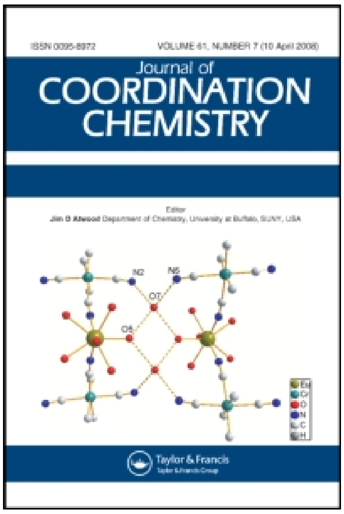

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THE OXIDATION OF URANIUM(IV) BY POLYVALENT METAL IONS. A LINEAR FREE-ENERGY CORRELATION

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The validity of application of a linear correlation to the kinetics of oxidation of uranium(IV) by multicharged metal ions in aqueous perchlorate media has been examined. The plot of ΔG^* versus ΔG° for most of these redox reactions was fairly linear with a slope slightly smaller than that required by the Marcus theory. This behaviour suggests that at least some of these reactions proceed via outer-sphere mechanism.\The variation in the structure of reactants in the rate-determining step, in particular quadrivalent uranium from the hydrated U^{4+} to the oxytype oxidation states UO_2^+ or UO_2^{2+}, was found to play a very important role in the reaction kinetics. Reaction mechanisms consistent with the empirical rate laws and the kinetic parameters were discussed.

Keywords: Oxidation kinetics, uranium, outer-sphere mechanism

1. INTRODUCTION

Studies involving oxidation–reduction reactions of actinides have a special interest since these cations are multiequivalent systems. A question of basic importance in connection with these multiequivalent inorganic reactants, is whether the oxidation process is proceeding by a direct two-electron-transfer process in a single step or by two successive one-electron changes.

Many approaches have been made to explain the kinetics and mechanisms of redox reactions involving electron-transfer between inorganic cations in aqueous solutions.[1–9] The simplest type of electron-transfer is that in which neither the coordination number nor the coordinated ligands of the reaction partners are subjected to change during the net reaction, thus

$$M_1L_x^{n+} + M_2L_y^{m+} \rightleftharpoons M_1L_x^{(n-q)+} + M_2L_y^{(m+q)+} \qquad (1)$$

where M_1 and M_2 denote the inorganic oxidant and reductant, n and m stand for their valencies, x and y are the numbers of their coordinated ligands, respectively; and q is the number of electrons transferred.

On the other hand, if only a single element is involved in the reaction

$$*M^{n+} + M^{m+} \rightleftharpoons *M^{m+} + M^{n+} \qquad (2)$$

it may be called an electron-exchange reaction.

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Although the kinetics and mechanisms of oxidation of uranium(IV) by multicharged metal ions have been the subject of many investigators,[10-22] little attention has been focused on the Marcus theory correlation.[1,23]

In view of this context, the present work has been undertaken to gain some information on the aqueous chemistry of uranium(IV) and its interactions in noncomplexing media.

2. IONIC SPECIES OF URANIUM(IV) IN AQUEOUS SOLUTIONS

Under the experimental conditions of $[H^+] < 1\ \text{mol dm}^{-3}$ reported for the redox reactions listed in Table I, uranium(IV) tends to hydrolyze to give the $U(OH)^{3+}$ and/or $U(OH)_2^{2+}$ hydrolyzed species. The configuration and net charge of uranium(IV) ion in acid perchlorate media indicate the existence of tetravalent uranium as hydrated U^{4+} form.[24-27] The high ionic charge of U^{4+} can be reduced by elimination of protons from the water molecules coordinated to the sphere of uranium(IV) upon hydrolysis as follows

$$[(H_2O)_yU]^{4+} \overset{K_{h1}}{\rightleftharpoons} [(H_2O)_{y-1}U(OH)]^{3+} + H^+ \qquad (3)$$

$$[(H_2O)_{y-1}U(OH)]^{3+} \overset{K_{h2}}{\rightleftharpoons} [(H_2O)_{y-2}U(OH)]^{2+} + H^+ \qquad (4)$$

where K_{h1} and K_{h2} are the first and second hydrolysis constants of U^{4+}, respectively, and y is the hydration number.* At 25°C and ionic strength of $1.0\ \text{mol dm}^{-3}$, the values of K_{h1} and K_{h2} were found to be 2.8×10^{-3} and $5.0 \times 10^{-4}\ \text{mol dm}^{-3}$, respectively.[26-28]

2.1. *Analysis of Data*

Analysis of the kinetic data of these tested redox reactions is generally based on two main processes: the determination of the reaction rate and the speculation of the reaction mechanism. Therefore, it is natural to divide the task of these analyses into two distinct stages. The first is discovering the sequence of elementary steps by which a complicated reaction is accomplished. The second is to evaluate the rate constants of the individual steps in terms of activated complex formation.

The observed increase of the rate of reaction with decreasing the hydrogen ion concentrations for these redox reactions suggests that the hydrolyzed ions of the reductant and/or the oxidants may be the reactive species which play the main role in the reaction kinetics. However, the extent of the hydrolysis in some cases is small enough, and the stoichiometric concentrations of the reactants are essentially identical with that of the unhydrolyzed ions.

2.2. *Interpreting the Rate Laws*

Though the form of the rate law gives the formulas of the activated complexes involved in the reaction, the law tells nothing about the actual species which react.

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* The number of solvent water molecules in the coordination sphere around U^{4+} is eight.[26]

Hence, we have chosen to formulate mechanisms in terms of the net reactions of principal species, one for each distinguishable activated complex. If rapid equilibria are established either before or after the rate-determining step they are included in these net reactions. This procedure avoids writing out the kinetically indistinguishable steps, but requires that the rate of each net reaction be explicitly stated. The net activation processes and the kinetic data listed in Tables 1 and 2 are based on the transition state theory.[29] It is assumed that the reactants are in a quasi-equilibrium with the activated complex for the rate-determining step and, hence, the rate of reaction is proportional to the concentration of the activated complex formed. The net equation is the sum of the equation for the formation of the activated complex in the actual rate-determining step and the equation for any rapid equilibria which occur prior to the rate controlling steps. In most of these redox reactions a rapid equilibrium is attained:

$$U^{4+} + Z\,H_2O \underset{\text{fast}}{\overset{K_h}{\rightleftharpoons}} [U(OH)_Z]^{(4-Z)+} + Z\,H^+ \tag{5}$$

or/and

$$M^{n+} + Z\,H_2O \underset{\text{fast}}{\overset{K_h}{\rightleftharpoons}} [M(OH)_Z]^{(n-Z)+} + Z\,H^+ \tag{6}$$

followed by one of the rate-determining steps

$$[U(OH)_Z]^{(4-Z)+} + M^{n+} \xrightarrow[\text{slow}]{k} \text{Product} \tag{7}$$

$$U^{4+} + [M(OH)_Z]^{(n-Z)+} \xrightarrow[\text{slow}]{k} \text{Product} \tag{8}$$

The rate-law would be expressed by the form

$$\text{Rate} = kK'_h[U^{4+}][M^{n+}]/[H^+]^p \tag{9}$$

and the net activation process is

$$U^{4+} + M^{n+} + Z\,H_2O \overset{\text{fast}}{\rightleftharpoons} [*]^{(4+n-Z)+} + Z\,H^+ \xrightarrow[\text{slow}]{k} \text{Product} \tag{10}$$

where M denotes the polyvalent oxidant metal ion, n stands for its valency; Z the number of hydrolyzed water molecules; K'_h or the hydrolysis constant* for U^{4+}; k the apparent rate constant; p the order with respect to the hydrogen ion, and [*] stands for the activated complex, respectively.

For a reaction which proceeds by more than one path, a net equation for the formation of each activated complex should be indicated in each net activation process.

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* In case of U(IV)–Ce(IV),[19] K'_h represents the hydrolysis constant of Ce^{4+}.

3. MECHANISMS OF REACTIONS

Two alternative reaction mechanisms for the oxidation of uranium(IV) by polyvalent metal ions may be considered. The first mechanism involves a simultaneous two-electron change in a single step

$$\mathrm{U(IV)} + \mathrm{M}^{n+} \longrightarrow \mathrm{U(VI)} + \mathrm{M}^{(n-2)+} \tag{11}$$

The second mechanism involves two successive one-electron-transfer, being

$$\mathrm{U(IV)} + \mathrm{M}^{n+} \xrightarrow{\text{slow}} \mathrm{U(V)} + \mathrm{M}^{(n-1)+} \tag{12}$$

followed by

$$\mathrm{U(V)} + \mathrm{M}^{n+} \xrightarrow{\text{fast}} \mathrm{U(VI)} + \mathrm{M}^{(n-1)+} \tag{13}$$

or the disproportionation of U(V)[30]

$$\mathrm{U(V)} + \mathrm{U(V)} \xrightarrow{\text{fast}} \mathrm{U(VI)} + \mathrm{U(IV)} \tag{14}$$

Reactions (13) and (14) are hardly likely to proceed simultaneously. If they are, the overall rate-law would not be first order for each of the reactants as is observed experimentally. It is well known that reaction (14) is slow compared with reaction (13), since the latter involves the breaking of an M–O bond, but the former does not.[17,18,30] Consequently, the reaction mechanism can be expressed by the first two steps. Again, assuming the steady-state approximation for U(V), the rate of formation of the products will give a rate expression similar to that defined by equation (9). This in turn confirms the suggested reaction mechanism for the two-electron changes defined by Eqs. 12–14.

If the coordination shells are unchanged not only in the net reaction but remain intact throughout its entire course, the reaction may be called an outer-sphere electron-transfer. But, if one or more ligands become common to the coordination shells of both reactants during the course of reaction, the reaction is called an inner-sphere electron-transfer. The distinction between these two types of reaction will clarify the detailed reaction mechanism which is experimentally difficult to achieve.

3.1. Simultaneous Two-Electron-Transfer Mechanism: Oxidation of U(IV) by Tl^{3+}, $[PtCl_6]^{2-}$ and NpO_2^+ ions

In connection with the redox reactions of uranium(IV) involving Tl^{3+},[10] $[\mathrm{PtCl_6}]^{2-}$,[11] and $\mathrm{NpO_2^+}$ [13] as oxidants at the top of Table I, a question of basic interest is whether electron-transfer process proceeds through a simultaneous two-electron change in a single step or by successive one-electron-transfer. If the transition states of both reductant and oxidant are unstable, a simultaneous two-electron-transfer mechanism such as that in the oxidation of U(IV) by Tl^{3+}[10] and $[\mathrm{PtCl_6}]^{2-}$[11] ions is more favourable one from the energetic point. Here, both the intermediate states of the reductant, U(V), and the oxidants, Tl(I) and Pt(III), are

TABLE I

The net activation processes and rate constants for the oxidation of U(IV) by metal ion oxidants in 1.0 mol dm^{-3} $HClO_4$ at 25°C.

Net activation process	k_{obs} dm^3 mol^{-1}s^{-1}	I mol dm^{-3}	E,(a) oxidant Volt	$[H^+]^p$(d)	Ref.
$U^{4+} + Tl^{3+} + Y(H_2O) = [*]^{(7-Y)+} + YH^{+(b)}$	3.9×10^{-2}	2.9	0.30	−1.39	10
$U^{4+} + [PtCl_6]^{2-} + 2H_2O = [*]^0 + 2H^+$	6.3×10^{-3}	1.0	0.72	−2.00	11
$U^{4+} + [IrCl_6]^{2-} + YH_2O = [*]^{(2-Y)+} + yH^+$	2.8×10^{-3}	1.0	0.87	−1.50	12
$U^{4+} + NpO_2^+ + H_2O = [*]^{4+} + H^+$	8.0×10^{-6}	1.0	0.74	−2.00	13
$U^{4+} + Np^{4+} + H_2O = [*]^{7+} + H^+$	5.0×10^{-5}	1.0	0.15	−2.50	13
$U^{4+} + NpO_2^{2+} + H_2O = [*]^{5+} + H^+$	2.2×10	2.0	1.14	−0.97	14
$U^{4+} + Fe^{3+} + YH_2O = [*]^{(7-Y)+} + YH^+$	1.3×10	1.02	0.77	−1.81	15
$U^{4+} + [Fe(CN)_6]^{3-} + YH_2O = [*]^{(1-Y)} + YH^+$	3.9×10	1.0	0.72	−1.45	16
$U^{4+} + PuO_2^{2+} + YH_2O = [*]^{(6-Y)+} + YH^+$	3.1	2.0	0.91	−1.20	17
$U^{4+} + Pu^{4+} + YH_2O = [*]^{(8-Y)+} + YH^+$	3.2×10	2.0	1.01	−1.03	18
$U^{4+} + Ce(OH)^{3+(c)} + H_2O = [*]^{6+} + H^+$	8.7×10^3	2.0	1.70	−1.20	19
$U^{4+} + HCrO_4^- + YH_2O = [*]^{(3-Y)+} + YH^+$	6.3×10^4	3.0	1.2	−1.20	20
$U^{4+} + VO_2^+ + YH_2O = [*]^{(5-Y)+} + YH^+$	4.9×10^4	1.0	1.02	−0.40	21
$U^{4+} + MnO_4^- = [*]^{3+}$	9.2×10^3	1.0	1.52	—	22

(a) W. Latimer, "Oxidation potentials", 2nd Edn., Prentice-Hall, Englewood Cliffs, New Jersey, 1952; G. Milazzo, S. Caroll and V.K. Sharma, "Tables of standard Electrode Potentials", John Wiley and Sons, New York, 1978.

(b) Y indicates the presence of two pathways, one of which at least involves hydrogen ion dependency.

(c) Ce^4 is the only hydrolyzed species in the redox reaction.

(d) p is the order with respect to hydrogen ion dependence.

unstable. On the contrary, if the oxidation of U(IV) by Tl^{3+}, $[PtCl_6]^{2-}$ or NpO_2^+ proceeds via two successive one-electron transfer, a chain reaction mechanism similar to that observed in U(IV)-O_2 reaction[31] should be expected. The experimental observations of these reactions indicated the absence of such a chain reaction mechanism.[10,11,13]

In view of this fact and the insensitivity of their reaction rates to the added catalysts such as Cu^{2+} and Hg^{2+} cations, it may be reasonable to suggest a simultaneous two-electron-transfer in a single step as a reaction mechanism for these redox reactions in accordance with the discussions made by Westheimer,[32] and Higginson and Marshall.[33]

It is interesting to speculate about the possible causes of the slowness of these reactions. It seems that neither the formal oxidation potential nor the charge on the activated complex has any remarkable effect on the rate of oxidation as shown in Table I. Hence, the slow rates of oxidation may be explained in part by the necessity of the structure for both oxidant and reductant to change in the rate-determining step. This will require some rearrangement of the coordinated water molecules or ligands about the reactants, in order to approach them closely enough from the configuration of the products as is expressed by the following equations

$$Np^{V}O_2^{+} + U^{IV} = Np^{III} + U^{VI}O_2^{2+} \qquad (15)$$

$$[Pt^{IV}Cl_6]^{2-} + U^{IV} = [Pt^{II}Cl_4]^{2-}\ U^{VI}O_2^{2+} \qquad (16)$$

$$Tl^{III} + U^{IV} = Tl^{I} + U^{VI}O_2^{2+} \qquad (17)$$

without regard to H^+ or H_2O molecules. In these reactions, the structure of uranium(IV) was subjected to change from the hydrated form to the oxytype structure; while neptunium(V), plantinum(IV) and thallium(III) on the other hand are subjected to change from the oxytype and octahedral structures to the hydrated and tetrahedral forms, respectively.

In view of this tentative interpretation and the experimental observations, these redox reactions are suggested to proceed via inner-sphere two-electron-transfer mechanisms rather than via an outer-sphere one, since there does not appear any experimental confirmation of outer-sphere two-electron-transfer mechanism.[34]

Moreover, the kinetics of oxidation of uranium(IV) by hexachloroplatinate(IV)[11] and hexachloroiridate(IV)[12] showed that the oxidation process is rather complex and consists of two distinct stages. The initial stage was fast and interpreted in terms of formation of $[(H_2O)_yU^{IV}.Cl_6M^{IV}]$ binuclear complex intermediate, followed by a slower reaction involving the transfer of electrons from the reductant U^{IV} to the oxidant M^{IV}. The formation of these binuclear intermediates was confirmed spectrophotometrically in visible regions by the slight increase of the optical densities over those of the initial reductants, $[PtCl_6]^{2-}$ and $[IrCl_6]^{2-}$ on mixing with U(IV) at lower temperature. It was also confirmed by the presence of $[PtCl_6]^{2-}$ and $[IrCl_6]^{2-}$ oxidant ions in the initial stage of reaction i.e., no reduction occurred.

The rate constants observed for these two redox reactions (Table I) are consistent with either inner- or outer-sphere mechanisms since uranium(IV) is known to be labile,[35] whereas hexachloroplatinate(IV)[36] and hexachloroiridate(IV)[37] on the other hand are extremely inert. These facts suggest two possible electron-transfer processes. First a complex is formed with at least one chloride bridge from the inert oxidant to the labile $[U^{IV}(H_2O)_y]$ coordination sphere at the initial rapid stage

$$(H_2O)_yU^{IV} + M^{IV}Cl_6 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [(H_2O)_yU^{IV}.Cl_6M^{IV}] \quad (18)$$

and the electron-transfer from U^{IV} to M^{IV} is followed at the slower stage; k_1 and k_{-1} denote the rate constants for the forward and reverse reactions. The second suggestion represents a rapid electron transfer with formation of a binuclear intermediate complex

$$(H_2O)_yU^{IV} + M^{IV}Cl_6 \rightleftharpoons [(H_2O)_yU^{(IV+q)+}\ Cl_6M^{(IV-q)+}] \quad (19)$$

followed by a slow process resulting from the decay of the successor redox step. The possibility that the fast step involves an outer-sphere ion-pairing between the reactants, followed by a slow electron-transfer within the pair would remain to be considered. Ion-pairing should be in turn a diffusion controlled process whereas the intermediates form with $k_1 > 10^3\ dm^3\ mol^{-1}\ s^{-1}$.[11,12] However, the higher energy bands observed in the spectra of the intermediates were larger than those expected for an outer-sphere ion pair. Consequently, the suggestion of outer-sphere ion pairing mechanism is omitted, and the inner-sphere type remains the more favourable one. The latter mechanism involves the releasing of protons from water coordinated to U(IV)

$$[(H_2O)_yU^{IV}.Cl_6M^{IV} \xrightarrow{\text{fast}} [(H_2O)_{y-Z}U^{IV}(OH)_Z.Cl_6M^{IV}] + ZH^+ \quad (20)$$

followed by the transfer of electrons from U^{IV} to M^{IV} ion

$$[(H_2O)_{y-Z}U^{IV}(OH)_Z.Cl_6M^{IV}] \xrightarrow{\text{slow}} (H_2O)_{y-Z}U^{(IV+q)+}(OH)_Z.Cl_6M^{(IV-q)+} \quad (21)$$

The presence of hydrolytic species which would deprotonate on electron-transfer may indicate that the present reaction proceeds via inner-sphere mechanism rather than by an outer-sphere one. This is in good agreement with that previously reported[11] for the oxidation of U(IV) by $[PtCl_6]^{2-}$ ion.

The rates of bridged complexes in electron-transfer have been demonstrated by Taube and Mayer in their pioneering work.[38] It may then be inferred that the composition of the activated complexes is $(H_2O)_{y-1}(OH)U^{IV}....Cl—M^{IV}Cl_5$ and $(H_2O)_{y-2}(OH)_2U^{IV}\begin{smallmatrix}\text{- - Cl}\\ \text{- - Cl}\end{smallmatrix} > M^{IV}Cl_4$

3.2. *Successive One-Electron-Transfer Mechanism*

On the other hand, the oxidation of uranium(IV) by other metal ions[14-20] (Table I) is suggested to proceed by two successive one-electron-transfer mechanisms. This suggestion was confirmed by the sensitivity of the rate of oxidation for most reactions to the added catalyst such as Cu^{2+} and Hg^{2+} ions where an appreciable increase in the observed rate constants was noticed. This fact can be interpreted by the fast reaction between the added catalyst and the formed unstable intermediate uranium(V) as follows,

$$U(IV) + M^{n+} \xrightarrow{\text{slow}} U(V) + M^{(n-1)+} \quad (12)$$

$$\mathrm{U(V) + Cu(II) \xrightarrow{fast} U(VI) + Cu(I)} \qquad (22)$$

or

$$\mathrm{U(V) + Hg(II) \xrightarrow{fast} U(VI) + Hg(I)} \qquad (22')$$

The main characteristics of these redox reactions are the appearance of a term in the rate law inversely proportional to fractional first- or second-order powers with respect to the hydrogen ion concentration. The non-integral inverse order in $[H^+]$ can be interpreted in terms of simultaneous contribution from two separate paths inversely first- and second-orders, respectively. This fact can be explained by the tendency of U(IV) to hydrolyze prior to the rate-determining step* in order to resemble more closely the transition states of the product;[39]

$$[H_2O\text{–}U\text{–}OH_2]^{4+} \rightleftharpoons [O{=}U{=}O]^+ + 4H^+ + e^- \qquad (23)$$

In this diagram, only two water molecules are shown. The overall reaction requires the removal of four protons from the hydration sphere around uranium(IV) ion. The appearance of these inverse-orders with respect to the $[H^+]$ dependence indicates that there are at least two pathways involving hydrogen ions for the rate-determining steps. Consequently, the most likely reaction mechanism which coincides with the hydrolysis assumptions of uranium(IV) may be expressed by the following competitive reactions,

$$[(H_2O)_yU]^{4+} + M^{n+} \rightleftharpoons [*]^{(4+n)+} \xrightarrow{k_0} \text{product} \qquad (24)$$

$$-H^+ \Big\downarrow\!\!\Big\uparrow K_{h1}$$

$$[(H_2O)_{y-1}U(OH)]^{3+} + M^{n+} \rightleftharpoons [*]^{(3+n)+} \xrightarrow{k_1} \text{product} \qquad (25)$$

$$-H^+ \Big\downarrow\!\!\Big\uparrow K_{h2}$$

$$[(H_2O)_{y-2}U(OH)_2]^{2+} + M^{n+} \rightleftharpoons [*]^{(2+n)+} \xrightarrow{k_2} \text{product} \qquad (26)$$

Considering that reactions (24), (25) and (26) are the rate-determining steps, the rate with change in the hydrogen ion concentration may be written as

$$\text{Rate} = \frac{k_0 + k_1'[H^+]^{-1} + k_2'[H^+]^{-2}}{1 + K_{h1}[H^+]^{-1} + K_{h2}[H^+]^{-2}} [M^{n+}][U(IV)]_T \qquad (27)$$

where $k_1' = k_1K_{h1}$, $k_2' = k_2K_{h1}K_{h2}$ and $[U(IV)]_T$ is the analytical concentration of uranium(IV)

$$[U(IV)]_T = [U^{4+}] + [U(OH)^{3+}] + [U(OH)_2^{2+}] \qquad (28)$$

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* In the case of U(IV)–Ce(IV)[19] reaction, Ce^{4+} is the only hydrolyzed species; while in U(IV)–MnO_4^- reaction no hydrolysis occurs under the experimental conditions used.

Generally, the empirical rate-law of the stoichiometric overall reaction is expressed by the form

$$\text{Rate} = k_{\text{obs}}[\text{U(IV)}][\text{M}^{n+}] \tag{29}$$

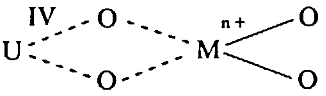
where k_{obs} is the observed second-order rate constant. Comparing equation (27) with (29), we obtain the following relationship:

$$k_{\text{obs}} = \frac{k_0 + k'_1[\text{H}^+]^{-1} + k'_2[\text{H}^+]^{-2}}{1 + K_{\text{h1}}[\text{H}^+]^{-1} + K_{\text{h1}}K_{\text{h2}}[\text{H}^+]^{-2}} \tag{30}$$

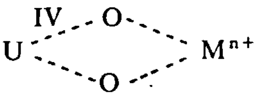
In reactions in which U^{4+} and/or M^{n+} are hydrolyzed, the hydrolysis constant of the oxidant should appear in the rate-expression.[15,18]

3.3. Oxidation of U(IV) by $HCrO_4^-$, VO_2^+ and MnO_4^- Ions

The fast rates of oxidation observed for U(IV)-$HCrO_4^-$,[20] U(IV)-VO_2^+,[21] and U(IV)-MnO_4^-[22] reactions at the bottom of Table I, were attributed to the transfer of oxygen atoms from the oxidants to U(IV) prior to the rate controlling steps.* These transferred oxygen atoms form a sort of bridge which facilitates the transfer of electrons from U^{IV} to the oxidants,[22] thus



or



(MnO_4^-, $HCrO_4^-$) (VO_2^+)

As reported previously,[22] a plot of ΔG° versus $\Delta G^{\ddagger}$ for these redox reactions was fairly linear, but the observed slope was found to be very much less than 0.5 as required by the Marcus theory.[1] This indicated that at least some of these reactions were proceeding via ion-pairing mechanism.

3.4. Oxidation of U(IV) by NpO_2^{2+}, Fe^{3+}, $[Fe(CN)_6]^{3-}$, PuO_2^{2+} and Pu^{4+} Ions

Furthermore, the moderate rates of oxidation observed in the oxidation of U(IV) by NpO_2^{2+},[14] Fe^{3+},[15] $Fe(CN)_6^{3-}$,[16] PuO_2^{2+},[17] and Pu^{4+}[18] lie at the middle of Table I may be explained by the necessity of the structure of only one reactant mainly, U(IV), to change from the hydrated form U^{4+} to the oxytype state UO_2^+ in the rate-determining step.

$$\text{U}^{\text{IV}} + \text{M}^{n+} \longrightarrow \text{U}^{\text{V}}\text{O}_2^+ + \text{M}^{(n-1)+} \tag{31}$$

4. INTERPRETING THE THERMODYNAMIC PARAMETERS

Although the rate law provides no information regarding inner- or outer-sphere nature, some information can be obtained by examining the magnitudes of the rate

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* Taking into consideration the energy required for the transfer of oxygen atoms.

constants for the exchange reactions of the two oxidation–reduction couples in each cross reaction based on Marcus theory.[1,23] If the rate constant of the redox reaction is greater than the rate of substitution, then the reaction should be necessarily of the outer-sphere type.[40–42] Unfortunately, no data were available on the rate of substitution of U(IV) ion. Again, the thermodynamic parameters of a series of common reactions may be considered as good evidence in support of the reaction mechanism.[43,44] The thermodynamic parameters were evaluated from Eyring's equation of the absolute rate theory.[29] The values listed in Table 2 were calculated by using the least-squares method. It has been suggested[41] that the redox reactions fall into two classes, one of positive entropies and large enthalpies of activation, and the other of negative entropies and small enthalpies of activation. The $\Delta S^{\neq}$ values for a group of outer-sphere reactions tend to be more positive than $\Delta S^{\neq}$ for a set of inner-sphere reactions which tend to be more negative. The activation parameters shown in Table II fall within the range of the first class, whereas $\Delta S^{\neq}$ values are ranging between -41 and $+135\,J\ K^{-1} mol^{-1}$. The difference in the free energies of activation arises mainly from the enthalpies terms. The variety within these values is not surprising when an allowance is made for the hydrolysis of U(IV) throughout the oxidation process, where the apparent rate constants are the product of the rate constant and the equilibrium constants as defined by equation (30). The positive entropies of activation can be explained on the basis of a high electronic transition probability between the two reactant ions owing to the U(IV) hydrolysis that lowers the energy barriers since the transition states will resemble more closely the products. The process of removing protons has higher hydrolytic thermodynamic parameters for ΔS° and ΔH° values of positive sign.[24–28]

TABLE II

Activation parameters of the oxidation of U(IV) by metal ion oxidants.

Oxidant	Pathway*	$\Delta S^{\neq}/J\ K^{-1} mol^{-1}$	$\Delta H^{\neq}/kJ^{-1} mol^{-1}$	$\Delta G^{\neq}/kJ\ mol^{-1}$	Ref.
Tl^{3+}	k_1'	41.8	102.8	90.4	10
	k_2'	29.3	90.7	82.0	
$[PtCl_6]^{2-}$	k_2'	130.4	136.0	97.1	11
$[IrCl_6]^{2-}$	k_1'	67.8	110.4	90.2	
	k_2'	78.9	115.6	92.1	12
NpO_2^+	k_2'	135.0	130.8	90.6	13
Np^{4+}	k_2'	−86.1	60.6	86.1	13
NpO_2^{2+}	k_1'	86.1	60.6	66.9	14
Fe^{3+}	k_1'	60.6	88.2	70.1	
	k_2'	101.6	97.4	67.1	15
$[Fe(CN)_6]^{3-}$	k_1'	48.3	85.3	71.0	16
	k_2'	82.2	98.7	73.9	
PuO_2^{2+}	k_1'	14.2	73.6	69.4	17
	k_2'	75.7	89.5	66.9	
Pu^{4+}	k_2'	125.8	101.6	64.1	18
Ce^{4+}	k_1'	25.9	58.5	50.8	19
$HCrO_4^-$	k_0	33.0	55.6	45.8	20
	k_1'	—	—	—	
VO_2^+	k_0	−41.8	35.6	48.0	21
	k_1	125.4	84.9	47.5	
MnO_4^-	k_0	30.5	62.9	53.8	22

* k_0, k_1' and k_2' denote non-proton, one-proton and two-proton pathways, respectively.

In order to understand the dependence of the reactivity upon reaction variables, in particular the reactants structure and the reaction medium, the rate and equilibrium data had led to the formulation of a number of empirical correlations.[39] The general form of these correlations is a linear relationship between $\Delta G°$ and $\Delta G^{\ddagger}$ for a series of reactions involving similar reaction mechanisms for the same reductant.

The similarity between the kinetics of the oxidation of U(IV) by NpO_2^{2+}, Fe^{3+}, $[Fe(CN)_6]^{3-}$, PuO_2^{2+}, Pu^{4+} and Ce^{4+} ions with that of U(IV)–VO_2^+, U(IV)–$HCrO_4^-$ and U(IV)–MnO_4^- reactions, may suggest the possibility of existence of a similar free energy relationship.[22] As shown in Fig. 1, a plot of $\Delta G°$ versus $\Delta G^{\ddagger}$ for one-electron change was fairly linear with slope of 0.25 ± 0.02. However, this value is smaller than that of 0.5 as predicted by Marcus theory[23] for an outer-sphere mechanism. It may suggest that at least some of these redox reactions proceed via outer-sphere mechanism since the two values are of the same order of magnitude.

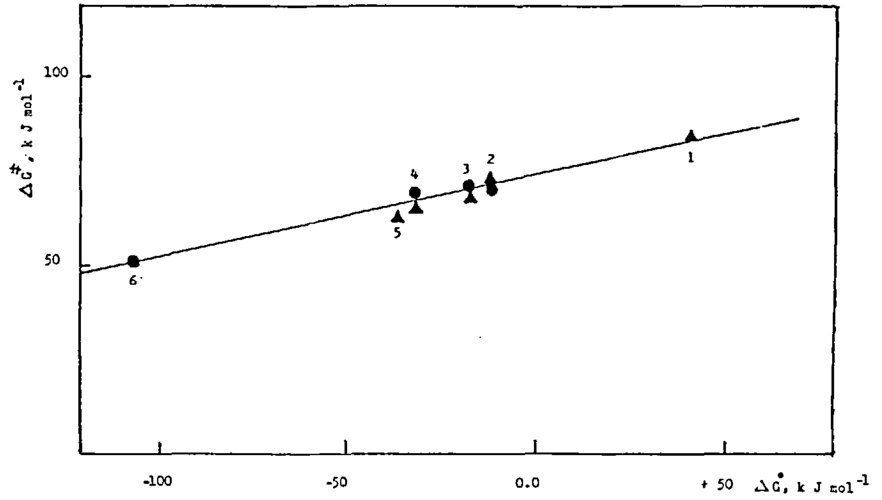

FIGURE 1 A linear free-energy relationship for the oxidation of uranium(IV) by some multicharged metal ions in aqueous $HClO_4$. (1) NP^{4+}; (2) $[Fe(CN)_6]^{3-}$; (3) Fe^{3+}; (4) PUO_2^{2+}; (5) Pu^{4+}; (6) Ce^{4+}. (●): k_1' pathway; (▲): k_2' pathway.

The degree of orientation of the solvent molecules toward an ion is generally affected by the charge of that ion, i.e. the number of the solvent molecules around the activated complex is affected by its charge which in turn tends to increase or decrease the entropy of activation. As shown in Table II, it seems quite likely that the charge on the activated complex has no such effect.

In view of these tentative interpretations, the structural changes of the reactants, in particular uranium(IV) in the rate-determining step plays a very important role in the kinetics of these redox reactions. This means that the change in the structure of uranium(IV) from the hydrated form U^{4+} to the oxytype oxidation state UO_2^+ or UO_2^{2+} may be considered as a determining factor in elucidation of the reaction mechanism.

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