

REDOX REACTIONS OF COBALT CYANIDE COMPLEXES. VIII.\*  
 OXIDATION-REDUCTION PROPERTIES AND BEHAVIOUR  
 OF THE PRODUCT OF FIXATION OF MOLECULAR OXYGEN  
 WITH AQUEOUS SOLUTIONS OF  $[\text{Co}(\text{CN})_5]^{3-}$

J. HANZLÍK and A. A. VLČEK

*J. Heyrovský Institute of Physical Chemistry and Electrochemistry,  
 Czechoslovak Academy of Sciences, 11840 Prague 1*

PE 128 / 38.1973. 4-6 Received February 2nd, 1972

Oxidation-reduction properties of the product of a redox-addition reaction between molecular oxygen and pentacyanocobaltate(II) ion,  $[(\text{CN})_5\text{Co}-\text{O}_2-\text{Co}(\text{CN})_5]^{6-}$  (*I*), were studied. The latter decomposes at  $\text{pH} < 12$  in two stages with the formation of an intermediate product,  $[\text{Co}(\text{CN})_5\text{O}_2]^{4-}$  (*II*). Oxygen bound in *I* and *II* is so stabilized by coordination that it does not undergo reduction. A reduction mechanism of *II* on the dropping mercury electrode was proposed and the kinetics of its decomposition in buffered aqueous solutions was studied. The decomposition rate constants were determined as  $k_{(\text{H}_3\text{O}^+)} = (1.2 \pm 0.2) \cdot 10^4 \text{ M}^{-1} \text{ s}^{-1}$  (*I* 0.15) and  $k_{(\text{H}_2\text{PO}_4^-)} = (3.5 \pm 0.5) \cdot 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$  (*I* 0.35) at 308 K; the activation energy  $E_a = (26 \pm 2) \text{ kcal/mol}$ .

The mode of fixation of molecular oxygen by natural carriers such as hemoglobines or hemocyanines, its transport and reversible setting free were already partly elucidated. Nevertheless, an insufficient amount of data has been obtained by studies of natural systems<sup>1,2</sup>. To obtain more information, synthetic carriers of molecular oxygen have been studied<sup>3</sup> such as  $[\text{Co}(\text{CN})_5]^{3-}$  on the first place.

The redox properties of products of the reaction between pentacyanocobaltate(II) and molecular oxygen were studied to find out the oxidation-reduction changes in this system, to elucidate the nature of the fixed oxygen bond and to check the ability of  $[\text{Co}(\text{CN})_5]^{3-}$  to transfer molecular oxygen.

#### EXPERIMENTAL

**Chemicals.** The complex  $\text{K}_6[\text{Co}_2(\text{CN})_{10}\text{O}_2] \cdot \text{H}_2\text{O}$  (*I*) was prepared after Haim and Wilmarth<sup>4</sup> with the use of the Schlenk flask technique<sup>5</sup>. All other chemicals used as starting materials for preparation or for buffer solutions were of reagent grade (Lachema, Brno).

**Apparatus and equipment.** Polarographic measurements were made on an LP 60 type polarograph (Laboratorní přístroje, Prague) with a pen recorder EZ 4 of a sensitivity of  $3.5 \cdot 10^{-10} \text{ A/cm}$ . The *iR* drop in the electrolytic circuit was eliminated by an automatic compensator based

\* Part VII: This Journal 38, 650 (1973).



on an operating amplifier<sup>6</sup>. Both polarographic and kinetic measurements were made in a universal modular electrolytic vessel<sup>7</sup>. The dropping mercury electrode had a drop time  $t_1 = 4.20$  s at a height of mercury column of 50 cm and at a potential of 0 V in 0.1M-KCl; the rate of flow of mercury was  $m = 1.60$  mg/s (measured under mercury). All potential values are referred to a silver chloride powder electrode in a saturated potassium chloride solution<sup>8</sup>. The vibrating platinum electrode was in the form of a platinum wire 1 mm in length and 0.5 mm in diameter sealed in glass; vibrations of a frequency of 50 c.p.s. were realized by an adapted vibrator available on the market<sup>14</sup>.

Products of the electrode process were studied with the aid of a Kalousek commutator (constructed in the Institute's electronic laboratory) and by electrolysis at constant potential on a mercury pool electrode. A preparative electronic potentiostat with an output voltage of 90 V and maximum current of 1 A was constructed also in the Institute's electronic laboratory. Coulometric measurements during electrolyses were made with an AMEL 558 type integrator. All kinetic measurements were made in Sørensen phosphate buffers, pH values were measured with a PHM 4 pH meter (Radiometer, Copenhagen), a glass electrode G-200 B and a reference SCE with a precision to within  $\pm 0.05$  pH. The ionic strength was controlled by addition of KCl. Weighed amounts of *I* (solid) in small polyethylene vessels were inserted into the reaction vessel and dissolved in the electrolyte. Owing to good solubility of the complex, its dissolution time (during stirring with an electromagnetic stirrer and a stream of inert gas) was negligible against the half time of the studied reaction.

## RESULTS AND DISCUSSION

### *Oxidation-Reduction Properties of Complex I*

An aqueous solution of the complex *I* at pH > 12 has a deeply red-brown colour and gives a single polarographic reduction wave (*D*) in the potential range from +0.2 to -1.9 V ( $E_{1/2} = -1.42$  V in 0.5M NaOH) independent of time; its height is directly proportional to the concentration of *I*. The dependence of the limiting current of wave *D* on the square root of the height of mercury column gives a straight line passing through the origin of coordinates, an evidence that the electrode process is in the corresponding potential range controlled by diffusion of the depolarizer. By comparison of the wave *D* with that of the complex<sup>14</sup>  $[(CN)_5Co-OC_6H_4O-Co(CN)_5]^{6-}$  it follows that the electrode process involves transfer of six electrons (assuming the same reaction mechanism and similar diffusion coefficients). This conclusion is supported by coulometry with a mercury pool electrode at -1.6 V. The polarographic wave in logarithmic coordinates shows an irreversible character and its half-wave potential depends on concentration of the base electrolyte, on the sort and charge of the cation (Fig. 1) but not on the sort of the anion:

0.05M-NaOH + 1M:	LiCl	NaCl	KCl	RbCl	CsCl
$E_{1/2}$ , V:	-1.48	-1.37	-1.34	-1.32	-1.31
0.05M-NaOH + 0.1M:	KCl	BaCl <sub>2</sub>	LaCl <sub>3</sub>		
$E_{1/2}$ , V:	-1.45	-1.3	-1.25		

The observed shifts of  $E_{1/2}$  values can be attributed to the influence of the double layer on irreversible electrode processes. The complex *I* is reduced on the negatively charged electrode surface and since it has a large negative formal charge ( $-6$ ) its approximation to the electrode is hindered by electrostatic repulsion. Thus, the reduction becomes more difficult. The energy of an ion in the double layer is determined by the  $\psi$  potential which depends on the base electrolyte concentration approximately as<sup>9</sup>  $|\psi| = \pm(RT/zF) \ln C_s + \text{const}$ . In our case, the minus sign applies. The value of  $|\psi|$  decreases with increasing  $C_s$  resulting in an easier reduction. In the case of such a highly charged ion it can be assumed that the transfer of an electron from the electrode to the depolarizer proceeds through ion pairs which diminish the charge of the particle and enable the formation of an activated bridge complex of the type electrode-cation-depolarizer. Its formation is facilitated by higher concentration of the cation, its greater polarizability, and lower dielectric constant of water in the electrode double layer<sup>10</sup>.

The products of the electrode process with  $\tau_{1/2} < 20$  ms were studied with the aid of the Kalousek commutator; the reduction products of *I* are at the given conditions and potentials polarographically inactive. This conclusion was substantiated by constant-potential electrolysis on a mercury pool cathode. The only possible electroinactive species which can be considered as a reduction product at our conditions is  $[\text{Co}(\text{CN})_5\text{H}]^{3-}$  formed<sup>11</sup> by protonation of the primary product,  $[\text{Co}(\text{CN})_5]^{4-}$ . The central Co atom in the oxidation state +3 is obviously reduced at the electrode by two electrons. Other two electrons are consumed in reduction of the  $\mu$ -peroxo group:

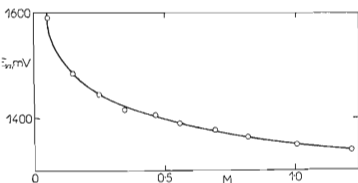
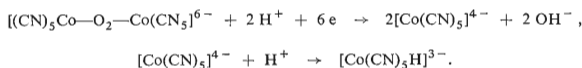


FIG. 1

Dependence of  $E_{1/2}$  for Reduction Wave of *I* on Concentration of  $\text{NaClO}_4$

$2 \cdot 10^{-3}\text{M}$  solution of *I* in  $0.5\text{M-NaOH}$ .

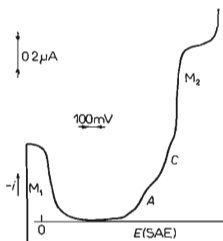


FIG. 2

Polarogram of Decomposition Products of *I* in Aqueous Buffer

$0.05\text{M}$  Borate buffer, pH 9.2; *I* 0.2, 298 K. Beginning from +0.2 V.

The polarographic behaviour of the compound *I* suggests that in the redox reaction between  $[\text{Co}(\text{CN})_5]^{3-}$  and molecular oxygen<sup>4</sup> electrons are completely transferred from cobalt to oxygen and the bridge ligand has the structure of  $\text{O}_2^{2-}$ . The peroxy group is so stabilized by coordination that it is not reducible. The species *I* is reduced as a whole in the potential range expected for reduction of Co(III) complexes analogously as in polarography of  $\mu$ -peroxy complexes studied by Vlček<sup>12</sup>.

By using a platinum vibration electrode, the potential range was extended to the region of probable oxidation of *I*. Although the complex  $[(\text{CN})_5\text{Co}^{\text{III}}-\text{O}_2-\text{Co}^{\text{IV}}.(\text{CN})_5]^{5-}$  was chemically synthesized<sup>13</sup>, oxidation of the complex *I* on the platinum electrode was not observed.

The complex *I* is stable only in strongly alkaline solutions and is rapidly decomposed in buffered solutions of  $\text{pH} < 12$ . The kinetics of its decomposition could not be studied by our experimental techniques. The species  $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$  was found polarographically to be the dissociation product. The other product is  $[\text{Co}(\text{CN})_5.\text{O}_2]^{4-}$  (*II*) formed by splitting off  $\text{Co}(\text{CN})_5$  from *I*:



A solution of *I* at 9–12 is practically an equimolar mixture of these species and its composition changes only very slowly at ambient temperature.

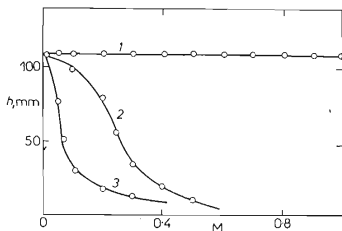


FIG. 3

Influence of Anions on Height of Wave  $M_1$  for Reduction of *II*

Wave height in relative units.  $0.05\text{M}-\text{Na}_2\text{B}_4\text{O}_7$ , 293 K; 1  $\text{ClO}_4^-$ ; 2  $\text{Cl}^-$ ; 3  $\text{Br}^-$ .

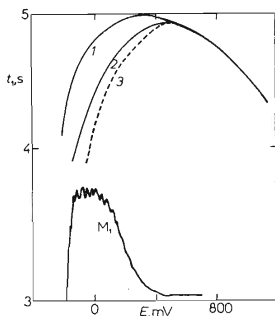


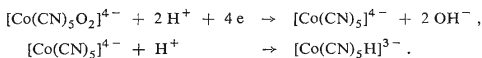
FIG. 4

Dependence of Drop Time on Applied Voltage (mV)

1  $0.5\text{M}-\text{Na}_2\text{B}_4\text{O}_7$ ; 2  $5 \cdot 10^{-3}\text{M}$  *II* added; 3  $5 \cdot 10^{-3}\text{M}$   $[\text{Co}(\text{CN})_5\text{H}]^{3-}$ .  $M_1$  denotes reduction wave of *II*.

Oxidation-Reduction Properties of  $[(\text{CN})_5\text{Co}-\text{O}_2]^{4-}$ 

The species *II* is formed by decomposition of *I* in buffered solutions of  $\text{pH} < 12$ . Fig. 2 shows a polarogram of a nearly equimolar mixture (light red solution) of  $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$  and *II*. The total limiting current is the same as with species *I* (assuming the same analytical concentration) and corresponds to transfer of six electrons. Waves *A* and *C* correspond to reduction of  $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$ . Limiting currents of waves  $M_1$  and  $M_2$  were corrected for time change (from kinetic data) and, in addition, wave  $M_2$  was corrected with regard to the behaviour of  $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$  since waves *C* and  $M_2$  could not be separated enough by choosing a suitable medium. The dependence of the limiting current on the height of mercury column shows that waves  $M_1$  and  $M_2$  are controlled by diffusion. A comparison with  $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$  (as internal standard) suggests that wave  $M_2$  is a four-electron one. All products of the electrode process in this wave are polarographically inert. The polarographic behaviour of *II* (wave  $M_2$ ) is an evidence for its assumed stoichiometry and oxidation states of its components. The central  $\text{Co(III)}$  is reduced by two electrons to  $\text{Co(I)}$  and at the same time  $\text{O}_2^{2-}$  is reduced by two electrons. The end products are the corresponding hydride and  $\text{OH}^-$ :



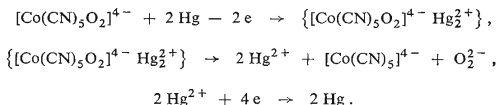
The reduction wave  $M_1$  of *II* starts from the potential of mercury dissolution, is controlled by diffusion and is directly proportional to the concentration of *II*. In buffered solutions containing no deformable anions, wave  $M_1$  is a two-electron one. The only electroactive product found in this step is  $\text{O}_2^{2-}$ . A two-electron reduction of the complex *II* results in its decomposition to give  $\text{H}_2\text{O}_2$  and  $[\text{Co}(\text{CN})_5\text{H}]^{3-}$ .

The height of wave  $M_1$  decreases with increasing concentration of deformable anions and with their deformability (Fig. 3); the reduction of *II* is probably facilitated by adsorption forces in the interface. Deformable anions which are strongly adsorbed at potentials more positive than the electrocapillary zero block the electrode surface and thus hinder the reduction of the complex *II*. The dependence of drop time on potential (Fig. 4) shows that the final reduction product of *II*,  $[\text{Co}(\text{CN})_5]^{4-}$ , is in the mentioned potential range strongly adsorbed; adsorption of the depolarizer is not excluded. The limiting current of wave  $M_1$  decreases with increasing negative potential under all studied conditions to the residual and charging current of the base electrolyte irrespective of the solution composition (ionic strength,  $\text{pH}$ , kind of ions) or temperature.

This effect can be explained as follows. The complex *II* bears a high negative charge ( $-4$ ), hence its reduction on the positively charged mercury surface is facilitated both by coulombic attraction and adsorption. With decreasing positive charge of the interface, the attraction weakens and the reduction becomes more difficult. At potentials more negative than the electrocapillary

zero, the electrode process is stopped by repulsion between the depolarizer and the electrode. In addition, the reduction product is desorbed (Fig. 4) whereby the activation energy of the electrode process increases. Since the drop of the limiting current of wave  $M_1$  is independent of ionic strength it seems that electrostatic forces (responsible for the current drop in reduction of anions) are not the only reason for this effect.

The reduction of the complex *II* in wave  $M_1$  proceeds most probably through formation of compounds with mercury since wave  $M_1$  is observed only if a mercury electrode is used. On electrodes from other materials (Pt, Au, C) no reduction wave of *II* corresponding to  $M_1$  was observed. We assume the following electron transfer mechanism:



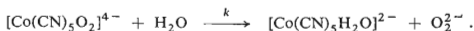
The observed cathodic current corresponds in substance to reduction of  $\text{Hg}_2^{2+}$ ; we have to deal with a "mercury assisted" process involving a close interaction of the depolarizer with the electrode surface in accord with the properties of wave  $M_1$ . At a sufficiently high negative potential the mentioned process is stopped and another reduction mechanism starts in wave  $M_2$ .

### Decomposition Kinetics of Complex II

The complex *II* is very stable in weakly alkaline solutions. Its decomposition kinetics was determined polarographically at lower pH and elevated temperature from the decrease of wave  $M_1$  and increase of waves *A* and *C* at the expense of  $M_2$  (Fig. 2); simultaneously a new wave due to reduction of  $\text{H}_2\text{O}_2$  appeared. The total limiting current ( $A + C + M_2$ ) is independent of time. In less acidic solutions, the waves *A* and *C* slightly increase probably as a result of an interaction between the electrode reaction products and  $\text{H}_2\text{O}_2$ .

The decomposition of the complex *II* in buffered solutions is governed by first-order reaction kinetics,  $d[\text{II}]/dt = -k[\text{II}]$ ; the logarithm of the height of wave  $M_1$  (as well as  $M_2$ ), which is proportional to the concentration of *II*, depends linearly on time. The rate constants determined from the slope of this dependence are summarized in Table I. The dependence of  $\log k$  on pH is linear with a slope of  $-1$  and the rate constant depends linearly on the buffer concentration, hence we have to deal with a general acid catalysis:  $k = \sum k_i[\text{HA}_i]$ , where  $k_i$  denotes catalytic rate constant and  $\text{HA}_i$  general acid. We found:  $k_{(\text{H}_3\text{O}^+)} = (1.2 \pm 0.2) \cdot 10^4 \text{M}^{-1} \text{s}^{-1}$  ( $I$  0.15),  $k_{(\text{H}_2\text{PO}_4^-)} = (3.5 \pm 0.5) \cdot 10^{-3} \text{M}^{-1} \text{s}^{-1}$  ( $I$  0.35) at 308 K. The activation energy of dissociation,  $E_a$ , was determined from the slope of the linear dependence of  $\log k$  on  $1/T$  as  $26 \pm 2$  kcal/mol, a value close to that<sup>14</sup> for dissociation of  $[\text{Co}(\text{CN})_5\text{—O—C}_6\text{H}_4\text{OH}]^{4-}$ , 25.5 kcal/mol. The negative slope of the dependence of  $\log k$  on the

square root of ionic strength suggests that oppositely charged ions enter into the activated complex:



The latter two were found as final products of the decomposition of *II* in aqueous buffered solutions, an evidence that during the redox reaction between molecular oxygen and pentacyanocobaltate(II) an unpaired electron is completely transferred from the latter into the vacant  $\pi$  orbits of oxygen. This is in accord with the high electronegativity of oxygen causing a shift of the electron density from the central atoms toward the bridge ligand. Hence, the reaction of  $[\text{Co}(\text{CN})_5]^{3-}$  with  $\text{O}_2$  proceeds by a pure redox-addition mechanism<sup>15</sup> evidenced already with *p*-benzoquinone<sup>14</sup> and its derivatives<sup>16</sup>.

TABLE I  
Representative Experimental Rate Constants for Decomposition of *II* at Various Conditions

	Temperature 308 K, [HA] 0.1M												
pH	6.18	6.80	7.32	8.03	6.87	6.87	6.87	7.62	7.62	7.62	7.32	7.32	7.32
$\mu$	0.15	0.15	0.15	0.15	0.35	0.35	0.35	0.15	0.25	0.35	0.15	0.15	0.15
$k \cdot 10^4, \text{s}^{-1}$	79	19.5	5.75	1.10	9.50	8 <sup>a</sup>	6.5 <sup>b</sup>	3.85	2.70	2.30	5.75	10.30 <sup>c</sup>	21.0 <sup>d</sup>

<sup>a</sup> [HA] = 0.05M; <sup>b</sup> [HA] = 0.025M; <sup>c</sup> 313 K; <sup>d</sup> 318 K.

The primary, very stable product of the redox reaction is a binuclear diamagnetic  $\mu$ -peroxo complex. It could be assumed that the interaction between two  $\text{Co}(\text{CN})_5$  groups and  $\text{O}_2$  leads to an electron activation of the latter causing splitting of the O—O bond analogously to activation of molecular hydrogen<sup>17</sup>. However, the stabilization of oxygen in the complex *I* after the redox addition is so strong that the  $\text{O}_2^{2-}$  group does not show its redox properties. Even after splitting off a  $\text{Co}(\text{CN})_5$  group and formation of the mononuclear complex *II*, where  $\text{O}_2^{2-}$  is one of the monodentate ligands, an independent reduction of the  $\mu$ -peroxo group was not observed. At potentials more anodic than  $E_{1/2}$  for reduction of  $\text{H}_2\text{O}_2$ , only "mercury assisted" reduction of the complex proceeds; at potentials more cathodic the bound peroxo group is reduced only during reduction of the central atom.

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Translated by K. Míčka.