

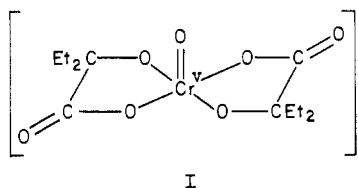
Electron Transfer. 76. Reduction of Carboxylato-Bound Chromium(V) with Uranium(IV)¹

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The chelated chromium(V) complex sodium bis(2-ethyl-2-hydroxybutyrate)oxochromate(V) (I) reacts rapidly with an equimolar quantity of uranium(IV) at pH 2-4, yielding UO_2^{2+} and a bis-chelated hydroxycarboxylato derivative of $(\text{H}_2\text{O})_2\text{Cr}^{\text{III}}$. Reactions in the presence of an excess of the ligand anion, 2-ethyl-2-hydroxybutyrate (Lig^-), pass through an intermediate which corresponds to that intervening in reductions of chelate I with $\text{Fe}(\text{II})$ or VO^{2+} and which has been previously characterized as a $\text{Cr}(\text{IV})$ species. Both the formation of this intermediate and its consumption are inhibited by H^+ and by excess Lig^- . Analyses of kinetic profiles, obtained with U^{IV} in excess, indicate that the Cr^{IV} intermediate is formed predominantly by electron transfer from the species $\text{U}^{\text{IV}}(\text{Lig})\text{OH}^{2+}$ to chelate I at a bimolecular specific rate (21°C , $\mu = 0.50\text{ M}$) of $1.9 \times 10^2\text{ M}^{-1}\text{ s}^{-1}$ and that this intermediate is reduced by U^{IV} (rather than by U^{V}) at a specific rate of $>10^3\text{ M}^{-1}\text{ s}^{-1}$. The $\text{U}(\text{V})$ intermediate formed in both of these 1e transfer steps appears to be lost by disproportionation to U^{IV} and U^{VI} , leading to the observed overall 1:1 stoichiometry. It is proposed that, as is the case for reductions by $\text{Ti}(\text{OH})^{3+}$, both steps in the primary reduction proceed predominantly by outer-sphere routes, throughout which the bis-chelated structural arrangement about chromium is maintained.

The straightforward preparation of water-soluble complexes of chromium(V), described in 1979,² revived interest in the role of this unusual oxidation state in redox transformations. It is now clear that the reduction of $\text{Cr}(\text{V})$ can proceed by one of several mechanistic variations, depending upon the nature of the electron donor. With "even-electron" basic reductants such as hydrazine³ and hydroxylamine,⁴ reduction appears to entail preliminary coordination to the $\text{Cr}(\text{V})$ center, followed by internal electron transfer. The latter act, in the case of N_2H_4 , is a 2e transaction leading directly to $\text{Cr}(\text{III})$, whereas with NH_2OH , a net transfer of 4e occurs, leading to a NO^+ complex of $\text{Cr}(\text{I})$. With 1e metal-center reductants, reactions must proceed through the still less usual oxidation state $\text{Cr}(\text{IV})$. This state is especially reactive and eludes detection in reactions with $\text{Ti}(\text{III})$,⁵ $\text{Ce}(\text{III})$,⁶ and $\text{Eu}(\text{II})$,⁷ but strongly absorbing transients having the properties of $\text{Cr}(\text{IV})$ were detected in reductions by $\text{Fe}(\text{II})$ ⁸ and VO^{2+} .⁷ The present extension deals with reduction of the $\text{Cr}(\text{V})$ chelate I with



$\text{U}(\text{IV})$. Reflecting the recognized stability of $\text{U}(\text{VI})$ (as UO_2^{2+}), quadrivalent uranium is generally taken to be a 2e reductant. There is, however, substantial evidence indicating intervention of uranium(V) in certain reductions of UO_2^{2+} ,⁹ and this points to the possibility that the $\text{U}(\text{IV})$ - $\text{Cr}(\text{V})$ reaction, may proceed, at least in part, by 1e steps and that the two unusual states $\text{U}(\text{V})$ and $\text{Cr}(\text{IV})$ may thus coexist, for a significant time, in the systems at hand. If so, this would constitute the first instance (to our knowledge) in which $\text{U}(\text{V})$ is generated by oxidation, rather than by reduction.

Experimental Section

Materials. Sodium bis(2-ethyl-2-hydroxybutyrate)oxochromate(V) (complex I) was prepared as its monohydrate as described² and was purified by recrystallization from acetone-chloroform.⁷ Stock solutions of uranyl perchlorate, $\text{UO}_2(\text{ClO}_4)_2$, were prepared by dissolving UO_3 (an Alfa product) in 1 M HClO_4 at 60°C and were analyzed spectrophotometrically.¹⁰ Solutions of $\text{U}(\text{III})$ were prepared by reducing $\text{UO}_2(\text{ClO}_4)_2$ with zinc amalgam¹¹ and were converted to $\text{U}(\text{IV})$ by air oxidation.^{12,13} Lithium perchlorate was prepared as described by Dockal¹⁴ and recrystallized twice before use. The "ligand acid", 2-hydroxy-2-ethylbutyric acid (Aldrich) was used as received, but its purity was checked acidimetrically.^{15a} Cation-exchange resin (Bio-Rad 50W-X2;

200-400 mesh) was pretreated before use as described.^{15b}

Stoichiometric Studies. The stoichiometry of the reaction of chromium(V) chelate I was determined by spectrophotometric titration in a buffer containing 0.05 M 2-ethyl-2-hydroxybutyric acid and an equivalent quantity of its sodium salt (pH 3.3). The ionic strength was kept near 0.5 M by addition of LiClO_4 . Typically, a series of solutions containing 0.004 M $\text{Cr}(\text{V})$ was mixed with known concentration of $\text{U}(\text{IV})$, keeping the total volume constant. After 5 min, the spectrum of each mixture was recorded at 350-800 nm. Plots of absorbance, (at 510 and 415 nm) vs. the molar ratio $[\text{U}^{\text{IV}}]/[\text{Cr}^{\text{V}}]$ exhibited "break points" at 1.00 ± 0.05 , indicating that the principal reactions involved equivalent quantities of the two reagents.

Examination of the $\text{Cr}(\text{III})$ Reaction Products. A reaction mixture consisting of equal quantities of chromium(V) chelate I and $\text{U}(\text{ClO}_4)_4$, along with 0.05 M each of the "ligand acid" and its sodium salt, exhibited maxima at 587 ($\epsilon = 47\text{ M}^{-1}\text{ cm}^{-1}$) and 420 nm ($\epsilon = 74\text{ M}^{-1}\text{ cm}^{-1}$). In addition, shoulders at 475, 455, 430, 400, and 380 nm were observed, but these could be shown to be characteristic of UO_2^{2+} in the presence of the ligand buffer. When the reaction mixture was subjected to separation on a cation-exchange column (length 7 cm; capacity 4 mequiv) at 2°C , a green eluate passed through the column quickly. This eluate contained 54% of the chromium taken^{16,17} and exhibited spectral characteristics of

- (1) Sponsorship of this work by the National Science Foundation (Grant 8313253) is gratefully acknowledged.
- (2) Krumpolc, M.; Roček, J. *J. Am. Chem. Soc.* **1979**, *101*, 3206.
- (3) Srinivasan, V. S.; Gould, E. S. *Inorg. Chem.* **1981**, *20*, 3176.
- (4) Rajasekar, N.; Subramaniam, R.; Gould, E. S. *Inorg. Chem.* **1983**, *22*, 971.
- (5) Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 2645.
- (6) Rajasekar, N.; Gould, E. S. *Inorg. Chem.* **1983**, *22*, 3798.
- (7) Fanchiang, Y.-T.; Bose, R. N.; Gelerinter, E.; Gould, E. S. *Inorg. Chem.*, in press.
- (8) Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 2832.
- (9) See, for example: (a) Imai, H. *Bull. Chem. Soc. Jpn.* **1957**, *30*, 873. (b) Newton, T. W.; Baker, F. B. *Inorg. Chem.* **1965**, *4*, 1166. (c) Mastragostino, M.; Saveant, J.-M. *Electrochim. Acta*, **1968**, *13*, 751. (d) Ekstrom, A.; Farrar, Y. *Inorg. Chem.* **1972**, *11*, 2610. (e) Ekstrom, A. *Ibid.* **1973**, *12*, 2455; **1974**, *13*, 2237.
- (10) Marck, W. J.; Booman, G. L.; Elliott, M. C.; Rein, J. E. *Anal. Chem.* **1959**, *31*, 1130.
- (11) Loar, M. K.; Sens, M. A.; Loar, G. W.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 330.
- (12) $\epsilon_{522\text{nm}}$ for $\text{U}(\text{III})$ in 1.0 M HClO_4 was found to be $145\text{ M}^{-1}\text{ cm}^{-1}$ (lit.¹³ $147\text{ M}^{-1}\text{ cm}^{-1}$). λ_{max} (ϵ) for $\text{U}(\text{IV})$ in 1.0 M HClO_4 were as follows: 672 nm ($27\text{ M}^{-1}\text{ cm}^{-1}$), 648 (61), 550 (23), 495 (32), 485 (25), 428 (18).
- (13) Stewart, D. C., Report No. ANL-4812; Argonne National Laboratory: Argonne, IL, 1952; p 12.
- (14) Dockal, E. R.; Everhart, E. T.; Gould, E. S. *J. Am. Chem. Soc.* **1971**, *93*, 5661.
- (15) (a) The purity of this acid varied from 95 to 99%, depending on the "lot" taken. The principal impurity was water. Examination of the acid by GLC showed a trace of 3-pentanone as the only volatile organic impurity. (b) Gould, E. S. *J. Am. Chem. Soc.* **1967**, *89*, 5792.
- (16) Total chromium eluted from the column, analyzed by oxidizing the fractions with H_2O_2 ,¹⁷ constituted 95% of that taken as $\text{Cr}(\text{V})$. In our systems, this oxidation also yielded a yellow precipitate. The latter was dissolved in 1 M HClO_4 at 60°C , yielding a spectrum identical with that of $\text{UO}_2(\text{ClO}_4)_2$.
- (17) See, for example: Haupt, G. W. *J. Res. Natl. Bur. Stand., Sect. A* **1952**, *48*, 414.

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the reaction mixture before separation (λ_{max} at 587 and 420 nm, together with the UO_2^{2+} shoulders. On standing, a steady decrease in absorption occurred, and the band at 588 nm shifted to 570 nm ($\epsilon = 26 \text{ M}^{-1} \text{ cm}^{-1}$). An additional green band was eluted from the column with 0.5 M HClO_4 ; the latter fraction showed maxima at 580 and 410 nm in addition to the several " UO_2^{2+} shoulders" described above. The band at 580 nm ($\epsilon = 37 \text{ M}^{-1} \text{ cm}^{-1}$) gradually shifted to 570 nm ($\epsilon = 24 \text{ M}^{-1} \text{ cm}^{-1}$) when this eluted fraction was allowed to stand for 6 h at room temperature. The chief conclusion from these studies (amplified in the Discussion) is that the predominant Cr^{III} product is a unipositive bis chelate of $\text{Cr}(\text{H}_2\text{O})_2^{3+}$, which undergoes slow aquation in solution and faster aquation in contact with cation-exchange resin.

Changes in the Spectrum of U(IV) with Addition of 2-Ethyl-2-hydroxybutyrate. The spectrum of U(IV) undergoes modest but unmistakable changes in the region 320–825 nm upon addition of 2-ethyl-2-hydroxybutyric acid buffer, suggesting the formation of at least two U^{IV} -ligand complexes. For examples, the U^{IV} peak of at 625 nm is shifted to 630 nm with addition of a 1:1 quantity of the ligand anion, but addition of further anion shifted the band back to 620 nm. Nearly limiting spectra were obtained with 0.08–0.10 M ligand anion. If the equilibrium constant for the first ligation, ($\text{U}^{\text{IV}} + \text{Lig}^- \rightleftharpoons \text{U}^{\text{IV}}\text{Lig}$), is assumed to be very large, the observed changes beyond 1:1 addition may be used to estimate the formation constant of $\text{U}^{\text{IV}}(\text{Lig})_2$. The equation employed is (1), where D is the observed optical density at a particular

$$D = \frac{[\text{U}]_t}{1 + K_2[\text{Lig}] + K_2[\text{U}]_t} (\epsilon_1(1 + K_2[\text{U}]_t) + \epsilon_2 K_2[\text{Lig}^-]) \quad (1)$$

wavelength, ϵ_1 and ϵ_2 are the extinction coefficients for $\text{U}^{\text{IV}}\text{Lig}$ and $\text{U}^{\text{IV}}(\text{Lig})_2$ at that wavelength, $[\text{U}]_t$ is the total concentration of U(IV), and $[\text{Lig}^-]$ is the ligand anion concentration, corrected for formation of $\text{U}^{\text{IV}}\text{Lig}$. Nonlinear least-squares refinement of spectral data at 620 nm (16 points at pH 3.3) yields $K_2 = 88 \pm 17 \text{ M}^{-1}$, $\epsilon_1 = 19 \text{ M}^{-1} \text{ cm}^{-1}$, and $\epsilon_2 = 37 \text{ M}^{-1} \text{ cm}^{-1}$ whereas data at 500 nm yield $K_2 = 60 \pm 3 \text{ M}^{-1}$, $\epsilon_1 = 10 \text{ M}^{-1} \text{ cm}^{-1}$, and $\epsilon_2 = 23 \text{ M}^{-1} \text{ cm}^{-1}$.¹⁸ At $[\text{Lig}^-] > 0.2 \text{ M}$, further small changes in spectra appeared, possibly due to formation of a third complex, $\text{U}^{\text{IV}}(\text{Lig})_3$.

Kinetic Measurements. The U(IV)–Cr(V) reaction, using complex I, was monitored at 510 nm with a Durrum–Gibson stop flow spectrophotometer. Experiments were carried out under pseudo-first-order conditions using excess U(IV). Total ionic strength was maintained near 0.5 M by addition of LiClO_4 . In most cases, kinetic profiles^{19a} exhibited a small increase, followed by a large decrease in absorbance, although at low ligand anion concentrations (<0.02 M), only a large near-exponential decrease, with marginal distortion early in the reaction, was observed. Depending upon reagent concentrations, maximal absorbances, when they could be seen, occurred 50–200 ms after mixing. The biphasic profiles were considered to be composites of two consecutive pseudo-first-order processes, and rate constants were computed from an iterative nonlinear least-squares treatment^{19b} using eq 2, where D_0 and D_∞ represent the

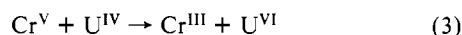
$$D = D_0 e^{-k_0 t} + \frac{A \epsilon k_0}{k_1 - k_0} (e^{-k_0 t} - e^{-k_1 t}) + \frac{D_\infty}{k_1 - k_0} (k_0 e^{-k_1 t} - k_1 e^{-k_0 t}) + D_\infty \quad (2)$$

initial and final absorbance, D represents the absorbance at time t , k_0 and k_1 are the rate constants for formation and decay of an intermediate species, A is the initial concentration of Cr^{V} , and ϵ is the extinction coefficient of the intermediate.

Uncertainties in the value of the lower rate constant, k_0 , were estimated to be 5%. A much more severe error, ca. 15%, applies to the larger rate constant, k_1 , reflecting the very small increases in absorbance.

Results and Discussion

Spectrophotometric titration of Cr(V) with U(IV) yields a "break point" near a mole ratio of 1.0, indicating that the net reaction may be represented schematically as



The principal chromium(III) product formed when $\text{Cr}(\text{V})$ chelate I is reduced, in the presence of excess ligand anion, with

Table I. Kinetic Data for Reduction of (Carboxylato)chromium(V) with U(IV) (21 °C, $\mu = 0.50 \text{ M}$)

$10^3[\text{Cr}^{\text{V}}],^a$ M	$10^3[\text{U}^{\text{IV}}],$ M	$[\text{Lig}^-],^b$ M	$[\text{HLig}],^c$ M	pH	$k_0',^d$ $\text{M}^{-1} \text{ s}^{-1}$	$10^{-2}k_1',^e$ $\text{M}^{-1} \text{ s}^{-1}$
0.89	5.9	0.044	0.056	3.20	48 (42)	8
0.89	11.7	0.044	0.056	3.20	43 (45)	8
0.89	23.4	0.027	0.073	2.87	51 (49)	10
0.91	8.8	0.0040 ^f	0.016	2.70	99 (91)	
0.91	8.8	0.0140 ^f	0.036	2.89	85 (98)	
0.88	8.8	0.029	0.041	3.15	55 (63)	10
0.88	8.8	0.069	0.081	3.23	22 (24)	3
0.88	8.8	0.094	0.106	3.25	16 (15)	1.4
0.50	5.9	0.044	0.306	2.46	20 (17)	2.4
0.40	5.9	0.044	0.206	2.63	24 (22)	3
0.45	5.9	0.044	0.106	3.25	34 (32)	4
0.44	5.9	0.044	0.056	3.20	48 (42)	7
0.44	5.9	0.044	0.031	3.45	56 (49)	10
0.43 ^g	3.4	0.075	0.075	3.30	23 (22)	
0.43 ^g	3.4	0.100	0.100	3.30	16 (14)	
0.43 ^g	3.4	0.130	0.130	3.30	12.1 (9.2)	

^aChromium(V) was added as sodium bis(2-ethyl-2-hydroxybutyrate)-oxochromate(V) (I). ^b2-Ethyl-2-hydroxybutyrate; concentration adjusted for 1:1 stoichiometric formation of uranium(IV)–ligand complex, $\text{U}^{\text{IV}}\text{Lig}$. ^c2-Ethyl-2-hydroxybutyric acid. ^dSecond-order specific rates for slower kinetic component, estimated from analyses of the biphasic kinetic curves as $k_0/[\text{U}^{\text{IV}}]$ (eq 2). Values in parentheses are calculated from rate law 4, taking a as 0.73 s^{-1} , b as 40 M^{-1} , c as 59 M^{-1} , and d as $3.8 \times 10^{-3} \text{ M}$ (see text). ^eSecond-order specific rates for the more rapid kinetic component, estimated from analyses of the biphasic kinetic curves as $k_1/[\text{U}^{\text{IV}}]$ (eq 2). ^fNo rising portion of the kinetic curve was observed at these low values of $[\text{Lig}^-]$. ^gRuns were carried out on the Cary spectrophotometer, with conventional mixing. Only the slower kinetic component (k_0) could be observed.

Ti(III),⁵ Fe(II),⁸ Eu(II),⁷ or V(IV)⁷ has been taken to be a 1+ bis chelated hydroxycarboxylato complex of $(\text{H}_2\text{O})_2\text{Cr}^{\text{III}}$. The relatively high extinction coefficients²⁰ ($\epsilon_{587} = 47$, $\epsilon_{420} = 74 \text{ M}^{-1} \text{ cm}^{-1}$) of the predominant Cr(III) product in the present reaction, together with its low affinity for sulfonate cation-exchange resin, indicate that we are dealing with the same Cr(III) species here. Slow decomposition (aquation) of our product in aqueous solution, and faster decay in contact with polysulfonic acid resin, correspond to behavior exhibited by (carboxylato)chromium(III) complexes in earlier studies.²¹

As with the VO^{2+} –Cr(V)⁷ and Fe(II)–Cr(V)⁸ systems, an intermediate species absorbing more strongly at 515 nm than either U(IV) or Cr(V) (or their sum) is observed when these reagents are mixed in the presence of excess ligand. Here, however, the rising portion of the kinetic profile is much less pronounced than was seen with the earlier reductants.

Analysis (according to eq 2) of the kinetic curves obtained with excess U(IV) yields two pseudo-first-order rate constants, k_0 and k_1 , both of which are proportional to $[\text{U}^{\text{IV}}]$. Second-order specific rates, obtained by dividing k_0 and k_1 by $[\text{U}^{\text{IV}}]$, are sensitive to pH and, to a more marked degree, upon the concentration of added carboxylate ligand, $[\text{Lig}^-]$. Kinetic data are summarized in Table I.

Of the two pseudo-first-order rate constants, k_0 and k_1 , one reflects the growth of the observed intermediate and the other its disappearance. The ambiguity associated with assignment of rate constants to such kinetic components has been emphasized, both by us⁸ and by others.²² If the larger rate constant is assigned to the growth and the lesser to the decay, calculation of the maximum degree of conversion to the intermediate²² and thence its apparent extinction coefficient at 515 nm yields the value $400 \pm 30 \text{ M}^{-1} \text{ cm}^{-1}$. If this assignment of rates be reversed, the resulting extinction coefficient is $1200 \pm 100 \text{ M}^{-1} \text{ cm}^{-1}$ (pH 3.3,

(18) We suspect that poor agreement between K_2 values at the two wavelengths reflects the relatively small differences between ϵ_1 and ϵ_2 , as well as possible formation of minor amounts of $\text{U}^{\text{IV}}(\text{Lig})_3$.

(19) (a) Representative absorbances, pertaining to a single kinetic run, are compared with values calculated by using eq 2 in the supplementary table. (b) A nonlinear least-squares program (written in Basic for the Apple II Computer) was kindly provided by Professor J. H. Espenson and was used with minor modifications.

(20) Visible spectra of (carboxylato)chromium(III) complexes of diverse types have been summarized by Fanchiang.⁷

(21) See, for example: (a) Gould, E. S. *J. Am. Chem. Soc.* **1968**, *90*, 1740 (footnote 10). (b) Hollaway, W. F.; Srinivasan, V. S.; Gould, E. S. *Inorg. Chem.* **1984**, *23*, 2181.

(22) See, for example: Espenson, J. H. "Chemical Kinetics and Reaction Mechanisms"; McGraw-Hill: New York, 1981; Chapter 4.

Table II. Mechanistic Features of Reductions of Chelated Chromium(V) with Various Inorganic Reducing Agents^a

reductant	<i>n</i> ^b	reacn type ^c	predominant reactive oxidizing species	predominant reactive reducing species	ref
N ₂ H ₅ ⁺	2	IS	Cr ^V (Lig)O(OH)	N ₂ H ₅ ⁺ , ^c N ₂ H ₂	3
NH ₃ OH ⁺	4 ^d	IS	Cr ^V (Lig)O(OH)	NH ₃ OH ⁺ ^c	4
Ce(III) ^e	1	IS	Cr ^V (Lig)O(OH)	Ce(OAc) ₂ ⁺ ^c	6
Ti(III)	1	OS	Cr ^V O(Lig) ₂ ⁻	TiOH ²⁺ , Ti(Lig)OH ⁺	5
Fe(II)	1	IS	Cr ^V O(OH)(Lig) ₂ ²⁻	Fe ²⁺ , Fe(Lig) ⁺	8
V(IV)	1	IS	Cr ^V O(Lig) ₃ ²⁻	VO ²⁺ , VO(Lig) ⁺	7
U(IV)	1	OS	Cr ^V O(Lig) ₂ ⁻	U ^{IV} (Lig)(OH) ²⁺	this work

^aReactions of the Cr(V) chelate I in aqueous media, pH 2–4. Supporting electrolyte was LiClO₄. Buffers were acetic, pivalic, or 2-ethyl-2-hydroxybutyric acids, along with the corresponding carboxylate anions. Lig⁻ = 2-ethyl-2-hydroxybutyrate. ^bNumber of electrons involved in the initial electron transfer. ^cPrecursor complex formed with loss of 1 H⁺. ^dPrincipal product was Cr^I(NO⁺). ^eCe(III) catalysis of the disproportionation of Cr(V). ^fIS = inner sphere; OS = outer sphere.

[Lig⁻] = 0.05 M). The latter value agrees closely with the molar absorbance reported for the analogous intermediate in the Cr(V) reductions by Fe(II)⁸ and V(IV),⁷ an intermediate that from its mode of formation, its reactivity with 1e reductants, and its ease of disproportionation has been taken to be a chromium(IV) complex. We thus favor a pattern in which the lesser rate constant, *k*₀, corresponds to formation of Cr^{IV} and the larger, *k*₁, to its subsequent reaction with U(IV).²³ The relatively small increase in absorbance preceding the near-exponential decay reflects the high ratio of *k*₁ to *k*₀ (10–20, depending upon ligand concentration and pH) in these systems.

The bimolecular rate constant, *k*₀[′], pertaining to the growth of the Cr^{IV} intermediate is found to conform to (4), which we have

$$k_0' = \frac{a}{(b[\text{Lig}^-] + 1)(c[\text{Lig}^-][\text{H}^+] + [\text{H}^+] + d)} \quad (4)$$

rewritten in its algebraically equivalent form, (5), applicable to the present system, where [Cr^V]_t and [U]_t are the total concen-

$$\text{rate} = \frac{[\text{Cr}^{\text{V}}]_t [\text{U}]_t k_{\text{lim}} K_A}{(K_L [\text{Lig}^-] + 1)(K_L' [\text{Lig}^-][\text{H}^+] + [\text{H}^+] + K_A)} \quad (5)$$

trations of added Cr^V and U^{IV}, and [Lig⁻] is the total concentration of added carboxylate anion (adjusted for formation of the 1:1 complex, U^{IV}Lig). Nonlinear least-squares refinement²⁴ of *k*₀[′] values yields *a* = *k*_{lim}*K*_A = 0.73 ± 0.17 s⁻¹, *b* = *K*_L = 40 ± 8 M⁻¹, *c* = *K*_L[′] = 59 ± 14 M⁻¹, and *d* = *K*_A = (3.8 ± 1.2) × 10⁻³ M (corresponding to p*K*_A = 2.42). Table I also compares observed rates with those calculated from (4).

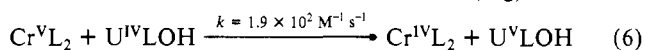
This rate law for growth of the intermediate is consistent with an activated complex formed from one unit each of Cr(V) and U(IV); however, we see that not all of the metal centers are kinetically active. One reagent pool is partially converted to an inactive species by extra ligation (association constant *K*_L) whereas the other is partially depleted both by protonation (*K*_A) and by ligation (*K*_L[′]) of the protonated form.

Although several possibilities exist, we note that *K*_L corresponds quite closely to the equilibrium constant previously determined, 51 ± 7 M⁻¹,⁷ for attachment of an extra ligand to the Cr(V) chelate I, whereas *K*_L[′] approaches the constant, determined in this study, for formation of U^{IV}(Lig)₂ from U^{IV}Lig. The value of *K*_A is a reasonable one for deprotonation of U^{IV}Lig, for this should be a somewhat weaker acid than the completely aquated form of U(IV) (p*K*_A 1.76).²⁵ Rate laws (4) and (5) then indicate the active U^{IV} species to be U^{IV}(Lig)OH, whereas U^{IV}Lig and U^{IV}-(Lig)₂ are much less active or inactive. Similarly, Cr^V(Lig)₂ may be taken to be the active Cr^V species, with Cr^V(Lig)₃ inactive. The limiting specific rate, *k*_{lim}, for formation of the Cr(IV) intermediate

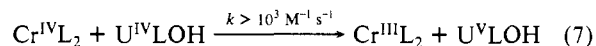
at low [Lig⁻] and high pH may then be calculated as 1.9 × 10² M⁻¹ s⁻¹.

Because the values for *k*₁, the more rapid kinetic component (pertaining to disappearance of Cr^{IV}), are derived from relatively small departures from simple exponential behavior in our kinetic curves, these must be considered much less precise than values of *k*₀. It seems clear, however, that *k*₁, like *k*₀, is first order in U(IV), but falls off with increases in [Lig⁻] and [H⁺]. Iterative refinement of *k*₁ values to determine more exact dependencies on these concentrations is not justified.

Our data then indicate that the principal route for reduction of Cr(IV) chelate I with U(IV) is initiated by a single-electron transfer between the chelate oxidant and U^{IV}(Lig)OH



and that this is followed by reduction of the Cr(IV) intermediate by a second unit of U(IV)²⁶



The alternative possibility, reduction of the Cr^{IV} intermediate by a U^V species, is not in accord with our finding that the disappearance of Cr^{IV} (kinetic component *k*₁) is first order in U(IV).

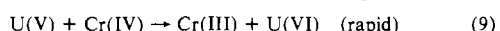
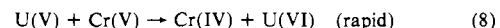
The present study sheds no direct light on the fate of the U(V) intermediate(s). Bimolecular disproportionation (2U^V → U^{IV} + U^{VI}) would be consistent with the observed overall 1:1 stoichiometry of the primary reaction, and we believe this to be a reasonable follow-up step. This disproportionation, in the absence of chelating ligand, has been studied in detail and has been found to be rapid in 1 M HClO₄ but negligibly slow above pH 2.^{26a} In our system, however, U(IV) and, almost certainly, U(V) and U(VI), as well, are ligated species, with the ligand environments about the three oxidation states resembling each other more closely than can be the case for the nonligated cations in aquo systems. This similarity would be expected to increase the U(V,VI) and U(IV,V) self-exchange rates, an effect which, by the arguments of Marcus,²⁷ should accelerate disproportionation.²⁸

The primary Cr(III) product, to which we have assigned a bis chelated structure, is not thermodynamically favored, for it is observed to undergo slow aquation in the reaction medium taken. As in earlier studies with 1e reductants,^{5,7,8} we suspect that its

(26) The active reducing species in step 7 is represented as U^{IV}LOH to reflect the retardation of this process (*k*₁[′] in Table I) with increases in [Lig⁻] and [H⁺]. Neither the degree of protonation nor the degree of ligation is certain.

(27) (a) Marcus, R. A. *J. Phys. Chem.* **1963**, *67*, 853. (b) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1963**, *15*, 155.

(28) A pair of rapid follow-up reactions, represented schematically as (8) and (9), involving Cr(V) and Cr(IV) is consistent with the observed 1:1



stoichiometry. If these were to contribute significantly to the overall reaction sequence, the kinetic components here examined would constitute only one-half of the total production and decay of Cr(IV), with the more rapid decay, (9), adding an additional component to the kinetic picture. We have examined kinetic profiles, both early and late in the reaction, and find no irregularities indicative of an additional reaction fraction.

(23) In further support of our assignment of consecutive rate constants, it was noted that absorbances immediately after mixing correspond closely to the sums of the known absorbances of the reactants. If the reverse sequence (rapid *k*₁ as growth, slower *k*₀ as decay) were correct, the initial absorbance should be greater than this sum.

(24) In this refinement, which minimized the function [(*k*₀[′])_{obsd} - (*k*₀[′])_{calcd}]², individual data points were unweighted. Values of [H⁺] were calculated from the concentrations of the ligand carboxylic acid and its anion, taking *K*_A for the acid³ as 5.0 × 10⁻⁴ M.

(25) McKay, H. A. C.; Woodhead, J. L. *J. Chem. Soc.* **1964**, 717.

structure is related to the original Cr(V) chelate (I) and that the ligand environment has persisted in both steps of the redox sequence ($\text{Cr}^{\text{V}} \rightarrow \text{Cr}^{\text{IV}}$ and $\text{Cr}^{\text{IV}} \rightarrow \text{Cr}^{\text{III}}$). This structural integrity would be expected if both steps proceeded by an outer-sphere mechanism, but it would not demand such a mechanistic inference.

It has been pointed out⁵ that the reductions of Cr(V) chelate (I) and its Cr(IV) analogue with TiOH^{2+} are each more rapid than ligand substitution reactions at Ti(III) centers, leading to the conclusion that both of these electron transfers are predominantly outer-sphere processes. The ratio of specific rates, $k_{\text{Cr(IV)}}/k_{\text{Cr(V)}}$, for reductions by TiOH^{2+} has been found to exceed 20. Such a ratio should, by the Marcus model for outer-sphere reactions,²⁷ be very nearly independent of the reductant chosen, and ratios much nearer to unity observed subsequently for Cr(V,IV) reductions by Fe^{2+} and VO^{2+} were taken to suggest that these reductants utilize a bridge mechanism in reactions with Cr(V).^{7,8} The ratio of limiting specific rates (>10) here noted for $\text{U}^{\text{IV}}(\text{Lig})\text{OH}$ appears to be consistent with an outer-sphere path for reductions by this actinide center, but reservations on this point are not unjustified.²⁹

The mechanism here proposed for the initial reaction between Cr(V) and U(IV) leads one to ask why the species $\text{U}^{\text{IV}}(\text{Lig})\text{OH}$ and $\text{Cr}^{\text{V}}(\text{Lig})_2$ should, under our conditions, be so much more reactive than other closely related metal complexes in the same solution. Since attachment of a negative ligand to a reducing metal center increases electron availability and, hence, generally makes it a more effective reductant, we would expect $\text{U}^{\text{IV}}(\text{Lig})\text{OH}^{2+}$ to be a more powerful reductant than either $\text{U}^{\text{IV}}(\text{Lig})^{3+}$ or $\text{U}^{\text{IV}}\text{OH}^{3+}$. Similarly straightforward reasoning leads us to predict that removal of a negative ligand from $\text{Cr}^{\text{V}}(\text{Lig})_3$ would make it a more effective oxidant. The kinetic advantage that $\text{U}^{\text{IV}}(\text{Lig})\text{OH}^{2+}$ appears to enjoy over the bis-ligated complex, $\text{U}^{\text{IV}}(\text{Lig})_2$, in our system cannot, however, be attributed to simple differences in electron density but may conceivably reflect the circumstance that $\text{U}^{\text{V}}\text{O}(\text{Lig})^{2+}$ is the predominant form of pentapositive uranium

in the medium used. If so, the reorganizational requirements (involving alteration of ligation and/or solvation) associated with oxidation of $\text{U}^{\text{IV}}(\text{Lig})\text{OH}^{2+}$ to its U(V) analogue would be minimal for this particular U(V,IV) interconversion, and this feature should be reflected in a more favorable specific rate. Detailed study of coordination equilibria in uranium(V)-carboxylate systems is needed to substantiate this conjecture.

Table II summarizes the assigned characteristics of a number of reductions of carboxylato-bound chromium(V) examined to date. Although there are only seven entries, we see considerable variation with respect to mechanism, to the number of electrons accepted in the initial transfer, and to selectivity among ligation and protonation levels of the Cr(V) oxidant. As additional reductants are examined, further mechanistic diversity is to be expected, and preliminary studies³⁰ of reductions of chelate I with HSO_3^- and with Mn(II) point to fulfillment of this expectation.³¹

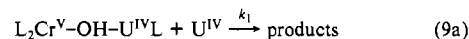
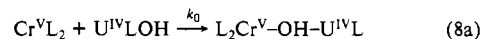
Acknowledgment. The authors are indebted to Professor Milton Manes for valuable discussions.

Registry No. I, 97042-89-2; $\text{UO}_2(\text{ClO}_4)_2$, 13093-00-0.

Supplementary Material Available: A table comparing representative absorbances constituting a single kinetic run with values calculated by using eq 2 (2 pages). Ordering information is given on any current masthead page.

(30) Srinivasan, V. S.; Bose, R., unpublished experiments, Kent State University, 1982 and 1985.

(31) A reviewer has suggested the following mechanism (which bypasses Cr^{IV}) for the Cr(V)-U(IV) reaction:



Although this sequence is consistent with the observed kinetics, we feel that it is less satisfactory than the $\text{Cr}^{\text{V}} \rightarrow \text{Cr}^{\text{IV}} \rightarrow \text{Cr}^{\text{III}}$ sequence proposed in the text since (a) the extinction coefficient of the intermediate corresponds closely to that of the Cr(IV) species observed in the reductions of Cr(V) with Fe(II) and VO^{2+} and (b) the role of the second U(IV) in reaction 9 appears to be mechanistically tenuous.

(29) See, for example: Gould, E. S. *Inorg. Chem.* **1979**, *18*, 900.