Europium and Ytterbium Amalgams

BY HERBERT N. MCCOY

Amalgams of some of the rare earth metals may be made by the electrolysis of alcoholic solutions of their anhydrous chlorides with a mercury cathode.[1] The high resistance of these solutions makes the use of a high voltage necessary while the chlorine liberated at the anode diminishes the electrical efficiency. The use of aqueous solutions[2] has hitherto proved unsatisfactory[3] for the reason that much hydroxide or basic salt is deposited on the mercury cathode, if the solution is neutral; while, if acid, hydrogen is given off. In either case, little or no pure amalgam is formed. The potassium double carbonates, tartrates and citrates of certain rare earths give water solutions that are particularly well suited for the preparation of amalgams. Still more convenient are solutions of potassium citrate and a rare earth acetate, made alkaline with potassium carbonate. When such solutions of europium or ytterbium are electrolyzed with a mercury cathode amalgams are formed at low voltage with good current efficiency.

In an electrolysis more or less potassium amalgam is also formed especially when the cathode current density is too great or the current is continued after the rare earth element has been deposited. The mixture of potassium and europium amalgams can be freed from the former by the action of water. Practically all the potassium goes into solution before the europium begins to react. This observation led to the thought that amalgams of these rare earths might also be formed by the direct action of sodium or potassium amalgam on alkaline double salt solutions without use of the current. This surmise was confirmed by experiment.

When more than 1.38% of europium is present in an amalgam the excess forms crystals having the composition $Hg_{10}Eu$. A second compound, Hg_2Eu_3, stable at a dull red heat is obtained by distilling off the excess mercury in a high vacuum.

Ytterbium amalgam was made with almost as good yield, both electrically and by the direct action of potassium amalgam, as was that of europium. The ytterbium oxide used was made by and obtained from Prof. Joseph K. Marsh[4] in exchange for europium material.

Experimental

Europium Amalgam.—Potassium citrate solution was made from 25 g. of citric acid, potassium carbonate and 80 ml. of water. Twenty-five grams of europium acetate[5] in 60 ml. of warm water was added. The clear solution was made distinctly alkaline with 5 g. more of potassium carbonate. This solution was electrolyzed in a 250-ml. beaker with 200 g. of mercury as cathode and a spiral of heavy platinum wire as anode. During the electrolysis the solution was stirred by power.

A current of two amperes, or 0.06 amp. per square cm. of cathode surface, produced by eight volts, with two ohms external resistance, deposited practically all of the europium in the solution (9.47 g.) in six and one-quarter hours; a current efficiency of 40%. The temperature was kept at 25 to 35° by a cooling bath.

During most of the electrolysis some Eu^{++} was present in the solution as shown by the bleaching of litmus paper. Shortly after the solution failed to bleach litmus, the electrolysis was considered complete. The solution poured from the amalgam was clear and pale yellow in color. It showed no absorption bands and consequently was practically free from europium.

The amalgam was a mixture of liquid and crystals. It contained but little potassium. The latter could be almost completely removed by stirring the mixed amalgams with water until europium hydroxide appeared in the solution. After being dried, the europium amalgam could be kept unchanged in a stoppered bottle. About a score of electrolyses were made using various solutions containing a total of 146 g. of europium carbonate, citrate and acetate. The best electrolyte tried was that formed by a solution of potassium citrate and europium acetate.

Solid Amalgams, $Hg_{10}Eu$ and Hg_2Eu_3.—By filtration through a platinum cone a crystalline amalgam could be separated from the mercury solution. The filtrate was analyzed by treating a weighed portion with dilute hydrochloric acid until all its europium content had passed into solution as europous chloride. The latter was oxidized to europic chloride, precipitated as oxalate, and ignited to oxide. The mercury was washed, dried, and weighed: 65.232 g. of liquid amalgam, filtered at 22°, gave 98.60% of mercury and 1.38% of europium. The crystalline amalgam was freed from excess mercury solution by pressure and analyzed similarly.

Anal. Calcd. for $Hg_{10}Eu$: Hg, 93.05; Eu, 6.95. Found: Hg, 92.96; Eu, 7.04.

Metallic europium has been made by Trombe.[6] The small amount prepared (about one gram) of 98% purity made a further attempt at its preparation desirable. With this aim, the liquid and crystalline amalgams were sub-

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[1] Audrieth, Meints and Hopkins, THIS JOURNAL, **53**, 1805 (1931); Jukkola, Audrieth and Hopkins, *ibid.*, **56**, 303 (1934).

[2] Hopkins and Audrieth, *Trans. Am. Electrochem. Soc.*, **66**, 135 (1934).

[3] "Inorganic Syntheses," Vol. I, 1939, p. 15.

[4] Marsh, *J. Chem. Soc.*, 1367 (1937).

[5] McCoy, THIS JOURNAL, **61**, 2455 (1939).

[6] Trombe, *Compt. rend.*, **206**, 1380 (1938).

jected to distillation in a high vacuum obtained by a mercury vapor pump supported by a Cenco Hi-Vac pump. This was followed by heating the residue in the field of a radio-frequency generator. The distillations were carried out in the Electronic Products Laboratory of this city, where Mr. Richard Seaman had the pumps as well as a high frequency apparatus set up for work on X-ray bulbs. It is a pleasure to express my thanks to Mr. Seaman for his skillful coöperation in the construction of the Pyrex and quartz glass apparatus used and for the privilege of using his equipment.

In a typical experiment, heat for the preliminary distillation was furnished by a coil of nichrome wire on an asbestos covered 35-mm. aluminum cylinder, 75 mm. high, surrounding the 32-mm. Pyrex distillation vessel. A regulated voltage (with a "Variac") permitted the mercury of 190 g. of 5% amalgam to be volatilized very slowly without spattering or bumping. In three and one-half hours the temperature had reached the point of incipient fusion of the aluminum cylinder (660°). Although this temperature was maintained half an hour longer nothing further vaporized.

The residue in the tube was fused to a coherent mass by removing the cylindrical heater and surrounding the Pyrex tube with the coil of a radio-frequency circuit of 500 kilocycles. This means of heating had the merit that heat was generated in the metal while the surrounding Pyrex tube remained temporarily much cooler. The high frequency coil was 20 cm. in diameter and consisted of seven turns of 0.25-inch copper tubing. The generator had 40 k. w. power, which could be applied in ten steps. A fraction of the maximum power quickly caused the contents of the tube to glow and the metal to sinter to lumps of an alloy which, on analysis, was found to be Hg_2Eu_3.

Although the Pyrex tube was noticeably attacked the alloy was but superficially contaminated. In the experiment described 14 g., in five lumps, resulted after the alloy had been cleaned by physical means. This alloy was analyzed in the same way as was $Hg_{10}Eu$: 2.2683 g. of alloy gave 1.0630 g. of mercury and 1.3936 g. of Eu_2O_3, equal to 1.2040 g. of Eu.

Anal. Calcd. for Hg_2Eu_3: Hg, 46.7; Eu, 53.3. Found: Hg, 46.8; Eu, 53.0.

The alloy, Hg_2Eu_3, is a metallic solid of pale yellow tint. Its density is 7.94. It can be easily scratched with a file. It may be kept without noticeable change under gasoline and is fairly stable in dry air at room temperature.

In one experiment 14 g. of Hg_2Eu_3 was heated in a quartz tube, in a high vacuum. After two minutes of heating with a Méker burner the metal began to glow whereupon it suddenly reacted with the tube with the formation of a black deposit (silicon ?) at the place of contact and a sublimate containing mercury and europium.

In another experiment 10 g. of cleaned lumps of Hg_2Eu_3 was put in a small magnesium oxide crucible supported on a tripod in a Pyrex bell jar, 70 mm. in diameter and 153 mm. high. After evacuation a high frequency field was applied. The alloy quickly became red hot. A faint glow of gas suddenly gave way to a very bright light that filled the entire jar. This light died down after two or three minutes as a sublimate condensed on the walls of the jar. After about ten minutes the current was stopped. When cold the crucible was found to be practically empty, (Trombe[6] had observed that europium distills in argon at 50 mm. pressure) and much of the vaporized mercury and europium had recombined on the walls of the jar. That some separation of the components had occurred was shown by the fact that 10 to 20% of the mercury was found free in the bottom of the jar and that apparently free europium formed thin silvery patches on the walls of the jar. These were much less readily attacked by dilute hydrochloric acid than the alloy. While radio-frequency heating has certain advantages, these seem to be offset by the difficulty of temperature control.

Ytterbium Amalgam.—One gram of ytterbium oxide (containing 5% of lutecium oxide) was dissolved in hydrochloric acid, precipitated with potassium carbonate and the filtered precipitate dissolved in acetic acid to form the acetate (the oxide is too weak a base to react with acetic acid directly). The acetate was added to a slightly alkaline solution of 8 g. of potassium citrate and diluted to 80 ml. The solution was electrolyzed with a mercury cathode and platinum anode at 30 to 35°. Eight volts and 2 amperes were used and a stream of carbon dioxide to minimize oxidation and stir the solution. The electrolyte was decanted after two hours and the amalgam washed well with water, with which it reacted slowly. The washed amalgam, treated with hydrochloric acid, gave hydrogen and a bright yellowish green solution that bleached litmus paper. This solution contained ytterbous chloride,[7] $YbCl_2$. Water and air soon caused oxidation to colorless ytterbic chloride, $YbCl_3$. This gave an oxalate that yielded 0.22 g. of oxide, Yb_2O_3, or 22% of that taken.

The citrate solution decanted from the electrolysis still contained ytterbium. It was stirred with potassium amalgam for two and one-half hours. The solution was decanted and the remaining amalgam washed with water. When treated with hydrochloric acid, it behaved like that produced by electrolysis, giving hydrogen and a yellowish green solution of ytterbous chloride. This in turn yielded 0.25 g. of the oxide. The filtrate from the amalgam, after evaporation and decomposition of the citrate by heat, gave an oxalate that yielded 0.50 g. of oxides, part of which was probably lutecium oxide. The total amount of recovered oxides was 0.97 g. from the 1 g. of starting material.

The results here recorded on amalgam formation show a marked difference from those obtained by Yntema[8] and by Ball and Yntema,[7] who electrolyzed aqueous solutions of the chlorides of europium and ytterbium, plus sulfuric acid, with a mercury cathode. They got europous and ytterbous sulfate, respectively, without amalgam formation. The difference in products formed in the two cases was doubtless due to the absence of the sulfate ion in the present experiments and by the use of a citrate solution which permitted an alkaline instead of an acid electrolyte to be used.

Summary

1. Aqueous solutions of the acetates of europium and ytterbium in potassium citrate give

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[7] Ball and Yntema, THIS JOURNAL, **52**, 4264 (1930).

[8] Yntema, *ibid.*, **52**, 2782 (1930).

amalgams upon (a) electrolysis, (b) treatment with potassium amalgam.

2. Solid amalgams $Hg_{10}Eu$ and Hg_2Eu_3 were prepared.

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Chlorination of Ethylenic Compounds Containing a Reactive Group with *t*-Butyl Hypochlorite in Methanol Solution[1]

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Introduction

Irwin and Hennion[1] recently described the addition reactions of *t*-butyl hypochlorite in reactive solvents with a number of ethylenic hydrocarbons. The present work extends this study to some ethylenic compounds containing reactive groups, notably allyl chloride, methallyl chloride, allyl alcohol, cinnamic acid, cinnamaldehyde and crotonaldehyde. Most of the reactions were carried out in excess methanol as a reactive solvent and resulted in the addition of a chlorine atom and the methoxyl group to the unsaturated carbon atoms. In all cases the methoxyl group took the position normally occupied by the negative addendum in directed additions to these compounds.

Certain reactive groups in the ethylenic reagents caused side reactions. The action of *t*-butyl hypochlorite in methanol on allyl alcohol yielded two by-products. The first was found to result from the addition of a chlorine atom and the alloxyl group to allyl alcohol. The same product was obtained by the action of *t*-butyl hypochlorite on allyl alcohol in the absence of methanol. The second by-product was assumed to result from the addition of chlorine and the methoxyl group to the alloxyl group of the first by-product. This conclusion was confirmed by synthesis of the compound by the action of *t*-butyl hypochlorite in methanol on the first by-product. Cinnamic acid gave, besides the expected addition compound, the methyl ester of this product. Crotonaldehyde underwent the expected addition with simultaneous oxidation of the compound thus formed to the acid. Actually, the methyl ester of the acid was isolated. The addition product from cinnamic aldehyde did not appear to be oxidized under these conditions. The reagents, products, yields, etc., are summarized in Table I.

The positions taken by the addenda in these reactions were established in various ways. The structure of the addition compound from allyl chloride was established by the close agreement in physical properties with the 1,3-dichloro-2-methoxypropane reported by Fairbourne.[3] The chloro-methoxyl addition product from allyl alcohol, upon reaction with phosphorus pentachloride, yielded a substance which corresponded satisfactorily with the addition product from allyl chloride. Both of the addition products from cinnamic acid have been described and their structures proved by Jackson.[4] The direction of addition to cinnamaldehyde was proved by oxidizing the addition product to the corresponding acid, which was found to be identical with the acid isolated from the addition reaction with cinnamic acid. In the addition products of crotonaldehyde and methallyl chloride and in the by-products of addition to allyl alcohol the orientations of the addenda were not proved but assigned by analogy.

The procedure used in the addition reactions was nearly uniform except that the temperature was varied slightly according to the reactivity of the ethylenic compound employed.

Experimental

Reagents.—*t*-Butyl hypochlorite was prepared by the method of Chattaway,[5] as modified by Irwin and Hennion.[1]

Allyl chloride, methallyl chloride and allyl alcohol were Shell Chemical Company products. The allyl chloride (b. p. 44°) and methallyl chloride (b. p. 70–71°) were distilled. The other chemicals were reagent grade or the equivalent.

Action of *t*-Butyl Hypochlorite on Allyl Chloride in Methanol Solution.—One-half mole (38.5 g.) of allyl chlo-

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[1] Paper 8 on halogenation in reactive solvents; previous paper, THIS JOURNAL, **63**, 858 (1941).

[2] Instructor, St. Vincent College, Latrobe, Pa., on leave of absence.

[3] Fairbourne, *J. Chem. Soc.*, 2232 (1929).

[4] Jackson, THIS JOURNAL, **48**, 2166 (1926).

[5] Chattaway, *J. Chem. Soc.*, **123**, 2999 (1923).