REDOX REACTIONS OF COBALT CYANIDE COMPLEXES. VI.*
THE KINETICS AND MECHANISM OF THE REDUCTION OF PENTACYANOCOBALTATE(II) WITH SODIUM BOROHYDRIDE

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The kinetics of the reduction of $Co(CN)_5^{3-}$ with sodium borohydride was investigated and the most likely mechanism for the oxidation-reduction reaction was proposed. The species BH_4^- is inactive toward $Co(CN)_5^{3-}$. It undergoes hydrolysis in solution, which is generally an acid catalyzed reaction, forming a series of intermediates and, finally, metaborate. The actual active species is BH_3OH^-, the first intermediate in the hydrolysis of BH_4^-, which enters a fast redox reaction with $Co(CN)_5^{3-}$ ($k \sim 10^6 M^{-1} s^{-1}$). The rate determining step is the formation of the BH_3OH^- species ($k_{H_3O^+} = (2 \cdot 6 \pm 0 \cdot 1) \cdot 10^6 M^{-1} s^{-1}$, 25°C, $\mu = 0 \cdot 2$).

It is well known that $Co(CN)_5^{3-}$ acts as a homogeneous hydrogenation catalyst[1]. It activates molecular hydrogen[2] and can even transfer it to certain unsaturated organic compounds[3]. The final product of the activation of molecular hydrogen by pentacyanocobaltate(II) is assumed to be the corresponding hydride complex, $Co(CN)_5H^{3-}$ (see[4]). This species appears in all the proposed mechanisms for the homogeneous hydrogenation of organic substances catalyzed by pentacyanocobaltate(II) as the actual active species.

The identity of the $Co(CN)_5H^{3-}$ species and the final product of the chemical reduction of $Co(CN)_5^{3-}$ or $Co(CN)_5X^{3-}$ ($X = H_2O$, Cl, Br, I) with the amalgams or the borohydrides of the alkali metals, or of their electrochemical reductions[4–6], has also been proven. The electrochemical preparation of $Co(CN)_5H^{3-}$ has already been described[7]. In spite of the wide use of the borohydrides of the alkali metals in preparative and analytical chemistry, there exist only a few detailed kinetic studies of the reduction of inorganic substances with these strong reducing agents.

This work contains a study of the kinetics and mechanism of the reaction between $Co(CN)_5^{3-}$ and BH_4^-, with the purpose of finding the optimal conditions for the preparation of $Co(CN)_5H^{3-}$ in this way.

EXPERIMENTAL

Chemicals and Apparatus

The preparation of pentacyanocobaltate(II) and all the kinetic studies were carried out in a protective atmosphere of inert gas, by the Schlenk type glassware technique using a vacuum-inert gas

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line[8]. Argon was purified under dry conditions by passing it over the BTS-catalyst. $K_6[Co_2(CN)_{10}] . 4 H_2O$ was prepared according to Adamson[9]. The solid phase of the Adamson salt was used everywhere where the presence of free cyanide was undesirable. In the remaining cases, an aqueous solution of this salt, prepared by the titration of a solution of cobalt(II) chloride with an aqueous solution of potassium cyanide in an inert atmosphere, was used directly. For this purpose an automatic pipette, adapted for work in an inert atmosphere, was used (Fig. 1). The aqueous solution of $Co(CN)_5H^{3-}$ was prepared by the electrolysis of $Co(CN)_5Br^{3-}$ at a constant potential (-1.5 V vs S.C.E.) on a mercury pool electrode in an electrolysis vessel constructed for work in an inert atmosphere[12]. $NaBH_4$ (Metal Hydrides, Inc.) was recrystallized from a solution of dimethylether diethylene glycol (Diglyme). The active hydrogen content in the sodium borohydride preparations was determined argentometrically[13]. All the remaining chemicals used either as starting materials for the preparations or to prepare buffers were of p.a. purity (Lachema, Brno).

The kinetic studies were carried out in a thermostated polarographic vessel produced by the firm Metrohm. The time dependence of the concentration changes of species in the reaction solution was monitored polarographically on the instrument LP-55 (Laboratorní přístroje, Prague) with photographic recording and a galvanometer sensitivity of $2.8 . 10^{-8}$ A/mm/m. The capillary used had the parameters: $m = 1.60$ mg/s, $t_1 = 4.20$ s (at the potential of the calomel electrode in a $0.1M$-KCl solution). As reference electrode was used a silver chloride electrode with a saturated solution of potassium chloride (with a potential of $+40$ mV vs S.C.E. at 20°C)[12]. Weighed amounts of borohydride were added directly into the solution of the complexes in the solid phase in polyethylene weighing vessels. The time necessary for dissolving the added borohydride was made negligible compared to $\tau_{1/2}$ of the studied reactions by intensive stirring (by an electromagnetic stirrer and by a stream of inert gas).

All kinetic studies were carried out in borate buffers. The pH of the buffer solutions was measured with the pH-meter PHM-4 (Radiometer, Copenhagen) with the glass indicator electrode G-200B and reference saturated calomel electrode. The precision was not less than ± 0.05 pH units. The ionic strength was maintained by additions of potassium chloride. The visible and ultraviolet spectra of the solutions were registered on the Unicam SP 800 spectrophotometer.

RESULTS AND DISCUSSION

Reaction Kinetics

The time change of the concentration of the starting materials, $Co(CN)_5H^{3-}$ and BH_4^-, was followed from the variations of the polarographic limiting diffusion currents for the one-electron reduction of $Co(CN)_5^{3-}$ ($E_{1/2} = -1.2$ V vs S.C.E.) (wave I)[5,6] and for the eight-electron oxidation of BH_4^- ($E_{1/2} = -0.15$ V $vs.$ S.C.E) (wave II, Fig. 2). The proven end products of the studied redox reaction are metaborate and $Co(CN)_5H^{3-}$. Both species are polarographically inactive. The existence and concentration of $Co(CN)_5H^{3-}$ were found by the presence and analysis of the absorption band at λ 305 nm (ε 620), corresponding to the first $d-d$ transition of this species[4].

On addition of sodium borohydride, in a concentration comparable to that of the complex ($\sim 10^{-3}M$ solutions), to an aqueous solution of $Co(CN)_5^{3-}$, there instantaneously occurs a gradual change in colour from the original olive green (corresponding to a solution of $Co(CN)_5^{3-}$) to yellow-orange. Simultaneously are noticeable

evolution of bubbles of gas. During the course of the reaction the polarographic picture exhibits a decrease of waves *I* and *II*. In the absorption spectra in the ultra-violet and visible range can simultaneously be observed a decrease of the band, $\lambda\,278$ nm $(\varepsilon\,6000)$ and the formation and growth of a band at $\lambda\,305$ nm $(\varepsilon\,620)$. The rate of change in the absorbance of the reaction solution and the decrease of pola-rographic waves *I* and *II*, which corresponds to the reaction rate, increases with de-creasing pH, with increasing temperature, with increasing ionic strength and con-centration of borohydride.

The conversion of the reactants to the proven reaction final products formally corresponds to summary equation (A)

$$BH_4^- + 2\,H_2O + 2\,Co(CN)_5^{3-} \;\rightarrow\; BO_2^- + 2\,Co(CN)_5H^{3-} + 3\,H_2 \,. \quad (A)$$

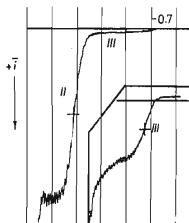The course of the reaction is determined by the experimentally found kinetic rela-tion (I):
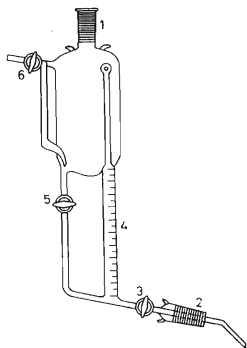
FIG. 2

Polarographic Picture of the Oxidation of Sodium Borohydride in Aqueous Solution

Wave *II* with $E_{1/2} = -0.15$ V (S.C.E.) in 0·5M-NaOH, from -0.7V. 210 mV/absc.; wave *III* with $E_{1/2} = -0.65$ V (S.C.E.) in bo-rate buffer (0·05M), I 0·5, 20°C, after 7 minutes of hydrolysis, from -0.9 V; $S^{II} = 1/500$; $S^{III} = 1/10$.

$$-\frac{d[BH_4^-]}{dt} = -\frac{d[Co(CN)_5^{3-}]}{dt} = k[BH_4^-][H_3O^+] = k'[BH_4^-], \qquad (1)$$

where

$$k' = k[H_3O^+].$$

The reaction rate, defined as the time change in the concentration of $Co(CN)_5^{3-}$, or of BH_4^-, does not depend on the concentration of $Co(CN)_5^{3-}$ ($5 . 10^{-3}$M-BH_4^-, pH 9·40, 25°C, I 0·2):

$[Co(CN)_5^{3-}]$, M	$5 . 10^{-4}$	$1 . 10^{-3}$	$2·5 . 10^{-3}$	$4 . 10^{-3}$	$5 . 10^{-3}$
$k . 10^4$, s^{-1}	10·8	11·5	11·0	10·2	11·0

The experimental linear dependence of the reaction rate on the concentration of borohydride and the linear dependence, log k'–pH, demonstrate a first order reaction with respect to both reacting species. The relatively narrow range of pH and borohydride concentration was determined by the method used. In buffered solution, the reaction order is decreased and it eventually appears as pseudo-first-order. Representative values of the rate constant k' in dependence on pH are given in Table I.

Values of k' measured from 20°C–35°C (pH 9·77, I 0·2):

t, °C	20	25	30	35
$k' . 10^4$, s^{-1}	3·0	4·35	6·0	7·85

At various ionic strengths the following values were found (25°C, pH 9·40):

I	0·2	0·3	0·4	0·5	0·6
$k' . 10^4$, s^{-1}	11·0	24·5	42	72·5	120

The determined catalytic rate constant has the value ($k_{H_3O^+} = (2·6 \pm 0·1) . 10^6$ M^{-1} s^{-1}, 25°C, I 0·2) and the determined activation energy of the process is $E_a = 11·8$ kcal/mol).

The decay of borohydride in an aqueous solution is a general acid catalyzed reaction[14–16] summarily given by equation (B)

$$BH_4^- + H_3O^+ + 2H_2O \rightarrow H_3BO_3 + 4H_2. \qquad (B)$$
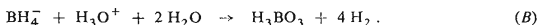
The reaction rate in buffered solution is given by relation (2)

$$-\frac{d[BH_4^-]}{dt} = [BH_4^-] . \sum_i k_{HA_i}[HA_i], \qquad (2)$$

HA_i is a general acid in the Brönsted sense. The contribution of the rate constant of the spontaneous reaction, $k_{H_2O} = 1·2 . 10^{-9}M^{-1} s^{-1}$, 25°C, I 1·0 (see[17]) and the catalytic rate constant $k_{H_3BO_3} = (1 \pm 5) . 10^{-4}M^{-1} s^{-1}$, 25°C, I 0·50 (see[18]) to the overall rate constant $k' = \sum k_i$ is negligible considering the high value of the catalytic rate constant, $k_{H_3O^+}$.

TABLE I

Values of the Rate Constants for the Reaction between $Co(CN)_5^{3-}$ and BH_4^-
$2 . 10^{-3}M$-$Co(CN)_5^{3-}$, $5 . 10^{-3}M$-BH_4^-, I 0·2, 25°C.

pH	8·30	8·50	8·70	8·95	9·17	9·32	9·40
$k' . 10^4$, s^{-1}	100	87	48	24	18·5	13·0	11·0

pH	9·77	9·94	10·15	10·40
$k' . 10^4$, s^{-1}	4·35	3·15	1·60	1·10

Mechanism

From the experimental results follows identity between kinetic laws (*1*) and (*2*). Since the reaction rate does not depend on the concentration of $Co(CN)_5^{3-}$ and the reaction course of the hydrolysis of borohydride alone is not influenced by the presence of the complex, the slowest step, controlling the overall rate of the studied reaction and the structure of the activated complex, must be identical with the slowest step and the transition state in the case of the hydrolysis of borohydride in aqueous solution.
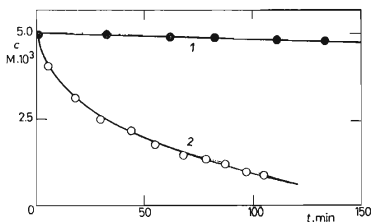

Fig. 3

Time Dependence of the Change of Concentration of the Species BH_4^- monitored on Wave *II*.
Aqueous solution of sodium borohydride: *1* in 0·5M-NaOH, 25°C; *2* borate buffer (0·05M); pH 9·48, 25°C, I 0·5.

The dependence of the reaction rate on pH shows that the actual active species coming into interaction with $Co(CN)_5^{3-}$ is not the species BH_4^-. In strongly alkaline solution (pH > 13), in which the particle BH_4^- is stable (used[13] in the argentometric determination of BH_4^-), the reaction almost ceases, as is noticeable from Fig. 3. The degree of conversion corresponds only to the negligible degree of decay of BH_4^- in this medium. With increasing acidity of the solution, the rate of decay of borohydride increases and with it the rate of reduction of $Co(CN)_5^{3-}$. It is evident that the actual active species must be one of the species resulting from the hydrolytic decay of borohydride.
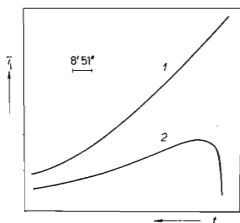

Fig. 4

Time Variations of the Concentration of the Species BH_4^- and BH_3OH^- During the Hydrolysis of Sodium Borohydride in an Aqueous Buffered Solution

Borate buffer (0·05M); pH 9·38; I 0·2; $5 \cdot 10^{-3}$M BH_4^-. Registered anodic current at potential: $1 - 0·05$ V vs S.C.E. (wave II), S 1/500; $2 - 0·5$ V vs S.C.E. (wave III), S 1/25.

It has been shown that the decay of borohydride occurs gradually through a series of ionic and non-ionic species[10,11,20,21].

In the partially hydrolyzed solution of borohydride were definitely identified species BH_4^-, BH_3OH^-, and $B(OH)_4^-$. The remaining species ($BH_2(OH)_2^-$, $BH(OH)_3^-$, and non-ionic species) are probably present only in very low concentrations because of their short life-times. The final product of the decay of borohydride is the borate, $B(OH)_4^-$, which is inactive with respect to the studied reaction.
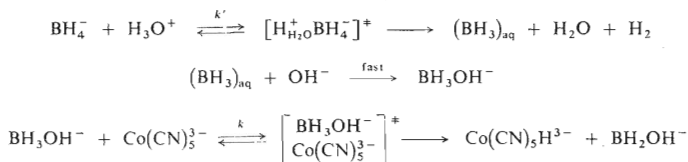
The species BH_3OH^- is the first hydrolytic product of borohydride and is polarographically active $(E_{1/2} = -0·65$ V vs S.C.E.)[14,15] – wave III (Fig. 2). The time dependence of the concentration of this species in slightly alkaline solution exhibits a maximum (Fig. 4) and shows that wave III belongs to the oxidation of intermediate B in the consecutive reaction

$$A \xrightarrow{\ k_1\ } B \xrightarrow{\ k_2\ } C \qquad (A = BH_4^-, B = BH_3OH^-, C = B(OH)_4^-).$$
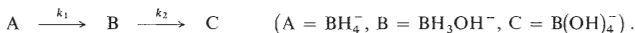
In the presence of $Co(CN)_5^{3-}$, the anodic current of the oxidation of BH_3OH^- does not appear at all. Similarly, if a solution of $Co(CN)_5^{3-}$ is added to an already hydrolyzed solution of borohydride, the concentration of BH_3OH^- drops instantly to below the sensitivity of the method used ($<10^{-6}$M). The actual active species is thus BH_3OH^- or some precursor other than BH_4^-.

The primary product of the decay of BH_4^- is borane[22]. Its notable properties as a Lewis acid, given by its atomic configuration and electronic structure, cause a very fast reaction with any donors of electrons present. As donors of electrons must be considered both OH^-, and the species $Co(CN)_5^{3-}$. (There are known borane adducts with complexes of transition metals with metal-boron bonds[23].) Cyanide ligands are also potential electron donors. Although cyanide complexes with the bridge bond M—CN—B are known[24], the basicity of the bonded cyanide group, in the case of the cyanide complexes of cobalt, is by 20 orders lower than the basicity of the active centre on the central atom[25]. It would then also be possible to consider BH_3 as the actual reducing agent. However, since, with increasing ionic strength of the solution, the rate constant also increases (the dependence log $k'-\sqrt{I}$ is linear with a positive slope), species with charges of the same polarity enter the activated complex, *i.e.* most probably $Co(CN)_5^{3-}$ and BH_3OH^-. Quantitative conclusions concerning the size of the charges of the species entering the activated complex, which result from the Brönsted–Christiansen–Scatchard equation, cannot be drawn in the case of the polarographic method, since the appropriate quantitative relationships are exactly valid only in solutions of low ionic strength.

In the proposed mechanism of the oxidation–reduction reaction between $Co(CN)_5^{3-}$ and BH_4^- there is a bimolecular attack of active species with weak interaction

$$BH_4^- + H_3O^+ \xrightleftharpoons{k'} [H_{H_2O}^+BH_4^-]^* \longrightarrow (BH_3)_{aq} + H_2O + H_2$$

$$(BH_3)_{aq} + OH^- \xrightarrow{fast} BH_3OH^-$$

$$BH_3OH^- + Co(CN)_5^{3-} \xrightleftharpoons{k} \begin{bmatrix} BH_3OH^- \\ Co(CN)_5^{3-} \end{bmatrix}^* \longrightarrow Co(CN)_5H^{3-} + BH_2OH^-$$

The species BH_2OH^- reacts instantly in a number of subsequent degradation reactions with H_3O^+ to give metaborate.

The overall reaction rate is limited by the rate of dissociation of the species BH_4^- ($k' \sim 10^4\ M^{-1}\ s^{-1}$) and thus $k \gg k'$. The values of the rate constants, found during the reaction of $Co(CN)_5^{3-}$ with other substrates have values of about $10^6 M^{-1}\ s^{-1}$.

In the mechanism is assumed the transfer of hydride hydrogen from the species BH_3OH^- to $Co(CN)_5^{3-}$. However, it is not possible to exclude also the possibility that the primary step of the reaction is the reduction of $Co(CN)_5^{3-}$ to $Co(CN)_5^{4-}$ and subsequent reaction with water to give $Co(CN)_5H^{3-}$. The possibility of distinguishing these two paths is not provided even by using isotope methods.

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