

## Hydrothermal Preparation of Some Rare Earth Trihydroxides and Some Rare Earth Oxide Hydroxides at Temperatures up to 900°C and Pressures up to 55 kb

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Hydrothermal methods have been used in the preparation of some rare earth trihydroxides and rare earth oxide hydroxides using pressure bombs, lined with pure silver or pure gold, at temperatures up to 500°C and pressures up to 700 atm.<sup>1-6</sup> It has, however, been reported, that compounds containing hydroxyl groups can be prepared at higher temperatures and pressures. In an investigation by Wilhelmi<sup>7</sup> of the system MoO<sub>3</sub>-MoO<sub>2</sub> at 25 kb using a girdle high-pressure apparatus,<sup>8</sup> a partial transformation of MoO<sub>3</sub> to Mo<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub> was observed. It was assumed that the hydrogen necessary for the reduction of MoO<sub>3</sub> came from pyrophyllite, which can give off hydrogen in the temperature interval 600-1000°C.<sup>7</sup> In an investigation by Waintal<sup>9</sup> of the system Fe<sub>2</sub>O<sub>3</sub>-In<sub>2</sub>O<sub>3</sub> at 110 kb and 1200°C using a high-pressure belt apparatus, indium oxide hydroxide was obtained. An investigation was undertaken to prepare rare earth hydroxide phases using temperatures over 500°C and pressures of 50-55 kb, in order to obtain hydroxide phases with densities greater than the densities of the known rare earth trihydroxides and rare earth oxide hydroxides.

Holmium oxide hydroxide, HoOOH, prepared according to Ref. 1, was treated in a belt high-pressure apparatus at 50 kb and 800°C for 1 h. The apparatus has been described by Waintal.<sup>9</sup> The X-ray powder pattern of the crystalline product, taken with a Guinier camera, using FeK $\alpha_1$  radiation, indicated a complete transformation of the monoclinic holmium oxide hydroxide to a new phase. All lines of the powder pattern were indexed on the basis of a tetragonal unit cell with the cell param-

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eters given in Table 1. The new phase was assumed to be a tetragonal modification of holmium oxide hydroxide. The change in volume by the transformation from the monoclinic to the tetragonal modification is -6%.

Table 1. Unit cell parameters for the tetragonal modification of some rare earth oxide hydroxides using FeK $\alpha_1$ =1.93597 Å. Standard deviations in parantheses.

MOOH	a (Å)	c (Å)
Dy	5.57(3)	5.446(9)
Ho	5.541(6)	5.410(2)
Er	5.517(4)	5.383(1)
Tm	5.507(4)	5.364(1)
Yb	5.48(2)	5.326(4)

The high-pressure belt apparatus has been used in the hydrothermal preparation of some rare earth trihydroxides and the tetragonal modification of some rare earth oxide hydroxides at the experimental conditions given in Table 2. The starting

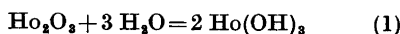
Table 2. Experimental conditions for hydrothermal preparations. Reaction time: 1 h.

Starting material	Pressure kb	Temp. °C	Product <sup>a</sup>
Nd(OH) <sub>3</sub>	55	700	Nd(OH) <sub>3</sub>
Sm <sub>2</sub> O <sub>3</sub>	55	700	Sm(OH) <sub>3</sub>
Eu <sub>2</sub> O <sub>3</sub>	55	700	Eu(OH) <sub>3</sub>
Gd <sub>2</sub> O <sub>3</sub>	55	700	Gd(OH) <sub>3</sub>
Dy <sub>2</sub> O <sub>3</sub>	55	700	Dy(OH) <sub>3</sub> DyOOH
Ho <sub>2</sub> O <sub>3</sub>	55	900	Ho(OH) <sub>3</sub> HoOOH
Er <sub>2</sub> O <sub>3</sub>	55	700	ErOOH
Tm <sub>2</sub> O <sub>3</sub>	50	800	TmOOH
Yb <sub>2</sub> O <sub>3</sub>	55	700	YbOOH

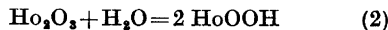
<sup>a</sup> All trihydroxides are the usual known modification and all oxide hydroxides are the new tetragonal modification.

materials were wetted with a 50% solution of NaOH in water, and were kept in platinum ampoules, with a volume of 26 mm<sup>3</sup>. The crystalline products were in some

cases still moist after the experiments. The formation of the trihydroxides or of the oxide hydroxides is dependent on the amount of solution used. In the reactions



and



the volume difference between product and reaction mixture is greatest for (1), and the formation of the trihydroxide is to be expected, when sufficient solution is present. Powder patterns of all products were obtained as for the tetragonal modification of holmium oxide hydroxide, and the rare earth oxide hydroxide phases were indexed, using the tetragonal unit cell parameters given in Table 1.

Single crystals of tetragonal ytterbium oxide hydroxide were prepared from a mixture of ytterbium oxide and solid sodium hydroxide. The mixture was allowed to absorb humidity from the atmosphere for a few min, and was then placed in a platinum ampoule and treated in the high-pressure belt apparatus at 50 kb and 800°C for 1 h. The sample was then slowly cooled to 600°C over a period of 30 min, followed by fast cooling to room temperature. The crystals were washed with water and dried at room temperature.

A single crystal was investigated by precession methods using MoK $\alpha$ -radiation ( $\lambda = 0.7107 \text{ \AA}$ ). Photographs were taken of  $hk0$ ,  $hk1$ ,  $hk2$ , and  $hhl$ . The reflections  $h00 = 2n + 1$  are absent. The symmetry of the photographs are in agreement with the space group  $P4_2m$  (No. 113). The crystal structure determination of the compound is in progress.

The present investigation shows, that high-pressure modifications of hydroxides can be obtained by hydrothermal synthesis at very high temperatures and pressures, and that a new experimental hydrothermal technique can be applied, using high-pressure belt apparatus.

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Received October 6, 1970.

## Stereoselective Synthesis of Triglochinic Acid, (*E*)-2-Butene-1,2,4-tricarboxylic Acid, Derived from the Cyanogenic Glucoside Triglochinin

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In a previous communication,<sup>1</sup> the isolation and constitutional assignment of a novel cyanogenic glucoside, triglochinin (IX), were described. This glucoside, unique within the group of cyanogenic glycosides in containing carboxylic functions in the aglycone,<sup>2</sup> was shown to decompose on enzymic or acid catalyzed hydrolysis to a hitherto unknown carboxylic acid, triglochinic acid (VI), along with glucose and HCN.<sup>1</sup> The (*E*)-configuration of the title compound (VI) has presently been elucidated by synthesis as depicted in the scheme below. It follows, provided the degradations of triglochinin (IX) are not accompanied with rearrangements at the 3,4-double bond, that the configuration of this double bond is (*E*). Further studies of the stereochemistry of the glucoside (IX) are in progress.

Condensation of acetaldehyde with 1-methoxycarbonylethylidetriphenylphosphorane (Wittig reaction) has been shown to furnish a mixture of methyl (*E*)-2-methyl-2-butenolate (methyl tiglate) and its stereoisomer (methyl angelate) in the