

KINETICS AND MECHANISM OF REDUCTION OF Fe(III) SALICYLATE COMPLEX BY ASCORBIC ACID

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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. Ascorbic acid. Reduction behaviour shows that reduction is much fast and pH dependent. A mechanism to account for observation is also proposed. The mechanism conforms to the following rate law.

$$\text{Rate} = k_{\text{obs}} [\text{Fe Sal}^+]$$

Where

$$k_{\text{obs}} = \frac{k_1 k_3 [\text{H}^+] + k_4}{k_2 + k_3 [\text{Asc.}]}$$

INTRODUCTION

Salicylic acid is very weak acid and is important clinically (Churchill, 1963). Its absorption spectra is in the ultra violet region. OR and COOR groups are in the ortho-position form intensely colored complex with Fe(III). Several authors i.e. (Babko, 1945; BertinBatsch, 1952; Argen, 1954; Vareille, 1955 and Chaneley *et al.*, 1956) have examined the iron(III) salicylic acid complexes spectrophotometrically but some others i.e. (Shchigol *et al.*, 1961; Tsin Jao *et al.*, 1962; Ernst *et al.*, 1963; Romain *et al.*, 1965) examined the complex by oxidation reduction potentiometry, usually combined with pH measurements.

All they suggested that Fe(III) form three complexes with salicylic acid of formulae FeSal, FeSal₂' and FeSal₃' where Sal represents 'O-C₆H₄ - COO'. In order to study the kinetics, the complex formation of salicylic acid with iron(III) was investigated. A preliminary account of part of this work has been published (Park, 1963). The violet complex (FeSal₂+) formed in an acid medium in a pH range of 1.5-2.0. As the pH of the solution increases and there is an adequate excess of salicylic acid, the conc. of (Sal) anion also rises and other complexes are formed at pH 4. There is 50 % conversion of violet (FeSal₂+) in to red violet (FeSal₂') and at pH 9 this complex unite with another (Sal) anion to form yellow complex (FeSal₃') The wavelength of maximum absorptio:l (A_{max}) and its molar absorptivity coefficient (c) values of this

complex (FeSal₂+) observed is same i .e.528 nm & 1520 lit. mOrl/m,1 as obtained in the literature (McBryde, 1970). The spectra of Fe(III) complex with salicylic acid showed the typical shift to lower values of A_{max} and higher values of c with increasing pH. The kinetics of Fe(III) salicylate complex on reduction to Fe(II) enable us to follow the reaction at the A_{max} of the complex.

MA TERIALS AND METHODS

- i. FeCb.6H₂O was obtained from E. Merck and its stock solutions were maintained at 0.1M HN0₃ to suppress polymerization. Fe(III) was standardized spectrophotometrically with orthophenanthroline.
- ii. Fe (III) salicylate was prepared by taking 5 fold greater concentration of salicylic acid than Fe(III) i.e. [FeIII] = 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 prepared in formate buffer. The c values were calculated at A_{max} by monitoring absorption spectra at particular pH spectrophotometrically and shown in (Fig. I). The complex is stable in the pH range ~ 3.5.
- iii. .Ascorbic acid: Freshly prepared solutions were used for reduction purpose. The solutions prepared from the stock are in the followings concentration range:
5 x 10⁻³ M

.. 2 X 10⁻² M

Table 1: Pseudo First Order Reduction Rate Constants of [Fe Sal] + Complex by Ascorbate

[Fe III] 1×10^{-3} mol / l pH 2.25
 [Salicylic acid] 5×10^{-3} mol / l 528 nm

[Asc] mol / l X 10 ³	kobs 20°C	kobs 25°C	kobs 30°C	kobs 35°C
5	0.0188	0.0247	0.0281	0.0460
7	0.0225	0.0375	0.0444	0.0374
9	0.0239	0.0485	0.0550	0.0834
20	0.0346	0.0666	0.0805	0.1406

Table 2: Pseudo First Order Reduction Rate Constants of [Fe Sal+] Complex By Ascorbate

[Fe III] 1×10^{-3} mol / l pH 2.50
 [Salicylic acid] 5×10^{-3} mol / l 528 nm

[Asc] mol/l x 10 ³	kobs 20°C	kobs 25°C	kobs 30°C	kobs 35°C
5	0.0141	0.025	0.0366	0.0424
7	0.0200	0.0345	0.0470	0.0653
9	0.0280	0.0435	0.0665	0.0834
20	0.0400	0.0660	0.0875	0.1248

Table 3: Pseudo First Order Reduction Rate Constants of [Fe Sal+] Complex By Ascorbate

[Fe III] 1×10^{-3} mol / l pH 3.0
 [Salicylic acid] 5×10^{-3} mol / l 528 nm

[Asc] mol / l x 10 ³	kobs 20°C	kobs 25°C	kobs 30°C	kobs 35°C
5	0.0196	0.0240	0.0255	0.0370
7	0.0265	0.0334	0.0426	0.0668
9	0.0306	0.0422	0.0592	0.0788
20	0.0405	0.0518	0.0757	0.1377

All the solutions were prepared in de-ionized distilled water.

Methodology (Kinetic Measurements):

All kinetic experiments were performed under pseudo first order condition with reductant in excess over the complex. pH measured with glass electrode to an orion SA model nO-pH meter having resolution :t 0.001 pH unit. The temperature was controlled by means of circulating water from a thermostatic water bath. The kinetics measurements were taken at 528 nm. The experiment was repeated with various concentrations

of reductant at pH 2.25, 2.50, 3.0, 3.5. As the complex is highly coloured and its reduced form is colorless. The addition of reductant to a solution of the complex, the concentration of ferric species was reduced and the absorbance decrease. From the change in absorbance the rates were followed spectrophotometrically by monitoring decrease in absorbance at 528 nm. Plots of $\ln(A_t - A_x)$ vs. time were linear for up to 85% of the reactions 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.

Table 4: Pseudo First Order Reduction Rate Constants of [Fe Sal+] Complex By Ascorbate

[Fe^{III}] 1x10⁻³ mol / l pH 3.5
 [Salicylic acid] 5x10⁻³ mol / l 528 nm

[Asc] mol / l x10 ³	k _{obs} 20°C	k _{obs} 25°C	k _{obs} 30°C	k _{obs} 35°C
5	0.0196	0.0315	0.0333	0.0586
7	0.0228	0.0352	0.0466	0.0668
9	0.0313	0.0416	0.0663	0.0755
20	0.0419	0.0542	0.0804	0.1111

This mechanism conforms to the following rate law:

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

Rate of formation of product = k₃[FeSal⁺⁺] [Asc] + k₄ [FeSal⁺] [Asc]

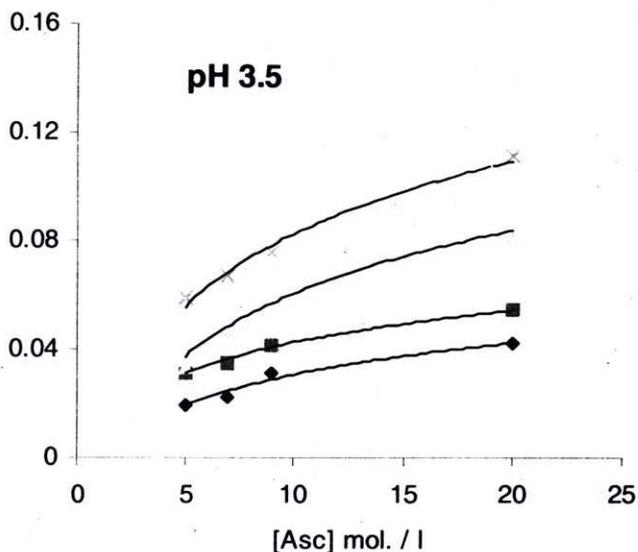
$$k_{obs} = \left[\frac{k_1 k_3 [H^+]}{k_2 + k_3 [Asc]} + k_4 \right]$$

So at low [Asc] : k₃[Asc] << k₂
 Therefore, k_{obs} appear to be linearly proportional to [Asc] i.e. (Initial slope) and k_{obs} become.

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

i.e. k_{obs} α [Asc] : only up to lower concentration of [Asc]

In the light of trends of k_{obs} variation with [Asc.] and pH we proposed the mechanism. In the mechanism, protonation is followed by reduction as indicated by direct [H⁺] dependence, so in this condition the k_{obs} will increase with increasing concentration of [Asc] which can be seen in the (Figs. 2-5) but up to certain lower limit of conc. of [Asc].



Applying steady rate approximation for [FeSal⁺⁺], rate of appearance and disappearance will be equal. On deriving these equation and substitution these values we get a final rate equation.

$$\text{Rate} = \left[\frac{k_1 k_3 [H^+]}{k_2 + k_3 [Asc]} + k_4 \right] [Asc] [FeSal^+]$$

A careful examination of (Figs. 2-5) however reveals that at the highest [Asc], the leveling off is not complete we believe that at these high [Asc], the k₄ pathway i.e. direct reduction of complex is also going on along with the other k₃ path and reduction becomes more effective.

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