# KINETICS AND MECHANISM OF REDUCTION OF Fe (III) SALICYLATE COMPLEX BY HYDROQUINONE

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**ABSTRACT**

The violet color complex $FeSal^+$ was prepared by reaction of Salicylic acid and Ferric Chloride in acidic medium up to pH 3.5 in formate buffer at ionic strength 0.1 M. Reduction kinetics of $FeSal^+$ complex at pseudo first order condition have been studied spectrophotometrically by a reductant i.e. Hydroquinone. Reduction behaviour shows that reduction is much fast and pH dependent. A mechanism to account for observation is also proposed along with the rate law.

**Keywords:** (Sal) represent $^-O\text{-}C_6H_4\text{-}COO^-$, $k_{obs}$, observed rate constant.

## INTRODUCTION

Salicylic acid is very weak acid and is important clinically. Its absorption spectra is in the ultra violet region. The $OH^-$ and $COOH^-$ groups are in the ortho-position. Salicylic acid forms intensely colored complex with Fe(III). It is reported in the literature that salicylates form complex with transition metal ions either spectrometrically or redox potentiometrically usually combined with pH measurements.

Perrin (1958) has examined the complex between $Ni^{+2}$ ion and some substituted Salicylic acid spectrometrically in aqueous solution. Complex formation and stability constant of ferric salicylates were determined by (Ernst and Menshi 1963) spectrometrically. Several others authors have examined the stability constant (Gupta *et al*., 1981). Potentiometric studies of Fe(III) complexes of some substituted salicylic acid were performed by Jahagirdar (1974).

All they suggested that Fe(III) form three complexes with salicylic acid of the formulae, $FeSal^+$,$FeSal_2^+$ and $FeSal_3^-$ where Sal represents $^-O\text{-}C_6H_4 - COO^-$. It was found that as pH of solution increased in an excess of salicylic acid, the concentration of (Sal) anion also increased.

Moreover, some other complexes were also formed at pH 4. There is 50% conversion of violet $FeSal^+$ into red violet $FeSal_2^+$ and at pH 9 this complex unite with another (Sal) anion to form yellow $FeSal_3^-$. The stability constant value of $FeSal^+$ complex was determined by Martell and Smith (1977). The dissociation constant of $Fe^{III}$-salicylate complex in aqueous media was studied and its absorption characterstic in the 420-640 nm range was compared with the literature value (Bertin Batsh, 1976).

McBryde (1970) described the improved method for determining the extinction coefficient of the first and second complex. The wavelength of maximum absorption i.e. $\lambda_{max}$ of the 1:1 complex of salicylic acid is 528 nm and its molar absorptivity coefficient i.e. $\varepsilon$ = 1520 lit $mol^{-1}$ $cm^{-1}$. The spectra of Fe(III) complex with salicylic acid showed the typical shift to lower values of $\lambda_{max}$ and higher values of $\varepsilon$ with increasing pH.

A recent work (Rostislav Sipos *et al.,* 2008) showed the solution properties of FeIII complexes with fluro-salicylic acid spectra, specification and redox stabilities were investigated by pH potentiometry combined with UV. Visible spectrophotometery.

Electron absorption spectra of the complexes based on pH and the metal ligand ratio in the visible region were obtained. Redox stability was monitored as an ability to undergo both spontaneous and photo-induced reduction of Fe(III) to Fe(II). Complexes do not undergo any redox changes when in dark, neither in methanol nor in water while alcoholic solution of complexes is stable under the influence of incident visible radiation. Steady state irradiation of the methanolic systems by visible light lead to photo-induction of Fe(III) to Fe(II),the quantum yield of Fe(II) photo formation was determined.

The objective of our study is two folds:

Firstly to investigate the 1:1 complex of Fe(III) with salicylic acid i.e., $FeSal^+$. The violet complex $(FeSal)^+$ formed in an acid medium in a pH range of 1.5-2.0 with $\lambda_{max}$ found to be 528nm and its' $\varepsilon$ value 1520 lit $mol^{-1}cm^{-1}$.

Secondly to study the reduction kinetics of Fe(III) salicylate complex to Fe(II) salicylate complex by hydroquinone reductant at the $\lambda_{max}$ 528nm.

## EXPERIMENTALS

i. $FeCl_3.6H_2O$ was obtained from E. Merck and its stock solutions were maintained at 0.1M $HNO_3$ to

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suppress polymerization. Fe(III) were standardized spectrophotometrically with ortho-phenanthroline.

ii. Fe(III) salicylate was prepared by taking 5 fold greater concentration of salicylic acid than Fe(III) i.e. [$Fe^{III}$] = 1 x $10^{-3}$ M, [Salicylic acid] = 5 x $10^{-3}$ M .The complex of 5 x $10^{-4}$ M was obtained by equal volume mixing of Fe(III) and salicylic acid solution .The solutions were made in formate buffer. The ε values were calculated at $\lambda_{max}$ by monitoring absorption spectra at particular pH spectrometrically and shown in fig 1.

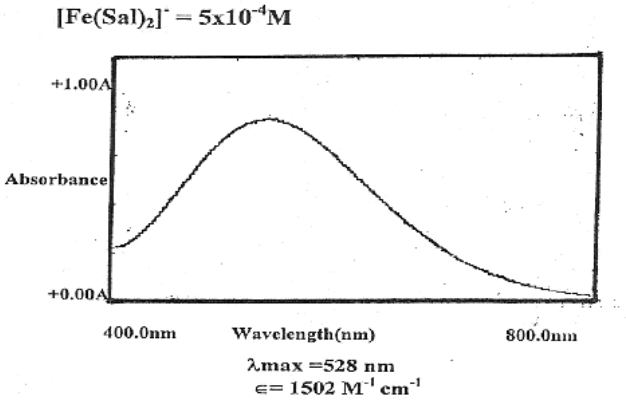


**Fig. 1**: Absorption spectrum of $[Fe(Sal)2]^-$ complex at pH 2.25 and 25°C.

The complex is stable in the pH range ≤ 3.5

iii. Hydroquinone: Freshly prepared solutions were used for reduction purpose.

Solutions prepared from the stock are in the following concentration range:

5 x $10^{-3}$ M ⟶ 2 x $10^{-2}$ M

All the solutions were prepared in deionized distilled water.

***Kinetics measurements***

All kinetics experiments were performed under pseudo first order condition with reductant concentration in excess over the complex. pH were measured with glass electrode to an orion SA model 720-pH meter having resolution ± 0.001 pH unit. The temperature was controlled by means of circulating water from a thermostatic water bath.

The kinetics measurements were taken at wavelength 528 nm. The experiment was repeated with various concentration of reductant at pH 2.25, 2.50, 3.0, 3.50. As the complex is highly colored and its reduced form is colorless. The addition of hydroquinone to a solution of the complex, the concentration of ferric specie was reduced and the absorbance decreased

From the change in absorbance, the rates were followed spectrophotometrically by monitoring decrease in absorbance at 528 nm. Plots of ln ($A_t$-$A_\alpha$) vs. time were linear for up to 85% of the reaction, conforming first order behavior in complex .The slopes of these plots gives $k_{obs}$. Where each $k_{obs}$ represents an average of at least 3 determinations.

## RESULTS

The observed rate constants ($k_{obs}$) at different pH and temperatures with Hydroquinone are given in tables 1-4. Plots of these tables are shown in figs. 2-5. $k_{obs}$ vs. [$H_2Q$] plots at a given pH and temperature are linear initially but level off at high [ $H_2Q$ ].

The calculated values of 1/ $k_{obs}$ and 1/ [$H_2Q$] at different temperatures and pH are plotted and shown in figs.6-9. The acid hydrolysis rate constants ($k_1$) are obtained which are listed in table 5, $k_1$ are found to increase with increase of pH and temperature.

The values of ratio of $k_2$ / $k_3$ obtained at different pH and temperature are given in table 4.

## DISCUSSION

When different plots of $k_{obs}$ vs. [$H_2Q$] at different pH are compared, it is observed that rates increase with pH. To account for observation data a possible reduction mechanism proposed and rate law consistent with the observation can be derived.

$$[\,FeSal^{+}] + H^{+} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [FeSal^{++}] \xrightarrow[[H_2Q]]{k_3} Fe^{II}, \text{ etc}$$

This mechanism conforms to the following rates.

Rate of formation of product = $k_3[FeSal^{++}]\,[H_2Q]$ (1)

Applying steady rate approximation for [$FeSal^{++}$], rate of appearance and disappearance will be equal i.e.

$$\frac{d\,[\,Fe\,Sal^{++}\,]}{dt} = -\,\frac{d\,[\,Fe\,Sal^{++}\,]}{dt} \qquad (2)$$

$$k_1[Fe\,Sal^{+}]\,[H^{+}] = k_2[\,Fe\,Sal^{++}\,] + k_3\,[Fe\,Sal^{++}]\,[H_2Q] \quad (3)$$

$$k_1\,[\,Fe\,Sal^{+}\,]\,[\,H^{+}] = [\,Fe\,Sal^{++}\,]\,[\,k_2 + k_3\,(\,H_2Q)]$$

and obtain the following equation,

$$[\,Fe\,Sal^{++}] = \frac{k_1\,[\,Fe\,Sal^{+}\,]\,[\,H^{+}]}{[\,k_2 + k_3\,[\,H_2Q]]}$$

Substituting this value in equation (1) the rate becomes

$$[\text{Fe Sal}^{++}] = \frac{k_1 k_3 [H^+] [H_2Q] [\text{Fe Sal}^+]}{[k_2 + k_3 [H_2Q]]}$$

i.e. Rate = $k_{obs}$ [ Complex ] Where

$$k_{obs} = \frac{k_1 k_3 [H^+] [H_2Q]}{[k_2 + k_3 [H_2Q]]}$$

So at low $[H_2Q]$ :- $k_3[H_2Q] << k_2$

Therefore, $k_{obs}$ appear to be linearly proportional to $[H_2Q]$ i.e. (Initial slope) and $k_{obs}$ become.

$$k_{obs} = \frac{k_1 k_3 [H^+][H_2Q]}{k_2}$$ i.e.

$k_{obs}$ α $[H_2Q]$

we proposed the mechanism in the light of trends of observed rate constant ($k_{obs}$), variation with concentration of $[H_2Q]$ & pH . In the mechanism, protonation is followed by reduction as indicated by direct $[H^+]$ dependence. So at this condition the $k_{obs}$ will increase with increasing concentration of $[H_2Q]$ but up to low concentration of $[H_2Q]$.

A careful examination of figs.2-5 however, reveal that at the highest $[H_2Q]$, the level off portion is achieved i.e. $k_{obs}$ now become constant and is independent of $[H_2Q]$ at particular pH. It means that at this level- off portion, saturation kinetics has been achieved which showing the maximum limit of reducing power of reductant i.e. $[H_2Q]$.

The acid hydrolysis rate constants ($k_1$) are found to increase with increase of pH and temperature.

The values of ratio of $k_2 / k_3$ obtained at different pH and temperature do not permit evaluation of activation parameters. Hence certain trends are noticeable.

**Tables 1-4:** Reduction rate constant ($k_{obs}$) of $[\text{Fe Sal}^+]$ by $[H_2Q]$ with different pH at $\lambda_{max}$ 528nm [FeIII]= $1\times10^{-3}$ mol/l [Salicylic acid] = $5\times10^{-3}$ mol/l

**pH 2.25**

| $[H_2Q]$ mol/l×$10^3$ | $k_{obs}$ 20°C | $k_{obs}$ 25°C | $k_{obs}$ 30°C | $k_{obs}$ 35°C |
|---|---|---|---|---|
| 5 | 0.00023 | 0.0031 | 0.0036 | 0.0041 |
| 7 | 0.0025 | 0.0041 | 0.0053 | 0.0063 |
| 9 | 0.0029 | 0.0045 | 0.0055 | 0.0075 |
| 20 | 0.0044 | 0.0061 | 0.0082 | 0.0107 |

**pH 2.50**

| $[H_2Q]$ mol/l×$10^3$ | $k_{obs}$ 20°C | $k_{obs}$ 25°C | $k_{obs}$ 30°C | $k_{obs}$ 35°C |
|---|---|---|---|---|
| 5 | 0.00141 | 0.0019 | 0.0032 | 0.0041 |
| 7 | 0.0017 | 0.0028 | 0.0035 | 0.0058 |
| 9 | 0.0021 | 0.0033 | 0.0045 | 0.0073 |
| 20 | 0.0032 | 0.0053 | 0.0081 | 0.0115 |

**pH 3.0**

| $[H_2Q]$ mol/l×$10^3$ | $k_{obs}$ 20°C | $k_{obs}$ 25°C | $k_{obs}$ 30°C | $k_{obs}$ 35°C |
|---|---|---|---|---|
| 5 | 0.0012 | 0.0021 | 0.0025 | 0.0045 |
| 7 | 0.0016 | 0.0027 | 0.0039 | 0.0053 |
| 9 | 0.0018 | 0.0029 | 0.0044 | 0.0059 |
| 20 | 0.0025 | 0.0039 | 0.0053 | 0.0079 |

**pH 3.5**

| $[H_2Q]$ mol/l×$10^3$ | $k_{obs}$ 20°C | $k_{obs}$ 25°C | $k_{obs}$ 30°C | $k_{obs}$ 35°C |
|---|---|---|---|---|
| 5 | 0.0010 | 0.0015 | 0.0021 | 0.0032 |
| 7 | 0.0013 | 0.0018 | 0.0030 | 0.0042 |
| 9 | 0.0016 | 0.0025 | 0.0040 | 0.0074 |
| 20 | 0.0022 | 0.0036 | 0.0057 | 0.0097 |

**Table 5**: Protonation rate constant ($k_1$) by $[H_2Q]$ at different pH and temperatures

| $k_1$ Protonation Rate Constant | | | | |
|---|---|---|---|---|
| pH | 20°C | 25°C | 30°C | 35°C |
| 2.25 | 1.92 | 3.51 | 5.65 | 5.86 |
| 2.50 | 1.62 | 2.75 | 5.27 | 5.45 |
| 3.00 | 1.26 | 2.41 | 4.72 | 5.27 |
| 3.50 | 1.18 | 2.39 | 3.16 | 3.64 |

**Table 6**: Ratio of rate constants at different temperatures and pH by $[H_2Q]$

| $k_2 / k_3 \times 10^3$ | | | | |
|---|---|---|---|---|
| pH | 20°C | 25°C | 30°C | 35°C |
| 2.25 | 8.50 | 12.40 | 19.50 | 12.90 |
| 2.50 | 12.50 | 15.60 | 22.83 | 14.35 |
| 3.00 | 10.06 | 15.00 | 22.69 | 14.59 |
| 3.50 | 12.80 | 20.01 | 16.50 | 10.90 |

When different plots of $k_{obs}$ vs. $[H_2Q]$ at different pH are compared, it is observed that rates increase with pH.

To account for observation data a possible reduction mechanism proposed and rate law consistent with the observation can be derived.

$$[\text{FeSal}^+] + H^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [\text{FeSal}^{++}] \xrightarrow[[H_2Q]]{k_3} Fe^{II}, \text{etc}$$

This mechanism conforms to the following rates.

Rate of formation of product=$k_3[\text{FeSal}^{++}]$ $[H_2Q]$ (1)

Applying steady rate approximation for $[\text{FeSal}^{++}]$, rate of appearance and disappearance will be equal i.e.

$$\frac{d[Fe\,Sal^{++}]}{dt} = -\frac{d[Fe\,Sal^{++}]}{dt} \quad (2)$$

$$k_1 [Fe\,Sal^{+}][H^{+}] = k_2 [Fe\,Sal^{++}] + k_3 [Fe\,Sal^{++}][H_2Q] \quad (3)$$

$$k_1 [Fe\,Sal^{+}][H^{+}] = [Fe\,Sal^{++}][k_2 + k_3 (H_2Q)]$$

and obtain the following equation:

$$[Fe\,Sal^{++}] = \frac{k_1 [Fe\,Sal^{+}][H^{+}]}{[k_2 + k_3 [H_2Q]]}$$

Substituting this value in equation (1) the rate becomes

$$[Fe\,Sal^{++}] = \frac{k_1 k_3 [H^{+}][H_2Q][Fe\,Sal^{+}]}{[k_2 + k_3 [H_2Q]]}$$

i.e. Rate = $k_{obs}$ [ Complex ] Where

$$k_{obs} = \frac{k_1 k_3 [H^{+}][H_2Q]}{[k_2 + k_3 [H_2Q]]}$$

So at low $[H_2Q]$ :- $k_3[H_2Q] << k_2$

Therefore, $k_{obs}$ appear to be linearly proportional to $[H_2Q]$

i.e. (Initial slope) and $k_{obs}$ become.

$$k_{obs} = \frac{k_1 k_3 [H^{+}][H_2Q]}{k_2} \quad \text{i.e.}$$

$$k_{obs} \;\alpha\; [H_2Q]$$

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A careful examination of figs. 2-5 however, reveal that at the highest $[H_2Q]$, the level off portion is achieved i.e., $k_{obs}$ now become constant and is independent of $[H_2Q]$ at particular pH. It means that at this level off portion, saturation kinetics has been achieved which showing the maximum limit of reducing power of reductant i.e., $[H_2Q]$.

The calculated values of $1/k_{obs}$ and $1/[H_2Q]$ at different temperatures and pH are plotted and shown in figs. 6-9. The acid hydrolysis rate constants ($k_1$) are obtained which

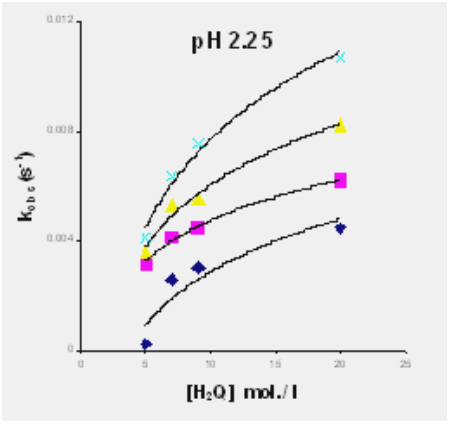


Fig. 2

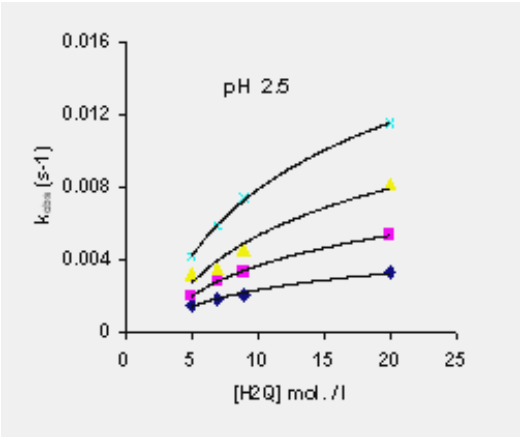


Fig. 3

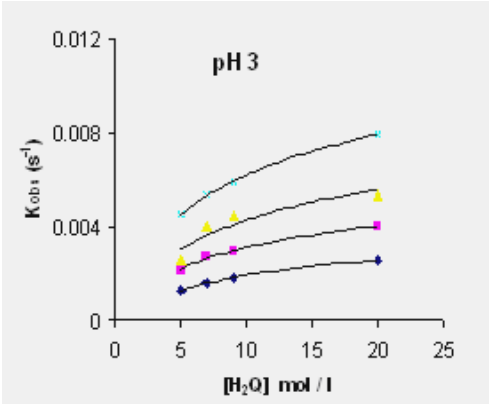


Fig. 4

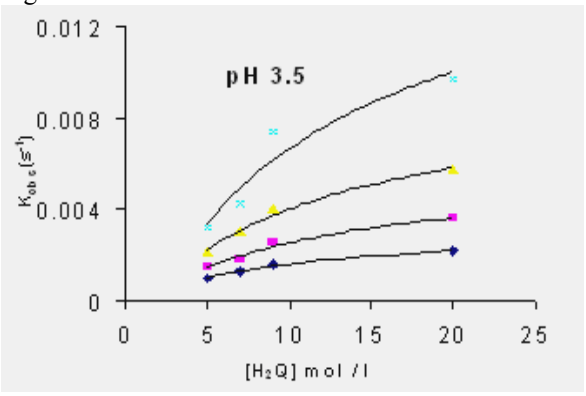


Fig. 5

**Figs. 2-5**: Tempeture dependence of reduction rate constant of [$FeSal^+$] complex by hydroquinone.

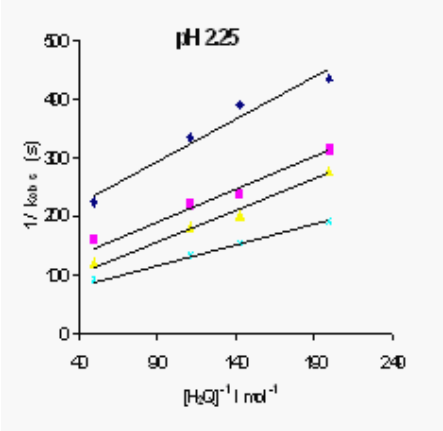


Fig. 6

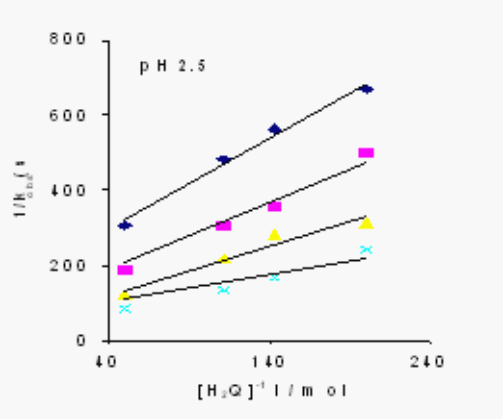


Fig. 7

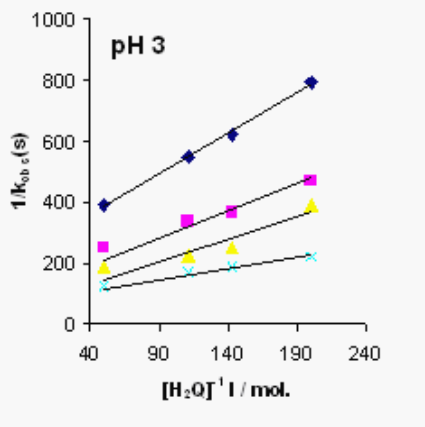


Fig. 8

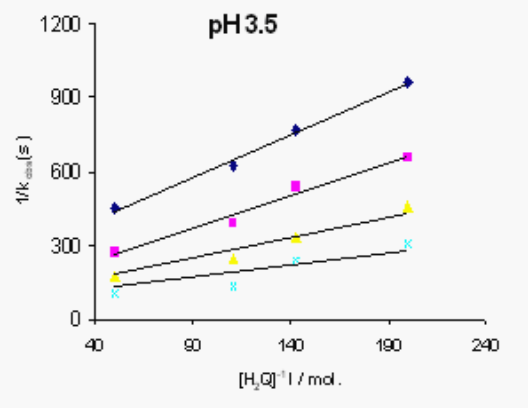


Fig. 9

**Figs. 6-9**: Variation of 1 / $k_{obs}$ vs. 1/ [$H_2Q$] at different temperatures.

are listed in table 5, $k_1$ are found to increase with increase of pH and temperature.

The ratio of $k_2/k_3$ obtained at different pH and temperature are given in table 4. These values do not permit evaluation of activation parameters. Hence certain trends are noticeable.

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