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Electron Transfer. 107. The Chromium(VI)–Uranium(IV) Reaction. Parallel One- and Two-Electron Paths[1]

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Reduction of $HCrO_4^-$ with U(IV) in solutions buffered by 2-ethyl-2-hydroxybutanoic acid (HLig) and its salt (Lig^-) is rapid and leads to a mixture of bis chelates of Cr(IV), Cr(V), and Cr(III), each derived from the buffering anion. The ratio of products approaches 3:1:1 and is nearly independent of [Lig^-]. Kinetic patterns suggest that the complexes $U^{IV}(Lig^-)$ and $U^{IV}(Lig^-)_2$ are active reductants but that $U^{IV}(Lig^-)_3$ is inactive. With U(IV) in excess, Cr(IV) is slowly reduced to Cr(III), a reaction which must involve intervention of U(V). The U(IV)–Cr(IV) reaction appears to proceed through a precursor complex ($K_{assn} = 5 \times 10^3$ M^{-1}), the pool of which is depleted both by protonation and extraligation. With Cr(VI) in excess, Cr(IV) is slowly lost by comproportionation ($Cr^{IV} + Cr^{VI} \rightarrow 2Cr^V$), a transformation which has been observed also in Cr(VI)–As(III) and Cr(VI)–Mo^V_2 systems. Cr(III), formed quickly in the initial stage of conversion in quantity equivalent to Cr(V), cannot arise from the Cr(V)–U(IV) or the Cr(IV)–U(IV) reaction, both of which are too slow, but is instead produced by reduction of Cr(IV) with U(V). ESR studies show that rapid reductions of excess $HCrO_4^-$ with $Mo_2O_4^{2+}$, HSO_3^-, or Sn(II) in our buffer system likewise yield, along with major quantities of Cr(IV), minor amounts of Cr(V), thus pointing to competitive $1e^-$ and $2e^-$ transactions with these reductants. Reduction by As(III) under the same conditions, however, yields only Cr(IV).

The preparation of aqueous solutions of chromium(IV), stabilized through ligation by anions of branched α-hydroxy acids such as 2-ethyl-2-hydroxybutanoic acid (I)[2] has expedited the

$$\underset{\text{I}}{(C_2H_5)_2C(OH)COOH}$$

examination of redox transformations of this atypical oxidation state. Earlier studies indicated that Cr(IV), as expected, is consumed very rapidly by the $1e^-$ reductants Ti(III),[3] Fe(II),[4] and V(IV).[5] However, the oxidations of reagents generally considered to be $2e^-$ donors, when they can be observed, are likely to utilize more circuitous routes.

The present report deals both with the generation of Cr(IV) from the reaction of Cr(VI) with U(IV) and with its reduction using this tetrapositive actinide center. For this system, we report evidence of the intermediacy of U(V), a less usual state that is generally prepared by the reduction of U(VI)[6,7] rather than by oxidation of U(IV).[8] Moreover, we find that reduction of Cr(VI) proceeds in part by a $1e^-$ path, which competes, to a measurable extent, with the expected $2e^-$ transaction.

Experimental Section

Materials. Sodium dichromate (MCB, Reagent Grade) and the "ligand acid", 2-ethyl-2-hydroxybutanoic acid (HLig, I) (Aldrich), were used as received. Solutions of U(IV) were prepared by dissolving UCl_4 (Strem) in 1.0 M $HClO_4$ and were standardized spectrophotometrically; $\epsilon_{max}^{648} = 61$ M^{-1} cm^{-1}.[8] Master solutions of U(IV), which were buffered with the ligand acid (I) and its salt, were prepared fresh under N_2 each day. Solutions of $NaClO_4$, used as a supporting electrolyte in kinetic experiments, were prepared by the reaction of $NaHCO_3$ with $HClO_4$.

Stoichiometric Experiments. Stoichiometry of the Cr(VI)–U(IV) reaction in buffers (pH 3.3) of the ligand acid, HLig, and its anion, Lig^-, were evaluated both with excess U(IV) and excess Cr(VI). For determinations with excess U(IV), a series of buffered solutions containing 0.012 M U(IV) were mixed with known concentrations of Cr(VI), while the volume was kept constant. After 5 min, the absorbance at 420 nm (a Cr(III) maximum) was recorded. Plots of absorbance vs the molar ratio $[Cr^{VI}]/[U^{IV}]$ exhibited "breakpoints" at 0.63. Determinations with excess Cr(VI) were made in a similar manner, by measuring the increases in absorbance at 510 nm (a Cr(V) maximum) 60 min after mixing. Poorly defined breakpoints were observed at $[Cr^{VI}]/[U^{IV}] = 1.69 \pm 0.10$.

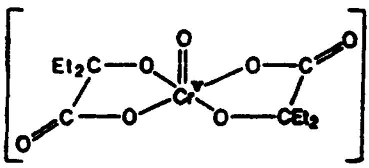
Table I. ESR Experimental Data[a] for the Initial Formation of Cr(V) from Reductions of Cr(VI)

reductant	$[Cr^{VI}]$, mM	[Red], mM	$[Cr^V]$,[b] mM	$[Cr^V]/[Red]$
As(III)	1.00	0.50	<0.005	<0.01
U(IV)	2.00	0.50	0.10	0.20
	4.00	0.50	0.096	0.19
	2.00	1.00	0.192	0.19
$Mo_2O_4^{2+}$	1.00	0.50	0.080	0.16
HSO_3^-	1.00	0.50	0.023	0.046
Sn(II)	0.32	0.16	0.04	0.25

[a] Reactions were carried out in solutions 0.05 M each in 2-ethyl-2-hydroxybutanoic acid (I) and its sodium salt (pH 3.3). [b] Estimated from intensity of the ESR signal at $g = 1.98$, extrapolated to zero time (see Experimental Section).

For comparison, the (faster) reaction with Cr(VI) in excess was studied in the absence of ligand buffer (in 0.1 M $HClO_4$) at 350 nm (a Cr(VI) maximum) by using a 10-s waiting period. Under these conditions, each mole of U(IV) was found to consume only 0.67 ± 0.02 units of Cr(VI).

In addition, the formation of Cr(IV) in buffered solutions could be monitored at 510 nm by adding known qunties of U(IV) to an excess of Cr(VI) and then measuring the absorbance only 8 s after mixing, i.e., before the much slower Cr(VI)–Cr(IV) comproportionation reaction[2] could intrude significantly. Breakpoints obtained in this manner were at $[Cr^{VI}]/[U^{IV}] = 0.98 \pm 0.02$. Moreover, absorbance values thus obtained were used to estimate the moles of Cr(IV) formed (as described in the Results).



II

ESR Studies. The reactions of excess Cr(VI) with several reductants were examined by ESR spectroscopy in order to estimate the extent of formation of Cr(V) in any initial rapid reaction. Measurements were calibrated by using 0.0002–0.002 M solutions of the known sodium salt of bis(2-ethyl-2-hydroxybutanoato)oxochromate(V) (complex II), which exhibits a single peak at $g = 1.98$ with a line width of 2.5 G.[5] Cr(IV) is ESR-silent under our conditions, whereas signals due to Cr(III) complexes are exceptionally broad and do not interfere with the monitoring of Cr(V).[5] Chromium(VI) and a deficiency of the reductant, were mixed in a solution buffered by an equimolar mixture (0.05 M each) of ligand acid I and its salt. The intensity of the Cr(V) signal, which increased slowly with time due to the Cr(IV)–Cr(VI) reaction, was extrapolated to zero time. In this manner, the reaction of Cr(VI) with As(III) was

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(5) Fanchiang, Y.-T., Bose, R. N.; Gelerinter, E.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 4679.

(6) See, for example: (a) Newton, T. W.; Baker, F. B. *Inorg. Chem.* **1965**, *4*, 1166. (b) Ekstrom, A.; Farrar, Y. *Inorg. Chem.* **1972**, *11*, 2670. (c) Ekstrom, A. *Inorg. Chem.* 1973, *12*, 2455; **1974**, *13*, 2237.

(7) Pillai, G. C.; Ghosh, S. K.; Gould, E. S. *Inorg. Chem.* **1988**, *27*, 1868.

(8) See, however: Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 94.

shown to form no detectable Cr(V) on initial mixing. Analogous experiments using U(IV), $Mo_2O_4^{2+}$, HSO_3^-, and Sn(II) (Table I) indicated that Cr(V) was formed along with Cr(IV) during initial rapid reductions of $HCrO_4^-$.

Examination of the Reaction Products. For the reaction with excess U(IV), mixtures (10 mL) contained 0.15 mmol of Cr(VI), 0.23 mmol of U(IV), and 1.5 mmol each of the ligand acid (I) and its salt and exhibited pH 3.25. These were allowed to react for 30 min and were then subjected to cation-exchange chromatography (Dowex 50-X8, 400 mesh, H^+ form)[9] at 2 °C. The major green fraction, comprising 80% of the chromium recovered, was eluted with distilled water and exhibited maxima at 589 ($\epsilon = 48$) and 423 nm ($\epsilon = 75$ M^{-1} cm^{-1}). A minor fraction, eluted with 0.5 M $NaClO_4$, absorbed at 579 ($\epsilon = 41$) and 417 nm ($\epsilon = 59$ M^{-1} cm^{-1}).

For the reaction with excess Cr(VI), mixtures (2.0 mL) were 0.0030 M in U(IV) and 0.0060 M in Cr(VI) and were buffered as above. After 1-h reaction time, these showed a spectrum which, after correction for the small known quantity of Cr(III) present (see Results), corresponded to that of the bischelated Cr^VO complex, II; $\epsilon_{max}^{510} = 187$ M^{-1} cm^{-1} (reported: 184 in 0.050 M Lig^-).[5]

When buffered reaction mixtures made with excess Cr(VI) were passed through an anion-exchange column (Dowex 1X2-400, ClO_4^- form), the first few drops, eluted with water alone, exhibited a maximum at 571 nm, characteristic of ligated Cr(III). This absorbance was superimposed on the tail of the spectrum of Cr(V), a portion of which was also eluted with water, and meaningful estimates of ϵ were not possible. No such green fraction was observed when the solution from the reaction of As(III) with excess Cr(VI) was treated in the same manner.

Kinetic Measurements. Reactions were followed by measuring absorbance changes at 510 nm (an absorption maximum for Cr(IV)). The rapid formation of Cr(IV) from Cr(VI) and U(IV) was examined in a Durrum-Gibson stop-flow instrument, whereas the much slower reactions of Cr(IV) with excess U(IV) or excess Cr(VI) were monitored in either a Beckman Model 5260 or a Cary 14 recording spectrophotometer. Solutions were buffered with measured quantities of the ligand acid, 2-ethyl-2-hydroxybutanoic acid (HLig, I), and its sodium salt (Na^+Lig^-).[10] Ionic strength was maintained at 0.5 M by addition of $NaClO_4$ solution.

Reactions were generally run under pseudo-first-order conditions, using at least a 9-fold excess of one of the redox reagents.[11] Rate constants associated with the resulting exponential curves were evaluated by using either semilogarithmic plots of absorbance differences vs reaction time or unweighted nonlinear least-squares fitting of data points to the relationship describing simple first-order transformations. Specific rates for replicate runs diverged by less than 5%.

Results

When the Cr(VI)–U(IV) reaction is carried out at low pH in an unbuffered solution, the products are U(VI) and Cr(III), regardless of the ratio of reactants. However, stoichiometry in our carboxylate buffers is found to depend on the reagent in excess. With excess U(IV), 3 mol of U(IV) consume very nearly 2 mol of Cr(VI), again yielding Cr(III)

$$3U^{IV} + 2Cr^{VI} \rightarrow 3U^{VI} + 2Cr^{III} \qquad (1)$$

whereas with Cr(VI) in excess, the net stoichiometry ($[Cr^{VI}]/[U^{IV}]$) is found to be 1.69 ± 0.10. Here the principal product is the bis chelate of Cr(V) (complex II), as identified by its spectrum,[5] with the departure from 2:1 stoichiometry, (2), demonstrating partial conversion to a lower oxidation state of chromium.

$$2Cr^{VI} + U^{IV} \rightarrow 2Cr^{V} + U^{VI} \qquad (2)$$

In solutions buffered by the ligand acid, reactions 1 and 2 are seen to proceed, at least in part, through the same strongly absorbing pink Cr(IV) intermediate, formed rapidly from equimolar quantities of the two redox partners.

$$Cr^{VI} + U^{IV} \rightarrow Cr^{IV} + U^{VI} \qquad (3)$$

Table II. Chromium Oxidation States Formed in the Rapid Cr(VI)–U(IV) Reaction[a]

$[Cr^{VI}]$, M × 10^4	$[U^{IV}]$, M × 10^4	$[Lig^-]$, M	ΔAbs, 510 nm	$[Cr^V]/[U^{IV}]$[b]	$[Cr^{IV}]/[U^{IV}]$[c]	$[Cr^{III}]/[U^{IV}]$[c]
4.0	1.00	0.050	0.139	0.19	0.67	0.16
4.0	2.0	0.050	0.287		0.69	0.15
4.0	3.0	0.050	0.423		0.67	0.15
20.0	4.0	0.050	0.534		0.65	0.18
20.0	8.0	0.050	1.014		0.61	0.20
4.0	1.00	0.0125	0.098		0.73	0.12
4.0	2.0	0.0125	0.190		0.71	0.13
4.0	3.0	0.0125	0.255		0.63	0.18
10.0	2.0	0.35	0.351		0.72[d]	0.14
10.0	4.0	0.35	0.692		0.71[d]	0.15
10.0	6.0	0.35	1.008		0.69[d]	0.16

[a] Reactions were carried out in solutions buffered by equimolar quantities of 2-ethyl-2-hydroxybutanoic acid (HLig) and its sodium salt (Na^+Lig^-) (pH 3.3–3.4) at 25 °C; waiting period, 8 s. [b] Ratio obtained from ESR measurements (see Table I). [c] Calculated from eqs 6 and 7, by taking $\epsilon_4 = 1293$ and $\epsilon_5 = 172$ M^{-1} cm^{-1} at $[Lig^-] = 0.0125$ M, $\epsilon_4 = 2032$ and $\epsilon_5 = 181$ M^{-1} cm^{-1} at $[Lig^-] = 0.050$ M, and $\epsilon_4 = 2383$ and $\epsilon_5 = 189$ M^{-1} cm^{-1} at $[Lig^-] = 0.35$ M. [d] $[Cr^{III}]$ taken to be equal to $[Cr^V]$; see text.

As with the Cr(VI)–Mo^V_2 system,[2] differing overall stoichiometries then stem mainly from reduction of the Cr(IV) intermediate with excess reductant or, alternatively, from its oxidation to Cr(V) with excess Cr(VI).

Although reduction of Cr(VI) proceeds predominantly through Cr(IV), a portion bypasses this state, being instead initiated by the formation of Cr(V). ESR measurements (Table I), carried out after the initial consumption of Cr(VI) is complete, point to the formation of 0.19 mol of Cr(V)/mol of U(IV) added to excess Cr(VI), apart from that formed slowly in the known[2] Cr(VI)–Cr(IV) reaction. This conversion appears to be very nearly independent of the ratio of reactants taken.

In addition, absorbance data at 510 nm (Table II), also collected before the Cr(VI)–Cr(IV) reaction proceeds significantly, tell us that even at this early stage we are dealing with a mixture containing both Cr(V) and Cr(IV). Although the absorbance of Cr(III) ($\epsilon_{510} = 22$ M^{-1} cm^{-1}) may be neglected relative to that of Cr(IV) and Cr(V), an inventory of reducing equivalents (eq 4), in conjunction with the observed absorbance change (eq 5), indicates that some Cr(III) is also formed, even with Cr(VI) in excess.

$$2\Delta[U^{IV}] = [Cr^V] + 2[Cr^{IV}] + 3[Cr^{III}] \qquad (4)$$

$$\Delta Abs = \epsilon_4[Cr^{IV}] + \epsilon_5[Cr^V] \qquad (5)$$

Yields of Cr(III), Cr(IV), and Cr(V) resulting from the initial Cr(VI)–U(IV) reaction, obtained from a combination of (4), (5), and the $[Cr^V]/[U^{IV}]$ ratio, 0.19 (determined by ESR), are compared in Table II.[12] The rapid reaction is seen to generate Cr(V), -(IV), and -(III) in a ratio close to 1:3:1, a proportion which does not vary significantly with the ratio of redox reagents or with the buffer concentration. The sums of the yields are nearly unity,

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(9) Separations were carried out on a 5-cm column, capacity 2 mequiv. For estimation of molar absorbances of the Cr(III) products, aliquots were oxidized with basic H_2O_2, and the total chromium content was determined as CrO_4^{2-}. (See: Haupt, G. W. *J. Res. Natl. Bur. Stand. Sect. A* **1952**, *48*, 41.) Note that the absorbances of the fraction eluted with water, but not that of the fraction eluted with $NaClO_4$, were corrected for contribution of U(VI) present. In the buffer system used, virtually no U(VI) remains in cationic form.[8]

(10) Redox reactions were generally initiated immediately after buffering the reagents. Chromium(VI) is known to react slowly with aqueous solutions of the ligand acid,[2] whereas buffered solutions of U(IV) were found to be more susceptible to air oxidation than U(IV)–$HClO_4$ solutions.

(11) Observed specific rates for the initial rapid Cr(VI)–U(IV) reaction were adjusted upward, by taking into consideration a specific rate of mixing estimated as 1.7 × 10^3 s^{-1} associated with our stop-flow instrument. See: Dickson, P. N.; Margerum, D. W. *Anal. Chem.* **1986**, *58*, 3153.

(12) Equations used in these calculations were (6) and (7), where ϵ_4 and ϵ_5

$$[Cr^{IV}] = \frac{\Delta Abs - R[U^{IV}]\epsilon_5}{\epsilon_4} \qquad (6)$$

$$[Cr^{III}] = \frac{[U^{IV}](2\epsilon_4 + 2R\epsilon_5 - R\epsilon_4) - 2\Delta Abs}{3\epsilon_4} \qquad (7)$$

pertain to the two oxidation states of chromium and R is the $[Cr^V]/[U^{IV}]$ ratio, found to be 0.19 in the ESR experiments.

Table III. Representative Kinetic Data for the Cr(VI)–U(IV) Reaction[a]

$[U^{IV}]$, M × 10^5	$[Cr^{VI}]$, M × 10^4	[LigH]	$[Lig^-]$	pH	$10^{-5}k$,[b] $M^{-1}\ s^{-1}$
4.0	2.0	0.050	0.050	3.28	2.5 (2.8)
4.0	7.5	0.050	0.050	3.30	2.5 (2.8)
4.0	7.5	0.050	0.050	3.30	2.4[c] (2.8)
10.0	10.0	0.050	0.050	3.28	2.4 (2.8)
100	1.0	0.050	0.050	3.30	2.3 (2.8)
10.0	15.0	0.050	0.050	3.30	2.4 (2.8)
4.0	3.5	0.035	0.025	3.19	3.6 (3.7)
4.0	3.5	0.125	0.025	2.62	4.0 (3.7)
4.0	3.5	0.010	0.010	3.29	4.8 (4.7)
4.0	3.5	0.0125	0.0125	3.30	4.3 (4.5)
4.0	3.5	0.025	0.025	3.29	4.0 (3.7)
4.0	3.5	0.037	0.037	3.29	3.4 (3.2)
4.0	3.5	0.075	0.075	3.28	2.2 (2.3)
4.0	3.5	0.10	0.10	3.28	2.0 (1.96)
4.0	3.5	0.15	0.15	3.30	1.57 (1.50)
4.0	3.5	0.20	0.20	3.31	1.17 (1.22)
4.0	3.5	0.25	0.25	3.32	1.03 (1.03)
4.0	3.5	0.30	0.30	3.32	0.91 (0.89)

[a] Reactions were run at 22 °C; $\mu = 0.50$ M ($NaClO_4$); progress was monitored at 510 nm. U(IV) was added as UCl_4; Cr(VI) was added as $Na_2Cr_2O_7$. Solutions were buffered with mixtures of 2-ethyl-2-hydroxybutanoic acid (LigH, I) and its sodium salt (Na^+Lig^-). [b] Bimolecular specific rates; parenthetical values were calculated from eq 8, by using parameters in text. [c] 0.005 M Cl^- was added.

Table IV. Kinetic Data for the Cr(IV)–U(IV) Reaction[a]

$[Cr^{VI}]_0$, M × 10^4	$[U^{IV}]$,[b] M × 10^4	[LigH]	$[Lig^-]$	pH	10^2k,[c] s^{-1}
0.50	2.50	0.050	0.050	3.30	6.1 (6.4)
0.50	4.5	0.050	0.050	3.28	10.3 (10.3)
0.50	4.5	0.050	0.050	3.28	9.9[d] (10.3)
1.00	6.5	0.050	0.050	3.30	12.4 (13.3)
1.00	6.5	0.050	0.050	3.30	9.5[e]
1.50	8.5	0.050	0.050	3.31	15.8 (15.8)
2.00	9.0	0.050	0.050	3.32	16.1 (16.4)
1.50	13.5	0.050	0.050	3.28	19.9 (20.0)
2.00	18.0	0.050	0.050	3.28	24 (23)
2.5	22.5	0.050	0.050	3.30	26 (26)
0.50	4.5	0.020	0.020	3.30	16.5 (16.1)
0.50	4.5	0.025	0.025	3.29	14.9 (14.7)
0.50	4.5	0.037	0.037	3.29	12.2 (12.2)
0.50	4.5	0.075	0.075	3.32	7.5 (7.9)
0.50	4.5	0.100	0.100	3.32	6.7 (6.4)
0.50	4.5	0.125	0.125	3.29	6.2 (5.4)
0.50	4.5	0.30	0.050	2.51	4.5 (4.1)
0.50	4.5	0.20	0.050	2.68	5.8 (5.3)
0.50	4.5	0.130	0.050	2.89	6.8 (7.0)
0.50	4.5	0.100	0.050	3.02	7.9 (8.1)
0.50	4.5	0.025	0.050	3.63	12.5 (12.2)
0.50	4.5	0.015	0.050	3.82	13.3 (13.1)

[a] Reactions were run at 24 °C; $\mu = 0.50$ M ($NaClO_4$); progress was monitored by using the absorbance decrease at 510 nm. U(IV) was added as UCl_4; Cr(IV) was generated in the preliminary rapid Cr(VI)–U(IV) reaction (Table III). Solutions were buffered with mixtures of 2-ethyl-2-hydroxybutanoic acid (LigH, I) and its sodium salt (Na^+Lig^-). [b] $[U^{IV}]$ adjusted for loss of reductant in the initial rapid generation of Cr(IV). [c] Unimolecular specific rates; parenthetical values were calculated from eq 16, by using accompanying kinetic parameters in text. [d] 0.012 M Cl^- was added. [e] Reaction in D_2O.

being thus in accord with the 1:1 $[Cr^{VI}]:[U^{IV}]$ stoichiometry found independently to obtain for this conversion.[13] Moreover, if the subsequent slow Cr(IV)–Cr(VI) reaction consumes one additional Cr(VI) for each Cr(IV), the indicated distribution is consistent with the net loss of 1.6 Cr(VI) per U(IV) after long waiting periods with Cr(VI) in excess. The 3:2 stoichiometry observed with U(IV) in excess reminds us that complete conversion to Cr(III) under these conditions is not altered by intervention of partially reduced intermediates.

The spectrum ($\epsilon_{589} = 48$; $\epsilon_{423} = 75\ M^{-1}\ cm^{-1}$) of the predominant Cr(III) product formed with an excess of U(IV) in buffered solutions corresponds closely to that of the complex formed when the Cr(V) chelate (II) is reduced with ascorbic acid in a similar medium.[14] The structure assigned to this product is that of a bischelated species derived from the buffering hydroxy acid with one additional (monodentate) carboxylate ligand. The elution behavior of this product, showing that it is devoid of positive charge, is in agreement with this picture, as is the apparent decomposition (partial aquation) in contact with polysulfonate resin.[15]

Kinetic data for the initial stage of the Cr(VI)–U(IV) reaction in our buffered systems are assembled in Table III. Reactions are first order in both redox reagents, and rates are seen to be independent of acidity within the (relatively narrow) range examined. Inhibition by the added ligand anion, Lig^-, is quite marked and is in accord with the rate law (8), where $[Cr^{VI}]_T$ and

$$\frac{-d[Cr^{VI}]}{dt} = \frac{-d[U^{IV}]}{dt} = [Cr^{VI}]_T[U^{IV}]_T\left(\frac{k_0 + k'K'[Lig^-]}{1 + K'[Lig^-] + K'K''[Lig^-]^2}\right) \quad (8)$$

$[U^{IV}]_T$ are the total concentrations of the redox reagents. The denominator of (8) is consistent with the partition of U(IV) into three species formed by successive substitutions of Lig^- for bound water; moreover, the numerator tells us that only the first two of these contribute to the overall rate. Earlier spectral examination of the U(IV)–Lig^- system under these conditions[8] pointed to a very large formation constant for the 1:1 complex and partial conversion to 2:1 and 3:1 complexes

$$U^{IV}{}_{aq} \xrightarrow[K > 10^4]{Lig^-} U^{IV}(Lig^-) \underset{K' = 60}{\overset{Lig^-}{\rightleftharpoons}} U^{IV}(Lig^-)_2 \underset{K''}{\overset{Lig^-}{\rightleftharpoons}} U^{IV}(Lig^-)_3 \quad (9)$$

Thus, the inactive species may be taken as the 3:1 complex, with the 2:1 and 1:1 active and $[U^{IV}{}_{aq}]$ negligible.

If K' is taken as the reported[8] value, 60 M^{-1}, refinement yields the specific rates $k_0 = (5.9 \pm 0.5) \times 10^5\ M^{-1}\ s^{-1}$ (pertaining to $U^{IV}(Lig^-)$), $k' = (3.2 \pm 0.6) \times 10^5\ M^{-1}\ s^{-1}$ (pertaining to $U^{IV}(Lig^-)_2$), and $K'' = 10 \pm 2\ M^{-1}$.

With U(IV) in excess, the very rapid growth of Cr(IV) is followed by its slow reduction to Cr(III). Rate data for this transformation appear in Table IV. This reaction is seen to exhibit kinetic saturation. Rates are very nearly proportional to $[U^{IV}]$ at low concentrations of the reductant but approach a limiting value at high concentrations, pointing to a rate proportional to the concentration of a Cr(IV)–U(IV) complex. Moreover the conversion is inhibited by the ligating anion, Lig^-, and by increasing acidity as well. Of the several sequences consistent with the observed kinetic patterns, the most reasonable appears to be (10)–(15). The reaction is represented as proceeding through

$$U^{IV}(Lig^-) + H^+ \overset{1/K_A}{\rightleftharpoons} U^{IV}(LigH) \quad \text{(inactive)} \quad (10)$$

$$U^{IV}(Lig^-) + Lig^- \overset{K_L}{\rightleftharpoons} U^{IV}(Lig^-)_2 \quad \text{(inactive)} \quad (11)$$

$$U^{IV}(LigH) + Lig^- \overset{K_L'}{\rightleftharpoons} U^{IV}(LigH)(Lig^-) \quad \text{(inactive)} \quad (12)$$

$$U^{IV}(Lig^-) + Cr^{IV} \overset{K_P}{\rightleftharpoons} U^{IV}(Lig^-)Cr^{IV} \quad (13)$$

$$U^{IV}(Lig^-)Cr^{IV} \xrightarrow{k} Cr^{III}(Lig^-) + U^V \quad (14)$$

$$U^V + Cr^{IV} \rightarrow Cr^{III} + U^{VI} \quad \text{(very rapid)} \quad (15)$$

precursor complex $U^{IV}(Lig^-)Cr^{IV}$, the pool of which is partially depleted by protonation (eq 10) and extraligation (eqs 11 and 12). This sequence generates the rate law (16).

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(13) Although the spectrophotometric titration at 510 nm monitors the growth of a mixture of products, this growth necessarily parallels the loss of Cr(VI).

(14) Ghosh, S. K.; Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1987**, *26*, 2684.

(15) See, for example: Gould, E. S. *J. Am. Chem. Soc.* **1968**, *90*, 1740 (footnote 10).

$$\frac{-d[\mathrm{Cr^{IV}}]}{dt} = \frac{2[\mathrm{Cr^{IV}}][\mathrm{U^{IV}}]kK_PK_A}{K_A + [\mathrm{H^+}] + K_AK_L[\mathrm{Lig^-}] + K_L'[\mathrm{H^+}][\mathrm{Lig^-}] + K_PK_A[\mathrm{U^{IV}}]} \quad (16)$$

In treatment of data according to (16), K_A and K_L have been kept at reported[8] values, 3.8×10^{-3} and 60 M^{-1}. Refinement then yields $k = 0.20 \pm 0.01$ s^{-1}, $K_P = (5.0 \pm 0.5) \times 10^3$ M^{-1}, and $K_L' = (3.7 \pm 0.4) \times 10^2$ M^{-1}. As expected, the "extraligation constant" (K_L') for U^{IV}(LigH) is greater than that (K_L) for $U^{IV}(Lig^-)$, which bears a smaller positive charge. Note that the limiting specific rate for this reaction is $2k$, reflecting the rapid "follow-up reaction", (15).

With Cr(VI) in excess, the growth of Cr(IV) is followed by the slow Cr(IV)–Cr(VI) comproportionation (eq 17). This is the reaction seen also when Cr(IV) is prepared by the oxidation of

$$\mathrm{Cr^{IV} + Cr^{VI} \rightarrow 2Cr^{V}} \quad (17)$$

H_3AsO_3 or $Mo_2O_4^{2+}$ by excess $HCrO_4^-$ in the same buffer.[2] The specific rate, 8.3×10^{-3} s^{-1}, observed for this reaction (pH 3.27, $[\mathrm{Cr^{VI}}] = 5.0 \times 10^{-3}$ M, $\mu = 0.50$ M, 24 °C) corresponds to those pertaining to the As(III) (8.4×10^{-3}) and Mo^V_2 (9.6×10^{-3} s^{-1}) systems under the same conditions.[16,17]

Discussion

The most notable implications of the present work are (a) the competition, during the initial rapid reduction of Cr(VI), between two- and one-electron processes (reactions 3 and 18) and (b) the intervention of the atypical state, U(V), in the reductions of both Cr(VI) and Cr(IV).

The third reduced state, Cr(III), formed quickly from Cr(VI) in quantity very nearly equivalent to Cr(V) (Table II), cannot arise from the Cr(IV)–U(IV) reaction, which has been shown here to be much too slow, nor from the Cr(V)–U(IV) reaction, which has been demonstrated[8] to proceed through Cr(IV). It must instead be produced from the rapid reaction between U(V) and Cr(IV) (eq 15). The preliminary phase of the overall reaction then entails three redox components:

$$\mathrm{Cr^{VI} + U^{IV} \rightarrow Cr^{IV} + U^{VI}} \quad (3)$$

$$\mathrm{Cr^{VI} + U^{IV} \rightarrow Cr^{V} + U^{V}} \quad (18)$$

$$\mathrm{Cr^{IV} + U^{V} \rightarrow Cr^{III} + U^{VI}} \quad \text{(rapid)} \quad (15)$$

Since the ratio $[\mathrm{Cr^{IV}}]/[\mathrm{Cr^{V}}]$ initially produced is found to vary inappreciably with the concentration of buffer, (3) and (18) must be similarly dependent on $[\mathrm{Lig^-}]$. Rate law (8) represents the sum of (3) and (18). Its denominator, which reflects the speciation of U(IV), applies to both steps, and we further infer that the ratio k_0/k', which pertains to reductions by $U^{IV}(Lig^-)$ and $U^{IV}(Lig^-)_2$, is nearly the same for the $2e^-$ and $1e^-$ transactions. Specific rates contributing to the predominant change, producing Cr(IV), may then be estimated as 81% of those for the net loss of U(IV), i.e. $(4.8 \pm 0.4) \times 10^5$ and $(2.6 \pm 0.5) \times 10^5$ M^{-1} s^{-1} for reductions by $U^{IV}(Lig^-)$ and $U^{IV}(Lig^-)_2$. The remainder of the overall change may be assigned to (18), the rapid formation of Cr(V).

Inhibition of the Cr(VI)–U(IV) reactions resulting from anation of U(IV) by Lig^- brings to mind similar trends recorded for the U(IV)–Cr(V) reaction in the same buffer system[8] and for the U(IV)–BrO_2^- reaction in carbonate buffers.[18] The effect is the reverse of what would be expected on electronic grounds alone, since substitution of negative for uncharged ligands should increase the electron availability at the reducing center. We suspect then that each of these reactions requires preliminary bonding of a peripheryl oxygen of the oxidant to uranium (i.e., that they are inner-sphere processes) and that these buffering anions compete with the added oxidant for the necessary coordination positions about the reductant.

The final stage of reaction with excess U(IV), the slow reduction of Cr(IV), is accompanied by the reduction, also to Cr(III), of the minor fraction of Cr(V) formed in the preliminary fast conversion (Table I). The latter state, like Cr(IV), has a maximum near 510 nm but with an extinction coefficient only about 10% as great. Since the Cr(V)–U(IV) reaction thus accounts for only about 2% of the total absorbance change, it does not significantly interfere with our monitoring the loss of Cr(IV).

Kinetic behavior during this stage stands in contrast to that observed in the As(III)–Cr(VI) and Mo^V_2–Cr(VI) systems.[2] Whereas Cr(IV) is reduced smoothly (albeit slowly) by U(IV), its reaction with H_3AsO_3 was not detected and that with the $Mo_2O_4^{2+}$ ion required unimolecular activation of the reductant, proceeding at a rate nearly independent of $[\mathrm{Cr^{IV}}]$. Since the reduction is necessarily a $1e^-$ change, this portion of the sequence provides more direct evidence for the intermediacy of U(V) than that arising from consideration of the initial stages.

It has long been recognized that reductants characteristically regarded as $2e^-$ donors can be induced to undergo single-electron changes, given sufficient driving force and the absence of complementary oxidants.[19] This study points to an even greater degree of flexibility among such reagents, for even with a facile two-unit route at hand, U(IV), Mo^V_2, HSO_3^-, and (most unexpectedly) Sn(II) are seen to utilize minor, but perceptible, single-electron paths. In this sense, As(III), despite scattered reports hinting at compromised behavior,[20] may be considered the "purest" of the $2e^-$ reductants here examined.

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Registry No. HLig, 3639-21-2; $HCrO_4^-$, 15596-54-0; U(IV), 7440-61-1.

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(16) In a brief evaluation of the solvent isotope effect associated with the Cr(VI)–Cr(IV) reaction (15), the ratio k_{H_2O}/k_{D_2O} was found to be 1.37 at pH 3.22 and 1.36 at pH 2.00 (25 °C, $\mu = 0.50$ M). This relatively modest effect appears to rule out a mechanism featuring simultaneous transfer of a proton and an electron, as suggested for the analogous Ru(IV)–Ru(II) comproportionation in bpy-coordinated systems ($k_{H_2O}/k_{D_2O} = 16.1$).[17]

(17) Binstead, R. A.; Meyer, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 3287.

(18) Jhanji, A. K.; Gould, E. S. *Int. J. Chem. Kinet.*, in press.

(19) See, for example: Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*, 2nd ed.; Wiley: New York, 1968; p 497.

(20) See, for example: Woods, R.; Kolthoff, I. M.; Meehan, E. J. *J. Am. Chem. Soc.* **1963**, *85*, 2385, 3324.