



KINETIC INVESTIGATION OF THE REDOX REACTION BETWEEN TRIS (1, 10-ORTHOPHENANTHROLINE) IRON(III) AND ETHYLENEDIAMMINETETRAACETATEIRON(II)

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(Received April 15, 2003 and accepted in revised form November 4, 2003)

The kinetics of the reduction of tris(1,10-orthophenanthroline)iron(III) ion by ethylenediamminetetraacetateiron(II) ion has been investigated spectrophotometrically. The redox reaction was carried out under the pseudo-first order conditions. The rate of electron transfer between ethylenediamminetetraacetateiron(II) ion and tris(1,10-orthophenanthroline)iron(III) ion was measured at different pH values. Pseudo-first order kinetics was observed with respect to each reductant and oxidant and an inverse fractional order in $[H^+]$. Rate law and redox mechanism have been deduced. The values of specific rate constant, k_1 , and equilibrium constant, K , between protonated and deprotonated forms of ethylenediamminetetraacetateiron(II) ion were calculated and found to be $230.31 \pm 4.45 M^{-1}s^{-1}$ and $219.72 \pm 3.45 M^{-1}$ respectively. Different thermodynamic functions like ΔG° , ΔG^\ddagger , ΔS^\ddagger , ΔH^\ddagger and E_a have also been computed.

Keywords: Electrochemistry/ Redox chemistry, Chemical kinetics, Reaction mechanism / Outer space complex, Thermodynamics

1. Introduction

Investigations pertaining to electron exchange reactions and their kinetics have been reported [1-4]. Complexes with mixed oxygen and nitrogen donor ligands such as ethylenediammine-tetraacetic acid, EDTA, are well known. It has been observed that hydrogen ion dependent terms are common feature of the rate equations of most of the metal / metal carboxylate ion exchange reactions. Day and Siddall interpreted that the protonation of the free carboxylate arms like EDTA is responsible for the blocking of ring formation in the complex. This will facilitate the removal of the ligand from the metal ion [5-7]. Newton [8] explained the mechanism of the exchange of Y^{3+} in the redox couple of $Y^{3+}/YDCTA^-$, trans-1, 2-Diaminocyclohexane-N, N, N', N'- tetraacetic acid monohydrate (DCTA) involving co-ordinated water molecule. The exchange of polyaminocarboxylic acid ligands between two metal ions is highly dependent upon the solution conditions. Metal ion attack, spontaneous dissociation, metal ion catalysis and coordinated anion effect are the factors that influence the rate of exchange of polyaminocarboxylic ligands [9]. Naqvi and Farrukh [10] have studied the kinetics of the reduction of Ferric-1,10-phenanthroline with uranium(IV) EDTA. Numerous kinetic studies related to electron

exchange reactions have been made on +2 and +3 states of iron [11-15]. An interesting feature of co-ordination chemistry of Fe^{III} is a marked preference for O-donor as opposed to N-donor ligands. Amines of Fe^{III} are unstable and dissociate in water. Some chelating ligands such as bipyridine and phenanthroline when attack metal or metal ion, cause high crystal field splitting and this provide sufficient energy to pair the metal electrons in lower energy levels. This phenomenon is known as spin-pairing. Induction of this spin-pairing produces more stable complexes. However, these Fe^{III} complexes are less stable than their corresponding Fe^{II} complexes. Thus deep-red aqueous solutions of $[Fe(o-phen)_3]^{2+}$ is indefinitely stable while deep-blue solution of $[Fe(o-phen)_3]^{3+}$ slowly turns khaki coloured as polymeric hydroxo specie is formed. Generally, iron(III) is stabilized by negatively charged ligands such as anion of EDTA whereas complexation with iron(II) is favoured by neutral ligand e.g. bipyridine and phenanthroline, which permit some delocalisation in π -orbitals. These form stronger complexes with iron(II). This is because iron(III) carries an additional positive charge compared to iron(II), so its correspondingly greater ability to polarize the co-ordinated ligands produces intense, charge transfer absorption at much lower energies than iron(II). Consequently

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iron(III) complexes generally have lower molar absorption coefficient than iron(II) complexes [16]. Most of the redox reactions that have both reacting specie in their complex forms either may be inert or even one of them is labile e.g. $[\text{Fe}(\text{EDTA})]^{2-}$ and $[\text{Fe}(\text{o-phen})_3]^{3+}$, proceed through outer sphere complex mechanism because both of them are inert. During this electron transfer reaction the coordination shells of the two reactants remain as unaltered and no bond breaking or bond formation occurs.

This paper narrates the kinetic study of electron transfer reaction between $[\text{Fe}(\text{EDTA})]^{2-}$ and $[\text{Fe}(\text{o-phen})_3]^{3+}$. Results have been concluded by comparing the data from two independent kinetic measurement methods. The mechanism is being proposed through formulating the role of hydrogen ion concentration in the progress of the reaction. Rate law has been derived and activation parameters are computed.

2. Experimental

All the solutions were prepared in the same manner as described earlier [17].

2.1. Kinetic measurements

To measure the kinetics of the reduction of iron(III) complex of orthophenanthroline with iron(II) complex of ethylenediaminetetraacetate, kinetic runs were made in 1-cm quartz cell having a 3 ml volume of the reaction mixture. Measurements were carried out under the pseudo-first order conditions with $[\text{reductant}] \gg [\text{oxidant}]$ (2 – 20 times). For integration method, the progress of the reaction was monitored by observing the absorbance, A_t , as a function of time at a wavelength of 510 nm. Straight-line graphs pertaining to the equation of pseudo-first order reaction, $\ln(a-x) = -kt + \ln a$, were plotted by replacing the concentration terms to the absorbance terms i.e. $\ln(A_\infty - A_t) = -kt + \ln A_\infty$ (Figures 1 and 2). Where A_∞ stands for the absorbance at infinite time and it was recorded when no further change in the absorbance could be monitored. For initial rate method, initial rate was calculated from the slope by drawing the tangent on absorbance-time curve at $t=0$ on kinetic mode of spectrophotometer. Initial rates are then plotted versus first power of concentration of both reacting specie (Figures 3 and 4). Another graph was plotted between initial rate and product of concentration of two reactants to prove an overall second order reaction.

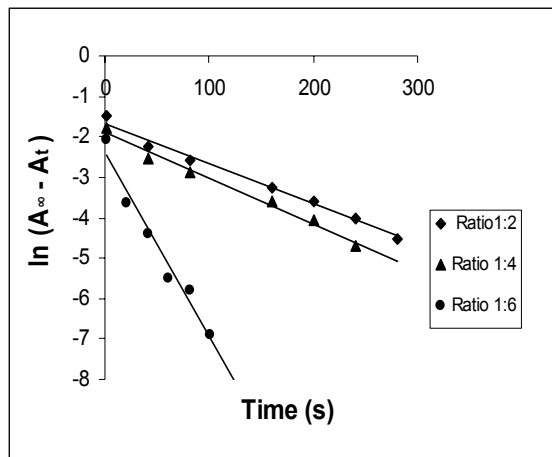


Figure 1. Plot of $\ln(A_\infty - A_t)$ vs. time at constant $[\text{Fe}(\text{o-phen})_3]^{3+}$ and varying $[\text{Fe}(\text{EDTA})]^{2-}$.

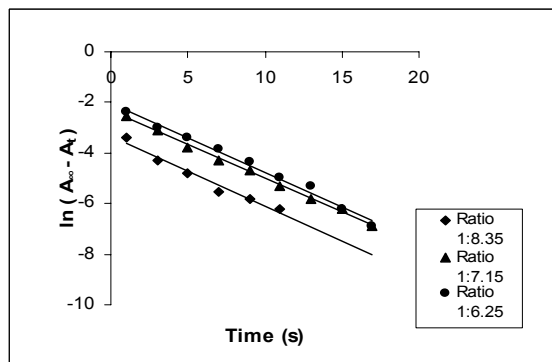


Figure 2. Plot of $\ln(A_\infty - A_t)$ vs. time at constant $[\text{Fe}(\text{EDTA})]^{2-}$ and varying $[\text{Fe}(\text{o-phen})_3]^{3+}$.

2.2. Instrumentation

Kinetic measurements were carried out on Shimadzu UV-160A, UV-visible spectrophotometer, using quartz cells. pH measurements were carried out on digital HANNA pH meter (HI - 8314 model). Temperature controlled runs were carried out by Thermostat (HAAKE KT 33).

3. Results and Discussion

Initial rate and integration methods were used to study the kinetics between tris (1,10-orthophenanthroline)iron(III) ion and ethylenediaminetetraacetateiron(II) ion.

3.1. Integration method

In this method, differential equation of rate law is integrated to observe the dependence of concentration of specie as a function of time. Integrated equation for first order reaction is given as

$$\ln(a-x) = -kt + \ln a \quad (1)$$

$$\text{where } \ln(a-x) = \ln(A_\infty - A_t)$$

$$\text{and } \ln a = \ln A_0$$

equation (1) becomes

$$\ln(A_\infty - A_t) = -kt + \ln A_0$$

3.1.1. Effect of $[\text{Fe}(\text{EDTA})]^{2-}$ on the pseudo-first order rate constant (k_{obs})

The data were recorded using integration method as shown in Table 1 by plotting $\ln(A_\infty - A_t)$

versus time at constant tris(1,10-orthophenanthroline)iron(III) ion. These first order plots were found to be linear for different molar ratios (2 – 20 times) of tris (1,10-orthophenanthroline)iron(III) ion to ethylenediaminetetraacetateiron (II) ion indicating first order dependence on $[\text{Fe}(\text{EDTA})]^{2-}$ as displayed in Fig 1. Values of pseudo-first order rate constant, k_{obs} , were evaluated from the slopes of plots.

3.1.2. Effect of $[\text{Fe}(\text{o-phen})_3]^{3+}$ on the pseudo-first order rate constant (k_{obs})

At constant ethylenediaminetetraacetateiron (II) ion and varying tris(1,10-orthophenanthroline)

Table 1. Kinetic rate data for the reduction of $[\text{Fe}(\text{o-phen})_3]^{3+}$ by $[\text{Fe}(\text{EDTA})]^{2-}$. At constant oxidant and varying reductant concentration using integration method.

$\lambda_{\text{max}} = 510 \text{ nm}$, $\epsilon = 11000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, $\text{pH} = 3.5$, $\text{Temperature} = 30^\circ\text{C}$

Molar Ratio	Time (s)	$[\text{Fe}(\text{EDTA})]^{2-}_0$ $\times 10^3 \text{ (M)}$	$[\text{Fe}(\text{o-phen})_3]^{3+}_0$ $\times 10^4 \text{ (M)}$	$\ln(A_\infty - A_t)$	$k_{\text{obs}} \text{ (s}^{-1}\text{)}$
2:1	1	0.33	1.67	-1.500	0.011 ± 0.00047
	41			-2.253	
	81			-2.590	
	121			-2.918	
	161			-3.244	
	201			-3.611	
	241			-4.017	
	281			-4.509	
	321			-5.809	
	361			-6.907	
4:1	1	0.67	1.67	-1.789	0.0142 ± 0.00060
	41			-2.538	
	81			-2.864	
	121			-3.218	
	161			-3.611	
	201			-4.074	
	241			-4.710	
	281			-5.521	
	321			-6.907	
	6:1			1	
21		-3.649			
41		-4.422			
61		-5.115			
81		-5.809			
101		-6.907			

Table 2. Kinetic rate data for the reduction of $[\text{Fe}(\text{o-phen})_3]^{3+}$ by $[\text{Fe}(\text{EDTA})]^{2-}$. At constant reductant and varying oxidant concentration using integration method. $\lambda_{\text{max}} = 510 \text{ nm}$, $\epsilon = 11000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, $\text{pH} = 3.5$, Temperature = 30°C

Molar Ratio	Time (s)	$[\text{Fe}(\text{EDTA})]^{2-}_0$ $\times 10^3 \text{ (M)}$	$[\text{Fe}(\text{o-phen})_3]^{3+}_0$ $\times 10^4 \text{ (M)}$	$\ln(A_\infty - A_t)$	k_{obs} (s^{-1})
8.35:1	1	1.67	2.00	-3.411	0.276 ± 0.00335
	3			-4.268	
	5			-4.828	
	7			-5.521	
	9			-5.809	
	11			-6.214	
7.16:1	1	1.67	2.33	-2.563	0.330 ± 0.00250
	3			-3.123	
	5			-3.772	
	7			-4.268	
	9			-4.710	
	11			-5.298	
	13			-5.809	
	15			-6.214	
	17			-6.907	
6.25:1	1	1.67	2.67	-2.375	0.362 ± 0.00224
	3			-2.975	
	5			-3.411	
	7			-3.863	
	9			-4.342	
	11			-4.961	
	13			-5.298	
	15			-6.214	
	17			-6.214	
	19			-6.907	

iron(III) ion concentrations, the first order plots of $\ln(A_\infty - A_t)$ versus time were linear for different sets of experiment. This shows first order reaction with respect to oxidant. (Table 2, Fig. 2). Values of pseudo-first order rate constant, k_{obs} , were evaluated from the slope of plots.

3.2. Initial rate method

In this method, rate in change in the concentration, dx/dt , is recorded prior to any extensive chemical change. Initial rates are

measured from the slopes by drawing the tangent at $t = 0$. Initial rates are then plotted versus concentrations. Rate law for pseudo-first reaction is given as,

$$\text{Rate} = k [\text{Conc.}]$$

3.2.1 Effect of $[\text{Fe}(\text{EDTA})]^{2-}$ on the pseudo-first order rate constant (k_{obs})

Initial rate method was applied by plotting the initial rates versus initial concentrations of ethylenediaminetetraacetateiron(II) ion,

(Rate = $k_{\text{obs}}[\text{Fe}(\text{EDTA})^{2-}]^n$). The plots of initial rate versus initial concentration of ethylenediammine-tetraacetateiron(II) ion at constant tris(1,10-orthophenanthroline)iron(III) ion concentration produced straight line passing through the origin, indicating first order dependence of the rate on $[\text{Fe}(\text{EDTA})^{2-}]$ (Table 3, Fig. 3). Graphical values of

pseudo-first order rate constant, k_{obs} (graphical), were calculated from the slope of the plots. Calculated values of pseudo-first order rate constant, k_{obs} (calculated) were determined from the formula $k_{\text{obs}} = \text{Rate} / [\text{Conc}]$. An overall second order reaction was found having the rate constant, k_1 , value of $242.4 \pm 3.23 \text{ M}^{-1}\text{s}^{-1}$.

Table 3. Dependence of initial rate on $[\text{Fe}(\text{o-phen})_3]^{3+}$ and $[\text{Fe}(\text{EDTA})^{2-}]^2$
 $\lambda_{\text{max}} = 510 \text{ nm}$, $\epsilon = 11000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, Temperature = 30°C

Set No.	pH	$[\text{Fe}(\text{EDTA})^{2-}]_0$ $\times 10^3 (\text{M})$	$[\text{Fe}(\text{o-phen})_3]^{3+}_0$ $\times 10^4 (\text{M})$	Initial Rate (Abs/s)	* k_{obs} (s^{-1}) Calculated	** k_{obs} (s^{-1}) Graphical
A	2.8	0.33	1.67	0.14	0.038	0.035 ± 0.00045
B		0.67	1.67	0.27	0.036	
C		1.00	1.67	0.40	0.036	
D		1.67	1.67	0.50	0.027	0.258 ± 0.00207
E		1.67	1.00	0.25	0.227	
F		1.67	1.33	0.43	0.294	
G		1.67	2.00	0.63	0.286	
H		1.67	3.00	0.79	0.239	
I		1.67	3.67	0.84	0.208	
A	3.5	0.33	1.67	0.26	0.071	0.042 ± 0.00031
B		0.67	1.67	0.36	0.048	
C		1.00	1.67	0.46	0.042	
D		1.33	1.67	0.58	0.039	0.357 ± 0.00148
E		1.67	0.33	0.13	0.358	
F		1.67	0.67	0.27	0.366	
G		1.67	1.00	0.40	0.363	
H		1.67	1.33	0.52	0.355	
I		1.67	2.00	0.66	0.300	
A	4.2	0.33	1.67	0.30	0.083	0.048 ± 0.00049
B		0.67	1.67	0.40	0.054	
C		1.00	1.67	0.49	0.045	
D		1.33	1.67	0.62	0.042	0.371 ± 0.00152
E		1.67	0.33	0.14	0.385	
F		1.67	0.67	0.28	0.379	
G		1.67	1.00	0.42	0.382	
H		1.67	1.33	0.54	0.369	
I		1.67	1.67	0.67	0.365	

$$*k_{\text{obs}} = \frac{\text{Initial rate (Abs.s}^{-1}\text{)}}{\text{Conc. (M)} \times \epsilon (\text{M}^{-1}\text{cm}^{-1}) \times b (\text{cm})}$$

$$\frac{\text{Initial rate (Abs.s}^{-1}\text{)}}{\epsilon (\text{M}^{-1}\text{.cm}^{-1}) \times b (\text{cm})} = **k_{\text{obs}} [\text{Conc.}] (\text{M}) \quad (\text{Abs.} = \text{absorbance})$$

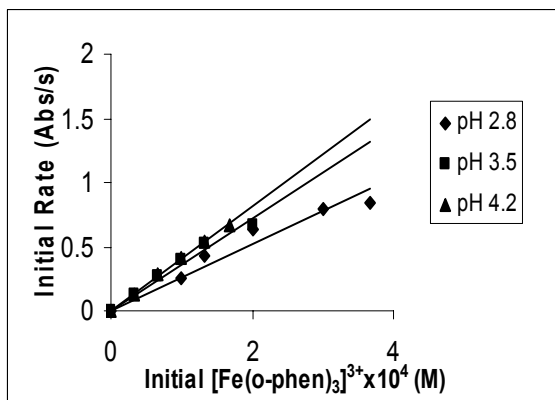


Fig.4. Plot of initial rates vs. $[\text{Fe}(\text{o-phen})_3]^{3+}$.

Table 4. Dependence of k_{obs} on $[\text{H}^+]$.

pH = 3.5, $[\text{Fe}(\text{EDTA})^{2-}] = 1.67 \times 10^{-3} \text{ M}$,
 $[\text{Fe}(\text{o-phen})_3]^{3+} = 1.33 \times 10^{-4} \text{ M}$, Temperature = 30°C

$k_{\text{obs}} (\text{s}^{-1})$	$1/k_{\text{obs}} (\text{s})$	$[\text{H}^+] \times 10^4 (\text{M})$
0.258	3.876	15.84
0.357	2.801	3.16
0.371	2.695	0.63

3.2.2. Effect of $[\text{Fe}(\text{o-phen})_3]^{3+}$ on the pseudo-first order rate constant (k_{obs})

When ethylenediaminetetraacetateiron(II) ion, having several fold excess concentration over tris(1,10-orthophenanthroline)iron(III) ion, was kept constant, the plots of initial rate versus initial concentrations of tris(1,10-orthophenanthroline)iron(III) ion gave straight line with zero intercept indicating that reaction is first order in oxidant. (Table 3, Fig. 4). Pseudo-first order rate constant ' k_{obs} ' with respect to $[\text{Fe}(\text{o-phen})_3]^{3+}$ were calculated from the slope of the plots.

3.3. Effect of k_{obs} on $[\text{H}^+]$

Change in absorbance was recorded as a function of time at three different pH values viz. 2.8, 3.5 and 4.2 in order to study the effect of $[\text{H}^+]$ on observed rate constant, k_{obs} . An increase in rate constant was observed with a decrease in $[\text{H}^+]$ which indicates inverse fractional order kinetics with respect to $[\text{H}^+]$. The same was substantiated by plotting the graph between $1/k_{\text{obs}}$ and $[\text{H}^+]$ which was found to be linear with positive slope (Table 4, Fig. 5).

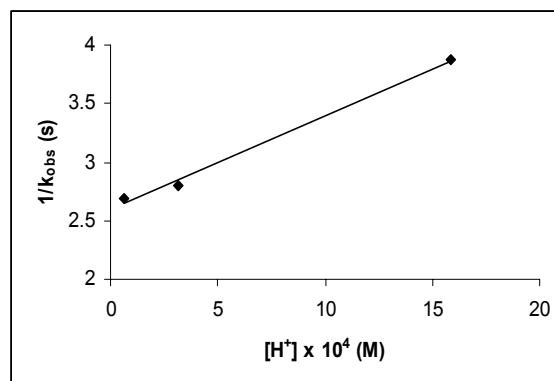


Figure 5. Plot of $1/k_{\text{obs}}$ vs. $[\text{H}^+]$, for the determination of order of reaction with respect to $[\text{H}^+]$.

Table 5. Thermodynamic Functions.

$[\text{Fe}(\text{EDTA})^{2-}] = 1.67 \times 10^{-3}$, $[\text{Fe}(\text{o-phen})_3]^{3+} = 1.67 \times 10^{-4}$, pH=3.5

Thermodynamic functions	Values
ΔG°	$-118 \pm 0 \text{ kJmol}^{-1}$
ΔG^\ddagger	$+35.3 \pm 1.67 \text{ kJmol}^{-1}$
ΔS^\ddagger	$-45.0 \pm 1.23 \text{ JK}^{-1}\text{mol}^{-1}$
ΔH^\ddagger	$+21.6 \pm 0.79 \text{ kJmol}^{-1}$
E_a	$+24.06 \pm 1.11 \text{ kJmol}^{-1}$

3.4. Effect of temperature on pseudo-order rate constant

To study the effect of temperature on k_{obs} , kinetic runs were carried out by varying the temperature in the range of 25 to 40°C. The residual conditions were kept unaltered. Various thermodynamic functions were calculated by applying different kinetic equations (Table 5). Standard free energy was calculated by using equation $\Delta G^\circ = -nFE^\circ$ and its value is found as -118 kJmol^{-1} . It is a theoretical value calculated from E° ($\Delta G^\circ = -nFE^\circ$) so has 0. Negative value of ΔG° signifies that reaction is feasible. Value of activation energy, E_a $24.06 \pm 1.11 \text{ kJmol}^{-1}$, was calculated from the slope when Arrhenius equation

i.e. $\ln k_{\text{obs}} = \ln A - \frac{E_a}{RT}$, was plotted between $\ln k_{\text{obs}}$

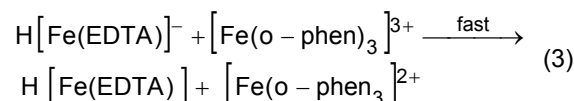
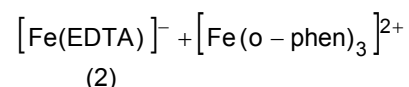
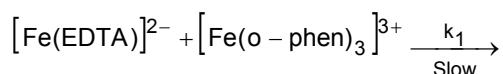
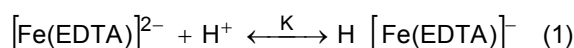
versus $1/T$. This positive value of activation energy realizes that reaction rate gets increased with an increase in temperature. By plotting data according to the equation of transition state theory,

$\ln \frac{k_{\text{obs}}}{T} = \ln \frac{k_B}{h} + \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT}$, enthalpy and entropy of activation, ΔH^\ddagger and ΔS^\ddagger , were calculated from the slope and intercept and found to be $21.6 \pm$

0.79 kJmol⁻¹ and -45.0±1.23 JK⁻¹mol⁻¹ respectively. Once ΔH^\ddagger and ΔS^\ddagger are known, free energy of activation, ΔG^\ddagger , was calculated from equation $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$. These positive values of ΔH^\ddagger and ΔG^\ddagger , and negative value of ΔS^\ddagger indicate that activated complex is less probable and the low rates of the reaction are observed.

4. Mechanism

Equations (1 – 3), are suggested to control the mechanism of the reaction.



The rate of reaction is given by

$$\text{Rate} = k_1 [\text{Fe}(\text{EDTA})]_F^{2-} [\text{Fe}(\text{o-phen})_3]^{3+} \quad (4)$$

Contemplating that the protonation of $\text{H}[\text{Fe}(\text{EDTA})]^-$ is quick, equilibrium constant for the formation of protonated specie is shown as

$$K = \frac{\text{H}[\text{Fe}(\text{EDTA})]^-}{[\text{H}^+][\text{Fe}(\text{EDTA})]_F^{2-}} \quad (5)$$

Where

$$[\text{Fe}(\text{EDTA})]_F^{2-} = [\text{Fe}(\text{EDTA})]_O^{2-} - \text{H}[\text{Fe}(\text{EDTA})]^-$$

$[\text{Fe}(\text{EDTA})]_F^{2-}$ is free concentration of ethylenediaminetetraacetateiron(II) ion.

$[\text{Fe}(\text{EDTA})]_O^{2-}$ is the total concentration of ethylenediaminetetraacetateiron(II) ion.

Substituting $\text{H}[\text{Fe}(\text{EDTA})]^-$ in equation (5) and rearranging.

$$[\text{Fe}(\text{EDTA})]_F^{2-} = \frac{[\text{Fe}(\text{EDTA})]_O^{2-}}{1 + K[\text{H}^+]}$$

Substituting for $[\text{Fe}(\text{EDTA})]_F^{2-}$ in equation (4), we have

$$\text{Rate} = \frac{k_1 [\text{Fe}(\text{EDTA})]_O^{2-} [\text{Fe}(\text{o-phen})_3]^{3+}}{1 + K[\text{H}^+]} \quad (6)$$

As pseudo first order conditions prevail, first order rate constant is taken as

$$k_{\text{obs}} = \frac{k_1 [\text{Fe}(\text{EDTA})]_O^{2-}}{1 + K[\text{H}^+]} \quad (7)$$

taking reciprocals on both sides eq (7) becomes

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k_1 [\text{Fe}(\text{EDTA})]_O^{2-}} + \frac{K[\text{H}^+]}{k_1 [\text{Fe}(\text{EDTA})]_O^{2-}} \quad (8)$$

To validate the mechanism, graph between $1/k_{\text{obs}}$ versus $[\text{H}^+]$ was plotted and found to be linear. The constants K and k_1 were calculated from the slope and intercept and were found to be $219.72 \pm 3.45 \text{ M}^{-1}$ and $230.31 \pm 4.45 \text{ M}^{-1}\text{s}^{-1}$ respectively. A good agreement was found between recalculated rate constant from equation 8 and experimental rate constant.

5. Conclusions

This work is an attempt to investigate the redox reaction between two complex ions in pseudo-first order conditions. Similar reactions have been reported in the literature but the investigators have used the experimental conditions that confirm to second order conditions. Further to date the role of pH on such reactions involving two complex ions has been examined. This presentation is novel in another aspect that it reports on the mechanism of electron transfer between $[\text{Fe}(\text{EDTA})]^{2-}$ and $[\text{Fe}(\text{o-phen})_3]^{3+}$ complexes and this has not been studied prior to this investigation. Further two independent methods have been used to study the same redox reaction and both produce concurrent results.

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