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KINETICS AND MECHANISM OF THE COMPLEX FORMATION BETWEEN HEXACYANOFERRATE (II) AND CHROMIUM (III)

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Kinetics of reaction between hexacyanoferrate (II) and Cr(III) has been followed spectrophotometrically at 480nm. The reaction follows an overall first order kinetics, being first order in Cr(III) and zero order in $Fe(CN)_6^{4-}$. The rate increases with increase in *p*H upto a *p*H of 4.4. The salt effect is negative and primary exponential in character. The rate decreases with an increase in dielectric constant, a plot between $\log k$ *vs* $1/D$ being linear. Various thermodynamic parameters, for the reaction have been evaluated. Chemical analysis corresponds to the formula $K[Cr.Fe(CN)_6OH].2H_2O$. A reaction mechanism to explain the above results has been proposed.

Key Words : Kinetics; Mechanism; Chromium (III); Hexacyanoferrate (II); Spectrophotometry

INTRODUCTION

The interaction of metal ions like Cr(III), Mo(VI), Ti(IV) with hexacyanoferrate presents some interesting features in the field of ferrocyanogen complexes. Some of these form soluble complexes while others form insoluble complexes under different conditions. Malik and co-workers[1] on the basis of various physico-chemical studies, reported the formation of a 1 : 1 complex between Cr(III) and hexacyanoferrate(II). However, a survey of literature indicated that the kinetic study of this complex formation has not been carried out so far. In an earlier paper,[2] findings were reported on the kinetics of interaction of hexacyanoferrate with Mo(VI). In continuation, the authors have studied the kinetics of Cr(III) interaction with hexacyanoferrate(II), results for which are presented in this paper.

EXPERIMENTAL

An aqueous solution of potassium hexacyanoferrate(II) was prepared from an Analar, BDH sample by direct weighing and its concentration was checked by standard potassium permanganate.[3] Aqueous solution of chromic chloride was standardized iodometrically after oxidizing the solution of chromate by Na_2O_2.[4] Sodium acetate-hydrochloric acid buffer was used to maintain the *p*H of solutions.

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All other reagents used were of analytical grade. The reaction vessels used were of pyrex glass and were coated on the out side with Japan black to exclude the possibility of photo-chemical reaction.

The pH measurements were carried out on a Cambridge Bench type pH-meter using glass electrode. The spectrophotometric measurements were made on Unicam SP 500 Spectrophotometer.

Polarographic measurements were made on a Toshniwal mannual polarograph using scalamp galvanometer in the external circuit and a fisher capillary with a drop time of 3–4sec (open circuit) and capillary constant $(m^{2/3}t^{1/6})$ of 1.807.

Kinetic Measurements

On mixing an aqueous solution of hexacyanoferrate (II) with an aqueous solution of chromic chloride a yellowish red colour developed which slowly becomes reddish brown on keeping. The λ_{max} for the reddish brown coloured solution of the complex thus obtained was found to be 480nm. Further, the λ_{max} of the reaction mixture did not change with time. It is worthwhile to point out here that both the reactants do not have any appreciable absorbance at this wavelength. The progress of the reaction was therefore followed by measuring the absorbance at regular intervals of time at a wavelength of 480nm.

<div align="center">RESULTS AND DISCUSSION</div>

Kinetic Behaviour

The reaction was studied at varying concentration of reactants, by turn, keeping the other constant. Initial rates in terms of (dx/dt) (where x is the absorbance after time t), were evaluated by plane mirror method of Latashaw.[5] The order of reaction was then evaluated by Van't Hoff's differential method (Table I). It was observed that the order in Cr(III) was one, while the reaction showed zero order in $Fe(CN)_6^{4-}$, thus giving an overall first order kinetics for this reaction. Further, a plot of log $(a-x)$ vs time was linear confirming that the reaction follows first order kinetics. The specific rate was found to increase as the concentration of Cr(III) increased (Table II). However, specific rate (k) was independent of initial concentration of $Fe(CN)_6^{4-}$ (Table III). It was observed that in an unbuffered solution, the pH changed from 4.30 to 4.40, during the course of reaction. The increase in pH during the course of reaction suggested that probably hydrolysis of the ferrocyanide takes place during the course of reaction.

The reaction was studied at different pH ranging between 1.02–4.4. Results for these studies are given in Table IV. Higher pH than 4.4 could not be investigated due to precipitation. It is seen that the specific rate increases with an increase in pH and reaches its maximum value at pH 4.4. Hence, all kinetic measurements were made at a pH of 4.4 maintained by using sodium acetate hydrochloric acid buffer. The results at varying ionic strength (by using KCl as neutral salt) indicated (Table V) that increase in ionic strength decreases the rate of reac-

<div align="center">TABLE I</div>

Effect of [Cr(III)] and [Fe(CN)$_6^{4-}$ *on the rate, KCl* $= 1.0 \times 10^{-1}$ *mol dm*$^{-3}$, *Temperature* $= 303\ K$

[Cr(III) $\times 10^2$ mol dm^{-3}	[Fe(CN)$_6^{4-}$] $\times 10^2$ mol dm^{-3}	$\left(\dfrac{dx}{dt}\right)_i$
2.0	1.0	7.32
1.33	1.0	2.60
1.00	1.0	2.09
0.50	1.0	0.97
1.0	2.0	7.24
1.0	1.33	7.29
1.0	0.50	7.21

<div align="center">TABLE II</div>

Effect of chromic chloride on the first order rate constant at constant ionic strength

$\left[Fe(CN)_6^{4-}\right] = 1.0 \times 10^2$ mol dm^{-3}; Temp. $= 303$ K, [KCl] $= 0.1$ mol dm^{-3} pH $= 4.4$

[Cr(III)] $\times 10^2$ mol dm^{-3}	$k \times 10^3$ min^{-1}
2.00	24.9
1.33	24.03
1.00	24.86
0.66	23.66
0.50	23.03

<div align="center">TABLE III</div>

Effect of $\left[Fe(CN)_6^{4-}\right]$ *on first order rate constant at constant ionic strength*

[Cr(III)] $= 1.0 \times 10^2$ mol dm^{-3}; Temp $= 303$ K [KCl] $= 0.1$ mol dm^{-3}; pH $= 4.4$

$\left[Fe(CN)_6^{4-}\right] \times 10^2$ mol dm^{-3}	$k \times 10^3$ min^{-1}
2.00	24.08
1.33	24 10
1.00	24.03
0.50	23.94

tion. A plot between log k vs $I^{1/2}$ was found to be linear inaicating that the negative salt effect was primary exponential in character. The nature of the salt effect suggested that the rate determining step must be a reaction between two oppositely charged ions.[6] Further, different ions investigated viz., K$^+$, Na$^+$, Mg^{++}, Cl$^-$, Br$^-$, I$^-$, NO$_3^-$, NO$_2^-$, ClO$_4^-$, SO$_4^{2-}$ did not have any specific inhibitory effect.
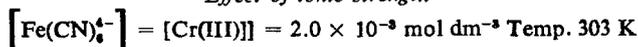
Reaction was studied at varying dielectric constant of the medium brought about by changing the ratio of water in water-methanol, water-ethanol and water-
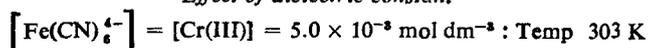
TABLE IV

Effect of pH

$\left[Fe(CN)_6^{4-}\right]$ = [Cr(III) = 2.0 × 10⁻³ mol dm⁻³ Temperature = 303 K: [KCl] = 0.1 mol dm⁻³
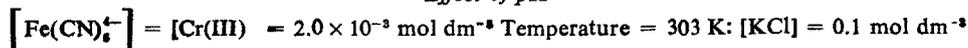
pH	$k \times 10^3$ min⁻¹
1.02	1.80
1.75	3.47
2.50	9.58
3.27	13.11
4.00	16.28
4.4	17.42
4.84	ppt

TABLE V

Effect of ionic strength

$\left[Fe(CN)_6^{4-}\right]$ = [Cr(III)]] = 2.0 × 10⁻³ mol dm⁻³ Temp. 303 K

[KCl] × 10² mol dm⁻³	$k \times 10^3$ min⁻¹
1	20.1
3.3	19.6
4	19.4
5	18.9
6	18.5
8	18.0
10	17.4

TABLE VI

Effect of dielectric constant

$\left[Fe(CN)_6^{4-}\right]$ = [Cr(III)] = 5.0 × 10⁻³ mol dm⁻³ : Temp 303 K

%	Methanol + water		Ethanol + water		Dioxane + water	
	D	$k \times 10^3$ (min⁻¹)	D	$k \times 10^3$ (min⁻¹)	D	$k \times 10^3$ (min⁻¹)
10	75·3	10.70	74.0	11.50	72.2	12.4
15	77.3	14.30	71.1	15.50	68.3	16.3
20	70.1	17.90	69.2	19.10	64.4	21.0
25	68.2	19.30	66.6	22.0	60.60	22.40
30	64.9	20.90	62.40	24.00	56.60	25.70
40	61.0	23.60	58.00	26.20	48.90	27.20

dioxane mixtures.[7,8] The results (Table VI) showed that decrease in dielectric constant resulted in an increase of the rate. A plot between log k and $\dfrac{1}{D}$ was

found to be linear in each case, further suggesting that the rate determining step involved a reaction between two oppositely charged ions.[9] The different thermodynamic parameters as evaluated by studying the reaction at five different temperatures (Fig. 1) were, $Ea = 69.7 \pm 1.0$kJ/mol, $\triangle S = 101.0 \pm 1.4$ JK^{-1} mol^{-1} and $A = 5.26 \times 10^6$ s^{-1}. A positive value of entropy of activation confirmed that the rate determining step involved reaction between two oppositely charged ions.

STOICHIOMETRY AND CHARACTERISATION OF COMPLEX

Stoichiometry of 1 mole of $CrCl_3$: 1 mole of $K_4Fe(CN)_6$ was obtained by Job's method.[10] The complex was isolated from equimolar mixture of the reactants, which was allowed to stand for two hours by adding absolute alcohol, filtered and washed with 25 per cent ethanol and dried over CaO in a dessicator for 24 hrs. Water of hydration was determined by heating the complex, iron was estimated by standard procedure,[4] chromium was estimated iodometrically and nitrogen was estimated by Kjeldahl's method.[11] Potassium was estimated by flame photometry. The results of chemical analysis were—

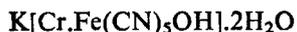| Element per cent	C	H	N	Fe	O	K	Cr
Found	18.24	1.62	21.12	16.85	14.63	11.92	15.62
Calculated for K[Cr.Fe(CN)₆OH].2H₂O	18.19	1.52	21.21	16.92	14.55	11.85	15.76
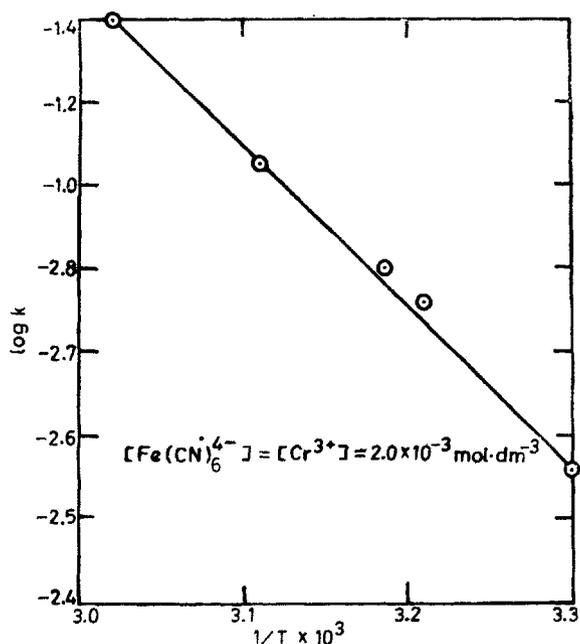
FIG 1 Arrhenius plot

On the basis of the above analysis the following formula for the complex was obtained—

$$K[Cr.Fe(CN)_5OH].2H_2O$$

The structure of this complex may be similar to that of prussian blue[12] where Fe(II) are replaced by Cr(III).

MECHANISM

On the basis of kinetic evidences presented in this paper, product isolated and taking into account the close similarity in kinetic behaviour of this reaction to that reported for Mo(VI) interaction with hexacyanoferrate(II),[2] the following reaction mechanism for the complex formation between hexacyanoferrate(II) and Cr(III) is suggested.

$$Fe(CN)_6^{4-} + H_2O \underset{Fast}{\overset{K_1}{\rightleftharpoons}} [Fe(CN)_5 (H_2O)]^{3-} + CN^- \qquad ...(1)$$

$$CN^- + H_2O \underset{Fast}{\overset{K_2}{\rightleftharpoons}} HCN + OH^- \qquad ...(2)$$

$$[Fe(CN)_5 (H_2O)]^{3-} + OH^- \underset{Fast}{\overset{K_3}{\rightleftharpoons}} [Fe(CN)_5 OH)]^{4-} + H_2O \qquad ...(3)$$

$$Cr(III) + 2CN^- \underset{Slow}{\overset{K_4}{\longrightarrow}} Cr(CN)_2^+ \qquad ...(4)$$

$$Cr(CN)_2^+ + [Fe(CN)_5 OH)]^{4-} \underset{Fast}{\overset{K_5}{\longrightarrow}} [CrFe(CN)_5 OH]^- + 2CN^- \qquad ...(5)$$
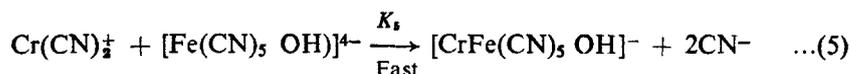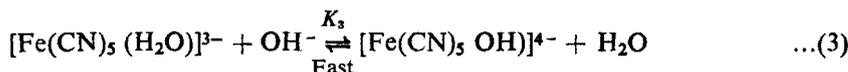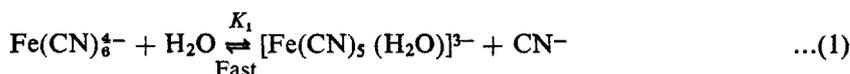
In the proposed mechanism, steps 1 to 3 are in accordance with the observations of Malik et al.[13] and as such are rapid equilibrium processes. Thus, reaction (4) may be supposed to be the rate determining process, which is a reaction between Cr(III) and CN^- two oppositely charged ions. The $Cr(CN)_2^+$ intermediate formed rapidly interacts with $[Fe(CN)_5 OH)]^{4-}$ by process (5) to give the final product, which has been confirmed by elemental analysis. The formation of complex $Cr(CN)_2^+$ by process (4) was confirmed polarographically, using Lingane's method. It was observed that the $E_{1/2}$ of $CrCl_3$ in 0.1M KCl as supporting electrolyte was shifted to more positive potential by the addition of KCN. From the slop of the plot of $E_{1/2}$ vs log $[CN^-]$ the coordination number is calculated to be 2.1 and hence the formula obtained is $Cr(CN)_2^+$. Further, the λ_{max} for the spectrum of the system — $CrCl_3$ + KCN also shifts with time, again indicating the formation of $Cr(CN)_2^+$ as confirmed polarographically. Furthermore, the reaction was found to be catalysed by CN^-, which also supports the participation of CN^- in the rate determining step. Thus taking stage (4) to be rate determining step, the rate law can be presented as

$$\left(\frac{dx}{dt}\right) = \frac{d [CrFe(CN)_5 OH]^-}{dt} = k [Cr(III)] [CN^-]^2$$

which reduces to $dx/dt = k[Cr(III)]$, since the concentration of CN^- at any moment is very small. The above rate law is in accordance with all the kinetic features observed.

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