

Kinetic and Mechanism of Oxidation of Ethylenediamine-tetraacetic Acid by Alkaline Hexacyanoferrate(III)

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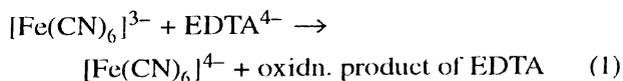
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The kinetics of oxidation of ethylenediaminetetraacetic acid (EDTA) by hexacyanoferrate(III) have been studied spectrophotometrically ($\lambda = 420$ nm) at pH = 11.0, $I = 0.5$ mol dm⁻³ (NaClO₄) and temperature 45°. The examination of rate data shows that the rate law is $d[\text{Fe}(\text{CN})_6]^{3-}/dt = k_f [\text{Fe}(\text{CN})_6]^{3-} [\text{EDTA}^{4-}]$ with a second order rate constant $k_f = 4.5 \times 10^{-2}$ dm³ mol⁻¹ s⁻¹. The rate of reaction has been followed as a function of pH in the range 7.5–12.0. The rate is found to increase. The reactive species of EDTA are H₂L²⁻, HL³⁻ and L⁴⁻. The resolved rate constants due to the reaction of [Fe(CN)₆]³⁻ with EDTA⁴⁻, HEDTA³⁻ and H₂EDTA²⁻ are calculated. The effect of ionic strength is found to be positive. The activation parameters are also calculated from Arrhenius plots. An electron transfer mechanism is suggested for the reaction.

Potassium ferricyanide is a potential oxidising agent and there are a large number of reports on the oxidation of a variety of organic and inorganic compounds by it¹. In the recent past, the kinetics and mechanism of ligand exchange reaction between polyamino-carboxylatoferrate(III) with cyanide ion has been investigated extensively². It was observed that the above reactions involved three observable stages in general. The first stage of the reaction is the stepwise addition of cyanide ion to the complex and finally the coordinated amino carboxylate is unwrapped from the coordination sphere of the metal ion. The second stage of the reaction involves the reaction of excess cyanide ion with [Fe(CN)₅OH]³⁻ formed in the first stage of reaction forming [Fe(CN)₆]³⁻. The third and the last stage of reaction involves the oxidation of aminocarboxylate released in the first stage of reaction by the [Fe(CN)₆]³⁻ formed in the second stage of the reaction. The third stage of reaction could not be studied in detail due to complications in the reaction system. In most of the kinetic studies available in literature, rarely any attention has been paid to resolve the rate constants due to various protonated and unprotonated forms of the oxidant. Thus this has enhanced our interest to make an independent kinetic study of the third stage of reaction (Eqn.1) in detail to understand the

reactivities of various protonated and unprotonated forms of EDTA with [Fe(CN)₆]³⁻ over the entire pH region of reaction (Eq. 1),



Results and Discussion

The reaction between [Fe(CN)₆]³⁻ and EDTA⁴⁻ exhibits first order dependence each in [Fe(CN)₆]³⁻ and [EDTA⁴⁻] over a wide range of EDTA⁴⁻ concentration. The pseudo-first order rate constant (k_{obs}) and second order rate constant (k_f) for the reaction system are listed in Table 1. The dependence of k_{obs} on [EDTA⁴⁻] follows straight line at three temperatures and passes through the origin (Fig.1). This indicates that the reaction is first order with respect to [EDTA⁴⁻]. Thus variation in the oxidation rate constants are consistent with the interaction of [EDTA]⁴⁻ with [Fe(CN)₆]³⁻ in the rate-determining step. In the reaction of [Fe(CN)₆]³⁻ with [EDTA]⁴⁻, [Fe(CN)₆]³⁻ is reduced to [Fe(CN)₆]⁴⁻ followed by oxidation of [EDTA]⁴⁻. The oxidation products are identified to be iminodiacetic acid, glycollic acid.

The hexacyanoferrate(II) is added externally in the concentration range 6×10^{-4} to 7×10^{-3} mol dm⁻³ in

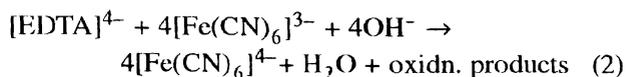
TABLE 1—DEPENDENCE OF PSEUDO-FIRST ORDER RATE CONSTANTS (k_{obs}) ON THE CONCENTRATION OF EDTA AT DIFFERENT TEMPERATURES

$[\text{Fe}(\text{CN})_6^{3-}] = 5 \times 10^{-4} \text{ M}$, $\text{pH} = 11 \pm 0.2$, $I = 0.5 \text{ mol dm}^{-3}$ (NaClO_4)

$10^2 [\text{EDTA}^{4-}]_{\text{T}}$	$10^4 k_{\text{obs}}$			$10^2 k_f = k_{\text{obs}} / [\text{EDTA}]_{\text{T}}$		
	25°	35°	45°	25°	35°	45°
1.0	1.41	2.40	5.31	1.41	2.40	5.31
1.5	1.83	3.54	7.19	1.22	2.36	4.79
2.0	2.21	4.52	8.37	1.11	2.26	4.19
2.5	2.42	5.48	10.47	1.00	2.19	4.19
3.0	3.29	6.52	13.43	1.10	2.17	4.48
	Average $k_f \times 10^2 =$			1.17	2.28	4.59
				± 0.16	± 0.10	± 0.47

the reaction mixture in the beginning. It does not retard the rate of reaction, indicating the reaction to be essentially irreversible. The addition of cyanide ion in the concentration range 3×10^{-2} to $8 \times 10^{-2} \text{ mol dm}^{-3}$ also does not affect the rate of reaction to any noticeable extent. This observation rules out the possibility of prior dissociation of $[\text{Fe}(\text{CN})_6]^{3-}$. The reaction

stoichiometry is verified titrimetrically and is given by equation (2),



Effect of ionic strength on reaction : The effect of ionic strength on the rate of reaction was also studied. The product of the charges ($Z_A Z_B$) on the reacting species in the rate-determining step was obtained from the slope of Bjerrum's plot of $\log(k_f)$ vs $\sqrt{I} / (1 + \sqrt{I})$. Interestingly, the values of $Z_A Z_B (= 5.50)$ is much smaller than the expected value when the only reactants were $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{EDTA}]^{4-}$. This result is not entirely unexpected because $[\text{EDTA}]$ and other polyaminocarboxylates are known to form complexes with alkali metals of moderate stabilities³. In the present reaction, three K^+ ions are released from dissociation of $\text{K}_3[\text{Fe}(\text{CN})_6]$ and a large excess of Na^+ ions is present due to the addition of NaClO_4 for maintaining ionic strength. Thus a significant concentration of EDTA is complexed with either Na^+ or K^+ and hence smaller effective value of $Z_A Z_B$ than expected. A second factor which also appears to affect the value of $Z_A Z_B$ is the possible ion-pair formation between $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{EDTA}]^{4-}$ with cations present in sufficiently large concentration in the reaction medium.

Dependence of rate on pH and resolution of rate constants : The reaction between $[\text{Fe}(\text{CN})_6]^{3-}$ and EDTA^{4-} was studied in the pH range 7.5–12.0 at 45° and $I = 0.5 \text{ M}$ (NaClO_4). The species distribution of EDTA at various pH values was computed on a computer using a programme developed by Perrin and Sayce⁴. It is seen that the predominant species of EDTA in the above pH range are H_2L^{2-} , HL^{3-} and L^{4-} . The species H_2L^{2-} , HL^{3-} and L^{4-} exist in varying proportions depending upon pH of the solution. The plot of second order rate constant (k_f) with pH is revealed that the rate of reaction increases linearly with increase in pH in the region 7.5–10.0 and levels off beyond pH 10.0. The following rate law (Eqn. 3) which fits into the above pH-dependence is given as

$$\text{Rate} = k_f [\text{Fe}(\text{CN})_6^{3-}] [\text{L}]_{\text{T}} \quad (3)$$

The term $[\text{L}]_{\text{T}}$ includes all the protonated and

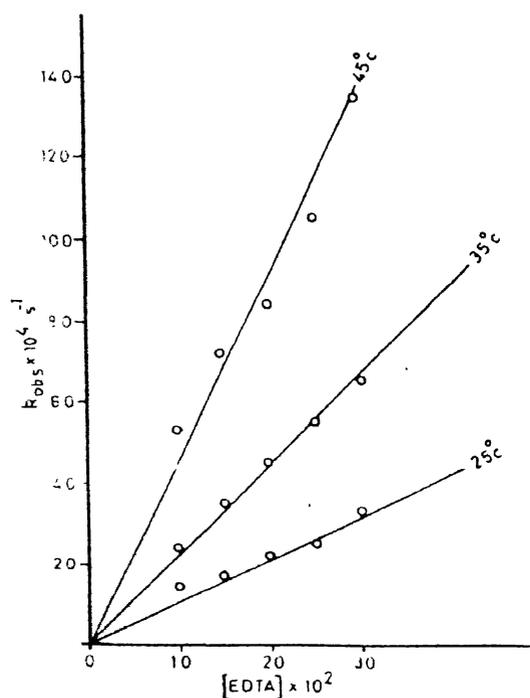


Fig. 1. Dependence of pseudo-first order rate constants on $[\text{EDTA}^{4-}]$ [Reaction conditions as in Table 1].

unprotonated species of EDTA in the whole pH region. $[\text{Fe}(\text{CN})_6]^{3-}$ is not protonated in the above pH region. The rate of oxidation of EDTA by $[\text{Fe}(\text{CN})_6]^{3-}$ is not due to single species of EDTA. Thus the equation (3) can be expressed by equation (4),

$$\begin{aligned} \text{Rate} &= [\text{Fe}(\text{CN})_6]^{3-} \left\{ k_1 [\text{L}^{4-}] + k_2 [\text{HL}^{3-}] + k_3 [\text{H}_2\text{L}^{2-}] \right\} \\ &= [\text{Fe}(\text{CN})_6]^{3-} \left\{ k_1 [\text{L}^{4-}] + k_2 K_1 [\text{H}^+] [\text{L}^{4-}] + k_3 K_2 K_1 [\text{H}^+]^2 [\text{L}^{4-}] \right\} \\ &= [\text{Fe}(\text{CN})_6]^{3-} [\text{L}^{4-}] \left\{ k_1 + k_2 K_1 [\text{H}^+] + k_3 K_1 K_2 [\text{H}^+]^2 \right\} \end{aligned} \quad (4)$$

where k_1 , k_2 and k_3 are the rate constants for the reaction of $[\text{Fe}(\text{CN})_6]^{3-}$ with L^{4-} , HL^{3-} and H_2L^{2-} respectively, and K_1 and K_2 are the respective protonation constants of EDTA. On comparing equations (3) and (4) one gets

$$k_1 \frac{[\text{L}]_1}{[\text{L}^{4-}]} = k_1 + k_2 K_1 [\text{H}^+] + k_3 K_1 K_2 [\text{H}^+]^2 \quad (5)$$

$$\text{where, } \frac{[\text{L}]_1}{[\text{L}^{4-}]} = 1 + K_1 [\text{H}^+] + K_1 K_2 [\text{H}^+]^2$$

At $\text{pH} > 10$, the term $[\text{H}^+]^2$ can be omitted and equation (5) is simplified to equation (6),

$$k_1 \{1 + K_1 [\text{H}^+]\} = k_1 + k_2 K_1 [\text{H}^+] \quad (6)$$

The plot of left-hand-side of equation (6) vs $[\text{H}^+]$ was a straight line, the slope of the line giving the value of rate constant k_2 for the reaction of $[\text{Fe}(\text{CN})_6]^{3-}$ with $[\text{HEDTA}]^{3-}$ equal to $3.1 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The intercept of the plot gives the rate constant k_1 for the reaction of $[\text{Fe}(\text{CN})_6]^{3-}$ with $[\text{EDTA}]^{4-}$ equal to $4.5 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. On rearranging equation (5) and taking logarithm, one gets

$$\begin{aligned} \log \frac{k_1}{[\text{H}^+]} \left\{ 1 + K_1 [\text{H}^+] + K_1 K_2 [\text{H}^+]^2 - k_1 - k_2 K_1 [\text{H}^+] \right\} \\ = \log(k_3 K_1 K_2) + \log [\text{H}^+] \end{aligned} \quad (7)$$

A plot of left-hand-side of equation (7) vs $\log [\text{H}^+]$

was found to be linear and the intercept gives the value of k_3 equal to $5.24 \times 10^{-17} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This is in agreement with the experimental observation that the rate of reaction is extremely slow below $\text{pH} 7.5$.

Effect of temperature on rate of reaction : The rate of reaction between $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{EDTA}]^{4-}$ determined in the temperature range $25\text{--}45^\circ$, follows Arrhenius equation. The activation parameters for the reaction of $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{EDTA}]^{4-}$ were calculated using the above plots and found to be $\Delta H^\ddagger = 48.78 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = 265.85 \text{ JK}^{-1} \text{ mol}^{-1}$.

Spectral studies of reaction : A repetitive scan of the present system was recorded (Fig. 2). It is seen that the peak heights at $\lambda = 420, 325$ and 303 nm decrease continuously with time. This is due to consumption of $[\text{Fe}(\text{CN})_6]^{3-}$ with time. $[\text{Fe}(\text{CN})_6]^{4-}$ is also known to have weak absorption band at 325 nm but it

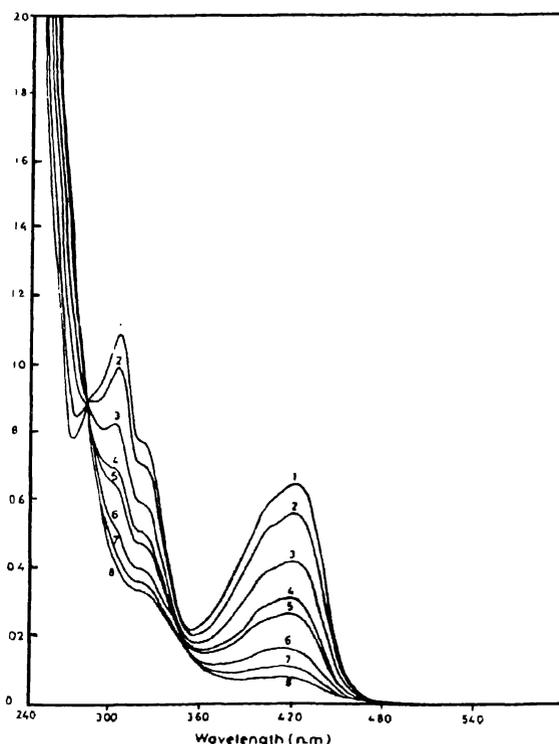


Fig. 2. Repetitive spectral scan of the reaction mixture during a typical kinetic run; $[\text{Fe}(\text{CN})_6]^{3-} = 5 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{EDTA}^{4-}] = 2 \times 10^{-2} \text{ mol dm}^{-3}$, $\text{pH} = 11.0$, $I = 0.5 \text{ mol dm}^{-3}$ (NaClO_4), $\text{temp.} = 26 \pm 0.1^\circ$; Curves 1–8 were recorded after time intervals of 1, 5, 10, 20, 25, 40, 55 and 70 min respectively

is not observed in this scan because being buried in the shoulder of $[\text{Fe}(\text{CN})_6]^{3-}$ at 325 nm. An isosbestic point is observed at 280 nm which suggests the coexistence of $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{4-}$ together. The peaks of oxidation products of EDTA are in the uv-region where EDTA has strong absorption and are therefore not possible to identify. No new peak is observed in the scan because no reaction intermediate is possibly present in a noticeable concentration. Two specific tests for $[\text{Fe}(\text{CN})_6]^{4-}$, with ammonium molybdate and with thorium nitrate, were found to be positive and thus confirming the formation of $[\text{Fe}(\text{CN})_6]^{4-}$ as one of the reaction products⁵.

The results suggest for an outersphere electron transfer mechanism from hexacyanoferrate(III) to the EDTA in a bimolecular step. The highly negative value of entropy of activation suggests for a highly charged activated complex in the bimolecular process.

Experimental

The disodium salt of ethylenediaminetetraacetic acid (Sigma), potassium hexacyanoferrate(III) (A.R., Sarabhai M.) and sodium cyanide (May Baker) were used as such. Sodium perchlorate (A.R., B.D.H.) was used to maintain the ionic strength. Sodium hydroxide or perchloric acid was used to maintain pH at any desired value. Standard buffers (B.D.H.) were used to standardise pH meter. Sodium cyanide was standardised argentometrically⁶. The other chemicals used were of guaranteed reagent grade. Double-distilled water was used throughout.

A Spectronic-20 spectrophotometer (Milton Roy, U.S.A.) fitted with a circulatory arrangement for thermostating the cell compartment was used for monitoring the progress of reaction. The temperature of reagents was maintained ($\pm 0.1^\circ$) at a desired tempera-

ture using a self-designed thermostat. Electronic spectra were recorded on a Shimadzu UV-240 spectrophotometer. pH measurements were made on a Toshniwal CL-46 pH meter.

Kinetics of reaction between EDTA^{4-} and $[\text{Fe}(\text{CN})_6]^{3-}$ were studied under pseudo-first order conditions using large excess of $[\text{EDTA}^{4-}]$. The reaction was monitored spectrophotometrically at 420 nm. (λ_{max} of $[\text{Fe}(\text{CN})_6]^{3-}$, $\epsilon = 1020 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) at pH = 11.0, $I = 0.5 \text{ M}$ (NaClO_4) and temperatures 25, 35 and 45°. The solutions of hexacyanoferrate(III) and EDTA^{4-} were pre-equilibrated at the required temperature for at least 30 min before mixing. The pH and ionic strength of each solution were adjusted each time before equilibrating the reactants. The pseudo-first order rate constants (k_{obs}) were calculated from the slopes of $\log(A)$ vs time plots, where (A) refers to the absorbance of the remaining hexacyanoferrate(III) at any time (t) at 420 nm. The reaction was monitored for at least three half-lives.

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