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Preparation of Quaternary Ammonium Borohydrides from Sodium and Lithium Borohydrides

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The metathetical preparation of a new type of borohydride containing a quaternary ammonium cation is described. Tetramethyl-, tetraethyl- and benzyltrimethylammonium borohydrides have been prepared by metathetical reactions from sodium borohydride and lithium borohydride. Several properties of these compounds are described.

Discussion

The metathetical reaction of alkali metal borohydrides with unsubstituted or partially substituted ammonium salts might be expected to yield ammonium borohydrides. This reaction, however, evidently gives other products, the nature of which leads in some cases to the supposition that while an ammonium borohydride may be formed momentarily, it decomposes almost immediately. Thus, ethereal lithium borohydride reacts with ammonium chloride[2] and with mono-, di- and trimethylammonium chlorides[3] according to the over-all equations

$$NH_4Cl + LiBH_4 \longrightarrow NBH_6 + LiCl + H_2$$
$$3CH_3NH_3Cl + 3LiBH_4 \longrightarrow B_3N_3H_3(CH_3)_3 + 3LiCl + 9H_2$$
$$(CH_3)_2NH_2Cl + LiBH_4 \longrightarrow (CH_3)_2NBH_2 + LiCl + 2H_2$$
$$(CH_3)_3NHCl + LiBH_4 \longrightarrow (CH_3)_3N{:}BH_3 + LiCl + H_2$$

The instability of the unsubstituted or partially substituted ammonium borohydrides is due in part to the presence of a hydrogen atom on the nitrogen[4] and in part to the weakly basic character of the cation. Thus, the borohydrides of the more strongly basic alkali metals are far more stable both thermally and toward hydrolysis. Accordingly, it may be expected that a borohydride having a quaternary ammonium cation, will be more stable than a borohydride having, say, a dimethylammonium cation. Unfortunately, most quaternary ammonium salts are insoluble in non-aqueous, non-hydroxylic solvents such as ethers; and in fact, show appreciable solubility only in a very few highly polar solvents, especially water. Therefore, it is not feasible to attempt metathetical reactions under the conditions employed previously in the case of partly substituted ammonium compounds. Moreover, the reactivity of the metal borohydrides with water has militated against the use of this medium for the preparation of new borohydrides. However, we have shown that aqueous phase metathesis constitutes an excellent method for the preparation of the quaternary ammonium borohydrides and that hydrolytic losses are less than anticipated.

Aqueous Metatheses with Sodium Borohydride.—Aqueous phase reactions were carried out in accordance with the general equation

$$R_4NX + NaBH_4 \longrightarrow R_4NBH_4 + NaX$$

Here, X represents hydroxide, halide, phosphate, carbonate, acetate or oxalate. Both water and dilute ethyl alcohol were employed as solvents and the vacuum dried reaction products were washed with water or 95% ethyl alcohol.

For tetramethylammonium borohydride, the best procedure was found to be a metathesis involving the quaternary hydroxide, since the resulting dried mixture of borohydride and sodium hydroxide could then be leached with 95% ethyl alcohol in which the latter is quite soluble and the former almost insoluble. Moreover sodium borohydride reacts more rapidly with ethyl alcohol than with water and (if present in the reaction product) would thus be removed. High yields of 99+% tetramethylammonium borohydride were obtained in this manner. The tetraethyl compound is more soluble in 95% ethyl alcohol and is also more susceptible to hydrolysis. Thus it was obtained in variable but considerably poorer yields.

Similar metatheses employing tetramethylammonium chloride and bromide were successful, but as expected from the solubilities of the four solids involved, none of the reactions gave more than 70–90% yields. Tetramethylammonium chloride in 95% ethyl alcohol gave a crude product containing 76% of the expected quaternary borohydride with evident reaction of the sodium borohydride with the solvent. Aqueous metatheses of the quaternary fluoride and phosphate appear preferable to those of the chloride or bromide on the basis of the lower solubility of sodium fluoride and triphosphate. (The latter metathesis is successful only at 0°.) Neither acetate nor oxalate metathesis offers any apparent advantages.

Aqueous Metatheses with Lithium Borohydride.—Although lithium borohydride ordinarily reacts violently with water, it was discovered that if the pure compound is introduced anaerobically at or below 0°, a solution results with but minor loss of activity. Air-free distilled water is employed. The resulting solution is sufficiently stable to permit its use over a period of hours.

The insolubility of lithium fluoride and phosphate permits almost quantitative reaction of the respective quaternary ammonium salts with lithium borohydride. Of the two metatheses, that employing the fluoride gave better yields in the case of benzyltrimethylammonium borohydride and quantitative yields of tetramethyl- and tetraethylammonium borohydrides. Various mixtures of lower amines, alcohols and water were investigated in a rather cursory manner and appear to offer no advantages over water. Those solvents in

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[2] H. I. Schlesinger and G. W. Schaeffer, *et al.*, University of Chicago, Final Report, Navy Contract N6ori-20 T. O. 10 (1947–1948).

[3] G. W. Schaeffer and E. R. Anderson, THIS JOURNAL, **71**, 2143 (1949).

[4] We are indebted to one of the referees for this observation and the comment that the case is analogous to the increasing ease of formation of N-dimethylaminoborine from trimethylamineborine and dimethylamineborine, respectively.

which lithium borohydride is soluble, *e.g.*, lower ethers and amines, do not dissolve quaternary ammonium salts. Aqueous amines are apparently no better than water (90% isopropylamine–10% water dissolves only 0.27 g./100 g. of tetramethylammonium borohydride); aqueous cyclic ethers were not investigated nor were secondary or tertiary alcohols.

Properties.—The three borohydrides prepared are stable hygroscopic microcrystalline solids comparable to sodium borohydride and lithium borohydride. They burn quietly but rapidly on ignition, leaving a slight ash. They are not ignited by friction nor by moistening with water or ethyl alcohol. Spontaneous ignition by pouring or handling in humid air has not been observed although the tetramethyl and benzyltrimethyl compounds deteriorate very rapidly when so handled. The materials keep well in an ordinary screw-top bottle, however. The densities at 25° of the tetramethyl, tetraethyl and benzyltrimethyl compounds are, respectively, 0.813, 0.927, 0.638 g./cc., measured by helium displacement.

All three compounds are soluble in water with reaction and they react with methanol. The tetramethyl compound has the solubilities shown in Table I and is insoluble in diethyl ether, isopropylamine, pyridine, chloroform, dioxane, tetrahydrofuran, ethyl cellosolve, N-methylmorpholine. The rate of reaction with water at room temperature follows approximately the increasing sequence: tetramethyl-, benzyltrimethyl-, tetraethylammonium borohydride, although the *p*H and presence of trace impurities such as heavy metal ions have a profound effect. The tetramethyl compound is less reactive toward water than sodium borohydride and the tetraethyl compound considerably less reactive than lithium borohydride. Hydrolysis yields four mols of hydrogen per mol borohydride and is presumed to proceed according to the reaction

$$R_4NBH_4 + 2H_2O \longrightarrow (R)_4NBO_2 + 4H_2$$

(The resulting quaternary ammonium salt of a weak acid should be capable of further hydrolysis to yield the labile hydroxide which decomposes in boiling water to give volatile ROH and R_3N.) The rate of hydrolysis of tetramethylammonium borohydride (5.8 *M*) in water at 40° is nearly constant over a period of 100 hours at 0.04% of original weight per hour based on the above equation. This rate is decreased to 0.02% per hour by the presence of $(CH_3)_4NOH$ in the amount of 5% of the weight of borohydride.

Table I

Solubility of Tetramethylammonium Borohydride

Solvent	Solubility g./100 g. at *T* °C.
Water	48 (20°) 61 (40°)
Ethyl alcohol	0.5 (25°)
95% Ethyl alcohol	1.42 (25°)
Acetonitrile	0.4 (25°)

Solid tetramethylammonium borohydride decomposes slowly *in vacuo* at 150°, rapidly at 250° yielding principally trimethylamineborine and methane. It does not ignite spontaneously in air at this temperature, but volatilizes leaving no residue. In an evacuated sealed glass bulb, it decomposes at the average rate of 0.095% per hour at 150°, 4.1% at 175°, 33.3% at 195°, and 4.16% per minute at 225°. The $\log_{10}$ rate of decomposition is evidently inversely proportional to the reciprocal of the absolute temperature over this range. At 220–250°, the trimethylamineborine rapidly sublimes away from the borohydride in the form of pure, acicular crystals (96% yield). Hydrogen and trimethylamine (4% yield) were observed as decomposition products, indicating two possible courses for the reaction. The small amount of pure white non-volatile residue (2% of the original weight) contained sodium, carbon, hydrogen and nitrogen and presumably boron and oxygen, which could not be determined. It is thought to consist of $NaBO_2$, $NaBH_4$ and possibly polymeric substances.

Experimental

Materials.—Commercial $NaBH_4$ and $LiBH_4$ were purified by extraction with water and isopropylamine[5] and diethyl ether, respectively, to yield products approaching 100% purity as measured by hydrogen evolved from acidified water. Tetramethyl- and tetraethylammonium chloride, bromide, iodide and hydroxide were obtained from Eastman Kodak Co. and the Paragon Division of the Matheson Co. Benzyltrimethylammonium chloride was provided by the Commercial Solvents Co. All were used as received. (Exposure of the hydroxides to air was kept to a minimum.) The quaternary salts other than those cited above were made by metathesis or by neutralization of the base by the desired acid to the appropriate end-point. Benzyltrimethylammonium hydroxide was prepared from the aqueous chloride *via* solid silver oxide. (It was necessary to stir under an inert atmosphere for four days.) A preferable method for preparing fluorides from the chlorides or bromides was used subsequently and involved the aqueous reaction with soluble silver fluoride prepared by dissolving silver oxide in dilute HF to a *p*H of from 6 to 7. The quaternary chloride or bromide is added to a solution of silver fluoride until a trace of chloride ion is detected. After brief boiling to coagulate the precipitated silver chloride or bromide, the solution is filterd and evaporated. The crystalline compound $(CH_3)_4NF\cdot 2H_2O$ is obtained by evaporation at 80°. It is extremely hygroscopic. Tetramethylammonium carbonate was prepared by saturating the aqueous hydroxide with CO_2 to a phenolphthalein end-point and subsequently adding an equal amount of the hydroxide to convert the bicarbonate to carbonate. The acetates were prepared from the iodides and silver acetate in preference to neutralization of the hydroxide.

Preparation of Tetramethylammonium Borohydride.—Solid sodium borohydride, 8.5 g. (0.22 mole) was added to 20 g. of $(CH_3)_4NOH$ (0.22 mole) dissolved in 90 g. water, the mixture giving an almost clear solution. This was evaporated to dryness *in vacuo* and the white solid broken up in a dry-box under dry argon. It was then extracted with 90 cc. of 95% ethyl alcohol and filtered by suction without precaution to exclude air. The filter cake was washed with two 50-cc. portions of cold 95% alcohol, then dried *in vacuo* for 18 hours at 70–80°; yield 18.5 g. (93%) of white microcrystalline product. *Anal.* Calcd.: B, 12.17; H (active), 4.50; H, (total), 18.1; C, 53.9; N, 15.83. Found: B, 12.13; H (active), 4.49; H (total), 17.9; C, 52.4; N, 16.4; Na, 0.6; total accounted for 99.43%. The ratio B/H (active) was 1:3.98; C/H (organic) was 1:3.04. A similar run in which the product was crystallized three times from water without an alcohol extraction gave a 61% yield of a product of 94% purity. Active hydrogen determinations were made by a standard method based on the volume of hydrogen obtained on acid hydrolysis. Nitrogen determinations were made by the Dumas method and were high for all compounds of this type. An aqueous

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

metathesis using the quaternary phosphate with filtration at 0–2° of the precipitated Na_3PO_4 gave a 90% crude product containing less than 1% phosphate, the balance being borate. A similar metathesis using the oxalate gave a 79% crude product containing 6.8% sodium oxalate and considerable borate. Similarly, an acetate metathesis gave an 86% crude product containing 12% $NaBO_2$. Metatheses based on the quaternary chloride, bromide and iodide with $NaBH_4$ were shown by solubility considerations not to be feasible in water. Use of aqueous isopropylamine and aqueous ethyl alcohol as media resulted in no substantial improvement.

An alternative typical preparation using lithium borohydride as a starting material is as follows: An aqueous solution containing 2.11 g. (0.97 mole) of lithium borohydride was prepared by adding 50 cc. of distilled, degassed, ice-water to the hydride under argon. The solution was promptly added to 8.92 g. of $(CH_3)_4NF$ (0.96 mole) and stirred. The precipitated LiF was removed on a sintered glass funnel and the clear filtrate evaporated *in vacuo* at room temperature. The solid was taken up in the minimum amount of water, filtered, evaporated and finally dried 3 hours at 100° in high vacuum; crude yield 98.5%, purity 95%. *Anal.* B, 12.5; H (active), 4.30; H, (total), 17.0; C, 50.6; N, 15.9.

Preparation based on metatheses involving the other cations cited were carried out in substantially the same manner using stoichiometric proportions.

Aqueous phosphate metathesis with filtration of the precipitated Li_3PO_4 gave a crude product of 78% purity containing borate. Aqueous carbonate metathesis with filtration of precipitated Li_2CO_3 gave a product of 89% purity containing 1.1% lithium and significant amounts of borate. Aqueous oxalate metathesis similarly gave a product of 72% purity.

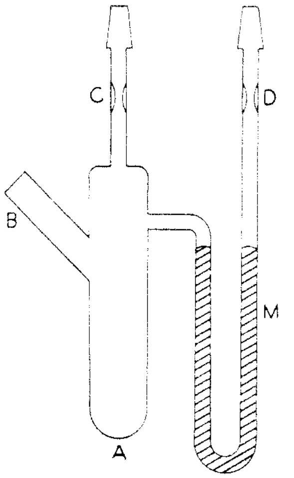

Fig. 1.—A, decomposition tube; B, side arm for introducing sample; C, D, seal-off constrictions; M, manometer.

Preparation of Tetraethylammonium Borohydride.—The preparation from the quaternary hydroxide and sodium borohydride was complicated by the greater reactivity of $(C_2H_5)_4NBH_4$ with water. The preparation from the quaternary fluoride and lithium borohydride was carried out exactly as described in the analogous case of the tetramethyl compound. An 82% yield of product analyzing 95% $(C_2H_5)_4NBH_4$ was obtained. *Anal.* B, 7.46; H (active), 2.78; H (total), 16.68; N, 9.66; ratios B/H, 1:4; C/H (organic), 1:2.50; B/C, 1:8; N/C, 1:7.14. Found: B, 7.39; H (active), 2.63; H (total), 15.5; N, 10.37; Li, 1.52; ratios: B/H (active), 1:3.83; C/H (organic), 1:2.42; B/C, 1:7.73; N/C, 1:7.14; total accounted for 98.18%. (As noted above, nitrogen values appear to be high by the Dumas method. The Kjeldahl procedure is not applicable.) Preparation by hydroxide metathesis in water gave a nearly quantitative yield of product accompanied by 10% inactive impurity. In alcohol, however, decomposition occurred. Aqueous chloride metathesis gave a product of 76% purity accompanied by Et_4NBO_2, which later is soluble in alcohol.

Preparation of Benzyltrimethylammonium Borohydride.—The only preparative method investigated was the aqueous reaction of the quaternary fluoride with lithium borohydride. Stoichiometric proportions of the reactants in water solution were mixed and evaporated to dryness *in vacuo* as in the case of the tetraethyl compound. A crude yield of 100% was obtained, the purity by active H content being only 89%. The product had a slight yellowish tinge. *Anal.* Calcd.: B, 6.56; H (active), 2.42; H (total), 12.20; C, 72.75; N, 8.49. Found: B, 6.19; H (active), 2.15; H (total), 11.30; C, 68.0; N, 12.45; Li, 0.24; Cl, 1.18; accounted for 99.36%. The formula of the product is largely established by the stoichiometry and the yield since the analysis presented unexplained discrepancies.

Thermal Stability of Solid Tetramethylammonium Borohydride.—The rates of decomposition were determined in the Pyrex apparatus shown in Fig. 1. The cleaned and degassed tube was attached to a manifold by the standard taper joints and mercury added to the desired level. The weighed sample was introduced under argon through tube B which was then sealed off. The tube was re-evacuated to 10^{-4} mm. and pure dry argon admitted to a pressure which was calculated to increase to approximately one atmosphere at the planned operating temperature. Tubes C and D were then sealed off and the entire apparatus placed in a constant temperature (±1°) oven. After a short induction period, decomposition set in as low as 150° as evidenced by development of pressure.

The stability of an aqueous solution containing 52 g. $(CH_3)_4NBH_4$ in 100 g. of water was carried out by observing the pressure change in a similar bulb completely immersed in an oil-filled thermostat controlled to ±0.5°.

Pyrolysis of Tetramethylammonium Borohydride.—Decomposition was carried out at 220–225° in a Pyrex sublimation tube attached to a calibrated vacuum line provided with conventional cold-traps and manometer. Sublimation commenced almost immediately with the deposition of long, needle-like crystals near the cool upper portion of the tube; yield of product 96% (based on the equation $(CH_3)_4NBH_4 \rightarrow (CH_3)_3NBH_3 + CH_4$); m.p. 93–94° (correct for trimethylamineborine). *Anal.* C, 49.40; H, 16.58; N, 19.22; B, 14.84. Found: C, 49.38; H, 16.64. N, 19.33; B, 14.65 by difference. Trimethylamine was condensed, identified by its vapor pressure of 6 mm. at −80° and measured by the pressure exerted in a calibrated portion of the vacuum line. No attempt was made to measure the yield of methane accurately when it was found to contain a small amount of non-condensable gas, presumably hydrogen. It was isolated by condensation followed by pump-off of the contaminating gas and identified by its vapor pressure of 12 mm. at −195°. From the known volume of the system, it was possible to estimate the yield of methane as approximately 95%.

Solubility of Tetramethylammonium Borohydride.—Samples of 99+% fine powder were weighed into test-tubes in an argon-filled dry-box and the tubes closed with culture-tube rubber stoppers. Portions of solvent insufficient to dissolve the contents were added and solid–solution equilibrium attained by shaking in a thermostat. Aliquots of the supernatant liquid were quickly pipetted into tared flasks and evaporated *in vacuo*. The dry residues were heated at 100° *in vacuo*, cooled, weighed and analyzed for active hydrogen.

The density of solids was measured by helium displacement in a modified Schumb–Rittner apparatus.[6]

Acknowledgment.—The data reported herein were obtained under a contract with the Fairchild Engine and Airplane Corporation on the Air Force sponsored NEPA Project. Density determinations were made in this Laboratory by Henry W. Kruschwitz, Jr.

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[6] W. C. Schumb and E. S. Rittner, This Journal, **65**, 1692 (1943).