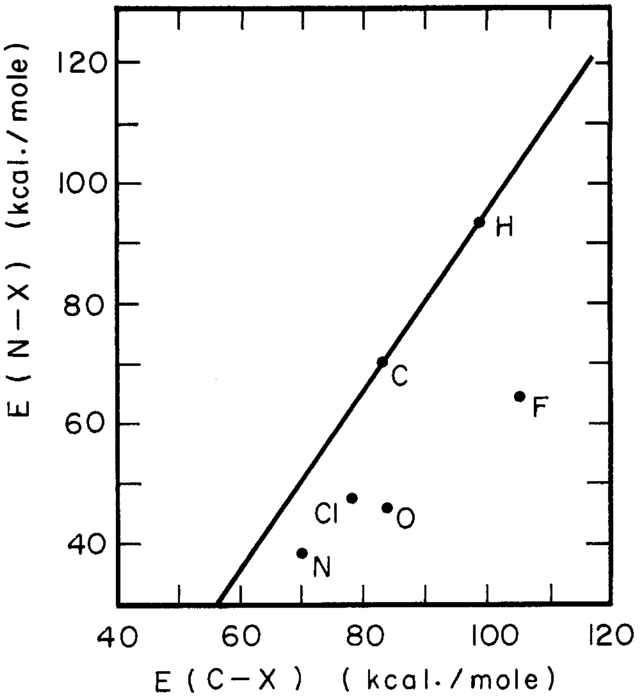

Fig. 4.—N–X bond energies *vs.* C–X bond energies.

bond. The H–H bond is weak because of poor overlap of the 1s-orbitals.[4]

When F–X, O–X, and N–X bond energies are plotted against C–X bond energies (Fig. 2–4), the points corresponding to very electronegative X atoms fall below the expected curve. In accordance with our contention that bond weakening increases with increasing electronegativity of the X atom, the points for X = F show the greatest discrepancies, the points for X = O show the next greatest discrepancies, and the points for X = Cl and N show relatively small discrepancies.

(4) In molecular H_2 the 1s-orbitals of the atoms cannot overlap strongly because of the spherical symmetry of the orbitals and the proton–proton repulsion. However, when a hydrogen atom forms a bond to an atom which offers a highly directional bonding orbital (*e.g.*, sp^3), the hydrogen atom can "immerse itself" in the other atom's bonding orbital, and thus very strong orbital overlap can be achieved.

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Boron Hydrides.[1] VII. The Metal Ion Catalyzed Hydrolysis of Sodium Borohydride in Heavy Water

Sir:

We wish to describe a hitherto unknown aspect of the hydrolysis of sodium borohydride. If the hydrolysis

$$BH_4^- + H_3O^+ + 2H_2O \longrightarrow H_3BO_3 + 4H_2 \qquad (1)$$

is performed in heavy water, analysis of the gas has been reported to vary greatly with the investigator[2,3] and a large solvent deuterium isotope effect was reported.[4]

We wish to report that the changes in isotopic composition are due to *metal ion catalyzed reactions* and that *micromolar* amounts of heavy metals will greatly change the composition of the gas. More important the reaction is an extremely useful technique to convert D^+ or T^+ in water into reductive D^- or T^- for isotopic synthesis, in some aspects almost as useful as the D^+ to D^- and T^+ to T^- exchange we reported previously.[1,5]

The data are presented in Table I for Co, Pd, and Pt. It is obvious that *micromolar* amounts of heavy metals can produce the strange results of ref. 2–4. One microgram of cobalt can reduce the amount of HD from 98 to 82%. The catalytic effect of the preformed cobalt catalyst finally levels off at 64% D_2. Platinum is the best catalyst both for hydrolysis[6] and the exchange. The last entry in the table demonstrates that even minute amounts of supported platinum can produce very high D_2 concentrations. The use of D_2 produced from this reaction or the hydrolysis–exchange of trimethylamine borane[1] in D_2O has obvious and immediate synthetic utility to produce controlled amounts of D_2 gas for reductive deuterogenations. The controlled external generation of D_2 gas extends

$$NaBH_4 \xrightarrow[\text{excess } D_2O]{\overset{Pt/C}{Na_2CO_3}} 4 \text{ moles of } D_2\uparrow \qquad (2)$$

the synthetic utility of the borohydride hydrogenator.[5,6]

The mechanism of the exchange is not clear. In other experiments the hydrolysis in deuterium oxide was allowed to proceed from 10 to 80% (as measured by the gas evolution) and the catalyst removed by ultrafiltration. The borohydride remaining was pure BH_4^- (D less than 2%) as determined by reduction of benzophenone to produce pure benzhydrol, $(C_6H_5)_2$-CHOH, which was analyzed for deuterium content.

Likewise the gas once formed does not exchange with the solvent in the presence of the catalyst and borohydride (see footnote of Table I). Experiments are in progress to modify the catalysis so that sodium borodeuteride could possibly be produced by a very convenient exchange technique.

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(1) Paper VI: R. E. Davis, A. E. Brown, R. Hopmann, and C. L. Kibby, *J. Am. Chem. Soc.*, **85**, 487 (1963).

(2) T. Freund, *J. Inorg. Nucl. Chem.*, **9**, 246 (1959). See the footnote on p. 249.

(3) W. L. Jolly and R. Mesmer, *J. Am. Chem. Soc.*, **83**, 4470 (1961). $NaBD_4$ in water gave 95.62% HD, 3.10% H_2, and 1.28% D_2. Hydrolysis of $NaBH_4$ in D_2O at pD of 7 gave 83.30% HD, 7.94% H_2, and 17.78% D_2 during the last 40% of reaction.

(4) In an earlier paper we reported the solvent isotope effect of reaction 1 by two techniques to be 4.9 and 3.0 [*J. Am. Chem. Soc.*, **84**, 885 (1962)]. These high results have been traced to metal ion catalysis. Measurement of the solvent isotope effect in D_2O–H_2O mixtures places $k_{H_3O^+}/k_{D_3O^+}$ at 1.3 using mass spectral analysis. This value agrees better with the value of 1.56 reported by Mesmer and Jolly [*Inorg. Chem.*, **1**, 608 (1962)] and is in the range to be expected for the solvent isotope effect of a general acid catalyzed reaction. It was our two original high values, reported without comment, that started the investigations reported in the present paper.

(5) Cyclohexene can be converted to 1,2-dideuteriocyclohexane using the easily controlled external generation of D_2 from $NaBH_4$–Pt/C–D_2O using the techniques of Brown [*J. Am. Chem. Soc.*, **84**, 1493, 1494, 1495 (1962)].

(6) H. C. Brown and C. A. Brown, *ibid.*, **84**, 1493 (1962).

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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(7) Alfred P. Sloan Fellow, 1962–1964.

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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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