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The Redox Reactions of Complex Cobalt(II) Cyanides.
XI. The Kinetics and Mechanism of the Redox Addition Reaction of Pentacyanocobaltate(II) with 1,4-Naphthoquinone in Aqueous Solution

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The following reaction scheme was proposed on the basis of kinetic measurements on the reaction system $Co(CN)_5^{3-}$*–1,4-naphthoquinone (NQ), whose behaviour was studied in dependence on the ionic strength and by finding the reaction orders with respect to the reactants.*

$$NQ + Co(CN)_5^{3-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (NC)_5Co{\cdot}NQ^{3-\bullet} \qquad K_1$$

$$(NC)_5Co{\cdot}NQ^{3-\bullet} + Co(CN)_5^{3-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (NC)_5Co{\cdot}NQ{\cdot}Co(CN)_5^{6-} \qquad K_2$$

$$NQ + (NC)_5Co{\cdot}NQ{\cdot}Co(CN)_5^{6-} \rightleftharpoons \text{products } (P) \qquad K_3$$

It then holds for the rate of decrease in the amount of pentacyanocobaltate and for the rate of formation of products (P) in system with a large excess of $Co(CN)_5^{3-}$ *that*

$$-d[Co(CN)_5^{3-}]/dt = 2d[P]/dt =$$
$$= 2k_1k_2[Co(CN)_5^{3-}]^2{\cdot}[NQ]/(k_{-1} + k_2[Co(CN)_5^{3-}])$$

The derived rate relationship was confirmed experimentally and the rate constant k_1 *(*9.08×10^4 M^{-1} s^{-1}*) was found. The proposed mechanism is further confirmed by the dependence of the experimentally determined overall equilibrium constant*

$$K = [P]_{eq}/\{[Co(CN)_5^{3-}]_{eq}^2{\cdot}([NQ]_o - 2[P]_{eq})^2\}$$

on the ionic strength. The dependence of the logarithm of constant K on $\sqrt{I}/(1 + \sqrt{I})$ *yields a straight line with slope 9.1. The products of this reaction, which are quite unstable and thus cannot be analysed directly, have an intense absorption band at 500 nm.*

Differences between the mechanism of the reaction of $Co(CN)_5^{3-}$ *with 1,4-naphthoquinone and the mechanism of the reaction with 1,4-benzoquinone are discussed.*

Introduction

Compared with the reactions of pentacyanocobaltate(II) with 1,4-benzoquinone (BQ) and 2-methyl-1,4-benzoquinone (TQ), it was clear from preliminary experiments [1] that the mechanism of the reaction of $Co(CN)_5^{3-}$ with 1,4-naphthoquinone (NQ) is different. While the reaction of $Co(CN)_5^{3-}$ with both BQ and TQ (in systems with $[Co(CN)_5^{3-}]_o \geqslant 2[Q]_o$) proceeded in two irreversible steps [2], with quantitative production of a binuclear bridge complex as the final product (*i.e.* in a concentration equal to $[Q]_o$), it was known of the reaction of pentacyanocobaltate(II) with 1,4-naphthoquinone only that the stoichiometry of the reaction loss in the amount of $Co(CN)_5^{3-}$ and NQ is rather 1:1. No final product could be found in preliminary experiments on this system.

This work was carried out in order to explain these differences in the reaction behaviour of the $Co(CN)_5^{3-}$, NQ system on the basis of determination of the detailed mechanism.

Experimental

Chemicals

Doubly distilled water was employed in all the measurements. The second distillation was carried out in an all-quartz apparatus from the firm VEB Quarzschmelze, Berlin Staaken. The commercial substances were of *p.a.* purity (Lachema) and, except for 1,4-naphthoquinone, were used without further purification. 1,4-Naphthoquinone was purified by sublimation and its solutions were prepared fresh for each group of parallel measurements. The concentration of the 1,4-naphthoquinone solution was determined photometrically on the basis of confirmation of the linearity of the absorbance dependence on the concentration for the most intense bands at 340 nm (ϵ = 3080 ± 80 M^{-1} cm^{-1}) and at 252 nm (ϵ = (2.23 ± 0.14) × 10^4 M^{-1} cm^{-1}). Although at most 5 × 10^{-4} M aqueous solutions of 1,4-naphthoquinone can be prepared at 20 °C, far more soluble sodium 1,4-naphthoquinone-2-sulphonate was not used in the kinetic measurements. Use of this substance would complicate the comparison with the first steps in the earlier studied reactions of pentacyanocobaltate(II) with benzoquinone, where the $Co(CN)_5^{3-}$ ion interacts with a neutral molecule.

Measurement of the Absorption Spectra

The absorption spectra of stable solutions in the visible and UV regions were measured on a Unicam SP 800 spectrophotometer.

Kinetic measurements were carried out on a stopped-flow apparatus with spectrophotometric monitoring of the concentration changes [3]. The dead time of the apparatus, τ_s, at a flow rate of 30 cm^3/s is 4.5 ms; the measurement can be carried out in the region 220–1150 nm. The procedure of kinetic measurement and the method of evaluation of the kinetic recording are described in a previous work [2]. All the kinetic measurements were carried out in the absence of oxygen under an argon atmosphere, which was freed of traces of oxygen on a column with BTS catalyst granules (Badische Anilin und Soda Fabrik).

Because of the instability of $Co(CN)_5^{3-}$ anion in water and its sensitivity to atmospheric oxygen, solutions of $Co(CN)_5^{3-}$ were prepared fresh for each measurement directly in the valve block of the flow-through apparatus by mixing oxygen-free solutions of cobalt(II) chloride and sodium cyanide. The ratio of concentrations of $[CN^-]:[Co^{2+}]$ was always greater than 8. As demonstrated in an earlier work, on entrance into the mixing point of the measuring kinetic cell, the concentration of this solution of $Co(CN)_5^{3-}$ corresponded to the adjusted concentration of divalent cobalt, $[Co^{2+}]$, except for a decrease caused by the reaction of pentacyanocobaltate(II) with traces of dissolved oxygen, *i.e.* the initial concentration of pentacyanocobaltate(II), $[Co(CN)_5^{3-}]_0$ immediately after mixing in the mixer of the kinetic cell with further components was lower than $[Co^{2+}]$* by less than 9 × 10^{-6} M.

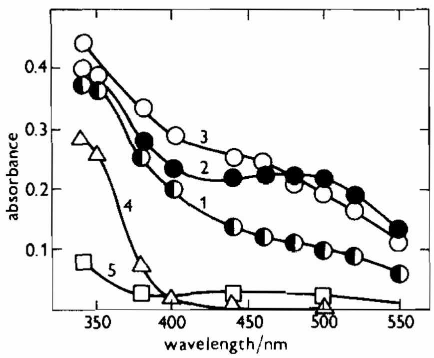

Fig. 1. The transition absorption spectrum of $Co(CN)_5^{3-}$, NQ at characteristic time intervals from the beginning of the reaction. Curve 1: 4.5 ms; curve 2: 150 ms; curve 3: 50 s from the beginning of the reaction. $[Co^{2+}]$ = 2.5 × 10^{-4} M; $[NQ]_0$ = 0.82 × 10^{-4} M; $[CN^-]_0$ = 1.25 × 10^{-3} M. For comparison, the spectra of the reactants alone in corresponding concentrations are also given. Curve 4: $[NQ]_0$ = 0.82 × 10^{-4} M; curve 5: $[Co^{2+}]$ = 2.5 × 10^{-4} M; $[CN^-]_0$ = 1.25 × 10^{-3} M. The $[OH^-]_0$ concentration was always 1 × 10^{-2} M.

Determination of Bands for Optimal Kinetic Study

The decease in the concentration of pentacyanocobaltate(II) was measured at 970 nm. No other reaction species absorbs at this wavelength and the molar absorption coefficient of $Co(CN)_5^{3-}$ at this wavelength is 299 M^{-1} cm^{-1} (ref. [4]). As the reaction mixture of pentacyanocobaltate(II) and 1,4-naphthoquinone is red immediately after mixing and its colour changes to orange-yellow, the absorption spectra of the given reaction system were measured point by point over the 340–550 nm region. Figure 1 depicts the absorption spectra of the described reaction system at characteristic time intervals from initiation of the reaction by mixing the initial components. Curve 1 represents the course of the absorbance (designated in further text as a_s)** of the reaction system for the instant of attainment of the effective centre of the observation point (*i.e.* after the dead time, τ_s, 4.5 ms). Curve 2 depicts the absorption spectrum for the instant when the absorbance of the reaction system reaches a maximum at 500 nm (*i.e.* approx. 150 ms from initiation of the reaction). The values of the absorbance for the given instant of attainment of the maximum value at 500 nm are indicated in the subsequent text as a_m. Further, the absorbance of the reaction system slowly changed over the whole studied wavelength region from the a_m values to the values depicted by

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*The term $[Co^{2+}]$ in this work indicates the value the concentration of divalent cobalt would attain in the mixing chamber of the kinetic cell if none of the components of the studied system reacted with Co^{2+}. The initial concentrations of the other components are indicated by index O in agreement with the previous definition indicating the concentration of the given component immediately after mixing in the mixer of the kinetic cell.

**Absorbance values designated by small letter a are values recalculated to unit length of the observation channel, *i.e.* the measured absorbance values divided by the length of the observation channel (2.34 cm).

curve 3. The course represents the absorption spectrum of the described reaction system aged by 50 s from the instant of mixing. For comparison, the absorption spectra of the initial components alone are given in Fig. 1.

Curve 4 indicates the course of a_s in the system formed by injecting a 1.64×10^{-4} *M* solution of 1,4-naphthoquinone into 2×10^{-2} *M* NaOH and agrees with the spectrum of a stable solution with the corresponding concentration of 1,4-naphthoquinone in neutral medium*. Curve 5 indicates the course of a_s in the system after injection of 5×10^{-4} *M* $Co(CN)_5^{3-}$ into the solution of 2×10^{-2} *M* NaOH under anaerobic conditions.

Direct measurement of the decrease in the concentration of 1,4-naphthoquinone in the described reaction system could not be carried out simply. As can be seen in Fig.1, the change in the absorption spectrum at 340 nm as a result of the reaction is small. At 251 nm both the initial substances and the products absorbed to a similar degree. In addition, the transmittance of the reaction system at this wavelength is less than 1% even from initial concentrations $[NQ]_0$ equal to 3×10^{-5} *M.*

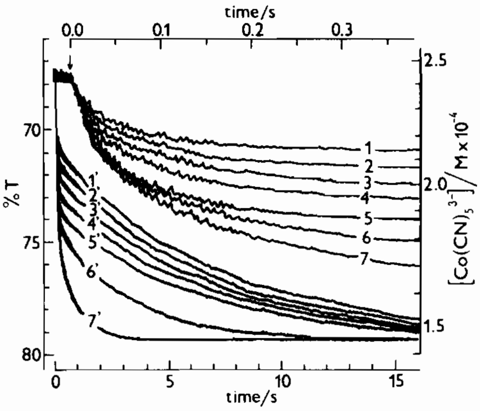

Fig. 2. The time course of the transmittance at 970 nm in the reaction system containing $Co(CN)_5^{3-}$ and NQ in dependence on the ionic strength and pH of the reaction system. Curve numbers 1–7 (or 1'–7') correspond to the number of the experiment given with the initial concentration values in Table I. The upper time axis is valid for curves 1–7, the lower corresponds to the dashed curves 1'–7'.

Results

Dependence on the Ionic Strength

The behaviour of the $Co(CN)_5^{3-}$, NQ system in dependence on the ionic strength is characteristic for this system. Figure 2 depicts the time course of the decrease in the concentration of pentacyanocobaltate(II) in the $Co(CN)_5^{3-}$, NQ reaction system measured at 970 nm. In the individual experiments in Fig. 2, the ionic strength of the system is increased from curve 1 to curve 5 for identical initial concentrations of $Co(CN)_5^{3-}$ and NQ. In experiments 5, 6 and 7, the pH value changes at a constant ionic strength.

Curves 1–7 in Fig. 2 depict the decrease in the concentration of $Co(CN)_5^{3-}$ up to 400 ms after reactant mixing. The bottom group of curves 1' to 7' correspond to experiments (1–7) for a time longer than 15 s. It can be seen in Fig. 2 that, with increasing concentration of indifferent electrolyte and for identical initial concentrations of the initial reactants, the decrease in the amount of pentacyanocobaltate(II) is greater in the rapid initial phase indicated in the upper group of curves. The magnitude of the decrease in the initial phase for ratio $[Co(CN)_5^{3-}]_0 : [NQ]_0 > 1$ is always less than the initial concentration of 1,4-napthoquinone. In contrast to the earlier described reactions with benzoquinones the course of the decrease in the amount of $Co(CN)_5^{3-}$ in the reaction with NQ can be measured practically from the initial concentration values, except for the decrease during time τ_s. This decrease up to the attainment of the observation point can be explained by extrapolation of the measured course (1–7) to the initial concentration of $[Co(CN)_5^{3-}]_0$. The overall reaction decrease in the concentration of $Co(CN)_5^{3-}$ – corresponding to curves 1'–7' – approaches $[Co(CN)_5^{3-}]_0 - [NQ]_0$ as a limiting value (provided that $[Co(CN)_5^{3-}]_0 > [NQ]_0$). The slow decrease in the concentration of $Co(CN)_5^{3-}$ after a rapid, but observable decrease in the rapid phase, is controlled by first order kinetics. The half-time of the subsequent slow decrease in the concentration of $Co(CN)_5^{3-}$ does not change with the ionic strength of the reaction system. For curves 1'–5' the half-time has the same value 4 ± 0.5 s and it is apparent that the decrease in this part is more than 100 × slower than in the initial rapid phase.

It is apparent in curves 6 and 7 that increasing the pH leads to no change in the initial rate of the decrease in the concentration of $Co(CN)_5^{3-}$ provided that the ionic strength is maintained (Curve 5) but

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*Similarly as with benzoquinone, it can be expected that 1,4-naphthoquinone will be unstable in alkaline medium in which the described experiments were carried out. Study of the course of the transmittance of the mixture formed by injecting 1,4-naphthoquinone into a strongly alkaline medium indicates that the change in the initial concentration of 1,4-naphthoquinone in time τ_s is negligibly small even in 0.01 *M* NaOH (*i.e.* less than 2×10^{-6} *M*). Further changes in time of the transmittance of this system as a result of disproportionation processes of 1,4-naphthoquinone in the described alkaline medium proceed many times slower than the time changes in the transmittance of the $Co(CN)_5^{3-}$, NQ system in the same NaOH medium of concentration 0.01 *M*.

that the subsequent slow decrease in the concentratin of $Co(CN)_5^{3-}$ in the second phase is more rapid. For curve 6′ measured for the described reaction system with pH ≈ 10.8, the half-time of the subsequent slow decrease is 2.04 s and for the system with pH ≈ 12.4 the half-time is 0.6 s.

The dependence of the time course of the transmittance on the ionic strength of the $Co(CN)_5^{3-}$, NQ reaction system measured at 500 nm (*i.e.* on the band with the maximum difference between absorbance values a_m and a_s) (see Fig. 1) is depicted in Fig. 3.

It is apparent from these curves that increasing the ionic strength in the system measured at 500 nm increases the initial increase in the absorbance at a rate corresponding to the rate of the initial phase of the decrease in the concentration of $Co(CN)_5^{3-}$.

The time course of the decrease in the absorbance at 500 nm, following after the rapid increase cannot easily be described kinetically. In this stage the reaction system is apparently already rather complicated and a detailed study lies outside the scope of this work. Nonetheless, it appears from the experiments carried out that the change in the absorbance in the region around 500 nm in this phase of the studied reaction system corresponds to at least two processes with different rates. After the initial rapid increase in the absorbance in the region 440–550 nm, a decrease occurs over the whole region, which could depend on the slow phase of the decrease in the concentration of $Co(CN)_5^{3-}$. On this decrease is superimposed the slower absorbance change corresponding to a new absorbance increase at 420 nm. It is apparent from the course at 500 nm that the system in this phase is limiting to a composition which is determined primarily by the initial concentration of 1,4-naphthoquinone and which is dependent on the pH of the reaction system.

It is apparent from Figs. 2 and 3 that both the initial phase of the decrease in the concentration of $Co(CN)_5^{3-}$ and the rapid increase in the absorbance at 500 nm are much faster than the subsequent changes. Attainment of the maximum absorbance value at 500 nm or the end of the initial rapid phase of decrease in the concentration of $Co(CN)_5^{3-}$ represents attainment of a pseudoequilibrium stage which is slowly perturbed by subsequent changes.

Table I lists the initial concentrations of the individual components for the described experiments investigating the effect of the ionic strength. For the individual measurements Table I lists the values of the concentration of $[Co(CN)_5^{3-}]_m$ recorded at the

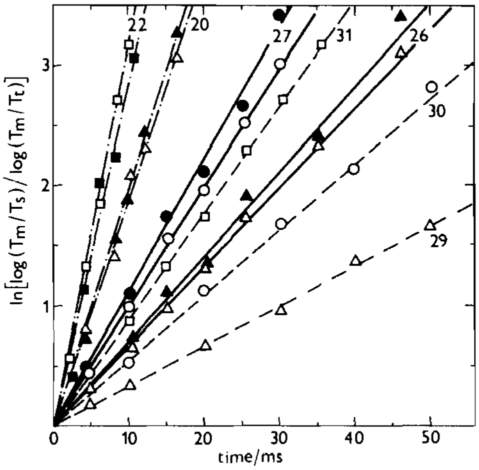

Fig. 4. Demonstration of the evaluation of the transmittance curve for a system with an order excess of $Co(CN)_5^{3-}$ for 970 nm (solid figures) and 500 nm (open figures). The numbers correspond to the experiment numbers in Table II. $[Co^{2+}]/10^{-3}$ *M*: – – – 0.63, ——— 1.0, –·–·– 1.9. Ionic strength/10^{-2} *M*: for triangles 1.6, for circles 2.8, for squares 7.2.

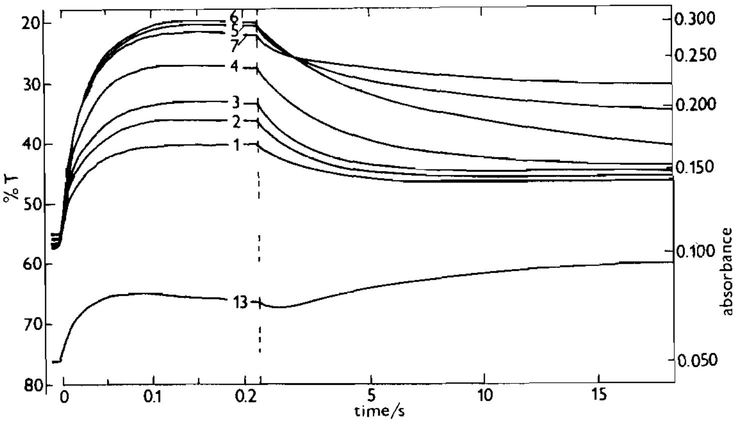

Fig. 3. The time dependence of the transmittance at 500 nm in the $Co(CN)_5^{3-}$, NQ system in dependence on the ionic strength. The initial concentration values for the individual experiments are given under the corresponding number in Table I. The dotted line designates a change in the time scale.

TABLE I. The Values of Pentacyanocobaltate(II) Concentration $[Co(CN)_5^{3-}]_m$ and Corresponding Absorbance Values a_m (550 nm) in Dependence on the Ionic Strength and pH of the Reaction System.

Exp. no.	$[Co^{2+}]$ $M \times 10^{-4}$	$[NQ]_0$ $M \times 10^{-5}$	$[CN^-]_0$ $M \times 10^{-3}$	$[OH^-]_0$ $M \times 10^{-2}$	$[ClO_4^-]_0$ $M \times 10^{-2}$	I $M \times 10^{-3}$	$[Co(CN)_5^{3-}]_m$ $M \times 10^{-4}$	a_m
1	2.5	9.9	1.25	–	0.25	5.75	2.17	0.164
2	2.5	9.9	1.25	–	0.5	8.25	2.11	0.181
3	2.5	9.9	1.25	–	0.75	10.75	2.08	0.201
4	2.5	9.9	1.25	–	1.25	15.75	2.02	0.242
5	2.5	9.9	1.25	–	2.25	25.75	1.94	0.294
6	2.5	9.9	3.75	–	–	25.75	1.90	0.301
7	2.5	9.9	1.25	2.5	–	28.25	1.85	0.279
8	2.5	7.9	1.25	0.05	–	3.75	2.32	0.080
9	2.5	9.2	1.25	–	6.2	65.25	1.86	0.371
10	2.5	8.2	1.25	1	–	13.25	2.05	0.218
11	1.5	5.2	1.75	–	2.25	25.45	1.27	0.063
12	1.5	9.8	1.75	–	0.25	5.45	1.24	0.079
13	1.5	10.0	1.75	–	0.5	8.45	1.21	0.082
14	1.5	10.1	1.75	–	2.25	25.45	1.13	0.130
15	3.5	4.6	1.25	–	2.20	26.05	3.20	0.158
16	3.5	9.8	1.25	–	2.20	26.05	2.88	0.361
17	3.5	9.8	1.25	2.20	–	26.05	2.82	0.384

instant of attaining the maximum values of absorbance at 500 nm, along with the corresponding values of the absorbance a_m. The absorbance values a_m are found with an error of ±0.003, the values of the concentration of $Co(CN)_5^{3-}$ with an error of $\pm 4 \times 10^{-6}$ *M*.

The absorbance values a_m plotted against the corresponding decrease in the concentration of pentacyanocobaltate(II), Δ_{Om}, calculated as the difference $[Co^{2+}] - [Co(CN)_5^{3-}]_m$, yield a linear dependence with a slope of 6.38×10^3 M^{-1} cm^{-1} (line 1, Fig. 5).

Kinetics and Reaction Orders

In systems with initial concentrations $[Co(CN)_5^{3-}]_0 : [NQ]_0 > 10$, the course of the increase in the transmittance at 970 nm and the decrease in the transmittance at 500 nm are controlled by pseudo-first order kinetics. The experimentally determined values $\ln(\log(T_m/T_s)/\log(T_m/T_t))$* plotted against time yields (Fig. 4) a linear dependence for the transmittance at both wavelengths. The values of the slopes of these dependences, *i.e.* k_{obs}, are given in Table II and are the average of at least three parallel measurements with a relative error of 5% (500 nm) and 8–10% (970 nm). It is clear from the table that the k_{obs} values for both wavelengths for a given initial concentration $[Co(CN)_5^{3-}]_0$ and a given ionic strength value are independent on the initial concentration of 1,4-naphthoquinone. The reaction order in these systems with respect to 1,4-naphthoquinone is thus unity. The rate of decrease in the concentration of $Co(CN)_5^{3-}$ and the rate of increase in the absorbance at 500 nm in the reaction system with excess $Co(CN)_5^{3-}$ is controlled by the same process and thus

$$\frac{-d[Co(CN)_5^{3-}]}{dt} = \frac{d(a_{500}/\epsilon_{ef})}{dt} = k_{obs} \cdot [NQ] \qquad (1)$$

ϵ_{ef} is the slope of the a_m *vs.* $[NQ]_0$ dependence in graph 5 with the significance of the effective molar absorption coefficient of the reaction system at 500 nm.

It is apparent from Table II that the reaction order for $Co(CN)_5^{3-}$ in the described system is greater than unity, as the values of the ratio of the slopes k_{obs} and the corresponding initial concentration $[Co(CN)_5^{3-}]_0$ are not constant but increase with increasing concentration $[Co(CN)_5^{3-}]_0$. It is further apparent that values k_{obs} increase for given initial concentrations $[Co(CN)_5^{3-}]_0$ with increasing ionic strength and thus

$$k_{obs} = f\{([Co(CN)_5^{3-}]_0)^b, I\}\ 2 > b > 1 \qquad (2)$$

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*T_s is the transmittance of the reaction system at the instant of attaining the observation point, T_t is the transmittance at time t. Values T_m were recorded in systems with $[Co(CN)_5^{3-}]_0 \gg [NQ]_0$ after a time greater than five times the reaction half-time. Compared with systems with concentrations of $Co(CN)_5^{3-}$ and NQ of the same order, the values of the transmittance at 970 nm and 500 nm change much more slowly after attaining the value T_m. In agreement with convention, it would be better to designate this as T_∞; however, symbol T_m is retained to maintain the connection with previous experiments.

TABLE II. The Values of Rate Constant k_{obs}.

Expt. no.	$[Co^{2+}]$ $M \times 10^{-3}$	$[NQ]_0$ $M \times 10^{-5}$	I $M \times 10^{-2}$	500 nm		970 nm	
				k_{obs} s^{-1}	$k_{obs} \times 10^{-4}$ $[Co^{2+}]$ M^{-1} s^{-1}	k_{obs} s^{-1}	$k_{obs} \times 10^{-4}$ $[Co^{2+}]$ M^{-1} s^{-1}
18	1.9	11.8	1.6	186.2	9.8	188.2	9.9
19	1.9	8.3	1.6	187.8	9.9	180.4	9.5
20	1.9	5.1	1.6	189.2	10.0	194.1	10.2
21	1.9	5.6	2.8	251.1	13.2	260.5	13.7
22	1.9	5.6	7.2	308.1	16.2	301.4	15.9
23	1.0	9.2	1.6	70.1	7.0	63.6	6.4
24	1.0	5.8	1.6	64.2	6.4	67.3	6.7
25	1.0	4.4	1.6	67.7	6.8	66.7	6.7
26	1.0	3.0	1.6	66.3	6.6	61.0	6.1
27	1.0	3.0	2.8	101.2	10.1	111.4	11.1
28	1.0	3.0	7.2	153.6	15.4	161.3	16.1
29	0.63	1.1	1.6	33.1	5.3	–	–
30	0.63	1.1	2.8	56.6	9.0	–	–
31	0.63	1.1	7.2	90.1	14.3	–	–

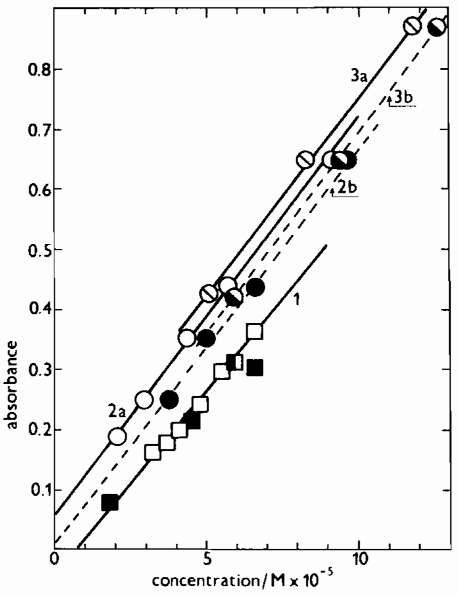

Fig. 5. Dependence of absorbance value a_m (500 nm) on the reaction decrease in concentration. Line 1 represents the dependence of the a_m values from Table I (systems with varying ionic strength) plotted against the decrease in the concentration of $Co(CN)_5^{3-}$, Δ_{Om}. □ points were obtained by plotting experiments 1–5 and 9, ◧ points correspond to experiment 6, ■ points to experiments 7, 8 and 10. Lines 2a and 3a are the dependences of the a_m values from Table III on the $[NQ]_0$ values; lines 2b and 3b were obtained by plotting the same a_m values against the Δ_{Om} values from Table III.

Reaction Stoichiometry

It is apparent from the reaction decrease in the concentration of $Co(CN)_5^{3-}$ in systems with a large excess of pentacyanocobaltate(II) (see Table III) that the overall decrease given by the difference $[Co^{2+}] - [Co(CN)_5^{3-}]_m$ (Δ_{Om}) is equal to the original concentration of 1,4-naphthoquinone in these systems, except for a small, practically constant contribution. (This contribution, which is less than 9×10^{-6} *M*, by which the decrease in the concentration of pentacyanocobaltate(II) is greater than the initial concentration $[NQ]_0$, corresponds to the reaction of $Co(CN)_5^{3-}$ with traces of dissolved oxygen). Plotting of the absorbance value a_m *vs.* the overall reaction decrease in the concentration of pentacyanocobaltate(II) Δ_{Om} in Graph 5 yielded straight lines 2b and 3b. Straight lines 2a and 3a were obtained by plotting the a_m values against the initial concentration $[NQ]_0$. Straight lines 2a, 2b, 3a and 3b have the same slope ($(6.42 \pm 0.20) \times 10^3$ M^{-1} cm^{-1}). The shift of 2a relative to 2b or 3a relative to 3b is a result of the mentioned decrease in the concentration of

TABLE III. The Balance of Reaction Decrease in Concentration in Systems with $[Co(CN)_5^{3-}]_0 \gg [NQ]_0$.

Expt. no.	$[NQ]_0$ $M \times 10^{-5}$	$[Co(CN)_5^{3-}]_m$ $M \times 10^{-4}$	Δ_{Om} $M \times 10^{-5}$	a_m
18	11.8	17.74 ± 0.02	12.6 ± 0.4	0.865
19	8.3	18.08 ± 0.08	9.2 ± 0.7	0.645
20	5.1	18.41 ± 0.11	5.9 ± 0.9	0.420
23	9.2	9.03 ± 0.02	9.7 ± 0.3	0.647
24	5.8	9.34 ± 0.06	6.6 ± 0.5	0.435
25	4.4	9.50 ± 0.11	5.0 ± 0.9	0.356
26	3.0	9.63 ± 0.19	3.7 ± 1.4	0.250

$Co(CN)_5^{3-}$ by reaction with O_2 and the shift of the corresponding straight lines 2 relative to 3 is a result primarily of the absorbance of $Co(CN)_5^{3-}$ at 500 nm. Straight line 1 in graph 5 was obtained, as mentioned, by plotting absorbance a_m *vs.* the corresponding decrease in the concentration of pentacyanocobaltate(II), Δ_{Om}, for the systems given in Table I, *i.e.* for systems whose concentration $[Co(CN)_5^{3-}]_0$ is of the same order as concentration $[NQ]_0$. As the concentration of Co^{2+} is four times less than in straight line 2, line 1 should practically pass through the origin of the coordinate system. Line 1 is, however, shifted by a concentration value corresponding primarily to the decrease in the $Co(CN)_5^{3-}$ concentration as a result of the reaction with traces of oxygen and the decrease in subsequent reactions which proceed in these systems more rapidly than in systems with an excess of $Co(CN)_5^{3-}$ of one order of magnitude. Direct measurement of the decrease in the concentration of NQ was not possible for reasons listed above under experimental. It is, however, apparent from the agreement of the slopes of the dependences in graph 5 that, both in systems with initial concentrations $[Co(CN)_5^{3-}]_0 \gg [NQ]_0$ and in other systems described containing $Co(CN)_5^{3-}$ and NQ, the ratio of the reaction decrease in the concentrations of the initial components is basically unity. It is also apparent that the ratio of the decrease in the concentration of any of the initial components to the increase in the concentration of the components (designated further as products (P)), absorbing at 500 nm with effective molar absorption coefficient $\epsilon_{ef} = 6.4 \times 10^3 \ M^{-1} \ cm^{-1}$ is constant and thus

$$[Co(CN)_5^{3-}]_0 - [Co(CN)_5^{3-}] \doteq [NQ]_0 - [NQ] \doteq (1/\nu)P \qquad (3)$$

where ν is the stoichiometric factor which cannot be determined without direct analysis of the products or without forming a concept of the reaction mechanism. Because of further decomposition, direct analysis of the products could not be carried out.

Relationship (3) is almost precisely valid (*i.e.* within experimental limits) in systems containing $Co(CN)_5^{3-}$ in excess of orders of magnitude or in systems with high ionic strength. The linearity of the dependences in graph 5 indicates that, if the reaction mixture contains intermediates, for which it can be assumed that their molar absorption coefficients in the wavelength region around 500 nm are of the same order as the absorption coefficient of products P, the concentrations of these intermediates are small and stationary.

Proposed Mechanism and Discussion

The experimental results obtained indicate basic differences in the behaviour of the reaction system $Co(CN)_5^{3-}$, NQ and the reactions of pentacyanocobaltate(II) with 1,4-benzoquinone studied earlier. It was primarily demonstrated that, in contrast to the system described earlier, in the system studied here the decrease in the concentration of pentacyanocobaltate(II) can be followed from the beginning.

A difference in the overall reaction stoichiometry was also demonstrated. A marked difference was found in that, with constant initial concentrations of the initial reactants, the overall reaction decrease in the concentrations of pentacyanocobaltate(II) (expressed as the difference $[Co(CN)_5^{3-}]_0 - [Co(CN)_5^{3-}]_m$) and the corresponding value of the absorbance a_m depends on the ionic strength of the reaction system. There is also a difference between the compared reaction systems in the reaction order with respect to $Co(CN)_5^{3-}$ found from kinetic measurements with a large excess of pentacyanocobaltate(II). While this order is unity for both BQ and TQ systems, in the reaction with 1,4-naphthoquinone the experimentally determined order with respect to $Co(CN)_5^{3-}$ is not an integral number and its value lies between one and two (see eqn. (2)).

These basic differences in the compared reaction systems, together with other experimental facts given in the previous paragraphs, whose interpretation in connection with the discussion of the proposed reaction mechanism will be given below, lead to the following scheme for the reaction mechanism:

$$NQ + Co(CN)_5^{3-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (NC)_5Co{\cdot}NQ^{3-\cdot} \qquad K_1 \qquad (4)$$

$$(NC)_5Co{\cdot}NQ^{3-\cdot} + Co(CN)_5^{3-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (NC)_5Co{\cdot}NQ{\cdot}Co(CN)_5^{6-} \qquad K_2 \qquad (5)$$

$$NQ + (NC)_5Co{\cdot}NQ{\cdot}Co(CN)_5^{6-} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \text{products (P)} \qquad K_3 \qquad (6)$$

This proposal is based on the assumption that the primary reaction step in this reaction system is again the reaction of $Co(CN)_5^{3-}$ anions with 1,4-naphthoquinone molecules which, analogous to the already described reactions of pentacyanocobaltate(II) with benzoquinone, leads to formation of the $(NC)_5Co{\cdot}NQ^{3-\cdot}$ anion radical. This step involves reaction of the $Co(CN)_5^{3-}$ species with an electrically neutral molecule (which cannot thus be, in itself strongly dependent on the ionic strength of the system). However, the magnitude of the overall reaction decrease in the concentration of $Co(CN)_5^{3-}$, Δ_{Om} (where this decrease can be followed practically from the beginning) is affected, as is the magntiude of the increase in the absorbance at 500 nm, by the ionic strength of the reaction system. To explain this behaviour of the described system, it is necessary to assume that the formation of the anion radical $(NC)_5Co{\cdot}NQ^{2-\cdot}$ is a reversible process. Considering the small decrease Δ_{Om} in systems with low ionic strength with comparable concentrations $[Co^{2+}]$ and $[NQ]_0$, this equilibrium is shifted toward the initial components. The assumption of the first step as a reversible process completes the earlier conclusions on the reactivity of the 1,4-benzoquinone series towards $Co(CN)_5^{3-}$ in dependence on the standard redox potential of the one-electron reduction of this quinone. Accordingly, quinones with standard potentials of single-electron reduction less than about 0.22 V do not react with pentacyanocobaltate(II), while quinones with potentials higher than this value react readily [1]. 1,4-Naphthoquinone has just this potential.

According to the second step of the proposed reaction mechanism, the reverse decomposition of the anion radical $(NC)_5Co{\cdot}NQ^{3-\cdot}$ competes with addition of a further $Co(CN)_5^{3-}$, where the equilibrium in this step is shifted toward the products with increasing ionic strength and increasing concentration of pentacyanocobaltate(II).

The last step (6) then considers the determined reaction stoichiometry, according to which the decrease in the concentration of $Co(CN)_5^{3-}$ is equal to the decrease in the amount of 1,4-naphthoquinone, assuming rapid interaction of the binuclear product of the second step with a further 1,4-naphthoquinone molecule. The process is similar to the rapid reversible disproportionation reaction of quinones with their completely reduced forms, which, in alkaline media, leads to formation of the semiquinone radical with a rate constant of the order of 10^6–10^8 M^{-1} s^{-1} (ref. [5, 6]). It is highly probable that provided the binuclear complex $(NC)_5Co{\cdot}NQ{\cdot}Co(CN)_5^{6-}$ is formed in the reaction system, the proposed reaction (6) must also occur. In contrast to the reactions of $Co(CN)_5^{3-}$ with the benzoquinones described earlier, the studied system contains both the binuclear complex $(NC)_5Co{\cdot}NQ{\cdot}Co(CN)_5^{6-}$ as well as 1,4-naphthoquinone. 1,4-Naphthoquinone is in this system in concentration an order greater than the concentration of the binuclear complex.

The composition of the final reaction products (the products of reaction (6)), manifested in an intense absorption band at 500 nm, could not be found by any direct method. The proposed mechanism suggests two possibilities, either the dimer $\{(NC)_5CoNQ\}_2^{6-}$ or an equimolar mixture of radicals $NQ^{-\cdot}$, $(NC)_5CoNQCo(CN)_5^{5-\cdot}$. As a mixture of these radicals or a mixture of radicals with the dimer should not change with the ionic strength of the initial concentration of the reactants, to retain the linearity of the dependence in graph 5, it is more probable that the final product is the dimer $\{(NC)_5CoNQ\}_2^{6-}$. Stoichiometric factor ν in eqn. (3) then equals 2 and the dimer should have a molar absorption coefficient (500 nm) equal to 1.26×10^4 M^{-1} cm^{-1}. The stability of the dimer should increase with increasing ionic strength, resulting in a further shift of the equilibrium towards formation of this agglomerate.

Another possible interaction of the $(NC)_5CoNQ^{3-\cdot}$ species – the intermediate formed in the first step – other than reaction with $Co(CN)_5^{3-}$, would be reaction with a further 1,4-naphthoquinone molecule, followed by rapid redox addition with $Co(CN)_5^{3-}$. A further variation of the reaction mechanism could involve direct recombination of the anion radical $(NC)_5CoNQ^{3-\cdot}$ forming the $\{(NC)_5CoNO\}_2^{6-}$ dimer. Both of these possibilities, like the suggestion above, would explain the reaction stiochiometry found as well as the increase in the initial rate of disappearance of $Co(CN)_5^{3-}$ or the increase in absorbance at 500 nm with increasing ionic strength. The reaction order for the initial components, found from measurements in presence of a multifold excess of pentacyanocobaltate(II), confirm the proposed reaction mechanism in which the reaction following the formation of the ion-radical $(NC)_5CoNQ^{3-\cdot}$ is addition of a further $Co(CN)_5^{3-}$ species, as will be shown below. For $[Co(CN)_5^{3-}]_0 \gg [NQ]_0$, solution of this reaction mechanism is based on the assumption of a stationary concentration of the intermediates formed in the first and second steps, *i.e.* $d[(NC)_5CoNQ^{3-\cdot}]/dt = d[(NC)_5CoNQCo(CN)_5^{6-}]/dt = 0$. This assumption is quite justified considering the identical course of the disappearance of $Co(CN)_5^{3-}$ and the increase in the absorbance at 500 nm, found for the given concentration ratio. For systems with $[Co(CN)_5^{3-}]_0 \gg [NQ]_0$ it is further assumed that $k_1[Co(CN)_5^{3-}][NQ] \gg k_{-2}[(NC)_5CoNQCo(CN)_5^{6-}]$, $k_2[Co(CN)_5^{3-}][(NC)_5CoNQ^{3-\cdot}] \gg k_{-3}[P]$ and $k_3[NQ] \gg k_{-2}$.

Under these assumptions, the rate of disappearance of pentacyanocobaltate(II) or the rate of increase in the concentration of the products is given by

$$-\frac{d[Co(CN)_5^{3-}]}{dt} = \frac{2d[P]}{dt} =$$

$$= \frac{2k_1k_2[Co(CN)_5^{3-}]^2[NQ]}{k_1 + k_2[Co(CN)_5^{3-}]} \tag{7}$$

It then holds for the rate constants found from experimental measurements with $[Co(CN)_5^{3-}]_0 \gg [NQ]_0$ (see Table II and eqn. (1)) that

$$k_{obs} = \frac{2k_1k_2[Co(CN)_5^{3-}]^2}{k_{-1} + k_2[Co(CN)_5^{3-}]} \tag{8}$$

It is apparent from graph 6 that plotting the value $2[Co^{2+}]^2/k_{obs}$ *vs.* $[Co^{2+}]$, in agreement with relationship

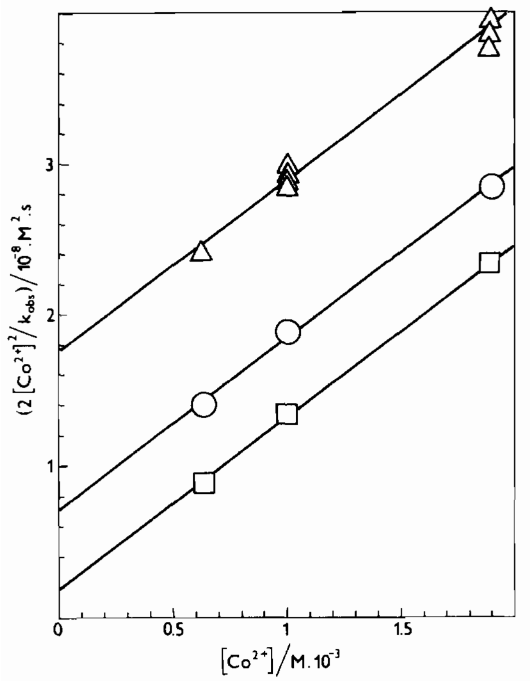

Fig. 6. Rate constant k_1 found from k_{obs} values (see Table II). Ionic strength/10^{-2} *M*: for square points 7.2, for circles 2.8 and for triangles 1.6.

$$\frac{2[\text{Co(CN)}_5^{3-}]^2}{k_{obs}} = \frac{1}{k_2K_1} + \frac{[\text{Co(CN)}_5^{3-}]}{k_1} \qquad (9)$$

leads to linear dependences with identical slopes for various ionic strength values, $[\text{Co(CN)}_5^{3-}] \approx [\text{Co}^{2+}]$. The reciprocal slope value is 9.08×10^4 M^{-1} s^{-1} and corresponds to rate constant k_1. The logarithm of the reciprocal value of the intercept on graph 6, $(k_{obs}/2[\text{Co}^{2+}]^2$ for $[\text{Co}^{2+}] \rightarrow 0)$, plotted *vs.* $\sqrt{I}/(1+\sqrt{I})$ yields straight lines with slopes of 9.6.

Behaviour of the described reaction system in the first rapid phase of the reaction changes is interpreted as attainment of an equilibrium, value of which is dependent on the ionic strength. Overall equilibrium constant is equal, according to the proposed reaction mechanism to

$$K = \frac{k_1 \cdot k_2 \cdot k_3}{k_{-1} \cdot k_{-2} \cdot k_{-3}} = \frac{[P]_{eq}}{[\text{Co(CN)}_5^{3-}]^2_{eq}\ [NQ]^2_{eq}} \qquad (10)$$

where subscript $_{eq}$ denotes the equilibrium concentrations of the individual components.

To simplify the evaluation of the dependence on ionic strength, the fact is neglected that the real equilibrium could not be attained (because of the slow decomposition of the product, the reaction of pentacyanocobaltate(II) with water and others). There are two justifications for such neglection. At first, the decomposition reactions are much slower than the attainment of the equilibrium and at second, this simplification causes only a small systematic error in an absolute value of the overall equilibrium constant which has very small influence on evaluated dependence on the ionic strength.

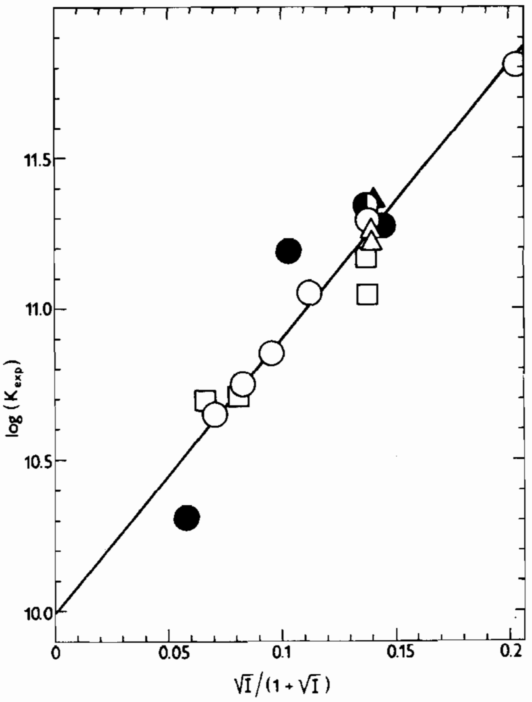

Fig. 7. The dependence of K_{exp} on the ionic strength. Point designation for experiments (see Table I): ○ exp. 1–5 and 9, ◐ exp. 6, ● for exp. 7, 8 and 10, □ for exp. 11–14, △ exp. 15, 16 and ▲ exp. 17.

Experimentally, the overall equilibrium constant K_{exp} was then calculated from the relationship

$$K_{exp} = \frac{[P]_m}{[\text{Co(CN)}_5^{3-}]^2_m([NQ]_0 - 2[P]_m)^2} \qquad (11)$$

where

$$P_m = (a_m - \epsilon_{\text{Co(CN)}_5^{3-}} \times [\text{Co(CN)}_5^{3-}]_m)/2\epsilon_{ef} \qquad (12)$$

$\epsilon_{\text{Co(CN)}_5^{3-}}$ (≈ 60 M^{-1} s^{-1}) is the molar absorption coefficient of the pentacyanocobaltate(II) at 500 nm. ϵ_{ef} is the effective molar absorption coefficient equal to the slope in graph 5 (the values of absorbance a_m and the values of $[\text{Co(CN)}_5^{3-}]_m$ were substituted from Table I).

The values of $\log K_{exp}$ plotted against $\sqrt{I}/(1+\sqrt{I})$ (see graph 7) yield linear dependences with a slope of 9.1.

The dependence of the logarithm of the equilbrium constant K_{exp}, the dependence of the logarithm of the reciprocal of the intercept value from graph 6 on the ionic strength, and especially the slopes found

TABLE IV. Comparison of Standard Potentials E°_1 of Given Quinones with the k_1 Values.

	E°_1/V ref. 8	$k_1/M^{-1}\ s^{-1}$
1,4-Benzoquinone	0.433	$\geqslant 2 \times 10^8$
2-Methyl-1,4-benzoquinone	0.399	$\geqslant 1.5 \times 10^8$
1,4-Naphthoquinone	0.244	9.08×10^4

for these dependences further confirm the proposed reaction mechanism. According to this scheme, the dependence of both quantities on the ionic strength I is given by the rate constant k_2, which is only one corresponding to the reaction of two ions with the same charge, −3. The determined values of the slopes of these dependences then agree with the product of the charges of the reactants in the second step.

The proposed reaction mechanism thus satisfactorily explains all the experimental data and it can thus be assumed that the reaction of 1,4-naphthoquinone with $Co(CN)_5^{3-}$ proceeds according to this proposed reaction scheme.

The perceptible qualitative differences in the mechanism between the reaction of pentacyanocobaltate(II) with p-benzoquinone or toluquinone and with 1,4-naphthoquinone are reflected in the different reaction course, different reaction stoichiometry and different products, and are primarily due to the differences in the rates of the first step. It is clear from the qualitative comparison in Table IV that, in agreement with the decrease in the standard redox potential E°_1 for the redox reaction quinone–semiquinone [8] from 1,4-benzoquinone to 1,4-naphthoquinone, the rate constant of the first step also decreases. Because the rate of the subsequent steps in the reaction system containing pentacyanocobaltate(II) and 1,4-naphthoquinone is comparable or higher (in dependence on the ionic strength) than the rate of the first step, interaction between $(NC)_5CoNQCo(CN)_5^{6-}$ (the intermediate in the second reaction step) with 1,4-naphthoquinone occurs. Reactions of this type could not be studied in the 1,4-benzoquinone (or toluquinone)–pentacyanocobaltate(II) system. As was mentioned in a previous work, when $[Co(CN)_5^{3-}]_0 \geqslant 2[Q]_0$, all the benzoquinone reacted with $Co(CN)_5^{3-}$ before the binuclear product was formed in an observable concentration. In systems with more than a stoichiometric amount of 1,4-benzoquinone, all the $Co(CN)_5^{3-}$ disappeared in the first step, so that the binuclear complex could not be formed. It is, however, known that the binuclear bridge complex $(NC)_5CoQCo(CN)_5^{6-}$ reacts with oxidants and very probably also with 1,4-benzoquinone [7].

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