

rigorous purification the m. p. can be raised to 88–89°. On catalytic hydrogenation the alcohol absorbs 0.9–1.0 mole of hydrogen.<sup>6</sup>

Three grams of a non-alcoholic liquid were recovered from the volatile fraction obtained during the above ethyl borate treatment. The substance polymerized very rapidly on heating and this property, together with the rotation, refractive index, and method of preparation, indicates that it was probably impure carvopinone.<sup>3</sup>

(6) Joshei, Hall and Palkin, *Ind. Eng. Chem., Anal. Ed.*, **13**, 447 (1941).

BUREAU OF AGRICULTURAL CHEMISTRY AND ENGINEERING  
U. S. DEPARTMENT OF AGRICULTURE  
WASHINGTON, D. C. RECEIVED OCTOBER 27, 1941

### The Separation of Ytterbium from Accompanying Rare Earths by Means of its Amalgam

BY HERBERT N. MCCOY AND R. PHILIP HAMMOND

The preparation of ytterbium amalgam by the electrolytic method described earlier<sup>1</sup> has been repeated, using a larger amount (4 g. of oxide) of the same starting material. The electrolyses were carried to the point where no further amalgam formation took place. The rare earths from amalgams and from residual electrolytes were then extracted as chlorides called I and II, respectively. Chloride I formed much the larger part of the material; chloride II amounted to about 0.1 g.

From chlorides I and II spectrograms were made using a replica grating of 15,000 lines per inch (5906 lines per cm.) and a graphite arc source. These spectrograms for the region 2500 to 4600 Å., accompanied by that of iron, were enlarged photographically to give prints with a dispersion of one Å. per mm. The enlarged prints were examined with the aid of Massachusetts Institute of Technology wave length tables<sup>2</sup> and more than 250 of the strong lines identified.

The spectrogram of chloride I was that of ytterbium containing a much smaller proportion of europium. No lines of other rare earths could be found on this spectrogram. That of chloride II showed in addition to some remaining ytterbium and europium, the presence of gadolinium, terbium, dysprosium, yttrium, erbium, thulium and lutecium. The presence of holmium was probable but could not be established with certainty because its strong lines were masked by those of other elements present.

(1) McCoy, *THIS JOURNAL*, **68**, 1622, 3432 (1941).

(2) "Massachusetts Institute of Technology Wave Length Tables," George W. Harrison, John Wiley and Sons, Inc., New York, N. Y., 1939.

This work shows that of the rare earths contained in the starting material only ytterbium and europium form amalgams by the method used. If the small proportion of europium present had first been removed, as might easily have been done by fractional crystallization as dimethyl phosphates,<sup>3</sup> bromates<sup>4</sup> or ethyl sulfates<sup>5</sup> the separation of ytterbium from the rare earths that usually accompany it would have been complete.

(3) Morgan and James, *THIS JOURNAL*, **36**, 10 (1914).

(4) James and Bissel, *ibid.*, **36**, 2060 (1914).

(5) Urbain, *Compt. rend.*, **126**, 835 (1898).

PRIVATE LABORATORY  
1226 WESTCHESTER PL.  
LOS ANGELES, CALIF.

LABORATORY OF  
LINDSAY LIGHT & CHEMICAL CO.  
WEST CHICAGO, ILLINOIS  
RECEIVED JANUARY 2, 1942

### The Purification of Thorium Chloride Octahydrate

BY CHESTER B. KREMER

In connection with previous researches on thorium compounds as well as in recent work in the production of thorium dioxide catalysts, the necessity of obtaining pure thorium chloride octahydrate arose. Thorium chloride "c. p." as purchased on the market contains appreciable amounts of iron and silica. Purification by simple recrystallization is difficult because of the tenacity with which iron compounds are retained by the salt and the formation of concentrated solutions, sirupy in nature, which will not deposit crystals. However, it is possible to obtain pure  $\text{ThCl}_4 \cdot 8\text{H}_2\text{O}$  by a method which in part is based upon a slight modification of the Gooch and Havens method for the determination of aluminum.

Specially prepared asbestos for the following operations is obtained by boiling a high grade variety repeatedly with concentrated hydrochloric acid until free of detectable iron and then washing thoroughly with distilled water.

Two hundred grams of the "c. p." salt is dissolved in just enough 6 *M* hydrochloric acid for complete solution, filtered through asbestos and then extracted twice with ethyl ether,<sup>1</sup> this operation removing practically all of the iron.<sup>2</sup> The solution is then evaporated to small volume on a hot plate. Excess silica precipitates out and is filtered off through asbestos. The filtrate is cooled to 0° and dry hydrogen chloride bubbled in until the solution is saturated with the gas. An equal volume of ethyl ether is

(1) Isopropyl ether may be employed; see Dodson, Forney and Swift, *THIS JOURNAL*, **68**, 2573 (1936).

(2) Langmuir, *ibid.*, **22**, 102 (1900).

added and the mixture agitated with hydrogen chloride gas until it becomes homogeneous. From this solution thorium chloride octahydrate precipitates as pure white crystals, which are filtered off, washed with ether and dried. A sample of the salt when dissolved in water gives a negative thiocyanate test for iron.

DEPARTMENT OF CHEMISTRY  
THE CITY COLLEGE  
NEW YORK, N. Y.

RECEIVED JANUARY 6, 1942

### The Action of Monoethanolamine on Ethyl Bromomalonate

BY CHESTER B. KREMER, M. MELTSNER AND H. HINDIN

In the course of work being carried out in these Laboratories dealing with the synthesis of diureides, the condensation of monoethanolamine with ethyl bromomalonate was attempted. As ordinarily carried out, we find condensation does not result; rather the bromine atom in the ester is replaced by hydrogen. This reaction is analogous to the action of alkaline reagents and halogen acids on similar compounds containing active halogen atoms.

The ethyl bromomalonate was prepared by the action of bromine on ethyl malonate dissolved in carbon tetrachloride. The product was carefully purified by several distillations through a column under reduced pressure. The fraction boiling at 126–127° under 18 mm. pressure was used.

Forty-six grams of monoethanolamine (0.752 mole) and 90 g. of the ethyl bromomalonate (0.376 mole) were refluxed together for six hours. On cooling, the mixture separated into two layers, the lower one eventually solidifying. The solid material was identified as monoethanolamine hydrobromide. The liquid upper layer was extracted with diethyl ether, thus effecting separation from any excess monoethanolamine, and the ether extract dried over anhydrous magnesium sulfate. The ether was distilled off and the resulting liquid fractionated. A low-boiling fraction, b. p. 58–60° (2 mm.), was shown to be ethyl malonate by its refractive index ( $n_D^{20}$  1.4144) and density ( $d_4^{20}$  1.055). The yield was 11 g. A higher boiling fraction (36 g.), b. p. 92–93° (2 mm.), was identified by its boiling point and density ( $d_4^{20}$  1.426) as unchanged ethyl bromomalonate.

DEPARTMENT OF CHEMISTRY  
THE CITY COLLEGE  
NEW YORK, N. Y.

RECEIVED JANUARY 6, 1942

### The Mutarotation of $\alpha$ -D-Glucose in Dioxane-Water Mixtures at 25°

BY H. H. ROWLEY<sup>1</sup> AND WARD N. HUBBARD

The mutarotation of  $\alpha$ -D-glucose has been an object of study for many years by numerous investigators. Though the majority of the experiments concerned this phenomenon in aqueous solution both with and without catalysts, a few have been studied in mixed aqueous solvents. Worley and Andrews<sup>2</sup> studied the mutarotation in methanol-water mixtures; Richards, Faulkner and Lowry<sup>3</sup> in both methanol-water mixtures and ethanol-water mixtures; Lowry and Faulkner<sup>4</sup> in pyridine-water mixtures; and more recently Rowley<sup>5</sup> in ethanol-water mixtures at 25°. The mutarotation of glucose in solution is believed by many to be catalyzed by acids and bases and since water is a complete catalyst, having both acidic and basic properties, the reaction is fairly rapid in pure water. Absolute methanol is amphiprotic and apparently a complete catalyst but much inferior to pure water<sup>6</sup> as is absolute ethanol.<sup>5</sup> On the other hand, pyridine is not amphiprotic but is a fairly strong base so mixtures of this solvent and water should be a fair catalyst for the mutarotation.

In continuing the studies of the mutarotation of  $\alpha$ -D-glucose in mixed aqueous solvents, it was decided to use an inert organic solvent which probably does not itself catalyze the reaction. Unlike the alcohols, which have been used in previous studies, dioxane has no apparent acid group and its basic properties are probably relatively weak. Thus it might be assumed that its catalytic effect on the mutarotation will be exceedingly small. This appears to be justified by subsequent experimental work. Since  $\alpha$ -D-glucose is fairly soluble in mixtures up to ninety weight per cent. of dioxane, the mutarotation of this sugar was studied in dioxane-water mixtures at 25°.

### Discussion of Results

The solutions were made by dissolving a weighed amount of pure anhydrous  $\alpha$ -D-glucose in dioxane-water mixtures of known composition. The concentration ranged from 4.0 g. of sugar/

(1) Present address: Department of Chemistry, Lawrence College, Appleton, Wisconsin.

(2) Worley and Andrews, *J. Phys. Chem.*, **31**, 742, 1880 (1927).

(3) Richards, Faulkner and Lowry, *J. Chem. Soc.*, 1733 (1927).

(4) Lowry and Faulkner, *ibid.*, **127**, 2883 (1925).

(5) Rowley, *THIS JOURNAL*, **62**, 2563 (1940).

(6) Rowley and Bailey, *ibid.*, **62**, 2562 (1940).