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Redox Potentials of Chromium(V)/(IV), -(V)/(III), and -(IV)/(III) Complexes with 2-Ethyl-2-hydroxybutanoato(2−/1−) Ligands

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Abstract: The formal reduction potentials of $[Cr^{V/IV}(O)L_2]^{-/2-}$ and $[Cr^{V}(O)L_2]^{-}/[Cr^{IV}(O)L(LH)]^{-}$ (L = ehba = 2-ethyl-2-hydroxybutanoato(2−)) are 0.44 and 0.65 V, respectively, from cyclic voltammetric measurements. Potentiometric titrations using the $[Fe(CN)_6]^{4-}$ reduction of $[Cr^{V}(O)L_2]^{-}$ yielded a formal potential of 0.84 V for the $[Cr^{V}(O)L_2]^{-}/[Cr^{III}L_2(H_2O)_2]^{-}$ redox couple. By using the values of $Cr^{V/IV}$ and $Cr^{V/III}$ couples, formal potentials for the $[Cr^{IV}(O)L_2]^{2-}/[Cr^{III}L_2(H_2O)_2]^{-}$ and $[Cr^{IV}(O)L(LH)]^{-}/[Cr^{III}L_2(H_2O)_2]^{-}$ couples were calculated to be 1.24 and 1.03 V, respectively. Most of these potential data differ markedly from those estimated by Ghosh and Gould (*J. Am. Chem. Soc.* **1993**, *115*, 3167−3173; *J. Chem. Soc., Chem. Commun.* **1992**, 195−196) for the same complexes. The spectra of the Cr(IV) complexes were also examined by reduction of $[Cr(O)L_2]^{-}$ with pulse radiolysis. The structures of the Cr(IV) complexes, $[Cr(O)L_2]^{2-}$, $[Cr(O)(L)(LH)]^{-}$, and $[Cr(O)(LH)_2]$, have been assigned on the basis of X-ray crystallography for isostructural V(IV) complexes. Finally, the equilibria among the Cr(V) or Cr(IV) complexes with excess ligand appear to be due to complexes involving one or two ehba ligands per chromium, as established by the isolation and characterization of the Cr(V) dimer, $\{[Cr(O)_2(ehba)]_2\}^{2-}$. These new redox potentials, along with the reinterpretation of literature data, will aid in understanding the redox chemistry involved in Cr(VI/V) oxidations of organic substrates and Cr(VI)-induced cancers.

Introduction

Recently, Ghosh and Gould[1] estimated the reduction potentials for the $Cr^{V/IV}$, $Cr^{IV/III}$, and $Cr^{V/III}$ redox couples, all of which are coordinated to two bidentate 2-ethyl-2-hydroxybutanoate(2−) (ehba) ligands. The formal potential for the CrV/IV redox couple reported by these authors[1] appears to be 0.85 V higher than that measured directly from the cyclic voltammetry and differential pulse voltammetry experiments by our two research groups.[2,3] Furthermore, the potential for the $Cr^{IV/III}$ couple reported by these authors in an initial communication[1b] differs considerably from that appearing in the full article.[1a] The unusually large discrepancy between direct electrochemical measurements[2,3] and those estimated by potentiometry[1] has prompted us to reexamine the reduction potentials of the above mentioned redox couples. Since the $Cr^{V/IV}$ potential was used to estimate the potentials for other redox couples, and further these potentials were then used to calculate the self-exchange rate constants for the various redox partners,[1] an accurate determination of these formal potentials is highly desirable. In this paper we report the reduction potentials of various chromium oxidation states from direct electrochemical measurements. In addition, the reported solution equilibria[1] between the Cr(V) and Cr(IV) complexes with excess ligand are not consistent with the detailed EPR experiments on Cr(V) in solution[4,5] and the X-ray crystallographic structures of Cr(V),[6] V(V),[7] and V(IV)[8] complexes with the same ligand. The recent isolation of the Cr(V) dimer, $\{[Cr(O)_2(ehba)]_2\}^{2-}$,[9] which has been characterized by EXAFS as having the same structure as the V(V) dimer,[7] has also prompted us to reexamine the structures of the species involved in the ligand exchange chemistry within the various oxidation states.

The redox potential data for high oxidation states of Cr complexes are essential in the evaluation of the oxidizing power of these species. This has many implications in understanding the mechanisms and selectivities of Cr(VI) oxidations of organic substrates. Furthermore, complexes of the poorly-characterized Cr(V) and Cr(IV) oxidation states are considered to be carcinogens and mutagens.[4,10] Reactions of Cr(VI) with glutathione and other cellular reducing agents afford long-lived Cr(V) and Cr(IV) intermediates.[11−15] Cr(V) complexes with

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2-hydroxy acid ligands, e.g., bis(2-ethyl-2-hydroxybutanoato(2−))oxochromate(V), are models for the complexes formed with lactate and citrate.[16] Such ligands are found in wide concentration ranges within cells and their complexes with Cr(V) are likely to form intracellularly. The ehba model complexes are also known to damage circular, supercoiled plasmid DNA.[4,17] Recent studies into the ligand exchange chemistry of Cr(V) complexes and the relative thermodynamic stabilities of different Cr(V) complexes suggest that such species may be significant intracellular species.[18] Cr(IV) intermediates generated by V(IV) reductions of Cr(V)[19] increase both cleavage of circular supercoiled DNA and mutations in bacteria.[8] Finally, Cr(V) peptide analogs also damage DNA and cause mutations in bacterial and mammalian cells.[20] Therefore, a knowledge of the redox potentials of $Cr^{V/IV}$ and $Cr^{IV/III}$ couples is important in understanding both the relative importance of these two reactive oxidation states in oxidative DNA cleavage and the structures and reactivities of these intermediates in the oxidation of organic substrates. As a consequence, the redox chemistries of these oxidation states with ehba have been reinvestigated here to gain new insight into the chemistry of the high oxidation states.

Experimental Section

Reagents. Sodium bis(2-ethyl-2-hydroxybutanoato(2−))oxochromate(V) hydrate, $Na[Cr^V(O)L_2]\cdot H_2O$, was prepared following the literature method,[21] and the dimer, $Na_2\{[Cr(O)_2(L)]_2\}0.5(LH)\cdot 3.5H_2O$ was prepared by a similar method, except using less ligand in the synthesis.[9] ***Caution:*** *Cr(VI) complexes are carcinogenic and Cr(V) complexes are mutagenic and potentially carcinogenic. Due care must be taken to avoid breathing dusts of the compounds and contact with the skin.* The protonated V(IV) complex, $[VIV(O)(LH)L]^-$, was also synthesized by the published method.[8] Potassium hexacyanoferrate(II) (ACS reagent) was used without further purification.

Physical Measurements. Cyclic voltammograms were recorded on a potentiostat/galvanostat (Model 273, PAR) or a BAS 100 Electrochemical Analyzer. These experiments were performed using a glassy carbon working electrode, saturated calomel or Ag/AgCl/KCl(sat) reference electrodes, and a Pt-wire as an auxiliary electrode. Full *iR* compensation was performed with the BAS instrument. Potassium chloride (0.1 M) was used as the supporting electrolyte for cyclic voltammetry experiments in aqueous solution. The $E_{1/2}$ values were determined by an arithmetic average, $E_{1/2} = (E_{pc} + E_{pa})/2$ where E_{pc} and E_{pa} are the reduction and oxidation peak potentials.

Potentiometric titrations were carried out on an Orion potentiometer that was calibrated with a standard cell, fitted with an aqueous KCl salt-bridge. Potentials at the equivalence points were determined from derivative plots. Potentiometric titrations were performed in the presence of $ehbaH_2$ (5×10^{-3} M) to reduce the loss of ligand from the Cr center. The pH was adjusted with HCl. Aliquots of Cr(V) solutions were added to either Sn(II) or $[Fe(CN)_6]^{4-}$ solutions of known concentrations and the potentials were recorded.

Spectrophotometric titrations on the V/ehba complexes were performed on a Hewlett-Packard 8452A Diode Array UV/vis spectrophotometer. The titrations were performed in 0.2 M $ehbaH_2$/ehbaH buffers at 25 °C.

Reduction of $[Cr(O)(ehba)_2]^-$ by $[Fe(CN)_6]^{4-}$ was carried on a stopped-flow instrument (Durram D110) using excess Fe(II) complex. The ionic strength was maintained at 0.10 M with KCl and the pH was adjusted by adding HCl. The reaction was monitored at 460 and 420 nm. An exponential growth in absorbance was observed at both wavelengths. Rate constants were obtained by non-linear least-squares fit of the absorbance−time data according to

$$A_t = (A_0 - A_\infty)e^{-kt} + A_\infty \tag{1}$$

where A_t, A_0, and A_∞ are the absorbances at time t, $t = 0$, and infinite time. The reproducibility of the rate constants is within 5%.

The pulse radiolysis facility at AINSE consists of a 1 MeV van de Graaff electron accelerator delivering single pulses (3.4 μs) of fast electrons through the thin wall (0.3 mm) of a "suprasil" cell with an optical path length of 1 cm. A remotely-operated peristaltic pump provides fresh solution for each pulse. Concentrations of light absorbing species were monitored by a beam of light from a 450-W high-pressure xenon lamp. This beam traversed the irradiated portion of the solution before entering a Bausch & Lomb high-intensity monochromator with a 250−700-nm grating. Changes in light transmission were measured with a 1P28 photomultiplier and then amplified and processed by a Compucard 250 (Gauge Applied Science Inc.) and an IBM-compatible 486 PC. The pulse trigger/amplifier unit incorporated variable delays, signal back-off, and sample-hold facilities to enable the initial light level to be measured with minimum exposure of the solution to light. Absorbance values and kinetic rate constants were calculated by a software program based on that developed by Thornton and Laurence.[22] The dose per pulse was monitored by using an aerated solution of KNCS (5 mM) as a dosimeter and taking the molar extinction coefficient of $(NCS)_2^{\bullet-}$ as 7600 M^{-1} cm^{-1} at 480 nm[23] and $G((NCS)_2^{\bullet-}) = 2.8$.

Radiolysis of water produces e_{aq}, $^{\bullet}OH$, and $H^{\bullet}$. The hydroxy radicals were scavenged with *tert*-butyl alcohol (1% v/v) and the major species present in solution was the aquated electron at the pH values studied (≥3.78). Solutions were also purged for 15 min with nitrogen to prevent interference from dissolved oxygen. NaehbaH/$ehbaH_2$ buffer solutions were made by dissolving equimolar amounts of NaOH (Merck, A.R. Grade) and 2-ethyl-2-hydroxybutanoic acid ($ehbaH_2$, Aldrich, A.R. Grade) in an appropriate volume of distilled water. Solution pH values were determined with an Activon Model 210 pH meter fitted with a BJ321 calomel electrode. $[Cr(O)L_2]^-$/NaehbaH/$ehbaH_2$ solutions were prepared by dissolving appropriate amounts of the complex in the above described buffer. The pH was adjusted, where necessary, using $HClO_4$.

Some EPR measurements were performed on an IBM 200D-SRC instrument. Detailed data acquisition and retrieval procedures are elaborated elsewhere.[12b] In addition, a Bruker ESP 300 spectrometer operating at ~9.6 GHz was also used for recording spectra and obtaining double integrals and second-derivative spectra. The instrument was calibrated with a Hewlett Packard 5352B frequency counter and a Bruker ESP300 gaussmeter. Second-order corrections were used to calculate A_{iso} values. Dynamic magnetic susceptibility measurements were performed following a newly-developed NMR method.[24]

Results

Redox Chemistry. The cyclic voltammograms of $[Cr^V(O)L_2]^-$ exhibit a quasireversible one-electron redox couple in the pH range 3.5 to 5. The separation between the oxidation and reduction waves was found to be 65 mV at a scan rate of 20 mV s^{-1} at 25 °C. The $E_{1/2}$ value, 0.195 V vs SCE (Figure 1a), is independent of pH in the range 4−5 and of the nature of the electrolytes (Cl^- or ClO_4^-). These results indicate that the $E_{1/2}$

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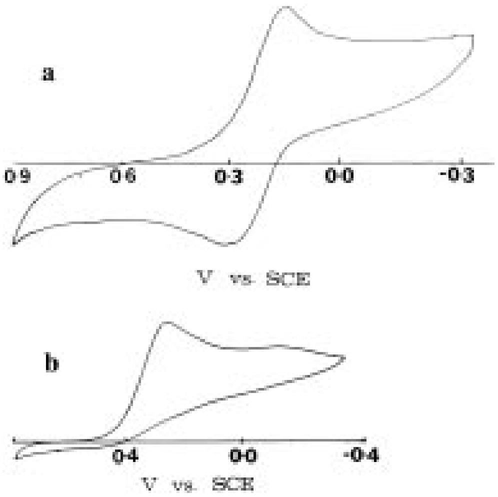

Figure 1. Cyclic voltammograms of sodium bis(2-ethyl-2-hydroxybutanoato(2−))oxochromate(V) at (a) pH 4.0 and (b) pH 2.0 in 0.1 M KCl.

value, 0.44 V vs NHE, relates to the electrode reaction

$$[Cr^{V}(O)L_2]^- + e^- \rightleftharpoons [Cr^{IV}(O)L_2]^{2-} \quad (2)$$

An anodic shift of 60 mV was observed on lowering the pH from 3.5 to 2.5. This is consistent with the electrode reaction

$$[Cr^{V}(O)L_2]^- + H_3O^+ + e^- \rightleftharpoons [Cr^{IV}(O)(LH)L]^- + H_2O \quad (3)$$

for which a formal potential, 0.64 V vs NHE, is calculated. Voltammograms recorded below pH 2.1 exhibit only one cathodic wave due to an irreversible two-electron reduction:[2]

$$[Cr^{V}(O)L_2]^- + 2H_3O^+ + 2e^- \rightleftharpoons [Cr^{III}(OH_2)_2L_2]^- + H_2O \quad (4)$$

Two equivalents of the hexacyanoferrate(II) complex reduces the Cr(V) complex to Cr(III), without any measurable concentrations of Cr(IV) intermediates, as judged by the monophasic appearance of the absorbance−time traces recorded at several wavelengths. The second-order rate constant for this reduction reaction was determined to be $3.7 \pm 0.1 \times 10^2$ M^{-1} s^{-1} at pH 2.8 and 25 °C. Since no Cr(IV) intermediates were detected, the reduction of Cr(V) to Cr(IV) should be taken as the rate-determining step, and, subsequently, the reduction of Cr(IV) to Cr(III) must be fast.

$$[Cr^{V}(O)L_2]^- + [Fe(CN)_6]^{4-} \xrightarrow{RDS} [Cr^{IV}(O)(L/LH)L]^{2-/-} + [Fe(CN)_6]^{3-} \quad (5)$$

$$[Cr^{IV}(O)(L/LH)L]^{2-/-} + [Fe(CN)_6]^{4-} \xrightarrow{fast/H^+} [Cr^{III}(OH_2)_2L_2]^- + [Fe(CN)_6]^{3-} \quad (6)$$

Since the reduction by the cyano complex is reasonably fast, we have exploited this reaction in a potentiometric titration. The equivalence point of the potentiometric titration for the reaction

$$[Cr^{V}(O)L_2]^- + nH_3O^+ + 2[Fe(CN)_6]^{4-} \rightarrow [Cr^{III}(OH_2)_2(H_xL)_2]^{x-1} + 2[Fe(CN)_6]^{3-} + (n-1)H_2O \quad (7)$$

is related to

$$3E_{eq} = 2E^\circ_{Cr(V/III)} + E'_{Fe(III/II)} + 0.059 \log[H^+]^n \quad (8)$$

Table 1. Potential[a] Data Related to $Cr^{V}-[Fe^{II}(CN)_6]^{4-}$ Titrations

pH	E_{eq}, V	$E'_{Fe(III/II)}$, V[b]	$E^\circ_{Cr(V/III)}$, V
1.0	0.47	0.32	0.60
2.0	0.39	0.23	0.59
2.9	0.36	0.18	0.62
3.2	0.32	0.16	0.59

[a] Potentials are with respect to SCE. [b] $I = 0.1$ M KCl/HCl.

Table 2. Formal Potentials for Various Chromium Redox Couples

electrode reaction	potential in V *vs* NHE
$[Cr^{V}(O)L_2]- + e^- \rightleftharpoons [Cr^{IV}(O)L_2]^{2-}$	0.44
$[Cr^{V}(O)L_2]^- + H^+ + e^- \rightleftharpoons [Cr^{IV}(O)(LH)L]$	0.65
$[Cr^{V}(O)L_2]^- + 2H^+ + e^- \rightleftharpoons [Cr^{IV}(O)(LH)_2]$	0.85
$[Cr^{V}(O)L_2]^- + 2H^+ + 2e^- \rightleftharpoons [Cr^{III}(OH_2)_2L_2]^-$	0.84
$[Cr^{IV}(O)L_2]^{2-} + 2H^+ + e^- \rightleftharpoons [Cr^{III}(OH_2)_2L_2]^-$	1.24
$[Cr^{IV}(O)(LH)L]^- + H^+ + e^- \rightleftharpoons [Cr^{III}(OH_2)_2L_2]^-$	1.03
$[Cr^{IV}(O)(LH)_2] + H_2O + e^- \rightleftharpoons [Cr^{III}(OH_2)_2L_2]^-$	0.83

where $E'_{Fe(III/II)}$ is the reduction potential of the cyano-Fe(III)/Fe(II) couple under the experimental conditions. Since the values of $E'_{Fe(III/II)}$ are known to vary with pH,[25] these values were determined under our experimental conditions and directly applied to eq 8. A plot of $3E_{eq} - E'_{Fe(III/II)}$ *vs* pH afforded a slope of −0.12, indicating that the value of n in eq 7 is 2. Table 1 summarizes E_{eq}, $E'_{Fe(III/II)}$, and $E^\circ_{Cr(V/III)}$ values. As can be seen, the $[Fe(CN)_6]^{3-/4-}$ potentials vary considerably over the pH range examined. The reductions are quasireversible with $\Delta E_p = 80-110$ mV at pH 1.0 and scan rates of 20−100 mV s^{-1}. The value of ΔE_p was highest (250 mV) at pH 3.2, with a scan rate of 100 mV s^{-1} (Figure 2).

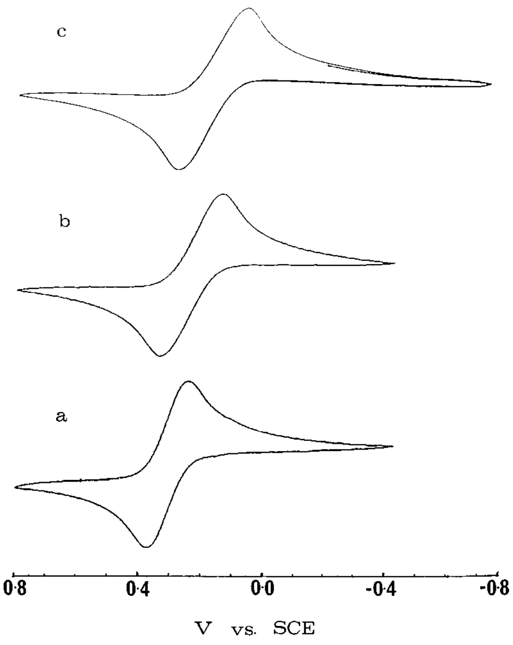

Figure 2. Cyclic voltammograms of $K_4[Fe(CN)_6]$ in 0.1 M HCl/KCl at pH (a) 1.0, (b) 2.0, and (c) 2.9.

The $E^\circ_{Cr(V/III)}$ value, 0.84 V *vs* NHE, listed in Table 2 corresponds to the electrode half-reaction:

$$[Cr^{V}(O)L_2]^- + 2H_3O^+ + 2e^- \rightleftharpoons [Cr^{III}(OH_2)_2L_2]^- + H_2O \quad (9)$$

By using eqs 2 and 9, and eqs 3 and 9, the reduction potentials for $[Cr^{IV}(O)L_2]^{2-}/[Cr^{III}L_2(OH_2)_2]^-$ and $[Cr^{IV}(O)(LH)(L)]^-/$

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$[Cr^{III}L_2(H_2O)_2]^-$ redox couples were calculated as 1.24 and 1.03 V, respectively, *vs* NHE (Table 2).

In non-aqueous solvents, such as ethanol, methanol, and 2-propanol, the redox behavior is similar to that observed in water. In the alcohol solvents, an equilibrium between mono- and bis(ehba) complexes has been established by EPR spectroscopy.[5]

Pulse Radiolysis. When buffered solutions (pH = 3.78, 50 mM LH_2/LH) of $[Cr^V(O)L_2]^-$ are reduced with $e^-(aq)$, a transient Cr(IV) species is observed, which decays to a long-lived ($t_{1/2} > 1$ s) Cr(IV) species with an intense band centered at 515 ± 2 nm ($\epsilon_{max} = 1.5 \times 10^4$ M^{-1} cm^{-1}). The rate constant for transformation into the new complex was 340 s^{-1} under the reaction conditions. The buffers alone showed no changes in absorption spectra in this region when they were irradiated. The nature of the species generated changed as a function of both the concentration of the ligand and the pH in a complex fashion. As the concentration of the buffer was reduced, the value of the molar extinction of the Cr(IV) species was reduced and new species were observed. In 5 mM $ehbaH_2$/ehbaH buffer, two peaks were observed at ~470 and ~570 nm, with ϵ_{max} values of ~910 and 1000 M^{-1} cm^{-1}, respectively. The apparent rate constant for the rearrangement is also reduced by an order of magnitude to 31 s^{-1}. An additional low-energy peak at ~600 nm is observed at higher pH values (6.93).

Solution Chemistry of Cr(V) Complexes. Dissolution of either $[Cr(O)L_2]^-$ or the dimer in water produced solutions with identical EPR spectra ($g_{iso} = 1.9784$, $A_{iso} = 18.5$ G) in which the outer ^{53}Cr hyperfine peaks were resolved into two distinct resonances due to the presence of two geometric isomers.[5] The ratio of the ^{53}Cr hyperfine peaks does not change with the concentration of the Cr (0.1−5 mM), the pH (0−5), or the added ligand concentration (0−100 mM). However, the UV/vis spectra of the monomer and dimer differ notably when dissolved in water and their spectra are consistent with the changes that are observed in the ligand dependence of the spectrum of $[Cr(O)L_2]^-$.[19]

Solution Chemistry of V(IV) Complexes. The crystallographically-characterized $[V(O)(ehba)(ehbaH)]^-$ [8] can be deprotonated to form $[V(O)(ehba)_2]^{2-}$ and protonated to form $[V(O)(ehbaH)_2]^0$ as shown by spectrophotometric titrations at the isosbestic points for the successive deprotonations. One isosbestic point was observed at 360 nm (pH 2.7−3.5) corresponding to the first deprotonation and two others at 400 and 640 nm were observed in the pH range 4−8.1 corresponding to the second deprotonation. The pK_{a1} and pK_{a2} values obtained from this titration are 3.2 and 4.3, respectively. When excess ehbaH/$ehbaH_2$ buffer is not added to solution, the complex is oxidized in air to form $\{[V(O)_2(ehba)]_2\}^{2-}$.[8] The same complex is formed even in the presence of ehbaH/ehbaH2 buffer, but its rate of formation decreases with increasing concentration of the ligand buffer and presumably arises from oxidation of mono-chelated ehba monomers and/or dimers.

Magnetic Measurements of the Reduction of Cr(VI) by As(III). The magnetic moment of the Cr(IV) species produced by reduction of Cr(VI) by As(III) was remeasured under the conditions reported previously.[1] The magnetic susceptibility measurements[24] yielded an uncorrected magnetic moment of 3.3 ± 0.1 μ_B at 295 K, immediately after the reactants were mixed. The susceptibility slowly increases and nearly approaches the value for a Cr(III) species. The corrected susceptibility is expected to be higher than 3.3 μ_B due to the diamagnetic correction, however, an exact molecular formula of the complex is required to make such a correction. In any event, the initial magnetic moment is significantly higher than that reported for a Cr(IV) complex (2.9 μ_B).[1]

Discussion

The formal potentials of the $Cr^{IV/III}$ couples are more positive than the corresponding $Cr^{V/IV}$ couples showing that Cr(IV) is a superior oxidizing agent than Cr(V). Since reduction of Cr(IV) to Cr(III) is more favored than the reduction of Cr(V) to Cr(IV), Cr(IV) species should not be observed at the electrode surface, unless there is a large kinetic barrier for its reduction at this potential. Since a quasireversible one-electron redox process corresponding to $Cr^V + e^- \rightleftharpoons Cr^{IV}$ is observed,[2] the lack of conversion of Cr(IV) to Cr(III) is due to an extremely sluggish electrokinetic process for the reduction of the Cr(IV) intermediate(s). Marked structural dissimilarities between Cr(IV) and Cr(III) complexes are most likely to contribute to this process. The chromium(V) complex has a distorted trigonal-bipyramidal geometry[6,26] and, as discussed below, the chromium(IV) complexes are likely to remain as five-coordinate oxo complexes, like their V(IV) analogs.[8] Therefore, the conversion of a five-coordinate oxochromate(IV) complex to a six-coordinate diaqua chromium(III) product in the pH range 3.5−5 requires major structural changes and, hence, a high activation barrier. Since two protonations of the oxo group are required on reduction of the oxochromium(IV) species at the electrode surface to form the diaqua complex, this process will be facilitated by a reduction in the pH. As expected, when pH is lowered to 2.0, protonation is rapid and only one two-electron reduction wave is observed that corresponds to the irreversible reduction of Cr(V) to Cr(III).

The measured potential for the $[Cr^{V/IV}(O)L_2]^{-/2-}$ couple is 0.85 V lower than that reported by Ghosh and Gould.[1] Similarly, Cr(V/III) and Cr(IV/III) redox potentials are overestimated by 0.5 and 0.3 V, respectively.[1] However, in order to compare Cr(V/III) and Cr(IV/III) reduction potentials, the nature of the various Cr(V)/(III) species must be defined. The potentiometric data over the pH range 1−3.2 show that two protons are associated with the reduction of the $[Cr^V(O)L_2]^-$ complex. The pK_a values of aqua ligands coordinated to Cr(III) are such that deprotonation of the aqua ligands will not be an influence on the redox chemistry in the pH range that has been studied, hence, the reduction of $[Cr^V(O)L_2]^-$ is most likely to result in the formation of $[Cr^{III}(OH_2)_2L_2]^-$ as indicated in eqs 5 and 6. It is difficult to compare our Cr(V/III) reduction potential with that reported by Ghosh and Gould[1] for they defined their Cr(III) species as a mixture of $[Cr(OH_2)_2(HL)_2]^+$ and $[Cr(HL)_3(OH_2)]$, in which the cationic bis-chelate dominates. The nature of the Cr(III) products was addressed on the basis of their interactions with cationic exchange resins. The majority of Cr(III) products generated by Ti(III),[27] Fe(II),[28] and V(IV)[19] reductions of $[Cr^V(O)L_2]^-$ in the presence of added $ehbaH_2$/ehbaH buffer did not adsorb on cation exchange resins. In any event, the cationic bis(ligated) complex would require four protons during the reduction:

$$[Cr^V(O)L_2]^- + 4H_3O^+ + 2e^- \rightleftharpoons [Cr^{III}(OH_2)_2(LH)_2]^+ + 3H_2O \quad (10)$$

For such a reaction, a slope of −0.24 is expected in the ($3E_{eq} - E'_{Fe(III/II)}$) *vs* pH plot of the potentiometric data. Theoretically, a reduction potential of 1.04 V *vs* NHE can be calculated for

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[26] Krumpolc, M.; De Boer, B.; Roček, J. *J. Am. Chem. Soc.* **1978**, *100*, 145−153.

[27] Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 2645−2647.

[28] Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 2832−2835.

reaction 10 (although our data do not require that treatment) by extrapolating our potentiometric data to pH 3. This extrapolated value differs from that reported by Ghosh and Gould[1] by 0.3 V. Likewise, taking into account the difference in formulations of Cr(IV), potential discrepancies between the present study and that by Ghosh and Gould[1] are estimated to be in the range of 0.1 to 0.3 V, depending on the nature of the complex. The further discrepancies in the redox potentials, after the problem of use of the right equation is taken into account, are a little more difficult to pinpoint. Crucial to the previous analysis is that the molar absorptivity of a Cr(IV) intermediate (thought to be $[Cr^{IV}(OH)_2L_2]^{2-}$) can be calculated on the assumption that it is generated stoichiometrically in situ by the reduction of Cr(VI) by As(III).[1] These authors presented two main arguments to substantiate the nature and concentrations of the Cr(IV) species.[29] These were that the magnetic moment of the intermediate is 2.9 μ_B (measured by the Evans method),[30] which corresponds to two unpaired electrons, and that the intermediate is EPR silent. Such a result is not consistent with our magnetic susceptibility measurements[24] that yielded an uncorrected magnetic moment of 3.3 ± 0.1 μ_B at 295 K, immediately after the reactants were mixed. However, after diamagnetic corrections have been made, which cannot be done accurately without a knowledge of the structures of all of the paramagnetic species in solution, the magnetic moment is significantly higher than that expected for a solution containing only Cr(IV). A further complication is that the susceptibility slowly increases and nearly approaches the value for a Cr(III) species. Reduction of Cr(VI) to a mixture of EPR-silent dimeric Cr(V),[4,31] Cr(IV), and Cr(III) products is not ruled out by the previous data and the magnetic data reported here may be consistent with such complications.[1] Such parallel pathways that yield Cr(V) and Cr(III) products have been documented by Haight and co-workers.[32] Therefore, our magnetic susceptibility data do not support a single Cr(IV) species in solution. If this is the case, it would lead to complications in the previous analysis of the potentiometric data when the Cr(IV) species was partially reduced with $[Fe^{II}(Me_2bpy)_3]^{2+}$, $[Fe^{II}(Me_2phen)_3]^{2+}$, or $[Fe^{II}(Me_4phen)_3]^{2+}$ (Me_2bpy = 4,4′-dimethyl-2,2′-bipyridine, Me_2phen = 5,6-dimethyl-1,10-phenanthroline, Me_4phen = 3,4,7,8-tetramethyl-1,10-phenanthroline). It should be noted that $[Fe^{II}(Me_2phen)_3]^{2+}$ employed in these redox reactions was generated in situ, by adding hexaaquairon(II) to an excess of the ligand.[1] It has been shown that phen ligands react with the Cr(V) (and presumably more rapidly with Cr(IV) species) to reduce them to Cr(III),[33] probably via oxo transfer reactions.[4] This could have caused complications with the redox data[1] obtained with the Me_2phen complex and would explain the discrepancy for this complex in some of the calculated parameters compared to the other Fe(II) complexes.[1] These potential complications highlight the difficulty of obtaining reliable reduction potentials for Cr redox chemistry using potentiometric data obtained from highly reactive Cr(IV) species generated *in situ*. This difficulty is compounded by the complexity of ligand exchange chemistry that occurs in all oxidation states and which is discussed in the following sections. Thus, it is likely that an approach presented here, *i.e.*, where the Cr(V/IV) redox potential, measured directly by cyclic voltammetry, is combined with potentiometric data obtained from isolated Cr(V) species, will yield more reliable reduction potential data.

The potential data[1] are also inconsistent with the chemistry of an intermediate that undergoes a disproportionation reaction to form Cr(V) and Cr(III) products. In fact, allowing 5% error in their potentials,[1] identical formal potentials for all three redox couples, $Cr^{V/IV}$, $Cr^{V/III}$, and $Cr^{IV/III}$, have emerged. Finally, these potential data along with rate constants for a variety of redox reactions were used to calculate the self-exchange rates for $Cr^{V/IV}$ and $Cr^{IV/III}$ redox couples.[1] In the light of the new potential data reported here, these exchange rates should be revised.

The chemistry of Cr(IV) was investigated further by the use of pulse radiolysis, but the results need to be considered with some caution because of small concentrations of $H^{\bullet}$ produced at the low pH conditions, which could cause additional products to those formed from the reduction chemistry of e^{-}(aq). Like the $HO^{\bullet}$ radicals, the $H^{\bullet}$ radicals will be scavenged by *t*-BuOH, albeit much less efficiently, to produce the *t*-$BuOH^{\bullet}$ radical.[34] However, neither $H^{\bullet}$ nor $BuOH^{\bullet}$ is expected to cause serious interferences, since their reactions (and particularly that of the latter) are much slower that those of the aquated electron.[34] A further complication is that the presence of small amounts of H_2O_2, which are generated as a secondary product from the radiolysis,[34] could react with Cr(V) and/or Cr(IV) to produce highly colored transients that could increase the absorbance in the region where Cr(IV) species absorb. The reaction of H_2O_2 with $[Cr(O)L_2]^-$ under the conditions of the radiolysis experiments has been studied[35,36] and is too slow to be a significant interference on the time scale of the pulse radiolysis experiments. However, the reaction of Cr(IV) may be considerably faster and it is possible that this could result in some complications in these experiments.

The extinction coefficient of the Cr(IV) species was obtained from the calculated dose in the pulse radiolysis experiments, since no reactions were observed with the buffer alone. These values suggest that either the Cr(IV) concentration has been overestimated in the work by Ghosh and Gould[1] or there are some side reactions in the pulse radiolysis experiments that may result in highly-absorbing transients in the same region. While the pulse radiolysis experiments are consistent with the magnetic measurements that suggest that the Cr(IV) concentration has been overestimated using the As(III) reduction of Cr(VI), the pulse radiolysis experiments are not definitive.

Nature of the Ligand-Dependent and pH-Dependent Cr(V) and Cr(IV) Equilibria. The likelihood that the Cr(V) equilibria involving ehba do not involve tris(ehba) complexes has been discussed in some detail previously.[4] The EPR and UV/vis evidence presented here further substantiates that mono- and bis(ehba) complexes are involved in such equilibria. As pointed out previously,[4,5] there is no evidence for Cr(V) complexes containing three ehba ligands and such complexes are not expected to form for steric reasons, since all of the ligands of the five-coordinate complex are within van der Waals contact and there is no room for a sixth ligand.[6] Initially, the equilibrium

$$[Cr^{V}(O)L_2]^{-} + LH_2 \rightleftharpoons [Cr^{V}(O)L_2(LH)]^{2-} + H^{+} \quad (11)$$

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(29) (a) Ghosh, M. C.; Gould, E. S. *Inorg. Chem.* **1990**, *29*, 4258−4262; **1991**, *30*, 491−494. (b) Ghosh, M. C.; Gelerinter, E.; Gould, E. S. *Inorg. Chem.* **1992**, *31*, 702−705.

(30) Evans, D. F. *J. Chem. Soc.* **1959**, 2003−2005. Note that the Evans method was designed originally for CW instruments utilizing an electromagnet. The magnitude of frequency change of an inert marker due to a paramagnetic substance produced by the old CW instruments is different from that generated by superconducting solenoids.

(31) Nishino, H.; Kochi, J. K. *Inorg. Chim. Acta* **1990**, *174*, 93−102.

(32) Haight, G. P.; Jursich, G. M.; Kelso, T. M.; Merrill, P. J. *Inorg. Chem.* **1985**, *24*, 2740−2746.

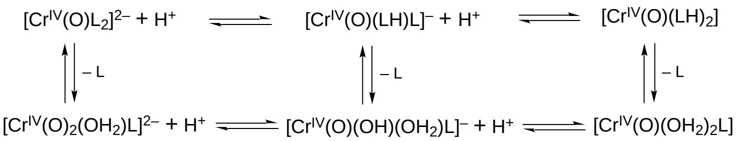
(33) Dillon, C. T. Ph.D. Thesis, University of Sydney, 1995.

(34) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513−886. Wardman, P. *J. Phys. Chem. Ref. Data* **1989**, *18*, 1637-1657.

(35) Ghosh, S. K.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 3357−3359.

(36) Judd, R. J. Ph.D. Thesis, University of Sydney, 1992.

Scheme 1



relating to the coordination of the third ligand onto the "open" basal site of a presumed square pyramid of the parent compound was described by one of us,[19,37] solely based on the change in molar absorptivity at 510 nm as a function of [L]. The alternative explanation of an equilibrium between mono- and bis-ehba complexes was also considered to explain the dependence on [L],[19] but was not favoured in this or subsequent publications. In the light of the structural data that show that the complex exists as a sterically-hindered, distorted trigonal bipyramid,[6] and the recent EPR results that do not support a formation of an octahedral complex,[5] the spectral changes at 510 nm are related to eq 12 or a similar equilibrium in which the monochelate complex is six-coordinate:

$$[\mathrm{Cr^V(O)L_2}]^- + \mathrm{H_3O^+} + \mathrm{H_2O} \rightleftharpoons [\mathrm{Cr^V(O)(OH)(OH_2)L}] + \mathrm{LH_2} \quad (12)$$

The similarity in the electrochemical behavior of $[\mathrm{Cr(O)L_2}]^-$ in water and in monodentate alcohols, such as ethanol and methanol, where two irreversible reduction peaks are observed, is also consistent with the proposed equilibria between complexes with one and two ehba ligands. Here, it has been established by the dependence of the Cr(V) EPR signals on concentration that an equilibrium exists of the type shown in (13).[5]

$$[\mathrm{Cr^V(O)L_2}]^- + 3\mathrm{ROH} \rightleftharpoons [\mathrm{Cr^V(O)(OR)_3L}]^{2-} + \mathrm{LH_2} + \mathrm{H^+} \quad (13)$$

Similar arguments pertain to the Cr(IV) solution chemistry where six-coordinate species with the bulky ehba ligands are unlikely. Strong evidence in support of this notion is provided by the X-ray structure of $[\mathrm{V(O)(ehba)(ehbaH)}]^-$,[8] which is also very sterically crowded despite having longer metal—ligand bond lengths. This structure also leads to the conclusion that the pH dependence of the Cr(IV) equilibria has an origin similar to that of the analogous V(IV) complexes, i.e., the protonation/deprotonation equilibria involve the alcohol groups of the ehba ligands rather than the oxo groups and/or the addition of an $\mathrm{OH^-}$ group to form a six-coordinate complex, as presumed in the Ghosh and Gould publications.[1] In support of this notion, the pH region where the Cr(V/IV) redox potentials are sensitive to $[\mathrm{H^+}]$ is the same as that where the two protonations of $[\mathrm{V(O)(ehba)_2}]^{2-}$ occur to produce $[\mathrm{V(O)(ehbaH)(ehba)}]^-$ and $[\mathrm{V(O)(ehbaH)_2}]$, respectively. All of this information points the likelihood that the Cr(IV) equilibria are best represented by those outlined in Scheme 1 (or something similar), rather than those proposed previously.[1,29] This also explains the large electrokinetic barrier for the reduction of Cr(IV) to Cr(III), since the rearrangement that occurs for this step is far greater than that required for the Cr(V/IV) couples. Hence, the reason for the observation of a chemically-reversible Cr(V/IV) couple in the cyclic voltammetry, even though Cr(IV) is a stronger oxidant than Cr(V), is due to the reorganizational energy barrier for the subsequent reduction to Cr(III).

Other evidence to support the notion that the Cr(IV) complexes exist in an equilibrium between mono- and bis-ehba complexes arises from the fact that the V(IV) complexes are oxidized by air to form the dimer $\{[\mathrm{V^V(O)_2(ehba)}]_2\}^{2-}$. Since the ease of oxidation increases with decreasing ehbaH concentration, this is presumed to arise from oxidation of mono-ehba V(IV) species. Further, since the spectra of the V(IV) complexes are independent of the ehbaH/ehbaH$_2$ buffer concentration at values above 0.1 M, this makes the presence of complexes with three ehba ligands extremely unlikely. This would be even less likely for Cr(IV) complexes, since complexes with this d^2 electronic configuration are expected to have shorter bond lengths and hence greater steric impediment to form six-coordinate complexes than their d^1 V(IV) analogs.

Conclusions

The chemistries of Cr(V) and Cr(IV) differ significantly from those reported previously,[1] since the re-evaluation of the chemistry shows clearly that Cr(IV) is a much stronger oxidant than Cr(V). This has marked implications in understanding chromium redox chemistry in relation to the mechanisms of Cr(VI)-induced cancers[8] and Cr(VI) oxidations of organic substrates. In addition, accurate redox data are needed in the evaluation of rate constants for electron self-exchange using the Marcus relationship.

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