

KINETIC STUDY OF REDOX REACTION OF U(IV) WITH FERRICYANIDE IONS

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The kinetics and mechanism of the redox reaction between U(IV) and ferricyanide ions were studied on the basis of the dependence of the limiting diffusion current of ferricyanide on time. The reaction is of first order with respect to the concentration of both ferricyanide and U(IV) ions. From the temperature dependence of the measured rate constant, activation parameters were determined with the use of the Eyring equation at two ionic strength values. From the dependence of the rate constant on concentration of hydrogen ions at different temperatures, the thermodynamic constants of the hydrolytic equilibrium of U^{4+} ions were derived as $\Delta G^\circ = -1.92 \text{ kcal mol}^{-1}$, $\Delta H^\circ = (11.8 \pm 0.5) \text{ kcal mol}^{-1}$ and $\Delta S^\circ = (33 \pm 1.3) \text{ cal K}^{-1} \text{ mol}^{-1}$ together with activation parameters of the elementary redox reaction $\Delta H^\ddagger = (5.08 \pm 0.6) \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = (-32.9 \pm 1.8) \text{ cal K}^{-1} \text{ mol}^{-1}$. A reaction mechanism is proposed and discussed according to which the elementary redox reaction is an interaction of the $HFe(CN)_6^{2-}$ ion with UOH^{3+} .

The kinetics and mechanism of oxidation of U(IV) were studied by a number of authors^{1-4,7}. Oxidation of U(IV) by Pu(IV), Fe(III) or Ce(IV) ions proceeds in two consecutive one-electron steps¹⁻³, the intermediate and final products being U(V) and UO_2^{2+} ions, respectively. Harkness and Halpern⁴ studied the kinetics of oxidation of U(IV) by Tl(III) ions and considered a two-electron transfer as more probable. The kinetics of the redox reaction between U(IV) and Fe(III) ions in 1-2M-HClO₄ was studied by Betts² who found the overall reaction order $n = 2$ and assumed a slow, rate-determining one-electron step. He could not explain unambiguously the fact that the reaction was approximately of second order with respect to hydrogen ions, and attributed it to one of the following competitive reactions: a) $UOH^{3+} + FeOH^{2+} \rightarrow Fe^{2+} + U(V)$, b) $U^{4+} + Fe(OH)_2^+ \rightarrow Fe^{2+} + U(V)$, c) $U(OH)_2^{2+} + Fe^{3+} \rightarrow Fe^{2+} + U(V)$. These reactions are kinetically equivalent and therefore it could not be decided which of them prevails.

In view of the unexplained features of the oxidation mechanism of U(IV) by Fe(III) ions, we decided to study the kinetics of oxidation of U(IV) ions by ferricyanide, which has not been described hitherto in the literature.

EXPERIMENTAL

The kinetics of oxidation of U(IV) ions by ferricyanide was studied polarographically by recording the time dependence of the limiting diffusion current of ferricyanide at $-0.08 \text{ V vs N.C.E.}$ with a type OH-102 polarograph (Radelkis). An electrolytic Kalousek cell was tempered with the aid

of a Hoesppler ultrathermostat. The dropping mercury electrode had a rate of flow $m = 1.6 \text{ mg/s}$ and drop time $t = 3.8 \text{ s}$ in distilled water on open circuit at a height of mercury column $h = 50 \text{ cm}$. The measured solution was in an atmosphere of pure nitrogen. A solution of U(IV) ions was prepared by electroreduction of uranyl acetate on a mercury pool cathode; their concentration was determined cerimetrically. Potassium ferricyanide and other chemicals were of reagent grade. The reactant solutions were freshly prepared before every measurement. They and the reaction mixture were protected against light. The ionic strength was maintained constant by addition of sodium perchlorate. The values of rate constants given in the present paper are average from four independent measurements which are accurate to within $\pm 7\%$.

RESULTS

The reaction under consideration was studied both at equivalent ratio of reactants ($1 \cdot 10^{-3} \text{ M-K}_3\text{Fe(CN)}_6 + 5 \cdot 10^{-4} \text{ M-U(IV)}$ ions) and at an excess of U(IV) ions in 1 M-HClO_4 . In the former case the reaction is of second order with respect to Fe(CN)_6^{3-} ions, in the latter it is of first order. The second-order rate constant $k_2 \text{ (s}^{-1} \text{ mol}^{-1} \text{ l)}$ was calculated from the equation

$$1/i - 1/i_0 = k_2 t / \alpha, \quad (1)$$

where i denotes limiting diffusion current of ferricyanide at time t , i_0 its initial value and α diffusion current constant. The first-order rate constant $k_1 \text{ (s}^{-1} \text{)}$ is given by

$$\ln(i_0/i) = k_1 t. \quad (2)$$

The k_1 values found experimentally are directly proportional to the concentration of U(IV) ions, the proportionality constant being equal to k_2 . The rate equation at constant pH can therefore be written as

$$-d[\text{Fe(CN)}_6^{3-}]/dt = 2k_2[\text{Fe(CN)}_6^{3-}][\text{U(IV)}]. \quad (3)$$

Activation parameters of the studied reaction were determined from the dependence of the k_2 value on temperature on the basis of the Eyring equation

$$-\ln(k_2 h / kT) = \Delta H^\ddagger / RT - \Delta S^\ddagger / R, \quad (4)$$

where k denotes Boltzmann constant and h Planck constant. The ΔH^\ddagger and ΔS^\ddagger values were calculated by the least squares method and are given in Table I.

The rate constant decreases with increasing concentration of hydrogen ions at constant ionic strength; the dependence of $\log k_2$ on pH is linear (Fig. 1) enabling to determine the corresponding reaction order as -1 independent of temperature. The k_2 value is inversely proportional to ionic strength (Table II) and decreases also with increasing concentration of chloride ions at constant ionic strength (Table III); this dependence is linear with the slope -1 . From the temperature dependence of the rate constants the influence of ionic strength and concentration of Cl^- ions on activation parameters was obtained (Table I). At a sufficiently high concentration of Cl^-

ions (about 1.5M) the k_2 value becomes independent of ionic strength in the interval $\mu = 1.5-2.5$.

After the reaction in solution was finished, the reaction products were determined quantitatively in accord with the overall equation

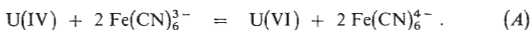


TABLE I
Dependence of Activation Parameters on Ionic Strength and Concentration of Chloride Ions

I	Cl^- M	ΔH^\ddagger kcal mol $^{-1}$	ΔS^\ddagger cal K $^{-1}$ mol $^{-1}$
1.5	0	22.6 \pm 0.9	+19.7 \pm 1.8
1.5	1.46	22.2 \pm 0.8	+16.8 \pm 1.6
1.0	0	22.2 \pm 0.9	+19.4 \pm 2.0

TABLE II
Dependence of Rate Constant on Ionic Strength
 $5 \cdot 10^{-4}\text{M-U(IV)} + 10^{-3}\text{M-K}_3\text{Fe(CN)}_6 + 1\text{M-HClO}_4$, 25°C.

I	1.0	2.0	3.0
k , s $^{-1}$ mol $^{-1}$ l	5.57	3.2	1.97

TABLE III
Dependence of Rate Constant on Concentration of Chloride Ions
 $5 \cdot 10^{-4}\text{M-U(IV)} + 10^{-3}\text{M-K}_3\text{Fe(CN)}_6 + 1\text{M-HClO}_4$, $I = 1.5$, 25°C.

Cl^- , M	0	0.56	0.96	1.46
k , s $^{-1}$ mol $^{-1}$ l	3.2	2.56	2.19	1.76

DISCUSSION

The influence of H_3O^+ ions on the measured rate constant can be explained on the assumption that U(IV) reacts in the form of UOH^{3+} ions which are formed by hydrolysis:



Since the hydrolysis proceeds rapidly, the observed rate of oxidation of U(IV) by ferricyanide ions can be expressed as

$$-d[\text{Fe}(\text{CN})_6^{3-}]/dt = 2k_0[\text{UOH}^{3+}][\text{Fe}(\text{CN})_6^{3-}]. \quad (5)$$

Introducing the equilibrium constant of hydrolysis

$$K = [\text{UOH}^{3+}][\text{H}_3\text{O}^+]/[\text{U}^{4+}] \quad (6)$$

and the analytical concentration of U(IV) ions

$$[\text{U(IV)}] = [\text{U}^{4+}] + [\text{UOH}^{3+}] \quad (7)$$

we can write the rate equation in the absence of Cl^- in the form

$$-d[\text{Fe}(\text{CN})_6^{3-}]/dt = 2k_0K[\text{Fe}(\text{CN})_6^{3-}][\text{U(IV)}]/(K + [\text{H}_3\text{O}^+]). \quad (8)$$

By comparing this result with Eq. (3) we obtain

$$k_2 = k_0K/(K + [\text{H}_3\text{O}^+]), \quad (9)$$

or

$$1/k_2 = 1/k_0 + [\text{H}_3\text{O}^+]/k_0K, \quad (10)$$

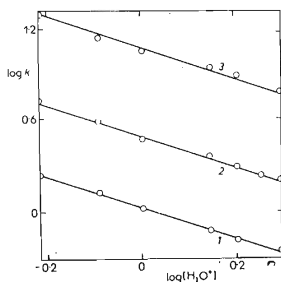


FIG. 1

Dependence of Rate Constant on Concentration of Hydrogen Ions

$5 \cdot 10^{-4}\text{M-U(IV)} + 10^{-3}\text{M-K}_3\text{Fe}(\text{CN})_6$,
I 2.0, 1 15°C; 2 25°C; 3 40°C.

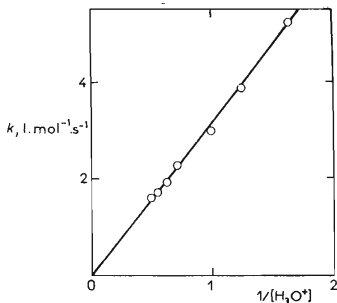


FIG. 2

Dependence of Rate Constant on Reciprocal Concentration of Hydrogen Ions

$5 \cdot 10^{-4}\text{M-U(IV)} + 10^{-3}\text{M-K}_3\text{Fe}(\text{CN})_6$,
I 2.0, 25°C.

which can be used in determining the true rate constant k_0 and the hydrolytic constant K . From Eq. (10) and from the dependence of the measured rate constant on concentration of hydrogen ions at various temperatures, the thermodynamic quantities of the hydrolytic equilibrium (Table IV) and activation parameters of the elementary redox reaction (Table V) were determined. In Table IV our data are compared with those of other authors^{2,5,6} found by independent methods; the agreement is good showing the correctness of the assumed mechanism according to which the elementary reaction step is the reaction between ferricyanide and UOH^{3+} ions.

In the case of a parallel reaction of U^{4+} besides UOH^{3+} ions with ferricyanide, the dependence of the rate constant on concentration of hydrogen ions should be given by

$$k_2 = k_4 + k_3 K / [\text{H}_3\text{O}^+], \quad (11)$$

where k_3 and k_4 denote rate constants of the reaction between ferricyanide and UOH^{3+} or U^{4+} ions, respectively. However, the dependence of k_2 on $1/[\text{H}_3\text{O}^+]$ is a straight line passing through the origin of coordinates (Fig. 2) in accord with Eq. (9) for $[\text{H}_3\text{O}^+] \gg K$ and not with (11).

Activation parameters of the elementary step (Table V) are in good agreement with those for reactions of a similar type⁷. It is surprising that the activation entropy is

TABLE IV
Thermodynamic Constants of Hydrolysis $\text{U}^{4+} + \text{H}_2\text{O} = \text{UOH}^{3+} + \text{H}^+$

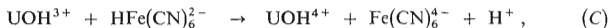
$K_{25^\circ\text{C}}$	ΔG^0 kcal mol ⁻¹	ΔH^0 kcal mol ⁻¹	ΔS^0 cal . K ⁻¹ mol ⁻¹	Cit.
0.039 (I 2.0)	1.92	11.8 ± 0.5	+33 ± 1.3	this work
0.075 (I 0.19)	1.532	10.7 ± 1	+31	2
0.05 (I 0.19)		11.7	+36	6
		11.0		5

TABLE V
Activation Parameters of Elementary Redox Reaction

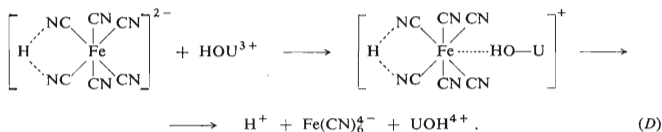
T, K	$k_0, \text{s}^{-1} \text{mol}^{-1} \text{l}$	$\Delta H^\ddagger, \text{kcal mol}^{-1}$	$\Delta S^\ddagger, \text{cal K}^{-1} \text{mol}^{-1}$
288	53	5.08 ± 0.6	-32.9 ± 1.8
298	81	—	—
313	118	—	—

negative, whereas in the case of an interaction between oppositely charged ions it should be positive. Similar discrepancies in some redox reactions of U(IV) ions were pointed out by Newton and Rabideau⁷ who attributed them to a large difference in ionic radii of both reactants and to participation of ClO_4^- ions in activated complex.

The elementary reaction step can be written as



since in the presence of perchloric acid in concentrations 0.6M or more the prevailing form of ferricyanide ions is $\text{HFe}(\text{CN})_6^{2-}$ with respect to $\text{p}K_A = 1.4$ (ref.⁸). This is more reactive owing to a polarization effect of the H^+ ion bound to the CN^- ligand. The polarization effect can strongly influence the geometry of the coordination sphere and promote the formation of a OH bridge bond between both reactants in an activated complex according to



The scheme (D) shows the first reaction step, which is slow and rate-determining, and the subsequent oxidation of U(V) ions by ferricyanide as a rapid step. The polarization effect of a proton on the coordination sphere of ferricyanide in its reaction with iodide in acid medium was pointed out by Indelli and Guaraldi⁹.

The influence of ionic strength on the rate constant corresponds roughly to the Bjerrum equation; deviations may be due to a high ionic strength and to high charges of both reactants.

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