second-order rate constants (k_2) for the reactions of β-nitrostilbenes with deuterated X-benzylamines ($XC_6H_4CH_2ND_2$) in acetonitrile at 25.0 °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	1.90 (±0.01)	0.739 (±0.004)	2.57 ± 0.02[a]
p-OMe	*p*-Me	2.79 (±0.02)	1.07 (±0.05)	2.61 ± 0.02
p-OMe	H	4.49 (±0.04)	1.69 (±0.09)	2.66 ± 0.03
p-OMe	*p*-Cl	9.39 (±0.06)	3.46 (±0.02)	2.71 ± 0.02
p-OMe	*p*-Br	11.3 (±0.9)	4.12 (±0.03)	2.75 ± 0.03
p-Cl	*p*-OMe	0.890 (±0.004)	0.368 (±0.002)	2.42 ± 0.02
p-Cl	*p*-Me	1.15 (±0.06)	0.462 (±0.003)	2.49 ± 0.02
p-Cl	H	1.78 (±0.01)	0.698 (±0.006)	2.55 ± 0.03
p-Cl	*p*-Cl	3.24 (±0.01)	1.25 (±0.08)	2.59 ± 0.02
p-Cl	*p*-Br	3.69 (±0.02)	1.41 (±0.01)	2.62 ± 0.02

[a] Standard deviations.

Table 5 Kinetic isotope effects on the second-order rate constants(k_2) for the reactions of β-cyano-4′-nitrostilbenes with deuterated X-benzylamines ($XC_6H_4CH_2ND_2$) in acetonitrile at 30.0 °C

X	Y	$k_H \times 10^3/M^{-1}\ s^{-1}$	$k_D \times 10^3/M^{-1}\ s^{-1}$	k_H/k_D
p-OMe	*p*-OMe	1.17 (±0.08)	0.518 (±0.004)	2.26 ± 0.02[a]
p-OMe	*p*-Me	1.56 (±0.01)	0.664 (±0.005)	2.35 ± 0.02
p-OMe	H	2.52 (±0.02)	1.04 (±0.01)	2.42 ± 0.03
p-OMe	*p*-Cl	4.50 (±0.03)	1.78 (±0.01)	2.53 ± 0.02
p-OMe	*p*-Br	4.74 (±0.03)	1.82 (±0.02)	2.61 ± 0.03
p-Cl	*p*-OMe	0.399 (±0.003)	0.186 (±0.002)	2.15 ± 0.02
p-Cl	*p*-Me	0.490 (±0.004)	0.223 (±0.002)	2.21 ± 0.03
p-Cl	H	0.681 (±0.005)	0.293 (±0.003)	2.32 ± 0.03
p-Cl	*p*-Cl	1.05 (±0.07)	0.438 (±0.005)	2.41 ± 0.03
p-Cl	*p*-Br	1.07(±0.08)	0.441 (±0.006)	2.43 ± 0.04

[a] Standard deviations.

Table 6 Activation parameters[a] for the reactions of β-nitrostilbenes (NBS) and β-cyano-4′-nitrostilbenes(CNS) with X-benzylamines in acetonitrile

		$\Delta H^{\neq}$/kcal mol^{-1}		$-\Delta S^{\neq}$/cal mol^{-1} K^{-1}	
X	Y	NSB	CNS	NSB	CNS
p-OMe	*p*-OMe	3.7	7.0	53	48
p-OMe	*p*-Br	3.8	6.8	50	46
p-Cl	*p*-OMe	4.8	6.9	51	51
p-Cl	*p*-Br	4.6	7.5	49	47

[a] Calculated by the Eyring equation. The maximum errors calculated (by the method of Wiberg, ref. 9) are ±0.9 kcal mol^{-1} and ±3 eu for $\Delta H^{\neq}$and $\Delta S^{\neq}$, respectively.

NO_2. The large negative entropy of activation (−46 to −53 eu †) is consistent with a four-centered constrained TS structure, **III**.

In summary, the addition of benzylamine to β-nitrostilbene (NSB) and β-cyano-4′-nitrostilbene (CNS) in acetonitrile takes place in a single step to form a neutral product by a concurrent C_α–N and H–C_β bond formation with a four-membered cyclic transition state structure, **III**. The rate of amine addition to CNS in acetonitrile is much lower than that expected from the rate sequence exhibited in aqueous solution. This rate depression together with that of NBS can be explained by the TS stabilization due to the direct resonance effect (σ^- or R^-) of the activating groups, Z,Z′, in the TS in acetonitrile, quite in contrast to the TS stabilization by the simple polar electron-withdrawing effect of Z,Z′ in aqueous solution. The negative sign of ρ_{XY} is consistent with the rate-limiting addition of a nucleophile (X) to the substrate (Y). The somewhat larger magnitude of ρ_{XY} is interpreted to represent stronger interaction between the substituents in the nucleophile and substrate due to weaker resonance electron withdrawing power of Z,Z′ in the amine additions to NSB and CNS in acetonitrile. The kinetic isotope effect ($k_H/k_D > 2.0$) involving deuterated benzylamines ($XC_6H_4CH_2ND_2$) and the low $\Delta H^{\neq}$ with large negative $\Delta S^{\neq}$ are in line with the TS proposed.

† 1 eu = 1 cal mol^{-1} K^{-1} = 4.184 J mol^{-1} K^{-1}.

Experimental

Materials

Merck GR acetonitrile was used after three distillations. The benzylamine nucleophiles, Aldrich GR, were used after recrystallization

Preparations of β-nitrostilbenes and β-cyano-4′-nitrostilbenes

The β-nitrostilbenes and β-cyano-4′-nitrostilbenes were prepared by the literature methods of Robertson[11] and Schonne *et al.*[12]

Kinetic measurements

The reaction was followed spectrophotometrically by monitoring the decrease in the concentration of [NSB] and [CNS] at λ_{max} of the substrate to over 80% completion. The reactions were studied under pseudo-first-order conditions, [Substrate] = 6.0×10^{-5} M and [BA] = (5.0–11.0) × 10^{-2} M at 25.0 ± 0.1 °C for NBS, and [BA] = (3.0–4.5) × 10^{-1} M at 30.0 ± 0.1 °C for CNS. The second-order rate constant, k_2, was determined from the slope of the plot ($r > 0.995$) of k_{obs} *vs.* [BA] with more than four concentrations of benzylamine, carried out more than three runs, and was reproducible to within ±3%.

Product analysis

The analysis of final products 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_3CN. For the reaction of NSB [p-$ClC_6H_4CH{=}C(NO_2)C_6H_5$] with benzylamine at 25 °C; initially we found a peak for CH in the reactant, p-$ClC_6H_4CH{=}C(NO_2)C_6H_5$, at 8.20 ppm, which was gradually reduced, and new two peaks for CH–CH in the product, p-$ClC_6H_4(C_6H_5CH_2NH)CH{-}CH(NO_2)C_6H_5$, grew at 4.75 and 5.45 ppm as the reaction proceeded. For the reaction of CNS [p-$ClC_6H_4CH{=}C(CN)(4\text{-}NO_2C_6H_4)$] with benzylamine at 30 °C, initially we found a peak for CH in the reactant, p-$ClC_6H_4CH{=}C(CN)(p\text{-}NO_2C_6H_4)$, at 7.61 ppm, which was gradually reduced, and new two peaks for CH–CH in the product, p-$ClC_6H_4(C_6H_5CH_2NH)CH{-}CH(CN)(p\text{-}NO_2C_6H_4)$, grew at 3.96 and 4.68 ppm as the reaction proceeded. No other peaks or complications were found during the reaction except the 3 peak height changes indicating that the reaction proceeds with no other side reactions.

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