nesium was always present to avoid too high a concentration of free bromine in the ether. The reaction was accelerated by efficient stirring. From 5-20 ml. of liquid bromine, reagent quality, was vaporized at a controlled rate into the reaction vessel, which was cooled below room temperature.[7] The large heat of formation always kept the ether solution at a higher temperature than the surrounding bath. At the completion of a run, the two-layer system was decanted or syphoned from the excess magnesium into a dry flask where crystallization was brought about by cooling. Occasionally, seeding with a small crystal of magnesium bromide trietherate, or cooling below 0°, was necessary to start crystallization.

Purification.—With small scale preparations, careful control will result in a product with a minimum of impurities. However, on a larger scale, the bromination of ether and subsequent removal of brominated products becomes a major difficulty. To remove the greater portion of the impurities, the increased solubility of the product in benzene-ether solutions[7] is utilized. Immediately after a preparation, the two-layer system is practically colorless. The trietherate of magnesium bromide is crystallized in an ice-bath and the supernatant liquid containing some of the impurities is decanted. The cold crystals are treated with anhydrous benzene and allowed to stand at room temperature. The solid crystal mass crumbles to the dietherate with the excess ether dissolving in the benzene. At the same time, some of the magnesium bromide and most of the impurities dissolve in the ether-benzene solution. The mixture is cooled to 0° and filtered rapidly, the crystals being washed with cold benzene. The moist crystals are transferred to the desolvator, a 15 × 5 cm. glass tube closed at one end and fitted with a wide-mouthed ground cap and stopcock. The ether is drawn off gradually by attaching to a water aspirator for several hours while the temperature is raised to 150-175°. A final heating of one hour with the desolvator connected to an oil vacuum pump completes the desolvation, leaving a white residue that breaks up easily into a fine solid. Depending on the quantity of bromine used, 20-40 g. of anhydrous material is obtained. Yields of 60-70%, based on magnesium consumed, are obtained by the above procedure. Higher yields of 90-95% can be obtained by omitting the benzene purification, but the product may contain 5-10% impurities.

Analysis.—The analysis was made by treating a 3-6-g. sample with 5-10 ml. of 95% ethyl alcohol, dissolving in water and diluting to 250 ml. The direct combination of anhydrous magnesium bromide and water is vigorous enough to cause some decomposition and loss of hydrogen bromide. Aliquot portions of the solution were analyzed separately for magnesium by the sulfate method[5] and for bromide by the Volhard method.[8] Calculating as anhydrous magnesium bromide, two typical runs gave analyses of 99.3 and 99.6% from bromide analyses and 99.9 and 100.0%, respectively, from magnesium analyses.

Discussion

The principal difficulty in this preparation is the removal of impurities from the bromination of ether when more than a few grams of magnesium bromide are prepared. Some of these impurities are soluble in ether and do not interfere but others are closely associated with the magnesium bromide and are exceedingly difficult to separate.

The exact nature of the organic impurities is not known but a great deal of work on their removal indicates that they may be polymeric organomagnesium compounds or possibly solvates other than diethyl etherates, which are easily decomposed by certain other organic substances.[9]

Whatever the nature of the impurities, it was found that the benzene purification should be carried out immediately after the preparation was made. On standing, with exposure to dry air, the solution frequently became dark and this dark impurity was not removed by the benzene treatment.

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[7] The addition of benzene to the ether solution was found to increase the solubility of magnesium bromide and to lower the temperature at which crystallization occurred without interfering with the reaction. About 3% benzene by volume lowered the freezing point below 20°, 9% lowered it below 14° and 14% benzene kept the two-layer system liquid below 10°. About 25% benzene rendered the two-layer system completely miscible at room temperature.

[8] Kolthoff and Sandell, "Textbook of Quantitative Inorganic Analysis," revised ed., The Macmillan Co., New York, N. Y., 1943, p. 573.

[9] Menschutkin, *Z. anorg. Chem.*, **62**, 45 (1909).

NORMAN, OKLAHOMA RECEIVED MARCH 2, 1950

The Rare Earth Metals and their Compounds. XII. Carbonates of Lanthanum, Neodymium and Samarium

BY MURRELL L. SALUTSKY[1] AND LAURENCE L. QUILL

Pure crystalline rare earth carbonates are difficult to prepare by the two commonly used methods, namely, the precipitation of the compounds by alkali carbonates or bicarbonates from rare earth salt solutions or the conversion, in aqueous suspension, of rare earth hydroxides to carbonates by carbon dioxide. However, the hydrolysis of rare earth trichloroacetates [$Nd(C_2Cl_3O_2)_3$] in a homogeneous phase reaction yields a pure crystalline carbonate

$$2Nd(C_2Cl_3O_2)_3 + 3HOH \longrightarrow 3CO_2 + 6CHCl_3 + Nd_2(CO_3)_3$$

Experimental

Approximately 10 g. of a rare earth oxide is dissolved with warming in slight excess of 25% trichloroacetic acid. This solution is diluted to 500 ml. with distilled water and heated on a steam-bath for about six hours after the carbonate precipitate is initially formed. The carbonate is filtered by suction, washed with distilled water, and air dried. The precipitated carbonate may be washed with alcohol and then ether in order to hasten drying. Since all of the rare earth cannot be precipitated by this reaction, the filtrate is treated with oxalic acid to recover the remaining rare earth as the oxalate.

A slight excess of trichloroacetic acid is required to dissolve the rare earth oxide, but the carbonate will not precipitate until the excess acid has been decomposed. The time required for the initial formation of the carbonate is dependent upon the amount of the excess acid and the temperature of the bath. The *pH* range during precipitation is 4.5-5.5.

The carbonates were analyzed by igniting weighed samples of a particular carbonate in a muffle furnace at a temperature of 925°. The resulting oxides were weighed and the per cent. rare earth oxide in the carbonate calculated. Other weighed samples were treated with dilute hydrochloric acid to liberate carbon dioxide which was collected on ascarite in an absorption bottle and weighed. The per cent. carbon dioxide in the carbonate and the mole ratio CO_2/R_2O_3 were calculated. The percentage H_2O was determined by difference and not verified experimentally. The analyses for lanthanum, neodymium, and samarium carbonates are listed in Table I.

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[1] Abstracted from a doctoral thesis submitted to the Michigan State College, 1950.

TABLE I

ANALYSES OF RARE EARTH CARBONATES

Carbonate	% R_2O_3	% CO_2	% H_2O	$\frac{CO_2}{R_2O_3}$	$\frac{H_2O}{R_2O_3}$	Suggested formula
Lanthanum	58.55	23.60	17.85	2.98	5.51	$La_2(CO_3)_3 \cdot 5.5H_2O$
Neodymium	65.80	25.35	8.85	2.95	2.51	$Nd_2(CO_3)_3 \cdot 2.5H_2O$
Samarium	65.88	23.43	10.69	2.82	3.14	$Sm_2(CO_3)_3 \cdot 3H_2O$

Conclusions.—It was concluded that the carbonates are normal carbonates of the formula $R_2(CO_3)_3 \cdot xH_2O$. This conclusion is based upon a comparison of the experimental and calculated values for the mole ratio CO_2/R_2O_3. This ratio is 3 for normal carbonates, 2 for $R(OH)CO_3$, and 6 for $R(HCO_3)_3$. It is observed from Table I that the mole ratios are approximately 3 in all cases, with the value for the samarium being the lowest; this could indicate a slight tendency toward basic salt formation which would be expected since samarium is the least basic of the elements studied.

The preparation of anhydrous neodymium carbonate was attempted. Samples of neodymium carbonate were dried under different conditions and analyzed for neodymium oxide and carbon dioxide. The mole ratios CO_2/Nd_2O_3 and H_2O/Nd_2O_3 are listed in Table II.

TABLE II

EFFECT OF HEAT ON HYDRATED NEODYMIUM CARBONATE

Sample	Drying conditions	% Nd_2O_3	% CO_2	% H_2O	$\frac{CO_2}{Nd_2O_3}$	$\frac{H_2O}{Nd_2O_3}$
A	Air dried[a]	65.8	25.4	8.8	2.96	2.50
B	1 hr. at 110°	68.2	26.7	5.1	3.00	1.40
C	12 hr. at 110°	70.8	27.9	1.3	3.02	0.34
D	3 days at 120°	71.4	27.8	0.8	2.98	0.21
$Nd_2(CO_3)_3$ (theoretical)		71.8	28.2	0.0	3.00	0.00

[a] Washed first with alcohol and ether.

The mole ratio CO_2/Nd_2O_3 remained approximately 3 for the above drying conditions; the mole ratio H_2O/Nd_2O_3 decreased continually, indicating dehydration. For an extended drying period an essentially anhydrous neodymium carbonate (Sample D) was obtained.

The preparation of rare earth normal carbonates by the decomposition of the trichloroacetates from hot water solution is very satisfactory since no interfering ions, such as the alkali ions, are introduced into the reaction mixture.

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Magnesium in Fourfold Coördination in Glass

BY RUSTUM ROY

Incident to other investigations[1] on the use of molar refraction data to indicate the coördination of ions, some interesting data regarding the coördination of Mg^{2+} in glass were encountered.

Fajans and Kreidl[2] have shown that the coördination number of Zn^{2+} is related to the molar volume. Previous work of Fajans and co-workers[3a,b,c,d] has demonstrated a relationship between molar refraction and molar volume. They have also shown a relationship in cesium and ammonium halides, between molar refraction and coördination number. Safford and Silverman[4] have presented evidence to show that a change of coördination of an ion alters the molar refraction contribution of the ion or more correctly of the group immediately surrounding the ion. These authors have shown that the Al^{3+} in fourfold coördination in glass or in certain crystals has a molar refraction contribution of 12.3 (calculated for Al_2O_3), whereas in sixfold coördination it is 10.5. Kreidl[5] first indicated that MgO may assume both "basic" and "acidic" properties in glass. Huggins[6] later pointed out that the magnesium ion may be surrounded "by but four oxygen neighbours" in some glasses containing magnesium, and Dietzel[7] has recently mentioned the possibility that Mg^{2+} may go partly into fourfold coördination in glass.

The data referred to at the outset substantiating the above claims regarding the fourfold coördination of Mg^{2+} are shown in Table I. The refractive indices and densities are reasonably well established and may be found either in Larsen and Berman[8] or in the "Data on Chemicals for Ceramic Use."[9] It will be seen that the difference in molar refraction between the crystalline and glassy states is about 0.65. It is known that Mg^{2+} is in sixfold coördination in enstatite and diopside. This difference in molar refractivity of crystals and glasses, when compared with that for Al^{3+}

TABLE I

MOLAR REFRACTION DATA

Substance		d	$\bar{n}$	R^a	Δ
$MgSiO_3$	Enstatite	3.175	1.646	11.48	0.63
$MgSiO_3$	Glass	2.757	1.5801	12.11	
$^1/_2(CaMg(SiO_3)_2)$	Diopside	3.275	1.676	12.44	.67
$^1/_2(CaMg(SiO_3)_2)$	Glass	2.854	1.607	13.11	
MgO	Periclase	3.5761	1.738	4.538	.64
$MgAl_2O_4$	Spinel	3.578	1.719	5.18[b]	
$Ca_2MgSi_2O_7$	Akermanite	2.944	1.635	33.19	.09
$Ca_2MgSi_2O_7$	Glass	2.955	1.641	33.28	

[a] The values of molar refraction are obtained by the Lorentz–Lorenz equation $R = (n^2 - 1)\ M/(n^2 + 2\ )d$, see references (2) and (4). [b] This is obtained by subtracting 10.50 as the contribution of Al_2O_3 with Al^{3+} in sixfold coördination,[4] from the total value of 15.68.

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