The Polarography of Bis(dipyridyl)cobalt(III) Complexes.

Unstable Univalent Cobalt Complexes

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Vlček¹⁾ and Waind et al.²⁾ found that the tris(dipyridyl) complex ion, $[Co^{III}dip_3]^{3+}$, is reversibly reduced to the cobalt(I) state through cobalt(II) ion, $[Co^{II}dip_3]^{2+}$, the

¹⁾ A. A. Vlček, Nature, 180, 573 (1957); Z. Elektrochem., 61, 1014 (1957); Z. physki. Chem. Sonderheft (Internationales Polarographisches Kolloquium, Dresden) (1958), p. 143.
2) G. M. Waind and B. Martin, J. Inorg. & Nuclear Chem., 8, 551 (1958).

TABLE I. HALF-WAVE POTENTIALS OF THE DIPYRIDYL COBALT(III) COMPLEXES (25°C)

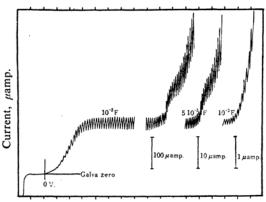
Compound	$E_{1/2}$ of 1st wave $Co(III) \rightarrow Co(II)$	$E_{1/2}$ of 2nd wave $Co(II) \rightarrow Co(I)$	Supporting electrolyte
[Co gly dip ₂]Cl ₂	-0.14	ca1.4	1 F KCl
[Co ala dip ₂]Cl ₂	-0.20	ca1.4	1 F KCl
[Co tyrosine dip ₂]Cl ₂	-0.19	-1.36	1 F KCl
[Co leuc dip ₂]Cl ₂	ca 0.25	-1.37_{8}	1 F KCl
[Co OCOCCH ₃ dip ₂]Cl ₂	-0.37_{3}	-1.39_{5}	1 F KCl, 0.0032% Tween 80 ²)
[Co dip ₃](ClO ₄) ₈ ·3H ₂ O	-0.14	-1.32	0.1 г KNO ₃ , 5·10 ⁻² м dip
	+	-1.10_{4}	1 F KCl
[Co dip ₃] (ClO ₄) ₂		-0.91	1 F LiCl, ethanolic soln.1)

Concentration of the complex; $2 \cdot 10^{-2}$ F

Voltage unit; V. vs. S.C.E.

Tween 80=Polyoxyethylene sorbitan mono-oleate

dropping mercury electrode (DME) in a 1 F lithium chloride ethanolic solution or in a potassium nitrate aqueous solution containing excess dipyridyl. In the present report, the mixed ligand complexes of the [Co^{III}dip₂Y] type are examined polarographically. It is found that unstable univalent cobalt complexes are formed during the course of reduction, where the bidentate ligand, Y, expresses the ion, NH2CH2COO- (glycinate), NH₂CH(CH₃)COO⁻ (alaninate), NH₂CH(CO-O-)CH₂CH(CH₃)₂ (leucinate), HOC₆H₄C₂H₃-(NH₂)COO⁻ (tyrosinate), or CH₃C(NO)COO⁻ (α -keto-propionic acid oximate) respectively³). All the complexes treated here are new ones which were prepared from the praseo-salt, [Co Cl₂ dip₂] Cl, by the substitution reaction.



Applied potential, V. vs. S.C.E. 100mV./absc.

Fig. 1. Dependence of the second wave for the complex, [Co^{III}gly dip₂]Cl₂, on the concentration of the complex.

Supporting electrolyte; $0.5 \text{ F } \text{K}_2\text{SO}_4$ aq. soln. Concn. of the complex; 10^{-2} , $5 \cdot 10^{-3}$, 10^{-3} F/l . $E_{1/2}$ of 1st wave=-0.11 V. vs. S.C.E. $E_{1/2}$ of 2nd wave=-1.31 V. vs. S.C.E.

* dip=2,2'-dipyridyl

These bis(dipyridyl)cobalt(III) complexes gave irreversible two-step waves at the DME in 1 F potassium chloride or in 0.5 F potassium sulfate supporting electrolyte. The first wave is well-defined, but the second one can be discerned only at a concentration of the complex higher than 10^{-2} F. The first and second waves, each corresponding to an acceptance of one electron, represent the reduction of cobalt(III) \rightarrow cobalt(II) and of cobalt(II) \rightarrow cobalt(I) respectively.

Figure 1 shows the polarograms of glycinatobis(dipyridyl)cobalt(III) chloride at various concentrations. Upon a decrease in the concentration, the second wave disappears into the current-rise of the hydrogen wave because of the glycine partly liberated from the complex on the way of reduction.

The following processes of the electrode reaction are considered to be most plausible:

The more the concentration of the original complex increases, the more the electrode reaction proceeds along path A rather than along path B. Thus, such an unstable cobalt-(I) complex as [Co^Igly dip₂] can be detected at a high concentration only by means of polarography.

Table I shows the half-wave potentials of the cobalt(III) complexes studied. As most of the second waves were fairly well covered by the hydrogen wave because of the amino acid liberated from the complex, the half-wave potentials could not necessarily be determined exactly. The oscillopolarograms of the $dE/dt \sim E$ (potential) curves also indicated that the

³⁾ M. Murakami, S. Senoh, N. Matsusato, H. Itatani and J. W. Kang, J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi), 83, 734, 737 (1962).

reduction process takes place in two stages at the DME.

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