PART-A

Uncatalysed Reactions
CHAPTER II

Oxidation of thiosulphate by hexacyanoferrate(III) in aqueous perchloric acid medium – a kinetic and mechanistic study by stopped flow method

Thiosulphate (S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-}) ion is a moderately strong reducing agent, that has been widely used to fix photographic images, to extract silver from ore, as an antidote cyanide poisoning, as a mordant in the dye industry and to determine oxidizing agents by an indirect procedure that involves iodine as intermediate. With iodine, thiosulphate ion is oxidized quantitatively to tetrathionate (S\textsubscript{4}O\textsubscript{6}\textsuperscript{2-}) according to the half reaction,

\[
2\text{S}_2\text{O}_3^{2-} \rightarrow \text{S}_4\text{O}_6^{2-} + 2e^-.
\]

The most important iron(III) cyanide complex is the hexacyanoferrate(III) anion, [Fe(CN)\textsubscript{6}\textsuperscript{3-}], a mild oxidant with the Fe\textsuperscript{3+} center bound in octahedral geometry to six cyanide ligands. Studies involving hexacyanoferrate(III) as an oxidant in acid media are limited\textsuperscript{1-4} by the fact that its reduction potential\textsuperscript{5} of the couple is small ([Fe(CN)\textsubscript{6}\textsuperscript{3-}] / [Fe(CN)\textsubscript{6}\textsuperscript{4-}] : 0.356V). Hexacyanoferrate(III) forms different species in acid media\textsuperscript{1-6}. The mechanism may be quite interesting due to the formation of different intermediates of hexacyanoferrate(III). Hence, we have investigated the kinetics of oxidation of thiosulphate by hexacyanoferrate(III) in aqueous perchloric acid medium in order to understand the behavior of the active species of hexacyanoferrate(III) and to arrive at a suitable mechanism.
EXPERIMENTAL

Materials and methods

The solutions were prepared in water, which had been twice distilled in all glass unit in the presence of potassium permanganate. Reagent grade chemicals were used throughout. The stock solution of oxidant, hexacyanoferrate(III), was prepared by dissolving potassium hexacyanoferrate(III) (BDH) in water and the concentration was ascertained by iodometric titration. A stock solution of thiosulphate was prepared by dissolving sodium thiosulphate (AR) in water and the solution was standardized by known procedure. Perchloric acid (70%, E.Merck) was used to keep constant acidity. The ionic strength was kept constant by using sodium perchlorate solution. The sodium perchlorate solution was obtained by neutralization of perchloric acid by sodium carbonate, the neutralization point at pH 7.00 ± 0.15 being controlled potentiometrically. Hexacyanoferrate(II) solution was obtained by dissolving potassium hexacyanoferrate(II) (BDH) in water and standardizing with standard cerium(IV) solution. The tetrathionate solution was prepared in water.

Kinetic studies

Kinetic measurements were carried out at 25 ± 0.1 °C and at constant acidity and ionic strength. Reactions were initiated by mixing previously thermosttated solutions of Fe(CN)₆³⁻ and S₂O₃²⁻ which also contained the required amounts of perchloric acid and sodium perchlorate. The kinetics were followed under pseudo-first order conditions with S₂O₃²⁻ in excess. Since the
initial reaction was too fast to be monitored by usual methods, the course of reaction was followed by monitoring the decrease in absorbance of hexacyanoferrate(III) in a 1 cm quartz cell placed in the thermostatted compartment of a varian Cary-50 Bio UV-Vis spectrophotometer connected to a rapid kinetic accessory (HI-TECH SFA-12) at 420nm as a function of time. Application of Beer’s law under the reaction conditions was verified between $1.0 \times 10^{-4}$ and $1.0 \times 10^{-3}$ mol dm$^{-3}$ of Fe(CN)$_6^{3-}$ and extinction coefficient, $\varepsilon$ was found to be $1000 \pm 50$ dm$^3$ mol$^{-1}$ cm$^{-1}$ (Fig. II(i) (p.31)). The kinetics were followed more than 85% completion of the reaction and good first order kinetics were observed. An example run is given in Table II (i) (p.32). The first order rate constant, $k_{\text{obs}}$ was obtained from the plot of $\log [\text{Fe(CN)}_6^{3-}]$ versus time. The first order plots were linear over three half lives (Fig. II (ii) (p.33)). The first order rate constants, $k_{\text{obs}}$ (Table II (iii) (p.38)) were average of minimum four independent kinetic runs and were reproducible within $\pm 5\%$. The decomposition of sodium thiosulphate was checked under our experimental conditions and found that the decomposition was very slow, being less than 1\% in 1 h and 0.4\% in 10 min. which is very less in comparison with the reaction between Fe(CN)$_6^{3-}$ and S$_2$O$_3^{2-}$. In 4 min. more than 85\% oxidation of S$_2$O$_3^{2-}$ by Fe(CN)$_6^{3-}$ was completed. Hence, no correction for the decomposition of S$_2$O$_3^{2-}$ was made under our experimental conditions. However, always freshly prepared and standardized thiosulphate solution was used in each kinetic run.
Verification of Beer's law for the hexacyanoferrate(III) concentrations at 420 nm in aqueous perchloric acid at 25°C.
Table II (i)

Oxidation of sodium thiosulphate by hexacyanoferrate(III) in aqueous perchloric acid medium at 25 °C

Example run

\[ [\text{Fe(CN)}_6^{3-}] = 2.0 \times 10^{-4}; \quad [\text{S}_2\text{O}_3^{2-}] = 5.0 \times 10^{-3}; \]

\[ [\text{HClO}_4] = 0.50; \quad I = 0.60/\text{mol dm}^{-3} \]

| Time (min) | Optical density (420 nm) | \[\text{Fe(CN)}_6^{3-}\] \times 10^{-4} (mol dm^{-3}) | \[6 + \log [\text{Fe(CN)}_6^{3-}] \]
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<tr>
<td>3.2</td>
<td>0.0092</td>
<td>0.092</td>
<td>0.964</td>
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First order plots of the oxidation of thiosulphate by hexacyanoferrate(III) in aqueous perchloric acid medium at 25 °C

\([\text{Fe(CN)}_6^{3-}] \times 10^4 \text{ mol dm}^{-3}: (1) 0.5, (2) 1.0, (3) 2.0, (4) 3.0, (5) 4.0, (6) 5.0\)
**RESULTS**

**Stoichiometry and product analysis**

Different sets of reactant concentrations were mixed at \([\text{HClO}_4] = 0.50\) mol dm\(^{-3}\) and at ionic strength \(I = 0.60\) mol dm\(^{-3}\), were kept over 1 h in a closed container under nitrogen atmosphere at 25°C. When \([\text{Fe(CN)}_6^{3-}] > [\text{S}_2\text{O}_3^{2-}]\), the remaining \(\text{Fe(CN)}_6^{3-}\) concentration was assayed by measuring the absorbance at 420 nm, whereas, under the conditions \([\text{S}_2\text{O}_3^{2-}] > [\text{Fe(CN)}_6^{3-}]\), when \(\text{Fe(CN)}_6^{3-}\) had fully reacted, i.e., immediately after the optical density at 420 nm became zero, qualitatively analysis for the sulphur containing products were carried out. The addition of mercury(I) nitrate to a reaction solution produced a yellow precipitate, which became black on heating, thus indicating the presence of tetrathionate ions, \((\text{S}_4\text{O}_6^{2-})\). Experiments were carried out to estimate the consumption of thiosulphate ions \((\text{S}_2\text{O}_3^{2-})\) corresponding to different initial concentrations of hexacyanoferrate(III) \((\text{Fe(CN)}_6^{3-})\). The number of moles of \(\text{S}_2\text{O}_3^{2-}\) consumed was estimated by determining at the end of the reaction, the amount of unconsumed \(\text{S}_2\text{O}_3^{2-}\) by means of iodometric titration. Since the analysis was performed when the optical density had reached zero, i.e., all the \(\text{Fe(CN)}_6^{3-}\) was reduced to \(\text{Fe(CN)}_6^{4-}\), the number of moles of \(\text{Fe(CN)}_6^{3-}\) consumed was equal to the initial moles of \(\text{Fe(CN)}_6^{3-}\). The results indicate the stoichiometry as 1:1, i.e., one mole of \(\text{S}_2\text{O}_3^{2-}\) requires one mole of \(\text{Fe(CN)}_6^{3-}\) (Table II (ii) (p.35)) as shown in equation 1.

\[
2 \text{Fe(CN)}_6^{3-} + 2 \text{S}_2\text{O}_3^{2-} \rightarrow 2\text{Fe(CN)}_6^{4-} + \text{S}_4\text{O}_6^{2-} \tag{1}
\]
Table II (ii)

Stoichiometry of the oxidation of sodium thiosulphate by hexacyanoferrate(III) in perchloric acid medium at 25 °C

\[
[HClO_4] = 0.5; \quad I = 0.60/mol \text{ dm}^{-3}
\]

<table>
<thead>
<tr>
<th>([\text{Fe(CN)}_6^{3-}] \times 10^4) (mol dm(^{-3}))</th>
<th>([\text{S}_2\text{O}_3^{2-}] \times 10^4) (mol dm(^{-3}))</th>
<th>([\text{Fe(CN)}_6^{3-}] \times 10^4) (mol dm(^{-3}))</th>
<th>([\text{S}_2\text{O}_3^{2-}] \times 10^4) (mol dm(^{-3}))</th>
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<tr>
<td>(4.0)</td>
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<td>(1.98)</td>
<td></td>
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</tbody>
</table>
It was found, however, that if the final reaction solution was analyzed some time after completion of the reaction, or immediately after reaction for experiments with higher initial Fe(CN)$_6^{3-}$ and S$_2$O$_3^{2-}$ concentrations, trithionate (S$_3$O$_6^{2-}$) was formed along with a build-up of S$_2$O$_3^{2-}$ ions. Thus, the initial products of the direct reaction between S$_2$O$_3^{2-}$ and Fe(CN)$_6^{3-}$ ions appear to be S$_4$O$_6^{2-}$ and Fe(CN)$_6^{4-}$ as shown the above equation 1. The S$_4$O$_6^{2-}$ ions undergo subsequent disproportion to S$_3$O$_6^{2-}$ and S$_2$O$_3^{2-}$ on long standing$^9$. The decomposition of S$_4$O$_6^{2-}$ to higher and lower polythionate ions has also been reported in literature$^{10}$.

**Reaction orders**

The reaction orders have been determined from the slopes of log $k_{obs}$ versus log (concentration) plots by varying the concentration of reductant and perchloric acid in while keeping the others constant.

**Effect of [hexacyanoferrate(III)]**

At constant concentrations of thiosulphate, perchloric acid and at constant ionic strength, the hexacyanoferrate(III) concentration was varied in the range of 5.0 x 10$^{-5}$ to 5.0 x 10$^{-4}$ mol dm$^{-3}$. The pseudo first order rate constants, $k_{obs}$ were almost constant (Table II (iii) (p.38)), for different concentrations of hexacyanoferrate(III), indicates first order with respect to hexacyanoferrate(III) concentration. The pseudo-first order plots under these conditions were linear and almost parallel (Fig. II (ii) (p.33)) over 75% completion of the reaction at different initial concentrations of
hexacyanoferrate(III) also confirming the first order with respect to hexacyanoferrate(III) concentration.

**Effect of [thiosulphate]**

The effect of thiosulphate concentration on the reaction was studied at constant concentrations of oxidant, acid at constant ionic strength of $I = 0.60$ mol dm$^{-3}$. The thiosulphate concentration was varied in the range of $5.0 \times 10^{-4}$ to $5.0 \times 10^{-3}$ mol dm$^{-3}$. The $k_{\text{obs}}$ values increased with increase in the concentration of thiosulphate (Table II (iii) (p.38)). From the plot of log $k_{\text{obs}}$ versus log $[S_2O_3^{2-}]$, the value of slope was found to be unity, indicating first order with respect to thiosulphate concentration ((Fig. II (iii) (p.39)).

**Effect of [HClO$_4$]**

Increasing the perchloric acid concentration accelerates the rate of reaction at constant ionic strength and at other conditions constant (Table II (iii) (p.38)). The order with respect to acid concentration, from log - log plot of $k_{\text{obs}}$ versus (concentration) (Fig. II (iii) (p.39)), was found to be less than unity in the concentration range of $0.05 - 0.50$ mol dm$^{-3}$ (Table II (iii) (p.38)).

Hexacyanoferrate(III) forms different protonated species in acid media as shown in equilibria (2) – (4) with the stability constants $\beta_1(=K_1)$, $\beta_2 = (K_1K_2)$ and $\beta_3(=K_1K_2K_3)$ belonging to the species with one, two and three protons respectively$^{10}$.

\[
\begin{align*}
&\text{Fe(CN)}_6^{3-} + H^+ \rightleftharpoons H\text{Fe(CN)}_6^{2-} \quad K_1 \\
&H\text{Fe(CN)}_6^{2-} + H^+ \rightleftharpoons H_2\text{Fe(CN)}_6^- \quad K_2 \\
&H_2\text{Fe(CN)}_6^- + H^+ \rightleftharpoons H_3\text{Fe(CN)}_6 \quad K_3
\end{align*}
\]
Table II (iii)

Effect of variation of hexacyanoferrate(III), thiosulphate and perchloric acid on the oxidation of thiosulphate by hexacyanoferrate(III) in aqueous perchloric acid media at 25 °C and at I = 0.60 mol dm$^{-3}$

<table>
<thead>
<tr>
<th>[Fe(CN)$_6^{3-}$] x $10^4$ (mol dm$^{-3}$)</th>
<th>[S$_2$O$_3^{2-}$] x $10^3$ (mol dm$^{-3}$)</th>
<th>[HClO$_4$] (mol dm$^{-3}$)</th>
<th>$k_{obs} \times 10^2$ (s$^{-1}$)</th>
<th>$k_{cat} \times 10^2$ (s$^{-1}$)</th>
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Order with respect to thiosulphate and perchloric acid concentrations on the oxidation of thiosulphate by hexacyanoferrate(III) in aqueous perchloric acid medium at 25 °C

(Conditions as in Table II (iii) (p.38))
The reported equilibrium constants of the different species are $K_3 < K_2 < K_1 < 10$, the value of $K_1$ being nearly ten in the media under present study. While the singly protonated species is expected to form extensively in the high acid media used herein, the doubly and triply protonated species to form to a lesser extant.

**Effect of initially added products**

The effect of initially added products $\text{Fe(CN)}_6^{4-}$ and $\text{S}_4\text{O}_6^{2-}$ were studied in the $1.0 \times 10^{-4}$ to $5.0 \times 10^{-4}$ mol dm$^{-3}$ concentration range, keeping reactant concentrations and other conditions constant. No significant effects of products on the reaction rate were observed.

**Effect of dielectric constant and ionic strength**

The effect of dielectric constant was studied by varying the ethanoic acid-water(v/v) content in the reaction mixture with all other conditions being maintained constant. Since the dielectric constants of aqueous ethanoic acid are not available in the literature, they were computed from the pure liquid values$^{11}$: The dielectric constant of reaction medium at various compositions of ethanoic acid-water (v/v) was calculated by using the following equation.

$$D = D_1 V_1 + D_2 V_2$$

where $V_1$ and $V_2$ are the volume fractions and $D_1$ and $D_2$ are dielectric constants of water and acetic acid as 78.5 and 6.15 at 25°C.

For example at 20% ethanoic acid

$$D = 78.5 \times 80/100 + 6.15 \times 20/100. = 64.03$$
The values are given in Table II(iv)(p.42). The dielectric constant(D) of the reaction medium was changed by using acetic acid. As the acetic acid content of the medium increased from 0 – 50 % (v/v), the rate of reaction did not change appreciably (Table II(iv) (p.42)).

The effect of ionic strength was studied by varying the sodium perchlorate concentration in the reaction medium. The ionic strength was varied from 0.60 to 3.0 mol dm$^{-3}$ at constant concentrations of hexacyanoferrate(III), thiosulphate and perchloric acid. It was found that the rate constant, $k_{obs}$, increased with increasing concentration of sodium perchlorate (Table II (iv) (p.42)). The plot of log $k_{obs}$ versus $I^{1/2}$ is linear with a positive slope (Fig. II (iv) (p.43)).

**Test for free radicals**

To test the presence of free radicals, the reaction mixture was mixed with acrylonitrile and kept in an inert atmosphere for 24h. Dilution with methanol and there was no formation of a white precipitate, indicating the absence of free radicals in the reaction.

**Effect of temperature**

The activation parameters for the reaction were studied by using linear regression analysis (also known as the method of least squares). In generalized notation, the formula for a 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
Table II (iv)

Effect of variation of ionic strength and dielectric constant on the oxidation of thiosulphate by hexacyanoferrate(III) in aqueous perchloric acid at 25 °C.

\[
\begin{align*}
[\text{Fe(CN)}_6^{3-}] &= 2.0 \times 10^{-2}; \\
[S_2\text{O}_3^{2-}] &= 5.0 \times 10^{-3}; \\
[H\text{ClO}_4] &= 0.50 / \text{mol dm}^{-3}
\end{align*}
\]

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<th>(I/2)</th>
<th>(k_{\text{obs}} \times 10^2)</th>
<th>(1/D \times 10^2)</th>
<th>(k_{\text{obs}} \times 10^2)</th>
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<td>1.732</td>
<td>2.48</td>
<td>60.61</td>
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Fig. II (iv)

Effect of ionic strength on the oxidation of thiosulphate by hexacyanoferrate(III) in aqueous perchloric acid medium at 25 °C

(Conditions as in Table II (iv) (p.42))
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 common linear regression analysis is that which minimises the sum of the squares of the derivatives 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

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

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

where 'n' is number of data points and the summation are for all data points in the set. These data were subjected to least squares analysis.

The rate of reaction was measured at four different temperatures, 20, 25, 30 and 35°C by varying perchloric acid and thiosulphate concentrations. The rate of reaction increased with increase in temperature. The rate constant (k), of slow step of Scheme 1 were obtained from the intercept of the plot of \([\text{S}_2\text{O}_3^{2-}]/k_{\text{obs}}\) versus 1/[H⁺] at four different temperatures (Table II (v) (p.47)). The data are subjected to least square analysis and are tabulated in Table II (v)(p.47).

The energy of activation for the rate determining step was obtained from the Arrhenius plot \(\log k_{\text{obs}}(Y^*_{\text{calc}})\) versus 1/T (Fig. II (v) (p.46)), from which activation parameters were calculated (Table II (v) (p.47).
The activation energy of the reaction is calculated by

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

The entropy of activation is calculated by

\[ \frac{\Delta S^\#}{4.576} = \log k - 10.753 - \log T + \frac{E_a}{4.576 T} \]

where \( k \) is in sec\(^{-1}\), \( T \) is in Kelvin and \( E_a \) is in cal mol\(^{-1}\).

The enthalpy of activation is calculated by

\[ \Delta H^\# = E_a - RT \]

The free energy of activation is calculated by

\[ \Delta G^\# = \Delta H^\# - T\Delta S^\# \]

and the \( \log A \) is calculated by

\[ \log A = \log k + \frac{E_a}{2.303RT} \]

**DISCUSSION**

The hexacyanoferrate(III) oxidation of thiosulphate occurs in measurable quantities in presence of 0.50 mol dm\(^{-3}\) perchloric acid at 25 °C and has a stoichiometry of 1:1, i.e., one mole of thiosulphate requires one mole of hexacyanoferrate(III). The order with respect to hexacyanoferrate(III) and thiosulphate concentrations were found to be unity. No effect of added products were observed. As the perchloric acid concentration increases the rate of the reaction also increases.
Fig. II (v)

Effect of temperature on the oxidation of thiosulphate by hexacyanoferrate(III) in aqueous perchloric acid medium with respect to slow step of Scheme 1

(Conditions as in Table II (v) (p.47))

\[
\begin{array}{cccccc}
1/T \times 10^3 & 3.180 & 3.240 & 3.300 & 3.360 & 3.420 & 3.480 \\
\log k (Y^* \text{ calc.}) & -2.400 & -2.500 & -2.600 & -2.700 & -2.800 \\
\end{array}
\]
Table II (v)

Effect of temperature on the slow step of the mechanism of oxidation of thiosulphate by hexacyanoferrate(III) in aqueous perchloric acid medium

Effect of temperature

<table>
<thead>
<tr>
<th>Temperature (T) (K)</th>
<th>1/T x 10³ (x)</th>
<th>k x 10³ (dm³ mol⁻¹ s⁻¹)</th>
<th>log k (Y)</th>
<th>log k (Y*calc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>3.4129</td>
<td>1.82</td>
<td>-2.7399</td>
<td>-2.40618</td>
</tr>
<tr>
<td>298</td>
<td>3.3557</td>
<td>2.22</td>
<td>-2.6536</td>
<td>-2.17708</td>
</tr>
<tr>
<td>303</td>
<td>3.3003</td>
<td>2.90</td>
<td>-2.5376</td>
<td>-1.99541</td>
</tr>
<tr>
<td>308</td>
<td>3.2467</td>
<td>3.50</td>
<td>-2.4559</td>
<td>-1.74083</td>
</tr>
</tbody>
</table>

Activation parameters

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>E_a (kJ mol⁻¹)</td>
<td>33 ± 2</td>
</tr>
<tr>
<td>( \Delta H^# ) (kJ mol⁻¹)</td>
<td>30 ± 2</td>
</tr>
<tr>
<td>( \Delta S^# ) (J K⁻¹mol⁻¹)</td>
<td>-20 ± 3</td>
</tr>
<tr>
<td>( \Delta G^# ) (kJ mol⁻¹)</td>
<td>11 ± 0.3</td>
</tr>
<tr>
<td>log A</td>
<td>8.0 ± 0.4</td>
</tr>
</tbody>
</table>
The effect of acid on the reaction rate is to accelerate the reaction at constant reactant concentration and at constant ionic strength, this suggest the involvement of one or more protonated species\textsuperscript{11}. The less than unit order in acid concentration is due to its involvement in the formation of different hexacyanoferrate(III) species in acid media. As discussed in the result section, hexacyanoferrate(III) forms different protonated species in acid media\textsuperscript{10}. Among different protonated species the active form of oxidant was found to be $\text{HFe(CN)}_6^{2-}$.

The mechanism (Scheme 1) involves the formation of the above species in a prior equilibrium, which reacts with thiosulphate ion to give the product, hexacyanoferrate(II) and $\text{S}_2\text{O}_3^{-}$. The formed $\text{S}_2\text{O}_3^{-}$, in a later fast step decomposes to give the another product tetrathionate, $\text{S}_4\text{O}_6^{2-}$. Based on the above, the mechanism shown in Scheme 1 is proposed.

$$\begin{align*}
\text{Fe(CN)}_6^{3-} + \text{H}^+ & \quad \xrightleftharpoons[K_1]{\quad} \quad \text{HFe(CN)}_6^{2-} \\
\text{HFe(CN)}_6^{2-} + \text{S}_2\text{O}_3^{-} & \quad \xrightarrow{k_{\text{slow}}} \quad \text{S}_2\text{O}_3^{-} + \text{HFe(CN)}_6^{3-} \\
2\text{S}_2\text{O}_3^{-} + \text{H}^+ & \quad \xrightarrow{\text{fast}} \quad \text{S}_4\text{O}_6^{2-}
\end{align*}$$

Scheme 1

The oxidation of thiosulphate by hexacyanoferrate(III) is a complementary reaction and may take place due to the intervention of reactive $\text{S}_2\text{O}_3^{-}$ species. The formations of such species are also observed in the literature\textsuperscript{12}.
Scheme 1 leads to the following rate law (9) which explains the observed orders in hexacyanoferrate(III), thiosulphate and acid.

\[
\text{Rate} = \frac{-d[\text{Fe(CN)}_6^{3-}]}{dt} = k [\text{Fe(CN)}_6^{3-}] [S_2O_3^{2-}] \\
= k K_1 [\text{Fe(CN)}_6^{3-}] [S_2O_3^{2-}] [H^+] 
\] (5)

But, the total concentration of hexacyanoferrate(III) is given by,

\[
[\text{Fe(CN)}_6^{3-}]_t = [\text{Fe(CN)}_6^{3-}]_f + [\text{HFe(CN)}_6^{2-}] \\
= [\text{Fe(CN)}_6^{3-}]_f \{ 1 + K [H^+] \} \\
[\text{Fe(CN)}_6^{3-}]_f = \frac{[\text{Fe(CN)}_6^{3-}]_t}{1 + K_1 [H^+]} 
\] (6)

Where ‘t’ and ‘f’ refers to total and free

In the same way,

\[
[H^+]_t = [H^+]_f + K_1 [HFe(CN)_6]^{2-} \\
[H^+]_t = [H^+]_f \{ 1 + K_1 [\text{Fe(CN)}_6^{3-}] \} \\
[H^+]_f = \frac{[H^+]_t}{1 + K_1 [\text{Fe(CN)}_6^{3-}]} 
\] (7)

In view of the low concentration of hexacyanoferrate(III) used in the experiment, the term \(K_1[\text{Fe(CN)}_6^{3-}]\) is neglected in equation (7) in comparison with unity.

Hence,

\[
[H^+]_t = [H^+]_f 
\] (8)
Substituting equations (6) and (8) in equation (5) and omitting subscripts we obtain equation (9).

\[
\begin{align*}
\text{Rate} &= \frac{-d\left[\text{Fe(CN)}_6^{3-}\right]}{dt} = \frac{k K_1 \left[\text{Fe(CN)}_6^{3-}\right] \left[S_2O_3^{2-}\right] \left[H^+\right]}{1 + K_1 \left[H^+\right]} \\
&\quad \text{or} \\
\frac{\text{Rate}}{[\text{Fe(CN)}_6^{3-}]} &= k_{\text{obs}} = \frac{k K_1 \left[S_2O_3^{2-}\right] \left[H^+\right]}{1 - K_1 \left[H^+\right]}
\end{align*}
\]

\[\text{(9)}\]

The rate law (9) can be rearranged to equation (10) which is suitable for verification.

\[
\left[S_2O_3^{2-}\right] = \frac{1}{k_{\text{obs}}} + \frac{1}{k K_1 \left[H^+\right]}
\]

\[\text{(10)}\]

According to equation (10) the plot of \([S_2O_3^{2-}] / k_{\text{obs}}\) versus 1/\([H^+]\) should be linear and are found to be so Fig. II (vi) (p.51). The intercept and slope of such plot lead to the values of \(k\) and \(K_1\) as 2.23 ± 0.03 dm\(^3\) mol\(^{-1}\) s\(^{-1}\) and 13.6 ± 0.4 dm\(^3\) mol\(^{-1}\) respectively. Using these values, rates under different experimental conditions were calculated and found to be in good agreement with experimental values (Table II (iii) (p.38)). The thermodynamic quantities of the first step of Scheme 1 were evaluated from the slopes and intercepts of the plots of \([S_2O_3^{2-}] / k_{\text{obs}}\) versus 1/\([H^+]\) at four different temperatures. The values of \(K_1\) at 20, 25, 30 and 35\(^{0}\)C are given in Table II (vi) (p.52). A van’t Hoff plot was drawn for the variation of \(K_1\) with temperature (i.e., log \(K_1\) versus 1/T) and the values of enthalpy of reaction \(\Delta H\), entropy of activation \(\Delta S\) and free energy of reaction \(\Delta G\) are given in Table II (vi) (p.52).
Verification of rate law (9) in the form of (10) for the oxidation of thiosulphate by hexacyanoferrate(III) in acid medium

(Conditions as in Table II (iii) (p.38))
Table II (vi)

Effect of temperature on the first equilibrium step of scheme 1

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>$K_1$ (dm$^3$ mol$^{-1}$)</th>
<th>Thermodynamic quantities</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>15.50</td>
<td>$\Delta H = -31 \pm 3$ k J mol$^{-1}$</td>
</tr>
<tr>
<td>298</td>
<td>13.09</td>
<td>$\Delta S = -66 \pm 2$ J K$^{-1}$ mol$^{-1}$</td>
</tr>
<tr>
<td>303</td>
<td>9.90</td>
<td>$\Delta G = -11 \pm 0.4$ k J mol$^{-1}$</td>
</tr>
<tr>
<td>308</td>
<td>8.42</td>
<td></td>
</tr>
</tbody>
</table>
The effect of ionic strength and dielectric constant on the rate qualitatively explains the reaction between two negatively charged ions as in Scheme 1. The moderate values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were both favorable for electron transfer processes. The observed modest enthalpy of activation and relatively low entropy of activation and higher rate constant of slow step indicate that oxidation presumably occurs by an inner–sphere mechanism.

**FINDINGS OF CHAPTER II**

The kinetics of oxidation of thiosulphate by hexacyanoferrate(III) in an aqueous perchloric acid medium has been studied spectrophotometrically by stopped flow method at 25°C. The stoichiometry is 1:1, i.e., one mole of thiosulphate consumes one mole of hexacyanoferrate(III). The reaction products are identified as $\text{Fe(CN)}_6^{4-}$ and $\text{S}_4\text{O}_6^{2-}$. The reaction is first order with respect to hexacyanoferrate(III) and thiosulphate concentrations. Increase in perchloric acid concentration increased the rate of reaction. Added products do not have any significant effect on the rate of reaction. The effect of ionic strength and dielectric constants are also studied on the reaction rate. The active species of oxidant is understood to be $\text{HFe(CN)}_6^{3-}$. A suitable mechanism is proposed and the reaction constants of the different steps involved have been evaluated. Activation parameters have also been calculated with respect to the slow step of the mechanism and discussed.

**IMPORTANCE OF THE CHAPTER II**

The reaction between hexacyanoferrate(III) and thiosulphate occurs with measurable velocity in acid media. The main active species of
hexacyanoferrate(III) is considered as $\text{HFe(CN)}_6^{2-}$, although other species might be active to much lesser extent. The role of hydrogen ion is crucial to the reaction. The description of the mechanism is consistent with all the experimental evidence.
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