lium on Spheron 6 and Spheron C range from 93 to 34 cal./mole.

5. The heat of adsorption, as defined by the B.E.T. "*c*" value is in substantial agreement with the calculated heat curves.

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A Polarographic Study of Cobalt Cyanide Complexes[1]

By David N. Hume[2] and I. M. Kolthoff

The characteristic properties of a solution of a cobaltous salt in excess alkali cyanide have frequently been attributed to the presence of hexacyanocobalt(II)ate ions.[3] There is much evidence, however, that in at least moderately concentrated solutions the complex which is formed is a pentacyanide rather than a hexacyanide.[4] The oxidation state of the cobalt in these solutions has never been definitely established. In the present investigation, a study of the reduction at the dropping mercury electrode of various cobalt complexes in cyanide medium has led to an understanding of the nature and identity of the complex cobalt ions formed in cyanide medium.

Experimental

The usual polarographic technique was employed. Details of the apparatus and methods have been described in a previous communication.[5] The capillary had a drop time of 3.18 sec. and a value of 1.98 for $m^{2/3}t^{1/6}$ in 0.1*M* potassium chloride at a potential of 0.0 v. against the saturated calomel electrode.

The reduction of cobalt(II) salts in potassium cyanide as a supporting electrolyte was first studied. In agreement with previous investigators[3d,3e] well-defined reduction waves were found for 0.002 *M* cobalt solutions in 0.1 *M* and 1.0 *M* potassium cyanide. The height of these waves was observed to be almost exactly one half that of the corresponding wave in potassium chloride, implying a one-electron reduction (Fig. 1). The shape of the waves obviously indicated irreversibility and no effort was made at analysis. It was also noted that the half wave potential was shifted to more positive values with increasing cyanide concentration, a confirmation of the irreversibility of the electrode reaction. The solutions obtained were yellow-green in color.

Previous investigators had interpreted the apparent one-electron reaction as a reduction of cobalt(III) hexacyanide ion produced spontaneously by water-oxidation of the cobalt(II) hexacyanide ion initially formed. In order to test this hypothesis, pure potassium hexacyanocobalt(III)ate (cobalticyanide) was prepared by the method of Benedetti-Pichler.[6] The product was obtained in large, clear, very pale yellow crystals which dissolved readily in water giving a clear solution. Polarograms were taken on millimolar solutions of the pure complex salt in 0.1 *M* and 1.0 *M* potassium cyanide as a supporting electrolyte.

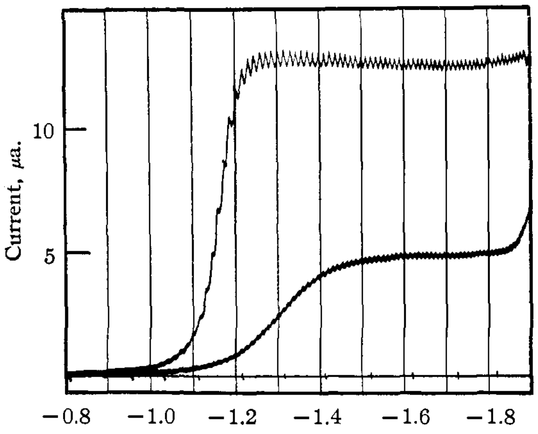

Fig. 1.—Polarograms of 0.002 *M* $CoCl_2$: upper curve in 0.1 *M* KCl; lower curve 1.0 *M* KCN.

No reduction of the cobalt complex could be observed prior to the discharge of potassium ion; the polarograms were identical with the residual current of the cyanide supporting electrolyte. The following experiments were therefore devised to determine the nature of the complex formed by solution of cobaltous salts in alkali cyanide.

A solution of 0.200 millimole of cobaltous chloride in 50 ml. of 1.0 *M* potassium cyanide was titrated amperometrically with 0.100 *M* potassium ferricyanide with exclusion of oxygen. After each addition of reagent and a wait of 2 or 3 minutes, the current at cathode potentials of −0.8 v. and −1.7 v. was measured. The cobalt is not reduced at −0.8 v. but gives a diffusion current at −1.7 v. Ferricyanide is reduced in cyanide medium at all attainable potentials of the dropping electrode, while ferrocyanide gives no wave. Hence any current at −0.8 v. must be due to unreacted ferricyanide. The result is shown in Fig. 2. The ferricyanide was consumed until one mole had been added per mole of cobalt. During the titration, the color of the solution changed from pale yellow-green to deep yellow and the diffusion current at −1.7 v. increased steadily, being approximately doubled by the end of the titration. The wave of the cobalt compound became more drawn-out and the half-wave potential shifted to more negative values (approximately −1.4 v.). The experiment clearly showed, therefore, that cobalt (II) chloride dissolved in excess potassium cyanide solution in the absence of air remains in the divalent state. Furthermore, the oxidized product obtained by treatment with ferricyanide is definitely not cobalt(III) hexacyanide ion, as the latter gives no wave.

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(1) Taken from a portion of the Doctorate thesis of David N. Hume, 1943. Presented in part at the Chicago Meeting of the American Chemical Society, September, 1946.

(2) Du Pont Fellow in Chemistry 1942-1943. Present address: Massachusetts Institute of Technology, Cambridge 39, Massachusetts.

(3) (a) G. Grube and P. Schächterle, *Z. Elektrochem.*, **32**, 565 (1926); (b) R. Peters, *Z. physik. Chem.*, **26**, 217 (1898); (c) T. M. Lowry, *Chem. Ind.*, **42**, 318 (1923); (d) N. V. Emelianova, *Rec. trav. chim.*, **44**, 529 (1925); (e) G. Sartori, *Gazz. chim. ital.*, **66**, 688 (1936).

(4) (a) E. Rupp and F. Pfenning, *Chem. Z.*, **34**, 322 (1910); (b) P. Edelmann, "Dissertation," Dresden T. H., 1915, p. 44; (c) E. Müller and H. Lauterbach, *Z. anal. Chem.*, **62**, 23 (1923); (d) E. Müller and W. Schlüttig, *Z. anorg. allgem. Chem.*, **134**, 327 (1924); (3) S. Glasstone and J. C. Speakman, *Analyst*, **55**, 93 (1930).

(5) D. N. Hume and I. M. Kolthoff, This Journal, **65**, 1897 (1943).

(6) A. A. Benedetti-Pichler, *Z. anal. Chem.*, **50**, 257 (1927).

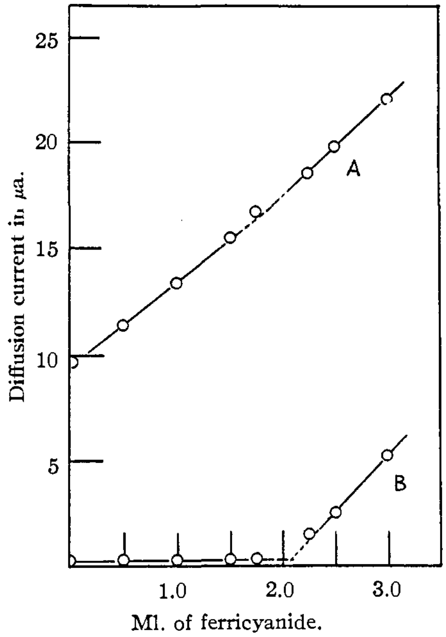

Fig. 2.—Amperometric titration of cobalt chloride with potassium ferricyanide in 1 *M* cyanide medium: (A) diffusion current at −1.7 v.; (B) diffusion current at −0.8 v.

Further experiments were performed in which 0.05 *M* cobaltous chloride solutions 1 *M* in potassium cyanide were heated in boiling water and samples taken in intervals for polarographic analysis. It was observed that the solutions first changed to an orange-yellow color while the polarographic wave decreased and became more drawn out. Amperometric titrations with ferricyanide showed that most of the cobalt had been oxidized after one hour. After three hours heating or standing overnight at room temperature, the solutions became almost colorless and yielded no polarographic wave. From this it was concluded that heating or standing in excess alkali cyanide ultimately converts the cobalt to the hexacyanocobalt(III)ate ion.

In order to establish the nature of the cobalt(II)cyanide complex first formed, experiments were performed in which cobalt chloride solutions were titrated with potassium cyanide, and *vice versa*. In agreement with previous investigators,[4] it was observed that good endpoints were obtained at a ratio of one cobalt to five cyanide ions regardless of whether the endpoint was located potentiometrically or by observation of the appearance or disappearance of the precipitate of cobalt cyanide. From this it would appear that the initial product obtained on dissolving cobalt(II) salts in excess potassium cyanide is the $[Co(H_2O)(CN)_5]^{\equiv}$ ion. Since direct oxidation should result in the $[Co(H_2O)(CN)_5]^{=}$ ion, which can be obtained unambiguously by another method, proof of the identity of the two products would establish the structure of the cobalt(II) complex. A solution of pure potassium aquopentacyanocobalt(III)ate was therefore prepared. It was obtained without difficulty by the method of Ray[7] and Ray and Dutt[8] from cobaltous chloride through thiosulfato pentammine cobalt(III) chloride, potassium thiosulfato pentacyano cobalt(III) ate and silver aquopentacyanocobalt(III)ate, and found to have the properties described by them. In 1.0 *M* potassium cyanide as a supporting electrolyte, it gave a single wave, identical in shape with that obtained after oxidation of divalent cobalt with ferricyanide in the same medium (Fig. 3). The observed half wave potential of −1.45 v. is in satisfactory agreement with that obtained from the other product.

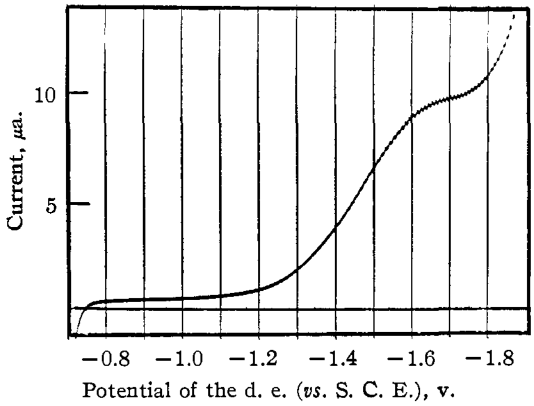

Fig. 3.—Polarogram of $[Co(H_2O)(CN)_5]^{=}$ ion in 1 *M* KCN.

An attempt was made to study the polarographic characteristics of the hexacyanocobalt(II)ate ion. Potassium hexacyanocobalt(II)ate was obtained as a finely crystalline violet precipitate by addition of a slight excess of potassium cyanide to a 0.1 *M* cobalt nitrate solution at −20°.[9] On transferring a sample of the solid to a 1 *M* potassium cyanide solution in the polarograph cell the solid immediately dissolved giving a clear pale yellow-green solution and the polarogram obtained was the same as that found on direct addition of cobalt nitrate to 1.0 *M* potassium cyanide.

The one-electron reduction of the cobalt(II) cyanide complex and the two-electron reduction of the cobalt (III) cyanide complex imply the existence of cobalt(I) as a cyanide complex formed at the surface of the dropping electrode. Grube and Schächterle[3a] in 1926 reported evidence for the formation of univalent cobalt by reduction of alkaline potassium hexacyanocobalt(III)ate solution at a cobalt cathode and with potassium amalgam. We observed a similar result when sodium amalgam was used as the reducing agent. The initially colorless solution slowly changed to red-orange with very little evolution of hydrogen. The same effect was observed when cobalt nitrate with five equivalents of cyanide added was used as the starting material. Samples of these reduced solutions were examined polarographically in 1.0 *M* potassium cyanide as a supporting electrolyte. In each case a small wave characteristic of the pentacyanocobalt(II)ate ion was observed. The height corresponded to only 5–10% of the total cobalt present. Addition of ferricyanide increased the height of the wave and gradually shifted it, ending with the characteristic wave of the pentacyanocobalt(III)ate ion. The cobalt(I) complex was not oxidizible anodically at the dropping electrode.

Discussion

The most striking characteristic of the cobalt cyanide complexes is the irreversibility of the oxidation and reduction steps involved. None of the complex ions studied were reversibly reduced at the dropping electrode, and none were oxidized at all. The potential of a quiet mercury electrode in the cobalt(II) solutions was the same as that of a mercury electrode in a cyanide solution of the same concentration but with cobalt absent. For the measurement of the potential of cobalt(II)–cobalt(III) couple in cyanide medium, the mer-

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(7) P. R. Ray, *J. Indian Chem. Soc.*, **4**, 64, 325 (1927).

(8) P. R. Ray and N. K. Dutt, *Z. anorg. allgem. Chem.*, **234**, 65 (1937).

(9) A. Descamps, *Ann. Chim. Phys.*, [5] **24**, 78 (1881).

cury electrode whether dropping or quiet is completely useless. The value commonly accepted[10] for the oxidation potential of that couple is due to Grube and Schächterle.[3a] From the potential of a platinized platinum electrode in a strongly alkaline solution of cobalt(III)hexacyanide partially reduced at a cobalt cathode, they calculated a result in terms of a hypothetical hexacyanocobalt(II)ate–hexacyanocobalt(III)ate electrode reaction. In addition to the error in formulation of the electrode reaction, a more serious difficulty exists. Both hydroxide ions and platinum are known to catalyze the water oxidation of the cobalt(II) cyanide complex. The potential which was measured differed from the potential of a hydrogen electrode in a solution of the same alkalinity by only a few millivolts: undoubtedly no more than experimental error. The potential which was reported (-0.81 v. on the hydrogen scale, European sign convention) must therefore be considered only as a lower limit on the reducing strength of the couple involved.

Summary

Polarographic investigation of the reduction of cobalt cyanide complexes has led to the following conclusions.

1. Addition of excess alkali cyanide to a solution of a cobalt(II) salt results in the immediate formation of the aquopentacyanocobalt(II)ate ion, reducible at the dropping electrode to a cobalt(I) complex.
2. Oxidation of the cobalt(II) complex yields aquopentacyanocobalt(III)ate, also reducible at the dropping electrode to a cobalt(I) complex.
3. Prolonged treatment of the aquopentacyano complexes with excess cyanide ultimately yields the hexacyanocobalt(III)ate ion, not reducible at the dropping electrode.
4. The cobalt(I) complex is neither reducible nor oxidizable at the dropping electrode.
5. The commonly accepted value for the potential of the cobalt(II)–cobalt(III) couple in cyanide medium cannot be considered valid.

CAMBRIDGE, MASSACHUSETTS
MINNEAPOLIS, MINNESOTA RECEIVED OCTOBER 28, 1948

[10] W. M. Latimer, "Oxidation Potentials," Prentice-Hall, New York, N. Y., 1938.

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

The Behavior of Oxygenated Organic Compounds in Acid Media[1]

BY MELVIN S. NEWMAN, RAYMOND A. CRAIG[2] AND ALFRED B. GARRETT

When oxygenated organic compounds are dissolved in strong protonic acids they generally accept a proton from the solvent to form a positively charged intermediate which may or may not undergo further change.[3] Evidence as to the fate of these conjugate acids has been obtained, among other sources, from the measurements of freezing point depression of solvent sulfuric acid[3,4] and from the nature of the reaction products isolated when the sulfuric acid solutions were poured into water or certain alcohols.[4] The further behavior of the species BH^+ forms the topic for the present discussion.

$$B + HA \longrightarrow BH^+ + A^- \qquad (1)$$

Alcohols[5]

In the case of solutions of alcohols in sulfuric acid three types of cryoscopic behavior have been noted.

$$ROH + H_2SO_4 \rightleftarrows ROH_2^+ + HSO_4^- \quad [i = 2]^{6} \qquad (2)$$

$$ROH + 2H_2SO_4 \rightleftarrows RHSO_4 + H_3O^+ + HSO_4^- \quad [i = 3] \qquad (3)$$

$$ROH + 2H_2SO_4 \rightleftarrows R^+ + H_3O^+ + 2HSO_4^- \quad [i = 4] \qquad (4)$$

For example, *i*-factors of 2 have reported for *t*-butyl and *t*-amyl alcohols[7]; *i*-factors of about 3 for several primary alcohols,[7] and an *i*-factor of 4 for triphenylcarbinol.[3,8] It appears reasonable to suppose that the first step in each of these cases involves a proton transfer to yield an oxonium compound, ROH_2^+. Two questions arose as to the further behavior of such oxonium compounds. (1) Why should an *i*-factor of only 2 be obtained with *t*-alcohols[7] when in reactions in acid media *t*-compounds often react most rapidly? (2) Are the conjugate acids of alcohols, ROH_2^+, thermally unstable at ordinary temperatures, or is some solvent effect operative?

In order to obtain information on the first topic, we have re-investigated the behavior of *t*-butyl alcohol in sulfuric acid and have also studied triethylcarbinol. When these alcohols are *carefully* (see Experimental Part for details) dissolved in sulfuric acid initial *i*-factors of slightly

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[1] The work herein reported is taken from the Ph.D. thesis of R. A. Craig, The Ohio State University, March, 1948.

[2] Standard Oil Company of Indiana Fellow, 1946–1947. Present address: Experimental Station, du Pont, Wilmington, Delaware.

[3] For background discussion see Hammett "Physical Organic Chemistry," McGraw-Hill Book Company, New York, N. Y., 1940, pp. 45–48, 53–56 and 277–285.

[4] (a) Newman, THIS JOURNAL, **63**, 2431 (1941); (b) Newman, Kuivila and Garrett, *ibid.*, **67**, 704 (1945); (c) Newman, *ibid.*, **64**, 2324 (1942).

[5] In this paper monofunctional compounds containing only carbon, hydrogen and oxygen and a few silicon organic compounds will be considered.

[6] The *i* refers to the van't Hoff *i* factor which means essentially the number of particles produced from one particle of solute.

[7] Oddo and Scandola, *Gazz. chim. ital.*, **39**, II, 1 (1909).

[8] Hammett and Deyrup, THIS JOURNAL, **55**, 1900 (1933).