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Outer-Sphere Mechanism in the Oxidation of Pyrrole-2-Carboxaldehyde by Hexacyanoferrate (III) Complex.

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Abstract

The kinetics and mechanism of base-catalyzed oxidation of pyrrole-2-carboxaldehyde with hexacyanoferrate (III) is reported. The reaction showed first order with respect to aldahyde , alkali and hexaeyanoferrate(III). The kinetic data suggest that the oxidation involves the formation of an anion of the substrate undergoes oxidation with hexaeyanoferrate(III) via outer sphere mechanism process. The free radical thus produced is further oxidized to form the final products. A suitable mechanism was proposed and rate law was derived as

$$-\frac{d[\mathrm{Fe(CN)_6}]^{3-}}{dt} = \frac{2\mathrm{k_1k_2[RC(OH)_2][Fe(CN)_6]^{3-}[OH^-]}}{\mathrm{k_{-1}[H_2O]}}$$

Key words: pyrrole-2-carboxaldehyde, hexaeyanoferrate(III), outer sphere mechanism.

I. Introduction

The mechanisms of oxidation-reduction of transition metals complexes have received a great deal of attention over the last years.[1-4] Hexacyanoferrate(III) has been extensively used to oxidize number of organic and inorganic compounds in alkaline media.[5-17] However, the oxidation of organic substrates proceeds through outer sphere mechanism, with the electron transfer occurring from the reductant to the central atom via a cyanide ligand.[18]

The alkaline hexacyanoferrate(III) ion acts as an electron-abstracting reagent in redox reactions. A free-radicals intermediate are produced from the oxidation of some substrates, while oxidation of others does not involve the production of such radicals. [19-21]

The present paper deals with kinetics and mechanism of base-catalyzed oxidation Pyrrole-2-carboxaldehyde (Figure 1) with hexacyanoferrate (III) to achieve additional information of this system.

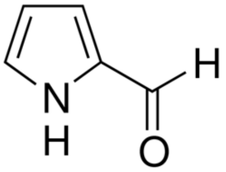


Fig. 1. Chemical structures of Pyrrole-2-carboxaldehyde

II. Materials and Methods

Pyrrole-2-carboxaldehyde were purchased from Aldrich and used as received. All chemicals used were of reagent grade, and doubly distilled water was used throughout the work. A solution of Ligand was prepared by dissolving an appropriate amount of ligand in doubly distilled water. The required concentration of ligand was prepared from its stock solution. A solution of $\mathrm{Fe(CN)_6}^{-3}$ was prepared by dissolving $\mathrm{K_3Fe(CN)_6}$ in $\mathrm{H_2O}$ and standardized iodometrically. [22] potassium hydroxide and potassium nitrate were employed to maintain the required alkalinity and ionic strength, respectively, in reaction solutions.

Kinetic measurements

All kinetic measurements were performed under pseudo first-order conditions where [Substrate] was always in large excess over $[\mathrm{Fe(CN)_6}^{-3}]$. The reaction was initiated by mixing the thermostatted solutions of $\mathrm{Fe(CN)_6}^{-3}$ and Substrate, which also contained the required concentration of KOH and KNO3. The progress of the reaction was monitored by measuring the decrease in the absorbance of $\mathrm{Fe(CN)_6}^{-3}$ in the reaction solution at 420 nm vs. time, using a Unicam UV/VIS spectrophotometer with 1.0 cm cell. The isolation method was used in this study where the concentration of the substance to be monitored is changed with the others kept constant. Aqueous solutions are prepared by making a constant total volume for all runs.

The pseudo first order rate constants in each case were obtained from the plots of the ln(A_∞ -A_t) versus time t were made (where A_∞ and A_t are the absorbances at infinity and at time t respectively), which were linear to about 80% at various reactant concentrations. The temperature was kept constant at 35º ± 1ºC, $[OH^-]$= 0.02 mol dm^{-3} and the ionic strength was maintained constant at 0.3mol dm^{-3} (KNO_3).

Reaction order

The reaction orders were determined from the slopes of log k_{obs} vs. logc plots by varying the concentrations of oxidant, reductant, and alkali in turn while keeping the others constant.

III. Effect of sodium hydroxide concentrations

To study the effect of alkali concentration on the rate of reaction, $[OH^-]$ was varied in the range of 0.10 to 0.50 (mol.dm^{-3}) at constant concentrations of HCF(III) and ligand at a ionic strength of 0.3 (mol.dm^{-3}). The rate constants of the reaction were found to increase with increase in $[OH^-]$ (Table **1**). Plot of log k_{obs} versus log $[OH^-]$ was linear with a slope of 0.99 suggesting the reaction to be first order with respect to $[OH^-]$ figure (2).

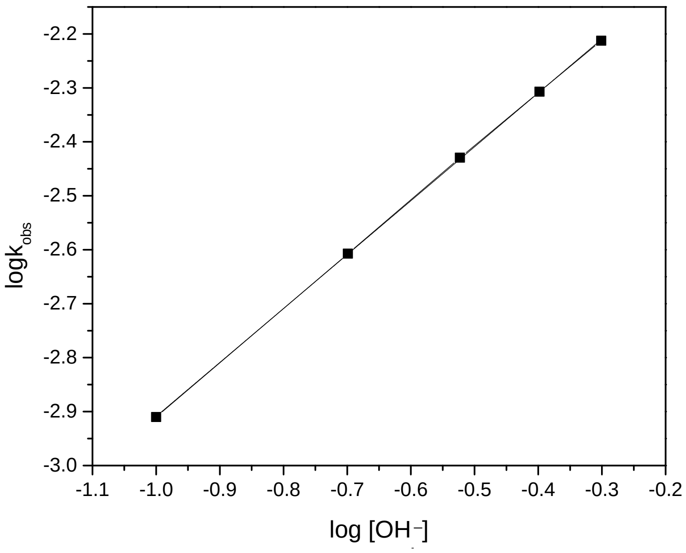


Fig. 2. Effect of $[OH^-]$ on oxidation of RCHO by HCF(III) in alkaline solution

Effect of pyrrole-2-carboxaldehyde(RCHO)

Reaction was carried out keeping all experimental conditions constant and by varying initial concentration of pyrrole-2-carboxaldehyde from 1.0×10^{-3} to 5.0×10^{-3} (mol.dm^{-3}). It was found that the rate of reaction increases with increasing [RCHO] (Table **1**). Plot of log k_{obs} versus log [RCHO] was linear with a slope of 1.010 suggesting the reaction to be first order with respect to [RCHO]. figure(3)

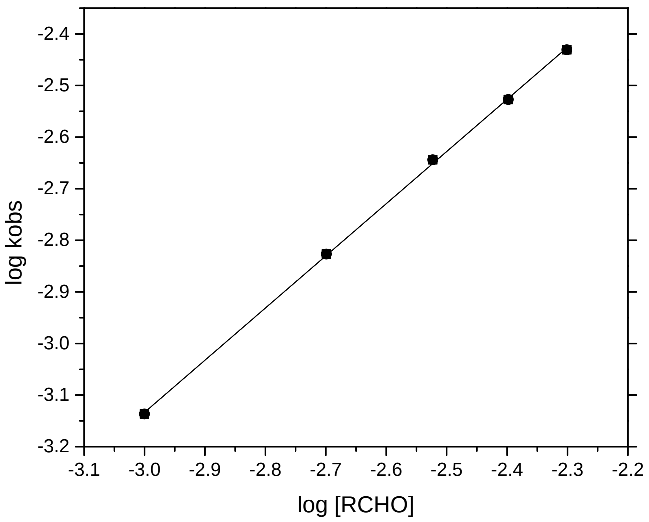


Fig. 3. Effect of oxidation[RCHO] by HCF(III) in alkaline solution

Table I. Effect of Variations of $[Fe(CN)6^{-3}]$, [RCHO],and $[OH^{-}]$ on the Oxidation of RCHO by $Fe(CN)_6^{3-}$ at 35 °C, $I = 0.30$ mol·dm^{-3}

[HCF(III)] X 10^4 (mol.dm^{-3})	[RCHO] X10^3 (mol.dm^{-3})	$[OH^-]$ (mol.dm^{-3})	K_{obs} X 10^{-3} (min^{-1})
2	5	0.3	1.86
4	5	0.3	3.69
6	5	0.3	5.54
8	5	0.3	7.39
10	5	0.3	9.27
4	1	0.3	0.73
4	2	0.3	1.49
4	3	0.3	2.27
4	4	0.3	2.97
4	5	0.3	3.71
4	5	0.1	1.23
4	5	0.2	2.47
4	5	0.3	3.72
4	5	0.4	4.93
4	5	0.5	6.13

Effect of ionic strength

The influence of ionic strength on the rate constant was also studied employing potassium nitrate solution for maintaining ionic strength in the range of (0.01 to 0.05 mol.dm^{-3})at constant concentrations of $[Fe(CN)_6^{-3}]$ 4.0x10^{-4} mol.dm^{-3}, [RCHO] 5.0x10^{-3} mol.dm^{-3} and $[OH^{-}]$ 0.3 mol.dm^{-3}. The values of k_{obs} were found to increase with increasing the ionic strength(Table 2), suggesting that the reaction takes place between ions of similar charges.

A plot of log k_{obs} vs $\sqrt{I}/(1+\sqrt{I})$according to extended Brönsted–Debye–Hückel equation [23], was found to be linear with positive slope as shown in Fig. 4.The rate constant at infinite dilution (k_0) is 1.18 × 10^{-3} min^{-1} and the product of the charges ZAZB ≈3. This is the same expected value considering the proposed mechanism, which involves a collision between a monovalent $((RCO(OH))^{-}$and a trivalent anion$(Fe(CN)_6^{-3})$ in the rate-determining step.

The rate was found to increase with increase in ionic strength indicating a positive salt effect.

Table(2). Effect of Ionic strength on the Oxidation of RCHO by HCF(III) in Aqueous Alkaline Medium at 30 °C.

[I]	$\sqrt{I}/(1+\sqrt{I})$	k_{obs} x10^3	Log k_{obs}
0.01	0.0909	2.36	-2.62774
0.02	0.1238	3.11	-2.50668
0.03	0.1476	3.71	-2.43063
0.04	0.1666	4.23	-2.37322
0.05	0.1827	4.82	-2.31679

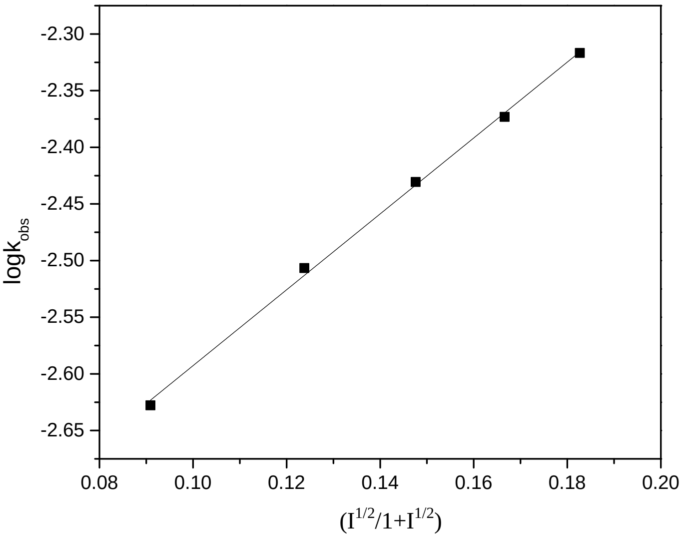


Fig. 4. Effect of [ionic strength] on oxidation of RCHO by HCF(III) in alkaline solution.

IV. Effect of Initially Added Products

The effect of initially added $K_4[Fe(CN)_6]$ product on the rate of reaction was also studied in the range of 1.0×10^{-4}–5.0×10^{-4} mol·dm^{-3} at35 ◦C at constant $[Fe(CN)_6^{-3}]$, [RCHO], $[OH^-]$, and ionic strength. As the initial concentration of $(Fe(CN)_6^{-4})$ is increased, the rate of reaction progressively decreased, i.e. it retarded the oxidation process (Table 3). A similar behavior has been observed in some redox reactions involving the formation of similar intermediates. [24–25]

Moreover, the effect of K^+ on the rate was also studied by varying the [KCl] in the same concentration range that of K4[Fe(CN)6]. The added KCl did not alter the rate of reaction. Hence, retardation on the rate of reaction was due to $(Fe(CN)_6^{-4})$ only.

Table 3: Effect of Added Product, $Fe(CN)_4^{-6}$, on the Oxidation of RCHO by HCF(III) in Aqueous Alkaline Medium at 30 ˚C.

$[Fe(CN)_6^{-4}] \times 10^{-5}$ (mol.dm^{-3})	1.0	2.0	3.0	4.0	5.0
k_{obs} X 10^{-3}	2.86	2.53	2.20	1.91	1.72

V. Free Radical Detection

The intervention of free radicals in the reaction was examined as follows. The reaction mixture, to which a known quantity of acrylonitrile scavenger had been initially added, was kept for 1 h in a nitrogen atmosphere, followed by large excess of methanol did not lead to the formation of precipitate This suggests that free radicals might not likely be involved in this reaction.

Thermodynamic Parameters

The rate of reaction was measured at different temperatures (298 – 318 K) at constant concentrations of reactants and other conditions being constant. The rate of reaction was increased with increasing the temperature. The values of k_{obs} at different temperature were given in Table 4. The activation energy Ea was calculated from the slope of Arrhenius plot of $\ln k_{obs}$ *versus* 1/ T. Eyring's plot of ln k_{obs}/T *versus* 1/T were linear (r = 0.999) (Fig. 5) and the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were obtained from the slope and intercept of the Eyring's plot. Arrhenius and thermodynamic activation parameters are given in table 5.

Table(4): Effect of temperatures on the rate of oxidation of RCHO by HCF(III) in aqueous alkaline medium at different temperatures.

T(K)	(1/T)x 10^3	k_{obs} x 10^3	Ln(k_{obs})	Ln(k/T)
298	3.36	2.75	-5.8962	-11.59325
303	3.30	3.20	-5.7446	-11.45834
308	3.25	3.72	-5.59403	-11.32413
313	3.19	4.18	-5.47744	-11.22365
318	3.14	4.67	-5.3666	-11.12865

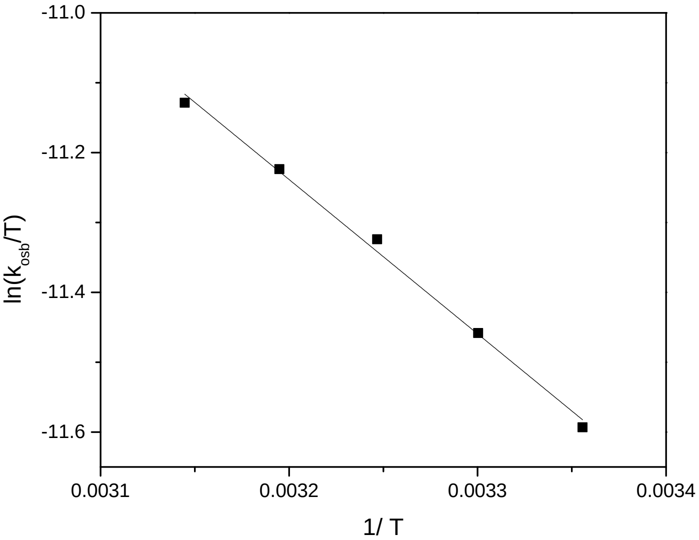


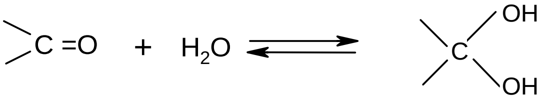
Fig. 5.Effect of temperatures on the rate of oxidation of RCHO by HCF(III) in alkaline solution.

Table(5): Arrhenius and thermodynamic activation parameters for the oxidation of RCHO by HCF(III) in aqueous alkaline medium at different temperatures.

Thermodynamic Parameters	Ea (k J mol^{-1})	ΔH‡ (k J mol^{-1})	ΔS‡ (J K^{-1} mol^{-1})	ΔG$^{‡}_{308}$ (k J mol^{-1})	A (dm^{3} mol^{-1}s^{1})
Parameters Values	20.04	18.37	-231.72	88.58	9.15

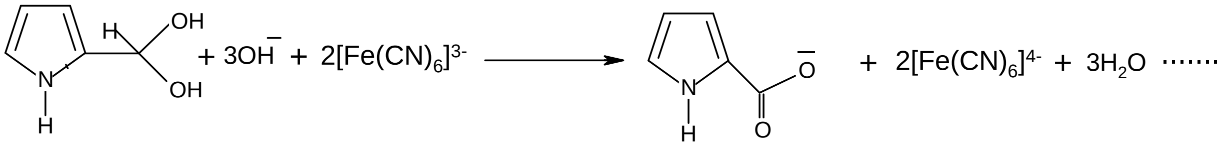
VI. Results and Discussion

There has been reported that carbonyl compounds undergo reversible hydration in aqueous solution in the presence of acid or base catalysis. [26-27] In several ways its oxidation resembles that of aliphatic alcohols. In the present case also, one might assume that the hydrate formation occur as according to the following equilibrium:



VII. Determination of stoichiometric factors

A reaction mixture, containing known an excess of hexacyanoferrate(III) over pyrrole-2-carboxaldehyde, was allowed to stand in the presence of sodium hydroxide at 30 °C. After the completion of reaction, the result showed that one mole of ligand consumed two moles of hexacyanoferrate(III) according to the stoichiometric equation (2)



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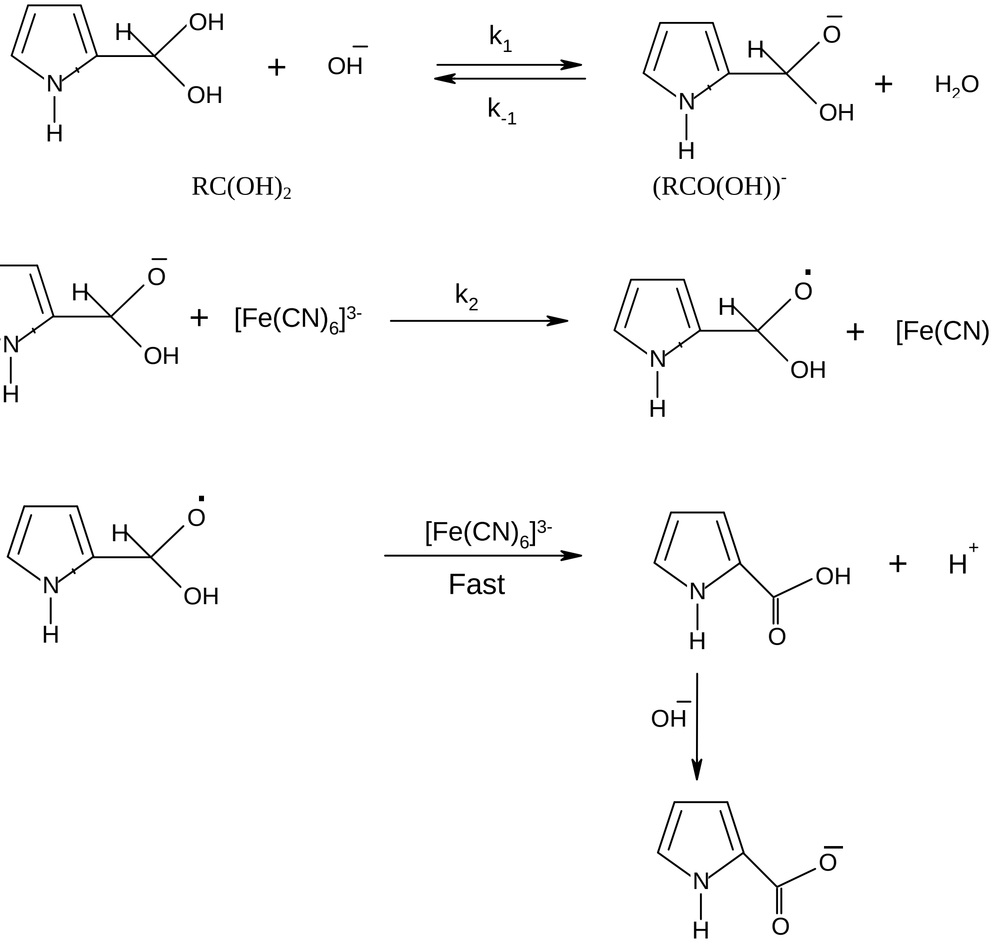
The main oxidation product pyrrole-2-carboxylic acid was extracted with chloroform, the solvent was removed under reduced pressure to give a white solid. The product was dissolved in a minimum amount of methanol and precipitated with diethyl ether.

The crystalline powder was collected by filtration, washed with ether (2 × 30 ml), and dried to afford the LCOOH as a white powder. The product was characterized by elemental analysis and The recorded IR spectra of aldehyde and its oxidation product showed a decay of the band at 1725 cm−1 of aldehyde due to(C=O) . Typical bands assigned to pyrrole-2-carboxaldehyde spectra were located at 1720 cm^{-1} is due to the CO double bond, the broad band centered in the range 2900-3250 cm^{-1} is caused by the presence of the OH and a band near 1400 cm^{-1} comes from the CO single bond.

On the basis of the results probable scheme of oxidation of the hydrated pyrrole-2-carboxaldehyde (RC(OH)$_2$)by hexacyanoferrate(III)) ion via the formation of anion $(RCO(OH))^-$as an intermediate might be considered as follows be:



$RC(OH)_2$ $(RCO(OH))^-$

The formate ion is much more stable towards oxidation due to its mesomeric structure.

Now assuming steady state condition for the concentration of $(RCO(OH))^-$, the rate law might be derived as follows:

$$-\frac{d[RCO(OH)]^-}{dt} = k_1[RC(OH)_2][OH^-] - k_{-1}\left[\left(RCO(OH)\right)^-\right][H_2O] - k_2\left[\left(RCO(OH)\right)^-\right][Fe(CN)_6]^{3-} \quad \ldots\ldots..3$$

Now keeping the experimental conditions in mind and solving equ.(2) the final rate equation will be:

$$-\frac{d[Fe(CN)_6]^{3-}}{dt} = \frac{2k_1k_2[RC(OH)_2][Fe(CN)_6]^{3-}[OH^-]}{k_{-1}[H_2O] + k_2[Fe(CN)_6]^{3-}} \ldots\ldots\ldots\ldots 4$$

To the first approximation, if we assume that $k_{-1}[H_2O] \gg [Fe(CN)_6]^{3-}$, the rate law (4) reduces to (5):

$$-\frac{d[Fe(CN)_6]^{3-}}{dt} = \frac{2k_1k_2[RC(OH)_2][Fe(CN)_6]^{3-}[OH^-]}{k_{-1}[H_2O]} \ldots\ldots\ldots\ldots 5$$

According to equation (4), the rate law clearly explains the experimental results i.e., first order kinetics with respect to hexaeyanoferrate(III), pyrrole-2-carboxaldehyde and hydroxide ion concentration. These results suggest that the reaction proceeds via a charge transfer process as it has already been observed in the course of the oxidation of acetone, ethylmethyl ketone, formaldehyde and 1,4,7,10-tetraazacyclododecane-1-carbaldehyde by aqueous alkaline hexacyanoferrate(III) .[28-30] Furthermore, the experimental values of $\Delta S^‡$ and $\Delta G^‡$ were both favourable for electron transfer processes. The high negative values of $\Delta S^‡$ indicates that the intermediate complex is more ordered than the reactants due to loss of degree of freedom.[31]

VIII. Conclusion

The oxidation of pyrrole-2-carboxaldehyde yields the corresponding pyrrole-2-carboxylic acid as the product. The reaction is first order with respect to aldahyde , alkali and hexaeyanoferrate(III). The effects of ionic strength suggest the participation of ions in the rate determining step as represented by the proposed mechanism. Moreover, the high negative values of $\Delta S^{\neq}$ provided support for the formation of a rigid activated complex with fewer degrees of freedom.A mechanism in terms of active species of oxidant is proposed and the rate law is derived and verified.

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