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Kinetics and Mechanism of the Reaction between 1,2-Diaminopropanetetraacetatoferrate(III) and Cyanide Ion

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Abstract

The present study examines the kinetics and mechanism of the system $[FePDTA(OH)]^{2-}$ + $5CN^-$ $\rightleftharpoons$ $[Fe(CN)_5OH]^{3-}$ + $PDTA^{4-}$ at pH = 11.0 ± 0.02, $I = 0.25$ M and temperature = 25 ± 0.1 °C. The reaction has been studied spectrophotometrically at 395 nm (λ_{max} of $[Fe(CN)_5OH]^{3-}$). The data show that the reaction has three distinguishable stages; the first stage is formation of $[Fe(CN)_5OH]^{3-}$, the second is conversion of $[Fe(CN)_5OH)]^{3-}$ to $[Fe(CN)_6]^{3-}$ and last is reduction of $[Fe(CN)_6]^{3-}$ to $[Fe(CN)_6]^{4-}$ by the released ligand, *viz.*, PDTA. The first reaction shows variable order dependence on cyanide concentration, one at high cyanide concentration and two at low cyanide concentration. The second reaction exhibits first order dependence on the concentration of $[Fe(CN)_5OH]^{3-}$ as well as cyanide. The reverse reaction between $[Fe(CN)_5OH]^{3-}$ and PDTA is first order in $[Fe(CN)_5OH]^{3-}$ and PDTA, and inverse first order in cyanide. On the basis of forward and reverse rate studies, a five-step mechanism has been proposed for the first reaction.

Introduction

The complete displacement of 1,2-diaminopropanetetraacetate ion from iron(III) by cyanide is slow and requires that four cyanide ions be present in the rate-determining step. The fifth cyanide then adds to form pentacyanohydroxoferrate(III) in a rapid step. Similar mechanisms have also been proposed for the reaction of cyanide ion with some polyaminocarboxylates of Fe(III) [1–3], Co(II) [4, 5], Mn(III) [6] and Ni(II) [7, 8].

In this communication we present our results on the reaction (1) in further confirmation of the mechanism proposed by us earlier [1–3]. The rates of these reactions are highly dependent upon the total cyanide concentration and are inversely proportional to the stability of aminocarboxylato iron(III) complexes [9]. The reverse rate studies lend further support to the proposed mechanistic scheme. Other supporting evidence has also been provided.

$$[FePDTA(OH)]^{2-n} + 5CN^- \rightleftharpoons [Fe(CN)_5OH]^{3-} + PDTA^{4-} \qquad (1)$$

Experimental

The tetra acid form of PDTA in purified and recrystallized form (Sigma Chemical Co; U.S.A.), ferric nitrate (Thomas and Baker), sodium cyanide (M and B Ltd., U.K.), sodium perchlorate (E. Merck, F.R.G.) and sodium ferricyanide (G.R., SDS) were used in this study.

Sodium aquapentacyanoferrate(II) was prepared from sodium nitroprusside (AR, B.D.H) by a literature method [10]. It was then oxidized to aquapentacyanoferrate(III) by hydrogen peroxide and then converted to pentacyanohydroxoferrate(III) by increasing the pH to a value higher than 10 [11]. Ferric perchlorate was prepared by a method described in an earlier communication [2] and was used for the preparation of 1,2-diaminopropanetetracetatoferrate(III). A ten percent excess of ligand over a stoichiometric requirement was added to ferric perchlorate solution to ensure complete formation of the aminocarboxylato complex. Sodium cyanide was standardized argentometrically [12]. Perchloric acid or sodium hydroxide were used to maintain pH at any required value.

A Toshniwal spectrophotometer model RL-02 with a circulatory arrangement for thermostatting the cell compartment was used for all kinetic studies of these reactions. The temperature of both reactants was maintained at 25 ± 0.1 °C by placing them in an ultracryostat model 2 NBE (G.D.R.). A Cary 17D and a Shimadzu (UV-190) double beam spectrophotometer were used for obtaining repetitive scans of reaction mixtures. All pH measurements were made on an Elico digital pH meter model LI-120 using B.D.H. standard buffers for standardization.

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Kinetic Measurements

The rate of $[Fe(CN)_5OH]^{3-}$ formation was measured spectrophotometrically at 395 nm (λ_{max} of $[Fe(CN)_5OH]^{3-}$, $\epsilon = 1740$ M^{-1} cm^{-1}) [13] at pH = 11.0, $I = 0.25$ M ($NaClO_4$) and 25 °C. The forward reactions were run in the presence of a large excess of CN^- and all gave pseudo first order plots. At this wavelength, $[FePDTA(OH)]^{2-}$ also absorbs appreciably, so corrections were applied for the absorbance of $[Fe(CN)_5OH]^{3-}$ at this wavelength. The pseudo first order rate constants were obtained by plotting log C_A *vs.* time (t) over at least 70% of the reaction where C_A is the concentration of $[FePDTA(OH)]^{2-}$ at any time t. A formula has been derived for the calculation of C_A as given in eqn. (2), based on reactions (3) and (4).

$$C_A = \frac{(\epsilon_B C_A{}^0 - A_t)}{\epsilon_B - \epsilon_A} \tag{2}$$

$$[FePDTA(OH)]^{2-} + 5CN^- \rightleftharpoons [Fe(CN)_5OH]^{3-} + PDTA^{4-} \tag{3}$$

$$[Fe(CN)_5OH]^{3-} + CN^- \rightleftharpoons [Fe(CN)_6]^{3-} + OH^- \tag{4}$$

where $A \equiv [FePDTA(OH)]^{2-}$, $B \equiv [Fe(CN)_5OH]^{3-}$, ϵ_A and ϵ_B are their corresponding ϵs. $C_A{}^0$ is the initial concentration of $[FePDTA(OH)]^{2-}$. The kinetics of the reverse reaction were also followed spectrophotometrically by the disappearance of $[Fe(CN)_5OH]^{3-}$ at 395 nm.

Results

The forward reaction shown in eqn. (1) is first order in the $[FePDTA(OH)]^{2-}$ complex and showed a variable order dependence in total cyanide ion concentration. Thus:

$$\text{rate} = \frac{d[Fe(CN)_5OH^{3-}]}{dt} = k_f[FePDTA(OH)(CN)_x{}^{-2-x}]\,[CN^-]_T{}^{4-x} \tag{5}$$

where x may be 0, 1, 2 or 3, though $x = 0.1$ could not be verified in this case. With a large excess of cyanide present, pseudo first order kinetics is observed.

For the rate determining step

$$\text{rate} = \frac{d[Fe(CN)_5OH^{3-}]}{dt} = k_{obs}[FePDTA(OH)(CN)_3{}^{5-}] \tag{6}$$

where $k_{obs} = k_f[CN^-]$. Table I lists the observed rate constants at varying concentration of total cyanide.

TABLE I. Cyanide Dependence of Observed Forward Rate Constant, pH = 11.0 ± 0.02; $I = 0.25$ M ($NaClO_4$); Temperature = 25 ± 0.1 °C. $[FePDTA(OH)^{2-}] = (3-5) \times 10^{-4}$ M

$10^2 \times [CN^-]_T$ (M)	k_{obs} (s^{-1})
1.0	4.79×10^{-6}
2.0	1.26×10^{-5}
3.0	1.84×10^{-5}
4.0	4.13×10^{-5}
6.0	6.23×10^{-5}
7.0	6.91×10^{-5}
8.0	7.04×10^{-5}
9.0	8.91×10^{-5}
10.0	9.29×10^{-5}
12.5	1.15×10^{-4}
15.0	1.31×10^{-4}
20.0	1.57×10^{-4}
25.0	1.79×10^{-4}

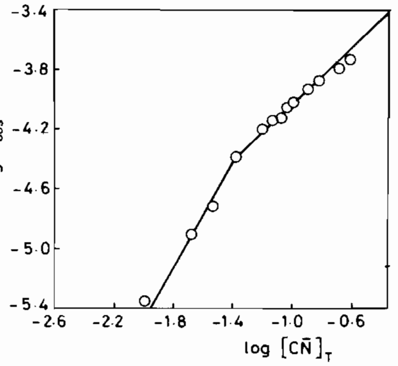

Fig. 1. Cyanide dependence of the observed pseudo first order rate constants in the reaction of cyanide ion with $[FePDTA(OH)]^{2-}$; pH = 11.0 ± 0.02; $I = 0.25$ M ($NaClO_4$), temperature = 25 ± 0.1 °C, $[FePDTA(OH)^{2-}] = (3-5) \times 10^{-4}$ M.

A plot of log k_{obs} as a function of log $[CN^-]_T$ is shown in Fig. 1. The slope of this plot is very close to one at high cyanide ion concentration and close to two at low cyanide ion concentration. It is proposed that mixed cyano complexes are formed in very low concentration during the reaction, which is supported by a small but definite instantaneous increase in the absorbance immediately after mixing. The subsequent changes are slower. The stability constants of these monocyano to tetracyano complexes have been determined by a kinetic method described earlier [9].

Kinetics of the Reverse Reaction

The stability constant of $[FePDTA]^{1-}$ is significantly less (log K_{FePDTA} = 21) [14] than that of

$[Fe(CN)_5OH]^{3-}$ (log β_5 = 43.6)*. However, using dilute concentrations of $[Fe(CN)_5OH]^{3-}$ and a fairly high concentration of $PDTA^{4-}$, it is possible to measure the reverse reaction rate (eqn. (1)). The rate of decomposition of $[Fe(CN)_5OH]^{3-}$ under these conditions does not obey a simple rate equation. The reverse reaction rate is first order with respect to $[Fe(CN)_5OH^{3-}]$ and $PDTA^{4-}$ and is inversely proportional in the free cyanide concentration. The data fit the following rate eqn. (7).

$$-\frac{d[Fe(CN)_5OH^{3-}]}{dt} = \frac{k_r[Fe(CN)_5OH^{3-}][PDTA^{4-}]}{[CN^-]} \quad (7)$$

The integrated rate expression is shown in eqn. (8):

$$A_i - A_t - A_i \ln\frac{A_t}{A_i} = -\frac{\epsilon l k'_{obs} t}{5} \quad (8)$$

In this expression $k'_{obs} = k_r[PDTA^{4-}]$, A_i and A_t are the absorbances at time $t = 0$ and t = t, respectively, and ϵ is the molar extinction coefficient of $[Fe(CN)_5\text{-}OH)]^{3-}$ at the wavelength at which the reaction is monitored (395 nm); l is the path length.

A plot of left hand side of eqn. (8) *vs.* t was found to be a straight line. The values of k'_{obs} were calculated from the slopes of the above plots. The values of rate constants calculated from these plots are listed in Table II.

TABLE II. Kinetics of Decomposition of $[Fe(CN)_5OH]^{3-}$ by PDTA, pH = 11.0 ± 0.02; I = 0.75 M ($NaClO_4$), Temperature = 25 ± 0.1 ℃. $[Fe(CN)_5(OH)^{3-}]$ = (4–8) × 10^{-5} M

$10^2 \times [PDTA]_T$ (M)	$10^{10} \times k'_{obs}$ ($M\ s^{-1}$)	$10^9 \times k_r$ ($= K_5^{-1}k_4$)^a (s^{-1})
8	6.58	8.2
10	8.2	8.2
12	10.9	9.08
18	15.9	8.8

^{a}Average = 8.57 × 10^{-9} s^{-1}.

Effect of Ionic Strength on the Forward Reaction

The rate of forward reaction (1) increased with increasing ionic strength of the medium. The ionic strength was maintained each time before mixing the two reactants, thus keeping pH, temperature and concentrations constant during these measurements. The forward second order rate constants obeyed eqn. (9), due to Bronsted–Bjerrum–Christiansen [15].

$$\log k_f = \log k_0 + \frac{2AZ_AZ_B\sqrt{I}}{1 + B\sqrt{I}} \quad (9)$$

where B is a constant which increases with increasing size of the ion, A is also a constant and given more generally by $A = 1.82 \times 10^6/(DT)^{3/2}$, D is the dielectric constant of the medium, and T is the absolute temperature. In this formulation, k_f = specific rate constant, k_0 is the specific rate constant at zero ionic strength, and Z_A and Z_B are the charges on the two reactant species. At 25 ℃, the above equation reduces to

$$\log k_f = \log k_0 + \frac{1.02Z_AZ_B\sqrt{I}}{1 + \sqrt{I}} \quad (10)$$

because A = 0.509 and B = 1.

The rate data obey eqn. (9) up to I = 0.1 M. The plots of log k_f *vs.* $\sqrt{I}/(1 + \sqrt{I})$ are given in Fig. 2.

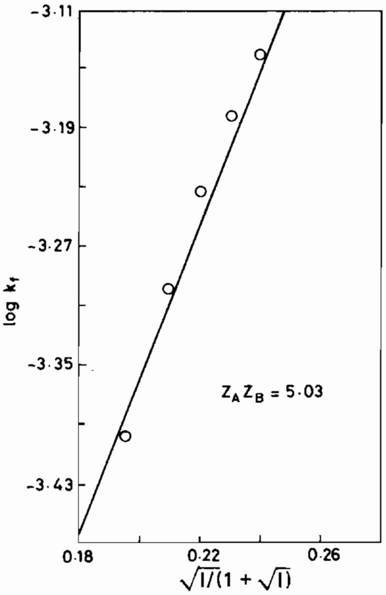

Fig. 2. Effect of ionic strength on the forward rate constants for $[FePDTA(OH)]^{2-}$–CN^- reaction pH = 11.0 ± 0.01, I = 0.25 M ($NaClO_4$), temperature = 25 ± 0.1 ℃, $[FePDTA\text{-}(OH)^{2-}]$ = 5 × 10^{-4} M.

The value of Z_AZ_B (5.03) calculated from the slopes of these plots agrees very well with the expected value 5. This agreement gives additional support to the postulate that the fourth step is the rate-determining one in the five-step mechanism (*vide supra*) proposed on the basis of the kinetic data obtained for the forward and reverse reactions.

Dependence of the Forward Reaction on pH

The rate of the forward reaction (eqn. (1)) was studied over the pH range 10.2–11.0 and found to increase in this pH range (Table III). Surprisingly, there is no levelling of the rate constant at this

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*log β_5 = 43.9 determined by authors spectrophotometrically at 25 ℃, I = 0.25 M ($NaClO_4$).

TABLE III. Effect of pH on the Rate of Reaction between $[FePDTA(OH)]^{2-}$ and Cyanide Ion, pH = 11.0 ± 0.02; I = 0.25 M ($NaClO_4$); Temperature = 25 ± 0.1 °C. [FePDTA-$(OH)^{2-}$] = 5×10^{-4} M; [CN^-] = 0.1 M.

pH	k_{obs} (s^{-1})
10.3	5.39×10^{-6}
10.5	2.16×10^{-5}
10.7	3.06×10^{-5}
11.0	9.29×10^{-5}
11.4	3.46×10^{-4}
11.7	1.19×10^{-3}

high pH. This increase in the rate constant in the above pH range can not be explained as solely due to the different reactivities of CN^- and HCN because cyanide exists as CN^- above pH 9. The increased rate can perhaps be accounted for by the formation of $[FePDTA(OH)_2]^{3-}$ or even $[FePDTA(OH)_3]^{4-}$. These species have smaller stability constants compared to $[FePDTA(OH)]^{2-}$ and hence are expected to react faster. It is not possible to resolve the rate constants because of the complexity of the subsequent reactions involving the conversion of $[Fe(CN)_5OH]^{3-}$ to $[Fe(CN)_6]^{3-}$ and the hydroxide-concentration-dependent reduction of latter to $[Fe(CN)_6]^{4-}$.

Temperature Dependence of the Forward and Reverse Reaction Rates

The temperature dependence of the forward and reverse rates was found to follow the Arrhenius equation over the temperature range 25–45 °C. The activation parameters for the forward and reverse reactions have been listed in Table V. These values of activation parameters are consistent with our proposed mechanim (*vide supra*).

Evidence for Other Reactions Occurring in the System

Deviations from linearity are observed in the pseudo first order plots of log C_A *vs.* time (not shown) which are negative in presence of low cyanide but positive at high cyanide concentrations. These deviations are, therefore, not due to reversibility. The chances of reversibility are very small, firstly, because the stability constant of $[Fe(CN)_5OH]^{3-}$ is very high compared to that of $[FePDTA(OH)]^{2-}$, and, secondly, because the excess cyanide present would not allow the reverse reaction to occur to any appreciable extent. It is reasonable to suppose that

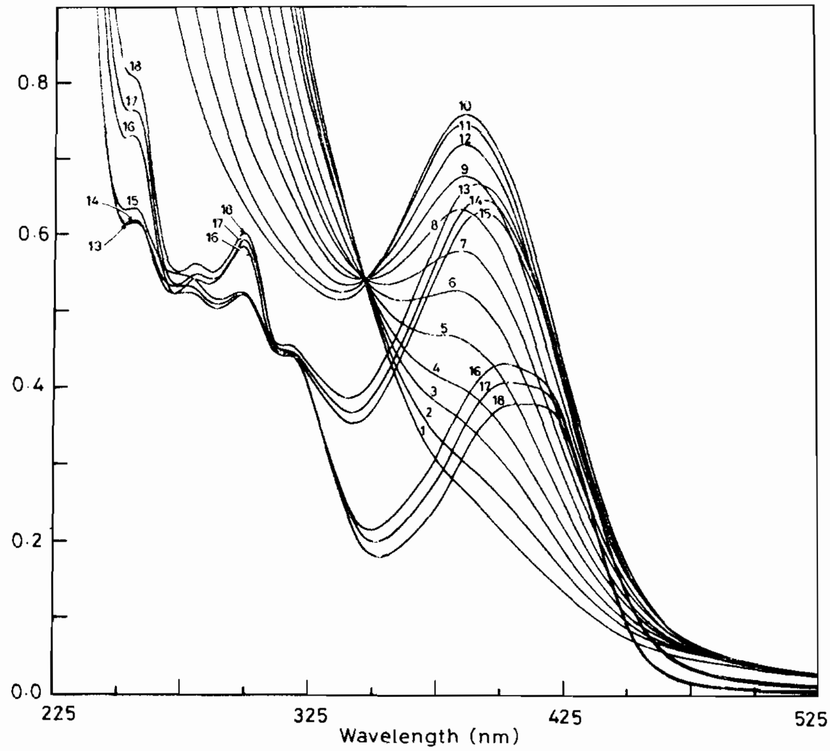

Fig. 3. Repetitive scan of the reaction mixture during a typical kinetic run: $[FePDTA(OH)^{2-}]_T = 5 \times 10^{-4}$ M, $[CN^-]_T$ = 0.1 M, pH = 11.4 ± 0.02, I = 0.25 M ($NaClO_4$), temperature = 30 ± 0.1 °C. No. (min/h): 1(5), 2(9), 3(15), 4(21), 5(30), 6(41), 7(51), 8(1.1), 9(1.3), 10(1.6), 11(2.0), 12(2.3), 13(5.5), 14(6), 15(7), 16(19), 17(22), 18(24).

the observed deviations are due to the fact that some other reactions involving cyanide are also occurring in the reaction system.

Evidence for these reactions is provided by repetitive spectral scans of the reaction mixture at suitable intervals, as shown in Fig. 3. The spectra are very revealing and contain wealth of information about all the reactions taking place in this system. There is a continuous increase in the height of the 395 nm peak, which is the λ_{max} of $[Fe(CN)_5OH]^{3-}$ at the beginning of the reaction, but as the concentration of $[Fe(CN)_5OH]^{3-}$ builds up (nearly 75% of the theoretical maximum value), the same compound reacts with excess cyanide to form $[Fe(CN)_6]^{3-}$. The lowering in the peak height of 395 nm with a shift towards 410–420 nm (λ_{max} region of $[Fe(CN)_6]^{3-}$) confirms this conclusion. This is further supported by the appearance of two new peaks in the UV region, one at 300 nm and the other at 257 nm. The heights of both peaks increase with time. These peaks are due to the formation of $[Fe(CN)_6]^{3-}$ in the second stage of reaction.

Finally, an additional peak appears at around 322 nm; it is attributed to the formation of $[Fe(CN)_6]^{4-}$ formed due to the reduction of $[Fe(CN)_6]^{3-}$ by $PDTA^{4-}$. The formation of $[Fe(CN)_6]^{4-}$ as the final product was also confirmed by two specific tests, *viz.*, the ammonium molybdate and thorium nitrate [16] tests, which were found to be positive in the latter part of reaction but not in the beginning.

An isosbestic point seen at 350 nm during the course of reaction indicates the conversion of $[FePDTA(OH)]^{2-}$ to $[Fe(CN)_5OH]^{3-}$. A second isosbestic point at around 313 nm corresponds to an equilibrium between $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$.

Reaction Between $[Fe(CN)_5OH]^{3-}$ *and* CN^-

The kinetics of the formation of $[Fe(CN)_6]^{3-}$ by the reaction of pentacyanohydroxoferrate(III) and cyanide ion at pH = 10.5, temperature = 30 °C and I = 0.25 M ($NaClO_4$) has been independently studied spectrophotometrically at 395 nm. This reaction exhibits first order dependence in $[Fe(CN)_5OH]^{3-}$ as well as in cyanide, but shows second order dependence overall. The calculated rate constants for this stage of the reaction are given in Table IV. The activation parameters for this reaction have been calculated and are listed in Table V.

TABLE IV. Cyanide Dependence of Observed Pseudo First Order Rate Constants for the Reaction of CN^- with $[Fe(CN)_5(OH)]^{3-}$, pH = 10.5 ± 0.02; I = 0.25 M ($NaClO_4$); temperature = 25 ± 0.1 °C $[Fe(CN)_5(OH)^{3-}]$ = 1 × 10^{-4} M.

$10^2 \times [CN^-]_T$ (M)	k_{obs} (s^{-1})	k_2[a] (M^{-1} s^{-1})
2.0	6.64×10^{-5}	3.32×10^{-3}
3.5	1.36×10^{-4}	3.88×10^{-3}
4.0	1.53×10^{-4}	3.82×10^{-3}
5.0	1.79×10^{-4}	3.58×10^{-3}
8.0	2.83×10^{-4}	3.53×10^{-3}

[a] Average = 3.62×10^{-3} M^{-1} s^{-1}.

The mechanism of oxidation of some aminocarboxylates, *viz.*, EDTA, HEDTA and NTA, by $[Fe(CN)_6]^{3-}$ has been reported by earlier workers [17]. The oxidation of DTPA was investigated by us [18]. All these oxidations were found to follow the same mechanism. The oxidation of PDTA should also fall in line and has, therefore, not been pursued. $[Fe(CN)_6]^{4-}$ is one of the products of these reactions. The aminocarboxylates give carbon dioxide, glycollic acid and low molecular weight aminocarboxylates as possible products.

Discussion

A combination of the forward and reverse rate studies for the reaction of $[FePDTA(OH)]^{2-}$ with cyanide ion in alkaline medium leads us to suggest a mechanism presented in eqns. (11)–(15) in further confirmation of the mechanism proposed by us earlier [2, 3].

$$[FeL(OH)]^{2-n} + CN^- \underset{(fast)}{\overset{K_1}{\rightleftharpoons}} [FeL(OH)(CN)]^{1-n} \qquad (11)$$

TABLE V. Activation Parameters

Forward reactions	Reverse reaction
(i) $[FePDTA(OH)]^{2-} + 5CN^- \rightarrow [Fe(CN)_5(OH)]^{3-} + PDTA^{4-}$ (E_a = 37.4 kJ, $\Delta H^{\neq}$ = 34.90 kJ, $\Delta S^{\neq}$ = −44.3 e.u., p_z = 1.19×10^3 cm^{-1})	(iii) $[Fe(CN)_5(OH)]^{3-} + PDTA^{4-} \rightarrow [FePDTA(OH)]^{2-} + 5CN^-$ (E_a = 74.9 kJ, $\Delta H^{\neq}$ = 72.4 kJ, $\Delta S^{\neq}$ = −37.2 e.u., p_z = 4.30×10^4 cm^{-1})
(ii) $[Fe(CN)_5(OH)]^{3-} + CN^- \rightarrow [Fe(CN)_6]^{3-} + OH^-$ (E_a = 39.0 kJ, $\Delta H^{\neq}$ = 36.6 kJ $\Delta S^{\neq}$ = −40.4 e.u. and p_z = 8.6×10^3 cm^{-1})	

TABLE VI. Rate Constants for Various Stages of Reactions

Reactions	Experimental conditions
1. $[\mathrm{FePDTA(OH)}]^{2-} + \mathrm{CN}^-$ $k_4 = 9.0 \times 10^{-4}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ $k_4K_3 = 3.14 \times 10^{-2}\ \mathrm{M}^{-2}\ \mathrm{s}^{-1}$	As in Table I
2. $[\mathrm{Fe(CN)_5(OH)}]^{3-} + \mathrm{PDTA}^{4-}$ $k_r = K_5^{-1}k_4 = 8.57 \times 10^{-9}\ \mathrm{s}^{-1}$	As in Table II
3. $[\mathrm{Fe(CN)_5(OH)}]^{3-} + \mathrm{CN}^-$	$[\mathrm{Fe(CN)_5OH^{3-}}] = 10^{-4}$ M $[\mathrm{CN}^-] = (2.0\text{–}10.0) \times 10^{-2}$ M
$k_2 = 3.62 \times 10^{-3}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$	pH = 10.5, $I = 0.25$ M, temperature = 30 ∓ 0.1 °C

$$[\mathrm{FeL(OH)(CN)}]^{1-n} + \mathrm{CN}^- \overset{K_2}{\rightleftharpoons} [\mathrm{FeL(OH)(CN)_2}]^{n-} \quad \text{(fast)} \qquad (12)$$

$$[\mathrm{FeL(OH)(CN)_2}]^{n-} + \mathrm{CN}^- \overset{K_3}{\rightleftharpoons} [\mathrm{FeL(OH)(CN)_3}]^{(n+1)-} \quad \text{(fast)} \qquad (13)$$

$$[\mathrm{FeL(OH)(CN)_3}]^{(n+1)-} + \mathrm{CN}^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} [\mathrm{FeL(OH)(CN)_4}]^{(n+2)-} \quad \text{(r.d.s.)} \qquad (14)$$

$$[\mathrm{FeL(OH)(CN)_4}]^{(n+2)-} + \mathrm{CN}^- \overset{K_5}{\rightleftharpoons} [\mathrm{Fe(CN)_5OH}]^{3-} + \mathrm{L}^{n-} \quad \text{(fast)} \qquad (15)$$

where L ≡ PDTA^{4-} and n = charge on PDTA = 4. The forward reaction proceeds through the rapid pre-equilibrium addition of three cyanides prior to the rate-determining step, which occurs when the fourth cyanide ion adds to the complex.

Our results on the forward and reverse rate study show that the fifth step is a fast one compared to fourth one. The application of the steady state approximation to $[\mathrm{FeL(OH)(CN)_4}]^{(n+2)-}$ in the postulated mechanism gives the following rate equation for the reverse reaction, which has also been confirmed experimentally.

$$\text{Rate} = \frac{k_r[\mathrm{Fe(CN)_5OH^{3-}}]\,[\mathrm{PDTA^{4-}}]}{[\mathrm{CN}^-]} \qquad (16)$$

where $k_r = k_{-4}/K_5^{-1}$ and $K_5^{-1} = k_{-5}/k_5$

The variable order dependence in cyanide concentration for the forward reaction, which varies from one to two, combined with the observation on the reverse reaction leads to the proposition that the first two steps are quite fast and that stable 1:1:1 and 1:1:2 intermediates, *viz.*, $[\mathrm{FeL(OH)(CN)}]^{1-n}$ and $[\mathrm{FeL(OH)(CN)_2}]^{n-}$, form immediately following the mixing of the reactants. At the low cyanide concentrations where these steps could have been observed, the rate is too slow to be observed experimentally. Though there is no direct evidence for the formation of 1:1:1 and 1:1:2 complexes in the present reaction system, similar types of mixed cyano complexes have been envisaged for the reactions of cyanide ion with Co(II) CYDTA [4, 5], Mn(III) CYDTA [6], Ni(II)DTPA, Ni(II)TMDTA and Ni(II)TTHA complexes [7, 8] investigated earlier.

In this work we could observe only first and second order dependences in cyanide, though in our earlier study [2, 3] an order starting from one at very high cyanide concentration to three at low cyanide ion concentration was observed. One reason for missing the third and fourth order in the present system may be the structural differences of the $[\mathrm{FePDTA(OH)}]^{2-}$ complex in comparison to other aminocarboxylato(hydroxo) complexes. These structures have not been reported so far, except for $[\mathrm{FeEDTA(OH)}]^{2-}$ [19] and $[\mathrm{FeCyDTA(OH)}]^{2-}$ [20].

As the concentration of cyanide increases from low to high, the reactant becomes $[\mathrm{FeL(OH)(CN)_2}]^{n-}$ and $[\mathrm{FeL(OH)(CN)_3}]^{(n+1)-}$, which accounts for the observed second and first order in cyanide. As stated above, lower orders in cyanide could not be observed because the reaction becomes too slow to be followed experimentally.

We have shown that a linear free energy relationship (LFER) exists between the step rate constants and the respective stability constants of the particular intermediates reacting in the step. Thus, it has been established that for three FeL(OH) complexes where L = EDTA, HEDTA and DTPA:

$$\log(k_4) = \log(k_r\beta_5) - \log\beta_{113} \qquad (16)$$

$$\log(k_4\mathrm{K}_3) = \log(k_r\beta_5) - \log\beta_{112} \qquad (17)$$

$$\log(k_4K_3K_2) = \log(k_r\beta_5) - \log\beta_{111} \qquad (18)$$

$$\log(k_4K_3K_2K_1) = \log(k_r\beta_5) - \log\beta_{110} \quad (\text{or} \log K_{\mathrm{FeL(OH)}}) \qquad (19)$$

The relationship does not hold true in case of FePDTA(OH). Such behaviour is not unusual with PDTA and has also been reported in NiL–CN^- reaction systems [21]. This deviation is attributed to the steric requirements of methyl group and its effect on the course of the reaction mechanism. A low $\Delta S^{\neq}$ for the forward reaction and high $\Delta S^{\neq}$ for the reverse reaction point to an associative mechanism rather than a dissociative one. These observations are consistent with the rate-determining step (eqn. (14)) proposed in the five-step mechanistic scheme.

Finally, it has been demonstrated that $[Fe(CN)_5OH]^{3-}$ is not a final product of the reaction of $[FePDTA(OH)]^{2-}$ with cyanide. A repetitive scan of the reaction mixture (Fig. 3) shows that two more reactions are occurring in the reaction system. Thus the overall reaction of $[FePDTA(OH)]^{2-}$ in presence of a sufficiently large excess of cyanide ion is made up of three distinguishable stages:

(i) Formation of $[Fe(CN)_5OH]^{3-}$ from $[FePDTA(OH)]^{2-}$

(ii) Conversion of $[Fe(CN)_5OH]^{3-}$ to $[Fe(CN)_6]^{3-}$

(iii) Reduction of $[Fe(CN)_6]^{3-}$ to $[Fe(CN)_6]^{4-}$ due to reaction with $PDTA^{4-}$ released in stage (i).

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