**Acknowledgment.** We thank Dr. William H. Orme-Johnson and Neil Bastian for assistance in obtaining EPR spectra and the Camille and Henry Dreyfus Foundation (Young Faculty Grant to A.M.S.), the Research Corp., and the National Institutes of Health (Grant GM 33882) for support of this research.

**Registry No.** $H_2(OEP)$, 2683-82-1; $H_2(OEP)^+$, 43078-00-8; $H_2(OEP)^{2+}$, 113773-40-3; $H_2(OEC)$, 991-74-2; $H_2(OEC)^+$, 113773-46-9; $H_2(OEC)^{2+}$, 113773-41-4; $H_2(OEiBC)$, 72260-12-9; $H_2(OEiBC)^+$, 73069-22-4; $H_2(OEiBC)^{2+}$, 73068-83-4; $H_2(MOEC)$, 74071-46-8; $H_2(MOEC)^+$, 113686-71-8; $H_2(MOEC)^{2+}$, 113773-42-5; $H_2(DMOEiBC)$, 113686-70-7; $H_2(DMOEiBC)^+$, 113686-72-9; $H_2(DMOEiBC)^{2+}$, 113773-43-6; Ni(OEP), 24803-99-4; $Ni(OEP)^+$, 74876-13-4; $Ni(OEP)^{2+}$, 24803-99-4; Ni(OEC), 28375-46-4; $Ni(OEC)^+$, 113773-44-7; $Ni(OEC)^{2+}$, 113773-45-8; Ni(OEiBC), 39001-94-0; $Ni(OEiBC)^+$, 113686-73-0; $Ni(OEiBC)^{2+}$, 113686-74-1; Ni(MOEC), 113686-75-2; $Ni(MOEC)^+$, 113686-76-3; $Ni(MOEC)^{2+}$, 113686-77-4; Ni(DMOEiBC), 113686-80-9; $Ni(DMOEiBC)^+$, 113686-78-5; $Ni(DMOEiBC)^{2+}$, 113686-79-6; $[(p\text{-}BrC_6H_4)_3N][SbCl_6]$, 24964-91-8; $[(p\text{-}CH_3C_6H_4)_3N][SbCl_6]$, 65644-87-3; $Br_2$, 7726-95-6.

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# Electron Transfer. 91. Reactions of Carboxylato-Bound Chromium(V) with Arenediols[1]

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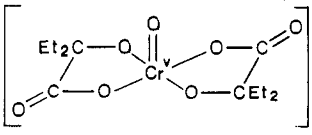
*Received October 15, 1987*

The chromium(V) chelate bis(2-ethyl-2-hydroxybutanoato)oxochromate(V) (I) oxidizes the arenediols hydroquinone and 2,3-dihydroxybenzoic acid in solutions buffered with the ligand acid, 2-ethyl-2-hydroxybutanoic acid, and its anion. The observed 1:1 stoichiometry of these reactions corresponds to the formation of the related quinone and Cr(III). The Cr(III) product from the reaction of excess hydroquinone is a bis chelate derived from the ligand anion, having, in addition, a ligand derived from the diol. With 2,3-dihydroxybenzoic acid, the diol appears to have coordinated to Cr(III) as a bidentate ligand. Both reactions are catalyzed by Cr(IV) and pass through semiquinone radicals, $ArO_2H^\bullet$, for which Cr(IV) and Cr(V) compete. Suggested reaction sequences for the two reductants feature bimolecular steps involving Cr(V) + $Ar(OH)_2$, Cr(V) + $ArO_2H^\bullet$, and Cr(IV) + $ArO_2H^\bullet$ (reactions 3, 4, and 6 in the text) but differ in the reaction of Cr(IV) with $Ar(OH)_2$, which is bimolecular with hydroquinone but exhibits kinetic saturation with 2,3-dihydroxybenzoic acid, indicating the formation of a strongly associated complex of the latter with Cr(IV). The suggested reaction sequences, in conjunction with rate constants for the individual steps derived from least-squares refinements of the data, reproduce the experimental kinetic curves. Dependencies of the component specific rates on the concentration of the ligand anion, $[Lig^-]$, indicate that partition of Cr(V) and Cr(IV) between ligation levels affects the reactions with hydroquinone but not those with dihydroxybenzoic acid. Acid catalysis of the Cr(IV)–$Ar(OH)_2$ step ($k_5$) for the latter diol points to partial protonation of the Cr(IV)–diol complex (p$K$ = 3.5). Comparisons of calculated electron-transfer rates with those for known outer-sphere reactions indicate that at least three of the four steps involving each diol proceed through bridged activated complexes. In contrast to earlier systems utilizing the proposed mechanism, the prominence of autocatalysis in the oxidation of hydroquinone is limited by the poor selectivity ($Cr^{IV}$ vs $Cr^{V}$) of the semiquinone radical rather than by the selectivity of the diol itself. Autocatalysis is not observed in the oxidation of 2,6-dihydroxynaphthalene.

In our investigations of the redox chemistry of carboxylato complexes of chromium(V),[3] we have encountered considerable diversity in kinetic behavior. The 2e reductants $Sn^{II}$, $H_2O_2$, and $N_2H_4$ generate uncomplicated exponential decay curves.[4] This apparent simplicity extends also to reductions by $Ti^{III}$ and $IrCl_6^{3-}$ despite the intervention of Cr(IV),[4a,5] for these donors react much more rapidly with Cr(IV) than with the less strongly oxidizing state[6] Cr(V). With $VO^{2+}$ and $Fe^{2+}$,[7] specific rates for the two successive steps are more nearly the same, and the buildup and loss of a Cr(IV) transient are clearly reflected in biphasic traces.

With reductants having both 1e and 2e capabilities, at least four different transfers may occur. Suitable interrelationships between rates for such components may lead to autocatalysis,[3,6a,8] and in some instances, the Cr(IV) intermediate is seen to grow slowly but decay suddenly, leading to a kinetic profile typifying a clock reaction.[6a,8a,c] Although autocatalytic reductions were initially described for the inorganic anions bisulfite,[6a] hypophosphite,[8b] and iodide,[8a] analogous behavior has been noted also for the organic reductants ascorbic acid,[8c] thiolactic acid,[9] and cysteine.[9] Each of these may undergo 1e oxidation to an organic radical which, in turn, rapidly reacts with both Cr(V) and Cr(IV).

The present report deals with reactions of the $Cr^{V}(=O)$ bis chelate of 2-ethyl-2-hydroxybutyric acid (I) with several dihydroxybenzene derivatives having structures allowing their conversion to quinones. With diols it was anticipated that intervention of 1e oxidation products, semiquinones, might be reflected in mechanistic variation. Although a number of such systems were characterized by unusually complex kinetic patterns



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[1] Sponsorship of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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**Table I.** Stoichiometries of the Reactions of Chromium(V) Chelate I with Arenediols[a]

| reductant | amt, mmol | | | $\Delta$[red]/-$\Delta$[$Cr^V$] |
|---|---|---|---|---|
| | $Cr^V$ | red | $\Delta$red | |
| 2,3-dihydroxybenzoic acid[b] | 0.073 | 0.209 | 0.080 | 1.09 |
| | 0.090 | 0.368 | 0.106 | 1.18 |
| | 0.115 | 0.312 | 0.125 | 1.13 |
| hydroquinone[c] | 0.0126 | 0.0129 | | 1.02 |
| | 0.0189 | 0.0181 | | 0.98 |
| | 0.0252 | 0.0278 | | 1.10 |

[a] Chromium(V) was added as the sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (the $Na^+$ salt of I); reactions were carried out in solutions buffered by the parent hydroxy acid and its sodium salt (see Experimental Section). [b] Loss of reductant determined by difference iodometrically. [c] Stoichiometry was determined by spectrophotometric titration.

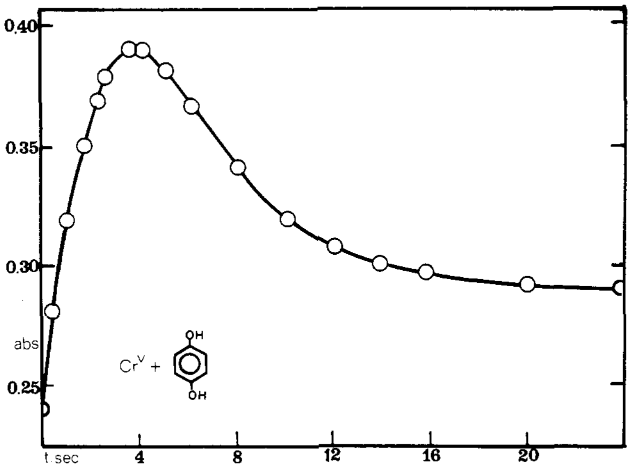

**Figure 1.** Kinetic profile at 600 nm for reduction of Cr(V) chelate I (2.5 × $10^{-3}$ M) with hydroquinone (6.3 × $10^{-3}$ M) at 24 °C. The supporting medium was 0.050 M each in 2-ethyl-2-hydroxybutyric acid and its sodium salt and was 0.35 M in $LiClO_4$; the pH was 3.32. The solid line is the experimental curve, whereas the circles indicate absorbances calculated from the sequence (3)–(6) in the text by taking $k_1$ and $k_3$ as 6.8 and 168 $M^{-1}$ $s^{-1}$ and the ratio $k_2/k_4$ as 1.14. Extinction coefficients used ($M^{-1}$ $cm^{-1}$): Cr(III), 58; Cr(IV), 474; Cr(V), 48. Mixing time: 0.005 s. Optical path length: 2.00 cm.

or the formation of strongly absorbing organic products (or both), experiments with hydroquinone (HQ) and 2,3-dihydroxybenzoic acid (DHB) led to reasonable pictures.

## Experimental Section

**Materials.** Sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (the $Na^+$ salt of anion I)[7a,10] and lithium perchlorate (used, after two recrystallizations, in kinetic experiments)[11] were prepared as described. The "ligand acid", 2-hydroxy-2-ethylbutanoic acid, and the various substituted benzenediols (Aldrich products) were generally used as received, as was hydroquinone (an Eastman product). However, 2,3-dihydroxybenzoic acid required two recrystallizations from methanol before yielding satisfactory kinetic results. 2,3-Dihydroxyacetophenone was prepared from 2,3-dimethoxybenzonitrile by the procedure of Baker and Smith[12] and was recrystallized from hexane. Cation-exchange resin (Dowex 50-,8, 400 mesh, $H^+$ form) was pretreated as described[13] and was converted to its $Na^+$ form by washing with saturated $NaHCO_3$.

**Stoichiometric Studies.** The stoichiometry of the reduction of Cr(V) anion I with excess 2,3-dihydroxybenzoic acid was determined by carrying out the reactions in solutions buffered at pH 3.3 by the ligand acid and its sodium salt (each 0.2 M); total volumes were 3 mL. After 1 h, the mixtures were treated with excess $KI_3$ and then allowed to stand an additional 30 min, after which that portion of the $I_3^-$ not consumed by the dihydroxy acid was titrated with standard $Na_2S_2O_3$.

The stoichiometry of the (much faster) reaction of Cr(V) with hydroquinone was evaluated by spectrophotometric titration at pH 3.3 in a 1.00-cm cell at 500 nm. Plots of absorbance vs added hydroquinone gave sharp breakpoints near 1:1 mole ratios.

Results for both reductants are summarized in Table I.

**Examination of the Cr(III) Reaction Products.** Reaction mixtures were 0.015–0.027 M in Cr(V) and 0.060–0.10 M in reductant and were buffered by equimolar quantities of the ligand acid and its sodium salt. These were allowed to react for 30–60 min at room temperature, were extracted with benzene to remove any uncomplexed quinone, and then were subjected to ion-exchange chromatography[14] at 2 °C. The Cr(III) products passed unchanged through anion-exchange resin but were absorbed on cation-exchange resin. The predominant Cr(III) product, corresponding to 85–95% of the Cr(V) taken, was eluted slowly with water in each case. Spectral characteristics of the products from reactions with three of the diol reductants are summarized in Table II. Treatment of these solutions with 0.1 M $HClO_4$ brought about rapid shifts in peak positions but left extinction coefficients nearly unchanged. The products from the three reductions appear to be different, and none corresponds to the Cr(III) product(s) arising from reduction of Cr(V) chelate I with ascorbic acid[8c] or vanadium(IV).[7a]

**Kinetic Measurements and Estimation of Specific Rates.** Reductions with hydroquinone were monitored by recording absorbance changes at 500 nm with a Durrum-Gibson stop-flow spectrophotometer. The slower reductions with 2,3-dihydroxybenzoic acid were followed on a Cary 14 recording spectrophotometer at 600 nm. Total ionic strength was kept at 0.4 M by adding twice-recrystallized $LiClO_4$, whereas pH values were regulated by adding measured quantities of 2-ethyl-2-hydroxybutanoic acid ($pK_A$ = 3.32)[4b] and its sodium salt. When the reductant was taken in excess, kinetic profiles featured the growth of a strongly absorbing intermediate and then its consumption (e.g., Figure 1). The shapes of the curves were like that of a reaction in which the first-order formation of a strongly absorbing transient is followed by its first-order decay. However, iterative nonlinear least-squares refinement of absorbance data appropriate for such a biphasic sequence[7b,15] converged for some, but not all, runs involving 2,3-dihydroxybenzoic acid and for none of the runs with hydroquinone. Moreover, even when convergence was achieved, calculated absorbances during the final stages of reaction decreased less markedly than those observed, indicating autocatalysis. Fits of all curves obtained with both of these reductants to an autocatalytic sequence (see Discussion) were accomplished initially with the program "INTEGRAL" to produce curves that were compared to those observed.[6a,16,17] Selected rate constants giving approximate agreement between observed and calculated absorbances were then refined further by using an iterative nonlinear least-squares procedure.[18,19] Parameters resulting from these refinements reproduced the observed curves closely (Figure 1).

Kinetic experiments were carried out with a number of additional arenediols. Treatment of Cr(V) complex I with catechol, resorcinol, 4-nitrocatechol, and 6,7-dihydroxy-2-naphthalenesulfonic acid resulted in the formation of deeply colored species that could not be characterized, whereas 3,4-dihydroxybenzoic acid and 2,3-dihydroxyacetophenone yielded unusually complex kinetic profiles that we could not disentangle.

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(10) Krumpolc, M.; Roček, J. *J. Am. Chem. Soc.* **1979**, *101*, 3206.

(11) Dockal, E. R.; Everhart, E. T.; Gould, E. S. *J. Am. Chem. Soc.* **1971**, *93*, 5661.

(12) Baker, W.; Smith, A. R. *J. Chem. Soc.* **1936**, 346.

(13) Gould, E. S. *J. Am. Chem. Soc.* **1967**, *89*, 5792.

(14) Separations were carried out by using 5-cm columns, capacity 2 mequiv. For estimations of extinction coefficients of Cr(III) species, aliquots were oxidized with basic $H_2O_2$, and the total chromium content was determined as chromate. (See, for example: Haupt, G. W. *J. Res. Natl. Bur. Stand., Sect. A* **1952**, *48*, 414.)

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

(16) Kinetic fits, which utilized a fourth-order Runge–Kutta integration technique,[17] were accomplished by a FORTRAN-77 program on an IBM 3081D computer system. The FORTRAN-IV version of the program, for which we thank Professor Gilbert Gordon (Miami University, Oxford, OH), was modified to incorporate the appropriate differential equations and stoichiometric relationships. Copies of the modified program may be obtained from R.N.B.

(17) (a) Margenau, H.; Murphy, G. M. *The Mathematics of Physics and Chemistry*; Van Nostrand: New York, 1943; p 469. (b) Wiberg, K. In *Investigations of Rates and Mechanisms of Reactions*; Lewis, E. S., Ed.; Techniques of Chemistry, 3rd ed., Vol. VI, Part I; Wiley: New York, 1974; p 764.

(18) This program, which was developed by R. Moore and T. W. Newton of Los Alamos National Laboratory, was obtained from Professor Gilbert Gordon. The FORTRAN-IV version was changed, with the help of Dr. J. W. Reed, to FORTRAN-77 in order to adapt to the IBM 3100 system. The program, which minimizes the function $(Abs_{calcd} - Abs_{obsd})^2$, uses the Gaussian method described by McWilliams and co-workers.[19] Trial values of the rate constants were those obtained from the "INTEGRAL" procedure. Individual experimental points were unweighted.

(19) McWilliams, P.; Hall, W. S.; Wegner, H. E. *Rev. Sci. Instrum.* **1965**, *33*, 76.

**Table II.** Major Cr(III) Products from Reaction of Cr(V) Chelate I with Arenediols[a]

| reductant | $[Cr^V]$, M | [red], M | $\epsilon_1$[b] | $\lambda_1$[b] | $\epsilon_2$ | $\lambda_2$ | % Cr[c] |
|---|---|---|---|---|---|---|---|
| hydroquinone | 0.0145 | 0.0663 | 48 (53)[b] | 570 (578) | 69 (74) | 438 (428) | 86[d] |
| 2,3-dihydroxybenzoic acid | 0.0203 | 0.060 | 208 (215) | 570 s (570 s) | $2 \times 10^4$ ($2 \times 10^4$) | 300 (300) | 95 |
|  | 0.0212 | 0.023 | 215 | 565 s | $2 \times 10^4$ | 300 | 90 |
| 2,6-dihydroxynaphthalene | 0.0268 | 0.102 | 48 (49) | 562 (582) | 61 (73) | 430 (408) | 83 |
| ascorbic acid[e] |  |  | 55 | 588 | 70 | 414 |  |
| $VO^{2+}$[f] |  |  | 49 | 588 | 61 | 415 |  |

[a] Reactions were carried out in solutions buffered by equimolal concentrations of 2-ethyl-2-hydroxybutyric acid and its sodium salt. Fractions were eluted from Dowex 50–X7 cation-exchange resin with water (see Experimental Section). [b] Absorption maxima ($\lambda$ values) are in nm; $\epsilon$ values are in $M^{-1}$ $cm^{-1}$. Parenthetic values refer to spectra recorded immediately after acidification with 0.1 M $HClO_4$. [c] Percent Cr(V) taken found in major fraction. [d] Minor fraction (12% of $Cr^V$ taken) eluted as $Cr(H_2O)_6^{3+}$. [e] Reference 8c. [f] Reference 7a.

**Table III.** Kinetic Parameters for the Reduction of Carboxylato-Bound Chromium(V) with Hydroquinone[a]

| [HQ], M | pH | [LigH][b] | $[Lig^-]$[c] | $k_1$[d,e] | $10^{-2}k_3$[d,e] | $k_2/k_4$[d,e] | $\epsilon_{Cr(IV)}$[d,f] |
|---|---|---|---|---|---|---|---|
| 0.0063 | 3.34 | 0.050 | 0.050 | 6.8 | 1.7 | 1.1 | 4.7 |
| 0.0125 | 3.34 | 0.050 | 0.050 | 6.0 | 1.6 | 1.8 | 4.3 |
| 0.0250 | 3.36 | 0.050 | 0.050 | 6.1 | 1.5 | 2.2 | 4.1 |
| 0.0375 | 3.32 | 0.050 | 0.050 | 6.3 | 1.6 | 1.9 | 4.3 |
| 0.0250[g] | 3.33 | 0.050 | 0.050 | 6.4 | 1.5 | 2.0 | 4.0 |
| 0.0250 | 3.35 | 0.10 | 0.10 | 5.2 | 1.9 | 1.3 | 4.6 |
| 0.0250 | 3.34 | 0.20 | 0.20 | 4.1 | 2.4 | 1.5 | 5.2 |
| 0.0250 | 3.37 | 0.30 | 0.30 | 3.5 | 2.8 | 1.2 | 5.2 |
| 0.0250 | 4.08 | 0.050 | 0.30 | 3.3 | 2.9 | 1.9 | 6.0 |
| 0.0250 | 3.74 | 0.10 | 0.30 | 3.9 | 2.4 | 1.4 | 5.7 |
| 0.0250 | 3.62 | 0.15 | 0.30 | 4.6 | 2.3 | 1.4 | 5.2 |
| 0.0250 | 3.51 | 0.20 | 0.30 | 4.6 | 2.3 | 1.1 | 5.2 |

[a] Reactions were carried out at 24 °C; $\mu$ = 0.4 M ($LiClO_4$); chromium(V), 0.0025 M unless otherwise indicated, was added as sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I). [b] 2-Ethyl-2-hydroxybutyric acid. [c] 2-Ethyl-2-hydroxybutyrate. [d] Parameters obtained from nonlinear least-squares refinements in which observed absorbances were compared with those obtained by integration of differential equations based on the sequence (3)–(6). (See text and ref 6a and 16.) [e] Values of $k_1$ and $k_3$ are in $M^{-1}$ $s^{-1}$; $k_2/k_4$ is dimensionless. [f] $M^{-1}$ $cm^{-1}$ × $10^{-2}$ (500 nm). [g] $[Cr^V]$ = 0.0050 M.

The oxidation of 2,6-dihydroxynaphthalene appeared to yield straightforward biphasic traces with no detectable autocatalysis, but the limited solubility of this diol was reflected in very shallow kinetic curves.[20] Oxidation of 1,4-dihydroxy-2-naphthoic acid, which was still less soluble, did not yield a useful profile.

## Results and Discussion

Stoichiometric experiments with the diol in excess (Table I) indicate that the primary reactions utilize equimolar quantities of the two redox partners and may thus be represented

$$Cr^VO + Ar(OH)_2 \rightarrow Cr^{III} + Ar({=}O)_2 + H_2O \qquad (2)$$

where "Ar(=O)$_2$" represents a 2e oxidation product, a quinone.

The elution characteristics of the major Cr(III) products correspond to those of uncharged species, and their relatively high extinction coefficients (Table II) indicate the formation of bischelated complexes.[21] Since products from three of the diols are different, both from each other and from the bis chelates formed by reduction with metal ions,[4a,7] we infer that the aromatic species has entered the coordination sphere of Cr(III), and the submergence of the usual peak near 400 nm into the "tail" of the strong aromatic absorbance band of the product from 2,3-dihydroxybenzoic acid is in accord with such intrusion. Substitution of an aryloxy group for the more strongly ligating $H_2O$ would be anticipated, in analogy with observations in the $(NH_3)_5Co^{III}$ series, to shift the band maximum near 415 nm to the region 430–440 nm,[22] as is seen for the products from hydroquinone and 2,6-dihydroxynaphthalene. The spectral changes occurring when these complexes are acidified suggest an expected[22] rapid aquation. In the product from 2,3-dihydroxybenzoic acid, which is somewhat more stable in acid, the reductant is probably bound to Cr(III) through its carboxyl function as well.

Kinetic curves feature the formation and subsequent disappearance of an intermediate that absorbs in a range characteristic of chelated Cr(IV) species.[7-9] Although data from a few runs conform satisfactorily to a pair of consecutive first-order processes, in most instances the observed drop in absorbance during the final stages of reaction is significantly more severe than that for an uncatalyzed sequence, indicating perceptible autocatalysis (see Figure 1).

The four-step sequence (3)–(6), which resembles that proposed for the Cr(V)–$NO_2^-$ system,[3b] correlates data from all runs with hydroquinone in excess. Intermediates are the semiquinone ($ArO_2H^•$) and Cr(IV).

$$Cr^V + Ar(OH)_2 \xrightarrow{k_1} Cr^{IV} + ArO_2H^• + H^+ \qquad (3)$$

$$Cr^V + ArO_2H^• \xrightarrow{k_2} Cr^{IV} + Ar({=}O)_2 + H^+ \qquad (4)$$

$$Cr^{IV} + Ar(OH)_2 \xrightarrow{k_3} Cr^{III} + ArO_2H^• + H^+ \qquad (5)$$

$$Cr^{IV} + ArO_2H^• \xrightarrow{k_4} Cr^{III} + Ar({=}O)_2 + H^+ \qquad (6)$$

Expression of the sequence (3)–(6) as differential kinetic equations, application of the steady-state approximation to the semiquinone radical, $ArO_2H^•$, and utilization of the Runge–Kutta integration procedure were carried out as described for the reduction of Cr(V) by $HSO_3^-$.[6a] Values of $k_1$, $k_3$, and the ratio $k_2/k_4$ were allowed to vary independently. Integration then yielded the concentrations of Cr(III), Cr(IV), Cr(V), and quinone at 0.5-s

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[20] Kinetic runs carried out with 2,6-dihydroxynaphthalene ($10^{-3}$ M) and Cr(V) ($2 \times 10^{-4}$ M) in 5% aqueous acetone (pH 2.5–3.5, $\mu$ = 0.4 M) yielded approximate specific rates for the formation ($k_1$) and consumption ($k_2$) of the Cr(IV) intermediate. The former parameter exhibited acid dependence and kinetic saturation

$$(k_1)_{obsd} = \frac{k_{lim}[H^+]}{K_A + [H^+]} \qquad (1)$$

with $k_{lim}$ = 33 $M^{-1}$ $s^{-1}$ and $K_A = 5 \times 10^{-4}$ M whereas $k_2 = 2 \times 10^2$ $M^{-1}$ $s^{-1}$ (with virtually no acid dependence). The extinction coefficient of the Cr(IV) intermediate is $5 \times 10^2$ $M^{-1}$ $cm^{-1}$ at 510 nm. The stoichiometry of this reaction, $[red]/[Cr^V]$, is 1.1. Properties of the Cr(III) product are included in Table II.

[21] Electronic spectra of a number of carboxylato complexes of Cr(III), both chelated and nonchelated, have been tabulated by Fanchiang.[7a]

[22] Reid, R.; Fan, F.-R. F.; Fanchiang, Y.-T.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 2766. The positions of the (very broad) maxima at 560–580 nm are less informative.

**Table IV.** Kinetic Parameters for the Reduction of Carboxylato-Bound Chromium(V) with 2,3-Dihydroxybenzoic Acid (DHB)[a]

| [DHB], M | pH | [LigH][b] | [Lig⁻][c] | $k_1$[d,e] | $k_5$[d,e] | $k_2/k_4$[d,e] | $\epsilon_{Cr(IV)}$[d,f] |
|---|---|---|---|---|---|---|---|
| 0.0050[g] | 3.34 | 0.050 | 0.050 | 1.6 | 0.020 | 2.6 | 8.6 |
| 0.0050[h] | 3.32 | 0.050 | 0.050 | 1.5 | 0.023 | 2.2 | 9.2 |
| 0.0015[g] | 3.32 | 0.050 | 0.050 | 1.6 | 0.023 | 1.9 | 10.5 |
| 0.0030[g] | 3.32 | 0.050 | 0.050 | 1.7 | 0.025 | 2.8 | 8.7 |
| 0.0060 | 3.32 | 0.050 | 0.050 | 1.8 | 0.023 | 2.9 | 9.0 |
| 0.015 | 3.32 | 0.050 | 0.050 | 1.5 | 0.027 | 2.0 | 9.0 |
| 0.020 | 3.32 | 0.050 | 0.050 | 1.5 | 0.022 | 1.5 | 8.5 |
| 0.030 | 3.32 | 0.050 | 0.050 | 1.6 | 0.024 | 0.81 | 8.6 |
| 0.040 | 3.32 | 0.050 | 0.050 | 1.5 | 0.029 | 0.54 | 8.6 |
| 0.010 | 3.35 | 0.10 | 0.10 | 1.3 | 0.048 | 1.8 | 7.9 |
| 0.010 | 3.33 | 0.20 | 0.20 | 1.2 | 0.048 | 1.8 | 8.6 |
| 0.010 | 3.84 | 0.050 | 0.20 | 2.7 | 0.014 | 2.2 | 8.8 |
| 0.010 | 3.55 | 0.10 | 0.20 | 1.8 | 0.030 | 2.1 | 8.7 |
| 0.010 | 3.03 | 0.20 | 0.10 | 1.2 | 0.050 | 2.5 | 9.0 |
| 0.010 | 2.77 | 0.20 | 0.050 | 1.2 | 0.054 | 3.1 | 8.2 |

[a] Reactions were carried out at 25 °C; $\mu$ = 0.4 M ($LiClO_4$); chromium(V), added as the sodium salt of chelate I, was 0.0010 M unless otherwise indicated. [b] 2-Ethyl-2-hydroxybutyric acid. [c] 2-Ethyl-2-hydroxybutyrate. [d] Parameters obtained from refinements based on the sequence (3), (4), (10), (6). (See text, Table III, and ref 6a and 16.) [e] Values of $k_1$ are in $M^{-1}$ $s^{-1}$ and $k_5$ in $s^{-1}$; $k_2/k_4$ is dimensionless. [f] $M^{-1}$ $cm^{-1}$ × $10^{-2}$ (600 nm). [g] $[Cr^V] = 5 \times 10^{-4}$ M. [h] $[Cr^V] = 1.5 \times 10^{-3}$ M.

intervals, and incorporation of the extinction coefficients of the three chromium oxidation states gave calculated absorbances at each point.[23] The set of parameters conforming most closely to the observed traces was used as a set of trial values for an iterative least-squares refinement.[18]

Values of $k_1$, $k_3$, $k_2/k_4$, and $\epsilon_{Cr(IV)}$ yielding optimum fits to experimental curves for the hydroquinone system are given in Table III. Absorbances calculated from a representative set of parameters are compared to the corresponding observed trace in Figure 1.

The hydroquinone–Cr(V) reaction ($k_1$) and that with Cr(IV) ($k_3$) are seen to respond in opposite directions to addition of the parent ligand anion (Lig⁻). Reaction with Cr(V) is retarded by excess ligand, with $k_1$ conforming to eq 7 where $a = 3.5 \pm 0.2$

$$k_1 = a + b/[\mathrm{lig}^-] \qquad (7)$$

$M^{-1}$ $s^{-1}$ and $b = 0.14 \pm 0.02$ $s^{-1}$, whereas the Cr(IV) step is accelerated by ligand (eq 8) with $c = 130 \pm 9$ $M^{-1}$ $s^{-1}$ and $d$ =

$$k_3 = c + d[\mathrm{Lig}^-] \qquad (8)$$

520 ± 48 $M^{-2}$ $s^{-1}$.[24] Both (7) and (8) reflect the partition of oxidants between ligation levels. Evidence for intrusion of an additional ligand anion in the coordination sphere of Cr(V) chelate I has been presented.[7a] As is the case for the oxidations of U(IV)[25] and S(IV),[6a] the "extraligated" species, bearing an additional unit of negative charge, is the less facile oxidant. However the apparent improvement in the oxidizing effectiveness of Cr(IV) on analogous anation, if it is not an artifact,[26] is without obvious precedent.

Although the reductions with 2,3-dihydroxybenzoic acid yield profiles of character similar to those with hydroquinone, the disappearance of the Cr(IV) intermediate is much less sensitive to the concentration of the reductant taken. Individual runs conform to the sequence (3)–(6), but correlation of data for all 15 experiments requires that we recognize formation of a 1:1 complex, $Ar(OH)_2{\cdot}Cr^{IV}$, with the rate of electron transfer proportional to its concentration. Treatment of absorbance data for this system involves replacement of step 5 with step 10 and the

$$Ar(OH)_2 + Cr^{IV} \xrightleftharpoons{K} Ar(OH)_2{\cdot}Cr^{IV} \xrightarrow{k_5} Cr^{III} + ArO_2H^{\bullet} + H^+ \qquad (10)$$

assumption that conversion to the 1:1 complex is virtually complete. Refinement, using a procedure otherwise similar to that for the hydroquinone reduction, yields the parameters listed in Table IV. The nearly constant values of $k_5$ as the concentration of reductant is increased from 0.0015 to 0.040 M confirms the quantitative conversion of $Cr^{IV}$ to the diol complex within this concentration range.[27]

In this instance, kinetic parameters show no systematic variation with the concentration of ligand anion, but are affected by $[H^+]$. Values of $k_1$ drop off with increases in acidity

$$k_1 = e + f/[H^+] \qquad (11)$$

with $e = 0.89 \pm 0.10$ $M^{-1}$ $s^{-1}$ and $f = (2.5 \pm 0.3) \times 10^{-4}$ $s^{-1}$, whereas $k_5$ is subject to acid catalysis and exhibits kinetic saturation

$$k_5 = \frac{k_{\mathrm{lim}}[H^+]}{K_A + [H^+]} \qquad (12)$$

where $k_{\mathrm{lim}} = 0.068 \pm 0.011$ $s^{-1}$ and $K_A = (3.3 \pm 1.5) \times 10^{-4}$ M.

Since the reductant ($pK_1$ = 2.70)[28] is largely deprotonated within much of our pH range, we attribute the inverse-$[H^+]$ term in (11) to a path involving a small concentration of a very reactive dianion. The acidity constant, $K_A$, in (12), which pertains to the $Cr^{IV}$–$Ar(OH)_2$ step, is almost certainly associated with a protonation equilibrium at the Cr(IV) center. Its value (which is imprecisely determined from our data) may be compared with the $K_A = 4 \times 10^{-4}$ M, reported for a similar Cr(IV) intermediate[7a] in the absence of aromatic ligands.

The Cr(III) products from both reductions undergo eventual aquation in our media and are therefore not thermodynamically favored. Both reactions yield predominantly bis chelates. Since the hydroxy groups in hydroquinone cannot chelate, the rings in the product from this reaction are formed by the oxy and carboxylato groups in the Cr(V) reactant.[29] Hence, chelation may be taken to survive in all steps entailing Cr(V) and Cr(IV). The

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(23) Values of $\epsilon_{Cr(V)}$ and $\epsilon_{Cr(III)}$ were calculated from the initial and final absorbances of the reaction mixtures and were kept fixed, but $\epsilon_{Cr(IV)}$ was allowed to "float". Absorbance of the quinone was considered negligible at the wavelengths chosen.

(24) The final four values in Table III suggest a modest acid dependence for $k_1$ in the hydroquinone reaction. However, refinement of all data on the basis of trinomial expression

$$k_1 = a + b[\mathrm{Lig}] + b'[H^+] \qquad (9)$$

yields values of $b'$ statistically indistinguishable from zero.

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

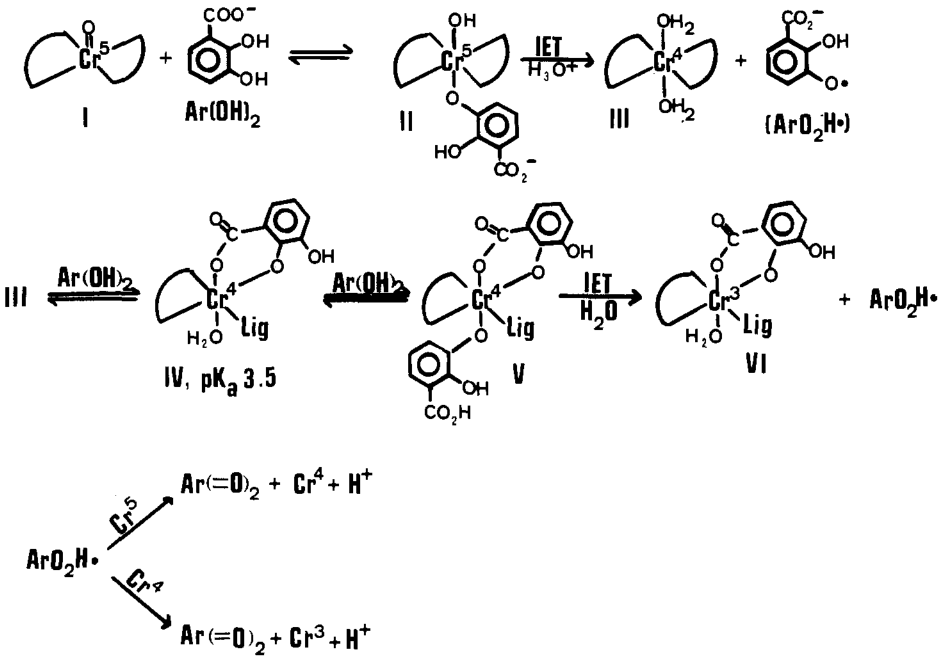
(26) It is well to emphasize here, as in earlier work,[6a] that parameters obtained from these multivariant refinements must be considered much less precise than those derived from exponential or simple biphasic traces.

(27) An estimate of the formation constant of this complex is, in principle, possible from measurements at still lower reductant concentrations where the initial step, (3), becomes inconveniently slow.

(28) Avdeef, A.; Sofen, S. R.; Brigante, T. L.; Raymond, K. N. *J. Am. Chem. Soc.* **1978**, *100*, 5362. This value pertains to 27 °C and $\mu$ = 0.1 M. Under the same conditions, $pK_2$ = 10.1.

(29) Note that the parent ligand coordinates as a dianion in the Cr(V) reactant, I, but as a monoanion at the much less acidic Cr(III) center(s) in the products.

**Scheme I**



attachment of a diol molecule at the chromium center probably takes place mainly at the Cr(IV) level, for this state is known to be more substitution labile than Cr(III) or Cr(V).[8b] A similar conclusion may be drawn concerning ligand incorporation in the reduction by 2,3-dihydroxybenzoic acid, but here the improved acid stability of the Cr(III) product and the more pronounced spectral alteration (Table II) suggest that one (but not both) of the rings may be derived from the diol, with attendant breakage of "one arm" of the original chelating ligand (i.e. complex VI in Scheme I).

Rate constants for the initial Cr(V)–hydroquinone step ($k_1$ = 3–7 $M^{-1}\ s^{-1}$) are about $10^2$ times that for reaction of this Cr(V) complex with the outer-sphere reductant $IrCl_6^{3-}$ ($3 \times 10^{-2}$).[4a] Recorded values for the formal potential (1.14 V)[30] and the self-exchange rate ($5 \times 10^7\ M^{-1}\ s^{-1}$)[31] pertaining to $Ar(OH)_2/ArO_2H^{\bullet}$ (for hydroquinone) allow us to compare the two systems on the basis of the Marcus model.[32] Using the self-exchange rate for $IrCl_6^{3-/4-}$ ($2.3 \times 10^5\ M^{-1}\ s^{-1}$)[33] and its reported formal potential (0.92 V),[34] we calculate[35] a specific rate less than $10^{-2}\ M^{-1}\ s^{-1}$ for the outer-sphere oxidation of hydroquinone. On this basis, the $Cr(V)–Ar(OH)_2$ reaction may be taken to proceed preponderantly by an inner-sphere path. The same conclusion applies somewhat more forcefully to $k_1$ for the oxidation of DHB (for which a formal potential of 1.25 V and a self-exchange rate of $6 \times 10^7\ M^{-1}\ s^{-1}$ have been reported.[30,31])

Earlier estimates of the selectivities of metal-center reductants reacting with both Cr(IV) and Cr(V) via outer-sphere paths indicated that the tetrapositive state is 10–60 times as reactive as the pentapositive state,[4a,5,25] a rate ratio that, according to the formalism of Marcus,[32] should be nearly independent of the reductant in the absence of a significant inner-sphere component. An outer-sphere oxidation of hydroquinone by Cr(IV) would then be expected to proceed at a specific rate less than 0.6 $M^{-1}\ s^{-1}$ under our conditions, whereas observed ($k_3$) values are seen to fall in the range 150–300 $M^{-1}\ s^{-1}$. In this case as well, we may infer that an inner-sphere path predominates. A similar comparison for the reaction of 2,3-dihydroxybenzoic acid with Cr(IV) ($k_5$) is complicated by the observed kinetic saturation, but the very existence of a Cr(IV)–DHB complex supports (but does not demand) an inner-sphere route for this step also. And that is not all; the observed "inversions" in relative rates for oxidation of $ArO_2H^{\bullet}$ radicals ($k_2/k_4$) which, in most cases, react with Cr(V) about twice as rapidly as with Cr(IV), point to an important inner-sphere route for the $Cr(V)–ArO_2H^{\bullet}$ step ($k_2$) but are noncommital as to the mechanism of the $Cr(IV)–ArO_2H^{\bullet}$ component.[36] Thus, rate comparison with previous systems indicate the intervention of bridged activated complexes in three of the four steps in the suggested mechanisms.

The sequence shown as Scheme I attempts to accommodate our observations pertaining to the oxidation of 2,3-dihydroxybenzoic acid. Species II and V are "precursor complexes", i.e., intermediates in the inner-sphere steps involving the diol.[37,38]

**Table V.** Autocatalytic Reductions of Chelated Chromium(V)[a]

| reductant | $k_1/k_3$[b] | $k_2/k_4$[c] | ref |
|---|---|---|---|
| A. Strongly Autocatalytic Systems Exhibiting Clocklike Profiles | | | |
| $HSO_3^-$ | 0.005–0.01 | 20–36 | 6a |
| ascorbate | 0.005–0.01 | 7–19 | 8c |
| $I^-$ | 0.017–0.03 | 40–50 | 8a |
| B. Weakly Autocatalytic Systems | | | |
| $NO_2^-$ | 20–50 | 3–10 | 3b |
| $H_2PO_2^-$ | 0.16–0.3 | 2–3 | 8b |
| thiolactate | 0.1–0.4 | 2–8 | 9 |
| cysteine | 0.1–0.5 | 6–15 | 9 |
| hydroquinone | 0.01–0.04 | 1–2 | *d* |
| 2,3-dihydroxybenzoic acid | *e* | 0.8–3 | *d* |

[a] Reactions of the Cr(V) chelate I in aqueous media, pH 2–4. Solutions were buffered with 2-ethyl-2-hydroxybutyric acid and its anion. [b] Relative rates at which the reductant reacts, via 1e transfer, with the Cr(V) reactant and the Cr(IV) intermediate. [c] Relative rates at which the radical intermediate from the reductant reacts with Cr(V) and Cr(IV) (see, for example, the sequence (2)–(5) in text). [d] This work. [e] Ratio cannot be calculated because of kinetic saturation associated with the $Cr(IV)–Ar(OH)_2$ step (see text).

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(30) Pelizzetti, E.; Mentasti, E.; Pramauro, E. *J. Chem. Soc., Perkin Trans. 2* **1978**, 620.

(31) McAuley, A.; Spencer, L.; West, P. R. *Can. J. Chem.* **1985**, *63*, 1198.

(32) See, for example: Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

(33) Hurwitz P.; Kustin, K. *Trans. Faraday Soc.* **1966**, *62*, 427.

(34) George, P.; Hanania, G. I. H.; Irvine, G. H. *J. Chem. Soc.* **1957**, 3048. This value was measured at 20.3 °C.

(35) Loar, M. K.; Fanchiang, Y.-T.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 3689.

(36) Gould, E. S. *Inorg. Chem.* **1979**, *18*, 900.

(37) Complexes II and V may be considered analogous to ester-like intermediates, which are thought to intervene in the oxidations of alcohols with Cr(VI) and Cr(V).[38]

(38) See, for example: (a) Mitewa, M.; Bontchev, P. R. *Coord. Chem. Rev.* **1985**, *61*, 241; (b) Beattie, J. K.; Haight, G. P., Jr. *Prog. Inorg. Chem.* **1972**, *17*, 97.

Internal electron transfer (IET) within II and V yields the radical $\mathrm{ArO_2H}^{\bullet}$, for which Cr(V) and Cr(IV) compete in 1e oxidations to the quinone "Ar(=O)$_2$". The latter competition (as measured by the ratio $k_2/k_4$) is related to the extent of autocatalysis. Two molecules of the diol have been incorporated into intermediate V, for the diol unit that appears in the ligand sphere of the (substitution-inert) Cr(III) product, VI, cannot be that which undergoes oxidation to the $\mathrm{ArO_2H}^{\bullet}$ radical. Since the $\mathrm{Ar(OH)_2}$–Cr(IV) step ($k_5$) in this reaction exhibits no kinetic dependency on [diol], we infer that conversion to V is rapid and essentially complete under our reaction conditions. An analogous scheme may be applied to the oxidation of hydroquinone, but chelation is precluded with this 1,4-diol. In an alternate path, $\mathrm{ArO_2H}^{\bullet}$ formed in the initial internal electron transfer remains bound to Cr(IV) while undergoing a second 1e oxidation to yield Cr(III) and quinone. Although conceptually simple, this cannot be a major contributor, for release of free $\mathrm{ArO_2H}^{\bullet}$ appears to be essential for the observed catalysis.

In the consideration of the reactions of Cr(V) with the several "ambifunctional" reductants (Table V) that utilize sequences related to (3)–(6), it has been noted[3b] that the most dramatic autocatalysis and the appearance of clocklike behavior are associated with the greatest reversals in selectivities toward Cr(V) and Cr(IV) when these reductants are compared with the radicals that they generate, i.e., when the differences between the ratios $k_1/k_3$ and $k_2/k_4$ are most marked. Moreover, there is considerably less variation in the latter ratio than in the former, and in previous instances, the severity of autocatalysis was determined principally by the selectivity of the primary reductant. This is not the case with reduction by hydroquinone, for which $k_1/k_3$ is found to lie very close to the corresponding ratio for iodide, a strongly autocatalytic reductant. Were it not for the poor selectivity of the semiquinone radical, we should observe a clock reaction in this reaction as well.[39]

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

**Registry No.** I, 84622-43-5; hydroquinone, 123-31-9; 2,3-dihydroxybenzoic acid, 303-38-8; catechol, 120-80-9; resorcinol, 108-46-3; 4-nitrocatechol, 3316-09-4; 6,7-dihydroxy-2-naphthalenesulfonic acid, 92-27-3; 3,4-dihydroxybenzoic acid, 99-50-3; 2,3-dihydroxyacetophenone, 13494-10-5; 2,6-dihydroxynaphthalene, 581-43-1; 1,4-dihydroxy-2-naphthoic acid, 31519-22-9.

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(39) It is reasonable to ask what structural characteristics of the reagents summarized in Table V govern their reactivities and those of their radicals. We see no straightforward relationship between these reactivities and the formal potentials of the reductants, their geometric or electronic structures (and those of the radicals), and the identity of the nucleophilic sites from which electrons are removed. We thus remain puzzled on this important point.

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# Electron Transfer. 92. Reductions of Vitamin $B_{12a}$ (Hydroxocobalamin) with Formate and Related Formyl Species[1]

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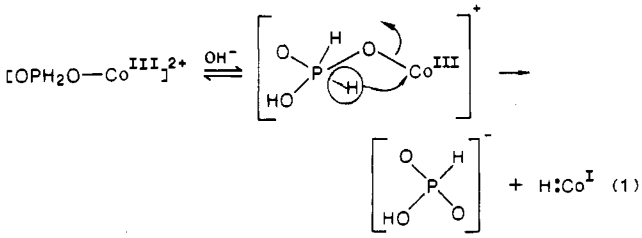
*Received November 12, 1987*

Vitamin $B_{12a}$ (hydroxocobalamin) is reduced to $B_{12r}$ (cob(II)alamin) with formate in aqueous media. One unit of formate consumes nearly two molecules of $B_{12a}$. At formate concentrations below 0.1 M, reactions are first order in both reagents. Rates vary with pH, approach a maximum in the range pH 5–7, and conform to eq 4 in the text, indicating that the active species are the formate anion and the protonated form of $B_{12a}$. At formate concentrations exceeding 0.1 M, the formate dependence exhibits kinetic saturation, pointing to the formation of a $B_{12a}$–formate complex having $K_{\mathrm{assn}} = 4.6\ \mathrm{M}^{-1}$. The reaction is inhibited moderately by acetate and thiocyanate but severely by imidazole. The observed deuterium isotope effect, $k_{\mathrm{HCOO^-}}/k_{\mathrm{DCOO^-}} = 1.8$, is very close to that reported for the Cannizzaro reaction of benzaldehyde and is thus consistent with a path entailing migration of hydride from a formyl carbon to cobalt. The proposed mechanism for this reaction (sequence (6) – (9)) then features an internal hydride shift ($k = 0.016\ \mathrm{s}^{-1}$) within a $B_{12a}$–formate complex to yield a protonated $\mathrm{Co^I}$ ($B_{12s}$-like) intermediate, which very rapidly undergoes a comproportionation reaction with unreacted $B_{12a}$. The reduction proceeds inconveniently slowly, or not at all, with a number of formyl-substituted carboxylic acids in which the aldehydo group is not properly positioned for hydride migration to carboxyl-bound $\mathrm{Co^{III}}$ or, in the case of glyoxylic acid, is nearly completely converted by hydration to its less reactive *gem*-diol form.

A recent report[2] described the reduction of cobalt(III) by bound hypophosphite and presented evidence that this transformation, which does not occur with phosphite or with free hypophosphite, proceeds via base-induced internal hydride transfer from P(I) to Co(III), (1), yielding a Co(I) species, which then rapidly reduces unreacted Co(III) to Co(II) (2). In considering the extension of this type of reaction to other systems, we noted that formate, potentiometrically a weaker reductant than hypophosphite,[3,4] functions as a hydride donor toward a number of metal centers.[5] The formato complex $\mathrm{HCO_2Co(NH_3)_5}^{2+}$ was nevertheless found to survive conditions much more severe than those bringing about



$$\mathrm{H{:}Co^{I}} + [\mathrm{Co^{III}{-}OPH_2O}]^{2+} \longrightarrow 2\mathrm{Co^{II}} + \mathrm{H_3PO_2} \qquad (2)$$

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(1) Sponsorship of this work by the National Science Foundation (Grant No. 8619472) is gratefully acknowledged.

(2) Linn, D. E., Jr.; Gould, E. S. *Inorg. Chem.* **1987**, *26*, 3442.

(3) The formal potential for the 2e oxidation of hypophosphorous acid is listed[4a] as −0.50 V at pH 0 (25 °C), and that for $\mathrm{H_2PO_2}^-$, as −1.57 V at pH 14. The potential appropriate for P(I) in the medium at hand (pH near 5) is then approximately −0.90 V. The potential for 2e oxidation of formate to $\mathrm{CO_2}$ lies near −0.4 V at pH 7.[4b]

(4) (a) Latimer, W. H. *Oxidation Potentials*, 2nd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1952; p 111. (b) See, for example: Fruton, J. S.; Simmonds, S. *General Biochemistry*, 2nd ed.; Wiley: New York, 1958; p 299.

(5) See, for example: (a) Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1962**, 5075. (b) King, A. D., Jr.; King, R. B.; Yang, D. B. *J. Am. Chem. Soc.* **1980**, *102*, 1028. (c) King, A. D., Jr.; King, R. B.; Sailers, E. L., III. *J. Am. Chem. Soc.* **1981**, *103*, 1867. (d) Darensbourg, D. J.; Rokicki, A. *Organometallics* **1982**, *1*, 1685. (e) Bar, R.; Sasson, Y. *Tetrahedron Lett.* **1981** *22*, 1709. (f) Strauss, S. H.; Whitmire, K. H.; Shriver, D. F. *J. Organomet. Chem.* **1979**, *174*, C59. (g) Krautler, B.; Caderas, C. *Helv. Chim. Acta* **1984**, *67*, 1891. (h) Linn, D. E., Jr. Ph.D. Thesis, University of Georgia, 1983; Chapters 3, 7.

0020-1669/88/1327-1625$01.50/0