

## Oxidation of Salicylaldehyde by Alkaline Hexacyanoferrate(III)-A Kinetic and Mechanistic Study

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**Abstract:** The kinetics of oxidation of salicylaldehyde by hexacyanoferrate(III) in aqueous alkaline medium was studied. An inverse fractional order with respect to substrate shows the substrate inhibition. A first order dependence in hexacyanoferrate(III) concentration and a fractional order in alkali were found. A retarding effect was observed by one of the products i.e. hexacyanoferrate(II). Increasing ionic strength and dielectric constant of the medium were found to increase rate of the reaction. The effect of temperature on the rate of reaction has also been studied and activation parameters have been evaluated. A mechanism based on the experimental results is proposed and the rate law is derived.

**Key words:** Oxidation; salicylaldehyde; substrate inhibition; inverse fractional order; 2-Hydroxy benzaldehyde; Potassium hexacyanoferrate(III)

### 1. Introduction

Hexacyanoferrate(III) has been proven to be an efficient oxidant for a wide variety of organic substrates, because the  $CN^-$  ligands are resistant to substitution reactions and thereby outer-sphere electron transfer is the preferred oxidation pathway. Therefore, oxidations are normally clean, devoid of side reactions, which greatly facilitate the monitoring<sup>1-2</sup>. The oxidation of reducing sugars<sup>3</sup>, phenols and naphthols<sup>4</sup>, vanillin<sup>5</sup>, enolizable and non-enolizable aldehydes<sup>2</sup> by this oxidant in alkaline medium have been studied.

2-hydroxy benzaldehyde otherwise known as salicylaldehyde plays a vital role in synthesis of Schiff base<sup>6</sup> and some compounds with anti-cancer<sup>7</sup>, anti microbial<sup>8-9</sup> and anti inflammatory<sup>10</sup> properties. Even though there are reports for oxidation of salicylaldehyde by other methods<sup>11-13</sup>, a systematic kinetic and mechanistic study is still lacking. The present work reports the kinetics of oxidation of salicylaldehyde by hexacyanoferrate(III) in alkaline medium and evaluates the reaction constants. Mechanistic aspects are also discussed.

### 2. Experimental

#### 2.1. Materials and Methods

All the chemicals (AR grade) were purchased from SD fine chemicals Ltd., and used without further purification. A solution of hexacyanoferrate(III) was prepared by dissolving  $K_3[Fe(CN)_6]$  in double distilled water and standardized iodometrically<sup>14a</sup>. NaOH and KCl were employed to maintain the required alkalinity and ionic strength respectively.

## 2.2. Kinetic Measurements

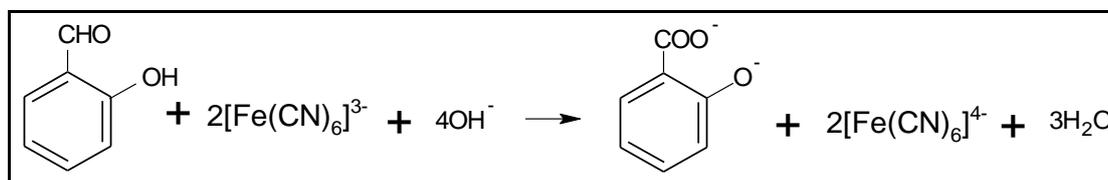
All kinetic measurements were performed under pseudo first-order conditions where [salicylaldehyde] was always in excess over hexacyanoferrate(III), at a constant ionic strength of  $1.0 \text{ mol.dm}^{-3}$  in alkaline medium at temperature of  $(30.0 \pm 0.1)^\circ\text{C}$ . The reaction was initiated by mixing the thermostatted solutions of hexacyanoferrate(III) and salicylaldehyde which also contained the required concentration of NaOH and KCl. The progress of the reaction was followed by observing the disappearance of hexacyanoferrate(III) titrimetrically. Pseudo first- order rate constants,  $k_{\text{obs}}$ , were obtained (Tables I and II) from the slopes of plots of  $\log_{10}[\text{Fe}(\text{CN})_6^{3-}]$  versus time; the plots were linear and the  $k_{\text{obs}}$  values were reproducible to within  $\pm 2\%$ .

**Table I: Effect of Variations of  $[\text{Fe}(\text{CN})_6^{3-}]$ , [Substrate] and  $[\text{OH}^-]$  on the Oxidation of Salicylaldehyde by  $\text{Fe}(\text{CN})_6^{3-}$  at  $30^\circ\text{C}$ ,  $I = 1.0 \text{ mol}\cdot\text{dm}^{-3}$**

$[\text{Fe}(\text{CN})_6^{3-}] \times 10^3$ ( $\text{mol}\cdot\text{dm}^{-3}$ )	[Substrate] $\times 10^2$ ( $\text{mol}\cdot\text{dm}^{-3}$ )	$[\text{OH}^-]$ ( $\text{mol}\cdot\text{dm}^{-3}$ )	$k_{\text{obs}} \times 10^4$ ( $\text{s}^{-1}$ )
4	5	0.8	3.81
5	5	0.8	3.79
6	5	0.8	3.8
7	5	0.8	3.81
5	4	0.8	4.05
5	5	0.8	3.79
5	6	0.8	3.53
5	7	0.8	3.32
5	5	0.4	2.18
5	5	0.6	2.57
5	5	0.8	3.79
5	5	1.0	4.66

## 2.3. Stoichiometry and Products Analysis

Different sets of reaction mixtures containing varying ratios of reactants to  $[\text{Fe}(\text{CN})_6^{3-}]$  in the presence of constant amount of  $\text{OH}^-$  and KCl were kept for about 24 hours at  $30^\circ\text{C}$  in a closed vessel. The remaining hexacyanoferrate(III) was estimated titrimetrically. The results indicated that two moles of hexacyanoferrate (III) consumed 1 mol of salicylaldehyde as given in the following equation.



The stoichiometric ratio suggests that the main reaction products are salicylic acid and  $\text{Fe}(\text{CN})_6^{4-}$ . The product salicylic acid is identified by its spot test<sup>15</sup>, isolated by acidifying the reaction mixture followed by ether extraction and confirmed by IR spectrum and its melting point at  $157.8^\circ\text{C}$ . (Experimental value  $159^\circ\text{C}$ ). The characteristic IR absorption bands at  $1663 \text{ cm}^{-1}$ ,  $2924 \text{ cm}^{-1}$ ,  $2854 \text{ cm}^{-1}$ ,  $1287 \text{ cm}^{-1}$  &  $3396 \text{ cm}^{-1}$  confirmed the presence of carboxylic acid group, the IR bands at  $1294 \text{ cm}^{-1}$ ,  $1352 \text{ cm}^{-1}$  &  $3784 \text{ cm}^{-1}$  confirmed the hydroxyl group and the same at  $759 \text{ cm}^{-1}$  &  $800 \text{ cm}^{-1}$  confirmed the presence of ortho disubstituted aromatic compound. The concentration of the reduction product,  $\text{Fe}(\text{CN})_6^{4-}$ , was estimated<sup>14b</sup> by titrating against a Ce(IV) solution.

## 3. Results and Discussion

### 3.1. Effect Of [Hexacyanoferrate(III)]

The rates were measured by varying the concentration of hexacyanoferrate(III) varied in the range of  $4.0 \times 10^{-3}$  to  $7.0 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ , keeping all other reactant concentrations and ionic strength as constant

(Table 1). The constancy in the value of rate constants irrespective of the concentration of the hexacyano ferrate(III) confirmed the first order dependence on hexacyanoferrate(III). This was also confirmed from the linearity of plots of  $\log_{10} [\text{hexacyanoferrate(III)}]$  versus time ( $r = 0.999$  and  $s \leq 0.004$ ) for up to 80% completion of the reaction.

### 3.2. Effect of [Salicylaldehyde]

A typical kinetic run is shown in Table II. A plot of  $\log[\text{hexacyanoferrate(III)}]$  against time is linear for the reaction ( $r = 0.988$ ) (Fig. 1.a). When the [substrate] was varied in the range of  $4.0 \times 10^{-2}$  to  $7.0 \times 10^{-2}$  mol.dm<sup>-3</sup> at 30°C keeping all other concentrations and conditions constant (Table I). The  $k_{\text{obs}}$  values decreased with increasing concentration of salicylaldehyde showing negative fractional order dependence on [salicylaldehyde]. Similar effects were reported in alkaline ferricyanide oxidation of sorbitol & mannitol<sup>16</sup> and aromatic aldehydes<sup>17</sup>, potassium periodate oxidation of myo-inositol<sup>18</sup> and D-sorbitol & D-mannitol<sup>19</sup> in alkaline medium.

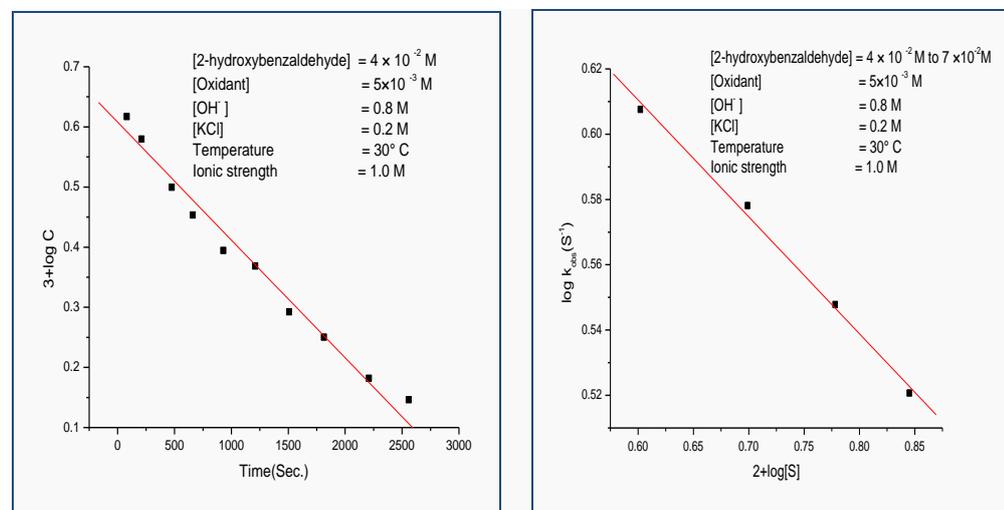
A plot of  $\log k_{\text{obs}}$  against  $2 + \log[\text{salicylaldehyde}]$  is linear with negative slope. ( $= -0.4$ ) ( $r = 0.997$ ) (Fig. 1.b).

The double reciprocal plot (Graph of  $1/k_{\text{obs}}$  versus  $1/[\text{Substrate}]$ ) is given in fig.3.

**Table II: Order with respect to [Substrate]**

[Substrate]= $4 \times 10^{-2}$ (mol.dm <sup>-3</sup> ); [OH <sup>-</sup> ] = 0.8 (mol.dm <sup>-3</sup> ); [oxidant] = $5 \times 10^{-3}$ (mol.dm <sup>-3</sup> ), Ionic strength=1.0(mol.dm <sup>-3</sup> )										
Time (s)	80	211	476	660	930	1210	1508	1814	2209	2559
$10^3 [k_{\text{obs}}]_t$	4.54	3.80	3.16	2.84	2.48	2.18	1.96	1.78	1.52	1.40

$k_{\text{obs}}$  was found to be  $= 4.05 \times 10^{-4} (\text{s}^{-1})$



**Fig. 1 (a) First order plot:  $\log[\text{hexacyanoferrate (III)}]$  against time(b) Plot of  $\log k_{\text{obs}}$  against  $2 + \log [\text{salicylaldehyde}]$**

### 3.3. Effect of [Alkali]

The dependence of the reaction rate on hydroxide ion has been studied in the range 0.40 to 1.00 mol.dm<sup>-3</sup> keeping the concentration of substrate and oxidant constant at ionic strength 1.0 mol.dm<sup>-3</sup> showed the values of the rate constants increased with increasing [OH<sup>-</sup>]. (Table 1) The order was found to be less than unity ( $\approx 0.54$ ). A plot of  $\log k_{\text{obs}}$  against  $\log [\text{OH}^-]$  is linear. (fig.3)

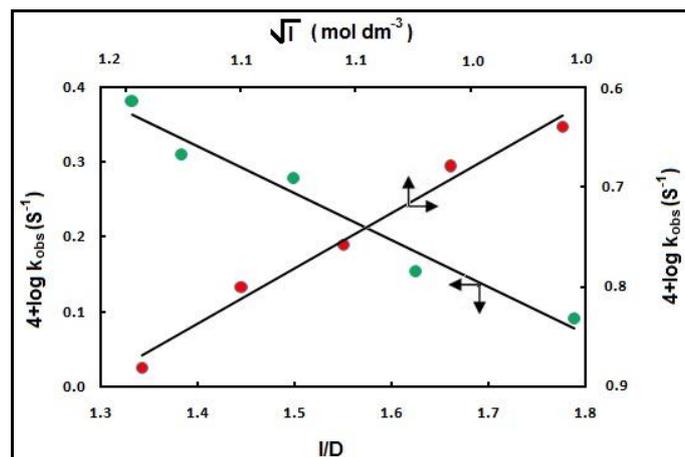
### 3.4. Effect of Ionic Strength and Solvent Polarity

The change in the ionic strength was effected by the addition of potassium chloride of known strength. The values of rate constants at different ionic strengths are calculated in Table III. It is clear that the rate of

reaction is increased by the addition of KCl which confirms reaction between similarly charged species in the rate determining step.

**Table III: Effect of varying Ionic strength on reaction rate**

[Substrate]= $5 \times 10^{-2}$ mol.dm $^{-3}$ ; [OH $^{-}$ ] = 0.8 mol.dm $^{-3}$ ; [oxidant] = $5 \times 10^{-3}$ mol.dm $^{-3}$ .					
$I$ (mol.dm $^{-3}$ )	1.00	1.10	1.20	1.30	1.40
$10^4 k$ (s $^{-1}$ )	3.79	4.07	5.39	5.52	6.77



**Fig.2. Effect of ionic strength and dielectric constant of the medium on oxidation of salicylaldehyde by hexacyanoferrate(III)**

As the dielectric constant of the medium is decreased, a decrease in rate of oxidation is observed (Fig. 2).

### 3.5. Effect of Initially Added Product

The effect of initially added product hexacyanoferrate(II) on the rate of reaction was also studied in the range of  $1.0 \times 10^{-3}$  to  $4.0 \times 10^{-3}$  mol.dm $^{-3}$  at 30°C by keeping ionic strength and other concentrations constant (Table IV). It has retarding effect on the rate of oxidation, revealing that the step in which hexacyanoferrate(II) is formed as a product must be reversible.

**Table IV: Effect of Added Product, hexacyanoferrate (II), on the Oxidation of salicylaldehyde by Hexacyanoferrate(III) in Aqueous Alkaline Medium**

[salicylaldehyde] = $5 \times 10^{-2}$ mol.dm $^{-3}$ ; [OH $^{-}$ ] = 0.8 mol.dm $^{-3}$ ; [Hexacyanoferrate(III)] = $5 \times 10^{-3}$ mol.dm $^{-3}$ ; $I = 1.0$ mol.dm $^{-3}$					
$[\text{Fe}(\text{CN})_6^{4-}] \times 10^3$	0	1	2	3	4
$k_{\text{obs}} \times 10^4$ (s $^{-1}$ )	3.79	3.1	2.56	2.49	2.05

### 3.6. Effect of Temperature

The oxidation of salicylaldehyde by alkaline hexacyanoferrate (III) was carried out in the temperature range 303-323 K and it was observed that the rate of reaction increased with an increase in temperature (Table V).

**Table V: Effect of Temperature on the Oxidation of salicylaldehyde by Hexacyanoferrate(III) in Aqueous Alkaline Medium**

[salicylaldehyde] = $5 \times 10^{-2}$ mol.dm <sup>-3</sup> ; [OH <sup>-</sup> ] = 0.8 mol.dm <sup>-3</sup> ; [Hexacyanoferrate(III)] = $5 \times 10^{-3}$ mol.dm <sup>-3</sup> ; I= 1.0 mol.dm <sup>-3</sup>					
Temperature (K)	303	308	313	318	323
$k_{\text{obs}} \times 10^4$ (s <sup>-1</sup> )	3.79	5.83	6.25	8.76	10.6

The activation parameters corresponding to the rate constants were evaluated from the Arrhenius plots of  $\log_{10}k_{\text{obs}}$  versus  $1/T$  which was linear with  $r = 0.99$ . (Table VI)

**Table VI: Activation Parameters for the Oxidation of Salicylaldehyde by Hexacyanoferrate(III) in Aqueous Alkaline Medium**

$E_a$ (kJ mol <sup>-1</sup> )	$\Delta H$ (kJ mol <sup>-1</sup> )	$\Delta S$ (J.K <sup>-1</sup> mol <sup>-1</sup> )	$\Delta G$ (kJ. mol <sup>-1</sup> )
39.98	37.3±0.1	-127 ± 5	77 ± 3

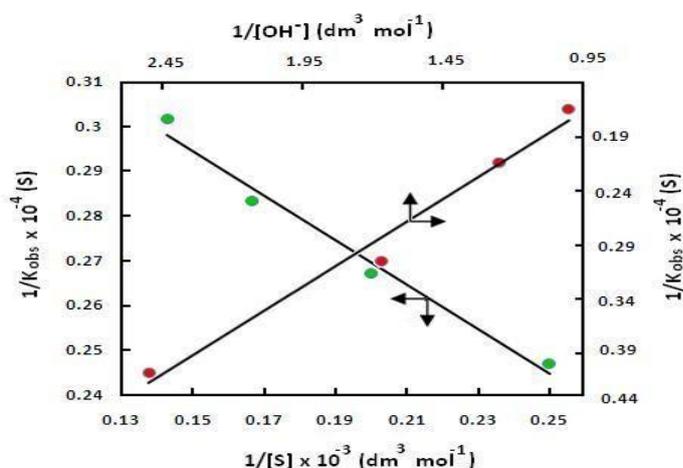
The intramolecular hydrogen bonding energy of salicylaldehyde has been computed as 11 kcal /mol<sup>20</sup>. This accounts for experimentally determined higher value of activation energy 39.98 kJ/mol (Table VI). Negative value of  $\Delta S$  supports the formation of the activated complex in the slow step.

### 3.7. Test for Free Radicals

The interference of free radicals was tested by adding few drops of methyl acrylate to the mixture of solution of salicylaldehyde in NaOH and hexacyanoferrate(III). As there occurred turbidity, interference of free radicals was confirmed.

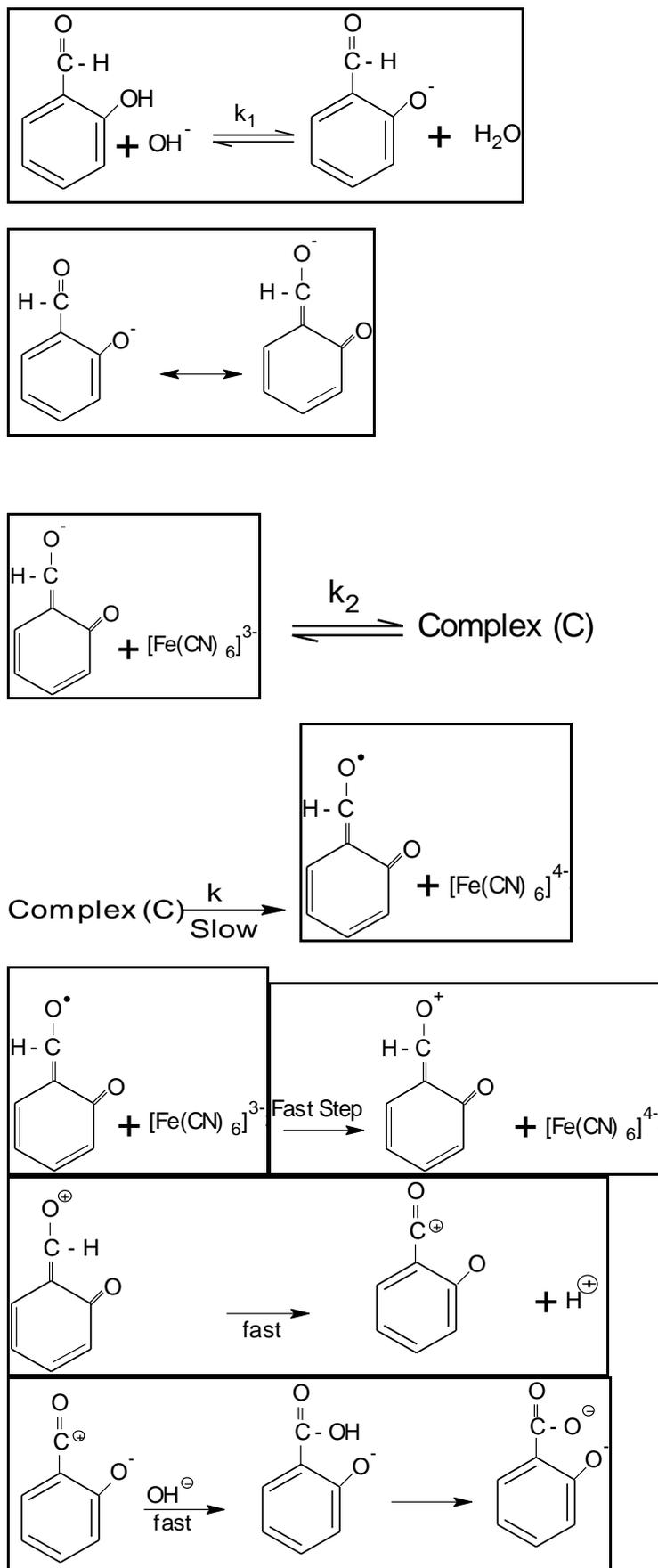
### 3.8. Mechanism of Reaction

The reaction being first order in [oxidant], inverse fractional order in [salicylaldehyde], fractional order in [OH<sup>-</sup>] and being retarded by the addition of hexacyanoferrate(II) can be accommodated in the following Scheme 1. The oxidation was initiated by the formation of the anion of salicylaldehyde. The anion can transfer an electron to hexacyanoferrate(III), resulting in the formation of a radical is the slow and rate determining step. The formation of complex occurs primarily before the slow step. The second molecule of hexacyanoferrate(III) abstracts an electron from the radical and subsequently leads to the formation of products. The formation of complex is proven kinetically based on derived rate law by the non-zero intercept (Fig.3) of graph of  $1/k_{\text{obs}}$  versus  $1/[\text{Substrate}]$ .

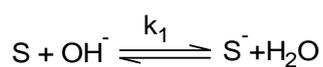


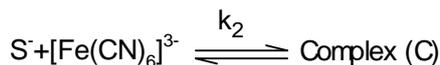
**Fig.3. Graph of  $1/k_{\text{obs}}$  versus  $1/[\text{Substrate}]$  and  $1/k_{\text{obs}}$  versus  $1/[\text{OH}^-]$  showing non-zero intercept**

Scheme 1

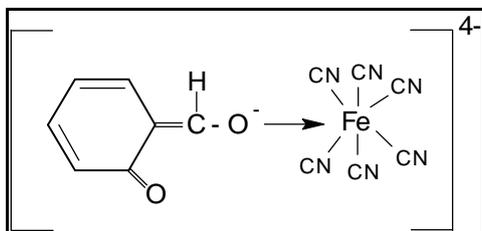


The rate law is given as follows;





The probable structure of the complex is given as:



$$\frac{-dFC}{dt} = k_2[S^-][FC] \quad \text{-----} \quad \longrightarrow (1)$$

$$\frac{-dFC}{dt} = \text{Rate} = k[\text{Complex}] \quad \text{-----} \quad \longrightarrow (2)$$

Applying steady state approximation for Complex 'C'

$$[\text{Complex}] = \frac{k_2[S^-][FC]}{k[\text{Radical}][FC]} \quad \text{-----} \quad \longrightarrow (3)$$

Substituting the terms in equation (3) & (2) and simplifying we get,

$$\text{Rate} = \frac{kk_1k_2[S][OH^-][FC]}{(1+k_1[OH^-])(1+k_1k_2[S][OH^-])(1+k_2[FC])} \quad \text{-----} \quad \longrightarrow (4)$$

As the concentration of  $Fe(CN)_6^{4-}$  used in the study is very low, term  $(1+k_2[FC])$  tends to unity. Then equation (4) becomes,

$$\text{Rate} = \frac{kk_1k_2[S][OH^-][FC]}{(1+k_1[OH^-])(1+k_1k_2[S][OH^-])} \quad \text{-----} \quad \longrightarrow (5)$$

#### 4. Conclusions

The kinetic studies clearly demonstrate that oxidation of salicylaldehyde by hexacyanoferrate(III) in alkaline medium is favored by the formation of the outer-sphere formation of  $Fe(CN)_6^{4-}$  and free radicals in slow step which is followed by the rapid oxidation of free radicals by  $Fe(CN)_6^{3-}$  to give products. Even though it involves the retardation by one of the products and substrate inhibition at higher concentrations, the overall mechanistic sequence described here is consistent with product, mechanistic and kinetic studies.

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