Kinetics of addition of thiophenol to para-substituted β-nitrostyrenes and β-methyl-β-nitrostyrenes

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The kinetic studies of the nucleophilic addition of thiophenol (PhSH) to para-substituted derivatives of β-nitrostyrene (βNS) and β-methyl-β-nitrostyrene (βMNS) have been investigated spectrophotometrically in 50%(v/v) acetonitrile-water at four different temperatures. The reaction follows first order with respect to each substrate and fractional order with respect to thiophenol in both the cases. On the basis of kinetic results, a stepwise mechanism involving the formation of zwitterionic addition complex in an equilibrium step followed by its conversion into product via proton transfer catalytic route by the thiophenol has been proposed for β-nitrostyrene and non-catalytic proton transfer has been proposed for β-methyl-β-nitrostyrene. Based on the rate law derived, a plot of [PhSH]/kkobs against I/[PhSH] is linear for β-nitrostyrene and a plot of 1/kobs against 1/[PhSH] is linear for β-methyl-β-nitrostyrene. The effect of solvent composition on the reaction rate indicates that the increase in the polarity of the medium increases the reaction rate in both reaction series. The study of the effect of substituents in the two reaction series shows that the electron-withdrawing substituents accelerate the reaction rate and the electron-releasing substituents retard it. Good Hammett correlations have been observed for both the series.

Nitroolefins are useful intermediates in organic synthesis and are important structural units that can be used as starting materials for many classes of compounds. Nitroalkenes, being markedly electron-deficient, readily undergo addition reaction with many different nucleophiles, and act as good Michael acceptors. Nucleophilic addition reactions of α,β-unsaturated nitro compounds are the most extensively investigated subjects in mechanistic organic chemistry and biochemistry. The addition reactions of thiols to various α,β-unsaturated activated compounds such as thiomethoxy benzylidene Meldrum’s acid, bicyclopropylidene, benzylidene Meldrum’s acid and chalcones are reported.

A careful literature survey revealed that there is no kinetic study on the reaction of β-nitrostyrene and β-methyl-β-nitrostyrene with thiophenol. The present work reports the investigation on kinetics of addition of thiophenol to β-nitrostyrene, β-methyl-β-nitrostyrene and their para-substituted derivatives in 50%(v/v) aqueous acetonitrile at different temperatures.

Materials and Methods

β-Nitrostyrene, β-methyl-β-nitrostyrene and their para-substituted derivatives were prepared by the method of Worrall. Thiophenol was prepared by literature method. The solutions of β-nitrostyrenes, β-methyl-β-nitrostyrenes and thiophenol were prepared in appropriate solvent system (50% (v/v) acetonitrile-water).

Kinetic measurement

The kinetics of the reaction were studied spectrophotometrically by monitoring the decrease in the optical densities of initial concentration of the substrate at 311 nm for β-nitrostyrene and at 313 nm for β-methyl-β-nitrostyrene under pseudo-first order conditions ([substrate] << [PhSH]) in 50% (v/v) acetonitrile-water mixture. Hitachi-Model 200-20 spectrophotometer was used with quartz cells of 1 cm path length. The concentration of substrate was kept at 1.00 × 10⁻⁴ mol dm⁻³ for both substrates. The concentration of thiophenol was kept at 1.00 × 10⁻³ mol dm⁻³ for β-nitrostyrene and at 6.00 × 10⁻³ mol dm⁻³ for β-methyl-β-nitrostyrene. The pseudo-first order rate constant, kobs, was computed from the slope of the plot of log [absorbance] versus time. Duplicate runs showed that the rates were reproducible within ± 3%. The kobs were evaluated for various para-substituted derivatives by monitoring the decrease in the OD at the corresponding λmax values.
Product analysis

\( \beta \)-Nitrostyrene/\( \beta \)-methyl-\( \beta \)-nitrostyrene and thiophenol were mixed under kinetic conditions and kept overnight. The mixture was diluted with water and the product was extracted with ether. The ether layer was washed with dilute sodium hydroxide solution, then with water and dried with anhydrous sodium sulphate. The separated white solid after the removal of solvent was recrystallised from ethanol and was identified as \( \text{C}_6\text{H}_5\text{-CH(S-C}_6\text{H}_5\text{-CH}_2\text{-NO}_2 \) (I) for \( \beta \)-nitrostyrene. The melting point of the product was found to be 70-71°C (lit.\(^{14}\) 72-73°C). The product of this reaction was confirmed from spectral techniques and also by preparing authentic sample\(^{15}\).

In the case of \( \beta \)-methyl-\( \beta \)-nitrostyrene the separated white solid was recrystallised from ethanol and was identified as \( \text{C}_6\text{H}_5\text{-CH(S-C}_6\text{H}_5\text{-CH}_3\text{-NO}_2 \) (II). The melting point of the product was found to be 118-19°C. The product of this reaction was confirmed from spectral techniques. IR spectrum in KBr disc of the product showed the following characteristic bands: 3500-3300 (OH-stretching), 3070 (C=H, aromatic), 2937 (C-H, aliphatic stretching), 1448 (C-H bending, asy) and 700 (C-S, stretching).

\(^1\)H NMR spectra (300 MHz; CDCl\(_3\)) of II show two signals at 8.79 and 4.98 ppm each integrating for one proton. Another singlet at 1.88 ppm integrating for three protons is presumably due to CH\(_3\)-proton. The aromatic protons give a multiplet integrating for ten protons suggesting both phenyl and phenylthio groups are present in the molecule. An examination of the CH-COSY spectrum reveals that the three-proton singlet correlates with carbon signal at 12.45 ppm while another singlet integrating for 1 H correlates with carbon signal at 58.34 ppm. Interestingly, another singlet at 8.79 ppm does not provide any correlation peak in CH-COSY spectrum disclosing that it is not attached to any carbon. All the above spectral observations are in consonance with structure II.

A high \( \delta \) value for the hydroxyl proton may be due to hydrogen bonding as in structure III. The \(^{13}\)C NMR spectra (75.47 MHz; CDCl\(_3\)) show signals at 157.4 (C=N), 137.8, 134.4, 133.0, 129.3, 129.0, 128.6, 128.3, 128.0 (aromatic), 58.3 (C-H) and 12.4 (CH\(_3\)) ppm.

Stoichiometric analysis

The stoichiometry of the reaction was determined by UV-Visible spectrophotometric method. Excess of \( \beta \)-nitrostyrene/\( \beta \)-methyl-\( \beta \)-nitrostyrene was mixed with thiophenol and allowed to stand for 24 hr at room temperature to ensure completion of the reaction. From the value of optical density the stoichiometry of the reaction was found to be 1:1. The observed stoichiometric equation is shown in Equations 1 and 2 respectively for \( \beta \)-nitrostyrene and \( \beta \)-methyl-\( \beta \)-nitrostyrene.

Results and Discussion

Effect of [substrate] and [thiophenol] on reaction rate

The rate of addition reactions of \( \beta \)-nitrostyrene and \( \beta \)-methyl-\( \beta \)-nitrostyrene with thiophenol in 50% (v/v) acetonitrile-water mixture was followed by monitoring the disappearance of UV absorption maxima of the substrates. The plot of log (OD) versus time is linear showing first order dependence on [substrate]. The rates of nucleophilic addition of thiophenol to \( \beta \)-nitrostyrene and \( \beta \)-methyl-\( \beta \)-nitrostyrene were measured at various initial concentrations of the substrates in 50% (v/v) acetonitrile-water mixture at 35°C. The relevant data are given in Table I. The variation of

\[ \text{C}_6\text{H}_5\text{-CH} - \text{C} = \text{N} / \text{O} + \text{C}_6\text{H}_5\text{SH} \rightarrow \text{C}_6\text{H}_5\text{-CH} = \text{C} / \text{N} \]  

\[ \text{C}_6\text{H}_5\text{-CH} - \text{C} = \text{C} / \text{N} + \text{C}_6\text{H}_5\text{SH} \rightarrow \text{C}_6\text{H}_5\text{-CH} - \text{C} / \text{N} \]
[substrate] at constant [thiophenol] does not alter the pseudo-first order rate constants (Table 1) confirming the first order dependence on substrate.

The effect of [thiophenol] on the rate of addition reaction of β-nitrostyrene/β-methyl-β-nitrostyrene was studied by varying the [PhSH] and keeping other factors as constant. The rate constant increases with the increase in [thiophenol]. The plot of log $k_{obs}$ versus log [PhSH] is linear with a slope of 1.523 ($r = 0.999$) for β-nitrostyrene and with a slope of 0.542 ($r = 0.990$) for β-methyl-β-nitrostyrene indicating that the order in thiophenol is fractional in both the cases.

**Mechanism for the addition of PhSH to βNS/βMNS**

From the above kinetic and experimental observations, a mechanism involving the formation of zwitterionic addition complex (Z) in the first fast equilibrium step followed by its conversion into product via catalytic proton transfer by the participation of the second molecule of thiophenol for β-nitrostyrene and proton transfer from the thiophenol to nitro group in a non-catalytic route has been proposed for β-methyl-β-nitrostyrene (Scheme 1).

Applying steady state approximation to the above reaction mechanism the rate law derived for β-nitrostyrene is as shown in Equation (3). and for β-methyl-β-nitrostyrene is as shown in Equation (4).

### Table 1—Effect of varying [thiophenol] and [substrate] on the rate of addition reaction at 35°C in 50% (v/v) acetonitrile-water

<table>
<thead>
<tr>
<th>β-Nitrostyrene</th>
<th>β-Methyl-β-nitrostyrene</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^4$ [βNS] (mol dm$^{-3}$)</td>
<td>$10^4$[PhSH] (mol dm$^{-3}$)</td>
</tr>
<tr>
<td>1.00</td>
<td>0.200</td>
</tr>
<tr>
<td>1.00</td>
<td>0.800</td>
</tr>
<tr>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>0.400</td>
<td>1.00</td>
</tr>
<tr>
<td>0.800</td>
<td>1.00</td>
</tr>
<tr>
<td>1.20</td>
<td>1.00</td>
</tr>
<tr>
<td>1.00</td>
<td>12.0</td>
</tr>
</tbody>
</table>

$^a$ The error quoted in $k_{obs}$ is 95% CL of the student $t_{22}$. 

![Scheme 1](image-url)
The effect of solvent on the rate of addition of thiophenol on β-nitrostyrene and β-methyl-β-nitrostyrene at 35°C.

<table>
<thead>
<tr>
<th>Percentage of CH₂CN (v/v)</th>
<th>10⁹ kobs (s⁻¹)</th>
<th>1/D</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>5.00 ± 0.03</td>
<td>0.0178</td>
</tr>
<tr>
<td>55</td>
<td>8.26 ± 0.07</td>
<td>0.0172</td>
</tr>
<tr>
<td>50</td>
<td>11.6 ± 0.1</td>
<td>0.0166</td>
</tr>
<tr>
<td>45</td>
<td>20.7 ± 0.2</td>
<td>0.0161</td>
</tr>
<tr>
<td>40</td>
<td>28.1 ± 0.5</td>
<td>0.0156</td>
</tr>
</tbody>
</table>

1. The error quoted in kobs is 95% CL of the student t²².

\[ \frac{k_{\text{obs}}}{Kc[\text{PhSH}]} = \frac{1}{K} + \frac{1}{k_c} \text{ vs. } \frac{1}{D} \]

The constants K and k_c were calculated from the slope and intercept of the plot of [PhSH]/kobs versus 1/[PhSH] for β-nitrostyrene and plot of 1/kobs versus 1/[PhSH] for β-methyl-β-nitrostyrene.

Cason et al.² reported the formation of C₆H₆CH(SPh)CH(CH₃)NO₂ in the reaction of β-methyl-β-nitrostyrene with thiophenol in benzene or ethanol. However, in the present study the product isolated under kinetic condition is found to be 1,4-addition product. Such type of 1,4-addition is also reported in some of the addition reactions of nitroolefins.¹⁸

Effect of solvent

The effect of dielectric constant on the rate of the addition reaction was studied by varying water composition in the reaction medium (Table II). The reaction rate increases with the increase in water composition in the reaction medium in both cases indicating the formation of polar transition state. In the transition state the negative charge is delocalised into the NO₂ moiety. The plot of log kobs versus 1/D (D = total dielectric constant of the medium) was found to be linear (r = 0.975; slope = -3.45 for β-nitrostyrene and r = 0.994; slope = -1.64 for β-methyl-β-nitrostyrene). The negative slope of the plot indicates that the reaction occurs between dipolar molecules in both the reactions. Solvent effect has been taken as evidence for the formation of a charge-separated activated complex in the rate-determining step in these reactions.

Substituents effect

In order to understand the electronic effects of para-substituents on the addition reactions and to gain more information regarding the nature of the transition state, the rate of addition of thiophenol to several para-substituted β-nitrostyrenes and β-methyl-β-nitrostyrenes have been measured at different temperatures viz., 25°C, 30°C, 35°C and 40°C and the relevant data are presented in Tables III and IV. Analysis of equilibrium constant values (K) in Table IV reveals that temperature has no effect on these values for both reaction series even though they proceed through different reaction paths.

The rate data clearly indicate that the electron-withdrawing substituents increase the rate while electron-releasing substituents retard it in both the cases. Comparing the rate constant, k_c, of β-nitrostyrene with that of β-methyl-β-nitrostyrene it is found that the k_c value is higher for β-nitrostyrene than for β-methyl-β-nitrostyrene (Table III). The equilibrium constant is
also higher for β-nitrostyrene (Table IV). This may be due to the deactivation of the carbon-carbon double bond by electron-releasing methyl group in the β-position of the β-methyl-β-nitrostyrene, making the α-carbon less electrophilic. The validity of the Hammett equation in this reaction has been tested by correlating the rate constants with the Hammett σ-constants. Both $k_c$ and $K$ values were correlated separately with the Hammett σ-constants. When log $k_c$ values are correlated with the Hammett σ-constants, a fairly good correlation is obtained for the addition reactions of β-nitrostyrenes ($r = 0.852$; $\rho = 0.967$; $s = 0.063$; $\psi = 0.285$; $n = 10$ at $35^\circ C$). The correlation is improved when exalted sigma constants are used for electron-releasing substituents ($\rho = 0.562$; $r = 0.994$; $s = 0.047$; $\psi = 0.122$; $n = 10$ at $35^\circ C$) as the electron-releasing substituents largely stabilise the reactant through mesomeric interaction. The equilibrium constant ($K$) values are also correlated well with the Hammett σ-constants for the reaction of β-nitrostyrene if the p-NO$_2$ substituent is not included ($\rho = 0.844$, $r = 0.987$, $s = 0.053$, $\psi = 0.180$; $n = 9$ at $35^\circ C$).

The value of $K$ for p-NO$_2$ substituent in β-nitrostyrene is much lower than expected in terms of its σ-constant (Table IV). In the case of β-methyl-β-nitrostyrene all the K values fit into the Hammett plot including p-nitro derivative. Generally in β-nitrostyrene α-carbon atom is more electrophilic than in β-methyl-β-nitrostyrene due to electron releasing methyl group in β-position. The development of positive charge at α-carbon increases its reactivity with
The rapid formation of zwitterion. This positive charge development is decreased by electron-releasing substituents and increased by electron-attracting substituents at para-position in β-nitrostyrene. This trend is revealed from the K values for the formation of zwitterion in the addition reaction of thiophenol with β-nitrostyrene (Table IV).

But the K value for p-nitro-β-nitrostyrene (K = 0.737 × 10³ dm³ mol⁻¹) is even lower than that of β-nitrostyrene (K = 0.818 × 10³ dm³ mol⁻¹) itself at 35°C. Nitro group at para-position increases further the development of positive charge at α-carbon due to inductive and resonance effect. However, the development of such kind of positive charge at α-carbon does not favour the formation of zwitterionic intermediate in the case of p-nitro-β-nitrostyrene. The transition state leading to zwitterion is less stabilised than expected. In β-methyl-β-nitrostyrene the extent of development of positive charge on α-carbon has been reduced by the presence of methyl group at β-carbon and hence good correlation is obtained including the K value for p-nitro derivative.

For the addition reaction of β-methyl-β-nitrostyrene with thiophenol good correlation is obtained when log \( k_e \) values are plotted against the Hammett \( \sigma \)-constants (\( \rho = 0.843 \pm 0.036; \ r = 0.994; \ s = 0.053; \ \psi = 0.122; \ n = 10 \) at 35°C). The equilibrium constants K also correlate well with the Hammett \( \sigma \)-constants (\( \rho = 1.091, \ r = 0.996, \ s = 0.051, \ \psi = 0.100; \ n = 10 \) at 35°C).

**Thermodynamic parameters**

Activation parameters were also evaluated from the plot of log \( k_e \) versus 1/T for both cases and the relevant data are presented in Table V. The \( \Delta S \)' values are all negative as expected for bimolecular reactions but they do not remain constant within the series. In such cases the variation of \( \Delta S \)' is linearly related to changes in \( \Delta H \) by compensation plot²⁹. The plot of \( \Delta H \) against \( \Delta S \)' is linear (\( r = 0.975 \) for β-nitrostyrene and \( r = 0.989 \) for β-methyl-β-nitrostyrene). The existence of linear relationship between \( \Delta H \) and \( \Delta S \)' indicates that a single mechanism is operating throughout these two series. The \( \Delta S \)' values are higher for β-methyl-β-nitrostyrenes than β-nitrostyrenes. This is due to the greater solvation of the transition state in β-methyl-β-nitrostyrene than in β-nitrostyrene as there is larger delocalisation involving the NO₂ group.

As explained by Exner²¹ the isokinetic relationship in the addition reaction of thiophenol to β-nitrostyrene and β-methyl-β-nitrostyrene has been examined from the plot of log \( k_e \) (40°C) versus log \( k_e \) (25°C). The plots of log \( k_e \) (40°C) versus log \( k_e \) (25°C) are linear for both the series (\( r = 0.998 \) for β-nitrostyrene and \( r = 0.999 \) for β-methyl-β-nitrostyrene). From these Exner plots, the isokinetic temperatures (\( \beta \)) were calculated as 197 K for β-nitrostyrenes and 205 K for β-methyl-β-nitrostyrenes.

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