Lade 5579 (full paper)

MASTER

MAR 8 1963

78255

THE PREPARATION AND THERMAL DECOMPOSITION OF
SOME RARE EARTH CARBONATES*

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MASTER

CONF 20-27

ABSTRACT

The preparation of the carbonates of lanthanum, cerium, praseodymium, neodymium, samarium, europium, and gadolinium by precipitation from homogeneous solution is described. Trichloroacetic acid is used as the source of the carbonate ion. In order to obtain the theoretical ratio of carbonate ion to rare earth ion, in general, it is necessary that the reaction be carried out under a pressure of carbon dioxide.

The thermal decomposition of these compounds in vacuum, water vapor and carbon dioxide was studied with an automatic recording vacuum thermobalance.

The course of the respective decompositions is shown by the pyrolysis curves. They may be described as follows: $M_2(CO_3)_3 \cdot xH_2O \rightarrow M_2(CO_3)_3 \rightarrow M_2O_2CO_3 \rightarrow M_2O_3 \cdot yCO_2 \rightarrow M_2O_3$ where x varies from compound to compound and the composition $M_2O_3 \cdot yCO_2$ ($y < 1$) is not always observed. Cerium carbonate is a special case.

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Introduction - The carbonates of the rare earth elements have customarily been prepared by precipitation of the lanthanon ion from a solution of alkaline bicarbonate saturated with carbon dioxide. If the normal alkaline carbonate is used, basic carbonates or double carbonates are formed.¹

A method involving precipitation from homogeneous solution in which the carbonate ion is supplied by the hydrolysis of trichloroacetate ion has been described by Salutsky and Quill². They reported the preparation, by this method, of the normal carbonates of lanthanum, neodymium, and samarium. However, the ratio of CO_2 to R_2O_3 was slightly low for lanthanum and neodymium and significantly low for samarium. The attempt to repeat this work at Los Alamos, where the barometric pressure is about 580 mm Hg, resulted in compounds having a deficiency in carbonate ion. The suggestion was made that the cause was the low barometric pressure and this was born out by further investigations.

This paper reports the preparation of the normal carbonates of lanthanum, cerium, praseodymium, neodymium, samarium, europium, and gadolinium, and a study of their thermal decomposition in vacuum, water vapor, and carbon dioxide.

Compound Preparation - The starting materials were the commercially available oxides, nominally 99.9% purity which were checked by spectroscopic analysis. Except for cerium, the carbonates were prepared by dissolving the oxide in an aqueous solution containing a slight excess of trichloroacetic acid and heating to decompose the trichloroacetate ion. The starting solutions were prepared by dissolving 10 grams of the oxide in 250 ml of the trichloroacetic acid solution, heating until precipitation started, cooling, adding crystals of trichloroacetic acid until the precipitate just dissolved, and diluting to 300 ml. The trichloroacetate solution of Ce(III) was prepared by dissolving the dioxide in hot, concentrated sulfuric acid, cooling, filtering off the $\text{Ce}(\text{SO}_4)_2$, dissolving in hot water, reducing the ceric to cerous with hydrogen peroxide, precipitating the hydroxide from homogeneous solution with urea, filtering, and dissolving the hydroxide in trichloroacetic acid solution. The solution was tested for sulfate ion with barium chloride and the process of precipitation of the hydroxide, filtration, and dissolution in trichloroacetic acid was repeated until all the sulfate ion was removed. The result was a colorless, clear solution of cerous trichloroacetate. The trichloroacetate ion concentration was adjusted as for the other solutions.

The decomposition of the trichloroacetate solutions was carried out at atmospheric pressure (~ 580 mm) in air in a covered beaker, and at 200-300 p.s.i., and 1000 p.s.i. of carbon dioxide pressure. The temperature was in the range of 80° to 90° . The times at these temperatures were about 20 minutes for the atmospheric pressure preparations, one hour for the 200-300 p.s.i. preparation and 8 to 10 hours for the 1000 p.s.i. preparations. Twenty minutes is not long enough for a quantitative yield, but a short time was used for the atmospheric

pressure runs to reduce the likelihood of hydrolysis.

The preparations in pressurized carbon dioxide were carried out in the apparatus shown in Figure 1. This is a Pyrex lined stainless steel pressure vessel, with a thermometer well, designed to stand a pressure of 2000 p.s.i. The contents were stirred magnetically with a Pyrex coated stirring bar (Teflon coated in a few of the runs, but the Teflon abraded and contaminated the product) while being heated in a hot water bath or on a Pyro-Magnestir (Labline, Inc.).

The carbonates were washed thoroughly with acetone or ethanol and then water until the washings were free of chloride by the Beilstein test, then again with acetone or ethanol and finally with ethyl ether. They were analyzed by conventional combustion analysis for carbon and hydrogen. The oxide was ignited at 1000° and weighed as the sesquioxide except for cerium, which was weighed as CeO_2 , and praseodymium, which was weighed as Pr_6O_{11} after heating over night. The results are shown in Table I.

Table I
Results of Analysis of Rare Earth Carbonate Preparations
made at Different Pressures of Carbon Dioxide

Element	580 mm (air)		200-300 PSIG		1000 PSIG	
	$\text{CO}_2/\text{R}_2\text{O}_3$	$\text{H}_2\text{O}/\text{R}_2\text{O}_3$	$\text{CO}_2/\text{R}_2\text{O}_3$	$\text{H}_2\text{O}/\text{R}_2\text{O}_3$	$\text{CO}_2/\text{R}_2\text{O}_3$	$\text{H}_2\text{O}/\text{R}_2\text{O}_3$
La	2.98	7.99	3.01	8.01	2.99	6.44
Ce	2.79	4.89	2.98	7.97	2.93	3.30
Pr	3.04	7.87	2.98	7.96	2.97	4.57
Nd	2.93	4.80	3.01	8.28	2.94	2.14
Nd*			3.00	2.09		
Sm	2.71	2.37	2.98	2.50	2.95	2.14
Eu	2.77	3.19	2.97	2.20	2.96	2.17
Gd	2.63	3.91	2.99	2.44	2.97	2.17

*In this preparation the pressure was 100 PSIG and the temperature was about 93°.

The uncertainty in the $\text{CO}_2/\text{R}_2\text{O}_3$ ratios is about 0.01 but differences of 0.02 or 0.03 from the theoretical 3.00 are not considered significant. The uncertainty in the $\text{H}_2\text{O}/\text{R}_2\text{O}_3$ ratios is about 0.04.

The carbonates were also examined by X-ray diffraction. At the time of writing this preliminary version of this paper, the results of the X-ray examination are not complete. They will be reported at the meeting and included in the final draft of the paper.

Thermal Decomposition - The thermal decomposition of the carbonates prepared at 200-300 PSIG was studied in vacuum, in water vapor, and in carbon dioxide with a recording vacuum thermobalance³. The resulting

curves are shown in Figures 2 - 8. They have many characteristics in common. In vacuum there is an initial loss of water leading to a more or less well defined plateau at a weight loss corresponding to the anhydrous normal carbonate. This plateau is most prominent for La, Ce, Pr and Nd and least prominent for Sm, Eu, and Gd. Continuation of the temperature rise leads to decomposition of the carbonate. For La and Pr there is a definite indication of a plateau at a weight loss corresponding to the formula $R_2O_2CO_3$. For the others this composition is barely evident, if at all. Cerium is a special case because oxidation to Ce(IV) apparently takes place in this region.

In water vapor there is no evidence for any intermediate hydrates between the starting material and the anhydrous carbonate except that for $Nd_2(CO_3)_3 \cdot 8H_2O$ there is a suggestion of a plateau at about the right place for the dihydrate.

The starting material for the runs in carbon dioxide was the anhydrous carbonate prepared by dehydrating the hydrated carbonate at a temperature below the decomposition point of the anhydrous carbonate. In all cases, except for cerium which will be discussed later, there is a definite plateau for the monocarbonate, $R_2O_2CO_3$. The decomposition of this compound to give the oxide proceeded through an intermediate step for Nd, Sm, Eu and Gd. The composition of this intermediate varied from compound to compound, being $Nd_2O_3 \cdot 0.75 CO_2$, $Sm_2O_3 \cdot 0.80 CO_2$, $Eu_2O_3 \cdot 0.12 CO_2$ and $Gd_2O_3 \cdot 0.87 CO_2$ respectively. This intermediate compound was not found for La and is uncertain for Pr.

Several runs were made on neodymium carbonate and the intermediate was not always found, and where found, it was not always of the same composition.

The temperatures of decomposition of the various carbonates are shown on an expanded scale in Figure 9. There is a general trend toward lower decomposition temperatures at higher atomic weights for the monocarbonates and also for the compound intermediate between it and the oxide, but the correlation is not perfect. Gd and Eu seem to be in reverse order for the monocarbonate. For the normal carbonates, La has the highest decomposition temperature, but otherwise the order is not clear, possibly because the decomposition temperatures lie so close together that rate effects mask any trend.

Lanthanum oxide will take up enough CO_2 in a few minutes to form $La_2O_2CO_3$ as is shown in Figure 2. This result was not observed for the other oxides. When neodymium oxide was held for several hours at a temperature ($\sim 670^\circ$) in the region where the monoxide was expected to form, it did indeed form slowly. In the case of gadolinium oxide, the monocarbonate did not form, even after many hours.

X-ray examination of the various solid decomposition products is being undertaken and the results will be reported at the meeting, and in the final draft of the paper.

Discussion - The carbonates of the rare earth elements have been studied by Preiss and co-workers^{4,5} (La, Ce, Pr, Nd), Ambrozhi et al.⁶ (La, Ce, Pr, Nd, Sm), Wendlandt and George⁷ (La, Pr, Nd, Sm, Eu, Gd), Sklyarenko et al.⁸ (La), and Domingues and co-workers^{9,10} (La, Ce, Pr, Nd, Sm). These different investigators have not always found the same numbers of waters of hydration for a given rare earth carbonate, and it is probable that the amount of hydration water depends on the temperature of preparation and subsequent history of the product. Only Preiss and Rainer⁵ studied the thermal decomposition in a carbon dioxide atmosphere, the other studies being carried out in air. All the investigators agree on the existence of the normal carbonates, $R_2(CO_3)_3$ and monocarbonates, $R_2O_2CO_3$, except for cerium in the latter case. The compound $Nd_2O_3 \cdot \frac{1}{2} CO_2$ intermediate between the monocarbonate and the oxide, was found by Preiss and Rainer⁵ and by Ambrozhi et al.⁶. It has also been observed in the thermal decomposition of neodymium oxalate^{10,11}. Similar compounds for the other rare earth elements have not been reported. The interpretation of the thermal decomposition of cerous carbonate is complicated by the concurrent oxidation of the cerium to the ceric state and the previous investigators are not in agreement.

The work reported here is in qualitative agreement with the previous work and is more quantitative and more extensive. The reversibility of the decomposition of $La_2O_2CO_3$ and $Nd_2O_2CO_3$ has been demonstrated. The presence of an intermediate carbonate between the monocarbonate and the oxide has been shown for samarium, europium, and gadolinium, and confirmed for neodymium. An inverse correlation has been shown between the temperature of decomposition of the monocarbonate and the atomic number of the rare earth element, i.e., a direct relation between decomposition temperature and basicity.

Acknowledgments - The authors wish to thank T. W. Newton for his helpful suggestions, Raymond George for help in compound preparation, and F. H. Ellinger for X-ray diffraction analysis.

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Figure 4.

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Figure 5.

Figure 6.

Figure 7.