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, pH 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)$_2$Co]($C_6H_2N_3O_7$), 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)$_2$Co]$_2$PtCl$_6$ 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 (κ = +0.029 × 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_{mol}^{25} for cobalticinium picrate is −194 ± 2 × 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.

(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)$_2$Fe,[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)$_2$Fe]$^+$, which is designated the ferricinium ion, are formed. The analogous ruthenium compounds, ruthenocene, (C_5H_5)$_2$-Ru, and the ruthenicinium salts have also been prepared,[3] as have salts of the ion [(C_5H_5)$_2$Co]$^+$ which is referred to as the cobalticinium ion.[4]

(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) G. Wilkinson, ibid., 74, 6148 (1952).

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./mM./1. mg.$^{2/3}$ sec.$^{-1/6}$.

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)$_2$Fe = [(C_5H_5)$_2$Fe]$^+$ + e$^-$; E_0 = −0.56 v. (versus the normal hydrogen electrode)
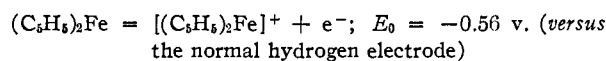
The polarographic behavior of the ferricinium perchlorate in a neutral aqueous 0.1 M sodium perchlorate supporting electrolyte was studied; the perchlorate solution was prepared by dissolving ferricinium picrate in an equivalent amount of perchloric acid solution, and ether extracting the picric acid. 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

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

alcoholic to aqueous supporting electrolyte. The result confirms other chemical evidence that the ferricinium ion in neutral aqueous solution partially decomposes quite rapidly to form some ferrocene.

The Ruthenocene–Ruthenicinium Ion System.—Ruthenocene has similarly been found to give a well defined anodic wave at the dropping mercury electrode; the supporting alcoholic electrolyte used was the same as the one used for ferrocene. The half-wave potential was $+0.26$ v. *versus* the S.C.E. The value of the polarographic constant, $i_d/Cm^{2/3}t^{1/6}$ was found to be 1.62 $\mu a./mM/1.$ mg.$^{2/3}$ sec.$^{-1/2}$.

A controlled potential oxidation at a mercury anode of 23.0 mg. of ruthenocene in 50 ml. of the same supporting electrolyte has been made at a potential of 0.40 v. *versus* the S.C.E. The initial current of 6.7 ma. decreased to 0.1 ma. in 60 minutes electrolysis. During the course of the electrolysis an insoluble yellow crystalline solid, ruthenicinium perchlorate, precipitated from the solution. The quantity of electricity measured as before was 8.76 coulombs, agreeing well with the calculated value, 9.57 coulombs, for a one-electron oxidation. The solid was removed leaving a pale yellow solution of ruthenicinium perchlorate in the supporting electrolyte; a polarogram of this solution gave a well defined wave at a potential of $+0.22$ v. *versus* the S.C.E. The separated perchlorate was dissolved in water and the solution made 0.1 M in sodium perchlorate; after removal of oxygen with nitrogen, a cathodic wave with a half-wave potential of $+0.11$ v. *versus* the S.C.E. was obtained; ruthenicinium perchlorate slowly separated from this solution in which it is very sparingly soluble.

The Cobalticinium Ion.—Solutions of cobalticinium perchlorate were prepared from cobalticinium picrate solutions by use of an anion exchange resin column. In an oxygen free, 0.1 M sodium perchlorate aqueous supporting electrolyte at pH 6.2, the cobalticinium ion gave a well-defined cathodic wave at the dropping mercury electrode. The half-wave potential was -1.16 v. *versus* the S.C.E. The value of the polarographic constant, $i_d/Cm^{2/3}t^{1/6}$, was found to be 1.77 $\mu a./mM/1.$ mg.$^{2/3}$ sec.$^{-1/2}$.

Unsuccessful attempts were made to prepare cobaltocene, $(C_5H_5)_2Co$, by controlled potential electrolysis of a neutral one millimolar cobalticinium perchlorate solution. A mercury cathode and divided cell were used, and the potential was -1.5 v. *versus* the S.C.E. The initial current was 7.0 ma. which decreased very slowly being 5 ma. after 60 minutes electrolysis. On continued electrolysis, the polarographic wave for the cobalticinium ion disappeared, indicating that complete destruction of the complex occurs, rather than the simple oxidation of cobaltocene by water.

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Acetylated Thioacetals of D-Glucosamine

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Wolfrom, Lemieux and Olin[2] reported that the mercaptalation and acetylation of N-acetyl-2-amino-2-deoxy-D-glucose (II, N-acetyl-D-glucosamine)[3,4] produced a crystalline product, m.p. 126–127°, $[\alpha]^{22}D$ $-32°$ (chloroform), which was described as a pentaacetyl derivative. Further investigation shows that this substance was actually a tetraacetyl derivative obtained in low yield and not again encountered in subsequent preparations. The correct pentaacetyl derivative V is herein described: m.p. 75–77°, $[\alpha]^{23}D$ $+1°$ (c 4, chloroform). Kent[5] has reported, without experimental detail, the same substance with the constants: m.p. 160–161°, $[\alpha]^{23}D$ $+2°$ (c 1, chloroform). It is then apparent that either the melting point of Kent is in error or we have at hand a low melting dimorph. N-Acetyl-2-amino-2-deoxy-D-glucose diethyl thioacetal (III, N-acetyl-D-glucosamine diethyl mercaptal) has been described by Wolfrom, Lemieux and Olin[2]; m.p. 130–131°, $[\alpha]^{23}D$ $- 35°$ (c 4, water). This compound has now been prepared from N-acetyl-2-amino-2-deoxy-D-glucose (II) by an improved method and the above constants verified. For this compound Kent[5] has reported the constants: m.p. 121–122°, $[\alpha]^{23}D$ $-24°$ (c 0.4, water). It is apparent that his preparation was impure. Kent[5] further records that he treated 2-amino-2-deoxy-D-glucose (D-glucosamine) hydrochloride (I) at room temperature with ethanethiol and hydrochloric acid (the recorded[5] density of 1.4 is undoubtedly in error). Treatment of 2-amino-2-deoxy-D-glucose hydrochloride (I) with ethanethiol in the concentrated hydrochloric acid of commerce (ca. 12 N) gave a very slow reaction from which we obtained after hydrogen chloride removal, 2-amino-2-deoxy-D-glucose diethyl thioacetal (IV); m.p. 109–110°, $[\alpha]^{23}D$ $-24°$ (c 1, water). Kent[5] records for the hydrochloride: m.p. 75–76°; $[\alpha]^{22}D$ $-18°$ (c 0.16, water). Acetylation of our preparation of 2-amino-2-deoxy-D-glucose diethyl thioacetal (IV) led to the above-mentioned pentaacetyl derivative V while de-O-acetylation of this yielded N-acetyl-2-amino-2-deoxy-D-glucose diethyl thioacetal (III)
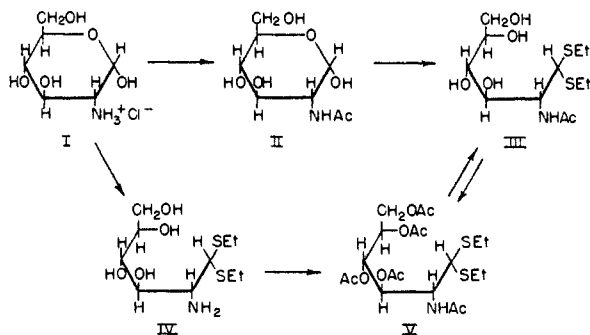
(1) Special Postdoctoral Research Fellow of the National Institutes of Health, United States Public Health Service.

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