a manual instrument, using a Leeds and Northrup Type HS galvanometer as current-measuring instrument. A diagram of the circuit will be presented elsewhere. All electrical components were calibrated, and the bridge potential was checked with a Type K potentiometer at the time of use. The internal resistance of the cell under the conditions employed was found to be 210 ohms, while the additional resistance contributed by the galvanometer and its shunts was only 0.3 ohm.

Plots of $-E_{\text{d.e.}}$ against $\log (i/(i_d - i))$ for these and similar data indicate that the reduction is thermodynamically reversible.[1] Independent diffusion current measurements, made with the same capillary, gave $I = 3.205 \pm 0.009$ in 0.10 F potassium nitrate and 3.85 ± 0.01 in 0.10 F potassium nitrate–0.88 F ammonia. Then, by the fundamental equation for the reduction of a complex to the metal[1]

$$(E_{1/2})_c - (E_{1/2})_s = 0.02957 \log \frac{3.205\, K f_c}{3.85 f_s} - 0.1183 \log C_{NH_3} \quad (1)$$

where the subscripts c and s refer to the ammino- and aquo- complexes, respectively, K is the dissociation constant of the ammino- complex, and f_c and f_s the activity coefficients of the two complexes, which, for want of experimental data, we shall consider to be equal.

Table II summarizes the measurements at ammonia concentrations between 0.12 and 3.6 F. From these data and equation (1), one computes $K = 1.26\ (\pm 0.02) \times 10^{-7}$, and, with the value of the cadmium–cadmium ion standard potential given by Harned and Fitzgerald[2]

$$Cd + 4NH_3 \longrightarrow Cd(NH_3)_4^{++} + 2e;\ E^0 = 0.606_0 \text{ v. (N. H. E.)}$$

TABLE II

EFFECT OF AMMONIA CONCENTRATION ON HALF-WAVE POTENTIAL OF CADMIUM(II) IN 0.10 F POTASSIUM NITRATE

All measurements were made with *ca.* 0.6 millimolar cadmium at 25.00 ± 0.01°

C_{NH_3}, F	$E_{1/2}$ *vs.* S. C. E., volt	$(E_{1/2})_c - (E_{1/2})_s + 0.1183 \log C_{NH_3}$
0	−0.5777	......
0.1267	− .6776	−0.2065
.310	− .7243	− .2066
.433	− .7407	− .2060
.550	− .7535	− .2064
.812	− .7758	− .2068
1.120	− .7899	− .2065
1.389	− .8033	− .2078
1.890	− .8206	− .2103
2.79_0	− .8441	− .2135
3.56_5	− .8604	− .2172
	Mean ($C_{NH_3} < 1.2\ F$)	−0.2064 ± 0.0002

Further, with the standard free energy of NH_3 (aq.) given by Latimer,[3] $F_{Cd(NH_3)_4^{++}} = -53{,}280$ cal.

$$F^0_{Cd(NH_3)_4^{++}} = -53{,}280 \text{ cal.}$$

Previously Lingane had found −0.578 v. for the half-wave potential of cadmium in 0.1 F potassium nitrate[4] and −0.81 v. in 1 F ammonia–1 F ammonium chloride.[5] Neglecting, as here, correction for activity effects, Euler[6] found 1×10^{-7} for the dissociation constant of the ammino- complex from potentiometric measurements.

The deviation in concentrated ammonia solutions is probably to be attributed to the formation of such complexes as $Cd(NH_3)_5^{++}$.

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(1) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1946, pp. 161–165.

(2) H. S. Harned and M. E. Fitzgerald, THIS JOURNAL, **58**, 2624 (1936).

(3) W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solution," Prentice-Hall, Inc., New York, N. Y., 1938, p. 305.

(4) J. J. Lingane, THIS JOURNAL, **61**, 2099 (1939).

(5) J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **15**, 583 (1943).

(6) H. Euler, *Ber.*, **36**, 3400 (1903).

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The Preparation of Calcium D-Arabonate from Calcium 2-Keto-D-gluconate by Electrolytic Bromine Oxidation

BY C. L. MEHLTRETTER, W. DVONCH AND C. E. RIST

Isbell and Frush and others[1] have shown that aqueous solutions of D-glucose in the presence of calcium carbonate can be oxidized to calcium D-gluconate in nearly quantitative yield with bromine generated electrolytically. By prolonging the electrolysis so as to consume twice the current required for the conversion of D-glucose to D-gluconic acid, Cook and Major[2] were able to isolate calcium 5-keto-D-gluconate in small amount.

In a study of the oxidation of calcium D-gluconate by electrolytic bromine whereby 4 faradays of electricity per mole of gluconate was used, we obtained calcium D-arabonate as well as the calcium salts of 5-keto-D-gluconic and oxalic acids. The crude calcium D-arabonate was converted to D-arabobenzimidazole,[3] from which the yield was calculated to be 9%. Electrolysis with 8 faradays per mole of calcium D-gluconate resulted in a 17% yield of calcium D-arabonate. The presence of 2-keto-D-gluconic acid could not be detected in any of the oxidized solutions.

The transformation of calcium D-gluconate to arabonate suggested that calcium 2-keto-D-gluconate is first formed and is then rapidly decarboxylated and oxidized to calcium D-arabonate. Honig and Tempus[4] proposed such a mechanism for the hypobromite oxidation of D-glucose because both 2-keto-D-gluconic and D-arabonic acids were

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(1) (a) Isbell and Frush, *J. Research Nat. Bur. Standards*, **6**, 1145 (1931); (b) Helwig (to Rohm and Haas Co.) U. S. Patent 1,937,273 (Nov. 28, 1933); (c) Fink and Sommers, *Trans. Electrochemical Soc.*, **74**, 625 (1938).

(2) Cook and Major, THIS JOURNAL, **57**, 773 (1935).

(3) Moore and Link, *J. Biol. Chem.*, **133**, 293 (1940).

(4) Honig and Tempus, *Ber.*, **57**, 787 (1924).

obtained as products of the reaction. However, a repetition of their work by Reichstein and Neracher[5] produced mainly 5-keto-D-gluconic acid and only questionable traces of 2-keto-D-gluconic acid. Under acidic conditions Ohle and Berend[6] were able to oxidize barium 2-keto-D-gluconate with barium permanganate to barium D-arabonate in small yield.

We have electrolyzed calcium 2-keto-D-gluconate in aqueous solution at 30° and have obtained calcium D-arabonate in a yield of 65%. Oxidation at 5 to 10° produced 84% of calcium D-arabonate. The absence of objectionable by-products allowed 90% of the product formed to be crystallized directly from the reaction mixture as practically pure calcium D-arabonate pentahydrate. These facts furnish evidence that the mechanism suggested by Honig and Tempus[4] is correct and that both 2-keto-D-gluconic and 5-keto-D-gluconic acids are produced by the hypobromite oxidation of glucose or gluconic acid, the 2-keto acid being converted to D-arabonic acid almost immediately.

Experimental

Oxidation of Calcium D-Gluconate.—A liter of solution was prepared for electrolysis by dissolving 56.1 g. (0.125 mole) of calcium D-gluconate monohydrate and 8 g. of calcium bromide in water. Oxidation took place in a 1500-ml. beaker containing two graphite electrodes ($3 \times 7^1/_2 \times {}^5/_{16}$ inches) placed 2 inches apart and immersed about 4 inches. The solution was stirred mechanically and 1 ampere of current passed through for 13.4 hours (0.5 faraday) at 6 to 7 volts. A short time after the electrolysis was begun, the cell temperature rose to 30° and remained at approximately that temperature for the duration of the reaction. The oxidized solution was filtered from 0.5 g. of calcium oxalate and had a reducing value equivalent to 12% of calcium 5-keto-D-gluconate. The latter was isolated in 7.4% yield from half of the solution by the method of Cook and Major.[2] The other half of the reaction mixture was concentrated *in vacuo* to 100 ml. and the calcium salts precipitated by the addition of 1 liter of ethanol. Reaction of the calcium salts with *o*-phenylenediamine[3] gave 9% of crude D-arabobenzimidazole. The more soluble D-glucobenzimidazole remained in solution and was not recovered. Recrystallization of the crude material from 50% ethanol yielded D-arabobenzimidazole of m. p. 234–235° (dec.); $[\alpha]^{25}\mathrm{D}$ $-49.6°$ (c, 2; 5% citric acid solution). The picrate melted at 161–162°. For L-arabobenzimidazole, Moore and Link[3] reported a melting point of 235° (dec.); $[\alpha]^{25}\mathrm{D}$ $+49.2°$ and a picrate which melted at 158°.

Oxidation of Calcium 2-Keto-D-gluconate.—A solution of 60.1 g. (0.125 mole) of calcium 2-keto-D-gluconate trihydrate and 8 g. of calcium bromide in 1 liter of water was electrolyzed by the procedure used for calcium D-gluconate. The oxidation was rapid as at no time could bromine be detected. During the reaction, it was necessary to reverse the polarity of the electrodes periodically to remove a deposit of calcium carbonate from the cathode. After the passage of 16.5 ampere-hours (0.62 faraday) of current at a reaction temperature of 5 to 10° the solution had practically no reducing value. Substantially complete oxidation of the calcium 2-keto-D-gluconate had occurred. The oxidized solution was heated on the steam-bath for two hours with 10 g. of calcium carbonate to convert D-arabonolactone present to calcium D-arabonate. The hot mixture was filtered from excess calcium carbonate and the clear filtrate concentrated *in vacuo*. Practically pure calcium D-arabonate pentahydrate crystallized out. The product was collected on a filter and washed with 95% ethanol. The air-dried salt weighed 43.1 g. which is a yield of 75% of theory. It had a specific rotation at 25° of $-3.5°$ (c, 1.00; water) and contained 8.73% calcium. D-Arabobenzimidazole of m. p. 234–235° was obtained from the product in 72% yield. The melting point of a mixture with authentic D-arabobenzimidazole was unchanged. Pure calcium D-arabonate pentahydrate has a calcium content of 8.71% and $[\alpha]^{25}\mathrm{D}$ $-3.0°$ (c, 1.00; water).

The mother liquor contained 5.8 g. of dissolved calcium D-arabonate which was isolated as D-arabobenzimidazole. The total yield of calcium D-arabonate was therefore 84% of the theoretical.

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[5] Reichstein and Neracher, *Helv. Chim. Acta*, **18**, 892 (1935).

[6] Ohle and Berend, *Ber.*, **60**, 1159 (1927).

[7] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Not copyrighted.

The Equilibrium between Ammonia and Hydrogen Telluride[1]

BY F. F. MIKUS[2] AND S. J. CARLYON[2]

In a previous paper,[3] the equilibrium between ammonia and hydrogen selenide has been reported. The investigation has been extended to include the next member of the sulfur family. In this work the equilibrium constants for the dissociation of ammonium hydrotelluride according to the reaction $NH_4HTe(s) \rightleftarrows H_2Te\ (g) + NH_3\ (g)$ were determined in the temperature range of 2.5–25°.

Hydrogen telluride was prepared in a manner similar to that described for the preparation of hydrogen selenide in the previous paper. Extreme precautions to eliminate all air from the system had to be taken as the hydrogen telluride decomposed immediately upon contact with the slightest trace of air. The preparation of anhydrous ammonia and the method of determining the equilibrium have also been described in the previous paper.

Equilibrium pressures over the temperature range 2.5–25° are given in Table I. Three different samples were used at the various temperatures. The equilibrium pressure was obtained by subtracting the difference between the levels of the mercury in the buret and the leveling bulb from the barometric pressure.

Since the total pressure, P, is equal to the sum of the partial pressures of NH_3 and H_2Te, which are found in equivalent amounts as the products of the decomposition of NH_4HTe, the equilibrium constant, $K_p = (P/2)^2$. Determinations made with excesses of H_2Te and NH_3 did not yield con-

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[3] F. F. Mikus and F. J. Poss, THIS JOURNAL, **71**, 429 (1949).