KINETIC STUDY OF THE REDUCTION OF FERRIC- 1, 10-ORTHOPHENAN-THROLINE WITH URANIUM (IV) DCTA

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The kinetics and mechanism of the reduction of ferric 1,10 orthophenanthroline by uranium (IV) trans – 1,2 – cyclohexanediaminetetraacetate was investigated in aqueous hydrochloric acid at 30^0C, at ionic strength 0.01-mole dm^{-3} and pH 3.5. Rate law for the formation of [Fe (opt)$_3$]$^{2+}$ was established through spectroscopic measurements at constant and varying pH by isolation method. Order of reaction with respect to each reactant ([U(IV) DCTA] and [Fe (opt)$_3$]$^{3+}$ was investigated by plotting a graph of ln A$_\infty$-A$_t$ vs time at different temperature ranges. Each reactant was found to follow first order. At pH 3.5 the over all order of reaction was found to be second, having the value of 0.73 M^{-1} s^{-1} and rate law is suggested to be $\frac{d}{dt}\left[Fe(opt)_3\right]^{+2} = K_1\left[U(IV)DCTAH^+\right]\left[Fe(opt)_3\right]^{+3}$. Different thermodynamic functions for the reaction were E$_a$ = 35 $\pm$ 0.6 kJ mol^{-1}, $\Delta H^\#$ = 2.4 $\pm$ 0.2 kJ mol^{-1} and $\Delta S^\#$ = -149 $\pm$ 3 J mol^{-1}k^{-1}. Activation energy for the reaction was calculated with the help of A rhenius equation. Other activation parameters ($\Delta S^{\neq}$, $\Delta H^{\neq}$) were determined from the slope and intercept of Eyring equation .At different pH values the rate law was observed as rate = K k$_1$ [H$^+$]^n [U (IV) DCTA] [Fe (opt)$_3$]$^{+3}$, where K is equilibrium constant for the protonation reaction

[U (IV) DCTA] + [H$^+$] = [U(IV) DCTA H$^+$] and k$_1$ is the specific rate constant for the redox reaction [U (IV) DCTA H$^+$] + [Fe(opt)$_3$]$^{+3}\rightarrow$ [U (V) DCTA] + [Fe (opt)$_3$]$^{2+}$.

Keywords: Reduction, [U (IV) DCTA], Kinetics, [Fe (opt)$_3$]$^{3+}$, Isolation method

1. Introduction

So far a number of studies pertaining to mechanism of electron transfer between metal complexes in solution have been reported [1-5] . A broader review of behavior of electron exchange reactions in aqueous solutions has recently appeared [6]. An electron transfer reaction between [U (IV) EDTA] and [Fe (opt)$_3$]$^{3+}$ has been investigated recently [7] and that mechanism has been proposed to be an outer sphere bimolecular electron transfer. This paper describes the results of an electron transfer reaction between [U(IV)DCTA] and [Fe (opt)$_3$]$^{3+}$. To make the reaction mixture at desired pH hydrochloric acid medium was used. This was done to avoid the complication due to the additional complexation of [U (IV) DCTA] with any of the anions routinely present in buffer mixtures. The redox potentials of the half cell reaction [U (IV) DCTA] +2e$^-$ $\rightarrow$ [U(VI) DCTA] couple has been calculated as 0.96 V as compared to that of [Fe (opt)]$^{3+}$+ e$^-$ $\rightarrow$ [Fe (opt)$_3$]$^{2+}$

couple being 1.02 V. So the reaction is thermodynamically favourable. An appropriate mechanism pertaining to kinetic data has been proposed and relevant activation parameters are being reported.

2. Experimental

2.1. Standard solution of [Fe (opt)$_3$]$^{3+}$

Solutions were prepared by mixing the appropriate volumes of orthophenthroline and Fe (III) standard solutions. Ferric nitrate Fe (NO$_3$)$_3$. 6H$_2$O and orthophenanthroline of BDH analar grade, were used [10].

2.2. Uranium (IV) stock solution

Uranous solution was obtained by catalytic hydrogenation method [11]. Analysis for uranous was performed by using K$_2$Cr$_2$O$_7$ [12] as well as ceric sulphate [13].

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2.3. Uranous DCTA complex, [U(IV) DCTA 2H₂O]

Disodium salt of DCTA of Merck analar grade, was used as a ligand. Standard solution of uranium (IV) was warmed to 40–50 ℃. Subsequently an amount of disodium salt of DCTA having 10% excess concentration over corresponding U (IV) concentration was introduced to it with vigorous stirring and warming. Soon as the grayish green crystals of U(IV) DCTA started appearing stirring and warming was stopped (prolonged heating results in black precipitates) . The grayish green crystals were filtered through Whatman 542 filter paper, washed with water and 99% absolute alcohol. Finally, the crystals were dried with ether. [U (IV) DCTA . 2H₂O] crystals were kept constant in dry place to avoid moisture. All solutions were prepared in aqueous medium.

The following results were obtained from the analysis of the complex

U(IV) DCTA·2H₂O	%U(IV)	% H	% C	%N
Error	± 2.64	± 0.3	± 0.3	± 0.3
Calculated	38.62	27.38	3.68	4.54
Analysed	37.60	27.10	3.06	4.21

U (IV) analysis in [U(IV) DCTA· 2H₂O] was performed by means of $K_2Cr_2O_7$ using sodium salt of diphenylamine sulphonic acid as an indicator [12]. The % age of carbon, hydrogen and nitrogen was analyzed by using CHN analyzer. *

Spectrophotometric analysis gave the spectrum of [U(IV) DCTA] having λ_{max} 660 nm with low value of molar absorptivity $\varepsilon = 48.50$ $M^{-1}cm^{-1}$, which is the same as reported in the literature [14]. Spectral studies on [U(IV) EDTA] and [U(IV) DCTA] [14] show that both of these complexes have same λ_{max}. This observation suggested that DCTA ligand does not change the CF splitting energy value of U (IV). The solubility of the complex in water is low and it is of the order of 10^{-3} M at room temperature [15].

2.4. Instrumentation

Kinetic measurements were carried out on Schimadzu UV-Visible, 160 A spectrophotometer. Temperature controlled runs were carried on Themomix – 1440 B, Mettler Toledo MP 220, pH measurements were made on a Kent model 7020 pH meter.

2.5. Kinetic measurements

All the solutions for the reaction were prepared in an inert atmospheric condition. The kinetic study of the reduction of the [Fe (opt)₃]³⁺ was carried out under the pseudo first order conditions, with [U(IV) DCTA] ten time excess over [Fe(opt)₃]³⁺. This was done in order to ascertain the influence of [Fe (opt)₃]³⁺ concentration over the reaction rate, independent of [U(IV)DCTA] concentration, The reaction was followed by recording absorbance at 510 nm where [Fe(opt)₃]²⁺ has its maximum absorption, which is the main reaction product. The concentration of the components of the reaction mixture were predetermined and they were kept at desired temperature on thermostatic bath. Using nitrogen gas cylinder extra pure nitrogen gas was bubbled to reduce the chances of the air oxidation of the [U (IV) DCTA] solution. The reaction mixture was prepared in 4 ml UV- visible cell having path length of 1cm and it was sealed by serum cap to avoid any oxidation.

Table 1. Effect of [Fe (opt)₃]³⁺ on k_{obs}

[U(IV)DCTA] = 6× 10⁻⁴ M , pH = 3.5

Temperature = 30 ⁰C , μ = 0.01 M

[Fe (opt)₃]³⁺/ 10⁵	k_{obs}* /10⁴ s⁻¹
3.0	7.35 ± 0.02
3.5	7.3 ± 0.03
4.0	7.32 ± 0.04
4.5	6.6 ± 0.03
5.0	7.0 ± 0.04

*Average of triplicate measurements

3. Results and Discussion

3.1. Determination of order of reaction with respect to [Fe (opt)₃]³⁺

The results of kinetic measurements for the reduction of [Fe (opt)₃]³⁺ are being reported in Tables 1 and 2. These reactions were carried out under pseudo first order conditions. Concentration of [U(IV)DCTA] was maintained at ten times over the concentration of [Fe (opt)₃]³⁺. Rate constant pertaining to psuedo first order conditions was calculated by plotting ln (Aα - At) vs time, for varying concentrations of[Fe (opt)₃]³⁺ (Fig. 1). As shown in Table 1 these values of the rate constant are reasonably constant while the concentration of

[Fe (opt)$_3$]$^{3+}$ increased at constant concentration of [U (IV) DCTA].

Table 2. Effect of [U(IV) DCTA] Concentration on k$_{obs}$

[Fe (opt)$_3$] = 3.0×10^{-5}M, pH 3.5
Temperature = 30 ^{0}C, μ = 0.01 M

[U (IV) DCTA] / 10^{-4}	k$_{obs}$* /10^{-4} s^{-1}
6.0	7.35 ± 0.02
6.5	7.91 ± 0.03
7.0	8.4 ± 0.02
7.5	8.66 ± 0.03
8.0	9.58 ± 0.02
8.5	10.1 ± 0.03
9.0	10.8 ± 0.05
9.5	11.4 ± 0.02
10	11.98 ± 0.06

*Average of triplicate measurements

3.2. Indirect determination of order of reaction with respect to [U(IV) DCTA]

The order of reaction with respect to the other reactant i.e. [U (IV) DCTA] was also investigated . By varying [U (IV) DCTA] concentration pseudo first order onstant k$_{obs}$ value was calculated, while the other parameters were kept constant. The value of k$_{obs}$ increases with an increase in the concentration of [U(IV)DCTA] complex (Table 2). Through the plot of k$_{obs}$ values against [U (IV) DCTA] concentration a straight line is obtained passing through the origin showing that the order of reaction with respect to [U (IV) DCTA] concentration is also first. The slope of the plot was evaluated as   second order rate constant k = 71.59 M^{-1}min^{-1} .

Table 3. Effect of pH on k$_{obs}$

[Fe (opt)$_3$]$^{3+}$ = 3.0×10^{-5} M , Temperature = 30 ^{0}C

[U (IV) DCTA] = 6.0×10^{-4}M , μ = 0.01 M

pH	k$_{obs}$*/ 10^{-4} s^{-1}
4.0	1.43 ± 0.02
3.8	3.55 ± 0.04
3.5	7.35 ± 0.03
3.2	12.4 ± 0.02

*Average of triplicate measurements

3.3. Dependence of the hydrogen ion concentration:

The studies on the effect of hydrogen ion concentration on the reaction rate at the constant temperature (30^{0}C) are summarized in Table 4.

Table 4. Effect of Ionic Strength on k$_{obs.}$

[Fe (opt)$_3$]$^{3+}$ = 3.0×10^{-5} M , Temperature = 30 ^{0}C

[U (IV) DCTA] = 6.0×10^{-4}M , pH = 3.5

Ionic strength /M	k$_{obs}$ / 10^{-4} s^{-1}
0.01	7.35± 0.04
0.02	7.3 ± 0.02
0.03	7.3 ± 0.03
0.04	7.41 ± 0.04
0.05	7.46 ± 0.05

The order of the reaction with respect to hydrogen ion concentration was calculated by formulating the following equation.

$$\text{Rate} = k^{'}\left[H^+\right]^n \left[U(IV) \text{ DCTA}\right]\left[Fe\ (opt)_3\right]^{3+}$$

$$k_{obs} = k'\left[H^+\right]^n \text{ and}$$

$$k' = Kk_1$$

In the preceeding equation k' [H]^n is the k$_{obs}$ for each experiment. K is equilibrium constant for the protonation of [U(IV)DCTA] and k$_1$ is the specific rate constant for the reaction of [U (IV) DCTA H$^+$] and [Fe (opt)$_3$]$^{3+}$. The value of "n" can therefore be evaluated from slope of a plot of log [H$^+$] against log k$_{obs}$ at constant temperature. The value of "n" thus determined equals to 1.15.This is nearly equal to the first power. So, it is suggested that the rate of oxidation of [U (IV) DCTA] by [Fe (opt)]$^{3+}$ is dependent on the first power of hydrogen ion concentration

3.4. Effect of temperature on the reaction

The thermodynamic parameters are determined by monitoring the effect of temperature on rate. The results are shown in Table 5. The rate of reaction was found to increase from 65.36 to 76.70 M^{-1} min^{-1} while the temperature increased from 15^{0}C to 40^{0}C. A plot of lnk$_1$ against 1/T is linear. Thermodynamic parameters are listed in Table 6. Activation energy for the reaction calculated with the help of Arrhenius equation

$$\ln k = -E_a / RT + \ln A.$$

Table 5. Effect of Temperature on k_1

[Fe (opt)$_3$]$^{3+}$ = 3.0×10^{-5} M , pH = 3.5 [U (IV)DCTA] = 6.0×10^{-4} M , μ = 0.01M

| Temperature ^{0}C	k_{obs}/ s^{-1} 10^{-4}	k_1 / mole^{-4} dm^3 s^{-1}
20	2.22	0.37 ± 0.02
25	3.12	0.52 ± 0.03
30	4.5	0.73 ± 0.05
35	5.34	0.89 ± 0.03
40	6.12	1.02 ± 0.07
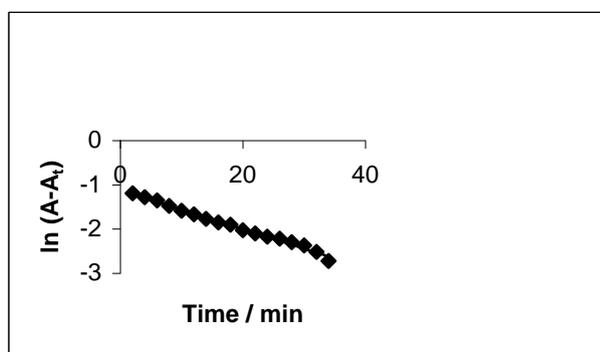
Figure 1. A typical kinetic plot for the determination of k_{obs}

Table 6. Thermodynamic Parameters

$\Delta H^{\#}$/ kJ/mole	$\Delta S^{\#}$/ J/mole	E_a/ kJ/mole	ΔG°/ kJ/ mol
2.417 ± 0.2	- 149.2 ± 3	35.1 ± 0.6	-40.4 ± 0.4

Other activation parameters ($\Delta S^{\neq}$, $\Delta H^{\neq}$) were determined from the slope and intercept of Eyring equation $\ln k = \ln(kT/h) + \Delta S^{\neq}/R - \Delta H^{\neq}/RT$

4. Proposed Mechanism

The reaction between [U(IV DCTA] and [Fe (opt)$_3$]$^{3+}$ follows the second order rate law with dependence of hydrogen ion concentration. This is a two-electron transfer process. In the first step [U (IV)DCTA] gets protonated to [U(IV)DCTA(H$^+$)] which subsequently oxidizes to reactive intermediate specie [U(V)DCTA(H$^+$)] and that it oxidizes itself to [U(VI)DCTA(H$^+$)].

$$[U(IV)DCTA] + H^+ \xleftrightarrow{K} [U(IV)DCTAH^+] \text{Fast} \quad (1)$$

$$\begin{aligned} &[U(IV)DCTAH^+] + [Fe(opt)_3]^{3+} \xrightarrow{k_1} \\ &[U(V)DCTA(H^+)] \; [Fe(opt)_3]^{2+} \end{aligned} \quad (2)$$

$$\begin{aligned} &[U(V)DCTA(H^+)] + [Fe(opt)_3]^{3+} \xrightarrow{k_2} \\ &[U(VI)DCTA(H^+)] + [Fe(opt)_3]^{2+} \end{aligned} \quad (3)$$
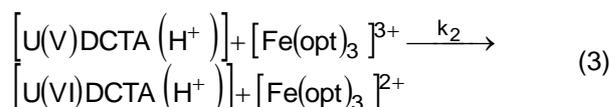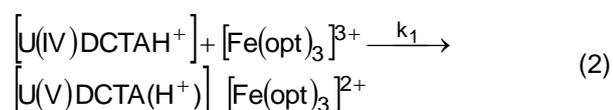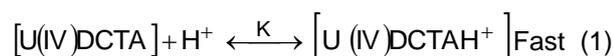
$$\text{Rate} = \frac{d[Fe(opt)_3]^{2+}}{dt} = k_1[U(IV)DCTA(H^+)] \\ [Fe(opt)_3]^{3+} \quad (4)$$

$$\frac{d[Fe(opt)_3]^{2+}}{dt} = k_{obs}[Fe(opt)_3]^{3+} \quad (5)$$

Where

$$k_{obs} = k^{'}[U(IV)DCTA] \quad (6)$$

For different pH

$$\begin{aligned} \text{Rate} &= \frac{d[Fe(opt)_3]^{2+}}{dt} \\ &= Kk_1[H^+]^n[U(IV)DCTA][Fe(opt)_3]^{3+} \end{aligned} \quad (7)$$

In the proposed mechanism k_1 is identified as specific rate constant for second order rate equation for the reaction [U (IV) DCTA(H$^+$)] and [Fe (opt)$_3$]$^{3+}$. K is equilibrium constant for the reaction [U(IV) DCTA] + [H] = [U (IV) DCTA H]$^+$. Out of the three proposed pathways, the second will be the slowest. 3 and 1 are assumed to be fast steps. These assumptions are justified as (1). There is an equilibrium between the protonated and deprotonated forms of the [U (IV) DCTA] with a low value of K (2) For the redox process reactive species are [U (IV) DCTA] and [U (IV) DCTA (H$^+$)]. This observation is supported by the response of redox reaction to ionic strength and pH (Tables 3, 4). Further to that we find that, the rate of protonation increases with the decrease of pH (Table 5). This observations is understandable as the protonation of co-ordinated complex facilitates the unwrapping of ligand and U (IV) thus freed, is made available for the redox reaction [8]. While comparing the two redox processes that of [U (IV) EDTA] [7] and the present reaction of [U (IV) DCTA] with [Fe (opt)$_3$]$^{3+}$ it is suggested that the mechanism of both reactions is same. However, the rate of the later is much slower than that of [U (IV) EDTA]. It can be explained by considering the presence of additional cyclohexane ring in DCTA complex, which makes it bulky molecule. Stability of the ring in co-ordinated [U (IV) DCTA] is

influenced by the steric factor rather than basicity of the molecule [9]. Steric factor stabilizes the [U (IV) DCTA] complex and the basicity of the ligand has no significant role or influence in this case. Higher stability of the complex works against the opening of the ring. The rate constant decreases accordingly in the order [U(IV) EDTA] > [U (IV) DCTA]. That is of inverse order of stability constants, which are, 25.6 for [U (IV) EDTA] and 26.9 [U (IV) DCTA]. Thermodynamic parameters also favour the observation. E_a of [U (IV) DCTA] is higher than that of the [U(IV) EDTA] reaction with [Fe $(opt)_3]^{3+}$. Negative value of entropy of activation ($\Delta S^{\neq}$) shows that the transition state is less probable and that the electron transfer reaction is likely to be slow [6].

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