Studies on the kinetics and mechanism of complex formation in the reactions of ferron with iron(III) and uranium(VI)

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The equilibria and kinetics of the reactions of ferron (7-iodo-8-hydroxyquinidine-5-sulphonic acid) with iron(III) and uranium(VI) have been followed by stopped flow spectrophotometry under the conditions of mono-complex formation. The equilibrium constants obtained spectrophotometrically have been compared with those obtained from kinetic studies. In the case of iron(III), in the acidity range, \([H^+] = (2.8-10.0) \times 10^{-7}\) mol dm\(^{-3}\), among the different possible reaction pathways, the reaction has been found to proceed mainly through the interaction of \(Fe(OH)(aq)^{2+}\) and partially deprotonated form \((LH^-)\) of the ligand. In the case of uranium(VI), in the acidity range, \([H^+] = (2.5-25.0) \times 10^{-7}\) mol dm\(^{-3}\), a dual path mechanism involving \(UO_2(aq)^{2+}\) and \(UO_2(OH)(aq)^{+}\) and the partially deprotonated \((LH^-)\) form of the ligand is consistent with the observations. The results in each case are in agreement with the Eigen mechanism and the characteristic water exchange rates have been obtained in each case, as a rough estimate, from the experimental data. Activation parameters \((\Delta H^*\) and \(\Delta S^*)\) for each path have been determined and compared.

Though studies on kinetics and mechanism of ligand substitution reaction at iron(III) centre have received much attention\(^1-^4\) such studies at uranium(VI) centre have received so far very little attention\(^8-^9\). In aqueous solution, uranium(VI) predominantly exists as an oxo-ion, \(UO_2^{2+}\) in which the axial positions are extremely inert\(^9\) but the equatorial positions are fairly labile and ligand substitution occurs preferably at the equatorial positions\(^5-^8\). Both \(UO_2(aq)^{2+}\) and \(Fe(aq)^{3+}\) are prone to hydrolysis\(^15\) and both the hydrolytic products, i.e. \(M(OH)(aq)^{(n-1)+}\) and unhydrolysed species, \(M(aq)^{n+}\), may participate kinetically in ligand substitution process. In such cases, if the ligand can participate in protolytic equilibria, then the total number of possible reactive species increases largely. Consequently, the number of possible reaction pathways involving all the available species gets proliferated and the kinetic interpretation may get complicated\(^1,^6,^17\). In fact, many reaction paths (for example, \(M(aq)^{n+} + L\) and \(M(OH)(aq)^{(n-1)+} + LH\)) become kinetically indistinguishable due to proton ambiguity. In such cases, it is necessary to choose between the alternatives by examining\(^1,^6,^17\) reasonableness of the rate constants. The present paper discusses and compares the relative importance of different paths from the viewpoint of kinetics at iron(III) (d-block element) and uranium(VI) (f-block element) centres in the reaction with the title ligand. In fact, such a comparison of kinetic behaviour between the d-block and f-block metal ions is scanty in literature.

Materials and Methods

Standard stock solutions of iron(III) perchlorate in perchloric acid media, sodium perchlorate and perchloric acid were prepared as described\(^4\) earlier. Standard stock solution of uranyl perchlorate was prepared as reported earlier\(^8\). The ligand (A.R., BDH) was used without further purification and weighed amounts were taken to prepare the solutions. All other chemicals used were of reagent grade. Doubly distilled water was used to prepare all the solutions.

Apparatus and procedure

The spectra of the freshly prepared complexes in solution were recorded using a Carl-Zeiss spectrophotometer (VSU-2P, Jena, Germany). The kinetic runs were carried out in a Canterbury model stopped-flow spectrophotometer (SF-3A, Hi-tech, UK) coupled with an oscilloscope (Advance Instruments OS 1000A) and a microprocessor (Apple-II) with the help of which the pseudo-
first order rate constants were calculated. The flow module of the SF-3A had arrangements for thermostating (±0.05°C) the reacting solutions and the observation cell of the flow module. Under the pseudo-first order conditions (\(T_M/T_L\geq 10\) where \(T_M\) and \(T_L\) are the total metal and ligand concentrations respectively), uranium(VI) forms a reddish yellow complex while iron(III) forms a light green complex with the title ligand in solution. For uranium(VI), the kinetic runs were recorded at 380 nm where the difference in absorbance between the complex and the starting materials is sufficiently high. For iron(III), the reaction was followed at the \(\lambda_{max}\) (625 nm) of the complex. For uranium(VI) system, the pH measurements were done with a Systronics (India) pH meter-335. From the pH meter readings, actual \([H^+]\) values were calculated from a calibration curve. Ionic strength was adjusted to 1.0 mol dm\(^{-3}\) (for iron(III) system) and 0.1 mol dm\(^{-3}\) (for uranium(VI) system) with an adequate amount of NaClO\(_4\).

Results and Discussion

Under the experimental conditions of kinetic studies: \(T_{Fe}=(2.0-5.0)\times 10^{-3}\) mol dm\(^{-3}\), \(T_L=2 \times 10^{-4}\) mol dm\(^{-3}\), \([H^+]=(2.8-10.0)\times 10^{-2}\) mol dm\(^{-3}\); \(T_u=(0.50-2.50)\times 10^{-1}\) mol dm\(^{-3}\), \(T_L=(0.50-1.00)\times 10^{-4}\) mol dm\(^{-3}\), \([H^+]=(2.5-25.0)\times 10^{-5}\) mol dm\(^{-3}\), from the known values of hydrolysis constant \((K_h)\) (ref. 15) of Fe(aq)\(^{3+}\) \((K_h=4.09 \times 10^{-5}\) at 40°C, \(I=1.0\) mol dm\(^{-3}\)) and UO\(_2\)(aq)\(^{3+}\) \((K_h=2.14 \times 10^{-5}\) at 25°C) and successive acid dissociation constants \(^{19}\) \((pK_{a(1)}=2.25, pK_{a(2)}=6.83\) at 25°C) of the ligand LH\(^{2+}\) the following protolytic equilibria of the reactants can be reasonably considered.

\[
M(aq)^{n+} \rightleftharpoons M(OH)(aq)^{n-1+} + H^+, \quad \text{(fast)} \quad \ldots \ (i)
\]

\[
LH^2+ \rightleftharpoons LH^- + H^+, \quad \text{(fast)} \quad \ldots \ (ii)
\]

For the formation of mono-complex, the following possible reactions along with the fast equilibria (i) and (ii) can be considered.

\[
M(aq)^{n+} + LH^2+ \rightleftharpoons ML^{(n-2)+} + 2H^+, \quad \left( Q = \frac{k_1}{K_{-1}} \right) \quad \ldots \ (iii)
\]

\[
M(OH)(aq)^{n-1+} + LH^2+ \rightleftharpoons (ML^{(n-2)+}) + H^+, \quad \left( Q = \frac{k_2}{K_{-2}} \right) \quad \ldots \ (iv)
\]

\[
M(aq)^{n+} + LH^- \rightleftharpoons ML^{(n-2)+} + H^+, \quad \left( Q = \frac{k_3}{K_{-3}} \right) \quad \ldots \ (v)
\]

\[
M(OH)(aq)^{n-1+} + LH^- \rightleftharpoons ML^{(n-2)+}, \quad \left( Q = \frac{k_4}{K_{-4}} \right) \quad \ldots \ (vi)
\]

Under the pseudo-first order conditions \((T_M/T_L\geq 10)\), the above possible reaction paths (iii-vi) along with the fast protolytic equilibria (i and ii) lead to Eq. (1)

\[
k_{obs} = \frac{T_M[H^+]}{[H^+]Q} + \frac{[H^+]Q}{K_{a(1)}[H^+] + K_h} \quad \ldots \ (1)
\]

where,

\[
P = k_1[H^+] + [k_2K_h + k_3K_{a(1)}] + k_4K_hK_{a(1)}[H^+]^{-1}
\]

Equation 1 on rearrangements gets reduced to Eqs (2) and (3)

\[
k_{obs} = \frac{k_1[H^+] + [k_2K_h + k_3K_{a(1)}] + k_4K_hK_{a(1)}[H^+]^{-1}}{B} \quad \ldots \ (2)
\]

where,

\[
B = \frac{T_M[H^+]}{[H^+]Q} + \frac{[H^+]Q}{K_{a(1)}[H^+] + K_h}
\]

or,

\[
k_{obs} = \frac{k_1[H^+]}{K_{a(1)}} + \left[ \frac{K_h}{K_{a(1)}} k_2 + k_3 \right][H^+] + k_4K_h \quad \ldots \ (3)
\]

where, \(B = \frac{BK_{a(1)}}{[H^+]Q}\).

At a fixed \([H^+]\), according to Eq. 1, the plots \(k_{obs}\) versus \(T_M\) are linear (Figs 1 and 2) with positive slopes and intercepts from which \(Q\) could be evaluated (Table 1) by using relationship (4),

\[
Q = \frac{\text{slope}}{\text{intercept}} \left[ [H^+]Q + K_{a(1)}[H^+] + K_h \right] \quad \ldots \ (4)
\]
The Q values could be evaluated from spectrophotometric equilibrium study. For the reactions (i-iii), we have the following relationship (5),

\[
\frac{1}{A - A_0} = \frac{[H^+]^2 [1 + K_a[H^+]] [1 + K_a[H^+]]}{T_M Q T_L \varepsilon l} + \frac{1}{T_L \varepsilon l} \quad \ldots \ldots (5)
\]

where A = absorbance of the reacting solution at equilibrium, \(A_0\) = absorbance of the solution under identical conditions at the same wavelength in the absence of the ligand, \(\varepsilon\) = molar extinction coefficient of the complex, \(l\) = path length of the cell.

Hence, from the linear plot of \(1/(A - A_0)\) versus \([H^+]^2/T_M\) (Fig. 3), Q values could be evaluated as follows.

\[
Q = \frac{\text{intercept}}{\text{slope}} [1 + K_a[H^+]][1 + K_a[H^+]]^{-1} \quad \ldots \ldots (6)
\]

The Q values obtained from kinetic studies (Eqs 1 and 4) and spectrophotometric studies (Eqs 5 and 6) are in good agreement (Table 1).

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**Table 1**—Thermodynamic parameters of the equilibrium constant of the mono-complex formation in the reactions of ferron with iron(III) and uranium(VI) (experimental conditions are given in the text and Figs 1, 2, and 3).

<table>
<thead>
<tr>
<th>Method of measurement</th>
<th>(Q/\text{mol dm}^{-3}), (for iron(III) system)</th>
<th>(10^2 Q/\text{mol dm}^{-3}) (for uranium(VI) system*)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>40°</td>
<td>45°</td>
</tr>
<tr>
<td>Spectrophotometric study</td>
<td>4.8 ± 0.1</td>
<td>6.0 ± 0.1</td>
</tr>
<tr>
<td>Kinetic study</td>
<td>5.0 ± 0.2</td>
<td>5.9 ± 0.1</td>
</tr>
<tr>
<td>(\Delta H^0) (kJ mol(^{-1}))</td>
<td>33.5 ± 7.0</td>
<td>33.5 ± 7.0</td>
</tr>
<tr>
<td>(\Delta S^0) (JK(^{-1}) mol(^{-1}))</td>
<td>133.5 ± 7.0</td>
<td>133.5 ± 7.0</td>
</tr>
</tbody>
</table>

*aQ = Q/Ka1;*  
*bObtained by using the average values of equilibrium constants.*
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Fig. 3—Spectrophotometric evaluation of the equilibrium constant in the reaction of ferron with iron(III) (Eq. 5). $T_{Fe} = (2.5-8.0) \times 10^{-3}$ mol dm$^{-3}$, $[H^+] = 0.15$ mol dm$^{-3}$, $T_I = 2.5 \times 10^{-4}$ mol dm$^{-3}$, $I = 1.0$ mol dm$^{-3}$, cell path length = 2.0 cm, $\lambda = 625$ nm, A (50°C), B (45°C) and C (40°C).

Fig. 4—Evaluation of rate constants in the reaction of ferron with iron (Eq. 2). $T_{Fe} = 5.0 \times 10^{-3}$ mol dm$^{-3}$, $T_I = 2.0 \times 10^{-4}$ mol dm$^{-3}$, $[H^+] = (0.02-0.10)$ mol dm$^{-3}$, $I = 1.0$ mol dm$^{-3}$, A (40°C), B (45°C), C (50°C).

Table 2—Kinetic parameters of complex formation in the reactions of ferron with iron(III) and uranium(VI). Experimental conditions are given in detail in Figs 4 and 5.

<table>
<thead>
<tr>
<th>System</th>
<th>Temp/°C</th>
<th>$10^{-4} k_3$ (dm$^3$ mol$^{-1}$ s$^{-1}$)</th>
<th>$10^{-4} k_4$ (dm$^3$ mol$^{-1}$ s$^{-1}$)</th>
<th>$10^{-4} k_{-4}$ (dm$^3$ mol$^{-1}$ s$^{-1}$)</th>
<th>$10 k_{ad}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uranium(VI)-ferron</td>
<td>20</td>
<td>4.68 ± 0.08</td>
<td>43.21 ± 0.35</td>
<td>9.67 ± 0.14</td>
<td>116.30 ± 2.20</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>6.40 ± 0.15</td>
<td>46.00 ± 0.50</td>
<td>11.70 ± 0.15</td>
<td>178.00 ± 2.60</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>8.81 ± 0.15</td>
<td>48.80 ± 0.50</td>
<td>14.10 ± 0.10</td>
<td>266.00 ± 2.50</td>
</tr>
<tr>
<td>$\Delta H^*$ (kJ mol$^{-1}$)</td>
<td>44.4 ± 2.2</td>
<td>6.6 ± 0.4</td>
<td>-63.2 ± 2.5</td>
<td>59.0 ± 3.4</td>
<td></td>
</tr>
<tr>
<td>$\Delta S^*$ (JK$^{-1}$ mol$^{-1}$)</td>
<td>-5.1 ± 0.6</td>
<td>-115.4 ± 5.4</td>
<td>-25.0 ± 1.5</td>
<td>-24.10 ± 2.0</td>
<td></td>
</tr>
<tr>
<td>Iron(III)-ferron</td>
<td>40</td>
<td>1.35 ± 0.08</td>
<td>0.76 ± 0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>2.00 ± 0.05</td>
<td>1.23 ± 0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>2.90 ± 0.10</td>
<td>1.93 ± 0.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta H^*$ (kJ mol$^{-1}$)</td>
<td>62.0 ± 3.0</td>
<td>76.7 ± 2.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta S^*$ (JK$^{-1}$ mol$^{-1}$)</td>
<td>30.5 ± 3.0</td>
<td>-24.10 ± 2.0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

By using the values of $Q$ and acid dissociation constants of LH$^+$, formation constant ($\beta_1$) of the mono-complex could be evaluated by using Eq. (7)

$$\beta_1 = \frac{Q}{K_{s(1)} K_{s(2)}} \quad \ldots (7)$$

For iron(III) system, thus, the estimated value ($\log \beta_1 = 9.45$ at 25°C) is in fairly good agreement with the reported value$^{20}$ ($\log \beta_1 = 9.45$ at 25°C). For uranium(VI) system, the estimated value is: $\log \beta_1 = 5.98$ at 25°C. It indicates that iron(III) forms stabler complex than uranium(VI).

For the iron(III) system, the plot of $k_{obs}/B$ versus $[H^+]^{-1}$ is linear (Fig. 4) passing through the origin. Hence, according to Eq. 2, all other reaction paths except path (vi) are kinetically non-existent. Thus Fe(OH)$^{2+}$ and the partially dissociated ligand, LH$^-$ are only kinetically important. The corresponding forward ($k_4$) and backward ($k_{-4}$) rate constants are evaluated along with their activation parameters (Table 2). According to Eigen mechanism$^{21}$ the overall rate constant ($k = k_{ex} K_{os}$) depends on the outer-sphere association constant ($K_{os}$) and the first order rate constant of water exchange ($k_{ex}$). In the present case, LH$^-$ form of the ligand is the reactive species in which the ne-
Table 5—Evaluation of rate constants in the reaction of ferron with uranium(VI) [Eq. 3]. $T_1 = 10^{-3}$ mol dm$^{-3}$, $T_2 = 10^{-4}$ mol dm$^{-3}$, $[H^+] = (0.25-2.50) \times 10^{-4}$ mol dm$^{-3}$, $I = 0.1$ mol dm$^{-1}$, A (20°C), B (25°C) and C (30°C).

The negative charge imparted by the $\text{SO}_3^-$ group remains at the remote site with respect to the binding sites. Hence, it is reasonable to consider that in the outer-sphere complex, mainly ion-dipole interaction exists and in such cases, $K_{\text{ex}}$ has been estimated as $\sim 0.2$ mol$^{-1}$ dm$^3$. Using this value, $k_{\text{ex}}$ becomes $2.0 \times 10^4$ s$^{-1}$ at 25°C which is within the range $(0.1-8.0) \times 10^4$ s$^{-1}$ found at 25°C for different types of ligands of quite different structures, binding sites and basicity. This observation is in conformity with the interchange dissociative ($I_d$) mechanism in the present case.

For the uranium(VI) system, the plots $k_{\text{obs}}/B_1$ versus $[H^+]$ are linear (Fig. 5) with positive slope $=(K_{\text{ex}}/K_{\text{ex}(1)}) \times k_2 + k_3$ and intercept $(= k_3 K_{\text{ex}})$. In comparison with Eq. 3, this indicates the nonexistence of the path (iii) from the standpoint of kinetics. From the intercept of the plot (Fig. 5), $k_3 = 11.7 \times 10^5$ mol$^{-1}$ dm$^3$ s$^{-1}$ at 25°C which could be evaluated without any ambiguity, but as $k_3$ (path iv) and $k_3$ (path v) have same hydrogen ion dependence, they suffer from proton ambiguities and thus they remain kinetically indistinguishable. Now considering the Eigen mechanism to operate at $\text{UO}_2(\text{OH})(\text{aq})^2^+$ centre in the $k_4$ path, the estimated water exchange rate constant becomes $6.0 \times 10^5$ s$^{-1}$ at 25°C which is close to the reported value $k_{\text{ex}} = 10^5$ s$^{-1}$ at $\text{UO}_2(\text{aq})^{2^+}$ centre. Here it is worth mentioning that for the f-block metal ion centres like uranium(VI) and cerium(IV), the reactivity of the hydroxo species and unhydrolysed species is not widely different. Unfortunately, the kinetic results at the mono-hydroxo centre of uranium(VI) are virtually unavailability in literature to generalise the conclusion. However, if the dissociative mechanism operates at $\text{UO}_2(\text{aq})^{2^+}$ centre, then operation of the same mechanism at the mono-hydroxo centre is not unlikely as in the case of iron(III) and cerium(IV). Now let us critically examine the relative contribution of $k_2$ and $k_3$ path to the observed slope (Fig. 5). For a representative set, we have:

$$\frac{K_{\text{ex}}}{K_{\text{ex}(1)}} k_2 + k_3 = 6.4 \times 10^4, \text{at } 25^\circ\text{C} \quad \ldots \ldots (8)$$

Now by considering the values of $K_{\text{ex}}$ (ref. 15) and $K_{\text{ex}(1)}$ (ref. 19) in the present case, we get $k_2/k_3 = 10^{-3}$ at 25°C. Hence, according to Eq. 8, the contribution of $k_2$ to the observed slope with respect to $k_3$ becomes significantly attributable for the condition: $k_2/k_3 < 10^{-3}$ which is unlikely, as it would lead to water exchange rate at $\text{UO}_2(\text{OH})(\text{aq})^+^+$ centre: $k_{\text{ex}} = 10^8$ s$^{-1}$ which is not possible (estimated $k_{\text{ex}} = 6 \times 10^5$ s$^{-1}$ from $k_4$ path). Thus, reasonably we can consider that the observed slope is mainly due to the $k_3$ path and the overall process goes through the paths (v) and (vi). From the evaluated $k_3$ values, according to the dissociative mechanism, the water exchange rate becomes ca. $3.2 \times 10^5$ (taking $K_{\text{ex}} = 0.2$ mol$^{-1}$ dm$^3$ for ion-dipole interaction). This estimated value is in good agreement with the reported value$^{12}$ and estimated values from kinetic data in the interaction of chromotropic acid and its derivatives, and 4-(2-pyridylazo) resorcinol. Thus for both the hydrolysed and unhydrolysed species of uranium(VI), dissociative ($D$) or interchange dissociative ($I_d$) mechanism can be argued. Here, it is worth mentioning that in $\text{UO}_2(\text{aq})^{2^+}$ and $\text{UO}_2(\text{OH})(\text{aq})^+$ the axial oxygens are extremely inert$^{12}$ and remain unaffected during the substitution process. In the limiting $S_\text{ex}1$ (or D) mechanism, the intermediate trigonal bipyramid species having $D_{3h}$ symmetry is unfavoured$^6$ from the standpoint of participation of uranyl $d$- or $f$-orbitals in bond formation. But, the dissociative interchange mechanism can operate.

In comparison with the interaction at iron(III) and uranium(VI), it appears that for iron(III), only the hydroxo-species is reactive ($I_d$ process) but for uranium(VI) both the hydrolysed and unhydrolysed species are almost equally reactive ($I_d$ process). In fact for iron(III), due to the enhanced reactivity$^{1,4}$ of the hydroxo-species i.e. $\text{Fe(OH)}(\text{aq})^{2^+}$ compared to the unhydrolysed one i.e. $\text{Fe}(\text{aq})^{2^+}$, very often the unhydrolysed species looses its kinetic importance. But for f-block cen-
tres like uranium(VI)\(^8\) and cerium(VI)\(^23\), no such difference in reactivity is observed. Besides, for iron(III), the relatively unreactive unhydrolysed species adopts\(^1\)\(^4\) a different mechanism which is probably an associative interchange \((I_\alpha)\) mechanism. In the \(k_4\) path, the higher rate constant for uranium(VI) compared to iron(III) may be accounted for its lower \(\Delta H^*\) values. In terms of rate constants, the lower equilibrium constant for uranium(VI) compared to that of iron(III) is due to higher backward rate constant \((k_{-4})\) for uranium(VI) system.

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