Kinetics of Reaction of Uranium(IV) and Hexachloroiridate(IV) in Acid Perchlorate Solutions. Evidence for a Binuclear Intermediate

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The kinetics of oxidation of uranium(IV) with hexachloroiridate(IV) in aqueous perchlorate media at a constant ionic strength of 1.0 mol dm^{-3} has been reinvestigated using stopped-flow and conventional spectrophotometric techniques. There are two distinct stages in the reaction: the initial stage is fast and interpreted as being the formation of a $[(H_2O)_nU^{IV}\cdot Cl_6Ir^{IV}]^{2+}$ binuclear intermediate (rate of formation k_1 Å 6.86 × 10^3 dm^3 mol^{-1} s^{-1}, decomposition k_{-1} = 3.91 s^{-1}), followed by a slower stage which was explained as the transfer of electrons from U^{IV} to Ir^{IV} following the loss of one or two protons from water molecules of $(H_2O)_nU^{IV}$. A tentative reaction mechanism consistent with the kinetic results is discussed.

The estimated reduction potentials for the $[IrCl_6]^{2-}$–$[IrCl_6]^{3-}$ (0.87 V) and U^{V}–U^{IV} (−0.58 V) couples[1] provide assurance that reaction (1) is highly favoured thermodynamically.

$$U^{IV} + [IrCl_6]^{2-} \longrightarrow U^{V} + [IrCl_6]^{3-} \qquad (1)$$

Preliminary experiments indicated the occurrence of an initial rapid reaction, followed by a much slower one. In an analogous kinetic study performed on the hexachloroplatinate(IV) oxidation of uranium(IV), Hassan *et al.*[2] observed the formation of a $[(H_2O)_nU^{IV}\cdot Cl_6Pt^{IV}]^{2+}$ binuclear intermediate at the initial stage of reaction, followed by transfer of electrons from the reductant to the oxidant.

Many actinide ions react in aqueous perchlorate media to form binuclear intermediates. More direct evidence for the formation of these complex ions has been obtained from spectrophotometric studies.[3-5] The reaction mechanisms elucidated for some redox reactions involving actinyl ion with other metal ions have also provided evidence of such complex formation.[6-10] The formation of such intermediates is not unique to actinide ions but also includes transitional-metal ions.[11-13]

The oxidation of Cr^{II} by $[IrCl_6]^{2-}$ represents a good example of inner-sphere processes in which the bridging ligand is supplied by the oxidizing agent.[14,15] Therefore, the oxidation of U^{IV} by $[IrCl_6]^{2-}$ was thought to be a useful test of the postulates that ligand transfer would occur if the oxidizing agent was substitution inert and contained relatively good bridging ligands and if the reducing agent was substitution labile or if it expanded its co-ordination sphere upon oxidation.

In view of this and current interest in reactions in which binuclear intermediates are formed,[2] the present reaction seems to merit further investigation[16] with a view to gaining unequivocal information on the ionic interaction of uranium(IV) in non-complexing media and making a comparison with the reaction mechanism for the U^{IV}–$[PtCl_6]^{2-}$ reaction since Pt^{IV} resembles Ir^{IV} in d-orbital configuration.

Experimental

Sodium hexachloroiridate(IV) $Na_2[IrCl_6]$ of AnalaR quality (Ventron Corp.) was used without further purification. Solutions of $[IrCl_6]^{2-}$ were freshly prepared before each experiment by dissolving the appropriate amounts of the reagent in perchloric acid solution to minimize the rate of aquation.[15,17] Uranium(IV) perchlorate solutions were prepared and standardized spectrophotometrically as described earlier.[18] Sodium perchlorate was prepared by neutralization of a slurry of sodium carbonate (AnalaR) with 60% perchloric acid (BDH). Solid sodium perchlorate was obtained by partial crystallization followed by three recrystallizations as described previously.[2]

All other reagents were of analytical grade and their solutions were prepared by dissolving the requisite amounts of the samples in doubly distilled water. The ionic strength of the reaction mixture was maintained constant at 1.0 mol dm^{-3} using sodium perchlorate as a non-complexing agent.

Kinetic Measurements.—All kinetic runs were carried out under pseudo-first-order conditions with uranium(IV) present initially in a large excess over $[IrCl_6]^{2-}$. The course of the reaction was followed by recording the decrease in absorbance of $[IrCl_6]^{2-}$ at its absorption maximum, 489 nm, as a function of time. It was verified that there was no interference from other reagents at this wavelength. The absorption spectra of the reactants and typical traces of the spectral changes are shown in Fig. 1.

The initial rapid part of the reaction was investigated using a Durrum-Gibson stopped-flow apparatus with a fully thermostatted compartment [Fig. 1(*b*)], while the slow stage was studied on a Shimadzu uv-vis 210 A double-beam spectrophotometer using cells of pathlength 1 cm [Fig. 1(*c*)].

Results

Stoichiometry.—The stoichiometry of the overall reaction of $[IrCl_6]^{2-}$ with excess U^{IV} in 1.0 mol dm^{-3} $HClO_4$ and at unit ionic strength was determined spectrophotometrically. The unreacted U^{IV} was estimated periodically at its absorption maximum, 648 nm, till completion of reaction. A stoichiometric ratio of 0.5 ± 0.01 ($[U^{IV}]_{consumed}/[IrCl_6{}^{2-}]_0$) was obtained at several initial concentrations of U^{IV}. This indicates that the stoichiometry of the overall reaction is as in equation (2).

$$U^{4+} + 2[IrCl_6]^{2-} + 2H_2O \longrightarrow [UO_2]^{2+} + 2[IrCl_6]^{3-} + 4H^{+} \qquad (2)$$

Dependence of Reaction Rate on $[IrCl_6]^{2-}$ *and* $[U^{IV}]$.—Plots of $\ln(A_t - A_\infty)$ *versus* time, where A_t and A_∞ represent the absorbances at time t and infinite time, respectively, were linear for over three half-lives of the reaction with respect to the initial rapid part and the slow reaction. This indicates that both the

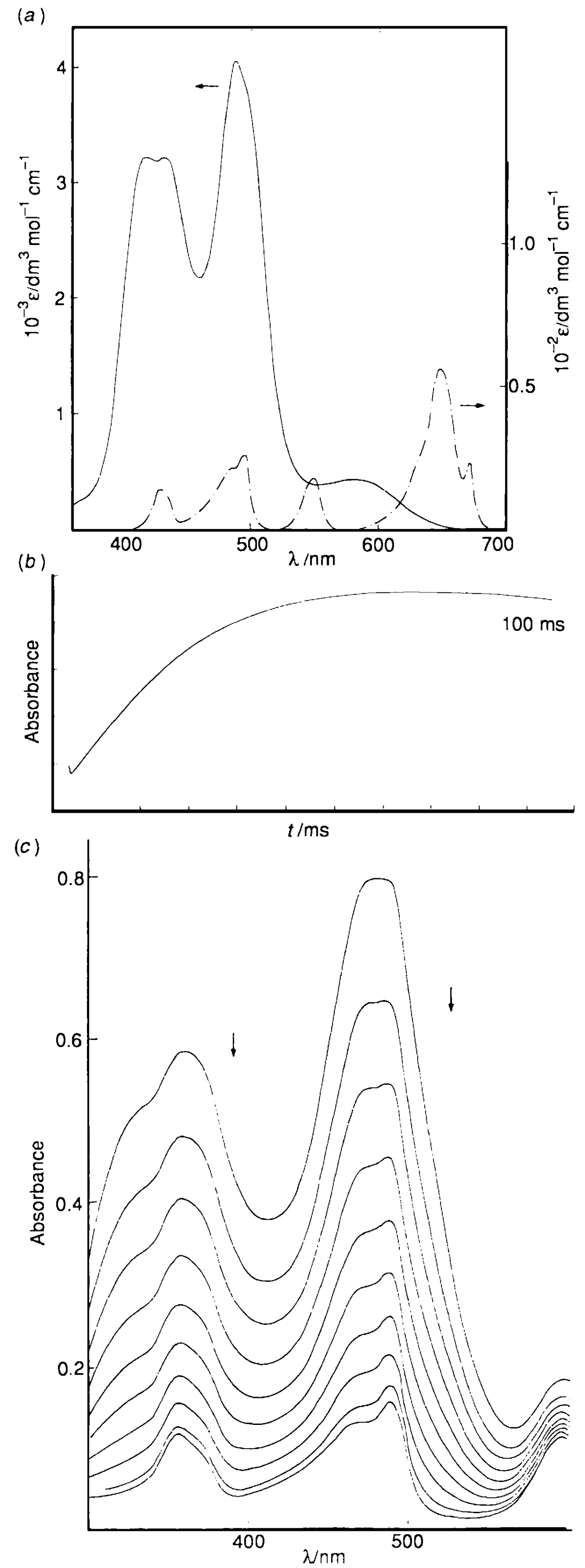

Fig. 1 (*a*) Absorption spectra of U^{IV} (– - · –) and $[IrCl_6]^{2-}$ (— —) in 1 mol dm^{-3} $HClO_4$. $[U^{IV}] = 1.31 \times 10^{-2}$ and $[IrCl_6]^{2-} = 2.03 \times 10^{-4}$ mol dm^{-3} at 25 C. (*b*) Typical reaction trace of the initial rapid stage of the oxidation of uranium(IV) by hexachloroiridate(IV) ion. $[U^{IV}] = 5.36 \times 10^{-3}$, $[IrCl_6]^{2-} = 2.03 \times 10^{-4}$, $[H^+] = 1.0$ and $I = 1.0$ mol dm^{-3} at $\lambda = 489$ nm and 21 C. (*c*) Spectral changes in the slow stage of the oxidation of uranium(IV) by hexachloroiridate(IV) ion. Concentrations as in (*b*), 20 C and scanning intervals of 1 min after mixing

initial and slow reactions are first order with respect to $[IrCl_6]^{2-}$.

The initial part of the reaction was too fast to be measured by the conventional spectrophotometric method and could hardly be considered as the rate of oxidation of uranium(IV) by $[IrCl_6]^{2-}$ when considering the relatively slow rates of oxidation of uranium(IV) by other metal-ion oxidants.[19-24] Therefore, the most reasonable reaction mechanism which may be suggested is the rapid formation of a binuclear intermediate followed by the slow transfer of an electron from U^{IV} to Ir^{IV} [equation (3)], followed by either (4) or (5) the disproportion-

$$(OH_2)_nU^{IV} + 2[IrCl_6]^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [(H_2O)_nU^{IV}\cdot Cl_6Ir^{IV}]^{2+} \xrightarrow[\text{slow}]{k} U^V + [IrCl_6]^{3-} \qquad (3)$$

$$U^V + [IrCl_6]^{2-} \xrightarrow{\text{fast}} U^{VI} + [IrCl_6]^{3-} \qquad (4)$$

$$U^V + U^V \xrightarrow{\text{fast}} U^{VI} + U^{IV} \qquad (5)$$

ation of U^V, where k_1 and k_{-1} denote the rate constants for the forward and reverse reactions and k is the rate constant for electron transfer.

It is well known that reaction (5) is relatively slow[25] compared with (4) since it probably involves the breaking of a U–O bond of UO_2^+ species* whereas reaction (4) does not; consequently reactions (4) and (5) are hardly likely to proceed simultaneously and the overall reaction may be expected to comprise the first two steps. On the basis of a steady-state assumption for U^V, the rate law for the formation of the product $[IrCl_6]^{3-}$ is described in equation (6).

The formation of such a binuclear reaction intermediate was confirmed by a slight increase in the absorbance over that of the initial $[IrCl_6]^{2-}$ observed in the visible region on mixing with uranium(IV) at lower temperatures. Compared with hexachloroiridate(IV), the binuclear complex has negligible absorption at 489 nm. Extrapolation of the data back to the time of mixing yields a reasonable lower limit for the molar absorption coefficient of the residual absorption of the intermediate over and above that of $[IrCl_6]^{2-}$, *i.e.* in the range 35–50 dm^3 mol^{-1} cm^{-1}. Calculation of this value by methods reported elsewhere[7,11] gave results in good agreement with those observed.

In the presence of a large excess of uranium(IV) over $[IrCl_6]^{2-}$ the pseudo-first-order plots were fairly linear with slopes corresponding to the observed first-order rate constants. As shown in Fig. 2, the plots of the observed first-order rate constants k_{obs} *versus* $[U^{IV}]_0$ for the initial rapid stage gave satisfactory straight lines from whose slopes and intercepts the values of k_1 and k_{-1} were determined. A run at $[H^+] = 1.0$ and $[IrCl_6]^{2-} = 2.03 \times 10^{-4}$ mol dm^{-3} and 21 C gave $k_1 = 6.86 \times 10^3$ dm^3 mol^{-1} s^{-1} and $k_{-1} = 3.91$ s^{-1}, respectively.

The rate of decomposition of the binuclear intermediate in the slow stage of reaction may be expressed by the rate law (6).

$$-d[(H_2O)_nU^{IV}\cdot Cl_6Ir^{IV}]^{2+}/dt = k[(H_2O)_nU^{IV}\cdot Cl_6Ir^{IV}]^{2+} \qquad (6)$$

When uranium(IV) is present in a large stoichiometric excess over $[IrCl_6]^{2-}$ and using the total concentration of the binuclear complex, equation (7) can be written where k' and k

$$k' = kK[U^{IV}]/1 + K[U^{IV}] \qquad (7)$$

refer to the observed and apparent rate constants of the slow

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* It is possible that reaction (5) need not involve U–O bond breaking but may occur *via* protonation to give U–OH_2. It still however should be slow because it is binuclear.

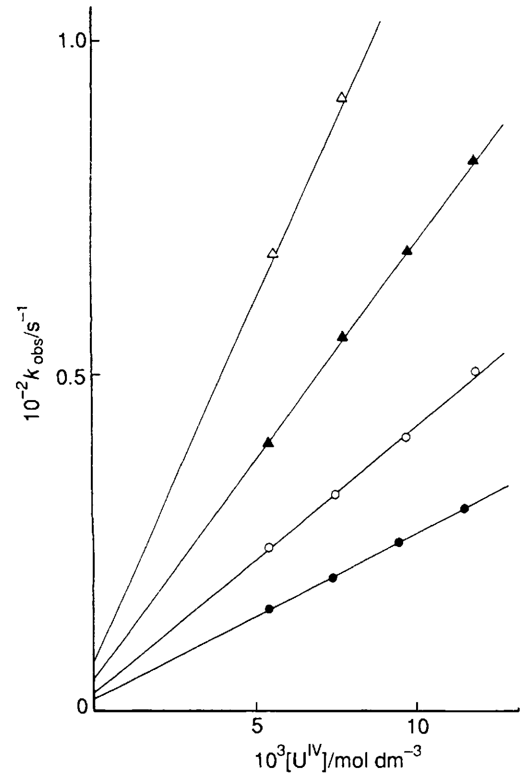

Fig. 2 Dependence of the observed rate constant on $[U^{IV}]$ for the initial rapid reaction. $[IrCl_6]^{2-} = 2.03 \times 10^{-4}$, $[H^+] = 1.0$, $I = 1.0$ mol dm^{-3} and 6 (●), 11 (○), 16 (▲) and 21 °C (△)

reaction and K is the formation constant of the binuclear complex. The value of K was evaluated from k_1 and k_{-1} and found to be 1.75×10^3 dm^3 mol^{-1} at 21 °C. Under our experimental conditions of $K[U^{IV}] \geqslant 8.8$, equation (7) reduces to $k' \approx k$ which can be used to express the kinetics of decomposition of the binuclear intermediate during the slow stage. A run at $[H^+] = 1.0$, $[U^{IV}] \approx 5 \times 10^{-3}$ and $[IrCl_6]^{2-} = 2.03 \times 10^{-4}$ mol dm^{-3} and 25 °C gave $k' = 1.34 \times 10^{-3}$ s^{-1} (where k' denotes the observed first-order rate constant for electron transfer in the slow reaction).

Dependence of Reaction Rate on Ionic Strength.—In order to investigate the effect of ionic strength on the rate of electron transfer, kinetic runs were performed at $[H^+] = 1.0$ mol dm^{-3} and 30 °C with increasing addition of $NaClO_4$ up to 3.5 mol dm^{-3}. The values of k' were found to decrease with increasing ionic strength. At $I = 2.0$ and 3.0, $[U^{IV}] = 5.01 \times 10^{-3}$ and $[IrCl_6]^{2-} = 2.03 \times 10^{-4}$ mol dm^{-3}, fixed $[H^+]$ and temperature, $k' = 1.83 \times 10^{-3}$ and 1.37×10^{-3} s^{-1}, respectively.

Dependence of Reaction Rate on the Hydrogen-Ion Concentration.—To clarify the influence of $[H^+]$ on the rates of formation and decomposition of the formed intermediate, kinetic measurements were performed in solutions of $HClO_4$–$NaClO_4$ of different $[H^+]$ and constant ionic strength and temperature. A decrease in acid concentration was found to accelerate the rate of oxidation, though no change was observed in the rate of binuclear formation within the range of acid concentration used ($[H^+] = 0.2$–1.0 mol dm^{-3}).

Plots of the observed first-order rate constants k' against the reciprocal of $[H^+]$ gave curves passing through the origin. The curvature suggests that the hydrogen-ion dependence of k' is more complicated. It was determined from the empirical equation $\ln k' = \ln[H^+]^n$ (ref. 26) where n was found to be intermediate between -1 and -2, suggesting a mixed-order reaction.

Dependence of Reaction Rate on Temperature.—To determine the activation parameters, the rapid and slow reactions were observed at various temperatures and constant $[H^+]$ and ionic strength. Use of the Eyring equation gave good straight lines and from the slopes and intercepts the enthalpies and entropies of activation were determined using the method of least squares and a Hitachi computer (705 Fortran).

Discussion

Two distinct stages in the kinetics of this reaction were observed, an initial rapid reaction followed by a much slower one at longer times.

Sullivan[7] reported that a 1:1 complex was formed when neptunium(V) and chromium(III) ions are mixed in perchloric acid [equation (8)] without electron transfer. On the other

$$Np^V + Cr^{III} \rightleftharpoons [Np^V{\cdot}Cr^{III}] \qquad (8)$$

hand, the reduction of uranium(VI) by chromium(II)[11,27] proceeds *via* an intermediate binuclear complex with simultaneous transfer of electrons from Cr^{II} to U^{VI} [equation (9)]. The main

$$U^{VI} + Cr^{II} \rightleftharpoons [U^V{\cdot}Cr^{III}] \qquad (9)$$

question in connection with this redox reaction is whether the formation of the intermediate binuclear complex occurs with or without electron transfer. Another point is whether the electron transfer proceeds through successive one-electron changes $U^{IV} \longrightarrow U^V \longrightarrow U^{VI}$ or by a simultaneous two-electron transfer in a single step $U^{IV} \longrightarrow U^{VI}$.

Two possible modes for electron transfer in the U^{IV}–$[IrCl_6]^{2-}$ reaction may be considered. The first involves rapid formation of a binuclear complex with a chloride bridge from the inert $[IrCl_6]^{2-}$ into the labile $(H_2O)_nU^{IV}$ co-ordination sphere,

$$(H_2O)_nU^{IV} + Ir^{IV}Cl_6 \rightleftharpoons [(H_2O)_nU^{IV}ClIr^{IV}Cl_5]^{2+} \qquad (10)$$

followed by electron transfer from U^{IV} to Ir^{IV} in the slower stage. The formula $(H_2O)_nU^{IV}$ (where $n = 8$ is most probable[28]) is employed since the absence of a hydrogen-ion dependence of the rate of binuclear complex formation has been established. The formation of such an intermediate is supported by the presence of $[IrCl_6]^{2-}$ ion after the initial rapid stage which means that no reduction of iridium(IV) has occurred.

The second mode represents a rapid electron transfer with formation of the binuclear intermediate [equation (11)]

$$(H_2O)_nU^{IV} + Ir^{IV}Cl_6 \rightleftharpoons [(H_2O)_nU^V{\cdot}Cl_6Ir^{III}]^{2+} \qquad (11)$$

followed by a slow process resulting from the decay of the intermediate.

The increase in k' values with decrease in the hydrogen-ion concentration suggests that hydrolysed ions of uranium(IV) may be the reactive species. The inverse non-integral order with respect to the hydrogen-ion dependence of the rate constant also suggests that at least two pathways involving the hydrolysed species contribute to the slow reaction. Since the rate of binuclear complex formation was found to be pH-independent in the range of $[H^+]$ used, the most likely reaction mechanism involves decomposition of the intermediates $[(H_2O)_nU^{IV}{\cdot}Cl_6Ir^{IV}]^{2+}$ (k_1), $[(H_2O)_{n-1}(OH)U^{IV}{\cdot}Cl_6Ir^{IV}]^+$ (k_2) and $[(H_2O)_{n-2}(OH)_2U^{IV}{\cdot}Cl_6Ir^{IV}]$ (k_3) in the rate-determining steps.

Hence, the change in the rate of decomposition of the binuclear intermediates with change in the hydrogen-ion concentration can be written as in equation (12) where K_{a1} and

$$-\frac{d[(H_2O)_nU^{IV}{\cdot}Cl_6Ir^{IV}]^{2+}}{dt} = \frac{k_1 + k_2K_{a1}[H^+]^{-1} + k_3K_{a1}K_{a2}[H^+]^{-2}}{1 + K_{a1}[H^+]^{-1} + K_{a1}K_{a2}[H^+]^{-2}} \cdot [(H_2O)_nU^{IV}{\cdot}Cl_6Ir]_T \qquad (12)$$

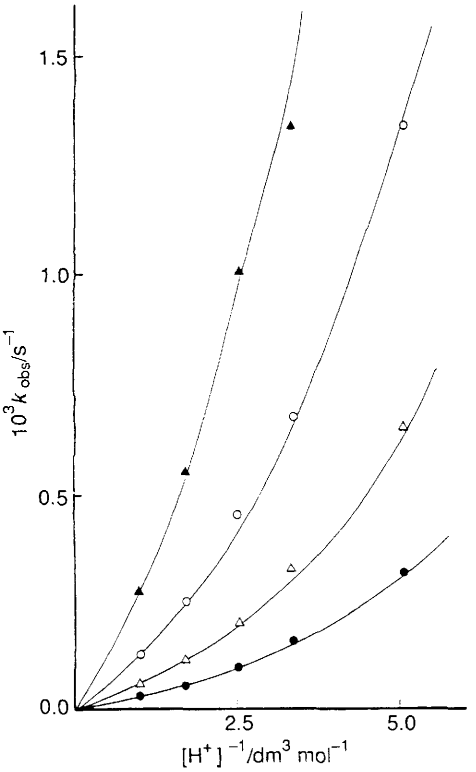

Fig. 3 Hydrogen-ion dependency for the slow stage. $[U^{IV}] = 5.36 \times 10^{-3}$, $[IrCl_6]^{2-} = 2.03 \times 10^{-4}$ and $I = 1.0$ mol dm^{-3} at 15 (●), 20 (△), 25 (○) and 30 °C (▲)

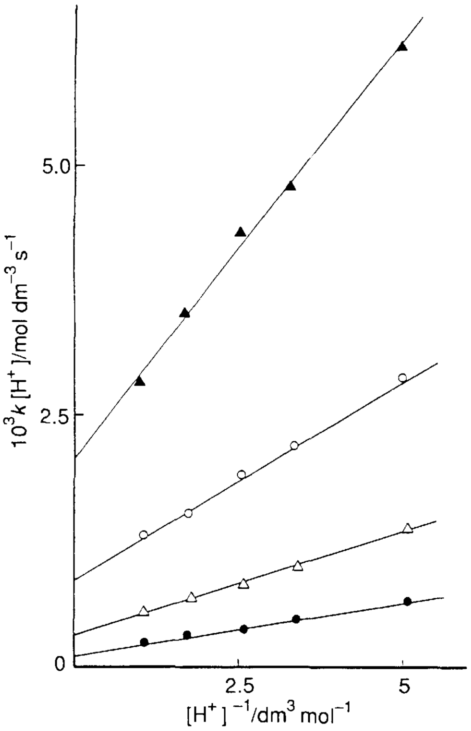

Fig. 4 Plots of $k[H^+]$ *vs.* $[H^+]^{-1}$ for the slow stage. Details as in Fig. 3

K_{a2} are the hydrolysis constants for $(H_2O)_nU^{IV}$ and $[(H_2O)_nU^{IV}{\cdot}Cl_6Ir^{IV}]_T$ is the analytical total concentration of the binuclear intermediate. However, the experimental results described are not in agreement with rate equation (12) since plots of k' against $[H^+]^{-1}$ gave curves passing through the origin as shown in Fig. 3.

This means that the first term, k_1, corresponding to the unhydrolysed species $[(H_2O)_nU^{IV}{\cdot}Cl_6Ir^{IV}]^{2+}$ is relatively small, and hence its reaction can be neglected. Then, the reactions involving the decomposition of the hydrolysed species may therefore be considered as the sole mechanism of electron transfer. Assuming that $k_{a1}K_{a2}[H^+]^{-2}$, $K_{a1}[H^+]^{-1} \ll 1$,[28,29] equation (12) may be simplified to (13) where $k_2' = k_2K_{a1}$ and

$$\text{Rate} = k' = k_2'[H^+]^{-1} + k_3'[H^+]^{-2} \qquad (13)$$

$k_3' = k_3K_{a1}K_{a2}$, respectively. According to equation (13), a plot of $k'[H^+]$ *versus* $[H^+]^{-1}$ should be linear as shown in Fig. 4.

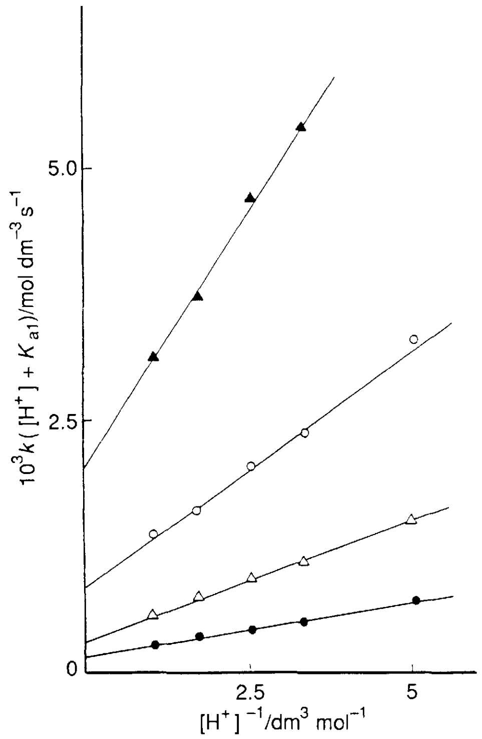

Fig. 5 Plot of $k([H^+] + k_{a1})$ *vs.* $[H^+]^{-1}$ for the slow stage. Details in Fig. 3

Table 1 The rate constants k_2' and k_3' at various temperatures in the oxidation of uranium(IV) by hexachloroiridate(IV) in the slow stage of the reaction $[U^{IV}] = 5.36 \times 10^{-3}$, $[IrCl_6]^{2-} = 2.03 \times 10^{-4}$ and $I = 1.0$ mol dm^{-3}

	T/°C			
	15	20	25	30
$10^4k_2'$/mol dm^{-3} s^{-1}	2.18	3.80	9.17	20.67
$10^4k_3'$/mol^2 dm^{-6} s^{-1}	0.84	2.03	3.92	9.50

Another interpretation might also be suggested considering that $K_{a1}K_{a2}[H^+]^{-2} \ll (1 + K_{a1}[H^+]^{-1})$ in equation (12).[28,29] Consequently equation (12) can now be rewritten in the form (14). Assuming that the K_{a1} values are nearly equal to the

$$k'([H^+] + K_{a1}) = k_2' + k_3'[H^+]^{-1} \qquad (14)$$

hydrolysis constants of uranium(IV),[28,29] plots of the left-hand side against $[H^+]^{-1}$ should be linear as experimentally observed (Fig. 5), which in turn confirms this suggestion. The calculated thermodynamic parameters for k_2' and k_3' using either equation (13) or (14) were found to be nearly the same. The values of k_2' and k_3' are summarized in Table 1.

The hexachloroiridate(III) formed can exist in two forms $[IrCl_6]^{3-}$ and/or $[IrCl_5(OH_2)]^{2-}$. It was possible to identify the two species and determine the relative amounts of each by spectrophotometric and ion-exchange techniques.[15] The

Table 2 Activation parameters of the binuclear complex formation and electron-transfer processes in the oxidation of uranium(IV) by hexachloroiridate(IV) and hexachloroplatinate(IV) ions

Reaction	Pathway	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta G^{\ddagger}$/kJ mol^{-1}	Ref.
U^{IV}–$[IrCl_6]^{2-}$	k_1	74.54 ± 2.31	70.92 ± 0.59	48.71 ± 1.28	This work
	k_{-1}	−73.89 ± 3.14	45.98 ± 1.22	68.00 ± 2.16	
	k_2'	67.84 ± 1.48	110.38 ± 1.29	90.16 ± 1.73	This work
	k_3'	78.86 ± 2.53	115.63 ± 1.43	92.10 ± 2.18	
U^{IV}–$[PtCl_6]^{2-}$	k_1	77.51 ± 2.39	72.29 ± 0.72	49.19 ± 1.43	2
	k_{-1}	−99.61 ± 4.92	40.50 ± 1.37	70.18 ± 2.84	
	k_3'	130.42 ± 14.51	136.02 ± 4.53	97.15 ± 8.85	2

spectrum of hexachloroiridate(III) shows a peak at 358 nm (ε = 74 dm^3 mol^{-1} cm^{-1}), while of aquapentachloroiridate(III) gives a peak at 347 nm (ε = 100 dm^3 mol^{-1} cm^{-1}). Pulson and Garner[30] have found that solutions of $[IrCl_6]^{3-}$ and $[IrCl_5(OH_2)]^{2-}$ can be oxidized rapidly by chlorine to the corresponding iridium(IV) complexes. Our experimental results indicate that the final species upon reduction of Ir^{IV} is only $[IrCl_6]^{3-}$ ion.

Although the rate laws provide no information on whether electron transfer is of inner- or outer-sphere nature, some information may be expected by examining the magnitude of the rate constant. If the rate constant of the redox step is greater than the rate of substitution the reaction is necessarily of the outer-sphere type.[31,32] Unfortunately, no data are available on the rate of substitution of uranium(IV). Therefore, the rate constant observed for the present redox reaction may be interpreted in terms of either an inner- or outer-sphere mechanism since $(H_2O)_nU^{IV}$ is known to be labile whereas $[IrCl_6]^{2-}$ is extremely inert to substitution with, at 50 °C, the rate constant for aquation of the first chloride being 10^{-6} s^{-1}.[30]

The possibility that the fast step involves an outer-sphere ion pairing of $(H_2O)_nU^{IV}$ and $[IrCl_6]^{2-}$ followed by slow electron transfer within the pair remains to be considered. Ion pairing should be in turn diffusion controlled whereas the intermediate forms with $k_1 = 6.86 \times 10^3$ dm^3 mol^{-1} s^{-1}. The perturbations in the spectrum of the intermediate from that of $[IrCl_6]^{2-}$ (Fig. 1), especially at higher energy, seem larger than would be expected for an outer-sphere ion pair. By these arguments an outer-sphere mechanism is excluded and the favoured mechanism is of the inner-sphere type[33–35] involving release of protons from water molecules co-ordinated to uranium(IV) followed by transfer of electrons from U^{IV} to Ir^{IV} [equation (15)] where y denotes the released protons.

$$[(OH_2)_{n-y}U^{IV}\text{·}Cl_6Ir^{IV}]^{2+} \xrightarrow{\text{slow}} [(H_2O)_{n-y}U^{V}\text{·}Cl_6Ir^{III}]^{2+} \quad (15)$$

The loss of protons from the hydration sphere of $(H_2O)_nU^{IV}$ prior to the rate-determining step is presumed to lower the energy barriers because the the transition states will more closely resemble the products [equation (16)]. This O–U–O

$$(H_2O{-}U{-}OH_2)^{4+} \rightleftharpoons (O{=}U{=}O)^{+} + 4H^{+} + e \quad (16)$$

configuration, which simulates the structure of both uranium-(V) and -(VI), has frequently been postulated in actinide reactions.[36,37] The role of protons in the oxidation of uranium-(VI) has attracted considerable interest. The overall reaction occurring when uranium(IV) reacts with $[IrCl_6]^{2-}$ is the formation of 1 mol of U^{VI} per 2 mol of $[IrCl_6]^{2-}$ as defined by equation (2), and the release of 2 mol of hydrogen ions per mol of $[IrCl_6]^{2-}$ is observed. This means that two protons are lost in the formation of the O–U–O core of the activated complex.[38–41]

The kinetics of oxidation of uranium(IV) by $[PtCl_6]^{2-}$ ion showed that the decomposition of the hydrolysed species of the intermediate complex, $[(H_2O)_{n-2}(OH)_2U^{IV}\text{·}Cl_6Pt^{IV}]$, was the only pathway in the rate-determining step. Therefore, a simultaneous two-electron transfer in a single step was proposed in this system. On the other hand, two reaction pathways for the decomposition of the hydrolysed species, $[(H_2O)_{n-1}(OH)U^{IV}\text{·}Cl_6Ir^{IV}]^{+}$ and $[(H_2O)_{n-2}(OH)_2U^{IV}\text{·}Cl_6Ir^{IV}]$, were observed in the oxidation of uranium(IV) by $[IrCl_6]^{2-}$ ion. Hence, successive one-electron transfer changes are probable for this reaction. This suggestion was based on the estimated redox potential of the relevant U^{V}–U^{IV} couple (−0.58 V) along with the value for the $[IrCl_6]^{2-}$–$[IrCl_6]^{3-}$ couple (0.87 V).[18]

Kinetic parameters for a series of common reactions may be considered as good evidence in support of the reaction mechanism. Unfortunately, the kinetic parameters k_2 and k_3 could not be evaluated because of non-availability of the hydrolysis constants K_{a1} and K_{a2} at various temperatures. Although some attempts were made to evaluate these constants from the experimental data, the results were not satisfactory. Therefore, the apparent rate constants k_2' and k_3' are composite quantities of the rate constants and the hydrolysis constants. The activation parameters for k_2' and k_3' are summarized in Table 2, along with the corresponding values for the oxidation of uranium(IV) by $[PtCl_6]^{2-}$ ion. The high enthalpies and entropies of activation observed for k_2' and k_3' are in part directly attributed to the hydrogen-ion dependence, since the apparent rate constants are the product of the rate constants and the hydrolysis constants. The differences in the activation parameters of the k_3' pathway observed in the U^{IV}–$[PtCl_6]^{2-}$ and –$[IrCl_6]^{2-}$ reactions may be explained in part by the dissimilarity of their transition states since Pt^{IV} tends to change its structure from octahedral to tetrahedral on reduction whereas Ir^{IV} does not.

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Received 26*th February* 1991; *Paper* 1/00923K