

ter employing this substance has been proposed and the effects of different conditions upon the behavior have been examined. A null method of comparison has been proposed and found satisfactory to 3% in absolute value. Other variations of the standard actinometer (as the tempera-

ture coefficients) were investigated with the aid of this null method. Other actinometers which used monochloroacetic acid and crystal violet leucocyanide were tested and found to be less desirable.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ILLINOIS]

Observations on the Rare Earths. XLIV. Preparation of Anhydrous Rare Earth Compounds by the Action of Fused and Solid "Onium" Salts on the Oxides

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Recent studies on the solubilities of rare earth compounds in non-aqueous solvents¹ and on the preparation of rare earth amalgams by electrolysis of non-aqueous solutions of their salts² have brought about the necessity of preparing anhydrous rare earth compounds, reasonably free from basic materials, and in considerable quantities. The compounds most extensively used in these studies are the halides which are exceptionally difficult to prepare in the anhydrous form. None of the many methods previously suggested for their preparation have proved entirely satisfactory when applied to relatively large quantities.

It has been found that oxides of typical rare earth elements such as lanthanum, neodymium, samarium and yttrium dissolve in such fused salts as pyridine hydrochloride,^{2d} ammonium nitrate,^{2a} hydrazine hydrochloride, hydroxylamine hydrochloride, ammonium thiocyanate³ and ammonium acetate.⁴ They react with solid ammonium chloride, ammonium bromide and ammonium iodide. These reactions are all of the same general character and may be represented by the typical equation



This reaction is readily understood if it is recognized that "onium" salts in the fused and solid states are acids according to the Brönsted defini-

(1) Hopkins and Quill, *Proc. Nat. Acad. Sci.*, **19**, 64 (1933).

(2) (a) Audrieth, Jukkola, Meints and Hopkins, *THIS JOURNAL*, **53**, 1805 (1931); (b) Meints, Hopkins and Audrieth, *Z. anorg. allgem. Chem.*, **211**, 237 (1933); (c) Jukkola, Audrieth and Hopkins, *THIS JOURNAL*, **56**, 303 (1934); (d) Hopkins and Audrieth, *Trans. Am. Electrochem. Soc.*, **66**, 135 (1934).

(3) The resulting product composed of an intimate mixture of rare earth thiocyanate and excess ammonium thiocyanate is soluble in alcohol, acetone, pyridine and liquid ammonia.

(4) Lanthanum and neodymium oxides dissolve quite readily in fused ammonium acetate, whereas only incomplete reactions occur when the less basic rare earth oxides are employed. If these melts are heated in a vacuum at temperatures between 130–150° residues consisting essentially of the anhydrous acetates may be obtained.

tion.⁵ In spite of the fact that water is one of the reaction products, the presence of excess ammonium chloride, by virtue of its acidic nature, prevents the hydrolysis of the lanthanum chloride. Hence, when carried out under proper conditions the above reaction and others of the same type may be used for the preparation of anhydrous rare earth compounds.

Experimental

Preparation of Anhydrous Rare Earth Chlorides.⁶—When ammonium chloride and oxides of the rare earth elements are mixed by grinding together in a mortar the odor of ammonia becomes distinctly noticeable, indicating that some reaction takes place even at room temperature. Up to a temperature of about 190° the reaction appears to be a very slow one, but above this temperature it proceeds vigorously. If twice the theoretical amount of ammonium chloride is used (for instance, 150 g. of NH_4Cl to 75 g. of Nd_2O_3) the reaction mixture soon becomes completely soluble in water.⁷ A considerable portion of the

(5) Audrieth and Schmidt, *Proc. Nat. Acad. Sci.*, **20**, 221 (1934).

(6) Various methods are listed in the literature for the dehydration of hydrated chlorides by heating in the presence of an excess of ammonium chloride. These procedures usually involve the addition of a large excess of ammonium chloride to a saturated solution of the chloride, after which the solution is evaporated to dryness and the mixture heated carefully by itself or in an atmosphere of hydrogen chloride. The method described by the authors not only eliminates this cumbersome procedure, but effects a considerable saving of time. The essential principle of preventing basic salt formation by the presence of the "onium" salt seems not to have been clearly defined heretofore and its elucidation (see Ref. 5) has enabled the authors to apply this method to the preparation of many other anhydrous chlorides.

It should be pointed out that Hodgkinson [*J. Soc. Chem. Ind.*, **33**, 445 (1914)] describes a method for the preparation of anhydrous chlorides, by mixing the oxides with a small excess of ammonium chloride and gradually dropping the mixture into a red hot crucible. Repeated trials of this method have shown that complete reaction is never obtained and that considerable loss of material is involved.

(7) In the case of cerium dioxide complete conversion to the chloride was not obtained.

excess ammonium chloride may then be driven off by continued heating in air. However, any attempt to drive off all of it in this manner invariably results in the formation of some basic material. The excess ammonium chloride is therefore best removed by heating the mixtures at 300–320° in a vacuum in an all-glass apparatus designed specifically for this purpose.

The anhydrous chlorides prepared by this method are obtained in finely powdered form. They are extremely hygroscopic and hiss on addition of water. Their water solutions are usually clear. No ammonia can be detected upon heating with excess sodium hydroxide. The chlorides are also readily soluble in alcohol and have been used successfully for the preparation of rare earth amalgams.²

Yields of 85 to 95% were obtained. The remaining rare earth material was not lost, but was recovered almost quantitatively from material adhering to the vessels and that used in solubility tests during the course of the reaction. Analyses of typical batches of rare earth chlorides prepared in this manner are given in Table I.

TABLE I

Nature of oxide	Cl, %		Rare earth, %	
	Calcd.	Found	Calcd.	Found
95% La, 5% Pr	43.35	43.46	56.65	56.61
60% La, 40% Pr	43.22	43.29	56.78	56.28
Pure Nd ₂ O ₃	42.43	42.77	57.57	57.3

Preparation of Anhydrous Rare Earth Bromides.—Ammonium bromide was found to react readily with rare earth oxides. By carefully heating the reaction mixture in air a completely soluble product could be obtained. This mixture was then heated in a vacuum at about 300° to remove the excess ammonium bromide. The anhydrous bromides prepared in this way were usually completely water soluble. The following is an analysis of lanthanum bromide prepared in this manner.

	La, %		Br, %	
Required for LaBr ₃	36.70		63.30	
Found	36.52	36.27	62.62	62.16

Reaction of Ammonium Iodide with Rare Earth Oxides and Sulfides.—Solid ammonium iodide and lanthanum oxide react readily at 200°. However, even if the reaction was carried out in a vacuum the final product was always insoluble in

water and found to have the approximate composition required for the compound, LaOI.

The reaction of ammonium iodide upon rare earth sulfides⁸ was also investigated in a preliminary fashion. The rare earth sulfides were found to react with excess ammonium iodide in an evacuated, sealed Pyrex tube at 450–500°. The odor of hydrogen sulfide was distinctly noticeable when the tubes were opened. The reaction mixture was then heated in vacuum until all volatile substances were removed completely. The product, which was bluish-gray in color, was only partially soluble in water. Analysis for the iodine–rare earth ratio in the water soluble portion indicated that at least partial reaction with formation of the normal iodide had taken place. Further work is being done on this problem.⁹

Summary

1. Reactions between rare earth oxides and a number of fused "onium" salts are described.
2. Rare earth oxides react at higher temperatures with ammonium chloride and ammonium bromide to yield the corresponding halides. The excess of "onium" salt may be removed by heating in a vacuum to give the anhydrous rare earth chlorides and bromides.
3. Rare earth sulfides, prepared by reduction of the sulfates with sugar charcoal, react partially with solid ammonium iodide at 450–500°. Attempts to prepare the anhydrous iodides by the action of ammonium iodide upon rare earth oxides resulted in the formation of the basic iodide.

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(8) Rare earth sulfides are generally prepared by heating the sulfates or oxides in a stream of hydrogen sulfide at red heat. This method is not readily adaptable to the preparation of large quantities. It was found that the anhydrous rare earth sulfates could be reduced readily to the sulfides by heating with an excess of sugar charcoal at bright red heat for about an hour. The resulting product contained small amounts of carbon and possibly some rare earth oxides. Sulfides prepared in this manner were used in the current investigation. Their preparation and a study of their properties will be made the subject of a future communication.

(9) Various other reactions were investigated in an attempt to prepare anhydrous rare earth iodides. Anhydrous lanthanum chloride was heated in a vacuum with excess ammonium iodide. The resulting product contained both iodine and chlorine. Repeated addition of ammonium iodide and heating failed to displace all the chlorine from the product. The reaction between anhydrous lanthanum acetate and ammonium iodide went only partially to completion. Thermal decomposition of anhydrous lanthanum iodate yielded the pure basic iodide, LaOI. Ammonium iodide and lanthanum chloride react in absolute ethanol to precipitate some of the ammonium chloride. Here again the reaction could not be made to go to completion.