

Kinetics of reaction of *para*-substituted β -nitrostyrenes and β -methyl- β -nitrostyrenes with *n*-butylamine

A Shunmugasundaram*, T Lekshmana Thanulingam & R Murugesan

Department of Chemistry, V.H.N.S.N. College, Virudhunagar 626 001

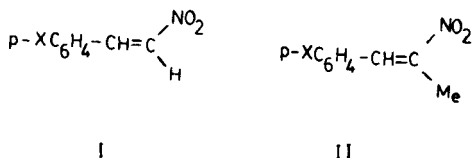
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The kinetics of addition of *n*-butylamine to β -nitrostyrene and β -methyl- β -nitrostyrene and their *para*-substituted derivatives in acetonitrile at four different temperatures have been followed spectrophotometrically. The order in [substrate] is unity and in [*n*-butylamine] it is non-integral. On the basis of the observed kinetic data, a stepwise mechanism involving the formation of zwitterionic addition complex in an equilibrium step followed by conversion into the reaction product via proton transfer in catalytic route by the amine has been proposed. The study of effect of substituents in these reactions shows that the electron-withdrawing substituents accelerate the reaction and electron-releasing substituents retard it. Good Hammett correlations have been observed in both the reaction series.

Though the addition of charged nucleophiles to an activated carbon-carbon double bond is a well studied reaction¹⁻⁴, studies involving the addition of electroneutral nucleophiles is limited. Herein we report the kinetic results of the addition of *n*-butylamine to β -nitrostyrenes (I) and β -methyl- β -nitrostyrenes (II).

Materials and Methods

All the β -nitrostyrenes (I) and β -methyl- β -nitrostyrenes (II) were prepared by literature methods^{5,6} and recrystallised from ethanol. *n*-Butylamine was rendered anhydrous and distilled under N₂ atmosphere. Triethylamine was rendered free from primary and secondary amine impurities and distilled over sodium. Acetonitrile was dried for one day over P₂O₅, refluxed for 5 hr over P₂O₅ and distilled through a fractionating column, and the middle fraction, (b.p. 82°) was collected.



Kinetic procedure

The rate measurements were carried out under pseudo-first order conditions ([amine] \gg [substrate]) in acetonitrile spectrophotometrically, monitoring the disappearance of UV absorption maxi-

ma at 451, 350, 325, 311, 313, 315, 317, 297, 300 and 307 nm for *p*-NMe₂, *p*-OMe, *p*-Me, H, *p*-F, *p*-Cl, *p*-Br, *p*-CF₃, *p*-CN and *p*-NO₂- β -nitrostyrenes and 440, 344, 321, 307, 309, 310, 311, 290, 289, 304 nm for *p*-NMe₂, *p*-OMe, *p*-Me, H, *p*-F, *p*-Cl, *p*-Br, *p*-CF₃, *p*-CN and *p*-NO₂- β -methyl- β -nitrostyrenes respectively. All the reactions followed first order kinetics as judged by the linearity of plots of log(absorbance) versus time. From the slope of these plots the pseudo-first order rate coefficients were calculated.

Product analysis

Equal amounts of β -nitrostyrene and *n*-butylamine were mixed under the kinetic conditions and kept overnight. Acetonitrile was removed under reduced pressure and the liquid residue distilled under reduced pressure (165°C/10 mm) to afford a yellow liquid, which was characterised as 1-butylamino-1-phenyl-2-nitroethane (C₆H₅-CH(*n*-C₄H₉NH)-CH₂NO₂) on the basis of ¹H NMR spectrum.

Results and Discussion

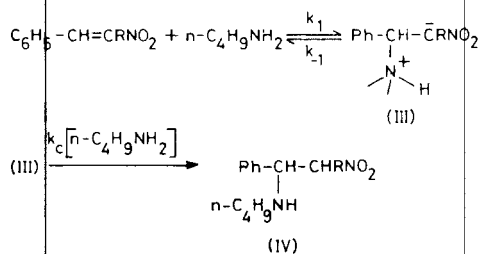
The rates of nucleophilic addition reaction of β -nitrostyrenes and β -methyl- β -nitrostyrenes with *n*-butylamine were measured at various initial [substrate] and [*n*-C₄H₉NH₂] (Tables 1 and 2). The plots of log (absorbance) versus time were linear showing first order dependence on [substrate]. The log-log plots of *k*_{obs} versus [*n*-C₄H₉NH₂] were linear with slopes of 1.76 for β -nitrostyrenes

Table 1 -- Effect of varying $[\beta\text{-nitrostyrene}]$ and $[n\text{-C}_4\text{H}_9\text{NH}_2]$ on the rate at 30°C

$[\beta\text{-Nitrostyrene}] \times 10^5$ (mol dm ⁻³)	$[n\text{-C}_4\text{H}_9\text{NH}_2] \times 10^3$ (mol dm ⁻³)	$k_{\text{obs}} \times 10^3$ (s ⁻¹)
4.56	9.00	2.52 ± 0.01
5.48	9.00	2.54 ± 0.01
7.00	9.00	2.69 ± 0.02
8.22	9.00	2.56 ± 0.01
7.00	5.00	0.985 ± 0.009
7.00	7.00	1.69 ± 0.01
7.00	15.0	6.59 ± 0.04
7.00	20.0	11.0 ± 0.1
7.00	25.0	16.6 ± 0.1

 Table 2 -- Effect of varying $[\beta\text{-methyl-}\beta\text{-nitrostyrene}]$ and $[n\text{-C}_4\text{H}_9\text{NH}_2]$ on the rate at 30°C

$[\beta\text{-Methyl-}\beta\text{-nitrostyrene}] \times 10^5$ (mol dm ⁻³)	$[n\text{-C}_4\text{H}_9\text{NH}_2] \times 10^2$ (mol dm ⁻³)	$k_{\text{obs}} \times 10^3$ (s ⁻¹)
4.86	5.81	1.80 ± 0.01
6.07	5.81	1.79 ± 0.01
7.00	5.81	1.77 ± 0.04
8.50	5.81	1.81 ± 0.01
7.00	4.64	1.20 ± 0.02
7.00	6.97	2.41 ± 0.01
7.00	8.13	3.13 ± 0.03
7.00	9.29	3.91 ± 0.02
7.00	10.4	4.71 ± 0.09



SCHEME 1

and 1.70 for $\beta\text{-methyl-}\beta\text{-nitrostyrenes}$ indicating that the order in $[n\text{-C}_4\text{H}_9\text{NH}_2]$ is non-integral. From the above kinetic observation a mechanism involving the formation of zwitterionic addition complex (III) in the first equilibrium step followed by conversion into the product via proton transfer in catalytic route by the participation of the second molecule of $n\text{-butylamine}$ (Scheme 1) is proposed.

The application of the steady-state hypothesis to this mechanism gives rate Eq. (1)

$$k_{\text{obs}} = \frac{K_1 k_c [n\text{-C}_4\text{H}_9\text{NH}_2]^2}{1 + K_1 [n\text{-C}_4\text{H}_9\text{NH}_2]} \quad \dots (1)$$

where $K_1 = k_1/k_{-1}$

Bernasconi *et al.*⁷ and Popov *et al.*⁸ also proposed similar type of mechanism for the amine addition to activated ethylene bond. Bernasconi *et al.* also observed rate-limiting proton transfer from zwitterionic intermediate to the base on the addition of amine to 1,1-diphenyl-2,2-dinitroethylene⁹, benzylidenemalonitrile¹⁰, $\alpha\text{-cyano-4-nitrostilbene}$, and $\alpha\text{-cyano-2,4-dinitrostilbene}$ ¹¹ in the 1:1 dimethyl sulphoxide-water (v/v) solvent mixture. The plots of second order rate constant k_2 versus $[n\text{-C}_4\text{H}_9\text{NH}_2]$ for the reaction of $\beta\text{-nitrostyrene}$ and $\beta\text{-methyl-}\beta\text{-nitrostyrene}$ in acetonitrile at 30°C are found to be linear ($r=0.999$). This observation is quite opposite to that observed in the addition of $n\text{-butylamine}$ to *trans*-(2-furyl)nitroethylene in acetonitrile where a curvilinear plot was observed⁸. The obtention of the curvilinear plot was explained on the basis of formation of the zwitterionic addition complex followed by the conversion into the reaction product by means of both non-catalytic and base-catalysed proton transfer processes. The linearity of the plot in the present study can be explained on the basis of conversion of the zwitterionic addition complex (III) into the reaction product (IV) by means of catalytic route by $n\text{-butylamine}$ (Scheme 1).

The participation of the second molecule of the amine in the conversion of intermediate (III) into the product IV may be explained in terms of general base catalysis as follows:

The kinetics of the reaction of $\beta\text{-nitrostyrene}$ and $\beta\text{-methyl-}\beta\text{-nitrostyrene}$ with $n\text{-butylamine}$ were studied in the presence of triethylamine as catalyst. The results obtained with varying $[(\text{C}_2\text{H}_5)_3\text{N}]$ on the interaction of $\beta\text{-nitrostyrene}$ and $\beta\text{-methyl-}\beta\text{-nitrostyrene}$ with $n\text{-butylamine}$ are given in Tables 3 and 4. The dependence of k_{obs} on $[(\text{C}_2\text{H}_5)_3\text{N}]$ at fixed [substrate] and $[n\text{-C}_4\text{H}_9\text{NH}_2]$ is linear. Plots of $\log k_{\text{obs}}$ versus $\log [(\text{C}_2\text{H}_5)_3\text{N}]$ is linear with slope 0.656 ($r=0.999$) for $\beta\text{-nitrostyrene}$ and 0.268 ($r=0.995$) for $\beta\text{-methyl-}\beta\text{-nitrostyrene}$ indicating that the order in $[(\text{C}_2\text{H}_5)_3\text{N}]$ is non-integral. Under the reaction conditions triethylamine does not add on to $\beta\text{-nitrostyrene}$ and $\beta\text{-methyl-}\beta\text{-nitrostyrene}$. It may

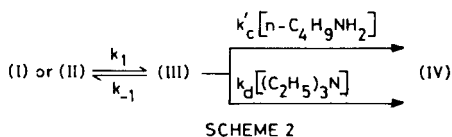
Table 3 – Effect of varying $[(C_2H_5)_3N]$ in the reaction of β -nitrostyrene with *n*-butylamine at 30°C [β -nitrostyrene] = 7×10^{-5} mol dm⁻³; [*n*-C₄H₉NH₂] = 5×10^{-3} mol dm⁻³

$[(C_2H_5)_3N] \times 10^3$ (mol dm ⁻³)	$k_{obs} \times 10^3$ (s ⁻¹)
2.0	1.20 ± 0.01
4.0	1.88 ± 0.01
6.0	2.39 ± 0.01
8.0	2.94 ± 0.01
10.0	3.46 ± 0.02
12.0	3.94 ± 0.01
14.0	4.23 ± 0.01

Table 4 – Effect of varying $[(C_2H_5)_3N]$ in the reaction of β -methyl- β -nitrostyrene with *n*-butylamine at 30°C [β -Methyl- β -nitrostyrene] = 7×10^{-5} mol dm⁻³; [*n*-C₄H₉NH₂] = 6×10^{-2} mol dm⁻³

$[(C_2H_5)_3N] \times 10^2$ (mol dm ⁻³)	$k_{obs} \times 10^3$ (s ⁻¹)
1.89	1.71 ± 0.01
3.78	1.92 ± 0.01
5.66	2.20 ± 0.02
7.55	2.37 ± 0.01
9.44	2.57 ± 0.02
11.3	2.69 ± 0.01
13.2	2.82 ± 0.01
15.1	2.92 ± 0.02
18.9	3.08 ± 0.02

be concluded that triethylamine is involved only in the proton transfer in the intermediate (III) from the nitrogen ammonium atom to the carbanion centre. The proton transfer may be effected by triethylamine through k_d route in parallel to k_c route (Scheme 2).



Application of the steady-state hypothesis to Scheme 2 leads to rate law (2).

$$k_{obs} = \frac{k_1 k'_c [n-C_4H_9NH_2]^2 + k_1 k_d [n-C_4H_9NH_2] [(C_2H_5)_3N]}{k_{-1} + k_d [(C_2H_5)_3N] + (k_1 + k'_c) [n-C_4H_9NH_2]} \quad \dots (2)$$

The linear dependence of k_{obs} on [triethylamine] complies with the condition

$$k_{-1} \gg k_d [(C_2H_5)_3N] + (k_1 + k'_c) [n-C_4H_9NH_2].$$

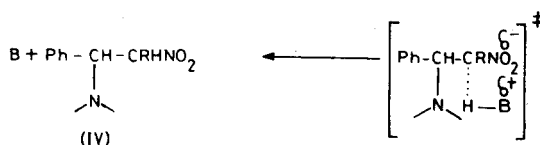
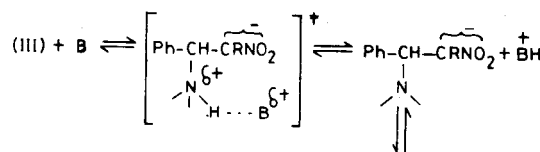
Eq. (2) is now reduced to Eq. (3).

$$\frac{k_{obs}}{[n-C_4H_9NH_2]} = \frac{K_1 k'_c [n-C_4H_9NH_2] + K_1 k_d [(C_2H_5)_3N]}{\dots} \quad \dots (3)$$

The catalytic rate constant for the reaction route with the participation of tertiary amine (k_d) may be found from the slope ($K_1 k_d$) of the plot of $k_{obs}/[n-C_4H_9NH_2]$ versus $[(C_2H_5)_3N]$ at fixed [*n*-C₄H₉NH₂]. The calculated k_d is 1.58 and 0.018 dm³ mol⁻¹ s⁻¹ for β -nitrostyrene and β -methyl- β -nitrostyrene respectively. The catalytic rate constant for the reaction route with the participation of *n*-butylamine in the presence of triethylamine (k'_c) may be calculated from the intercept of the above plot. The values of k'_c are calculated to be 1.03 and 0.062 dm³ mol⁻¹ s⁻¹ for β -nitrostyrene and β -methyl- β -nitrostyrene respectively. The values of K_1 were obtained from Eq. (1). The proton transfer catalysed by *n*-butylamine or triethylamine (B) may be represented by Scheme 3 which is similar to that proposed by Popov *et al.*⁸

The rates of *n*-butylamine addition to several *para*-substituted β -nitrostyrenes and β -methyl- β -nitrostyrenes at different [*n*-C₄H₉NH₂] at four different temperatures were also measured. From these observed pseudo-first order rate constants k_c for the slow step and K_1 for the formation of zwitterionic addition complex were evaluated by modifying Eq. (1) (see Eq. 4).

$$\frac{[n-C_4H_9NH_2]}{k_{obs}} = \frac{1}{K_1 k_c [n-C_4H_9NH_2]} + \frac{1}{k_c} \quad \dots (4)$$



SCHEME 3

The constants K_1 and k_c are calculated from the slope and intercept of the plot of $[n\text{-C}_4\text{H}_9\text{NH}_2]/k_{\text{obs}}$ against $1/[n\text{-C}_4\text{H}_9\text{NH}_2]$. The values of k_c and K_1 for the various *para*-substituted β -nitrostyrenes and β -methyl- β -nitrostyrenes are presented in Tables 5 and 6.

The rate constant k_c is higher for β -nitrostyrenes as compared to β -methyl- β -nitrostyrenes. The equilibrium constant is also higher for β -nitrostyrenes. This may be due to the deactivation of the carbon-carbon double bond by electron releasing methyl group in the β -position of β -methyl- β -nitrostyrenes and making the α -

carbon less electrophilic. The rate data clearly indicate that electron-withdrawing substituents increase the rate while electron-donating substituents retard it. The equilibrium constant K_1 also shows that the formation of zwitterionic addition complex is facilitated by electron-withdrawing groups and is retarded in the case of electron-donating groups. k_c and K_1 values were correlated with the Hammett σ -constant and the results calculated at 30°C are given in Table 7. The positive ρ -value obtained for both β -nitrostyrenes and β -methyl- β -nitrostyrenes suggests that the reaction centre is electron-rich in the transition state and is

Table 5 – Effect of structural variation on the rate, equilibrium constant and activation parameters of addition of *n*-butylamine to β -nitrostyrene and *para*-substituted β -nitrostyrenes in acetonitrile.

Substituent	k_c dm ³ mol ⁻¹ s ⁻¹				ΔH^\ddagger kJ mol ⁻¹	$-\Delta S^\ddagger$ JK ⁻¹ mol ⁻¹	K_1 dm ³ mol ⁻¹				$-\Delta H$ kJ mol ⁻¹	$-\Delta S$ JK ⁻¹ mol ⁻¹
					(at 30°C)	(at 30°C)					(at 30°C)	(at 30°C)
	25°	30°	35°	40°C			25°	30°	35°	40°C		
NMe ₂	0.143	0.189	0.234	0.334	39.6	128	4.16	2.92	2.23	1.48	52.3	163
OMe	0.494	0.567	0.675	1.01	38.7	122	10.7	8.89	6.76	3.71	53.2	157
Me	0.703	0.939	1.27	1.43	35.3	129	25.6	16.6	12.7	9.54	50.1	142
H	1.10	1.37	1.43	1.57	14.9	193	48.6	32.2	27.7	23.7	36.0	90.0
F	1.52	1.74	1.88	2.14	14.7	192	50.1	40.6	35.1	28.9	27.8	60.9
Cl	2.60	2.81	3.69	4.26	24.7	155	59.6	45.5	37.0	31.0	33.7	79.4
Br	2.32	2.52	3.28	4.03	27.2	148	66.7	49.1	38.3	30.8	39.8	99.1
CF ₃	4.27	5.12	6.08	7.20	24.5	151	136	107	82.1	64.5	38.6	88.8
CN	6.08	6.98	7.42	8.41	13.6	184	161	150	119	87.0	32.1	64.1
NO ₂	6.85	8.10	8.74	9.57	14.3	181	251	172	148	118	37.6	81.3

Table 6 – Effect of structural variation on the rate, equilibrium constants and activation parameters of addition of *n*-butylamine to β -methyl- β -nitrostyrene and *para*-substituted β -methyl- β -nitrostyrenes in acetonitrile

Substituent	k_c dm ³ mol ⁻¹ s ⁻¹				ΔH^\ddagger kJ mol ⁻¹	$-\Delta S^\ddagger$ JK ⁻¹ mol ⁻¹	K_1 dm ³ mol ⁻¹				$-\Delta H$ kJ mol ⁻¹	$-\Delta S$ JK ⁻¹ mol ⁻¹
					(at 30°C)	(at 30°C)					(at 30°C)	(at 30°C)
	25°	30°	35°	40°C			25°	30°	35°	40°C		
NMe ₂	0.021	0.023	0.031	0.036	27.6	185	0.941	0.807	0.574	0.531	31.9	107
OMe	0.047	0.056	0.064	0.071	18.6	208	6.03	4.85	4.11	3.52	27.6	78.1
Me	0.070	0.076	0.104	0.116	26.0	180	7.94	7.18	4.61	3.99	38.8	112
H	0.080	0.105	0.115	0.139	24.6	183	10.3	7.59	6.24	5.27	34.3	96.3
F	0.101	0.115	0.137	0.159	21.4	193	16.1	14.4	11.3	9.46	28.4	71.7
Cl	0.116	0.145	0.155	0.165	14.9	212	26.4	19.4	19.2	18.3	19.7	40.5
Br	0.116	0.134	0.149	0.162	14.8	213	31.0	26.5	22.8	21.9	18.6	34.0
CF ₃	0.227	0.247	0.268	0.290	10.2	223	73.2	57.8	46.2	37.1	35.1	82.1
CN	0.246	0.305	0.314	0.328	11.4	217	106	78.6	66.7	51.8	35.9	82.2
NO ₂	0.301	0.375	0.406	0.451	17.7	195	157	132	116	94.1	25.8	44.6

Table 7 – The results of correlation for the reaction of addition of *n*-butylamine to β -nitrostyrenes and β -methyl- β -nitrostyrenes at 30°C

Substrate	Parameters used for correlation	ρ	r	s	ψ	n
β -nitrostyrene	$\log k_c$ versus σ	1.055 ± 0.084	0.996	0.050	0.099	10
	$\log K_1$ versus σ	1.141 ± 0.140	0.990	0.083	0.158	10
β -methyl- β -nitrostyrene	$\log k_c$ versus σ	0.748 ± 0.040	0.998	0.024	0.071	10
	$\log K_1$ versus σ	1.354 ± 0.120	0.995	0.071	0.112	10

thus consistent with the proposed mechanism. Further it is found that the rate constant k_c increases with increase in temperature and that the equilibrium constant decreases with temperature. This observation may be accounted for by assuming the presence of a pre-equilibrium step in the reaction. As the temperature increases the equilibrium is shifted to left.

The Arrhenius activation energies for the catalytic route (ΔH^\ddagger and ΔS^\ddagger) and the ΔH and ΔS for the equilibrium step are presented in Tables 5 and 6. The ΔH^\ddagger values are not high and ΔS^\ddagger values are all negative. ΔH and ΔS are negative indicating that in both the reaction series formation of zwitterionic addition complex occurs in the equilibrium step. The plots of ΔH^\ddagger against ΔS^\ddagger for β -nitrostyrenes ($r=0.974$) and β -methyl- β -nitrostyrenes ($r=0.956$) are linear. Exner plots of $\log k_c$ at 40°C versus $\log k_c$ at 25°C is also linear for both β -nitrostyrenes ($r=0.994$) and β -methyl- β -nitrostyrenes ($r=0.995$). The linearity observed in compensation plots and Exner plots shows that in this reaction series all the substituted compounds follow an identical mechanism.

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