plexes[36] of the type $L_2AuS_2CNR_2$ also show an apparent increase in the C$\overset{\cdot\cdot}{-}$N double-bond character as the electron-withdrawing ability of L is increased.

We have noted that an acceptable correlation exists between the C$\overset{\cdot\cdot}{-}$N bond order[37] as judged by Bernstein's relationship[38] and the tendency of the nickel(II) dithiocarbamates to form base adducts. The greater the C–N bond order, the less is the tendency of the nickel(II) complex to form a base adduct, providing other factors are maintained constant. This type of an electronic effect and the role it plays in metal-influenced ligand reactions has been little explored to date. It is apparent from the work reported here, however, that base interactions (adduct formation) with the metal can influence properties of the ligand substantially, even properties associated with ligand atoms well removed from the metal.

**Acknowledgment.**—We acknowledge several stimulating discussions with Professors J. Lewis and A. Wojcicki regarding this work.

[36] H. J. A. Blaauw, R. J. F. Nivard, and G. J. M. Van Der Kerk, *J. Organometal. Chem.* (Amsterdam), **2**, 236 (1964).

[37] J. P. Fackler, Jr., and D. Coucouvanis, submitted for publication.

[38] A. J. Bernstein, *J. Chem. Phys.*, **15**, 284 (1947).

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CONTRIBUTION FROM THE CHEMICAL LABORATORY AT NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS,
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# Redox Reactions of Cobalt–Cyanide Complexes. II.[1] Reaction of Pentacyanocobaltate(II) with *p*-Benzoquinone. Properties of $[(CN)_5CoOC_6H_4OCo(CN)_5]^{6-}$

BY A. A. VLČEK[2] AND J. HANZLÍK

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Pentacyanocobaltate(II) ion reacts very rapidly with *p*-benzoquinone to form the bridge species $[(CN)_5CoOC_6H_4OCo(CN)_5]^{6-}$ (I). The organic ligand in I is isoelectronic with the dianion of hydroquinone, but owing to the influence of Co atoms, it shows a higher degree of π-electron delocalization, as can be deduced from spectroscopic and electrochemical properties. Compound I is not oxidized electrochemically, but shows a four-electron reduction analogous to that of other cobalt(III)-pentacyano complexes. I undergoes a two-step decomposition in aqueous solution. Both steps show general acid catalysis. The products of the first step are $[Co(CN)_5H_2O]^{2-}$ and $[(CN)_5CoOC_6H_4OH]^{3-}$ (II). The ligand in II resembles hydroquinone in its spectroscopic and electrochemical behavior. II shows a two-electron oxidation, the product of which is an unstable complex, $[Co(CN)_5(quinone)]^{2-}$, which decomposes to quinone and $[Co(CN)_5H_2O]^{2-}$. II also shows a normal cobalt(III)-cyanide complex reduction. II itself decomposes in solution with the formation of $[Co(CN)_5H_2O]^{2-}$ and hydroquinone. The mechanism of reductions by $Co(CN)_5^{3-}$ is discussed and it is deduced that these reactions proceed mostly *via* a redox addition mechanism, the oxidizing agent (or its fragments) being reduced and coordinated to the cobalt atom at the same time. One-electron agents give monomolecular species whereas two-electron agents give bridged complexes.

Solutions of cobaltous pentacyanide catalyze the hydrogenation of several groups of organic compounds or reduce these compounds (see ref 3 for review). However, except for the reaction with organic halides,[4] no other reaction has been studied in detail. In the reactions with some substrates, deviations from the expected course of reaction are observed[3] which indicate that the process might involve several intermediates and complicated steps.

In the course of our systematic study of the oxidation–reduction reactions of cobalt cyanide complexes, the reaction between cobaltous pentacyanide and *p*-benzoquinone has been studied.

## Experimental Section

**Preparation of $[K_6Co(CN)_5C_6H_4O_2Co(CN)_5]\cdot 2H_2O$.**—To 50 ml of a carefully deaerated aqueous solution of 3 g of $CoCl_2\cdot 6H_2O$, 30 ml of a deaerated solution containing 4.1 g of KCN (reprecipitated from aqueous solution by ethanol) is added at 0° under nitrogen. To the resulting deep green solution 100 ml of an ethanolic, deaerated solution of 0.7 g of *p*-benzoquinone (cooled to 0°) is added slowly with strong stirring and cooling in a nitrogen atmosphere. The color changes immediately to deep red. At the end of the addition of the quinone solution, a red-brown precipitate starts to form (in some cases, especially when the addition of quinone solution is rapid, red oil is first formed which becomes crystalline on longer stirring of the solution at 0°). After 5–10 min of stirring, the precipitate is collected on a filter under nitrogen and washed several times with deaerated ethanol and ether. The resulting material (*ca.* 3.6 g, *i.e.*, about 75%) is dissolved rapidly in a very small amount of water at 0° and reprecipitated rapidly with ethanol (precooled to 0°). It is advisable to precipitate only about three-fourths of the material; otherwise contamination with the decomposition products tends to be high. The precipitate is collected on a filter in a nitrogen atmosphere, washed with ethanol and ether, and dried under vacuum over $P_2O_5$. *Anal.*[5] Calcd for $K_6[(CN)_5CoOC_6H_4OCo(CN)_5]\cdot 2H_2O$: C, 25.39; N, 18.51; H, 1.06. Found: C, 25.8; N, 18.44; H, 1.16.

**Potentiometric Titration.**—A Beckman Model 9 potentiometer with a bright platinum electrode combined with a commercial

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[1] Part I: A. A. Vlček and F. Basolo, *Inorg. Chem.*, **5**, 156 (1966).

[2] This work was started during the leave of absence of A. A. V. from the J. Heyrovský Institute of Polarography, Czechoslovak Academy of Sciences, Prague, Czechoslovakia. He is a recipient of a Senior Foreign Scientist National Science Foundation Fellowship at Northwestern University, 1964–1965.

[3] J. Kwiatek, I. L. Mader, and J. K. Seyler, Advances in Chemistry Series, No. 37, American Chemical Society, Washington, D. C., 1963, p 201.

[4] J. Halpern and J. P. Maher, *J. Am. Chem. Soc.*, **87**, 5361 (1965).

[5] The analysis was performed by Micro-Tech, Skokie, Ill.

saturated calomel electrode was used for potentiometric titrations. All titrations were performed in a nitrogen atmosphere.

To prevent the decomposition of the products, the titration was in most cases carried out at 0°. However, even this did not prevent a partial decomposition and fluctuating results were observed. The final titration was carried out in such a way that for each point on the curve a new solution was taken and the total amount of the second agent corresponding to the designated point on the curve was added. Readings were thus always made with fresh solutions. Reproducibility of the titration done in this way was better than 5%.

**Polarographic Measurements.**—These were performed on an LP-60 Model self-recording polarograph of Laboratorní přístroje (Prague, Czechoslovakia) using the normal polarographic vessel with a silver–silver chloride electrode in saturated potassium chloride solution as a reference electrode. All measurements were carried out in an argon atmosphere. The sample was dissolved directly in the vessel after carefully deaerating the electrolyte solution. The beginning of the polarographic registration took place within 10 sec after dissolving the sample. For the study of the mechanism of the electrode process, the Kalousek commutator was used.

**Spectra.**—Infrared spectra were taken on a Perkin-Elmer grating infrared Model 337 spectrophotometer using Nujol mulls.

A Cary Model 14 spectrophotometer was used for recording the visible and ultraviolet spectra.

As the compound studied decomposes rather rapidly in solution, spectra have to be taken in the shortest possible time after dissolution in cold solution. To achieve this a flow apparatus depicted in Figure 1 is used. The volumetric flask is filled with the desired volume of the solvent and the known amount of the sample to be studied is introduced in a thin-walled glass bubble (G). Argon is passed through the solution by inlet A with stopcocks 1 closed, 3 open, and 2 in the position A–B. After deaerating the solution (after *ca.* 20 min) the glass bubble with the sample is broken by the magnetic stirrer (M), stopcock 3 is closed, 1 opened, and 2 put into the position B–C. Under the pressure of the gas, the solution flows into the spectrophotometric cell (S), which can be either placed directly in the spectrophotometer compartment or, after closing stopcocks 4 and 5, disconnected from the apparatus and transferred into the compartment. The time necessary for filling the cell is about 5 sec. With the cell in the compartment the very first stages of the reaction can be followed.

**Kinetic Measurements.**—The rate of the decomposition of the complex was followed spectrophotometrically or polarographically. Owing to the overlapping of the absorption bands of the complex and of the products of its decomposition, the spectrophotometric method could be used only in the first stages of the reaction. The polarographic method made it possible to follow the whole reaction. The main measurable quantity in this case was the concentration of the $Co(CN)_5H_2O^{2-}$ complex formed. Under special conditions, both the concentration of $Co(CN)_5H_2O^{2-}$ and that of the intermediate and the over-all concentration of cobalt were measured simultaneously.

## Results

**Reaction of $Co(CN)_5^{3-}$ with *p*-Benzoquinone.**—The spectrophotometric study of this reaction, using the typical bands of $Co(CN)_5^{3-}$ at 280 and 967 mμ, shows that upon the addition of 1 equiv of *p*-benzoquinone exactly 2 equiv of $Co(CN)_5^{3-}$ disappears from the solution. However, the expected hydroquinone and $Co(CN)_5H_2O^{2-}$ bands do not appear, a new very strong band at 435 mμ being formed.

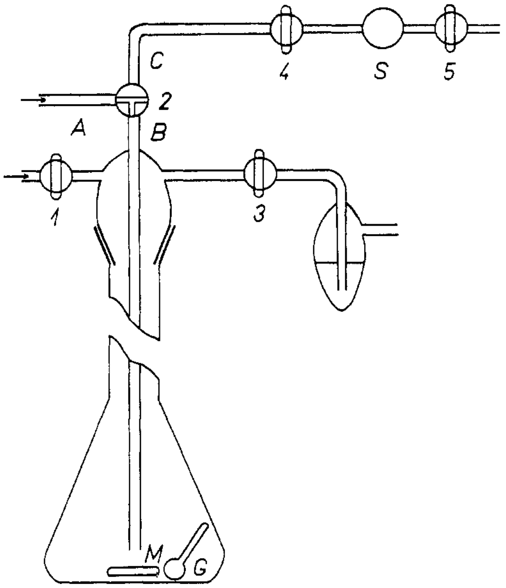

Figure 1.—Apparatus for rapid dissolving and filling of the spectrophotometric cell (see text for explanation).

The polarographic study of this reaction shows a similar result: The characteristic reduction wave of $Co(CN)_5^{3-}$ at $\sim -1.3$ v decreases upon the addition of *p*-benzoquinone, again exactly in the ratio of 2 equiv of Co(II)/1 equiv of *p*-benzoquinone, and a new wave at about $-1.5$ v (see later) is formed, no current attributable to the oxidation of hydroquinone being observed.

The reaction discussed also influences the simultaneous reduction of *p*-benzoquinone and $Co(CN)_5Br^{3-}$ at the dropping-mercury electrode. The reduction wave of $Co(CN)_5Br^{3-}$ does not appear in presence of *p*-benzoquinone unless

$$D_q^{1/2}[\text{quinone}] \leq 2D_c^{1/2}[\text{Co(CN)}_5\text{Br}^{3-}] \qquad (1)$$

($D_q$ and $D_c$ are the diffusion coefficients of *p*-benzoquinone and $Co(CN)_5Br^{3-}$, respectively.) Instead a wave at more negative potentials (around $-1.5$ v, depending upon the ionic strength of the solution) is observed, the over-all limiting current also being about 20% smaller than the sum of limiting currents of *p*-benzoquinone and $Co(CN)_5Br^{3-}$.

This behavior can be explained in the following way. $Co(CN)_5^{3-}$ is formed as the product of the reduction of $Co(CN)_5Br^{3-}$ [6] and diffuses into the solution. Along its path, it meets the *p*-quinone diffusing toward the electrode and reduces it forming a species which is reducible at more negative potentials. In this way part of the quinone is reduced chemically and thus escapes the electrode reaction. Condition 1 defines the stoichiometry of the reaction, which is identical with that deduced from direct observations of the reaction between $Co(CN)_5^{3-}$ and *p*-benzoquinone.

The same result is obtained by a potentiometric titration of a $Co(CN)_5^{3-}$ solution with a solution of *p*-benzoquinone (see Figure 2a).

In this connection it should be mentioned that pentacyanocobaltate(II) solutions can be used as good titrating agents or can be easily titrated with oxidizing agents. The potential of a bright platinum electrode in a solution of $Co(CN)_5^{3-}$ with an excess of about 0.1 equiv of

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(6) H. Matschiner, Ph.D. Thesis, Polarographic Institute, Prague, 1964 (to be published); A. A. Vlček, *Pure Appl. Chem.*, **10**, 61 (1965).

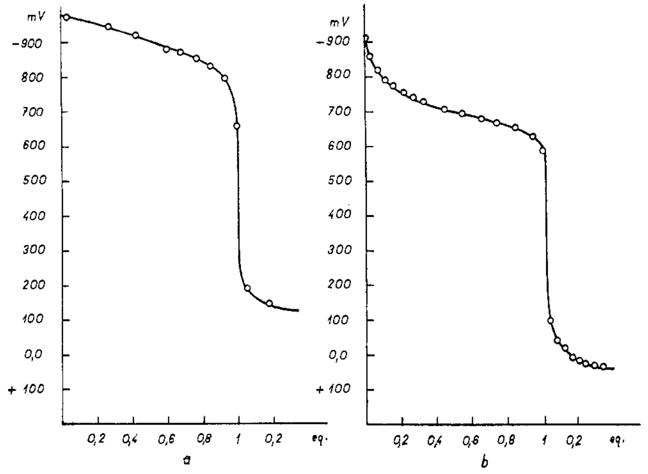

Figure 2.—Potentiometric titration of pentacyanocobaltate(II) solution with *p*-benzoquinone (a) and iodine (b). $10^{-2}$ *M* $Co(CN)_5^{3-}$, 0°.

KCN and containing an equivalent amount of $Co(CN)_5H_2O^{2-}$ has a potential of about −0.94 v (sce). The titration curve of $Co(CN)_5^{3-}$ alone shows the general pattern of a potentiometric titration curve. The potential at which half-equivalence is reached ($E_f^0$) depends, however, on the titrating agent and also slightly upon the starting concentration of the cobaltous pentacyanide. For the titration with iodine it was observed that $E_f^0 = -0.70$ v (sce) (see Figure 2b); for that with *p*-benzoquinone $E_f^0 = -0.86$ to $-0.90$ v (sce). The potential usually reaches a constant value within 1–2 min. The meaning of the $E_f^0$ value, as well as the nature of the redox couple determining the potential of the electrode, is not quite clear and is being studied.[7] However, for present purposes, the experiments show unambiguously that potentiometric titrations using $Co(CN)_5^{3-}$ are possible and can be used to determine the stoichiometry of the reactions of cobalt(II)–pentacyanide.

From these experiments, as well as on the basis of other evidence (see later), we conclude that a bridge compound (I) is formed, in complete analogy with some other reactions of $Co(CN)_5^{3-}$ with oxidizing agents:[1] $[(CN)_5CoOC_6H_4OCo(CN)_5]^{6-}$ (I). It has to be emphasized, that species I is formed as the only product of the reaction even in solutions containing a very large excess of cyanide ions.

Preliminary experiments on the determination of the rate and mechanism of the reaction between $Co(CN)_5^{3-}$ and *p*-benzoquinone, performed with the use of the stopped-flow method, indicate that the primary step is a reaction of one $Co(CN)_5^{3-}$ ion with one molecule of *p*-benzoquinone. This reaction is very fast; the preliminary value of the rate constant was calculated as $\sim 5 \times 10^6\ M^{-1}\ sec^{-1}$.

**Properties of the Bridge Complex.**—The deep red bridge complex (I) is stable in the solid state, even in the presence of air. It is extremely soluble in water and almost insoluble in common organic solvents. In solution a rather rapid decomposition takes place. This decomposition seems to be faster and more complicated in the presence of oxidizing agents. This is especially important in preparative experiments. When a solution of $Co(CN)_5^{3-}$ is added to a solution of benzoquinone containing an excess of quinone, complicated products are formed which cannot be completely converted into the bridge compound by the addition of an excess of $Co(CN)_5^{3-}$.

Aqueous solutions of I show one intense band at 23,000 cm$^{-1}$ with $\epsilon$ 8 × $10^3$. There is no band in the infrared region nor near 33,000 cm$^{-1}$, where typical bands of free quinone or hydroquinone are located.

The infrared spectrum of I shows the typical bands due to CN groups and to the organic ligand, as well as to the $Co(CN)_5$ group. The observed frequencies are as follows (in cm$^{-1}$): 3200 (m), 2140 (m), 2120 (s), 2080 (w), 1620 (m), 1485 (s), 1226 (s) (with weak shoulders at 1245, 1260), 1108 (w), 1095 (w), 862 (m–w), 854 (m–w), 792 (m), 585 (vw); 545 (vw), 465 (w), 419 (m) (with a shoulder at 427). The group of bands at 2100 cm$^{-1}$ is due to the $CN^-$ group and the bands in the region 550–420 cm$^{-1}$ are common to most complexes containing a $Co(CN)_5$ group. The remaining bands are due to the organic ligand. There is a similarity of this part of spectrum to that of hydroquinone. However, the spectrum of the complex is much simpler and some bands are shifted as compared with the free hydroquinone. This is especially the case of the 1485-cm$^{-1}$ band (1515 cm$^{-1}$ (s) in free hydroquinone) and of the 1226-cm$^{-1}$ band (a group of five bands between 1190 to 1265 cm$^{-1}$ (m) in free hydroquinone).

Complex I undergoes a four-electron reduction at the dropping-mercury electrode. The limiting current due to this reduction is diffusion controlled and increases linearly with the concentration of I. The over-all electrode process as well as the electrode reaction proper is completely irreversible, as follows from the analysis of potential–current dependence and from the experiments by ac techniques. Hydroquinone is the only electroactive product detected (1 equiv of hydroquinone/1 equiv of I). The half-wave potential of the reduction process depends strongly upon the concentration of the supporting electrolyte (see Figure 3) and is

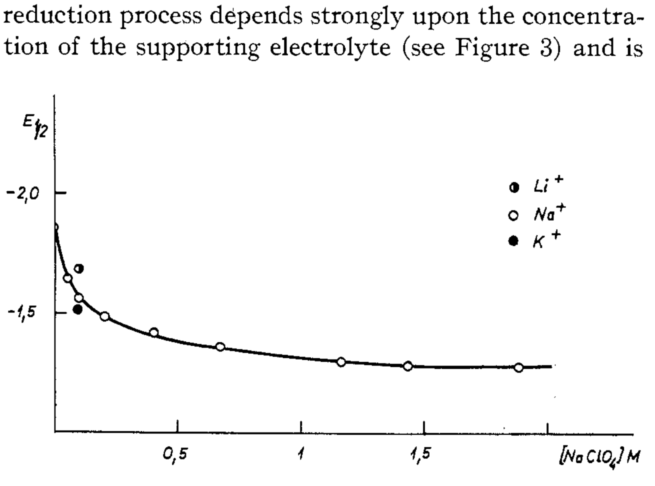

Figure 3.—Dependence of the half-wave potential of I at the dropping-mercury electrode upon the ionic strength measured at 0°.

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[7] (a) G. Grube, *Z. Elektrochem.*, **32**, 565 (1926); (b) D. N. Hume and I. M. Kolthoff, *J. Am. Chem. Soc.*, **71**, 867 (1949).

shifted toward more positive potentials with increasing ionic strength. The pronounced positive shift is observed also by changing the cation of the supporting electrolyte in the series $Li^+ < Na^+ < K^+ < Rb^+$. There is no dependence upon the anion of the supporting electrolyte nor upon the pH in the region 9–11.5. This behavior fits into the pattern of the reduction of other cobalt(III)–cyanide complexes.[6] The results show furthermore that there is a great electrostatic hindrance in the reduction process, connected with the high negative charge of the depolarizing particle.

According to these results and in analogy with the mechanism of other cobalt(III)–cyanide complexes[6] the reduction mechanism of I can be written

$$\begin{tikzcd} \mathrm{I} \arrow[r, Rightarrow, "4e"] & 2\mathrm{Co(CN)_5}^{4-} \arrow[d, "H^+"] + \text{hydroquinone} \\ & 2\mathrm{Co(CN)_5H}^{3-} \end{tikzcd}$$

No oxidation of I at a mercury dropping or a platinum vibrating electrode up to +1.1 v has been detected in neutral and alkaline solutions up to pH ~13. Similarly, no reduction attributable to the organic ligand was found.

**Decomposition in the Solution.**—The spectrophotometric as well as polarographic results show that I undergoes a two-step decomposition in aqueous solution. The relative rates of these two steps make it possible to follow, under certain conditions, these two consecutive reactions separately.

In the first step one $Co(CN)_5H_2O^{2-}$ ion is formed per one particle of I, together with an intermediate product which decomposes with a smaller rate than I giving a second equiv of $Co(CN)_5H_2O^{2-}$ and 1 equiv of hydroquinone. This stoichiometry has been confirmed independently by polarographic and spectrophotometric measurements.

The first step of decomposition of I is manifested in the spectrum by the decrease of the band at 435 mμ, by the broadening of this band on the side of lower wavelengths, and by the shift of the band maximum toward the value 370 mμ which seems to be characteristic for the intermediate species. At the same time a new band at 279 mμ and a double band at 316 and 323 mμ develop (in 0.04 *M* NaOH; in neutral solutions only one band at 307 mμ is formed). During the second step of decomposition the band at 370 mμ decreases and bands of hydroquinone are formed (depending on pH, between 290 and 310 mμ). In completely decomposed solutions, bands corresponding to $Co(CN)_5H_2O^{2-}$ (380 mμ) and to hydroquinone are detected.

When the polarographic behavior of this system is followed during decomposition, the wave of $Co(CN)_5H_2O^{3-}$ appears and increases with time. At the same time a new oxidation wave ($E_{1/2}$ = +0.02 v) is formed with the same rate as the wave of $Co(CN)_5H_2O^{3-}$. This oxidation wave reaches a limiting value when approximately 1 equiv of $Co(CN)_5H_2O^{2-}$ appears in the solution, *i.e.*, when the first step of decomposition is almost complete. During the second step the limiting oxidation current remains constant, but the oxidation wave shifts toward more negative potential and changes its shape at the same time until it reaches the value and shape corresponding to that of the oxidation of hydroquinone in the given medium. During the first step the reduction wave of I disappears and a new wave, badly separated from the wave of I as well as from the second reduction wave of $Co(CN)_5H_2O^{2-}$, is formed. The total limiting reduction current remains constant throughout the whole process, confirming thus the consumption of two electrons per one cobalt atom in the reduction process of I. The oxidation wave observed at +0.02 v during the first step is obviously due to the oxidation of the intermediate species which is characterized by the 370-mμ band. The time dependence of the various forms is shown in Figure 4.

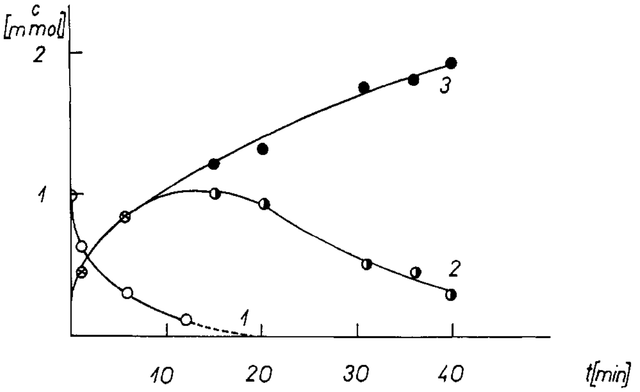

Figure 4.—Change of concentration of various species during the decomposition of I. Decomposition was followed polarographically in a solution of pH 9.64 (0.1 *M* boric acid + borate) and 0.25 *M* KCl at 30°: (1) species I; (2) species II; (3) $Co(CN)_5H_2O^{2-}$.

The intermediate species formed during the decomposition can be, on the basis of the evidence quoted above, formulated as $[(CN)_5CoOC_6H_4OH]^{3-}$ (II).

The decomposition of I as well as of II is generally acid catalyzed, as can be seen from the influence of pH and buffer concentration upon the rates of these reactions. The over-all rates of both steps decrease with increasing ionic strength. However, owing to the necessity to work at rather high concentrations of buffer and indifferent salts, a quantitative evaluation of the linear $(\log k)-\sqrt{\mu}$ dependence is not possible. The nature of the anion of the strong acid does not have any influence upon the rate of the decomposition. Table I summarizes some of the experimental data.

Both reactions are greatly accelerated by increasing the temperature. However, the estimated activation parameters ($\Delta H^{\ddagger}$ = 50 kcal and $\Delta S^{\ddagger}$ = +97 eu for the first step) seem to be unrealistic which might be connected with the catalytic nature of the process.

**Properties of II.**—All attempts to isolate species II have failed. Owing to its lability, it was impossible to separate it from the large admixtures of $Co(CN)_5H_2O^{2-}$. Thus the properties of II were studied only in reaction mixtures.

From the analysis of the time dependence of the

TABLE I
MEAN VALUES OF RATE CONSTANTS FOR THE DECOMPOSITION OF I

| pH | [HA],[a] *M* | [KCl], *M* | $10^4k$, $M^{-1}$ sec$^{-1}$ |
|---|---|---|---|
| | First Step (25°) | | |
| 9.24 | 0.10 | 0.25 | 13.0 |
| 9.64 | | | 7.1 |
| 9.80 | | | 5.0 |
| 10.07 | | | 3.05 |
| 9.24 | 0.10 | 0.25 | 13.0 |
| | | 0.50 | 4.6 |
| | | 0.75 | 3.6 |
| | | 1.00 | 2.9 |
| 9.53 | 0.05 | 1.0 | 2.3 |
| | 0.10 | | 1.72 |
| | 0.15 | | 1.15 |
| | Second Step (30°) | | |
| 9.52 | 0.1 | 0.25 | 5.7 |
| 9.56 | | | 5.0 |
| 9.64 | | | 3.6 |
| 9.70 | | | 2.9 |
| 9.80 | | | 1.9 |
| 9.52 | 0.1 | 0.25 | 5.7 |
| | | 0.50 | 2.0 |
| | | 0.75 | 0.8 |
| | | 1.00 | 0.38 |
| 9.29 | 0.05 | 0.375 | 6.9 |
| | 0.10 | | 7.5 |
| | 0.15 | | 8.6 |

[a] Total concentration of the acid and anion.

spectrum it follows that species II shows a band at 27,000 cm$^{-1}$ with $\epsilon \sim 2000$ and a band at 32,700 cm$^{-1}$ in water or a double band at 31,600 and 31,000 cm$^{-1}$ in alkaline solutions. Furthermore, the band appearing at 36,000 cm$^{-1}$ can also be ascribed to species II. The series of bands around 31,000 cm$^{-1}$ is similar but distinguishable from the bands of hydroquinone. The band at 27,000 cm$^{-1}$ is analogous to the bands observed for the intermediates of the decomposition of the analogous $\mu$-SO$_2$ complex.[1]

The electrochemical behavior of II can be studied in the reaction mixtures without difficulties. Correcting the observed current–potential curves for the known behavior of $Co(CN)_5H_2O^{2-}$, the reduction wave at $-1.52$ v (pH 10.55, 0.2 *M* borate buffer, 0°) and the oxidation wave at $+0.02$ v (pH 8.2, borate buffer) are seen to be due to the reduction and oxidation of II. Both of these processes are diffusion-controlled two-electron changes. By studying the reduction process with Kalousek's commutator, hydroquinone was detected as the only electroactive product of the reduction process. However, an inspection of the oxidation process reveals the existence of two products reducible at $+0.02$ and $-0.05$ v, respectively. The product reducible at $-0.05$ v was identified as free quinone whereas the second product, reduced reversibly at $+0.02$ v, is obviously the oxidized form of II. The ratio of the concentrations of the products formed changes with temperature. At 0° the oxidized form of II represents about 80% of the products whereas at 30° quinone is the main product (about 90%). This points to the conclusion that the electrode reaction proper of the oxidation of II proceeds reversibly; the oxidized form of II is formed as the primary product and decomposes rather rapidly giving $Co(CN)_5H_2O^{2-}$ and quinone. The electrochemical behavior of II can be summarized as

$$\begin{tikzcd}
Co(CN)_5(\text{quinone})^{2-} \arrow[r, leftrightarrow, "2e"] \arrow[d] & \text{II} \arrow[r, Rightarrow, "2e"] & Co(CN)_5^{4-} + \text{hydroquinone} \arrow[d, "H^+"] \\
Co(CN)_5H_2O^{2-} + \text{quinone} & & Co(CN)_5H^{3-}
\end{tikzcd}$$

From the comparison of the electrode behavior of II with the behavior of other cobalt(III)–cyanide complexes, as well as with that of hydroquinone, it can be concluded that only the organic ligand in II is involved in the oxidation process. At a mercury dropping electrode the potential of the oxidation of the hydroquinone bound in II is about 70 mv more positive than that of the free hydroquinone in the same medium,[8] showing that hydroquinone bound in the complex is more stable toward the oxidation than the free compound.

## Discussion

The reducing strength of pentacyanocobaltate(II) ion cannot be expressed quantitatively, for the measurements of the redox potentials do not provide us with data which would make it possible to specify the standard redox potential (*vide ante*). In this situation only a comparison of the reactivity of $Co(CN)_5^{3-}$ toward various redox systems can be used to estimate its reducing strength. From a series of potentiometric and amperometric titrations,[9] it follows that $Co(CN)_5^{3-}$ is able to reduce oxidized forms of systems having $E^0$ more positive than about $-0.5$ to $-0.55$ v (*vs.* standard hydrogen electrode). Thus sulfite ion is not reduced in alkaline solution, but undergoes a reaction after slight acidification.[1] The same holds for nitrite ion.[9] Analogously $\gamma,\gamma$-dipyridyl does not react with pentacyanocobaltate(II) in neutral or alkaline solutions; a partial reduction is observed only upon acidification to pH 5.5–6. Similarly, anthraquinone $\beta$-sulfonate is also reduced only partially.[9]

The reducing strength of pentacyanocobaltate(II) depends, however, to a great extent upon the ability of the compounds, or of their fragments, being reduced to coordinate in their reduced forms to the $Co(CN)_5$ unit. The results presented as well the study of several other processes[1,3,4,9,10] point to the conclusion that this coordination process is quite a general feature for reactions in which pentacyanocobaltate(II) ion is the reducing agent proper.[11] One-electron oxidizing agents

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(8) It has to be noted that at a bright platinum vibrating electrode this difference is +300 mv, most probably due to an incomplete reversibility of the system or to adsorption effects more pronounced at the platinum electrode than at the mercury electrode.

(9) A. A. Vlček, unpublished results.

(10) J. Halpern and S. Nakamura, "Proceedings of the VIIIth International Conference on Coordination Chemistry," V. Gutmann, Ed., Vienna, 1964, p 271.

(11) However, for the reaction between pentacyanocobaltate(II) ion and some cobaltic complexes, $Co(CN)_6^{3-}$ was found as the main product. On the basis of the rate law of these reactions, it was concluded[10] that an outer-sphere mechanism operates in these cases, the $Co(CN)_6^{4-}$ species being the reducing agent proper. The rather limited material on this type of reaction does not make any rationalization possible.

usually react to a product or intermediate of the general form $Co(CN)_5X^{n-}$; two-electron oxidizing agents give a bridge species, $Co(CN)_5XCo(CN)_5^{n-}$. The stability of these products or intermediates and the possibility to detect their formation depend strongly upon the nature of X and of the medium. Some of the bridge species decompose rather rapidly in neutral and acid solutions so that their formation cannot be detected under these conditions by standard techniques.

All of these observations raise the important question of the ability of $Co(CN)_5^{3-}$ to coordinate a sixth ligand and of the structure of the species formed.

Pentacyanocobaltate(II) is known to exist as a diamagnetic dimer in the solid.[12] In solution, however, a paramagnetic species exists which is supposed to be monomeric with coordination number 5.[12] As the Co–Co bond gets broken by dissolution, the monomeric units $Co(CN)_5^{3-}$ must be stabilized by interaction with the solvent which would compensate for the stabilizing effect of the metal–metal bond. Stabilization in solution can be due to solvation only or to solvation plus coordination of one solvent molecule in the sixth position. However, the bonding of the sixth ligand would be rather weak, for the single unpaired electron would occupy the $a_1$ $\sigma$-antibonding orbital, so that $Co(CN)_5^{3-}$ can be regarded as special, predominantly existing with coordination number 5, and any stronger coordination of a sixth ligand to $Co(CN)_5^{3-}$ is improbable unless *the ligand has the ability to accommodate the unpaired electron in a vacant orbital* either fully localized on the ligand or involved in the metal–ligand bond. Such a vacant orbital might be a $\sigma$-bonding or nonbonding orbital in the final complex (*e.g.*, halogens, $SO_2$) or a vacant $\pi$-orbital of the ligand (*e.g.*, oxygen, *p*-quinone).

$Co(CN)_5^{3-}$ is thus able to coordinate strongly a sixth ligand only if the coordination process is accompanied by a simultaneous intramolecular redox process, fully or partially transferring the electron from the $Co(CN)_5^{3-}$ unit into the new ligand. This process which can be described as the *redox addition* represents at the same time the primary step in most electron-transfer reactions of pentacyanocobaltate(II) and can be, owing to its specific features, regarded as a special type of the more general inner-sphere mechanism of redox reactions. Most reactions in which $Co(CN)_5^{3-}$ is the reducing agent proper seem to proceed by this mechanism.

The redox addition mechanism involving actually no structural changes in the $Co(CN)_5$ unit (except for solvation changes) is fully in agreement with the high rates of most reductions by $Co(CN)_5^{3-}$ which in some cases are exceeded only by the rates of reduction by the hydrated electron and which show that the electron in pentacyanocobaltate(II) is readily available.

In this way it is quite easy to understand the course of the reaction of pentacyanocobaltate(II) with *p*-benzoquinone. The unpaired electrons of two $Co(CN)_5^{3-}$ units are accepted into the $2b_{2g}$ orbital of *p*-quinone[13] which is vacant and slightly bonding.[14,15] The reaction proceeds in two steps, as follows from the linear dependence of its rate upon the concentration of $Co(CN)_5^{3-}$ and *p*-benzoquinone: primarily a highly unstable species $[Co(CN)_5(\text{quinone})]^{3-}$ is formed which reacts very rapidly with a second $Co(CN)_5^{3-}$ to form I. Species I is thermodynamically stable; however, in solution it undergoes a two-step splitting by the attack of proton donors. The uncatalyzed hydrolysis or a splitting under the influence of ligands able to coordinate to cobalt atom proceeds extremely slowly. From this it can be concluded that the splitting in solution is induced only by the protonation of the oxygen attached to the cobalt atom.

The electron transfer in I seems to be complete, for in both steps of the decomposition the complex of trivalent cobalt, $Co(CN)_5H_2O^{2-}$, is formed.[16] This conclusion is supported by the course of the reduction process at the dropping-mercury electrode which shows the features characteristic for the Co(III) complexes. Furthermore, I differs from the analogous complexes formed in the reaction with oxygen in that no oxidation of the [Co–L–Co] unit is observed. I should thus be formulated as a complex of trivalent cobalt with a rather small delocalization of highest occupied orbital in the cobalt atoms.

The ligand L in the bridge species I is thus isoelectronic with the dianion of hydroquinone ($Q^{2-}$). The comparison of the properties of $Q^{2-}$ with that of L indicates, however, that there are considerable differences in behavior, and it has to be concluded that the electronic levels and distribution in L differ to a great extent from those in $Q^{2-}$.

The most striking difference is in the redox properties. Whereas free hydroquinone is easily oxidized, no oxidation of the organic ligand in I at a dropping-mercury or platinum electrode has been detected showing thus that the organic ligand in I is highly stabilized toward oxidation by coordination and the corresponding complex with oxidized ligand (or less probably with oxidized central atom) is by far less stable than species I itself.[17] This *relative* instability of oxidized forms of I does not necessarily mean an intrinsic instability which would result in decomposition but is connected primarily with an increased ionization potential of the reduced form of the bound ligand as compared with its free form. This confirms also that during the reduction of *p*-benzoquinone the electrons are accepted into the $2b_{2g}$ orbital. The ligand L is a ten-$\pi$-electron system, of the general form *p*-$YC_6H_4Y$, the $b_{2g}$ orbital being the highest occupied level. The properties of this orbital, especially the extent to which this orbital

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(12) A. Adamson, *J. Am. Chem. Soc.*, **73**, 5710 (1951).

(13) Here and in the subsequent text we use the group-theory symbols based on the symmetry of the isolated ligand.

(14) L. E. Orgel, *Trans. Faraday Soc.*, **52**, 1172 (1956).

(15) G. N. Schrauzer and H. Thyrst, *Theoret. Chim. Acta*, **1**, 172 (1963).

(16) In the decomposition of the $\mu$-$SO_2$ species, the first step gives $Co(CN)_5H_2O^{2-}$ whereas during the second step an intramolecular redox reaction takes place, pentacyanocobaltate(II) being formed in alkaline solution: J. Hanzlík and A. A. Vlček, submitted for publication.

(17) It has to be pointed out that all attempts to prepare oxidation products of I, even though one would expect theoretically two such products, failed. A complicated mixture of the oxidation products of hydroquinone and $Co(CN)_5H_2O^{2-}$ was always observed.

has a bonding or antibonding character and the magnitude of the conjugation between the p electrons of the substituents Y and the $\pi$ system of the ring, depend strongly upon the nature of substituent Y,[18] expressible in the HMO calculations by the parameters $h$ and $k$ in the definition of Coulomb and resonance integrals (see, *e.g.*, ref 18). The difference in the behavior of L and $Q^{2-}$ amounts to a stabilization of the $2b_{2g}$ level and an increased conjugation between Y and the ring. The organic ligand in I can thus be regarded as being more closely a ten-$\pi$-electron system than the hydroquinone which is regarded to be very close to a six-$\pi$-electron system.[19] This effect, which can be accounted for by ascribing a higher $h$ parameter to the $-OCo(CN)_5$ groups than to oxygen itself, is connected with the increase of electron attraction of oxygen atoms due to their coordination to cobalt atoms (coordination effect) and to an interaction of the $\pi$ levels of L with the $\pi$ levels of the $Co(CN)_5$ groups. The $2b_{2g}$ level might be stabilized not only because of the coordination effect but also because of the interaction with $\pi$-antibonding orbitals of the $Co(CN)_5$ groups. The $3b_1$ orbital (vacant, antibonding) is able, on the other hand, to interact, probably only weakly, with the $\pi$ levels of $Co(CN)_5$ groups. All of these effects are consistent not only with the observed stabilization toward the oxidation but also with the disappearance of the L–L transition in I (*vide ante*). The observed absorption band at 23,000 $cm^{-1}$ is most probably a charge-transfer band from the $2b_{2g}$ level of L into the lowest $\sigma$-antibonding level of the complex localized to a great extent on the metal atoms.

According to this picture of the electron configuration of L in I, the oxygen–carbon bond would be left with some double-bond character but at the same time with electron density in $\pi$-antibonding orbitals. The infrared frequency of L which can be ascribed to the C–O stretch is in the single C–O bond region and is even lower that in $H_2O$. The force constant of the C–O bond in I is influenced by the electron density in $\pi$-bonding as well as antibonding orbitals and by the coordination of oxygen which might decrease the $\sigma$-bond contribution to the force constant of the C–O bond, as is also the case in some other complexes.

The organic ligand in species II, on the other hand, resembles very closely the free hydroquinone (in redox as well as in spectral properties). Obviously, the splitting off of one $Co(CN)_5$ group from I causes a decrease of the above-discussed influences and brings the electronic configuration of the ligand in II closer to that of hydroquinone.

The primary product of electrochemical oxidation of II is a species which is actually a $\sigma$-bonded quinone complex, $[Co(CN)_5(quinone)]^{2-}$. The stability of this species in aqueous solution is rather low, undergoing a simple hydrolysis without any further intramolecular redox process.

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[18] C. A. Coulson, A. Streitwieser, Jr., M. D. Poole, and J. I. Brauman, "Dictionary of $\pi$-Electron Calculations," Pergamon Press, New York, N. Y., 1965.

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# Kinetics of Some Substitution Reactions of *trans*-Bis(dimethylglyoximato)cobalt(III) Complexes[1]

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Kinetic measurements are reported for a number of anation reactions of *trans*-$Co(DH)_2(NO_2)OH_2$ and *trans*-$Co(DH)_2(I)OH_2$, where $DH^-$ is the dimethylglyoximate ion, $HON{=}C(CH_3)C(CH_3){=}NO^-$. The reactions were found to exhibit second-order kinetics, the order of increasing reactivity of the anions examined being $Cl^- < Br^-$, $NO_2^- < N_3^-$, $NCS^- < HSO_3^-$. For a number of the reactions, activation parameters as well as equilibrium measurements also are reported. The results, which are consistent with either SN1 or SN2 substitution mechanisms, are discussed and compared with those for related substitution reactions of other cobalt(III) complexes including the cobalamins.

## Introduction

This paper describes some kinetic studies on a number of substitution reactions of *trans*-bis(dimethylglyoximato)cobalt(III) complexes, notably the anation reactions of nitroaquobis(dimethylglyoximato)cobalt(III) and iodoaquobis(dimethylglyoximato)cobalt(III)

$$trans\text{-}Co(DH)_2(X)OH_2 + Y^- \longrightarrow trans\text{-}Co(DH)_2(X)Y^- + H_2O \quad (1)$$

where $DH^- = HON{=}C(CH_3)C(CH_3){=}NO^-$, $X^- = NO_2^-$ or $I^-$, and $Y^- = NO_2^-, Cl^-, Br^-, NCS^-, N_3^-$, or $HSO_3^-$. These studies were undertaken in the context of the extensive continuing general interest, reflected in numerous recent investigations,[2-5] in the kinetics and mechanisms of the substitution reactions

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