Oxidation of thiosulphate by hexacyanoferrate(III) in aqueous perchloric acid medium — A kinetic and mechanistic study

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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 Fe(CN)$_6^{3-}$ and S$_4$O$_6^{2-}$. The reaction is first order with respect to hexacyanoferrate(III) and thiosulphate concentrations. Increase in perchloric acid concentration increases the rate of reaction (order=0.40). Added products do not have any significant effect on the rate of reaction. The effect of ionic strength and dielectric constants on the reaction rate has also been studied. The active species of oxidant is indicated to be 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.

Keywords: Kinetics, Reaction mechanisms, Oxidations, Thiosulphate, Hexacyanoferrate

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Thiosulphate (S$_2$O$_3^{2-}$) ion is a moderately strong reducing agent, that has been widely used to fix photographic images, extract silver from ore, as an antidote to 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$_4$O$_6^{2-}$) according to the half reaction, $2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$. The most important iron(III) cyanide complex is the hexacyanoferrate(III) anion, [Fe(CN)$_6^{3-}$], a mild oxidant with the Fe$^{3+}$ center bound in octahedral geometry to six cyanide ligands. Studies involving hexacyanoferrate(III) as an oxidant in acid media are limited$^{1-4}$ by the fact that reduction potential$^5$ of the couple is small (${[\text{Fe(CN)}_6^{3-}]/{[\text{Fe(CN)}_6^{4-}] : 0.356V}$). Hexacyanoferrate(III) forms different species in acidic media$^{1-6}$. The mechanism may be quite interesting due to the formation of different intermediates of hexacyanoferrate(III). Hence, we have investigated the kinetics and mechanism 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).

Experimental

All solutions were prepared in water, which had been twice distilled in an 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 titrometric titration$^7a$. A stock solution of thiosulphate was prepared by dissolving sodium thiosulphate (AR) in water and the solution was standardized by known procedure$^7b$. Perchloric acid (70%, E. Merck) was used to maintain 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$^7c$.

Kinetic measurements were carried out at 25 ± 0.1°C and at constant acidity and ionic strength. Reactions were initiated by mixing previously thermostatted solutions of Fe(CN)$_6^{3-}$ and S$_2$O$_3^{2-}$ which also contained the required amounts of perchloric acid and sodium perchlorate. The kinetics was followed under pseudo-first order conditions with S$_2$O$_3^{2-}$ 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 420 nm 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, $C$, was found to be $1000 \pm 50$ dm$^{-3}$ mol$^{-1}$ cm$^{-1}$. The first order rate constant, $k_{obs}$, was obtained from the plot of log(absorbance) versus time (Fig. 1). The first order plots were linear over three half lives (Fig. 1). The first order rate constants are average of minimum four independent kinetic runs and reproducible within $\pm 5\%$.

The decomposition of sodium thiosulphate was checked under our experimental conditions and it was found that the decomposition was very slow, being less than 1% in 1 hr and 0.4% in 10 min. which is very slow in comparison with the reaction between Fe(CN)$_6^{3-}$ and S$_2$O$_3^{2-}$. Hence, no correction for the decomposition of S$_2$O$_3^{2-}$ was made under the experimental conditions. However, always freshly prepared and standardized thiosulphate solution was used in each kinetic run.

**Results and discussion**

Different sets of reactant concentrations were mixed at [HClO$_4$] = 0.50 mol dm$^{-3}$ and at ionic strength $I = 0.60$ mol dm$^{-3}$, and kept for 1 h in a closed container under nitrogen atmosphere at 25°C. When [Fe(CN)$_6^{3-}$] $> [S_2O_3^{2-}]$, the remaining Fe(CN)$_6^{3-}$ concentration was assayed by measuring the absorbance at 420 nm, while, under the conditions [S$_2$O$_3^{2-}$] $> [Fe(CN)_6^{3-}]$, when Fe(CN)$_6^{3-}$ had fully reacted, i.e., immediately after the optical density at 420 nm became zero, qualitative 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$^8$ of tetrathionate ions (S$_4$O$_6^{2-}$). Experiments were carried out to estimate the consumption of thiosulphate ions (S$_2$O$_3^{2-}$) corresponding to different initial concentrations of hexacyanoferrate(III) (Fe(CN)$_6^{3-}$). The number of moles of S$_2$O$_3^{2-}$ consumed was estimated by determining at the end of the reaction, the amount of unconsumed S$_2$O$_3^{2-}$ by iodometric titration$^7b$. Since the analysis was performed when the optical density had reached zero, i.e., all the Fe(CN)$_6^{3-}$ was reduced to Fe(CN)$_6^{4-}$, the number of moles of Fe(CN)$_6^{3-}$ consumed was equal to the initial moles of Fe(CN)$_6^{3-}$. The results indicate the stoichiometry as 1:1, i.e., one mole of S$_2$O$_3^{2-}$ requires one mole of Fe(CN)$_6^{3-}$ as shown in Eq. 1.

$$2\text{Fe(CN)}_6^{3-} + 2\text{S}_2\text{O}_3^{2-} \rightarrow 2\text{Fe(CN)}_6^{4-} + \text{S}_4\text{O}_6^{2-} \quad \ldots(1)$$

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 in Eq. 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 reaction orders have been determined from the slopes of log$^k_{obs}$ versus log(concentration) plots by varying concentrations of thiosulphate or perchloric acid separately, while keeping the other constant. The plots of log(absorbance) versus time, were linear and almost parallel over three half lives of the reaction for different initial hexacyanoferrate(III) concentration (Fig. 1) which indicates unit order with respect to hexacyanoferrate(III) concentration. This was also confirmed by the almost constant values of the rate constants, $k_{obs}$, for different hexacyanoferrate(III) concentrations (Table 1). The thiosulphate concentration was varied in the concentration range $5.0 \times 10^{-3} - 5.0 \times 10^{-2}$ mol dm$^{-3}$ at constant concentrations of other reactants. The order with respect to thiosulphate concentration was also found to be unity.

The effect of initially added products, Fe(CN)$_6^{2-}$ and S$_4$O$_6^{2-}$, were studied in the 1.0×10$^{-5}$ to 5.0×10$^{-5}$ mol dm$^{-3}$ concentration range, keeping reactants concentrations and other conditions constant. No significant effects of products on the reaction rate were observed.
Increasing the perchloric acid concentration at constant ionic strength and at other conditions constant accelerates the rate of reaction. The order with respect to acid ion concentration, from log-log plots of $k_{obs}$ versus concentration, was found to be less than unity in the concentration range of 0.05-0.50 mol dm$^{-3}$ (Table 2). 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.$^{10}$

Fe(CN)$_6^{3-}$ + H$^+$ $\rightleftharpoons$ HFe(CN)$_6^{2-}$ $K_1$ ... (2)

HFe(CN)$_6^{2-}$ + H$^+$ $\rightleftharpoons$ H$_2$Fe(CN)$_6^{-}$ $K_2$ ... (3)

H$_2$Fe(CN)$_6^{-}$ + H$^+$ $\rightleftharpoons$ H$_3$Fe(CN)$_6$ $K_3$ ... (4)

The reported equilibrium constants of the different species are $K_1$ > $K_2$ > $K_3$ > 10, the value of $K_1$ being nearly ten in the media used in the 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 form to a lesser extent.

At constant concentrations of reactants, with other conditions constant, the ionic strength was varied between 0.60 and 3.0 mol dm$^{-3}$. The rate was found to increase with increasing ionic strength. A plot of log $k_{obs}$ versus $\sqrt{I}$ is linear with positive slope. The dielectric constant ($D$) of the reaction medium was changed by using acetic acid. As the acetic acid content of the medium was increased from 0-50% (v/v), the rate of reaction did not change appreciably.

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 the slow step in Scheme 1 was obtained from the intercept of the plot of $[S_2O_3^{2-}]/k_{obs}$ versus $1/[H^+]$ at four different temperatures (Table 2). The energy of activation for the rate determining step was obtained from the plot of log $k$ versus $1/T$, from which activation parameters were calculated (Table 2). The thermodynamic quantities of the first step of Scheme 1 were evaluated from the slopes and intercepts of the plots of $[S_2O_3^{2-}]/k_{obs}$ versus $1/[H^+]$ at four different temperatures. The values of $K_1$ at 20, 25, 30 and 35°C are given in Table 2. 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 2.

The hexacyanoferrate(III) oxidation of thiosulphate occurs in measurable quantities in the 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 both hexacyanoferrate(III) and thiosulphate concentrations was found to be unity. No effect of added products was observed. As the perchloric acid concentration increases the rate of the reaction also increases. The effect of acid on the reaction rate is to accelerate the reaction at constant reactant concentration and at constant ionic strength.

### Table 1 — Effect of variation of [Fe(CN)$_6^{3-}$], $[S_2O_3^{2-}]$ and $[HClO_4]$ on the oxidation of $S_2O_3^{2-}$ by Fe(CN)$_6^{3-}$; [Temp. = 25°C; $I = 0.60$ mol dm$^{-3}$]

<table>
<thead>
<tr>
<th>[Fe(CN)$_6^{3-}$]×10$^4$ (mol dm$^{-3}$)</th>
<th>$[S_2O_3^{2-}]$×10$^4$ (mol dm$^{-3}$)</th>
<th>$[HClO_4]$ (mol dm$^{-3}$)</th>
<th>$k_{obs}$×10$^2$ (s$^{-1}$)</th>
<th>$k_{obs}$×10$^3$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>5.0</td>
<td>0.5</td>
<td>0.99</td>
<td>0.96</td>
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<td>0.5</td>
<td>1.02</td>
<td>0.96</td>
</tr>
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<td>5.0</td>
<td>0.5</td>
<td>1.05</td>
<td>0.96</td>
</tr>
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<td>5.0</td>
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</tr>
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<td>0.09</td>
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<tr>
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<td>5.0</td>
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<td>0.96</td>
</tr>
</tbody>
</table>

### Table 2 — Effect of temperature on the Fe(CN)$_6^{3-}$-S$_2$O$_3^{2-}$ reaction and the thermodynamic parameters

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>$k$ (dm$^3$ mol$^{-1}$s$^{-1}$)</th>
<th>$K_1$ (dm$^3$ mol$^{-1}$)</th>
</tr>
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<tbody>
<tr>
<td>293</td>
<td>1.82</td>
<td>15.50</td>
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<tr>
<td>298</td>
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<td>308</td>
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<td>8.42</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Activation parameters</th>
<th>$E_a$ (kcal mol$^{-1}$)</th>
<th>$\Delta H^\circ$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^\circ$ (kJ mol$^{-1}$ K$^{-1}$)</th>
<th>$\Delta G^\circ$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_a$</td>
<td>$33 \pm 2$ kcal mol$^{-1}$</td>
<td>$30 \pm 2$ kcal mol$^{-1}$</td>
<td>$-20 \pm 3$ JK$^{-1}$ mol$^{-1}$</td>
<td>$-66 \pm 2$ JK$^{-1}$ mol$^{-1}$</td>
</tr>
<tr>
<td>$\Delta H^\circ$</td>
<td>$11 \pm 0.3$ kcal mol$^{-1}$</td>
<td>$-11 \pm 0.4$ kcal mol$^{-1}$</td>
<td>$8.0 \pm 0.4$</td>
<td>$8.0 \pm 0.4$</td>
</tr>
<tr>
<td>$\log A$</td>
<td>$8.0 \pm 0.4$</td>
<td>$8.0 \pm 0.4$</td>
<td>$8.0 \pm 0.4$</td>
<td>$8.0 \pm 0.4$</td>
</tr>
</tbody>
</table>
This suggests the involvement of one or more protonated species\textsuperscript{11}. The order in acid concentration was found to be less than unity. 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 above, hexacyanoferrate(III) forms different protonated species in acid media\textsuperscript{10}. Among the different protonated species the active form of oxidant was found to be HFe(CN)\textsubscript{6}\textsuperscript{2--}.

The mechanism (Scheme 1) involves the formation of the above species in a prior equilibrium, which results in the formation of different hexacyanoferrate(III) species in acid media. As discussed above, hexacyanoferrate(III) forms different protonated species in acid media\textsuperscript{10}. Among the different protonated species the active form of oxidant was found to be HFe(CN)\textsubscript{6}\textsuperscript{2--}.

The oxidation of thiosulphate by hexacyanoferrate(III) is a complementary reaction and may take place due to the intervention of the reactive S\textsubscript{2}O\textsubscript{3}\textsuperscript{2--} species. The formation of such species are also observed in the literature\textsuperscript{12}.

Scheme 1 leads to the rate law (9) which explains the observed orders in hexacyanoferrate(III), thiosulphate and acid.

\[
\text{Rate} = \frac{-d[\text{Fe(CN)}_6^{3-}]}{dt} = k [\text{Fe(CN)}_6^{3-}] [\text{S}_2\text{O}_3^{2-}] [\text{H}^+] \\
= k K_1 [\text{Fe(CN)}_6^{3-}] [\text{S}_2\text{O}_3^{2-}] [\text{H}^+] \\
\]

(5)

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 species. Similarly,

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

(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 Eq. 7 in comparison with unity.

Hence,

\[
[H^+]_t = [H^+]_f \\
\]

(8)

Substituting Eqs. (6) and (8) in Eq. (5) and omitting subscripts we obtain Eq. (9).

\[
\text{Rate} = \frac{-d[\text{Fe(CN)}_6^{3-}]}{dt} = k K_1[\text{Fe(CN)}_6^{3-}] [\text{S}_2\text{O}_3^{2-}] [\text{H}^+] \\
= k K_1 [\text{S}_2\text{O}_3^{2-}] [\text{H}^+] \\
\]

(9)

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

\[
\frac{[\text{S}_2\text{O}_3^{2-}]}{\text{k}_{\text{obs}}} = \frac{1}{k K_1[\text{H}^+]} + \frac{1}{k} \\
\]

(10)

According to Eq. (10), the plot of \([\text{S}_2\text{O}_3^{2-}] / \text{k}_{\text{obs}}\) versus 1/[H\textsuperscript{+}] should be linear and is found to be so. The intercept and slope of this plot lead to the values of \(k\) as 2.23 ± 0.03 dm\textsuperscript{3} mol\textsuperscript{-1} s\textsuperscript{-1} and 13.6 ± 0.4 dm\textsuperscript{3} mol\textsuperscript{-1} respectively. Using these values, rates under different experimental conditions were calculated and found to be in good agreement with experimental values (Table 1).

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 \(\Delta H^\#\) and \(\Delta S^\#\) are 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 the oxidation presumably occurs by an inner-sphere mechanism.

The study shows that the reaction between hexacyanoferrate(III) and thiosulphate occurs with measurable rate in acidic media. The main active
species of hexacyanoferrate(III) is considered to be HFe(CN)$_6^{2-}$, although there may be other species active to a much lesser extent. The role of hydrogen ion is crucial to the reaction.

References