Chapter VI

Kinetic and Mechanistic study of oxidation of Indole 3-butyric acid by alkaline Hexacyanoferrate (III)

Oxidation of a variety of organic compounds by potassium hexacyanoferrate (III), (HCF (III)) has been studied by a number of workers\textsuperscript{1-4}. The earlier studies on alkaline HCF (III) oxidation of the organic compounds showed that the anions derived from the organic acids are oxidised by HCF (III) ion\textsuperscript{3}. However Speakman and Waters\textsuperscript{5} have suggested complex mechanism for the oxidation of aldehydes, ketones, and paraffins. Singh and co-workers\textsuperscript{6} suggested that the oxidation of formaldehyde takes place by a free radical mechanism.

Indole 3-butyric acid, (IBA) and such closely related compounds such as indole 3-acetic acid, (IAC) and 1-naphthlene acetic acid, (NAA) are used in horticultural practices such as plant growth regulators. They have a property of promoting root formation when applied to stems and cuttings of some plants. The potassium salts of IBA and NAA, as well as the methyl esters of these compounds, are the most effective forms since they have the advantage of solubility in water\textsuperscript{7}. To the best of our knowledge there are no reports on mechanistic studies of IBA oxidation by any oxidant. In view of the lack of literature on the oxidation of IBA by HCF (III) and in order to explore the mechanistic aspects of HCF (III) oxidation in alkaline medium, we have chosen IBA as a substrate. The present study aims at
getting more definite information regarding the mechanism of oxidation of IBA by alkaline hexacyanoferrate (III) ions on the basis of kinetic results.

EXPERIMENTAL

Since the initial reaction was too fast to monitor by the usual method, kinetic measurements were performed on a Hitachi 150-20 spectrophotometer connected to a rapid kinetic accessory (HI-TECH SFA-12).

Materials and methods

Potassium hexacyanoferrate (III) used was B.D.H. Analar and its standard solution was prepared in doubly distilled water. Its strength was checked iodometrically. Indole 3-butyric acid is insoluble in water, but soluble in aqueous alkaline solution. Therefore the solution of Indole 3-butyric acid (IBA) (S.D.Fine) was prepared by dissolving appropriate amount of sample in dilute NaOH solution. Hexacyanoferrate (II) solution was prepared by dissolving a known amount of K₄Fe(CN)₆ (BDH) in water. Sodium hydroxide (Merck) and sodium perchlorate (BDH) were used to provide the required alkalinity and to maintain the ionic strength, respectively.

Reaction-time curves

The reaction time - curves were found to be of S-shape throughout the entire range of reaction. The initial rates were relatively fast in the early stages, followed by a decrease in the reaction rate over longer time periods. As the reaction is of two stage nature, the oxidation obeys the rate expression \( (A_t - A_\infty) = B_0 e^{-k_f t} + P_0 e^{-k_s t} \). Here, \( k_f \) and \( k_s \) are the first order rate constants for the fast and
slow reactions, while $B_0$ and $P_0$ represent the absorbance change for the fast and slow reacting species, respectively. The rate constants, presented in Table VI(i)(p.200) were obtained by drawing a straight line through the fast time linear portion ($k_t$) of the first-order plot and extrapolating the line back to zero time ($B_0$). The rate of oxidation, $k_s$, for the slow oxidation reaction was obtained from plots of the form $-\ln \left[ (A_t - A_{\infty}) - (A_{t'} - A_{\infty}) \right]$ versus time. The quantity $(A_t - A_{\infty})$ represents the experimental point and $(A_{t'} - A_{\infty})$ represents the extrapolated point at time $t'$ as shown in Figure VI (i) (p.201).

**KINETIC MEASUREMENTS**

All kinetic measurements were performed under pseudo first-order conditions where [indole 3-butyric acid] was always $\geq 10$ fold in excess over [HCF (III)] at a constant ionic strength of 0.50 mol dm$^{-3}$ in alkaline medium at a constant temperature of $25.0 \pm 0.1^\circ C$ respectively. The reaction was initiated by mixing the thermostatted hexacyanoferrate (III) and indole 3-butyric acid solutions which also contained the required amounts of sodium hydroxide and sodium perchlorate. The progress of the reaction was followed by measuring the absorbance of hexacyanoferrate (III) in the reaction solution in a 1cm quartz cell of a thermostatted compartment of a Hitachi model 150-20 spectrophotometer at its absorption maximum, 420 nm as a function of time where the other constituents of the reaction mixture do not absorb significantly. The application of Beer's law for hexacyanoferrate (III) at 420 nm, under the reaction conditions had earlier been verified giving $\varepsilon = 1060 \pm 20$ dm$^3$ mol$^{-1}$ cm$^{-1}$. Pseudo first-order rate constants
Table VI (i)

Effect of variation of [Indole 3-butyric acid], [HCF (III)] and [OH⁻] on the oxidation of indole 3-butyric acid by alkaline hexacyanoferrate (III) at 25°C, I=0.50 mol dm⁻³.

<table>
<thead>
<tr>
<th>[IBA] x 10⁻³ (mol dm⁻³)</th>
<th>[HCF(III)] x 10⁻⁴ (mol dm⁻³)</th>
<th>[OH⁻] x 10⁻¹ (mol dm⁻³)</th>
<th>1st stage</th>
<th>2nd stage</th>
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<tbody>
<tr>
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<td></td>
<td>k_f x 10⁻³ (s⁻¹)</td>
<td>k_f x 10⁻³ (s⁻¹)</td>
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<td>18.1</td>
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<td>11.5</td>
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<td>4.0</td>
<td>2.0</td>
<td>18.5</td>
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*Experimental and Calculated

Error ± 5%
Figure VI (i)

First order plot of (a) $\log (A_t - A_\infty)$ versus time and (b) $\log [(A_t - A_\infty) - (A_t - A_\infty)]$ versus time in alkaline medium, for the oxidation of indole 3-butyric acid by aqueous alkaline hexacyanoferrate (III) at 25°C,

$[\text{HCF (III)}] = 4.0 \times 10^4$, $[\text{IBA}] = 4.0 \times 10^{-3}$, $[\text{OH}^{-}] = 1.0 \times 10^{-1}$ and $I = 5.0 \times 10^{-1}$/mol dm$^{-3}$.
were obtained from the plots of log \((A_t - A_{\infty})\) versus time and the plot of log \([\left( A_t - A_{\infty} \right) - \left( A_t' - A_{\infty} \right)]\), an example run is given in Table VI (ii) (p.203). The plot of log \((A_t' - A_{\infty})\) versus time and the plot of log \([\left( A_t - A_{\infty} \right) - \left( A_t' - A_{\infty} \right)]\) versus time indicates two stage processes and both the stages are linear up to 90% completion of the reaction, and \(k_{obs}\) values were reproducible within ±5%, where the first fast stage follows second slow stage process (Fig. VI (i) (p.201)). Such type of two stage processes are observed in a few cases\(^9\).

In view of the modest concentrations of alkali used in the reaction medium, attenuation 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 with glass vessels and cells, indicating that the surfaces play no important role in the reaction rate.

The effect of dissolved oxygen on the rate of the reaction was checked by preparing the reaction mixture and following the reaction in an atmosphere of nitrogen. No significant difference between the results obtained under nitrogen and in presence of air was observed. In view of the ubiquitous contamination of carbonate in basic solutions, the effect of carbonate on the reaction was also studied. Added carbonate up to \(1.0 \times 10^{-3} \text{ mol dm}^{-3}\) showed no effect on the reaction rate. However, fresh solutions were used while performing the experiments.

In alkaline medium during the progress of the reaction, the colour of the solution changed from yellow to almost colourless, which is verified by titration for HCF (II)\(^10\). A regression analysis of experimental data in order to obtain the regression coefficient, \(r\) and
Table VI (ii)

An Example run for the oxidation of indole 3-butyric acid by aqueous alkaline hexacyanoferrate (III) at 25 °C

\[
[HCF(III)] = 4.0 \times 10^{-4}; \quad [IBA] = 4.0 \times 10^{-3};
\]
\[
[H^+] = 0.10; \quad I = 0.50/\text{mol dm}^{-3}.
\]

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Optical density (420 nm)</th>
<th>( \log (A_r - A_a) )</th>
</tr>
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<td>-0.3990</td>
</tr>
<tr>
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<td>1.8</td>
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Error ± 5%. 

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RESULTS

Stoichiometry and Product Analysis

The reaction mixture containing excess HCF (III) concentration over indole 3-butyric acid were mixed in presence of 0.10 mol dm$^{-3}$ NaOH, adjusted to a constant ionic strength of 0.50 mol dm$^{-3}$ and allowed to react for about 4h at 25.0 ± 0.1°C. The remaining HCF (III) was then analysed spectrophotometrically. The results indicated that eight moles of HCF (III) were consumed by one mole of IBA according to equation (1).

$$\text{CH}_2\text{CH}_2\text{CH}_2\text{C}$$OH + 8[Fe(CN)$_6$]$^{3-}$+ H$_2$O $\rightarrow$ CO$_2$ + 8[Fe(CN)$_6$]=$^{4-}$+ 8 H$^+$

(1)

The reaction product was eluted with ether, and submitted to spot test$^{11}$, which revealed the presence of aldehydic group. The presence of triple bond and –CHO group were also confirmed by finding its IR spectrum$^{12}$. IR (KBr) showed bands at (u) 2057 cm$^{-1}$ for C≡C stretching, 1672 cm$^{-1}$ and 2851 cm$^{-1}$ for carbonyl (>C=O) and –CH stretching respectively. However, the other product in alkaline medium, hexacyanoferrate (II), Fe(CN)$_6$$^4-$, was identified$^{10}$ by a known method.

The product aldehyde does not undergo further oxidation under the present kinetic conditions, since the test for the probable oxidation product of aldehyde i.e. acid was negative.
REACTION ORDERS

The order each in indole 3-butyric acid and alkali was investigated by varying one of these concentrations while keeping all other concentrations and conditions constant and studying the effect of its concentration on the rate of the reaction. The resulting data were employed to plot log $k_{obs}$ versus log concentration graphs and the orders were obtained from such graphs.

Effect of [Hexacyanoferrate (III)]

Kinetic data were collected for initial [HCF (III)] in the (0.60-6.0) x10⁻⁴ mol dm⁻³ range. The reaction followed two stage processes (Fig. VI (i) (p.201)). All the experiments exhibited an identical characteristic, an initial fast reaction followed by a slower one. The plots of log $(A_t - A_\infty)$ versus time and the plot of log $[(A_t - A_\infty) - (A_t' - A_\infty)]$ ($r > 0.9961$, $s \leq 0.02847$ I stage, $r > 0.9981$, $s \leq 0.02811$ II stage) for different initial concentrations of HCF (III) had two distinct straight lines for the fast and slow stages of the reaction. The fairly constant $k_f$ ($s^{-1}$) values for the fast stage and $k_s$ ($s^{-1}$) values for the slow stage confirms that fast and slow depletions in HCF (III) follow first order kinetics (Table VI (i) (p.200)).

Effect of [Indole 3-butyric acid]

The concentration of indole 3-butyric acid was varied in the range of (0.85-8.5) x10⁻³ mol dm⁻³ keeping all other reactants concentrations and conditions constant. In alkaline medium the $k_f$ and $k_s$ values (Table VI (i) (p.200)) increased with increase in concentration of indole 3-butyric acid indicating less then unit order (0.78 I stage, 0.68 II stage, Fig. VI (ii) (p.206)) dependence on [substrate] in
Figure VI (ii)

Order of reaction with respect to [IBA] and [OH\(^{-}\)] on the oxidation of indole 3-butyric acid by aqueous alkaline hexacyanoferrate (III) at 25° C.

(Conditions as in Table VI (i) (p.200)).
both the stages \( (r > 0.9996, s \leq 0.04431 \text{ I stage}, r > 0.9886, s \leq 0.05434 \text{ II stage}) \).

**Effect of [Alkali]**

To study the effect of \([\text{OH}^-]\), on the rate of the reaction, \([\text{OH}^-]\) was varied from \((0.02 - 0.20) \times 10^{-2} \text{ mol dm}^{-3}\) at constant concentration of HCF (III) and indole 3-butyric acid, maintaining a constant ionic strength of \(5.0 \times 10^{-1} \text{ mol dm}^{-3}\). It was found that, in both the stages the rate increased with increase in \([\text{OH}^-]\) concentration (Table VI (i) (p.200). The order in both the stages was less than unity \((0.75 \text{ I stage}, 0.67 \text{ II stage}, \text{Fig. VI (ii) (p.206)}), (r > 0.9991, s \leq 0.03311 \text{ I stage}, r > 0.9977, s \leq 0.03423 \text{ II stage}).

**Effect of Initially Added Reaction Products**

The initial addition of the other product, HCF (II), in the range of \((1.0 - 1.5) \times 10^{-4} \text{ mol dm}^{-3}\) keeping other conditions constant had a retarding effect on the rate of the reaction (Table VI (iii) (p.208)).

**Effect of Ionic Strength**

The effect of ionic strength was studied by varying the sodium perchlorate concentration. The ionic strength of reaction medium was varied from \(0.10\) to \(0.50\) \text{ mol dm}^{-3}\) at constant concentrations of hexacyanoferrate, indole 3-butyric acid and \([\text{OH}^-]\) as given in Table VI (iv) (p.209). It was found that in both the stages the rate constant increased with increasing concentration of \(\text{NaClO}_4\) and the plots of log \(k_{obs}\) versus \(1^{1/2}\) \((r>0.9867, s \leq 0.02516 \text{ I stage}, r>0.9745, s \leq 0.02035 \text{ II stage})\) were linear with positive slope (Fig. VI (iii) (p.210)).
Table VI (iii)

Effect of product, HCF (II) on the oxidation of indole 3-butyric acid by alkaline hexacyanoferrate (III) at 25°C.

\[ [\text{HCF(III)}] = 4.0 \times 10^{-4}, \quad [\text{IBA}] = 4.0 \times 10^{-3}, \quad [\text{OH}^-] = 1.0 \times 10^{-1} \quad \text{and} \quad I = 5.0 \times 10^{1} \text{ mol dm}^{-3} \]

<table>
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<tr>
<th>[HCF(II)] x 10^4 (mol dm^{-3})</th>
<th>1st stage $k_f \times 10^3$ (s^{-1})</th>
<th>2nd stage $k_s \times 10^3$ (s^{-1})</th>
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Table VI (iv)

Effect of variation of ionic strength (I) and solvent polarity (D) on the oxidation of indole 3-butyric acid by aqueous alkaline hexacyanoferrate (III) at 25°C.

\[
\begin{align*}
[HCF(III)] &= 4.0 \times 10^{-4}; \\
[IBA] &= 4.0 \times 10^{-3}; \\
[OH^+] &= 1.0 \times 10^{-1}; \\
I &= 5.0 \times 10^{-1} \text{ mol dm}^{-3}.
\end{align*}
\]

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<th>I (mol dm(^{-3}))</th>
<th>I stage (k_f \times 10^3) (s(^{-1}))</th>
<th>II stage (k_s \times 10^3) (s(^{-1}))</th>
<th>% of t-butanol*</th>
<th>D</th>
<th>I stage (k_f \times 10^3) (s(^{-1}))</th>
<th>II stage (k_s \times 10^3) (s(^{-1}))</th>
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*t-butanol-water (v/v)

Error ± 5%.
Figure VI (iii)

Effect of ionic strength (I) and dielectric constant (D) on the oxidation of Indole 3-butyric acid by aqueous alkaline hexacyanoferrate (III) at 25°C.

(Conditions as in Table VI (iv) (p.209)).
Effect of Solvent Polarity

The relative permittivity (D) effect was studied by varying t-butyl alcohol-water content in the reaction mixture with all other conditions being constant. Attempts to measure the relative permittivity were not successful. However, they were computed from the values of pure liquids\(^{13}\). There is no reaction of the solvent with the oxidant. It was found that in both the stages the rate constant \(k_{\text{obs}}\) decreased with the decrease in the dielectric constant of the medium as given in Table VI (iv) (p.209). The plots of \(\log k_{\text{obs}}\) versus \(1/D\) (\(r > 0.9834\), \(s \leq 0.04610\) \(r > 0.9867\) I stage, \(r > 0.9745\), \(s \leq 0.02035\) II stage) were linear with negative slope (Fig. VI (iii) (p.210)).

Test for Free Radicals

The intervention of free radicals in the reaction was examined as follows. The reaction mixture to which a known quantity of acrylonitrile scavenger had been added initially was kept for one hour in an inert atmosphere. On diluting the reaction mixture with methanol, no precipitate was resulted, indicating the absence of free radical.

Effect of Temperature

The rate of reaction was measured at different temperatures under varying Indole 3-butyric acid (IBA). Indole 3-butyric acid is unstable above 30\(^{\circ}\)C. Therefore effect of temperature was studied at lower temperatures. The rate of reaction decreased with the decrease of temperature. The rate constants, \(k\) of the slow step of scheme 1 was obtained from intercept and slope of \(1/k_{\text{obs}}\) versus
1/[IBA] and used to calculate the activation parameters. The values of k (dm$^3$ mol$^{-1}$ s$^{-1}$) for the 1st. and 2nd. stage, at 10, 15, 20 and 25°C are incorporated in Table VI (v) (p.213). The activation parameters corresponding to these constants were evaluated from the plot of log k (Y*caid.) versus 1/T (Fig. VI (iv) (p.214) r>0.9948, s<0.02195 1 stage, r>0.9891, s<0.0152 II stage) and are tabulated in Table VI (vi a) (p.215).

The thermodynamic quantities for the first equilibrium step in scheme 1 can be evaluated as follows: The hydroxyl ion concentration as in Table VI (i) (p.200) was varied at four different temperatures and the $K_i$ value was determined at each temperature. The values of $K_i \times 10$ (dm$^3$ mol$^{-1}$) were obtained as 2.78, 3.95, 5.25 and 6.03 at 10, 15, 20 and 25°C, respectively. A van’t Hoff’s plot was made for the variation of $K_i$ with temperature (i.e., log $K_i$ versus 1/T, r>0.9859, s<0.0219). The values of thermodynamic quantities are given in Table VI (vi b) (p.215). A comparison of these values with those values obtained for the slow step shows that the reaction before the rate-determining step is fairly slow and involves high activation energy.

**DISCUSSION**

Variation of the concentrations each of the oxidant (HCF (III)), substrate (IBA) and alkali while keeping the others constant showed that the reaction exhibits first - order in oxidant, and less than unit order in substrate and alkali concentrations (Table VI (i) (p.200)).

The reaction between IBA and HCF (III) in NaOH has a stoichiometry of
Table VI (v)

Effect of temperature on the slow step of the mechanism of oxidation of indole 3-butyric acid by alkaline hexacyanoferrate (III).

\[ \text{[HCF(III)]} = 4.0 \times 10^{-4}; \quad \text{[IBA]} = 4.0 \times 10^{3}; \]
\[ \text{[OH]} = 1.0 \times 10^{1}; \quad I = 5.0 \times 10^{1}/\text{mol dm}^3. \]

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<th>Stage II</th>
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<tr>
<td>(K)</td>
<td>(dm$^3$ mol$^{-1}$ s$^{-1}$)</td>
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Calculated.
Figure VI (iv)

Effect of temperature on the slow step of the mechanism of oxidation of indole 3-butyric acid by aqueous alkaline hexacyanoferrate (III).

(Conditions as in Table VI (v) (p.213)).
Table V (vi)

Thermodynamic activation parameters for the oxidation of indole 3-butyric acid by aqueous alkaline hexacyanoferrate (III)

\[[\text{HCF(III)}] = 4.0 \times 10^4; \quad [\text{IBA}] = 4.0 \times 10^4; \]
\[[\text{OH}^-] = 1.0 \times 10^1; \quad I = 5.0 \times 10^{-1} /\text{mol dm}^{-3}.\]

(a) Thermodynamic activation parameters with respect to slow step of scheme 1.

<table>
<thead>
<tr>
<th>Activation parameters</th>
<th>1st stage</th>
<th>1nd stage</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_a) (kJ mol(^{-1}))</td>
<td>28 ± 1</td>
<td>36 ± 2</td>
</tr>
<tr>
<td>(\Delta H^\circ) (kJ mol(^{-1}))</td>
<td>26 ±1</td>
<td>34 ± 1</td>
</tr>
<tr>
<td>Log (A)</td>
<td>3.5 ± 0.2</td>
<td>4.6 ± 0.2</td>
</tr>
<tr>
<td>(\Delta S^\circ) (JK(^{-1}) mol(^{-1}))</td>
<td>-187 ± 6</td>
<td>-166 ± 6</td>
</tr>
<tr>
<td>(\Delta G^\circ) (kJ mol(^{-1}))</td>
<td>81 ± 4</td>
<td>83 ± 3</td>
</tr>
</tbody>
</table>

(b) Thermodynamic quantities with respect to first step of scheme 1.

<table>
<thead>
<tr>
<th>Thermodynamic quantities</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta H) (kJ mol(^{-1}))</td>
<td>37 ± 2</td>
</tr>
<tr>
<td>(\Delta S) (JK(^{-1}) mol(^{-1}))</td>
<td>-119 ± 4</td>
</tr>
<tr>
<td>(\Delta G) (kJ mol(^{-1}))</td>
<td>2.0 ± 0.1</td>
</tr>
<tr>
<td>Error ± 5%</td>
<td></td>
</tr>
</tbody>
</table>

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It has been observed that the presence of ferrocyanide, \([\text{Fe (CN)}_6]^{4-}\), retards the rate of reduction of ferricyanide by IBA. However, the retardation is small, increase in the initial concentration of the ferrocyanide produced only a 4% reduction in rate, and has been attributed to a secondary salt effect\(^{14}\). Based on the experimental results, a mechanism can be proposed for which all the observed orders in each constituent such as [oxidant], [reductant] and [OH\(^-\)] may be well accommodated.

Oxidation of indole 3-butyric acid by hexacyanoferrate (III) in NaOH media is a non-complementary reaction with oxidant undergoing eight equivalent changes. In most of the oxidation reactions, hexacyanoferrate (III) resembles Cu (II), which involves free radical formation and rapidly oxidises it\(^{15-17}\). Hexacyanoferrate (III) – hexacyanoferrate (II) system, which has higher redox potential than Cu (II) - Cu (I), substantiates better possibility of the rapid oxidation of the free radical with hexacyanoferrate (III) in the alkaline medium and the rapid oxidation of the free radicals might completely mask the polymerization. Sometimes the vinyl compounds themselves are oxidised under the experimental conditions used and the test for free radical fails\(^{18}\). In the present study, the experimental results suggest that indole 3-butyric acid reacts with OH\(^-\) in a prior equilibrium step to form an anionic form of IBA, which is evidenced by the earlier work\(^{19}\). The oxidation reaction proceeds via formation of a complex between anionic form of the substrate and oxidant, which decomposes in a slow step to a free radical with the formation of CO\(_2\) and hexacyanoferrate (II). The free radical further reacts with one mole of HCF (III) in aqueous media in a fast step to give another intermediate product,
indole 3-propanol and HCF (II). The intermediate product so formed further reacts
with two moles of HCF (III) in a fast step to give another intermediate product
indole 3-propenol and HCF (II). Indole 3-propenol further reacts with two moles of
HCF (III) in a fast step to give indole 3-propynol as the intermediate product and
HCF (II). The intermediate product so formed in presence of two moles of HCF
(III) undergoes oxidation to the final products, indole 3-propynal and
hydrocyanoferrate (II) (HCF (II)), satisfying the stoichiometric observations. The
results can be accommodated by scheme 1.
Spectroscopic evidence for the complex formation between oxidant and substrate was obtained from UV/Vis spectra of the HCF (III) and HCF (III) - indole 3-butyric acid mixture. A hypsochromic shift of about 8nm from 420 to 412 nm is observed. Analogous effects upon complex formation between a substrate and an oxidant have been observed in other investigations. Further the formation of complex is also proved kinetically by the non-zero intercept of the plot of 1/k_{obs} versus 1/[IBA] (Fig. VI (v) (p.222)). The observed modest enthalpy of activation and a relatively low value of the entropy of activation, as well as a higher rate.
constant for the slow step, indicates that the oxidation presumably occurs \textit{via} inner-sphere mechanism. This conclusion is supported by earlier observations\textsuperscript{21}. Scheme 1 is in accordance with the generally well-accepted principle of noncomplementary oxidations taking place in sequences of one electron steps.

**Scheme 1 leads to the following rate law**

\[ \text{Rate} = k \ [C] \]

\[ = k \ K_1 \ K_2 \ [\text{Fe (CN)}_6^{3-}]_t \ [\text{IBA}]_t \ [\text{OH}^+]_t \]  \hspace{1cm} (2)

\[ [\text{IBA}]_t = [\text{IBA}]_f + [\text{IBA}]^- + [C] \]

\[ = [\text{IBA}]_f + K_1 \ [\text{IBA}] \ [\text{OH}^+] + K_2 \ [\text{Fe (CN)}_6^{3-}]_t [\text{IBA}]^- \]

\[ = [\text{IBA}]_f + K_1 \ [\text{IBA}] \ [\text{OH}^+] + K_1 K_2 \ [\text{Fe (CN)}_6^{3-}]_t [\text{IBA}]_t \ [\text{OH}^+] \]

\[ = [\text{IBA}]_t (1 + K_1 [\text{OH}^+] + K_1 K_2 [\text{Fe (CN)}_6^{3-}]_t [\text{OH}^+]) \]

Therefore \[ [\text{IBA}]_f = [\text{IBA}]_t \]

\[ = \frac{[\text{IBA}]_t}{(1 + K_1 [\text{OH}^+] + K_1 K_2 [\text{Fe (CN)}_6^{3-}]_t [\text{OH}^+])} \]  \hspace{1cm} (3)

\[ [\text{OH}^+]_t = [\text{OH}^+]_f + K_1 K_2 [\text{Fe (CN)}_6^{3-}]_t [\text{IBA}]_t \]

\[ = [\text{OH}^+]_f + K_1 [\text{IBA}] [\text{OH}^+]_f + K_1 K_2 [\text{Fe (CN)}_6^{3-}]_t [\text{IBA}] [\text{OH}^+] \]

\[ = [\text{OH}^+]_f (1 + K_1 [\text{IBA}] + K_1 K_2 [\text{Fe (CN)}_6^{3-}]_t [\text{IBA}]) \]  \hspace{1cm} (4)

\[ [\text{Fe (CN)}_6^{3-}]_t = [\text{Fe (CN)}_6^{3-}]_f + C \]

\[ = [\text{Fe (CN)}_6^{3-}]_f + K_1 K_2 [\text{Fe (CN)}_6^{3-}]_t [\text{IBA}] [\text{OH}^+] \]

\[ = [\text{Fe (CN)}_6^{3-}]_t (1 + K_1 K_2 [\text{IBA}] [\text{OH}^+]) \]

\[ [\text{Fe (CN)}_6^{3-}]_f = \frac{[\text{Fe (CN)}_6^{3-}]_t}{1 + K_1 K_2 [\text{IBA}] [\text{OH}^+]} \]  \hspace{1cm} (5)

Substituting equations (3) (4) and (5) in equation (2)
Rate = \frac{kK_1K_2[\text{Fe (CN)}_6^{3-}][\text{IBA}][\text{OH}^{-}]}{(1+K_i[\text{IBA}][\text{OH}^{-}])[1+K_1[\text{IBA}]+K_1K_2[\text{Fe (CN)}_6^{3-}][\text{OH}^{-}])} (6)

The term \{K_iK_2[\text{Fe(CN)}_6^{3-}][\text{OH}^{-}]\} in the denominator of equation (6) is negligibly small compared to 1+K_i[\text{OH}^{-}] and the term \{1+K_i[\text{IBA}]+K_1K_2[\text{Fe(CN)}_6^{3-}][\text{IBA}]\} in the denominator of equation (6) approximate to unity, in view of low concentration of Fe (CN)_6^{3-} used. Therefore equation (6) becomes

\frac{d[\text{Fe (CN)}_6^{3-}]}{dt} = \frac{kK_1K_2[\text{Fe (CN)}_6^{3-}][\text{IBA}][\text{OH}^{-}]}{(1+K_i[\text{OH}^{-}])[1+K_1K_2[\text{IBA}][\text{OH}^{-}])} (7)

\frac{\text{Rate}}{[\text{Fe (CN)}_6^{3-}]} = k_{\text{obs}} = \frac{kK_1K_2[\text{IBA}][\text{OH}^{-}]}{(1+K_iK_2[\text{IBA}][\text{OH}^{-}]+K_i[\text{OH}^{-}]+K_1^2K_2[\text{IBA}][\text{OH}^{-}]^2)} (8)

In view of the low concentration of OH^-, IBA and low value of K_i, the term

K_i^2K_2[\text{OH}^{-}]^2[\text{IBA}] in the denominator of equation (8) becomes negligibly small compared to unity.

Therefore equation (8) becomes

k_{\text{obs}} = \frac{kK_1K_2[\text{IBA}][\text{OH}^{-}]}{(1+K_1K_2[\text{IBA}][\text{OH}^{-}]+K_i[\text{OH}^{-}]}) (9)

Equation (9) can be rearranged to the following form, which is used for verification of the rate law.

\frac{1}{k_{\text{obs}}} = \frac{1}{kK_1K_2[\text{IBA}][\text{OH}^{-}]} + \frac{1}{k} (10)

According to equation (10), the plots of 1/k_{\text{obs}} versus 1/[IBA] (r > 0.9988, s \leq 0.03415 I stage, r > 0.9960, s \leq 0.03301 II stage) and 1/k_{obs} versus 1/[OH^{-}] (r
> 0.9960, s ≤ 0.0145 I stage, r > 0.9979, s ≤ 0.01885 II stage) should be linear, as verified in Figure VI (v) (p.222)). The slope and intercept of such plots lead to the values of $k$, $K_1$, and $K_2$ at 25°C as $(3.67 \pm 0.14) \times 10^2$ s$^{-1}$, $(6.03 \pm 0.30) \times 10^1$ dm$^3$ mol$^{-1}$, and $(2.02 \pm 0.07) \times 10^3$ dm$^3$ mol$^{-1}$ for the I stage and $(1.51 \pm 0.07) \times 10^2$ s$^{-1}$, $(6.48 \pm 0.22) \times 10^1$ dm$^3$ mol$^{-1}$, and $(2.52 \pm 0.08) \times 10^3$ dm$^3$ mol$^{-1}$ for the II stage respectively. Using these values, rate constants under different experimental conditions were calculated and compared with experimental data (Table VI (i) (p.200)). There is a reasonable agreement between them.

The effect of increasing ionic strength on the rate explains qualitatively the reaction between two negatively charged ions, as seen in Scheme 1. The effect of solvent on the reaction kinetics has been described in earlier literature$^{22-26}$. For the limiting case of a zero angle approach between two dipoles or an ion-dipole system, Amis$^{27}$ has shown that a plot of log $k_{obs}$ versus $1/D$ is linear with a negative slope for a reaction between a negative ion and a dipole or two dipoles, and with a positive slope for a positive ion-dipole interaction. However, in the present study, an increase in the content of acetic acid in the reaction medium leads to the decrease in the reaction rate, which is not in agreement with Amis theory$^{27}$.

Applying the Born equation, Laidler and Eyring derived the equation (11).

\[
\ln k = \ln k_0 + \frac{NZ^2e^2}{2DRT} (\frac{1}{r} - \frac{1}{r^*})
\]

(11)
Figure VI (v)
The plots of (a) $1/k_{\text{obs}}$ versus $1/[\text{IBA}]$ and (b) $1/k_{\text{obs}}$ versus $1/[\text{OH}^-]$ (Verification of rate law (9) in the form of (10)).

(Conditions as in Table VI (i) (200)).
Where $k_0$ is the rate constant in a medium of infinite dielectric constant and $r$ and $r^*$ refer to the radius of the reacting species and the activated complex, respectively. It can be seen from the equation (11) that the rate should be greater in a medium of lower dielectric constant when $r^* > r$. There is a possibility of intermolecular hydrogen bonding, that could stabilise the transition state, increasing the size of the activated complex by attracting solvent molecules due to a solvation effect. The fairly high positive values of $\Delta H^\#$ and $\Delta G^\#$ (Table VI (vi a) (p.215)) also indicate that the transition state is highly solvated, which results in an increase in the size of transition state. It is likely that $r^* > r$ for indole 3-butyric acid, thus explaining the experimental observations. Hence one can expect intermolecular hydrogen bonding between two molecules of IBA, since they contain a carboxylic group (-COOH). Such type of hydrogen bonding is common for molecules having -COOH, -COOH and -OH etc\textsuperscript{28}. The observed modest activation energy and sizeable entropy of activation supports a complex transition state in the reaction. The negative value of the entropy of activation indicated that the complex is more ordered than the reactants\textsuperscript{29}.

**Reason for the two stages**

Details regarding the occurrence of two successive stages, fast and slow, might be suggested that these stages be probably due to creation of an optimum concentration of some intermediates\textsuperscript{30}. It might be possible that, upto a certain range of HCF (III) concentration (first fast stage), the active species of oxidant is reactive, due to attainment of optimum concentration of the active species. While
in the second stage (second slow stage) of the reaction, the rate becomes slower
due to deactivation of the active species as one of the products, HCF (II) retards the
rate.

*Importance of chapter VI*

The kinetic measurements were performed with rapid kinetic accessory
(HITECH, SFA-12) attached to spectrophotometer. The reaction exhibits two
successive steps, a fast and slow stage. Activation parameters with respect to slow
step of the proposed mechanism for both the stages are evaluated and discussed.
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