The Preparation and Some Properties of the Cobalticinium Salts

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In view of the unusual stability of "ferrocene," bis-cyclopentadienyliron, $(C_5H_5)_2Fe$,[1] it would seem that the sandwich structure suggested[2] for the compound is a very stable one, and that other transitional metals with suitable electronic structures might well adopt a similar configuration to form either neutral compounds analogous to ferrocene, or metal hydrocarbon ions, depending on the oxidation state of the metal in the complex.

The methods of formation of ferrocene and of ruthenocene, the value for the oxidation potentials of these compounds to the unipositive ions, and the magnetic susceptibilities of ferrocene and the ferricinium salts, suggest that the metals in the neutral compounds are in the +2 oxidation state while in the ions, they are in the +3 oxidation state. The reaction of cyclopentadienylmagnesium bromide with a +3 cobalt or rhodium compound might therefore be expected to lead to a unipositive cobalt hydrocarbon ion isoelectronic with ferrocene. Salts of the ion $[(C_5H_5)_2Co]^+$ have now been prepared; they are designated cobalticinium salts by analogy with the ferricinium and ruthenicinium salts, although they might more properly be called salts of bis-cyclopentadienylcobalt(III).

Experimental

The metal acetylacetonate was used in the preparation of ruthenocene[3] and this technique is again used. Cobaltic acetylacetonate was prepared by treating the black hydrated oxide resulting from alkaline bromine oxidation of cobaltous chloride with acetylacetone; after standing for two days the mixture was centrifuged and the product crystallized from benzene. The addition of the dark green acetylacetonate in benzene to cold cyclopentadienylmagnesium bromide in benzene, produces instantaneously a bright yellow precipitate; an excess of the Grignard reagent, sufficient to react with all the carbonyl groups present in the acetylacetone was used. On addition of ice water to the product, the yellow precipitate dissolves giving a yellow solution; the yellow compound is a cobalticinium salt which is produced by an apparently simple metathetical reaction such as

$$2Co(C_5H_7O_2)_3 + 4(C_5H_5)MgBr = 2[Co(C_5H_5)_2]Br + MgBr_2 + 3Mg(C_5H_7O_2)_2$$

The mixture was extracted several times with ether and the large quantities of insoluble matter removed by centrifugation. The hot aqueous solution was then freed from magnesium salts by addition of barium hydroxide solution; after removal of magnesium hydroxide, the excess barium was removed by addition of an equivalent amount of dilute sulfuric acid. Using cobaltic acetylacetonate labeled with Co^{60}, it is found that the compound reacts completely to give the cobalticinium ion, all of which appears in the aqueous solution; no activity appeared in the ether extracts or in the aqueous solution in a form other than the metal hydrocarbon ion.

Final purification of the cobalticinium salt solution was made by precipitation of the picrate, by addition of a saturated solution of picric acid to the solution containing about 0.15 g./ml. of cobalticinium ion. The picrate was recrystallized from dilute picric acid solution; a yield of about 65% was obtained at this state. The recovery of all solutions and precipitation of the ion from neutral or faintly acid solutions by sodium 2,4-dinitrophenolate has given yields of about 95% based on the amount to be expected from complete reaction of the acetylacetonate. Conversion of the picrate or the 2,4-dinitrophenolate to other salts in aqueous solution is made by ether extraction of the organic acid after addition of the appropriate amount of mineral acid, and by anion exchange resin (Dow A2) columns.

In aqueous solution cobalticinium salts are exceedingly stable, in contrast to the ferricinium and ruthenicinium salts. The ion is unaffected by boiling with either aqua regia or concentrated sulfuric acid for 15 minutes or so, or with dilute alkalies alone or even in the presence of hydrogen peroxide. Fuming with perchloric acid however rapidly destroys the ion and analysis of cobalticinium salts and of solutions has been made by destruction in this manner. The cobalt was then determined either polarographically, or by the volumetric method involving the alkaline perborate oxidation of cobaltous solutions.[4] The chemical behavior of the cobalticinium ion in aqueous solution is much like that of a large alkali metal ion. The salts of common acids are very soluble in water, but have eluded attempts to crystallize them; on evaporation of chloride, bromide or sulfate solutions, only viscous liquids result, and some decomposition occurs. With large anions, crystalline salts are more easily obtained.

From hydrochloric acid solutions containing as little as 0.1 mg./ml. of cobalticinium ion, silicotungstic acid gives a pale yellow precipitate, resembling in this respect cesium and the ferrocinium and ruthenicinium ions. This precipitate can be metathesized with hot mercurous nitrate solutions, the excess of which can be removed by hydrochloric acid leaving a pure cobalticinium salt solution; a separation from ammonium salts is thus possible.

With sodium 2,4-dinitrophenolate and sodium 2,4-dinitro-1-naphthol-7-sulfonate, solutions of ~ 0.1 mg./ml. concentration give yellow crystals in about 10 minutes, and at higher concentrations, immediate precipitates; both these precipitates are much less soluble than the picrate. The analysis of the 2,4-dinitrophenolate, when precipitated from faintly acid solution and recrystallized twice, corresponds to a molecular complex of the formula $[(C_5H_5)_2Co](C_6H_3O_5N_2)\cdot 2C_6H_4O_5N_2$. Sodium α-naphthol-β-sulfonate gives a yellow precipitate with the cobalticinium ion, but there is no reaction with sodium 6-chloro-5-nitrotoluene-3-sulfonate. A further similarity to rubidium and cesium is the formation of a yellow ferric chloride–antimony chloride complex on addition of antimony trichloride in glacial acetic acid to ferric chloride solutions containing as little as 0.01 mg. of cobalticinium ion. The addition of a saturated solution of potassium permanganate to a fairly concentrated solution of cobalticinium salt (1–2 mg./ml.) gives a brown precipitate sparingly soluble in water and dilute acids.

The ultraviolet absorption spectrum of cobalticinium perchlorate in aqueous solution is shown in Fig. 1. The solutions used were prepared from the picrate by anion exchange

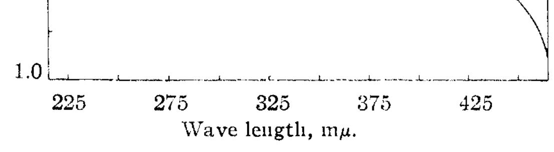

Fig. 1.—Ultraviolet absorption spectrum of cobalticinium perchlorate in water; Beckman spectrophotometer, silica cells, 25°.

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[1] First reported by T. J. Kealy and P. L. Pauson, *Nature*, **168**, 1039 (1951). See also Miller, Tebboth and Tremaine, *J. Chem. Soc.*, 632 (1952).

[2] G. Wilkinson, M. Rosenblum, M. C. Whiting and R. B. Woodward, THIS JOURNAL, **74**, 2125 (1952).

[3] G. Wilkinson, *ibid.*, **74**, 6146 (1952).

[4] E. H. Swift, "System of Chemical Analysis," Prentice-Hall, Inc., New York, N. Y., 1939, p. 344.

and were determined polarographically. Measurements taken at 242 and 278 mμ show that Beer's law is obeyed over a concentration range of 0.03 to 0.3 millimolar and at 336 mμ from 0.3 to 3.0 millimolar.

Attempts at reduction in aqueous solution by chemical reagents failed, which is not surprising in view of the reduction potential for the cobalticinium ion.[5] Cobalticinium hydroxide has been made in aqueous solution by the action of freshly prepared silver oxide on the chloride solution; from titration curves of the base with 0.1 *N* hydrochloric acid, *p*H measurements being made with a Beckman Model G instrument with glass and saturated calomel electrodes, the ionization constant of the base has been determined to be 8.2×10^{-3}.

Cobalticinium picrate $[(C_5H_5)_2Co](C_6H_2N_3O_7)$, is obtained as orange needle crystals which explode readily on heating, making carbon and hydrogen analysis difficult. Analyses gave C, 45.51; H, 3.36; N, 9.88; Co, 14.07; (calcd. C, 46.1; H, 2.88; N, 10.06; Co, 14.11). The solubility of the picrate in water at 25° is 3.0 g./liter.

The chloroplatinate $[(C_5H_5)_2Co]_2PtCl_6$ has been made by evaporation almost to dryness of cobalticinium chloride and chloroplatinic acid solutions and precipitation of the salt with absolute alcohol; the salt was then crystallized from water. Analyses gave C, 30.61; H, 2.81; Co, 15.01; Pt, 24.80; Cl, 27.10 (calcd. C, 30.55; H, 2.55; Co, 14.95; Pt, 24.85; Cl, 27.14).

The addition of a solution of potassium triiodide to a dilute solution of a cobalticinium salt gives a brown precipitate of cobalticinium triiodide; the ion thus resembles the ferricinium and ruthenicinium ions in forming triiodides very sparingly soluble in water. Analyses gave Co 10.30, I 66.77 (calcd. Co 10.32, I 66.71).

Since the cobalticinium ion is isoelectronic with ferrocene, its salts should be diamagnetic. The magnetic susceptibility of cobalticinium picrate has been measured by the Gouy split tube method using air ($\kappa = +0.029 \times 10^{-6}$ c.g.s. unit) and water (-0.72×10^{-6} c.g.s. unit) as standards. The values obtained were independent of field strength; the measurements were repeated after recrystallization of the picrate, and two packings of the tube with the powdered picrate were made in each case. The molar susceptibility χ^{25}_{mol} for cobalticinium picrate is $-194 \pm 2 \times 10^{-6}$ c.g.s. unit.

I am indebted to Mr. J. A. Page for polarographic measurements, and to Prof. R. B. Woodward, Dr. M. C. Whiting and Mr. M. Rosenblum for helpful discussions.

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(5) J. A. Page and G. Wilkinson, THIS JOURNAL, **74**, 6149 (1952).

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The Polarographic Chemistry of Ferrocene, Ruthenocene and the Metal Hydrocarbon Ions

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In a previous communication, a structure for "ferrocene," bis-cyclopentadienyliron $(C_5H_5)_2Fe$,[1] has been given,[2] in which the iron atom is symmetrically placed between two cyclopentadienyl rings; it was further shown that on oxidation salts of the unipositive ion $[(C_5H_5)_2Fe]^+$, which is designated the ferricinium ion, are formed. The analogous ruthenium compounds, ruthenocene, $(C_5H_5)_2Ru$, and the ruthenicinium salts have also been prepared,[3] as have salts of the ion $[(C_5H_5)_2Co]^+$ which is referred to as the cobalticinium ion.[4]

The polarographic behavior of these compounds has now been studied. Polarograms were obtained using a Sargent Model 11 instrument, and a divided H-cell with a saturated calomel reference electrode; chloride ion was excluded from the polarographic solution by means of a potassium nitrate–agar plug. This was necessary because the chloride ion gives an anodic wave in the alcohol solutions employed, which interferes with the polarographic waves of ferrocene and ruthenocene.

The Ferrocene–Ferricinium Ion System.—Ferrocene has been found to give a well defined reversible anodic wave at the dropping mercury electrode in a 90% ethanol, 0.1 *M* sodium perchlorate and 0.01 *M* perchloric acid supporting electrolyte. The half-wave potential is +0.31 *versus* the S.C.E. No change in the potential was observed between neutral and 0.01 *M* perchloric acid solutions, but the presence of perchloric acid improves the definition of the polarographic wave. The value of the polarographic constant in the supporting electrolyte, $i_d/Cm^{2/3}t^{1/6}$, was found to be 1.27 μa./m*M*./l. $\text{mg.}^{2/3}\ \text{sec.}^{-1/2}$.

Controlled potential oxidation of ferrocene in the above supporting electrolyte using the potentiostat of Lingane and Jones[5] was carried out at a mercury anode at a potential of +0.40 v. *versus* the S.C.E. The anode compartment was separated from the cathode by a fritted disc and a potassium nitrate–agar plug. The cathode compartment was filled with dilute nitric acid solution, and a platinum cathode was used. Twenty-two and a half milligrams of ferrocene in the supporting electrolyte was oxidized. The initial current of 8.4 ma. decreased to 0.1 ma. in 60 minutes electrolysis, and the original yellow solution changed during the electrolysis to the deep blue color characteristic of ferricinium salt solutions. The quantity of electricity consumed during the electrolysis, 10.6 coulombs, was determined by a silver titration coulometer. The theoretical value for a one-electron oxidation step is 11.6 coulombs.

A polarogram of the ferricinium salt solution resulting from the electrolysis, showed a well defined cathodic wave with a half-wave potential of +0.30 v. *versus* the S.C.E., agreeing, within the limits of experimental error, with the half-wave potential for the oxidation of ferrocene. The ferrocene–ferricinium ion couple is hence a thermodynamically reversible system in the alcoholic supporting electrolyte.

$$(C_5H_5)_2Fe = [(C_5H_5)_2Fe]^+ + e^-;\ E_0 = -0.56 \text{ v. } (\textit{versus} \text{ the normal hydrogen electrode})$$

The polarographic behavior of the ferricinium perchlorate in a neutral aqueous 0.1 *M* sodium perchlorate supporting electrolyte was studied; the perchlorate solution was prepared by dissolving ferricinium picrate in an equivalent amount of perchloric acid solution, and ether extracting the picric acid. A freshly prepared solution, after removal of oxygen with nitrogen, showed a combined anodic–cathodic polarographic wave, with a half-wave potential of +0.16 v. *versus* the S.C.E.; the shift in half-wave potential is due to the change from an

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[3] G. Wilkinson, *ibid.*, **74**, 6146 (1952).

[4] G. Wilkinson, *ibid.*, **74**, 6148 (1952).

[5] J. J. Lingane and S. L. Jones, *Anal. Chem.*, **22**, 1169 (1950).