

REDOX REACTIONS OF COBALT CYANIDE COMPLEXES. VII.*

THE KINETICS AND MECHANISM OF THE REDUCTION OF POTASSIUM BROMOPENTACYANOCOBALTATE(III) WITH SODIUM BOROHYDRIDE

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The kinetics of the reduction of $[\text{Co}(\text{CN})_5\text{Br}]^{3-}$ with sodium borohydride was followed and the most probable mechanism of the oxidation-reduction reaction was proposed. A simultaneous hydrolytic reaction of BH_4^- with H_2O , which suppresses the borohydride reduction efficiency, competes with the reaction between $[\text{Co}(\text{CN})_5\text{Br}]^{3-}$ and BH_4^- . The BH_4^- species is inactive towards $[\text{Co}(\text{CN})_5\text{Br}]^{3-}$. It is hydrolyzed in a reaction with water with formation of the intermediate, BH_3OH^- , and of the final product, $\text{B}(\text{OH})_4^-$, and of molecular hydrogen. BH_3OH^- is the active particle in the reaction with $\text{Co}(\text{CN})_5\text{Br}^{3-}$. The reaction is autocatalyzed in an induction period, during which the catalytically active particle and final reaction product, $[\text{Co}(\text{CN})_5\text{H}]^{3-}$, is formed. The overall rate determining step is the dissociation of the binuclear bridged complex with formation of $[\text{Co}(\text{CN})_5]^{3-}$, which then undergoes a fast reaction with BH_3OH^- , yielding $[\text{Co}(\text{CN})_5\text{H}]^{3-}$ ($k_c \approx 50\text{M}^{-1}\text{s}^{-1}$, $E_a \approx 22\text{ kcal/mol}$).

The kinetics and mechanism of the reaction between $[\text{Co}(\text{CN})_5]^{3-}$ and BH_4^- , in which $[\text{Co}(\text{CN})_5\text{H}]^{3-}$ is formed, have been described^{1,2}. Since both the preparation of $[\text{Co}(\text{CN})_5]^{3-}$ and manipulation with this substance in the solid state and in solution are experimentally difficult, an attempt was made to use complex cyanides of trivalent cobalt for the preparation of $[\text{Co}(\text{CN})_5\text{H}]^{3-}$ solutions. The identity of the final products of the chemical and electrochemical reduction of $[\text{Co}(\text{CN})_5]^{3-}$ and $[\text{Co}(\text{CN})_5\text{X}]^{3-}$ ($\text{X} = \text{H}_2\text{O}, \text{Cl}, \text{Br}, \text{I}$) has already been proven^{1,2}. The electrochemical preparation of $\text{Co}(\text{CN})_5\text{H}^{3-}$ solutions has also been dealt with in previous papers^{3,4}.

Elucidation of the kinetics and mechanism of the homogeneous chemical reduction of $[\text{Co}(\text{CN})_5\text{Br}]^{3-}$ with sodium borohydride, with the purpose of finding the optimum conditions for the preparation of $\text{Co}(\text{CN})_5\text{H}^{3-}$ solutions, constitutes the contents of the present paper.

EXPERIMENTAL

$\text{K}_3[\text{Co}(\text{CN})_5\text{Br}]$ was prepared as described by Adamson⁵ from $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Br}_2$ by reaction⁶ with KCN . To obtain as pure a substance as possible, it was necessary to carry out all operations in solutions cooled with a mixture of finely ground ice and water. The complex precipitation with

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ethanol also had to be carried out very carefully, just to the first turbidity. In this way it was possible to obtain very pure preparations, with the lowest content of the undesirable aquocomplex. The substance purity was preferably checked polarographically. All other chemicals were of p.a. purity (Lachema, Brno).

Instruments and equipment were identical with those used in the previous work^{1,2}. Kinetic measurements were carried out exclusively in borate buffers with sufficient capacity (0.05M). The pH was checked before and after the reduction with potassium borohydrate.

RESULTS AND DISCUSSION

Reaction Kinetics

The study of the kinetics of the homogeneous $[\text{Co}(\text{CN})_5\text{Br}]^{3-}$ reduction with sodium borohydride is chiefly based on recording time variations in the polarographic limiting diffusion currents of polarographically active species. All species, whose concentration changes with time could be followed during the course of the reaction, are summarized in Table I. For experimental reasons (a considerable amount of hydrogen is liberated during the reduction), spectral methods were used for identification of the final product of the $[\text{Co}(\text{CN})_5\text{H}]^{3-}$ homogeneous chemical reduction, which is polarographically inactive (Table I and Fig. 1). On addition of solid sodium borohydride to an aqueous buffered $[\text{Co}(\text{CN})_5\text{Br}]^{3-}$ solution, the BH_4^- reaction with water begins immediately on dissolution. An instantaneous decrease in the BH_4^- concentration, the appearance of the BH_3OH^- species and an increase in its concentration are observable. The $[\text{Co}(\text{CN})_5\text{Br}]^{3-}$ concentration is almost unchanged within an interval from the dissolution of solid borohydride (~ 5 s) to several tens

TABLE I

Species Followed During the Homogeneous Redox Reaction between $\text{Co}(\text{CN})_5\text{Br}^{3-}$ and BH_4^- and Their Polarographic and Spectral Characteristics

n Number of electrons in the electrode process at the dropping mercury electrode.

Species	Polarography		Symbols	Spectra	
	$E_{1/2}$, V(s.c.e.) ^a	n		λ nm	ϵ $\text{mol}^{-1} \text{l cm}^{-1}$
$[\text{Co}(\text{CN})_5\text{Br}]^{3-}$	-0.8	+1	A	400	360
	-1.32	+1	C		
$[\text{Co}(\text{CN})_5]^{3-}$	-1.32	+1	C	278	6 000
$[\text{Co}(\text{CN})_4]^{3-}$	-1.2	+1	B	360	7 000
BH_4^-	+0.105	-8	I	—	—
BH_3OH^-	-0.65	—	II	—	—

^aValid for solution of pH 8.2; I 0.5; 25°C.

of seconds (depending upon the reaction conditions). After this induction period, a decrease in the $[\text{Co}(\text{CN})_5\text{Br}]^{3-}$ concentration is manifested by a decrease in the limiting currents of its reduction waves, the $i_d^A : i_d^B$ ratio being constant. Simultaneously, the concentration of the hydrolysis intermediate, BH_3OH^- , decreases immediately after the induction period. In cases of comparable concentrations of the reactants, the BH_3OH^- concentration decreases below the detection limit of the method used ($< 10^{-6}\text{M}$). The anodic faradaic current of the BH_3OH^- oxidation at the dropping mercury electrode completely disappears. Only the residual and the capacity currents can be observed (Fig. 2). In the spectrum, a decrease in the band at λ 400 nm (ϵ 360) can be observed after the induction period, along with formation and increase in the band at λ 278 nm (ϵ 6000). Simultaneously, strong hydrogen evolution occurs. The complex reduction is a slower reaction than the borohydride reaction with water. The reducing ability of the borohydride solution is diminished due to this parallel reaction. For this reason, a large excess of borohydride (more than 100 times the molar concentration) was required to carry out the total complex reduction. For example, a buffered $[\text{Co}(\text{CN})_5\text{Br}]^{3-}$ solution of $1 \cdot 10^{-3}\text{M}$ concentration, at pH 9.5 (I 0.4), was completely reduced with sodium borohydride of $8 \cdot 10^{-2}\text{M}$ concentration only after 9 h.

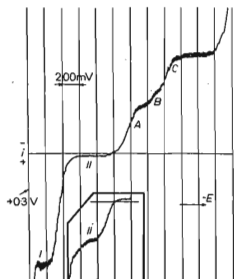


FIG. 1

The Polarographic Behaviour of the Reactants in a Buffered Aqueous Solution

Borate buffer, pH 9.65; I 0.5; 25°C ; I and II immediately after dissolving sodium borohydride; $S^I = 1 : 500$; $S^{II} = 1 : 10$, sensitivity for the cathodic portion of the curve, $1 : 100$.

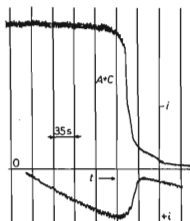


FIG. 2

An Example of the Induction Period Shown on the Limiting Currents of the Wave of $[\text{Co}(\text{CN})_5\text{Br}]^{3-}$ Reduction ($2 \cdot 10^{-3}\text{M}$, Waves A and C) and Wave II (the lower curve) of the Oxidation of the Species BH_3OH^- in a Buffered Solution ($1 \cdot 10^{-1}\text{M}$ - NaBH_4)

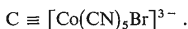
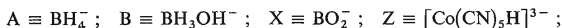
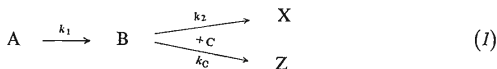
Borate buffer + 4M - KCl , 0.05M ; pH 9.8; $S^{A+C} = 1 : 50$, $S^{II} = 1 : 30$; 25°C .

The time necessary for complete reduction was sufficiently long for undesired substitution or dissociation reactions of the initial complex to take place. This is chiefly the substitution of the heteroligand with water^{7,8} with formation of $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$ which is manifested by a shift in the $E_{1/2}$ of wave A to more negative potentials. The presence of free cyanide ions in these solutions documents a gradual substitution of the cyanide ligands with the solvent molecules, the initial co-ordination number being preserved. Newly formed particles (with the probable composition $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$, $[\text{Co}(\text{CN})_4(\text{H}_2\text{O})_2]^{-}$) are reduced with borohydride in the same way as the parent species, $[\text{Co}(\text{CN})_5\text{Br}]^{3-}$.

An increase in the concentration of $[\text{Co}(\text{CN})_5]^{3-}$ in the reaction solution was not observed ($i_d^A : i_d^B$ was constant during the whole reaction). For the study of the kinetics of the given reaction, it was first necessary to find those reaction conditions under which, on one hand, the reaction rate would be sufficient, and on the other hand, it would be possible to avoid all complicating effects. Thus reactant concentrations of the same order and relatively low pH values were employed.

The time dependence of the BH_4^- species concentration is not affected by the presence of $[\text{Co}(\text{CN})_5\text{Br}]^{3-}$ either during the induction period or after it. It is obvious that the BH_4^- species does not take a direct part in the complex reduction. It undergoes independent hydrolysis, forming a number of intermediates, and borate and hydrogen gas as the final products^{9,10}. The actual active species is the BH_3OH^- particle, as in the case of the $[\text{Co}(\text{CN})_5]^{3-}$ reduction, which is formed by direct dissociation of BH_4^- and is removed by two independent paths. The first path is the redox reaction with $[\text{Co}(\text{CN})_5\text{Br}]^{3-}$, the other is the reaction with water. Since the BH_3OH^- concentration assumes kinetically significant values only after the induction period, the rate of disappearance of this species must be higher than, or, in the limiting case, equal to the rate of its formation. The intermediate concentration is minimal and thus the procedure for the pseudo-stationary state¹¹ can be advantageously used as a justifiable approximation in the mathematical treatment of the reaction scheme.

The reaction can be described by the following scheme:



The following basic kinetic equations describe the reaction scheme:

$$-d[\text{A}]/dt = k_1[\text{A}], \quad -d[\text{C}]/dt = k_c \cdot [\text{C}] \cdot [\text{B}], \quad (2), (3)$$

$$k_1 \cdot [A] = k_2[B] + k_c[B] \cdot [C]. \quad (4)$$

On eliminating $[B]$, relation (5) can be obtained, giving the time dependence of the concentration of C, corrected for the decrease in the concentration of B through the competing reaction with water:

$$\ln [C]_0/[C] = (k_c \cdot k_1/k_2) [A]_0 [(1 - e^{-k_1 t})/k_1] - (k_c/k_2) ([C]_0 - [C]). \quad (5)$$

By plotting the dependence of $\ln [C]$ (or the logarithm of a value which is directly proportional to the concentration of C in solution) against the term $(1 - e^{-k_1 t})/k_1$, called the "corrected time", a linear dependence was obtained (Fig. 4), proving that the reaction is of the first order with respect to the concentration of $[\text{Co}(\text{CN})_5\text{Br}]^{3-}$. The distortion of the time dependence due to the induction period is negligible compared to the time necessary for following the reaction. The k_c/k_2

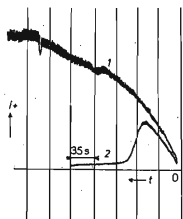


FIG. 3

The Induction Period on the Time Dependence of the Limiting Current of Wave II of the BH_3OH^- Oxidation in a Buffered Solution

1 $5 \cdot 10^{-3}\text{M-NaBH}_4$; 2 as 1 in the presence of $2 \cdot 10^{-3}\text{M} \cdot [\text{Co}(\text{CN})_5\text{Br}]^{3-}$. Borate buffer (0.05M); pH 9.38; I 0.4; 25°C ; $S^{II} = 1:10$.

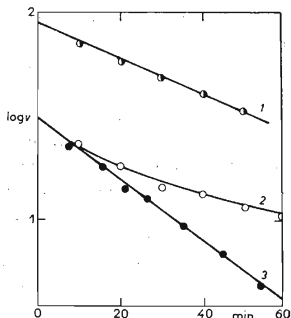


FIG. 4

Evaluation of the Time Dependence of the $[\text{Co}(\text{CN})_5\text{Br}]^{3-}$ Concentration Changes During BH_4^- Reduction in a Buffered Solution

1 The dependence of the log of the limiting current of wave I on time; 2 the dependence of the log of the limiting current of the complex reduction (A + C), during the reaction with borohydride, on time. 3 Corrected time given on the abscissa; coordinates the same; borate buffer (0.05M); pH 9.46; I 0.4; $5 \cdot 10^{-3}\text{M-NaBH}_4$; $2 \cdot 10^{-3}\text{M} \cdot [\text{Co}(\text{CN})_5\text{Br}]^{3-}$; 25°C .

value can be obtained from this linear dependence, if the value of the rate constant, k_1 , is known for the given reaction conditions and for the initial borohydride concentration. The absolute value of k_c was only assessed because k_2 , obtained from the relation

$$t_{\max} = (1/(\alpha - 1)) \ln \alpha \quad (6)$$

($\alpha = k_2/k_1$, t_{\max} is the time corresponding to the maximum on the time dependence of the BH_3OH^- concentration during the BH_4^- hydrolysis in the given medium), could be determined only to within one order of magnitude for experimental and calculation reasons ($k_2 \approx 5 \cdot 10^3 \text{ M}^{-1} \text{ s}^{-1}$; $k_c \approx 50 \text{ M}^{-1} \text{ s}^{-1}$, 25°C , $I = 0.4$). The dependence of the reaction rate on the BH_4^- analytical concentration, followed within the concentration range, $5 \cdot 10^{-4} \text{ M} - 5 \cdot 10^{-3} \text{ M}$, at a constant concentration of the complex ($2 \cdot 10^{-3} \text{ M} [\text{Co}(\text{CN})_5\text{Br}]^{3-}$) is linear. The dependence of the log of the reaction rate on pH is also linear, with a slope of -1 . Thus the reaction within the phase is, after the induction period, formally of the first order with respect to BH_4^- , H_3O^+ , and $[\text{Co}(\text{CN})_5\text{Br}]^{3-}$ concentrations. The reaction activation energy, assessed from the linear dependence $\log(k_c/k_2)$ on $1/T$, is 22 kcal/mol.

The reaction rate is affected by changes in the ionic strength of the solution. The $\log(k_c/k_2)$ vs \sqrt{I} dependence is linear with a positive slope. Thus particles with charges of the same sign enter the activated complex of the reduction reaction of $\text{Co}(\text{CN})_5\text{Br}^{3-}$ itself, since the slope, which is determined by the factor $z_A z_B$, has a positive value.

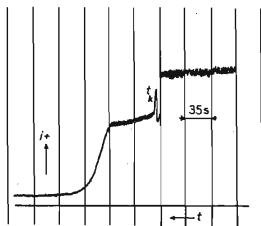
Reaction Mechanism

The actual reaction between the species $[\text{Co}(\text{CN})_5\text{Br}]^{3-}$ and BH_3OH^- is slow. This is indicated by the very small decrease in the concentrations of these species during the induction period (Figs 2 and 3). Since an induction period appears even in borohydride solutions which contain intermediates of the hydrolytic decomposition before addition of $[\text{Co}(\text{CN})_5\text{Br}]^{3-}$, it is not caused by subsequent reactions in the

FIG. 5

The Induction Period on the Time Dependence of the Limiting Current of Wave II of the Oxidation of Species BH_3OH^- after the Addition of $[\text{Co}(\text{CN})_5\text{Br}]^{3-}$.

Borate buffer (0.05M); pH 9.38; I 0.25; 21°C . $5 \cdot 10^{-3} \text{ M-NaBH}_4$; 15 minutes hydrolysis. $2 \cdot 10^{-3} \text{ M-Co}(\text{CN})_5\text{Br}^{3-}$ added at time t_k .

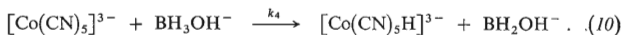
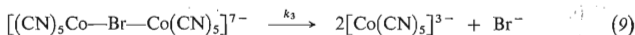
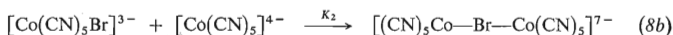
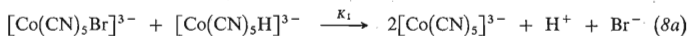


BH_4^- — H_2O system (Fig. 5). If the $[\text{Co}(\text{CN})_5\text{H}]^{3-}$ concentration is, at time $t = 0$, very small compared to the $[\text{Co}(\text{CN})_5\text{Br}]^{3-}$ concentration (a concentration ratio $< 10^{-3}$) no induction period is observed; the overall reaction course is not affected by the presence of $[\text{Co}(\text{CN})_5\text{H}]^{3-}$, i.e. the reaction course is, already at $t = 0$, entirely identical with that otherwise observed only after the induction period. Thus it can be assumed, with great probability, that the reaction is catalyzed by the reaction product.

The reaction mechanism is represented by the following scheme: A. the uncatalyzed reaction:



B. the catalyzed reaction:



The uncatalyzed reaction path, A, (Eq. (7)), through which the catalyst is generated, is very slow and results in the induction period. The catalyzed reaction path, B, assumes an interaction between the species $[\text{Co}(\text{CN})_5\text{Br}]^{3-}$ and the catalyst in the first step. Since the polarographic picture of the $[\text{Co}(\text{CN})_5\text{Br}]^{3-}$ reduction (Fig. 1) is not affected by the presence of the hydride (not even as far as the time dependence is concerned), establishment of a fast equilibrium must be assumed, a kinetically significant amount of $[\text{Co}(\text{CN})_5]^{3-}$ being its product (Eqs (8–9)). This species enters a very fast reaction¹² with BH_3OH^- (Eq. (10)), $k_4 \approx 10^6 \text{M}^{-1} \text{s}^{-1}$, with formation of the final reaction product and of the fragment BH_2OH^- , which yields borate after subsequent fast reactions with water.

The proven low reactivity of $[\text{Co}(\text{CN})_5\text{H}]^{3-}$ and, on the other hand, the extreme reactivity of the $[\text{Co}(\text{CN})_5]^{4-}$ species which is in an acid–base equilibrium with the hydride³, support the assumption of reaction path (8a). The first step in the oxidation–reduction disproportionation reaction (8b) is the formation of the activated complex – a bridged binuclear particle. Although direct detection of such intermediates is possible only with some systems^{13,14} it appears that formation of bridged

binuclear complexes as primary products of an electron transfer reaction with a strong component interaction is a general feature of these reactions¹⁵⁻¹⁹. The overall rate determining step after the induction period is the dissociation of the bridged binuclear complex, following the intramolecular redox process (9).

It follows from the experimental material assembled^{12,20,21} that the BH_4^- species is inactive in solution for the reduction of the complex cyanides of cobalt, ferricyanide, and numerous simpler oxidizing agents. On the contrary, the species BH_3OH^- , which is the first intermediate in the BH_4^- hydrolytic decomposition, is relatively stable and exhibits a high redox reactivity towards the above substrates.

Properties of $[\text{Co}(\text{CN})_5\text{H}]^{3-}$

$[\text{Co}(\text{CN})_5\text{H}]^{3-}$ is the final product of the oxidation-reduction reaction between $[\text{Co}(\text{CN})_5\text{X}]^{3-}$ or $[\text{Co}(\text{CN})_5\text{X}]^{3-}$ ($\text{X} = \text{H}_2\text{O}, \text{Cl}, \text{Br}, \text{I}$) and BH_4^- . The electrochemical behaviour of the hydride as well as its formation as the final product of the electrode reduction of complex cobalt cyanides unambiguously verify that the σ -electron pair of the Co—H bond is shifted towards the central atom. The hydride behaves rather like a species with a central atom in a lower oxidation state. On the contrary, certain conclusions concerning the spectral properties of the hydride lead to the formulation of the complex as a species with a central atom in the oxidation state +3. By direct comparison of the first $d-d$ transitions in complexes of the type $[\text{Co}(\text{CN})_5\text{X}]^{3-}$ a spectrochemical series² can be formed for various heteroligands, from which it is apparent that the simplest heteroligand, hydride, forms a slightly stronger ligand field than cyanide. In agreement with this, $[\text{Co}(\text{CN})_6]^{3-}$ is reduced at -1830 mV (S.C.E.)¹⁸ in 1M-KCl, while $[\text{Co}(\text{CN})_5\text{H}]^{3-}$ is, in aqueous medium, inactive within the accessible potential range (up to -2.4 V (S.C.E.)). This fact reflects the high activation energy of the hydride reduction process. From the point of view of acid-base properties, $[\text{Co}(\text{CN})_5\text{H}]^{3-}$ behaves like a very weak acid. The determined $\text{pK} \approx 18-19$ is in agreement with earlier determinations^{3,4}.

Preparation of $[\text{Co}(\text{CN})_5\text{H}]^{3-}$ solutions. The importance of the preparation of $[\text{Co}(\text{CN})_5\text{H}]^{3-}$ solutions is given by the role of this species in the homogeneous hydrogenization of organic substrates¹⁹, catalyzed by $[\text{Co}(\text{CN})_5]^{3-}$. There are basically three known preparation methods: a) homogeneous activation of molecular hydrogen with a $[\text{Co}(\text{CN})_5]^{3-}$ solution; b) reduction of complex cobalt cyanides with borohydride; c) electrochemical reduction of complex cobalt cyanides.

Procedure a) can be used only for very low concentrations when the established equilibrium can be shifted in favour of the product by changes in the complex concentration and the partial pressure of molecular hydrogen. As has been shown in previous studies¹², and in the present study, procedure b) is least suitable. The BH_4^- reaction with $[\text{Co}(\text{CN})_5\text{Br}]^{3-}$ is very slow and for increasing the reaction rate the reaction conditions must be changed in a way unsuitable for further manipulation (an increase in μ , a decrease in pH), not to mention the fact that a considerable excess of borohydride must be used to achieve complete reduction. For this reason, the time necessary for decaying of the reduction activity of the system, given by borohydride and its de-

composition intermediates, becomes longer. Moreover, the solution is saturated with molecular hydrogen, which is liberated during borohydride decomposition with water.⁹

The most advantageous procedure for preparation of $[\text{Co}(\text{CN})_5\text{H}]^{3-}$ solutions appears to be procedure c). By electroreduction of a solution of complex cobalt cyanides at a mercury pool electrode at a constant potential (-1.5 V (s.c.e.)) a defined hydride solution can be prepared³ up to the concentrations used for preparations, in a short time and without the presence of the reaction products from a reducing agent.

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