CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE
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A Study of Some Cyano Complexes of Rhenium

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Potassium hexachlororhenate(IV) reacts with potassium cyanide in aqueous solution to give as chief product the new compound $K_4ReO_2(CN)_4$, obtained as a grayish-black solid by precipitation with ethanol. Solutions of this compound, alone or in the presence of added potassium cyanide, when treated with potassium borohydride yield the hitherto unreported compound, $K_3Re(OH)_3(CN)_3$, precipitated by ethanol as a dark blue solid. In the presence of chloride ion, however, borohydride reduction of $K_4ReO_2(CN)_4$–KCN mixtures gives $K_5Re(CN)_6$ as the chief product. The same result is obtained when K_2ReCl_6–KCN mixtures are treated with borohydride. In the absence of cyanide, K_2ReCl_6 reacts with borohydride to form hydrated rhenium(IV) oxide.

Introduction

Mixtures of potassium hexachlororhenate(IV) and potassium cyanide in aqueous solution have served as starting materials in the production of both potassium hexacyanorhenate(I),[1] through reduction by potassium amalgam, and potassium tetracyanodioxorhenate(V),[2] by oxidation with hydrogen peroxide. In connection with both of these preparations it was reported that when potassium hexachlororhenate(IV) and potassium cyanide were mixed in aqueous solution a marked color change rapidly ensued, from the light green color of the rhenium complex to deep black. In spite of this evidence for chemical reaction in the initial mixture, however, no attempt to isolate a product appears to have been described.

In the investigation to be described in this report a new compound, potassium tetracyanodioxorhenate(IV), has been isolated from mixtures of this kind. Furthermore, a comparative study has been made of the action of potassium borohydride on aqueous solutions of potassium hexachlororhenate(IV), with and without added potassium cyanide, and on aqueous potassium tetracyanodioxorhenate(IV), with and without added potassium chloride. This work has brought to light some interesting differences in the nature of the rhenium products obtained under these different circumstances. For example, both of the rhenium(IV) compounds investigated are reduced to rhenium(I) by borohydride if chloride and cyanide are present either through addition or as part of the original compound. On the other hand, in the absence of chloride potassium tetracyanodioxorhenate(IV) reacts with borohydride to give a rhenium(III) compound, potassium tricyanotrihydroxorhenate(III), which has not been described previously. In the absence of cyanide potassium hexachlororhenate(IV) simply undergoes hydrolysis when treated with borohydride, the principal product being hydrated rhenium(IV) oxide.

Experimental

Materials.—Potassium hexachlororhenate(IV) was prepared from C.P. spectroscopically analyzed potassium perrhenate, purchased from the University of Tennessee. At first the method of Hurd and Reinders[3] was employed; later, the method of Rulfs and Meyer,[4] using hypophosphorous acid as the reducing agent, was found to be more convenient. The potassium cyanide and potassium chloride used both were Baker's Analyzed Reagent grade. The potassium borohydride was purchased from Metal Hydrides, Inc., Beverly, Massachusetts. Deaerated water was used in preparing solutions of these salts. For the potassium analyses, sodium tetraphenylborate, *puriss.*, was used as purchased from the Aldrich Chemical Company. Solutions of this reagent were filtered prior to use.

Analytical Methods.—Rhenium was determined by precipitation as nitron perrhenate,[5] after oxidation of the rhenium to perrhenate with hydrogen peroxide in basic solution. The original sample to be analyzed was treated with approximately 25 ml. of water, 10 ml. of 30% hydrogen peroxide, and 6 ml. of 5 *N* sodium hydroxide. This mixture was heated below the boiling point until it became colorless, after which it was evaporated to about 10 ml., then diluted, and the evaporation and dilution repeated until the excess hydrogen peroxide had been destroyed. The sample finally was made up to 100 ml., and suitable aliquot parts were taken for analysis. Potassium was de-

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[1] D. Clauss and A. Lissner, *Z. anorg. u. allgem. Chem.*, **297**, 300 (1958).

[2] W. Klemm and G. Frischmuth, *ibid.*, **230**, 215 (1937).

[3] L. C. Hurd and V. A. Reinders, *Inorg. Syntheses*, **1**, 178 (1939).

[4] C. L. Rulfs and R. J. Meyer, *J. Am. Chem. Soc.*, **77**, 4505 (1955).

[5] W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, and J. I. Hoffman, "Applied Inorganic Analysis," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1953, p. 321.

termined by precipitation as potassium tetraphenylborate.[6] Cyanide analyses were done in the manner described in a previous paper.[7]

Determination of the oxidation state of rhenium was accomplished by ascertaining the rhenium content and the quantity of dichromate required to effect oxidation of the rhenium to perrhenate, following the technique of Geilmann and Wrigge.[8]

Apparatus and General Procedure.—The reaction vessels were of approximately 100 to 200 ml. capacity, made from 45 mm. or larger Pyrex tubing to the top of which was sealed the outer part of a standard taper ground glass joint of approximately the same diameter. Near the bottom of the vessel was sealed a fritted glass filter of medium porosity below which the tube was drawn down and sealed to a stopcock tube. The latter tube could be inserted through a stopper into a filter flask, thereby permitting the contents of the vessel to be filtered with suction. A three-necked head carrying a matching standard taper inner joint could be attached to the top of the reaction vessel and, by means of suitable ground glass joints, gas inlet and outlet tubes and a dropping funnel were inserted into the head. When the apparatus was assembled, the gas inlet tube extended nearly to the fritted disk in the lower part of the chamber. It thus was possible to add reagent solutions, to stir the reaction mixtures with a current of nitrogen, and to carry out filtration and washings while maintaining a nitrogen atmosphere in the reaction vessel at all times.

A number of the solid products were extracted with hot methanol in order to free them of excess potassium cyanide, potassium chloride, or potassium borohydride. These extractions were carried out in a conventional Soxhlet apparatus. After having been suitably washed or extracted, all of the solid products finally were washed with diethyl ether and dried in a vacuum desiccator over magnesium perchlorate before being taken for analysis.

Reaction of Potassium Hexachlororhenate(IV) with Potassium Cyanide.—To a solution of potassium hexachlororhenate(IV) (2 g. in 30 ml.), contained in the reaction vessel described above, was added a solution of potassium cyanide (12 g. in 25 ml.), whereupon a white solid appeared in the light green solution. Within a few minutes the solid disappeared and the color of the solution changed to a deep black. The mixture was agitated with a current of nitrogen for about 30 min., and then filtered into 100 ml. of ethanol. The grayish-black solid which appeared at this point was filtered out, washed with ethanol and ether, dried, and then extracted with methanol for from 1 to 5 days, until no test for cyanide was given by the fresh extract. The residue finally was dried and analyzed as outlined above. Mean values of concordant analyses obtained from different preparations are given below.

Anal. Calcd. for $K_4ReO_2(CN)_4$: K, 32.66; Re, 38.91; CN, 21.74. Found: K, 32.50; Re, 38.73; CN, 21.70; oxidation no. of Re, 4.12.

Portions of the product prepared in this manner were used in several of the experiments which are described below.

Potassium Hexachlororhenate(IV) with Potassium Cyanide and Potassium Borohydride.—A mixture of potassium hexachlororhenate(IV) and potassium cyanide, prepared as described in the preceding paragraph, was treated with a solution of potassium borohydride (2 g. in 25 ml.), and the mixture stirred with nitrogen for 12 hr. At the end of this period a dark olive-green solid was separated from the liquid which now had a cherry-red color. The solid was extracted with methanol for three days, dried, and analyzed. Qualitative tests[9] showed the absence of chloride.

Anal. Calcd. for $K_5Re(CN)_6$: K, 36.34; Re, 34.64; CN, 29.02. Found: (two different preparations) K, 40.50, 39.90; Re, 33.18, 33.07; CN, 24.90, 25.24; oxidation no. of Re, 0.97, 1.01.

The cherry-red filtrate was run into 150 ml. of ethanol from which at the end of from 1 to 3 days a small amount of a feathery red solid was deposited. This solid dissolved in water to give a red solution which when treated with a current of oxygen, or violently shaken in air, turned green. The presence of a little borohydride would, however, cause the color to revert to red. Addition of ethanol to the green solution resulted in the formation of a small amount of green solid. The quantities of both the red and the green solid were so small that complete analyses could not be obtained. Oxidation number determinations were made, however, with these results: red solid, 4.05, 4.10; green solid, 4.90, 4.95.

Potassium Hexachlororhenate(IV) with Potassium Borohydride.—Solutions of potassium hexachlororhenate(IV) and potassium borohydride were mixed in approximately the same amounts and concentrations as were used in the preceding experiment, but no potassium cyanide was added. A finely divided brown solid appeared, and was separated, washed successively with water, ethanol, and ether, then dried and analyzed. The product gave no test for potassium or chloride.

Anal. Found: Re, 62.60; oxidation no. of Re, 4.05.

Reaction of Potassium Tetracyanodioxorhenate(IV) with Potassium Borohydride.—Potassium tetracyanodioxorhenate(IV), prepared as described in an earlier section, was dissolved in water (1 g. in 20 ml.) and treated with aqueous potassium borohydride (2 g. in 20 ml.). There was no immediate visible change, but at the end of 17 hr. the mixture had assumed an intense opaque blue color. Stirring by means of a current of nitrogen was continued for an additional 24 hr., the solution by that time having been evaporated to about 20 ml. When this solution was filtered into 150 ml. of ethanol a precipitate appeared which, after separation, extraction with methanol for two days, and drying, was obtained as a dark blue crystalline power.

Another run was carried out in the same way, except that potassium cyanide (6.5 g.) was added to the mixture at the start. The solid product presented the same appearance as that from the previous experiment. Analyses of the products obtained in both runs are given below, the first percentage in each case applying to the product obtained in the absence of added potassium cyanide.

Anal. Calcd. for $K_3Re(OH)_3(CN)_3$: K, 27.11; Re,

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(6) K. Sporek and A. F. Williams, *Analyst*, **80**, 347 (1955).

(7) L. C. Smith, J. Kleinberg, and E. Griswold, *J. Am. Chem. Soc.*, **75**, 449 (1953).

(8) W. Geilmann and Fr. W. Wrigge, *Z. anorg. u. allgem. Chem.*, **222**, 56 (1935).

(9) W. W. Scott, "Standard Methods of Chemical Analysis," 5th Ed., D. Van Nostrand Company, Inc., New York, N. Y., 1939, p. 261.

43.06; CN, 18.04. Found: K, 27.25, 27.16; Re, 42.88, 43.07; CN, 17.93, 17.83; oxidation no. of Re, 3.13, 3.05.

Potassium Tetracyanodioxorhenate(IV) with Potassium Cyanide, Potassium Chloride, and Potassium Borohydride.—Solutions of potassium tetracyanodioxorhenate(IV) (1.5 g. in 15 ml.), potassium cyanide (8 g. in 15 ml.), potassium chloride (0.5 g. in 10 ml.), and potassium borohydride (2 g. in 20 ml.) were mixed together in the reaction vessel and stirred with nitrogen for 48 hr. Filtration of the mixture yielded a bluish-green solid and a reddish-brown filtrate, from which an additional quantity of solid was deposited slowly. The solid was washed with methanol until the washings gave no precipitate with silver nitrate, then dried and analyzed.

Anal. Calcd. for $K_5Re(CN)_6$: K, 36.34; Re, 34.64; CN, 29.02. Found: K, 37.34; Re, 34.56; CN, 28.33; oxidation no. of Re, 1.10.

Discussion of Results

The results presented above show unequivocally that when aqueous potassium hexachlororhenate(IV) is treated with potassium cyanide the principal product is potassium tetracyanodioxorhenate(IV), $K_4ReO_2(CN)_4$. This substance was obtained in yields ranging from 65 to 80%, based on K_2ReCl_6, part of the loss perhaps arising from some dissolution of the compound during prolonged methanol extraction.

The nature of the product obtained in this work is strikingly different from the octacyanorhenate(V) compound, $K_3Re(CN)_8$, which has been reported[10] to result from the reaction between potassium hexaiodorhenate(IV) and potassium cyanide in methanol solution. In pointing out the contrast in these results, it must, of course, be emphasized that the work of Colton, Peacock, and Wilkinson was carried out in methanol, presumably in the presence of air. Surprisingly, however, these investigators report that potassium octacyanorhenate(V) is sufficiently stable toward hydrolysis that it can be recrystallized from water, or even evaporated repeatedly with water in order to hydrolyze the excess potassium cyanide to potassium hydroxide, which then is extracted by methanol.

The difficulty commonly experienced in preparing fully cyanated complex compounds of rhenium from aqueous solutions is illustrated not only by the present work with rhenium(IV) in which, even with a large excess of potassium cyanide, the chief product is an oxocyano compound, but it also has been repeatedly exemplified in the work of other investigators on cyano complexes of rhenium(V). Allusion already has been made to the production of potassium tetracyanodioxorhenate(V), $K_3ReO_2(CN)_4$, by oxidation of K_2ReCl_6 with hydrogen peroxide in the presence of potassium cyanide.[2] The same compound has been produced from rhenium(IV) oxide in a similar manner.[11] It also is formed when potassium perrhenate is reduced with hydrazine in the presence of potassium cyanide,[12] and when potassium oxopentachlororhenate(V), K_2ReOCl_5, is warmed with potassium cyanide in alkaline solution.[13] Thus, in aqueous solution at least, it appears that partially hydrolyzed cyano complexes of rhenium(IV) and rhenium(V) are the normal products, rather than the fully cyanated complex compounds.

A further illustration of the ready formation of partially hydrolyzed cyano complexes of rhenium is provided by the behavior of $K_4ReO_2(CN)_4$ when treated with potassium borohydride. The chief product, obtained in approximately 70% yield, is potassium tricyanotrihydroxorhenate(III), $K_3Re(OH)_3(CN)_3$. Even when conducted in the presence of a large excess of potassium cyanide, the course of the reaction is the same.

It is of especial interest to note that, in contrast to the behavior just described, mixtures of $K_4ReO_2(CN)_4$ and potassium cyanide *in the presence of chloride* react with borohydride to give rhenium(I) rather than rhenium(III). The same result is obtained by the action of borohydride on mixtures of potassium cyanide with K_2ReCl_6, where, of course, chloride already is present. The principal product is undoubtedly $K_5Re(CN)_6$, although the analytical results suggest that even here there may be a small proportion of some partially hydrolyzed cyano complex of rhenium(I) mixed with the fully cyanated compound. The chloride ion appears here to be acting in some manner to facilitate the reduction of rhenium to the +1 state. That it can act as an electron-transfer agent in promoting certain oxidation–reduction reactions has been demonstrated.[14]

The fact that potassium borohydride reacts with K_2ReCl_6 alone in aqueous solution to yield hydrated rhenium(IV) oxide is further evidence

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[10] R. Colton, R. D. Peacock, and G. Wilkinson, *J. Chem. Soc.*, 1374 (1960).

[11] G. T. Morgan and G. R. Davies, *ibid.*, 1858 (1938).

[12] G. T. Morgan, *ibid.*, 554 (1935).

[13] B. Jezowska-Trzebiatowska and J. Danowska, *Z. physik. Chem.* (Leipzig), **212**, 29 (1959).

[14] See, for example, H. Taube and E. L. King, *J. Am. Chem. Soc.*, **76**, 4053 (1954); H. Taube and H. Myers, *ibid.*, **76**, 2103 (1954).

for the ready hydrolysis of hexachlororhenate(IV) ion in alkaline medium. It also may reflect an inability of chloride ion to stabilize oxidation states lower than four sufficiently well to permit their formation in these circumstances.

It may be mentioned that the two compounds $K_4ReO_2(CN)_4$ and $K_3Re(OH)_3(CN)_3$ have not been reported previously. Some evidence for the existence of a red rhenium(IV) compound and a green rhenium(V) compound also has been given above, but characterization of these materials must await further work.

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The Mechanism of Racemization of the Hexadentate Complex of Cobalt(III) with Ethylenediaminetetraacetic Acid

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The rate of racemization of the optically active hexadentate complex of cobalt(III) with ethylenediaminetetraacetic acid, *d*-[Co(EDTA)]$^-$, has been determined as a function of *p*H and temperature. Racemization proceeds very slowly in acidic media by a *p*H-independent path, for which $\Delta E_a = 40.6$ kcal./mole and $\Delta S^* = 20.6$ cal./deg. mole. The reaction is explained in terms of a unique intramolecular inversion process. A strong base catalysis of racemization also has been observed, providing a second order path for which $\Delta E_a = 32.7$ kcal./mole and $\Delta S^* = 54.7$ cal./deg. mole. In view of the structure of the cobalt complex and the details of its reaction in basic media, the possibility exists that the mechanism involves nucleophilic attack by an OH^- ion with simultaneous increase of the coördination number of the central atom to seven and the formation of a symmetrical intermediate.

Introduction

Dwyer, Gyarfas, and Mellor[1] reported that the optically active forms of [Co(EDTA)]$^-$ are stable in aqueous solutions at 30° for two weeks, and that racemization occurs at 100° with an approximate half-life of 170 minutes. They suggested that the mode of racemization might depend on the breaking of at least one Co–O bond and that racemization could occur at elevated temperatures through a five-coördinate intermediate in which a certain group in the partially dissociated ligand is temporarily replaced by a solvent molecule. Detailed study of the stereochemical model reveals that the multiply connected nature of the ligand requires that any racemization proceeding through a dissociative mechanism must be accompanied by extensive rearrangement or by reduction of the penta- or hexadentate linkage to tetradentate. Also, earlier studies on the conversion of pentadentate cobalt–EDTA complexes reveal that dissociative mechanisms lead to substitution with complete retention of enantiomeric configuration.[1-3] Since the attainment of a tetradentate structure must proceed stepwise, the process should be aided by increased hydrogen ion concentrations. This follows from the equilibrium given in equation 1 and the fact that the conversion of [Co(H–EDTA)H_2O] into the hexadentate complex (equation 2) is slower than the corresponding reaction for [Co(EDTA)H_2O]$^-$ (equation 3).[2,4]

$$[\mathrm{Co(H\text{-}EDTA)H_2O}] \rightleftharpoons \mathrm{H^+} + [\mathrm{Co(EDTA)H_2O}]^- \quad (1)$$

$$[\mathrm{Co(H\text{-}EDTA)H_2O}] \longrightarrow [\mathrm{Co(EDTA)}]^- + \mathrm{H_2O} + \mathrm{H^+} \quad (2)$$

$$[\mathrm{Co(EDTA)H_2O}]^- \longrightarrow [\mathrm{Co(EDTA)}]^- + \mathrm{H_2O} \quad (3)$$

Base acceleration of the substitution reactions of cobalt(III) ammines has been explained on the

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[1] F. P. Dwyer, E. C. Gyarfas, and D. P. Mellor, *J. Phys. Chem.*, **59**, 296 (1955).

(2) I. A. W. Shimi and W. C. E. Higginson, *J. Chem. Soc.*, 260 (1958).

(3) M. L. Morris and D. H. Busch, *J. Phys. Chem.*, **63**, 340 (1959).

(4) R. Dyke and W. C. E. Higginson, *J. Chem. Soc.*, 1998 (1960).