Short Communications

Oxidation of Cerium(III) to Cerium(IV) Ion by Means of Cobalt(III) Ion

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Cobaltous carbonate, suspended in a solution of sodium or potassium bicarbonate, is oxidized by hydrogen peroxide to a green soluble cobaltic complex¹. Job² and several other authors have shown — by measuring the oxidative power — that cobalt is trivalent in the green solution. Reduction of the green trivalent cobalt compound may be carried out by addition of excess of standard ferrous pyrophosphate and titration of the excess with permanganate^{2,3}. Metzl⁴ has determined cobalt volumetrically by first converting it into the green cobaltic complex. After addition of sodium hydroxide and boiling, all cobalt is precipitated as cobaltic hydroxide, which can be dissolved in sulfuric acid containing potassium iodide. The iodine formed is then titrated with sodium thiosulphate.

From an analytical point of view the green cobaltic carbonate ion (it is reasonable to assume that the green cobaltic complex is either $[\text{Co}(\text{CO}_3)_2]^{---}$ or mixed carbonate hydroxo ions) may act as a source of cobaltic aquo ion. When the green solution is acidified with a considerable excess of sulfuric or nitric acid, the blue cobaltic aquo ion is formed. Cobaltic ion is one of the most powerful oxidants known; the reduction potential of Co(III)/Co(II) is about 1.8 volts. However, solutions containing cobaltic aquo ion are not stable, because water acts as a reducing

agent. The stability seems to increase with increasing acid concentration. — In the present preliminary investigation it is shown that cerous ion can be oxidized quantitatively to ceric ion by means of cobaltic ion.

Preparation of the cobaltic carbonate solution. 0.01 mole cobaltous nitrate was dissolved in 250 ml water. 75 g sodium bicarbonate was added and the flask agitated for one minute. Thereafter 2 ml 30 % hydrogen peroxide, diluted with water to 250 ml, were added gradually while rotating the contents of the flask. After dilution to 1 liter the still undissolved sodium bicarbonate went into solution. The clear green liquid was left until next day to make sure that the excess of hydrogen peroxide was quite destroyed. Fortunately the complex cobaltic ion exerts a strong catalytic influence on the decomposition of hydrogen peroxide, so, in all likelihood, the excess is destroyed within a few minutes.

The normality of the cobaltic solution was determined as follows: 50 ml of the green solution was run into 30 ml 2 *M* sulfuric acid plus 2 g potassium iodide. The iodine formed was then titrated with thiosulphate. The results were very reproducible. The carbon dioxide formed by the neutralization seems to expel the oxygen from the solutions. Anyhow, aeration of the solutions with carbon dioxide does not alter the titer. To make sure that the titer thus found really is identical with the content of cobalt, the cobalt was determined by electrolysis. The average normality found by titration was 0.00938. Two electrolytic determinations gave molarity with respect to cobalt 0.00936 and 0.00938.

It seems impossible to make the cobaltic carbonate solution much more than 1/100 molar even if the solution is saturated with sodium bicarbonate. The excess of cobalt will yield a brown precipitate. The ca. 1/100 molar solution keeps its titer fairly well, but when stored for months the titer

decreases considerably with precipitation of brown hydroxide. It seems that the solution remains more constant when sodium bicarbonate is present in excess (solid salt on the bottom of the container).

Oxidation of cerous ion. A comparison of the reduction potential of Co(III)/Co(II), which is about 1.8 volts, with that of Ce(IV)/Ce(III), which is about 1.5 volts, shows that it is theoretically just possible to oxidize cerous ion quantitatively by means of cobaltic ion in the usual analytical concentration range. The following experiments confirm this.

An about 0.05 M cerous nitrate solution was prepared and analyzed. Evaporation of a sample and ignition to CeO₂ gave the molarity 0.0515 (mean of 3 determinations). The colour of the CeO₂ showed that it was not quite pure, but with a slight content of other rare earths. The true content of cerous ion in the solution was determined by oxidation with sodium bismuthate^{5,6} and titration with hydrogen peroxide of the Ce(IV) formed. Two determinations gave 0.0511 M and 0.0511 M.

The cerium content in 20 ml of the 0.0511 M solution was now oxidized with cobaltic ion as follows: 30 ml conc. sulfuric acid were diluted with water to 100 ml. After cooling 20 ml cerous nitrate solution were added. 150 ml ca. 0.01 M cobaltic carbonate solution were now gradually added. The Ce(III) was oxidized nearly immediately, and the colour of the solution showed excess of cobaltic ion. The solution was now heated to decompose the cobaltic ion, and boiled for one minute, to expel the oxygen formed. The ceric ion formed was now titrated with hydrogen peroxide. Two determinations gave 0.0509 M and 0.0510 M.

Cobaltic ion may be used for many other quantitative oxidations, for example oxidation of chromic chromium to chromate chromium.

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Separation of Saturated Straight Chain Fatty Acids II. Qualitative Paper Ionophoresis

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When analysing the homologous series of saturated straight chain fatty acids the separation can be achieved by paper ionophoresis. Barnett^{1,2} describes the separation of long chain fatty acids — from capric to stearic acid — using 3 N aqueous ammonia as solvent. The analysis is, however, difficult to carry out because of the high volatility of ammonia. In the procedures described below this difficulty is avoided by substituting ammonia with sodium hydroxide.

The acids from acetic to pelargonic acid can be separated from each other ionophoretically by means of aqueous sodium hydroxide buffered with boric acid to pH 9.0. The mobilities of these acids at +25° C and at a voltage of 5 V/cm were as follows: acetic 31, propionic 27, butyric 25, valeric 23, caproic (hexoic) 21.5, α -nonylic (heptoic) 20, caprylic (octoic) 19, and pelargonic (nonoic) acid 18 mm/h.

The acids from acetic to palmitic acid can be separated from each other ionophoretically by using a 0.2 N solution of sodium hydroxide in glycerol and a temperature of +90° C. The short chain acids are separable with the method described below but their location on the glycerolic paper is rather cumbersome because of the slow absorption of the indicator solution and because of the disturbing effect of the atmospheric carbon dioxide. Therefore the description will be limited to the separation of the acids from caproic acid upwards. As an interesting detail may be mentioned that it is possible to follow the movement of all these acids throughout the analysis by dissolving a suitable indicator, e. g. phenolphthalein, in the glycerol solution and removing the carbon dioxide from the air-tight reaction chamber equipped with a window. The mobilities of different acids at a voltage of 20 V/cm were as follows: caproic 7.7, α -nonylic 6.6, caprylic 5.8, pelargonic 5.3, capric (decoic) 4.9,