[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF THE U. S. NAVAL ORDNANCE TEST STATION]

Observations on Several Compounds of Lithium and Oxygen. I[1a,1b]

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A new method of preparation for $LiO_2H \cdot H_2O$ ($Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$) is described. The formula $Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$ for this compound is discounted. Cell constants, densities and possible space groups are reported for $LiO_2H \cdot H_2O$ and Li_2O_2. X-Ray diffraction studies indicate that LiO_2H and Li_2CO_4 do not exist at room temperature. A dehydration study showed that no fractional hydrate of less than one exists for LiOH.

Introduction

Earlier workers[2-4] have prepared lithium hydroperoxide 1-hydrate which they represented by a dualistic formula approximating $Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$. This compound is of interest both from a structural standpoint and as an intermediate in the preparation of pure lithium peroxide and oxide.

Incomplete powder diffraction data have been reported earlier for Li_2O_2,[3] Li_2O,[5] $LiOH \cdot H_2O$,[6] LiOH[7] and Li_2CO_3.[7] Crystal structure determinations have been made for $LiOH \cdot H_2O$[8] and LiOH.[9] Although Fehler[10] mentions having taken powder patterns of $Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$ and LiO_2H, his experimental data were not published.

Partington[11] recently reported the preparation of a lithium peroxycarbonate, Li_2CO_4, by action of carbon dioxide on "$Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$," or on lithium peroxide containing a requisite amount of water. He found that 30% hydrogen peroxide was without action on lithium carbonate.

De Forcrand[12] mentioned the existence of a hydrate of lithium hydroxide corresponding to $4Li_2O \cdot 5H_2O$ or $LiOH \cdot {}^1/_8H_2O$ produced by heating lithium hydroxide 1-hydrate rapidly to 450° in a stream of hydrogen. On the other hand, he found that the 1-hydrate was completely dehydrated to lithium hydroxide by heating at 140°. Pickering[13] ran the freezing point curve of lithium hydroxide and water which indicated the existence of $LiOH \cdot H_2O$ and possibly $LiOH \cdot 0.13H_2O$ in one of two runs. The inflection point indicating the existence of the latter is most likely an experimental error as it was not present in a second run.

The present paper presents a method for the preparation of lithium hydroperoxide 1-hydrate which is both simple and rapid. This compound has been identified as the same compound as was earlier represented by $Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$.

Powder diffraction data for lithium–oxygen compounds have been extended and these data made more complete. Improved cell constants and possible space groups are reported for Li_2O_2. Crystals of lithium hydroperoxide 1-hydrate prepared by the method of De Forcrand[2] were examined both optically and by powder, rotation and Weissenberg X-ray methods. Preliminary structure data are reported.

An X-ray powder diffraction study to determine whether Li_2CO_4 exists as a definite compound, was undertaken. An investigation of the dehydration of lithium hydroxide 1-hydrate in a helium atmosphere was followed by means of X-ray powder diffraction methods.

Experimental

Methods.—The X-ray powder diffraction data were taken on Eastman Kodak Co. no-screen, X-ray film using a powder camera of 5.0 cm. radius, Type 52014 manufactured by North American Philips. The unstable and reactive materials being studied were sealed in thin-walled cellulose acetate tubes to protect them during the 1.5-hour exposures. Some of the substances were also examined using an automatic recording Philips High Angle Spectrometer Goniometer. The radiation was $CuK\alpha$ with Ni filter in both instances. This wave length is taken as 1.54 Å. except in calculating cell constants the value 1.542 Å. is used. The petrographic microscope for optical examinations was a Bausch and Lomb instrument employing calcite nicol prisms.

Preparations.—Lithium metal ribbon coated with petroleum jelly obtained from the Metalloy Corporation, Minneapolis, Minnesota, was employed as the starting material for all preparations. The protective coating was removed by dissolving in *o*-xylene. The hydrogen peroxide was 30% C.P. grade. The absolute alcohol was U.S.P. grade. The lithium carbonate was a C.P. grade J. T. Baker product.

(1) Lithium hydroperoxide 1-hydrate was prepared from 2 g. of lithium ribbon dissolved in 250 ml. of absolute alcohol contained in a 600-ml. beaker. The solution became quite hot and a voluminous precipitate of lithium ethoxide separated out. The lithium ethoxide was, in some instances, filtered and washed with small portions of absolute alcohol at 70° to remove traces of sodium and potassium that might be present as impurities in the lithium starting material. Twenty-five ml. of 30% hydrogen peroxide was added to the suspension of lithium ethoxide in 250 ml. of alcohol, with stirring. After standing for at least an hour with frequent stirring, the suspension was filtered by suction and the precipitate collected on a sintered glass filtering funnel. The product was washed with two 25-ml. portions of cold alcohol and dried by suction. All the above operations were performed in a helium-filled dry-box in order to avoid contamination by carbon dioxide. The hydroperoxide appears to be stable in contact with the mother liquor but is unstable after drying. It can be preserved for short periods by refrigeration in a closed container. The yield is 9.4 g., 56%, based on lithium.

Anal. Calcd. for $LiO_2H \cdot H_2O$: Li_2O, 25.8; O (peroxide), 27.6. Found: Li_2O, 25.4; O, 27.4.

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(1) (a) Published with the approval of the Technical Director, U. S. Naval Ordnance Test Station. The opinions contained herein are the author's and are not to be construed as official or reflecting the views of the Department of the Navy. (b) Tables of the X-ray powder diffraction data for $LiO_2H \cdot H_2O$, Li_2O_2, Li_2O, $LiOH \cdot H_2O$, LiOH and Li_2CO_3 may be obtained by ordering Document 3607 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $2.55 for photocopies (6 × 8 inches) readable without optical aid.

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Material prepared by the method of Pierron[4] gave a similar analysis. X-Ray powder diffraction patterns were identical for samples prepared by the method described here, by Pierron's and by De Forcrand's[2] methods.

(2) Lithium peroxide was prepared by dehydration of lithium hydroperoxide 1-hydrate over P_2O_5 in a vacuum desiccator at 20 mm. pressure. After standing 18 days[14] at room temperature, the material was completely dehydrated and analyzed as 99% Li_2O_2. The yield was quantitative. The anhydrous material may be preserved indefinitely in a dark bottle under refrigeration.

Anal. Calcd. for Li_2O_2: Li_2O, 65.0; O (peroxide), 34.9. Found: Li_2O, 64.5; O, 34.0.

(3) Lithium oxide was prepared by heating anhydrous lithium peroxide prepared according to (2) in an alundum boat contained in a combustion tube. A slow stream of dried oil-free helium was passed through the tube while the furnace temperature was slowly raised until the temperature of the sample was 450°. The heating was continued for six hours. The sample was then cooled and removed from the tube. The material was stored in a tightly sealed container to prevent absorption of water vapor and carbon dioxide. The yield was quantitative based on Li_2O_2.

(4) Lithium hydroxide 1-hydrate was prepared by reacting lithium ribbon with distilled water until large amounts of the compound separated from solution and the reaction of the solution with additional ribbon was very slow. The excess water was partially removed by dehydration over P_2O_5 at a pressure of 20 mm. and a temperature of 25° in a vacuum desiccator. When only a moist solid remained, the material was transferred to a vacuum desiccator containing anhydrous lithium hydroxide and allowed to reach equilibrium.

Anal. Calcd. for $LiOH{\cdot}H_2O$: Li_2O, 35.6; H_2O, 42.9. Found: Li_2O, 34.8; H_2O, 42.6.

(5) Lithium hydroxide was prepared by dehydration of lithium hydroxide 1-hydrate in a platinum micro crucible contained in a combustion tube at 140°. The sample was heated to constant weight in a slow stream of dried oil-free helium gas. The water evolved on drying was absorbed in anhydrone and weighed. The average loss of water was 42.6%. The platinum was not attacked at this temperature.

(6) Attempts were made to prepare a lithium peroxycarbonate in the following ways. (a) Lithium carbonate was added to 30% hydrogen peroxide in excess at room temperature, stirred frequently, and kept under refrigeration at 5° for 48 hours. The solid material present was then filtered and found to give a negative analysis for active oxygen. An X-ray powder diffraction pattern was taken and the material found to be lithium carbonate. (b) Lithium hydroperoxide 1-hydrate was placed in a vacuum desiccator over Dry Ice and the carbon dioxide pressure allowed to rise to slightly greater than atmospheric. The lithium compound absorbed carbon dioxide in an exothermic reaction with oxygen, hydrogen peroxide and water vapor as gaseous reaction products. The solid residue gave a negative test for active oxygen and was identified as lithium carbonate by a diffraction pattern. (c) Lithium hydroperoxide 1-hydrate was added in excess to absolute alcohol and cooled to −10°. Several small pieces of Dry Ice were dropped into the suspension which became more voluminous as carbon dioxide was absorbed. The suspension was washed with absolute alcohol by decantation and filtered, then washed with dry ether. The product was a fine white powder with considerable active oxygen content.

Anal. Found: Li_2O_2, 54.1; CO_2, 25; H, 3.0.

A diffraction pattern showed that the material was a mixture of the starting material and lithium carbonate. All lines were contributed by one of these two species. (d) "Lithium permonocarbonate," $Li_2CO_4{\cdot}H_2O$, preparation was attempted, following the directions given by Partington,[11] by action of dry carbon dioxide on lithium hydroperoxide 1-hydrate at −10°. The hydroperoxide used was prepared by the method of De Forcrand.[2] A diffraction pattern and a spectrometer goniometer pattern showed the product of the reaction to be a mixture of the original hydroperoxide hydrate and lithium carbonate. All diffraction lines present were common to one or the other of these two compounds.

(7) An attempt was made to isolate anhydrous lithium hydroperoxide. During a dehydration study of lithium hydroperoxide 1-hydrate over P_2O_5 at 20 mm. and 25°, a phase giving a lithium and active oxygen content corresponding to LiO_2H was found. A diffraction pattern showed that this material consisted of a mixture of $LiO_2H{\cdot}H_2O$ and Li_2O_2.

Results and Discussion

X-Ray Powder Diffraction Data.—Data were collected on film for all the compounds included in this study. Spectrometer goniometer patterns were limited to lithium hydroperoxide 1-hydrate, lithium peroxide, lithium hydroxide 1-hydrate and lithium carbonate. The other compounds were not stable enough in air for accurate work. These data are obtainable from the American Documentation Institute.[1b]

Preliminary Structure Data. (1) Lithium Hydroperoxide 1-Hydrate.—Small transparent crystals were prepared by the method of De Forcrand.[2] Several crystals were mounted in fine Pyrex capillaries. Both rotation and Weissenberg patterns were taken, rotating a crystal with dimensions of 0.49 × 0.14 × 0.14 mm. around its needle axis. The zero, first and second layer Weissenberg patterns were taken. The material was found to be orthorhombic, with possible space groups, Immm $-$ D_{2h}^{25}, $\mathrm{I2_12_12_1}$ $-$ D_2^9, or Imm $-$ C_{2v}^{20}. The unit cell dimensions were found to be as follows: a = 7.92 Å., b = 9.52 Å., c = 3.20 Å. The calculated density with 4 molecules per unit cell is 1.60; the experimental density at 25° was found pycnometrically to be 1.69. An optical examination of the crystal showed it to have parallel extinction under crossed nicol prisms, and an acute bisectrix interference pattern indicated it to be biaxial. Two refractive indices were determined by oil immersion methods using sodium D illumination. These were 1.458(α) and 1.526(γ). A complete structure determination is in progress.

(2) Lithium Peroxide.—It is not possible to grow sufficiently large crystals of this compound so the powder was employed. A goniometer spectrometer trace was used to evaluate the cell constants. Lithium peroxide is tetragonal with possible space groups; P4/m $-$ C_{4h}^{1}, P4 $-$ C_4^1, P4$\bar{4}$ $-$ S_4^1, $\mathrm{P42_1}$ $-$ D_4^2, $\mathrm{P\bar{4}2_1m}$ $-$ D_{2d}^3, or P4/mmm $-$ D_{4h}^1. The cell constants determined are compared with the earlier results of Aguzzi[3] and Fehler[10] in Table I. A complete structure determination is being attempted, using the available powder data.

TABLE I

CELL CONSTANTS OF LITHIUM PEROXIDE

	Cohen	Aguzzi	Fehler
a in Å.	5.445 ± 0.007	5.47	5.48
c in Å.	7.736 ± 0.034	7.73	7.74
c/a	1.421	1.41	1.41
d, calcd., g./cc.	2.66	2.64	2.62
d, exptl., g./cc.	2.26 (25°)	..	2.14
Molecules/unit cell	8	8	8

Existence of Li_2CO_4 and LiO_2H at Room Temperature.—The present work indicates that the structure Li_2CO_4, if it exists, is not stable enough at room temperature for an X-ray powder diffraction

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[14] A recent patent describes a faster method of preparing lithium peroxide by elimination of the water through distillation in an organic liquid; P. F. Winternitz, U. S. Patent 2,488,485 (Nov. 15, 1949).

pattern to be obtained. The fact that both $LiO_2H \cdot H_2O$ and Li_2CO_3 are present after treatment of the former with CO_2 tends to make the existence of Li_2CO_4 seem doubtful. It is not surprising that LiO_2H cannot exist at room temperature although Fehler[9] reported that the phase $Li_2O_2 \cdot H_2O_2$ or LiO_2H gave a well-defined Debye pattern.

Dehydration Study of Lithium Hydroxide 1-Hydrate.—The dehydration carried out in a stream of dry helium in the temperature range 125–140° gave anhydrous lithium hydroxide with no intermediate phase as shown by X-ray diffraction patterns and chemical analyses. Dehydration of the hydrate by quickly heating to 445° in the helium stream gave anhydrous lithium hydroxide with no intermediate phase as reported by De Forcrand.[12] On the basis of this work it may be concluded that no intermediate hydrate exists between $LiOH \cdot H_2O$ and LiOH.

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Heat Capacities at Low Temperatures and Entropies at 298.16°K. of Orthotitanates of Barium and Strontium

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Heat-capacity measurements of crystalline barium and strontium orthotitanates and of their equimolal solid solution were conducted over the temperature range 51 to 309°K. The results are regular, except those for barium orthotitanate in the region above 268°K. where there is evidence of approach to a heat-capacity peak. The entropies at 298.16°K. were obtained as 47.0 ± 0.5, 38.0 ± 0.3 and 45.8 ± 0.4 cal./deg. mole, respectively, for barium orthotitanate, strontium orthotitanate and the equimolal solid solution.

Introduction

In an earlier paper,[1] the authors reported low temperature heat capacities and entropies of crystalline barium and strontium metatitanates and of a solid solution containing 54.3 mole % of the former and 45.7 mole % of the latter. Analogous data for crystalline orthotitanates of barium and strontium and their equimolal solid solution appear in the present paper. No previous, similar data for any of these substances, or for any other orthotitanate, were found in the literature.

Materials.—Barium orthotitanate was prepared from reagent-grade barium hydroxide and titania (99.8% pure, after ignition). Stoichiometric quantities were intimately mixed, pressed into pellets, and heated for prolonged periods at temperatures up to 1350°. As is usual, several grindings, remixings and minor adjustments of composition were made during the preparation process. The final product analyzed 20.80% TiO_2 (as compared with the theoretical 20.67%), 0.34% CaO and 0.02% SiO_2. It is estimated from these results that the purity of this material is 99.2%. The X-ray diffraction pattern gave no evidence of unreacted oxides or of metatitanate. The existence of barium orthotitanate as a compound in the $BaO-TiO_2$ system is shown by the melting-point studies of Statton.[2]

Strontium orthotitanate was prepared in similar fashion from reagent-grade strontium carbonate and titania. Analysis of the final product gave 27.85% TiO_2 (as compared with the theoretical 27.82%), 0.17% CaO and 0.03% SiO_2; and the X-ray diffraction pattern gave no evidence of incomplete reaction. It is estimated that the purity of this material is 99.5%.

The equimolal solid solution was prepared by heating an intimate mixture of the two orthotitanates for prolonged periods at temperatures up to 1400°, with several intervening grindings and remixings. Analysis of the final product gave 23.77% TiO_2, which agrees within the limits of experimental error with the theoretical 23.72% calculated for the equimolal solid solution. The X-ray diffraction pattern was analogous to those for the individual orthotitanates.

Heat Capacities.—The heat capacities were determined with previously described apparatus.[3] The results, expressed in defined calories (1 cal. = 4.1833 int. joules), appear in Table I. Molecular weights accord with the 1949 International Atomic Weights. Sample masses employed in the measurements were 268.45, 217.47 and 250.56 g., respectively, of barium orthotitanate, strontium orthotitanate and the equimolal solid solution.

The heat capacities of strontium orthotitanate and the solid solution follow a regular course throughout the investigated temperature range. Values for barium orthotitanate also are regular between 51 and 268°K. At higher temperatures, the values take on an upward swing, which prevails to 309°K., indicating approach to a heat-capacity maximum. Measurements beyond 309°K. were precluded by temperature limitations of the apparatus. The extra heat absorption up to 298.16°K. is about 10 cal./mole. There is evidence that this upward swing is incompletely reversible. The three consecutive measurements labeled (b), (c) and (d) in Table I were obtained after cooling from 298.7 to 280.0°K. and rewarming to 296.2°K. Measurement (b) falls near normal extension of the results from below the transformation range, whereas (c) and (d) are over 2% higher. The measurement labeled (a) was obtained after heating to 308.9°K., cooling to room temperature, and holding for 4 days. This measurement is similar to (b).

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