STUDIES ON HYDRATED CERIC OXIDE

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Abstract—The results of physico-chemical studies on hydrated ceric oxide analysing to the formula CeO₃·2H₂O are presented. By thermogravimetric and differential thermal analysis, earlier findings on the stability of ceric hydroxide at higher temperatures have been disproved. Attempts have been made to elucidate the structure of the material from X-ray diffraction patterns and infra-red spectra. Results obtained from these studies suggest that hydration of ceric oxide destroys the fluorite structure.

THE oxidation product of cerous hydroxide has been variously described as ceric hydroxide, hydrated ceric oxide etc. (1-9) The author has developed a simple method (10)for the preparation of a product analysing to CeO₂·2H₂O which is used by him in the isolation of hexachloroceric acid crystals.⁽¹¹⁾ In view of the contradictory statements regarding the stability and composition of hydrous ceric oxide, a systematic study has been attempted by the present author. Results of thermal degradation, differential thermal analysis and X-ray examination of ceric oxide dihydrate are given in this paper.

EXPERIMENTAL

Pure cerous nitrate (25 g) was dissolved in about 500 ml water and cerous hydroxide precipitated with 2 N ammonium hydroxide. Hydrogen peroxide (30 vol) was then added with vigorous stirring till the precipitate became dark brown. The solution was kept on a water bath and stirred for 1 hr when the evolution of oxygen ceased and the precipitate became straw-yellow in colour. The precipitate was filtered off and washed free of soluble impurities. It was pressed between folds of filter paper, washed several times by decantation and then on a sintered funnel with dry dioxane. The adsorbed dioxane was removed by washing with dry petroleum ether. Finally a current of dry, carbon-dioxide-free air was passed for 1 hr. The product obtained was a dry, free-flowing, yellow powder. The material was analysed for water and cerium. (Found: Ce 67.15%; H₂O 17.52%; Calc. for CeO₂, 2H₂O: Ce 67.31%; H₂O 17.31%).

Thermogravimetric analysis

A known weight of the hydrous ceria, in a shallow platinum crucible, was placed in an electric muffle, the temperature of which could be maintained within $\pm 5^{\circ}$ C. After heating the sample for one hour at the desired temperature, the loss in weight was noted. The results are presented in Table 1.

Differential thermal analysis

The apparatus employed was essentially the same as described by NORTON, (12) except for the fact that the furnace was mounted vertically. Ignited alumina was used as the inert material and chromelalumel thermo-couples were used with cold junctions. The e.m.f. due to the differential temperature

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was measured with a high sensitivity (LEEDS and NORTHRUP) galvanometer and a lamp and scale arrangement. The furnace temperature was raised at the rate of 10°C/min and was measured by the null-point method. The results are given in Fig. 1.

Temperature (°C)	Loss in weight (g)	Loss of water (moles)
125	0.127	1.49
225	0.129	1.49
325	0.129	1.49
425	0.164	1.87
525	0.165	1.89
625	0.167	1.91
725	0.172	1.97
825	0.175	2.00

TABLE	1.—DEHYDRATION	AT	VARIOUS	TEMPERATURES
	Wt. of material t	ake	n = 1.0)00 g

X-Ray diffraction pattern

The instrument used was Philip's wide range diffractometer, an automatically recording Geiger counter instrument with CuK α radiation filtered through nickel and operated at 40 KVP and 15 mA. The scanning speed used in all these recordings was $2\theta/\min$. Diffraction patterns were taken with (1) a wet sample of the product obtained by oxidation of cerous hydroxide with hydrogen peroxide.



FIG. 1.-D.T.A. curve of ceric hydroxide; inert material alumina; rate of heating 10°C/min.

(2) a sample of the above oxidation product washed with dioxane and petroleum ether, (3) a sample after drying to constant weight at 110° C, and (4) a sample after ignition at 900° C.

Infra-red spectrum

A Grubb-Parsons double-beam, automatically recording instrument was used. Spectra were taken in Nujol mull of (1) a sample of the oxidation product of cerous hydroxide washed with dioxan and petroleum ether and analysing to $CeO_2 \cdot 2H_2O$ (Fig. 2) and (2) a sample of the above substance ignited at 900°C to give CeO_2 (Fig. 3).

Because of the colour and powdery nature of the substance, attempts to record the Raman spectrum were unsuccessful.*

* Private communication from Dr. R. S. KRISHNAN, Professor of Physics, Indian Institute of Science, Bangalore, India.

DISCUSSION OF RESULTS

The results of thermogravimetric and differential thermal analyses did not agree with the earlier findings of CARNELLY and WALKER⁽¹⁾ that ceric hydroxide was stable up to 600°C. Heating for 1 hr at 125°C removed 1.5 moles of water (Table 1) leaving a product corresponding to the formula $2\text{CeO}_2 \cdot \text{H}_2\text{O}$. This product is stable up to



FIG. 2.-Infra-red spectrum of ceric hydroxide in Nujol mull.

325°C as no appreciable loss in weight is noticed even at this temperature. There is a sudden increase in loss of water at 425°C, further dehydration taking place progressively with rise in temperature and becoming complete at 825°C. These observations are supported by the shape of the D.T.A. curve (Fig. 1). The peak at 123°C



FIG. 3.—Infra-red spectrum of product of igniting ceric hydroxide at 900°C, in Nujol mull.

corresponds to dehydration up to 2CeO_2 ·H₂O. Complete dehydration is indicated by the peak at 820°C. The shape of the curve suggests that changes between 350° and 650°C are negligible and that dehydration becomes more marked above 650°C, becoming complete at 820°C.

The X-ray diffraction patterns showed that the oxidation product of cerous hydroxide was poorly crystalline. Both the wet sample and the sample after washing with dioxan and petroleum ether (CeO₂·2H₂O) give identical patterns, showing no crystalline phase of particles of size greater than 30-40 Å. The fluorite structure was completely absent. But the product dried to constant weight at 110°C showed an increase in crystalline size and development of the fluorite pattern. Ignition at 900°C gave the fluorite pattern and spacing characteristic of CeO₂.

The observed peak at 2.97 μ in the infra-red spectrum of CeO₂2H₂O is within the frequency range for chelate compounds with strong intra-molecular bonds. In fact, the peak which is prominent in (Fig. 2) and which is absent in (Fig. 3) for the ignited material, has the shape and appearance, characteristic of strongly bonded OH absorption near 3000 cm⁻¹. The OH absorption band is shifted from the value (2.71 μ) of the unbonded OH in water to 2.97 μ , presumably due to intra-molecular bonding.

There is good agreement between the results of thermal degradation studies and differential thermal analysis of $CeO_2 \cdot 2H_2O$ with respect to its dehydration process. However, it is not clear from the X-ray and I.R. spectra whether the oxidation product of cerous hydroxide is hydrated ceria or ceric hydroxide. Success in recording the Raman Spectra might have helped in elucidating this problem.

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