Polarographic Studies of Metallic Complexes. VI[1]. *Tetracyanocobaltate(III) Complex*[2]

By Nobufumi MAKI and Ryutaro TSUCHIDA

(Received May 2, 1961)

In the earlier papers[3,4] it was reported that the pentacyanocobaltate(III) complexes are all reduced in one or two steps to cobalt(I) complexes at the dropping mercury electrode (DME)[5].

A similar polarographic behaviour was found in the case of tetracyanocobaltate(III) complex, $Na_5[Co(CN)_4(SO_3)_2]$[6].

Namely, disulphono-tetracyanocobaltate(III) ion[7] gave a well-defined wave of one step at the DME in 0.5 F sodium sulphite supporting electrolyte (Fig. 1). The current is controlled only by diffusion. The diffusion current and the concentration of the depolarizer are linearly related in the concentration range from 5×10^{-4} to 10^{-2} F.

The wave, corresponding to an acceptance of two electrons, represents the reduction to a univalent cobalt complex, whose formula is presumed analogously in the cases of cyanocobalt(I) complexes[4,8,9] to be the same as that of the oxidized form. Hence, the process of the electrode reaction is considered as follows:

$$[Co^{III}(CN)_4(SO_3)_2]^{5-}+2e^- \longrightarrow [Co^{I}(CN)_4(SO_3)_2]^{7-}$$

The above electrode process belongs to the quasi-reversible reaction polarographically. For further detail on this point, an oscillograph-polarographic study will be reported later.

The mechanism of the electron transfer and the change of the electronic configuration for the above reaction are explained by the atomic orbital method[10] as follows.

---

1) Part V of this series; N. Maki, Y. Shimura and R. Tsuchida, This Bulletin, **32**, 833 (1959).

2) Presented at the Symposium on Polarography, Kyoto, October, 1959.

3) N. Maki, J. Fujita and R. Tsuchida, *Nature*, **183**, 458 (1959).

4) N. Maki, ibid., **185**, 682 (1960).

5) D. N. Hume and I. M. Kolthoff, *J. Am. Chem. Soc.*, **71**, 867 (1949).

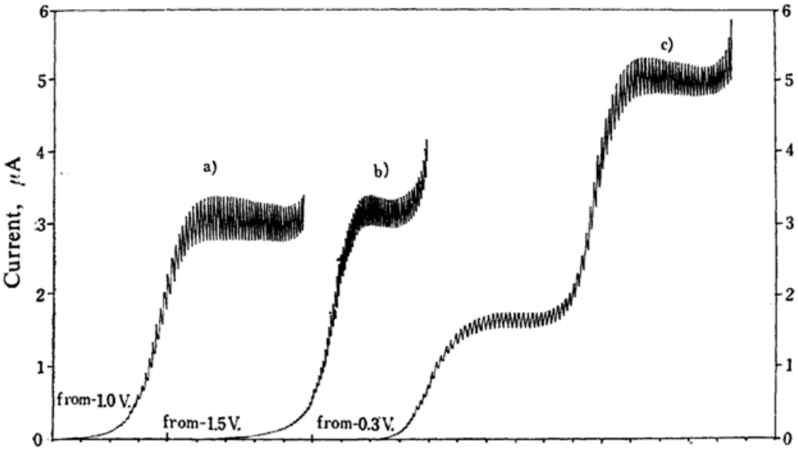
6) P. R. Rây and S. C. Chackrabarty, *Z. anorg. u. allgem. Chem.*, **211**, 173 (1933).

7) The "sulphono-group", which is SO_3^{2-} radical bound to the central metal ion by the sulphur atom, is distinguished from the "sulphito-group", OSO_2^{2-} bound by the oxygen.

8) N. Maki, *Nature*, **188**, 227 (1960).

9) W. P. Griffith and G. Wilkinson, *J. Chem. Soc.*, **1959**, 2757.

10) A. A. Vlček, *Collection Czechoslov. Chem. Communs.*, **20**, 894 (1955).



Applied Voltage (V. vs. S. C. E., 100 mV./absc.)

Fig. 1. Polarograms of sulphono- and sulphito-cobalt(III) complexes obtained at the concentration of 0.001 F complex ion in sodium sulphite supporting electrolyte (25°C). Each the height of the waves is seen to be proportional to the electron numbers of reduction process.

a) $Na_5[Co(CN)_4(SO_3)_2]$
Supporting salt : 0.5 F Na_2SO_3
Sensitivity : 0.04 μA/mm., Damping : 100, from −1.0 V. vs. S. C. E.
$E_{1/2}=-1.36$ V.

b) $K_4[Co(CN)_5SO_3]\cdot 2H_2O$
Supporting salt 1F Na_2SO_3
Sensitivity : 0.04 μA/mm., Damping : 200, from −1.5 V. vs. S. C. E.
$E_{1/2}=-1.54$

c) $[Co(NH_3)_5SO_3]Cl$
Supporting salt : 1F Na_2SO_3
Sensitivity : 0.04 μA/mm, Damping : 100, from −0.30 V. vs. S. C. E.
$E_{1/2}$ (1st wave) = −0.74 V., $E_{1/2}$ (2nd wave) = −1.30 V.
Voltage unit : vs. the saturated calomel electrode (S. C. E.), 100 mV./absc.

The acceptance of the electrons occurs in two stages.

$$d^2d^2d^2[D^2SP^3] \xrightarrow[e^-]{} d^2d^2d^2[D^2SP^3]d^1$$

$$\xrightarrow{} d^2d^2d^1[DSP^2][PD]$$

$$\xrightarrow[e^-]{} d^2d^2d^2d^2[DSP^2][PD]$$

First, the electron is accepted into the 4d peripheral orbitals temporarily, where it is held loosely, since the 3d atomic orbitals of Co(III) are fully occupied. After that the consecutive change of the electronic configuration and the placement of the electron in the stable 3d orbitals occur gradually. Thus, the electronic configuration of cobalt(I) complex is considered to consist of a coplanar structure through $3d4s4p^2$ hybrid orbital and a linear structure through 4p4d hybrid orbital separately, so the resulting cobalt(I) ion, $[Co^I(CN)_4\cdot(SO_3)_2]^{7-}$, may probably have a trans-configuration rather than that of cis-one.

Department of Chemistry
Osaka University
Kita-ku Osaka