[Contribution from Callery Chemical Company]

The Sodium–Diborane Reaction[1]

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Received September 26, 1957

The reaction of diborane with sodium amalgam in simple ethers yielded an equimolar mixture of sodium borohydride and NaB_3H_8. The new compound was characterized by X-ray, infrared and elemental chemical analyses and by its physical properties. A proposed reaction course involves intermediates of empirical composition $Na_2B_2H_6$ and NaB_2H_6.

Reactions of boron hydrides with sodium amalgam were first studied by Stock and co-workers[2-5] who found that after two or three days at room temperature sodium amalgam and diborane gave a solid having the empirical composition $Na_2B_2H_6$. Later investigators[6] revealed that sodium absorbed more diborane than required for the formation of $Na_2B_2H_6$. The X-ray pattern of their product indicated the presence of sodium borohydride and unidentified substances. The reaction of sodium with diborane was investigated in this Laboratory to determine the stoichiometry and identify the reaction products.

Results and Discussion

Ethyl and *n*-butyl ether were used as liquid media for the reaction of diborane with sodium amalgam.[1] The rate of reaction was considerably faster in the ethers than in the absence of reaction media. Complete reaction involving the consumption of one mole of diborane per gram atom of sodium was observed in one to two days. Since butyl ether was difficult to purify, partial hydrolysis of the hydridic materials occurred when butyl ether was used. Therefore, the products of reaction in ethyl ether were more thoroughly investigated.

The ultimate reaction products, having the empirical composition NaB_2H_6, consisted of an equimolar mixture of sodium borohydride and a new compound, NaB_3H_8.[7] The net reaction is defined by the equation

$$2Na + 2B_2H_6 \longrightarrow NaBH_4 + NaB_3H_8 \qquad (1)$$

Since NaB_3H_8 is soluble in ethyl ether it was readily separated from insoluble sodium borohydride. Quantitative isolation of the small quantity of product from a comparatively large reaction vessel containing large quantities of mercury was not realized. However, 80% recovery of NaB_3H_8 calculated from equation 1 was obtained from ether solution while insoluble residues corresponded analytically to sodium borohydride.

The white crystalline NaB_3H_8 is thermally stable at 200° and dissolves readily in ethers, liquid ammonia, methanol and water. Solution in water and in aqueous hydrogen chloride is accompanied by mild incomplete hydrolysis. The anhydrous compound readily absorbs water or ether. A hemi- and a mono-ethyl etherate are formed at 0°.

Although the over-all reaction between sodium and diborane is well-defined by equation 1, studies of the reaction and nature of the reaction products as a function of time (Table I) furnished evidence of intermediate reactions. A material of empirical composition $Na_2B_2H_6$ appeared to form early in the reaction process; after 4 hr. the sodium, although only partially consumed, had reacted in the proportion of about two gram atoms per mole of absorbed diborane. No unreacted sodium was recovered after 16 hr. and absorption of one mole of diborane per gram atom of sodium was nearly complete. Although the stoichiometry of equation 1 was fulfilled at this time, evidence was obtained for an intermediate of composition NaB_2H_6. In one instance a sample of the material of composition NaB_2H_6 removed immediately from the reaction gave an X-ray pattern dissimilar to that of sodium borohydride or NaB_3H_8. Subsequent X-ray examinations of the same sample indicated the gradual formation of sodium borohydride with simultaneous disappearance of the intermediate NaB_2H_6.

Table I

The Reaction of Diborane with Sodium Amalgam in Simple Ethers[a]

Time, hr.	Charged Na mg. atom	Charged B_2H_6, mmole	Consumed Na mg. atom	Consumed B_2H_6, mmole	Hydrogen evolved, mmole	Product formula Na:B:H
4	5.72	12.26	1.37	0.85	0.00	1.00:1.24:3.72
16	6.45	12.67	6.45	6.26	.00	1.00:1.94:5.83
44	6.15	12.21	6.15	6.18	.00	1.00:2.01:6.03
64[b]	6.94	12.23	6.94	6.78	.36	1.00:1.96:5.82
150	6.01	12.15	6.01	6.41	.18	1.00:2.13:6.37

[a] Approximately 11 mmoles of ether in each experiment. [b] *n*-Butyl ether was used. Ethyl ether was used in all other experiments.

The usual X-ray pattern of crude reaction products of composition NaB_2H_6 was identical to that of sodium borohydride. A satisfactory X-ray pattern for NaB_3H_8 was obtained only after extreme precautions were taken to avoid contact with air and ether vapors. None of the crude reaction products exhibited X-ray patterns typical of NaB_3H_8 since the patterns were obtained before the necessity of careful handling was realized. Although NaB_3H_8 was not detected by X-ray analysis of the crude reaction products, the infrared spectra clearly demonstrated that the samples were mixtures of NaB_3H_8 and sodium borohydride.

The experimental observations provided a basis upon which a reaction course may be tentatively proposed. This reaction course involves the for-

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(1) See W. V. Hough, L. J. Edwards and A. D. McElroy, This Journal, **78**, 689 (1956), for a preliminary report of this investigation.

(2) A. Stock and E. Kuss, *Ber.*, **56**, 789 (1923).

(3) A. Stock and E. Pohland, *ibid.*, **59**, 2210 (1926).

(4) A. Stock, "Hydrides of Boron and Silicon," the Cayuga Press, Ithaca, New York, 1933, pp. 58, 138

(5) A. Stock and H. Laudenklos, *Z. anorg. allgem. Chem.*, 178 (1936).

(6) J. S. Kasper, L. V. McCarty and A. E. Newkirk, This Journal, **71**, 2583 (1949).

(7) The committee on Boron Nomenclature with Dr. Kurt L. Loening of *Chemical Abstracts* as chairman, has recommended the name sodium octahydrotriborate (I).

mation of an intermediate of empirical composition $Na_2B_2H_6$, the further absorption of diborane to yield another intermediate of composition NaB_2H_6 and finally a transition of the material NaB_2H_6 to NaB_3H_8 and sodium borohydride. The X-ray data suggested that the transition of the intermediate NaB_2H_6 may occur in the solid phase. A solid phase transition, however, would seem more reasonable if NaB_2H_6 were dimeric. This representation of the course of reaction may be over-simplified.

Experimental

Materials.—Commercially available ethers were distilled from and stored over sodium hydride. An amalgam containing about 0.6 wt. % sodium was prepared in kilogram quantities by adding mercury to molten sodium in mineral oil. Diborane of 98–99% purity was used.

Reaction Stoichiometry.—High vacuum techniques were used and the experimental procedures were for the most part those commonly employed in the use of sealed tubes. As far as possible materials were handled *in vacuo* or in a dry box to assure minimum contact with air and moisture. The following procedure was employed in the studies of the reaction between sodium and diborane. The reaction tube (110–250 ml. capacity) was evacuated, degassed by direct flame heating, filled with nitrogen, capped and placed in a dry box. A weighed quantity of amalgam and a measured volume of ether were introduced. The tube was attached to a vacuum system, cooled with liquid nitrogen and evacuated. A measured quantity of diborane was condensed into the tube. The tube was sealed, warmed to room temperature and agitated in a wrist action shaker for the desired length of time. The sealed break-off tip was broken; hydrogen was pumped off and its volume was measured. The condensable volatile components were fractionated and the recovered diborane was measured. Purity of the recovered ether was determined by vapor pressure measurements and/or mass spectrometric analysis. A sample of the mercury phase was analyzed for sodium.

The stoichiometry of the reaction was calculated from the quantities of charged and recovered materials. Table I gives representative experimental data. In experiments lasting five days or more, diborane was consumed in excess of theory and traces of hydrogen and other volatile boron hydrides were detected.

In several cases, NaB_3H_8 was prepared in larger quantities to determine the amount of the compound formed in the reaction. In a typical experiment sodium amalgam, containing 80 mmoles of sodium, was charged in a two-liter reaction flask with 25 ml. of ethyl ether. About 87 mmoles of diborane was condensed into the bulb at $-196°$ and the bulb was sealed *in vacuo*. When the amalgam melted, the bulb was placed on its side and the amalgam was stirred with a magnetic stirring bar. After two days all volatile materials were removed and the solids were separated by extraction with ethyl ether in the dry box. An 83% yield, 2.1 g., of NaB_3H_8 was obtained. The ether-insoluble solid was sodium borohydride contaminated with mercury.

Identification of Products.—The X-ray diffraction patterns of the crude reaction products of empirical composition NaB_2H_6 (Table II, $NaB_2H_6{}^a$), obtained 12 to 24 hr. after isolation, were identical with the pattern of sodium borohydride. X-Ray examination immediately after isolation of the reaction product of empirical composition NaB_2H_6 (Table II, $NaB_2H_6{}^b$) indicated the absence of sodium borohydride and the presence of a previously unobserved material. None of the crude reaction products gave X-ray evidence for the presence of NaB_3H_8. Satisfactory X-ray patterns for NaB_3H_8 were obtained only after more than the usual precautions were taken to exclude moisture and ether from the sample.

The infrared spectra of the crude reaction products were consistent with an interpretation in terms of a mixture of sodium borohydride and NaB_3H_8. The prominent infrared spectral bands were as follows: $NaBH_4$ in KBr: 2280(S), 2250(S), 2145(S), 1125(S); $NaBH_4$ in triethylene glycol dimethyl ether: 2240 (broad); NaB_3H_8 in KBr: 2470(S), 2435(S), 2135(M), 2100(M), 1175(S), 1005(S), 795(M), 735(M); NaB_3H_8 in triethylene glycol dimethyl ether: 2440(S), 2395(S), 2135(M), 2080(M).

The complete hydrolysis of NaB_3H_8 in distilled water required several days at 100°. Chemical analyses were made by the measurement of the hydrogen evolved on hydrolysis and by the titration of the resulting solution for boron and sodium.

Anal. Calcd. for NaB_3H_8: Na, 36.1; B, 51.2; H (hydrolyzable), 141 mmole/g. Found: Na, 35.6, 34.5; B, 52.7, 51.7; H (hydrolyzable), 137, 142 mmole/g.

TABLE II

X-RAY PATTERNS

INTENSITIES AND *d*-VALUES

$NaBH_4$	3.559(m), 3.082(vs), 2.179(s), 1.859(w), 1.739(m), 1.541(w), 1.414(w), 1.378(m), 1.259(w), 1.186(w), 1.089(w), 1.027(w), 0.975(w), 0.929(w), 0.855(w), 0.824(w)
$NaB_2H_6{}^a$	3.60(m), 3.07(vs), 2.17(s), 1.85(m), 1.78(m), 1.53(w), 1.42(w), 1.37(m), 1.26(m)
$NaB_2H_6{}^b$	4.2(m), 3.3(s), 3.05(w), 1.81(w), 1.53(w), 1.36(m), 0.914(w), 0.791(w)
NaB_3H_8	5.67(m), 5.09(m), 4.66(m), 3.93(s), 3.67(s), 3.32(vs), 2.71(w), 2.35(s), 2.15(m), 2.02(w), 1.88(w), 1.64(w)

[a] An ethyl ether product—usual pattern. [b] An ethyl ether product—pattern of a freshly prepared sample.

An attempt was made to determine the molecular weight of NaB_3H_8 by measurement of the vapor pressures of liquid ammonia solutions at $-45°$. The calculated values of the molecular weight ranged from 13.6 in a 4.0 *m* solution to 53.2 in a 2.0 *m* solution. The variations in the results can probably be attributed to solvation of the compound.

Ethyl Ether Solvation.—The extent of solvation of NaB_3H_8 in ethyl ether was determined by observation of the equilibrium pressures resulting when successive small increments of ether were introduced to, or removed from, a flask containing a known weight of solid. The two plateaus in the 0° isotherm indicated the formation of a hemi- and a mono-etherate, with dissociation pressures of 4 and 10 mm., respectively.

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