[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF MICHIGAN AND IOWA STATE COLLEGE]

Preparation and Properties of Tetraalkylammonium Hexacyanocobaltates(III) and Hexacyanoferrates(III)

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Normal salts and acid salts of the tetraalkylammonium hexacyanocobaltates(III) and hexacyanoferrates(III) have been prepared from the corresponding hexacyanocobaltic(III) and hexacyanoferric(III) acids by the neutralization with tetraalkylammonium hydroxides. The normal salts of tetraalkylammonium hexacyanocobaltates(III) have been found to be useful as supporting electrolytes in polarography giving no interference in the range of +0.30 to −2.30 v. *vs.* S.C.E.

The preparation of the tetraalkylammonium salts of hexacyanocobaltic acid described in this paper was prompted by the possibility that they might be of interest as supporting electrolytes in polarography. Tetraalkylammonium halides as supporting electrolytes permit polarography into the far negative region (45° tangent potentials of −2.2 v. or more negative) but at the positive end limit polarography to about zero toward the saturated calomel electrode owing to the anodic formation of insoluble mercurous halides ("mercury free wave"). The hexacyanocobaltate(III) ion does not form insoluble or non-dissociated compounds with the mercurous ion and permits polarography as far positive +0.3 or 0.4 v. toward S.C.E., just as do the sulfates, nitrates and perchlorates of the alkali metals. In solutions of the alkali metals salts of sulfate, nitrate or perchlorate a terminal reduction wave is found around −1.5 v. Inasmuch as the hexacyanocobaltate(III) ion is not reduced at all at the dropping mercury electrode, it seemed possible that tetraalkylammonium hexacyanocobaltate(III) salts might provide a useful supporting electrolyte over the entire range from +0.3 to −2.2 v. toward the S.C.E.

The salts were prepared by the neutralization of hexacyanocobaltic acid ($H_3Co(CN)_6$) with the tetraalkylammonium hydroxide. When the base was added to the acid precipitation occurred, but on the addition of the acid to the base no precipitate formed. This led to the isolation of tetraalkylammonium acid salts of hexacyanocobaltic acid and similarly of hexacyanoferric acid. The preparation of these salts and their properties are now reported.

Experimental Work

Hexacyanocobaltic(III) Acid and Hexacyanoferric(III) Acid.—Hexacyanocobaltic(III) and hexacyanoferric(III) acids were prepared by passing a solution of potassium salts of these acids through a cation exchange column in the hydrogen form as described previously.[1,2] The decomposition of these acids in water was prevented to a great extent by using dim light and saturating them with the hydrogen cyanide gas. However, even under these conditions it was necessary to use the aqueous solutions within a short time after the preparation. Even in the dark, hexacyanoferric acid undergoes slow decomposition on standing.

Tetraalkylammonium Hydroxides.—Tetraalkylammonium hydroxides were prepared from their halide salts either by passage through an anion-exchange column in the hydroxyl form or by reaction with silver hydroxide. The latter method was preferred since it gave more concentrated hydroxide solutions than in the ion-exchange process.

Normal Salts.—Tetrabutylammonium, tetrapropylammonium, tetraethylammonium, tetramethylammonium hexacyanocobaltates(III) and hexacyanoferrates(III) were prepared by the neutralization of the corresponding hydroxides with these acids to *p*H of 7.0. The solution was evaporated under vacuum in a dim light. The residue was then dissolved in ethanol or in ethanol-water mixture and recrystallized. The tetrabutylammonium and tetrapropylammonium hexacyanocobaltates(III) and hexacyanoferrates(III) dissolved in absolute alcohol and ether mixture on cooling in Dry Ice–acetone bath. Ether was added to the cool solution until cloudiness appeared and then the solution was allowed to warm up to room temperature. Crystals were formed on the walls of the container. The crystals were filtered off and were rinsed with ether–alcohol mixture. The same procedure was followed for the crystallization of tetrabutylammonium, tetrapropylammonium, and tetraethylammonium hexacyanoferrates(III). The tetraethylammonium, tetramethylammonium hexacyanocobaltates(III) and tetramethylammonium hexacyanoferrate (III) were recrystallized from ethanol and water mixtures. The tetraalkylammonium salt was dissolved on warming, then the solution was cooled in an ice-bath until the precipitate formed. The crystals were filtered off and rinsed with cold ethanol. These crystals contained water of crystallization which could be removed on vacuum drying at 80° yielding anhydrous tetraethylammonium and tetramethylammonium hexacyanocobaltates(III). However, tetramethylammonium hexacyanoferrate(III) not only lost the water of crystallization but also underwent partial decomposition. At the temperatures above 165° even tetraalkylammonium hexacyanocobaltates decomposed yielding an intensely blue residue, cyanogen and the other decomposition products.

Acid Salts.—Tetrabutylammonium, tetrapropylammonium, tetraethylammonium and tetramethylammonium acid salts of hexacyanocobaltates(III) and hexacyanoferrates (III) were prepared by the neutralization of hexacyanocobaltic or hexacyanoferric acids with corresponding tetraalkylammonium hydroxides to an approximate *p*H of 2.2. The solution was chilled in an ice-bath and the formed crystals were filtered off, rinsed with acetone and air dried. The acid salts of tetrabutylammonium, tetrapropylammonium hexacyanocobaltates(III) and hexacyanoferrates (III) were formed immediately. Thus, better crystals could be obtained from more dilute solutions. The acid salts of tetraethylammonium, tetramethylammonium hexacyanocobaltates(III) and hexacyanoferrates(III) required more concentrated solutions and the crystals formed on cooling. On drying *in vacuo* at 80° the acid salts of hexacyanocobaltates(III) lost water of crystallization without decomposition. The acid salts of hexacyanoferrates(III) underwent reductive decomposition.

Analytical Methods.—The empirical formulas for the tetraalkylammonium hexacyanocobaltates(III) are deduced on the basis of the colorimetric determination of cobalt after washing with perchloric acid,[3] on the argentometric titration of hexacyanocobaltate(III)[4] and the micro determination of hydrogen and nitrogen. The acid salts of tetraalkylammonium hexacyanocobaltates(III) were analyzed in addition for neutral equivalent and water of crystallization present.

The empirical formulas of the tetraalkylammonium hexacyanoferrates(III) are based on the iodimetric determination of hexacyanoferrate(III) and the micro determination of hydrogen and nitrogen. The acid salts of tetraalkylammonium hexacyanoferrates(III) were analyzed in

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(1) Fr. Hein and H. Lilie, *Z. anorg. allgem. Chem.*, **45**, 270 (1952).

(2) B. Jaselskis and H. Diehl, *Anal. Chim. Acta*, **16**, 274 (1957).

(3) W. M. Wise and W. W. Brandt, *Anal. Chem.*, **26**, 693 (1954).

(4) R. Uzel and B. Jezel, *Coll. Czech. Chem. Comm.*, **7**, 497 (1935).

addition for neutral equivalent by potentiometric titration with the standard base. All of the hexacyanoferrates(III) on drying underwent reductive decomposition, yielding a mixture of ferrous ions, cyanogen, ferricyanide and other by-products.

Results

The results of the analyses of the various hexacyanocobaltates(III) are given in Table I, those on the hexacyanoferrates(III) in Table II.

Table I

Summary of Analysis of Tetraalkylammonium Hexacyanocobaltates(III)

Empirical formula	Mol. wt. Calcd.	Neut. equiv.	Co, % Found	Co, % Theor.	H_2O,[b] %
$(Bu_4N)_3Co(CN)_6$	941	..	6.22	6.26	..
$(Pr_4N)_3Co(CN)_6$	773	..	7.57	7.62	..
$(Et_4N)_3Co(CN)_6$[a]	635	..	9.23	9.28	..
$(Me_4N)_3Co(CN)_6$[a]	437	..	13.41	13.49	..
$(Bu_4N)H_2Co(CN)_6 \cdot 2H_2O$	495	248	11.82	11.91	7.25
$(Pr_4N)H_2Co(CN)_6 \cdot 2H_2O$	439	221	13.38	13.42	8.19
$(Et_4N)_2HCo(CN)_6 \cdot 2H_2O$	542	543	10.81	10.87	6.60
$(Me_4N)_2HCo(CN)_6 \cdot 2H_2O$	400	399	14.70	14.73	8.96

[a] Analyses are based on samples dried at 80° *in vacuo*. All other samples were analyzed on the air-dried basis. [b] Losing weight on heating at 80° *in vacuo*.

The results are in good agreement with the calculated molecular weights based on the empirical formulas proposed in the first column of these tables.

The analyses of the thermal decomposition products of hexacyanocobaltates(III) in a qualitative sense indicated the presence of $Co(CN)_3$, and those of hexacyanoferrates(III) suggested the presence of $Fe_3Fe(CN)_6$.

Table II

Summary of Analysis of Tetraalkylammonium Hexacyanoferrates(III)

Empirical formula	Mol. wt. calcd.	Neut. equiv.	Oxidation equiv.
$(Bu_4N)_3Fe(CN)_6$	938	..	943
$(Pr_4N)_3Fe(CN)_6$	770	..	774
$(Et_4N)_3Fe(CN)_6$	632	..	634
$(Me_4N)_3Fe(CN)_6 \cdot 2H_2O$[a]	470	..	472
$(Bu_4N)H_2Fe(CN)_6 \cdot 2H_2O$[a]	493	245	491
$(Pr_4N)HFe(CN)_6 \cdot 2H_2O$[a]	436	217	435
$(Et_4N)_2HFe(CN)_6 \cdot 2H_2O$[a]	539	539	541
$(Me_4N)_2HFe(CN)_6 \cdot 2H_2O$[a]	397	398	395

[a] Tetramethylammonium hexacyanoferrate(III) and all acid salts were analyzed on the air-dried basis.

Tetraalkylammonium hexacyanocobaltates(III) have no major advantages as supporting electrolytes in aqueous solution polarography over the tetraalkylammonium halides or potassium hexacyanocobaltate(III). Freshly prepared hexacyanocobaltate(III) supporting electrolytes permit polarography as far as +0.35 v. and up to −2.3 v. (45° tangent potential) toward S.C.E. Inasmuch as the hexacyanocobaltate(III) ion hydrolyses in aqueous solution yields aquopentacyanocobaltate(III) and hydrogen cyanide, the solutions cannot be stored for any length of time. However, the tetraalkylammonium hexacyanocobaltates(III) can be used as supporting electrolytes in organic solvents because of their solubility and their greater stability rather than in aqueous solutions. In addition, it is felt that uses for the acid salts of tetraalkylammonium hexacyanocobaltates(III) and hexacyanoferrates(III) may be found in neutralization and oxidation–reduction reactions in nonaqueous solutions.

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The Mechanism of Chemisorption: Nitrogen on Nickel

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The adsorption of nitrogen on nickel–silica catalyst samples at moderately low temperatures in the neighborhood of −78° produces a small reversible loss of magnetization as measured by the low frequency a.c. permeameter method. This effect is also observed with argon and with krypton. It is shown that the effects described cannot be due to molecular chemisorption and that they may be due to polarization of physically adsorbed molecules or to the dimensional changes caused by the adsorbed gases, or to both.

Introduction

It often has been stated that nitrogen is chemisorbed on nickel at low temperatures.[1–6]

The work of Schuit and DeBoer is of special significance to the present investigation because the nickel–silica catalyst samples used were prepared, in some cases, by quite similar methods. Their conclusion that nitrogen is chemisorbed appears to be based primarily on the fact that the quantity of nitrogen adsorbed at −78° depends on the amount of nickel present and not on the total surface as determined by nitrogen adsorption at −196°. This work carries the implication that there is no chemisorption of nitrogen on nickel at −196°.

Some further evidence is given by Suhrmann and Schulz[7] who found that nitrogen is adsorbed, in part irreversibly, on nickel films at −183° and that this causes an increase of electrical resistance of about 0.6%. It is, however, to be noted that

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(3) O. Beeck, W. A. Cole and A. Wheeler, *Disc. Faraday Soc.*, **8**, 314 (1950).

(4) O. Beeck, "Advances in Catalysis," Vol. II, Edited by W. Frankenburg, Academic Press, New York, N. Y., 1950, p. 151.

(5) B. M. W. Trapnell, *Proc. Roy. Soc.* (*London*), **A218**, 566 (1953).

(6) G. C. A. Schuit and N. H. DeBoer, *J. chim. phys.*, **51**, 482 (1954).

(7) R. Suhrmann and K. Schulz, *Z. Naturforsch.*, **10a**, 517 (1955).