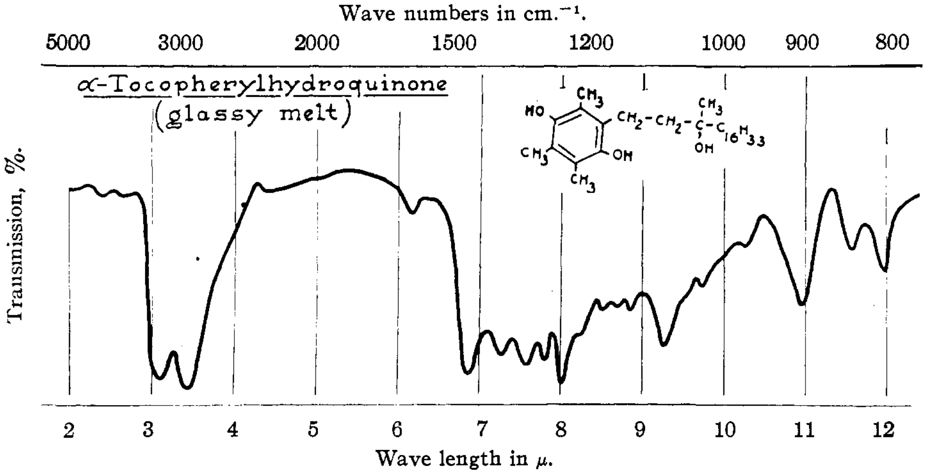

Fig. 1.—Infrared spectrum of α-tocopherylhydroquinone.

hours, formation of crystals occurred and continued slowly over the next three days. Melting point determinations of the white solid gave values of 59.5–61.4°. The infrared absorption spectrum (Fig. 1) may be distinguished readily from that of either α-tocopherol or α-tocopherylquinone. Hydrogen bonding is indicated by the broadening of the hydroxyl absorption band and the location of this band near 3.1 μ; unbonded phenolic hydroxyl groups usually absorb near 2.8 μ. Infrared absorption spectra of the corresponding tocopherol and tocopherylquinone[6] and data on the ultraviolet absorption spectrum of α-tocopherylhydroquinone[2] were published previously.

(6) Rosenkrantz, *J. Biol. Chem.*, **173**, 439 (1948).

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Studies of Non-aqueous Solvates. V. The Preparation of Anhydrous Magnesium Bromide in Diethyl Ether[1]

BY H. H. ROWLEY

The reaction of free bromine with magnesium in anhydrous diethyl ether to form the magnesium bromide–diethyl ether system has been known and studied for some time.[2–6] The present work describes the preparation of pure anhydrous magnesium bromide from this system.

Experimental

Apparatus.—The preparation of 2–3-g. samples of anhydrous magnesium bromide can be carried out in an Erlenmeyer flask with addition of liquid bromine from a dropping bottle. By slow addition of bromine and careful control of temperature a very pure product can be obtained with only a trace of impurities. For larger amounts of material an apparatus following the general design of Fig. 1 was found to be most suitable. To control the speed of the reaction, a bromine vaporizer (A) was used. Passage of dry nitrogen gas (15 ml./min.) through the bromine, which was heated to 50–55°, served to introduce bromine directly into the ether and also to provide the inert atmosphere which was found necessary. The bromine could be stopped at any time by manipulation of stopcocks (S_1, S_2, S_3) without halting nitrogen flow. The reaction vessel (B) was fitted with ground joints (M), a mercury seal (T) and spiral stirrer (N). In later runs, a 500-ml. round-bottom, three-necked standard taper flask was used with satisfactory results.

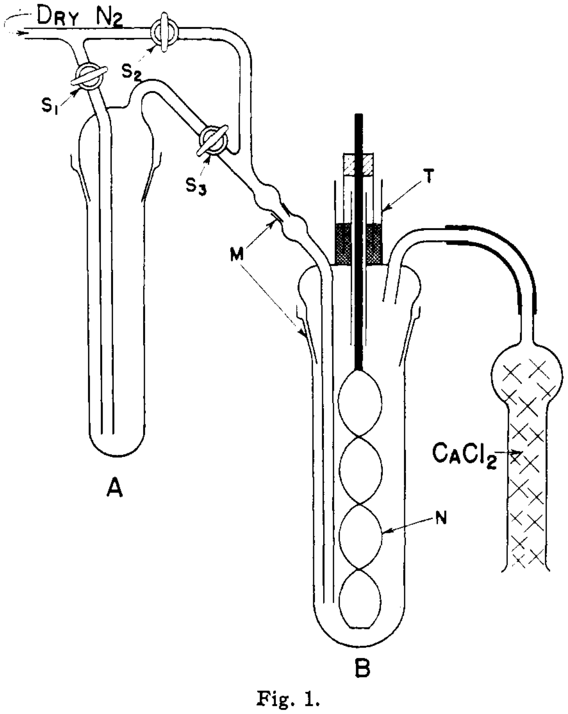

Fig. 1.

Procedure.—A typical run consisted of about 10 g. of magnesium turnings, Grignard quality, in 150 ml. of freshly distilled anhydrous diethyl ether. Excess mag-

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[1] Presented at the Fifth Southwest Regional American Chemical Society meeting, Oklahoma City, Okla., December 9, 1949.

(2) Zelinsky, *Chem. Zentr.*, **74**, II, 277 (1903).

(3) Menschutkin, *Z. anorg. Chem.*, **49**, 34 (1906).

(4) Evans and Rowley, THIS JOURNAL, **52**, 3523 (1930).

(5) Rowley, *ibid.*, **58**, 1337 (1936).

(6) Rowley, *ibid.*, **59**, 621 (1937).

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).

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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 *p*H 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.