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The Redox Reactions of Complex Cobalt(II) Cyanides.
X. The Kinetics and Mechanism of the Redox Addition Reaction of Pentacyanocobaltate(II) with 1,4-Benzoquinone and 2-Methyl-1,4-benzoquinone in Aqueous Solutions

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On the basis of stopped-flow kinetic measurements it was found that, in systems in which $[Co(CN)_5^{3-}]_0$ *is at least twice the initial concentration of the particular benzoquinone,* $Co(CN)_5^{3-}$ *reacts both with 1,4-benzoquinone (BQ) and with 2-methyl-1,4-benzoquinone (TQ) in two irreversible steps. In the first step, a very rapid redox-addition reaction of the initial components results in formation of a reactive intermediate, probably* $(NC)_5CoQ^{3-\cdot}$*, with ligand Q, which is isoelectronic with the anion of the corresponding benzosemiquinone. The consecutive–competitive reaction of the intermediate* $(NC)_5CoQ^{3-\cdot}$ *with a further pentacyanocobaltate(II) species in a further irreversible step results in quantitative formation of the binuclear bridge complex* $(NC)_5CoQCo(CN)_5^{6-}$*, discussed earlier. The lower limit for the rate constant of the first step was estimated to be* $k_1 \geqslant 2 \times 10^8$ M^{-1} s^{-1} *(BQ) and* $\geqslant 1.5 \times 10^8$ M^{-1} s^{-1} *(TQ) and the rate constant of the second step was found to be* $k_2 = 3.2 \times 10^4$ M^{-1} s^{-1} *(BQ) and* 3.0×10^4 M^{-1} s^{-1} *(TQ) (ionic strength → 0; 25 °C).*

In reaction system with $[Q]_0 > [Co(CN)_5^{3-}]_0$ *interaction of the* $(NC)_5CoQ^{3-\cdot}$ *species with benzoquinone was observed.*

In systems with identical initial concentrations of benzoquinone and $Co(CN)_5^{3-}$*, the* $(NC)_5CoQ^{3-\cdot}$ *intermediate decomposes after an induction period. A mechanism for this interactions was proposed.*

Introduction

Vlček and Hanzlík [1, 2] described binuclear bridge complexes of the type $(NC)_5CoQCo(CN)_5^{6-}$ (designated Z in the subsequent text), which are formed as the final product in the reaction of $Co(CN)_5^{3-}$ with 1,4-benzoquinone and some other substituted 1,4-benzoquinones. In the described binuclear complex, bridge ligand Q is isoelectronic with the dianion of the corresponding hydroquinone. It was found that the bridge complexes (Z) are formed only when the initial concentration of $Co(CN)_5^{3-}$ is at least twice the initial concentration of benzoquinone.

This work is concerned with determining the kinetics and detailed mechanism of formation of the already described binuclear product (Z) of the reaction of $Co(CN)_5^{3-}$ with 1,4-benzoquinone (BQ) and 2-methyl-1,4-benzoquinone (TQ). This study is limited to these two members of the previously studied series of substituted 1,4-benzoquinones, as they are the only two of the series of benzoquinones reacting with $Co(CN)_5^{3-}$ that are sufficiently soluble in water to permit kinetic measurements.

Experimental

Kinetic Measurements

All the kinetic measurements were carried out on a home-made stopped-flow apparatus [3]. The dead time (designated τ_s) of the kinetic cell of the flow-through apparatus at a flow-rate of 30 cm³/s is 4.5 ms. Concentration changes were followed spectrophotometrically over the region 220–1150 nm. The pump section of the apparatus has four pumps connected in two pairs by a block of control valves. This arrangement has the advantage that unstable initial reaction components can be prepared for each individual kinetic experiment by mixing corresponding precursors in the control valve block.

The recordings for kinetic experiments with large excesses of one of the initial components ($[Co(CN)_5^{3-}]_0 \gg [Q]_0$) were evaluated by plotting the dependence

$$\ln(\log(T_\infty/T_t)/\log(T_\infty/T_s)) = -t \cdot k_{obs} \quad (1)$$

where T_∞ is the transmittance of the reaction system for $t \to \infty$, T_t is the transmittance of the system for time t and T_s is the transmitttance of the system at the moment τ_s ($t \equiv 0$). The slopes (k_{obs}, [s^{-1}]) of these dependences were found by the least squares method. The initial concentration (indicated by index 0) is understood to be the concentration of the given component in the reaction mixture at the instant of initiation of the reaction after mixing in the mixing cell.

Reaction courses in systems controlled by second order kinetics were evaluated by graphical comparison of the experimental curves with theoretical shape of the transmittance plotted by the digitally controlled recorder of an HP 9820 calculator according to the relationship

$$T_t = T_n \cdot 10^{\epsilon_{ef}(\chi_n - \chi_t)} \qquad (2)$$

in which ϵ_{ef} is the effective molar absorption coefficient of the reaction system, T_n is the transmittance of the system for time $t \rightarrow n$ (usually the last recorded point). Quantity χ_t corresponds to the integral sum of the concentrations, whose change in time is controlled by second order kinetics, across the length of the observation channel according to relationship [4, 5] (3)

$$\chi_t = v/k \cdot \ln \frac{b - a \cdot \exp\{-k(b-a)[t + (l+d)/v]\}}{b - a \cdot \exp\{-k(b-a)(t + d/v)\}} \qquad (3)$$

where symbols a and b designate the initial concentrations of the reagents, v is the flow-rate [m/s], l is the distance between the point of mixing and the entrance into the observation channel (in our apparatus l = 0.8 cm), d is the length of the observation channel (2.34 cm) and χ_n is the value of χ_t for time t approaching n. The values of rate constants k [M^{-1} s^{-1}] were varied until the experimental and theoretical curves were identical.

All the kinetic measurements had to be carried out in the complete absence of oxygen under an argon atmosphere. This was freed of traces of oxygen by passing through a column filled with granules of BTS catalyst (Badische Anilin und Soda Fabrik).

Measurement of Absorption Spectra

The absorption spectra in the visible and ultraviolet regions were measured on a Unicam SP 800 spectrophotometer. To record spectra of substances sensitive to atmospheric oxygen, a flow-through quartz cuvette from the firm Helma adapted for measuring spectra in controlled anaerobic conditions was used in the Unicam SP 800 spectrophotometer (see Fig. 1). Solutions flowing through the cuvette came into contact with only glass, quartz glass, polytrifluorochloroethylene, of which the body of the cuvette adapter was made, and polytetrafluoroethylene (PTFE), of which the closing valves were made.

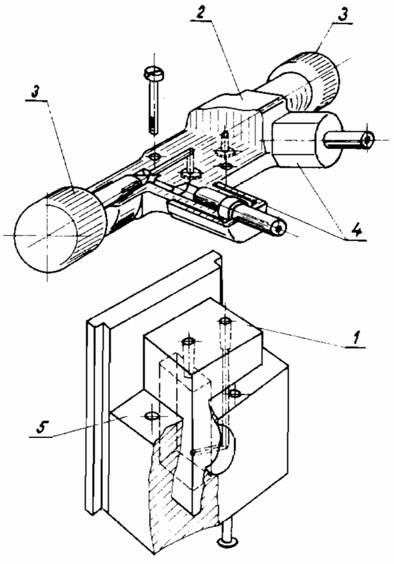

Fig. 1. Flow-through cuvette adapted for measurements under anaerobic conditions; 1) flow-through cuvette, 2) adapter body, 3) cone valves, 4) inlets with nuts and seals, 5) cuvette holder in the Unicam SP 800 spectrophotometer.

Chemicals

Water for solution preparation was doubly distilled. The second distillation was carried out in an all quartz apparatus from VEB Quarzschmelze, Berlin Staaken. Commercial products, where not otherwise designated, were of *p.a.* purity from Lachema and were employed without further purification. The content of cyanide in sodium cyanide (Lachema, *p.a.*), was determined several times. The product has a declared cyanide content (98%) and was used without further purification. Potassium cyanide was recrystallized from aqueous solution by precipitation with ethanol. 1,4-benzoquinone and 2-methyl-1,4-benzoquinone were purified by sublimation. A quinone solution was prepared fresh for each group of parallel measurements. The concentration of these solutions was found photometrically. The linear dependence of the absorbance on the concentration was tested for the most intense band for each component.

Preparation of $Co(CN)_5^{3-}$ Solutions

Because of the instability of aqueous solutions of the cyanides of divalent cobalt [6, 7], greater reliability of the measurement was ensured by preparation of the $Co(CN)_5^{3-}$ solution for each individual measurement directly in the valve block of the flow-through system by mixing an oxygen-free solution of cobalt(II) chloride and sodium cyanide.

The concentration ratio [CN^-] : [Co^{2+}] was always greater than 8. At a flow-rate of 30 cm^3 s^{-1}, this solution of $Co(CN)_5^{3-}$ 'aged' from the instant of mixing

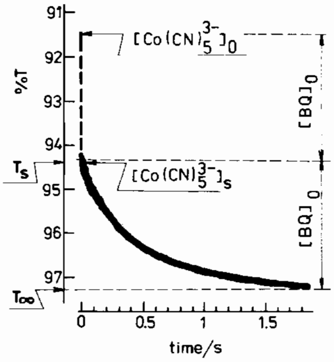

Fig. 2. Time course of the transmittance of the $Co(CN)_5^{3-}$, BQ reaction system. λ = 970 nm. $[Co(CN)_5^{3-}]_0 = 5.5 \times 10^{-5}$ *M*, $[BQ]_0 = 1.9 \times 10^{-5}$ *M*, $[CN^-]_0 = 2 \times 10^{-4}$ *M*.

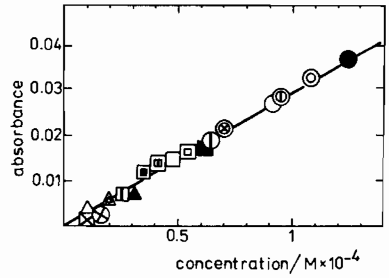

Fig. 3. Dependences reflecting the stoichiometry of the reaction of $Co(CN)_5^{3-}$ with 1,4-benzoquinone. 1) Single points: a_∞ values plotted against $[Co(CN)_5^{3-}]_0 - 2[BQ]_0$. 2) Double points: a_s *vs.* $[Co(CN)_5^{3-}]_0 - [BQ]_0$. 3) Solid points, see text. $[Co(CN)_5^{3-}]_0/M \times 10^{-4}$: for all round points 1.26, for all square points 0.62, for triangular points 0.31. $[BQ]_0$ can be read from graph 6 for identical points.

the initial components (Co^{2+} and CN^-) in the valve block to the instant of mixing in the mixing point in the kinetic cell with the second component of the studied reaction system by less than 100 ms. The period of injection for the experiment, determined by the volume of the syringe which stops the solution flow was about 170 ms. The convenience of this method of preparation of the $Co(CN)_5^{3-}$ solution was confirmed by direct observation of the formation of $Co(CN)_5^{3-}$ on the absorption band at 970 nm by-mixing the solutions of cobalt(II) and alkaline cyanide directly in the kinetic cell. It was shown that the concentration of pentacyanocobaltate(II) formed at the instant of passing the observation point (*i.e.* after a time of less than 4.5 ms) corresponds to the initial concentration of cobalt(II) less that consumed by traces of dissolved oxygen (the residual concentration of oxygen was less than 2×10^{-6} *M*).

Results and Discussion

Reaction Systems with Concentration Ratios of $[Co(CN)_5^{3-}]_0 \cdot [Q]_0 \geqslant 2$

Reaction stoichiometry

The time course of the concentration decrease of the pentacyanocobaltate(II) in the reaction systems with the given component ratio, measured at 970 nm, is given in Fig. 2 ($Co(CN)_5^{3-}$ is the only component of the given reaction system which absorbs at this wavelength). It is clear that the $Co(CN)_5^{3-}$ concentration decreases in these reaction systems, both for the reaction with 1,4-benzoquinone and for that with 2-methyl-1,4-benzoquinone (both further designated generally as Q), in two clearly defined steps. To the instant when the solution passes the observation point, the concentration of pentacyanocobaltate(II) decreases to value $[Co(CN)_5^{3-}]_s$, which is less than concentration $[Co(CN)_5^{3-}]_0$ by a value which is practically equal to the initial concentration of benzoquinone. A further decrease in the concentration of pentacyanocobaltate(II) below value $[Co(CN)_5^{3-}]_s$ could be observed with time and the concentration of $Co(CN)_5^{3-}$ approached the value $[Co(CN)_5^{3-}]_0 - 2[Q]_0$ in this step. The stoichiometry found for the reaction decrease of $Co(CN)_5^{3-}$ is given in Fig. 3. The absorbance of the reaction system a_s (recalculated for a unit length of the observation channel) at instant τ_s plotted against the $[Co(CN)_5^{3-}]_0 - [Q]_0$ values lies, within expérimental error, on the same straight line as abosrbance values a_∞ plotted against the concentration values $[Co(CN)_5^{3-}]_0 - 2[Q]_0$ (a_∞ applies for the reaction system in which the studied reaction has proceeded to completion). The values of absorbance a_s for the system formed by mixing a solution of $Co(CN)_5^{3-}$ with deoxygenated water (full dots) are plotted in Fig. 3 against $[Co(CN)_5^{3-}]_0$. The slope of the straight line evaluated by the least squares method has a value of 299 ± 35 M^{-1} cm^{-1} (= $\epsilon_{Co(CN)_5^{3-}}$ at 970 nm [8]).

The decrease in the amount of 1,4-benzoquinone or 2-methyl-1,4-benzoquinone was measured on bands at 247 nm and 251 nm, respectively. It was clear from these measurements that, in agreement with the decrease in the concentration of pentacyanocobaltate(II) in the first step, practically all Q disappeared up to the instant when the solution reached the observation point.

Figure 4 depicts the transition spectra of the described reaction system for the region 390–450 nm. The a_s values designate the values of the absorbance of the described reaction system at instant τ_s and a_∞ are the values of the absorbance corresponding to complete conversion of the minor reactant (benzoquinone) into the final binuclear bridge product (read 3 s after commencement of the reaction) (see also Fig. 6). It is clear from these spectra that the optimum conditions for following the formation of the final product (i.e. the greatest difference

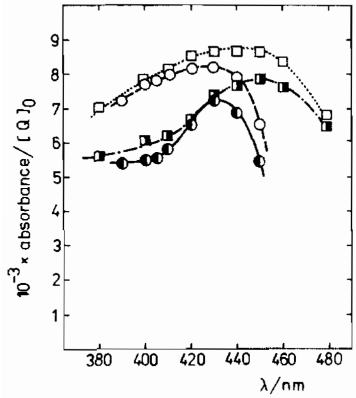

Fig. 4. Dependence of the $a_s/[Q]_0$ (◐, ◨) and $a_\infty/[Q]_0$ (○, □) values on for reaction system $Co(CN)_5^{3-}$, BQ (round points) and for the $Co(CN)_5^{3-}$, TQ system (square points).

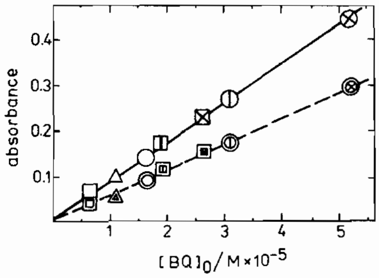

Fig. 5. Dependence of the a_s (dotted line – – –) and a_∞ (solid line ———) values for the $Co(CN)_5^{3-}$, BQ system on $[BQ]_0$. λ = 405 nm. The $[Co(CN)_5^{3-}]_0$ concentrations are given in Fig. 3.

between values a_s and a_∞) involved measurement at 405 nm (1,4-benzoquinone) and 410 nm (2-methyl-1,4-benzoquinone). Values a_s and a_∞ plotted against the initial concentration of 1,4-benzoquinone (Fig. 5) yield a straight line with a slope of 5450 ± 230 M^{-1} cm^{-1} (dotted line in Fig. 5) for a_s and a slope of 8160 ± 170 M^{-1} cm^{-1} for a_∞. The values of the slopes of the corresponding dependences of a_s and a_∞ at 410 nm for 2-methyl-1,4-benzoquinone are 5870 ± 180 M^{-1} cm^{-1} and 8510 ± 150 M^{-1} cm^{-1}, respectively. It is clear from the time change in the transmittance at 405 nm (Fig. 6) that the values of T_s, which are attained by the transmittance of the studied reaction system at the instant of passing the observation point, can only be explained by the presence of an intermediate, which is formed at the same rate as that at which Q disappears or at which the concentration of $Co(CN)_5^{3-}$ decreases in the first step. It is clear from Fig. 6 that the values of T_s are apparently the same as the values obtained by extrapolating the plotted time course to the instant of commencing the reaction ($t = -\tau_s$). It can

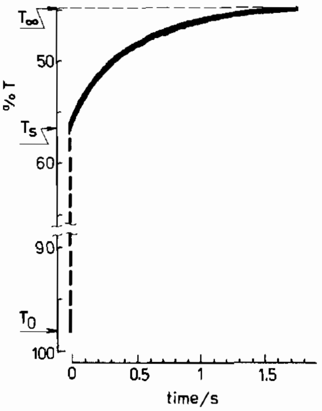

Fig. 6. Course of the transmittance at 405 nm for the $Co(CN)_5^{3-}$, BQ reaction system with time with initial concentration $[Co(CN)_5^{3-}]_0:[BQ]_0$ > 2. Concentrations $[Co(CN)_5^{3-}]_0$ and $[BQ]_0$ as in Fig. 2.

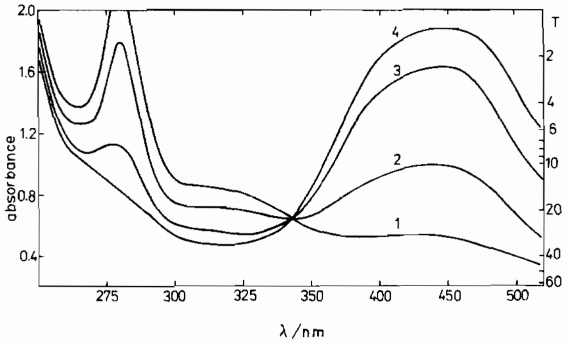

Fig. 7. Spectra of the $Co(CN)_5^{3-}$, TQ reaction system recorded 30 s after reaction initiation. $[Co(CN)_5^{3-}]_0 = 4.6 \times 10^{-4}$ *M*, $[TQ]_0/M \times 10^{-4}$ = 1) 0.64, 2) 1.15, 3) 1.9, 4) 2.32. $[CN^-]_0 = 3.5 \times 10^{-3}$ *M*, $[OH^-]_0 = 2.5 \times 10^{-1}$ *M*.

be seen that these values are much lower than the transmittance values T_0 which, considering the molar absorption coefficients of the initial components, the described systems attain at the instant of commencing the reaction (for the system in Fig. 6, the transmittance of the reaction system at the instant of commencing the reaction is not less than 95%, as none of the initial components has a molar absorption coefficient at 405 nm greater than 100 M^{-1} cm^{-1}). Identical conclusions can be drawn for the time change in the transmittance at 410 nm for the reaction system $Co(CN)_5^{3-}$, TQ.

The reaction stoichiometry obtained for the described reaction systems with an initial concentration ratio of $[Co(CN)_5^{3-}]_0:[Q]_0 \geqslant 2$ indicates that the decrease in the concentration of $Co(CN)_5^{3-}$ at the instant of attaining the observation point is practically equal to the initial concentration $[Q]_0$ and, considering that the overall reaction stoichiometry

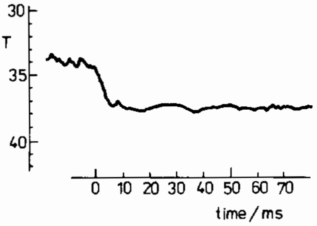

Fig. 8. Time dependence of the transmittance of the $Co(CN)_5^{3-}$, BQ system at 247 nm. $[Co(CN)_5^{3-}]_0 = 1.8 \times 10^{-5}$ *M*; $[BQ]_0 = 1.7 \times 10^{-5}$ *M*; $[CN^-]_0 = 2 \times 10^{-4}$ *M*.

found in earlier work [1, 2] is such that the final amount of final product Z is exactly equal to the amount of Q, it follows that both reaction steps are completely irreversible and involve no side reactions. It further follows that the concentration of the intermediate at instant τ_s must, within experimental error, be equal to the initial concentration $[Q]_0$. The slopes of the dependences of a_s on $[Q]_0$ at the given wavelength thus correspond to the absorption coefficients of the particular intermediates. The molar absorption coefficients of the final products Z for the given wavelength are equal to the slope of the dependence of a_∞ on $[Q]_0$.

Figure 7 gives the spectrum of the reaction system containing $Co(CN)_5^{3-}$ and TQ, measured in the cuvette depicted in Fig. 1. The cuvette was connected with the stopped-flow apparatus and was filled by injecting the reaction system formed by mixing the initial components in the kinetic cell of the flow-through apparatus. After completion of the injection the cuvette was transferred to the spectrophotometer so that recording began about 30 s after mixing. To retard the hydrolytic reaction in which the final product of the studied reaction decomposes [2], the measurement was carried out in 0.25 *M* NaOH. The maximum of the band at 450 nm, corresponding to the final product corresponds exactly to the determined stoichiometry. The sharp isosbestic point is characteristic of a reaction course which is not complicated by parallel reactions. The spectrum of the final product of the reaction of $Co(CN)_5^{3-}$ with 1,4-benzoquinone is described in paper [1].

Reaction kinetics and proposed mechanism

As has been demonstrated, the decrease in $Co(CN)_5^{3-}$ from value $[Co(CN)_5^{3-}]_0$ to value $[Co(CN)_5^{3-}]_s$ ($\approx [Co(CN)_5^{3-}]_0 - [Q]_0$) and the disappearance of practically all the benzoquinone occur in less than 4.5 ms. Only at the lowest concentrations where $[Co(CN)_5^{3-}]_0 \approx [Q]_0 = 2 \times 10^{-5}$ *M* was it possible, because of the large values of the molar absorption coefficients of the given benzoquinones, to observe a time decrease in the absorbance corresponding to the disappearance of the last traces of benzoquinone as a result of the studied reaction, by measuring the absorbance at 247 nm (BQ, $\epsilon = 1.96 \times 10^4$ M^{-1} cm^{-1}) or at 251 nm (TQ, $\epsilon = 2.04 \times 10^4$ M^{-1} cm^{-1}) (Fig. 8). The estimate of the lower limit for the rate constant for the first step corresponding to the disappearance of benzoquinone from the reaction mixture or the decrease in the concentration of pentacyanocobaltate(II) to value $[Co(CN)_5^{3-}]_0 - [Q]_0$ is 2×10^8 M^{-1} s^{-1} (BQ) or 1.5×10^8 M^{-1} s^{-1} (TQ).

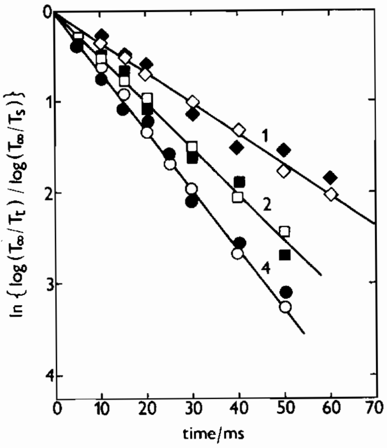

Fig. 9. Evaluation of kinetic measurements on the $Co(CN)_5^{3-}$, BQ system with $[Co(CN)_5^{3-}]_0 \gg [Q]_0$. Measurements at 970 nm are plotted as solid points, measurements at 405 nm are plotted as open points. The dependence numbers correspond to the experiment numbers in Table Ia).

The further decrease in the concentration of pentacyanocobaltate(II) from values $[Co(CN)_5^{3-}]_s$ to values $[Co(CN)_5^{3-}]_\infty$ and the increase in the absorbance at wavelengths of 405 nm and 410 nm from values a_s to values a_∞ was at least 100 times slower, depending on the ionic strength of the system. It is clear from Fig. 9 that, in reaction systems with a large excess of pentacyanocobaltate(II) over the initial concentration of benzoquinone, the dependences of the values of $\ln(\log(T_\infty/T_t)/\log(T_\infty/T_s))$ for both the studied time decrease in the concentration of pentacyanocobaltate and for the corresponding time increase in the absorbance at 405 nm (or 410 nm) are linear with identical slopes.

The formation of final product Z is thus controlled by the same process as the studied decrease in the concentration of pentacyanocobaltate(II) and the following rate equation is valid for both processes

$$\frac{d[Z]}{dt} = -\frac{d[Co(CN)_5^{3-}]}{dt} = \tag{4}$$

$$= k_2([Co(CN)_5^{3-}]_0 - [Q]_0 - [Z])\cdot(Q]_0 - [Z])$$

TABLE I. Values of the Rate Constant k_2, $I = 0.009\,M$, 25 °C, $[ClO_4^-] = 5\text{–}6 \times 10^{-3}\,M$.

Expt. no.	$[Co(CN)_5^{3-}]_0$ $M \times 10^{-4}$	$[Q]_0$ $M \times 10^{-5}$	k_{obs} s^{-1}	$k_2 \times 10^{-5}$ $M^{-1} \times s^{-1}$
a)	$Co(CN)_5^{3-}$, BQ system			
1	2.2	1.9	33.57	1.67
2	2.9	2.1	50.30	1.87
3	4.0	2.05	66.43	1.75
4	4.0	3.3	65.65	1.79
5	5.0	4.2	77.40	1.69
b)	$Co(CN)_5^{3-}$, TQ system			
1	2.1	1.7	29.53	1.53
2	3.0	1.9	39.90	1.42
3	4.0	2.2	55.94	1.48
4	5.0	3.0	70.5	1.50

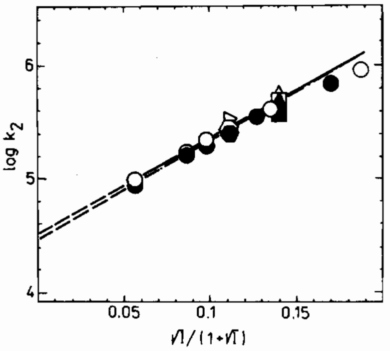

Fig. 10. Open circles: dependence of constant k_2 on the ionic strength in the $Co(CN)_5^{3-}$, BQ system; full circles the same dependence for the $Co(CN)_5^{3-}$, TQ system. $[Co(CN)_5^{3-}]_0 = 4 \times 10^{-4}\,M$; $[BQ]_0$, $[TQ]_0 \approx 3 \times 10^{-5}\,M$; $[CN^-]_0 = 2 \times 10^{-3}\,M$; $[ClO_4^-]_0 = 0\text{–}5 \times 10^{-2}\,M$. Angular points: effect of the OH^- concentration and free CN^- concentration on rate constant k_2. $[Co(CN)_5^{3-}]_0 = 3 \times 10^{-4}\,M$, $[BQ]_0$ (open points), $[TQ]_0$ (solid points) $\approx 2 \times 10^{-5}\,M$. $[CN^-]_0/M \times 10^{-2}$ = △, ▲: 2.35; ○, ●: 1.35; □, ■, ▷: 0.15. $[OH^-]_0/M \times 10^{-2}$ = □, ■: 2.25, △: 1.25.

The values of rate constant k_2 given in Table I were calculated as the ratio of slopes k_{obs} and the values of cncentration ($[Co(CN)_5^{3-}]_0 - [Q]_0$).

The cited experimental facts indicate a system of consecutive reactions

$$Co(CN)_5^{3-} + Q \xrightarrow{k_1} (NC)_5CoQ^{3-\cdot} \qquad (5)$$

$$Co(CN)_5^{3-} + (NC)_5CoQ^{3-\cdot} \xrightarrow{k_2} (NC)_5CoQCo(CN)_5^{6-} \qquad (6)$$

The first reaction step is the very rapid redox addition of benzoquinone to the $Co(CN)_5^{3-}$ complex anion forming the semiquinoid adduct $(NC)_5CoQ^{3-\cdot}$, an intermediate appearing as intense absorbance in the region 400–450 nm. The radical character of this intermediate was not directly provable; however, it is known from a number of papers, *e.g.* [9, 10], that the reduction of pentacyanocobaltate(II) when the substrate is a neutral molecule generally proceeds through radical intermediates. Further addtion of pentacyanocobaltate(II) to the semiquinoid anion radical then produces the binuclear bridge complex (Z).

The slope of the dependence of the rate constant k_2 on the ionic strength (Fig. 10) is in agreement with the product of the charges of the reacting species in the second step. The theoretical value of the slope of the dependence of the decadic logarithm of the rate constant k_2 on $\sqrt{I}/(\sqrt{I} + 1)$ for reaction species $Co(CN)_5^{3-}$ and $(NC)_5CoQ^{3-\cdot}$ according to the relationship

$$\log k = \log k^{\circ} + z_i \cdot z_j \cdot (\sqrt{I}/(\sqrt{I} + 1)), \qquad (7)$$

where z_i and z_j are the charges of the reactants, has a value of 9 (aqueous solutions, 25 °C). The values of the slopes found experimentally are 8.8 (BQ) and 8.9 (TQ). Fig. 10 also indicates that the rate of the reaction does not depend on the nature of the anion and is not affected by the concentration of free CN^- ions or by the concentration of hydroxide ions. The value of rate constant k_2 extrapolated to zero ionic strength for 1,4-benzoquinone has a value of $(3.2 \pm 0.5) \times 10^4\,M^{-1}\,s^{-1}$ and for 2-methyl-1,4-benzoquinone a value of $(3.0 \pm 0.3) \times 10^4\,M^{-1}\,s^{-1}$.

Reaction Systems with Concentration Ratios of $[Co(CN)_5^{3-}]_0 : [Q]_0 \leq 1$

In these systems the pentacyanocobaltate(II) concentration decreases below the detection limit

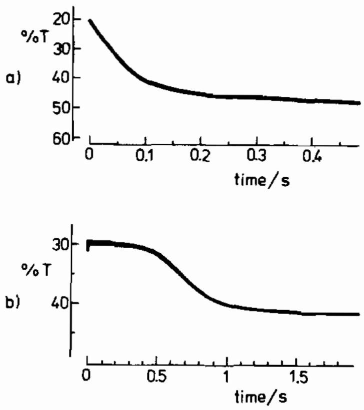

Fig. 11. Time dependence of the transmittance at 405 nm for the system with ratio $[\mathrm{Co(CN)_5^{3-}}]_0:[\mathrm{BQ}]_0 < 2$; $[\mathrm{CN^-}]_0 = 2 \times 10^{-4}$ *M*. a) $[\mathrm{Co(CN)_5^{3-}}]_0 = 5.5 \times 10^{-5}$ *M*, $[\mathrm{BQ}]_0 = 6.5 \times 10^{-5}$ *M*, b) $[\mathrm{Co(CN)_5^{3-}}]_0 = 5.5 \times 10^{-5}$ *M*, $[\mathrm{BQ}]_0 = 4.3 \times 10^{-5}$ *M*.

before attaining the observation point (*i.e.* in a time interval of less than 4.5 ms). In systems with initial concentrations of benzoquinone only slightly larger than the initial concentration of $\mathrm{Co(CN)_5^{3-}}$ the absorbance of these reaction systems a_s at 405 or 410 nm attains values corresponding to the appropriate linear dependence in Fig. 5 when plotted against a concentration equal to the initial concentration of pentacyanocobaltate(II) (minor reactant). Consequently, on attaining the observation point all the $\mathrm{Co(CN)_5^{3-}}$ is converted to $\mathrm{(NC)_5CoQ^{3-\bullet}}$.

After stopping the flow, the absorbance at 405 and 410 nm in the particular system decreases relatively rapidly (Fig. 11a) (the half-time for this decrease in Fig. 11a is 50 ms, while the half-time for the formation of product Z for the same initial concentration of pentacyanocobaltate(II) at an initial concentration of $[\mathrm{BQ}]_0 = 1.9 \times 10^5$ *M* is 300 ms). Neither the kinetics nor the mechanism of these absorbance decreases were studied in this paper in detail. It is clear from the measurements that were carried out in this area that the initial rate of absorbance decrease is increased by the residual concentration of unreacted Q and the reaction consists of decomposition of $\mathrm{(NC)_5CoQ^{3-\bullet}}$ induced by unreacted benzoquinone. In limiting cases, where for ratio $R = [\mathrm{Co(CN)_5^{3-}}]_0:[\mathrm{Q}]_0$ it held that $2 > R \geqslant 1$, the curves at 405 nm are characterized by a marked induction period (Fig. 11b).

Reaction steps (2) and (3) represent the complete mechanism of the formation of binuclear bridge complexes in systems with at least a two-fold excess initial $\mathrm{Co(CN)_5^{3-}}$ concentration compared with the initial concentration of benzoquinone. Decomposition of $\mathrm{(NC)_5CoQ^{3-\bullet}}$ in systems with excess Q can be interpreted by the assumption that the primary step involves electron transfer between the semiquinone (*i.e.* $\mathrm{(NC)_5CoQ^{3-\bullet}}$) of type $\mathrm{Q_i^{-\bullet}}$ and the quinone (*i.e.* BQ or TQ) of type $\mathrm{Q_j}$:

$$\mathrm{Q_i^{-\bullet}} + \mathrm{Q_j} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathrm{Q_i} + \mathrm{Q_j^{-\bullet}} \tag{8}$$

The values of the rate constants of the reactions involving exchange or transfer of electrons in aqueous solutions for 1,4-benzoquinone and its methyl derivates found for $i = j$ ($k_f = k_b$) from broadening of the EPR lines of the semiquinone anion radicals and for reactions where $i \neq j$, found on the basis of kinetic measurements by the pulse radiolysis method lie in the range 10^6–10^9 M^{-1} s^{-1} [11].

The decomposition of the anion-radical $\mathrm{(NC)_5CoQ^{3-\bullet}}$ in the presence of free Q can thus be written as

$$\mathrm{(NC)_5CoQ^{3-\bullet}} + \mathrm{Q} \rightleftharpoons \mathrm{(NC)_5CoQ^{2-}} + \mathrm{Q^{-\bullet}} \tag{9}$$

$$\mathrm{(NC)_5CoQ^{2-}} + \mathrm{H_2O} \longrightarrow \mathrm{(NC)_5CoOH_2^{2-}} + \mathrm{Q} \tag{10}$$

involving formation of an unstable substitution labile intermediate $\mathrm{(NC)_5CoQ^{2-}}$ which is also assumed to be a primary product of the electrochemical reaction involving oxidation of the products of the hydrolysis of the binuclear bridge compounds Z [1,2].

According to the proposed mechanism, benzoquinone acts as a catalyst in the decomposition of anion-radical $\mathrm{(NC)_5CoQ^{3-\bullet}}$, increasing the rate of substitution of anion-radical $\mathrm{Q^{-\bullet}}$ in species $\mathrm{(NC)_5CoQ^{-\bullet}}$ by a water molecule.

The decomposition of intermediate $\mathrm{(NC)_5CoQ^{3-\bullet}}$, a pathway other than reaction with benzoquinone, must be much slower. Otherwise, it would not be possible to explain formation of final product Z, which is quantitative even in systems with stoichiometric amounts of initial components (*i.e.* when $[\mathrm{Co(CN)_5^{3-}}]_0 = 2[\mathrm{Q}]_0$).

Measurements in which the first reaction step involves quantitative consumption of benzoquinone and the residual concentration of $\mathrm{Co(CN)_5^{3-}}$ is much lower than the concentration of the anion radical formed, *i.e.* when the solution does not contain free benzoquinone nor, eventually, $\mathrm{Co(CN)_5^{3-}}$ with which the radical anion $\mathrm{(NC)_5CoQ^{3-\bullet}}$ could react forming product Z, confirm that the presence of free quinone leads to an increase in the rate of decomposition of the semiquinoid adduct formed. The concentration of $\mathrm{(NC)_5CoQ^{3-\bullet}}$ in these systems decreases only after an induction period involving a slow decrease in the absorbance at 405 nm (or 410 nm). Two most probable mechanisms can be proposed for the decomposition of the anion radical in these systems with an induction period. In the absence of free benzoquinone in the reaction system, the decomposition of $(NC)_5CoQ^{3-\bullet}$ can occur either through a disproportionation reaction according to the equation

$$2\,(NC)_5CoQ^{3-\bullet} \overset{H^+}{\rightleftharpoons} (NC)_5CoQ^{2-} + (NC)_5CoQH^{3-} \qquad (11)$$

where species $(NC)_5CoQH^{3-}$ is an already described [1] relatively stable product in which ligand QH is isoelectronic with the hydroquinone anion, and where the substitution reaction of $(NC)_5CoQ^{2-}$ with water according to Eq. (9) releases free Q into the reaction system, or through a substitution reaction according to Eq. (12):

$$(NC)_5CoQ^{3-\bullet} \overset{H_2O}{\rightleftharpoons} (NC)_5CoOH_2^{2-} + Q^{-\bullet} \qquad (12)$$

Rapid disproportionation of the semiquinone radical anion $Q^{-\bullet}$ [12]

$$2\,Q^{-\bullet} \overset{H^+}{\rightleftharpoons} Q + QH^- \qquad (13)$$

leads to rapid establishment of equilibrium among species $Q^{-\bullet}$, Q and QH^-. Decomposition of the radical anion either through disproportionation or substitution is apparently slower than the reaction of $(NC)_5CoQ^{3-\bullet}$ with benzoquinone. The decomposition rate is apparently increased with the reappearance and increasing concentration of benzoquinone in the reaction system.

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