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Solution Redox Couples for Electrochemical Energy Storage

II. Cobalt(III)-Cobalt(II) Complexes with o-Phenanthroline and Related Ligands

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ABSTRACT

Co(III) and Co(II) complexes with o-phenanthroline, bipyridine, and related ligands were examined by voltammetric and coulometric techniques in aqueous H_2SO_4 media to investigate their suitability as redox couples for electrochemical energy storage systems and semiconductor photoelectrochemical cells. The Co(II) complex undergoes a rapid ($k° \sim 10^{-3}$ cm/sec) one-electron oxidation at a graphite or platinum electrode to yield the Co(III) complex. With several ligands both forms of the couple are very stable and show formal potentials shifted very negative (to $\sim 0.1V$ *vs.* SCE) from that of the aquo-Co(III/II) couple.

In a previous paper (1) we outlined past work in the area of redox flow cells and some of the requirements of soluble redox couples for use in such cells. These generally include high solubility, rapid charge transfer rates at the electrode surface, high stability of both forms of the redox couple, and, especially for photoelectrochemical cell applications, stabiliza-

tion of the electrode materials. The previous study (1) dealt with the Fe(III)/Fe(II) couple and its characteristics in aqueous solutions of o-phenanthroline (phen), bipyridine (bpy), and related ligands. In this paper we describe a parallel investigation of the Co(III)/Co(II) couple.

The electrochemical behavior of various bidentate complexes of Co has been investigated before, especially in connection with the determination of the

reversibility of the electrode reactions, in the determination of the stoichiometry of the complexes, and in voltammetric determinations (2-6). The electrochemistry of cobalt and its compounds is reviewed in detail by Maki and Tanaka (7). Because the redox potential of the uncomplexed Co(III)/Co(II) species in aqueous solution is high, and estimated at near 1.9V vs. NHE (7), Co^{3+} cannot be generated from the $+2$ species without simultaneous evolution of oxygen. However, π-bonding ligands such as phen or bpy complex the $+3$ form more strongly and shift the potential of the couple in a negative direction. This is consistent with the stronger complexation of the $d^6(t_{2g})$ form by π-bonding ligands, which for Co occurs in the $+3$ state (8, 9). Note that for iron the d^6 state is $+2$ so that the potential of the Fe(III)/Fe(II) couple is shifted in a positive direction by complexation with these ligands, as discussed previously (1). Moreover, as described below, both the $+2$ and $+3$ forms of the Co complexes are quite stable and appear suitable for redox battery applications.

Experimental

Reagents.—1,10(or o-)phenanthroline (phen), 2,9-dimethylphenanthroline (2,9-dmp), 4-methylphenanthroline (mp), and 4,7-dimethylphenanthroline (4,7-dmp) were obtained from Alfa Chemicals. The other chemicals used in this study were 2,2'-bipyridine (bpy) (Aldrich Chemical); tripyridine triazine (tpt) (J. T. Baker Company); $CoSO_4 \cdot 7H_2O$, reagent grade (Matheson, Coleman and Bell). All solutions were prepared with distilled water and were degassed with prepurified nitrogen.

Apparatus.—A Model 173 potentiostat in combination with a Model 179 digital coulometer (Princeton Applied Research Corporation, Princeton, New Jersey) was employed for all electrochemical experiments. The i-E and Q-t curves were recorded on a Houston Instruments Model 2000 X-Y recorder.

Procedure.—The details of the procedures employed in the present studies have been described previously (1). The solutions were purged with nitrogen gas before use. The complexes were prepared directly in the electrochemical cell by mixing known concentrations of cobalt(II) sulfate and the ligand. A mol ratio of ligand/Co(II) of greater than 3 was used. Controlled potential electrolysis was carried out with a large area graphite sheet electrode (area, 6.5 cm²) (Ultra Carbon, Sherman, Texas) with continuous nitrogen bubbling. All potentials in this study are reported with respect to an aqueous saturated calomel electrode (SCE). For cyclic voltammetric investigations, a single compartment cell with a solution capacity of 5 ml was employed, with either a platinum disk ($A = 0.114$ cm²) or graphite rod ($A = 0.12$ cm²) working electrode. The platinum electrodes were pretreated by fast pulsing between $+1.0$ and $-1.0V$ in H_2SO_4.

Results

Solubilities.—Table I is a list of the estimated solubilities of the complexes in aqueous 0.5M H_2SO_4. Uncomplexed Co(II) and Co(III)-sulfate salts are quite soluble and yield solutions with metal ion concentrations $\sim$1M. The solubilities of the complexes are $\sim$1M and yield deeply colored solutions. The ligands are soluble in acidic media to $\sim$2M.

$E^{\circ\prime}$ *values.*—The formal potentials $(E^{\circ\prime})$ of the various Co(II)/Co(III) complexes were evaluated from the cyclic voltammetric peak potentials at low scan rates (Table II). Note that the $E^{\circ\prime}$-values for these complexes are all shifted negatively by large amounts from the aquo Co(III)/(II) couple potential. Similar observations were reported by Farina and Wilkins (11) in potentiometric studies of complexation with π-bonding ligands at 0°C.

Table I. Solubilities of cobalt(II) complexes and ligands*

Substance†	Solubility (g/100 ml)	Concentration** (M)
$CoSO_4 \cdot 7H_2O$	28.1	1.0
Co(phen)₃SO₄	69.7	1.0
Co(tp)₂SO₄	52.4	1.0
Co(bpy)₃SO₄	63.1	1.0
Co(np)₃SO₄	83.2	1.0
Co(4-mp)₃SO₄	73.9	1.0
Co(2,9-dmp)SO₄	Insoluble	
Co(4,7-dmp)₃SO₄	8.09	0.1
1,10-Phenanthroline	40.0	2.2
2,2'-Bipyridine	31.6	2.0
Terpyridine	44.0	1.8

* Measured at 0.5M H_2SO_4 and at room temperature.
** Solubility was estimated by mixing the specified concentration of $CoSO_4 \cdot 7H_2O$ and an excess of ligand. The complex is precipitated at higher concentration of metal ion. The precipitate was then dissolved by adding 0.5M H_2SO_4 and the solubility estimated from dilution required to dissolve the precipitate.
† Abbreviations for the ligand names are indicated in Table II.

At a hanging mercury drop electrode (HMDE), another reversible peak at $-1.20V$ was observed with solutions of higher pH values ($\sim$6) (Fig. 1). This wave is attributed to the Co(II)/Co(I) complex (10). The insolubility of the Co(I) complex results in deposition of a blue compound on the electrode and produces a sharp peak on the anodic scan. The blue-black solid of Co(I) trisbipyridyl perchlorate was previously prepared by an electrochemical method (10).

Cyclic Voltammetric Measurements

Electron transfer kinetics.—Cyclic voltammetry (cv) was employed to estimate the heterogeneous electron transfer rate constants (12, 13) and to ascertain the stability of the coordinated Co(II) and Co(III) species. The results are given in Table II. Since the heterogeneous electron transfer rate constants, k°, are moderately large ($> 10^{-3}$ cm/sec), at low scan rates, v, the electrochemical behavior is characteristic of a nernstian reaction. When v is increased, the peaks shift and an increase in the ΔE_p values $(E_{pa} - E_{pc})$ is observed, indicating the effect of the finite heterogeneous electron transfer rate (11,
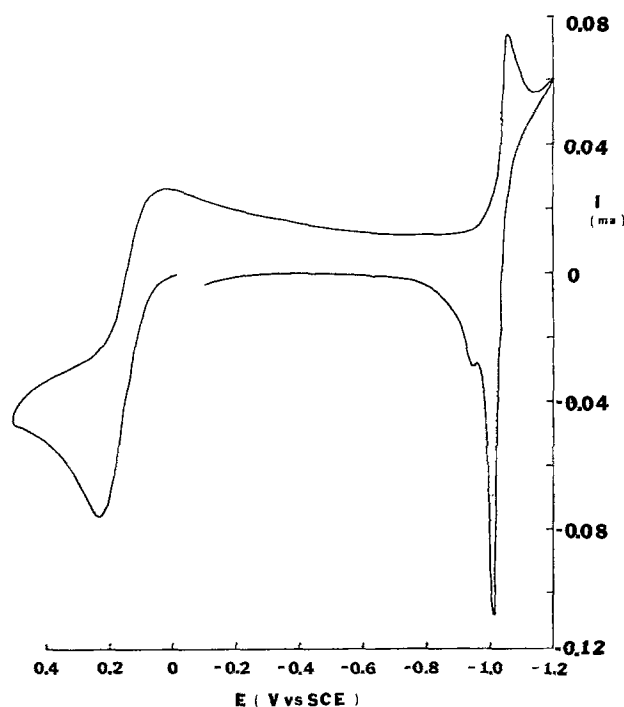

Fig. 1. Cyclic voltammetric curve for the oxidation of 12.4 mM Co(phen)₃²⁺ in 0.5M K₂SO₄. Working electrode: hanging mercury drop electrode. Reference electrode: aqueous saturated calomel electrode. $v = 0.05$ V/sec.

Table II. Thermodynamic and kinetic constants for cobalt(III/II) couples*

Ligands	$E^{\circ\prime}$ (V vs. SCE)	k° (cm sec^{-1})	k_t (sec^{-1})	D ($\times 10^6$ cm^2/sec)	Abbreviation of ligands
Aquo	1.9†				
Bipyridine	0.063	1.4×10^{-3}	$<10^{-7}$	1.8	bpy
o-Phenanthroline	0.14	0.81×10^{-3}	$<10^{-7}$	1.1	phen
4-Methyl-o-phenanthroline	0.04	0.52×10^{-3}	$<10^{-7}$	0.40§	mp
4,7-Dimethyl-o-phenanthroline	0.015	0.29×10^{-3}	$<10^{-7}$	0.43§	4,7-dmp
5-Nitrophenanthroline	0.37	1.8×10^{-3}	3.1×10^{-4}	1.5	np
Terpyridine	0.016	1.5×10^{-3}	$<10^{-7}$	1.7	tp
Tripyridinetriazine	0.73	Irreversible‡	$<10^{-7}$	—	tpt

* Measurements were made in 0.5M H_2SO_4 at platinum working electrode.
† Ref. (7).
‡ $E_{pc} = 0.52V$, $E_{pa} = 0.94V$ at $v = 0.01$ V/sec.
§ Adsorption might occur.

12). The rate itself can be obtained from the variation of E_{pa} or ΔE_p with v using the methods developed by Nicholson (13). From the $E_p - v$ behavior (assuming $\alpha = 0.5$), the value of ψ can be determined, where $\psi = k^{\circ}\pi$ $(aD_c)^{1/2}$, $a = nFv/RT$, and D_c is the diffusion coefficient of the complex. The diffusion coefficients of the Co(II) and Co(III) complexes were determined by chronocoulometry at a platinum disk electrode ($A = 0.114$ cm^2). For a planar electrode, the cumulative charge passed in oxidizing the diffusion reactant is given by (14)

$$Q = 2nFAD_r^{1/2}C_r^* t^{1/2}/\pi^{1/2} + Q_{dl} + nFA\Gamma_r \qquad [1]$$

where Q_{dl} is the double layer charge and $nFA\Gamma_r$ is the faradaic charge required to oxidize an amount, Γ_r, of adsorbed R. A typical plot of Q vs. t and $t^{1/2}$ is illustrated in Fig. 2. Diffusion coefficients, determined from the slopes of the Q-$t^{1/2}$ plots, are listed in Table II. The larger intercepts of the Q-$t^{1/2}$ plots found with the ligands mp and 4,7-dmp suggest that adsorption occurs in these cases. By substituting the relevant D-values into the above ψ expression, k° was obtained. For example, in a typical study with the Co(II)-tp complex in 0.5M H_2SO_4, the cv wave showed an $E_{pa} = +0.060V$ and on scan reversal E_{pc}
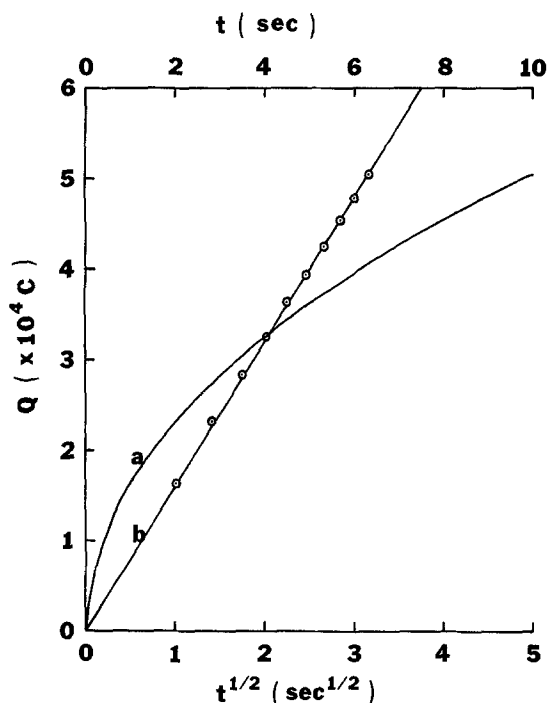
$= -0.028V$ at $v = 10$ mV/sec. When v increased, ΔE_p increased and at $v = 50$ mV/sec, $\Delta E_p = 112$ mV; $v = 0.1$ V/sec, $\Delta E_p = 125$ mV and $v = 0.2$ V/sec, $\Delta E_p = 150$ mV. From these values, an average value of $k^{\circ} = 1.5 \times 10^{-3}$ cm/sec was obtained.

The electron transfer rates of several of these Co-complexes have previously been measured in neutral media using a rotating platinum disk electrode. For Co(phen)$_3^{2+}$ a value of 4.8×10^{-2} cm/sec (15) and for Co(bpy)$_3^{2+}$, a value of 7.7×10^{-2} cm/sec (16) have been reported in 1M KCl medium. These values are an order of magnitude higher than in 0.5M H_2SO_4. This difference can probably be ascribed to the counterion and pH of the medium. The values of k° for Co(III/II) couple in 0.5M H_2SO_4 in the absence of added ligand could not be obtained, since the oxidation of the aquo Co(II) occurs beyond the background discharge potential.

The short-term stability of the complexes also could be obtained from the cv scans. The cyclic voltammetric curves of Co(II) complexes showed an initial anodic peak and a complementary cathodic peak arising from the reduction of Co(III) complex (see Fig. 3, 4, and 5). During the duration of the sweep, the Co(III) complexes were highly stable. The stability of Co(II) complexes was investigated by examining the cv curves after waiting periods of several hours following formation of the complex; no decom-
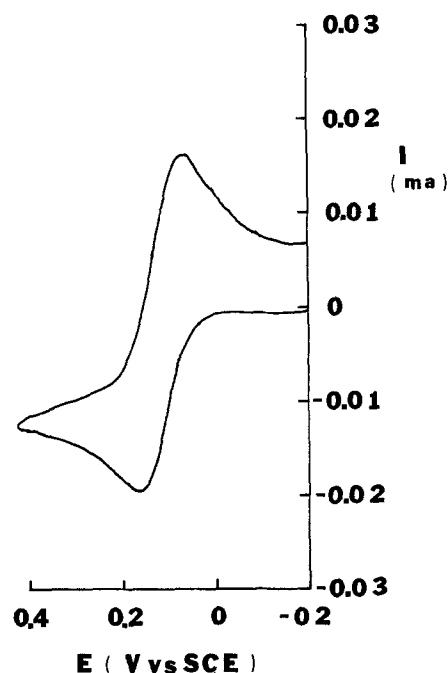
t (sec)

Fig. 2. Charge vs. time (curve a) and charge vs. (time)$^{1/2}$ (curve b) for 10 mM Co(bpy)$_3^{2+}$ in 0.5M H_2SO_4 in a chronocoulometric experiment. Working electrode: platinum disk. $E_i = -0.15V$, $E_f = 0.60V$.

Fig. 3a. Cyclic voltammetric curve for the oxidation of 10 mM Co(phen)$_3^{2+}$ before exhaustive electrolysis. Working electrode: platinum.
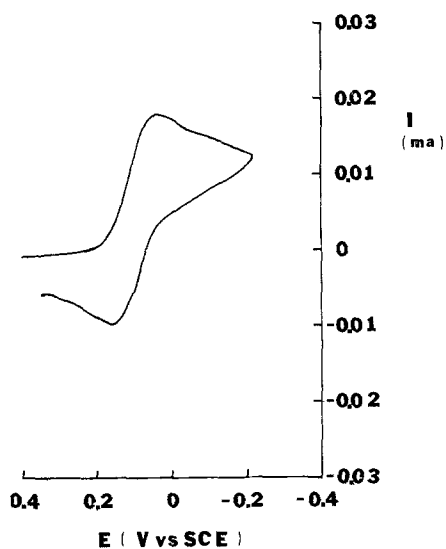
Fig. 3b. Cyclic voltammetric curve of the product of exhaustive electrolysis of $Co(phen)_3^{2+}$ conducted at graphite working electrode.
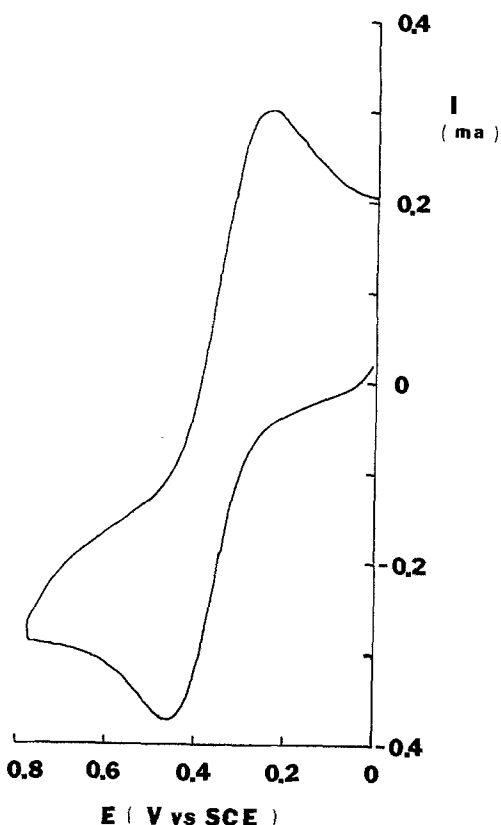

Fig. 4. Cyclic voltammetric curve of 10 mM $Co(np)_3^{2+}$ in 0.5M H_2SO_4 at graphite working electrode. $v = 0.10$ V/sec.

position of the complexes as evidenced by a decrease in i_{pa} was noticed. This stability can be contrasted to the behavior observed with several of the same Fe(III) complexes (e.g., np) where appreciable decomposition of the complex occurred, even on the cv time scale.

Controlled potential coulometric (CPC) *measurements.*—The stability for longer periods and current efficiency in the electrochemical oxidation-reduction processes were investigated by controlled potential electrolysis techniques. The oxidation of the Co(II) complexes, carried out at $+0.40V$ beyond the E_{pa} (from cv at low v) showed an n_{app} (faraday/mol) of 0.93-1.0. The lower values of n_{app} were found at higher
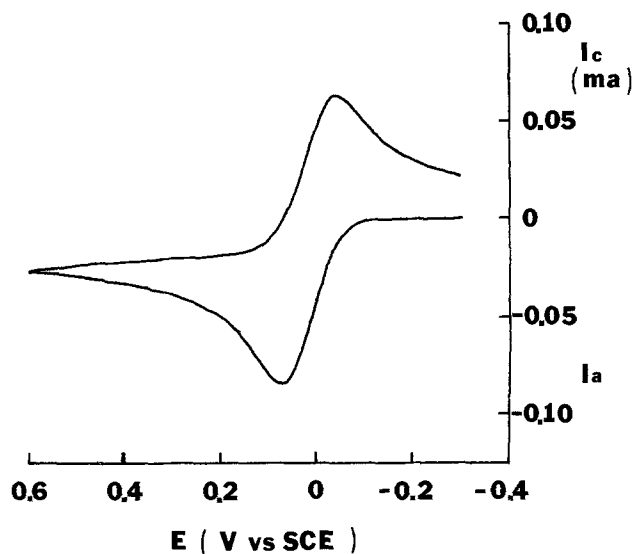

Fig. 5. Cyclic voltammetric curve of 10 mM $Co(tpd)_2^{2+}$ in 0.5M H_2SO_4 at $v = 0.05$ V/sec. Working electrode: platinum.

concentrations (0.2-0.5M) of the complex and can be attributed to some loss of the electroactive material because of diffusion into the counterelectrode compartment during the long term (1-2 hr) electrolysis. The current decayed smoothly to the background value and a plot of log i *vs.* t was linear (17). The product of the electrolysis, the Co(III) species, was examined by cv after different waiting periods. For example, the results in Fig. 3b demonstrate the stability of $Co(phen)_3^{3+}$; the magnitude of the cv peak current before and after electrolysis was identical, for waiting periods of at least 4 hr.

Reversal electrolysis, reduction of the electrogenerated Co(III), consumed essentially the same number of coulombs as in the forward electrolysis; the potential of the electrode was maintained at $-0.10V$ during these experiments. Repetitive electrolysis, cycling between the oxidized and reduced forms four times at 1 hr intervals, produced similar results (see Table III). With complexes of mp and tptz adsorption or some precipitation of the Co(III) complex on the electrode results in faster decay of the current and in-

Table III. Controlled potential electrolysis of cobaltous ions*

Mol taken	$Q_f{}^\circ$ (C)	Mol of Co^{2+} (oxdn)	$Q_b{}^\circ$ (C)	Mol of Co^{2+} recovered (redn)	n_{pp} (faradays/mol)
Co(bpy)₃²⁺					
1.12×10^{-3}	108.4	1.11×10^{-3}	111.3	1.15×10^{-3}	1.0
1.40×10^{-3}	136.0	1.41×10^{-6}	—		1.0
1.67×10^{-3}	162.1	1.68×10^{-3}			
4.5×10^{-4}	44.1	4.56×10^{-3}	46.5		
Co(phen)₃²⁺					
3.49×10^{-3}	300.2	3.11×10^{-3}	333.0	3.45×10^{-3}	0.92**
3.12×10^{-3}	301.0	3.12×10^{-3}	—	—	1.00
1.58×10^{-3}	136.0	1.41×10^{-3}			0.90
Co(np)₃²⁺					
7.17×10^{-4}	57.0	5.9×10^{-4}			0.82
2.07×10^{-4}	20.0	2.0×10^{-4}	22.4	2.3×10^{-4}	1.00
1.03×10^{-4}	10.0	1.0×10^{-4}	10.1	1.0×10^{-4}	1.00
3.10×10^{-4}	30.0	3.1×10^{-4}	30.9	3.2×10^{-4}	1.00
Co(tp)₂²⁺					
3.95×10^{-4}	38.1	3.95×10^{-4}	26.7	2.76×10^{-4}	1.0**
3.95×10^{-4}	37.9	3.92×10^{-4}			0.99
2.07×10^{-4}	20.0	2.07×10^{-4}	17.2	1.78×10^{-4}	1.0
1.55×10^{-4}	15.0	1.55×10^{-4}	13.4	1.38×10^{-4}	
1.03×10^{-4}	10.0	1.03×10^{-4}	9.8	1.01×10^{-4}	1.0
5.18×10^{-5}	5.0	5.18×10^{-4}	4.9	5.16×10^{-4}	

* ml solution in 0.5M H_2SO_4.
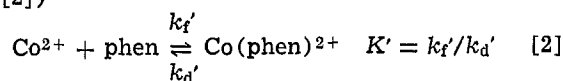** Diffusion of Co(II) complex to the counterelectrode compartment occurs.

complete electrolysis, presumably due to formation of an insulating film.

A brief investigation of the electrochemical reduction of the Co(II) complexes was also undertaken to see if the Co(II)/Co(I) couple is a possible candidate as the negative couple in a redox battery. The reduction of these complexes was examined in near neutral solutions of K_2SO_4; exhaustive electrolysis at a graphite electrode at $-1.10V$ resulted in a blue deposit on the electrode; this deposition caused a rapid decay of the electrolysis current (Fig. 6). Reversal electrolysis at $-0.30V$ removed the blue deposit from the electrode with the consumption of a smaller number of coulombs than for the forward electrolysis. In a typical electrolysis of 12.4 mM $Co(phen)_3{}^{2+}$ in 0.5M K_2SO_4 (15 ml) at a platinum electrode, a $Q_f = 1.10C$ and a $Q_b = 0.18C$ was reached. A similar result was obtained when a graphite electrode was used ($Q_f = 20.2C$ and $Q_b = 3.2C$). These results demonstrate that a large fraction of the Co(I) complex is lost through a chemical reaction. The $Co(bpy)_3{}^{2+}$ complex exhibited similar behavior. At a graphite electrode, exhaustive electrolysis at $-1.10V$, of 8.9 mM $Co(bpy)_3{}^{2+}$ consumed $Q_f = 23.8C$ and a film formed on the electrode. Reversal electrolysis at $-0.30V$ consumed $Q_b = 0.25C$. On the basis of these results, we conclude that the Co(I) complex is unstable and decomposes to a form which is not readily oxidizable.

Stability of Co(III) species.—Since a primary condition in the development of a storage battery is the long-term stability of the redox species in the two oxidation states, the Co(III)-complex stability was also studied spectrophotometrically. A solution of 10 mM Co(III)-phen complex with an absorption maximum at $\lambda_{450\,nm}$ ($\epsilon_{max} = 90$ M^{-1} cm^{-1}), showed no change in absorbance in 0.5M H_2SO_4 for at least 2 days. The rate of decrease in intensity showed that k_f was less than 10^{-7} sec^{-1} (where k_f is the first-order

rate constant for disappearance of the species). A similar k_f value was found with tp ($\lambda_{438\,nm}$, $\epsilon = 421$ M^{-1} cm^{-1}). The $+3$ complex with np was kinetically less stable, however, and showed a $k_f = 3.1 \times 10^{-4}$ sec^{-1}. This enhancement in the rate of decomposition by at least three orders of magnitude is possibly due to the presence of electron withdrawing groups in the ligand.

The stability of Co(II) complexes has been investigated previously (18-20). The equilibrium constants for these species favor formation of the complex. For example, for $Co(phen)^{2+}$, $K' = 2 \times 10^7$ (Eq. [2])

$$Co^{2+} + phen \underset{k_d{}'}{\overset{k_f{}'}{\rightleftharpoons}} Co(phen)^{2+} \quad K' = k_f{}'/k_d{}' \quad [2]$$

The decomposition of Co(II)-phen complex proceeds with a $k_d{}' = 1.5 \times 10^{-2}$ sec^{-1} while the rate of complexation in the reaction proceeds with a $k_f{}' = 3.1 \times 10^5$ M^{-1} sec^{-1}. The rate of complexation is generally of this order of magnitude with several of these ligands.

The stability of Co(II) complexes also depends, however, on the presence of O_2 in the medium. If O_2 gas is bubbled through a solution of 10 mM Co(II)-phen in 0.5M H_2SO_4, the cv peak at $E_{pa} = 0.13V$ decreases with time and on continuous bubbling of O_2, Co(II)-phen is converted to Co(III)-phen (Fig. 7). In preliminary experiments we found that the conversion of the Co(II) to Co(III) proceeded as a pseudo first-order reaction with a $k = 1.0 \times 10^{-4}$ sec^{-1}. This conversion has also been followed using a rotating disk electrode; the limiting currents in the cv curves are proportional to the concentration of the electroactive species (Fig. 8). The rate of conversion of $Co(bpy)_3{}^{2+}$ was followed by this procedure and gave a pseudo first order $k = 3.6 \times 10^{-5}$ sec^{-1}.

The near complete complexation of Co(II) with ligands like phen and bpy has been substantiated from equilibrium studies (21, 22). With phen, the equilibrium constants for the successive additions of the ligand are $K_1 = 10^7$, $K_2 = 10^6$, and $K_3 = 10^6$. The ligand addition reactions with bpy show $K_1 = 10^{5.7}$, $K_2 = 10^{5.6}$, and $K_3 = 10^{4.8}$. In this respect, the Co(II) complexes compare very well in stability with $Fe(bpy)_3{}^{2+}$, where $K_1 = 10^{4.3}$, $K_2 = 10^{3.7}$, and $K_3 = 10^{9.5}$ (23).

Discussion

Complexes of Co(II)-Co(III) appear to satisfy many of the general requirements of an energy storage redox couple. The stability of the complexes in the two oxidation states is remarkably high and the heterogeneous transfer rates at graphite electrodes appear adequate. Of course, more extensive studies under very long-term cycling and an economic evaluation would be required before such couples could be con-
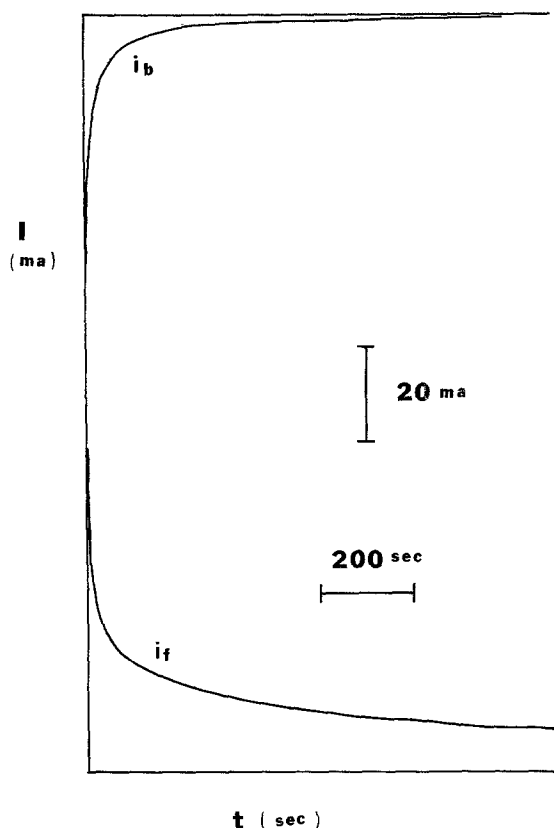

Fig. 6. Current-time curve during exhaustive electrolysis in 10 mM $Co(phen)_3{}^{2+d}$ at graphite electrode in 0.5M K_2SO_4 with its potential controlled at $-1.10V$ during reduction and reversal electrolysis at $-0.30V$.
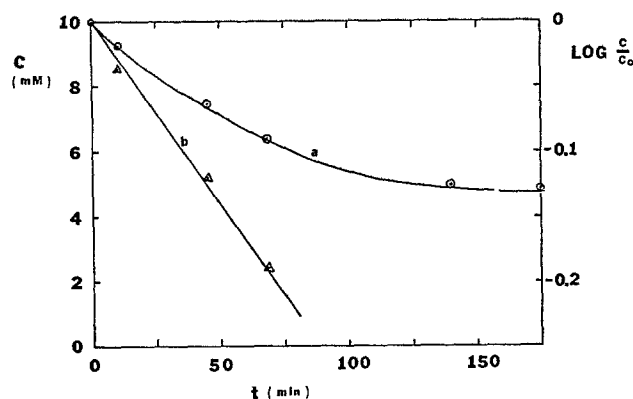

Fig. 7. Oxidation of 10 mM $Co(phen)_3{}^{2+}$ by oxygen: (a) concentration changes during continuous oxygen bubbling, (b) plot of log C/C_0 vs. t.
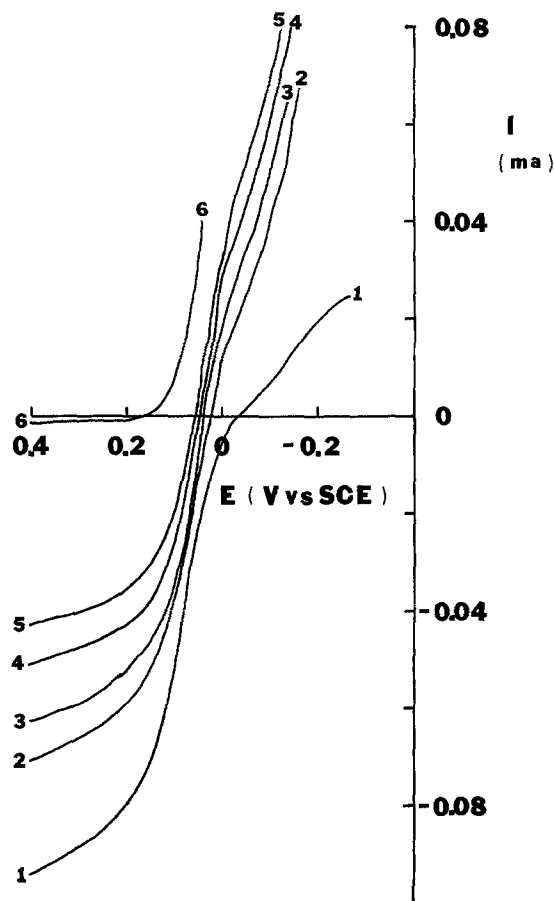
Fig. 8. Cyclic voltammetric curve during continuous bubbling of O_2 through 10 mM $Co(bpy)_3^{2+}$ at a rotating platinum disk electrode. $v = 0.01$ V/sec. The numbers on the curves represent the current values at different times: 1, 0.0; 2, 97; 3, 184; 4, 247; 5, 300 min, and 6, overnight (1230 min). The O_2 bubbling was stopped during the recording of cv curves.

sidered in practical battery systems. The major disadvantage of these complexes for a redox storage battery is that the $E^{o'}$-values are neither very positive (~0.38V for $Co(phen)_3^{2+}$ compared to 1.08V for $Fe(phen)_3^{2+}$) (1) nor negative. However, the use of these couples in semiconductor electrode photovoltaic cells is attractive, since these couples lie at potentials where neither extensive corrosion nor decomposition (e.g., via reactions at the electrodes or in solution leading to H_2 or O_2 evolution) should occur. The energy level corresponding to these E^o-values is sufficiently positive that it lies within the gap and should lead to reasonable output voltages with a number of small bandgap semiconductor materials (24). Preliminary experiments have demonstrated successful utilization of the Co(III/II)-phen system with several semiconductors (25) with high efficiency in cycling the redox couple.

There has been an active interest in the development of a redox battery with a single metal system for use in the positive half as well as in the negative half of a cell. The cation so chosen must be capable of undergoing oxidation on one side of the half-cell and reduction in the other half-cell. Cr(III) has been suggested for such a cell (26), but the Cr(VI)/Cr(III) couple is not well-behaved electrochemically. The present studies suggest Co complexes are potentially

useful, employing the Co(III)/Co(II) and Co(II)/Co(I) systems. These have the advantage of both being single electron transfer systems and indeed, the biological redox system involving Vitamin B_{12} involves, at least formally, these redox states. However, the results with the ligands employed here show that the Co(I) species, even in neutral media, were not sufficiently stable for this application. Alternate ligands are under investigation.

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