TABLE I

GAS ANALYSIS FOR COMPLETE HYDROLYSIS OF SODIUM BOROHYDRIDE WITH PREFORMED CATALYSTS IN 0.1 *M* $Na_2CO_3$ IN $D_2O$ AT 25.0 ± 0.05°

| Catalyst | Weight, mg. | $H_2$, %[e] | HD, %[e] | $D_2$, %[e] |
|---|---|---|---|---|
| O[a] | . . . | 0.8 | 98.7 | 0.5 |
| Co[b] | 0.001 | 1.7 | 82.2 | 16.1 |
| | 0.10 | 5.0 | 31.0 | 64.0 |
| | 1.00 | 4.7 | 30.2 | 65.1 |
| | 4.90 | 4.3 | 30.9 | 64.8 |
| | 11.3 | 3.8 | 30.4 | 65.8 |
| | 23.4 | 4.4 | 30.5 | 65.1 |
| | 30.2 | 4.8 | 32.8 | 62.4 |
| Pd/C[c] | 0.10 | 3.2 | 20.8 | 76.2 |
| | 1.20 | 3.0 | 25.1 | 71.9 |
| | 1.90 | 2.5 | 25.0 | 72.5 |
| | 5.00 | 1.0 | 21.5 | 77.5 |
| Pt/C[d] | 0.376 | 2.9 | 25.5 | 71.6 |
| | 0.617 | 3.2 | 20.8 | 76.2 |
| | 0.951 | 1.4 | 18.2 | 80.3 |
| | 1.594 | 0.4 | 7.7 | 92.2 |

[a] No added catalyst. Special techniques were used in an attempt to keep the materials free from metals. The $D_2O$ used was of 99.52 ± 0.03% isotopic purity. Mass of borohydride was always between 9 and 11 mg. in all this work in 5 ml. of $D_2O$. [b] Cobalt(II) chloride. Catalyst weight expressed as mg. of $Co_2B$ in 5.00 ml. of $D_2O$. Catalyst was preformed with 10 mg. of sodium borohydride and then used as a catalyst for another 10-mg. sample. [c] Commercial catalyst of 5% Pd on carbon (Englehard). Mass of catalyst suspended in 5 ml. of $D_2O$ expressed as mg. of metal. [d] Commercial 5% Pt on carbon (Englehard). Mass of catalyst has been expressed as mass of Pt in 5 ml. of $D_2O$. [e] Control experiments show that the data of Table I are not due to the catalyst reacting with the gaseous hydrogen produced. Although these catalysts can cause exchange between dissolved hydrogen gas and water, this exchange is much slower than the hydrolysis reactions observed here. (The entire system contains 99% D and 1% H, and this would be the isotopic composition for complete isotope equilibration. Our control experiments are confirmed by the data of U. Schindewolf, *J. chim. phys.*, **60**, 124 (1963).)

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## Convenient Preparation of the Dodecahydrododecaborate Ion

*Sir:*

In the previously reported preparation[1] of the $B_{12}H_{12}^{-2}$ ion the yields were very low and it was only a minor by-product of the reaction. We wish to report a much improved preparation.[2]

Decaborane has been shown to react with borohydride at room temperature in diethylene glycol dimethyl ether to form the $B_{10}H_{13}^-$ ion.[3]

$$B_{10}H_{14} + BH_4^- + R_2O \longrightarrow B_{10}H_{13}^- + R_2OBH_3 + H_2$$

At about 90° these products react further to form the $B_{11}H_{14}^-$ ion.[4]

$$B_{10}H_{13}^- + R_2OBH_3 \longrightarrow B_{11}H_{14}^- + H_2 + R_2O$$

With a second equivalent of borohydride this system undergoes further reaction at higher temperatures to form the $B_{12}H_{12}^{-2}$ ion.

$$B_{11}H_{14}^- + BH_4^- \longrightarrow B_{12}H_{12}^{-2} + 3H_2\uparrow$$

Dry diethylene glycol dimethyl ether, 23 ml., was added to 0.98 g. (8.0 mmoles) of decaborane and 0.64 g. (16.8 mmoles) of sodium borohydride. A yellow color developed and hydrogen was evolved. The mixture was refluxed under nitrogen with stirring until hydrogen evolution ceased. After chilling, 3.71 g. of white solid $Na_2B_{12}H_{12}\cdot$diglyme was filtered off and dried *in vacuo*. This solvate was dissolved in water and evaporated to dryness at room temperature on a rotary evaporator. This process was repeated three more times to afford the diglyme-free salt, 0.90 g. (60%).

Addition of triethylammonium chloride to an aqueous solution of the sodium salt and refrigeration caused the precipitation of white crystalline $[(C_2H_5)_3NH]_2B_{12}H_{12}$. *Anal.* Calcd. for $B_{12}C_{12}H_{44}N_2$: C, 41.7; H, 12.75; B, 37.4; N, 8.11. Found: C, 41.3; H, 12.7; B, 37.2; N, 8.09.

The infrared spectrum of the triethylammonium salt (KBr) showed all the reported absorption bands for the $B_{12}H_{12}^{-2}$ ion[1] with the exception of a weak band at 755 cm.$^{-1}$ and agreed with the spectrum[5] of an authentic specimen.

**Acknowledgment.**—We wish to express our appreciation to Callery Chemical Company for the sample of decaborane and for the elemental and spectral analyses.

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[1] A. R. Pitochelli and M. F. Hawthorne, *J. Am. Chem. Soc.*, **82**, 3228 (1960).

[2] Referees have informed us of three other procedures which also give much better yields, one by Greenwood from amine boranes and decaborane (*Proc. Chem. Soc.*, in press), and procedures starting with diborane by Miller, Miller, and Muetterties (*J. Am. Chem. Soc.*, in press) and by Schaeffer (*ibid.*, in press). We wish to thank Dr. Muetterties for a copy of the second paper in advance of publication.

[3] W. V. Hough and L. J. Edwards, Advances in Chemistry Series, No. 32, American Chemical Society, Washington, D. C., 1961, pp. 191–192.

[4] V. D. Aftandilian, H. C. Miller, G. W. Parshall, and E. L. Muetterties, *Inorg. Chem.*, **1**, 734 (1962).

[5] Kindly provided by Professor M. F. Hawthorne.

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