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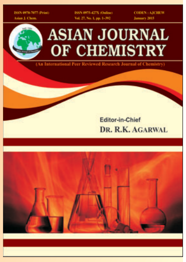

Kinetics and Mechanistic Study of Oxidation of Ethyl Vanillin by Alkaline Hexacyanoferrate(III)

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The kinetics of oxidation of ethyl vanillin by hexacyanoferrate(III) in aqueous alkaline medium was studied. The reactions are found to be fractional order with respect to substrate & hydroxide ion and first order with respect to oxidant. The rate-determining step is the outer-sphere formation of $Fe(CN)_6^{4-}$ and free radicals, which is followed by the rapid oxidation of free radicals by $Fe(CN)_6^{3-}$ to give products. The added product, hexacyanoferrate(II), had a retarding effect on the rate of reaction. Ionic strength and dielectric constant of the reaction medium have little effect on the reaction rate. 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.

Keywords: Oxidation, Ethyl vanillin, Kinetics, Mechanism, Potassium hexacyanoferrate(III).

INTRODUCTION

Potassium ferricyanide is an inorganic complex, used effectively as an oxidant for several organic compounds. 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[1].

Kinetics and mechanistic study of oxidation of several organic substrates by hexacyanoferrate(III) are well documented[2-9]. The oxidation of carbonyl compounds by this oxidant in alkaline medium has been studied by several workers[10-16]. The present study deals with the oxidation of ethyl vanillin by alkaline hexacyanoferrate(III) to explore the redox chemistry of hexacyanoferrate(III) in such media and to arrive at a suitable mechanism for the oxidation of ethyl vanillin by alkaline hexacyanoferrate(III) on the basis of kinetic results.

3-Ethoxy-4-hydroxybenzaldehyde, commercially known as ethyl vanillin has flavoring power two to four times stronger than vanillin[17]. It is also used as a chemical intermediate[18] and in perfumery[19]. The oxidation of ethyl vanillin by hexacyanoferrate(III) in aqueous alkaline medium is quite interesting because one may expect the transfer of electron from hydroxyl group which is an electron rich centre to oxidant. In contrary aldehydic group becomes electron rich and thereby undergoes oxidation because of immediate exclusion of proton from hydroxyl group by alkali.

EXPERIMENTAL

All the chemicals used are of AR grade and of SD fine chemicals Ltd. These were used without further purification. A solution of hexacyanoferrate(III) was prepared by dissolving $K_3[Fe(CN)_6]$ in distilled water and standardized iodometrically[20a]. 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 [ethyl vanillin] was always in excess over hexacyanoferrate(III), at a constant ionic strength in alkaline medium at a constant temperature of (30 ± 0.1) °C, respectively, unless otherwise stated. The reaction was initiated by mixing the thermostatted solutions of hexacyanoferrate(III) and ethyl vanillin, 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_{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 ±5 %.

Stoichiometry and products analysis: Reaction mixtures with different sets of concentrations of reactants where $[Fe(CN)_6^{3-}]$ was in excess over [ethyl vanillin] at a constant ionic strength and alkali were kept for about 8 h at 30 °C in a closed vessel. The remaining hexacyanoferrate(III) was estimated

TABLE-1
EFFECT OF VARIATIONS OF [Fe(CN)$_6^{3-}$], [ETHYL VANILLIN] AND [OH$^-$] ON THE OXIDATION OF ETHYL VANILLIN BY Fe(CN)$_6^{3-}$ AT 30 °C, I = 0.80 mol dm^{-3}

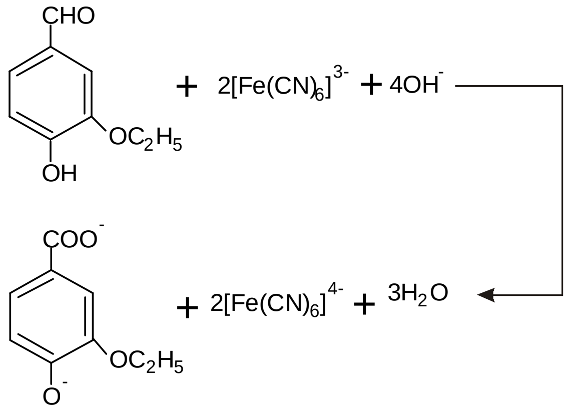
[Fe(CN)$_6^{3-}$] × 10^3 (mol dm^{-3})	[Ethyl vanillin] × 10^2 (mol dm^{-3})	[OH$^-$] (mol dm^{-3})	k$_{obs}$ × 10^3 (s^{-1})
2.0	5.0	0.40	1.46
3.0	5.0	0.40	1.46
4.0	5.0	0.40	1.46
5.0	5.0	0.40	1.42
4.0	4.0	0.40	0.82
4.0	5.0	0.40	0.93
4.0	6.0	0.40	1.16
4.0	7.0	0.40	1.50
4.0	5.0	0.35	1.40
4.0	5.0	0.55	1.84
4.0	5.0	0.65	2.10
4.0	5.0	0.75	2.70

TABLE-2
EFFECT OF VARYING IONIC STRENGTH ON REACTION RATE

[Substrate] = 5 × 10^{-2} mol dm^{-3}; [OH$^-$] = 0.4 mol dm^{-3}; [oxidant] = 3 × 10^{-3} mol dm^{-3}

I	0.588	0.688	0.788	0.888	0.988
10^4 k (s^{-1})	7.8	10.8	18.5	22.9	26.8

titrimetrically. The results indicated that 2 moles of hexacyanoferrate(III) consumed 1 mol of ethyl vanillin as in eqn. 1.



The stoichiometric ratio suggests that the main reaction products are 3-ethoxy 4-hydroxy benzoic acid and Fe(CN)$_6^{4-}$. The product 3-ethoxy 4-hydroxy benzoic acid is identified by its spot test[21]. It was also isolated by acidifying the reaction mixture followed by ether extraction and it was confirmed by IR spectrum. The characteristic absorption bands at 2980, 1681 and 1282 cm^{-1} confirmed the presence of carboxylic acid group and the same at 3691 cm^{-1} confirmed the hydroxyl group. The concentration of the reduction product, Fe(CN)$_6^{4-}$, was estimated by titrating against a Ce(IV) solution[20].

RESULTS AND DISCUSSION

Reaction order: The order with respect to [ethyl vanillin] and [alkali] were found by log$_{10}$ k$_{obs}$ *versus* log$_{10}$ (concentration) plots; these orders were obtained by varying the concentration of reductant and alkali in turn while keeping others constant.

Effect of [hexacyanoferrate(III)]: The [hexacyanoferrate(III)] was varied in the range, 2 × 10^{-3} to 5 × 10^{-3} mol dm^{-3} at fixed [ethyl vanillin], [OH$^-$] and ionic strength. The non-variation of the pseudo first-order rate constant at various concentrations of hexacyanoferrate(III) indicates the order in [hexacyanoferrate(III)] is unity (Table-1). This was also confirmed from the linearity of plots of log$_{10}$ [hexacyanoferrate(III)] *versus* time (r = 0.998 and s ≤ 0.005) for up to 60 % completion of the reaction.

Effect of [ethyl vanillin]: The substrate ethylvanillin, was varied in the range of 4 × 10^{-2} to 7 ×10^{-2} mol dm^{-3} at 30 °C keeping all other reactant's concentrations and conditions constant (Table-1). The k$_{obs}$ values were almost constant which underlines the first order dependence on ethyl vanillin. A plot of log k$_{obs}$ against log [ethyl vanillin] is linear with slope = 0.90.

Effect of [alkali]: The dependence of the reaction rate on hydroxide ion has been studied in the range 0.35 to 0.95 mol dm^{-3}. Table-1 shows the values of the rate constants at different [OH$^-$]. A plot of log k$_{obs}$ against log [OH$^-$]$_{actual}$ is linear with slope = 0.63. An attempt was made to find out whether the reaction would proceed in the absence of hydroxide ion or in the presence of bases other than hydroxide ion. For this purpose, a solution of the substrate in exactly equal molarity of hydroxide ion was prepared and reacted with hexacyanoferrate(III). The reaction did not proceed at all. So the reaction may be considered to be specific hydroxide catalyzed and not general base catalyzed.

Effect of ionic strength and solvent polarity: The ionic strength of the medium has been found to have considerable effect on the rate of oxidation of ethyl vanillin by alkaline hexacyanoferrate(III) Fig. 1. 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.

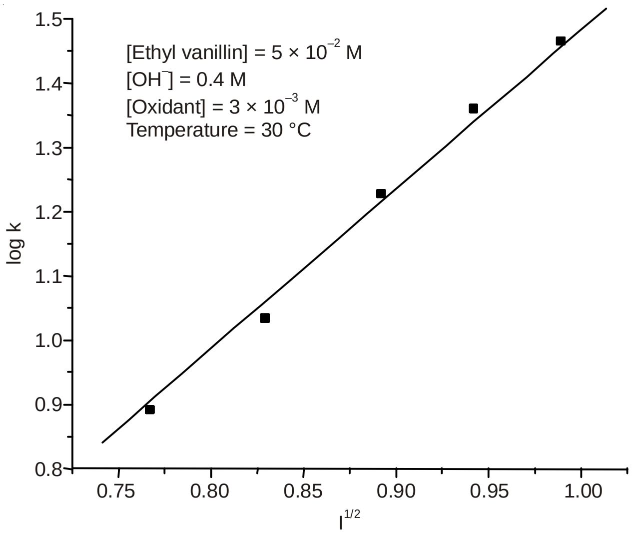


Fig. 1. Effect of ionic strength on oxidation of ethyl vanillin by hexacyanoferrate(III)

The addition of ethanol to the reaction mixture decreases the rate of oxidation. It is observed that the value of the rate constant decreases with decrease in the dielectric constant of the medium. The plot of log$_{10}$ k$_{obs}$ *versus* 1/D was linear with r = 0.997 (Fig. 2).

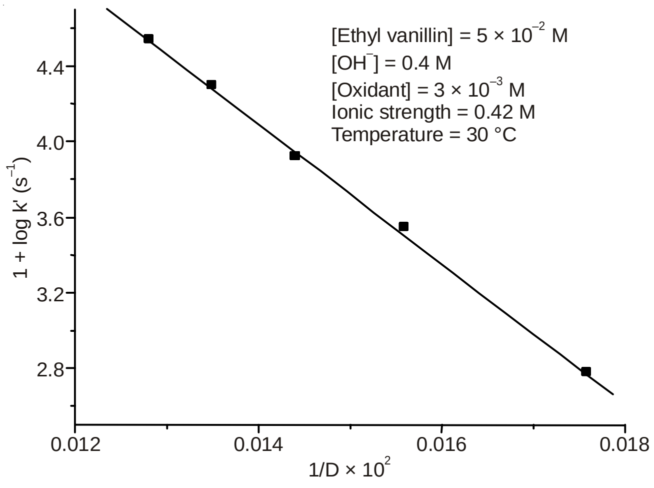


Fig. 2. Effect of solvent polarity on oxidation of ethyl vanillin by hexacyanoferrate(III) at 30 °C

Effect of initially added product: The effect of initially added product hexacyanoferrate(III) on the rate of reaction was also studied in the range of 1 × 10^{-3} to 4 × 10^{-3} mol dm^{-3} at 30 °C at constant [ethyl vanillin], [hexacyanoferrate(III)], [OH^-] and ionic strength. Hexacyanoferrate(II) was shown to have a retarding effect on rate of reaction (Table-3).

TABLE-3
EFFECT OF ADDED PRODUCT, HEXACYANOFERRATE(II), ON THE OXIDATION OF ETHYLVANILLIN BY HEXACYANOFERRATE(III) IN AQUEOUS ALKALINE MEDIUM AT 30 °C

[Ethylvanillin] = 5 × 10^{-2} mol dm^{-3}; [OH^-] = 0.4 mol dm^{-3}; [Hexacyanoferrate(III)] = 3 × 10^{-3} mol dm^{-3}; I = 0.42 mol dm^{-3}

$[Fe(CN)_6^{4-}] \times 10^3$	NIL	1	2	3	4
$k_{obs} \times 10^3$ (s^{-1})	1.6	1.39	1.35	1.02	0.98

Effect of temperature: The oxidation of ethyl vanillin by alkaline hexacyanoferrate(III) was carried out in the temperature range 302-323 K and it was observed that the rate of reaction increased with an increase in temperature (Table-4).

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 48.07 and 45.56 kJ mol^{-1}, respectively.

TABLE-4
EFFECT OF TEMPERATURE ON THE OXIDATION OF ETHYLVANILLIN BY HEXACYANOFERRATE(III) IN AQUEOUS ALKALINE MEDIUM

[Ethyl vanillin] = 5 × 10^{-2} mol dm^{-3}; [OH^-] = 0.4 mol dm^{-3}; [Hexacyanoferrate(III)] = 3 × 10^{-3} mol dm^{-3}; I = 0.42 mol dm^{-3}

Temperature (K)	302	308	314	318	323
$k_{obs} \times 10^3$ (s^{-1})	0.27	0.50	0.62	0.89	0.92

Entropy of activation at 302, 308, 314, 318 and 323 K are -101.28, -100.45, -102.52, -103.08 and -105.42 kJ mol^{-1}, respectively. The free energy of activation at 302, 308, 314, 318 and 323 K are 76.15, 76.45, 77.65, 78.20 and 79.43 kJ mol^{-1}, respectively.

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

Mechanism of reaction: The reaction being first order in [oxidant], first order in [ethyl vanillin] and first order in [OH^-] and the retarding effect of hexacyanoferrate(II) can be accommodated in the following **Scheme-I**. The oxidation was initiated by the formation of the anion of ethyl vanillin. The anion can transfer an electron to hexacyanoferrate(III), 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 rate law is given as follows;

$$EV + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} EV^- + H_2O$$

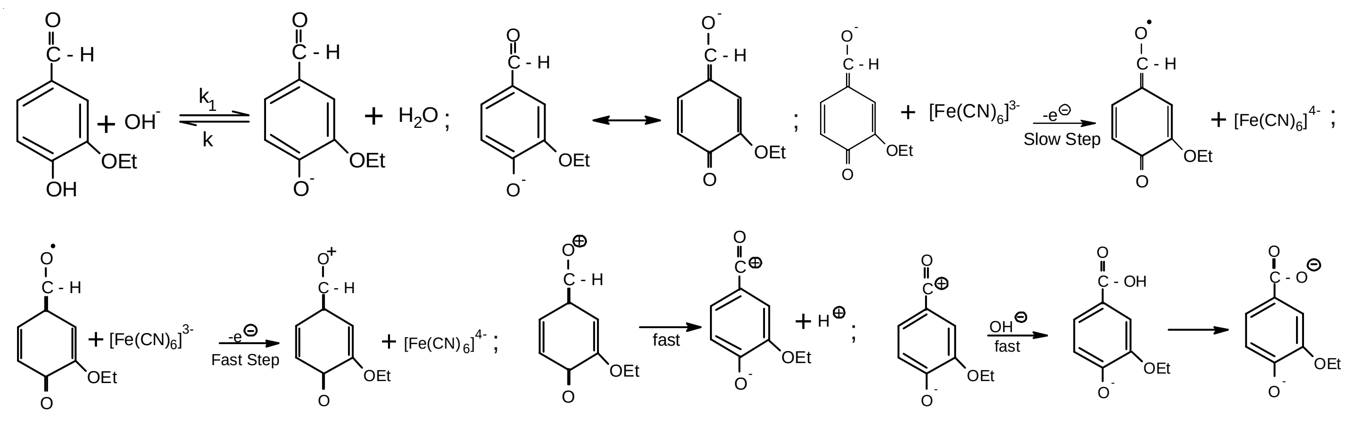
$$EV^- + FC \underset{k}{\overset{\text{Slow } k_2}{\rightleftharpoons}} \text{Radical R} + FC'$$

$$R + FC + OH^- \xrightarrow{k_3} \text{Products}$$

$$\frac{-dFC}{dt} = k_2[EV^-][FC] - k_{-2}[R][FC'] + k_3[R][FC]$$

Applying steady state approximation for radical R

$$[R] = \frac{k_2[EV^-][FC]}{k_3[FC] + k_{-2}[FC']}$$



Scheme-I

Substituting the terms in equations and simplifying we get:

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

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 becomes:

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

Conclusion

It is hereby concluded that one of the most important and widely used flavoring compounds ethyl vanillin can be oxidized by hexacyanoferrate(III) in alkaline medium. This happens through interference of free radical. The reaction may be considered to be specific hydroxide catalyzed. 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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