PART II

OXIDATIONS BY STABLE METAL COMPLEX
Chapter II

Oxidation of Vanillin by Hexacyanoferrate(III) in Aqueous Alkaline Medium
Since hexacyanoferrate(III) is a weak oxidant; has been widely used to oxidize numerous organic and inorganic compounds in alkaline media. The authors\textsuperscript{1,2} have suggested that alkaline hexacyanoferrate(III) ([Fe(CN)\textsubscript{6}]\textsuperscript{3-}) ion simply acts as an electron-abstracting reagent in redox reactions. However, Speakman and Water\textsuperscript{3} have suggested different paths of oxidation of aldehydes, ketones and nitroparaffines. Singh and co-workers\textsuperscript{4,5}, while discussing the oxidations of formaldehydes, acetones and ethyl methyl ketone have suggested that the oxidation takes place \textit{via} an electron transfer process resulting in the formation of a free radical intermediate.
3-methoxy-4-hydroxy benzenaldehyde, commercially called p-vanillin and in general vanillin (VAN), occurs in nature as a glucoside, which hydrolyzes to vanillin and sugar. It is a very popular flavouring reagent in the food industry and it is also useful in the synthesis of drugs; 40% of vanillin is consumed in manufacturing drugs such as Aldomet, L-dopa, and Trimethaprim. Vanillin is also used in the preparation of perfume and as a catalyst to polymerize methyl methacrylate. Vanillin has both phenolic and an aldehydic groups and is capable of undergoing three different types of reactions: those of aldehydic group, the phenolic hydroxyl, and aromatic nucleus. The aldehydic group undergoes certain typical aldehyde condensation reactions that allows various substitutions for the aldehyde group. The aldehydic group can also be partially or completely reduced. However, as a p-hydroxybenzaldehyde, vanillin does not undergo some very common aldehyde reactions, such as the Cannizzaro’s reaction and the bezoin condensation. If the hydroxyl group in vanillin is protected, it undergoes oxidation to vanillic acid. As a phenol, vanillin forms esters and ethers, and the nucleus is easily substituted by halogen and nitro groups. In comparison with most other aldehydes, vanillin is notable for its stability. Literature reveals that there are no reports on oxidation of vanillin except in a single case. Hence, in order to explore the mechanistic aspects of hexacyanoferrate(III) oxidation in alkaline medium, we have chosen vanillin as a substrate. The present work deals with the title reaction to investigate the redox chemistry of hexacyanoferrate(III) in such medium, and to arrive at suitable mechanism for the oxidation of vanillin by alkaline hexacyanoferrate(III).
EXPERIMENTAL

Materials and Methods

All chemicals used were of reagent grade. Doubly distilled water (from KMnO₄ in all-glass apparatus) was used throughout the work. Purity of the sample is checked by its melting point. Solution of vanillin (s. d-fine) was prepared by dissolving appropriate amount of recrystallised¹⁴ sample in distilled H₂O. A solution of [Fe(CN)₆]³⁻ was prepared by dissolving K₃[Fe(CN)₆] (BDH) in H₂O and standardized¹⁵a by adding 10 % KI solution in presence of zinc sulphate and the liberated iodine was titrated with standard sodium thiosulphate solution. The product, [Fe(CN)₆]⁴⁻ solution was prepared by dissolving pure samples of K₄[(Fe(CN)₆) and its concentration was checked¹⁵b volumetrically by titrating against standard ceric ammonium sulphate solution in sulphuric acid medium; N-phenylantranilic acid was used as an indicator. Another product vanillic acid was prepared by dissolving the crystals of vanillic acid sample (s. d-fine) in distilled water. NaOH and NaClO₄ were employed to maintain required alkalinity and ionic strength respectively. NaClO₄ solution is prepared by mixing equal [HClO₄] and [NaOH] solutions. Its pH is determined as 7. NaOH solution is prepared by dissolving required quantity of sample in distilled water and standardized using standard methods¹⁵.
Kinetics

All kinetic measurements were performed under pseudo first-order conditions where [Vanillin] was always in excess over [Fe(CN)$_6$]$^{3-}$ at a constant ionic strength of 0.80 mol dm$^{-3}$ in alkaline medium at a constant temperature of 30 ± 0.1 °C, respectively unless otherwise stated. The reaction was initiated by mixing the thermostatted solutions of [Fe(CN)$_6$]$^{3-}$ and vanillin solutions, which also contained the required concentrations of NaOH and NaClO$_4$. The progress of the reaction was followed spectrophotometrically by measuring decrease in the absorbance of [Fe(CN)$_6$]$^{3-}$ using Hitachi 150-20 spectrophotometer at its absorbance maximum, 420 nm, as a function of time where other constituents of the reaction mixture do not absorb significantly (Fig. II(1)(p.50)). An example run is given in Table II(1)(p.51). The application of Beer's law for [Fe(CN)$_6$]$^{3-}$ at 420 nm under the reaction condition verified in the range of 1.0 x 10$^{-4}$ to 1.0 x 10$^{-3}$ mol dm$^{-3}$ giving ε = 1060 ± 20 dm$^3$ mol$^{-1}$ cm$^{-1}$ (Fig. II(2)(p.52)). Pseudo first order rate constants, k$_{obs}$ were obtained from the slopes of plots of log [Fe(CN)$_6$]$^{3-}$ versus time; the plots were linear upto 40% completion of the reaction in alkaline medium and the k$_{obs}$ values were reproducible within ± 5%; deviation from linearity above 40% of reaction was due to the retarding effect of one of the products, [Fe(CN)$_6$]$^{4+}$ (discussed elsewhere). The results are also interpreted in terms of the initial rate of the reaction to avoid the complexities, which may arise due to interference by the product like [Fe(CN)$_6$]$^{4+}$. Initial rates were obtained from the tangents at the initial stages of concentration versus time curves by the plane mirror method$^{16}$ and were reproducible to within ± 5%. However, the k$_{obs}$ values were used to interpret the results throughout the study.
Figure II(1)

Spectrum of potassium hexacyanoferrate(III) in aqueous alkaline medium at 30 °C.

\[ [\text{Fe(CN)}_6^{3-}] = 4.0 \times 10^{-4}; \quad [\text{OH}^-] = 0.80; \]
\[ I = 0.80 \text{ mol dm}^{-3}. \]
Table II(1)

Example run for the oxidation of vanillin by hexacyanoferrate(III) in aqueous alkaline medium at 30°C.

\[ [\text{VAN}] = 4.0 \times 10^{-3}; \quad [\text{Fe(CN)}_6^{3-}] = 4.0 \times 10^{-4}; \]

\[ [\text{OH}^-] = 0.80; \quad \text{I} = 0.80 / \text{mol dm}^{-3}. \]

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Optical density (420 nm)</th>
<th>$[\text{Fe(CN)}_6^{3-}] \times 10^4$ (mol dm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.424</td>
<td>4.00</td>
</tr>
<tr>
<td>1.0</td>
<td>0.326</td>
<td>3.08</td>
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<tr>
<td>2.0</td>
<td>0.286</td>
<td>2.70</td>
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<td>3.0</td>
<td>0.258</td>
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<tr>
<td>4.0</td>
<td>0.236</td>
<td>2.23</td>
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<td>5.0</td>
<td>0.217</td>
<td>2.05</td>
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<tr>
<td>6.0</td>
<td>0.201</td>
<td>1.90</td>
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<td>7.0</td>
<td>0.187</td>
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<td>8.0</td>
<td>0.176</td>
<td>1.66</td>
</tr>
<tr>
<td>9.0</td>
<td>0.164</td>
<td>1.55</td>
</tr>
<tr>
<td>10</td>
<td>0.156</td>
<td>1.47</td>
</tr>
<tr>
<td>11</td>
<td>0.149</td>
<td>1.41</td>
</tr>
<tr>
<td>12</td>
<td>0.143</td>
<td>1.35</td>
</tr>
</tbody>
</table>
Verification of Beer's law at 420 nm with freshly prepared potassium hexacyanoferrate(III) in aqueous alkaline medium at 30 °C.

\[ [\text{Fe(CN)}_6^{3-}] = 4.0 \times 10^{-4}; \quad [\text{OH}^-] = 0.80; \]

\[ I = 0.80 \text{ / mol dm}^{-3}. \]
In view of modest concentrations of alkali used in the reaction medium, attention was also given to the effect of the surface of the reaction vessels on the kinetics. Use of polythene / acrylic ware and quartz or polyacrylate cells gave the same results as glass vessels and cells, indicating that the surfaces play no significant role on the reaction rate.

The effect of dissolved oxygen on the rate of reaction was checked by preparing the reaction mixture and following the reaction in an atmosphere of air and nitrogen. No significant difference between the results obtained under nitrogen and in presence of air was observed. In the view of ubiquitous contamination of CO$_3^{2-}$, its effect was also studied on the rate of reaction. Added CO$_3^{2-}$ up to 1.0 x 10$^{-3}$ mol dm$^{-3}$ showed no effect on reaction rate. However, fresh solutions were used while performing the experiment.

**Stoichiometry and Product Analysis**

Reaction mixtures with different sets of concentrations of [Fe(CN)$_6$]$_3^-$ and [Vanillin] at a constant ionic strength and alkali were kept for about 6 hours at 30 ± 0.1 °C in a closed vessel. When the [Fe(CN)$_6$]$_3^-$ was in excess its concentration was assayed spectrophotometrically by measuring the absorbance at 420 nm. The results indicated that two moles of [Fe(CN)$_6$]$_3^-$ consumed one mole of vanillin as in equation (1).

\[
\text{CHO} + 2 \text{[Fe(CN)$_6$]$_3^-$} + 4\text{OH}^- \rightarrow \text{COO}^- + 2 \text{[Fe(CN)$_6$]$_4^{3+}$} + 3\text{H}_2\text{O} \quad (1)
\]
The stoichiometric ratio suggests that the main reaction products are vanillic acid and [Fe(CN)$_6$]$^{4-}$. The vanillic acid is identified$^{17}$ by its spot test as in earlier work$^{13}$. It was also isolated$^{17}$ by acidifying the reaction mixture followed by ether and ethyl acetate extraction. Each extract was dehydrated with anhydrous Na$_2$SO$_4$ and decanted, the solvent was removed by evaporation. The residue is recrystallised from warm glacial acetic acid. It was confirmed by its melting point 206 °C (Lit. M. P. (208 ± 2) °C) and by IR spectrum (>C=O stretching at 1686 cm$^{-1}$ and -OH stretching at 3486 cm$^{-1}$). The other product, [Fe(CN)$_6$]$^{4-}$ was estimated$^{15b}$ by titrating against Ce(IV) solution.

RESULTS

Reaction Order

The order with respect to [Vanillin] and [alkali] were found by log $k_{obs}$ versus log (concentration) plots; and the obtained orders were also confirmed by differential method from the slope of the plot log(-dc/dt) versus log(concentration) using the equation log(± dc/dt) = logk + n logc, where 'n' is order of reaction.

Effect of [Hexacyanoferrate(III)]

The [Fe(CN)$_6$]$^{3-}$ was varied in the range, 8.0 x 10$^{-5}$ to 8.0 x 10$^{-4}$ mol dm$^{-3}$ at fixed [Vanillin], [OH$^-]$ and ionic strength (Table II(2)(p.55)). The non-variation in the pseudo-first order rate constant at various concentrations of [Fe(CN)$_6$]$^{3-}$ indicates, the order in [Fe(CN)$_6$]$^{3-}$ as unity (Fig. II(3)(p.56)). This was also confirmed from the linearity of plots of log (O.D) versus time ($r = 0.9886$ and s ≤ 0.005) up to 40% completion of the reaction.
Table II(2)

Effect of variation of [Fe(CN)₆]³⁻ and [Vanillin] on oxidation of vanillin by hexacyanoferrate(III) in aqueous alkaline medium at 30 °C.

\[ [\text{OH}^-] = 0.80; \quad I = 0.80 \text{ / mol dm}^{-3}. \]

<table>
<thead>
<tr>
<th>[Fe(CN)₆]³⁻ × 10⁴ (mol dm⁻³)</th>
<th>[Vanillin] × 10³ (mol dm⁻³)</th>
<th>( k_{\text{obs}} \times 10³ ) (s⁻¹)</th>
<th>Found</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
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<td>2.26</td>
<td>2.20</td>
<td></td>
</tr>
<tr>
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<td>4.0</td>
<td>2.54</td>
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</tr>
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<td></td>
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<td>3.03</td>
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<td>4.0</td>
<td>10</td>
<td>3.40</td>
<td>3.27</td>
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</tbody>
</table>
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Figure II(3)
First order plots of oxidation of vanillin by hexacyanoferrate(III) at various $[\text{Fe(CN)}_6]^{3-}$ in aqueous alkaline at 30 °C at 420 nm.

(Conditions as in Table II(2)(p.55)).

$[\text{Fe(CN)}_6]^{3-} = (1) \ 0.8 \times 10^{-4}, \ (2) \ 1.0 \times 10^{-4}, \ (3) \ 2.0 \times 10^{-4}, \ (4) \ 4.0 \times 10^{-4}, \ (5) \ 6.0 \times 10^{-4} \ \text{and} \ (6) \ 8.0 \times 10^{-4} / \text{mol dm}^{-3}$.
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Effect of [Vanillin]

The substrate, [Vanillin] was varied in the range, $1.0 \times 10^{-3}$ to $1.0 \times 10^{-2}$ mol dm$^{-3}$ at 30 °C keeping all other reactants’ concentrations and conditions constant (Table II(2)(p.55). The $k_{obs}$ values increased with increase in concentration of vanillin indicating an apparent less than unit order dependence on [Vanillin] ($\approx 0.6$) and was obtained from the plot of log $k_{obs}$ versus log [Vanillin] (Fig. II(4-A)(p.58)).

Effect of [Alkali]

The effect of [OH$^-$] on the rate of reaction was studied at constant [Vanillin], [Fe(CN)$_6$]$^{3-}$ and ionic strength of 0.80 mol dm$^{-3}$ at 30 °C. The rate constants increased with increase in [OH$^-$] and order was found to be less than unity ($\approx 0.6$) (Table II(3)(p.58) and (Fig. II(4-B)(p.59)).

Effect of Ionic Strength and Solvent Polarity

The effect of ionic strength was studied by varying the [NaClO$_4$] in the reaction medium. The ionic strength of the reaction medium was varied from 0.80 to 3.0 mol dm$^{-3}$ at constant [Fe(CN)$_6$]$^{3-}$, [Vanillin] and [OH$^-$]. It was found that as ionic strength increases the rate of the reaction increases (Table II(4)(p.60). The plot of log $k_{obs}$ versus $\bar{V}$ was linear with slope 0.5 (Fig. II(5-A)(p.61)). The dielectric constant (D) effect on the reaction medium was studied by varying the t-butyl alcohol-water content in the reaction mixture with all other conditions being constant. Attempts to measure the dielectric constants at various concentrations of alcohol and water (v/v) were not successful. However, they were computed from the values of pure liquids as in earlier work$^{18}$ using the following equation (p.62).
Table II(3)

Effect of \([OH^-]\) and \([Fe(CN)_6]^{4-}\) on the oxidation of vanillin by alkaline hexacyanoferrate(III) in aqueous alkaline medium at 30 °C.

\[
[VAN] = 4.0 \times 10^{-3}; \quad [Fe(CN)_6]^{3-} = 4.0 \times 10^{-4};
\]

\[I = 0.80 / \text{mol dm}^{-3};\]

<table>
<thead>
<tr>
<th>([OH^-]) (mol dm(^{-3}))</th>
<th>([Fe(CN)_6]^{4-}) x 10(^4) (mol dm(^{-3}))</th>
<th>(k_{obs} \times 10^3) s(^{-1})</th>
<th>Found</th>
<th>Calculated</th>
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<td>1.10</td>
<td>1.10</td>
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<td>-</td>
<td></td>
</tr>
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<td>0.6</td>
<td>1.80</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>0.80</td>
<td>0.8</td>
<td>1.75</td>
<td>-</td>
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<td>0.80</td>
<td>1.0</td>
<td>1.71</td>
<td>-</td>
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</table>
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Figure II(4)

A: Order in [VAN] on the oxidation of vanillin by hexacyanoferrate(III) in aqueous alkaline medium at 30 °C.

(Conditions as in Table II(2)(p.55))

B: Order in [OH'] on the oxidation of vanillin by hexacyanoferrate(III) in aqueous alkaline medium at 30 °C.

(Conditions as in Table II(3)(p.58))
### Table II(4)

Effect of variation of ionic strength (I) on the oxidation of vanillin by hexacyanoferrate(III) in aqueous alkaline medium at 30 °C.

\[
\text{[VAN]} = 4.0 \times 10^{-3}; \quad \text{[Fe(CN)₆]^{3-}} = 4.0 \times 10^{-4}; \\
\text{[OH']} = 0.80 / \text{mol dm}^{-3}.
\]

<table>
<thead>
<tr>
<th>I (mol dm⁻³)</th>
<th>√I</th>
<th>(k_{\text{obs}} \times 10^3) (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>0.89</td>
<td>2.27</td>
</tr>
<tr>
<td>1.0</td>
<td>1.0</td>
<td>2.60</td>
</tr>
<tr>
<td>1.2</td>
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<td>1.3</td>
<td>3.49</td>
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<tr>
<td>3.0</td>
<td>1.7</td>
<td>6.16</td>
</tr>
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</table>
Chapter II

A. Effect of ionic strength (I) on the oxidation of vanillin by hexacyanoferrate(III) in aqueous alkaline medium at 30 °C.

(Conditions as in Table II(4)(p.60))

B. Effect of dielectric constant (D) on the oxidation of vanillin by hexacyanoferrate(III) in aqueous alkaline medium at 30 °C.

(Conditions as in Table II(5)(p.63))
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\[ D = D_1 V_1 + D_2 V_2 \]

where \( V_1 \) and \( V_2 \) are volume fractions and \( D_1 \) and \( D_2 \) are dielectric constants of water and t-butyl alcohol as 78.5 and 10.9 at 25 \(^\circ\)C respectively. Earlier it was confirmed that there was no reaction of the solvent with the oxidant under the experimental conditions used. The rate constants, \( k_{\text{obs}} \) were decreased with decrease in the dielectric constant of the medium (Table II(5)(p.63). The plot of \( \log k_{\text{obs}} \) versus \( 1/D \) was linear (Fig. II(5-B)(p.61)) \((r = 0.9829 \text{ and } s \leq 0.005)\).

**Effect of Initially Added Products**

The effect of initially added products, vanillic acid and \([\text{Fe(CN)}_6]^{4-}\) on the rate of reaction was also studied in the concentration range, \(1.0 \times 10^{-4} \text{ to } 1.0 \times 10^{-3} \text{ mol dm}^{-3}\) at 30 \(^\circ\)C at constant \([\text{Fe(CN)}_6]^{3-}\), [Vanillin], [OH\(^{-}\)] and ionic strength. The added vanillic acid did not alter the rate of reaction. However, \([\text{Fe(CN)}_6]^{4-}\) had shown a retarding effect on rate of reaction (Table II(3)(p.58). The order was found to be \(\approx 0.3\) (Fig. II(6)(p.64)).

**Effect of Temperature**

The kinetics were studied at 30, 35, 40 and 45 \(^\circ\)C at \([\text{Fe(CN)}_6]^{3-} = 4.0 \times 10^{-4} \text{ mol dm}^{-3}\), [Vanillin] = \(4.0 \times 10^{-3} \text{ mol dm}^{-3}\), [OH\(^{-}\)] = \(0.80 \text{ mol dm}^{-3}\), \(I = 0.80 \text{ mol dm}^{-3}\), resulting in \(k_{\text{obs}}\) are tabulated in (Table II(6)(p.65).
Table II(5)

Effect of variation of dielectric constant (D) on the oxidation of vanilin by hexacyanoferrate(III) in aqueous alkaline medium at 30 °C.

\[
\begin{align*}
[VAN] &= 4.0 \times 10^{-3}; & [Fe(CN)_{6}]^{3-} &= 4.0 \times 10^{-4}; \\
[OH^-] &= 0.80; & I &= 0.80 / \text{mol dm}^{-3}
\end{align*}
\]

| Water (%) | t-butyl alcohol-water (%) v/v | D \( \times 10^3 \) & \( k_{obs} \times 10^3 \) (s\(^{-1}\)) |
|-----------|-----------------------------|------------------|------------------|
| 100       | 0                           | 78.5             | 2.26             |
| 95        | 5                           | 75.1             | 2.13             |
| 90        | 10                          | 71.7             | 2.00             |
| 85        | 15                          | 68.4             | 1.87             |
| 80        | 20                          | 65.0             | 1.74             |
Figure II(6)

Effect of product, $[\text{Fe(CN)}_6]^{4-}$ on the oxidation of vanillin by hexacyanoferrate(III) in aqueous alkaline medium at $30 \, ^\circ\text{C}$

(Conditions as in Table II(3)(p.58)).
Table II(6)

A. Effect of temperature on the oxidation of vanillin by hexacyanoferrate(III) in aqueous alkaline medium.

\[
\begin{align*}
[VAN] &= 4.0 \times 10^{-3}; \\
[Fe(CN)_6]^{3-} &= 4.0 \times 10^{-4}; \\
[OH^-] &= 0.80; \\
I &= 0.80 / \text{mol dm}^{-3}.
\end{align*}
\]

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>( k_{\text{obs}} \times 10^3 ) (s(^{-1}))</th>
<th>( \log k_{\text{obs}} ) (Y)</th>
<th>( 1/T \times 10^3 ) (X)</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>2.27</td>
<td>-2.6436</td>
<td>3.300</td>
</tr>
<tr>
<td>308</td>
<td>2.55</td>
<td>-2.5938</td>
<td>3.247</td>
</tr>
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<td>313</td>
<td>2.80</td>
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<td>3.195</td>
</tr>
<tr>
<td>318</td>
<td>3.15</td>
<td>-2.5017</td>
<td>3.145</td>
</tr>
</tbody>
</table>

B. Activation parameters for the oxidation of vanillin by hexacyanoferrate(III) in aqueous alkaline medium.

\[
\begin{align*}
[VAN] &= 4.0 \times 10^{-3}; \\
[Fe(CN)_6]^{3-} &= 4.0 \times 10^{-4}; \\
[OH^-] &= 0.80; \\
I &= 0.80 / \text{mol dm}^{-3}.
\end{align*}
\]

<table>
<thead>
<tr>
<th>( E_a ) (k J mol(^{-1}))</th>
<th>( \Delta H^\circ ) (k J mol(^{-1}))</th>
<th>( \Delta S^\circ ) (J K(^{-1}) mol(^{-1}))</th>
<th>( \Delta G^\circ ) (k J mol(^{-1}))</th>
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</thead>
<tbody>
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<td>17 ± 0.2</td>
<td>15 ± 0.2</td>
<td>-247 ± 10</td>
<td>91 ± 4</td>
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</tbody>
</table>
The activation energy for the reaction were calculated by using linear regression analysis (also known as method of least square). In generalized notation, the formula for the straight line is \( y = ax + b \). The most tractable form of linear regression analysis assumes that values of the independent variables ‘x’ are known without error and that experimental error is manifested only in values of the dependent variable ‘y’. Most sets of kinetic data approximate this situation, in as much as times of observation are more accurately measurable than the chemical or physical quantities related to reactant concentrations. The straight line selected by the common linear regression analysis is that which minimises the sum of the squares of the derivations of the ‘y’ variable from the line.

The slope ‘a’ and intercept ‘b’ parameters for the above equation can be calculated by linear regression analysis by any of several mathematically equivalent but different looking experiments. Most familiar are

\[
\text{Slope} : a = \frac{n \Sigma xy - \Sigma x \Sigma y}{n \Sigma x^2 - (\Sigma x)^2}
\]

\[
\text{Intercept} : b = \frac{\Sigma y \Sigma x^2 - \Sigma x \Sigma xy}{n \Sigma x^2 - (\Sigma x)^2}
\]

where ‘n’ is the number of data points and summation are for all data points in the set. These data were subjected to least square analysis and verified with experimental values. The activation energy was evaluated from the plot of \( \log k_{\text{obs}} \) versus \( 1/T \) as shown in Fig. II(7)(p.67) and are tabulated in Table II(6)(p.65). The activation energy of the reaction was calculated from the slope as

\[
E_a = -2.303 \times R \times \text{slope}
\]
Chapter II

Figure II(7)

Effect of temperature on the oxidation of vanillin by hexacyanoferrate(III) in aqueous alkaline medium.

(Data from Table II(6)(p65))
The other activation parameters were calculated as follows.

The Arrhenius factor ‘A’ was calculated by,
\[ \log A = \log k_{\text{obs}} + \frac{E_a}{2.303RT} \]

The entropy of activation was calculated by using the equation,
\[ k_{\text{obs}} = \left( \frac{kT}{h} \right) e^{\frac{\Delta S^\#}{R}} e^{-\frac{E_a}{RT}} \]

2.303 \log k_{\text{obs}} = 2.303 \log \left( \frac{k}{h} \right) + \frac{\Delta S^\#}{R} - \frac{E_a}{2.303RT}

\[ \log k_{\text{obs}} = \log \left( \frac{k}{h} \right) + \log T + \frac{\Delta S^\#}{2.303R} - \frac{E_a}{2.303RT} \]

\[ \frac{\Delta S^\#}{2.303R} = \log k_{\text{obs}} - \log \left( \frac{k}{h} \right) - \log T + \frac{E_a}{2.303RT} \]

On substituting the universal gas constant ‘R’ as 8.314 J K^{-1} mol^{-1}, the Boltzmann constant (k) = 1.3807 \times 10^{-23} J K^{-1} and the Plank’s constant (h) = 6.63 \times 10^{-34} J \text{ sec}.

\[ \frac{\Delta S^\#}{2.303 \times 8.314} = \log k_{\text{obs}} - \log \frac{1.3807 \times 10^{-23}}{6.63 \times 10^{-34}} - \log T + \frac{E_a}{2.303 \times 8.314 \times T} \]

\[ \frac{\Delta S^\#}{19.147} = \log k_{\text{obs}} - \log 11.753 - \log T + \frac{E_a}{19.147 \times T} \]

The \( k_{\text{obs}} \) should be in s^{-1}, the temperature in Kelvin, \( E_a \) results in J mol^{-1}; then \( \Delta S^\# \) J K^{-1} mol^{-1}.

The enthalpy of activation was calculated by,
\[ \Delta H^\# = E_a - RT \]

And the free energy of activation was from \( \Delta G^\# = \Delta H^\# - T\Delta S^\# \).
**Test for Free Radicals**

Since the reaction is of a non complementary type, the intervention of free radical during reaction is expected. It was tested by adding a monomer, acrylonitrile and kept for 24 hours under nitrogen atmosphere during the course of reaction and on diluting with methanol no copious precipitate was obtained. It is contrary to the expectation and discussed elsewhere.

**DISCUSSION**

The overall reaction is approximately second order, being first order in oxidant, fractional order each in vanillin and OH and the retarding effect of hexacyanoferrate(II) can be accommodated in the following Scheme 1.

\[
\begin{align*}
\text{C—H} & \quad \text{OCH}_3 \\
\text{OH} & \quad \text{OCH}_3 \\
\text{+ OH}^- & \quad \text{+ H}_2\text{O} \\
\end{align*}
\]

\[
\begin{align*}
\text{C—H} & \quad \text{OCH}_3 \\
\text{OH} & \quad \text{OCH}_3 \\
\text{+ [Fe(CN)}_6\text{]^{3-}} & \quad \text{Complex(C)} \quad \text{+ CN}^- \\
\end{align*}
\]

\[
\text{Complex(C)} \xrightarrow{k \text{ slow}} \text{OCH}_3
\]
The probable structure of the complex is

\[
\begin{align*}
\text{Scheme 1}
\end{align*}
\]

The oxidation of hexacyanoferrate(III) resembles with Cu(II) in which reaction occurs through intervention of free radical with rapid oxidation^{19-21}. The
redox potential of the \([\text{Fe(CN)}_6]^{3-}\)-[\text{Fe(CN)}_6]^{4+}\) is greater than the \(\text{Cu(II)}-\text{Cu(I)}\). Hence, there might be a rapid oxidation of free radical which could mask the polymerization of acrylonitrile. As found experimentally, sometimes the vinyl compounds themselves are oxidized under the experimental conditions used and the test for the free radicals fails\(^{22}\).

The retardation of rate of reaction due to the product, hexacyanoferrate(II) is not shown in the scheme 1. The retardation is only of about 10-15\%, (Table II(3)(p.58), Fig.II(6)(p.64). This may be due to secondary salt effect\(^{23}\) or it readily forms complex with substrate\(^{24}\) compared to hexacyanoferrate(III). This complex may be less reactive than the complex formed between hexacyanoferrate(III) and substrate as shown in the Scheme 1.

In the present study, the oxidation proceeds via, the formation of anion of vanillin; first it forms a complex with oxidant in a prior equilibrium state. This decomposes in a slow step to give a free radical by abstracting hydrogen atom and in the further fast steps anionic form of vanillic acid is formed as shown in Scheme 1. The rate law for Scheme 1 can be derived as,

\[
\text{rate} = -\frac{d[\text{Fe(CN)}_6]^{3-}}{dt} = k \text{ [Complex]}
\]

\[
= kK_2 [\text{VAN}]_d [\text{HCF}]_f
\]

Where, \([\text{VAN}]_d\) is the concentration of deprotonated vanillin and \([\text{HCF}]_f\) is concentration of hexacyanoferrate(III) in free state.

or \(\text{rate} = kK_2 [\text{VAN}]_f [\text{HCF}]_f [\text{OH}^-] \) (2)

\([\text{HCF}]_f = [\text{HCF}]_f + [\text{Complex}]\)
The [VAN]_f and [HCF]_f are calculated as below.

\[ [\text{HCF}]_f = \frac{[\text{HCF}]_r}{1 + K_1 K_2 [\text{VAN}]_r [\text{OH}^-]} \]

Similarly,

\[ [\text{VAN}]_r = [\text{VAN}]_r + [\text{VAN}]_d + [\text{Complex}] \]

\[ [\text{VAN}]_r = [\text{VAN}]_r \{ 1 + K_1 [\text{OH}^-] + K_1 K_2 [\text{OH}^-][\text{HCF}] \} \]

\[ [\text{VAN}]_r = \frac{[\text{VAN}]_r}{1 + K_1 [\text{OH}^-] + K_1 K_2 [\text{OH}^-][\text{HCF}]} \]

\( K_1 K_2 [\text{OH}^-][\text{HCF}] \) can be neglected as HCF is used in very very small concentration. Therefore,

\[ [\text{VAN}]_r = \frac{[\text{VAN}]_r}{1 + K_i [\text{OH}^-]} \]

Thus, on substituting [VAN]_r and [HCF]_r in equation (2), equation (3) results,

\[ \text{Rate} = \frac{d[\text{Fe(CN)}_6]^{3-}}{dt} = \frac{k K_1 K_2 [\text{Fe(CN)}_6]^{3-} [\text{VAN}]_r [\text{OH}^-]_r}{(1 + K_i [\text{OH}^-])(1 + K_1 K_2 [\text{VAN}] [\text{OH}^-])} \]

(3)

The denominator on right hand side of equation (3) should also contain a term \((1 + K_2 [\text{Fe(CN)}_6]^{3-})\) which is neglected as it almost tends to unity due to low concentrations of \([\text{Fe(CN)}_6]^{3-}\) used in the present study. The formation of complex is proved kinetically by the non-zero intercept graph of \(1/k_{\text{obs}}\) versus \(1/[\text{Vanillin}]\) (Table II(2)(p.55), Fig. II(8)(p.73)). The equation (3) can also be written as

\[ k_{\text{obs}} = \frac{k K_1 K_2 [\text{VAN}]_r [\text{OH}^-]_r}{(1 + K_i [\text{OH}^-])(1 + K_1 K_2 [\text{OH}^-][\text{VAN}] )} \]

(4)

or

\[ k_{\text{obs}} = \frac{k K_1 K_2 [\text{VAN}]_r [\text{OH}^-]_r}{1 + K_1 [\text{OH}^-] + K_1 K_2 [\text{OH}^-][\text{VAN}] + K_i^2 K_2 [\text{OH}^-]^2 [\text{VAN}]} \]

(5)

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Figure II(8)

Verification of rate law (6) of oxidation of vanillin by hexacyanoferrate(III) at 30 °C.

(Conditions as in Table II(2)(p.55), Table II(3)(p.58))
The term $K_1^2K_2[OH']^2[VAN]$, in equation (5) can be omitted due to the low concentrations of vanillin and OH'. Thus, equation (5) becomes,

$$
k_{obs} = \frac{kK_1K_2[VAN][OH']}{1 + K_1[OH'] + K_1K_2[OH'][VAN]}
$$

The equation (6) is verified in the following form and the subscripts, T are omitted.

$$
\frac{1}{k_{obs}} = \frac{1}{kK_1K_2[OH'][VAN]} + \frac{1}{kK_2[VAN]} + \frac{1}{k}
$$

The plots of $1/k_{obs}$ versus $1/[OH']$ ($r = 0.999$ and $s < 0.005$) and $1/k_{obs}$ versus $1/[Vanillin]$ ($r = 0.999$ and $s < 0.0048$) should be linear and found to be so in the Fig. II(8)(p.73). From the slopes and intercept of Fig. II(8)(p.73) the constants $k$, $K_1$ and $K_2$ were calculated as $4.8 (\pm 0.2) \times 10^3$ s$^{-1}$, $0.83 (\pm 0.04)$ dm$^3$ mol$^{-1}$ and $517 (\pm 2)$ dm$^3$ mol$^{-1}$ respectively. Using these values in equation (6), the rate constant for various concentrations of $[Fe(CN)_6]^{3-}$, vanillin and OH$^-$ were calculated and compared with experimental values. There is a good agreement between these values (Table II(2)(p.55), (Table II(3)(p.58).

The increasing effect of ionic strength on the rate of the reaction is also in the expected direction as similar charged species, $[Fe(CN)_6]^{3-}$ and anionic form of vanillin are involved in the reaction. The ion pairing between $[Fe(CN)_6]^{3-}$ and $K^+$ is well known$^{18,25}$. Thus the ion pairing between $Na^+$ and $[Fe(CN)_6]^{3-}$ might be reduced the expected value (i.e. 3) of slope (Fig. II(5A))(p.61). The similar ion paring is evidenced by other reactions$^{18,25}$ also.
The effect of solvent on the rate of reaction has been studied. An increase in rate with increase in dielectric constant of the medium supports the involvement of similar charged species (Scheme 1). The activated complex may be more polar than the reactants, $[\text{Fe(CN)}_6]^{3-}$ and vanillin anion which also may be a more solvated in the water than in the low dielectric medium compared to its reactants. The large negative value of $\Delta s^\circ (-247 \text{ J K}^{-1} \text{ mol}^{-1})$ also supports the reaction between highly charged species of $[\text{Fe(CN)}_6]^{3+}$ and vanillin anion to stabilize the activated complex. The activated complex could be more ordered than the reactants. It is also evidence by the small value of ‘k’.

**FINDINGS**

The commercially more valuable vanillin was oxidized by hexacyanoferrate(III) in alkaline medium. This occurs through intervention of free radical with the retarding effect of product, $[\text{Fe(CN)}_6]^{4+}$. The small value of ‘k’ in the rate determining step proves that the activated complex is highly ordered than the reactants which is also supported by the large negative value of $\Delta s^\circ$. The reaction constant like $K$ and $k$ are evaluated and the mechanism is confirmed.
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