TABLE I

COMPARISON OF SOME OF THE CURIUM BANDS IN SOLIDS WITH THOSE IN SOLUTION

1.3 *M* $HClO_4$[a] λ(mμ)	ε	Solid[21] CmF_3 λ(mμ)	Relative intensity[c]	Solid[b] CmF_3 λ(mμ)	Relative intensity	(Absorption)[25] $CmCl_3$ in $LaCl_3$ λ(mμ)	(Fluorescence)[25] $CmCl_3$ in $LaCl_3$ λ(mμ)
454.3	3.8	449.0	w				460.6
433.2	6.3						460.3
396.4	55.2	395.0	s				458.8
381.1	32.7	378.0	m			383.5	400.1
375.4	28.9	374.0	m			383.0	399.5
287.5	3.4			282.6	2	378.7	399.0
277.0	2.5			277.4	10	377.6	398.4
270.2	1.4			268.0	6		
				236.8	4		

[a] Present study. [b] D. C. Feay, UCRL-2547 (April 12, 1954). [c] W = weak or broad peak; m = moderately sharp peak; s = sharp peak.

band positions found. Using the same assumptions which gave good agreement between calculated and observed data for U(IV) indicates that the ^6I and ^6P levels should be the lowest excited levels over the ^8S ground state, with ^6I lying below ^6P. Calculations for Gd(III) result in the same relationships; however, evidence from the crystal absorption spectra of $Gd_2(SO_4)_3$ and $GdAc_3$ indicates that the ^6P state lies lowest over the ground level.[24] Similar considerations appear to apply to Cm(III), although there is presently no conclusive evidence.

Table I summarizes most of the presently available data on the curium absorption bands. A study of the fluorescence spectra of $CmCl_3$ in $LaCl_3$ has confirmed the presence of curium bands near 450 and 400 mμ, and they were ascribed to transitions between ^6P and the ^8S ground level.[25] A recent study of the absorption spectrum of CmF_3 gave good agreement with the results obtained in solution.[21]

(24) S. P. Cook and G. H. Dieke, *J. Chem. Phys.*, **27**, 1213 (1957).

(25) J. G. Conway, J. C. Wallman, B. B. Cunningham and G. V. Shalimoff, *ibid.*, **27**, 1416 (1957).

LEMONT, ILLINOIS

[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY DIVISION, BATTELLE MEMORIAL INSTITUTE]

Preparation of Anhydrous Rare Earth Chlorides for Physicochemical Studies[1]

BY J. F. MILLER, S. E. MILLER AND R. C. HIMES

RECEIVED MARCH 21, 1959

A method for synthesizing anhydrous rare earth chlorides is presented and discussed. This method, which is based on conversion of the oxides or mixtures of oxides by reaction with carbon tetrachloride vapor at elevated temperatures, yields chlorides which appear to be superior in quality to those prepared by several other methods which have been described in the literature and were investigated in this research.

Introduction

In precise studies of the physicochemical properties of materials, composition and purity of the samples to be studied are, obviously, of primary importance. Halides of the higher-valent metals such as U, W, Mo, Co, Fe, Al and the rare earth elements, present a special problem in this area. Because of the ease with which they hydrolyze, obtaining the anhydrous compounds, making up samples to a definite size or composition and preserving purity through any required sample transfers are very difficult. In the course of a recent investigation dealing with physical properties of the chlorides of the rare earth elements and yttrium, these difficulties were circumvented by devising a preparative method by which the required samples could be synthesized *in situ* (*i.e.*, within the containers in which they were to be studied). Details of this method, which is based on conversion of the oxide or mixture of oxides by reaction with carbon tetrachloride vapor at elevated temperatures, are discussed in this paper.

The method described here is suited to the preparation of either an individual rare earth chloride or mixtures of rare earth chlorides of predetermined compositions. The method is convenient; the necessary reaction can be carried out in a single small container (only about double the volume required to contain the sample in powder form), and the chlorides obtained appear to be superior to those prepared by the several other methods tested.

(1) Appreciation is expressed to Grace Research and Development Division, W. R. Grace and Company, for support of the work described in this paper and for permission to publish the results.

Discussion

Numerous methods of preparing anhydrous rare earth chlorides are described in the literature.[2] In the course of work which preceded development of the subject method, a number of these methods were investigated. Chlorination of oxides with ammonium chloride[3] and dehydration of the hydrated chlorides in dry HCl[4] proved to be cumbersome and failed to give complete conversion to the chlorides. The latter observation is in agreement with that of Harrison.[5] Further, serious sample losses occur as ammonium chloride or water is removed.

Chlorination of the oxides with HCl alone[6] or HCl in combination with a reducing agent[7] are reported as methods for preparing rare earth

(2) See J. B. Reed, B. S. Hopkins and L. F. Audrieth, "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., Inc., New York, N. Y., 1939, pp. 28–33.

(3) J. B. Reed, B. S. Hopkins and L. F. Audrieth, THIS JOURNAL, **57**, 1159 (1935).

(4) J. H. Kleinheksel and H. C. Kremers, *ibid.*, **50**, 959 (1928).

(5) E. R. Harrison, *J. Appl. Chem.*, **2**, 601 (1952).

(6) C. Matignon, *Ann. chim. phys.*, [8] **8**, 364 (1906).

(7) O. Petterson, *Z. anorg. Chem.*, **4**, 1 (1893).

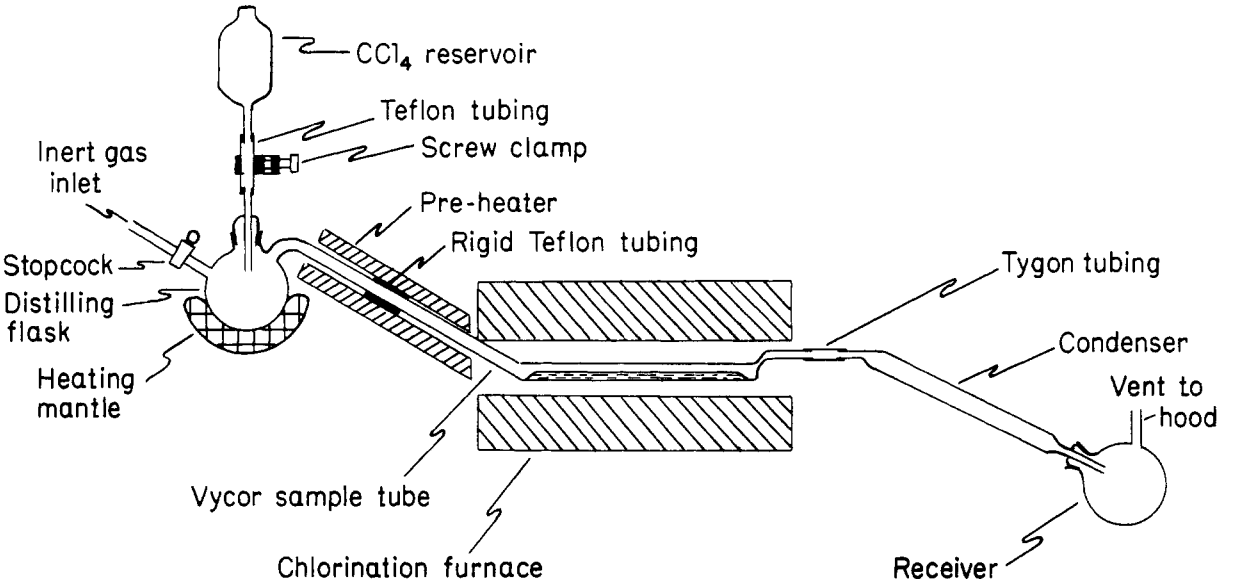

Fig. 1.—Schematic diagram of apparatus used to prepare anhydrous rare-earth chlorides.

chlorides. These reactions could not, however, be made to proceed with yttrium oxide.

Chlorination of the oxides with carbon tetrachloride at elevated temperatures (similar to the process described by Heisig and others[8] for preparing anhydrous chromic chloride) gave promising results, and this method was selected for development. The reaction presumably proceeds as

$$RE_2O_3 + CCl_4 \longrightarrow 2RECl_3 + 3COCl_2$$

and/or

$$2RE_2O_3 + 3CCl_4 \longrightarrow 4RECl_3 + 3CO_2$$

Accurately proportioned mixtures of the oxides used as starting materials can be made up by weighing[9] them in the reaction tube. No sample transfers, addition or removal of reagents (other than CCl_4 vapor and gaseous reaction products) are required. Thus, the preparation of anhydrous chloride samples by this method could readily be made quantitative. Some modification of the basic method referred to was necessary before acceptable rare earth chloride samples were obtained. Satisfactory procedures were developed empirically, and no attempts were made to shorten the chlorination cycle, although this may be possible.

Experimental Procedures

The sample to be chlorinated was contained in a Vycor tube which was suspended within an electric furnace. A schematic drawing of the apparatus is shown in Fig. 1. Sample tubes actually used have ranged in size from 13 mm. diameter × 7 cm. long to 25 mm. diameter × 25 cm. long. The chlorination furnace was designed so as to minimize the temperature gradient along the length of the sample tube. The inlet of the sample tube was attached to the sidearm of the distilling flask with a section of rigid Teflon tubing, and the outlet was connected to a condenser-receiver unit with a section of Tygon tubing. The Teflon was used repeatedly and appeared to be unaffected. However, it was necessary to replace the Tygon tubing after each run.

The carbon tetrachloride was fed dropwise, at the rate of 0.22 to 0.27 gram of carbon tetrachloride per cm.^{2} of sample tube cross-section per minute, from the reservoir down into the distilling flask and was flash-distilled through the system. Control over this flow rate, which initially presented a problem, was most satisfactorily obtained by adjusting a screw clamp on a short section of Teflon tubing between the carbon tetrachloride reservoir and the distilling flask. Temperature of the distilling flask was maintained at about 100° with an electric heating mantle. Temperature of the preheat section (the side arm which connected the distilling flask and the sample tube) was kept at about 120° through use of electric heating tape.

Temperature of the chlorination furnace was programmed as follows: 500° for 6 hr., 550° for 15 hr., 600–650° for 8 hr. Best results were obtained with a final chlorination temperature just below the liquidus temperature for the chloride composition being produced, but in no case exceeding 650°. At higher temperatures, two deleterious effects were observed: (1) inhibition of the reaction by a film of molten chloride which formed a barrier between the chlorinating agent and the unreacted oxide or oxychloride, and (2) pyrolytic decomposition of organic compounds formed in the course of reaction which resulted in contamination of the sample.

Upon completion of the reaction cycle, the system may be flushed with dry argon (or another inert gas) introduced through the inlet provided for that purpose. The sample tube then can be disconnected, quickly stoppered, and the rare earth chlorides may be transferred to another container in a dry box, if necessary. However, for most careful work, the sample container should be designed so that the desired studies can be made without removing the chlorides from the container. The container can then simply be connected to a vacuum system, evacuated and both inlet and outlet sealed off (fused seals). In view of the ease with which the rare earth chlorides form hydrates, this course, which was followed in the physical property study previously mentioned, is most desirable.

Results

Samples of the anhydrous trichlorides of Y, Gd, Dy, Ho and mixtures of these chlorides have been prepared by this method. Chloride determinations were made for a number of the samples by use of the gravimetric method (as AgCl). Normally, error for this analytical method should be less than ± 0.05%. As is shown by representative analytical results presented in Table I, however, the same type of scatter was obtained as has been reported by others[2] (*i.e.*, values fall both above and

(8) G. B. Heisig, B. Fawkes and R. Hedin, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, pp. 193–196.

(9) Checks made indicate that rare earth oxides calcined at 900° remain at constant weight through relatively long periods of exposure to the atmosphere.

TABLE I

CHLORIDE ANALYSES

Oxide	% Cl, by wt. Found	% Cl, by wt. Theoretical
Gd	40.2	40.4
50.1 Ho 49.9 Dy	39.3	38.5

below the theoretical values by margins ranging from several tenths to several per cent). One possible explanation for this scatter is based on consideration of precise composition of the rare earth oxides used as starting materials. Although accurate data cannot be obtained readily regarding concentrations of impurities present in the commercial grades of oxides (98–99%) typical analytical figures indicate that Y_2O_3 concentrations present in lots of Dy_2O_3 and Ho_2O_3 used ranged from a trace to 1.5%. If such Y concentrations are considered, then theoretical chloride value for the 50.1 Ho–49.9 Dy mixture could range between 38.5 and 40.0%, which would account for the apparently high chloride concentration found. Likewise, significant concentrations of Th, which are frequently found in the rare earth oxides, could account for apparently low chloride values. Nevertheless, it is felt that very sensitive indication as to the completeness of conversion was obtained by observing clarity of the materials when molten and the extent of reaction between the sample and the Vycor container. Samples produced by the other methods contained residual solids (oxides and oxychlorides) at temperatures above the melting points of the chlorides, and extensively attacked the Vycor containers. In contrast, samples prepared by the chlorination method described in this paper were perfectly clear when molten, and no attack on the containers was observed. No etching of the container walls or other evidence of attack could be detected, even after the chloride samples had been held in the molten state for extended periods of time (*e.g.*, 24 hours).

COLUMBUS, OHIO

[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY]

Separation of the Lanthanons at Amalgam Cathodes. III. Electrochemical Fractionation of the Lanthanons at a Lithium Amalgam Cathode[1]

BY E. I. ONSTOTT

RECEIVED JANUARY 31, 1959

Electrolyses of a monazite mixture, an yttrium–earth mixture and a terbium–dysprosium mixture at a lithium–amalgam cathode were studied. The separations obtained show that individual lanthanons are electrolyzed at different rates at a lithium–amalgam cathode. The relative ease of electrolysis is: europium, ytterbium, samarium, lanthanum and other lanthanons in the order of atomic number. Yttrium falls between erbium and thulium. Data were not obtained for lutetium. All of the lighter lanthanons through terbium can be relatively rapidly electrolyzed from aqueous lithium citrate electrolytes, but the rates of electrolysis of the heavier lanthanons except for ytterbium are quite slow from this electrolyte. Rates of electrolysis of the heavier elements are improved considerably by using a methanol electrolyte containing lithium acetate. It appears that europium and ytterbium, and possibly samarium, are rapidly electrolyzed because they are easily reduced to a lower valence state. However, the lanthanons which show only the (III) or higher valence in compounds appear to be reduced by a different mechanism, believed to entail formation of a hydrido species at the cathode surface. The rates of electrolysis of the (III) lanthanons vary widely depending on the electrolysis conditions, but the ratio of rates for any two of these lanthanons appears to be relatively constant. Separations can be predicted from the relative rates of electrolysis.

The electrochemical separation of europium from samarium[2,3] and the separation of samarium from gadolinium[3] proved to be so successful that the work has been extended to the lanthanide series.

Except for the work of McCoy,[4] there has been very little other research reported on the electrochemical separation of the lanthanons by electrolysis into mercury. Several researchers have used electrochemical techniques to prepare amalgams of some of the lanthanons by electrolysis from an ethanolic anhydrous chloride electrolyte.[5] Sodium amalgam was used by Marsh to extract preferentially europium, ytterbium and samarium[6] and by Moeller and Kremers to extract ytterbium from lanthanon mixtures.[7] West and Hopkins used sodium amalgam to prepare several rare earth amalgams by reaction with the anhydrous chlorides in ethanol.[8] Ytterbium separations with amalgam cathodes have been studied.[9]

In this paper the term "lanthanon (III)" is used to describe the lanthanons, including yttrium, which show only (III) or higher valence in compounds. Europium, ytterbium and samarium are thus not included in this designation.

Experimental

Analyses of the lanthanon mixtures were done by classic gravimetric, spectrophotometric and spectrographic procedures. The Cary Model 14X spectrophotometer and a Beckman Model D spectrophotometer were used for lanthanons with suitable absorption coefficients.[10] Europium tracer was used in the same manner as described previously.[2]

(1) Work done under the auspices of the Atomic Energy Commission.

(2) E. I. Onstott, THIS JOURNAL, **77**, 2129 (1955).

(3) E. I. Onstott, *ibid.*, **78**, 2070 (1956).

(4) H. N. McCoy, *ibid.*, **63**, 1622 (1941); **63**, 3432 (1941).

(5) L. F. Audrieth, E. E. Jukkola and B. S. Hopkins, *ibid.*, **53**, 1805 (1931); E. E. Jukkola, L. F. Audrieth and B. S. Hopkins, *ibid.*, **56**, 303 (1934); B. S. Hopkins and L. F. Audrieth, *Trans. Am. Electrochem. Soc.*, **66**, 135 (1934).

(6) J. K. Marsh, *J. Chem. Soc.*, 398 (1942); 531 (1943).

(7) T. Moeller and H. E. Kremers, *Ind. Eng. Chem.*, **17**, 798 (1945).

(8) D. H. West and B. S. Hopkins, THIS JOURNAL, **57**, 2185 (1935).

(9) H. N. McCoy, *ibid.*, **63**, 1622 (1941); H. N. McCoy and R. P. Hammond, *ibid.*, **64**, 1009 (1942); D. I. Ryabchikov, Yu. S. Sklarenko and N. S. Stroganova, *Zhur. Neorg. Khim.*, **1**, 1954 (1956); *C. A.*, **51**, 5595e (1957).

(10) T. Moeller and F. A. J. Moss, THIS JOURNAL, **73**, 3149 (1951); T. Moeller and J. C. Brantley, *Anal. Chem.*, **22**, 433 (1950); C. V. Banks and D. W. Klingman, *Anal. Chem. Acta*, **15**, 356 (1956); L. J.