although net 2e changes, proceed in 1e steps, with the overall rate determined by the initial transfer. The resulting radical may then react quickly with a second Co^I center or may undergo bimolecular disproportionation, yielding equivalent quantities of the dihydro compound and the original aromatic. Substantial chain termination by radical dimerization is not consistent with the observed stoichiometry.

Although additional systems should be examined, it thus appears that B_{12s} reductions of pyridine amides differ from those of α,β-unsaturated dicarboxylic acids and their esters where the superior reactivity of alkyne-derived oxidants and the overall stereospecificity of their conversion to alkenes support the intermediacy of a carbanion-like adduct, formed in a 2e process without intervention of an odd-electron species.[4b,c]

Acknowledgment. We thank Dr. Rathindra Bose for help in computational procedures and Ms. Arla McPherson for technical assistance.

Supplementary Material Available: Tables VI–VIII, giving kinetic data for the reactions of 2-pyridinecarboxamide, *N*-methylnicotinamide, and 1-methyl-3-carbamoylpyridinium perchlorate with B_{12s} (3 pages). Ordering information is given on any current masthead page.

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Electron Transfer. 106. Stabilized Aqueous Chromium(IV), As Prepared from the Chromium(VI)–Arsenic(III) Reaction[1]

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Received May 25, 1990

Reduction of $HCrO_4^-$ with H_3AsO_3 in solutions buffered by 2-ethyl-2-hydroxybutanoic acid (LigH) and its salt (Lig^-) yields stabilized pink solutions of Cr(IV). This atypical state is oxidized to a bis chelate of Cr(V) with excess Cr(VI), is reduced very slowly to chelated Cr(III) with excess Lig^-, but does not react with As(III). Variation of absorbance with [Lig^-] points to partition of Cr(IV) (eq 4) into two forms, II ($\epsilon_{510} = 53 \pm 22$) and II–Lig ($\epsilon_{510} = 2460 \pm 70$ M^{-1} cm^{-1}), related by a ligation constant of 90 ± 8 M^{-1} (25 °C; $\mu = 0.50$ M). The Cr(VI)–As(III) system features a $Cr^{VI}As^{III}$ complex ($K = 340 \pm 60$ M^{-1}). Reduction to Cr(IV) (rate law 6) proceeds through two paths, the first involving extra units of H^+ and Lig^- and the second requiring 2 H^+ and 2 Lig^-. The reaction $Cr^{IV} + Cr^{VI} \rightarrow 2Cr^V$ in this buffer appears to entail a $Cr^{IV}Cr^{VI}$ complex ($K = 50 \pm 9$ M^{-1}) and proceeds through a combination of an acid-independent route and a [H^+]-proportional route. This comproportionation corresponds to that observed when Cr(VI) is reduced with $Mo_2O_4^{2+}$ in the same medium. Chromium(IV) solutions prepared by reduction with excess As(III) are more stable than those prepared by using $Mo_2O_4^{2+}$, U(IV), or Sn(II), for the latter three reagents can undergo less favored $1e^-$ changes in the presence of the strongly oxidizing Cr(IV) center. Analogous $1e^-$ oxidation of As(III) cannot compete with the reduction of Cr(IV) by the ligand anion used.

Although chromium(IV) is generally considered to be an atypical oxidation state, awareness is increasing as to its role in the redox chemistry of that element. Kinetic studies have implicated this state as an intermediate in the reactions of chromium(VI) with both organic[2] and inorganic[3] reductants, and preparative oxidations using Cr(IV), generated in situ, have been described.[4] Of the Cr(IV) compounds that have been isolated and characterized,[5] nearly all undergo decomposition in aqueous media. A small number of diperoxo ammine complexes,[6] such as $Cr^{IV}(NH_3)_3(O_2)_2$, decompose only slowly in water, but the behavior of the metal center in such complexes is significantly modified by the presence of two peroxo ligands and by the expanded coordination sphere about seven-covalent chromium.

Chromium(IV) derivatives of 2-hydroxy carboxylates have been detected as transients when Cr(V) chelates derived from carboxylato ligands of this type are reduced with the $1e^-$ reagents U(IV), Fe(III), and VO^{2+}[7] or with species that can undergo both one- or two-electron reductions (such as bisulfite, nitrite, and ascorbate).[8] However, examination of such systems is complicated by the further rapid reductions of Cr(IV) by $1e^-$ transactions.

Table I. Stoichiometry of the Cr(VI)–As(III) Reactions[a]

10^4-[Cr^{VI}], M	10^4-[As^{III}], M	10^4-Δ[Cr^{VI}], M	10^4-Δ[As^{III}], M	Δ[Cr^{VI}]/Δ[As^{III}]
1.50	5.0		1.63	1.08
3.0	5.0		2.95	0.98
4.0	5.0		3.9	0.96
1.9[b]	7.5		2.05	0.93
3.8[b]	7.5		3.7	1.03
100	15.0	31		2.08
100	30	58		1.94
100	45	86		1.91
9.0[c]	4.0	2.7		0.67
9.0[c]	8.0	5.2		0.65
9.0[c]	12.0	7.7		0.64

[a] Cr^{VI} was added as $Na_2Cr_2O_7$; As^{III}, as H_3AsO_3. Solutions (pH 3.3) were buffered with equal concentrations (0.05 M) of the ligand hydroxy acid (I) and its sodium salt unless otherwise indicated. Reactions were monitored at 510 nm. [b] [HLig] = [Lig^-] = 5×10^{-3} M. [c] Reactions in 0.10 M $HClO_4$, carried out in the absence of ligating acid; these were monitored at 350 nm. Reaction time = 30 min.

We recently[9] reported the preparation of more stable Cr(IV) complexes in solution by treatment of Cr(VI) with the cationic reductant $[Mo^V_2O_4(H_2O)_6]^{2+}$ in aqueous media buffered by 2-ethyl-2-hydroxybutanoic acid [$(C_2H_5)_2C(OH)COOH$] (I) and its anion. The persistance of Cr(IV) in such systems results, in part, from the difficulty associated with the reactions of $(Mo^V)_2$ derivatives with $1e^-$ oxidants,[10] reactions that often appear to entail

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(1) Sponsorship of this work by the National Science Foundation (Grant 8619472) is gratefully acknowledged.

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(6) (a) Hoffman, K. A. *Ber. Dtsch. Chem. Ges.* **1906**, *39*, 3181. (b) House, D. A.; Hughes, R. G.; Garner, C. S. *Inorg.Chem.* **1967**, *6*, 1077. (c) Garner, C. S.; House, D. A. *Transition Met. Chem.* (*N.Y.*) **1970**, *6*, 59 (Table I).

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Table II. Absorbance Data for Solutions of Chromium(IV) in 2-Hydroxy-2-ethylbutanoate Buffers[a]

$[Lig^-]$, M[b]	pH	abs_{obsd}	abs_{calcd}[c]
0.0010	3.34	0.192	0.189
0.0035	3.31	0.44	0.47
0.0085	3.29	0.81	0.82
0.0125	3.36	0.97	0.94
0.020	3.27	1.27	1.17
0.025	3.35	1.30	1.26
0.050	3.28	1.52	1.52
0.100	3.27	1.65	1.66
0.20	3.26	1.69	1.75
0.30	3.30	1.73	1.78

[a] Data were taken in a 1.00-cm cell at 23 °C. Equimolar concentrations of 2-hydroxy-2-ethylbutanoate (lig^-) and its parent acid were maintained in each case. Absorbances (at 511 nm) were recorded after complete conversion of 7.5×10^{-4} M Cr^{VI} to Cr^{IV} by action of 0.005 M H_3AsO_3. Spectra were taken 30–200 s after mixing, i.e., before decay of Cr^{IV} is significant. [b] Values calculated from $[Lig^-]_{added}$, adjusted for initial formation of $CrI^V(Lig)_2$. [c] Values were calculated by using eq 5 in the text, taking ϵ_0 as 53 M^{-1} cm^{-1}, ϵ_1 as 2.46×10^3 M^{-1} cm^{-1}, and $K = 90$ M^{-1}.

unimolecular activation of the reductant[9,11] in a manner which is not yet clear.

We here describe the reaction of Cr(VI) with H_3AsO_3 (a reductant for which $1e^-$ paths are virtually excluded) in similarly buffered media. The Cr(IV) solutions so produced are sufficiently stable to allow examination of ligation equilibria by static methods.

Experimental Section

Materials. Sodium dichromate (MCB, reagent grade) and the "ligand acid", 2-ethyl-2-hydroxybutanoic acid (I) (Aldrich), were used as received. Solutions of As(III) were prepared by suspending reagent grade As_2O_3 (Fisher) in water and then adding 1.0 M NaOH dropwise, with continuous stirring, until solution was complete. Solutions of $NaClO_4$, used as a supporting electrolyte in kinetic experiments, were prepared by reaction of $NaHCO_3$ with $HClO_4$.

Stoichiometric Experiments. Stoichiometry of the Cr(VI)–As(III) reaction in buffers of the ligand acid (I) and its anion were determined with both excess As(III) and excess Cr(VI). Experiments with excess As(III) were carried out by adding measured deficiencies of Cr(VI) to the reductant, waiting 90 s for completion of the redox reaction, and then measuring the increase in absorbance at 510 nm. These changes were compared to those occurring quickly when As(III) was treated with a slight excess of oxidant. Determinations with excess Cr(VI) were made in an analogous manner, again at 510 nm (for conversion of Cr^{VI} to Cr^V), with waiting periods of 30–45 min. Results appear in Table I.

Examination of Reaction Products. For the reaction with excess As(III), mixtures (10 mL) contained 0.070 mmol of $Cr_2O_7^{2-}$, 0.80 mmol of As(III), and 1.0 mmol each of ligand acid and its sodium salt and exhibited pH 3.34. These were kept for 5 days at 25 °C (allowing complete destruction of Cr^{IV}) and were then subjected to cation-exchange chromatography (Dowex 50X8), 400 mesh, H^+ form).[12] The major green fraction, comprising 82% of the chromium recovered, was eluted with distilled water. It exhibited maxima at 587 ($\epsilon = 48$) and 427 nm ($\epsilon = 57$ M^{-1} cm^{-1}). A minor fraction, eluted with 0.5 M $NaClO_4$, showed peaks at 578 ($\epsilon = 38$) and 418 nm ($\epsilon = 52$ M^{-1} cm^{-1}).

For the reaction with excess Cr(VI), mixtures (2.0 mL) were 0.0025 M in As(III) and 0.0025 M in $Cr_2O_7^{2-}$ and were 0.025 M each in the ligand acid and its sodium salt (pH 3.32). After 1 h reaction time, solutions showed a spectrum corresponding to that of the bischelated Cr^VO complex of the ligand acid, $\epsilon_{max} = 180$ M^{-1} cm^{-1} (reported[7b]: 181 M^{-1} cm^{-1} in 0.025 M Lig^-).

To examine the spectrum of Cr(IV), 3.75×10^{-4} M $Cr_2O_7^{2-}$ was added to 5.0×10^{-3} M H_3AsO_3 in a measured quantity of ligand buffer. Spectra were taken immediately after mixing. Observed variation of absorbance at 511 nm with $[Lig^-]$ allowed estimation of the equilibrium constant pertaining to ligation of the Cr(IV) center (Table II).

Kinetic Measurements. Reactions were followed by measuring absorbance changes at 540 nm, employing either a Beckman Model 5260 or a Cary 14 recording spectrophotometer. Since $Cr_2O_7^{2-}$ reacts slowly with 2-ethyl-2-hydroxybutanoate buffers,[9] Cr(VI) was generally added to buffered solutions of As(III). In runs utilizing prebuffered Cr(VI), the redox reaction was initiated immediately after buffering. Ionic strength was maintained at 0.5 M by addition of $NaClO_4$ solution.

In experiments with excess Cr(VI), two readily separable exponential curves were obtained—an absorbance increase corresponding to the formation of Cr(IV) and a much slower decreases reflecting its reaction with Cr(VI). With excess As(III), the formation of Cr(IV)was again exponential, and this was followed by a very slow decay, which was poorly reproducible but appeared to be biphasic in nature with rates independent of $[As^{III}]$ taken. This component, which produced Cr(III) but not CrO_4^{2-}, was not studied in detail.

Rate constants for each of the exponential profiles were evaluated by using either semilogarithmic plots of absorbance differences vs reaction time or unweighted nonlinear least-squares fittings of data points to the relationship describing simple first-order transformations. Specific rates for replicate runs diverged by less than 6%.

Results and Discussion

The overall stoichiometry of the Cr(VI)–As(III) reaction in 2-ethyl-2-hydroxybutanoate buffers under the conditions employed is seen (Table I) to depend upon the reagent in excess. For short reaction times with excess As(III), nearly equimolar quantities of the two redox centers react, yielding the characteristic pink Cr(IV) species

$$Cr^{VI} + As^{III} \rightarrow Cr^{IV} + As^V \qquad (1)$$

whereas when Cr(VI) is in excess, formation of Cr(IV) is followed by its oxidation by Cr(VI), leading to 2:1 stoichiometry and the formation of a bis chelate of Cr^V (as characterized by its spectrum)[7b]

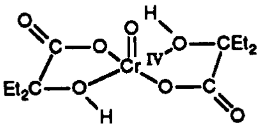
$$2Cr^{VI} + As^{III} \rightarrow 2Cr^V + As^V \qquad (2)$$

These reactions stand in contrast to the familar 2:3 stoichiometry observed in the absence of the stabilizing ligand

$$2Cr^{VI} + 3As^{III} \rightarrow 2Cr^{III} + 3As^V \qquad (3)$$

Carboxylate-stabilized Cr(IV) does not appear to react, under our conditions, with excess As(III). The observed slow decay (at a rate independent of $[As^{III}]$) very probably represents reduction by excess ligand[13] and yields, as a predominant product, a Cr(III) complex exhibiting spectral and elution properties corresponding to an uncharged tris(carboxylato) derivative. Its visible spectrum ($\epsilon_{587} = 48$; $\epsilon_{427} = 57$), is similar to, but not identical with, that of the product ($\epsilon_{584} = 49$; $\epsilon_{414} = 76$) from the much more rapid $(Mo^V)_2$–Cr^{VI} reaction,[9] which has been assigned a structure featuring two chelate rings and an additional monodentate carboxyl group. The shift in position of the stronger peak, as well as the observed difference in intensity, is consistent with the opening of one of the rings via aquation at the Cr^{III} center, a process that is known to occur with solutions of such carboxylato chelates on standing.[14]

Since the observed Cr(IV) complex is oxidized to a bis chelate of Cr(V) with excess Cr(VI) but reduced to a bis chelate of Cr(III) with $[Mo_2O_4(H_2O)_6]^{2+}$,[9] it too is almost certainly bischelated (structure II). It is further represented as an oxo species, featuring a $Cr^{IV}({=}O)$ linkage, in analogy with the known Cr(V) complexes



II

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(12) Separations were run on a 5-cm column, capacity 2 mequiv. For estimating 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.

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(14) (a) Butler, R. D.; Taube, H. *J. Am. Chem. Soc.* **1965**, *87*, 5597. (b) Spectral characteristics of a number of chelated and nonchelated (carboxylato)chromium(III) complexes have been summarized by Fanchiang.[7b]

Table III. Kinetic Data for the Reaction $Cr^{VI} + As^{III} \rightarrow Cr^{IV} + As^{V}$[a]

A. Reactions in Excess Cr(VI)[b]

$10^4[Cr^{VI}]$, M	[LigH],[d] M	pH	10^2k, s^{-1}[e]
3.0	0.050	3.33	7.5 (7.0)
5.0	0.050	3.32	12.4 (11.0)
7.5	0.050	3.34	16.3 (15.3)
10.0[f]	0.050	3.34	19.3 (19.1)
15.0[f]	0.050	3.34	26 (25)
20.0[f]	0.050	3.32	34 (31)
30.0[f]	0.050	3.32	40 (38)
50[f]	0.050	3.32	42 (47)
5.0	0.0125	3.35	1.7 (1.8)
5.0	0.0190	3.33	2.9 (2.9)
5.0	0.025	3.32	4.3 (4.2)
5.0	0.038	3.31	7.4 (7.4)
5.0	0.075	3.29	24 (20)
5.0	0.100	3.32	37 (32)
5.0	0.150	3.31	60 (63)
5.0	0.040[g]	3.13	7.5 (7.5)
5.0	0.060[g]	2.93	14.1 (14.7)
5.0	0.100[g]	2.73	28 (30)
5.0	0.140[g]	2.58	46 (53)

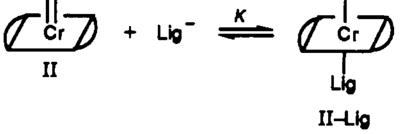
B. Reactions in Excess As(III)[c]

$10^4[As^{III}]$, M	[LigH],[d] M	pH	10^2k, s^{-1}[e]
3.0	0.050	3.34	7.4 (7.0)
5.0	0.050	3.32	12.2 (11.0)
7.5	0.050	3.32	15.8 (15.3)
10.0[h]	0.050	3.32	19.8 (19.1)
20.0[h]	0.050	3.32	33 (31)
30.0[h]	0.050	3.31	40 (38)
50[h]	0.050	3.32	46 (47)
5.0	0.0125	3.34	1.5 (1.8)
5.0	0.0190	3.33	2.6 (2.9)
5.0	0.025	3.31	4.1 (4.2)
5.0	0.038	3.30	8.1 (7.4)
5.0	0.075	3.31	23 (20)
5.0	0.100	3.32	33 (32)
5.0	0.040[g]	3.13	7.9 (7.5)
5.0	0.060[g]	2.91	14.1 (15.9)
5.0	0.100[g]	2.71	29 (33)
5.0	0.140[g]	2.59	50 (53)

[a] Reactions were run at 25.0 °C; $\mu = 0.50$ M ($NaClO_4$): progress was monitored at 540 nm. Cr(VI) was added as $Na_2Cr_2O_7$: As(III) was added as H_3AsO_3. Solutions were buffered with mixtures of 2-ethyl-2-hydroxybutanoic acid (LigH, I) and its sodium salt (Na^+Lig^-). [b] $[As(III)] = 5.0 \times 10^{-5}$ M unless otherwise indicated. [c] $[Cr(VI)] = 5.0 \times 10^{-5}$ M unless otherwise indicated. [d] $[LigH] = [Lig^-]$ unless otherwise indicated. [e] Unimolecular specific rates; parenthetical values are calculated from eq 6, taking K_P as 340 M^{-1}, a as 1.68×10^4 M^{-2} s^{-1}, and b as 6.1×10^8 M^{-4} s^{-1}. [f] $[As(III)] = 1.00 \times 10^{-4}$ M. [g] $[Lig^-] = 0.025$ M. [h] $[Cr(VI)] = 1.00 \times 10^{-4}$ M.

of this carboxylato ligand and a large number of familiar complexes of vanadium(IV).

For short reaction times, reduction with excess As(III) results in virtually quantitative conversion to Cr(IV) at ligand concentrations as low as 0.005 M. However the molar absorbance associated with the Cr^{IV} peak at 510 nm (but not its position) is seen to be strongly dependent on $[Lig^-]$. Absorbance data (Table II), taken 30–200 s after mixing, are treated in terms of a mobile equilibrium (4) between two Cr(IV) complexes, leading to eq 5,



II

II–Lig

(4)

$$\text{abs} = [Cr^4]_t \frac{\epsilon_0 + \epsilon_1 K[Lig^-]}{1 + K[Lig^-]} \quad (5)$$

where $[Cr^4]_t$ denotes the total Cr(IV) concentration, ϵ_0 and ϵ_1 are the extinction coefficients of the bis chelate (II) and the extra-

Table IV. Kinetic Data for the Reaction $Cr^{IV} + Cr^{VI} \rightarrow 2Cr^{V}$

$10^3[Cr^{VI}]$, M	[LigH],[b]	pH	10^3k, s^{-1}[c]
1.50	0.050	3.33	4.2 (3.3)
2.5	0.050	3.32	5.7 (5.2)
4.5	0.050	3.32	8.3 (8.6)
9.5	0.050	3.30	13.3 (15.0)
19.5	0.050	3.31	21 (23)
18.5[d]	0.050	3.32	20 (22)
19.9[e]	0.050	3.29	22 (23)
40	0.050	3.33	30 (31)
80	0.050	3.35	46 (37)
9.5	0.0125	3.37	12.8 (15.0)
9.5	0.100	3.32	12.9 (15.0)
4.5	0.040[f]	3.12	8.6 (9.0)
4.5	0.060[f]	2.95	9.2 (9.5)
4.5	0.100[f]	2.74	10.3 (10.5)
4.5	0.140[f]	2.58	11.7 (11.7)
4.5	0.180[f]	2.46	12.9 (13.0)
4.5	0.092[g]	2.26	16.5 (15.9)

[a] Reactions were run at 25 °C; $\mu = 0.5$ M ($NaClO_4$); progress was monitored at 540 nm. Cr(VI) was added as $Na_2Cr_2O_7$; Cr(IV) was generated by addition of H_3AsO_3 (5.0×10^{-4} M unless otherwise stated). Tabulated values of $[Cr^{VI}] = [Cr^{VI}]_{added} - [As^{III}]_{added}$ to accommodate the initial formation of Cr^{IV}. Solutions were buffered with mixtures of 2-ethyl-2-hydroxybutanoic acid (LigH, I) and its sodium salt (Na^+ Lig^-). [b] $[LigH] = [Lig^-]$ unless otherwise stated. [c] Unimolecular specific rates; parenthetical values were calculated from eq 7, taking K_c as 50 M^{-1}, k^0 as 0.043 s^{-1}, and k' as 7.9 M^{-1} s^{-1}. [d] $[H_3AsO_3]_{init} = 0.0015$ M. [e] $[H_3AsO_3]_{init} = 1.24 \times 10^{-4}$ M. [f] $[Lig^-] = 0.025$ M. [g] $[Lig^-] = 0.0080$ M.

ligated complex (II-Lig), and K is the indicated association constant. Refinement of absorbance values yields $\epsilon_0 = 53 \pm 22$ M^{-1} cm^{-1}, $\epsilon_1 = (2.45 \pm 0.07) \times 10^3$ M^{-1} cm^{-1}, and $K = 90 \pm 8$ M^{-1}. The latter value is nearly twice the constant (51 M^{-1}) reported[7b] for the corresponding equilibrium involving the analogous bis chelate of $Cr^{V}({=}O)$, which bears a -1 charge (since the hydroxycarboxylato ligands coordinate as dianions to this highly acidic center). The implication here is that these chelating ligands bind to $Cr^{IV}({=}O)$ (as to Cr^{III}) as monoanions and that the resulting bis chelate is uncharged.

Kinetic data for the formation of Cr(IV) from the Cr(VI)–As(III) reaction appear in Table III. With the oxidant in excess (part A), rates are seen to be very nearly proportional to $[Cr^{VI}]$ at low concentrations of the latter but approach a limiting value at higher concentrations. An analogous kinetic saturation with respect to $[As^{III}]$ is observed for reactions carried out with the reductant in excess (part B), thus indicating the formation of a Cr(VI)–As(III) complex. The reaction, irrespective of the reagent in excess, is strongly accelerated by both H^+ and Lig^-. Rates conform to eq 6, where K_p (taken to be the association constant

$$\frac{d[Cr^{IV}]}{dt} = \frac{K_p[As^{III}][Cr^{VI}]}{1 + K_p[R]}(a[H^+][Lig^-] + b[H^+]^2[Lig^-]^2) \quad (6)$$

of a Cr^{VI}–As^{III} precursor complex) is $(3.4 \pm 0.4) \times 10^2$ M^{-1}, $a = (1.68 \pm 0.17) \times 10^4$ M^{-2} s^{-1}, $b = (6.1 \pm 0.7) \times 10^8$ M^{-4} s^{-1}, and [R] represents the concentration of that redox reactant taken in excess. Rates calculated from (6) are compared with observed values in the same table.

This binomial rate law is consistent with a two-path reaction, with rates for both components proportional to the concentration of the Cr(VI)–As(III) complex. In addition, one path entails extra units of H^+ and Lig^- (or HLig), whereas the second requires two H^+ and two Lig^-. No saturation with respect to $[H^+]$ or $[Lig^-]$ is evident, indicating that only minor fractions of the Cr^{VI}–As^{III} adduct are converted to reactive species. A similar [HLig]-proportional term has been noted for the $(Mo^V)_2$–Cr^{VI} reaction,[9] in keeping with the suggestion that preassociation of the ligand acid with the Cr(VI) center is a common feature of these conversions to Cr(IV).

Data for decay of Cr(IV) in the presence of excess Cr(VI) appear in Table IV. Here again we see kinetic saturation with respect to Cr^{VI}, pointing, in this instance, to formation of a

Cr^{IV}–Cr^{VI} complex. Unimolecular specific rates for this reaction, which is acid-catalyzed, conform to (7), where K_c is association

$$k_{obsd} = \frac{K_c[Cr^{VI}]}{1 + K_c[Cr^{VI}]}(k^0 + k'[H^+]) \qquad (7)$$

constant for the $Cr^{VI}Cr^{IV}$ complex and k^0 and k' are the limiting specific rates (at high $[Cr^{VI}]$) for the acid-independent and $[H^+]$-proportional contributions. Refinement of specific rates according to (7) yields $K_c = (50 \pm 9)\ M^{-1}$, $k^0 = (4.3 \pm 0.5) \times 10^{-2}\ s^{-1}$, and $k' = (7.9 \pm 2.2)\ M^{-1}\ s^{-1}$. Agreement between these values and the analogous parameters pertaining to destruction of Cr(IV) formed by the reaction of $Mo_2O_4^{2+}$ with excess $Cr_2O_7^{2-}$ under similar conditions[9,15] shows that the same comproportionation process is in operation in the two systems.

In sum, several reductants that react preferentially as $2e^-$ reagents have been used to generate complexed Cr(IV) from $Cr_2O_7^{2-}$ in the aqueous buffer used. Of these, excess As(III) reacts in the most straightforward manner and gives the most stable solutions, which decay only by slow oxidation of the ligand. With $Mo_2O_4^{2+}$, U(IV), or Sn(II) in excess, Cr(IV) is reduced to Cr(III), in each case at a rate proportional to [reductant].[9,16] These conversions presumably require that the reagents assume their less usual roles as single electron donors—$Mo_2O_4^{2+}$ via unimolecular preactivation,[11] U(IV) via intervention of U(V), and Sn(II) (unexpectedly) through intermediacy of the highly atypical state Sn(III).[17] Work on the latter systems is continuing.[18]

Acknowledgment. We are grateful to Ms. Arla White for technical assistance.

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(15) The corresponding values recorded for the $(Mo^V)_2$–Cr^{VI} system are as follows: $K_c = 40 \pm 7\ M^{-1}$, $k^0 = (5.3 \pm 0.8) \times 10^{-2}\ s^{-1}$, and $k' = 8.8 \pm 1.8$ (25 °C, $\mu = 0.50$ M).

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(18) **Note Added in Proof**: The paramagnetic susceptibilities of our chromium(IV) complexes do not appear to vary significantly with their degree of ligation. Using the procedure of D. F. Evans (*J. Chem. Soc.* **1959**, 2003), we find the effective magnetic moment, μ_{eff}, of our Cr(IV) preparations to be 2.60, 2.65, and 2.90 μ_B at $[Lig^-]$ values of 0.010, 0.16, and 0.46 M.

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Proton-Coupled Electron Transfer in High-Valent Oxomanganese Dimers: Role of the Ancillary Ligands

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Received July 17, 1990

The aqueous electrochemistry of selected binuclear mixed-valence oxo-bridged manganese clusters has been investigated. For $[Mn^{III}Mn^{IV}(O)_2(bpy)_4]^{3+}$ (**1**, bpy = 2,2'-bipyridyl), it was observed that there is a substantial isotope effect ($k_H/k_D = 4.3$) for its electrochemical reduction, consistent with the proton-coupled electron transfer observed previously. Studies on $[Mn^{III}Mn^{IV}(O)_2(edda)_2]^-$ (**2**, edda = ethylenediamine-*N,N'*-diacetate) show that the $E_{1/2}$ values are also pH-dependent in a manner consistent with a one-proton/one-electron (slope of 0.07 ± 0.016 V/pH, $R = 0.99$) mechanism, as with **1**. For $[Mn^{III}Mn^{IV}(O)_2(bispicen)_2]^{3+}$ (**3**, bispicen = *N,N'*-bis(2-methylpyridyl)ethane-1,2-diamine), similar measurements indicate an EC mechanism where the electron transfer and protonation are kinetically decoupled. The current response as a function of pH was measured to determine a $pK_a \sim 8.35$ for $[Mn^{III}_2(O)(OH)(bispicen)_2]^{3+}$. Comparison of the electrochemical properties of **1**–**3** suggests that the proton-coupled mechanism is facilitated by low steric demand of the ancillary ligands and high basicity of the oxo bridges.

Acid–base equilibria are of great importance in redox processes because they can have large effects both on thermodynamic potentials and on electron-transfer kinetics. It has been suggested that enzymatic reactions such as the binding of dioxygen and the oxidation of water and peroxide proceed via mechanisms that involve proton-coupled electron transfer at oxo-bridged metal clusters.[1,2] The study of these reactions in oxo-bridged clusters is relevant to elucidating the primary processes in the function of redox enzymes such as uteroferrin, hemerythrin, catalase, and photosystem II (PS II).[1,2] Proton-coupled redox reactions can also initiate structural rearrangements of oxomanganese clusters.[3] We have previously observed concerted transfer of an electron and a proton in an oxo-bridged dimer, $[Mn^{III}Mn^{IV}(O)_2(bpy)_4]^{3+}$ (**1**, bpy = 2,2'-bipyridyl),[4,5] which has been studied extensively as a model for the Mn cluster in PS II.[6]

Electrochemical investigations of proton-coupled electron transfer in **1** lead to quasi-reversible cyclic voltammograms and a marked dependence on the nature of the electrode surface.[4,5] Cyclic voltammetry of **1** at activated glassy-carbon electrodes gave a heterogeneous rate constant $k_s = 5 \times 10^{-3}$ cm/s at pH 3.78.[4] This value is consistent with those obtained for proton-coupled electron transfer at terminal hydroxo complexes of ruthenium.[7] The $E_{1/2}$ for voltammograms of **1** is pH-dependent ($E_{1/2}$ = (0.99–0.059 pH) V vs SSCE) in a manner consistent with the assignment of this couple to eq 1.[4] The dependence of the

$$[Mn^{III}Mn^{IV}(O)_2(bpy)_4]^{3+} + e^- + H^+ \rightarrow [Mn^{III}_2(O)(OH)(bpy)_4]^{3+} \qquad (1)$$

heterogeneous kinetics of this reaction on the nature of the electrode surface is remarkable,[4,5] as it is for other proton-coupled reactions.[7] Voltammetric results for activated glassy carbon, tin-doped indium oxide, and edge-oriented pyrolytic graphite are consistent with a model where specific sites on the electrode surface mediate proton transfer to the metal complex.[5] Thus, a special interaction between the metal complex and the surface site is

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