

(b.p. 67.5–68° at 750 mm.). The over-all yield was 89%. The last column shows that even in the most favorable experiment 14.5% of the methyl borate was lost as part of the acid layer.

A mixture of 570 ml. (500 g.) of the azeotrope and 570 ml. of ligroin (b.p. 110°, previously washed with sulfuric acid) was treated with two portions of 20 ml. of sulfuric acid. Only 4.8% of the ester was lost and 98.1% of the methanol was removed. Distillation of the solvent led to 91.2% yield of ester boiling from 67.5–68.5°.

Azeotropic Separation.—A mixture of 2800 g. of the azeotrope and 1400 g. of carbon disulfide was fractionally distilled with the aid of the column employed for the preparation of the azeotrope. The carbon disulfide–methanol azeotrope distilled at 38°. The distillate separated into two layers, of which the lower one (97% carbon disulfide–3% methanol) was returned to the still. At the end of 45 hours of operation, methanol removal was complete, as indicated by the rise in boiling point to that of carbon disulfide, 46°. The products were a carbon disulfide–methanol fraction of 2105 g., a fraction from 46 to 67.5° of 88 g. (73% ester) and 1940 g. of pure methyl borate, b.p. 67.5–68.5°. The yield was 92.3%. The reaction time could probably be greatly decreased by the use of a more efficient column.⁶

Lithium Chloride Separation.—The effectiveness of a number of salts in separating the methanol from the azeotrope was studied. Data are summarized in Table IV.

The addition of 120 g. of anhydrous lithium chloride to 1000 g. of the azeotrope caused the mixture to separate into two layers.⁷ The lower one consisted of a solution of lithium

(6) The advantage of recycling a portion of the carbon disulfide is lost if the carbon disulfide–methanol mixture contains as little as 1.5% of methyl borate, for then separation into two layers does not occur. This difficulty is avoided by use of a good fractionating column.

(7) Although a smaller amount (80 g.) of the salt seems to saturate the solution, the larger quantity gives somewhat better results.

TABLE IV

EXTRACTION OF METHANOL FROM THE AZEOTROPE WITH SALTS

Salt used	LiCl	NaCl	CaCl ₂	Ca-(NO ₃) ₂	AlCl ₃	MgCl ₂	Zn-Cl ₂
G. salt per 135 g. azeotrope	13	30	14	30	8.0	15	46
Purity of methyl borate, %	99.6	98.0	92.5	90	85	98.2	99.6

chloride in methanol plus some suspended salt and contained from 3.6 to 4.0% of the methyl borate present in the azeotrope. The upper layer contained about 96% of the methyl borate of from 99.5 to 99.7% purity; the slight contamination was methanol.

The methanol was recovered from the lower layer by distillation. Below 90°, the small quantity of the methyl borate present distilled as the azeotrope. At a pot temperature of from 95 to 115°, 96% of the methanol was recovered practically pure. At this stage the lithium chloride was obtained partly as a powder and partly as readily powdered lumps.

By raising the temperature to 160°, the remaining 4% of the methanol could be recovered. When that was done, the lithium chloride was obtained as a hard cake which, though usable, was inconvenient to handle. It is, therefore, recommended that heating the residue above 115° be avoided if the lithium chloride is to be re-used in subsequent separations.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Sodium Borohydride, Its Hydrolysis and its Use as a Reducing Agent and in the Generation of Hydrogen¹

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Sodium borohydride reacts slowly with water ultimately to liberate 4 moles of hydrogen per mole of the compound at room temperature, or 2.4 l. per gram. The reaction is greatly accelerated by rise of temperature or by the addition of acidic substances, for which latter purpose boric oxide is convenient and effective when the objective is the generation of hydrogen. Particularly striking is the catalytic effect of certain metal salts, especially that of cobalt(II) chloride. Thus pellets of sodium borohydride containing only 5% of the cobalt salt react as rapidly as those containing 10 times that amount of boric oxide. The effect of the cobalt salt is ascribed to the catalytic action of a material of empirical composition, Co₂B, which is formed in the initial stages of the reaction.

The hydrolysis of sodium borohydride is of interest in connection with the use of the compound as a reducing agent in aqueous solutions² and because of its potential usefulness for the generation of hydrogen whenever or wherever the use of the compressed gas is inconvenient. Under appropriate conditions, 2.37 l. of hydrogen (gas at S.T.P.) are liberated per mole of the compound, as compared with 1.1 l. for calcium hydride and 2.8 l. for lithium hydride. At ordinary temperatures, however, only a very small percentage of the theoretical amount of hydrogen is liberated at an

appreciable rate, since the initial moderately rapid rate soon decreases after the borohydride and the water have been mixed. As a result, not only may the aqueous solution of the compound be effectively used as a chemical reagent, but a large part of the salt may actually be recovered unchanged from such solutions by removal of water *in vacuo*.³

It is evident that the decrease in the initial rate of hydrogen evolution is due to the increasing pH of the solution⁴ which in turn is caused by the formation of the strongly basic metaborate ion



Thus the initial generation of hydrogen may be

(3) H. I. Schlesinger, H. C. Brown, H. R. Hoekstra and L. R. Rapp, *THIS JOURNAL*, **75**, 199 (1953).

(4) See also M. Kilpatrick and C. D. McKinney, Jr., *ibid.*, **72**, 5474 (1950).

(1) New Developments in the Chemistry of Diborane and of the Borohydrides. IX. For an explanation of the nomenclature employed, see paper I, *THIS JOURNAL*, **75**, 186 (1953).

(2) (a) H. I. Schlesinger, H. C. Brown and A. E. Finholt, *ibid.*, **75**, 205 (1953). (b) S. W. Chaikin and W. G. Brown, *ibid.*, **71**, 122 (1949); unpublished work of G. W. Schaeffer and A. Stewart. (c) A. Stewart, Master's Thesis, University of Chicago (1948).