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The Catalytic Action of Fe(III) in the U(IV)-U(VI) Electron Exchange Reaction

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The catalytic action of ferric ions in the U(IV)–U(VI) electron exchange reaction has been studied in the presence of a high concentration of hydrochloric acid. The exchange rate is found to be accelerated by the addition of ferric ions; the observed rate law is given by:

$$R = k_0[\mathrm{U(IV)}][\mathrm{U(VI)}] + k_c[\mathrm{Fe(III)}]_0\sqrt{[\mathrm{U(IV)}][\mathrm{U(VI)}]}$$

An activation energy of 19.7 kcal/mol was calculated for the iron-catalyzed reaction in the U(IV)–U(VI) electron exchange reaction. This value is much smaller than that of 32.2 kcal/mol, which was found in the non-catalytic reaction. The kinetics and equilibrium of the reaction between Fe(III) and U(IV) have also been studied in order to investigate in detail the mechanism of the catalytic reaction. A one-electron-transfer mechanism producing U(V) as an intermediate is estimated from the rate law and supported by the kinetics and equilibrium studies of the Fe(III)–U(IV) reaction.

In the earlier papers dealing with the electron exchange reaction between U(IV) and U(VI) in concentrated hydrochloric acid,[1–4)] it was shown that the rate of the electron exchange reaction (1) markedly increased with the acidity;

$$^{235}\mathrm{U(IV)} + {}^{238}\mathrm{U(VI)} \rightleftarrows {}^{238}\mathrm{U(IV)} + {}^{235}\mathrm{U(VI)} \qquad (1)$$

The present investigation was undertaken in order to determine the electron exchange rate between U(IV) and U(VI) in the presence of the smallest amount of Fe(III) and in order to observe the catalytic action of Fe(III).

Experimental

All of the chemicals used in this work were analytical reagent grade. The preparation and analysis of materials for the exchange reaction and the procedure in the kinetic experiment have been described in detail elsewhere.[2,3)] The concentration of the Fe(III) stock solution was standardized for the potassium dichromate solution by passing an aliquot through a column of zinc amalgam. The desired concentrations of U(IV), U(VI), Fe(III), and hydrogen ions were obtained by adding appropriate amounts of hydrochloric acid and triply-distilled water. An aqueous solution of Fe(III) has an intense absorption maximum (*i.e.*, a molar extinction coefficient of 3.5×10^3 in 8M HCl) at 370 nm, whilst a negligibly small absorption and a weak absorption were observed at this wavelength in the solutions of Fe(II) and U(IV) and in U(VI) respectively. Therefore, the spectrophotometric determination of Fe(III) in the reaction mixtures was performed at 370 nm, using as a reference solution U(VI) which has the same concentration of U(VI) as the reaction mixtures. The spectrophotometric measurement was carried out by using a Shimadzu-50L recording spectrophotometer. The cell used for the measurement was filled with nitrogen gas and hermetically sealed to prevent the air oxidation of U(IV) and Fe(II). The electron exchange rate was measured by a mass-spectrometric analysis of the uranium isotope in U(VI).[2,3)]

Results and Discussion

Kinetics and Equiliblium of the Reaction between U(IV) and Fe(III). Betts studied the kinetics of the oxidation of U(IV) by Fe(III) at a low acidity[5)] and showed that the reaction proceeded *via* the following two steps:

$$\mathrm{U(IV)} + \mathrm{Fe(III)} \xrightarrow{k_2} \mathrm{U(V)} + \mathrm{Fe(II)} \qquad (2)$$

$$\mathrm{U(V)} + \mathrm{Fe(III)} \xrightarrow{k_3} \mathrm{U(VI)} + \mathrm{Fe(II)} \qquad (3)$$

Reaction (2) was found to be the rate-determining step, with a rate constant of 12.3 $\mathrm{M^{-1}\,s^{-1}}$ in 1M HCl at 24 °C.

In an attempt to gain a better understanding of the interaction between U(IV) and Fe(III), several investigations have been conducted in our laboratory in concentrated hydrochloric acid solutions. Since the concentration of U(IV), [U(IV)], was large enough in the kinetic run compared with the Fe(III) concentration, [Fe(III)], [U(IV)] may be regarded as constant during the reaction. If Reaction (2) is the rate-determining step, the rate law may be written as a first-order rate equation with respect to [Fe(III)]:

$$\ln\{[\mathrm{Fe(III)}]/[\mathrm{Fe(III)}]_0\} = -2k_2[\mathrm{U(IV)}] \qquad (4)$$

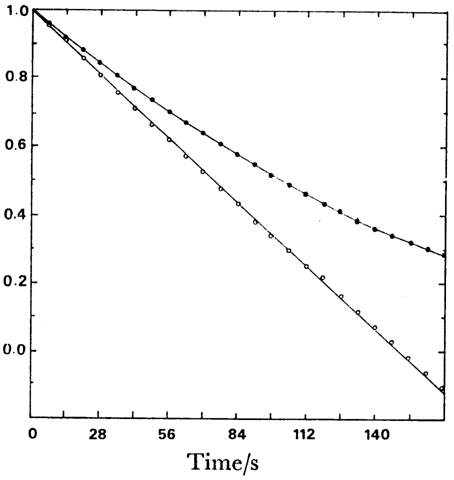

Fig. 1. Typical kinetic run for the oxidation of U(IV) by Fe(III) at 25 °C in 8 M HCl solution.
●: log {[Fe(III)]/[Fe(III)]$_0$} *vs.* time, *t*
○: Left-hand side of Eq. (7) *vs.* time, *t*
[Fe(III)]$_0$=2.9×10^{-4} M, [U(IV)]=1.88×10^{-2} M

where $[Fe(III)]_0$ denotes the initial concentration of Fe(III). As is shown in Fig. 1, a plot of $\log\{[Fe(III)]/ Fe(III)]_0\}$ against time, t, indicates a gradual departure from linearity. This fact suggests that the above-mentioned mechanism was unsuccessful under these conditions and leads us to assume that Reaction (2) is reversible:

$$U(IV) + Fe(III) \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} U(V) + Fe(II) \qquad (2')$$

Therefore, we may now write the following differential equation:

$$-\frac{d[Fe(III)]}{dt} = k_2[U(IV)][Fe(III)] - k_{-2}[U(V)][Fe(II)] + k_3[U(V)][Fe(III)] \qquad (5)$$

The application of a steady-state approximation to [U(V)] gives:

$$[U(V)] = \frac{k_2[Fe(III)][U(IV)]}{k_{-2}[Fe(II)]+k_3[Fe(III)]} \qquad (6)$$

The substitution of Eq. (6) into Eq. (5) and integration yields:

$$\log\left(\frac{[Fe(III)]}{[Fe(III)]_0}\right)-\frac{1}{2.303(k_3/k_{-2}-1)}\left(\frac{[Fe(III)]_0}{[Fe(III)]}-1\right) = -\frac{2k_2[U(IV)]}{2.303(1-k_{-2}/k_3)}t \qquad (7)$$

Although the values of k_2, k_{-2}, and k_3 in Eq. (7) are not known, the left-hand side of Eq. (7) can be calculated for an arbitrary value of k_3/k_{-2}. If the assumptions are valid, a plot of the value of the left-hand side in Eq. (7) against t should give a straight line for some value of k_3/k_{-2}. As may be seen in Fig. 1, a straight line was obtained by introducing the value of $k_3/k_{-2}=5.83$, which was computed by the least-square method. From the slope, k_2 was calculated at $0.32\ M^{-1}\ s^{-1}$. It should be noted that the linear correlation was kept, even when U(VI) had previously been added to the reaction mixture, and that the value of k_2 was independent of the U(VI) concentration. This fact reveals that the backward reaction in Eq. (3) is so slow that it makes no appreciable contribution to Eq. (7).

The value of k_2 obtained in 8M HCl is much smaller than that of $12.3\ M^{-1}\ s^{-1}$ which was reported by Betts in 1M HCl. Some experiments were made in an 8M $HClO_4$ solution in order to investigate why the rate is reduced in 8M HCl as compared with that in 1M HCl. Unlike in 8M HCl, a plot of $\log\{[Fe(III)]/ Fe(III)]_0\}$ *vs.* t gave a straight line under the conditions of $[U(IV)]=7.7\times10^{-3}$ M, $[Fe(III)]_0=3.8\times10^{-4}$ M and 8M $HClO_4$, and a much larger value of $2.4\ M^{-1}\ s^{-1}$ was obtained for k_2. Although this value is still smaller than that in 1M HCl, the effect of the hydrogen ion itself on the rate appears to be not very large, since the hydrolyzed species of U(IV) is more reactive with Fe(III) than U^{4+} at a low acidity.[12] Therefore, the high concentration of chloride ions seems to play a major role in reducing the reaction rate in 8M HCl. This is consistent with the findings in previous studies[13,14] that U(IV) is stabilized by forming a chloro complex in concentrated hydrochloric acid and that the oxidation rate by molecular oxygen is very slow compared with that in low acid concentrations. In addition, the redox potential between Fe(III) and Fe(II) may be changed in the presence of a high concentration of chloride ions. This change would influence the rate of the reaction between U(IV) and Fe(III) and would also play an important role in the mechanism where the reaction does not proceed by a simple first order with respect to Fe(III).

In the course of a kinetic study of the reaction between U(IV) and Fe(III), it has become apparent that the reduction of Fe(III) by U(IV) did not proceed to completion, no matter how large an excess of U(IV) was present. This can be seen in Fig. 2, where the absorption spectra were measured after the reaction between U(IV) and Fe(III) had reached equilibrium. The maximum peak at about 370 nm shows that trace amounts of Fe(III) are able to exist under the conditions mentioned above. The equilibrium concentration of Fe(III), $[Fe(III)]_{eq}$,* was estimated from the

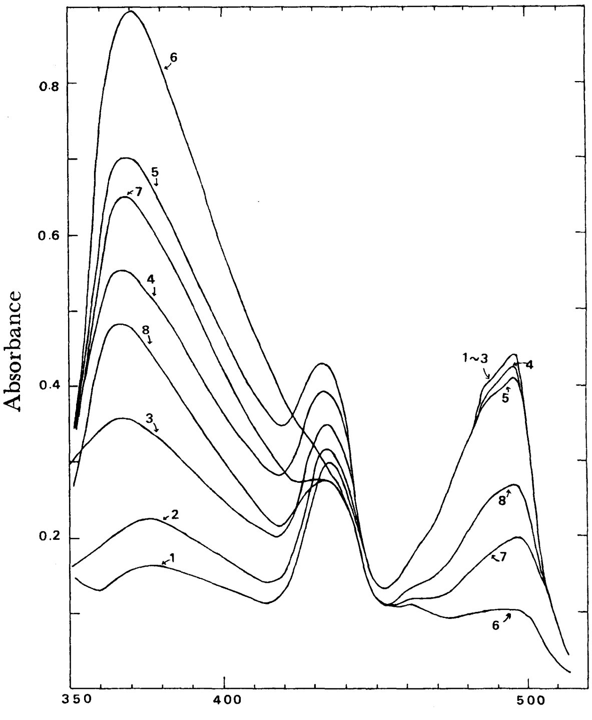

Fig. 2. Absorption spectra in the solution including Fe(III), Fe(II), U(IV), and U(VI) in 8 M HCl at 25 °C.

As reference solution, U(VI) which was the same concentration as in sample solution was used.

$[Fe(III)]_0$ is: (1) 1.40×10^{-3} M, (2) 1.96×10^{-3} M, (3) 2.80×10^{-3} M, (4) 4.20×10^{-3} M, (5) 5.60×10^{-3} M, while [U(IV)] and [U(VI)] are kept constant at 1.9×10^{-2} M and 2.1×10^{-2} M respectively.

[U(IV)] is: (6) 3.71×10^{-3} M, (7) 7.72×10^{-3} M, (8) 1.09×10^{-3} M, while $[Fe(III)]_0$ and [U(VI)] are kept constant at 3.6×10^{-3} M and 1.6×10^{-2} M respectively.

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* In the equations from (9) to (16), [ ] shows the equilibrium concentrations. However, in order to distinguish the equilibrium concentration of Fe(III) from the time-dependent concentration, [Fe(III)], in Eq. (7) or Fig. 1, inferior letters, eq, will be used, as in $[Fe(III)]_{eq}$.

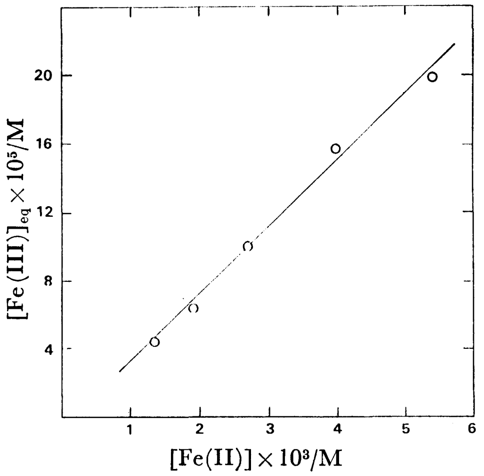

Fig. 3. Plot of $[Fe(III)]_{eq}$ *vs.* [Fe(II)] in Fe(III), Fe(II), U(IV), and U(VI) mixture.
[U(IV)] and [U(VI)] are kept constant at 1.8×10^{-2} M and 2.2×10^{-2} M respectively.

absorbance at this wavelength and was found to be associated with $[Fe(III)]_0$ and [U(IV)]. In Fig. 3, $[Fe(III)]_{eq}$ is plotted against [Fe(II)], which was calculated from the difference between $[Fe(III)]_0$ and $[Fe(III)]_{eq}$; a linear relationship is obtained. This might be explained stoichiometrically by the following reaction:

$$U(IV) + 2Fe(III) = U(VI) + 2Fe(II) \qquad (8)$$

If these species are in equilibrium, the equilibrium constant, K, is given by:

$$K = \frac{[U(VI)][Fe(II)]^2}{[U(IV)][Fe(III)]^2_{eq}} \qquad (9)$$

or

$$[Fe(III)]_{eq} = \frac{1}{\sqrt{K}}[Fe(II)]\sqrt{\frac{[U(VI)]}{[U(IV)]}} \qquad (10)$$

As is shown in Fig, 4, the concentration of Fe(III) yields a stright line when plotted as a function of $1/\sqrt{[U(IV)]}$, keeping the value of $[Fe(III)]_0$ constant; the intercept of the straight line is found to be 0, within the limits of experimental error. These results are evidence in support of Eq. (10). Unfortunately, the relationship between $[Fe(III)]_{eq}$ and [U(VI)] could not be experimentally examined, because Fe(III) seems to interact with U(VI) and the absorption peak of Fe(III) shifts slightly depending upon the U(VI) concentration. However, there seems no doubt that Eq. (10) can be used for a solution containing Fe(III), Fe(II), U(IV), and U(VI). The values of $\sqrt{K}$ calculated from Eq. (10) are listed in Table 1, with the concentrations of these species.

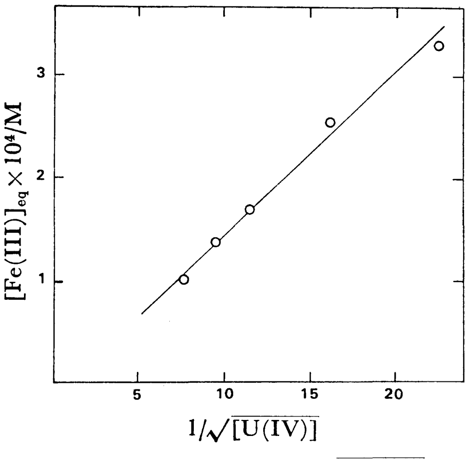

Fig. 4. Plot of $[Fe(III)]_{eq}$ *vs.* $1/\sqrt{[U(IV)]}$ in Fe(III), Fe(II), U(IV) and U(VI) mixture.
$[Fe(III)]_0$ and [U(VI)] are kept constant at 3.6×10^{-3} M and 1.6×10^{-2} M.

TABLE 1. EQUILIBRIUM CONCENTRATIONS AND EQUILIBRIUM CONSTANT IN Fe(III), Fe(II), U(IV), AND U(VI) MIXTURE AT 25 °C IN 8 M HCl SOLUTION

$[Fe(III)]_0$ $\times 10^3$ M	$[Fe(III)]_{eq}$ $\times 10^4$ M	[Fe(II)] $\times 10^3$ M	[U(IV)] $\times 10^2$ M	[U(VI)] $\times 10^2$ M	$\sqrt{K}$
5.60	1.99	5.40	1.73	2.27	31.2
4.20	1.57	4.04	1.80	2.20	28.5
2.80	1.00	2.70	1.86	2.14	29.0
1.96	0.63	1.90	1.90	2.10	31.6
1.40	0.44	1.36	1.93	2.07	32.0
3.63	3.30	3.30	0.195	1.64	30.4
3.63	2.54	3.38	0.371	1.63	29.3
3.63	1.74	3.46	0.727	1.63	31.2
3.63	1.37	3.49	1.09	1.63	32.9
3.63	1.00	3.53	1.62	1.62	37.2
1.13	0.83	1.05	0.308	1.80	30.7
2.26	1.73	2.09	0.255	1.88	31.9
				Average	31.3

TABLE 2. RATE CONSTANTS FOR THE Fe(III)-CATALYZED U(IV)-U(VI) ELECTRON EXCHANGE REACTION AT 30 °C IN 8M HCl SOLUTION

[U(IV)] $\times 10^2$ M	[U(VI)] $\times 10^2$ M	$[Fe(III)]_0$ $\times 10^5$ M	k $\times 10^5$ M^{-1} s^{-1}	k_C $\times 10^2$ M^{-1} s^{-1}
2.79	2.59	0	3.0	—
2.79	2.59	1.54	4.5	2.6_2
2.79	2.59	4.64	6.7	2.1_3
2.79	2.59	9.25	10.7	2.2_3
			Average	2.3_3

U(IV)–U(VI) Electron Exchange Reaction in the Presence of Fe(III). The U(IV)–U(VI) electron exchange reaction in the presence of Fe(III) was measured by the mass-spectrometric analysis described before, and the results were treated by using the McKay equation.[6] The rate constants in the presence of Fe(III) are listed in Table 2, along with various $[Fe(III)]_0$ values. It can be seen from Table 2 that the rate constants increase with $[Fe(III)]_0$. A plot of the rate constant, k, *versus* $[Fe(III)]_0$ yields a straight line (Fig. 5). The intercept of the line should give the rate constant in the absence of Fe(III); it agrees very closely with the value of 3.0×10^{-5} M^{-1} s^{-1} obtained in the previous paper. In Fig. 6, a plot of k *versus* $1/\sqrt{[U(VI)]}$ is shown under the conditions of constant $[Fe(III)]_0$ and [U(IV)] values; it gives a straight line. These results lead to the following rate law, although the [U(IV)] dependence on the rate has not yet been shown:

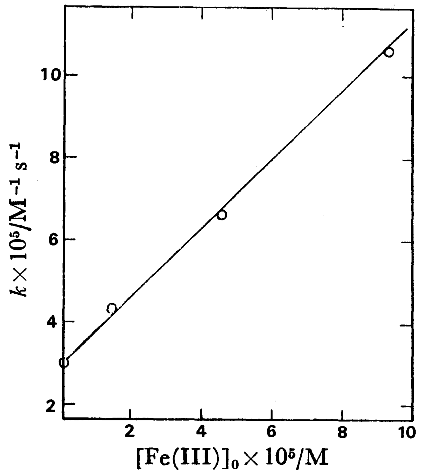

Fig. 5. Rate constant, k, as a function of $[\text{Fe(III)}]_0$ at 30 °C in 8 M HCl solution.
$[\text{U(IV)}]=2.79\times10^{-2}$ M, $[\text{U(VI)}]=2.59\times10^{-2}$ M.

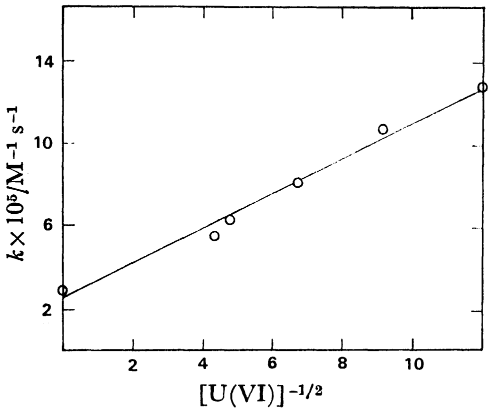

Fig. 6. Plot of k *vs.* $[\text{U(VI)}]^{-1/2}$.

TABLE 3. RATE CONSTANTS

[U(IV)] $\times10^2$ M	[U(VI)] $\times10^2$ M	[Fe(III)]$_0$ $\times10^5$ M	k $\times10^5$ M^{-1} s^{-1}	k_c $\times10^2$ M^{-1} s^{-1}
2.78	2.59	6.30	8.3	2.2_8
1.67	1.56	6.30	12.0	2.3_0

$$k = k_0 + \frac{k_c[\text{Fe(III)}]_0}{\sqrt{[\text{U(IV)}][\text{U(VI)}]}} \tag{11}$$

where k_0 and k represent the rate constants for the noncatalytic and catalytic paths respectively. In Table 3, the rate constants obtained from the kinetic runs under two different conditions are listed. As may be seen in Table 3, the two values of k_c are nearly equal and are in good agreement with those listed in Table 2. It thus appears that the kinetic order with respect to [U(IV)] in Eq. (11) well explains the experimental results.

The temperature dependence of k, ranging from 20 to 70 °C, is shown in Fig. 7. As may be seen in Fig. 7, the plots show a slight deviation from the linear relationship in the range of low temperatures. This result also implies that the U(IV)–U(VI) electron exchange, in which the least amount of Fe(III) is involved, consists of at least two reaction paths. A graph of

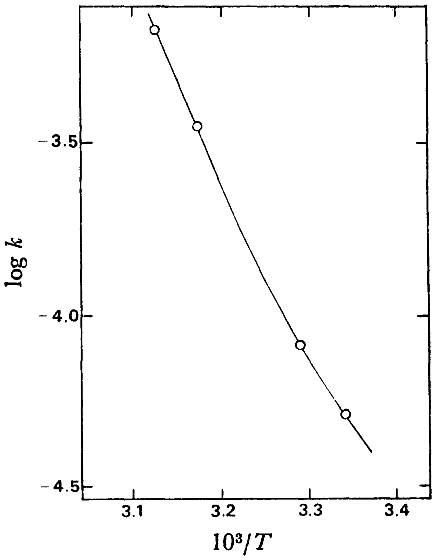

Fig. 7. Temperature dependence of k.

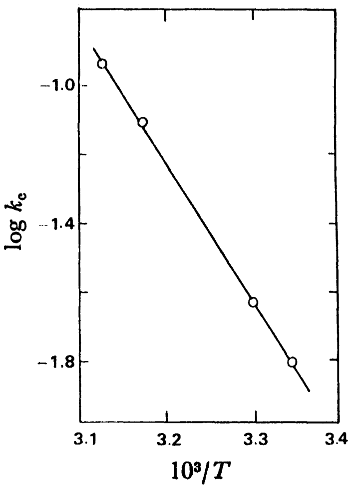

Fig. 8. Temperature dependence of k_c.

log k_c *versus* $1/T$ gives a straight line (Fig. 8), and the activation energy of 19.7 kcal/mol is calculated for the catalytic reaction. This value is much smaller than that of the non-catalytic reaction, that is, 32.2 kcal/mol.[2)]

From the results mentioned above, the most probable mechanism for a catalytic reaction is seemed to be a one-electron transfer reaction through the formation of U(V). The initiation step might be the oxidation of U(IV) by Fe(III) (k_2 path), followed by a faster reaction (k_3 path):

$$\text{U(IV)} + \text{Fe(III)} \rightleftharpoons \text{U(V)} + \text{Fe(II)} \tag{2}$$

$$\text{U(V)} + \text{Fe(III)} \rightleftharpoons \text{U(VI)} + \text{Fe(II)} \tag{3}$$

Gordon and Taube studied the electron exchange reaction between U(V) and U(VI):

$$\text{U(V)} + \text{U(VI)} \rightleftharpoons \text{U(VI)} + \text{U(V)} \tag{12}$$

and estimated that the rate constant was 52.0 M^{-1} s^{-1} in a 1.0 M $HClO_4$ solution.[7)] This value is much larger than that of k_2 (0.32 M^{-1} s^{-1}) obtained in a concentrated hydrochloric acid solution, as has been described above. Therefore, it would be reasonable to assume that Reaction (12) proceeds much faster than Reaction (2), so that the electron exchange (12) occurs immediately after the formation of U(V) by Reaction (2) (k_2 path).

On the basis of this assumption, the rate law for the Fe(III)-catalyzed reaction may be given by:

$$R_c = k_2[\mathrm{U(IV)}][\mathrm{Fe(III)}] \tag{13}$$

where R_c is the rate of the Fe(III)-catalyzed reaction. The substitution of Eq. (10) into Eq. (13) gives:

$$R_c = \frac{k_2}{\sqrt{K}}[\mathrm{Fe(II)}]\sqrt{[\mathrm{U(IV)}][\mathrm{U(VI)}]} \tag{14}$$

Hence, the overall exchange rate, R, and the rate constant, k, may be expressed by:

$$R = k_0[\mathrm{U(IV)}][\mathrm{U(VI)}] + \frac{k_2}{\sqrt{K}}[\mathrm{Fe(II)}]\sqrt{[\mathrm{U(IV)}][\mathrm{U(VI)}]} \tag{15}$$

and:

$$k = k_0 + \frac{k_2}{\sqrt{K}}\frac{[\mathrm{Fe(II)}]}{\sqrt{[\mathrm{U(IV)}][\mathrm{U(VI)}]}} \tag{16}$$

The disproportionation of U(V) may make some contribution to the U(IV)-U(VI) electron exchange reaction.[8-11]

$$2\mathrm{U(V)} \rightleftharpoons \mathrm{U(IV)} + \mathrm{U(VI)} \tag{17}$$

The rate law, however, is valid even if the disproportionation is faster than Reaction (12). In the course of a kinetic study of the oxidation of U(IV) by Fe(III), it may be clear that the disproportionation of U(V) is slow compared with Reaction (3) (k_3 path). This is because, if the disproportionation of U(V) were very fast, the reaction between U(IV) and Fe(III) would proceed simply by first-order with [Fe(III)], a plot of $\log\{[\mathrm{Fe(III)}]/[\mathrm{Fe(III)}]_0\}$ against t should give a straight line, and the linear relationship with respect to Eq. (7) as in Fig. 1 would not be obtained.

Since $[\mathrm{Fe(III)}]_0$ in Eq. (11) is nearly equal to [Fe(II)], as may be seen in Table 1, Eq. (16) is completely consistent with Eq. (11). This leads to the following relation:

$$k_c = k_2/\sqrt{K} \tag{18}$$

From the Fe(III)-catalyzed U(IV)-U(VI) electron exchange reaction, k_c can be obtained experimentally as $1.3\times10^{-2}\ \mathrm{M^{-1}\,s^{-1}}$ at 25 °C. On the other hand, k_2 and $\sqrt{K}$ were $0.32\ \mathrm{M^{-1}\,s^{-1}}$ and 31.3 respectively at 25 °C, as is shown in Fig. 1 and Table 1. From these results, $k_2/\sqrt{K}$ was calculated to be $1.0\times10^{-2}\ \mathrm{M^{-1}\,s^{-1}}$. The $k_2/\sqrt{K}$ ratio gives the estimated rate constant for the Fe(III)-catalyzed U(IV)-U(VI) electron exchange reaction, assuming the rate law (16) and assuming that the value of $1.0\times10^{-2}\ \mathrm{M^{-1}\,s^{-1}}$ is in satisfactory agreement, within the limits of experimental error, with that of $1.3\times10^{-2}\ \mathrm{M^{-1}\,s^{-1}}$ obtained by the direct measurement of the U(IV)-U(VI) electron exchange reaction. This final result supports very strongly the mechanism we have discussed in this paper.

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