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RESEARCH ARTICLE

KINETICS AND MECHANISTIC STUDY OF OXIDATION OF 4-HYDROXY BENZALDEHYDE BY ALKALINE HEXACYANOFERRATE (III)

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ABSTRACT

The kinetics of oxidation of 4-hydroxy benzaldehyde by hexacyanoferrate(III) in aqueous alkaline medium was studied. The first order dependence on concentration of hexacyanoferrate (III) and fractional order dependence on both 4-hydroxy benzaldehyde and alkali is supported by the derived rate law. A retarding effect was observed by one of the products hexacyanoferrate(II). Increasing ionic strength and dielectric constant of the medium increased the 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 elucidated.

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INTRODUCTION

Potassium hexacyanoferrate(III) an inorganic complex otherwise known as red prussiate, prussian red or potassium ferricyanide is used effectively as an oxidant for several organic and inorganic compounds. The oxidation of organic compounds by this oxidant in alkaline medium has been studied by several workers (Singh *et al*, 1969, Didcy *et al*, 1990, Sairabanu *et al*, 2009, Quadri *et al*, 2003, Timy P. Jose *et al*, 2006 and Radhakrishnamurti *et al* 1979). The oxidation-reduction reactions of hexacyanoferrate (III) ion are shown to be rapid whenever the process involves a simple electron transfer and to be slow and of complex mechanism if such a step cannot occur (Adamson AW. 1952).The oxidation of 4-hydroxybenzaldehyde was carried out in order to gain information about the slow step of the reaction and to explore a suitable mechanism for the oxidation of 4-hydroxy benzaldehyde by alkaline hexacyanoferrate(III) on the basis of kinetic results.

4-hydroxy benzaldehyde, one of the three isomers of hydroxy benzaldehyde is otherwise known as p-hydroxybenzaldehyde or p-formylphenol. It can be found in the orchids *Gastrodia elata* and *Galeola faberi* and in vanilla (Wikipedia). It is also used to prepare Vanillin (Douglass *et al*, 2007), aldehyde methacrylates and finds application in the manufacture of dental materials which can form strong and durable bonds with dentin (Joseph M. Antonucci 1978) and in chelating resins (Bunian *et al*, 2013). The kinetics and mechanism of oxidation of 4-hydroxy benzaldehyde by oxidants like potassium permanganate and peroxide in acid medium have been reported (Bhagwansing Dobhal *et al*, 2010 & Yoshiro Ogata and Iwao Tabushi 1959). However, there is no report for its oxidation in alkaline medium. This prompted us to undertake the present investigation. The present work reports the kinetics of oxidation of 4-hyroxy benzaldehyde by hexacyanoferrate(III) in alkaline medium and evaluates the reaction constants. Mechanistic aspects are also discussed.

Experimental

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 (Mendham. J., *et al*, 2009). NaOH and KCl were employed to maintain the required alkalinity and ionic strength respectively.

Kinetic Measurements

All kinetic measurements were performed under pseudo first-order conditions where [4-hydroxy benzaldehyde] was always in excess over hexacyanoferrate (III), at a constant ionic strength of 1.0 mol.dm^{-3} in alkaline medium at a temperature of (30.0 ± 0.1) $^{\circ}$C unless otherwise stated. The reaction was initiated by mixing the thermostatted solutions of hexacyanoferrate (III) and 4-hydroxy benzaldehyde, which also contained the required concentration of NaOH and KCl. The progress of the reaction was followed titrimetrically by observing the disappearance of hexacyanoferrate(III) at regular and convenient interval of time. Pseudo first- order rate constants, k_{obs}, were obtained (Tables 1 and 2) from the slopes of plots of $\log_{10}[Fe(CN)_6^{3-}]$ *versus* time; the plots were linear and the k_{obs} values were reproducible to within ±3%.

Stoichiometry and Products Analysis

Reaction mixtures with different sets of concentrations of reactants where $[Fe(CN)_6^{3-}]$ was in excess over [4-hydroxy benzaldehyde] at a constant ionic strength and alkali were kept for about 24 hours at 30°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 4-hydroxy benzaldehyde as in the following equation.

The stoichiometric ratio suggests that the main reaction products are 4-hydroxy benzoic acid and $Fe(CN)_6^{4-}$. The

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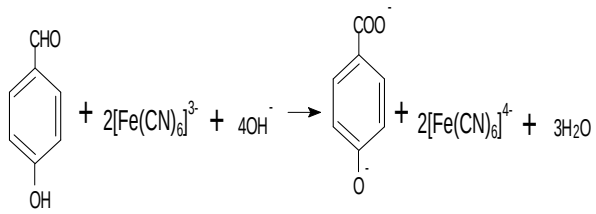


product 4-hydroxy benzoic acid was isolated by acidifying the reaction mixture followed by ether extraction and identified by its spot test (Feigl, F.,and Anger.V.,1996), melting point at 214.5°C (literature melting point is 215± 2°C) and IR spectrum. The characteristic absorption bands at 1679 cm^{-1}, 2961 cm^{-1} and 1287 cm^{-1} confirmed the presence of carboxylic acid group and the same at 3684cm^{-1} confirmed the hydroxyl group. The possibility of dimerisation of free radicals is ruled out as we did not get any kinetic evidence for the formation of such product. The concentration of the reduction product, $Fe(CN)_6^{4-}$, was estimated (Mendham. J., *et al*, 2009) by titrating against a Ce(IV) solution.

Table 1 Effect of Variations of $[Fe(CN)_6^{3-}]$, [4-hydroxy benzaldehyde], and $[OH^-]$ on the Oxidation of 4-hydroxy benzaldehyde by $Fe(CN)_6^{3-}$ at 30 °C, I = 1.0 mol·dm^{-3}

$[Fe(CN)_6^{3-}] \times 10^3$ (mol.dm^{-3})	[4-hydroxy benzaldehyde] $\times 10^2$(mol. dm^{-3})	$[OH^-]$ (mol. dm^{-3})	$k_{obs} \times 10^4$ (s^{-1})
4.0	5.0	0.80	3.90
5.0	5.0	0.80	3.90
6.0	5.0	0.80	3.88
7.0	5.0	0.80	3.89
5.0	4.0	0.80	3.50
5.0	5.0	0.80	3.90
5.0	6.0	0.80	4.30
5.0	7.0	0.80	4.90
5.0	5.0	0.40	2.60
5.0	5.0	0.60	3.30
5.0	5.0	0.80	3.90
5.0	5.0	1.00	5.10

RESULTS AND DISSCUSSION

Reaction Order

The order with respect to [4-hydroxy benzaldehyde] and [alkali] were found by $\log_{10} k_{obs}$ *versus* $\log_{10}$ (concentration) plots; these orders were obtained by varying the concentration of 4-hydroxy benzaldehyde and alkali in turn while keeping others constant.

Effect of [Hexacyanoferrate(III)]

The concentration of hexacyanoferrate (III) was varied in the range 4.0×10^{-3} to 7.0×10^{-3} mol.dm^{-3} and keeping all other reactant concentrations and ionic strength as constant and the rates were measured (Table 1). The constancy in the value of rate constants irrespective of the concentration of the hexacyanoferrate (III) confirms the first order dependence on hexacyanoferrate (III). This was also confirmed from the linearity of plots of $\log_{10}$ [hexacyanoferrate (III)] *versus* time (r = 0.999 and $s \leq 0.004$).

Effect of [4-Hydroxy Benzaldehyde]

The concentration of substrate 4-hydroxy benzaldehyde, was varied for the range of 4.0×10^{-2} to 7.0×10^{-2} mol.dm^{-3} at 30°C keeping all other reactant's concentrations and conditions constant (Table 1). The k_{obs} values increased with increasing concentration of 4-hydroxy benzaldehyde indicating an apparent less than unit order dependence on [4-hydroxy benzaldehyde]. (= 0.60)

Effect of [alkali]

The dependence of the reaction rate on hydroxide ion has been studied in the range 0.4 to 1.0 mol.dm^{-3} keeping the other conditions and concentrations constant showed the values of the rate constants increased with increasing $[OH^-]$. (Table 1) The order was found to be less than unity (= 0.65). A plot of log k_{obs} against log $[OH^-]$ is linear.

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

Table 2 Effect of variation of Ionic strength on reaction rate

[Substrate]=5×10^{-2}mol. dm^{-3}; $[OH^-]$ = 0.8 mol. dm^{-3}; [oxidant] = 5×10^{-3}mol. dm^{-3}

I	1.0	1.1	1.2	1.3	1.4
$10^4 k$ (s^{-1})	3.9	4.2	4.9	5.2	6.4

The addition of ethanol to the reaction mixture decreases dielectric constant of the medium. As the dielectric constant of the medium is decreased, a decrease in rate of oxidation is observed. The plot of $\log_{10} k_{obs}$ *versus* 1/D is linear. (r = 0.987) (Fig.1). This explains the involvement of similarly charged species. (Scheme 1)

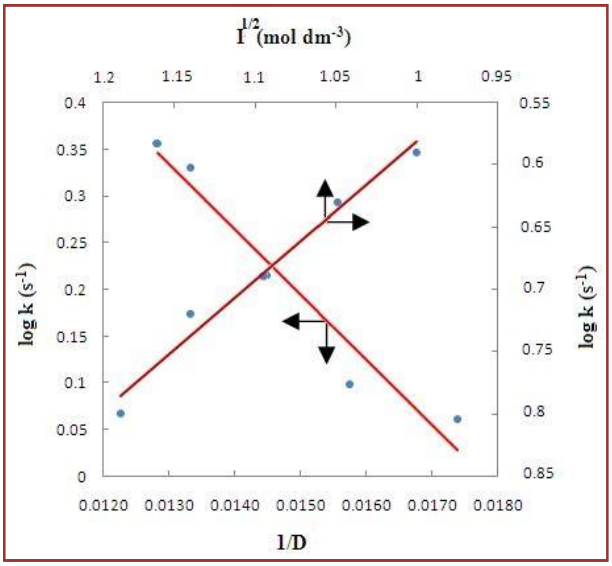


Fig.1 Effect of dielectric constant and ionic strength of the medium on oxidation of 4-hydroxy benzaldehyde by hexacyanoferrate(III)

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 1.0×10^{-3} to 4.0×10^{-3} mol.dm^{-3} at 30°C at constant $[OH^-]$, [4-hydroxy benzaldehyde], [hexacyanoferrate(III)] and ionic strength. Hexacyanoferrate(II) was shown to have a retarding effect on the rate of reaction. The effect is only meager revealing that the step in which hexacyanoferrate(II) is formed as a product must be reversible. (Table 3).

Table 3 Effect of added product, hexacyanoferrate (II), on the oxidation of 4-hydroxy benzaldehyde by hexacyanoferrate(III) in aqueous alkaline medium at 30°C

[4-hydroxy benzaldehyde] = 5×10^{-2} mol. dm^{-3}; [OH$^-$] = 0.8 mol. dm^{-3}; [Oxidant] = 5×10^{-3} mol. dm^{-3}; I = 1.0 mol. dm^{-3}					
$[Fe(CN)_6^{4-}] \times 10^3$ mol. dm^{-3}	0.0	1.0	2.0	3.0	4.0
$k_{obs} \times 10^4$ (s^{-1})	3.9	3.2	3.0	2.7	2.5

Effect of Temperature

The oxidation of 4-hydroxy benzaldehyde 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 4).

Table 4 Effect of temperature on the oxidation of 4-hydroxy benzaldehyde by hexacyanoferrate(III) in aqueous alkaline medium

[4-hydroxy benzaldehyde] = 5×10^{-2} mol. dm^{-3}; [OH$^-$] = 0.8 mol. dm^{-3}; [Oxidant] = 5×10^{-3} mol. dm^{-3}; I= 1.0 mol. dm^{-3}					
Temperature (K)	303	308	314	319	323
$k_{obs} \times 10^4$ (s^{-1})	3.9	4.0	5.2	6.8	7.5

The activation parameters corresponding to the rate constants were evaluated from the Arrhenius plots of $\log_{10}k_{obs}$ versus $1/T$ which was linear with r=0.99 and the energy of activation and enthalpy of activation are found to be 28.79 kJ mol^{-1} and 26.27±0.2 kJ mol^{-1} respectively. Entropy of activation and free energy of activation are -144.38 ± 2 J.K^{-1}mol^{-1} and 120± 2 kJ.mol^{-1} respectively.

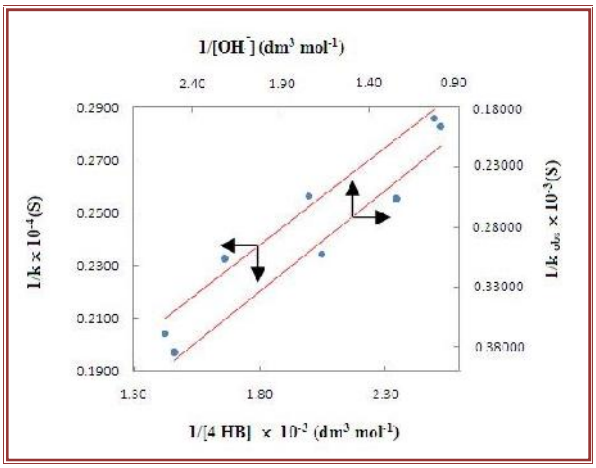


Fig.2 Verification of rate law
Graph of $1/k_{obs}$ *versus* 1/ [4HB] and $1/k_{obs}$ *versus* 1/ [OH$^-$] showing non-zero intercept

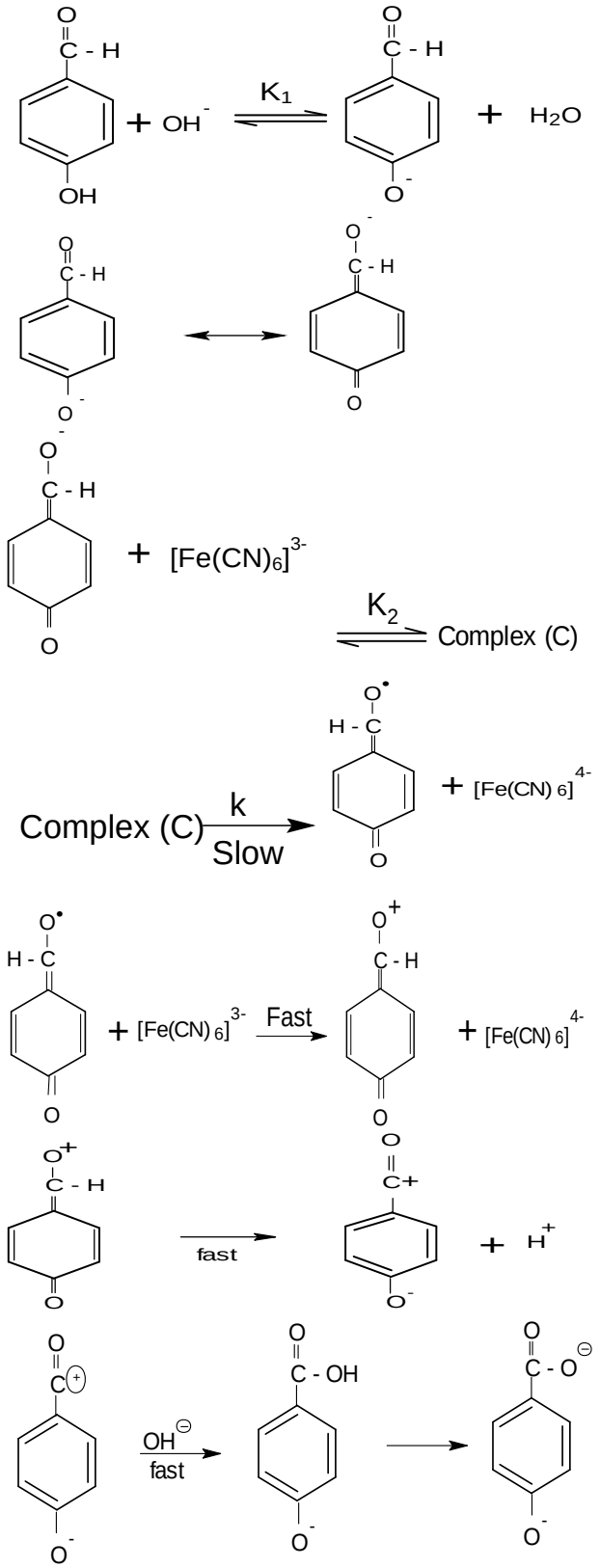
Test for Free Radicals

The interference of free radicals was tested by adding few drops of methyl acrylate to the solution of 4-hydroxy benzaldehyde in NaOH and hexacyanoferrate(III). As there occurred turbidity, interference of free radicals was confirmed.

Mechanism of Reaction

The overall reaction is approximately second order, being first order in [oxidant], fractional order in each [4-hydroxy benzaldehyde] and [OH$^-$] and the retarding effect of hexacyanoferrate(II) can be accommodated in the following Scheme 1. The oxidation was initiated by the formation of the anion of 4-hydroxy benzaldehyde. The anion can transfer an electron to hexacyanoferrate(III), forming an intermediate complex and resulting in the formation of a radical through slow step and is the rate determining 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 by the non-zero intercept graph of $1/k_{obs}$ *versus* 1/ [4HB] (Fig.2)

Scheme 1



The rate law is given as follows;

$$S + OH^- \underset{}{\overset{k_1}{\rightleftharpoons}} S^- + H_2O$$

$$S^- + [Fe(CN)_6]^{3-} \overset{k_2}{\rightleftharpoons} \text{Complex (C)}$$

$$\text{Complex (C)} \xrightarrow[\text{Slow}]{k} \text{Radical} + [Fe(CN)_6]^{4-}$$

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

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

Applying steady state approximation for Complex 'C'

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

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

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

---------- $\longrightarrow$ (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,

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

---------- $\longrightarrow$ (5)

Note: The abbreviations S & 4 HB represent 4-hydroxy benzaldehyde and FC & FC' represent hexacyanoferrate(III) and hexacyanoferrate(II) respectively.

CONCLUSIONS

The kinetic studies clearly demonstrate that oxidation of 4-hydroxy benzaldehyde by hexacyanoferrate(III) in alkaline medium is favored by 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 the overall mechanistic sequence described here is consistent with product, mechanistic and kinetic studies.

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