

REDOX REACTIONS OF COBALT CYANIDE COMPLEXES. IX.\*  
 OXIDATION-REDUCTION PROPERTIES AND DECOMPOSITION  
 OF  $(\text{CN})_5\text{CoNCFe}(\text{CN})_5^{6-}$

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Oxidation-reduction properties of the compound  $(\text{CN})_5\text{CoNCFe}(\text{CN})_5^{6-}$ , product of a redox addition reaction between  $\text{Co}(\text{CN})_5^{3-}$  and  $\text{Fe}(\text{CN})_6^{3-}$ , and its behaviour in aqueous buffered solutions were studied. In the course of the redox addition, the electron density is shifted entirely from the Co to the Fe atom. The resulting binuclear bridge complex is distinguished by a high thermodynamic and kinetic stability caused by a favourable electronic and atomic configuration.

In the preceding communications of this series, the oxidation-reduction reactions between pentacyanocobaltate(II) and *p*-benzoquinone<sup>1</sup> and its substituted derivatives<sup>2</sup>, molecular oxygen<sup>3</sup>, and sulphur dioxide<sup>4</sup> were studied. It was shown that all the mentioned reactions of electron transfer proceed by a mechanism characterized by a strong interaction of the components, namely by redox addition<sup>5</sup>.

The present work deals with oxidation-reduction properties of the product of the reaction between pentacyanocobaltate(II) and hexacyanoferrate(III) ions.

#### EXPERIMENTAL

The experimental equipment was described previously<sup>3</sup>. The rotating platinum disc electrode of a large area was manufactured in the Institute's workshop. The complex  $\text{Ba}_3[(\text{CN})_5\text{CoNCFe}(\text{CN})_5]$  was synthesized according to Haim and Wilmarth<sup>6</sup>, and its conversion with potassium sulphate yielded the corresponding potassium salt. An aqueous solution of pentacyanocobaltate(II) was prepared in the same way as described previously<sup>7</sup>. All chemicals used as starting substances for preparations or as buffer components were of reagent grade (Lachema, Brno). Potentials are given against saturated silver chloride electrode<sup>3</sup>.

#### RESULTS AND DISCUSSION

##### *Oxidation-Reduction Behaviour of $(\text{CN})_5\text{CoNCFe}(\text{CN})_5^{6-}$*

A redox addition reaction between pentacyanocobaltate(II) and hexacyanoferrate(III) in solution yields the binuclear bridge complex  $(\text{CN})_5\text{CoNCFe}(\text{CN})_5^{6-}$  (further: complex F) identified first

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by Haim and Wilmarth<sup>6</sup>. It forms a yellow-orange aqueous solution, which is stable in the presence of air at ambient temperature. The complex F can be considered as a stable intermediate product of the overall electron transfer reaction between pentacyanocobaltate(II) and hexacyanoferrate(III). Analogous compounds, but considerably less stable, were postulated in the oxidation of  $[\text{CoEDTA}]^{3-}$  (ref.<sup>8</sup>) and  $[\text{Co en}_3]^{3+}$  (ref.<sup>9</sup>) with hexacyanoferrate(III). The reaction under study is too rapid to be followed with our experimental technique. A potentiometric titration revealed an equimolar ratio of the reactants in the equivalence point.

The stoichiometry of the reaction was proved also polarographically. In the presence of hexacyanoferrate(III), the expected reduction of bromopentacyanocobaltate(III) does not proceed<sup>10</sup>. Instead, a wave ascribed to reduction of F appears at more negative potentials (Fig. 1). The reduction waves of bromopentacyanocobaltate(III) begin to appear as soon as the condition

$$\sqrt{D_p}[\text{Fe}(\text{CN})_6^{3-}] \cong \sqrt{D_c}[\text{Co}(\text{CN})_5\text{Br}^{3-}] \quad (1)$$

is fulfilled ( $D_p$  and  $D_c$  denote diffusion coefficients of the respective compounds in brackets). Nonadditive currents can be in this case elucidated as follows. The

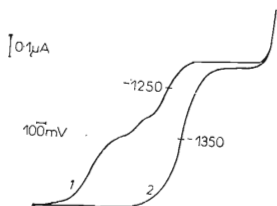


FIG. 1

Nonadditive Currents in Simultaneous Reduction of  $\text{Fe}(\text{CN})_6^{3-}$  and  $\text{Co}(\text{CN})_5\text{Br}^{3-}$  on Dropping Mercury Electrode

0.5M-KCl, from -0.4 V. 1 Reduction waves of  $\text{Co}(\text{CN})_5\text{Br}^{3-}$ ; 2 equivalent amount of  $\text{Fe}(\text{CN})_6^{3-}$  added.

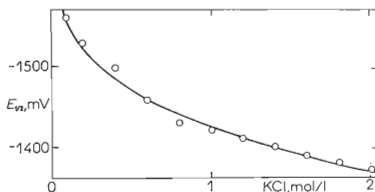


FIG. 2

Dependence of  $E_{1/2}$  for Reduction Wave of Complex F on Concentration of Indifferent Electrolyte

pentacyanocobaltate(II) ions, which are formed as intermediate product of the electroreduction of bromopentacyanocobaltate(III) ions, react rapidly in the close proximity of the electrode with hexacyanoferrate(III) ions, which diffuse from the bulk to the electrode. The reaction product, F, is reduced only at more negative potentials. Since the reaction is very rapid, the electrode process is controlled by diffusion.

The compound F is reduced at the dropping mercury electrode in both buffered and unbuffered aqueous solutions in a single step and the overall electrode process is in the potential range of the limiting current controlled by diffusion ( $i_1 \sim h^{1/2}$ ). This conclusion is substantiated by a plot of the  $i-t$  curve in logarithmic coordinates (exponent 0.2). The mean limiting current of the polarographic wave is directly proportional to the depolarizer concentration up to 0.01M and corresponds to a transfer of two electrons per one F molecule as determined both microcoulometrically and by comparison with the reduction wave of the complex  $(\text{CN})_5\text{Co}.\text{OC}_6\text{H}_4\text{O}.\text{Co}(\text{CN})_5^{6-}$ , the electrochemical behaviour of which is known<sup>1</sup>. The transfer of two electrons per F molecule is substantiated also by the nonadditive polarographic currents.

The logarithmic analysis of the polarographic reduction wave of F shows its irreversible character. The value of  $E_{1/2}$  depends strongly on the concentration of the supporting electrolyte (Fig. 2), on its cation:

0.5M chloride of:	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Cs <sup>+</sup>
$E_{1/2}$ , V	-1.68	-1.60	-1.48	-1.36

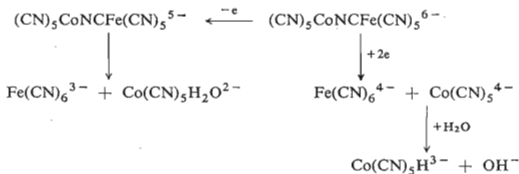
and the charge of the cation:

0.2M chloride of:	K <sup>+</sup>	Ba <sup>2+</sup>	La <sup>3+</sup>
$E_{1/2}$ , V	-1.52	-1.38	-1.25

These effects occurring with a highly charged depolarizer anion can be discussed in terms of ion pair formation and influence of the double layer on the rate of irreversible electrode processes similarly as in the analogous case<sup>3</sup> of the complex  $(\text{CN})_5\text{CoO}_2\text{Co}(\text{CN})_5^{6-}$ . The value of  $E_{1/2}$  is independent of pH in the range 7–13 and is shifted to more negative values with increasing temperature. The only polarographically active product found was hexacyanoferrate(II).

The complex F is oxidized on a platinum vibrating electrode ( $E_{1/2} = +0.35$  V in 2M-KCl). The number of transferred electrons cannot be determined with certainty but can be assumed to be one. The primary product thus formed contains both central atoms with the oxidation number +III, and decomposes to form hexacyanoferrate(III) and aquopentacyanocobaltate(III). These end products were determined by electrolysis on a platinum disc electrode of a large area. On a mercury electrode, no oxidation wave was observed in the attainable potential range.

The electrooxidation-reduction behaviour of the complex F can be described schematically as follows:



### Decomposition Kinetics of Complex F

The oxidation state of the central atoms can be judged from the polarographic behaviour of the complex F and from the observed products of its decomposition in aqueous buffered solutions. All hitherto studied (intermediate) products of the reaction of pentacyanocobaltate(II) with one- or two-electron oxidants decompose in aqueous solutions. Their stability depends on the character of the bridge ligand and of the medium. They decompose by reaction with proton donors to form a totally reduced substrate and Co(III) particle. The F complex is the most stable one of the studied products of redox addition reactions of the pentacyanocobaltate(II) ion. The stability of products increases in the following order of substrates:



To follow the kinetics of decomposition of the F complex by polarography as an analytical tool it was necessary to decrease the value of pH and increase the temperature of the solution. The influence of temperature on  $E_{1/2}$  was compensated by increasing the ionic strength.

The total limiting current remained constant during decomposition of the complex F. With proceeding decomposition a reduction wave of aquopentacyanocobaltate(III) appeared and grew at the expense of the reduction wave of F. From the time dependence of the latter it can be deduced that the decomposition of F in buffered solutions follows a first-order reaction kinetics. Representative values of the rate constant in dependence on pH and ionic strength are:

$\text{pH} (I = 0.55)$	6.10	6.25	6.41	6.60	6.85
$10^5 k, \text{s}^{-1}$	6.8	6.0	3.4	2.0	1.2
$I (\text{pH} = 6.25)$	0.75	0.55	0.35		
$10^5 k, \text{s}^{-1}$	3.8	6.0	9.4		

The dependence of  $\log k$  on pH is linear with a slope  $-1$ . With our experimental conditions it was not possible to study the dependence of  $k$  on the buffer capacity

and temperature. By analogy with systems studied previously, it can be assumed that the decomposition of F is a general acid-catalyzed reaction. The value of  $k$  decreases with increasing  $I$ .

The products of the decomposition of the complex F, determined polarographically, are aquopentacyanocobaltate(III) and hexacyanoferrate(II), which was detected in the medium of 0.1N- $H_2SO_4$  since its polarographic behaviour in the reaction medium used is complicated. The anodic part of the polarogram is identical with the known polarographic wave of hexacyanoferrate (II), (ref.<sup>11</sup>).

The decomposition of the particle F in buffered solutions proceeds according to the scheme



It is obvious from the experiments that in the course of the redox addition reaction between pentacyanocobaltate(II) and hexacyanoferrate(III) an electron is shifted entirely from the Co to the Fe atom. Both central atoms thus acquire the electron configuration  $d^6$ . The reason for the high stability of the complex F can be found in its favourable electronic and atomic configuration. Both  $\text{MX}_5$  groups attain a higher coordination number, 6, by coordination with the same common ligand. The complex F has then the structure of two octahedrons contacting each other by their peaks. The mode of its decomposition shows that the strength of the Fe—C bond is higher than that of the Co—N bond with respect to an attack by proton donors. The stabilization by coordination is reflected by a shift of the oxidation wave of the complex F by 50 mV toward positive values with respect to the free hexacyanoferrate(II).

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