CHAPTER IIA
OXIDATION OF CHROMIUM(III) BY ALKALINE HEXACYANOFERRATE(III)
The stable oxidation states of chromium are chromium(III) and chromium(VI). Chromium(VI) compounds such as chromates, dichromates and particularly chromic acid act as irritants of the skin and mucous membranes. Dermatitis results in the cases of some individuals who have become sensitised and allergic to chromium(VI) compounds. On the contrary, chromium, as chromium(III), appears to be an essential trace metal in mammalian metabolism and there is no evidence that chromium(III) compounds have any toxic effects. Testes, bones, liver and spleen have a high affinity for chromium, while the affinity of muscle and brain is low. Chromium(III) coordinates with proteins. The deficiency of chromium(III) in rats and monkeys leads to decrease in the glycogen reserve, and causes disturbance in utilisation of aminoacids in protein synthesis and a syndrome resembling diabetes. The biologically effective form of chromium is produced as a result of a sequence of reactions of chromium(III) with ligands including OH⁻, present in the biological system. Specially it is essential to determine which of many biological substances are most likely to contain chromium(III) in transportable form. To determine the chemical processes that affect the biological systems, the aqueous species of chromium(III) at all pH conditions along with the data
of chromium(III) to chromium(VI) transformation are required.

The chemistry of chromium(III) in alkaline medium is not well developed as is the case in acid medium. Only recently has it become known that the relatively high solubility of chromium(III) in solutions of pH > 11.5 is due to the species like Cr(OH)_4^- and that, in such solutions, presence of polymeric chromium(III) species were unlikely. The solubility of chromium(III) above pH 12 was also found to be subject to greater variability and it generally decreased with time. No oxidation studies of chromium(III) in alkaline medium have been made so far, studies in acid medium being available. The redox potentials of Fe(CN)_6^{4-}/Fe(CN)_6^{3-} and Cr(III)/Cr(VI) couples of -0.45V and +0.13V respectively in alkaline medium indicate that Fe(CN)_6^{3-} and Cr(III) may react with facility and this is so. The reaction affords an example of a study supplementing the scantily understood chemistry of chromium(III). The oxidation of chromium(III) by one equivalent oxidants is generally expected to proceed through chromium(IV) and chromium(V), yet little is known about such species in basic medium. Herein, the results of the study of the hexacyanoferrate(III)-chromium(III) reaction in
alkaline medium are furnished.

EXPERIMENTAL

Reagent grade chemicals and doubly distilled water were used. The second distillation was from permanganate in a glass still. Hexacyanoferrate(III) was prepared by dissolving potassium hexacyanoferrate(III) (BDH) in water. The solution was standardised$^7$ by adding a 10% potassium iodide solution in presence of zinc sulphate and the liberated iodine was titrated with standard sodium thiosulphate solution. Chromium(III) solution was prepared from chromium(III) potassium sulphate (BDH) in water and its concentration was checked$^7$ by oxidation to chromium(VI) with potassium persulphate in presence of 2 drops of 0.010 mol dm$^{-3}$ silver nitrate solution as a catalyst, the chromium(VI) being found with standard iron(II) solution using N-phenylanthranalic acid as indicator. Hexacyanoferrate(II) solution was prepared by dissolving potassium hexacyanoferrate(II) (BDH) in water and standardised$^7$ with cerium(IV) solution. The chromium(VI) was made from aqueous solution of potassium dichromate (BDH). Sodium hydroxide and sodium perchlorate were used to provide the required alkalinity and to maintain the ionic strength respectively in
reaction solutions.

Freshly dissolved chromium(III) in excess alkali gives rise to a spectrum in the visible region, the spectrum being similar to that of aqueous solution \( \text{Cr}^{3+}_{\text{aq}} \) except that some hyperchromicity is found as shown in fig. IIA(i) (p. 104). The chromium(III) solutions at pH greater than 12 used in this study were clear when freshly prepared and turbidimetry showed no insoluble material in such solutions over a period of approximately 40 hours; after this period, a low initial turbidity slowly developed into a full scale precipitate by 96 hours (Table IIA(ia); p.105). In view of this reason, kinetics were restricted to fresh solutions of chromium(III) except in case of the comparative studies made with solutions of around 36 hours standing. Solutions standing for 36 hours have been called in this study as 'aged' solutions.

Kinetic runs

Runs were followed under second order conditions at a constant temperature of 27±0.05°C unless otherwise stated. The reaction was initiated by mixing the thermostatted hexacyanoferrate(III) and chromium(III)
Fig. IIA(i) : Spectrum of Cr(III) in aqueous solution:
(a) in the absence of OH\(^-\)(----) and
(b) in the presence of OH\(^-\)(---).

\([\text{Cr(III)}] = 0.01, \quad [\text{OH}^-] = 0.20/\text{mol dm}^{-3}\)

temp. = 25°C.
Table IIA(ia) : Kinetics of formation of polynuclear chromium(III) species at 27°C.

\[ \text{[Cr(III)]} = 0.007; \quad \text{[OH}^-\text{]} = 0.20, \quad I = 0.30/\text{mol dm}^{-3} \]

<table>
<thead>
<tr>
<th>Time in hours</th>
<th>0</th>
<th>3</th>
<th>24</th>
<th>36</th>
<th>40</th>
<th>48</th>
<th>72</th>
<th>96</th>
</tr>
</thead>
<tbody>
<tr>
<td>NTU.</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>5</td>
<td>120</td>
<td>180</td>
<td>Ppt.</td>
</tr>
</tbody>
</table>

Table IIA(ib) : Solubility of chromium(III) as a function of pH.

\[ \text{[Cr(III)]} = 0.007 \text{ mol dm}^{-3} \]

<table>
<thead>
<tr>
<th>pH.</th>
<th>10</th>
<th>10.5</th>
<th>11.0</th>
<th>11.6</th>
<th>11.8</th>
<th>12.0</th>
<th>12.2</th>
<th>12.6</th>
<th>13.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>NTU.</td>
<td>Ppt.</td>
<td>Ppt.</td>
<td>180</td>
<td>83</td>
<td>67</td>
<td>40</td>
<td>22</td>
<td>Clear Solution</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Error ± 5%</td>
<td></td>
</tr>
</tbody>
</table>
solutions which also contained the required amounts of sodium perchlorate and sodium hydroxide. The reaction was followed by measuring the absorbance of chromium(III) in the reaction solution in a 1 cm cell in the thermostatted compartment of a Bausch and Lomb Spectronic 2000 spectrophotometer at 590 nm where other constituents of the reaction mixture do not absorb significantly. The obedience of the absorbance of freshly dissolved chromium(III) solution in alkali to Beer's law under the reaction conditions in 0.30 mol dm$^{-3}$ alkali in the concentration range of $1.0 \times 10^{-3}$ to $2.0 \times 10^{-2}$ mol dm$^{-3}$ chromium(III) had earlier been tested with the molar absorbancy index, $\varepsilon$, resulting as $25 \pm 1$ dm$^3$ mol$^{-1}$ cm$^{-1}$ (Fig. IIA(ii); p.107). The $\varepsilon$ value in case of chromium(III) solutions of 36 hours standing resulted as $30.5 \pm 1$ dm$^3$ mol$^{-1}$ cm$^{-1}$ (Fig. IIA(ii)). These values of $\varepsilon$ were also seen to be independent of OH$^-$ concentrations of $\geq 0.10$ mol dm$^{-3}$ or higher. Therefore, the $\varepsilon$ values of 25 and 30.5 were used in case of kinetics involving fresh and 'aged' chromium(III) solutions respectively.

In view of the reaction followed under second order conditions, the apparent second order constant, $k_{app}$, was obtained from plots of $(a-x)^{-1}$ versus time from runs involving equivalent concentrations of reactants. The
Fig. IIA(ii) : Verification of Beer's law in the case of
(a) freshly dissolved Cr(III) in alkali at
590 nm (-o-),
(b) 'aged' Cr(III) in alkali at 590 nm (-●-),
(c) Cr(VI) in alkali at 372 nm (-△-)
([OH\(^{-}\)] = 0.30 mol dm\(^{-3}\))

\[
[\text{Cr(VI)}] \times 10^4 \text{ mol dm}^{-3}
\]

\[
[\text{Cr(III)}] \times 10^2 \text{ mol dm}^{-3}
\]
initial rates were obtained from concentration versus
time curves from slopes of tangents at initial stages of
the reaction by plane mirror method. The $k_{app}$ and the
initial rates were reproducible within $\pm$ 5%. Example
runs of both fresh and aged solutions are given in tables
IIA(ii) (p.109) and IIA(iii) (p.110).

Runs under conditions of pH greater than 12 lead to
satisfactory results. However, at the lower $\text{OH}^-$
concentrations of less than around 0.10 mol dm$^{-3}$, the
reaction mixture tended to become turbid presumably due
to precipitation of chromium(III) hydroxide (Cr(OH)$_3$) as
shown in table IIA(ib) (p.105). For this reason, runs had
to be restricted to pH greater than 12. Chromium(III)
solutions under the reaction conditions of pH $> 12$ were
tested for turbidity using a Systronics Nephelo Turbidity
Meter - 131 and showed no interference from insoluble
material. The pH was measured with a pH meter after
appropriate calibration with known buffers and had a
precision of $\pm$ 0.05 unit.

In view of the modest concentrations of alkali used
in the reaction medium, attention was also given to the
effect of surface on the kinetics. Test solutions were
handled ab initio in polythene/acrylic ware and
Table IIA(ii) : Oxidation of chromium(III) by hexacyanoferrate(III) : Example run in case of freshly dissolved chromium(III) solution

\[ [\text{Cr(III)}] = 0.007; \quad [\text{Fe(CN)}_6^{3-}] = 0.021 \quad [\text{OH}^-] = 0.20 \]
\[ I = 0.70/\text{mol dm}^{-3}; \quad \text{temp. 27°C} \]

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Absorbance (590)</th>
<th>([\text{Cr(III)}] \times 10^3) mol dm(^{-3})</th>
<th>(1/[\text{Cr(III)}] \times 10^{-2}) dm(^3) mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.172</td>
<td>6.89</td>
<td>1.45</td>
</tr>
<tr>
<td>0.2</td>
<td>0.147</td>
<td>5.88</td>
<td>1.70</td>
</tr>
<tr>
<td>0.4</td>
<td>0.125</td>
<td>5.00</td>
<td>2.00</td>
</tr>
<tr>
<td>0.8</td>
<td>0.100</td>
<td>4.00</td>
<td>2.50</td>
</tr>
<tr>
<td>1.0</td>
<td>0.089</td>
<td>3.57</td>
<td>2.80</td>
</tr>
<tr>
<td>1.5</td>
<td>0.071</td>
<td>2.85</td>
<td>3.50</td>
</tr>
<tr>
<td>2.0</td>
<td>0.061</td>
<td>2.44</td>
<td>4.09</td>
</tr>
<tr>
<td>3.0</td>
<td>0.045</td>
<td>1.80</td>
<td>5.50</td>
</tr>
<tr>
<td>4.0</td>
<td>0.036</td>
<td>1.44</td>
<td>6.95</td>
</tr>
<tr>
<td>5.0</td>
<td>0.030</td>
<td>1.20</td>
<td>8.30</td>
</tr>
<tr>
<td>6.0</td>
<td>0.026</td>
<td>1.05</td>
<td>9.60</td>
</tr>
<tr>
<td>7.0</td>
<td>0.023</td>
<td>0.91</td>
<td>11.0</td>
</tr>
<tr>
<td>8.0</td>
<td>0.020</td>
<td>0.81</td>
<td>12.4</td>
</tr>
<tr>
<td>10.0</td>
<td>0.016</td>
<td>0.65</td>
<td>15.4</td>
</tr>
</tbody>
</table>
Table IIA(iii) : Oxidation of chromium(III) by hexacyanoferrate(III) at 27°C. Example run of 'aged' chromium(III) solution

\[
\begin{align*}
[Cr(III)] &= 0.007; \\
[Fe(CN)]_6^{3-} &= 0.021; \\
[OH^-] &= 0.25; \\
I &= 0.7/mol \text{ dm}^{-3}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Absorbance (590nm)</th>
<th>([Cr(III)] \times 10^3) mol dm(^{-3})</th>
<th>(1/[Cr(III)] \times 10^2) mol(^{-1}) dm(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.216</td>
<td>7.08</td>
<td>1.41</td>
</tr>
<tr>
<td>0.2</td>
<td>0.190</td>
<td>6.25</td>
<td>1.60</td>
</tr>
<tr>
<td>0.4</td>
<td>0.169</td>
<td>5.54</td>
<td>1.80</td>
</tr>
<tr>
<td>0.8</td>
<td>0.135</td>
<td>4.43</td>
<td>2.26</td>
</tr>
<tr>
<td>1.0</td>
<td>0.122</td>
<td>4.00</td>
<td>2.50</td>
</tr>
<tr>
<td>1.5</td>
<td>0.098</td>
<td>3.21</td>
<td>3.11</td>
</tr>
<tr>
<td>2.0</td>
<td>0.083</td>
<td>2.72</td>
<td>3.67</td>
</tr>
<tr>
<td>3.0</td>
<td>0.064</td>
<td>2.10</td>
<td>4.76</td>
</tr>
<tr>
<td>4.0</td>
<td>0.052</td>
<td>1.70</td>
<td>5.86</td>
</tr>
<tr>
<td>5.0</td>
<td>0.043</td>
<td>1.41</td>
<td>7.09</td>
</tr>
<tr>
<td>6.0</td>
<td>0.037</td>
<td>1.21</td>
<td>8.24</td>
</tr>
<tr>
<td>7.0</td>
<td>0.033</td>
<td>1.08</td>
<td>9.24</td>
</tr>
<tr>
<td>8.0</td>
<td>0.029</td>
<td>0.95</td>
<td>10.5</td>
</tr>
<tr>
<td>10.0</td>
<td>0.025</td>
<td>0.82</td>
<td>12.2</td>
</tr>
</tbody>
</table>
absorbance of reaction solutions followed under different OH$^-$ concentrations in quartz as well as polyacrylate cells. Both sets of results with quartz and polyacrylate cells agreed with the results obtained previously with glass vessels and the results are shown in table IIA(iv)(p.112). The details of construction of optical absorption cells from polyacrylate sheets is given in the appendix (p.142).

The effect of dissolved oxygen on the rate of the reaction was also 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 seen.

RESULTS

Stoichiometry

Different sets of concentrations of reactants in 0.20 mol dm$^{-3}$ sodium hydroxide at a constant ionic strength of 0.70 mol dm$^{-3}$ were kept for 8 hours at 27$^\circ$C under nitrogen atmosphere. The chromium(III) and chromium(VI) were analysed by spectrophotometry at 590 and 360 nm respectively. The absorption of chromium(VI)
Table IIA(iv) : Effect of variation of [OH\(^-\)] as well as surface of different vessels and cells on chromium(III) hexacyanoferrate(III) reaction at 25°C.

\[ [Cr(III)] = 0.007; \ [Fe(CN)_{6}^{3-}] = 0.021; \ I = 0.70/mol \ dm^{-3} \]

<table>
<thead>
<tr>
<th>[OH(^-)] mol dm(^{-3})</th>
<th>(Inl. rate(_{\text{expt}})) (\times 10^5) mol dm(^{-3}) s(^{-1})</th>
<th>(Inl. rate(_{\text{cal}})) (\times 10^5) mol dm(^{-3}) s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>Glass</td>
<td>Polyacrylate</td>
</tr>
<tr>
<td>0.10</td>
<td>5.30</td>
<td>5.30</td>
</tr>
<tr>
<td>0.15</td>
<td>6.68</td>
<td>6.65</td>
</tr>
<tr>
<td>0.20</td>
<td>9.00</td>
<td>9.10</td>
</tr>
<tr>
<td>0.25</td>
<td>10.6</td>
<td>10.5</td>
</tr>
<tr>
<td>0.30</td>
<td>11.1</td>
<td>11.1</td>
</tr>
<tr>
<td>0.35</td>
<td>14.5</td>
<td>14.5</td>
</tr>
<tr>
<td>0.45</td>
<td>15.3</td>
<td>15.2</td>
</tr>
<tr>
<td>0.50</td>
<td>16.8</td>
<td>16.5</td>
</tr>
</tbody>
</table>

# Calculation of initial rates was on the basis of equation(9) using \(K_{OH}\) and \(k\) as \(1.62 \pm 0.02 \text{ dm}^3\text{mol}^{-1}\) and \(2.50 \pm 0.2 \text{ dm}^3\text{mol}^{-1}\) s\(^{-1}\) respectively.

Error \(\pm 3\%\)
at 370 nm obeys Beer's law in alkaline medium under the conditions of reaction in the range of $1.0 \times 10^{-5}$ to $3.0 \times 10^{-4}$ mol dm$^{-3}$ and results in a molar absorbancy index, $\varepsilon$, of $4670 \pm 2\%$ dm$^3$ mol$^{-1}$ cm$^{-1}$ (Fig.IIA(ii), p. 107). The unreacted hexacyanoferrate(III) was also estimated by acidifying the reaction mixture with sulphuric acid in presence of zinc sulphate which prevents the back reaction of hexacyanoferrate(II) with chromium(VI). The total oxidant was then found by iodometry and after accounting for the chromium(VI) formed, the remaining oxidant concentration could be derived. The results support a 3:1 stoichiometry (Table IIA(v); p. 114) for the reaction:

$$3\text{Fe(CN)}_6^{3-} + \text{Cr(III)} \rightarrow 3\text{Fe(CN)}_6^{4-} + \text{Cr(VI)}; (1)$$

The stoichiometric results with 'aged' (36 hours) chromium(III) solutions were the same as with freshly prepared chromium(III) solutions (equation 1).

**Reaction order**

The order of the reaction was found from log-log plots of initial rates versus concentrations at constant alkalinity of 0.20 mol dm$^{-3}$ and ionic strength of 0.70
Table IIA(v) : Stoichiometry of Fe(CN)$_6^{3-}$-Cr(III) reaction

$[\text{OH}^-] = 0.20, \ I = 0.70/\text{mol dm}^{-3}, \ \text{temp.} \ 27\degree\text{C.}$

<table>
<thead>
<tr>
<th>[Cr(III)]x10$^2$ taken</th>
<th>[Fe(CN)$_6^{3-}$]x10$^2$ taken</th>
<th>[Cr(III)]x10$^2$ remaining</th>
<th>[Fe(CN)$_6^{3-}$]x10$^2$ remaining</th>
<th>[Cr(VI)]x10$^2$ found</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.70</td>
<td>2.10</td>
<td>-</td>
<td>-</td>
<td>0.70</td>
</tr>
<tr>
<td>0.70</td>
<td>1.00</td>
<td>0.35</td>
<td>-</td>
<td>0.34</td>
</tr>
<tr>
<td>0.70</td>
<td>0.50</td>
<td>0.53</td>
<td>-</td>
<td>0.17</td>
</tr>
<tr>
<td>1.0</td>
<td>1.0</td>
<td>0.67</td>
<td>-</td>
<td>0.33</td>
</tr>
<tr>
<td>1.0</td>
<td>5.0</td>
<td>-</td>
<td>2.0</td>
<td>1.0</td>
</tr>
<tr>
<td>0.70</td>
<td>4.0</td>
<td>-</td>
<td>1.9</td>
<td>0.70</td>
</tr>
</tbody>
</table>

# All concentrations are in mol dm$^{-3}$. 
mol dm$^{-3}$. At a fixed concentration of chromium(III) of 0.70x10$^{-2}$ mol dm$^{-3}$, the order in hexacyanoferrate(III) in the concentration range of 5.0x10$^{-3}$ to 5.0x10$^{-2}$ mol dm$^{-3}$ was nearly unity and at a constant hexacyanoferrate(III) concentration of 2.1x10$^{-2}$ mol dm$^{-3}$, the order in chromium(III) in the concentration range of 2.0x10$^{-3}$ to 2.0x10$^{-2}$ mol dm$^{-3}$ was $\approx 0.92$ (Table IIA(vi); p.116 and Fig. IIA(iii); p.117). The OH$^-$ order was found to be $\approx 0.94$ in the concentration range of 0.10 to 0.55 mol dm$^{-3}$ at constant ionic strength and all other reactant concentrations being constant (Table IIA(iv); p.112 and Fig. IIA(iv); p.118).

In view of the tendency of chromium(III) solution to undergo precipitation after standing for 36 hours, the effect of the time of standing of chromium(III) solution on reaction rate was also examined. It may be noted that the onset of 'slow' precipitation starts after about 40 hours (Table IIA(i)). Thus, the orders with respect to oxidant, reductant and OH$^-$ concentration were found in case of the reaction of hexacyanoferrate(III) with 'aged' chromium(III). The orders were found to be almost the same as in the case of the fresh solution, except that the order in oxidant had come down marginally (Table IIA(viii); p.119). However, the second order rate
Table IIA(vi): Effect of variation of [Cr(III)] and [Fe(CN)$_6^{3-}$] on chromium(III)-hexacyanoferrate(III) reaction at 27°C.

$[\text{OH}^-] = 0.20$; $I = 0.70/\text{mol dm}^{-3}$.

<table>
<thead>
<tr>
<th>[Cr(III)]x$10^3$ mol dm$^{-3}$</th>
<th>[Fe(CN)$_6^{3-}$]x$10^2$ mol dm$^{-3}$</th>
<th>Inl. rate$\times10^5$ mol dm$^{-3}$ s$^{-1}$</th>
<th>Exptl.</th>
<th>Calculated*</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>2.1</td>
<td>2.50</td>
<td>2.60</td>
<td></td>
</tr>
<tr>
<td>4.0</td>
<td>2.1</td>
<td>5.30</td>
<td>5.20</td>
<td></td>
</tr>
<tr>
<td>7.0</td>
<td>2.1</td>
<td>8.90</td>
<td>9.00</td>
<td></td>
</tr>
<tr>
<td>9.0</td>
<td>2.1</td>
<td>12.2</td>
<td>11.6</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>2.1</td>
<td>14.0</td>
<td>14.1</td>
<td></td>
</tr>
<tr>
<td>7.0</td>
<td>0.50</td>
<td>2.60</td>
<td>2.20</td>
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</tr>
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<td>7.0</td>
<td>0.70</td>
<td>3.30</td>
<td>3.00</td>
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</tr>
<tr>
<td>7.0</td>
<td>1.0</td>
<td>4.80</td>
<td>4.30</td>
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<td>7.0</td>
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<td>8.90</td>
<td>9.00</td>
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</tr>
<tr>
<td>7.0</td>
<td>4.0</td>
<td>17.2</td>
<td>17.0</td>
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<tr>
<td>7.0</td>
<td>5.0</td>
<td>22.1</td>
<td>21.4</td>
<td></td>
</tr>
</tbody>
</table>

* Calculation of initial rates on the basis of equation (9) using $K_{OH}$ and $k$ as $1.62 \pm 0.02$ dm$^3$ mol$^{-1}$ and $2.50 \pm 0.2$ dm$^3$ mol$^{-1}$ s$^{-1}$ respectively.

Error $\pm 3\%$
Fig. IIA(iii): Order in Cr(III) (−Δ−) and Fe(CN)$_6^{3−}$ (−•−) Fe(CN)$_6^{3−}$ oxidation of Cr(III).

(conditions as in table IIA(vi), p.116).
Fig. IIA(iv) : Order in OH⁻ :
Fe(CN)₆³⁻ oxidation of Cr(III).
(conditions as in table IIA(iv), p.112).
Table IIA(viii) : Effect of variation of [Cr(III)], [Fe(CN)₆³⁻] and [OH⁻] on chromium(III)-hexacyanoferrate(III) reaction at 27°C.

The Cr(III) solution was of 36 hours (aged).
I = 0.70 mol dm⁻³

Error ± 3%
constant, $k_{app}$, was dependent on the 'age' of the chromium(III) solution (Table IIA(vii); p.121 and fig.IIA(v), p.122).

**Effect of added products and ions**

Initially added products, chromium(VI) and hexacyanoferrate(II), in the concentration range of $2.0 \times 10^{-3}$ to $5.0 \times 10^{-2}$ mol dm$^{-3}$, did not have any significant effect on the reaction rate. The results were similar in the case of the reaction of the 'aged' chromium(III) solution (Table IIA(ix) p.123).

In view of the possibility that sulphate ions might affect results, an amount of sulphate ions added (as $\text{Na}_2\text{SO}_4$) up to $2.10 \times 10^{-2}$ mol dm$^{-3}$ (an amount of $1.40 \times 10^{-2}$ mol dm$^{-3}$ coming from the chrome alum used to prepare the chromium(III) stock solution is already present) did not show any significant change in results. Likewise, oxalate, thiocyanate, cyanide and sodium salt of EDTA did not affect the reaction in concentrations up to $2.10 \times 10^{-2}$ mol dm$^{-3}$.

**Effect of ionic strength and temperature**

The ionic strength of the reaction solution was
Table IIA(vii): Dependence of the apparent second order constant, $k_{app}$, on the duration of standing of Cr(III) solution in Cr(III)-Fe(CN)$_6^{3-}$ reaction at 27°C.

$[\text{Cr(III)}] = 0.007; \ [\text{Fe(CN)}_6^{3-}] = 0.021; \ \ [\text{OH}^-] = 0.25; \ I = 0.44/\text{mol dm}^{-3}$

<table>
<thead>
<tr>
<th>Time in hours</th>
<th>0</th>
<th>6</th>
<th>24</th>
<th>36</th>
<th>48</th>
<th>72</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{app} \text{ dm mol}^{-1} \text{s}^{-1}$</td>
<td>1.52</td>
<td>1.00</td>
<td>0.80</td>
<td>0.76</td>
<td>0.67</td>
<td>0.62</td>
</tr>
</tbody>
</table>

Error $\pm 3\%$
Fig. IIA(v) : Plot of $[\text{Cr(III)}]^{-1}$ vs. time : Fe(CN)$_6^{3-}$ oxidation of Cr(III)
(a) for freshly dissolved Cr(III)($\Theta$-) and
(b) 'aged' Cr(III)($\Lambda$-) in alkali.
(conditions as in tables IIA(ii) and IIA(iii), pp. 109, 103 respectively.)
Table IIA(ixa): Effect of added products on oxidation of chromium(III) by hexacyanoferrate(III) at 27°C.

\[
[\text{Cr(III)}] = 0.007; \quad [\text{Fe(CN)}_6^{3-}] = 0.021; \\
[\text{OH}^-] = 0.20; \quad I = 0.70/\text{mol dm}^{-3}
\]

<table>
<thead>
<tr>
<th>[Cr(VI)]x10^3 mol dm(^{-3})</th>
<th>Inl. ratex10^5 mol dm(^{-3}) s(^{-1})</th>
<th>[Fe(CN)_6^{4-}]x10^2 mol dm(^{-3})</th>
<th>Inl. ratex10^5 mol dm(^{-3}) s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>8.90</td>
<td>0.50</td>
<td>8.95</td>
</tr>
<tr>
<td>4.0</td>
<td>8.95</td>
<td>0.70</td>
<td>8.90</td>
</tr>
<tr>
<td>7.0</td>
<td>8.90</td>
<td>1.01</td>
<td>8.90</td>
</tr>
<tr>
<td>9.0</td>
<td>9.00</td>
<td>2.10</td>
<td>8.90</td>
</tr>
<tr>
<td>11</td>
<td>9.00</td>
<td>4.00</td>
<td>9.00</td>
</tr>
<tr>
<td>12</td>
<td>8.90</td>
<td>5.00</td>
<td>9.00</td>
</tr>
</tbody>
</table>

Table IIA(ixb): Activation parameters of chromium(III)-hexacyanoferrate(III) reaction.

\[
[\text{Cr(III)}] = 0.007; \quad [\text{Fe(CN)}_6^{3-}] = 0.021; \\
[\text{OH}^-] = 0.20; \quad I = 0.70/\text{mol dm}^{-3}
\]

<table>
<thead>
<tr>
<th>Temp.°C</th>
<th>(k_{\text{app}}) dm(^{-3}) mol(^{-1}) s(^{-1})</th>
<th>(\log k_{\text{app}})</th>
<th>((1/T)\times10^3) K(^{-1})</th>
<th>(-\Delta S^#)</th>
</tr>
</thead>
<tbody>
<tr>
<td>27</td>
<td>1.47</td>
<td>0.167</td>
<td>3.33</td>
<td>72.10</td>
</tr>
<tr>
<td>32</td>
<td>1.74</td>
<td>0.240</td>
<td>3.27</td>
<td>73.40</td>
</tr>
<tr>
<td>37</td>
<td>2.05</td>
<td>0.312</td>
<td>3.22</td>
<td>75.38</td>
</tr>
<tr>
<td>42</td>
<td>2.37</td>
<td>0.375</td>
<td>3.17</td>
<td>75.10</td>
</tr>
<tr>
<td>47</td>
<td>2.71</td>
<td>0.433</td>
<td>3.13</td>
<td>79.20</td>
</tr>
</tbody>
</table>

\(\Delta H^\# = 48.2\ \text{kJ mol}^{-1}\)
\(\Delta S^\# = -75\ \text{JK}^{-1}\text{mol}^{-1}\)
varied between 0.39 and 1.0 mol dm$^{-3}$ with sodium perchlorate at constant oxidant, reductant and OH$^- \cdot$ concentrations of $2.1 \times 10^{-2}$, $7.0 \times 10^{-3}$ and 0.20 mol dm$^{-3}$ respectively. The apparent second order rate constant, $k_{\text{app}}$, showed a near five-fold increase and log $k_{\text{app}}$ versus $I^-$ was linear with a slope of 2.0 (Fig.IIA(vi); p. 125). When the ionic strength was varied using lithium perchlorate instead of sodium perchlorate, the results were found to be identical.

In respect of the 'aged' chromium(III) solution (36 hours), the effect of the ionic strength was studied between 0.44 and 0.95 mol dm$^{-3}$ under similar conditions (except [OH$^-\cdot] = 0.25$ mol dm$^{-3}$ here) as used in case of fresh chromium(III) solution. The slope of log $k_{\text{app}}$ versus $I^-$ was again found to be nearly 2.0 (Table IIA(x); p.126) and Fig. IIA(vi) (p.125).

Kinetics were also studied at 27, 32, 37, 42 and 47°C at constant reactant concentrations (Table IIA(ix); p.123). From the data, the enthalpy of activation, $\Delta H^\#$, and entropy of activation, $\Delta S^\#$, were found to be 48.2 kJ mol$^{-1}$ and $-75\pm4$ JK$^{-1}$ mol$^{-1}$ respectively (Fig. IIA(vii),p. 127 and table IIA(ix); p.123).
Fig. IIA(vi) : Effect of ionic strength :
Fe(CN)$_3^-$ oxidation of Cr(III)
(a) for freshly dissolved Cr(III) (\(\cdot\)O\(\cdot\)) and
(b) 'aged' Cr(III) (\(\cdot\)\(\Delta\)\(\cdot\)) in alkali.

(conditions as in table IIA(x), p.126).
Table IIA(X): Effect of ionic strength on the apparent second order constant, $k_{app}$, of oxidation of chromium(III) by hexacyanoferrate(III) in alkali at 27°C.

$[\text{Cr(III)}] = 0.007; \quad [\text{Fe(CN)}_6^{3-}] = 0.021/\text{mol dm}^{-3}$

<table>
<thead>
<tr>
<th>I (mol dm$^{-3}$)</th>
<th>$k_{app}$ (dm$^3$mol$^{-1}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh Cr(III) solution</td>
<td>Aged Cr(III) solution</td>
</tr>
<tr>
<td>[OH$^-$] = 0.20 mol dm$^{-3}$</td>
<td>[OH$^-$] = 0.25 mol dm$^{-3}$</td>
</tr>
<tr>
<td>0.39</td>
<td>0.95</td>
</tr>
<tr>
<td>0.55</td>
<td>1.47</td>
</tr>
<tr>
<td>0.75</td>
<td>2.70</td>
</tr>
<tr>
<td>0.90</td>
<td>3.70</td>
</tr>
<tr>
<td>1.00</td>
<td>4.90</td>
</tr>
</tbody>
</table>

Error $\pm$ 4%
Fig. IIA(vii) : Effect of temperature on Fe(CN)$_6^{3-}$ oxidation of Cr(III) (conditions as in table IIA(ixb), p.123).
Rate law

The rate law (2) of oxidation of chromium(III) by hexacyanoferrate(III) follows from the experimental results.

\[ \text{Rate} = k [\text{Cr(III)}]^{0.92} [\text{Fe(CN)}_{6}^{3-}] [\text{OH}^{-}]^{0.94} \] (2)

The order in oxidant was less than unity in case of 'aged' chromium(III) solution.

DISCUSSION

Chromium(III) in an alkaline medium at pH > 11.5 exhibits greater solubility due to the predominence of the species \( \text{Cr(OH)}_{4}^{−} \) under the conditions of ionic strength 0.010 mol dm\(^{-3}\) at 22°C in aged solutions\(^2\). It is also found that slow formation of polynuclear species occurs as well as a decrease in solubility with time. It could therefore be expected that the insolubility in such solutions might be due to formation of such polynuclear chromium(III) in greater and greater proportion with time. In the present case, the solubility of chromium(III) in freshly prepared solutions is dependent on pH and increases rapidly with pH as shown in respect of 7.0x10\(^{-3}\).
mol dm$^{-3}$ solutions at 27°C (Table IIA(1b), p.105). As monitored by Nepheloturbidity meter, while solutions are clear above pH 12.2, the turbidity increases with acidity and precipitation occurs below pH of 10.15. Presumably on account of the slow formation of polynuclear species and, also to an increasing extent with time, the clear solutions of chromium(III) (7.0x10$^{-3}$ mol dm$^{-3}$) tend to become turbid beyond ~40 hours (Table IIA(1a), p.105). When kinetics were studied with chromium(III) solutions of different 'ages' from zero to 72 hours (other solutions freshly prepared), the rate constant, $k_{app}$, was found to have decreased with increasing 'age' of the chromium(III) solution (Table IIA(11), p.121). Although the reaction with 'aged' chromium(III) solution tends to slow down, kinetics of oxidation of both fresh and 'aged' chromium(III) solutions (upto 40 hours) occur smoothly and without interference. Only reactions under conditions of pH > 12 have been studied in this work for reasons detailed already. The solubility of chromium(III) above pH 12 has been ascribed to Cr(OH)$_4^{2-}$ formation and the spectrum under such conditions is similar to that of Cr$^{3+}_{aq}$ except that some hyperchromicity is found (Fig. IIA(1), p.104) in the former case ($\epsilon_{590} = 25+1$ as against 17 of Cr$^{3+}_{aq}$). Interestingly, Cr(OH)$_{6}^{3-}$, widely believed$^9$ to be responsible for the amphoterism of
chromium(III), is not one of the species in alkaline solutions. In terms of the formation equilibrium of Cr(OH)$_4^-$ from the rather low concentration of Cr(OH)$_3$ present in soluble form in such solutions, the small deviation of the reaction order in chromium(III) from unity may be explained as due to the total chromium(III) in the reaction being mainly split between these two forms. Attention may also be called to the fact that, polymeric chromium(III) species in such solutions, as in the present case, at ordinary temperatures and when the chromium(III) solution is freshly made, are almost completely absent. The order of less than unity in OH$^-$ concentration may also be understood in terms of the predominant chromium(III) species of Cr(OH)$_4^-$.

In terms of the pre-equilibrium involving chromium(III) and OH$^-$ and the generally well accepted principle of non-complementary oxidations taking place in sequences of one-electron steps, the mechanism of Scheme 1 is feasible. The order of unity in hexacyanoferrate(III) is well accommodated in Scheme 1.
As has been mentioned in the results section, chromium(III) solutions 'aged' up to 36 hours display kinetic features which are largely similar to those found in respect of the freshly prepared chromium(III) except that the reaction is now slower. The orders in chromium(III) and OH\textsuperscript{−} are not changed much, but the order in oxidant is now less than unity. The mechanism is still the same even at 36 hours, the slower reaction presumably being due to the less easily oxidisable chromium(III) species.

According to Scheme 1, the rate is given by eqn. (3)

\[
-d[\text{Cr(III)}]/dt = k[\text{Fe(CN)}_6^{3−}][\text{Cr(OH)}_4^{−}]
\]  

(3)
where

\[
[\text{Cr}(\text{III})]_T = [\text{Cr(OH)}_3^-] + [\text{Cr(OH)}_4^-]
\]  \hspace{1cm} (4)

From the first step of the Scheme 1,

\[
[\text{Cr}(\text{III})]_T = [\text{Cr(OH)}_3^-] + K_\text{OH}[\text{Cr(OH)}_3^-][\text{OH}^-]
\]  \hspace{1cm} (5)

or \[
[\text{Cr(OH)}_3^-] = [\text{Cr}(\text{III})]_T / (1 + K_\text{OH}[\text{OH}^-])
\]  \hspace{1cm} (6)

and therefore,

\[
[\text{Cr(OH)}_4^-] = \frac{K_\text{OH}[\text{Cr}(\text{III})]_T[\text{OH}^-]_T}{(1 + K_\text{OH}[\text{OH}^-]_T)(1 + K_\text{OH}[\text{Cr(III)}]_T)}
\]  \hspace{1cm} (7)

In (7), \([\text{OH}^-]_f\), the free \([\text{OH}^-]\) concentration is given by

\[
[\text{OH}^-]_f = \frac{[\text{OH}^-]_T}{(1 + K_\text{OH}[\text{Cr(III)}]_T)}
\]  \hspace{1cm} (8)

The rate of the reaction is therefore given by,

\[
\frac{-d[\text{Cr}(\text{III})]_T}{dt} = \frac{kK_\text{OH}[\text{Fe(CN)}_6^{3-}]_T[\text{Cr}(\text{III})]_T[\text{OH}^-]_T}{(1 + K_\text{OH}[\text{OH}^-]_T)(1 + K_\text{OH}[\text{Cr(III)}]_T)}
\]  \hspace{1cm} (9)

\[
= \frac{kK_\text{OH}[\text{Fe(CN)}_6^{3-}]_T[\text{Cr}(\text{III})]_T[\text{OH}^-]_T}{(1 + K_\text{OH}[\text{OH}^-]_T)}
\]  \hspace{1cm} (as \((1 + K_\text{OH}[\text{Cr(III)}]_T) = 1\)
The mechanism of Scheme 1 and the rate law (9) may be verified by rearranging it in the form of (10):

\[
\frac{[\text{Fe(CN)}_6^{3-}] [\text{Cr(III)}]_T}{\text{rate}} = \frac{1}{kK_{OH}} \frac{1}{[\text{OH}^-]_T} + \frac{1}{k}. \tag{10}
\]

The plot of left hand side against \(1/[\text{OH}^-]_T\) should be linear which is verified (Fig. IIA(viii), p.134); the slope and intercept lead to values of \(K_{OH}\) and \(k\) at \(27^\circ\text{C}\) as \(1.62 \, \text{dm}^3 \, \text{mol}^{-1}\) and \(2.5 \, \text{dm}^3 \, \text{mol}^{-1} \, \text{s}^{-1}\) respectively. From these values, rates for several experimental conditions may be calculated from (9) and compared with the experimentally found data. Such a comparison has been made in tables IIA(iv) (p.112) and IIA(vi) (p.116) and it is found that there is good agreement between the calculated and experimental rates.

The effect of increasing ionic strength on the rate is also in the expected direction on the basis of the reaction between the two negatively charged species, \(\text{Cr(OH)}_4^-\) and \(\text{Fe(CN)}_6^{3-}\). Ion pairing in case of \(\text{Fe(CN)}_6^{3-}\) with \(K^+\) is well known\(^\text{10}\). The ion pairing decreases with the size of ions and a value of less than 10 has been assumed for the formation constant\(^\text{11}\) of \(H^+\text{Fe(CN)}_6^{3-}\). Thus, ion pairing between \(\text{Na}^+\) and \(\text{Fe(CN)}_6^{3-}\) may be
Fig. IIA(ii) : Verification of rate law (9) :
\[ \text{Fe(CN)}_6^{3-} \text{ oxidation of Cr(III)} \]
(conditions as in table IIA(iv), p.112).
expected in the present case also and if ion pairs are more reactive than the unpaired ones, the increasing ionic strength favouring larger ion pairing may lead to increase in $k_{\text{app}}$ value. Thus, a part of the increase in $k_{\text{app}}$ value with ionic strength may be due to ion pairing. The reaction between Fe(CN)$_3^{3-}$ and Cr(OH)$_4^{-}$, leads to log $k_{\text{app}}$ vs. $I^{1/2}$ linear plot with a slope of +2 (Fig. IIA(vi), p.125) which is less than the value that may be expected.

The fact that the log $k_{\text{app}}$ vs. $I^{1/2}$ results are similar in case of 'aged' Cr(III) solutions to those of the reaction of fresh Cr(III) emphasizes the fact that no serious differences of mechanism exist between the two cases.

On the basis of the Scheme 1, $k_{\text{app}}$ is approximately equal to $k_{K_{\text{OH}}}$ and in any case, Cr(III) order deviates only a little from unity. The entropy of activation is less negative than is expected$^{12}$ on the basis of the reaction between two negative ions, one triply charged and the other singly charged. However, if ion pairing as discussed above is occurring between Na$^+$ and Fe(CN)$_3^{3-}$, this will contribute to a less negative $\Delta S^\#$ value.

The hexacyanoferrate(III) oxidation of chromium(III) in alkaline medium is facile and takes places with the intervention of chromium(IV) and chromium(V). In acid medium, chromium(V) has some stability and its esr
spectrum has been recorded and chromium(IV) is one of the most potent oxidants known in acid medium and can oxidise manganese(II) to manganese(III). While not much is known about these chromium species in basic medium, from scheme 1 it appears that they are much weaker oxidants in alkali. Chromium(VI) itself loses much of its oxidising capacity in basic medium and this trend appears to apply to its lower oxidation states as well.
Findings:

The reaction between chromium(III) and hexacyanoferrate(III) in acid medium does not occur but is facile in alkali due to the changes of the potentials of the two redox couples. The reaction is found to take place in one equivalent steps with intervention of intermediates, chromium(V) and chromium(IV). The reaction is much faster at higher OH$^-$ concentration and the kinetic data support the formation of complex, Cr(OH)$_4^-$; a value for the formation constant is also derived.

Work advisable:

More information on the formation of the species, of Cr(OH)$_4^-$ is advisable. Furthermore, while chromium(IV) is a potent oxidant and chromium(V) comparatively less so in acid, their oxidising abilities and stabilities in alkali are not known. A greater understanding of these chromium intermediates in alkaline solutions is desirable.

Importance of the results of Chapter IIA:

In the present work, we have examined the solubility
of chromium(III) at higher pH's which is due to the formation of species like Cr(OH)$_4^-$, but not Cr(OH)$_6^{2-}$ as reported in many text books. The oxidation of chromium(III) in alkaline solutions has been studied here for the first time. The spectrum of chromium(III) in basic solution is identical with that of Cr$^{3+}_{aq}$, with some hyperchromicity.
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APPENDIX

Construction of optical absorption cell of 1 cm path length by polyacrylate sheets

The required 1 cm cells could be constructed by either of two procedures:

i) Two pairs of plates (1.20 x 4.80 cm) and 1.00 x 4.80 cm were cut from 1 mm thick polyacrylate sheets and the edges smoothened with emery paper. Each pair forms parallel surfaces of the cell and, using a paste made of polyacrylate powder in chloroform (or methyl ethyl ketone), the plates are fashioned into a cell of 1 cm path length, with bottom and top made from 1.2 cm$^2$ plates prepared as before. The paste is carefully applied to the edges with a pointed glass rod. After allowing to dry, any leaks could be remedied with fresh applications of the acrylic paste. Repeated trials gave rise to very satisfactory results.

ii) In an alternative procedure, a wooden block with perfect dimensions of 1.0 x 1.0 x 4.8 in cm with very smooth surfaces could be used. The surfaces were greased and the two pairs of sheets, 1.2 x 4.8 (cm) and 1.0 x 4.8 (cm)
used to prepare the cell with the wooden block as support. The bottom was covered with a 1.2 cm$^2$ piece. The paste was used as before with care. Once the cell was ensured to be leak proof, a lid could also be prepared similarly. The dimensions of the wooden block were crucial in ensuring the 1 cm path length of the cell.

Calibration

The cells may be calibrated by comparison of the optical densities obtained with it using standard chromate (or copper sulphate) solutions with similarly measured optical densities using known cells or with known standard values.

The cells prepared in this manner were found to be satisfactory in the range of 280-900 nm. The sheets chosen to prepare the cells must be free from scratches. Polyacrylate is unaffected by dilute mineral acids and bases except hydrofluoric acid and ammonia. The pH range of 0-14 may be employed with upto around 5% acid or 30% bases. Inorganic compounds do not affect the cells. During normal use at ordinary temperature, no breakage or leakage can occur. The cells can be cleaned with soap water rinsing. However, brushing as well as use of organic solvents is to be avoided.