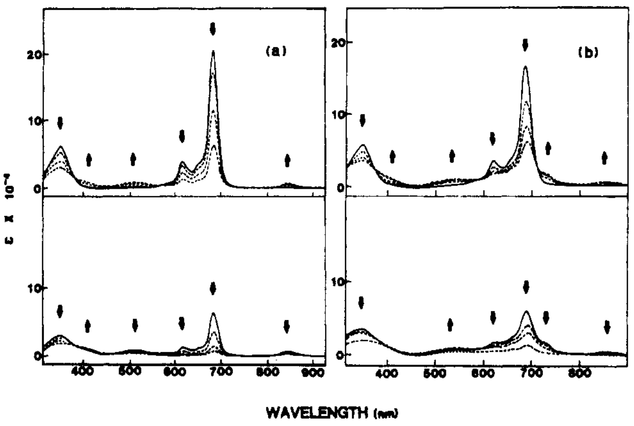


Figure 4. Electronic absorption spectra monitored during the first oxidation of (a) (Pc)Th$(acac)_2$ and (b) (Pc)U$(acac)_2$ in PhCN containing 0.2 M TBAP.

peaks may be related to reduction of the electrooxidized ligand.

Parts a and b of Figure 4 illustrate initial changes that occur in the electronic absorption spectra of (Pc)Th$(acac)_2$ and (Pc)U$(acac)_2$ upon controlled-potential oxidation in a thin-layer cell. Table II lists the wavelengths and molar absorptivities associated with these spectra. The initial spectra indicate an oxidation at the conjugated ring structure. However, upon rereduction at 0.00 V, the original spectra are not regenerated, thus indicating that the first oxidation is not reversible on a time scale of 5–8 min.

When (Pc)Th$(acac)_2$ is oxidized at 0.95 V for periods longer than 8 min, continual changes occur in the UV–visible spectra. Under these conditions all of the bands show a general decrease in intensity as the spectral detail disappears. This is illustrated by the spectra in Figure 4a. Also, after controlled-potential oxidation at 0.95 V the second oxidation peak on the voltammogram is greatly reduced in current, further demonstrating the presence of an irreversible chemical reaction. Finally, when the potential is set to +1.30 V, all of the absorption bands decrease in intensity, nearly to base line levels. The same result is observed for (Pc)U$(acac)_2$ and must be due to a demetalation or degradation of the phthalocyanine conjugated ring system.

An empirical formula, based on a limited data set, has been used to predict the first reduction and first oxidation potentials for (Pc)M$(L)_n$ complexes containing the metal ion in the plane of the phthalocyanine ring.[50,51] This formula is based on the size and charge of the metal ion in (Pc)M$(L)_n$. With this formula, the first oxidation of (Pc)U$(acac)_2$ is calculated to be 0.84 V and the first reduction to be −0.73 V. The first oxidation of (Pc)Th$(acac)_2$ is calculated to be 0.82 V and the first reduction to be −0.74 V. These calculated values are not in good agreement with the experimental values and suggest that the Th and U metals in (Pc)M$(acac)_2$ are not in the plane of the phthalocyanine ring or that a reduction or oxidation occurs at the metal center. This latter possibility is eliminated on the basis of ESR and spectroelectrochemical data.

In conclusion, the synthesis of (Pc)U$(acac)_2$ and (Pc)Th$(acac)_2$ provides a relatively easy route to 1:1 actinide–phthalocyanine complexes. The ^{1}H NMR data suggest a cis configuration of the acac ligands and a metal atom out of the plane of the phthalocyanine ring. The electrochemical data indicate ring-centered reactions and also support a structure with the metal out of the phthalocyanine ring.

Acknowledgment. The support of the National Science Foundation is gratefully acknowledged (Grants CHE-8515411 and INT-8413696).

Contribution from the Departments of Chemistry, Pittsburg State University, Pittsburg, Kansas 66762,
and Lebanon Valley College, Annville, Pennsylvania 17003

Phosphate-Mediated Electron Transfer during the Reduction of Cobalt(III) Complexes by Titanium(III)

Rathindra N. Bose,*[1a] Richard D. Cornelius,[1b] and Anne C. Mullen[1a]

Received March 5, 1986

The kinetics of electron-transfer reactions between hexaaquatitanium(III) and cobalt(III) complexes containing monodentate or bidentate ortho-, pyro-, or triphosphate were investigated at 25.0 °C in 1.0 M LiCl–HCl. The reactions are first order with respect to each of the reactants. The dependence of the rate upon the concentration of hydrogen ion indicates that at least one oxygen atom of the phosphate group must be deprotonated in order for the electron-transfer reaction to occur and that $TiOH^{2+}$ is the active reductant. The calculated rate constants for the reduction reactions of $TiOH^{2+}$ are within the range $(0.5–10) \times 10^4$ M^{-1} s^{-1} when a value of $K_a = 2.3 \times 10^{-3}$ M is used. An inner-sphere mechanism is proposed in which substitution on titanium(III) is the rate-limiting step followed by rapid electron transfer within the transient dinuclear intermediate. The efficiency of phosphate ligands in mediating electron transfer from titanium(III) to cobalt(III) is compared with that of other bridging ligands reported in the literature.

Introduction

The acceleration of the hydrolysis reactions of coordinated polyphosphates and nucleotides by certain complexes of platinum(II) and cobalt(III) has been reported previously from this and other laboratories.[2,3] On the basis of stoichiometric data, phosphorus-31 NMR data, and the dependence of the rate of hydrolysis upon the concentration of hydrogen ion, it has been suggested that coordinated hydroxide ion catalyzes the hydrolysis within a phosphate-bridged dinuclear intermediate. In these systems maximal acceleration of the rate was observed at neutral or basic pH.[3] In our continuing effort to understand the role of metal ions in phosphate hydrolysis reactions, we have begun to explore the possibility of using metal ions that might accelerate phosphate hydrolysis[4] at lower pH. Hexaaquatitanium(III), having a pK_a value in the range 1.9–2.7 dependent on the supporting electrolyte,[5] would be a likely candidate to catalyze phosphate hydrolysis of cobalt(III) polyphosphate complexes if

---

(1) (a) Pittsburg State University. (b) Lebanon Valley College.

(2) Bose, R. N.; Viola, R. E.; Cornelius, R. D. *Inorg. Chem.* **1984**, *23*, 1181–1182. Bose, R. N.; Viola, R. E.; Cornelius, R. D. *Inorg. Chem.* **1985**, *24*, 3989–3996.

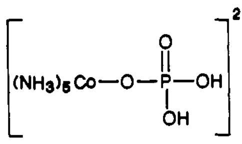
(3) (a) Haromy, t. P.; Gilletti, P. F.; Cornelius, R. D.; Sundaralingam, M. *J. Am. Chem. Soc.* **1984**, *106*, 2812–2818. (b) Norman, P. R.; Cornelius, R. D. *J. Am. Chem. Soc.* **1982**, *104*, 2356–2361. Cornelius, R. D. *Inorg. Chem.* **1980**, *19*, 1286–1290. Meyer, G.; Cornelius, R. D. *J. Inorg. Biochem.* **1984**, *22*, 249–258.

(4) The term "phosphate hydrolysis" refers to the hydrolysis reaction involving the cleavage of the P–O–P bond in polyphosphate to yield lower phosphates.

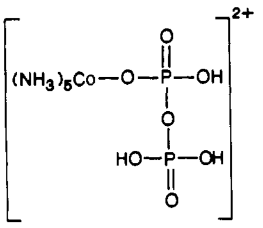
(5) Birk, J. P. *Inorg. Chem.* **1975**, *14*, 1724–1727. Pecsok, R. L.; Fletcher, A. N. *Inorg. Chem.* **1962**, *1*, 155–158. Paris, M. R.; Gregoire, C. L. *Anal. Chim. Acta* **1968**, *42*, 439.

0020-1669/87/1326-1414$01.50/0 © 1987 American Chemical Society

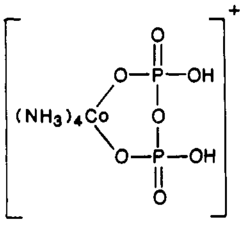
Chart I



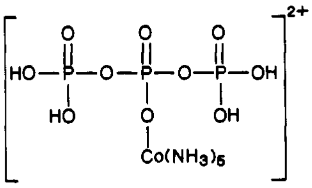
I



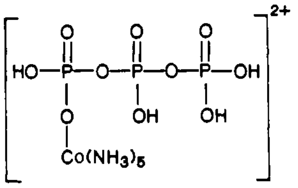
II



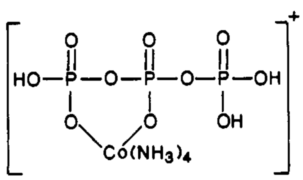
III



IV



V



VI

the titanium complex would form a phosphate-bridged intermediate with cobalt(III). Titanium(III) is also a unique reductant in that it reduces cobalt(III) complexes by both outer- and inner-sphere mechanisms with rate constants that span several orders of magnitude.[6-10] If the reduction of cobalt(III) phosphates were to proceed via an inner-sphere mechanism, the electron-transfer reaction might be coupled with phosphate hydrolysis, depending upon the rates of intramolecular hydrolysis and electron transfer within the binuclear intermediate.

In this paper we report our first results on the interaction of titanium(III) complexes with the well-characterized phosphato complexes of cobalt(III) shown in structures I–VI[3a,11,12] (Chart I). The results reported here describe the kinetics of the reduction of these complexes by titanium(III) in acidic aqueous solution.

Experimental Section

Reagents. The complex pentaammine(orthophosphato)cobalt(III) (I) was synthesized by following the procedure of Schmidt and Taube.[12] All other phosphato complexes, such as pentaammine(dihydrogen pyrophosphato)cobalt(III) (II), tetraammine(dihydrogen pyrophosphato)cobalt(III) (III), β- and γ-pentaammine(dihydrogen triphosphato)cobalt(III) (IV and V), and β,γ-tetraammine(dihydrogen triphosphato)cobalt(III) (VI), were prepared by following the procedure reported from this laboratory.[3a,11]

Stock solutions of titanium(III) were prepared by dissolving $TiCl_3$ (Aldrich) in 1.0 M HCl degassed with nitrogen and were standardized by dichromate titration.[13] The solutions were stored under nitrogen in a refrigerator. Subsequent standardization was made spectrophotometrically by using the molar asorptivity $\epsilon = 3.97\ M^{-1}\ cm^{-1}$ at 502 nm. The hydrogen ion concentration in the titanium(III) stock solution was determined by direct titration with standard sodium hydroxide solution.[14] Lithium chloride was prepared by neutralization of Li_2CO_3 with HCl. All other reagents were of analytical reagent grade and were used without further purification.

Stoichiometric Measurements. The stoichiometric coefficients of the redox reactions involving phosphato complexes of cobalt(III) and titanium(III) were determined spectrophotometrically at 520 and 380 nm. In a typical series of experiments, solutions at a fixed concentration of a (phosphato)cobalt(III) complex were mixed with titanium(III) solutions of varying concentrations. The ionic strength and concentration of hydrogen ion were kept constant at 1.0 M LiCl–HCl. The absorbance values were recorded for each of the solutions at the end of the reaction. The stoichiometries of the reactions were obtained from plots of absorbance vs. molar ratio.

In the titanium(III) reduction of pentaammine(orthophosphato)cobalt(III), the amount of cobalt(II) produced was quantitatively determined under conditions of limiting cobalt(III) concentration. The concentration of cobalt(II) was determined spectrophotometrically at 692 nm by following the method of Gould and Taube.[15]

Phosphate Estimation. The orthophosphate content in the products of the reaction of pentaammine(orthophosphato)cobalt(III) with titanium(III) was determined spectrophotometrically as phosphomolybdate blue.[16] Immediately after the completion of the redox reaction, the products were passed through a cation-exchange column (Bio-Rad AG 50W-X2; 1.5 × 5 cm column; H^+ form; 3-mequiv capacity) to remove titanium(IV) and cobalt(II). Free orthophosphate ion readily passed through the column. The column was washed with water (2 × 5 mL), and the eluate was subjected to analysis for phosphate.

The phosphate content in the products of the reactions of γ-pentaammine(dihydrogen triphosphato)cobalt(III) and β,γ-tetraammine(dihydrogen triphosphato)cobalt(III) with titanium(III) were determined by the same procedure as that outlined above. When the eluate was analyzed immediately after separation of cobalt and titanium, it was found to contain less than 0.1% orthophosphate product. When the eluate was allowed to stand, periodic analysis demonstrated the slow appearance of orthophosphate expected from the hydrolysis of triphosphate ion. In sample experiments standing overnight resulted in the hydrolysis of 85% of the triphosphate ion. Blank experiments containing identical concentrations of triphosphato complexes without titanium(III) were also conducted. The orthophosphate concentration found in these blank experiments was negligible even when the eluate was allowed to stand 24 h, a finding consistent with the removal of triphosphate along with the removal of cobalt(III) by ion exchange.

Kinetic Measurements. The kinetic experiments for slower reactions were performed either on a Cary 219 or on a computer-interfaced Varian DMS-100 spectrophotometer. A Durrum 110 stopped-flow instrument was used for monitoring faster reactions. The kinetics of the reduction of cobalt(III) complexes by titanium(III) were monitored by following the decrease in absorbance at 520 nm. The ionic strength was maintained at 1.0 M LiCl–HCl, and the temperature was kept constant at 25.0 °C. The kinetics were followed under both pseudo-first-order conditions with excess titanium(III) and under second-order conditions. When the kinetics were followed under pseudo-first-order conditions, the rate constants were evaluated from the slope of plots of log $(D - D_\infty)$ vs. time, where D and D_∞ are the absorbance values at time t and infinite time, respectively. These plots were linear over 3 half-lives, and the repro-

---

(6) Orhanovic, M.; Earley, J. E. *Inorg. Chem.* **1975**, *14*, 1478–1481. Olubuyide, O.; Earley, J. E. *Inorg. Chem.* **1981**, *20*, 3569–3571. Ali, S. Z.; Chalilpoyil, P.; Earley, J. *E. Inorg. Chim. Acta* **1981**, *48*, 57–59.

(7) Martin, A. H.; Gould, E. S. *Inorg. Chem.* **1975**, *14*, 873–877; **1976**, *15*, 1934–1936. Ram, M. S.; Martin, A. H.; Gould, E. S. *Inorg. Chem.* **1983**, *22*, 1103–1108.

(8) Thompson, G. A. K.; Sykes, A. G. *Inorg. Chem.* **1976**, *15*, 638–642.

(9) Hery, M.; Weighardt, K. *Inorg. Chem.* **1978**, *17*, 1130–1134.

(10) Bakac, A.; Orhanovic, M. *Inorg. Chim. Acta* **1977**, *21*, 173–175. Adegite, A.; Ojo, F. *Inorg. Chem.* **1977**, *16*, 477–479.

(11) Cornelius, R. D.; Hart, P. A.; Cleland, W. W. *Inorg. Chem.* **1977**, *16*, 2799–2805. Merritt, E. A.; Sundaralingam, M.; Cornelius, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 6152–6153.

(12) Schmidt, W.; Taube, H. *Inorg. Chem.* **1963**, *2*, 698–703.

(13) Pierson, R. H.; Gantz, E. C. *Anal. Chem.* **1954**, *26*, 1808–1810.

(14) The titration of titanium(III) with NaOH proceeds through the formation of a precipitate as reported by Davies and Earley (Davies, K. M.; Earley, J. E. *Inorg. Chem.* **1978**, *17*, 3350) according to the reaction[6]

$$4Ti^{3+} + O_2 + 12OH^- = 4TiO_2(s) + 6H_2O$$

Such a precipitate does not interfere with the detection of the end point using phenolphthalein indicator. The $[H^+]$ in the titanium solution was calculated by following the relationship

$$[H^+] = [OH^-] - 3[Ti^{3+}]$$

(15) Gould, E. S.; Taube, H. *J. Am. Chem. Soc.* **1964**, *86*, 1318–1328.

(16) Chen, P. A.; Toribara, Y. T.; Warner, H. *Anal. Chem.* **1956**, *28*, 1756–1758.

Table I. Acid Dissociation Constants (pK_a Values) of Various Phosphato Complexes at 25.0 °C in 1.0 M LiCl–HCl

complex	pK_1	pK_2	pK_3	pK_4
$[Co(H_2PO_4)(NH_3)_5]^{2+}$ (I)	3.2	8.6	...	...
	3.4[a]	8.6[a]		
$[Co(H_3P_2O_7)(NH_3)_5]^{2+}$ (II)	<–0.1[d]	3.3	5.6	...
$[Co(H_2P_2O_7)(NH_3)_4]^{+}$ (III)	<–0.1[d]	4.0	...	...
γ-$[Co(H_4P_3O_{10})(NH_3)_5]^{2+}$ (IV)	–0.1[d]	2.5	3.4	6.6
			3.45[b]	6.70[b]
β-$[Co(H_4P_3O_{10})(NH_3)_5]^{2+}$ (V)	<–0.1[d]	3.2	4.5	6.1
			4.37[b]	6.12[b]
β,γ-$[Co(H_3P_3O_{10})(NH_3)_4]^{+}$ (VI)	<–0.1[d]	2.3	5.7	...
		2.3[c]	5.7[c]	

[a] Reference 12. [b] Reference 3a. [c] Reference 21. [d] In 2.0 M LiCl–HCl.

ducibility of the rate constants was within 6%.

The rate constants under second-order kinetic conditions were computed by using a nonlinear least-squares computer program[17] for eq 1, where A and B represent [Co(III)] and [Ti(III)], respectively, and D_0 is the absorbance at $t = 0$.

$$D = D_0 + \frac{k_2B(D_\infty - D_0)[e^{(k_2B - k_2A)t} - 1]}{k_2Be^{(k_2B - k_2A)t} - k_2A} \qquad (1)$$

Acid Dissociation Constants. The acid dissociation constants of the phosphato complexes in the pH range 1–11 were determined by titrating solutions of the complexes at 1.0 M ionic strength (LiCl–HCl) with 1.0 M NaOH. Blank titrations using identical experimental conditions without the phosphato complex were also carried out. At a particular pH the amount of base used to titrate a complex was obtained from the difference between the reagent and blank titrations. At a given pH, the number of protons attached per molecule of a phosphato complex, n_H, was calculated by using this volume difference and the concentration of the phosphato complexes as described elsehwere.[19] The pK values were evaluated by stepwise calculation using the values of n_H. For the complexes that have successive acidity constants within 3 pH units, the pK values were evaluated by using the Noyes equation.[20]

Protonation constants in the range 0.1–2.0 M hydrogen ion were investigated spectrophotometrically. Values were obtained by using the absorbance readings of band maxima centered at 520 and 380 nm for solutions containing various concentrations of hydrogen ion.[12]

Results

Acid Dissociation Constants. All the phosphato complexes used in this study exhibit absorption bands at 520 and 380 nm.[3a,11,12] The acid dissociation constants for most of the complexes have been reported[3a,11,12,21] in the literature to be in the range pK_a = 2–11. Since the kinetic investigations described in the present study were carried out in acidic solutions below pH 2.0, the protonation steps of the phosphato complexes were investigated at hydrogen ion concentrations up to 2.0 M. Table I reports the pK_a values for the various phosphato complexes.

Table II. Rate Constants for the Reduction of Pentaammine(orthophosphato)cobalt(III) by Titanium(III) at 25.0 °C in 1.0 M LiCl–HCl

[Co(III)], mM	[Ti(III)], mM	[H$^+$], mM	10^2k_0, s^{-1}	k_2, M^{-1} s^{-1}
0.20	2.0	500	0.09	0.15 (0.6)[a]
0.97	12.7	250	2.2	1.7 (2.4)
0.97	12.7	180	6.9	5.4 (4.7)
1.10	12.0	180	6.0	5.0 (4.7)
0.40	6.0	180	2.8	4.7 (4.7)
0.40	4.1	180	2.1	5.1 (4.7)
0.36	4.2	128	3.7	8.8 (9.2)
0.94	6.3	128	6.2	9.8 (9.2)
0.94	9.5	128	9.2	9.7 (9.2)
0.94	12.7	128	12	9.4 (9.2)
0.40	4.6	110	5.3	12 (13)

[a] The values in parentheses are based on the least-squares fit of eq 3 with the value of k taken as 0.15 ± 0.01 M^{-1} s^{-1}.

Table III. Rate Constants for the Reduction of Monodentate and Bidentate Pyrophosphato Complexes of Cobalt(III) at 25.0 °C in 1.0 M LiCl–HCl

[Co(III)], mM	[Ti(III)], mM	[H$^+$], mM	$10^{-2}k_2$, M^{-1} s^{-1}
	$[Co(H_3P_2O_7)(NH_3)_5]^{2+}$ (II)		
0.52	1.2	642	0.79 (1.0)[a]
0.52	1.2	444	1.5 (1.6)
0.45	1.2	325	2.3 (2.2)
0.45	1.3	246	3.0 (2.9)
	$[Co(H_2P_2O_7)(NH_3)_4]^{+}$ (III)		
0.47	1.5	680	0.74 (0.94)
0.47	1.5	485	1.3 (1.3)
0.45	1.5	366	1.6 (1.7)
0.45	1.4	287	2.4 (2.2)

[a] The values in parentheses are the calculated rate constants according to eq 4 with the values of k taken as 71 ± 4 and 62 ± 5 s^{-1} for compounds II and III.

Stoichiometry. The plots of absorbance vs. molar ratio [Ti(III)]/[Co(III)] constructed from the spectrophotometric titration data show break points at a molar ratio of unity for all the redox reactions between titanium(III) and the phosphato complexes of cobalt(III). The stoichiometric ratios for the reactions of cobalt(III) phosphates and titanium(III) obtained from plots of absorbance vs. molar ratio are as follows: orthophosphato complex, I, 1.0 ± 0.05; monodentate pyrophosphato complex, II, 0.9 ± 0.1; bidentate pyrophosphato complex, III, 1.00 ± 0.05; β-monodentate triphosphato complex, IV, 1.05 ± 0.05; γ-monodentate triphosphato complex, V, 1.00 ± 0.05; β,γ-bidentate triphosphato complex, VI, 1.0 ± 0.1.

These results are consistent with the stoichiometry given by eq 2.

$$\mathrm{Ti(III) + Co(III) = Ti(IV) + Co(II)} \qquad (2)$$

Reduction of Pentaammine(orthophosphato)cobalt(III). The pseudo-first-order rate constants, k_0, computed at a particular hydrogen ion concentration increase linearly with increasing concentration of titanium(III). Second-order rate constants were calculated as $k_2 = k_0/[\mathrm{Ti(III)}]$. Table II gives the values of the rate constants at various concentrations of hydrogen ion. The rate data can adequately be described by the rate law

$$k_2 = k[H^+]^{-2} \qquad (3)$$

The magnitude of k evaluated from a least-squares fit[22] to eq 3 is 0.15 ± 0.01 M s^{-1}.

---

(17) The gradual increase in orthophosphate content over time is due to the slow hydrolysis reaction of triphosphate (see for example: Van Wazer, J. R.; Grifith, E. J.; Mccullough, J. F. *J. Am. Chem. Soc.* **1955**, *77*, 287–291) and is not related to the primary redox process.

(18) Fits to eq 1 were accomplished by using the nonlinear least-squares program FIT kindly supplied by Professor Gilbert Gordon, Miami University. A description of the algorithm of the program is given in the Los Alamos publication LA-2367 and addenda.

(19) Bose, R. N.; Ali, M. A. *J. Inorg. Nucl. Chem.* **1980**, *42*, 149–150. Rahman, M. A.; Ghosh, A. K.; Bose, R. N. *J. Chem. Technol. Biotechnol.* **1979**, *29*, 153–158. The values of n_H were calculated by using the expression

$$n_H = y - \frac{(v_2 - v_1)N}{(V + v_1)T}$$

where y is the number of replaceable hydrogen atoms, v_1 and v_2 are the volumes of NaOH solution of concentration N required for the titration of reagent and blank, and V is the initial volume of the complex of concentration T. The pK_a values were then obtained from a stepwise calculation by the expression

$$\mathrm{p}K_a = \mathrm{pH} + \log \frac{n_H}{y - n_H}$$

(20) Sarjeant, E. P. *Ionization Constants of Acids and Bases*; Wiley: New York, 1962; pp 51–57.

(21) Reibenspies, J.; Cornelius, R. D. *Inorg. Chem.* **1984**, *23*, 1563–1565.

(22) A nonlinear least-squares program (written in BASIC for the Apple II computer; see for example: Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 2832) was used to fit the rate data by using eq 3–5. The refined parameters are based on the unweighted individual data points. However, the values of k_1 for the two monodentate triphosphato complexes were calculated to be slightly higher (49 and 11 M^{-1} s^{-1} for the β- and γ-triphosphato complexes) if the weight was taken as inversely proportional to the magnitude of the rate constants.

Table IV. Rate Constants for the Reduction of Triphosphato Complexes of Cobalt(III) by Titanium(III) at 25.0 °C in 1.0 M LiCl–HCl

[Co(III)], mM	[Ti(III)], mM	[H$^+$], mM	$10^{-2}k_2$, M^{-1} s^{-1}
γ-[Co(H$_4$P$_3$O$_{10}$)(NH$_3$)$_5$]$^{2+}$ (IV)			
0.29	1.5	680	0.64 (0.64)[a]
0.20	1.2	525	0.66 (0.69)
0.20	1.2	360	0.89 (0.8)
0.20	1.2	165	1.1 (1.2)
0.29	1.0	100	1.7 (1.7)
β-[Co(H$_4$P$_3$O$_{10}$)(NH$_3$)$_5$]$^{2+}$ (V)			
0.36	1.5	683	0.31 (0.41)
0.36	1.5	485	0.47 (0.54)
0.36	1.4	287	0.87 (0.84)
0.36	1.3	167	1.6 (1.4)
0.36	1.5	90	2.3 (2.4)
β,γ-[Co(H$_3$P$_3$O$_{10}$)(NH$_3$)$_4$]$^{+}$ (VI)			
0.40	1.2	740	1.1 (1.2)
0.40	1.3	626	1.4 (1.4)
0.40	1.2	560	1.7 (1.6)
0.40	1.2	365	2.4 (2.4)

[a] The values in parentheses are the calculated rate constants according to eq 5 for compounds IV and V and eq 4 for compound VI. The values of the fitted parameters are presented in Table V and described in the text.

Table V. Values of k_1, k, and k_4 for the Reduction of Cobalt(III) Phosphato Complexes by Titanium(III) at 25.0 °C in 1.0 M LiCl–HCl

complex	k_1, M^{-1} s^{-1}	k, M^{-1} s^{-1}	$10^{-4}k_4$ or $k_{\mathrm{TiOH^{2+}}}$[b]
[Co(HPO$_4$)(NH$_3$)$_5$]$^+$ (I)		0.15[a]	10[c]
[Co(H$_3$P$_2$O$_7$)(NH$_3$)$_5$]$^{2+}$ (II)		71	3.1
[Co(H$_2$P$_2$O$_7$)(NH$_3$)$_4$]$^+$ (III)		62	2.7
γ-[Co(H$_4$P$_3$O$_{10}$)(NH$_3$)$_5$]$^{2+}$ (IV)	47	12	0.5
β-[Co(H$_4$P$_3$O$_{10}$)(NH$_3$)$_5$]$^{2+}$ (V)	10	21	0.9
β,γ-[Co(H$_3$P$_3$O$_{10}$)(NH$_3$)$_4$]$^+$ (VI)		89	3.9

[a] In M s^{-1}. [b] Calculated by using $K_a = 2.3 \times 10^{-3}$ M. [c] Calculated by using both K_a and $K_b = 6.3 \times 10^{-4}$ M^{-1}.

Reduction of Pyrophosphato Complexes of Cobalt(III). Table III lists the second-order rate constants for the reduction of the two pyrophosphato complexes at various hydrogen ion concentrations.[23] The variation of the second-order rate constants for the reduction of both the bidentate and monodentate pyrophosphato complexes with the concentration of hydrogen ion follows the rate law expressed by eq 4. A least-squares fit to eq

$$k_2 = k[\mathrm{H}^+]^{-1} \tag{4}$$

4 yielded the k values 72 ± 4 and 62 ± 5 s^{-1} for the monodentate and bidentate pyrophosphato complexes, respectively.

Reduction of (Triphosphato)cobalt(III) Complexes. The reactions in which titanium(III) reduces the triphosphato complexes IV–VI also follow second-order kinetics, first order with respect to each of the reactants. Table IV reports the rate constants at various hydrogen ion concentrations. Although the rates of the reactions for all three triphosphato complexes increase with decreasing [H$^+$], the rate law for the monodentate complexes differs from that of the bidentate complex VI. The monodentate complexes follow the rate law given by eq 5 while the rate data for

$$k_2 = k_1 + k[\mathrm{H}^+]^{-1} \tag{5}$$

the bidentate complex can adequately be described without the k_1 term. The nonlinear least-squares refinements yielded the values of k_1 and k as 47 ± 4 and 12 ± 1 for the γ-triphosphato complexes and 11 ± 3 and 21 ± 2 for the β-triphosphato complexes. The fitted value of k for the bidentate chelate was 89 ± 2 s^{-1}.

Discussion

Although the rates of the reduction of various phosphato complexes exhibit diverse dependence upon the concentration of hydrogen ion, a general mechanism can be formulated for all the redox reactions:

$$\mathrm{Ti^{3+} + H_2O \overset{K_a}{=} TiOH^{2+} + H_3O^+} \tag{6}$$

$$\mathrm{CoLH}^{n+} + \mathrm{H_2O} \overset{K_b}{=} \mathrm{CoL}^{(n-1)+} + \mathrm{H_3O^+} \tag{7}$$

$$\mathrm{CoL}^{(n-1)+} + \mathrm{Ti^{3+}} \xrightarrow{k_3} \text{products} \tag{8}$$

$$\mathrm{CoL}^{(n-1)+} + \mathrm{TiOH^{2+}} \xrightarrow{k_4} \text{products} \tag{9}$$

The notation LH represents a protonated phosphate ligand.

If k_3 is much less than k_4, then the contribution to the overall reaction from the k_3 pathway may be neglected. In that case the rate law for the above mechanism is given by eq 10. In chloride

$$k_2 = \frac{k_4K_aK_b}{(K_a + [\mathrm{H}^+])(K_b + [\mathrm{H}^+])} \tag{10}$$

medium the value of K_a has been reported to be 2.3×10^{-3} M.[4] The lowest hydrogen ion concentration used in the present investigation is 0.09 M, much greater than the value of K_a; i.e., $[\mathrm{H}^+] \gg K_a$. Given this condition, there are two limiting situations for which eq 10 can be reduced to a single term. If $[\mathrm{H}^+] \gg K_b$, then k_2 is expressed by eq 11, and if $[\mathrm{H}^+] \ll K_b$, then k_2 can be expressed by eq 12. For the orthophosphato complex the two

$$k_2 = \frac{k_4K_aK_b}{[\mathrm{H}^+]^2} \tag{11}$$

$$k_2 = \frac{k_4K_a}{[\mathrm{H}^+]} \tag{12}$$

pK_a values are 3.2 and 8.4, corresponding to K_a values that are much smaller than the lowest hydrogen ion concentration used. The observed inverse dependence on the square of the hydrogen ion concentration for k_2 is consistent with the rate expression found in eq 11. Using the value of $K_a = 2.3 \times 10^{-3}$ M and taking the value of K_b as 6.0×10^{-4} M (k_1), k_4 can be calculated to be 1×10^5 M^{-1} s^{-1} ((slope)/K_aK_b).

From an examination of the acid dissociation constants for the various phosphato complexes in Table I it can be concluded that there is at least one deprotonated phosphate site for each of the pyrophosphato complexes II and III and for each of the triphosphato complexes IV–VI. The inverse hydrogen ion dependence of k_2 for the bidentate and monodentate pyrophosphato complexes is consistent with eq 12. The values of k_4 can be calculated to be 3.1×10^4 and 2.7×10^4 M^{-1} s^{-1} for the monodentate and bidentate pyrophosphato complexes, respectively. For the β,γ-triphosphato chelate, the value of the limiting rate constant k_4 can be calculated to be 3.9×10^4. For the reduction of the two monodentate triphosphato complexes the non-zero intercepts in the plots of k_2 vs. $[\mathrm{H}^+]^{-1}$ suggest a possible contribution from the k_3 path of the reactions.

The inverse squared dependence of the reaction rate on the concentration of hydrogen ion suggests that at least one deprotonated oxygen atom in the phosphate group is required for reaction to occur. The same conclusion can be reached for the reductions of other phosphato complexes, since at least one oxygen atom in the phosphate group is deprotonated in the pH range investigated. A requirement for a deprotonated oxygen atom is consistent with the explanation that the electron transfer within a transient phosphate-bridged dinuclear intermediate is facilitated by the bridging ligand. The formation of a phosphate-coordinated titanium(III) intermediate finds support from the magnitude of

---

(23) The titanium(III) reductions of all the phosphato complexes reported here develop turbidity at low concentrations of hydrogen ion. The lowest hydrogen ion concentrations reported are those at which turbidity was not observed. The formation of turbid solutions may be due to the lower solubility of titanium(IV) phosphato complexes at lower concentrations of hydrogen ion.

(24) Lee, R. A.; Earley, J. E. *Inorg. Chem.* **1981**, *20*, 1739–1742.

the rate constant k_4. Earley and coworkers[25] have shown that the rate constants for the reduction of monopositively charged (oxalato)ruthenium(III) complexes by titanium(III) are within the range $(2-5) \times 10^4$ M^{-1} s^{-1}. The active reductant in this case is Ti^{3+}. The reduction of pentaammine(oxalato)cobalt(III) by $TiOH^{2+}$ has a rate constant of 8.6×10^4 M^{-1} s^{-1}.[6] In the case of ruthenium complexes the formation of an oxalato-bridged dinuclear intermediate has been suggested as the rate-limiting step followed by a rapid electron transfer through the bridging ligand.[24-26] Such an analysis probably also holds for the reduction of the (oxalato)cobalt(III) complex,[7] although the active reductant is $TiOH^{2+}$ ion.[27]

Rate processes limited by the electron-transfer step have also been suggested for the reduction of some monomeric and dimeric (carboxylato)ruthenium(III)[28] and -diruthenium(II,III) complexes.[29] In these cases the rate constants fall below the rate constant for substitution on titanium(III) but remain considerably higher than expected for the corresponding outer-sphere processes.

The reactive species of the phosphato complexes are monocations except for the pyrophosphato and triphosphato chelates III and VI. The rate constants for monocations lie in the narrow range $(0.5-10) \times 10^4$ M^{-1} s^{-1}, which overlaps with the range of values reported for the reduction of oxalato complexes of ruthenium(III) and cobalt(III). If the reductions of these oxalato complexes are taken to be substitution-limited processes, then the reductions of these monopositively charged phosphato complexes also appear to be limited by the rate of substitution on titanium(III). The reductions of the two remaining neutral species, the pyrophosphato chelate and β,γ-triphosphato chelate, may be limited by the electron-transfer step.

In the two-term rate law for the reduction of the two monodentate triphosphato complexes, the smaller term, k_1, is attributed to the reaction between $CoL^{(n-1)+}$ and Ti^{3+} as indicated by k_3 for eq 8 of the redox mechanism. The large value for the ratio of the rate constants k_4/k_1, $(1-8) \times 10^2$, implies that under the acidic conditions used here the reduction is predominantly accomplished by $TiOH^{2+}$. The absence of a k_1 term for the other phosphato complexes suggests that the analogous ratios of the rate constants are even greater than those observed for the two triphosphato complexes.

The k_1 term could also originate from the reaction shown as eq 13 in which [H$^+$] has opposite effects on the concentrations of oxidant and reductant and should correspond to the same composition of the activated complex as eq 8. This reaction would be unlikely if it were to proceed through an inner-sphere mechanism, since protonated ligands do not serve well as bridges. However, the reduction through an outer-sphere mechanism cannot be ruled out. Assuming that reaction 13 proceeds mainly through an outer-sphere process, and utilizing the rate ratio k_4/k_5, we conclude that the inner-sphere process should be at least 100 times faster than the corresponding outer-sphere reduction of these phosphato complexes.

$$CoLH^{n+} + Ti^{3+} \xrightarrow{k_5} \text{products} \qquad (13)$$

Thompson and Sykes[8] have reported that sulfate serves as a bridge in the titanium(III) reduction of the pentaammine(sulfato)cobalt(III) cation. Hard and soft acid–base interactions have been cited as playing a major role in determining the bridging ligand.[8] Redox reactions involving phosphate as a bridging ligand have not been explored except for the reaction of pentaammine(orthophosphato)cobalt(III) with chromium(II) which follows an inner-sphere mechanism.[12] The concepts of hard and soft acids and bases can explain the efficacy of sulfate and phosphate as bridging ligands by identifying titanium(III) as a hard acid and the coordinated sulfate and phosphate as hard bases. In contrast, the titanium(III) reduction of pentaammine(sulfato)ruthenium(III) follows an outer-sphere mechanism,[30] which suggests that the hard and soft acid–base concept alone may not be sufficient in predicting the bridging ligand in electron-transfer reactions. Earley and coworkers[31] have emphasized the importance of matching orbital symmetries of the bridging ligand and the redox partners to understand the details of the inner-sphere mechanism, especially for the Ti(III)–Ru(III) redox couples, where both the acceptor and the donor have t_{2g} symmetry. Since the intramolecular rates of electron transfer remain unknown in a substitution-limited redox reaction, the relative efficiencies of bridging ligands in mediating electron transfer cannot be compared. However, if we take an upper estimate of 10 M^{-1} for the formation constant of the transient intermediate, a lower limit of 10^3–10^4 s^{-1} can be calculated for the rate constant for intramolecular electron transfer. This estimated rate constant is within the values estimated[24,26] or observed[28,29] for the titanium(III) reduction of some (carboxylato)ruthenium complexes although the acceptor orbital in the cobalt(III) phosphates should have an e_g symmetry unless the activated Co(III)–Ti(III) complex has a high-spin configuration.

The hydrolysis of triphosphate results in the formation of orthophosphate and pyrophosphate ion.[2,3] Since the reduction of triphosphato complexes of cobalt(III) by Ti(III) did not yield orthophosphate as a product, we conclude that the phosphate hydrolysis reaction is slower than the electron-transfer reaction.

Acknowledgment. We are grateful to Professor Edwin S. Gould for valuable discussions and to Paul F. Filletti for the preparation of β- and γ-$Co(H_2P_3O_{10})(NH_3)_5$. This research was supported in part by National Science Foundation Grant No. CHE-8024043 and by Pittsburg State University. R.N.B. expresses his gratitude to Dr. Melvin L. Potts for arranging funds for the purchase of a DMS-100 UV–visible spectrophotometer.

---

(25) Adegite, A.; Earley, J. E.; Ojo, J. F. *Inorg. Chem.* **1979**, *18*, 1535–1539. Bose, R. N.; Earley, J. E. *Inorg. Chim. Acta* **1984**, *82*, L7.

(26) Bose, R. N.; Earley, J. E. *Inorg. Chem.* **1981**, *20*, 2739.

(27) Chaudhuri, P.; Diebler, H. *J. Chem. Soc., Dalton Trans.* **1977**, 596–599. These authors concluded that the rate constant of substitution of oxalate ion onto $TiOH^{2+}$ should not be different from that onto Ti^{3+}.

(28) Berrie, B. H.; Earley, J. E. *Inorg. Chem.* **1984**, *23*, 774–778.

(29) Bose, R. N.; Earley, J. E. *J. Chem. Soc., Chem. Commun.* **1983**, 59–60. Bose, R. N.; Wagner, P. A.; Earley, J. E. *Inorg. Chem.* **1984**, *23*, 1132–1134. Sasaki, Y.; Everhat, M. A.; Earley, J. E. *Polyhedron* **1985**, *4*, 317–320.

(30) Barone, P. Ph.D. Thesis, Georgetown University, 1983.

(31) Earley, J. E.; Barone, P.; Berrie, B. H.; Bose, R. N.; Lee, R. A. *Coordination Chemistry-20*; Banerjea, D., Ed.; Pergamon: New York, 1980; pp 65–69.