as a force field associated with this state. Similar phenomena have been observed by Feitknecht and Haberle.[10]

[10] W. Feitknecht and E. Haberle, *Helv. Chim. Acta*, **33**, 922 (1950).

McPherson Chemical Laboratory
The Ohio State University
Columbus, Ohio

Potassium, Rubidium and Cesium Borohydrides

By M. Douglas Banus, Robert W. Bragdon and Alfred A. Hinckley

Received February 17, 1954

The relatively small ionic potentials (= charge/radius) of the potassium, rubidium and cesium ions and the consequent low coördinating power of the ions suggested that the borohydrides of these metals would not form hydrates. Interest in these compounds was prompted by this consideration, because of the instability of the borohydride ion toward water. Sodium borohydride forms a dihydrate under normal atmospheric conditions and consequently has a poor shelf-life after exposure.

Potassium borohydride has been prepared by the absorption of diborane by potassium tetramethoxyborohydride[1] but none of its properties were reported. This is a difficult preparative method because of the unusual nature of the chemicals and equipment necessary. This note describes a simple method for the preparation of potassium borohydride, and in addition the hitherto unknown rubidium and cesium borohydrides by metathetical reactions from sodium borohydride.[2] In aqueous or alcoholic media the products are easily obtained in a pure form, are non-hygroscopic, and as such have good storage stability. Investigation of some of the properties and reactions of the potassium compound show it to be similar to sodium borohydride in many respects.

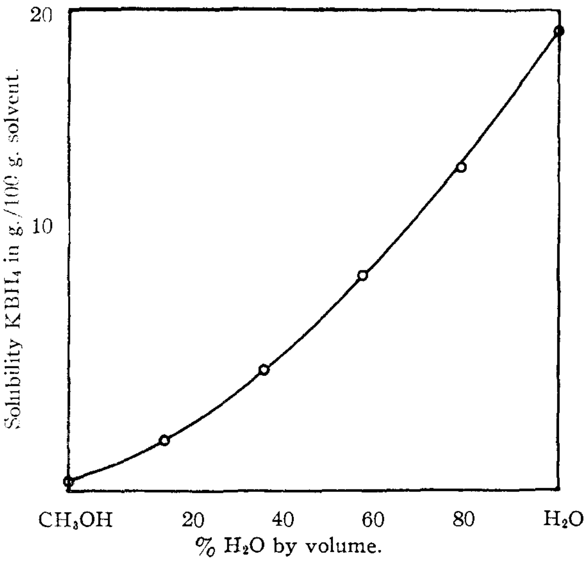

Fig. 1.—Solubility of potassium borohydride in methanol, water and methanol–water mixtures at 20°.

Experimental

Materials.—Commercial sodium borohydride from Metal Hydrides, Incorporated, was used for the preparation of potassium borohydride. For the preparation of the rubidium and cesium compounds, it was purified by the method of Davis, Mason and Stegeman.[3] Rubidium and cesium metals were obtained from the Fairmount Chemical Company. Organic compounds used in the reduction studies were obtained from the Eastman Kodak Company.

Preparation of Potassium Borohydride.—A solution of 74.2 g. of 94.7% sodium borohydride in 130 cc. of distilled water was added to a stirred solution of 133.2 g. of potassium hydroxide (85% assay) in 110 cc. of water. The resulting thick slurry was filtered through a medium-porosity, sintered glass disc under nitrogen pressure. The precipitate was washed with three 100-cc. portions of ice-cold, 95% ethanol. The product was then dried in a vacuum oven at 80° for three hours; 75.5 grams of potassium borohydride was obtained, representing a yield of 75.5%.

Anal. Calcd. for KBH_4: K, 72.48; B, 20.06; H, 7.47. Found: K, 73.3; B, 19.8; H, 7.25.

Preparation of Rubidium and Cesium Borohydrides.—10.8 grams of rubidium metal was dissolved in 750 cc. of absolute methanol to give a clear, water-white solution of rubidium methoxide. This solution was concentrated by distillation of the excess methanol to give a nearly saturated methoxide solution; 4.93 grams of 99.0% pure sodium borohydride dissolved in a minimum amount of methanol was added to the stirred methoxide solution. A white precipitate formed immediately, which was isolated by filtration on a medium-porosity, sintered glass disc, followed by two washes with methanol. The product was dried in a stream of nitrogen, then in a vacuum oven at 80° for two hours. The combined methanol washes were concentrated by evaporation to precipitate more product. This was filtered as before, and washed with 10–20 cc. of methanol and dried. A combined yield of 12.2 g., or 95.3% of theory, was obtained.

Anal. Calcd. for $RbBH_4$: Rb, 85.20; B, 10.78; H, 4.02. Found: Rb, 84.59; B, 10.74; H, 4.00.

Cesium borohydride was prepared by a similar procedure in 85% yield.

Anal. Calcd. for $CsBH_4$: Cs, 89.95; B, 7.32; H, 2.73. Found: Cs, 89.44; B, 7.37; H, 2.71.

Hygroscopicity of Potassium Borohydride.—A weighed sample of 99.0% potassium borohydride was placed in a hygrostat over a saturated, aqueous solution of ammonium chloride in contact with an excess of solid ammonium chloride. In this manner a constant humidity of 79.5% at 20° (13.8 mm.) was maintained. Exposure for 24 hours resulted in a weight gain of 0.85%. Further evidence of the good storage stability of potassium compound was found when exposure of a weighed sample to normal laboratory atmosphere for seven days resulted in no weight gain and no detectable change in purity.

Solubilities of Potassium Borohydride.—Solubility measurements were carried out by agitation of an excess of the solid with the solvent in a warm water-bath, followed by cooling of the mixture to the desired temperature. A portion of the solution was then removed with a pipet fitted with a glass wool plug to prevent entry of solids. The solution was weighed, the solvent vacuum evaporated, and the weight of the residue determined. Purity was checked in each case by chemical analysis. It was observed that heat was absorbed during solution in water and alcohols. Data for the solubility in aqueous methanol solutions are presented in Fig. 1. Potassium borohydride was observed to be very soluble in liquid ammonia, but no quantitative measurements were made. One hundred grams of 95% ethanol dissolved 0.25 g. of potassium borohydride at 25°. The compound is insoluble (<0.01%) in isopropylamine, benzene, hexane, ether, dioxane, tetrahydrofuran and acetonitrile.

Thermal Stability of Potassium Borohydride.—A small sample of 98.8% pure potassium borohydride was placed in

---

[1] H. I. Schlesinger, H. C. Brown H. R. Hoekstra and L. R. Rapp, This Journal, **75**, 199 (1953).

[2] J. Kollonitsch, *Nature*, **173**, 125 (1954), has recently described an analogous procedure for the preparation of lithium, magnesium and calcium borohydrides, the latter two at −20 to −50°.

[3] W. D. Davis, L. S. Mason and G. Stegeman, This Journal, **71**, 2775 (1949).

a fused silica tube, 1/2″ by 10″, fitted with a ${}^{19}/_{38}$ ₸ ground joint. The tube was attached to a vacuum system and evacuated to 10^{-4} mm. The sample was then gradually heated by an electric furnace. Decomposition commenced at about 500° with the evolution of hydrogen and the simultaneous distillation of potassium.

Densities and Refractive Indices of Sodium, Potassium, Rubidium and Cesium Borohydrides.—Powder densities were determined by the method of Schumb and Rittner.[4] Refractive indices were determined by the Becke Line and Half-Shadow techniques. The data are presented in Table I.

TABLE I

DENSITIES AND REFRACTIVE INDICES OF SODIUM, POTASSIUM, RUBIDIUM AND CESIUM BOROHYDRIDES

Compound	Density, g./cc. at R.T.	Refractive index
$NaBH_4$	1.04	1.547
KBH_4	1.11	1.490
$RbBH_4$	1.71	1.487
$CsBH_4$	2.11	1.498

Debye-Scherrer Powder Patterns of Potassium, Rubidium and Cesium Borohydrides.—X-Ray powder patterns were made by filling 1-mm. diameter glass capillaries with the finely powdered borohydrides. The photographs were made in a Debye-Scherrer camera of 114.6 mm. diameter using Cu Kα irradiation and four-hour exposure. "d" spacings were obtained by visual measurement, as were the intensities. These are listed in Table II, and can be considered as tentative values only.

TABLE II

DEBYE-SCHERRER POWDER PATTERNS

KBH_4		$RbBH_4$		$CsBH_4$	
d spacing, Å.	Intensity	d spacing, Å.	Intensity	d spacing, Å.	Intensity
3.84	MS	3.97	MS	4.17	MS
3.33	S	3.60	S	3.65	MS
2.36	MS	2.46	S	2.59	S
2.02	MS	2.11	MS	2.22	S
1.925	W	2.01	MW	2.12	W
1.675	VVW	1.750	VW	1.840	VVW
1.540	VW	1.610	MW	1.695	W
1.500	VW	1.565	MW	1.650	W
1.375	VW	1.435	MW	1.505	W
1.300	VVW	1.350	MW	1.425	VW
1.195	VVW	1.242	VW	1.250	VVW
		1.190	W	1.235	VVW
		1.175	W		

Comparison of Potassium Borohydride with Sodium Borohydride for the Reduction of Organic Compounds.—Methyl ethyl ketone was reduced to *s*-butyl alcohol (yield 85%), chloral hydrate to trichloroethanol (55%), and *m*-nitrobenzaldehyde to *m*-nitrobenzyl alcohol (90%). Yields reported in the corresponding reactions using sodium borohydride as reductant were 87, 61 and 82%.[5]

Acknowledgment.—The authors wish to acknowledge the assistance of Douglas S. Littlehale in carrying out the chemical analyses, and James B. Vetrano for the determination of refractive indices. X-Ray studies were carried out by Dr. Edward Washken, of Washken Laboratories, Cambridge, Massachusetts.

CHEMICAL RESEARCH LABORATORY
METAL HYDRIDES, INCORPORATED
BEVERLY, MASSACHUSETTS

---

[4] W. C. Schumb and E. S. Rittner, THIS JOURNAL, **65**, 1692 (1943).

[5] S. W. Chaikin and W. G. Brown, THIS JOURNAL, **71**, 122 (1949).

Isotopic Exchange Reactions in Triethylamine-Liquid Sulfur Dioxide Solutions

BY ROLFE H. HERBER[1] AND T. H. NORRIS

RECEIVED APRIL 15, 1954

In their extensive investigations of the chemistry of liquid sulfur dioxide solutions, Jander and coworkers[2] have described the reaction with the solvent of various amines. Evaporation of a solution of triethylamine (under strictly anhydrous conditions) reportedly leads to the formation of colorless crystals of m.p. 73°, corresponding to a 1:1 addition compound between amine and solvent. On the basis of not altogether convincing evidence, they deduce for this material the formula $[(Et_3N)_2SO]SO_3$ (I).

Jander's observations and conclusions have been most effectively disputed by Bateman, Hughes and Ingold,[3] who were unable to confirm his results. Under anhydrous conditions they could prepare no colorless crystalline substance, but only an orange-red liquid, corresponding to the 1:1 addition compound, with a melting point well below 0°. However, various saline materials could be obtained from this by absorption of water or oxygen; in particular the absorption of one mole of water yielded crystals with m.p. 74–75° which they identified with Jander's crystalline substance and to which they assigned the formula $(Et_3NH)(HSO_3)$ (II).

More recently, Jander has somewhat modified his position,[4] suggesting that formula I represents but a minor equilibrium form in solution of the 1:1 addition compound, which he concedes to be primarily monomeric. However, he continues to present chemical reactions as going *via* the dimeric thionyl form, and also still reports the addition compound as a white solid with m.p. 80°.[5] No reference is made to the triethylammonium bisulfite of Bateman, *et al.*[3]

In the course of other work on the chemistry of liquid sulfur dioxide solutions,[6] it was considered worthwhile to investigate this system a bit further by means of isotopic exchange reactions.

Experimental Procedure and Results

Reagent preparations, radioactivity techniques and vacuum line manipulations were similar to those already reported.[6a,c] The radiosulfur, S^{35}, was obtained from the U. S. Atomic Energy Commission. Eastman Kodak Co. (white label) triethylamine was dried over freshly cut sodium, frozen into a cold finger with liquid air and subjected to high vacuum pumping; prolonged contact with stopcock grease was avoided.

The Addition Compound and its Exchange with Sulfur Dioxide.—Some preliminary observations were made on the vapor pressure of triethylamine-sulfur dioxide mixtures. To a known small amount of the amine, successive incre-

---

[1] Department of Chemistry and Laboratory for Nuclear Science, Massachusetts Institute of Technology, Cambridge, Massachusetts. Taken from the Ph.D. thesis of Rolfe H. Herber, Oregon State College, August, 1952.

[2] K. Wickert and G. Jander, *Ber.*, **70**, 251 (1937).

[3] L. C. Bateman, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 243 (1944).

[4] G. Jander, "Die Chemie in Wasserähnlichen Lösungsmitteln," Springer-Verlag, Berlin, 1949, p. 283, *et seq.*

[5] G. Jander, ref. 4, pp. 225, 226.

[6] (a) J. L. Huston, THIS JOURNAL, **73**, 3049 (1951); (b) R. E. Johnson, T. H. Norris and J. L. Huston, *ibid.*, **73**, 3052 (1951); (c) R. H. Herber, T. H. Norris and J. L. Huston, *ibid.*, **76**, 2015 (1954).