

22°C was collected. Yield of IV: 0.50 g (5.44 mmoles).

$^{13}\text{C}-\text{C}_6\text{H}_5\text{N}_3\text{BF}_4$: (IV) was converted to (V) using a modification of Flood's method (Ref. 2). A mixture of 0.50 g (5.44 mmoles) of (IV), 1.38 ml conc. HCl and 1.38 ml H_2O was cooled to -8°C and maintained at this temperature during the preparation. A diazotization was effectuated by adding 0.4 g (5.8 mmoles) NaNO_2 in 1.1 ml water. Afterwards 0.1 g (1.02 mmoles) Na_2CO_3 was added under magnetic stirring. When all was dissolved 0.66 g (6.10 mmoles) NaBF_4 in 3 ml water was added. The mixture was stirred for 10 min and filtered. After washing with 1 ml water and 1 ml methanol at 0°C and drying *in vacuo* over P_2O_5 , 0.60 g (3.16 mmoles) of (V) was obtained.

$^{13}\text{C}-\text{C}_6\text{H}_5\text{F}$: Following Ref. 2 (V) was decomposed to (VI) on the vacuum-line at $110-117^\circ\text{C}$. All the volatile reaction products were passed through a trap cooled to *ca.* -80°C . Here (VI), all higher boiling substances, and part of the BF_3 condensed. After removal of BF_3 the residue was distilled. 0.24 g (2.54 mmoles) of (VI) was collected at a vapour pressure of 55 mm Hg at 22°C . The over-all yield of this five-step-preparation was *ca.* 15 %.

In the infrared spectrum of (VI) in the liquid phase, all absorption bands could be attributed to fluorobenzene or ^{13}C -fluorobenzenes. Isotope effects could be observed in the regions of CF-stretching vibrations at 1200 cm^{-1} and CH-stretching vibrations at 3020 cm^{-1} .

Microwave studies of the isotopic species are in progress.

1. Bak, B., Christiansen, J., Lipschitz, L. and Tormod Nielsen, J. *Acta Chem. Scand.* **16** (1962) 2318.
2. Flood, D. T. *Org. Syn. Coll. Vol.* 2 p. 295, (1955).
3. Vogel, A. I. *Textbook of Practical Organic Chemistry*. Longmans, Green & Co. 1957, p. 525.

Received February 22, 1966.

Hydrothermal Preparation of some Rare Earth Trihydroxides and Rare Earth Oxide Hydroxides

A. NØRLUND CHRISTENSEN

*Department of Inorganic Chemistry,
University of Aarhus, Aarhus C., Denmark*

Hydrothermal methods have been used in the preparation of oxide hydroxides of holmium, erbium, and ytterbium.¹ Microcrystals of $\text{Ce}(\text{OH})_3$, $\text{Tb}(\text{OH})_3$, $\text{Dy}(\text{OH})_3$, $\text{Ho}(\text{OH})_3$, $\text{Er}(\text{OH})_3$, $\text{Tm}(\text{OH})_3$, and DyOOH were prepared using similar methods. Hydrothermal preparation of rare earth trihydroxides and rare earth oxide hydroxides has been reported previously by other authors.²⁻⁵ Recently hydrothermal preparation of these compounds has been intensively investigated by Klevtsov and Sheina.⁶ The unit cell parameters which they report were calculated from powder patterns obtained with 57.3 mm and 114.6 mm Debye-Scherrer cameras. Since a Guinier camera of 114.6 mm diameter was used in the investigation reported here, and since the data processing by the author is probably more elaborate, the author considers his data to be of greater precision than other previously reported.

Microcrystals of the rare earth trihydroxides and rare earth oxide hydroxides were formed by treating freshly precipitated rare earth hydroxides with water or a sodium hydroxide solution in a 20 ml pressure bomb lined with pure silver. The balanced pressure technique was used. Table 1 gives the experimental conditions. The reaction products were identified from Guinier powder patterns. A quadruple camera of the de Wolff type was used. Purified sodium chloride was used as internal standard. The powder patterns had sharp lines and a reasonable precision in the determination of the unit cell dimensions was obtainable. The powder patterns were indexed by using a GIER-ALGOL least squares program which gives the powder lines the weight $\sin 2\theta$ and permits changes of the unit cell parameters step by step. The unit cell parameters obtained from the X-ray diffraction data for $\text{Ce}(\text{OH})_3$, $\text{Tb}(\text{OH})_3$, $\text{Dy}(\text{OH})_3$, $\text{Ho}(\text{OH})_3$, $\text{Er}(\text{OH})_3$, and $\text{Tm}(\text{OH})_3$ are listed in Table 2. The unit cell parameters are compared with

Table 1. Experimental conditions.

Temp. °C	Pressure atm.	Time h	Conc. of NaOH solution	Result	Crystal size mm
420	700	40		Ce(OH) ₃	0.001
245	45	40	2.2 m	Tb(OH) ₃	0.001
270	54	43	0.1 m	Dy(OH) ₃	0.001
500	500	60	1.0 m	DyOOH	0.001
260	46	66	2.9 m	Ho(OH) ₃	0.04
230	28	67	1.5 m	Er(OH) ₃	0.04
193	12	66	2.6 m	Tm(OH) ₃	0.04

some recently reported values.⁶ The powder patterns will be sent to the ASTM index.

Dy(OH)₃ and Ho(OH)₃ were analysed by EDTA titration.⁷ (Found: Dy 76.11. Calc. for Dy(OH)₃: Dy 76.12. Found: Ho 76.45. Calc. for Ho(OH)₃: Ho 76.38).

The unit cell parameters obtained from the X-ray powder pattern of DyOOH is listed in Table 3. The unit cell parameters of some other rare earth oxide hydroxides are given for comparison. The powder pattern of EuOOH reported by Rau and Glove⁸ was indexed by the author on the

basis of a monoclinic unit cell with $a = 6.12$ Å, $b = 3.72$ Å, $c = 4.39$ Å, $\beta = 109.0^\circ$, and independently by Bärnighausen⁹ using a similar unit cell. The setting used by Klevtsov and Sheina⁶ is different from the setting used by the author. If the axes $a' b' c'$ chosen in Ref. 6 are transformed according to the following scheme $a = -a' - c'$, $b = b'$, $c = a'$ the unit cell parameters given in Table 3 are obtained. The variation in the unit cell parameters illustrates the lanthanide contraction. This contraction can also be seen from Fig. 1 and Fig. 2

Table 2. Unit cell parameters for rare earth trihydroxides using $\text{CuK}\alpha_1 = 1.54051$ Å, $a_{\text{NaCl}} = 5.6389$ Å.

M(OH) ₃	a (Å)	c (Å)	Ref.
Ce	6.50 ± 0.01	3.82 ± 0.01	
Tb	6.312 ± 0.005 6.28	3.601 ± 0.005 3.57	6
Dy	6.280 ± 0.005 6.26	3.569 ± 0.005 3.56	6
Ho	6.255 ± 0.005 6.24	3.545 ± 0.005 3.53	6
Er	6.232 ± 0.005 6.225	3.518 ± 0.005 3.51	6
Tm	6.233 ± 0.005 6.21	3.501 ± 0.005 3.49	6

Table 3. Unit cell parameters for rare earth oxide hydroxides.

MOOH	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β	Ref.
Nd	6.24	3.805	4.39	108.1	6
Sm	6.13	3.77	4.36	108.6	6
Eu	6.10	3.73	4.34	108.6	6
	6.12	3.72	4.39	109.0	
	6.109	3.748	4.347	108.6	9
Gd	6.06	3.71	4.34	108.9	6
Tb	6.04	3.69	4.33	109.0	6
Dy	5.98	3.64	4.29	109.0	6
	6.02	3.66	4.33	109.0	
Ho	5.96	3.63	4.29	109.0	6
	5.96	3.64	4.31	109.1	1
Er	5.93	3.62	4.27	109.2	6
	5.94	3.62	4.30	109.3	1
Tm	5.89	3.59	4.25	109.3	6
Yb	5.88	3.58	4.25	109.4	6
	5.87	3.58	4.27	109.3	1
Lu	5.84	3.55	4.23	109.5	6

which shows the variation in the cubic root of the unit cell volumes of rare earth trihydroxides and rare earth oxide hydroxides *vs.* cation radius. The radii of the cations were those reported by Templeton and Dauben.¹⁰ A linear relationship between the unit cell dimensions and the cation radius for the *C*-type cubic rare earth oxide structures was reported by Roth and Schneider.¹³

The rare earth oxide hydroxides probably all have the holmium oxide hydroxide structure.¹ The infra-red spectra of DyOOH, HoOOH, ErOOH, and YbOOH have been obtained over the frequency

range 400 to 4000 cm^{-1} on a Perkin-Elmer Model 521 spectrophotometer. The pellet technique was used. A mixture of 4 mg of sample and 200 mg of CsI was used. The infra-red spectra all have a sharp absorption band close to the absorption band of a free OH ion.^{14,15} Table 4 gives the position of the absorption bands. For a comparison the positions of the absorption bands of the isostructural compounds EuOOH⁸ and YOOH¹⁶ are given. From the infra-red spectra only it is hard to draw any conclusions on the existence of hydrogen bonding in the rare earth oxide hydroxide structures.

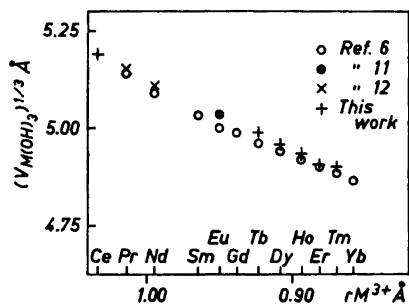


Fig. 1. Cubic root of the unit cell volumes (Å) of $\text{M}(\text{OH})_3$ *vs.* ionic radii of M^{3+} (Å). Unit cell parameters from the present work and from Refs. 6, 11, 12 have been used.

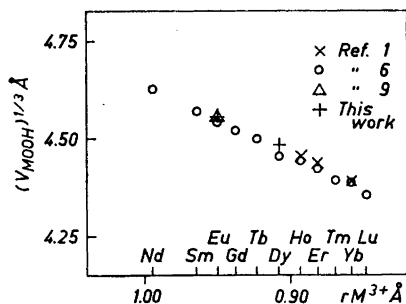


Fig. 2. Cubic root of the unit cell volumes (Å) of MOOH *vs.* ionic radii of M^{3+} (Å). Unit cell parameters from the present work and from Refs. 1, 6, 9 have been used.

Table 4. Absorption bands in infra-red spectra of MOOH.

MOOH	Absorption cm^{-1}	Ref.
Y	3610	16
Eu	3585	8
Dy	3600	
Ho	3610	
Er	3610	
Yb	3610	
Free OH^-	3580–3670	14
	3590–3650	15

Acknowledgements. I am indebted to Professor S. Brodersen of the Department of Chemical Physics, Aarhus University, for the use of the spectrophotometer, to Mrs. S. Andersen and Miss E. Brandt for recording the infra-red spectra, and to Professor S. E. Rasmussen for his interest in this work.

- Christensen, A. N. *Acta Chem. Scand.* **19** (1965) 1391.
- Shafer, M. W. and Roy, R. *J. Am. Ceram. Soc.* **42** (1959) 563.
- Fricke, R. and Seitz, A. *Z. anorg. Chem.* **254** (1947) 107.
- Fricke, R. and Dürrwächter, W. *Z. anorg. Chem.* **259** (1949) 305.
- Roy, R. and McKinstry, H. A. *Acta Cryst.* **6** (1953) 365.
- Klevtsov, P. V. and Sheina, L. P. *Izv. Akad. Nauk. SSSR., Neorg. Materialy* **1** (1965) 912.
- Schwarzenbach, G. *Die komplexometrische Titration*, Stuttgart 1960, p. 69.
- Rau, R. C. and Glover, Jr., W. J. *J. Am. Ceram. Soc.* **47** (1964) 382.
- Bärnighausen, H. *Acta Cryst.* **19** (1965) 1047.
- Templeton, D. H. and Dauben, C. H. *J. Am. Chem. Soc.* **76** (1954) 5237.
- Eick, H. A., Baenziger, N. C. and Eyring, L. *J. Am. Chem. Soc.* **78** (1956) 5987.
- Zachariasen, W. H. *Acta Cryst.* **1** (1948) 265.
- Roth, R. S. and Schneider, S. J. *J. Res. Natl. Bur. Std.* **64 A** (1960) 309.
- Cross, A. D. *Introduction to practical infra-red spectroscopy*, London 1960, p. 61.
- Bellamy, L. J. *The infra-red spectra of complex molecules*, London 1958, p. 96.
- Klevtsova, R. F. and Klevtsov, P. V. *Zh. Strukt. Khim.* **5** (1964) 860.

Received February 16, 1966.

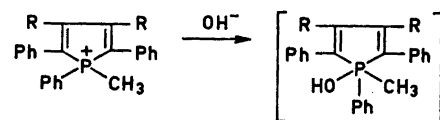
Alkaline Decomposition of Some Unsaturated Cyclic Phosphonium Compounds

KNUT BERGESEN

Chemical Institute, University of Bergen, Bergen, Norway

The alkaline decomposition of quaternary phosphonium compounds has been studied by several workers.¹⁻⁷ It has been found that the reaction of hydroxyl ions with alkyl- as well as aryl-substituted phosphonium compounds gives phosphine oxides and hydrocarbons as chief products. Depending on the stability of the leaving negatively charged organic group, the decomposition is known to obey third order¹⁻⁷ or second order kinetics.⁵ The order of readiness with which the hydrocarbon group is displaced by hydroxyl ions is: *p*-nitrobenzyl > benzyl > phenyl > methyl > phenethyl > ethyl higher alkyl groups.

This paper reports the hydrolysis of the five-membered unsaturated cyclic phosphonium compounds, 1,2,5-triphenyl-1-methyl phospholium iodide (III) and 1,2,3,4,5-pentaphenyl-1-methyl phospholium iodide (IV). Similar to the observation of Aksnes and Songstad⁸ for the decomposition of *p*-nitrobenzyl-substituted phosphonium compounds, the present compounds show second order kinetics: first order dependence on the concentration of phosphonium ion and first order on hydroxyl ion (Table 1). The hydrolysis results in cleavage of the five-membered ring at the P—C bond with formation of phosphine oxide; methyl phenyl (1,4-diphenyl-



III: R = H

IV: R = Ph



V: R = H

VI: R = Ph