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Electron Transfer. 82. Reduction of Carboxylato-Bound Chromium(V) with Hypophosphorous Acid[1a]

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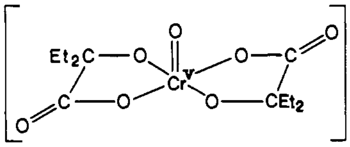
The bis-chelated chromium(V) anion bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I) reacts with an equimolar quantity of hypophosphorous acid in aqueous solutions buffered by the parent acid, 2-ethyl-2-hydroxybutyric acid, and its anion. Reactions pass through a mixture of strongly absorbing intermediates, the behavior of which corresponds to chromium(IV) species. By implication, phosphorus(II) transients are also involved. The preponderant Cr(III) products are $(H_2PO_2)Cr(H_2O)_5^{2+}$ and a mixture of hypophosphito and carboxylato derivatives of $(H_2O)_4Cr^{III}$. The chelate rings in the reactant survive in less than 2% of the recovered product. The observed kinetic profiles do not conform satisfactorily to a sequence of consecutive uncatalyzed processes. Instead, they accommodate an autocatalytic mechanism analogous to that proposed for the Cr(V)–HSO_3^- system, in which $H_2PO_2^-$ is oxidized by both Cr(V) and Cr(IV) to the $H_2PO_2^{\bullet}$ radical, for which Cr(V) and Cr(V) then compete (sequence 3–6 in the text). The rates of these reactions, when contrasted to the very sluggish intramolecular proton transfer (P–H to O–H), which limits the rates of other hypophosphite oxidations, indicate that the transformations at hand proceed through bridged transition states in which the strongly acidic Cr^V or Cr^{IV} center favors the mobilization of P-bound protons. Variation, with reaction medium, of specific rates involving Cr^{IV} indicates the operation of rapid ligand exchange processes at that oxidation level; these are reflected also in changes in the molar absorptivities of the Cr^{IV} intermediate and in the mix of Cr^{III} complexes recovered.

Chromium(V) chelates derived from α-hydroxycarboxylic acids have proved instructive in the experimental examination of redox mechanisms.[2] Complexes such as I are easily prepared, are stable in air, and dissolve in aqueous media, yielding solutions in which the unusual oxidation state Cr(V) persists for hours.[3] Conversions to Cr(III) with single-electron reductants pass through the still less usual state Cr(IV), the reactions of which may, in favorable instances,[4] also be studied. Reductions with "even-electron" reagents might be expected to bypass Cr(IV), and this appears to be so for reductions with hydrazine,[5] hydroxylamine,[6] and tin(II).[7]



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Evidence has been reported, however, that some reductants that are ordinarily considered to be two-electron donors (e.g. U(IV) and HSO_3^-) react with Cr(V) via one-electron transactions,[8] resulting in intervention not only of Cr(IV), but also a second metastable oxidation state (U^V or S^V) derived from the reductant. We here describe experiments which indicate that the reduction of bis chelate I with hypophosphorous acid, H_3PO_2, conforms to such a pattern and thus involves the formation and consumption of a P(II) species. The reaction is not unlike the reduction with S(IV),[8b] but autocatalysis by Cr(IV), which is prominent in the latter system, plays a much more subdued role in the present case.

Experimental Section

Materials. Sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (complex I) was prepared as its monohydrate as described[3] and was purified by recrystallization from acetone–chloroform.[4b] Lithium perchlorate, used as the supporting electrolyte in kinetic experiments, was prepared by the method of Dockal[9] and was twice recrystallized before use. The "ligand acid" 2-hydroxy-2-ethylbutyric acid (Aldrich) was used as received. Cation-exchange resin (Bio-Rad 50W-X2, 200–400 mesh) was pretreated as described.[10] Solutions of hypophosphorous acid were prepared by diluting the concentrated acid (Aldrich, "50%") with distilled water;[11] the concentrated acid was found, by using the procedure of Mitchell,[12] to be 9.03 M in H_3PO_2 and 0.40 M in H_3PO_3. Reaction of H_3PO_3 with our Cr(V) oxidant was shown to be negligible on the time scale used.

Table I. Stoichiometry of the Reaction of Chromium(V) Chelate I with Hypophosphorous Acid[a]

mmol of Cr^V	mmol of H_3PO_2	$\Delta(H_3PO_2)$, mmol[b]	$\Delta(Cr^V)/\Delta(H_3PO_2)$
0.170	0.403	0.177	0.96
0.061	0.179	0.062	0.98
0.090	0.179	0.088	1.02

[a] Chromium(V) was added as sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I); reactions were carried out in solutions buffered by the parent hydroxy acid and its salt. The reaction volume was 2.0 mL (see text). [b] Determined iodometrically by difference (see text).

Stoichiometric Studies. The stoichiometry of the reaction between Cr(V) chelate I and excess hypophosphorous acid was determined by carrying out the reaction in solutions buffered by the parent carboxylic acid (0.05 M) and an equivalent quantity of its anion (pH 3.3). After 60 min, a measured excess of KI_3 was added and the reaction mixture acidified with 0.5 M H_2SO_4. After another 45 min, the excess iodine was estimated by titration with standard $Na_2S_2O_3$. Results are summarized in Table I. Reaction between I_3^- and phosphorous acid was shown to be negligibly slow at pH 3.3.

Examination of the Cr(III) Reaction Products. Reaction mixtures, each 0.005 M in Cr(V) and buffered with equimolar quantities of the ligand acid and its sodium salt, were treated with measured quantities of excess H_3PO_2 at room temperature. Mixtures were subjected to cation-exchange chromatography[13] at 3 °C. Results of a representative separation are summarized in Table II. Between 88 and 95% of the total added chromium was recovered in the ion-exchange procedure.

All fractions eluted with $NaClO_4$ or $Th(ClO_4)_4$ solutions converted Ag(I) and Hg(II) to the respective metals and acidic MnO_4^- to Mn^{2+}.

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[1] (a) Sponsorship of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. (b) Present address: Department of Chemistry, Pittsburg State University, Pittsburg, KS 66762.

[2] Gould, E. S. *Acc. Chem. Res.* **1986**, *19*, 66.

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[8] (a) Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 94. (b) Bose, R. N.; Rajasekar, N.; Thompson, D. M.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 3349.

[9] Dockal, E. R.; Everhart, E. T.; Gould, E. S. *J. Am. Chem. Soc.* **1971**, *93*, 5661.

[10] Gould, E. S. *J. Am. Chem. Soc.* **1967**, *89*, 5792.

[11] In our hands, air oxidation of H_3PO_2 was not a problem. Solutions (ca. 10 M) were kept near 2 °C in loosely stoppered flasks for several weeks with loss of less than 1% of reducing titer.

[12] Mitchell, A. D. *J. Chem. Soc.* **1920**, 1322.

[13] Separations were carried out by using Bio-Rad 50W-X2 sulfonate resin,[4] H^+ form, 200–400 mesh, column length 5 cm, column capacity 2.0 mequiv. For estimation of molar absorbances 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.* (*U.S.*) **1952**, *48*, 414.

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Table II. Cation-Exchange Separation of Products from Reaction of Chromium(V) Chelate I with Hypophosphorous Acid[a]

fraction	eluant	ϵ_1[b]	λ_1[b]	ϵ_2	λ_2	Cr^{III}/P^{I}[c]	% Cr^V taken
1	H_2O	40	602	46	421	*d*	1.6
2	0.1 M $NaClO_4$	16	600	20	426	1.80	7.1
3	0.3 M $NaClO_4$	16	596	18	424	1.88	31.2
4	1.0 M $NaClO_4$	17	596	20	423	1.55	11.9
5	1.0 M $Th(ClO_4)_4$	16	596	16	418	1.03	39.9

[a] Chromium(V) (0.0050 M) was added as sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I); $H_2PO_2^-$ (0.025 M) was added as hypophosphorous acid. Reaction was carried out in solutions buffered with the parent hydroxy acid (0.2 M) and its sodium salt (0.2 M). Separations were carried out on sulfonate resin at 3 °C (see ref 13). [b] Absorption maxima (λ values) are in nm; ϵ values are in M^{-1} cm^{-1}. [c] Chromium was determined as CrO_4^{2-} (see ref 13); phosphorus(I) was determined iodometrically (see ref 18a). [d] Quantity of bound phosphorus(I) in this fraction, which contained a high concentration of unbound H_3PO_2, was not determined.

Table III. Representative Absorbance Data for Reduction of Chromium(V) with Hypophosphorous Acid (25 °C, μ = 1.0 M)[a]

time, s	Abs_{obsd}	$(Abs_{calcd})_B$[b]	$(Abs_{calcd})_{AC}$[c]	time, s	Abs_{obsd}	$(Abs_{calcd})_B$[b]	$(Abs_{calcd})_{AC}$[c]
0	0.758	0.758	0.757	240	0.278	0.281	0.269
20	0.863	0.893	0.848	260	0.223	0.239	0.220
40	0.893	0.930	0.892	280	0.181	0.203	0.179
60	0.883	0.907	0.893	300	0.143	0.173	0.145
80	0.853	0.848	0.859	320	0.118	0.148	0.118
100	0.783	0.770	0.799	340	0.096	0.127	0.097
120	0.718	0.688	0.723	360	0.081	0.110	0.081
140	0.633	0.604	0.639	380	0.070	0.095	0.069
160	0.553	0.525	0.553	400	0.061	0.083	0.059
180	0.477	0.453	0.471	420	0.053	0.074	0.052
200	0.403	0.388	0.395	440	0.050	0.066	0.047
220	0.333	0.331	0.328	∞	0.033		

[a] Chromium(V) (0.0049 M) was added as sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V); $[H_3PO_2]$ = 0.0602 M; the reaction solution was 0.40 M in 2-ethyl-2-hydroxybutyric acid and 0.20 M in its sodium salt. Data were taken at 510 nm in a 1.00-cm optical cell. [b] Calculated from biphasic eq 1, taking k as 0.0128 s^{-1}, ϵ_1 as 367 M^{-1} cm^{-1}, and A_0 as 0.758. [c] Absorbances calculated from autocatalytic sequence 3–6, taking k_1 and k_3 as 0.049 and 0.220 M^{-1} s^{-1}, the ratio k_2/k_4 as 1.90, and ϵ_1 as 352 M^{-1} cm^{-1}.

Moreover, each reduced I_3^- to I^- under conditions where hypophosphite, but not phosphite, was shown to react. The chromium(III)/phosphorus(I) ratio, determined iodometrically, was 1.5–1.8 for samples eluted with $NaClO_4$, but very near 1.0 for the slow-moving fraction which was eluted with $Th(ClO_4)_4$. Both ^1H and ^{13}C NMR spectra of the $NaClO_4$ eluates (but not of the $Th(ClO_4)_4$ eluate) exhibited methyl and methylene resonances characteristic of the carboxylate ligand. Electronic spectra were not affected by treatment with dilute $HClO_4$. The fraction of Cr(III) eluted with $Th(ClO_4)_4$ increased from 0.34 to 0.40 as the ratio of $[H_3PO_2]$ to $[Lig^-]$ in the generating mixture was increased from 0.063 to 0.25.

Kinetic Measurements and Estimation of Specific Rates. Reactions were monitored by following absorbance changes at 510 nm with a Cary 14 recording spectrophotometer. Total ionic strength was maintained near 1.0 M by addition of $LiClO_4$, and pH values were regulated by addition of measured quantities of 2-ethyl-2-hydroxybutyric acid (pK_A 3.32)[5] and its sodium salt. All runs were carried out at 25.0 ± 0.2 °C under "pseudo-first-order" conditions, most often with H_3PO_2 in at least tenfold excess.

When H_3PO_2 was taken in excess, a steep increase in absorbance, followed by a more gradual decrease, was observed. Depending upon reagent concentrations, maximal absorbances occurred 50–100 s after mixing. Profiles resembled those of systems in which the first-order generation of a strongly absorbing intermediate is followed by a first-order decay at a specific rate comparable to that of its formation. However, the usual iterative nonlinear least-squares refinement of absorbance data applicable to such sequences[4a,14] did not converge but indicated that the two specific rates were very nearly equal. An attempted refinement appropriate to this situation[4a,15] yielded calculated absorbances in only fair agreement with the observed; in particular, observed values during the last 25% of the reaction diminished more sharply than did the calculated values, suggesting an autocatalytic component. Close fits of the kinetic profiles to a sequence featuring autocatalysis by Cr(IV) (see Discussion) were achieved by using the computer program INTEGRAL to generate curves that were compared to those observed.[8b,16,17] Representative absorbances, pertaining to a single kinetic run, are compared in Table III with those calculated[16] by using eq 1 (applicable to an uncatalyzed biphasic system) and with those incorporating autocatalysis.

Results and Discussion

Stoichiometry experiments with H_3PO_2 in excess (Table I) indicate a net conversion which involves equimolar quantities of the two reagents and may thus be represented schematically

$$Cr^V + P^I \rightarrow Cr^{III} + P^{III} \qquad (2)$$

Of the chromium(III) products separated by cation-exchange chromatography (Table II), that eluted by water alone constitutes less than 2% of the total Cr(V) taken. Its high extinction coefficients (ϵ_{602} = 40, ϵ_{421} = 46 M^{-1} cm^{-1}) indicates that it is a bis chelate of Cr(III). It is not, however, the familar bis chelate $[(Lig)_2(H_2O)_2Cr^{III}]^+$, which is formed when Cr(V) complex I is reduced rapidly with metal-center reductants,[4,7] for its spectrum does not correspond to that of the diaquo derivative (ϵ_{585} = 48, ϵ_{415} = 61 M^{-1} cm^{-1}) and its elution behavior points to the absence of positive charge. It is most probably related to the diaquo chelate by replacement of one of the axial waters by a phosphite ligand. This component may be derived from a small fraction of the overall reaction proceeding by direct oxygen atom transfer from Cr(V) to hypophosphite, or it may be formed by a minor variant of the sequence of single-electron transactions proposed below.

The fraction eluted with $Th(ClO_4)_4$ has a charge greater than or equal to +2. Its Cr(III)/P(I) ratio (1.03) and its visible spectrum correspond closely to values reported[18a] for the hypo-

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(14) See, for example: (a) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1981; Chapters 4 and 5. (b) Bose, R. N.; Viola, R. E.; Cornelius, R. D. *J. Am. Chem. Soc.* **1984**, *104*, 3336.

(15) The relationship[4a] describing consecutive first order reactions with equal specific rates is

$$D_t = D_0e^{-kt} + \epsilon_1kA_0te^{-kt} - D_\infty e^{-kt}(1 + kt) + D_\infty \qquad (1)$$

where D_t is the total absorbance at time t, D_0 is the initial absorbance, k represents the two (equal) rate constants, A_0 is the initial reactant concentration, ϵ_1 is the extinction coefficient of the intermediate species, and D_∞ is the final absorbance.

(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 stoichiometry. Copies of the modified program may be obtained from RNB.

(17) (a) Margenau, H.; Murphy, G. M. *The Mathematics of Physics and Chemistry*; Van Nostrand: New York, 1943; p 469. (b) Wiberg, K. *Tech. Chem.* (*N.Y.*) **1974**, *6*, 764.

Table IV. Kinetic Parameters for the Reduction of Carboxyl-Bound Chromium(V) with Hypophosphite[a]

[Cr(V)], M	$[H_2PO_2^-]$, M	pH	$[Lig^-]$,[b] M	k_1,[c] $M^{-1}\ s^{-1}$	k_3,[c] $M^{-1}\ s^{-1}$	k_2/k_4[c]	$\epsilon_{Cr(IV)}$,[c,d] $M^{-1}\ cm^{-1}$
0.0049	0.0602	2.8	0.34	0.055	0.15	2.2	510
0.0049	0.0602	3.4	0.34	0.050	0.15	2.8	520
0.0049	0.0602	3.7	0.34	0.048	0.18	2.6	470
0.0049	0.0602	2.6	0.24	0.059	0.18	2.0	400
0.0049	0.0602	2.3	0.14	0.049	0.22	1.9	350
0.0038	0.0489	3.9	0.35	0.048	0.14	3.1	610
0.0037	0.0602	3.0	0.24	0.045	0.18	2.4	540
0.0073	0.1204	2.3	0.18	0.039	0.26	1.6	320

[a] Reactions were carried out at 25 °C; $\mu = 1.0$ M ($LiClO_4$) Chromium(V) was added as sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I). The pH was regulated by addition of measured quantities of 2-ethyl-2-hydroxybutyric acid (pK_A 3.32) and its sodium salt. [b] Ethyl-2-hydroxybutyrate. [c] Parameters obtained from best fit of integrated forms of the differential equations based on sequence 3–6 to the experimental kinetic curves (see text and ref 8b). [d] At 510 nm.

phosphito complex $(H_2PO_2)Cr(H_2O)_5^{2+}$. The fractions eluted with $NaClO_4$ have cation-exchange behavior corresponding to that of a +1 ion and are mixtures, for their spectra change measurably when the ratio of hypophosphite to carboxylate in the generating solution is altered. Their relatively low absorbances and the positions of their maxima suggest that they consist of unipositive derivatives of $(H_2O)_4Cr^{III}$ containing two carboxylato groups, two hypophosphito groups, or one of each. Attempts at further separation of these fractions were not successful.

In view of the recognized substitution-inert character of hexacovalent Cr(III),[18b] it may be reasonably supposed that the redistribution of ligands accompanying the net conversion of Cr(V) to Cr(III) has taken place before the formation of the latter oxidation state, i.e. at the Cr(IV) level.

Kinetic profiles at 510 nm (λ_{max} for Cr^V) indicate the rapid formation and subsequent decay of a strongly absorbing intermediate. The curves are similar in character to those obtained in the reductions of the Cr(V) chelate I with Fe^{2+} or VO^{2+},[4] which proceed through Cr(IV). In this case, however, patterns do not correspond acceptably to the superposition of first-order or pseudo-first-order processes, for perceptible acceleration during the later stages of reaction (Table III) points to a substantial degree of autocatalysis.

The autocatalytic sequence, (3)–(6), analogous to that proposed[8b] for the Cr(V)-HSO_3^- system, correlates our data satisfactorily. Intermediates are Cr(IV) and the $H_2PO_2^{\bullet}$ radical (abbreviated P^2).[19] Early in the reaction, only (3) and (4) are

$$Cr^V + P^1 \xrightarrow{k_1} Cr^{IV} + P^2 \qquad P^1 = H_2PO_2^- \tag{3}$$

$$Cr^V + P^2 \xrightarrow{k_2} Cr^{IV} + P_3 \qquad P^3 = H_2PO_3^- \tag{4}$$

$$Cr^{IV} + P^1 \xrightarrow{k_3} Cr^{III} + P^2 \tag{5}$$

$$Cr^{IV} + P^2 \xrightarrow{k_4} Cr^{III} + P^3 \tag{6}$$

significant, but as Cr(IV) accumulates, (5) becomes more important, boosting the level of the P^2 radical. The latter reacts more rapidly with Cr^V than with Cr^{IV}, but reaction with Cr^V regenerates Cr^{IV} via (4), resulting in autocatalysis.

Generation of the appropriate differential rate equations from sequence 3–6, application of the steady-state approximation to the radical P^2, and employment of the Runge–Kutta integration technique[17] (together with the reaction stoichiometry) were carried out in a manner parallel to that described[8b] for the reaction of Cr(V) with HSO_3^-. Values of k_1, k_3, and the ratio k_2/k_4 were allowed to vary. Integration then yielded the concentrations of each of the three chromium oxidation states and that of $H_2PO_2^-$ at 20-s intervals. Incorporation of extinction coefficients of Cr^V, Cr^{IV}, and Cr^{III} yielded calculated values for the optical density of the reaction mixture at each point.[20]

Values of the parameters k_1, k_3, k_2/k_4, and $\epsilon_{Cr(IV)}$ giving the closest agreement between calculated and observed absorbances are recorded in Table IV. Calculated absorbances obtained from a representative set of parameters are compared with experimental values in Table III. Absorbances, designated $(Abs_{calcd})_{AC}$, estimated on the basis of the autocatalytic mechanism are seen to lie much closer to the observed values than those, designated $(Abs_{calcd})_B$, calculated from a least-squares refinement based on a biphasic sequence without catalysis. The superiority of fit is most persuasive during the final stages of reaction.

The most novel facet of the present work is the indicated intermediacy of the hypophosphite radical, $H_2PO_2^{\bullet}$, (or its equivalent), a species that is derived, in the formal sense, from P(II). Although references to this oxidation state are scarce,[19] it almost certainly intervenes also in the oxidations of hypophosphite by such strong 1e acceptors as Ce^{IV}_{aq} and Co^{III}_{aq}.[21] Simplifications in our kinetic treatment preclude direct calculation of the concentrations of this radical during a given reaction, but a lower limit near 10^{-12} M at $t = 100$ s in the reaction described in Table III may be estimated[22] by assuming that k_2, the greatest of the four rate constants, cannot be greater than $10^{10}\ M^{-1}\ s^{-1}$, the diffusion-controlled limit for bimolecular reactions in water.[14a]

The approximate nature of our refinement procedure dictates caution in considering small changes in the derived parameters as the reaction conditions are altered. Nevertheless it seems clear that the Cr^{IV}–P^1 reaction (k_3), but not the Cr(V)–P^1 reaction (k_1), is retarded by excess ligand anion, Lig^-. This dependency is less steep than that described by an inverse proportionality, suggesting participation of Cr^{IV} in a rapid ligation equilibrium, with the more fully carboxylate-coordinated species somewhat less active than that with fewer carboxyls. The observed variation in $\epsilon_{Cr(IV)}$ with $[Lig^-]$ tells the same story, for the absorbance of this intermediate is greatest at high $[Lig^-]$ and low $[H_2PO_2^-]$. This dismantling of the ligand sheath originally about Cr(V) and the scission of

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(18) (a) Espenson, J. H.; Binau, D. E. *Inorg. Chem.* **1966**, *5*, 1365. These workers record λ_{max} values for this complex as 596 ($\epsilon = 15.6$) and 420 ($\epsilon = 17.3$) nm. (b) See, however: Ogino, H.; Masuko, A.; Ito, S.; Miura, N.; Shimura, M. *Inorg. Chem.* **1986**, *25*, 708.

(19) Reports dealing with derivatives of dipositive phosphorus are relatively uncommon. See, for example: (a) Baudler, M. *Z. Naturf.* **1959**, *14B*, 404. (b) Cordes, H.; Warkehr, E. *Z. Phys. Chem.* **1965**, *46*, 24. (c) Spandua, H.; Beyer, A. *Naturwissenschaften* **1959**, *46*, 400. (d) Toy, A. D. F. In *Comprehensive Inorganic Chemistry*; Bailar, J. C., Jr., Ed.; Pergamon: Oxford, England, 1973; Vol. 2, p 440.

(20) Values of $\epsilon_{Cr(III)}$ and $\epsilon_{Cr(V)}$ were taken from the final and initial absorbances of the reaction mixture and were kept fixed. The value of $\epsilon_{Cr(IV)}$ was allowed to vary.

(21) A number of oxidations of hypophosphite have been studied in detail, but these generally involve 2e oxidants or those for which there is ambiguity concerning the nature of the initial step (e.g., I_2 or CrO_4^{2-}). See, for example: (a) Haight, G. P.; Rose, M.; Preer, J. *J. Am. Chem. Soc.* **1968**, *90*, 4809. (b) Cooper, J. *J. Phys. Chem.* **1970**, *74*, 955. (c) Griffith, R. O.; McKeown, A.; Taylor, R. P. *Trans. Faraday Soc.* **1934**, *30*, 530. (d) Jenkins, W. A.; Yost, D. M. *J. Inorg. Nucl. Chem.* **1959**, *11*, 297.

(22) Application of the steady-state approximation to P^2 in sequence 3–6 yields (7).

$$[P^2] = \frac{k_1[Cr^V][P^1] + k_3[Cr^{IV}][P^1]}{k_2[Cr^V] + k_4[Cr^{IV}]} \tag{7}$$

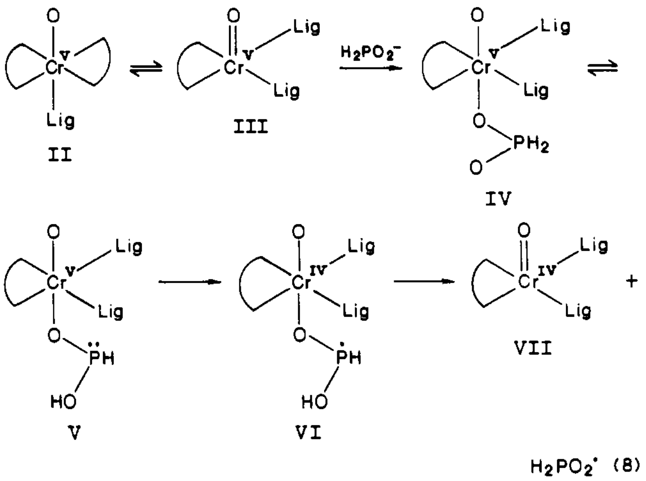
At $t = 100$ s in this reaction (described in Table III), $[P^1]$ is calculated as 0.058 M, $[Cr^V]$ as 0.0020 M, and $[Cr^{IV}]$ as 0.00135 M. The estimated upper limits of k_2 (10^{10}) and k_4 ($5 \times 10^9\ M^{-1}\ s^{-1}$) may be utilized in conjunction with k_1 (0.049) and k_3 ($0.22\ M^{-1}\ s^{-1}$) to obtain the indicated lower limit for $[P^2]$.

the chelate rings do not occur during the more rapid reductions of Cr(V) with 1e metal-center reductants.[4,8a] Ligand-exchange processes are favored here by the sluggishness of the Cr^{IV}–P^I reaction[23] and by the high concentration of $H_2PO_2^-$ used to allow the initial reaction to proceed at a convenient rate. Partition of the resulting Cr(III) products between hypophosphite-bound and carboxylate-bound species probably reflects the same equilibration process, for the ratio of the two types of ligation rises as the ratio $[H_2PO_2^-]/[Lig^-]$ in the reaction mixture is increased.

Jenkins and Yost[21d] have emphasized the importance of intramolecular proton transfer (P–H to O–H) in hypophosphite in determining its rates of oxidation by a variety of reagents. This transfer, however, proceeds with a half-life period greater than 2 days in the absence of Cr(V) in media similar to ours. Although there are other possibilities, the relatively high specific rates at which $H_2PO_2^-$ reacts with both Cr^V (k_1) and Cr^{IV} (k_3) in this study may then reasonably be attributed to preliminary coordination of the reductant to the strongly acidic Cr^V or Cr^{IV} center, thus mobilizing the P-bound protons.[24,25]

If, as we suspect, the Cr^V–P^I reaction proceeds through an oxygen-bridged intermediate, the bridge must arise from hypophosphite, rather than from the Cr(V) chelate, for there is no site on $H_2PO_2^-$ that can accommodate an incoming donor atom. An earlier study[4b] has shown that the Cr(V) chelate taken here undergoes additional ligation to form complex II (K_{assn} 51 M^{-1}) in the presence of an excess of the parent carboxylate anion; in the buffer systems used, only 5–12% of the added Cr(V) is present as the 5-coordinate species I. Loss of the axial carboxyl group from II would leave a place for ligation by $H_2PO_2^-$, but such a path should lead to values of k_1 that are dependent on $[Lig^-]^{-1}$, contrary to what is observed.

Our findings are consistent with sequence 8, in which breakage of one of the chelate rings in II (but not the departure of carboxylate) allows attachment of hypophosphite to form intermediate IV. The function of this intermediate is simply to hold the Cr^V and P^I centers in proximity; the bridging oxygen is not transferred.



The tautomeric shift IV → V is then facilitated by the nearby Cr^V. This leaves an exposed electron pair on phosphorus and precedes the act of electron transfer (V → VI).

Although it is conceivable that the Cr(IV)–P(II) intermediate VI, formed via internal electron transfer, might undergo a second act of transfer, yielding Cr(III)-bound phosphorus(III), the nature of the predominant Cr(III) products requires that the principal fate of VI is heterolysis to the $H_2PO_2^•$ radical (for which Cr^V and Cr^{IV} then compete in reactions 4 and 6) and a coordinatively unsaturated Cr^{IV} species, which, prior to further reduction, undergoes breakage of the chelate rings and the ligand redistribution reflected in the mix of Cr(III) products observed. The Cr(IV)–$H_2PO_2^-$ reaction (eq 3) which also appears to involve a bridged intermediate, may utilize a similar path, but one in which the participants are devoid of the chelate rings present in the Cr(V) reactant.

When autocatalysis in the Cr(V)–HSO_3^- system, leading to its "clocklike" character, was first described,[2,8b] it appeared that the proposed catalytic sequence might apply uniquely to the S(IV) reductant chosen. It is now evident, however, that a closely analogous mechanism operates not only in the Cr(V)–$H_2PO_2^-$ reaction at hand, but also in the reductions of Cr(V) with such diverse species as iodide, thiocyanate, and ascorbic acid.[26] Whether similar sequences can be established in the reductions of additional metal-center oxidants remains an open question.

Acknowledgment. The authors are grateful to Professor J. H. Espenson for valuable discussions.

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(23) For additional examples of slow reactions passing through Cr(IV) in which the ligand environment about that center is altered, see: (a) Plane, R. A.; Taube, H. *J. Phys. Chem.* **1952**, *56*, 33. (b) Ogard, A. E.; Taube, H. *Ibid.* **1958**, *62*, 357. (c) Rajasekar, N.; Gould, E. S. *Inorg. Chem.* **1983**, *22*, 3798.

(24) The ratios $k_{Cr(IV)}/k_{Cr(V)}$ for reactions of these oxidation states with $H_2PO_2^-$ (k_3/k_1) and with $H_2PO_2^•$ (k_4/k_2) are seen to lie below the estimated[25] lower limit ($k_{Cr(IV)}/k_{Cr(V)} > 20$) for outer-sphere reductions of these states by $Ti(OH)^{2+}$ in a similar medium. However, no obvious mechanistic inference may be drawn from this discrepancy since the predominant Cr(IV) species in this study are different from that in the Cr(V)–Ti(III) system.

(25) Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 2645.

(26) Ghosh, S. K., unpublished experiments, 1986.

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Electron Transfer. 83. Reductions of Unsaturated Esters with Vitamin B_{12s} (Cob(I)alamin)[1]

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The diesters of maleic and fumaric acid are rapidly reduced to succinic esters by vitamin B_{12s} (cob(I)alamin) in aqueous media. The dimethyl ester of acetylenedicarboxylic acid is reduced in two stages: the first (very rapid) stage yields a fumaric ester, which is then converted more slowly to succinate. Reactions are first order each in redox partners and are fastest at highest acidities. Kinetic behavior is consistent with the partition of B_{12s} into an inactive nonprotonated, a moderately reactive monoprotonated, and a very reactive diprotonated form. It is proposed that the latter is a Co–H species, having hydride-like character, which is oxidized at a specific rate $>10^4$ M^{-1} s^{-1} (25 °C). The relative reactivities of acetylenic and olefinic esters (rate ratios 10^4–10^5) indicate that these reactions, like those of the parent diacids, are heterolytic (2e) rather than homolytic (1e) in nature. The reduction of acetylenedicarboxylate to fumarate is a net trans addition for which an olefinic–carbanion intermediate, which may maintain its geometric configuration, is suggested.

The action of strong reducing agents on vitamin B_{12} yields B_{12r} (cob(II)alamin), which may be further converted to vitamin B_{12s} (cob(I)alamin).[2] This cobalt(I) complex reduces a number of diverse organic species in solution,[3] leading to its expanding ap-