The Polarography of o-Phenanthroline Cobalt(III) and Cobalt(II) Complexes

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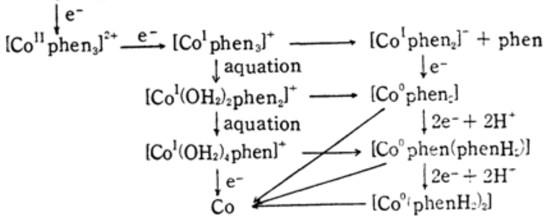
Vlček[1] and Waind et al.[2] found that the tris(dipyridyl) complex, $[\mathrm{Co^{III}\,dip_3}](\mathrm{ClO_4})_3\cdot 3\mathrm{H_2O}$, or $[\mathrm{Co^{II}\,dip_3}](\mathrm{ClO_4})_2$*, is reversibly reduced to cobalt(I) ions, $[\mathrm{Co^{I}\,dip_3}]^+$, at the dropping mercury electrode (DME). In the present communication, the tris(phenanthroline) cobalt(III) and cobalt(II) complexes, $[\mathrm{Co^{III}\,phen_3}]\mathrm{Cl_3}\cdot 7\mathrm{H_2O}$ and $[\mathrm{Co^{II}\,phen_3}]\mathrm{Cl_2}\cdot 8\mathrm{H_2O}$*, are found to be reduced irreversibly to the cobalt(0) state through cobalt(I) complexes in a 0.5 F sodium sulfate aqueous solution.

Figure 1 shows all the waves of the step-by-step reduction of the cobalt(III) complex. The cobalt(II) complex also gave the same waves after the second wave.

The first, the second and the third wave, each corresponding to an acceptance of one electron, represent the reduction of cobalt(III)→cobalt(II), of cobalt(II)→cobalt(I), and of cobalt(I)→cobalt(0) respectively. The limiting current of the waves, except that of the last one, is controlled only by diffusion. The diffusion current and the concentration of the complex are linearly related in the concentration range of $10^{-2}\sim 10^{-4}$ F. The third wave disappears into the catalytic maximum one, decreasing the concentration of the complex.

In absolute alcohol, the cobalt(I) ion, $[\mathrm{Co^{I}\,phen_3}]^+$, may dissociate into the $[\mathrm{Co^{I}\,phen_2}]^+$ ion, and so on. Therefore, without excess ligands, the reduction to the cobalt(I) state is almost irreversible (Table I). In an aqueous solution, the shape of the wave for this system is quite different from that of the usual current-voltage curve of the S-type, and the current-rise at the half-wave potential is almost at right angles to the line of galva zero. This phenomenon is considered to be due to the hydrophobic effect of the phenanthroline ligands or to the adsorption of the complex at the surface of the DME.

The processes of the electrode reaction are as follows:



The tris(bathophenanthroline)cobalt(III) chloride**, $[\mathrm{Co^{III}\,bathophen_3}]\mathrm{Cl_3}$, gave similar polarographic waves.

As for the oscillopolarograms of the dE/d$t\sim E$ (potential) curves, the cut-ins in the cathodic branch are generally larger than those in the anodic branch. This means that the electrode process is irreversible, even in the

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[1] A. A. Vlček, *Nature*, **180**, 573 (1957); *Z. Elektrochem.*, **61**, 1014 (1957); *Z. physik. Chem. Sonderheft* (Internationales Polarographisches Kolloquium, Dresden) (1958), p. 143.

[2] G. M. Waind and B. Martin, *J. Inorg. & Nuclear Chem.*, **8**, 551 (1958).

* dip = 2,2′-dipyridyl, $(\mathrm{C_5H_4N})_2$; phen = 1,10-phenanthroline, $\mathrm{C_{12}H_8N_2}$

** bathophen = 4,7-diphenyl-1, 10-phenanthroline, $\mathrm{C_{12}H_8N_2(C_6H_5)_2}$

TABLE I. HALF-WAVE POTENTIALS OF THE WAVES FOR THE COBALT(III) COMPLEXES OF THE LUTEO-TYPE (25°C)

Compound	$E_{1/2}$ of 1st wave Co(III)→Co(II)	$E_{1/2}$ of 2nd wave Co(II)→Co(I)	$E_{1/2}$ of 3rd wave Co(I)→Co(0)	Supporting electrolyte
[Co phen$_3$]Cl$_3\cdot$7H$_2$O	−0.08	-1.00_5	−1.34	0.5 F Na$_2$SO$_4$
[Co phen$_3$]Cl$_3\cdot$7H$_2$O	—	−1.62	—	1 F LiCl ethanolic soln.
[Co phen$_3$]Cl$_3\cdot$7H$_2$O	—	−0.83	—	1 F LiCl & 0.1 M phen. ethanolic soln.
[Co bathophen$_3$]Cl$_3$	+	−0.80	−1.11	1 F LiCl ethanolic soln.

Concentration of the complex, 10^{-2} F; voltage unit, V. vs. S. C. E.

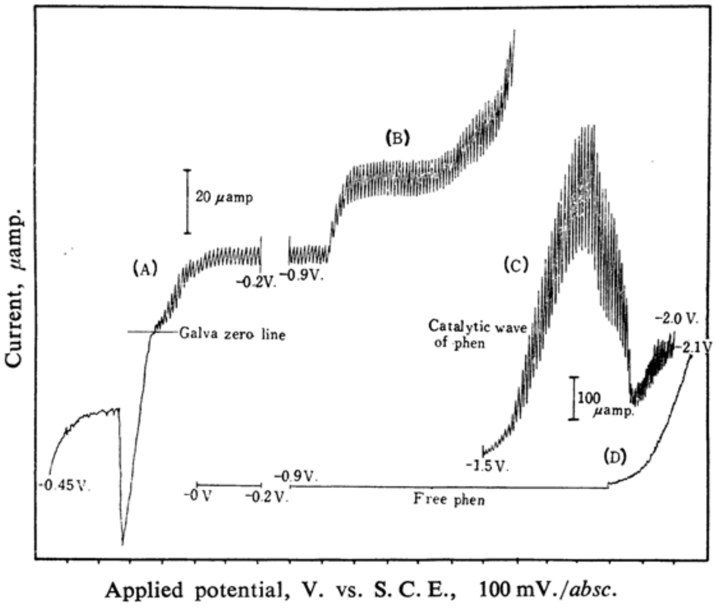

Fig. 1. The polarograms of the complex, [Co^{III} phen$_3$]Cl$_3\cdot$7H$_2$O obtained at the concentration of 10^{-2} M in 0.5 M Na$_2$SO$_4$ aqueous solution (25°C).

(A) Recorded from +0.45 to −0.2 V.; Sensitivity, 1.0 μamp./mm.
(B) Recorded from −0.9 to −1.6 V.; Sensitivity, 1.0 μamp./mm.
(C) Recorded from −1.5 to −2.1 V.; Sensitivity, 6.0 μamp./mm.
(D) The polarogram of 0.5 M Na$_2$SO$_4$ aqueous solution saturated with *o*-phenanthroline

$E_{1/2}$ of 1st wave = +0.08 V., $E_{1/2}$ of 2nd wave = -1.00_5 V., $E_{1/2}$ of 3rd wave = −1.34 V., voltage unit: V. vs. S. C. E.

presence of many excess ligands, due to the slower rate of oxidization.

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