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Kinetics and mechanism of the addition of benzylamines to β-nitrostyrenes in acetonitrile

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The kinetics and mechanism of the addition of benzylamines to β-nitrostyrenes in acetonitrile at 25.0 °C have been investigated. The addition reaction proceeds by two pathways, uncatalyzed (k_2) and catalyzed (k_3) paths. The kinetic isotope effects (k_H/k_D) involving deuterated benzylamine nucleophiles support the proposal that proton transfer from the amine to the β-carbon occurs concurrently with addition of the amine to the α-carbon. The transition state is predicted to have four- (**I**) and six-membered (**II**) cyclic structures for the k_2 and k_3 paths, respectively, with a tighter and more rigid structure for the uncatalyzed process. The cross-interaction constants, ρ_{XY}, are negative (-0.90 and -0.54 when the fall-off factor is taken into account) and the magnitude is larger for the uncatalyzed path than for the normal backside attack S_N2 reaction of benzyl derivatives with anilines (-0.6 to -0.8).

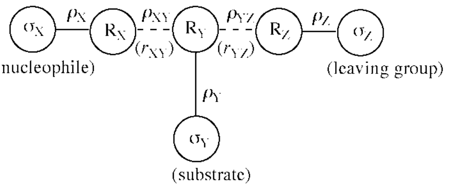
Introduction

In our endeavors to establish the cross-interaction constants, ρ_{ij} and β_{ij} in eqns. (1) and (2) (where i and j can be any two

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

$$\log (k_{ij}/k_{HH}) = \beta_i pK_i + \beta_j pK_j + \beta_{ij} pK_i pK_j \qquad (2)$$

fragments X, Y or Z, involved in a transition state (TS), *e.g.* Scheme 1), as a mechanistic tool for organic reactions,[1] we have shown that the sign of ρ_{XY} and β_{XY} (Scheme 1) for the bond-making step is negative while that of ρ_{YZ} and β_{YZ} for the bond-breaking step is positive in normal backside attack S_N2 reactions.[1,2] In general, the magnitude of ρ_{ij} (and β_{ij}) represents a change in the strength of interaction between the two fragments, i and j, on going from the reactants to the TS.[3] Thus the magnitude of ρ_{XY} is greater while that of ρ_{YZ} is smaller, when the TS is tighter with a larger degree of bond making (shorter r_{XY}) and a smaller degree of bond cleavage (shorter r_{YZ}).[3]



Scheme 1 Typical S_N2 transition state. R and σ represent reaction center and substituent on each fragment, *r* is the distance between fragments.

In the limiting case in which only bond *cleavage* occurs in the TS, *i.e.*, in the S_N1 TS, ρ_{YZ} was indeed positive and large.[4] In this work, we have studied the other limiting case, in which only bond *formation* takes place in the TS, using the nucleophilic addition reactions of benzylamines to (*E*)-β-nitrostyrenes.

Although mechanistic studies of nucleophilic additions to an activated olefins including β-nitrostyrene have been reported,[5] we have found no examples of reactions in which the structures (or substituents) of both the nucleophile (X) and the olefin (*e.g.* substituent Y in the β-nitrostyrene) are varied simultaneously.

We have carried out kinetic studies of addition reactions of benzylamines (BA) to (*E*)-β-nitrostyrenes (NS) in acetonitrile at 25.0 °C, eqn. (3). The main aim of this paper is to examine

$$XC_6H_4CH_2NH_2 + YC_6H_4CH{=}CHNO_2 \longrightarrow \begin{matrix} YC_6H_4CHCH_2NO_2 \\ | \\ NHCH_2C_6H_4X \end{matrix} \qquad (3)$$

the substituent effects (both X and Y) on this addition reaction, and to determine the cross-interaction constant, ρ_{XY}, for the exclusive addition step in the TS. The sign and magnitude of ρ_{XY} are expected to provide a useful guide for predicting the TS structure.

Results and discussion

The pseudo-first order rate constants (k_{obs}) for all reactions studied in this work obeyed eqn. (4), indicating that the

$$k_{obs} = k_2[BA] + k_3[BA]^2 \qquad (4)$$

addition of BA to NS is catalyzed by a second BA molecule. The k_2 (uncatalyzed) and k_3 (catalyzed) values were determined as the intercept and slope, respectively, of a linear plot of $k_{obs}/[BA]$ *vs.* [BA]. The details of the experimental conditions, *i.e.*, [BA], [NS], ranges of k_{obs} and extinction coefficient changes at λ_{max}, are given in the Experimental section (*vide infra*). The k_2 and k_3 values are summarized in Tables 1 and 2, where the Hammett (ρ_X and ρ_Y) and Brønsted (β_X) coefficients are also shown. Jalani *et al.* reported[5c] the k_2 and k_3 values with 28 X substituents but with Y = H only in eqn. (3). Comparison of their values at 25.0 °C with our k_2 and k_3 values in Tables 1 and 2 shows that our values are consistently greater, by a factor of 1.7. In their experimental section, they report that the k_{obs} values were evaluated from the linear plot of log[NS] *vs.* time. The slope of this plot is actually smaller by a factor of 2.303

Table 1 Second order rate constants ($k_2/10^{-2}$ dm^3 mol^{-1} s^{-1}) for the addition reactions of β-nitrostyrenes with X-benzylamines in acetonitrile at 25.0 °C. [NS] = 8.0 × 10^{-5} M and [BA] = 1.5–25 mM. ρ_X and ρ_Y are the Hammett coefficients for X and Y. β_X is the Brønsted coefficient for X

	Y				
X	*p*-Me	H	*p*-Cl	*p*-NO$_2$	$\rho_Y{}^{a}$
p-OMe	2.55 2.40^{b} 2.24^{c}	4.46	15.2	128 118^{b} 108^{c}	1.82 ± 0.09
p-Me	1.92	3.86	11.9	86.2	1.74 ± 0.08
H	1.42	2.63	7.78	61.4	1.73 ± 0.06
p-Cl	0.649 0.605^{b} 0.562^{c}	1.12	3.02	20.6 18.9^{b} 17.1^{c}	1.60 ± 0.05
$\rho_X{}^{d}$	−1.17 ± 0.11	−1.22 ± 0.15	−1.41 ± 0.14	−1.55 ± 0.19	$\rho_{XY}{}^{e} = -0.41$
$\beta_X{}^{f}$	1.20 ± 0.16	1.36 ± 0.14	1.51 ± 0.15	1.59 ± 0.29	

[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 0.998 in all cases. [b] At 15 °C. [c] At 5 °C. [d] The σ values were taken from D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420. Correlation coefficients were better than 0.985 in all cases. [e] Correlation coefficient was 0.997. [f] The pK_a values were taken from A. Fischer, W. J. Galloway and J. Vaughan, *J. Chem. Soc.*, 1964, 3588. Correlation coefficients were better than 0.991 in all cases. X = *p*-CH$_3$O were excluded from the Brønsted plot for β_X (benzylamine) due to unreliable pK_a value listed.

Table 2 Third order rate constants (k_3/dm^6 mol^{-2} s^{-1}) for the addition reactions of β-nitrostyrenes with X-benzylamines in acetonitrile at 25.0 °C. [NS] = 8.0 × 10^{-5} M and [BA] = 1.5–25 mM. ρ_X and ρ_Y are the Hammett coefficients for X and Y. β_X is the Brønsted coefficient for X

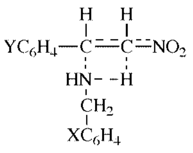
	Y				
X	*p*-Me	H	*p*-Cl	*p*-NO$_2$	$\rho_Y{}^{a}$
p-OMe	1.51 1.15^{b} 0.867^{c}	4.46	11.0	88.3 67.0^{b} 49.9^{c}	1.81 ± 0.13
p-Me	1.33	3.21	8.30	64.1	1.75 ± 0.08
H	0.833	2.33	5.84	40.3	1.72 ± 0.14
p-Cl	0.481 0.351^{b} 0.254^{c}	1.15	2.76	20.0 15.7^{b} 12.1^{c}	1.67 ± 0.08
$\rho_X{}^{d}$	−1.04 ± 0.06	−1.15 ± 0.08	−1.19 ± 0.08	−1.29 ± 0.02	$\rho_{XY}{}^{e} = -0.24$
$\beta_X{}^{f}$	1.10 ± 0.08	1.13 ± 0.11	1.21 ± 0.11	1.26 ± 0.01	

[a–f] Same as the footnotes for Table 1, except correlation coefficients, *r*: [a] $r \geqslant 0.994$. [d] $r \geqslant 0.995$. [e] $r \geqslant 0.996$. [f] $r \geqslant 0.995$.

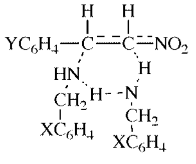
than the true k_{obs} value, since k_{obs} is the slope of a linear plot of ln[NS] (=2.303 log [NS]) *vs.* time.[6] If we multiply their k_{obs} value (and hence k_2 and k_3 values) by 2.303, our k_2 and k_3 values are consistently smaller by a factor of 1.2–1.3, which, we consider, is more appropriate since the difference in the temperature control may allow such small, but consistent, differences.

The magnitudes of ρ_X for k_2 (−1.2 to −1.6, which corresponds to −2.7 to −3.4 if the fall-off factor of 2.19[1a,7] is taken into account for the CH$_2$ group between substituent X and the functional center N) and β_X (1.2–1.6) are relatively large, compared to the corresponding values of ρ_X (−1.89 ± 0.13) and β_X (0.68)[8] for the addition of anilines.[5b] This is an indication of a greater degree of bond formation in the TS for the BA relative to aniline addition. The magnitude of ρ_Y is also large (ρ_Y = 1.6–1.8) suggesting that negative charge development at the $C_\alpha{=}C_\beta$ moiety should be large, which is consistent with the tight bond formation predicted by the large magnitude of ρ_X and β_X. In agreement with these trends, the cross-interaction constant, ρ_{XY}, is also large and negative ($\rho_{XY} = -0.41$, which corresponds to −0.90 when the fall-off factor is taken into account). The corresponding values for the normal backside attack S$_N$2 reaction of benzyl derivatives with anilines are *ca.* −0.6 to −0.8.[1,2]

Surprisingly, our k_3 values give very similar, only slightly smaller, magnitudes of ρ_X, β_X, ρ_Y and ρ_{XY} (−0.24, corresponding to −0.54 taking into account fall-off) to those for aniline addition. This may be taken as evidence for a slightly looser bond-making structure in the catalyzed TS. This is supported by the smaller k_H/k_D (>1.0) values for the catalyzed (k_3) process in Tables 3 and 4. The normal kinetic isotope effects (k_H/k_D > 1.0) involving deuterated benzylamines (XC$_6$H$_4$CH$_2$ND$_2$) provide evidence for partial N–H(D) bond cleavage in the TS.[1b] We presume that proton transfer to C$_\beta$ occurs concurrently with the C$_\alpha$–N bond formation in the TS, **I** and **II**. In the k_2 path,



I



II

relatively greater stretching of the N–H bond is required than in the k_3 path, so the k_H/k_D values are greater in general. This is consistent with a lesser degree of bond formation in the catalyzed path, as indicated by the smaller magnitude of the selectivity parameters, ρ_X, β_X and ρ_{XY}. For both paths, the largest k_H/k_D value is obtained for the X = *p*-OMe and Y =

Table 3 Kinetic isotope effects on the second-order rate constants for the reactions of β-nitrostyrenes with deuterated X-benzylamines in acetonitrile at 25.0 °C[a]

X	Y	$k_H/10^{-2}$ M^{-1} s^{-1}	$k_D/10^{-2}$ M^{-1} s^{-1}	k_H/k_D
p-OMe	*p*-Me	2.55 (±0.03)	0.992 (±0.002)	2.57 ± 0.06[b]
p-OMe	H	4.46 (±0.06)	1.56 (±0.03)	2.86 ± 0.06
p-OMe	*p*-Cl	15.2 (±0.2)	5.18 (±0.06)	2.93 ± 0.05
p-OMe	*p*-NO_2	128 (±3)	41.5 (±0.1)	3.08 ± 0.06
p-Cl	*p*-Me	0.649 (±0.005)	0.282 (±0.002)	2.30 ± 0.02
p-Cl	H	1.12 (±0.02)	0.420 (±0.006)	2.67 ± 0.04
p-Cl	*p*-Cl	3.02 (±0.04)	1.10 (±0.02)	2.74 ± 0.06
p-Cl	*p*-NO_2	20.6 (±0.4)	7.43 (±0.07)	2.77 ± 0.06

[a] Concentrations of NS and BA are the same as in Tables 1 and 2. [b] Standard deviations.

Table 4 Kinetic isotope effects on the third-order rate constants for the reactions of β-nitrostyrenes with deuterated X-benzylamines in acetonitrile at 25.0 °C[a]

X	Y	$k_H/10^{-2}$ M^{-2} s^{-1}	$k_D/10^{-2}$ M^{-2} s^{-1}	k_H/k_D
p-OMe	*p*-Me	1.51 (±0.04)	1.17 (±0.02)	1.29 ± 0.04[a]
p-OMe	H	4.46 (±0.06)	3.41 (± 0.05)	1.31 ± 0.03
p-OMe	*p*-Cl	11.0 (±0.2)	7.96 (±0.07)	1.38 ± 0.03
p-OMe	*p*-NO_2	88.3 (±0.9)	46.5 (±0.6)	1.90 ± 0.03
p-Cl	*p*-Me	0.481 (±0.004)	0.333 (±0.003)	1.44 ± 0.02
p-Cl	H	1.15 (±0.02)	0.650 (±0.001)	1.77 ± 0.04
p-Cl	*p*-Cl	2.76 (±0.05)	1.50 (±0.02)	1.84 ± 0.04
p-Cl	*p*-NO_2	20.0 (±0.3)	10.6 (±0.2)	1.87 ± 0.04

[a] Concentrations of NS and BA are the same as in Tables 1 and 2. [b] Standard deviations.

Table 5 Activation parameters[a] for the reactions of β-nitrostyrenes with X-benzylamines in acetonitrile at 25.0 °C[b]

X	Y	Reaction path	$\Delta H^‡$/kcal mol^{-1}	$-\Delta S^‡$/ cal mol^{-1} K^{-1}	$\Delta G^‡$/kcal mol^{-1}
p-OMe	*p*-Me	k_2	0.5	64	19.6
p-OMe	*p*-NO_2	k_2	0.9	55	17.3
p-Cl	*p*-Me	k_2	0.5	61	18.7
p-Cl	*p*-NO_2	k_2	1.0	58	18.3
p-OMe	*p*-Me	k_3	4.0	44	17.1
p-OMe	*p*-NO_2	k_3	4.6	32	14.1
p-Cl	*p*-Me	k_3	4.6	44	17.7
p-Cl	*p*-NO_2	k_3	3.8	41	16.0

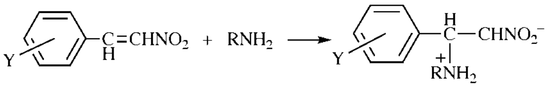
[a] Calculated by the Eyring equation. The maximum errors calculated (by the method of K. B. Wiberg, *Physical Organic Chemistry*, Wiley, New York, 1964, p. 378) are ±0.5 kcal mol^{-1} and ±2 eu for $\Delta H^‡$ and $\Delta S^‡$, respectively. [b] Concentrations of NS and BA are the same as in Tables 1 and 2.

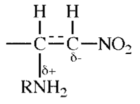
p-NO_2 set. This is quite reasonable, since for this set of substituents the extent of bond formation in the TS is the greatest with the largest magnitude of ρ_Y and ρ_X (β_X) values (Tables 1 and 2).

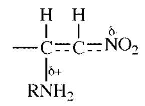
Finally, the activation parameters in Table 5 support the proposed mechanism. We note that in general the $\Delta H^‡$ values are higher but the negative $\Delta S^‡$ values are, in general, large. This is in accord with the greater degree of bond formation (exoergic) leading to less energy being required to break the π bond (endoergic) on C=C but *more rigid* four-membered TS, **I**, for the k_2 path. For the k_3 path, the six-membered TS, **II**, has a looser (than **I**) structure with smaller negative $\Delta S^‡$.

Table 6 The λ_{max} (nm) ranges of extinction coefficient (ε/dm^3 mol^{-1} cm^{-1}) and ($k_{obs}/10^{-4}$ s^{-1}) and percentage completion of reactions. [NS] = 8.0 × 10^{-5} M and [BA] = 1.5–25 mM

X	Y	λ_{max}/ nm	ε/dm^3 mol^{-1} cm^{-1}	$k_{obs}/10^{-4}$ s^{-1}	Completion (%)
p-OMe	*p*-Me	324	1.60–0.20	0.406–15.5	87.5
	H	311	1.50–0.18	0.751–37.1	88.0
	p-Cl	314	1.70–0.21	2.49–108	87.6
	p-NO_2	307	1.90–0.23	15.5–878	88.4
p-Me	*p*-Me	324	1.80–0.21	0.364–13.5	88.3
	H	311	1.55–0.19	0.579–29.4	87.7
	p-Cl	314	1.75–0.22	1.88–82.0	87.4
	p-NO_2	307	1.90–0.25	14.9–637	86.8
H	*p*-Me	324	1.42–0.17	0.224–8.93	88.0
	H	311	1.50–0.15	0.344–20.1	90.0
	p-Cl	314	1.20–0.15	1.30–56.1	87.5
	p-NO_2	307	1.75–0.20	9.47–385	88.6
p-Cl	*p*-Me	324	1.50–0.18	0.108–4.83	88.0
	H	311	1.75–0.22	0.180–9.78	87.4
	p-Cl	314	1.25–0.15	0.283–22.8	88.0
	p-NO_2	307	1.65–0.20	3.02–195	87.8


(5)


III


IV

It is well known that there is a charge imbalance in the TS for the addition reactions of amines to activated olefins such as β-nitrostyrenes,[5a,10] eqn. (5). The TS "imbalance" was attributed to a *lag* in the charge delocalization into the NO_2 moiety *behind* C–N bond formation in the TS.[5b,10] This sort of imbalance leads to an extreme structure in which negative charge builds up on the $C_β$ carbon, as in **III**, instead of delocalizing onto the NO_2 group, as in **IV**,[10] in the TS. Since the negative charge transferred from the amine to the substrate is *practically* localized on $C_β$ in the TS, the proton transfer to $C_β$ from the amine should become viable, and our proposal of the proton transferred TS structures, **I** and **II**, is supported. The low cost of energy ($\Delta H^‡$) required for the π-bond cleavage in the TS may also be partly attributable to the concurrent proton transfer. In view of the results of Bernasconi *et al.*,[5a] that there is considerable positive charge development on the amine nitrogen in the TS, the positive charge carried away by the transferring proton should be small, *i.e.*, the N···H bond stretching should be in its early stage in **I** and **II**.

In summary, the addition of benzylamines to (*E*)-β-nitrostyrenes in acetonitrile proceeds by two pathways, the uncatalyzed (k_2) and catalyzed (k_3) paths. Furthermore, the reaction is a one-step process, in which the proton transfer from benzylamine to the β-carbon occurs concurrently with the addition of benzylamine to the α-carbon. This assertion is supported by the observation of relatively large primary kinetic isotope effects, k_H/k_D > 1.0, for deuterated nucleophiles, $XC_6H_4CH_2ND_2$. The charge imbalance leading to a practically localized negative charge on $C_β$ in the TS, **III**, seems to provide support for the proposed concurrent proton transfer. Bond formation in the TS is more advanced in the k_2 (larger negative ρ_{XY}) than k_3 path, so that the k_2 path has a more rigid (more negative $\Delta S^‡$) four-membered structure with a greater degree of proton transfer.

Experimental

Materials

Solvent, acetonitrile (Merck GR) was used after three distil-

Table 7 The k_{obs} *versus* [BA] (benzylamine concentration/M) data in acetonitrile at 25.0 °C

X	Y	[BA] M	$k_{obs}/10^{-4}$ s^{-1}	$k_2/10^{-2}$ M^{-1} s^{-1}	k_3/M^{-2} s^{-1}	*R* corr. coeff.
p-OMe	*p*-Me	0.0015	0.406	2.55 ± 0.04	1.51 ± 0.03	0.999
		0.0030	0.975			
		0.0045	1.47			
		0.0060	1.96			
		0.0075	2.74			
		0.0100	4.03			
		0.0150	7.34			
		0.0200	11.32			
		0.0250	15.55			
p-OMe	*p*-Cl	0.0015	2.49	15.2 ± 0.3	11.0 ± 0.2	0.999
		0.0030	5.76			
		0.0045	9.21			
		0.0060	13.3			
		0.0075	17.3			
		0.0100	25.6			
		0.0150	47.1			
		0.0200	74.7			
		0.0250	108			
p-Me	*p*-Cl	0.0015	1.88	11.9 ± 0.4	8.30 ± 0.03	0.994
		0.0030	4.18			
		0.0045	7.17			
		0.0060	10.2			
		0.0075	14.7			
		0.0100	20.6			
		0.0150	34.8			
		0.0200	57.0			
		0.0250	82.0			
p-Me	*p*-NO$_2$	0.0015	14.9	86.2 ± 0.3	64.1 ± 0.2	0.996
		0.0030	32.7			
		0.0045	52.2			
		0.0060	74.4			
		0.0075	98.8			
		0.0100	147			
		0.0150	264			
		0.0200	420			
		0.0250	637			

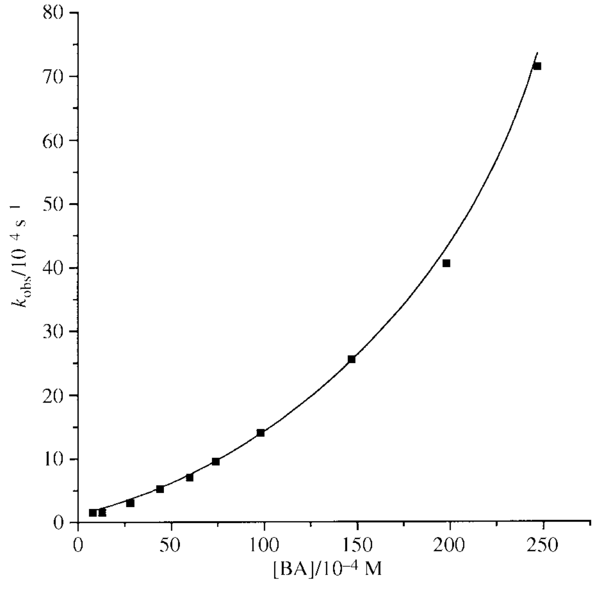


Fig. 1 The plot of k_{obs} *vs.* concentration of benzylamine for the reaction of (*E*)-*p*-chloro-β-nitrostyrene in MeCN at 25.0 °C.

lations. Benzylamines (Aldrich GR) were used after recrystallization. The β-nitrostyrenes were prepared by the literature method of Worrall.[11] The analytical data are as follows (IR: NICOLET 5BX FTIR; NMR: JEOL 400 MHz).

(*E*)-*p*-Methyl-β-nitrostyrene. Mp 97–99 °C; λ_{max} 324 nm; IR(KBr) ν_{max}/cm^{-1} 3100 (C–H, alkene), 1636 (C=C, alkene), 1595 (C=C, aromatic), 1431 (–CH$_2$ bend); ^{1}H NMR (400 MHz, CDCl$_3$) 2.41 (3H, s, –CH$_3$), 7.26 (2H, d, *m*-H, *J* 7.81 Hz), 7.44 (2H, d, *o*-H, *J* 8.31 Hz), 7.57 (1H, d, =CH, *J* 13.7 Hz), 7.99 (1H, d, =CH, *J* 13.7 Hz); ^{13}C NMR (100.4 MHz, CDCl$_3$) 143.1, 139.2, 136.3, 130.2, 129.2, 127.3, 100.6, 21.7.

(*E*)-β-Nitrostyrene. Mp 58–60 °C; λ_{max} 311 nm; IR(KBr) ν_{max}/cm^{-1} 3113 (C–H, alkene), 1629 (C=C, alkene) 1582, 1475 (C=C, aromatic), 1448 (–CH$_2$ bend); ^{1}H NMR (400 MHz, CDCl$_3$) 7.45 (2H, d, *m*-H, *J* 6.84 Hz), 7.55 (2H, d, *o*-H) 7.59 (1H, d, =CH, *J* 13.7 Hz), 8.01 (1H, d, =CH, *J* 13.7 Hz); ^{13}C NMR (100.4 MHz, CDCl$_3$) 139.1, 137.1, 132.2, 130.1, 129.4, 129.2.

(*E*)-*p*-Chloro-β-nitrostyrene. Mp 102–104 °C; λ_{max} 314 nm; IR(KBr) ν_{max}/cm^{-1} 3107 (C–H, alkene), 1636 (C=C, alkene), 1589 (C=C, aromatic), 1441 (–CH$_2$ bend); ^{1}H NMR (400 MHz, CDCl$_3$), 7.43 (2H, d, *m*-H, *J* 8.79 Hz), 7.49 (2H, d, *o*-H, *J* 8.79 Hz), 7.57 (1H, d, =CH, *J* 13.7 Hz), 7.97 (1H, d, =CH, *J* 13.7 Hz); ^{13}C NMR (100.4 MHz, CDCl$_3$) 137.7, 137.4, 130.0, 129.8, 129.3, 128.5, 127.3.

(*E*)-*p*-Nitro-β-nitrostyrene. Mp 194–196 °C; λ_{max} 307 nm; IR(KBr) ν_{max}/cm^{-1} 3101 (C–H, alkene), 1635 (C=C, alkene), 1594 (C=C, aromatic), 1431 (–CH$_2$ bend); ^{1}H NMR (400 MHz, CDCl$_3$) 7.64 (1H, d, =CH, *J* 13.7 Hz), 7.73 (2H, d, *m*-H, *J* 8.79 Hz), 8.04 (1H, d, CH, *J* 13.7 Hz), 8.32 (2H, d, *o*-H, *J* 8.79 Hz); ^{13}C NMR (100.4 MHz, CDCl$_3$) 136.7, 135.0, 129.7, 128.9, 128.3.

Kinetic measurements

The reaction was followed spectrophotometrically by monitoring the decrease in the concentration of β-nitrostyrene, [NS], at λ_{max} of the substrate to over 80% completion. The reaction was studied under pseudo-first-order conditions, $[NS] = 8.0 \times 10^{-5}$ M^{-1} and $[BA] = (1.5–25) \times 10^{-3}$ M^{-1} at 25.0 ± 0.1 °C. The pseudo-first-order rate constant, k_{obs}, was determined from the slope of the plot ($r > 0.993$) ln[NS] (2.303 log [NS]) *vs.* time. The uncatalyzed (k_2) and catalyzed (k_3) rate constants were determined by fitting the k_{obs} data to a parabolic curve, Fig. 1, of the k_{obs} *vs.* [BA] plot, eqn. (4), which corresponded to a linear plot of k_{obs}/[BA] *vs.* [BA] with an intercept of k_2 and slope of k_3. The two methods gave the same results within an experimental error of ±3%. The ranges of [BA] (1.5–25 mM] and the concentration of [NB] (8.0×10^{-5} M) were fixed in all cases. The ranges of k_{obs} and extinction coefficients changes at λ_{max} are summarized in Table 6. Representative data are shown in Table 7.

Product analysis

β-Nitrostyrene (0.05 mol) and benzylamine (0.5 mol) were reacted in acetonitrile at 25.0 °C. After more than 15 half lives, solvent was removed under reduced pressure and product was separated by column chromatography (silica gel, 20% ethylacetate–*n*-hexane). Analytical data are as follows.

$C_6H_5CH(NHCH_2C_6H_4OCH_3)CH_2NO_2$. Liquid; IR(KBr) ν_{max}/cm^{-1} 2993 (C–H, CH_2), 2958 (N–H, stretch), 2946 (C–H, CH_3), 1460 (C=C, aromatic), 1448 (C–H, CH_2); ^{1}H NMR (400 MHz, $CDCl_3$) 3.82 (3H, s, OCH_3), 4.30 (1H, t, CH, *J* 6.90 Hz), 4.76 (2H, d, benzylamine CH_2, *J* 3.01 Hz), 4.78 (2H, d, benzyl CH_2, *J* 6.10 Hz), 6.88–7.53 (9H, m, aromatic ring); ^{13}C NMR (100.4 MHz, $CDCl_3$) 134.0 130.7 129.4 128.9, 128.6, 128.5, 128.3, 127.2, 114.1, 113.8, 64.9, 55.2, 41.7.

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