Hexacyanoferrate (III), (HCF (III)) has been widely used to oxidise numerous organic and inorganic compounds in alkaline media. The authors\textsuperscript{1-2} have suggested that alkaline hexacyanoferrate (III) ion simply acts as an electron abstracting reagent in redox reactions. However, Speakman and waters\textsuperscript{3} have suggested different paths of oxidation of aldehydes, ketones and nitroparaffins. Singh and coworkers,\textsuperscript{4,5} while discussing the oxidations of formaldehyde, acetone and ethyl methyl ketone have suggested that the oxidation takes place via an electron transfer process resulting in the formation of a free radical intermediate.

Sulfanilic acid (p-aminobenzenesulfonic acid) (SAA) is an important and interesting compound, which finds number of applications in the syntheses of organic dyes, one of which is familiar indicator, methyl orange (I) (Helianthin) used as an indicator, and methyl orange (II) (from diazodised sulfanilic acid and 2-naphthol) is used for dying paper\textsuperscript{6}. The amide of sulfanilic acid (sulfanilamide) and certain related substituted amides are of considerable medical importance as the sulfa drugs. Although they have been supplanted to a wide extent by the antibiotics such as penicillin, terramycin, chloromycetin and aureomycin. The sulfa drugs still have their medical uses, and make up a considerable portion of the output of the pharmaceutical industry. The antibacterial activity and toxicity of a
sulfanilamide stems from a rather simple fact: Enzymes in the bacteria and inpatients confuse it for p-aminobenzenesulfonic acid (sulfanilic acid), which is an essential metabolite. In what is known as metabolite antagonism, the sulfanilamide competes with p-aminobenzenesulfonic acid (sulfanilic acid) for reactive sites on the enzymes, deprived of the essential metabolite the organism fails to reproduce and dies\textsuperscript{7}. Several studies have been reported on the oxidation of sulfanilic acid by other oxidants such as peroxomonophosphoric acid\textsuperscript{8}, periodate\textsuperscript{9}, \( \text{H}_2\text{O}_2 \)\textsuperscript{10}, Ce (IV)\textsuperscript{11}, persulfate (peroxy disulfate)\textsuperscript{12,13}. Different workers have identified different products by different oxidants for sulfanilic acid\textsuperscript{8-13}. Thus the study of sulfanilic acid becomes important because of its biological significance and selectivity towards the oxidants. In view of the lack of literature on the oxidation of sulfanilic acid by HCF (III), and in order to explore the mechanistic aspects of HCF (III) oxidation in alkaline medium, we have chosen sulfanilic acid as a substrate. The present study deals with the title reaction to investigate the redox chemistry of HCF (III) in such media, and to arrive at a suitable mechanism for the oxidation of sulfanilic acid 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

Reagent grade chemicals and doubly distilled water were used throughout. A solution of Fe(CN)$_6^{3-}$ was prepared by dissolving K$_3$Fe(CN)$_6$ (BDH) in H$_2$O and was standardized iodometrically$^{14}$. Sulfanilic acid is not only insoluble in organic solvents, but also nearly insoluble in water and in aqueous acids, but it is soluble in aqueous bases. These properties of sulfanilic acid are understandable when we realize that sulfanilic acid actually has the structure I which contains the $-\text{NH}_3^+$ and $-\text{SO}_3^-$ groups. Sulfanilic acid is a salt of special kind, called a dipolar ion sometimes called as a zwitterion$^7$. The hydrogen ion is attached to nitrogen rather than oxygen simply because the $-\text{NH}_2$ group is a stronger base than the $\text{SO}_3^-$ group.

In alkaline solution, the strongly basic hydroxide ion pulls hydrogen ion away from the weakly basic $-\text{NH}_2$ group to yield the p-aminobenzenesulfonate ion (II), which like most sodium salts, is soluble in water. Therefore the solution of sulfanilic acid (Merck) was prepared by dissolving appropriate amount of sample in warm and very dilute alkali. Hexacyanoferrate (II) solution was prepared by dissolving a known amount of K$_4$Fe(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.
KINETIC MEASUREMENTS

All kinetic measurements were performed under pseudo first-order conditions where [sulfanilic acid] was always ≥10 fold in excess over [HCF (III)] at a constant ionic strength of 2.50 mol dm$^{-3}$ in alkaline medium at a constant temperature of 30 ± 0.1°C respectively. The reaction was initiated by mixing the thermostatted hexacyanoferrate (III) and sulfanilic 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 were obtained from the plots of log [HCF (III)] versus time, an example run is given in Table V (i) (p.171). The plots were linear upto 75% completion of the reaction in alkaline medium and the $k_{obs}$ values were reproducible within ±5% and deviation from linearity was also observed due to the retarding effect of one of the products. The results are also interpreted in terms of initial rate of the reaction to avoid the complexities which may arise due to interference by the products. Initial rates were obtained from tangents at the initial stages of concentration versus time curves by the plane mirror method and were reproducible to within ±4%.
Table V (i)

An Example run for the oxidation of sulfanilic acid by aqueous alkaline hexacyanoferrate (III) at 30 °C

\[ [\text{HCF(III)}] = 5.0 \times 10^{-4}; \quad [\text{SAA}] = 10.0 \times 10^{-3}; \]
\[ [\text{H}^+] = 0.90; \quad I = 2.50 \text{ /mol dm}^3. \]

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Optical density (420 nm)</th>
<th>Log [HCF(III)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.526</td>
<td>-3.3043</td>
</tr>
<tr>
<td>0.2</td>
<td>0.500</td>
<td>-3.3263</td>
</tr>
<tr>
<td>0.4</td>
<td>0.471</td>
<td>-3.3522</td>
</tr>
<tr>
<td>0.6</td>
<td>0.443</td>
<td>-3.3789</td>
</tr>
<tr>
<td>0.8</td>
<td>0.417</td>
<td>-3.4051</td>
</tr>
<tr>
<td>1.0</td>
<td>0.391</td>
<td>-3.4331</td>
</tr>
<tr>
<td>1.2</td>
<td>0.368</td>
<td>-3.4594</td>
</tr>
<tr>
<td>1.4</td>
<td>0.347</td>
<td>-3.4849</td>
</tr>
<tr>
<td>1.6</td>
<td>0.327</td>
<td>-3.5107</td>
</tr>
<tr>
<td>1.8</td>
<td>0.309</td>
<td>-3.5353</td>
</tr>
<tr>
<td>2.0</td>
<td>0.293</td>
<td>-3.5584</td>
</tr>
<tr>
<td>2.2</td>
<td>0.278</td>
<td>-3.5812</td>
</tr>
<tr>
<td>2.4</td>
<td>0.265</td>
<td>-3.6020</td>
</tr>
<tr>
<td>2.6</td>
<td>0.254</td>
<td>-3.6204</td>
</tr>
<tr>
<td>2.8</td>
<td>0.243</td>
<td>-3.6396</td>
</tr>
</tbody>
</table>

Error ± 5%.
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 $1.0 \times 10^{-3}$ 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)$^{15}$. A regression analysis of experimental data in order to obtain the regression coefficient, $r$ and standard deviation, $s$ of plots from the regression line was performed with a Pentium-III personnel computer.

RESULTS

Stoichiometry and Product Analysis

The reaction mixture containing excess hexacyanoferrate (III) concentration over sulfanilic acid were mixed in presence of 0.90 mol dm$^{-3}$ sodium hydroxide, adjusted to a constant ionic strength of 2.5 mol dm$^{-3}$ and allowed to
react for about 4h at 30 ± 0.1°C. The remaining HCF (III) was then analysed spectrophotometrically. The results indicated that eight moles of HCF (III) were consumed by two moles of sulfanilic acid according to equation (1) (1:4), as shown in Table V (ii) (p.174). The reaction product was eluted with ether, and submitted to spot test\textsuperscript{16}, which revealed the presence of an azo, nitroso and keto groups. The presence of dye was also confirmed by finding its uv/vis spectrum\textsuperscript{17} and by its IR\textsuperscript{18} spectroscopy. IR (KBr) showed bands at (υ) 1727cm\textsuperscript{-1} (for carbonyl, >C=O stretching and 1375 cm\textsuperscript{-1} for N=N → O stretching). However, the other product, in alkaline medium is hexacyanoferrate (II), Fe(CN)\textsubscript{6}\textsuperscript{4-}, which was identified by titration\textsuperscript{15}. The product keto azoxydye, does not undergo further oxidation under the present kinetic conditions, since the test for probable oxidation product of ketone i.e acid and nitrosobenzene was negative.

**Identification of keto azoxy dye from its uv/vis spectrum.**

When uv/vis spectrum was observed at different pH i.e. from pH = 4 to pH = 7, no absorption is observed in the visible region but in the uv region at λ\textsubscript{max} = 278 nm, the extinction coefficient ε = 174.1 mol\textsuperscript{-1}cm\textsuperscript{-1} indicating π → π* transition due to carbonyl chromophore (>C=O). At high H\textsuperscript{+} ion concentration absorption is observed in the visible region at λ\textsubscript{max} = 601.6 nm, the ε = 13.1 dm\textsuperscript{3} mol\textsuperscript{-1}cm\textsuperscript{-1} indicating n → π* transitions\textsuperscript{19}. When we compare the uv/vis spectrum of azobenzene and azoxybenzene with that of the product keto azoxydye, it has been found that for azodye at λ\textsubscript{max} = 433nm, ε = 727 for azoxybenzene at λ\textsubscript{max} = 322nm, ε = 14700, in MeOH, where as for keto azoxybenzene, at λ\textsubscript{max} = 601.6nm, ε = 13.1 in...
Table V (ii)

Stoichiometry for the oxidation of sulfanilic acid by aqueous alkaline hexacyanoferrate (III) at 30° C.

\[ [\text{OH}^-] = 0.90; \quad I = 2.50 \text{ /mol dm}^{-3}. \]

<table>
<thead>
<tr>
<th>Taken</th>
<th>[HCF(III)] x 10^4</th>
<th>[SAA] x 10^4</th>
<th>[HCF(III)] x 10^4</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>1.0</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>2.0</td>
<td>2.08</td>
<td></td>
</tr>
<tr>
<td>6.0</td>
<td>1.0</td>
<td>2.05</td>
<td></td>
</tr>
<tr>
<td>8.0</td>
<td>2.0</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>4.0</td>
<td>0.5</td>
<td>2.01</td>
<td></td>
</tr>
</tbody>
</table>

Error ± 5%.
HCl, indicating forbidden transition. The shift in $\lambda_{\text{max}}$ value of the product towards longer wavelength may be due to increase in conjugation. Carbonyl group (>C=O) extends the conjugation of a chromophore by $-N\equiv N\rightarrow O$ resulting in a different absorption maximum with very low extinction coefficient.

**REACTION ORDERS**

The order each in sulfanilic 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 $k_{\text{obs}}$ versus log concentration graphs and the orders were obtained from such graphs.

**Effect of [Hexacyanoferrate]**,

The oxidant, HCF (III) concentration was varied in the range of $1.0 \times 10^{-4}$ to $10 \times 10^{-3}$ mol dm$^{-3}$ and the linearity of plot of log [HCF (III)] versus time (Fig. V (i) (p.176)) ($r >0.9987$, $s< 0.0255$) indicates the order in [HCF (III)] as unity. This was also confirmed by varying [HCF (III)]$_{0}$, which did not show any change in pseudo first order rate constants $k_{\text{obs}}$ (Table V (iii) (p.177)).

**Effect of [Sulfanilic acid]**

The substrate, sulfanilic acid, concentration was varied in the range of $2.0 \times 10^{-3}$ to $2.0 \times 10^{-2}$ mol dm$^{-3}$ at 30°C keeping all other reactants concentration and conditions constant (Table V (iii) (p.177). The apparent order in [SAA] was found to be less than unity (0.60) ($r >0.9949$, $s< 0.03417$) (Fig. V (ii) (p.178)).
Figure V (i)

First order plot of [HCF(III)] on oxidation of sulfanilic acid by aqueous alkaline hexacyanoferrate (III) at 30 °C.

(Conditions as in Table V (iii) (p. 177)).

[HCF (III)] x 10^{-4} \text{ mol dm}^{-3}: (1) 1.0, (2) 3.0, (3) 5.0, (4) 7.0 and (5) 10.
### Table V (iii)

Effect of variation of [sulfanilic acid], [HCF (III)] and [OH⁻] on the oxidation of sulfanilic acid by alkaline hexacyanoferrate (III) at 30°C, I=2.5 mol dm⁻³.

<table>
<thead>
<tr>
<th>[SAA] 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>kₜₐₜ x 10⁻³ (s⁻¹)</th>
<th>Initial rate x 10⁻⁷ (mol dm⁻³ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Expt*.</td>
<td>Cald*</td>
<td>Expt*.</td>
<td>Cald*</td>
</tr>
<tr>
<td>2.0</td>
<td>5.0</td>
<td>9.0</td>
<td>1.76</td>
<td>1.75</td>
</tr>
<tr>
<td>6.0</td>
<td>5.0</td>
<td>9.0</td>
<td>3.76</td>
<td>3.78</td>
</tr>
<tr>
<td>10</td>
<td>5.0</td>
<td>9.0</td>
<td>4.74</td>
<td>4.90</td>
</tr>
<tr>
<td>15</td>
<td>5.0</td>
<td>9.0</td>
<td>5.62</td>
<td>5.77</td>
</tr>
<tr>
<td>20</td>
<td>5.0</td>
<td>9.0</td>
<td>6.85</td>
<td>6.33</td>
</tr>
<tr>
<td>10</td>
<td>1.0</td>
<td>9.0</td>
<td>4.72</td>
<td>4.90</td>
</tr>
<tr>
<td>10</td>
<td>3.0</td>
<td>9.0</td>
<td>4.75</td>
<td>4.90</td>
</tr>
<tr>
<td>10</td>
<td>5.0</td>
<td>9.0</td>
<td>4.72</td>
<td>4.90</td>
</tr>
<tr>
<td>10</td>
<td>7.0</td>
<td>9.0</td>
<td>4.76</td>
<td>4.90</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>9.0</td>
<td>4.71</td>
<td>4.90</td>
</tr>
<tr>
<td>10</td>
<td>5.0</td>
<td>1.5</td>
<td>8.52</td>
<td>8.20</td>
</tr>
<tr>
<td>10</td>
<td>5.0</td>
<td>5.0</td>
<td>2.39</td>
<td>2.72</td>
</tr>
<tr>
<td>10</td>
<td>5.0</td>
<td>9.0</td>
<td>4.79</td>
<td>4.90</td>
</tr>
<tr>
<td>10</td>
<td>5.0</td>
<td>12</td>
<td>6.61</td>
<td>6.54</td>
</tr>
<tr>
<td>10</td>
<td>5.0</td>
<td>15</td>
<td>8.07</td>
<td>8.12</td>
</tr>
</tbody>
</table>

*Experimental and Calculated.

Error ± 5%
Figure V (ii)

Order of reaction with respect to [SAA] and [OH'] on oxidation of sulfanilic acid by aqueous alkaline hexacyanoferrate (III) at 30° C.

(Conditions as in Table V (iii) (p.177)).
Effect of Sodium hydroxide

The effect of increasing concentration of alkali was studied on the reaction rate at constant concentration of sulfanilic acid and HCF (III) at constant ionic strength of 2.50 mol dm\(^{-3}\) at 30\(^\circ\)C. The rate constants increased with the increase in alkali concentration. (Table V (iii) (p.177)), order = unity) (r >0.9976, s< 0.0536) (Fig. V(ii) (p.178)).

Effect of Initially Added Reaction Product

The initially added product, such as HCF (II), in the range of (1.0-1.5) x10\(^{-4}\) mol dm\(^{-3}\) keeping other conditions constants had a retarding effect on the rate of the reaction. As the initial concentration of HCF (II) is increased, the rate progressively decreased. This illustrates the retarding nature of the product (Table V (iv) (p.180)).

Effect of Ionic Strength

The effect of ionic strength was studied by varying the sodium perchlorate concentration. The ionic strength of the reaction medium was varied from 0.9 to 3.0 mol dm\(^{-3}\) at constant concentrations of HCF (III), sulfanilic acid and alkali as given in Table V (v) (p.181). It was found that the rate constant increased with increasing concentration of NaClO\(_4\), and the plot of log k\(_{obs}\) versus I\(^{1/2}\) was linear (r >0.9843, s< 0.0467) with positive slope (Fig. V (iii) (p.182)).

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.
Table V (iv)

Effect of product, HCF (II) on the oxidation of sulfanilic acid by alkaline hexacyanoferrate (III) at 30°C

\[
\begin{align*}
[HCF(III)] &= 5.0 \times 10^{-4}; \\
[OH^-] &= 9.0 \times 10^{-1}; \\
[SAA] &= 10.0 \times 10^{-3}; \\
I &= 2.50/\text{mol dm}^3.
\end{align*}
\]

<table>
<thead>
<tr>
<th>[HCF(II)] (x\ 10^4) (mol dm(^3))</th>
<th>(k_{obs}\ x10^3) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>4.65</td>
</tr>
<tr>
<td>5.0</td>
<td>4.57</td>
</tr>
<tr>
<td>8.0</td>
<td>4.24</td>
</tr>
<tr>
<td>12</td>
<td>3.80</td>
</tr>
<tr>
<td>15</td>
<td>3.23</td>
</tr>
</tbody>
</table>

Error ± 5%
Table V (v)

Effect of variation of ionic strength (I) and solvent polarity (D) on the oxidation of sulfanilic acid by aqueous alkaline hexacyanoferrate at 30°C.

\[
[HCF(III)] = 5.0 \times 10^{-4}; \quad [HCF(III)] = 1.10 \times 10^{-3};
\]
\[
[SAA] = 1.10 \times 10^{-3}; \quad [SAA] = 1.10 \times 10^{-3};
\]
\[
[OH^-] = 9.0 \times 10^{-1}; \quad [OH^-] = 9.0 \times 10^{-1};
\]

\[I = 2.50 \text{ mol dm}^{-3}.\]

<table>
<thead>
<tr>
<th>(I) \text{ (mol dm}^{-3})</th>
<th>(k_{\text{obs}} \times 10^3) \text{ (s}^{-1})</th>
<th>% of t-butanol*</th>
<th>(D)</th>
<th>(k_{\text{obs}} \times 10^3) \text{ (s}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9</td>
<td>2.89</td>
<td>5</td>
<td>75.12</td>
<td>4.80</td>
</tr>
<tr>
<td>1.4</td>
<td>3.20</td>
<td>10</td>
<td>71.74</td>
<td>4.78</td>
</tr>
<tr>
<td>2.0</td>
<td>3.83</td>
<td>15</td>
<td>68.36</td>
<td>4.78</td>
</tr>
<tr>
<td>2.5</td>
<td>4.79</td>
<td>20</td>
<td>64.98</td>
<td>4.76</td>
</tr>
<tr>
<td>3.0</td>
<td>5.33</td>
<td>25</td>
<td>61.60</td>
<td>4.73</td>
</tr>
</tbody>
</table>

*t-butanol-water (v/v)

Error ± 5%.
Figure V (iii)
Effect of ionic strength (I) on the oxidation of sulfanilic acid by aqueous acidic hexacyanoferrate (III) at 30° C.

(Conditions as in Table V (v) (p. 181)).
Attempts to measure the relative permittivity were not successful. However, they were computed from the values of pure liquids\textsuperscript{20} as given in chapter II. There is no reaction of the solvent with the oxidant under the experimental conditions. It was found that the rate constant did not change with decreasing dielectric constant of the medium Table V (v) (p.181).

**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 a nitrogen 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 [SAA]. The rate of reaction increased with the increase of temperature. The rate constants, $k$ of the slow step of scheme 1 were obtained from intercept and slope of $[\text{OH}^-]/k_{\text{obs}}$ versus $1/[\text{SAA}]$ and used to calculate the activation parameters. The values of $k$ ($s^{-1}$) are given in Table V (vi a) (p.184). The activation parameters corresponding to these constants were evaluated from the plot of log $k$ ($Y_{\text{cald.}}$) versus $1/T$ as shown in Figure V (iv) (p.185) ($r>0.9960$ $s \leq 0.08900$) and are tabulated in Table V (vi b) (p.184).
Table V (vi)
Effect of temperature on the slow step of the mechanism of oxidation of sulfanilic acid by alkaline hexacyanoferrate (III).

\[ [\text{HCF(III)}] = 5.0 \times 10^{-4}; \]
\[ [\text{SAA}] = 10.0 \times 10^{-3}; \]
\[ [\text{OH}^-] = 9.0 \times 10^{-1}; \]
\[ I = 2.50 /\text{mol dm}^{-3}. \]

(a) Values of rate constants

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>k (dm$^3$ mol$^{-1}$ s$^{-1}$)</th>
<th>$1/T \times 10^4$ (X)</th>
<th>Log k</th>
<th>$Y_{\text{calcd.}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>9.90</td>
<td>3.30</td>
<td>-2.00</td>
<td>-1.98</td>
</tr>
<tr>
<td>308</td>
<td>15.8</td>
<td>3.25</td>
<td>-1.83</td>
<td>-1.83</td>
</tr>
<tr>
<td>313</td>
<td>23.7</td>
<td>3.19</td>
<td>-1.62</td>
<td>-1.64</td>
</tr>
<tr>
<td>318</td>
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<tr>
<td>323</td>
<td>43.2</td>
<td>3.09</td>
<td>-1.36</td>
<td>-1.34</td>
</tr>
</tbody>
</table>

*Calculated.

(b) Thermodynamic activation parameters.

<table>
<thead>
<tr>
<th>Activation parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_a$ (kJ mol$^{-1}$)</td>
<td>$60 \pm 3$</td>
</tr>
<tr>
<td>$\Delta H^#$ (kJ mol$^{-1}$)</td>
<td>$58 \pm 3$</td>
</tr>
<tr>
<td>Log A</td>
<td>$8.4 \pm 0.4$</td>
</tr>
<tr>
<td>$\Delta S^#$ (JK$^{-1}$ mol$^{-1}$)</td>
<td>$-93 \pm 3$</td>
</tr>
<tr>
<td>$\Delta G^#$ (kJ mol$^{-1}$)</td>
<td>$86 \pm 4$</td>
</tr>
</tbody>
</table>

Error $\pm 5\%$. 

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Figure V (iv)

Effect of temperature on the slow step of the mechanism of oxidation of sulfanilic acid by aqueous alkaline hexacyanoferrate (III).

(Conditions as in Table V (vi) (p. 184)).
DISCUSSION

Variation of the concentrations each of the oxidant (HCF (III)), substrate (SAA) and alkali, while keeping the others constant showed that the reaction exhibits first-order in oxidant, alkali and less than unit order in substrate concentrations (Table V(iii) (p.177)). The reaction between SAA and HCF (III) in NaOH has a stoichiometry of 1:4. It has been observed that the presence of ferrocyanide, [Fe (CN)$_6$]$^{4-}$ retards the rate of reduction of ferricyanide by SAA. 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$^{21}$. 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 sulfanilic 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$^{22-24}$. 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$^{25}$. In the present study, the oxidation reaction proceeds via formation of a complex between
substrate and oxidant, which decomposes in presence of alkali in a slow step to a free radical derived from SAA 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, hydroxylamine benzene sulfonic acid, and HCF (II). The hydroxylamine benzene sulfonic acid so formed further reacts with two moles of HCF (III) in a fast step to give nitrosobenzene sulfonic acid and HCF (II). Another molecule of SAA reacts with two moles of HCF (III) in fast steps to give hydroxylamine benzene sulfonic acid as intermediate product and HCF (II). The two intermediate products namely nitrosobenzene sulfonic acid and hydroxylamine benzene sulfonic acid rearrange themselves in a fast step to azoxybenzene - 4,4'- disulfonic acid as another intermediate product, which in presence of two moles of HCF (III) under goes further oxidation to the final products, 2 keto azoxybenzene-4,4'- disulfonic acid and hexacyanoferrate (II) (HCF (II)), satisfying the stoichiometric observations. The results can be accommodated by scheme 1.

\[
\text{Scheme 1:}
\]

\[
\text{HO}_3\text{S}-\text{NH}_2 + [\text{Fe(CN)}_6]^{3-} \xrightleftharpoons{K} [\text{HO}_3\text{S}-\text{N}^- - [\text{Fe(CN)}_6]^{3-}] + \text{CN}^- \\
\text{Complex (C)}
\]

\[
\text{Complex (C)} + [\text{OH}^-] \xrightarrow{k_{\text{slow}}} \text{HO}_3\text{S}-\text{N}^- + [\text{Fe(CN)}_6]^{3-} + \text{H}_2\text{O}
\]

\[
[\text{Fe(CN)}_6]^{3-} + \text{CN}^- \xrightarrow{\text{fast}} [\text{Fe(CN)}_6]^{4-}
\]

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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) – sulfanilic acid mixture. A hypsochromic shift of about 5 nm from 290 to 285 nm is observed, and hyperchromicity is observed at of about 285 nm. 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 $[\text{OH}] / k_{\text{obs}}$ versus $1/[\text{SAA}]$ (Fig. V (v) (p. 191)). 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 via inner-sphere mechanism. This conclusion is supported by earlier observations. Scheme 1 is in accordance with the generally well-accepted principle of noncomplementary oxidations taking place in sequences of one electron steps.

The rate law of the reaction can be derived from scheme 1 as given below

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

Rate = $k K [\text{Fe (CN)}_6^{3-}]_r [\text{SAA}]_r [\text{OH}]_r$

Where $K = \frac{[\text{C}]}{[\text{Fe (CN)}_6^{3-}][\text{SAA}]}$

$[\text{SAA}]_r = [\text{SAA}]_r + C$

$= [\text{SAA}]_r + K [\text{Fe (CN)}_6^{3-}]_r [\text{SAA}]_r$

$= [\text{SAA}]_r \{1 + K [\text{Fe (CN)}_6^{3-}]_r \}$

Therefore,

$[\text{SAA}]_r = \frac{[\text{SAA}]_r}{\{1 + K [\text{Fe (CN)}_6^{3-}]_r \}}$

(2)
Similarly,
\[
[\text{Fe (CN)}_6^{3-}]_r = [\text{Fe (CN)}_6^{3-}]_f + C
- [\text{Fe (CN)}_6^{3-}]_f + K [\text{Fe (CN)}_6^{3-}]_f [\text{SAA}]
= [\text{Fe (CN)}_6^{3-}]_f \{1 + K [\text{SAA}]\}
\]

Therefore,
\[
[\text{Fe (CN)}_6^{3-}]_r = \frac{[\text{Fe (CN)}_6^{3-}]_f}{1 + K [\text{SAA}]}
\]

Substituting equation (3) and (4) in equation (2)

\[
\text{Rate} = - \frac{d[\text{Fe (CN)}_6^{3-}]}{dt} = \frac{k K [\text{Fe (CN)}_6^{3-}]_f [\text{SAA}][\text{OH}^-]}{(1+K[\text{SAA}]) (1+K[\text{Fe (CN)}_6^{3-}]_f)}
\]

\[
\text{Rate} = \frac{k K [\text{Fe (CN)}_6^{3-}]_f [\text{SAA}][\text{OH}^-]}{1+K[\text{SAA}]+K[\text{Fe (CN)}_6^{3-}]+K^2[\text{Fe (CN)}_6^{3-}]_f [\text{SAA}]}
\]

The terms \((K[\text{Fe (CN)}_6^{3-}])\) and \((K^2[\text{SAA}][\text{Fe (CN)}_6^{3-}])\) in the denominator of equation (6) approximate to unity in view of the low concentration of \(\text{Fe (CN)}_6^{3-}\) used and the observed first order with respect to \(\text{Fe (CN)}_6^{3-}\). Therefore equation (6) becomes

\[
\text{Rate} = \frac{k K [\text{Fe (CN)}_6^{3-}]_f [\text{SAA}][\text{OH}^-]}{1+K[\text{SAA}]}
\]

\[
\text{Rate} = \frac{k K [\text{SAA}][\text{OH}^-]}{1+K[\text{SAA}]}
\]

Equation (8) can be rearranged to the following form, which is used for verification of the rate law.

\[
\frac{[\text{OH}^-]}{k_{\text{obs}}} = \frac{1}{kk[\text{SAA}]} + \frac{1}{k}
\]

According to equation (9), the plots of \([\text{OH}^-]/k_{\text{obs}}\) versus \(1/[\text{SAA}]\) (\(r > 0.9990, s < 0.0148\)) should be linear, as verified in Figure V (v) (p.191). The slope and intercept of such plot leads to the values of \(K\) and \(k\) at 30°C as \((1.22 \pm 0.04) \times 10^2 \text{ dm}^3 \text{ mol}^{-1}, (9.9 \pm 0.4) \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{s}^{-1}\), respectively. Using these
Figure V (v)

The plot of $[\text{OH}^']/k_{\text{obs}}$ versus $1/[[\text{SAA}]]$ (Verification of rate law (8) in the form of equation (9))

(Conditions as in Table V (iii) (p.177)).
values rate constants under different experimental conditions were calculated and compared with experimental data (Table V (iii) (p.177). 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 negative value of the entropy of activation indicated that the complex is more ordered than the reactants. The observed modest activation energy and sizeable entropy of activation supports a complex transition state in the reaction.

Importance of chapter V

The oxidation of SAA with HCF (III) in alkaline medium involves the retardation by one of the products and the overall mechanistic sequence described here is consistent with product, mechanistic and kinetic studies. The reaction constants in the mechanism are evaluated. There is a good agreement between the observed and calculated rate constants under different experimental conditions.
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