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The Chemical Isolation of Samarium from Lanthanide Mixtures[1]

BY A. F. CLIFFORD AND H. C. BEACHELL

In efforts to separate the rare earth elements from each other a number of workers have successfully reduced from solution and isolated the elements europium[2] and ytterbium[3] in the divalent state. Samarium, however, has proved to be much more difficult to reduce in solution, although Marsh[4] has reported preparation of samarous compounds by dissolution of samarium amalgam in dilute acid and also by the simultaneous reduction of samaric and europic compounds in the presence of sulfate to precipitate the divalent ions. However, Marsh apparently found the reduction of samarium directly to the divalent state in the absence of europium to be extremely difficult.

In order to utilize the well-characterized divalency of samarium in its separation, it was proposed to employ a non-aqueous solvent to slow up the reoxidation of the divalent samarium by hydrogen ion. Inasmuch as the rare earth trichlorides are fairly soluble in ethanol and the dichlorides, like barium chloride, are reasonably insoluble, the chlorides were selected as the most likely to lead to a successful reduction. Most other rare earth salts were automatically ruled out because of insufficient alcohol-solubility in the trivalent state (fluorides, sulfates, acetates, etc.) or excessive solubility in the divalent state (iodides, etc.).

Experimental and Discussion

Preliminary experiments were carried out with a dilute solution of pure samarium trichloride (hydrated salt) (in which only faint traces of europium were detectable spectroscopically) in absolute ethanol containing a few drops of aqueous 12 N hydrochloric acid. It was found that when pieces of zinc, manganese, aluminum (in the presence of mercuric chloride), beryllium, thorium (which contained considerable carbide) and magnesium were added, although all reacted vigorously, only on the magnesium was there evidence of production of samarous chloride, $SaCl_2$. On the magnesium a deep red solid material formed, turning brown and disappearing when the acid became exhausted. Attempts to use calcium lithium and sodium were unsuccessful.

Identification of the substance as samarous chloride was based on its color,[5] its solubility in water to give

momentarily a Bordeaux red solution,[6] its metathesis by aqueous sulfuric acid to a water-insoluble orange sulfate,[7] which was slowly dissolved and destroyed by aqueous acids, and by its metathesis by alcoholic ammonium or sodium hydroxide to a green compound,[8] insoluble in ethanol but soluble in the polar solvent formamide (with decomposition), as would be expected of a pseudo-alkaline earth hydroxide. Samarous chloride was observed to dissolve in formamide to yield momentarily a deep green solution. Since the formamide had not been especially purified, this was probably samarous hydroxide or some basic samarous salt. Also, by metathesis with aqueous solutions of the appropriate alkali salts, were prepared the fluoride (deep brownish or purplish red, water insoluble), the citrate (orange, insoluble in, but unstable to, water) and the carbonate (brownish-orange, water-insoluble). These preparations show that the green compound which Holleck[8] reported as being either "carbonate or hydroxide" was in fact the hydroxide.

Metathesis of samarous chloride with ethanolic hydrogen peroxide or formic acid or aqueous oxalate or iodate resulted in immediate oxidation of the samarous ion, in the last case with reduction of the iodate to iodine.

It was found possible to obtain an unstable orange suspension of samarous sulfate, $SaSO_4$, by treating aqueous samarium chloride containing 5–10% ethanol with magnesium and a little sulfuric acid or better by treating a solution of samaric chloride and magnesium sulfate in 1:1 aqueous methanol with magnesium and a little hydrochloric acid. This approach had the dual disadvantage of the instability of the divalent sulfate and the low solubility of the trivalent sulfate.

It was observed also that samarous sulfate was produced by magnesium amalgam in neutral or slightly acid aqueous sulfate solutions. Likewise magnesium amalgam produced samarous chloride in neutral ethanolic chloride solutions. Both reactions, however, were complicated by simultaneous precipitation of trivalent hydroxides. Thorium amalgam had no effect on an ethanol solution from which magnesium amalgam would precipitate samarous chloride.

It was decided that the optimum conditions for reduction could be obtained by using a 50–50 mixture of dioxane with ethanol saturated with strontium and barium chlorides. (The reduction was found to be successful also in acetone and isopropanol.)

Using commercial didymium chloride or chloride prepared from didymium carbonate—both being chlorides of the mixed rare earths minus cerium in the proportion in which they occur in monazite) containing about 3% samarium, and the ethanol–dioxane solvent described above, a saturated solution of the trichlorides was made. To this were added magnesium and sufficient aqueous 12 N hydrochloric acid to give a vigorous reaction on warming gently. When the magnesium was completely coated with red samarous chloride the mixture was cooled to allow the magnesium to settle and the liquor decanted. The product was washed with 1:2 ethanol–acetone saturated with alkaline earth chlorides (found to destroy the samarous chloride less rapidly than ethanol–dioxane). The process was repeated several times with fresh magnesium, replenishing the acid as required. From time to time it was necessary to boil the solution to near dryness and redissolve to get rid of the accumulated water. The process was brought to a halt when the magnesium content rose to the point where mixed magnesium–rare earth chlorides began to crystallize out. (This series of salts

(1) From a thesis presented by A. F. Clifford to the faculty of the University of Delaware in partial fulfilment of the requirements for the M. S. degree, September, 1947.

(2) Yost, Russell and Garner, "The Rare Earth Elements and Their Compounds," John Wiley and Sons, Inc., New York, N. Y., 1947; Yntema, THIS JOURNAL, **52**, 2782 (1930); Jantsch, Alber and Grubitsch, *Monatsh.*, **53–54**, 305 (1929); McCoy, THIS JOURNAL, **57**, 1756 (1935); **58**, 1577 (1936); **58**, 2279 (1936); W. Pearce, master's thesis, University of Illinois, 1931 (quoted by Yost, Russell and Garner, p. 65).

(3) Ball and Yntema, THIS JOURNAL, **52**, 4246 (1930); Marsh, *J. Chem. Soc.*, 1367 (1937); Pearce, Naeser and Hopkins, *Trans. Electrochem. Soc.*, **69**, 557 (1936).

(4) Marsh, *J. Chem. Soc.*, 531 (1943).

(5) Matignon and Cazes, *Ann. chim. phys.*, [8] **8**, 417 (1906).

(6) Yost, Russell and Garner, ref. 2.

(7) Jantsch and Skalla, *Z. anorg. allgem. Chem.*, **193**, 391 (1930).

(8) Holleck, *Atti X° congr. intern. chim.*, **2**, 671 (1938).

apparently has minimum solubilities in alcohol for the lightest rare earths.) The collected product in dilute hydrochloric acid solution was analyzed spectrophotometrically for samarium and neodymium. By comparison of the two values, the samarium content was found to have been increased from 3 to about 30% of the total rare earths. A reprocessing of the product further increased the samarium content (on the same basis) to 74%.

Using ethanol without dioxane and bubbling in hydrogen chloride gas instead of using the aqueous acid, the reduction was repeated with somewhat better separation. Too high a hydrogen chloride concentration was found to prevent the formation of samarous chloride, but when only sufficient gas was present to cause gentle evolution of hydrogen from the magnesium, samarous chloride formed readily on the metal. Using the didymium chloride previously described, after a short initial period of reaction, a suspension of particles of free samarous chloride began to appear. The free samarous chloride thus formed was stable in the medium and could be readily centrifuged down. One batch of solid samarous chloride was observed to be apparently unchanged after being in contact with this liquid for twenty-four hours. It was possible to wash the free salt with acetone without much oxidation, but not with ethanol. This product was of greater purity, as regards rare earths, than that of the previous run, the first product in this case having better than 55% samarium as compared with 30% in the former case.

It was found that addition of dioxane under these conditions resulted in an orange-colored product much more sensitive to hydrogen chloride concentration. The use of dioxane in the anhydrous method was therefore considered undesirable.

It was attempted to reduce samarium out of similar solutions containing all the rare earths in their ratio in monazite sand (cerium about 48%, samarium 1-2%). The material used contained considerable iron. Neither hydrous nor anhydrous reduction was successful. However, when the material was freed from iron and the ethanolic solution diluted with more than an equal volume of dioxane, the hydrous method did give a reduced samarium compound. The compound obtained, however, was not the expected red chloride but the green hydroxide, even with fairly large quantities of hydrochloric acid. That this compound was the hydroxide, or at least a basic salt, was strongly indicated by the fact that it was metathesized by ethanolic hydrogen chloride to the red samarous chloride. Furthermore, it had previously been observed that in solutions containing too much water for formation of samarous chloride, a very thin film of greenish material formed on the surface of the reacting magnesium where presumably the hydrogen ion concentration was depleted.

No reduction was obtained from these solutions by the anhydrous method even with iron-free material. This particular reaction is probably of no use as a separation method due to the tendency of the trichlorides to crystallize out of the dioxane solution, but may be of use as a qualitative test.

Specific tests on more concentrated samarium solutions showed that the presence of iron in small quantity, although apparently making reduction more difficult, did not completely prevent reduction. Much more harmful was the presence of platinum. Reduction was never obtained in a solution which had contained platinum even after repeated reduction by magnesium and centrifuging out of the platinum metal. Apparently very minute traces of platinum (presumably under these conditions colloidal metal) catalyzed the reverse reaction, the oxidation of samarous by hydrogen ion, faster than the samarium could be reduced. The effect of colloidal metals on similar reductions has already been noted by Marsh.

The specificity of magnesium ($E_0 = 2.3$ v.) in the reaction and the inability of thorium ($E_0 = ca.$ 2.0 v.) to perform the reduction seem to place the normal oxidation potential for the samarous–samaric couple in ethanolic chloride solution between 1.9 and 2.3 v.

Compared with Laitinen's[9] experimental result of 1.15 v. for the ytterbous–ytterbic couple (for which Latimer[10] estimated 0.6 volt) a potential around 2 v. is much more likely than Latimer's estimate of 0.8 v. The extreme sensitivity to even the small hydrogen-ion concentration in absolute ethanol would appear to support the evidence for this high potential. It should be noted that this is somewhat greater than the normal reduction potential which would be deduced from the first wave of Noddack and Bruckl's[11] polarographic reduction of aqueous samarium sulfate—$E_0 = 1.72$ v.

Considering the relative reduction potentials of samarium, ytterbium, and europium, it becomes apparent that the first batch of samarium reduced should carry with it all the europium and ytterbium in the solution in the same way as their concentration by sulfate precipitation has been reported by Marsh, thus affording a very convenient means of concentrating these elements to the point where they can be separated from the samarium by the methods already reported in the literature. It is highly possible that thulous chloride, $TmCl_2$, can be prepared from thulium concentrates in the same way.

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Summary

Samarium has been separated from the other rare earth elements (except europium and ytterbium) by reduction of ethanolic solutions of rare earth trichlorides with magnesium and hydrochloric acid (aqueous or anhydrous), yielding red samarium dichloride, $SaCl_2$. Using aqueous hydrochloric acid and diluting largely with dioxane, even from very low samarium concentrations green samarous hydroxide is produced directly instead. This reaction may be of significance for qualitative detection of samarium. By metathesis of the dichloride, the sulfate (previously prepared), the hydroxide, citrate, carbonate and fluoride (new compounds), all water-insoluble, have been prepared. The poisoning effect of iron and particularly platinum on the reduction has been noted. In neutral ethanolic solution, samarous chloride was precipitated by magnesium amalgam. The reaction, however, was complicated by hydroxide precipitates. In neutral aqueous sulfate solution, samarous sulfate was likewise precipitated by magnesium amalgam, with the same complications. Addition of a little methanol in the last case aided the reaction. The potential for the samarous–samaric couple in ethanolic chloride solutions has been placed in the region of 1.9–2.3 v.

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(9) Laitinen, THIS JOURNAL, **64**, 1133 (1942); Laitinen and Taebel, Ind. Eng. Chem., Anal. Ed., **13**, 825 (1941).

(10) Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938.

(11) Noddack and Bruckl, Angew Chem., **50**, 362 (1937).