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Electron Transfer. 114. Structure–Reactivity Relationships in the Redox Series Chromium(V,IV,III) and Vanadium(V,IV,III)[1]

Manik C. Ghosh* and E. S. Gould*

Contribution from the Department of Chemistry, Kent State University, Kent, Ohio 44242

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Abstract: Aqueous solutions of the two atypical oxidation states Cr(IV) and Cr(V) are stabilized through chelation by the anion of 2-ethyl-2-hydroxybutanoic acid (HLig). Redox reactions of these states with a series of 1e⁻ reductants having structures dictating outer-sphere routes lead to calculated formal potentials of 1.35 V for $\mathrm{Cr^{IV/III}}$ and 1.29 V for $\mathrm{Cr^{V/IV}}$ with all three states participating as bis chelates. Measured specific rates for oxidations by Cr(IV), in conjunction with the modified treatment of Marcus, yield an estimated self-exchange rate of $10^{-0.51\pm0.40}$ $\mathrm{M^{-1}\ s^{-1}}$ for $\mathrm{Cr^{IV/III}}$, a value within the range characteristic of several octahedral complexes of 3d block centers, suggesting that there are no major structural alterations associated with interconversion of these two states, i.e., that both are 6-covalent in the ligand environment chosen. The Cr(IV) chelate does not react perceptibly with the oxo-acceptor reagents triphenylphosphine, Sb(III), $\mathrm{H_2AsO_3^-}$, and methionine, pointing to the absence of an oxo function. Rates for oxidations by Cr(V) are consistent with a $\mathrm{Cr^{V/IV}}$ self-exchange rate of $10^{-6.1\pm0.8}$ $\mathrm{M^{-1}\ s^{-1}}$, reflecting a much greater barrier, due in part to the change in coordination number and in part, presumably, to a change in the chromium–oxygen bond order associated with this interconversion. Rates for oxidations by $\mathrm{VO^{2+}}$ lead to an outer-sphere $\mathrm{V^{IV/III}}$ self-exchange rate of $10^{-7.6\pm1.4}$ $\mathrm{M^{-1}\ s^{-1}}$, well below the experimental rate, which is then presumed to pertain to a process which is predominantly inner-sphere. The contrast between the $\mathrm{V^{IV/III}}$ rate and the much greater $\mathrm{V^{V/IV}}$ value, $10^{-2\pm1}$ $\mathrm{M^{-1}\ s^{-1}}$, estimated by Macartney, may be attributed, at least partially, to the presence of V(=O) linakges in both V(V) and V(IV), but not in V(III). The present data then indicate that the redox series V(V,IV,III) (aquated) differs from Cr(V,IV,III) (chelated) in that the major structural change in the former is connected with the 4+/3+ component whereas that in the chelated chromium series is associated with 5+/4+.

Enhanced interest in the less usual oxidation states of chromium lying between Cr(III) and Cr(VI) reflects an increased appreciation of the roles played by such states, not only in inorganic redox mechanisms but also in organic synthesis[2] and in biosystems.[3]

Kinetic experiments by Westheimer[4] in 1949 implicated both Cr(IV) and Cr(V) as intermediates in the oxidations of alcohols with $\mathrm{HCrO_4^-}$, and the following decade witnessed an expanding body of evidence that both of these atypical states intervene also in the reactions of Cr(VI) with 1e⁻ reductants.[5] Over three dozen Cr(V) compounds have been reported,[2,6] and a more modest, but growing, array of Cr(IV) derivatives[7] have been characterized. Recently, Bakac and co-workers[8] have described the preparation of an unusually simple Cr(IV) species exhibiting behavior corresponding to the oxo cation $\mathrm{Cr^{IV}O^{2+}(aq)}$, which was found to decay in aqueous solution with a half-life of 45 s at room temperature.

Although only a small number of these compounds dissolve in water without oxidation of the medium or disproportionation, chelation by anions of branched α-hydroxy acids such as 2-ethyl-2-hydroxybutanoic acid (I) has been shown to stabilize aqueous solutions of both Cr(V)[9,19] and Cr(IV)[10] markedly. Mechanistic studies of a number of reductions of both states have been reported,[9b,10,11] and considerable versatility of action is evident. However, for more detailed considerations, knowledge of both the formal potentials and the rates of electron self-exchange associated with these states is desirable. We here report experiments allowing us to estimate these parameters and to compare them with the corresponding quantities pertaining to the more familiar vanadium(V,IV,III) triad.

$$\mathrm{(C_2H_5)_2C(OH)COOH}$$

I

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[1] Sponsorship of this work by the National Science Foundation (Grant 9019840) is gratefully acknowledged.

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[9] See, for example: (a) Krumpolc, M.; Rocek, J. *J. Am. Chem. Soc.* **1979**, *101*, 3206. (b) Gould, E. S. *Acc. Chem. Res.* **1986**, *19*, 66.

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Experimental Section

Materials. The "ligand acid", 2-ethyl-2-hydroxybutanoic acid ("HLig", I), trifluoromethanesulfonic (triflic) acid, lithium triflate, barium perchlorate, vanadyl sulfate, and cobalt(III) sepulchrate trichloride (all Aldrich products), sodium dichromate (MCB Reagent Grade), sodium hexachloroiridate(III) and -(IV) ($Na_3IrCl_6 \cdot xH_2O$ and $Na_2IrCl_6 \cdot 6H_2O$, Alfa products), sodium hexacyanoferrate(II) (Strem Chemicals), triphenylphosphine (MCB), L-methionine (Eastman Organic Chemicals), and the iron(II) complexes of 3,4,7,8-tetramethyl-1,10-phenanthroline and 4,4′-dimethyl-2,2′-bipyridine (G. F. Smith Chemicals) were used as received. Solutions of $NaClO_4$ were prepared by neutralizing $HClO_4$ with $NaHCO_3$. Sodium bis(2-ethyl-2-hydroxybutanoato)oxochromate(V) was prepared as described;[9a,12] master solutions were made each day in "ligand buffer" (0.05 M each in HLig and Lig$^-$) and stored in the dark. Chromium(IV) solutions were prepared in situ in ligand buffer by adding an excess of basic As(III) solution to buffered $Na_2Cr_2O_7$;[10] these solutions were used immediately. Solutions of the perchlorate, chloride, and triflate of VO^{2+} were prepared by treatment of $VOSO_4$ with the corresponding barium salt as described;[12] after removal of the precipitated $BaSO_4$ by centrifuging, concentrations of VO^{2+} were estimated spectrophotometrically.[12] Solutions of V(III) were prepared by reducing VO^{2+} to V^{2+}, using zinc amalgam in 1 M $HClO_4$, then mixing the resulting V(II) with a 10% excess of VO^{2+} 30 min before use. Hexaammineruthenium(III) triflate was prepared by treating a saturated solution of $Ru(NH_3)_6Cl_3$ (Matthey-Bishop) in 0.01 M triflic acid with 2.7 mol equiv of silver triflate, separating the precipitated AgCl, and then removing the water from the filtrate by rotary evaporation; this salt was converted to the corresponding ruthenium(II) complex by reduction with a known deficiency of Eu^{2+} under argon as described.[13] The iron(II) complex of 5,6-dimethyl-1,10-phenanthroline, $Fe(DMP)_3^{2+}$, was prepared in situ by treatment of $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ with a 5- to 10-fold excess of the heterocyclic ligand (Aldrich); the perchlorate salt of this complex is only slightly soluble in water. The iron(III) complex of 2,2′-bipyridyl, $Fe(bipy)_3(ClO_4)_3$, was prepared by a modification of the method of Burstall,[14] oxidizing the iron(II) complex with NaOCl and HCl, rather than with Cl_2. Cobalt(II) sepulchrate was prepared by reduction of the Co(III) complex with zinc amalgam under N_2 in the absence of added acid.[15]

Stoichiometric Experiments and Characterization of Reaction Products. Stoichiometries of six of the redox reactions were estimated spectrophotometrically, generally at wavelengths where absorbance changes were most marked. Changes observed upon addition of deficient quantities of the less strongly absorbing reagent to the colored coreagent were compared to changes resulting from addition of an excess.

The spectrum of the Ir product from the Cr(IV)–$IrCl_6^{3-}$ reaction was found to correspond to that of authentic K_2IrCl_6. The product mixture from this reaction, after removal of $IrCl_6^{2-}$ (using anion-exchange resin), was separated into two components on cation-exchange resin as described.[10a] The observed spectra[10b] of both fractions were characteristic of bis chelates formed by Cr(III) with the anion of the ligand acid, Lig$^-$.[10a] The major fraction was uncharged and exhibited maxima at 592 (ϵ = 50 M^{-1} cm^{-1}) and 417 (ϵ = 61) nm. Maxima of the minor fraction, which was eluted with 0.5 M $NaClO_4$, were at 572 (ϵ = 37) and 417 (ϵ = 48) nm. When the redox reaction was carried out in solutions with [Lig$^-$] = 0.2 M, the uncharged fraction constituted 80% of the total recovered chromium.

Estimation of Equilibrium Quotients. Two reactions of type 1 and one of type 2, although rapid, proceeded only partially to completion. For the Cr(IV)–Fe(II) reactions, the extent of conversion at equilibrium was estimated spectrophotometrically at 510 nm by measuring the loss of reactants upon adding known quantities of Fe(II) and adjusting slightly for the slow bimolecular disproportionation of Cr(IV)[16] and also for the gradual regeneration of Fe(II) from decomposition of $Fe^{III}L_3$.[14] For the

$$Cr^{IV} + Fe^{II}L_3^{2+} \rightarrow Cr^{III} + Fe^{III}L_3^{3+} \tag{1}$$

L = 5,6-Me$_2$-*o*-phen, 4,4′-Me$_2$bipy

$$Cr^{V} + 2Fe^{II}L_3^{2+} \rightarrow Cr^{III} + 2Fe^{III}L_3^{3+} \tag{2}$$

L = 4,4′-Me$_2$bipy

Cr(V)–Fe(II) reaction (2), the loss of the $Fe^{II}(Me_2bipy)_3^{2+}$ upon addition of Cr(V) was monitored at 528 nm. Profiles of the latter reaction ruled out an appreciable buildup of Cr(IV).

Partition of the bis chelated chromium(III) product between ligation levels [$Cr^{III}(Lig)_2 + Lig^- \rightleftharpoons Cr^{III}(Lig)_3$] was examined by measuring variations in the apparent molar absorbance, at 414 and 588 nm, of Cr(III) with changes of [Lig$^-$] in the medium. The Cr(III) product, generated by reduction of the corresponding oxochromium(V) chelate with excess Eu^{2+} in HLig–Lig$^-$ buffer,[12] was subjected first to anion exchange (to remove Lig$^-$), then to cation exchange.[10] Aliquots of the uncharged Cr(III) fraction were added to solutions in which [Lig$^-$] fell between 0.01 and 0.70 M. The equilibrium of interest was achieved after 8 h at 25 °C.

In addition, the acidity constant of $Cr^{III}(Lig)_2(H_2O)_2^+$ was estimated by noting changes in the absorbance ratio ($R = Abs_{410}/Abs_{480}$) as pH was allowed to vary between 1.0 and 5.5. Treatment of data as described[12] yielded $pK_A = 3.38 \pm 0.05$ and R values of 2.62 and 1.15 for the protonated and deprotonated forms.

Kinetic Experiments. Reactions were followed by measuring absorbance changes, employing either a Beckman Model 5260 recording spectrophotometer or a Durrum-Gibson stop-flow spectrophotometer equipped with an OLIS data acquisition operation system. Conversions were generally carried out under pseudo-first-order conditions, and concentrations were adjusted so that less than 10% of the reagent in excess was consumed during the collection of data. Ionic strength was generally maintained at 0.5 M by addition of NaCl, $NaClO_4$, or sodium triflate. Solutions were customarily buffered using measured quantities of 2-ethyl-2-hydroxybutanoic acid (HLig, I) and its sodium salt. All reactions yielded pseudo-first-order kinetic curves. Conversions were followed for at least 4 half-lives. For reactions using conventional mixing, rate constants were evaluated by using either semilogarithmic plots of absorbance differences vs reaction times or nonlinear least-squares fittings to the relationship describing first-order decay. For the three reactions proceeding only partially to completion, specific rates were evaluated using the procedure of King.[17] Specific rates greater than 50 s^{-1} were adjusted upward to accommodate the mixing rate associated with our stop-flow instrument, as described by Dickson.[18] Rate constants for replicate runs diverged by less than 7%. Although the oxidations of the tris chelate of Fe(II) featured the slow regeneration of Fe(II) after the oxidant had been consumed, this did not seriously interfere with evaluation of rates.

Additional Observations. The reduction of Cr(V) with $Ru(NH_3)_6^{2+}$ was too rapid to follow, even with stop-flow. In contrast, the slow decay of Cr(IV) (due to disproportionation) was not appreciably accelerated by addition of L-methionine (0.04 M), triphenylphosphine (0.04 M in 85% CH_3CN–H_2O), Sb^{III} (added as $SbCl_3$ in ligand buffer), or $H_2AsO_3^-$ (0.010 M).

Results

Earlier reports[10,11] described the preparation of pink aqueous solutions containing Cr(IV) by reduction of $HCrO_4^-$ with such 2e$^-$ reagents as H_3AsO_3, Sn(II), and U(IV) in solutions buffered with 2-ethyl-2-hydroxybutanoic acid (HLig, I) and its anion (Lig$^-$) and presented evidence, augmented in the present study, suggesting that Cr(IV) in these preparations exists predominantly as an uncharged bis chelate. Both the 5-coordinate oxo complex, II, and the 6-coordinate dihydroxo species, III, are consistent with this formulation, whereas a crystallographic study[19] supports the anionic oxo structure, IV, (in which each of the ligands carries a 2– charge) for the Cr(V) chelate. Both oxidation states undergo

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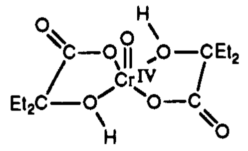

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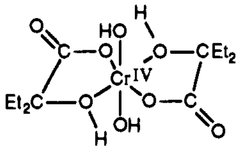

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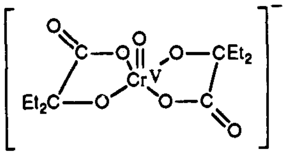


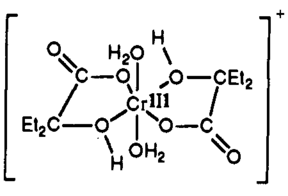
IV

anation with an additional unit of ligand (presumably in a unidentate manner) at high concentrations of the latter.[10,12]

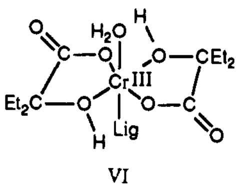
$$\mathrm{Ox} + \mathrm{Lig}^- \overset{K_L}{\rightleftarrows} \mathrm{Ox(Lig}^-) \qquad (3)$$

$$\mathrm{Ox} = \mathrm{Cr}^{IV},\ K_L = 90;\ \mathrm{Ox} = \mathrm{Cr}^{V},\ K_L = 51$$

Bis chelation persists in the Cr(III) reduction products. At the pH's used, these are the diaqua cation, V, and in cases where



V



VI

an "extraligated" oxidant contributes, the uncharged extraligated complex, VI.[10] Absorbance data for the Cr(III) product at varying concentrations of Lig^- (Table I) are consistent with (4), which

$$\mathrm{Abs} = [\mathrm{Cr^{III}}]_{tot}\frac{\epsilon_1 + \epsilon_2 Q_L[\mathrm{Lig}^-]}{1 + Q_L[\mathrm{Lig}^-]} \qquad (4)$$

is in accord with an equilibrium between V (extinction coefficient ϵ_1) and VI (ϵ_2), with Q the equilibrium quotient for the ligation reaction V + $\mathrm{Lig}^- \rightleftharpoons$ VI + H_2O. Treatment of data at 588 nm leads to $\epsilon_1 = 37\ M^{-1}\ cm^{-1}$, $\epsilon_2 = 50\ M^{-1}\ cm^{-1}$, and $Q_L = 6.5 \pm 0.9\ M^{-1}$. Similar refinements of absorbance data at 563 and 414 nm yield Q_L values 5.9 ± 1.0 and 5.3 ± 0.8 M^{-1}.

Estimated equilibrium quotinents (Table II), pertaining specifically to pH 3.3, are $10^{-1.0}$ for the reduction of Cr(IV) by $\mathrm{Fe^{II}(5,6\text{-}Me_2phen)_3^{2+}}$ and $10^{0.70}$ for its reduction by $\mathrm{Fe^{II}(4,4'\text{-}Me_2bipy)_3^{2+}}$. Since two protons are consumed in the full reactions (5), these quotients should be proportional to $[H^+]^2$. A plot of

$$2H^+ + \mathrm{Cr^{IV}(Lig)_2(OH)_2} + \mathrm{Fe^{II}} \rightarrow \mathrm{Cr^{III}(Lig)_2(H_2O)_2}^+ + \mathrm{Fe^{III}} \qquad (5)$$

observed Q's vs $[H^+]^2$ for the $\mathrm{Fe^{II}(Me_2phen)_3^{2+}}$ reaction (Figure 1) is seen to approach linearity with a slope $(3.5 \pm 0.5) \times 10^5\ M^{-2}$, the latter corresponding to $K_{eq} = 10^{5.5\pm0.1}$. Analogous treatment of data for the $\mathrm{Fe^{II}(Me_2bipy)_3^{2+}}$ reaction yields $K_{eq} = 10^{7.3}$.

These K's, in combination with the recorded[20] $E°$'s for the reductants (0.99 and 0.94 V), lead to formal potentials 1.33 and 1.37 V for $\mathrm{Cr^{IV/III}}$, values which are, as expected, considerably below those cited by Bose[21a] (1.61 V) and by Rocek[21b] (2.1 V) pertaining to solutions in the absence of ligands that stabilize Cr(IV).

Table I. Absorbance Data for Chelated Chromium(III) Reflecting the Equilibrium $\mathrm{Cr^{III}(Lig)_2 + Lig^- \rightleftharpoons Cr^{III}(Lig)_3}$ in 2-Hydroxy-2-ethylbutanoate Buffers[a]

$[\mathrm{Lig}^-]$ (M)[b]	$(\mathrm{Abs})_{obsd}$	$(\mathrm{Abs})_{calcd}$[c]
0.0174	0.689	0.685
0.0269	0.695	0.695
0.0365	0.697	0.704
0.0545	0.722	0.720
0.0923	0.746	0.745
0.1606	0.775	0.775
0.307	0.811	0.809
0.405	0.826	0.822
0.554	0.832	0.835
0.704	0.843	0.844

[a] Data were taken in a 1.00-cm cell at 25 °C. Solutions were buffered with a 1:9 mixture of 2-hydroxy-2-ethylbutanoic acid and its sodium salt; pH = 4.1–4.2. Absorbances at 588 nm were recorded after equilibration of 0.0178 M $\mathrm{Cr^{III}(Lig)_3}$ (complex VI in text) with the ligand buffer. Spectra were taken 8 h after mixing. [b] 2-Hydroxy-2-ethylbutanoate. [c] Values were calculated by using eq 4 in the text, taking $\epsilon_1 = 37.2\ M^{-1}\ cm^{-1}$, $\epsilon_2 = 49.5\ M^{-1}\ cm^{-1}$, and $Q_L = 6.5\ M^{-1}$.

The close approach to 1:2 stoichiometry observed for reductions of Cr(V) (Table III) points to nearly quantitative conversion to Cr(III); in none of these reactions is there evidence for appreciable accumulation of Cr(IV). The calculated reaction quotient for the Cr(V)–$\mathrm{Fe^{II}(Me_2bipy)_3}$ reaction, $10^{-0.51\pm0.20}$ at pH 3.3, when adjusted for the attendant consumption of protons, yields $K_{eq} = 10^{12.9}$, allowing us to estimate $E°$ for $\mathrm{Cr^{V/III}}$ as 1.32 V, a value very nearly the same in aqueous chloride as in perchlorate. The latter potential, in conjunction with $E°(\mathrm{Cr^{IV/III}}) = 1.35$ V, leads to 1.29 V for $E°(\mathrm{Cr^{V/IV}})$. Thus, Cr(IV) is a slightly stronger 1e^- oxidant than Cr(V), a difference in accord with the observed spontaneous bimolecular disproportionation of Cr(IV) ($2\mathrm{Cr^{IV}} \rightarrow \mathrm{Cr^{III}} + \mathrm{Cr^{V}}$),[16] a reaction for which our formal potentials yield an equilibrium quotient of 10 (25 °C, pH 3.3, μ = 0.50 M).

Since "extraligation quotients", pertaining to the reactions $\mathrm{Cr(Lig)_2 + Lig^- \rightleftharpoons Cr(Lig)_3}$, are comparable for the three oxidation states of interest, formal potentials associated with interconversion of triligated species lie close to those for diligated. Calculated values are 1.28 V for $\mathrm{Cr(Lig)_3^{IV/III}}$ and 1.31 V for $\mathrm{Cr(Lig)_3^{V/IV}}$.

All reactions examined are first order in each of the redox partners. Although three of the chromium systems exhibit kinetic dependencies on $[\mathrm{Lig}^-]$ (within the range 0.010–0.30 M), the others do not, indicating that specific rates associated with reductions of the chelated oxidant and its "extraligated" form, $\mathrm{Ox(Lig}^-)$, are nearly equal.

Representative kinetic data, associated with the Cr(IV)–$\mathrm{IrCl_6^{3-}}$ and the Cr(V)–$\mathrm{Fe^{II}(Me_2bipy)_3^{2+}}$ reactions, appear in Table IV. Both conversions are inhibited by excess ligand anion, and both sets of data are consistent with expression 6, which conforms to

$$\mathrm{rate} = [\mathrm{Ox}][\mathrm{Red}]\frac{k_1 + k_2K_L[\mathrm{Lig}^-]}{1 + K_L[\mathrm{Lig}^-]} \qquad (6)$$

competitive oxidations by Ox (with specific rate k_1) and $\mathrm{Ox(Lig}^-)$ (specific rate k_2) where K_L is the ligation constant ($\mathrm{Ox + Lig^- \rightleftharpoons Ox(Lig^-)}$).[22]

Kinetic parameters resulting from refinements in terms of (6) are listed in Table V, and calculated rates are compared to observed

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Table II. Estimated Equilibrium Quotients for Cr(IV)–Fe(II) and Cr(V)–Fe(II) Reactions[a]

type	oxidant (mM)	reductant (mM)	medium	λ (nm)	Q
1	Cr(IV) (0.02–0.15)	$Fe^{II}(Me_2phen)_3$ (0.015–0.08)	0.5 M NaCl	510	0.10 ± 0.02
1	Cr(IV) (0.015)	$Fe^{II}(Me_2bipy)_3$ (0.08)	0.5 M NaCl	510	5 ± 2[b]
2	Cr(V) (0.25–1.0)	$Fe^{II}(Me_2bipy)_3$ (0.018–0.036)	0.5 M $NaClO_4$[c]	528	0.31 ± 0.11
2	Cr(V) (0.20–5.0)	$Fe^{II}(Me_2bipy)_3$ (0.02–0.05)	0.5 M NaCl	528	0.34 ± 0.10

[a] Reactions were carried out at 25 °C; solutions were buffered with equal concentrations (0.05 M) of 2-ethyl-2-hydroxybutanoic acid (HLig, I) and its sodium salt (Lig^-); pH = 3.3. Values of the equilibrium quotient, Q, were estimated spectrophotometrically (see the Experimental Section). [b] See ref 16. [c] [HLig] = [Lig^-] = 0.010 M.

Table III. Stoichiometry of Redox Reactions of Chromium and Vanadium[a]

oxidant (mM)	reductant (mM)	λ (nm)	waiting period,[b] min	Δ[Ox]/Δ[Red]
Cr^{IV} (0.05–0.40)	$IrCl_6^{3-}$ (0.25–1.0)	487	0.5	1.12 ± 0.02
Cr^{IV} (0.16–0.64)	$Fe(CN)_6^{4-}$ (0.3–1.8)	420	0.5	0.97 ± 0.02
Cr^{IV} (0.07)	$Fe(CN)_6^{4-}$ (0.02–0.06)	510	0.5	1.03 ± 0.03
V^{IV} (50)	Co^{II}(sep) (10–30)	760	45	0.97 ± 0.05
$IrCl_6^{2-}$ (0.44)	V^{III}(aq) (0.13–0.39)	487	5	1.02 ± 0.04
$Fe^{III}(bipy)_3$ (0.2)	V^{III}(aq) (0.06–0.12)	522	25	0.92 ± 0.13
Cr^{V} (10)	$Fe(CN)_6^{4-}$ (1.6–4.0)	510	0.5	0.52 ± 0.02
Cr^{V} (0.2–0.4)	$IrCl_6^{3-}$ (1.4)	488	30	0.57 ± 0.06[c]

[a] Reactions were carried out in aqueous solutions at 25 °C. Chromium(IV) and –(V) were prepared as chelates of 2-ethyl-2-hydroxybutanoic acid (HLig, I) and used in solutions buffered by equal concentrations of HLig and Lig^- (see text). [b] Waiting period after each addition of the reactant in deficiency. [c] Ghosh, S. K.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 3357.

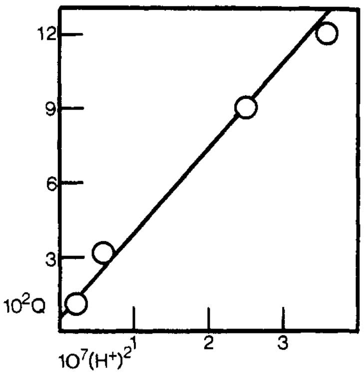

Figure 1. Variation, with $[H^+]^2$, of the observed reaction quotient, $Q = [Fe^{III}][Cr^{III}]/[Fe^{II}][Cr^{IV}]$, for the reduction of chelated Cr(IV) with $Fe^{II}(Me_2phen)_3^{2+}$ (Me_2phen = 5,6-dimethyl-1,10-phenanthroline): 25 °C; μ = 0.50 M (NaCl); 510 nm. The slope of the regression line, $Q = (3.5 \pm 0.5) \times 10^5[H^+]^2 + (4.7 \pm 2.3) \times 10^{-3}$, corresponds to the equilibrium constant for reaction 5 in the text.

values in Table IV.

Table V also summarizes rate laws and parameters for 10 additional redox systems, including two oxidations by VO^{2+} and a reduction by V(III). Oxidations by Cr(V) consume 2 equiv of each reductant taken, and since there is no accumulation of Cr(IV), the initial conversion to Cr(IV) is assumed to be rate-determining and the follow-up reduction ($Cr^{IV} \rightarrow Cr^{III}$) is taken to be rapid. Tabulated Cr(V) rates are therefore half the observed rate of loss of the reductant.

Oxidations by Cr(IV), as a group, are seen to be considerably more rapid than those by Cr(V), and these are, in turn, faster than the vanadium reactions (which are carried out in unbuffered media). When individual kinetic contributions from Ox and Ox(Lig^-) can be evaluated for the chromium reactions (k_1 and k_2 values), the former are somewhat greater. Both oxidations by VO^{2+} are pH-independent, whereas the reduction by V(III) proceeds at a rate proportional to $[H^+]^{-1}$.

Data in Table VI pertain to the reactions of Cr(IV) in media of widely varying ionic strengths. Specific rates involving three coreagents with different net charges are seen to be virtually invariant within the range μ = 0.10–2.0 M, i.e., all three reactions are characterized by negligible kinetic salt effects. This behavior strongly implies that the redox partner common to the three systems, Cr(IV), exists predominantly as an uncharged species and thus confirms an earlier suggestion on this point,[10] based in part on comparison of ligation constants.

Discussion

The structures of the transition-metal reductants used in the Cr(IV), Cr(V), and V(IV) reactions and their substitution-inert character dictate outer-sphere paths for these conversions. Although the estimated formal potential for $Cr^{IV/III}$ is more positive than that for $Cr^{V/IV}$, the difference between these values (0.06 V) is too small, on the basis of the Marcus model,[23] to accommodate, by itself, the much greater rates observed here for oxidations by Cr(IV). The major part of this divergence in reactivities may reasonably be attributed, at least in part, to a difference in self-exchange rates for the couples $Cr^{IV/III}$ and $Cr^{V/IV}$.

A preliminary account,[24] based on an approximate treatment of only a portion of these results, is in accord with such a conclusion. However, the diversity of charge types among the reductants and the range of $\Delta G°$ values associated with these reactions justify a more detailed treatment,[23c] in which the specific rate, k_{12}, of an electron-transfer reaction is represented as the sum of three terms

$$\ln(k_{12}) = \frac{1}{2}\left[\ln(k_{11}k_{22}K_{12}) + \frac{[\ln(K_{12}) + (w_{12} - w_{21})/RT]^2}{4\left[\ln\left(\frac{k_{11}k_{22}}{Z^2}\right) + \frac{w_{11} + w_{22}}{RT}\right]}\right] + \frac{w_{11} + w_{22} - w_{12} - w_{21}}{2RT} \quad (7)$$

where k_{11} and k_{22} are the self-exchange rates for the oxidant and reductant, K_{12} is the equilibrium constant for the redox reaction,

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(22) From (4) and k_1 and k_2 values for the Cr(IV)–$IrCl_6^{3-}$ reaction (Table IV), we calculate that 88% of this redox reaction should proceed via Ox(Lig^-) at [Lig^-] = 0.20 M. Partition between paths should be reflected in the mix of Cr(III) products formed. Examination of these products after cation-exchange separation indicates that nearly 80% of the recovered chromium product is "extraligated" (see the Experimental Section). Agreement here may be considered reasonable since slow aquation of Cr^{III}(Lig^-) is known to occur on contact with polysulfonate resin.[12]

(23) (a) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155. (b) Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1977**, *99*, 5615. (c) Creutz, C.; Sutin, N. In *Inorganic Reactions and Methods*; Zuckerman, J. J., Eds.; VCH Publishers: Deerfield Beach, FL, 1986; Vol. 15, p 1350.

(24) Ghosh, M. C.; Gould, E. S. *J. Chem. Soc., Chem. Commun.* **1992**, 195.

Table IV. Representative Kinetic Data for the Cr(IV)–$IrCl_6^{3}$ and Cr(V)–$Fe^{II}(Me_2bipy)_3^{2+}$ Reactions (25 °C; μ = 0.50 M)

Cr(IV) + $IrCl_6^{3-}$ (NaCl, 544 nm)					Cr(V) + $Fe^{II}(Me_2bipy)_3^{2+}$ ($NaClO_4$, 528 nm)[a]			
[Ox] (mM)	[Red] (mM)	$[Lig^-]^b$ (M)	pH	10^2k^c (s^{-1})	[Ox] (mM)	$[Lig^-]^b$ (M)	pH	k^a ($M^{-1}\,s^{-1}$)
0.050	0.50	0.050	3.32	2.9 (2.6)	0.50	0.0090	3.36	19.2(20)
0.050	1.00	0.050	3.34	5.5 (5.2)	1.00	0.0090	3.22	18.0(20)
0.20	1.50	0.050	3.31	7.8 (7.8)	0.50	0.0090	3.00	17.8(20)
0.20	2.0	0.050	3.34	10.2 (10.4)	0.50	0.0090	2.77	17.0(20)
0.20	3.0	0.050	3.31	14.0 (15.6)	0.50	0.022	3.19	15.0 (14.8)
0.050	0.50	0.10	3.26	2.5 (2.4)	0.50	0.045	3.22	13.2 (11.5)
0.050	0.50	0.20	3.27	2.1 (2.2)	0.50	0.067	3.19	10.0 (8.8)
0.050	0.50	0.030	3.40	3.0 (2.9)	0.50	0.090	3.21	6.5 (7.5)
0.050	0.50	0.015	3.47	3.2 (3.3)				
0.050	0.50	0.050	3.42	2.8 (2.6)				
0.050	0.50	0.050	3.04	2.7 (2.6)				
0.050	0.50	0.050	2.74	2.8 (2.6)				
0.050	0.50	0.050	2.46	2.7 (2.6)				

[a] [Fe(II)] = 3 × 10^{-5} M throughout. Second-order rate constants were calculated by the procedure of King,[17] taking the equilibrium quotient for the reaction as 0.31 (Table II). [b] Buffering anion (Lig^-) = 2-ethyl-2-hydroxybutanoate. [c] First-order specific rates; parenthetical values were calculated from (6) and parameters in Table V.

Table V. Rate Laws and Kinetic Parameters for Redox Reactions of Chromium(IV), Chromium(V), Vanadium(IV), and Vanadium(III)[a]

A. Oxidations by chromium(IV)[b,c]

reductant (R)	medium	λ (nm)	rate law	parameters[d]
$IrCl_6^{3}$	NaCl	545	$[Ox][R]\dfrac{k_1 + k_2K_L[L]}{1 + K_L[L]}$ (4)	$k_1 = 101 \pm 9$; $k_2 = 41 \pm 2$; $K_L = 90^e$
$Fe(CN)_6^{4-}$	$NaClO_4$	510	k[Ox][R]	$k = (1.89 \pm 0.11) \times 10^6$
$Fe(Me_2bipy)_3^{2+}$	$NaCF_3SO_3$	528	k[Ox][R]	$k = (1.5 \pm 0.3) \times 10^3$
$Fe(Me_4phen)_3^{2+}$	NaCl	498	k[Ox][R]	$k = (1.2 \pm 0.2) \times 10^3$
$Fe(Me_2phen)_3^{2+}$	NaCl	518	k[Ox][R]	$k = (8.8 \pm 1.0) \times 10^2$

B. Oxidations by Chromium(V)[h,f]

reductant (R)	medium	λ (nm)	rate law	parameters[d]
$Fe(CN)_6^{4-}$	$NaClO_4$	420	k[Ox][R]	$k = 135 \pm 30$
$Fe(Me_2bipy)_3^{2+}$	$NaClO_4$	528	(4)	$k_1 = 14 \pm 2$; $k_2 = 1.65 \pm 0.80$; $K_L = 51^g$
$Fe(Me_4phen)_3^{2+}$	$NaCF_3SO_3$	498	(4)	$k_1 = 3.4 \pm 0.1$; $k_2 = 1.35 \pm 0.05$; $K_L = 51^g$
$IrCl_6^{3}$	NaCl	488	k[Ox][R]	$k = (1.65 \pm 0.10) \times 10^{-2}$

C. Reactions of Vanadium[h]

oxidant	reductant (R)	medium	λ (nm)	rate law	parameters
VO^{2+}	$Co(sep)^{2+}$	1.1 M $NaClO_4$[i]	472	k[Ox][R]	$k = 0.33 \pm 0.04$
VO^{2+}	$Ru(NH_3)_6^{2+}$	0.6 M $NaCF_3SO_3$[j]	400	k[Ox][R]	$k = (1.86 \pm 0.13) \times 10^{-3k}$
$IrCl_6^{2}$	V(III)	1.0 M $NaClO_4$[i]	487	$k[Ox][R][H^+]^{-1}$	$k = 53 \pm 1\ s^{-1}$

[a] Reactions were carried out at 25 °C; μ = 0.50 M unless otherwise indicated. [b] Oxidant solutions were stabilized by buffers of 2-ethyl-2-hydroxybutanoic acid (Hlig) and its anion (Lig^-); pH = 2.4–3.4; [Lig^-] = 0.03–0.30 M. [c] [Ox] = 0.05–0.20 mM; [Red] = 0.01–3.0 mM. [d] Specific rates are listed in $M^{-1}\,s^{-1}$ unless otherwise indicated. [e] Reported anation constant for Cr(IV) (ref 10). [f] [ox] = 0.5–2.0 mM; [red] = 0.025–0.09 mM. [g] Reported anation constant for Cr(V) (ref 12). [h] Reactions were run in unbuffered solutions. [i] [H^+] = 0.01–0.10 M. [j] [H^+] = 0.012–0.024 M. [k] Reaction was strongly catalyzed by Cl^-; $(rate)_{cat}$ = 0.0082[Ox][Red][Cl^-] (25 °C).

Z^2 (ca. 10^{22} $M^{-2}\,s^{-2}$)[25,26] is the square of the collision frequency, and the *w*'s are electrostatic work contributions associated with the reactants, the products, and the two self-exchanging systems. Each *w* term is, in turn, calculated by (8), where *z*'s are the ionic

$$w_{cd} = 4.23 z_c z_d / a_{cd}(1 + 0.33\, a_{cd}\mu^{1/2}) \qquad (8)$$

charges on interacting species c and d, μ is the ionic strength of the medium, and a_{cd} is the distance of closest approach, as estimated from the presumed geometry of the encounter and reported atomic and ionic radii.

Values of k_{12} for the "cross-reactions" involving Cr(IV) are summarized in Table VII. Where kinetic contributions from both the oxidant and its extraligated form ($Cr^{IV}(Lig^-)$) were detected (k_1 and k_2 in Table V), the former rate has been taken.

Table VI. Reactions of Chromium(IV) at Varying Ionic Strengths[a]

coreagent	λ (nm)	$10^5[Cr^{IV}]$ (M)	10^4[coreagent]	μ (M)	k_{obsd} (s^{-1})
$HCrO_4^-$	510	80.0	100	0.10	0.0122
				1.00	0.0124
				2.00	0.0131
$IrCl_6^{3-}$	545	8.00	7.0	0.10	0.044
				1.00	0.041
				2.00	0.040
Sn(II)	510	7.0	8.5	0.10	0.131
				1.00	0.138
				2.00	0.138

[a] Reactions were carried out at 25 °C; buffering anion (Lig^-) (0.007 M) = 2-ethyl-2-hydroxybutanoate; pH = 3.04–3.36. Chromium(IV) was generated from the reaction of Cr(VI) and As(III) (see the Experimental Section). The supporting electrolyte was $NaClO_4$ for the $HCrO_4^-$ reaction and NaCl for the $IrCl_6^{3-}$ and Sn(II) reactions.

At 25 °C, log K_{12} may be taken as $\Delta E°/0.059$. However, the Marcus model requires that the partners in each of the contributing half reactions differ only in their electron count and not in their level of protonation. Since our predominant Cr(III) product, $Cr^{III}(Lig)_2(H_2O)_2^+$, has 2 more protons than the Cr(IV) oxidant (eq 5), the estimated $E°$ for Cr(IV,III), 1.35 V, must be converted to a value pertaining instead to $Cr^{III}(Lig)_2(OH)_2^-$. The treatment,

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(25) See, for example: (a) Rudgewick-Brown, N.; Cannon, R. D. *Inorg. Chem.* **1985**, *24*, 2463. (b) Sarala, R.; Rabin, S. B.; Stanbury, D. M. *Inorg. Chem.* **1991**, *30*, 3999. Utilization of alternate treatments,[26] in which values of this term range between 10^{20} and $10^{24.6}$ $M^{-2}\,s^{-2}$, does not significantly affect the calculated self-exchange rates.

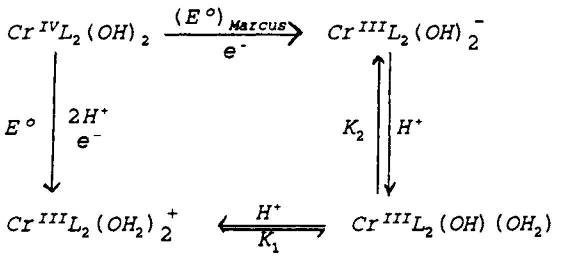
(26) (a) Martin, M. J.; Endicott, J. F.; Ochrymowycz, L. A.; Rorabacher. *Inorg. Chem.* **1987**, *26*, 3012. (b) Macartney, D. L.; Sutin, N. *Inorg. Chem.* **1983**, *22*, 3530.

Table VII. Calculated Self-Exchange Rates and Contributing Parameters for Redox Reactions Involving Cr(IV), Cr(V), V(IV), and V(III) (25 °C)

oxidant	reductant	μ (M)	$E°_{red}$	$\log(k_{22})$[a]	$\log(K_{12})$[b]	$\log(W_{12})$[c]	k_{12}	$\log(k_{11})$[d]
Cr(IV)[e]	$IrCl_6^{3-}$	0.50	0.87[f]	5.36[n]	−1.02	0.23	1.0×10^2	−0.77
($E°$ 0.81 V)	$Fe(CN)_6^{4-}$	0.50	0.36[g]	4.85[o]	7.7	0.51	1.9×10^6	−0.19
	$Fe(Me_4phen)_3^{2+}$	0.50	0.895[h]	8.5[p]	−1.45	0.34	1.2×10^3	−1.35
	$Fe(Me_2bipy)_3^{2+}$	0.50	0.94[h]	8.5[p]	−2.21	0.34	1.5×10^3[t]	−0.51
	$Fe(Me_2phen)_3^{2+}$	0.50	0.99[i]	8.5[p]	−3.06	0.34	8.8×10^2[t]	−0.06
Cr(V)[e]	$IrCl_6^{3-}$	0.50	0.87	5.36	−2.55	0.029	1.7×10^{-2}	−6.90
($E°$ 0.72 V)	$Fe(CN)_6^{4-}$	0.20	0.36	4.85	6.1	0.23	1.3×10^2	−6.41
	$Fe(Me_4phen)_3^{2+}$	0.20	0.895	8.5	−2.98	1.04	3.4	−6.43
	$Fe(Me_2bipy)_3^{2+}$	0.50	0.94	8.5	−3.74	0.75	14[t]	−4.00
	$Ru(NH_3)_6^{2+}$	0.20	0.067[j]	3.63[q]	11.1	1.65	$\geq 1 \times 10^5$	≥ -6.6
VO^{2+}	Co(sep)$^{2+}$	1.10	−0.30[k]	0.71[r]	10.9	0.026	0.33	−6.01
($E°$ −0.04 V)[m]	$Co^I(B_{12s})$	0.20	−0.61[l]	4.8[s]	16.2	0.99	130[u]	−9.43
	$Ru(NH_3)_6^{2+}$	1.00	0.067	3.63	4.6	0.018	1.9×10^{-3}	−7.31
$IrCl_6^{2-}$ ($E°$ 0.87 V)[f]	$V(OH)^{2+}$	1.00	0.17	5.36	11.9	1.63	2.5×10^4	−10.2

[a] Reported self-exchange rate refers to reductant coreagent except for reactions of $V(OH)^{2+}$. [b] log K_{12} for the "cross reaction" evaluated as $(E°_{ox} - E°_{red})/0.59$. [c] Sum of electrostatic work terms, evaluated from (8) in text. [d] Self-exchange rate for Cr or V system, estimated from (7) in text. [e] Reactions were carried out in buffers of 2-ethyl-2-hydroxybutanoic acid (I) and its anion. The Cr(V) compound was bis chelate IV. Values of $E°$ have been adjusted to accommodate differences in proton numbers between oxidized and reduced form (see text and ref 27). [f] George, P.; Hanania, I. H.; Irvine, D. H. *J. Chem. Soc.* **1957**, 3048. [g] Murray, R. C.; Rock, P. A. *Electrochim. Acta* **1968**, *13*, 969. [h] Brandt, W. W.; Smith, G. F. *Anal. Chem.* **1949**, *21*, 1313. [i] Reference 20. [j] Brown, G. M.; Krentzien, H. J.; Abe, M.; Taube, H. *Inorg. Chem.* **1979**, *18*, 3374. [k] Creaser, I. I.; Harrowfield, J. MacB.; Herlt, A. J.; Sargeson, A. M.; Springborg, J.; Geue, R. J.; Snow, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 3181. [l] Lexa, D.; Saveant, J.-M. *Acc. Chem. Res.* **1983**, *16*, 235. [m] Jones, G.; Colvin, J. H. *J. Am. Chem. Soc.* **1944**, *66*, 1563. See also ref 27. [n] Hurwitz, P.; Kustin, K. *Trans. Faraday Soc.* **1966**, *62*, 427. [o] Balasubramanian, P. N.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 3403. [p] Self-exchange rates taken to be the same as that for $[Fe(phen)_3]^{3+/2+}$ (ref 29a). [q] Meyer, T. J.; Taube, H. *Inorg. Chem.* **1968**, *7*, 2369. [r] Reference 15. [s] Pillai, G. C.; Ghosh, S. K.; Gould, E. S. *Inorg. Chem.* **1988**, *27*, 1868. [t] Reaction proceeded only partially to completion; specific rate was evaluated by the method of King (ref 17). [u] Pillai, G. C.; Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1987**, *26*, 3120.

Scheme I



analogous to that by Macartney,[27] utilizes the component steps indicated in Scheme I and leads to (9), where the K's represent successive acidity constants for the reduced form.

$$(E°)_{Marcus} = E° - 0.059(pK_1 + pK_2) \qquad (9)$$

From our experimental value of pK_1 (3.4) and several recorded K_1/K_2 ratios for aquated metal ions,[28a] we estimate pK_2 for our Cr(III) product III to be 5.7. Combining the two pK's leads to an estimated "electron-exchange-only" potential, $(E°)_{Marcus}$ of 0.81 ± 0.02 V for $Cr^{IV/III}$. The corresponding treatment of our $E°$ value for $Cr^{V/IV}$, 1.29 V, in conjunction with the reported[12] pK_1 of 3.5 for Cr(IV),[28b] yields a potential $(E°)_{Marcus}$ of 0.72 V pertaining to single-electron transfer from Cr(V) oxidant IV.

Values of k_{12} for Cr(IV), in combination with (7), lead to a calculated self-exchange rate, k_{11}, of $10^{-0.51\pm0.40}$ M^{-1} s^{-1} for $Cr^{IV/III}$. The indicated uncertainty, although sizable, is comparable to those for earlier estimates for other systems featuring transition-metal centers[26a,27,29] and is not unreasonable for treatments of this sort.

This $Cr^{IV/III}$ rate falls within the span characteristic of several octahedral aqua complexes of 3d block centers ($[TiOH]^{3+/2+}$, $\geq 10^{-3.5}$ M^{-1} s^{-1}; $V^{3+/2+}$, $10^{-2.0}$; $Mn^{3+/2+}$, $10^{-3.5}$; $Fe^{3+/2+}$, $10^{0.1}$) but lies substantially above that for $Cr^{3+/2+}$ ($\leq 10^{-4.7}$).[23c,30] The low value for the latter is commonly attributed to Jahn–Teller elongation of axial metal–ligand bonds in the reduced (d^4) member of this system.[30] The overall similarity suggests that, aside from $Cr^{3+/2+}$, the Franck–Condon barrier to self-exchange, which largely reflects the difference in bond lengths for the reduced and oxidized forms,[30] is not greatly different for these systems and that there are no major structural alterations attending interconversion of the principal Cr(III) and Cr(IV) species. The implication here is that both oxidation states are hexacovalent in the ligand environment chosen.[31-34]

Despite the limited roster of known Cr(IV) species,[7] some diversity of coordination geometry is associated with this state. Porphyrin derivatives are reported to be pentacovalent and to feature an oxochromium(IV) unit, $Cr^{IV}(=O)$,[35] and it has been proposed that the aqua cation of Cr(IV) has a closely related structure.[8] On the other hand, the Cr(IV) center in diperoxo complexes has been found to be 7-covalent, being bonded to three nitrogen and four oxygen atoms defining a pentagonal bipyramid.[36] Although the $Cr^{IV/III}$ self-exchange rate derived from our data

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(27) Macartney, D. H. *Inorg. Chem.* **1986**, *25*, 2222.

(28) (a) Recorded ΔpK_N values are 2.3 for $Cr(H_2O)_6^{3+}$, 2.0 for $Fe(H_2O)_6^{3+}$, 2.5 for $VO(H_2O)_4^{2+}$, and 2.8 for $Be(H_2O)_4^{2+}$. See: Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum: New York, 1976; Vol. 4, pp 1–14. (b) A ΔpK_N value of 2.3 is assigned also to the two successive deprotonation constants of $Cr^{IV}L_2(OH)_2$ in considering the $Cr^{V/IV}$ couple.

(29) (a) Macartney, D. H.; Sutin, N. *Inorg. Chem.* **1985**, *24*, 3403. (b) Howes, K. R.; Bakac, A.; Espenson, J. H. *Ibid.* **1988**, *27*, 791.

(30) Brunschwig, B. S.; Creutz, C.; Macartney, D. H.; Sham, T.-K.; Sutin, N. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 113.

(31) Earlier analysis of cross-reaction data for Fe^{2+} reductions of 10 different outer-sphere oxidants led to an apparent $Fe^{3+/2+}$ self-exchange rate of $10^{-3\pm1}$ M^{-1} s^{-1}.[32] Further investigations, both theoretical[30,33a-c] and experimental,[33d] provide strong (but not universally accepted)[34] support of the view that the greater rate (1.1 M^{-1} s^{-1}) pertains to an adiabatic outer-sphere exchange and that many cross reactions of Fe^{2+} are, to varying degrees, nonadiabatic.

(32) Macartney, D. H.; McAuley, A.; Olubuyide, O. A. *Inorg. Chem.* **1985**, *24*, 307.

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cannot rule out an oxo dihydroxo equilibrium ($Cr^{IV}(=O) \rightleftharpoons Cr^{IV}(OH)_2$) in which the 5-covalent complex II is a minor Cr(IV) contributor, it favors predominance of the 6-coordinate species III at that oxidation level.

In addition, we find that the Cr(IV) derivatives in the present study, in contrast to the aquachromium(IV) complex described by Scott and co-workers,[8] do not react perceptibly with the "oxo-acceptor" reagents, triphenylphosphine, Sb(III), H_2AsO_3 , and the thiyl-substituted amino acid, methionine, likewise indicating that our Cr(IV) species are devoid of the oxo function.

Rate constants for oxidation by Cr(V) are consistent with a k_{11} value of $10^{-6.1\pm0.8}$ for $Cr^{V/IV}$, some 5 orders of magnitude below that for $Cr^{IV/III}$ and well below the range taken to be typical of interconversions of octahedral aqua species. We cannot say, at this point, how much of this greater barrier to self-exchange may be attributed to differing coordination numbers of the two states and how much to the stretching of the Cr=O bond in IV during conversion to a Cr–O bond in III, but both of these factors may be assumed to contribute.

Comparison with the systems $V^{IV/III}$ and $V^{V/IV}$ as aqua ions (in the absence of chelating ligands) is instructive. Specific rates for oxidations by VO^{2+} (yielding $V(H_2O)_6^{3+}$) are notably low. After adjustment for differences in proton count,[27] our data yield a k_{11} value of $10^{-7.6\pm1.4}$ M^{-1} s^{-1}, applicable to $V^{IV}O(H_2O)_4^{2+} + e^- \rightarrow V^{III}(OH)_2(H_2O)_3^{+}$.[37] This appears to be one of the lowest rates thus far reported for a pair of transition-metal centers and lies far beneath the experimental exchange rate recorded by Furman and Garner.[38] However, the monomial inverse-$[H^+]$ kinetic dependence reported by these workers (who observed no acid-independent term), in conjunction with the recognized substitution-labile character of both states, indicates that here the observed rate describes a process which is nearly completely inner-sphere.[39,40]

Macartney[27] has estimated a $V^{V/IV}$ rate, pertaining to the couple $[VO(OH)]^{2+/+}$, in the range 10^{-3}–10^{-1} M^{-1} s^{-1}. Contrast between this and the much slower $V^{IV/III}$ exchange may then be attributed, at least in part, to the presence of oxovanadium linkages in both V(V), and V(IV), but not in V(III). The totality of the present data indicates that the redox series V(V,IV,III) (aquated) differs from Cr(V,IV,III) (chelated) in that the major structural change in the former is associated with its 4+/3+ component whereas that in the chromium series is associated with 5+/4+.

Note that the latter conclusion is in accord with the suggestion made some 30 years ago by King and Espenson,[5a,41] pertaining to the successive 1e⁻ changes in the reduction of Cr(VI) to Cr(III) in aqueous media at low pH. However, recent evidence[8] that Cr(IV) in aquo systems is an oxo species, as are Cr(VI) and (presumably) Cr(V), casts doubt that this proposal applies to the conversions for which it was intended. Somewhat paradoxically, however, it appears to be valid for the present chromium series, in which the intermediate states which existed only transiently in the earlier work, have been stabilized by chelation.

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[37] For this classification, acidity constants for successive deprotonations of $V(H_2O)_6^{3+}$ ($pK_1 = 2.5$; $pK_2 = 3.9$) are employed. See, for example: (a) Haim, A. *Prog. Inorg. Chem.* **1983**, *30*, 273. (b) Bard, A. J., Ed. *Standard Potentials in Aqueous Solution*; Marcell Dekker: New York, 1985; p 519.

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$$\text{rate} = k[V^{III}][V^{IV}][H^+]^{-1} \tag{10}$$

where $k = 2.6 \times 10^{-2}$ s^{-1} over the range 0.5–2.0 M $HClO_4$ (25 °C; $\mu = 2.5$ M).

[39] The $V^{IV/III}$ self-exchange rate estimated from the $IrCl_6^{2-}$–$V(OH)^{2+}$ reaction, $10^{-10.3}$ M^{-1} s^{-1} (Table VII), applies to a process at a different protonation level ($V^{IV}(OH)^{3+} \rightarrow V^{III}(OH)^{2+}$).[40] It nevertheless falls slightly below the mean $V^{IV/III}$ rate obtained here from oxidations by VO^{2+}. The similarity in calculated k_{11} values suggests that despite the availability of potential bridging ligands on the chloro-substituted oxidant, any inner-sphere path contributes negligibly to this reduction by $V(OH)^{2+}$.

[40] This treatment utilizes $E°(VO^{2+} \rightarrow V(OH)^{2+}) = 0.164$ V.[37b] Adjustment for differing proton contents[27] requires an estimate of pK_A of $V(OH)(H_2O)_4^{3+}$, which is taken to be 0.0, i.e. 5 units less than that for its conjugate base $VO(H_2O)_4^{2+}$.[37b]

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