(CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL CHEMISTRY OF THE AUSTRALIAN COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANIZATION]

Reduction of Water to Hydrogen by a Complex Cyanide of Cobalt

BY N. KELSO KING AND M. E. WINFIELD

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Mixtures of aqueous $CoCl_2$ and KCN which contain precipitated cobaltous dicyanide evolve H_2, and this reaction has been studied at 40° in dilute preparations, mostly at a cobalt concentration of 0.0133 *M*. Gas evolution is preceded by an induction period of about 15 minutes. The maximum rate of H_2 production is found at a mole ratio of cyanide to cobalt of about 4.1/1. Alkali metal ions increase the rate and Cs^+ is peculiarly effective. Methyl viologen in the ratio of 1 molecule per 40 atoms of cobalt has a strong promoter action, while at a ratio greater than 1/10 it is inhibitory. Addition of alkali up to about *p*H 9.7 increases the rate while further additions result in a sharp decrease. Pentacyanocobaltate(II) ion present in freshly prepared mixtures undergoes a series of decay reactions which may proceed for many hours. At least the first of these is a prerequisite to evolution of H_2 and it is accompanied by uptake of H^+. When Cs^+ is added to a precipitate-free solution, a yellow complex (possibly dinuclear) appears whose formation is accompanied or preceded by a substantial uptake of H^+.

Introduction

For about a century, mention has been made from time to time of the liberation of hydrogen gas which occurs when aqueous solutions of cobalt chloride and potassium cyanide are mixed. The reaction was regarded as extraordinary but of little practical value. With the recent interest in the deuterium exchange reaction catalyzed by cobalt cyanide solutions (Ogg,[1] Mills, Weller and Wheeler[2]), and the more general problems of hydrogenation in solution by metal complexes and hydrogenase (see reviews by Weller and Mills,[3] Halpern[4] or Winfield[5]), it has become important to study the mechanism of H_2 evolution.

In 1868 Descamps[6] wrote that H_2 was evolved by a solution in which the ratio of total moles of cyanide to cobalt (R) was about 6. The more recent results of Iguchi[7] showed H_2 evolution at R = 4 to 5 but not at 6 or more. Most authors believed that the over-all reaction could be expressed by

$$K_4[Co(CN)_6] + H_2O \longrightarrow K_3[Co(CN)_6] + KOH + {}^1/_2H_2$$

Ogg has proposed the mechanism[1]

$$[Co(CN)_6]^{4-} + H_3O^+ \longrightarrow [Co(CN)_6]^{3-} + H_2O + H$$
$$2H \longrightarrow H_2$$

In 1949 Hume and Kolthoff[8] showed that the compound believed to be $K_4[Co(CN)_6]$ had only five cyanide ligands, with possibly a water molecule in the sixth position, while in 1951 Adamson[9] suggested the formula $K_3[Co(CN)_5]$. More recent evidence from kinetic studies of H_2 uptake indicate the co-existence of small amounts of $[Co(CN)_6]^{4-}$ in solutions of the pentacyanocobaltate ion.[10] We now find that neither of these ions is directly responsible for H_2 evolution.

Experimental

Pressure Measurement.—The manometric technique and gas purification were essentially as described previously.[10,11] In some experiments the O_2-absorber in the center well of the Warburg respirometers was omitted, because of its tendency to absorb HCN. The procedure then was to shake vigorously the respirometers and contents for 20 minutes, while passing through them a stream of H_2, argon or N_2, before tipping the $CoCl_2$ into the KCN solution. Both methods led to the same rates of reaction.

To prevent loss of HCN during the flushing procedure, the gas first was passed through KCN solution of the same concentration and temperature as that in the respirometers. Air in the manometer capillary above the Brodie solution was removed by forcing the latter to the top of the capillary six times during the gassing period. Vessels were cleaned by boiling in sulfuric acid containing a little nitrate and rinsing twenty times with water. Where the reaction mixture contained acid, it was added with the $CoCl_2$ solution; where alkali, with the KCN solution.

A. R. grade chemicals were used with the exception that cesium chloride was purified by two recrystallizations from water–ethanol mixtures.

Anal. Calcd. for $CoCl_2 \cdot 6H_2O$: Co 24.77. Found: Co, 24.71. *Anal.* Calcd. for KCN: CN^-, 39.96. Found: CN^-, 39.76. *p*H of aqueous solution, theoretical.

***p*H Measurement.**—Solutions of each reactant were prepared with boiled water and were further freed from air by long gassing with O_2-free argon. The *p*H was determined by means of a glass electrode, together with a calomel electrode from which the leakage of KCl was so small that it did not influence the reaction rate of the cobalt complex.

Results

Rate of H_2 Evolution as a Function of R.—At 40° there is a maximum rate of gas evolution at *R* = 4.1 approximately (Fig. 1). It was necessary to obtain the points shown in the figure by averaging the results of a number of experiments since the H_2 evolution rates were not readily reproducible. The variability was not due to traces of foreign gases or foreign ions adsorbed on the walls of the Warburg vessels, nor to variations in pipetting, shaking rate, temperature or light intensity. Our experience is analogous to that of Rasmussen and Bjerrum with solutions of diaquobis-(ethylenediamine)-cobalt(III) ions.[12] They observed a variability in the aging of their solutions which they attributed to irregular rates of polymerization.

The rates of evolution which we have measured are maximum, attained only after an induction

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[1] R. A. Ogg, Jr., Abstracts 123rd Meeting of Amer. Chem. Soc., 1953, p. 24 P.

[2] G. A. Mills, S. W. Weller and A. Wheeler, private communication.

[3] S. W. Weller and G. A. Mills, "Advances in Catalysis," Vol. VIII, Academic Press, Inc., New York, N. Y., 1956, p. 163.

[4] J. Halpern, *Quart. Revs. Chem. Soc.*, **10**, 463 (1956).

[5] M. E. Winfield, *Revs. Pure Appl. Chem. (Australia)*, **5**, 217 (1955).

[6] M. A. Descamps, *Compt. rend.*, **67**, 330 (1868).

[7] M. Iguchi, *J. Chem. Soc. (Japan)*, **63**, 634 (1942).

[8] D. N. Hume and I. M. Kolthoff, THIS JOURNAL, **71**, 867 (1949).

[9] A. W. Adamson, *ibid.*, **73**, 5710 (1951).

[10] J. Bayston, N. K. King and M. E. Winfield, "Advances in Catalysis," Vol. IX, Academic Press, Inc., New York, N. Y., 1957, p. 312.

[11] N. K. King and M. E. Winfield, *Biochim. Biophys. Acta*, **18**, 431 (1955).

[12] S. E. Rasmussen and J. Bjerrum, *Acta Chem. Scand.*, **9**, 735 (1955).

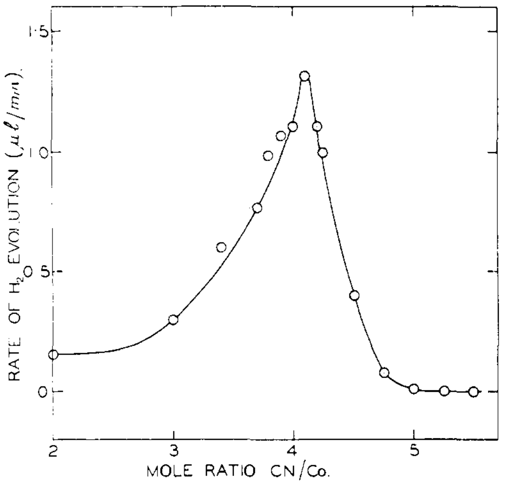

Fig. 1.—Dependence of the rate of H_2 evolution on the mole ratio of cyanide to cobalt. Rates are expressed in microliters per minute per 3.0 ml. of reaction mixture: cobalt molarity 0.0133; temperature 40°; N_2 atmosphere.

period lasting as much as 30 minutes (see for example Fig. 4).

Above $R = 5$ no precipitate is present and no H_2 evolution can be detected, except at temperatures approaching the boiling point of the solution. From this and the position of the peak in Fig. 1, it is clear that the hydrogen evolution which we have measured at 30 or 40°C. (as distinct from that at high temperature) depends upon the presence of a precipitate of cobaltous dicyanide.[9] The latter will be referred to as "catalyst" while recognizing that it may prove to be more correctly described as reactant.

Dependence on the Cobalt Concentration.—When R is held constant at 4.0 while the total concentration of cobalt [Co] is varied, the rate of H_2 evolution is a linear function of $[Co]^{4/3}$ (Fig. 2). This result is not interpreted readily, since the pH increases with concentration and the rate is sensitive to pH. The addition of KCl, noted in Fig. 2, serves to increase reproducibility without apparently altering the exponent $^4/_3$.

Dependence on pH.—It was expected that H_2 evolution would be favored by addition of acid and repressed by alkali because the source of the hydrogen atoms in the evolved gas must ultimately be the hydrogen ions of the solvent. Experiment shows that for small amounts of alkali the reverse is true (Fig. 3). Only after adding 0.12 mole of KOH per mole of cobalt do further additions of alkali decrease the rate of evolution. We may conclude that the rate is less dependent on hydrogen ion concentration than on the concentration of the cobalt complex which takes up H^+ and evolves H_2, and that the rate of formation of this complex is increased by K^+.

A satisfactory pH scale cannot be provided for Fig. 3. There is no regular relation between the pH immediately after mixing and the amount of acid or alkali added, as will be shown later (Fig. 8).

Alkali Metal Ions as Promoters.—Although we are unable to find a substance which will substitute for cobaltous dicyanide as catalyst, a number of "promoters" can be found which increase the rate of H_2 evolution in the presence of the catalyst. It will be recalled that KCl increases the rate of H_2 uptake by homogeneous cyanocobaltate(II) solutions.[7] King and Winfield[13] have shown that in both the homogeneous (R > 5) and in the heterogeneous ($R < 5$) regions of relative cyanide to cobalt concentrations the rate is increased by K^+ and the other alkali metal ions. We have now examined the effect on H_2 evolution and find that this too is stimulated but disproportionately more so by Cs^+ (Fig. 4).

A most striking result is that Cs^+ eliminates the induction period (Fig. 4). From measurements of

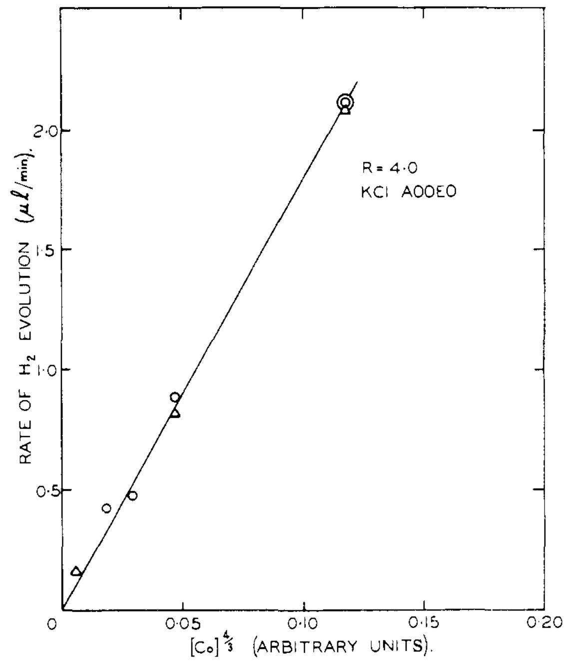

Fig. 2.—Dependence of the rate of H_2 evolution on the cobalt concentration, R being held constant at 4.0: cobalt molarity 0.0033 to 0.0133; KCl molarity 0.1; $R = 4.0$; temperature 40°; N_2 atmosphere.

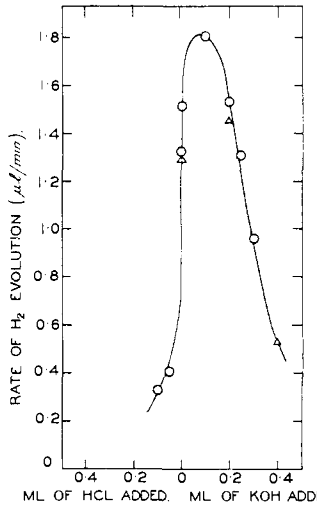

Fig. 3.—Dependence of rate of H_2 evolution on pH: cobalt molarity 0.0133; $R = 4.0$; temperature 40°; N_2 atmosphere. Both acid and alkali are 0.05 N.

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[13] N. K. King and M. E. Winfield, to be published.

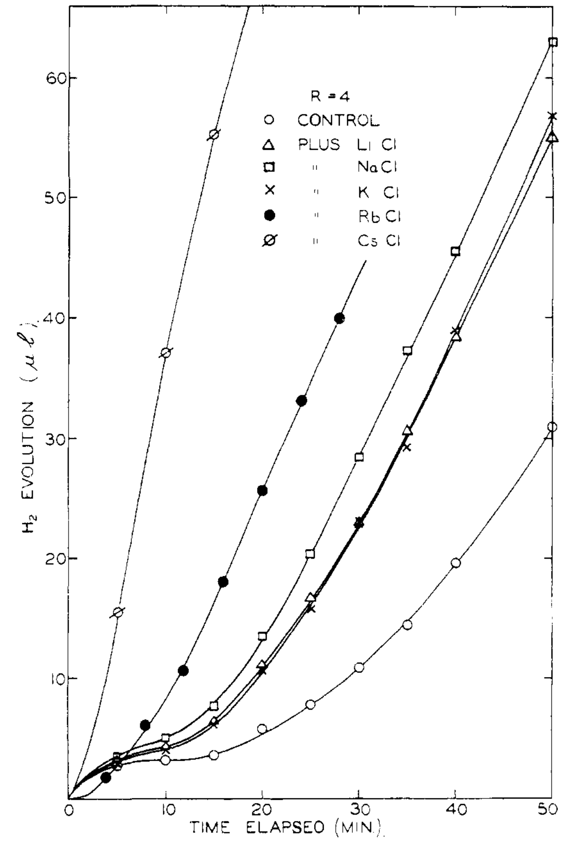

Fig. 4.—Stimulation of H_2 evolution by alkali metal ions: cobalt molarity 0.0133; salt molarity 0.03; R = 4.0; temperature 40°; N_2 atmosphere.

absorption spectra[13] and pH, as a function of time, it is clear that on adding Cs^+ most of the $[Co(CN)_5]^{3-}$ is converted to a new complex, apparently Co(III) or Co(IV), and that its formation involves uptake of hydrogen ion.

When the rate of H_2 evolution is plotted against the size of the promoter ion, its degrees of hydration or the electronegativity of the metal, it is seen that Cs^+ does not fall in the usual lyotropic series (Fig. 5).

Anion Effects.—Figure 6 shows that within the halogen series of anions the differences in promoter activity are relatively small, demonstrating that in an alkali metal chloride it is the cation, rather than the anion, which accelerates H_2 evolution.

Other Promoters.—We have tried a number of substances known to facilitate electron transfer or H-transfer. Of these the most effective was expected to be methyl viologen. It is a 1-electron acceptor whose oxidation-reduction potential is close to that of the hydrogen electrode. It nevertheless has an oxidizing action on cyanide complexes of Co^{II}, and it is only by working at unusually low dye concentrations that we can observe a stimulating rather than a poisoning of the H_2 evolution reaction (Fig. 7). At the optimum concentration of methyl viologen the rate is increased fivefold. The figure shows that in effectiveness other acceptors fall in a series related approximately to their oxidation-reduction potentials (methyl viologen

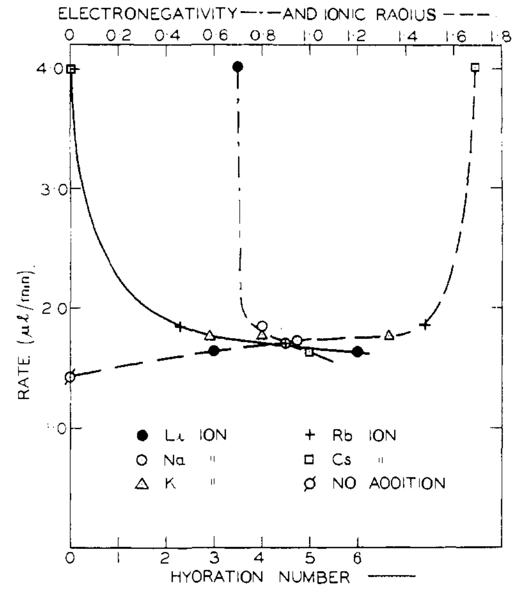

Fig. 5.—Stimulation of H_2 evolution as a function of the size of the promoting ion, its electronegativity and its degree of hydration: cobalt molarity 0.0133; LiCl, NaCl, KCl, RbCl or CsCl molarity 0.03; R = 4.0; temperature 40°; N_2 atmosphere.

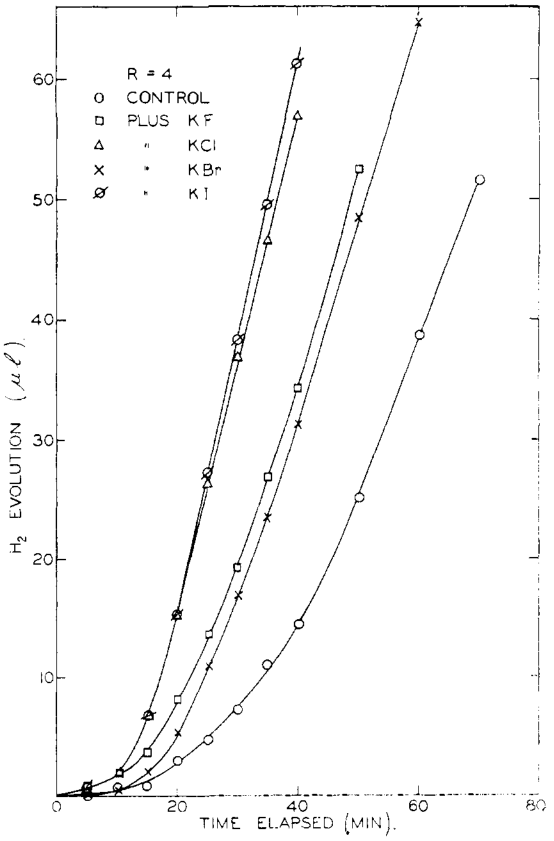

Fig. 6.—Effect of halogen anions on the rate of H_2 evolution: cobalt molarity 0.0133; potassium halide molarity 0.03; R = 4.0; temperature 40°; N_2 atmosphere. The times given refer to the time elapsed after mixing $CoCl_2$ with KCN and the halide.

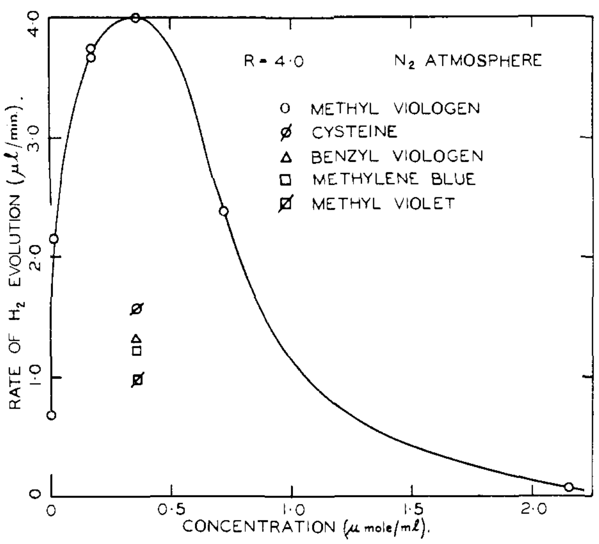

Fig. 7.—Stimulation of H_2 evolution by electron acceptors at very small concentrations, showing poisoning at higher concentrations: cobalt molarity 0.0133; electron acceptor concentration expressed in micromoles per ml. of reaction mixture; R = 4.0; temperature 40°; N_2 atmosphere.

-0.44 v., benzyl viologen -0.36, cysteine -0.34, methylene blue $+0.01$). It was shown also that promotion by cesium ion and by methyl viologen are not additive.

A weak stimulation was obtained with the following miscellaneous additives: isatin, cinnamate, gold, silver, copper and nickel. The use of metallic silver arose from the finding by Dwyer[14] that silver wire will reduce certain cobalt(III) complexes to the cobalt(II) state. We can find no evidence for such an effect with the cyanide complexes of cobalt.

When $R > 5$, H_2 is evolved if the solution is boiled[15] or if the concentration of reactants is very high. Both have been noted by a number of authors and we have observed what appear to be the same phenomena. It is not a simple matter to prove that a homogeneous evolution of H_2 can occur if the extra energy that is required is provided by heating, or by increasing the concentration of $[Co^{II}(CN)_5]^{3-}$ and thus making more negative the oxidation–reduction potential of the system. Precipitate of some description may well be present. According to Descamps[6] boiling leads to the formation of cobalt sesquioxide. $Co_2O_3 \cdot nH_2O$ is produced[16] on boiling a solution which contains $[Co^{III}(CN)_5 \cdot OH]^{3-}$ and the latter is a possible constituent of the preparations which evolve H_2.

Peters[15] makes the observation that instead of heating the solution it is sufficient to add platinized platinum, in order to bring about gas evolution. We have tested all of the promoters mentioned earlier in this section, and find that none can induce H_2 evolution from dilute solutions (0.0133 M) at 40° when R exceeds 5.

Change in *p*H with Time.—A freshly prepared mixture of aqueous $CoCl_2$ and KCN has a *p*H of between 9.5 and 10.5 at the concentrations usually employed in our experiments. Immediately after mixing the concentration of $[Co^{II}(CN)_5]^{3-}$ begins to fall, as a result of what we shall for convenience term decay reactions. They are accompanied by uptake of hydrogen ions in spite of the already high *p*H, indicating that the products of decay are very weak acids.

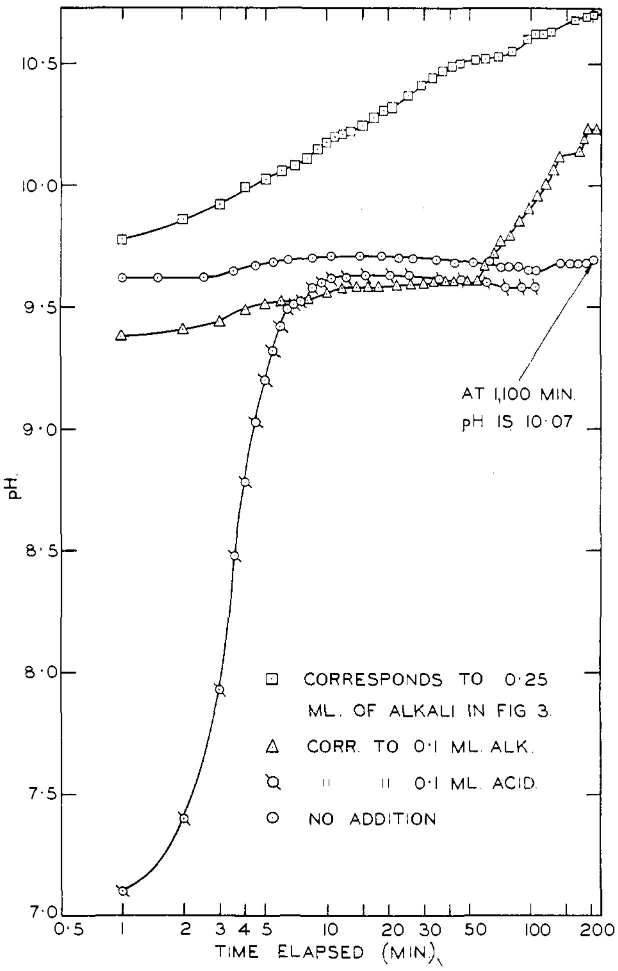

Fig. 8.—Change of *p*H of reaction mixture with time, with and without added acid or alkali: cobalt molarity 0.0133; R = 4.0; temperature 40°; argon atmosphere; 250 ml. of reaction mixture.

Figure 8 shows the *p*H changes which accompany the decay reactions and H_2 evolution under the conditions described for some of the evolution experiments of Fig. 3. We shall not attempt to interpret the curves except to point out that there are at least two stages of hydrogen ion uptake as well as an intermediate short-lived stage, not always detectable, in which the *p*H decreases. It is possible that the latter is due to incorporation of OH^- into a cobalt complex. At 25° little H_2 is evolved, and the *p*H is 0.4 or more units above the values shown in Fig. 8 for 40°. The region of *p*H decrease is more clearly defined.

Effect of Cesium Ion on Absorption Spectrum.[17]—Changes in absorption spectrum due to decay reac-

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(14) F. P. Dwyer, private communication.

(15) R. Peters, *Z. physik. Chem.*, **26**, 191 (1898).

(16) L. C. Smith, J. Kleinberg and E. Griswold, THIS JOURNAL, **75**, 449 (1953).

(17) We are indebted to Dr. J. B. Willis for measurements taken with a Beckman recording spectrophotometer.

tions were measured at 25° in the absence of precipitate ($R = 6$). Using the absorption band at 960 mμ as a measure[13] of the concentration of $[Co^{II}(CN)_5]^{3-}$, it will be seen from Fig. 9 that addition of Cs^+ causes a rapid loss of the pentacyanocobaltate(II) ion accompanied by formation of a complex which absorbs at 380–390 mμ.

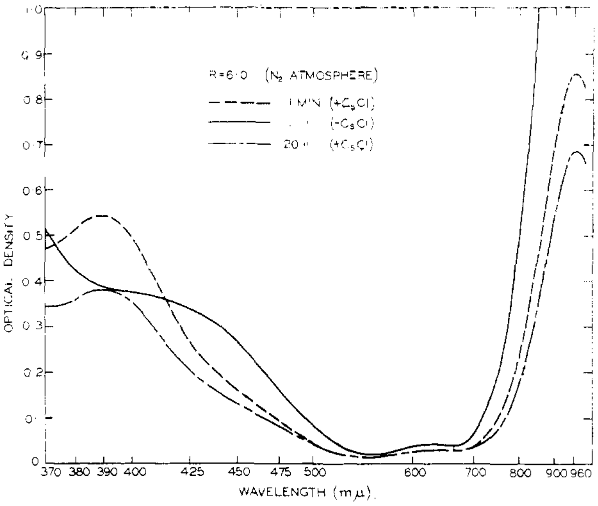

Fig. 9.—Change in absorption spectrum with time of a mixture of aqueous KCN and $CoCl_2$ showing the effect of added cesium ion: cobalt molarity 0.0066; cesium chloride molarity 0.1; $R = 6.0$; 25°; N_2 atmosphere.

*p*H measurements show that formation of the new complex is accompanied by uptake of hydrogen ion (Fig. 10). When KCN solution is added to the solution of $CoCl_2$ the *p*H rises, and in the presence of Cs^+ reaches a value of 11.17 during the time required for thorough mixing, compared with 10.45 without Cs^+. Later there are small *p*H increases which are not influenced by Cs^+ and these ultimately reach a total of 0.3 unit in both curves (final points not shown in figure).

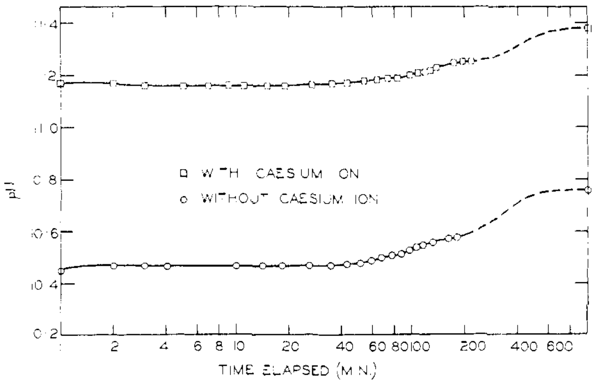

Fig. 10.—Change in *p*H of reaction mixture with time, with and without added cesium ions. Conditions as in Fig. 9.

It should be noted that immediately after mixing KCN and $CoCl_2$ solutions in the mole ratio 6/1 the solution contains, according to present views, nearly equimolar amounts of $K_3[Co(CN)_5]$ and KCN and only very small amounts of other cobalt species. If it were not for the presence of $K_3[Co(CN)_5]$ the KCN would impart to the solution a *p*H of 10.47 compared with 10.45 actually observed. The much higher *p*H obtained when Cs^+ is added suggests that Cs^+ promotes a reaction written provisionally as

$$2[Co^{II}(CN)_5]^{3-} + 2H^+ \longrightarrow [Co_2(CN)_{10}H_2]^{4-}$$

The structure of the product will be discussed elsewhere.[13]

At 40° $[Co^{II}(CN)_5]^{3-}$ is expected to decay much faster than is shown by the decline in height of the 960 mμ band in Fig. 9. The time required for disappearance of the pentacyanocobaltate(II) ion is thought to be the induction period of the H_2 evolution experiments, for example of Fig. 4.

Amount of H_2 Evolved.—At $R = 4.0$ the amount approaches 1 atom of hydrogen per 2 cobalt atoms (Fig. 11). Manchot and Herzog obtained 1 hydrogen atom per cobalt atom by boiling a solution which contained excess cyanide ion.[18] The two results are in accord if it is assumed that at R = 4 there is sufficient cyanide ion to permit only one half of the Co^{II} to be converted to Co^{III}, the final products being $Co^{II}(CN)_2$ and $[Co^{III}(CN)_6]^{3-}$.

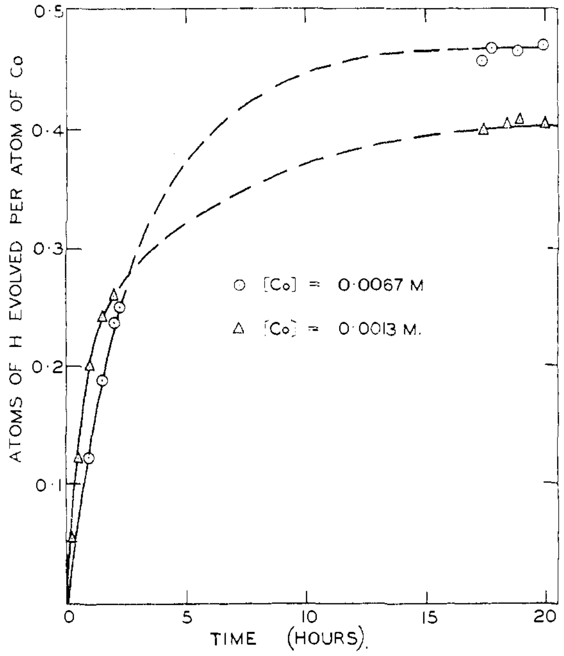

Fig. 11.—Amount of H_2 evolved at or near completion when $R = 4.0$: temperature 40°; N_2 atmosphere.

At $R = 6$

$$2[Co^{II}(CN)_5]^{3-} + 2HCN \longrightarrow 2[Co^{III}(CN)_6]^{3-} + H_2$$

At $R = 4$

$$/_3Co(CN)_2 + {}^4/_3[Co^{II}(CN)_5]^{3-} + H^+ \longrightarrow Co(CN)_2 + [Co^{III}(CN)_6]^{3-} + {}^1/_2H_2$$

Precipitate Color.—When suspensions containing solid dicyanide are prepared at 1° in a hydrogen atmosphere, and in a system thoroughly freed from O_2, the precipitate has a greyish pink or red color. After taking up considerable H_2 the suspension becomes green, and the lower the value of R the slower is the color change.

At 40° in hydrogen the colors are pinkish grey at $R = 3.5$; grey at $R = 3.6$ to 3.7; greenish grey at

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(18) W. Manchot and J. Herzog, *Ber.*, **33**, 1742 (1900).

R = 3.8 to 4.1. An hour later, after evolving appreciable H_2, they are only a little greener. When the gas atmosphere is nitrogen the color immediately after mixing the $CoCl_2$ and KCN solutions is orange. Following an induction period, H_2 evolution commences and is accompanied by a color change from orange to green. There is no direct correlation between the amount of H_2 evolved and the amount of green material formed.

In the presence of a little acid and an atmosphere of either H_2 or N_2 the initial precipitate is buff colored, while in the presence of alkali it is a deep green. Within a range of low alkali concentrations the amount of green material that is formed appears to be proportional to the amount of alkali added. KCl cannot substitute even in part for KOH. Alternate additions of acid and alkali destroy and reconstitute the green compound, and it can be reformed from the hydrosulfite complex by adding alkali. Thus it is fairly stable and probably has a definite composition rather than being an adsorption complex at the surface of particles of cobaltous dicyanide. Descamps[6] considered it to be $K_2Co[Co(CN)_6]$.

Discussion

According to the published literature there are only two or three compounds of cobalt present in significant amount immediately after mixing KCN solution with $CoCl_2$ in an inert atmosphere, namely, cobaltous dicyanide, pentacyanocobaltate(II) ion and possibly hexacyanocobaltate(II) ion. The composition and structure of none of these is known with certainty. In the early literature there are claims for two distinct cobaltous cyanides, one a dihydrate[19] and the other a trihydrate.[20] The probable nature of the pentacyanide ion is discussed by Adamson[9] and of the hexacyanide ion by King and Winfield.[13]

After a short period of aging the mixture contains several new ionic species. Disappearance of the pentacyanide is accompanied by the formation of a series of ions which are not readily isolated and identified, since they are continually undergoing chemical change. We have studied them chiefly by means of their absorption spectra.[13]

After prolonged aging there is presumably equilibrium and a smaller number of species. This final product we have attempted to investigate only when cyanide is present in excess. The solution then contains hexacyanocobaltate(III) ion together with a smaller amount of an orange complex which is characterized by absorption bands at 267 and 285 mμ.[13]

It is reasonably certain that the complex directly responsible for H_2 evolution is not a previously described compound of cobalt. We are working on the hypothesis that it is formed as follows: $[Co^{II}(CN)_5]^{3-}$ becomes attached by a double bridge to another cobalt complex at the surface of a particle of cobaltous dicyanide, the second partner being either $[Co^{II}(CN)_5]^{3-}$ or part of the solid itself. Each bridging cyanide group is reduced to an imine with uptake of H^+, the necessary electrons being derived from the cobalt atoms.

When the rate of H_2 evolution is measured at 1 atmosphere pressure of H_2, it is found to be one-tenth as fast as in an atmosphere of argon. This is not evidence for the reversibility of the H_2 evolution, but is due to an initial uptake of H_2 with a resulting decrease in concentration of $[Co^{II}(CN)_5]^{3-}$ which is the source of the H_2-evolving complex. Mills, Weller and Wheeler[2] have made the interesting observation that with a concentrated solution of pentacyanocobaltate ion in an atmosphere of H_2 the paramagnetism disappears and the pressure change ceases after several minutes at room temperature, but the solution then catalyzes the exchange reaction between D_2 and water. Here we apparently have as part of the exchange process an H_2 evolution reaction which is due to the reversal of H_2 uptake, and which therefore yields as product a reduced cobalt complex that can again take up D_2. In the H_2 evolution process in argon which we have described, there is no prior uptake of H_2 and the evolution is irreversible since the product is an oxidized complex.

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(19) N. V. Sidgwick, "The Chemical Elements and their Compounds," Vol. II, Oxford University Press, Oxford, 1951, p. 1380.

(20) "Gmelins Handbuch der anorganischen Chemie," Vol. 58, part 2, Verlag Chemie, Berlin, 1932, p. 364.

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Interaction of Rhodium(III) Solutions with 1,2,3-Benzotriazole[1]

BY RAY F. WILSON AND CHAVUS M. WOMACK, JR.

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Methods for the synthesis of several coördination type compounds formed in the interaction of rhodium with 1,2,3-benzotriazole are described.

As a result of a recently initiated study of the reactions between the platinum elements and 1,2,3-benzotriazole the preparations of several palladium compounds have been reported.[2,3] It was observed, also, that a solution of rhodium(III) chloride when reacting with 1,2,3-benzotriazole yielded a precipitate.[4]

The purpose of the present study was to examine the precipitate obtained from the rhodium(III) chloride–1,2,3-benzotriazole system and to prepare and investigate precipitates from analogous sys-

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(1) This work was supported by a grant from the National Science Foundation.

(2) R. F. Wilson and L. E. Wilson, THIS JOURNAL, **77**, 6204 (1955).

(3) R. F. Wilson, L. E. Wilson and L. J. Baye, *ibid.*, **78**, 2370 (1956).

(4) R. F. Wilson and L. E. Wilson, *Anal. Chem.*, **28**, 93 (1956).