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Kinetics and Mechanism of the Formation of the Chromium(III)–Uranium(V) Binuclear Complex

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The kinetics of the formation of the [Cr(III)·U(V)] binuclear complex have been measured by stopped-flow techniques. The rate of formation of the complex was found to be given by the expression $d(\text{complex})/dt = k[UO_2^{2+}][Cr^{2+}]$. The value of k is $(1.29 \pm 0.04) \times 10^4\ M^{-1}\ \text{sec}^{-1}$, at 14.5° and an ionic strength of 2.0, and is independent of acid concentration in the range 0.03–2.0 M $[H^+]$. The reaction has an activation energy of 1.38 ± 0.40 kcal mol^{-1}, and mechanisms consistent with the observed data are discussed.

Introduction

Recent studies on the mechanism of some redox reactions of the actinide ions have provided evidence for the formation of binuclear complexes between an actinyl ion and another metal ion. Thus the rate laws of the Fe(II)–Pu(VI),[1] V(III)–U(VI),[2] and V(III)–U(VI)[3] reactions are of a form which suggests the participation of binuclear complexes in the reaction mechanism. More direct evidence for the formation of binuclear complexes has been obtained from spectroscopic studies of mixtures of U(V)–Cr(III),[4] U(V)–U(VI),[5] of Np(V) with U(VI),[6] of Np(V) with Fe(III), Al(III), Ga(III), Sc(III), In(III), and Cr(III),[7] and of Pu(V) with Cr(III).[8]

The formation of these complexes is not unique to the actinide ions. The reaction of Cr(II) with V(IV) also produces a binuclear species, presumably Cr(III)·V(III), the rate constant for the formation of this complex being estimated as $>8 \times 10^3\ M^{-1}\ \text{sec}^{-1}$.[9] Similar species are believed to be formed between Cr(II) and V(III)[10] and between V(II) and V(IV).[11]

The binuclear complexes formed between U(V) and Np(V) with Cr(III) have been studied in some detail. Sullivan[7] showed that a 1:1 complex was formed very slowly when Cr(III) and Np(V) were mixed in perchloric acid solution. The complex could be isolated by ion exchange techniques and the equilibrium constant of reaction 1 was 2.62, the rate of formation of

$$\text{Np(V)} + \text{Cr(III)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\text{Np(V)}\cdot\text{Cr(III)}] \quad (1)$$

the complex being $5.8 \times 10^{-6}\ M^{-1}\ \text{sec}^{-1}$ at 25°.[7] An apparently analogous complex is formed very quickly and quantitatively when U(VI) and Cr(II) are mixed.[4] The absorption spectrum of the complex suggests that the species contains a Cr(III) ion so that the formation of the complex involves the reduction of the U(VI) (reaction 2). The mechanism of decomposition of

$$\text{U(VI)} + \text{Cr(II)} \longrightarrow [\text{U(V)}\cdot\text{Cr(III)}] \quad (2)$$

the intermediate was found to be very complex, and some evidence for the presence of two intermediates which differed in their reactivities was obtained. Gordon[12] has shown that efficient transfer of oxygen from the uranyl ion to the $[Cr(H_2O)_6]^{3+}$ takes place during the reaction.

For the above complexes it has been suggested that the actinyl oxygen atom replaces a coordinated water molecule in the inner coordination sphere of the Cr(III) ion (reaction 3). In the case of the reaction of Cr(III)

$$[Cr(H_2O)_6]^{3+} + [O\text{–}M\text{–}O]^{+} \longrightarrow [(H_2O)_5Cr\text{–}O\text{–}M\text{–}O]^{4+} + H_2O \quad (3)$$

with Np(V) no electron transfer occurs, and the rate of formation might be expected to be controlled by the rate at which the water molecules coordinated by Cr(III) are replaced by Np(V) ions. In the case of the U(V)·Cr(III) complex formed by the reaction of U(VI) and Cr(II) both electron transfer and replacement of coordinated water must occur. The replacement can occur at either Cr(II) or Cr(III), *i.e.*, before or after the electron transfer. Preliminary work in this laboratory showed that the formation of the binuclear U(V)·Cr(III) complex could be followed by stop-flow techniques, and a detailed study of the reaction was undertaken in an attempt to elucidate the mechanism of this reaction.

Experimental Section

Uranyl perchlorate solutions were prepared by dissolution of UO_3 in perchloric acid. The UO_3 used for this preparation was made either by heating uranyl nitrate at 300° or by the hydrogen peroxide precipitation method.[13] Both sources of UO_3 gave identical results. Chromium(III) perchlorate solutions were prepared from chromium metal or by the dissolution of chromium trioxide in approximately 1 M $HClO_4$ and reduction to Cr(III) with excess H_2O_2, followed by boiling to remove excess H_2O_2. The final solutions were analyzed for Cr(III)[14] and free acid.[15] Sodium perchlorate solutions, used to maintain the ionic strength of the solutions constant, were prepared by neutralizing standardized sodium hydroxide with standardized perchloric acid. All water used in these experiments was demineralized and distilled from alkaline permanganate.

For the runs in heavy water, the preparation of the reagents was identical with that above, except that deuterated perchloric

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[2] T. W. Newton and F. B. Baker, *ibid.*, **70**, 1943 (1966).
[3] T. W. Newton, *ibid.*, **62**, 943 (1958).
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[7] (a) J. C. Sullivan, *ibid.*, **84**, 4256 (1962); (b) J. C. Sullivan, *Inorg. Chem.*, **3**, 315 (1964).
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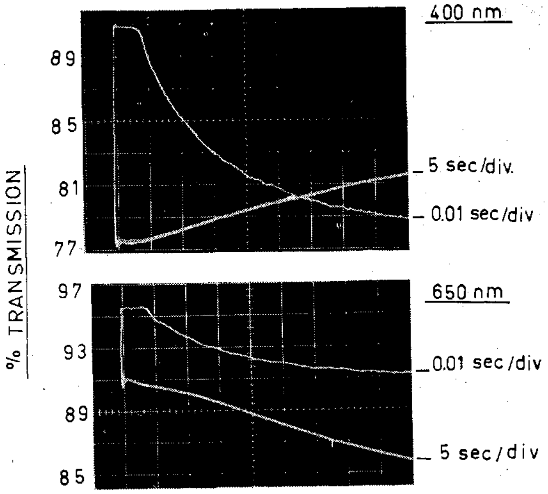

Figure 1.—Typical reaction traces obtained from the reaction of Cr(II) with U(VI) at 400 and 650 nm, [Cr(II)] = 5.046 × 10^{-3} *M*, [U(VI)] = 4.790 × 10^{-3} *M*, [H^+] = 1.0 *M*, 14.5°, and ionic strength = 2.0.

acid prepared according to the method of Sullivan, *et al.*,[16] was used. In this case the ionic strength was kept at 2.0 with sodium perchlorate (Merck) heated to constant weight at 140°.

The Pu(IV) solutions were prepared by dissolving high-purity plutonium metal (NBS Standards) in purified and standardized perchloric acid, followed by heating aliquots of the resulting solution to near dryness with perchloric acid and diluting to volume. The vanadyl perchlorate solutions were prepared from vanadyl sulfate (Analar) by treating a vanadyl sulfate solution with barium perchlorate (Merck), filtering the resulting precipitate, and making the solution up to the desired volume.

Reactant solutions of U(VI) and Cr(III) of the desired acidity and ionic strength were prepared by dilution of the stock solutions. The U(VI) solutions were degassed by flushing with high-purity nitrogen gas. The Cr(III) solutions were placed in a thermostated electrochemical cell made from a B54 socket, sealed with a Teflon stopper. An electrical contact was provided to the mercury pool cathode. The Teflon stopper was drilled to receive an inlet for nitrogen flushing, a Teflon tube ending in a standard taper through which samples could be withdrawn with a hypodermic syringe, and a tube fitted with a fine sinter containing the platinum anode immersed in 1 *M* $HClO_4$. The Cr(III) solutions in the cell were degassed by flushing with nitrogen gas for 30 min. The electrolysis was then started, and when complete, samples were withdrawn with a hypodermic syringe. A similar sample was withdrawn from the U(VI) solution. The syringes were sealed with Teflon syringe caps and placed in a thermostated water bath, operated at the same temperature as the stop-flow apparatus. The Cr(II) solutions prepared and stored in the above fashion were stable for at least 12 hr, provided that oxygen was excluded from the solutions and the hypodermic syringe. When the solutions had reached the required temperature, usually within 15 min, the solutions were transferred to the driving syringes of an Aminco-Morrow stopped-flow apparatus and the reactions measured as quickly as possible.

Results

Figure 1 shows typical reaction traces obtained by reacting Cr(II) with U(VI) in perchlorate media at 14.5°, using light of either 400 or 650 nm wavelength to follow the reaction. At 400 nm, the result indicates the occurrence of a fast reaction, shown by the rapid decrease in the transmission, followed by a much slower reaction indicated by the increase in transmission. This result is consistent with a reaction mechanism involving the rapid formation of an intermediate, followed by a much slower decomposition of the intermediate. Similar results are obtained at 650 nm except that at this wavelength the decomposition of the intermediate leads to a decrease in the transmission. These results are qualitatively identical with those described by Newton and Baker,[4] except that these authors, using conventional techniques, were unable to follow the formation of the intermediate.

Although the above results show that the formation of an intermediate can be followed using the stop-flow techniques, they do not show that the intermediate is identical with that described by Newton and Baker.[4] Assuming that the formation of the intermediate discussed by these authors is represented by the equation

$$\mathrm{Cr(II)} + \mathrm{U(VI)} \longrightarrow [\mathrm{Cr(III)}\cdot\mathrm{U(V)}] \qquad (4)$$

then at the completion of this reaction the absorbance (ABSF) of the reactant solution is given by the expression

$$\mathrm{ABSF} = a\epsilon^{\mathrm{U(VI)}} + b\epsilon^{\mathrm{Cr(II)}} + x\epsilon^{\mathrm{INT}} \qquad (5)$$

where a, b, and x are respectively the concentrations and $\epsilon^{\mathrm{U(VI)}}$, $\epsilon^{\mathrm{Cr(II)}}$, and ϵ^{INT} the molar extinction coefficients of U(VI), Cr(II), and [Cr(III)·U(V)]. If, as suggested by the previous investigation,[4] reaction 4 is quantitative and if conditions are chosen so that the initial U(VI) concentration is greater than the initial Cr(II) concentration, it can be readily shown that

$$\mathrm{ABSF} = [a_0 - b_0]\epsilon^{\mathrm{U(VI)}} + b_0\epsilon^{\mathrm{INT}} \qquad (6)$$

or

$$\epsilon^{\mathrm{INT}} = \frac{\mathrm{ABSF} - [a_0 - b_0]\epsilon^{\mathrm{U(VI)}}}{b_0} \qquad (7)$$

where a_0 and b_0 are respectively the initial U(VI) and Cr(II) concentrations.

The final absorbance can be obtained from the reaction trace, and the values of $\epsilon^{\mathrm{U(VI)}}$ at the appropriate wavelength can be measured independently. As shown in Table I, the values of ϵ^{INT} obtained in the present study at 14.5° and at various wavelengths are similar to those reported by Newton and Baker,[4] and the ratio of the extinction coefficients reported by these authors and those of the present study are essentially constant. Further, the values of ϵ^{INT} determined in this study are independent of initial Cr(II) and U(VI) concentrations (Table II). These results would thus suggest that the intermediate whose formation is represented by reaction traces such as those shown in Figure 1 and the binuclear species discussed by Newton and Baker are identical.

TABLE I

SUMMARY OF THE EXTINCTION OF COEFFICIENTS OF THE COMPLEX AT VARIOUS WAVELENGTHS

Wave-length, nm	Extinction coefficient		Ratio of values of ref 4/ present work
	Present work[a] 14.5°	Ref 4 0°	
400	26.2 ± 0.5	30.0	1.15
425	20.9 ± 0.4	27.8	1.34
450	12.7 ± 0.2	17.5	1.38
600	14.2 ± 0.5	19.8	1.39
650	10.1 ± 0.3	~12	

[a] [H^+] = 1.0 *M*, ionic strength = 2.0, 14.5°, $[\mathrm{U(VI)}]_0$ = 9.580 × 10^{-3} *M*, and $[\mathrm{Cr(II)}]_0$ = 2.523 × 10^{-3} *M*.

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[16] J. C. Sullivan, D. Cohen, and J. C. Hindman, *J. Amer. Chem. Soc.*, **79**, 3672 (1957).

TABLE II

EFFECT OF INITIAL Cr(II) AND U(VI) CONCENTRATIONS ON THE RATE CONSTANT FOR THE FORMATION OF THE COMPLEX[a]

10^3[Cr(II)], M	10^3[U(VI)], M	No. of determinations	ϵ^{INT}	$10^{-4}k$, M^{-1} sec^{-1}
1.262	4.790	4	24.8 ± 0.5	1.43 ± 0.08
2.523	4.790	4	26.9 ± 0.5	1.33 ± 0.06
2.523	7.185	4	27.2 ± 0.5	1.34 ± 0.09
2.523	9.580	17	26.2 ± 0.5	1.29 ± 0.04
2.523	11.975	4	27.4 ± 0.5	1.40 ± 0.10
5.064	11.975	8	28.4 ± 1.0	1.21 ± 0.10
5.064	23.950	4	25.8 ± 0.5	1.41 ± 0.07
2.523	2.515	3	25.4 ± 1.0	1.43 ± 0.08
5.046	5.029	4	27.6 ± 1.0	1.57 ± 0.15
10.92	10.06	4	25.0 ± 0.5	1.70 ± 0.08

[a] $[H^+] = 1.0$, ionic strength = 2.0, 14.5°, and 400 nm.

Since the molar extinction coefficient of Cr(II) is very low,[17] the absorbance (ABST) of the reaction mixture at any time during the formation of the intermediate is given by the expression

$$\mathrm{ABST} = [a_0 - x]\epsilon^{\mathrm{U(VI)}} + x\epsilon^{\mathrm{INT}} \qquad (8)$$

and hence

$$x = \frac{\mathrm{ABST} - a_0\epsilon^{\mathrm{U(VI)}}}{\epsilon^{\mathrm{INT}} - \epsilon^{\mathrm{U(VI)}}} \qquad (9)$$

The rate of formation of the intermediate is given by the equation

$$\frac{dx}{dt} = k[a_0 - x][b_0 - x] \qquad (10)$$

which on integration yields the equation

$$\frac{1}{a_0 - b_0} \ln \frac{b_0[a_0 - x]}{a_0[b_0 - x]} = kt \qquad (11)$$

Under the conditions used in the present study, the true time (t) elapsed since the start of the reaction is given by

$$t = t_{\mathrm{exp}} + \Delta t \qquad (12)$$

where t_{exp} is the experimentally measured time and Δt the dead time of the stop-flow apparatus. Thus eq 8 can be written

$$\frac{1}{a_0 - b_0} \ln \frac{b_0[a_0 - x]}{a_0[b_0 - x]} = kt_{\mathrm{exp}} + k\Delta t \qquad (13)$$

The value of the rate constant (k) can be determined from a plot of the left side of eq 13 against t_{exp}, the slope of the line being k while the intercept will be equal to $k\Delta t$. Typical plots of eq 10 of data obtained at various wavelengths are shown in Figure 2, and the data of Tables II and III show that the values of the rate constants obtained from these plots are independent of initial reactant concentration and of the wavelength of the analyzing light. The observed rate constant for samples in which $a_0 \approx b_0$ appeared to increase slightly with increasing initial reactant concentration suggesting possible complicating reactions. However, in those cases where $a_0 > b_0$, the results show no consistent relationship between the rate constant and the reactant concentration.

TABLE III

VALUES OF THE RATE CONSTANT DETERMINED AT VARIOUS WAVELENGTHS[a]

Wavelength, nm	No. of determinations	$10^{-4}k$, M^{-1} sec^{-1}
400	17	1.29 ± 0.05
425	4	1.20 ± 0.04
450	4	1.34 ± 0.04
600	4	1.28 ± 0.06
650	4	1.32 ± 0.12

[a] $[H^+] = 1.0$, $[Cr(II)]_0 = 2.523 \times 10^{-3}$ M, $[U(VI)]_0 = 9.580 \times 10^{-3}$ M, ionic strength = 2.0, 14.5°.

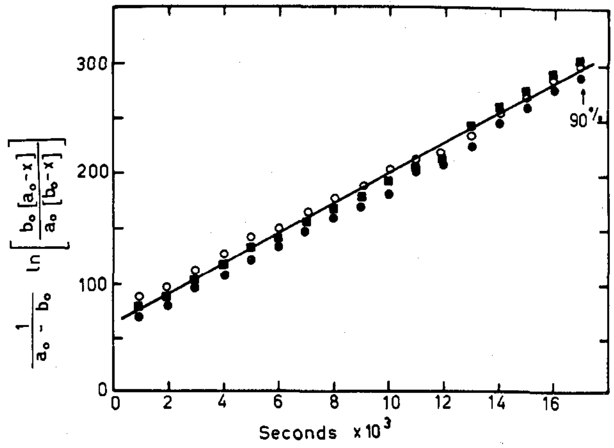

Figure 2.—Typical plots of the integrated rate equation, $[H^+] = 1.0$ M, 14.5°, and ionic strength = 2.0: ●, 400 nm, $[U(VI)] = 9.570 \times 10^{-3}$ M, $[Cr(II)] = 2.523 \times 10^{-3}$ M; ○, 600 nm, $[U(VI)] = 9.510 \times 10^{-3}$ M, $[Cr(II)] = 2.523 \times 10^{-3}$ M; ■, 650 nm, $[U(VI)] = 1.1976 \times 10^{-2}$ M, $[Cr(II)] = 5.046 \times 10^{-3}$ M.

The effect of acid concentration in the range 0.03–2.0 M at a constant ionic strength is summarized in Table IV. The results appear to show a slight increase in the rate constant with increasing acid concentration.

TABLE IV

EFFECT OF ACID CONCENTRATION ON THE RATE CONSTANT FOR THE FORMATION OF THE COMPLEX[a]

$[H^+]$, M	No. of determinations	ϵ^{INT}	$10^{-4}k$, M^{-1} sec^{-1}
2.02	4	27.7 ± 1.0	1.46 ± 0.05
1.75	4	27.6 ± 0.7	1.34 ± 0.05
1.02	17	26.2 ± 0.5	1.29 ± 0.04
0.78	4	26.2 ± 0.5	1.28 ± 0.04
0.45	4	26.2 ± 0.4	1.30 ± 0.07
0.25	4	26.2 ± 0.2	1.19 ± 0.05
0.030	4	26.0 ± 0.4	1.08 ± 0.03

[a] Ionic strength = 2.0, 14.5°, 400 nm, $[U(VI)]_0 = 9.570 \times 10^{-3}$ M, and $[Cr(II)]_0 = 2.523 \times 10^{-3}$ M.

The effect of temperature in the range 14.5–32° on the rate constant is summarized in Table V. The rate constant was found to increase slightly with increasing temperature. When weighted according to the inverse of the squares of the uncertainties of the measurements, a least-squares analysis yields a value of 1.37 ± 0.40 kcal mol^{-1} for the activation energy.[18]

The rate constant of the reaction was also determined in a fully deuterated solvent. At 14.5°, an ionic strength of 2.0, and an acid concentration of 1.0 M, the rate constant for the reaction is (8.26 ± 0.26) ×

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(17) A. Ekstrom, unpublished data.

(18) The least-squares analysis to calculate the activation energy and ionic strength dependency were carried out using the nonlinear least-squares program described by M. H. Lietzke, ORNL Report No. 3259 (1962).

TABLE V

EFFECT OF TEMPERATURE ON THE RATE CONSTANT FOR THE FORMATION OF THE COMPLEX[a]

Temperature, °C	No. of determinations	ϵ^{INT}	$10^{-4}k$ (obsd), M^{-1} sec^{-1}	$10^{-4}k$ (calcd),[b] M^{-1} sec^{-1}
14.5	17	26.2 ± 0.5	1.29 ± 0.04	1.31
17.5	4	26.6 ± 0.5	1.42 ± 0.06	1.34
24.7	3	26.7 ± 0.2	1.47 ± 0.08	1.42
28.5	3	26.7 ± 0.4	1.41 ± 0.05	1.46
29.2	3	25.8 ± 0.4	1.41 ± 0.04	1.47
32.0	3	27.4 ± 0.6	1.52 ± 0.02	1.50

[a] $[\mathrm{H}^+] = 1.0\ M$, ionic strength = 2.0, 400 nm, $[\mathrm{U(VI)}]_0 = 9.570 \times 10^{-3}\ M$, and $[\mathrm{Cr(II)}]_0 = 2.523 \times 10^{-3}\ M$. [b] Calculated from $\log k = \log A_0 - E_A/2.303RT$ with $\log A_0 = 5.16 \pm 0.29$, and $E_A = (1.38 \pm 0.40) \times 10^3$ cal mol^{-1}.

$10^3\ M^{-1}$ sec^{-1}, this being the average and mean error of ten determinations. Under identical conditions in H_2O, the rate constant is $(1.29 \pm 0.04) \times 10^4$, being the average and mean error of 17 determinations. The rate in D_2O is thus significantly slower than in H_2O, the ratio of $k_{\mathrm{H_2O}}/k_{\mathrm{D_2O}}$ being 1.56 under the specified conditions.

During the preliminary experiments it appeared that the rate of formation of the binuclear complex was strongly dependent on the ionic strength. This result is confirmed by the data presented in Table VI, which shows that the rate of the reaction increases by a factor of approximately 3 in the ionic strength range of 0.087–0.99. As shown in Table VI the observed ionic strength dependency is consistent with the extended Debye–Hückel theory, either with the constant *C* set equal to a value of 0.20 or alternatively with *C* treated as an unknown constant.

TABLE VI

EFFECT OF IONIC STRENGTH ON THE RATE CONSTANT FOR THE FORMATION OF THE COMPLEX[a]

Ionic strength	No. of determinations	$10^{-4}k$ (obsd), M^{-1} sec^{-1}	$10^{-4}k$ (calcd),[b] M^{-1} sec^{-1}	$10^{-4}k$ (calcd),[c] M^{-1} sec^{-1}
0.087	3	0.219 ± 0.005	0.216	0.218
0.112	3	0.247 ± 0.009	0.249	0.248
0.137	2	0.264 ± 0.010	0.272	0.275
0.162	3	0.310 ± 0.008	0.294	0.300
0.272	3	0.382 ± 0.008	0.376	0.395
0.422	3	0.508 ± 0.007	0.471	0.498
0.990	3	0.779 ± 0.005	0.804	0.782

[a] $[\mathrm{H}^+] = 0.03\ M$, 14.5°, $[\mathrm{U(VI)}]_0 = 9.580 \times 10^{-3}\ M$, $[\mathrm{Cr(II)}]_0 = 2.523 \times 10^{-3}\ M$, 400 nm. [b] Calculated from $\log k = \log k_0 + (A\Delta Z^2\mu^{1/2})/(1 + Ba\mu^{1/2}) + 0.200\mu$ with $\log k_0 = 2.703 \pm 0.002$, $a = (9.17 \pm 0.38) \times 10^{-8}$ cm, $A = 0.5028$, and $B = 0.3273 \times 10^8$. R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed, Butterworths, London, 1959, p 392. [c] Calculated from $\log k = \log k_0 + (A\Delta Z^2\mu^{1/2})/(1 + Ba\mu^{1/2}) + C\mu$ with $\log k_0 = 2.711 \pm 0.004$, $a = (6.89 \pm 0.58) \times 10^{-8}$ cm, $C = 0.036 \pm 0.051$, $A = 0.5028$, and $B = 0.3273 \times 10^8$. R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed, Butterworths, London, 1959, p 392.

An attempt was also made to measure the rate of the reaction of Pu(VI) with Cr(II). Previous studies[8] have shown that a Pu(V)–Cr(III) binuclear complex was formed by the oxidation of Pu(IV) by Cr(VI). Examination of the spectrum of the Pu(V)·Cr(III) complex showed that at 400 nm the spectrum of the complex is sufficiently different from Pu(VI) and Cr(II) so that using initial Pu(VI) and Cr(II) concentrations of 1.0×10^{-2} and $2.5 \times 10^{-3}\ M$, respectively, the formation of the Pu(V)·Cr(III) intermediate would be readily observable, if the species were formed and if its rate of formation was sufficiently slow. However, it was found that at 14.5° and 1 M H^+ the absorbance of the reactants increased to a constant value within the dead time of the stop-flow apparatus. The final absorbance was considerably less than that calculated if the product had been the Pu(V)·Cr(III) complex. A similar experiment, using only one-tenth of the above initial reactant concentrations also resulted in an "instantaneous" increase in the absorption.

A similar experiment in which Cr(II) (2.523×10^{-3} M) and V(IV) (1.0×10^{-2} M) in 1.5 M H^+ and at 14.5° were mixed also resulted in an "instantaneous" change in transmission at 400 nm. Thus while Espenson[9] showed that the rate constant for the formation of the Cr(III)·V(III) complex exceeded a value of $8 \times 10^3\ M^{-1}$ sec^{-1}, the present results show that the value is much larger than that of the analogous reaction between Cr(II) and U(VI).

Since the dead time of the stopped-flow apparatus is approximately 5 msec, the above results indicate that the second-order rate constants for the Pu(VI)–Cr(II) and V(IV)–Cr(II) reactions exceed values of approximately 10^5–10^6 and 10^4–10^5 M^{-1} sec^{-1}, respectively.

Discussion

The similarity between the extinction coefficients of the intermediate observed in the present study and those determined by Newton and Baker[4] leaves little doubt that the two species are the same. Since the species is believed to contain a Cr(III) moiety, the transfer of an electron as well as the replacement of coordinated water must occur if the species is prepared by reacting Cr(II) and U(VI).

The previous studies on the decomposition of the intermediate provided results which were interpreted as showing that a second intermediate, designated Cr·U*, was present in the reaction mixture.[4,12] It was suggested that this species was formed by a reaction or rearrangement of the first intermediate (equation 14). The rate of this conversion is presumably slow

$$[\mathrm{Cr(III)\cdot U(V)}]^{4+} \longrightarrow [\mathrm{Cr\cdot U}]^* \qquad (14)$$

compared to the formation of the first intermediate, since the present results show no evidence for the presence of the Cr·U* species.

The overall reaction occurring when Cr(II) reacts with U(VI) is the formation of 1 mol of U(IV) for each 2 mol of Cr(II) (equation 15). The decomposition

$$2\mathrm{Cr}^{2+} + \mathrm{UO_2}^{2+} + 4\mathrm{H}^+ \longrightarrow \mathrm{U}^{4+} + 2\mathrm{Cr}^{3+} + 2\mathrm{H_2O} \qquad (15)$$

of the intermediate has been shown[4] to result in the consumption of 2 mol of H^+ for each mol of Cr(II). The present results show that the rate of formation of the Cr(III)·U(V) intermediate is independent of acid concentration, the slight decrease in the rate constant with decreasing acid concentration being attributed to a medium effect resulting from the progressive replacement of H^+ ions by the Na^+ ions. The absence of any significant H^+ dependency also precludes any hydroxyl ion bridging in the complex.

Two reaction mechanisms for the formation of the intermediate may be considered, the first being the transfer of the electron prior to the replacement of a water molecule coordinated to Cr(II). This mechanism, corresponding to an outer-sphere mechanism, may be represented by eq 16–18. It is reasonable to suggest that the rate-controlling step in this mechanism would be the rate at which the UO_2^+ ion replaces a water molecule coordinated to Cr(III) (eq 8).

(a) Formation of outer-sphere ion pair

$$Cr^{2+}(H_2O)_6 + UO_2^{2+} \rightleftharpoons [Cr^{2+}(H_2O)_6]\cdot UO_2^{2+} \qquad (16)$$

(b) Electron transfer

$$[Cr^{2+}(H_2O)_6]\cdot UO_2^{2+} \longrightarrow [Cr^{3+}(H_2O)_6]\cdot UO_2^{+} \qquad (17)$$

(c) Replacement of coordinated water

$$[Cr^{3+}(H_2O)_6]\cdot UO_2^{+} \xrightarrow{k_{18}} [(H_2O)_5Cr^{3+}\cdot UO_2^{+}] + H_2O \qquad (18)$$

The inertness of $Cr^{III}(H_2O)_6$ to substitution is well established,[19] the rate constant for the replacement of water being approximately 3×10^{-5} sec^{-1} at 25°.[20] It is of interest to note that the rate constant for reaction 19 has a value of 5.80×10^{-6} sec^{-1}.[6] Since the present results show that the rate constant for the formation of the Cr(III)·U(V) intermediate is almost 10 orders of magnitude greater than the rate constant for reaction 19, it seems unlikely that this mechanism can account for the present results.

$$NpO_2^{+} + Cr^{3+}(H_2O)_6 \longrightarrow [(H_2O)_5Cr^{3+}\cdot NpO_2^{+}] + H_2O \qquad (19)$$

The second mechanism which may be considered involves the replacement of coordinated water before the electron transfer, *i.e.*, an inner-sphere electron transfer. This mechanism may be represented by eq 20 and 21.

(a) Formation of outer-sphere ion pair

$$Cr^{2+}(H_2O)_6 + UO_2^{2+} \overset{K_0}{\rightleftharpoons} [Cr^{2+}(H_2O)_6]\cdot UO_2^{2+} \qquad (20)$$

(b) Replacement of coordinated water

$$[Cr^{2+}(H_2O)_6]\cdot UO_2^{2+} \xrightarrow{k_{21}} [(H_2O)_5Cr^{2+}\cdot UO_2^{2+}] + H_2O \qquad (21)$$

(c) Electron transfer

$$[(H_2O)_5Cr^{2+}\cdot UO_2^{2+}] \xrightarrow{k_{22}} [(H_2O)_5Cr^{3+}\cdot UO_2^{+}] \qquad (22)$$

The formation of the outer-sphere ion pair is undoubtedly a diffusion-controlled process. Hence the formation of the Cr(III)–U(V) complex is controlled either by the rate at which a water molecule is replaced by the UO_2^{2+} ion in the inner coordination sphere of the Cr(II) ion (eq 21) or by the rate at which the electron is transferred from Cr(II) to U(VI). If the electron transfer is considered to be very fast, the experimentally determined rate constant (k) is related to k_{21} by the expression

$$k = k_{21}K_0 \qquad (23)$$

and it would be expected that the value of k_{21} should approach 10^8–10^9 sec^{-1}, since the lifetime of a particular water molecule in the coordination sphere of the Cr(II) ion is in the range 10^{-8}–10^{-9} sec.[21] Thus for this mechanism to be valid, K_0 has to have a value of $\sim 10^{-4}$–10^{-5} to account for the observed rate constant of $\sim 10^4$ M^{-1} sec^{-1}.

The value of K_0 is difficult to evaluate accurately. It has been suggested that the UO_2^{2+} ion has a linear structure in which the uranium atom carries a charge of 4+, while each of the oxygen atoms carries a charge of 1−.[22] To a first approximation, we can thus consider the outer-sphere ion pair as equivalent to one formed between a $Cr^{II}(H_2O)_6$ ion and a univalent anion. Using a value of 3.5 Å for the internuclear distance between the uranyl oxygen atom and the $Cr^{II}(H_2O)_6$ ion, K_0 is evaluated as approximately unity either by the Fuoss[23] or Bjerrum[24] theory. While it is probable that the values of K_0 calculated in this manner are upper limits since stereochemical effects are undoubtedly important, it is difficult to see that the value of K_0 can be as small as 10^{-4}–10^{-5}. The very much faster rate of formation of the analogous Cr(III)·V(III) intermediate is also difficult to explain by this mechanism.

Alternatively, an inner-sphere mechanism in which the rate-controlling step is the transfer of an electron may be considered. In this mechanism the rapid formation of the outer-sphere ion pair (eq 20) which rapidly and presumably rearranges reversibly to an inner-sphere complex between Cr(II) and uranium(VI) (eq 24) is followed by the transfer of the electron (eq 25).

$$[Cr^{2+}(H_2O)_6]\cdot UO_2^{2+} \overset{K_1}{\rightleftharpoons} [(H_2O)_5Cr^{2+}\cdot UO_2^{2+}] + H_2O \text{ (rapid)} \qquad (24)$$

$$[(H_2O)_5Cr^{2+}\cdot UO_2^{2+}] \xrightarrow{k_{24}} [(H_2O)_5Cr^{3+}\cdot UO_2^{+}] \text{ (rate controlling)} \qquad (25)$$

The value of the rate constant for the forward reaction of equation 24 is probably similar to the rate of water replacement at Cr(II), *i.e.*, of the order of 10^8–10^9 sec^{-1} at 25°. For this reaction mechanism the value of k_{25} is related to the experimental rate constant (k) by the expression $k_{25} = k/(K_0K_1)$. The values of K_0 and K_1 are not known with any confidence, and so the true value of k_{25} cannot be evaluated accurately, but it seems unlikely that K_0 and K_1 differ appreciably from unity,[25] so that k_{25} has a value which may be in the range of 10^3–10^5 M^{-1} sec^{-1}. It is clear, however, that the rate for the Cr(II)–U(VI) reaction is considerably slower than the equivalent Cr(II)–V(IV) reaction. This observation and the comparatively low value of k_{25} may be attributable to the greater difficulty of transferring f electrons compared to d electrons. It is of interest to note that the Eu(II)–V(III) reaction is also much slower than the equivalent Cr(II)–V(III) reaction, and an analogous explanation has been proposed to account for these latter observations.[26] The electron exchange reactions between certain transition metal ions are also believed to be slow because of spin restriction.[27]

For a reaction such as (25) above, the transfer of the electron will have to be preceded or followed by the rearrangement of the coordinated water molecules around the chromium ion, *i.e.*, as the electron is trans-

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[19] H. Taube and H. Myers, *J. Amer. Chem. Soc.*, **76**, 2103 (1954).

[20] J. P. Hunt and R. A. Plane, *ibid.*, **76**, 5960 (1954).

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[23] R. Fuoss, *ibid.*, **80**, 5059 (1958).

[24] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed, Butterworths, London, 1959, p 392.

[25] The value of the equilibrium constant for reaction 1 is 2.62,[7] and it may be expected that the value of K_1 would not be too different from this.

[26] A. Adin and A. G. Sykes, *J. Chem. Soc. A*, 1230 (1966).

[27] A. G. Sykes, *Advan. Inorg. Nucl. Chem.*, **10**, 153 (1968).

ferred across the Cr–O–U bridge, the water molecules around the Cr^{2+} ion will have to rearrange their positions to the one they would occupy around a Cr^{3+} ion. If this rearrangement must occur prior to the transfer of the electron, then an alternate interpretation of the present results is that the rate of the electron transfer is controlled by the rate at which the water molecules adjust their position to that which they would occupy around a Cr^{3+} ion.

For reaction 4 the temperature dependency of the observed rate constant yields values of 788 ± 395 cal mol^{-1} and -36.8 ± 1.3 eu for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. These values were obtained by fitting the experimental results to the equation $k = kT/he^{\Delta S^{\ddagger}/R}e^{-\Delta H^{\ddagger}/RT}$ by the nonlinear least-squares method, the data being weighted according to the reciprocals of the squares of the quoted errors. This compares to values of 25 kcal mol^{-1} and $+1.4$ eu for the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, respectively, for the formation of the Np(V)·Cr(IV) complex from Np(V) and Cr(III) ions.[7b] It would thus appear that there are basic differences in the mechanism of formation of the two species.

Using the mechanism indicated by eq 20, 24, and 25 it can be readily shown that

$$\Delta H^{\ddagger}(k_{25}) = \Delta H^{\ddagger}(k) - \Delta H(K_0) - \Delta H(K_1) \quad (26)$$

Where $\Delta H^{\ddagger}(k_{25})$ and $\Delta H^{\ddagger}(k)$ are the enthalpies of activation of reaction 25 and of the observed rate constant, and $\Delta H(K_0)$ and $\Delta H(K_1)$ the enthalpy changes associated with the equilibrium constants K_0 and K_1. The value of $\Delta H(K_0)$ can be estimated as ~1 kcal mol^{-1} from either the Bjerrum of Fuoss theory, the value being positive because of the dominance of the temperature dependency of the dielectric constant in the calculation. The value of $\Delta H(K_1)$ cannot be estimated, so that the enthalpy of activation for reaction 25 cannot be evaluated with any confidence.

The solvent D_2O effect for the reaction ($k_{H_2O}/k_{D_2O} = 1.56$) is of a comparable magnitude to that observed for other electron exchange and transfer reactions believed to proceed by inner-sphere mechanisms.[27] As these solvent effects can arise from several causes, this result does not provide further insight into details of the mechanism of the reaction.

The present results, in agreement with previous studies,[4] suggest that the reaction of Pu(VI) with Cr(II) does not result in a Cr(III)·Pu(V) intermediate even though the species can be formed by the reaction of Pu(IV) with Cr(VI).[8] The most likely explanation for this observation is that the Pu(VI)–Cr(II) reaction, which has a $\Delta G°$ value of -30.3 kcal mol^{-1} compared to -10.7 kcal mol^{-1} for the equivalent U(VI)–Cr(II) reaction, proceeds by an outer-sphere electron transfer mechanism (eq 27). As the rate constant for the disproportionation reaction of Pu(V) is probably much higher than the rate of substitution of water coordinated to Cr(III), the PuO_2^+ ion does not remain in the solution for a sufficient time to displace a water molecule from the Cr(III) coordination sphere. By comparison, the reduction of Pu(VI) with Fe(II), which has a $\Delta G°$ value of -3.3 kcal mol^{-1} has been shown to result in the formation of a binuclear intermediate believed to be a Pu(V)·Fe(III) species.

$$Cr^{2+}(H_2O)_6 + PuO_2^{2+} \longrightarrow Cr^{3+}(H_2O)_6 + PuO_2^{+} \quad (27)$$

Alternatively, the results obtained for the Pu(VI)–Cr(II) reaction may indicate that the Pu(V)–Cr(III) complex, although formed, reacts rapidly with Cr(II) to yield Pu(IV) and Cr(III). This interpretation would be consistent with the results obtained for the reaction of Np(VI) with Cr(II)[7b] which even in the presence of excess Np(VI) results in the formation of an appreciable yield of Np(IV).

In conclusion it may be noted that the preceding discussion has ignored the role of water molecules coordinated to the UO_2^{2+} ion. However, preliminary results[28] suggest that the rate of exchange of the four equatorially coordinated water molecules of the UO_2^{2+} ion with those of the bulk solution is quite rapid, and it seems unlikely that they play a prominent role in the formation of the Cr(III)·U(V) complex. It is also noted that Murman and Sullivan[29] have attempted to interpret their results for the formation and decomposition of the Cr(III)·Np(V) and Ru(III)·Np(V) complexes in terms of a mechanism in which the rate-controlling step of the reaction is related to the rate at which the neptunium(V) oxygen atom is replaced. It is doubtful, however, that this suggestion can be applied to the present situation where an electron transfer as well as the replacement of coordinated water is involved. Further, the rate of the U(VI)–Cr(II) reaction is nearly 10 orders of magnitude greater than those for the formation or decomposition of the Cr(III)·Np(V) and Ru(III)·Np(V) species discussed by Murman and Sullivan.

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