ate had $n^{25}\text{D}$ 1.4198, m.p. 11.3°; dioxane has[8,9] $n^{25}\text{D}$ 1.4201, m.p., 11.6°.

Solubility of Silver Perchlorate in Dioxane.—Silver perchlorate (*ca.* 1 g.), contained in a glass tube integral with a vacuum system, was dried by evacuation to 10^{-3} mm. mercury pressure for 18 hours. Dioxane (10 ml.), dried over sodium, was distilled through the vacuum system directly on to the silver perchlorate, and the tube then sealed and removed from the system. The tube and contents were left to stand at room temperature (25 ± 5°), with occasional shaking, for 20 days. The tube was then opened and 5 ml. of the supernatant liquid removed. This was evaporated to dryness under vacuum, the residue dissolved in water (2 ml.) and hydrochloric acid (2 ml. of 0.1 *N*) added; the solution remained quite clear, showing the absence of silver in the supernatant dioxane.

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[8] C. H. Schneider and C. C. Lynch, THIS JOURNAL **65**, 1063 (1943).

[9] J. Gillis and A. Delaunois, *Rec. trav. chim.*, **53**, 186 (1934).

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Racemization of Tris-(ethylenediamine)-cobalt(III) Ion in the Presence of Decolorizing Carbon

BY BODIE E. DOUGLAS

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The use of decolorizing carbon as a catalyst in the preparation of hexamminecobalt(III) salts prompted the investigation of the effect of decolorizing carbon on the racemization of tris-(ethylenediamine)-cobalt(III) ion. Optically active tris-(ethylenediamine)-cobalt(III) ion is very stable toward racemization. No change in rotation is observed for an aqueous solution of the complex after 24 hours on a steam-bath. However, in the presence of decolorizing carbon, racemization is complete in 2 minutes at 90°.

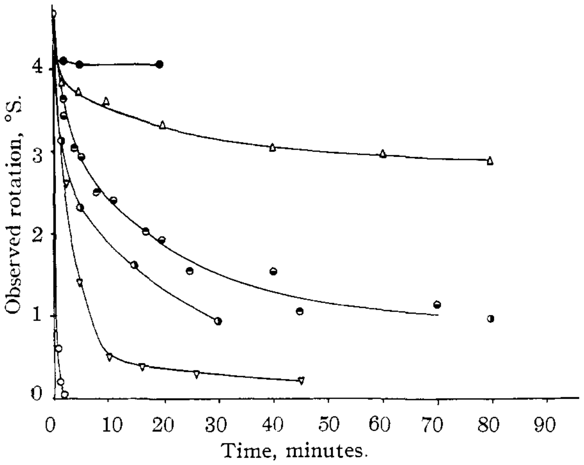

Fig. 1.—Rate of racemization of $Co(en)_3Cl_3$ in the presence of decolorizing carbon. The composition of the samples represented by circles was 1 g. of $Co(en)_3Cl_3$ and 1 g. of decolorizing carbon in 100 ml. of water at various temperatures: ●, 20.5°; ◒, ◓ and ◑, 57°; ○, 90°. The initial rotation for the curves represented by ● and ◑ was 4.1°S. because of incomplete resolution of the sample of the complex used. The samples represented by the triangles were maintained at 57° and differed only in the amount of decolorizing carbon present; △, 0.5 g. of carbon; ▽, 2.0 g. of carbon.

Experimental

Tris-(ethylenediamine)-cobalt(III) chloride was prepared according to the method of Work[1] and resolved by fractional crystallization of the chloro-*d*-tartrate salt as described by Werner.[2] The *d*-complex is less soluble as the chloro-*d*-tartrate salt and can be obtained in a very pure form. The *l*-form of the complex is very soluble as the chloro-*d*-tartrate salt and a solution of the complex tends to form a gel rather than crystals. The *l*-form of the complex was precipitated as the chloride salt with concentrated hydrochloric acid and recrystallized twice to separate it from the less soluble *dl*-form. The specific rotations using a sodium lamp as the light source were +159° and −155° as compared to Werner's values of +152° and −154°, respectively. The first optical rotations were obtained with a Schmidt and Haensch polarimeter which read to 0.01° by means of a vernier scale. The rate studies were carried out using a Bausch and Lomb saccharimeter which read to 0.1°S. (International Sugar scale) by means of a vernier scale. The readings obtained with the saccharimeter could be converted to circular degrees by means of the relationship 100°S. = 34.62° circular. Readings were made with both instruments on the same sample and found to be reproducible to within the reproducibility of the saccharimeter, or about 0.03° circular. Rotations were observed at room temperature for solutions containing 0.100 g. of tris-(ethylenediamine)-cobalt(III) chloride dissolved in enough water to give 10.00 ml.

The racemization rate studies were carried out as follows. The weighed sample of the complex was dissolved in the required volume of water and the solution was allowed to reach a constant temperature in a water-bath before the weighed sample of decolorizing carbon was added. A typical sample for the studies of the effect of temperature contained 1.00 g. of tris-(ethylenediamine)-cobalt(III) chloride, 1.00 g. of carbon and 100 ml. of water. Samples of the stirred suspension were removed with a pipet and filtered as rapidly as possible through a sintered glass filter using suction. The filtrate was then evaporated under an infrared lamp with an air stream blowing over the surface of the solution. Alcohol was added just before the water had been completely evaporated to give a powder on drying rather than a glassy solid. Samples of the active complex were subjected to the same treatment with the omission of the active carbon without change in rotation. Each observation at 90° was carried out with an individual sample of 0.15 g. of complex, 0.15 g. of carbon and 15 ml. of water because of the short and closely spaced time intervals.

Baker and Adamson decolorizing carbon was heated to 700° in a loosely covered crucible for 1 hour in a muffle furnace and bottled for future use. Carbon treated in this way gave reproducible results after 2 or 3 months.

Discussion of Results

The results are presented in Fig. 1. It is apparent that the rate of racemization of tris-(ethylenediamine)-cobalt(III) ion is dependent on the presence of relatively large amounts of active carbon and on the temperature. Samples heated with active carbon for 5 minutes at over 90° were optically inactive, but the absorption spectrum of a solution of the complex in the range of 330 to 725 mμ was the same as for a fresh sample of the complex. Therefore, the decrease in rotation is due to racemization, not decomposition. Samples which had stood in contact with carbon at room temperature for one-half hour or more showed practically no change in rotation on further standing. Samples heated to boiling for an hour or more after standing for at least a day at room temperature in the presence of carbon showed a slight decrease in rotation, but the decrease was never as great as 50% of the original rotation.

Additional data were obtained under somewhat

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[1] J. B. Work, "Inorganic Syntheses," Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 221.

[2] A. Werner, *Ber.*, **45**, 121 (1912).

different conditions, but the general pattern was not altered in any case. A levorotatory sample with an initial rotation of −4.4°S. was observed to be racemized completely in 1 minute 35 seconds at 90° under the same conditions as those described for the dextrorotatory sample reported in the figure.

No mathematical analysis was made of the curves because of the fact that the carbon becomes a less effective "catalyst" as time progresses. The carbon finally becomes essentially ineffective for bringing about further racemization, even at elevated temperatures. Further studies are planned with other complexes and other possible "catalysts."

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Ion Exchange as a Separations Method. VII. Near Optimum Conditions for the Separation of Fission Product Rare Earths with Lactic Acid Eluant at 87°

BY EDWARD C. FREILING AND LELAND R. BUNNEY

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Mayer and Freiling[1] have found lactic acid solutions to be considerably more selective than citric acid solutions for separating Eu, Sm and Tb by cation exchange chromatography. Using their results as a basis, near optimum conditions have been determined for separating the rare-earth activities known to be formed in uranium fission (*i.e.*, Y, La, Ce, Pr, Nd, Pm, Sm and Eu), together with Gd and Tb. This note presents the method used to achieve virtually complete separation of these activities from one another in 49 hr. using lactic acid eluants of various strengths at a *p*H of 3 and a temperature of 87°. The method is shown to be applicable to the precise radiochemical determinations of rare earth activities.

Experimental

Materials.—To obtain desired rare earth isotopes, uranyl nitrate was converted to U_3O_8 by ignition and bombarded with neutrons in the Oak Ridge Pile.

Eluant solutions were made up as described by Mayer and Freiling.[1] The strengths of the 1 *M* lactic acid solutions were based upon titrations with standard 0.1 *N* NaOH to the phenolphthalein end-point; no attempt was made to ensure dissociation of associated lactic acid. Solutions of strengths less than 1 *M* were made up by diluting the 1 *M* stock solutions.

Dowex-50 cation exchange resin 250 to 500 mesh was simultaneously cleaned and converted to the ammonium form by washing with *p*H 6 ammonium citrate solution and then graded to obtain that fraction which settled through 6 in. of water in 5 to 9 min. Subsequent microscopic examination revealed that the resin particle diameters were normally distributed with 98% of them falling between 29 and 62 μ.

Apparatus.—The apparatus used was essentially that of Mayer and Freiling[1] except that the inside diameter of the capillary was increased from 2 to 3 mm. and sintered glass in place of glass wool was used to support the resin bed. This substitution allowed faster and steadier flow rates to be maintained

Procedure.—The column was prepared by boiling 3.4 ml. of wet resin to remove air, slurrying the resin into a heated column, and allowing it to settle without flow of water.

The bombarded U_3O_8 was dissolved to 6 *N* HNO_3 to which had been added 20 mg. each of Ce, Pr, Nd and Sm carriers. The rare earth group was then isolated by the following series of fairly standard steps.[2] Fluoride precipitations in the presence of bromate ion and Zr holdback carrier removed U, Np, and most of the fission product contamination; hydroxide precipitations in the presence of Ba holdback carrier freed the samples from Ba and Sr activities; any remaining Zr activity was removed by precipitating zirconium iodate from nitric acid solutions using H_2O_2 to keep Ce in the trivalent state. At this point all contaminating activities had been removed and Ce could be separated from the other rare earths as ceric iodate by simply oxidizing the cerous ion with bromate ion. This oxidation was followed by a ceric iodate scavenging, after which the remaining rare earths were precipitated as the hydroxides.

The final precipitate of rare earth hydroxides was dissolved in a minimum amount of concentrated $HClO_4$, diluted to twice its volume, brought to a boil, and allowed to pass through the column. When the liquid level had dropped to within a centimeter of the top of the resin bed, the remainder of the column was filled with boiled, distilled water. After a milliliter of this had passed into the resin, the water was withdrawn, thus washing away unadsorbed activity. Activity adhering to the glass walls of the column, however, was sufficient to produce the small degree of tailing of the Y peak shown in Fig. 1. This activity can be removed, and the tail eliminated, by rinsing the column again with eluant.

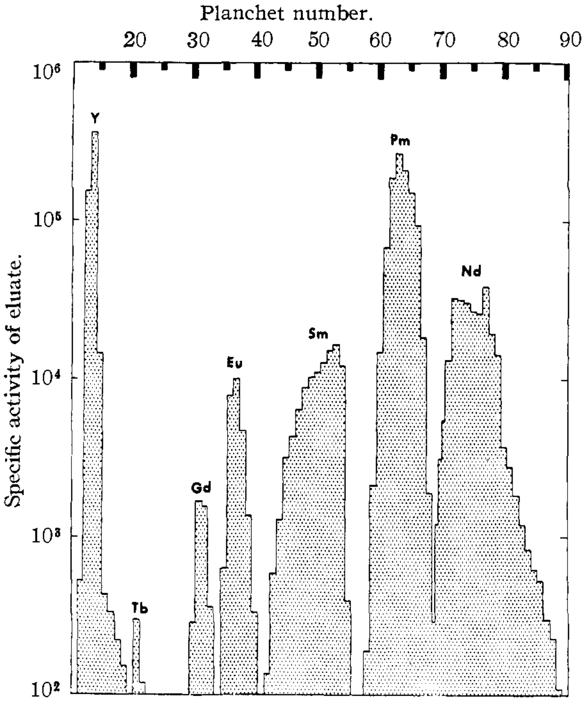

Fig. 1.—Elution history curve.

Depending upon the flow rate, fractions of 1 to 1.5 ml. were collected every half-hour in weighed polyethylene planchets. (It was sometimes found advantageous to reduce the collection time to 15 min. between peaks of difficultly separable rare earths.) The full planchets were reweighed and the volume of liquid reduced by evaporation with a heat lamp. The β-γ activity of each planchet was measured with a flow type proportional counter. An elution history curve was then prepared (Fig. 1) by plotting counts/min./g. of eluant *vs.* planchet number. This curve was used to de-

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(1) S. W. Mayer and E. C. Freiling, THIS JOURNAL, **75**, 5647 (1953).

(2) Coryell and Sugarman, "Radiochemical Studies: The Fission Products," National Nuclear Energy Series, McGraw-Hill Book Co., Inc., New York, N. Y., 1951.