Kinetics and Equilibrium Data for Base-catalysed Addition of Ethanol to β-Nitrostyrene

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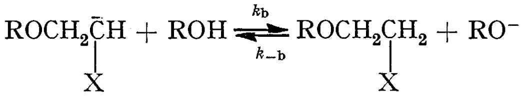
The kinetics of the addition of ethanol to β-nitrostyrene catalysed by sodium ethoxide has been studied. The observed rate equation is $R = A$[β-nitrostyrene] + B, where A and B are constants which depend on the initial concentrations of the olefin and catalyst. The mechanism of the reaction consists of reversible addition of the ethoxide ion to the olefin, followed by rapid protonation of the intermediate carbanion. A general approach has been developed for determining the forward (k_1) and backward (k_{-1}) rate constants of the addition step, which are $(1{\cdot}7 \pm 0{\cdot}3) \times 10^2$ l mol^{-1} min^{-1} and $(1{\cdot}1 \pm 0{\cdot}4) \times 10^{-6}$ min^{-1}, respectively.

THE addition of nucleophiles to activated double bonds has been extensively studied from the mechanistic viewpoint and several reviews are available.[1,2] The base-catalysed addition of alcohols to such olefins follows the general mechanism of Michael addition reactions,[2-11] namely, nucleophilic attack of the alkoxide ion on C_β to form an intermediate carbanion in the rate-determining step, followed by protonation [reactions (1) and (2)]. When the rate of the decomposition of the intermediate carbanion to the original reactants is comparable with the rate of its protonation, an equilibrium is established. This has been observed for the addition of trinitromethane to β-nitrostyrene,[12] the addition of various active methylenic compounds to acrylonitrile,[13] and the addition of alcohols to alkyl vinyl ketones [3,8,9,11] and vinyl sulphones.[10] We were interested in having quantitative data on the rate constants k_a and k_{-a} for nucleophilic attack at C_β. It was therefore the purpose of the present work to develop a general approach for determining these rate constants.

$$\mathrm{RO^- + CH_2{=}\underset{X}{CH} \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} RO{-}CH_2{-}\underset{X}{\bar{C}H}} \quad (1)$$



$$\mathrm{ROCH_2\underset{X}{\bar{C}H} + ROH \underset{k_{-b}}{\overset{k_b}{\rightleftharpoons}} ROCH_2\underset{X}{CH_2} + RO^-} \quad (2)$$

RESULTS AND DISCUSSION

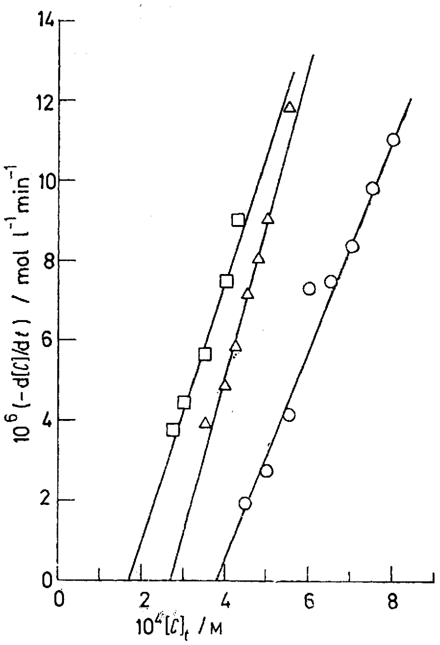
The rates of addition of ethanol to β-nitrostyrene catalysed by sodium ethoxide were measured in ethanol as solvent at 30°. The disappearance of β-nitrostyrene was followed by u.v. at 310 nm. The initial concentrations of olefin and base were changed in the range of $1{\cdot}29$—$9{\cdot}68 \times 10^{-4}$ and $0{\cdot}51$—5×10^{-4} M, respectively. For each kinetic run, a plot of R_t, the rate of reaction at time t, against $[C]_t$ the concentration of β-nitrostyrene at time t, gave a straight line with a slope A and an intercept B (Figure). Consequently, the experimental rate equation is (3). R_t Values were

$$R_t = -\mathrm{d}[C]_t/\mathrm{d}t = A[C]_t + B \qquad (3)$$

derived from the slopes of conversion curves at different t values. On integrating equation (3) equation (4) is obtained. The best conversion curve was plotted for

$$[C]_t = \{(A[C]_0 + B)\mathrm{e}^{-At} - B\}/A \qquad (4)$$

each run according to equation (4) using a computer and the values of A and B calculated. Deviations of the measured values of $[C]_t$ from those calculated were within ±5%. Detailed data for some of the kinetic runs are presented in the Experimental section (Table 2).



Plots of R_t against [β-nitrostyrene]$_t$: ○ run 10; △ run 11; □ run 14

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A rate equation similar to the observed equation (3) can be derived from the reactions (5) and (6). According

$$\mathrm{EtO^- + \mathit{Ph}CH{=}CHNO_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} EtOPhCH\bar{C}HNO_2} \quad (5)$$

$$\mathrm{EtOPhCH{-}\bar{C}HNO_2 + EtOH \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} EtOPhCHCH_2NO_2 + EtO^-} \quad (6)$$

to these reactions the rate of the addition reaction, measured as $R_t = -\mathrm{d}[\beta\text{-nitrostyrene}]/\mathrm{d}t$, is given by equation (7) where EtOC$^-$ stands for the intermediate

$$R = -\mathrm{d}[C]_t/\mathrm{d}t = k_1[\mathrm{EtO^-}][C]_t - k_{-1}[\mathrm{EtOC^-}] \quad (7)$$

carbanion. Assuming steady state conditions for EtOC$^-$, the rate equation (7) becomes (8) where EtOCH stands

$$R_t = k_1[\mathrm{EtO^-}][C]_t\left(\frac{k_2[\mathrm{EtOH}]}{k_{-1} + k_2[\mathrm{EtOH}]} - \frac{k_{-1}k_{-2}[\mathrm{EtO^-}][\mathrm{EtOCH}]_t}{k_{-1} + k_2[\mathrm{EtOH}]}\right) \quad (8)$$

for the addition product. Since the addition product was formed, it might be assumed that $k_2[\mathrm{EtOH}] \gg k_{-1}$. Equation (8) could then be simplified to (9). On

$$R_t = k_1[\mathrm{EtO^-}][C]_t - \frac{k_{-1}k_{-2}[\mathrm{EtO^-}][\mathrm{EtOCH}]}{k_2[\mathrm{EtOH}]} \quad (9)$$

substituting $[C]_0 - [C]_t$ for $[\mathrm{EtOCH}]_t$ in equation (9) equation (10) is obtained. This equation is identical

$$R_t = \left(k_1[\mathrm{EtO^-}] + \frac{k_{-1}k_{-2}[\mathrm{EtO^-}]}{k_2[\mathrm{EtOH}]}\right)[C]_t - \frac{k_{-1}k_{-2}[\mathrm{EtO^-}]}{k_2[\mathrm{EtOH}]}[C]_0 \quad (10)$$

to the experimently observed rate equation (3) where relationships (11) and (12) apply.

$$B = k_{-1}k_{-2}[\mathrm{EtO^-}][C]_0/k_2[\mathrm{EtOH}] \quad (11)$$

$$\begin{aligned} A &= k_1[\mathrm{EtO^-}] + k_{-1}k_{-2}[\mathrm{EtO^-}]/k_2[\mathrm{EtOH}] \quad (12)\\ &= k_1[\mathrm{EtO^-}] - B/[C]_0 \end{aligned}$$

It has been recently suggested that vinyl carbanion intermediates of the type $\mathrm{{>}C{=}\bar{C}X}$ (X = CN, CO$_2$R, NO$_2$, *etc.*) are involved in reactions of bases with αβ-unsaturated nitriles,[14-19] esters,[18,20] and nitro-compounds [21] having an α-vinyl hydrogen atom. The two acid–base equilibria (13) and (14), leading to the formation of vinyl carbanions, may occur in the system investigated here. As shown above, equation (10), which is similar to the observed equation (3), can be derived from equations (5) and (6). It might be therefore assumed that the equilibrium reactions (13) and (14) have relatively very small equilibrium constants and do not affect to any significant extent the rate of addition of ethanol to β-nitrostyrene.

$$\mathrm{EtO^- + PhCH{=}CHNO_2 \rightleftharpoons EtOH + PhCH{=}\bar{C}NO_2} \quad (13)$$

$$\mathrm{EtO(Ph)CH{-}\bar{C}HNO_2 + PhCH{=}CHNO_2 \rightleftharpoons EtO(Ph)CHCH_2NO_2 + PhCH{=}\bar{C}NO_2} \quad (14)$$

One of the following conditions may be associated with reactions (5) and (6) from which equation (10) was derived: (I) $k_1 \gg k_{-1}$, $k_2 \gg k_{-2}$; (II) $k_1 \ll k_{-1}$, $k_2 \ll k_{-2}$; (III) $k_1 \gg k_{-1}$, $k_2 \ll k_{-2}$; or (IV) $k_1 \ll k_{-1}$, $k_2 \gg k_{-2}$. If condition (I) applies, the reaction investigated should be irreversible. It can be shown that under such conditions equation (10) should change into a simple second-order reaction $R = -\mathrm{d}[C]_t/\mathrm{d}t = k_1[\mathrm{EtO^-}][C]_t$, which is different from the observed rate equation (3). Such kinetic behaviour was found in the case of the nucleophilic addition of alcohols to acrylonitrile,[4,6,7] methacrylonitrile,[6,7] and acrylic and methacrylic esters.[6,7] Condition (II) can be eliminated since it would lead to no addition reaction. When each of the two conditions (III) and (IV) is applied to equation (10), the general form of this equation is not changed. This was expected since in both cases the reaction should be reversible. These two conditions require that if the reaction were such that $k_2 \ll k_{-2}$, one should obtain from the kinetic rate measurements that $k_1 \gg k_{-1}$ [condition (III)], and if $k_2 \gg k_{-2}$, k_1 should be $\ll k_{-1}$ [condition (IV)]. Comparison of the relative acidities of EtOH and EtOCH could thus clearly indicate for any reversible addition reaction of this type, which of the two conditions controls the system. The equilibrium

TABLE 1

Rate constants for the addition of ethanol to β-nitrostyrene catalysed by sodium ethaxide

Run no.	10^4[β-nitro-sytrene]/ M	10^4 [EtO$^-$Na$^+$]/ M	$10^{-2}k_1$/ l mol^{-1} min^{-1}	$10^6 k_{-1}$/ min^{-1}	10^2K *
1	4·42	5·10	2·01	1·85	10·9
2	3·33	3·06	1·46	1·28	11·4
3	3·52	3·06	1·67	1·32	13·1
4	3·57	2·04	1·67	0·84	20·0
5	3·53	2·04	1·68	0·92	18·2
6	3·63	1·02	1·99	0·81	24·2
7	3·70	1·02	2·08	0·86	24·4
8	3·50	0·51	1·21	0·93	12·3
9	3·52	0·51	1·74	1·41	12·3
10	9·26	1·02	1·55	1·80	8·1
11	5·78	1·02	1·38	0·92	15·0
12	5·83	1·02	1·27	0·94	13·7
13	4·18	1·02	1·50	0·77	19·5
14	4·50	1·02	1·91	1·42	13·4
15	2·93	1·02	1·87	1·19	15·6
16	1·23	1·02	1·76	0·93	19·9

* Average $K = 15{\cdot}8 \pm 3{\cdot}9$.

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constant of reaction (6) is given by $K = k_2/k_{-2} = k_{a(\mathrm{EtOH})}/k_{a(\mathrm{EtOCH})}$, where $k_{a(\mathrm{EtOH})}$ and $k_{a(\mathrm{EtOCH})}$ are the acidic dissociation constants of EtOH and EtOCH, respectively. It can be assumed that $k_{a(\mathrm{EtOCH})} \simeq k_{a(\mathrm{CH_3CH_2NO_2})} \simeq 10^{-9}$.[22,23] It follows therefore that $k_2 \ll k_{-2}$ since $k_2/k_{-2} \simeq 10^{-18}/10^{-9} = 10^{-9}$.[24]

It was indeed found that $k_1 \gg k_{-1}$ and k_1/k_{-1} ratio *ca.* 10^8 was obtained (Table 1). Condition (IV) ($k_2 \gg k_{-2}$) is demonstrated by the EtOD–$\mathrm{EtO^-Na^+}$–cinnamonitrile system, where the ratio k_2/k_{-2} is *ca.* 10^7. A k_1/k_{-1} ratio of 10^{-8} ($k_1 \ll k_{-1}$) was obtained for this system from the kinetic rate measurements.[25] The values of k_1 and k_{-1} for each run could be calculated using equations (11) and (12) in the form $k_1 = (A + B/[C]_0)/[\mathrm{EtO^-}]$ and $k_{-1} = k_2B[\mathrm{EtOH}]/k_{-2}[\mathrm{EtO^-}][C]_0$. The average values of k_1 and k_{-1} obtained by this way (Table 1) were: $k_1 = (1{\cdot}7 \pm 0{\cdot}3) \times 10^2$ l mol^{-1} min^{-1} and $k_{-1} = (1{\cdot}1 \pm 0{\cdot}4) \times 10^{-6}$ min^{-1}. It should be noted that some error is involved in the values of k_1 and k_{-1}, since the available value of k_2/k_{-2} is not an accurate one (k_2/k_{-2} *ca.* 10^{-9}).

TABLE 2

Addition of ethanol to β-nitrostyrene catalysed by sodium ethoxide [a]

Run no:	10			11			14		
	t/min	$10^4[C]_{t,m}$ [b]/M	$10^4[C]_{t,c}$ [c]/M	t/min	$10^4[C]_{t,m}$/M	$10^4[C]_{t,c}$/M	t/min	$10^4[C]_{t,m}$/M	$10^4[C]_{t,c}$/M
	0		9·26	0		5·78	0		1·23
	4	8·82	8·70	4	5·55	5·47	3	1·16	1·17
	7	8·24	8·31	8	5·21	5·18	7	1·11	1·09
	10	8·00	7·97	11	4·89	4·97	12	1·00	1·00
	16	7·12	7·34	15	4·70	4·72	20	0·89	0·88
	21	7·01	6·90	23	4·24	4·27	33	0·73	0·73
	30	6·25	6·22	30	3·91	3·93	50	0·58	0·58
	46	5·23	5·36	45	3·28	3·34	75	0·44	0·46
	60	5·06	4·86	65	2·93	2·79	135	0·37	0·33
	130	3·86	3·90	80	2·48	2·49	265	0·28	0·30
				100	2·24	2·21			
				160	1·75	1·80			
A (min^{-1})		$2{\cdot}66 \times 10^{-2}$			$1{\cdot}96 \times 10^{-2}$			$2{\cdot}35 \times 10^{-2}$	
B (mol l^{-1} min^{-1})		$-9{\cdot}98 \times 10^{-6}$			$-3{\cdot}20 \times 10^{-6}$			$-6{\cdot}90 \times 10^{-6}$	

[a] The concentration of sodium ethoxide was $1{\cdot}02 \times 10^{-4}$M. [b] $[C]_{t,m}$ Measured concentration of β-nitrostyrene. [c] $[C]_{t,c}$ Calculated (by computer) concentration of β-nitrostyrene according to equation (4).

The overall addition reaction of ethanol to β-nitrostyrene, catalysed by sodium ethoxide, is given by equation (15). The equilibrium constant K for this

$$\mathrm{EtOH} + \mathrm{PhCH{=}CHNO_2} \xrightleftharpoons{\mathrm{EtO^-Na^+}} \mathrm{EtO(Ph)CHCH_2NO_2} \tag{15}$$

reaction is given by equation (16). The equilibrium

$$\begin{aligned} K &= [\mathrm{EtOCH}]_{\mathrm{eq.}}/[\mathrm{EtOH}][C]_{\mathrm{eq.}} \\ &= ([C]_0 - [C]_{\mathrm{eq.}})/[\mathrm{EtOH}][C]_{\mathrm{eq.}} \end{aligned} \tag{16}$$

concentration of β-nitrostyrene — $[C]_{\mathrm{eq.}}$ can be calculated for each run, since equation (3) converts at equilibrium into (17). The calculated equilibrium constant for reaction (15) in ethanol as solvent at 30° was

$$[C]_{\mathrm{eq.}} = -B/A \tag{17}$$

$K = (15{\cdot}8 \pm 3{\cdot}9) \times 10^{-2}$; values of K for each run are given in Table 1.

EXPERIMENTAL

Materials.—β-Nitrostyrene was synthesized [26] and purified by several crystallizations. Absolute ethanol was dried over magnesium and distilled under nitrogen. Alcoholic sodium alkoxide solutions were prepared by dissolving sodium in alcohol under reflux. All liquid materials, β-nitrostyrene in ethanol, ethanol, and alcoholic sodium alkoxide, were kept under pure nitrogen in flasks fitted with self-sealing rubber caps. Aliquot portions were removed with syringes by applying nitrogen pressure.

Kinetic Runs.—The addition reaction was carried out in a flask (150 ml) connected to high vacuum and nitrogen lines. The flask was fitted with a self-sealing rubber cup through which liquids were introduced by a syringe. The system was dried, evacuated, and flushed with dry nitrogen prior to the introduction of solvent and reactants. Samples were withdrawn at the required intervals through a capillary stopcock, by applying nitrogen pressure. The samples withdrawn were quenched with a solution of hydrochloric acid in propan-2-ol, and the concentration of β-nitrostyrene was then determined by u.v. spectroscopy.

Some representative kinetic rate measurements are presented in Table 2 from which plots of R_t against $[C]_t$ (Figure) can be drawn.

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