

Kinetic Study of the Reduction of Ferric-1, 10-orthophenanthroline with Uranium (IV) EDTA

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Summary: The kinetics and mechanism of the reduction of ferric 1,10 orthophenanthroline by Uranium (IV) ethylenediammine tetra acetate was investigated in aqueous hydrochloric acid at 25°C, ionic strength 0.01 mol dm⁻³ and pH 3.5. Rate law for the formation of Fe (II) opt was established through spectrophotometric measurement at constant and varying pH by isolation method. At pH of 3.5 and temperature of 25°C, the order of reaction was found to be second having the value of 221 M⁻¹ min⁻¹ and rate law is suggested to be $d/dt [Fe(opt)_3]^{2+} = K_1 [U(IV) EDTA H^+] [Fe(opt)_3]^{3+}$. Different thermodynamic functions for the reaction were $E_a = 3.37 \text{ KJ mol}^{-1}$, $\Delta G = -42 \text{ KJ mol}^{-1}$, $\Delta H = 2 \text{ KJ mol}^{-1}$ and $\Delta S = 148 \text{ JK}^{-1} \text{ mol}^{-1}$. At different pH values the rate law was observed as $\text{rate} = Kk_1[H^+] [U(IV) EDTA] [Fe(opt)_3]^{3+}$, where K is equilibrium constant for the reaction $[U(IV) EDTA] + [H^+] = [U(IV) EDTA H^+]$ and k_1 is the specific rate constant for the reaction $[U(IV)EDTA H^+] + [Fe(opt)_3]^{3+} \rightarrow [U(V)EDTA] + [Fe(opt)_3]^{2+}$

Introduction

Investigations pertaining to electron exchange reactions in aqueous solutions have been widely reported [1]. Mechanisms of electron transfer between inorganic complex ions in solution have received considerable attention [2,11]. This paper reports the results of studies on electron transfer reaction between [U(IV)EDTA] and [Fe(opt)₃]³⁺. The study was carried out in hydrochloric acid medium to minimize complications due to additional complexation of U(IV) EDTA with any of the anions routinely present in buffer mixtures. The redox potential of the half cell reaction $U(VI) EDTA + 2e^- \rightarrow U(IV)EDTA$ couple has been calculated as 0.80 V as compared to $Fe(III)opt + 1e^- \rightarrow Fe(II)opt$ couple 1.02 V, because of these values the reaction is thermodynamically favourable. An appropriate mechanism pertaining to kinetic data has been proposed and relevant activation parameters are being reported.

Results and Discussion

Determination of Order of Reaction with Respect to [Fe (opt)₃]³⁺

The results of the kinetic measurements of the reduction of [Fe (opt)₃]³⁺ are reported in Tables 1 and 2. Reaction were carried out under the arrangement that the concentration of U(IV)EDTA exceeded ten times over the corresponding concentration of [Fe (opt)₃]³⁺. Pseudo first order rate constant of the

reduction of [Fe (opt)₃]³⁺ is reasonably constant with the increasing concentration of [Fe (opt)₃]³⁺ at constant concentration of U(IV)EDTA, as shown in Table 1.

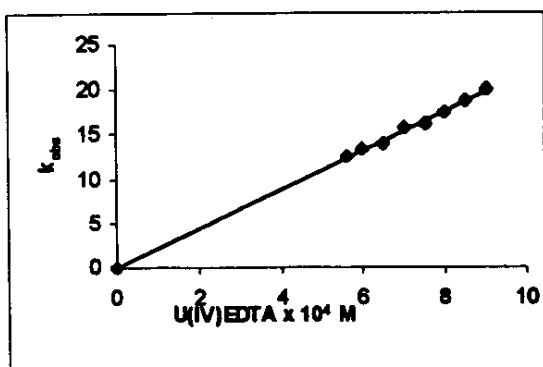
Table 1 Observed rate constants viz. Varying [Fe(opt)₃]³⁺ concentrations
 U(IV)EDTA = 6.0x10⁻⁴M, I = 0.01M,
 temperature = 25°C and pH = 3.5.

Run number	[Fe(Opt) ₃] ³⁺ (Mx10 ⁵)	Number of replicates	k _{obs} (min. ⁻¹)x10 ²
1	3.3	5	13.3
2	4.2	4	10.9
3	5.1	5	10.0

Indirect Determination of Order of Reaction with Respect to U (IV) EDTA

Another set of experiments was carried out to investigate the effect of varying U(IV)EDTA concentrations on the pseudo first order rate constant (k_{obs}) values. These results are shown in Table 2. k_{obs} values which increase with the increasing U(IV)EDTA complex concentration and demonstrate that reaction rate is also dependent upon U(IV)EDTA concentration. Figure 1 displays the plot of k_{obs} values against U(IV)EDTA concentration and straight line is obtained passing through the origin which shows the order of reaction with respect to U(IV)EDTA is also first. Since the over all order of reaction is second. The slope has been calculated

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Fig. 1: Effect on k_{obs} varying $[U(IV)EDTA]$

from this regression line and it gives the rate constant value as $221 \text{ M}^{-1} \text{ min}^{-1}$.

Table 2: Observed rate constants viz varying $U(IV)EDTA$ concentrations
 $[Fe(opt)_3]^{3+} = 3.3 \times 10^{-5} \text{ M}$, $I = 0.01 \text{ M}$, temperature = 25°C and $\text{pH} = 3.5$

Run number	$[U(IV)EDTA] (\text{M} \times 10^4)$	Number of replicates	$k_{obs} (\text{min}^{-1}) \times 10^2$
1	5.6	4	12.5
2	6.0	5	13.3
3	6.5	4	14.1
4	7.0	3	15.7
5	7.5	4	16.2
6	8.0	5	17.5
7	8.5	4	18.7
8	9.0	3	20.0

Dependence of the Rate on Hydrogen Ion Concentration

Table 3 summarizes the results for the studies on the effect of hydrogen ion concentration on the reaction rate, at a fixed temperature (25°C). The apparent order of the reaction with respect to hydrogen ion concentration at constant temperature was calculated by using the equation.

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

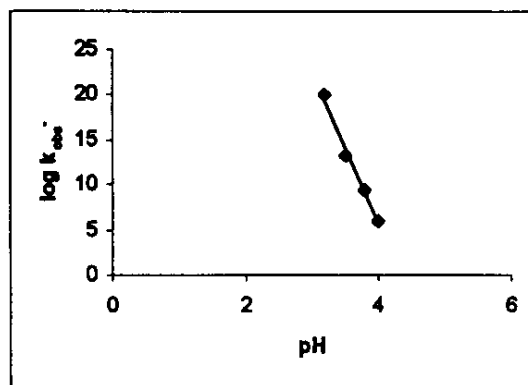
$$k_{obs} = k' (H^+)^n \quad \text{and} \quad k' = Kk_1$$

Table 3: Observed rate constants viz. varying pH

$[Fe(opt)_3]^{3+} = 3.3 \times 10^{-5} \text{ M}$, $U(IV)EDTA = 6.0 \times 10^{-4} \text{ M}$, $I = 0.01 \text{ M}$, and temperature = 25°C .

Run number	Number of replicates	pH	$k_{obs} (\text{min}^{-1}) \times 10^2$
1	4	4.0	6.0
2	4	3.8	9.5
3	5	3.5	13.5
4	3	3.2	20.0

In the above equation $k' [H^+]^n$ is to be identified with k_{obs} for each experiment. The value of n can therefore be evaluated from a plot of $\log [H^+]$ against $\log k_{obs}$ at constant temperature. This plot is shown in Figure 2 and the value of n thus determined equals 0.63. This result suggests that the rate of oxidation of $U(IV)EDTA$ by $[Fe(opt)_3]^{3+}$ is very nearly dependent upon the first power of hydrogen ion concentration.

Fig. 2: Variation of k_{obs} with pH at $T = 25^\circ \text{C}$, $I = 0.01 \text{ M}$

Effect of Temperature on the Reaction

In order to determine the thermodynamic parameters, temperature dependence of the rate was monitored, and the results are being shown in the Table 4. The rate of reaction was found to increase with temperature. The second order rate constant values increased from 190 to $475 \text{ M}^{-1} \text{ min}^{-1}$ with temperatures 15°C to 40°C respectively. A plot of $\ln k_1$ against $1/T$ is linear as shown in Figure 3 and the thermodynamic parameters obtained from this plot are shown in Table 5. The Thermodynamic parameters are $\Delta H = 2 \text{ KJ mol}^{-1}$, $\Delta S = 148 \text{ J mol}^{-1} \text{ K}^{-1}$, $E_a = 3.37 \text{ KJ mol}^{-1}$ and $\Delta G = -42 \text{ KJ mol}^{-1}$

Table 4: rate constants at different temperatures

$U(IV)EDTA = 6.0 \times 10^{-4} \text{ M}$, $[Fe(Opt)_3]^{3+} = 3.3 \times 10^{-5} \text{ M}$, $I = 0.01 \text{ M}$ and $\text{pH} = 3.5$

Run No.	Number of replicates	Temp ($^\circ \text{C}$)	$T^{-1}/^\circ \text{K} \times 10^4$	$k_1 (\text{M}^{-1} \text{ min}^{-1})$	$\ln k_1$
1	3	15	34.72	190	5.247
2	5	25	33.55	221	5.398
3	4	40	31.94	475	6.163

Table 5: The thermodynamic parameters of the reaction

ΔH K J mol ⁻¹	ΔS Joules K ⁻¹ mol ⁻¹	ΔG K Joules mol ⁻¹	E_a K Joules mol ⁻¹
2	148	-42	3.37

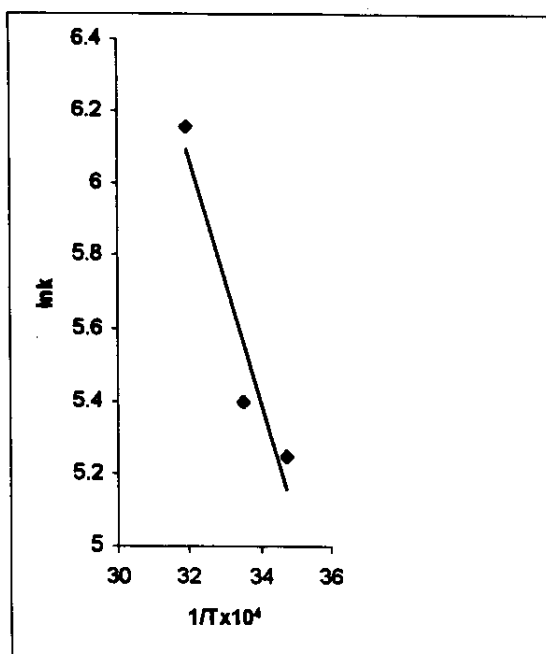
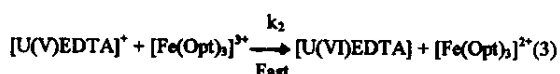
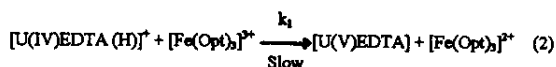


Fig. 3: Determination of thermodynamic parameters.

Proposed Mechanism



Rate Expressions

At pH of 3.5 and temperature of 25°C

$$\text{Rate} = d/dt [\text{Fe(opt)}_3]^{3+} = k_1 [\text{U(IV)EDTA(H)}]^+ [\text{Fe(opt)}_3]^{3+}$$

$$d/dt [\text{Fe(opt)}_3]^{3+} = k_{\text{obs}} [\text{Fe(opt)}_3]^{3+}$$

$$\text{where } k_{\text{obs}} = k_1 [\text{U(IV)EDTA(H)}]^+$$

At different pH values the rate law was observed as

$$\text{rate} = d/dt [\text{Fe(opt)}_3]^{3+} = Kk_1 [\text{H}^+] [\text{U(IV)EDTA}] [\text{Fe(opt)}_3]^{3+}$$

where K is equilibrium constant for the reaction $[\text{U(IV)EDTA}] + [\text{H}^+] = [\text{U(IV)EDTA(H)}]^+$

] and k_1 is the specific rate constant for the reaction $[\text{U(IV)EDTA(H)}]^+ + [\text{Fe(opt)}_3]^{3+} \rightarrow [\text{U(V)EDTA}] + [\text{Fe(opt)}_3]^{2+}$. Out of the above mentioned three pathways, the first and the last are expected to be fast where as the second one will be slower and rate determining step. This result indicates that (1) equilibrium between protonated and deprotonated forms of the reactant is rapid, (2) the protonation equilibrium constant is small, (3) both the forms i.e. U(IV)EDTA and U(IV)EDTA H⁺ are reactive, (4) the protonated form provides the more reactive pathway. The observation shows that the rate of oxidation gets enhanced as the pH is lowered could be very well understood by the tendency of protonation of U(IV)EDTA complex at a higher ion concentration. The protonation facilitates the release of free U(IV) whose oxidation has been reported to be faster than EDTA complex [9].

Experimental

Standard Solution of $[\text{Fe(opt)}_3]^{3+}$

Solutions were prepared by mixing appropriate volumes of orthophenanthroline and Fe(III) standard solutions. Ferric nitrate $[\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$ and orthophenanthroline standard solutions of BDH analar grade, were used [3].

Uranium (VI) Stock Solution

0.1 M stock solution of uranyl was prepared by dissolving an appropriate amount of BDH analar grade uranyl nitrate hexahydrate, $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, in 0.1 M HCl solution.

Stock Solution of Uranium (IV)

Uranous solution was obtained by catalytic hydrogenation method [4]. Analysis of uranous solution was performed by using $\text{K}_2\text{Cr}_2\text{O}_7$ [5] as well as ceric sulphate [6].

Uranous EDTA complex, $[\text{U(IV)EDTA} \cdot 2\text{H}_2\text{O}]$

Disodium salt of EDTA of BDH analar grade, was used as a ligand. Standard solution of uranium (IV) was warmed to 40-50°C. Subsequently an amount of disodium EDTA having 10% excess concentration over corresponding uranium (IV) was introduced to it with vigorous stirring. Soon as the greyish green crystals of U(IV)EDTA started appearing, stirring and warming was stopped (prolonged heating results into back precipitates). The greyish green crystals were then filtered through Whatman 542 filter paper, washed with water and

99% absolute alcohol. Finally the crystals were dried with ether. U (IV) EDTA.2H₂O crystals were kept in dry place to avoid moisture. All solutions were prepared in aqueous medium.

Analysis of U(IV) EDTA.2H₂O

The following results were obtained from analysis of the complex:

U(IV)EDTA.2H ₂ O	%U(IV)	%C*	%H*	%N*
Calculated	41.01	20.70	3.13	4.82
Analysed S.T.d	40.00	22.06	2.94	5.17
% Error	±2.467	±6.57	±6.07	±7.25

*with compliments to HBI Research Institute of Chemistry.

U(IV) analysis was performed by means of volumetric titration with K₂Cr₂O₇ using sodium salt of diphenylamine sulphonc acid as an indicator [5].

Spectrophotometric analysis gave the spectrum of U(IV)EDTA.2H₂O, having λ_{max} 660 nm which is same as reported in the literature [7]. The solubility of complex in water is low and it is of the order of 10⁻³ M at room temperature [8].

Instrumentation

Kinetic measurements were carried out on Bausch Lomb Spectronic 21*. All spectra were recorded on Shimadzu UV-visible, 160A spectrophotometer. Temperature controlled runs were carried on Thermomix-1440B, Braun Melsugen AG. pH measurements were made on a Kent model 7020 pH meter.

Kinetic Measurements

The kinetic study of the reduction of [Fe(opt)₃]³⁺ by U(IV)EDTA was carried out under pseudo order conditions, with U(IV)EDTA in ten times excess over [Fe(Opt)₃]³⁺, this was done in order to ascertain the influence of Fe(III)opt concentration over the reaction rate, independent of U(IV)EDTA concentration. The reactions were followed by recording absorbance at 510 nm where [Fe(Opt)₃]²⁺

has its maximum absorption, which is the main reaction product. The concentrations of components of the reaction mixture were predetermined and they were kept at desired temperatures on thermostatic bath. Using nitrogen gas cylinder extra pure nitrogen gas was bubbled through the mixture to eliminate oxygen, to reduce the chances of air oxidation of U (IV)EDTA solution. The reaction mixture was prepared in 5ml spectrometric cell having path length of 1cm. The cell was sealed by using a serum cap. Three ml of U(IV)EDTA aqueous solution at appropriate pH, 0.5 ml of 0.1 M sodium chloride to maintain ionic strength 0.01, and an appropriate volume of 0.1 M hydrochloric acid were added by a syringe and finally 1.5 ml of [Fe(opt)₃]³⁺ of differentin each concentration was introduced to initiate the reaction mixture

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