inert thiolate complex that is stable to oxidation and transchelation in vivo.[34] As demonstrated by UV–visible and Raman spectroscopy, the TcO^{3+} core is bound in square-based-pyramidal geometry to give $TcOS_4^-$ stoichiometry. As many as seven Tc atoms were observed to exchange into ZnMT, and Tc–S–Tc bridging is postulated to accommodate the $TcOS_4^-$ stoichiometry.

Metallothionein has functional groups appropriate for its conjugation to biologically important molecules. MT's conjugated to monoclonal antibodies maintain their immunoreactivity.[34] The kinetics of exchange of Tc(V) into MT are rapid and will allow efficient radiolabeling of MT-antibody conjugates with ^{99m}Tc immediately before use. The application of these ^{99m}TcMT-labeled MAb's in diagnostic nuclear medicine is ongoing.

Acknowledgment. We thank Pamela Mabrouk (MIT) for acquiring the Raman spectroscopy data and Alan Davison (MIT) for many helpful discussions. We thank Thomas H. Tulip for his critical reading of the manuscript.

Registry No. Cys, 52-90-4.

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[34] Brown, B. A.; Drozynksi, C. A.; Dearborn, C. B.; Hadjian, R. A.; Liberatore, F. L.; Tulip, T. H.; Tolman, G. L.; Haber, S. B. *Anal. Biochem.*, in press.

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Electron Transfer. 94. Internal Redox in Cobalt(III)-Bound Hypophosphite[1]

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The hypophosphito derivative of Co^{III}, $(NH_3)_5CoO_2PH_2^{2+}$, decomposes in basic media, yielding Co(II) quantitatively along with a 1:1 mixture of hypophosphite and phosphite. When this reaction is carried out in 0.014–0.60 M OH^- in the presence of Na_4EDTA, a strongly absorbing intermediate ($\epsilon_{295} = 1.1 \times 10^3$ M^{-1} cm^{-1}) is formed and then undergoes decay. Kinetic profiles are consistent with a pair of consecutive pseudo-first-order processes, each of which is also very nearly first order in OH^-. Isotopic labeling experiments with the $-PD_2$ analogue of the complex indicate a kinetic isotope effect, k_{PH_2}/k_{PD_2}, of 4.0 ± 0.5 for the first step in the sequence and 2.0 ± 0.2 for the second. Our results suggest that the reaction is initiated by removal of a P-bound proton from the hypophosphite ligand, forming conjugate base I. The latter then reacts with a second OH^- and undergoes a hydride shift from phosphorus to cobalt(III), generating a cobalt(I) species, which rapidly reduces an additional molecule of the Co(III) reactant to Co(II). If the reaction is carried out in the presence of a second cobalt(III) oxidant, the latter competes with the hypophosphito complex for the Co(I) intermediate, lowering the yield of free $H_2PO_2^-$. From the ratio of phosphite to hypophosphite, the relative reactivities of the external "trap" and the hypophosphito complex toward Co(I) may be estimated. The formato complex of $(NH_3)_5Co^{III}$ reacts over twice as rapidly as the analogous pyridine complex, a reversal of the selectivity observed in outer-sphere reduction series, thus implying the use of an inner-sphere path in the Co(I)–formato reaction. The complex $(NH_3)_5Co(NCS)^{2+}$ is an especially efficient trap for Co(I), reflecting the unusually soft character of the Co(I) center. The same transformation of the hypophosphito complex, when carried out at pH 8.7–11 in the absence of added NaOH, generates a straightforward exponential profile without indication of an intermediate and exhibits a kinetic isotope effect of only 2.1–2.3, indicating that the predominant mechanism under these conditions is different from that operating in the more strongly basic systems here examined.

The hypophosphito derivative of $(NH_3)_5Co^{III}$ may be prepared and stored without difficulty.[2,3] When treated with basic species in aqueous media, it undergoes an internal redox process, yielding Co(II) and equimolar quantities of free phosphite and hypophosphite (eq 1). It was proposed[3] that this transformation, which

$$2[(NH_3)_5Co(OPH_2O)]^{2+} + H_2O \xrightarrow{B:} 2Co^{II} + HPO_3^{2-} + H_2PO_2^- + 3NH_4^+ + 7NH_3 \quad (1)$$

does not proceed with uncoordinated hypophosphite or with bound or unbound phosphite, is initiated by a hydroxide-induced hydride shift from P(I) to Co(III), yielding a Co(I) intermediate, which then rapidly reduces unreacted Co(III) to Co(II).

The reaction appears to exhibit a straightforward kinetic picture at pH 9–11 but becomes complex in more highly basic solutions, passing through a strongly absorbing intermediate, although the net stoichiometry is unchanged. The present report deals with this reaction under the latter conditions. In addition to our attempt to address this complexity, we report experiments designed to bear upon the selectivity of the Co(I) intermediate toward several Co(III) oxidants.

Experimental Section

Physical Methods. ^1H and ^{31}P NMR spectra were recorded on a GN300 spectrometer using DSS and 85% external H_3PO_4 as chemical shift standards.[4] Infrared spectrometry was performed on a Perkin-Elmer 283 instrument. Kinetic measurements and UV–vis spectra were obtained on either a Beckman UV 5260 or Perkin-Elmer Lambda 4B spectrophotometer.

Materials. The $(NH_3)_5Co^{III}$ complex of hypophosphorous acid, $[(NH_3)_5CoO_2PH_2][ClO_4]_2$, and its $-PD_2$ analogue were prepared as described;[3] chromatographic purification of the deuteriated complex was carried out in D_2O rather than in H_2O. The deuterio derivative was found to contain 6% $[CoO_2PHD]^{2+}$ by ^{31}P NMR.[5] Additional $(NH_3)_5Co^{III}$ derivatives of H_2O,[6] formate,[7] pyridine,[8] and thiocyanate (N-bound)[9] were prepared by literature methods. Lithium perchlorate[10] was doubly recrystallized and Na_4EDTA (Aldrich) recrystallized once before use. Stock solutions of carbonate-free NaOH were standardized against potassium hydrogen phthalate (primary standard grade).

General Considerations. All solutions were rigorously deaerated prior to use, and all transfers were done by syringe under N_2. Determination of phosphite and hypophosphite in solutions containing both states utilized the iodometric method of Jones and Swift.[11]

Labeling Studies. Reaction of the hypophosphito complex (0.0125 M) with acetate buffer (0.015 M, pH 4) in D_2O was monitored by ^1H NMR.

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

[2] Sisley, M. J.; Jordan, R. B. *Inorg. Chem.* **1987**, *26*, 273.

[3] Linn, D. E., Jr.; Gould, E. S. *Inorg. Chem.* **1987**, *26*, 3442.

[4] "DSS" = $(CH_3)_3Si(CH_2)_2SO_3^-Na^+$; upfield singlet at $\delta = 0$. ^1H spectra were recorded with frequency 300.521 MHz, spectral width 4 kZh, pulse width 5 μs, and repetition time 5.3 s. Respective parameters for ^{31}P spectra were 121.652 MHz, 16 kHz, 3 μs, and 9.1 s. Each spectrum was generated from 32 768 data points.

[5] Infrared spectrometry (Nujol): ν_{P-H} 2397 cm^{-1}; ν_{P-D} 1710 cm^{-1}. The NMR characterization of these complexes has been described.[3]

[6] Goli, U. B.; Gould, E. S. *Inorg. Chem.* **1984**, *23*, 221.

[7] Gould, E. S.; Taube, H. *J. Am. Chem. Soc.* **1964**, *86*, 1328.

[8] Ram, M. S.; Gould, E. S. *Inorg. Chem.* **1983**, *22*, 2457.

[9] Carlin, R. L.; Edwards, J. O. *J. Inorg. Nucl. Chem.* **1958**, *6*, 217.

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

[11] Jones, R. T.; Swift, E. H. *Anal. Chem.* **1953**, *25*, 1272.

0020-1669/88/1327-3140$01.50/0

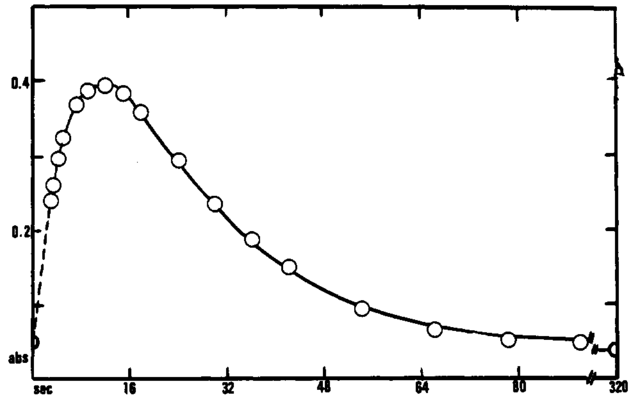

Figure 1. Kinetic profile at 320 nm for the base-induced internal redox reaction of $(NH_3)_5CoO_2PH_2^{2+}$ (0.0020 M) at 25 °C and $\mu = 3.0$ M ($LiClO_4$). The reaction was carried out under N_2 in a medium 0.20 M in NaOH and 0.14 M in Na_4EDTA. The solid line is the experimental curve, whereas the circles indicate absorbances calculated from eq 3, with k_0 and k_1 taken as 0.063 and 0.027 s^{-1} and ϵ_I as 355 $M^{-1}\ cm^{-1}$. The optical path length was 1.00 cm.

Table I. Kinetic Data for the Internal Redox Reactions of the Hypophosphito Derivative of $(NH_3)_5Co^{III}$, As Induced by Hydroxide[a,b]

$[OH^-]$, M	10^2k_0, s^{-1}	10^2k_1, s^{-1}	ϵ_I(320 nm), $M^{-1}\ cm^{-1}$
	A. Co(III)–O_2PH_2 Reaction		
0.014	0.84 (0.04)	0.224 (0.007)	*c*
0.025	1.52 (0.07)	0.40 (0.01)	*c*
0.050	2.33 (0.07)	0.74 (0.01)	*c*
0.10	4.6 (0.1)	1.15 (0.02)	296 (4)[d]
0.20	6.3 (0.3)	2.7 (0.1)	355 (12)[d]
0.30	8.0 (0.4)	3.6 (0.2)	281 (10)[d]
	B. Co(III)–O_2PD_2 Reaction		
0.10	1.04 (0.02)	0.56 (0.01)	*c*
0.20	1.45 (0.02)	1.19 (0.02)	*c*
0.30	2.35 (0.02)	2.23 (0.02)	*c*
0.40	2.47 (0.02)	2.27 (0.02)	*c*
0.50	4.7 (0.3)	2.20 (0.01)	286 (12)[d]
0.60	5.0 (0.3)	3.5 (0.2)	291 (10)[d]

[a] Reaction conditions: $[Co^{III}]_{init} = 0.001$–$0.002$ M; $[Na_4EDTA] = 0.14$ M; $\mu = 3.0$ M ($LiClO_4$); $T = 25$ °C; reactions carried out under N_2. [b] Values for rate constants were obtained by nonlinear least-squares refinements according to eq 3 in the text. Values in parentheses are estimated standard deviations. [c] The value of ϵ_1 was fixed at 290 $M^{-1}\ cm^{-1}$ in these refinements; k_0 and k_1 were allowed to vary. [d] Values of k_0, k_1, and ϵ_1 were allowed to vary in these refinements.

Table II. Component Kinetic Parameters for the Internal Redox Reaction of the Hypophosphito Derivative of $(NH_3)_5Co^{III}$, As Induced by Hydroxide[a] ($k_{obsd} = a[OH^-] + b$)

complex		10^2a, $M^{-1}\ s^{-1}$	10^2b, s^{-1}
Co^{III}–O_2PH_2	k_0	26.3 ± 1.9	0.89 ± 0.21
	k_1	12.3 ± 0.4	0.07 ± 0.04
Co^{III}–O_2PD_2	k_0	7.8 ± 0.8	0.04 ± 0.27
	k_1	5.3 ± 0.6	0.15 ± 0.21

[a] Reaction conditions are given in Table I. Specific rates k_0 and k_1 pertain to the growth and disappearance of the intermediate absorbing at 295 nm (see eq 3 and text). Parameters *a* and *b* were obtained by least-squares refinements of values of k_0 and k_1 in Table I, with individual rate constants weighted in inverse proportionality to the square roots of their values.

Rapid exchange ($t_{1/2} < 5$ min) of ammine protons with solvent deuterium was observed. Consequently, under the conditions employed ion our kinetic studies (see below), Co(III)-bound ND_3 ligands may be considered to be quickly converted to coordinated NH_3 groups in H_2O.

Reaction of the hypophosphite complex (0.11 M) and Na_4EDTA (0.41 M) in D_2O was monitored by ^{31}P NMR. Neither the –PHD nor the –PD_2 complex was found to accumulate appreciably over the course of the reaction (12 h).[12] In accordance with eq 1, the ^{31}P NMR spectrum of the resulting solution indicated the presence of nearly equal amounts of two phosphorus species,[13,14] although peaks were markedly broadened due to the presence of paramagnetic Co(II).

Kinetic Studies. Reactions were followed by measuring absorbance changes at 320 nm. The total ionic strength was maintained at 3.0 M by the addition of $LiClO_4$. Stock solutions of the hypophosphito complex were prepared in water, whereas those of its deuteriated analogue were prepared in dilute acetate buffer (pH 4; 0.15 M).[15] To ensure complete N-protonation of the ammine ligands in the –PD_2 complex, stock solutions of this derivative were allowed to incubate for 10 min in buffer before mixing with base.

When NaOH and Na_4EDTA were added in large excess, a rapid increase in absorbance was observed, reflecting the formation of an intermediate absorbing preferentially at 295 nm ($\epsilon = 1.1 \times 10^3\ M^{-1}\ cm^{-1}$) with a minimum at 275 nm ($\epsilon = 7 \times 10^2\ M^{-1}\ cm^{-1}$). Depending on reaction conditions, maximal absorbance occurred between 12 and 200 s after mixing.[16] Rate constants were evaluated by treating the kinetic profiles as successive pseudo-first-order processes according to (2).

$$Co^{III}\text{–}P^{I} \xrightarrow{k_0} \text{intermediate} \xrightarrow{k_1} \text{products} \qquad (2)$$

Absorbance–time profiles may be described by eq 3,[17] where *D* and D_∞

$$D = A_0\epsilon_A e^{-k_0t} + \frac{\epsilon_I A_0 k_0}{k_1 - k_0}(e^{-k_0t} - e^{-k_1t}) + \frac{D_\infty}{k_1 - k_0}(k_0e^{-k_0t} - k_1e^{-k_0t}) + D_\infty \qquad (3)$$

are the absorbances at time *t* and at infinite time, ϵ_A and ϵ_I are the extinction coefficients of the starting material ("Co^{III}–P^I") and the intermediate, and A_0 is the original concentration of Co(III). The two pseudo-first-order rate constants, k_0 and k_1, were evaluated by using an iterative nonlinear least-squares refinement.[18] Absorbances calculated from the final adjusted parameters, k_0, k_1, and ϵ_I, for a representative run are compared to the observed values in Figure 1.

In addition, a number of experiments were performed in which the Co(III)–hypophosphito complex was allowed to decompose in the presence of a measured amount of a second cobalt(III) derivative. These reactions were carried out in 0.41 M Na_4EDTA, a medium in which the decomposition of the hypophosphite complex has been found[3] to allow pseudo-first-order kinetics. Determination of the phosphite concentration[11] at the conclusion of the reaction allowed estimation of the relative rates at which the two competing Co(III) oxidants consumed the proposed (Co^I) intermediate.[19]

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(12) From the multiplicity patterns for these two species[3] it is estimated that, after 1 half-life (90 min), >8% CoO_2PHD and >4% CoO_2PD_2 would have been detectable.

(13) The ^{31}P NMR spectrum in D_2O shows $\delta = 8.4$ for phosphite ($J_{PH} = 550$ Hz) and $\delta = 1.8$ for hypophosphite. The latter resonance was broadened, implying that a smaller coupling, i.e. $J_{PD} = 80$ Hz, was present. Fre hypophosphite has been observed to undergo slow H/D exchange with solvent.[14]

(14) Fratiello, A.; Anderson, E. W. *J. Am. Chem. Soc.* **1963**, *85*, 519.

(15) The redox reaction of interest was not affected by the buffer, which was present at concentrations much lower than that of the added base.

(16) Attempts were made to follow the more rapid reactions with stopped-flow spectrophotometry, using a Durrum-Gibson instrument. Despite several modifications of technique, satisfactory reproducibility between runs was not achieved. We suspect that catalytic effects arising from traces of oxidized iron (solubilized in part by the EDTA) in the valve system are complicating the picture here.

(17) See, for example: (a) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1981; Chapter 4. (b) Wilkins, R. G. *The Study of Kinetics and Mechanisms of Reactions of Transition Metal Complexes*; Allyn and Bacon: Boston, MA, 1974; pp 20–24. (c) Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 2832.

(18) A nonlinear least-squares program (written in Basic for the Apple II computer) was kindly provided by Professor J. H. Espenson and was used with minor modification. Trial values for the two rate constants were obtained graphically from biphasic plots,[17b] and the parameters A_0, ϵ_A, and *D* were held invariant. Refinements in which k_0, k_1, and ϵ_I were allowed to float converged for the more rapid runs. For the slower runs, ϵ_I at 320 nm was held at 290 $M^{-1}\ cm^{-1}$ (the value obtained from the rapid runs), and the rate constants were allowed to vary. Individual data points were unweighted. Attempted refinements of the kinetic data in terms of more complex sequences involving four or more adjustable parameters yielded marginal improvements in the quality of fit, but interrelationships between parameters associated with the various runs did not lead to a reasonable mechanistic picture.

(19) The salts $Co(NH_3)_6(ClO_4)_3$ and $CoCl(NH_3)_5(ClO_4)_2$ were not sufficiently soluble in the medium at hand for use in such "trapping" experiments, whereas experiments with the very soluble complex *cis*-α-$Co(trien)Cl_2^+Cl^-$ (Sargeson, A. M.; Searle, G. H. *Inorg. Chem.* **1967**, *6*, 787) were complicated by the rapid hydrolysis of this oxidant.

Table III. Kinetic Deuterium Isotope Effects, k_{PH_2}/k_{PD_2}, for the Internal Redox Reaction of the Hypophosphito Derivative of $(NH_3)_5Co^{III}$, As Induced by Hydroxide[a]

$[OH^-]$, M	$(k_0)_{PH_2}/(k_0)_{PD_2}$	$(k_1)_{PH_2}/(k_1)_{PD_2}$
0.10	4.4	2.0
0.20	4.4	2.3
0.30	3.4	1.6

[a] Reaction conditions are specified in Table I. Specific rates k_0 and k_1 pertain to the growth and disappearance of the reaction intermediate absorbing at 295 nm (see eq 3 and text).

Results and Discussion

In all experiments the concentrations of OH^- and EDTA greatly exceed that of the Co(III) complex and are thus considered to remain constant within each run. The biphasic kinetic curves are analyzed as superpositions of two consecutive pseudo-first-order processes,[17] reflecting the growth and disappearance of an intermediate. The usual ambiguity pertaining to the association of the rate constants with such components[17a] is resolved in the present systems by assigning the greater rate of the growth of the transient and the lesser rate to its consumption. On the basis of this choice, the calculated value of ϵ_I is found to remain nearly constant (295 ± 20 M^{-1} cm^{-1} at 320 nm) for runs at varying basicities, whereas this is not the case with the reverse assignment.

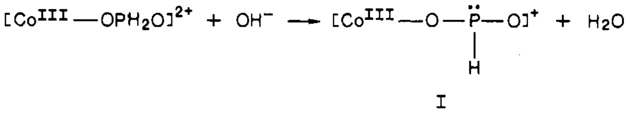
Kinetic data for reactions of the hypophosphito complex and for its $-PD_2$ analogue are summarized in Table I. Although kinetic parameters obtained from refinements of data conforming to these biphasic curves must be considered significantly less precise than those from simple exponential traces, it is clear that both k_0 and k_1 rise with increasing basicity. Least-squares analyses of k values in terms of (4) lead to the kinetic parameters in Table II.

$$k_{obsd} = a[OH^-] + b \qquad (4)$$

Since b, the $[OH^-]$-independent term, is seen to be statistically indistinguishable from zero for two of these parameters and marginal for a third, rates of both reaction components may be taken to be very nearly proportional to $[OH^-]$.

In addition, direct comparison of rates for the hypophosphito complex and for its $-PD_2$ analogue is possible in the range 0.1–0.3 M OH^- (Table III). The kinetic deuterium isotope effect, k_{PH_2}/k_{PD_2}, is found to be 4.0 ± 0.5 for the initial reaction yielding the intermediate and 2.0 ± 0.2 for the step in which the intermediate is consumed.

The $[OH^-]$ dependence and the large isotope effect associated with the initiation are consistent with rate-determining proton removal from phosphorus:



$$[Co^{III}-OPH_2O]^{2+} + OH^- \longrightarrow [Co^{III}-O-\underset{\underset{H}{|}}{\ddot{P}}-O]^+ + H_2O \qquad (5)$$

If it is assumed that we are dealing with a pure zero-point energy effect, an upper limit may be estimated by using (6),[20a] where

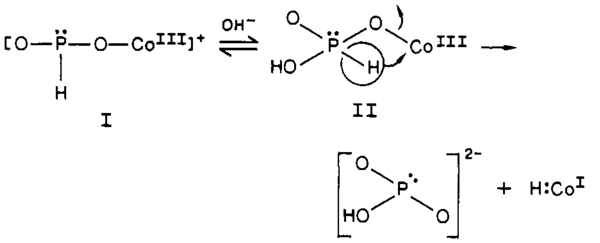
$$k_H/k_D = \exp\left\{\frac{hc}{2kT}(\nu_{P-H} - \nu_{P-D})\right\} \qquad (6)$$

ν values refer to the stretching frequencies of the bonds to that hydrogen being removed. Substitution of measured[5] P–H and P–D frequencies yields k_H/k_D = 5.3, a ratio only slightly higher than that observed for k_0. Moreover, the latter falls within the range applicable to measurably slow proton transfers near room temperature (3.0–9.8).[20b] On this basis we may reasonably take the observed intermediate to be the deprotonated monocation I.

Deprotonation of the phosphorus in the hypophosphito complex markedly shifts its charge-transfer band from 199 nm ($\epsilon = 1 \times 10^3$ M^{-1} cm^{-1}), probably reflecting the increased electron availability associated with the Co-bound oxygen when the ligand is in the conjugate base form. No shift of this magnitude is noted when the analogous bisphosphito complex, $(NH_3)_5Co(OPHO_2H)^{2+}$, is treated with base,[3] for this ligand loses its proton from the more distant OH group.[21]

The isotope effect assigned to the decay of the intermediate (k_1) lies close to those reported for hydride-transfer reactions from C–H species (1.8–1.9)[22] and is thus compatible with the hydride shift sequence proposed earlier.[3] However, this step, like the first, is first order in OH^-, suggesting the operation of a preequilibrium process, which does not, however, involve P-bound hydrogen.

Two possibilities come to mind. The first is attachment of OH^- to phosphorus in I, yielding intermediate II (with an expanded octet about phosphorus), within which a hydride shift to Co(III) yields a species that may be considered as either a hydride complex of Co(III) or a protonated form of Co(I):[23]

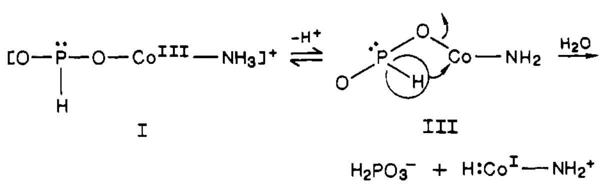


(7)

$$H{:}Co^I + [Co^{III}-OPH_2O]^{2+} \xrightarrow{\text{rapid}} 2Co^{II} + H_3PO_2 \qquad (8)$$

On the basis of known Co(III)–Co(I) reactions,[24] we would anticipate that the latter intermediate will reduce unreacted Co(III) very rapidly (reaction 8), accommodating the observed stoichiometry.

Alternatively, a proton may be removed from a ligated ammonia, yielding the conjugate base III. Here, it may be argued



(9)

that subsequent molecular rearrangement, which includes the analogous hydride shift, is favored by weaking of the Co–O bond by the $-NH_2$ group in much the same manner as deprotonation of Co(III)-bound ammonia in $Co(NH_3)_5X^{2+}$ facilitates departure of X^- in base-catalyzed hydrolysis.[25] This hydride shift would be followed by the analogous Co(III)–Co(I) comproportionation (eq 8). We favor the second of these paths since it does not require attack by OH^- at electron-rich phosphorus.

Since the Co(III)–Co(I) reaction (8) occurs after the rate-determining steps, the usual kinetic experiments are uninformative as to its rate. However, "trapping" studies, in which the hypo-

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(20) (a) See, for example: Melander, R.; Saunders, W. H., Jr. *Reaction Rates of Isotopic Molecules*; Wiley-Interscience: New York, 1980; pp 24–26. Among the several factors that can lower the ratio k_H/k_D are nonlinearity in the transition state and a substantial heavy-atom contribution to the reaction coordinate. Much higher values of this ratio are thought, in large part, to reflect tunneling effects. Equation (6) is generally inapplicable to reactions at elevated temperatures. (b) More O'Ferrall, R. A. In *Proton Transfer Reactions*; Caldin, E. F., Gold, V., Eds.; Chapman and Hall: London, 1975; Chapter 8.

(21) The charge-transfer band from the biphosphito complex shifts only from 193 to 205 nm on treatment with 0.2 M NaOH.

(22) See, for example: (a) Bartlett, P. D.; McCollum, J. D. *J. Am. Chem. Soc.* **1956**, *78*, 1441. (b) Wiberg, K. B. *J. Am. Chem. Soc.* **1954**, *76*, 5371. (c) Saunders, W. H., Jr. *Tech. Chem.* (*N.Y.*) **1974**, *6*, 222.

(23) See, for example: Pillai, G. C.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 4740.

(24) (a) Ryan, D. A.; Espenson, J. H.; Meyerstein, D.; Mulac, W. A. *Inorg. Chem.* **1978**, *17*, 3725. (b) Balasubramanian, P. N.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 1791.

(25) See, for example: Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*, 2nd ed.; Wiley: New York, 1967; p 177.

(26) The kinetic relationships here are rather more complex than those for the more usual competition experiments, in which both competing species are present in large (and nearly constant) excess over that reagent generating the reactive intermediate.

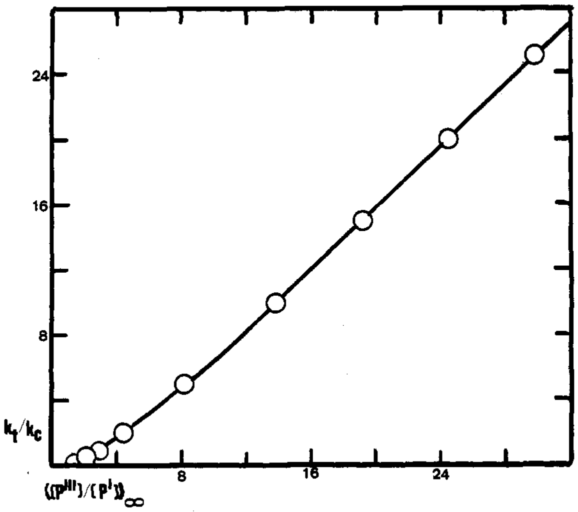

Figure 2. Relationship between the ratio of phosphite to hypophosphite, $[P^{III}]/[P^I]$, in the reaction product and the relative rates, k_t/k_c, at which the proposed Co(I) intermediate reacts with the "trapping reagent", Co^3X, and the hypophosphito complex, Co^3P^1 (see eq 10, 8′, and 11 in the text). Values of $[P^{III}]$ and $[P^I]$ were obtained by numerical integration of differential equations 13 and 15, with k_h taken as 1.0×10^{-4} s^{-1} and equal initial concentrations of Co^3P^1 and Co^3X.

phosphito complex decomposes in the presence of a second Co(III) derivative, allow us to compare the rates at which the Co(I) intermediate reacts with pairs of competing oxidants. If these experiments are carried out under conditions where the decomposition adheres to a pseudo-first-order pattern (excess EDTA, no added NaOH),[3] the applicable sequence may be represented schematically as (only the oxidation numbers are designated)

$$Co^3P^1 \xrightarrow{k_h} Co^1 + P^3 \qquad (10)$$

$$Co^1 + Co^3P^1 \xrightarrow{k_c} 2Co^2 + P^1 \qquad (8')$$

$$Co^1 + Co^3X \xrightarrow{k_t} 2Co^2 + X \qquad (11)$$

Here k_h, k_c, and k_t indicate the specific rates for the hydride shift, the comproportionation involving the reactant, and trapping by the complex Co^3X. This generates the differential rate equations (12)–(14). Applying the steady-state approximation to $[Co^1]$

$$-\frac{d[Co^3P^1]}{dt} = k_h[Co^3P^1] + k_c[Co^3P^1][Co^1] \qquad (12)$$

$$\frac{d[P^3]}{dt} = k_h[Co^3P^1] \qquad (13)$$

$$\frac{d[Co^1]}{dt} = k_h[Co^3P^1] - k_c[Co^1][Co^3P^1] - k_t[Co^1][Co^3X] \qquad (14)$$

and then substituting the resulting expression for $[Co^1]$ into (12) yields (15). Integration of this system in closed form is possible

$$-\frac{d[Co^3P^1]}{dt} = k_h[Co^3P^1] + k_h[Co^3P^1]\left(1 + \frac{k_t[Co^3X]}{k_c[Co^3P^1]}\right)^{-1} \qquad (15)$$

but cumbersome. A more convenient procedure utilized the Runge–Kutta integration technique[27] as applied to (13) and (15), with a 250-s time interval chosen between kinetic points. The ratio k_t/k_c was allowed to vary, whereas $[Co^3X]$, $[Co^3P^1]$, and k_h were assigned known values.[28] Integration then yielded $[P^1]$ (hypophosphite) and $[P^3]$ (phosphite) at various stages of the reaction and very near completion (>4 × 10^4 s). Figure 2, for example, shows the manner in which the ratio $([P^3]/[P^1])_\infty$ varies with k_t/k_c for a given ratio of competing oxidants. Comparisons of observed product ratios with those calculated by numerical integration in this manner yield the relative rates listed in Table IV.

Table IV. Relative Rates at Which Cobalt(III) Oxidants React with the Proposed Cobalt(I) Intermediate[a]

oxidant[b] (concn, M)	$[Co^{III}O_2PH_2^{2+}]_0$, M	$[P^{III}]/[P^I]$[c]	k_t/k_c[d]
$Ro(OH)^{2+}$ (0.105)	0.0874	1.65	0.20
$Ro(OH)^{2+}$ (0.105)	0.0300	2.37	0.14
$Ro(form)^{2+}$ (0.140)	0.0600	1.68	0.14
$(tren)CoCl_2^+$ (0.060)	0.060	5.19	>3.0[e]
$Ro(py)^{3+}$ (0.214)	0.0600	1.01	<0.06
$Ro(NCS)^{2+}$ (0.0175)	0.0175	34	30

[a] Competition experiments were carried out in 0.41 M Na_4EDTA at 20 °C under N_2. The reaction time was 2 × 10^4 s. [b] Abbreviations: Ro = "roseo" = $(NH_3)_5Co^{III}$; form = formate; trien = triethylenetetramine; py = pyridine. [c] Ratio of phosphite to hypophosphite in the reaction mixture determined iodometrically.[11] [d] Relative rates for reaction of the proposed cobalt(I) intermediate with added "trapping reagent", Co^3X (eq 11), and the generating complex, Co^3P^1 (eq 8′), obtained by comparing the ratio $([P^{III}]/[P^I])_\infty$ to values calculated by a numerical integration procedure (see text and Figure 2). [e] Basic hydrolysis of the dichloro complex to a less reactive monochloro oxidant competes with the redox transformations of interest. Only a lower limit is calculated for this trapping reagent.

Although only a few trapping reagents were examined, the rate ratios obtained indicate that the Co(I) intermediate utilizes an inner-sphere path in reactions with Co(III) oxidants having a bridging ligand. The outer-sphere reductant, $Ru(NH_3)_6^{2+}$, has been found to react with the pyridine derivative of $(NH_3)_5Co^{III}$ about 7 times as rapidly as with the corresponding formato complex,[29] a rate ratio that, according to the model of Marcus,[30] should be applicable to other outer-sphere reductants. Here, as with reductions by Cr^{2+}, Eu^{2+}, and V^{2+}, that ratio is reversed, pointing to the intervention of a bridged activated complex in reduction of the formato complex and, by implication, reductions of the hypophosphito and isothiocyanato derivatives as well. The relatively rapid reduction of the latter emphasizes the recognized[24b] unusually "soft" character of the Co(I) center.

Finally, it may be asked whether this transformation may take place without intervention of the strongly absorbing intermediate. At pH 8.7–11.0, the reaction, which is much slower, appears to generate a straightforward exponential kinetic profile without indication of the 295-nm transient.[3] Under these conditions, the overall conversion is very nearly first order in OH^-, indicating that only 1, rather than 2, unit of base is implicated. Moreover, the kinetic isotope effect, k_{PH_2}/k_{PD_2}, is found to be 2.1–2.3, suggesting that the hydride shift, but not the removal of a P-bound proton, is involved in activation. At the much higher pH values considered in the present study, however, this component does not compete effectively with the path entailing two hydroxide ions.

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[27] (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. (c) This procedure was 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.

[28] The value of k_h (5 × 10^{-5} s^{-1}) was obtained by monitoring the primary redox reaction under the corresponding conditions in the absence of trapping reagent. The ratio $[P^3]/[P^1]$ was, however, insensitive to k_h in the range (5–10) × 10^{-5} s^{-1}. Note that, in this system, $\Delta[P^1] = -\Delta[Co^3P^1] - \Delta[P^3]$.

[29] Fan, F.-R. F.; Gould, E. S. *Inorg. Chem.* **1974**, *13*, 2647.

[30] (a) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 970. (b) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.