Borohydride Reduction of Cobalt Ions in Water. Chemistry Leading to Nanoscale Metal, Boride, or Borate Particles

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The reduction of Co^{2+}(aq) by $NaBH_4$ has been studied with mechanistic and stoichiometric factors as the focus. The primary product of this reduction in aqueous solution is nanoscale Co_2B particles, which are formed possibly through the intermediacy of $[(H_2O)_5CoOH(BH_2)HOCo(H_2O)_5]^{3+}$, and this complex ion is reduced by electrons provided by 3 more mol of $NaBH_4$. The ratio of BH_4^-/Co^{2+} required is 2, and the overall balanced equation is

$$2CoCl_2 + 4NaBH_4 + 9H_2O \rightarrow Co_2B + 4NaCl + 12.5H_2 + 3B(OH)_3$$

However, a side reaction where $NaBH_4$ reacts directly with H_2O becomes important if sufficient time is available before Co^{2+} addition or if Co/Co_2B particles are allowed to catalyze it. In this way $NaBO_2$ can be formed that can react with Co^{2+} to give $Co(BO_2)_2$ as a product, which precipitates. A secondary product is metallic Co particles, which are formed by heat treatment of $Co_2B/Co(BO_2)_2$ mixtures, or by sacrificial oxidation of Co_2B. A tertiary product is Co_3B, and this is formed by heat treatment of a mixture of Co_2B and Co. These studies show that the primary product Co_2B is best prepared by rapid mixing of Co^{2+}(aq) with solid $NaBH_4$, and the Co_2B precipitate must be handled under anaerobic conditions. However, by adjusting conditions of reaction time, mixing procedure, and concentrations, a mixture of Co_2B and $Co(BO_2)_2$ can be produced, which upon heat treatment yields metallic Co nanoscale particles plus boron oxides. Magnetic and physical properties of the fresh Co_2B are as follows: surface area = 15.9 m^2/g, crystallite size = <2 nm, σ = 48 emu/g, Hc = 260 Oe. For Co particles, properties are as follows: surface area = 9.1 m^2/g, crystallite size = <2 nm, σ = 53 emu/g, Hc = 333 Oe.

Introduction

Borohydride reduction of metal ions has been used extensively for the removal of aqueous ions as well as the production of fine particles of metals and metal borides.[1-4] Despite this widespread use, the chemistry of this process is not well understood. As a result, the literature is replete with varying recipes and techniques commonly giving rise to products of different composition.

We have undertaken studies with mechanistic and stoichiometric factors as the focus in an effort to be able to predict and thus control the nature of the products formed from these reactions. Understanding and controlling the production of nanoscale magnetic particles is our goal.

It was noted in a recent letter that simply through mixing techniques and appropriate product handling, the controlled generation of Co_2B, metallic Co, or $Co(BO_2)_2$ may be achieved.[5] In this report the reaction steps leading to these products and the factors that influence the process are detailed. In addition, the ultrafine powders produced are characterized (magnetic properties, electron micrographs, X-ray patterns, and surface areas).

Experimental Section

General Procedures. All reactions were carried out in a 1000-mL three-necked round-bottom flask attached to a vacuum line of known volume and equipped with a mercury manometer. The flask had two side-arms arranged so that liquid could be added to the vessel in vacuo.[5] Distilled water was purged with argon for several hours prior to use. Total amounts of gas evolved during a reaction were determined by measurements of the pressures developed in a known volume. The percent of H_2 in the gas was determined by GC (using a column of molecular sieves powder at ambient temperature).

Sodium borohydride (99%) was purchased from Aldrich Chemical Co., Inc., and stored in an inert atmosphere box under argon. Aqueous solutions of $CoCl_2 \cdot 6H_2O$ (0.010, 0.025, 0.050, 0.10, and 1.0 M) were prepared using prepurged water. Unreacted Co^{2+} was determined titremetrically.[6] The pH of solutions were determined using an Extech 651 digital meter.

Heat treatments of powders were carried out in a quartz tube under argon. Generally samples were brought to desired temperature within 2–5 min and kept at that temperature for 2 h, after which they were allowed to rapidly cool to ambient temperature (5–10 min). X-ray powder diffraction data were collected on a SCINTAG 3000 machine with Ni $K\alpha$ filtered radiation. Pyrophoric samples were protected with mineral oil (Nujol) prior to powder diffraction studies. Magnetic properties of the different product powders were obtained from measurements on a SQUID magnetometer on weighed samples immobilized in paraffin in a quartz cell. Temperatures between 10 and 300 K were used with fields ranging from −1500 to 55 000 Oe. Electron microscopy data were obtained on a Jeol-100C instrument. Differential scanning calorimetry scans were obtained on a Perkin-Elmer 7 series thermal analysis system. Elemental analyses were obtained from Gailbraith Labs in

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Knoxville, TN. Surface areas were determined by BET measurements using nitrogen on a Flowsorb II 2300 instrument. Mass spectroscopic measurements were carried out on a Finnigan 4021C instrument.

A Typical Borohydride Reduction. The 1000-mL flask was charged with 0.15 g (4.0 mmol) of $NaBH_4$ under Ar and connected to the vacuum system. Under Ar flow four 60-mL syringes were charged with a total of 200 mL of 0.010 M $CoCl_2 \cdot 6H_2O$ in water. After evacuation of the flask, the aqueous cobalt solution was added over a 45-60 s period. During this time the solution turned black and a black precipitate appeared within 2 min. Hydrogen was evolved during the reaction and continued for 1 min after addition of all the cobalt ion solution. When gas evolution had ceased, the Hg manometer reading was recorded and GC analysis for H_2 carried out. The reaction chamber was then isolated and disconnected from the vacuum line. The contents of the reaction flask were filtered and washed with prepurged H_2O and acetone using standard inert atmosphere and Schlenk techniques and the resulting powder was dried in vacuo. The black, amorphous, pyrophoric powder of Co_2B (0.12 g) was collected in an inert atmosphere box. Elemental analysis of the crude dry powder yielded the following. Found: Co, 84.18; B, 7.92; Co/B ratio, 1.95. Calcd for Co_2B: Co, 91.6; B, 8.40. After thermal processing at 500 °C under Ar for 2 h, analysis showed Co, 94.25; B, 8.50; Co/B ratio, 2.03. The heat-processed sample was air stable and was examined by X-ray powder diffraction (XRD) which showed it to be Co_2B. Crystallite sizes were determined using the Scherrer equation ($t = 0.9\lambda/B \cos \theta_B$). The crude powder was also examined using XRD.

If the resulting black suspension obtained from the above reaction was filtered, washed and dried under ambient conditions, an air-stable powder was isolated. This powder showed a very broad line centered around the most intense line in metallic Co. Upon heat treatment at 500 °C under Ar for 2 h, lines corresponding to fcc metallic Co were obtained. However, if the powder was vacuum dried after filtration, an air-stable powder which showed lines corresponding to Co, Co_2B, and Co_3B in the XRD upon thermal processing was obtained.

Borohydride Reduction with Two-Stage Addition of Cobalt Ion Solution. In a typical reaction, the 1000-mL flask was charged with an appropriate weight of $NaBH_4$ so as to achieve a desired BH_4^-/Co^{2+} mole ratio. Then 200 mL of 0.010 M $CoCl_2 \cdot 6H_2O$ (2 mmol) was added. The reaction flask was connected to the vacuum system and evacuated and the Co^{2+} ion solution added in two 100-mL portions with each addition taking 60 s and a time interval of about 75 s in between additions. In the reaction with an overall BH_4^-/Co^{2+} of 2, a black suspension was apparent after the addition of the 100 mL of Co^{2+} solution with significant gas evolution. On addition of the second portion of solution, a bluish-green fluffy solid became apparent with minimal gas evolution. The solid product was filtered, washed with prepurged H_2O and acetone using standard inert atmosphere and Schlenk techniques, and dried in vacuo. An air stable powder (0.14 g) was isolated. Elemental analysis of the crude dry powder yielded the following: Found: Co, 67.49; B, 6.59; Co/B ratio, 1.88. Calcd for Co_2B: Co, 91.6; B, 8.40. Calcd for $Co(BO_2)_2$: Co, 40.9; B, 14.9. After heat processing under Ar at 500 °C for 2 h, the analysis indicated the following: Co, 79.38; B, 6.38; Co/B ratio, 2.28. The XRD of the heat-treated material showed lines corresponding to metallic Co.

If the resulting suspension from the above reaction was filtered, washed, and dried under ambient conditions, 0.21 g of a black blue-green air-stable solid was obtained. On heat treatment at 500 °C under Ar for 2 h, this sample showed significant weight loss as a result of water loss. XRD of the heat-processed samples indicated $Co_3(BO_3)_2$ and CoO. At high BH_4/Co^{2+} ratios (≥4), the two-stage addition reaction yielded the same products described in the typical borohydride reduction reactions.

Reactions were also carried out in which $NaBH_4$ (0.15 g, 4.0 mmol) was first treated with 20 mL of Co^{2+} solutions (0.010 M, 0.20 mmol) with the remaining 180 mL of Co^{2+} solutions (1.8 mmol) required for the desired BH_4^-/Co^{2+} ratio of 2 added at varying time intervals of 5, 8, 9, 12, and 15 min (Table VI). The resulting precipitates were isolated using standard inert atmosphere and Schlenk techniques. In the case where complete catalytic decomposition had occurred prior to the addition of the

Table I. Effects of BH_4^-/Co^{2+} Ratio

BH_4^-/Co^{2+} [a]	H_2 evolved,[b] mmol	H_2 predicted by Scheme I,[c] mmol	pH of filtrate[d]	unreacted Co^{2+} ions, mmol
0.2	(2.6)	(1.6)	7.6	1.8
0.5	(4.4)	2 (4)	7.3	1.4
1.0	8.3 (8.9)	6 (8)	7.7 (10.4)	1.1
1.5	12 (12)	10 (12)	7.9	0.6
2	14 (15)	14 (16)	8.4 (10.6)	0.1
3	22 (23)	22 (24)	9.0 (10.6)	0.1
4	30 (30)	30 (32)	9.3 (10.6)	0.01
5	38 (37)	38 (40)	9.5 (10.7)	0.01
6	44 (48)	46 (48)	9.6 (10.7)	0.05
10	74 (82)	78 (80)	10.1 (10.7)	9.4×10^{-3}
15	103 (114)	118 (120)	10.3	3.8×10^{-3}
20	170 (167)	158 (160)	10.4	3.8×10^{-3}

[a] 2.0 total mmol of $CoCl_2$ and mmol total of $NaBH_4$ varied from 0.4 to 40. [b] Shown in parentheses are mmoles of total gas evolved including H_2. [c] Shown in parentheses is the expected amount of H_2 that could be produced by the reaction $BH_4^- + 2H_2O \rightarrow BO_2^- + 4H_2$. [d] Shown in parentheses is the pH of equivalent solutions without any Co^{2+}.

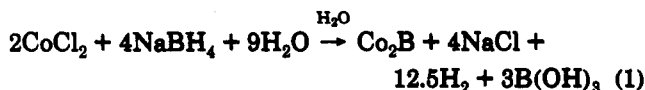remaining Co^{2+} solution (15 min), $Co(BO_2)_2$ (0.17 g) was obtained as the dominant product.

Results

Effect of BH_4^-/Co^{2+} Ratio. Addition of a 0.010 M Co^{2+} solution (200 mL) to solid $NaBH_4$ in the reaction vessel under static vacuum over a 45-60 s period yielded a black suspension regardless of the BH_4^-/Co^{2+} ratio. Table I summarizes the ratios employed, H_2 evolved, pH, and amount of unreacted Co^{2+}. The ratios were changed by varying the amount of solid $NaBH_4$ placed in the flask; the volume and molarity of the Co^{2+} aqueous solutions were held constant. The amount of time necessary for the reaction to come to completion ranged from 1 to 12 min depending on the amount of $NaBH_4$ used.

A black, pyrophoric powder was isolated upon filtration and washing with deoxygenated H_2O/acetone under airless conditions. This black material showed very broad lines in the X-ray diffraction (XRD) that were suggestive of solid Co_2B. Upon heat treatment at 350 and 500 °C under Ar, air-stable powders were obtained that were pure Co_2B, according to XRD. The ratio of BH_4^-/Co^{2+} did not change the identity of the product.

Gases evolved were carefully measured and plotted against this ratio (Figure 2). The filtrates from these reactions were analyzed for pH and residual Co^{2+} (Table I). For another comparison, the pH values of several solutions containing the same amount of $NaBH_4$ but no $CoCl_2$ were also determined. The pH values of these control solutions rose quickly and leveled off at about 10.7, whereas the reduced cobalt ion solutions slowly rose from about 7.5 to 10.4 (the higher pH for a BH_4^-/Co^{2+} ratio of 20).

These results show that the primary solid product is always Co_2B under these aqueous conditions and that the amount of H_2 generated is consistent with the output of eq 1 shown below plus a fractional operation of (2), and an equilibrium of $NaBO_2$ with water

$$2CoCl_2 + 4NaBH_4 + 9H_2O \xrightarrow{H_2O} Co_2B + 4NaCl +$$
$$12.5H_2 + 3B(OH)_3 \quad (1)$$

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 \quad (2)$$

$$NaBO_2 + H_2O \rightleftharpoons BO_2H + NaOH \quad (3)$$

It should be pointed out that in the absence of Co^{2+}, the $NaBH_4$ slowly reacts by eq 2, and as $NaBO_2$ concentration

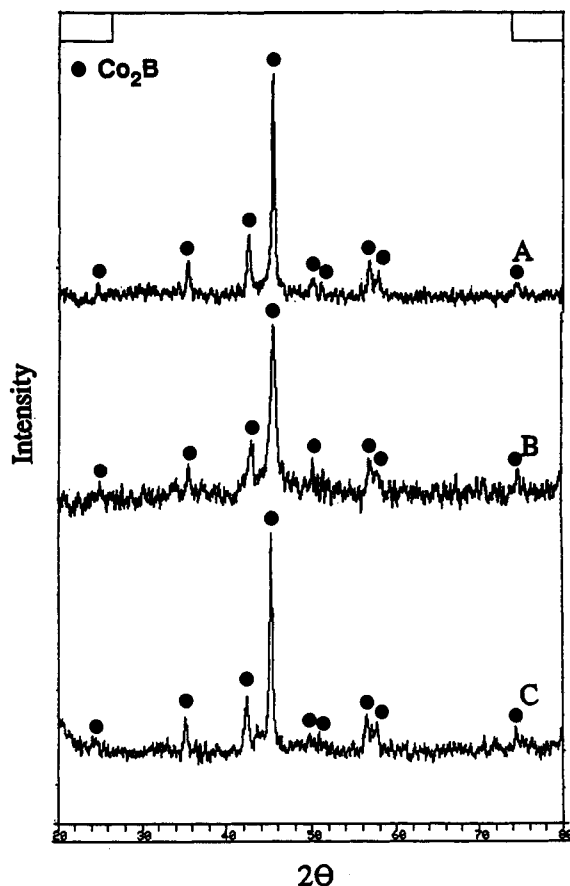**Figure 1.** Cobalt boride samples using differing BH_4^-:Co^{2+} ratios: A, BH_4^-:Co^{2+} ratio = 2; B, ratio = 4; C, ratio = 20.

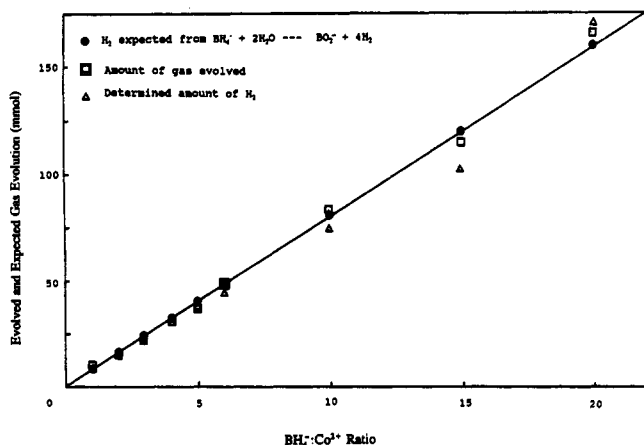**Figure 2.** Gas evolved verses BH_4^-:Co^{2+} ratio.

increases, equilibrium equation (3) becomes important, pushing the pH up. However, in the presence of Co^{2+} the main reaction path upon rapid mixing is eq 1, and pH is not affected much until rather large excesses of $NaBH_4$ are present, thereby making eqs 2 and 3 more important.

Effects of Prior Dissolution of $NaBH_4$. For selected BH_4^-/Co^{2+} ratios (Table II), reactions were carried out in the same manner as described above with the exception that 50 mL of argon-purged water was added to the reaction vessel to dissolve the $NaBH_4$ before the cobalt ion solution was added. These reactions again yielded only Co_2B as the solid product. No significant differences in gas evolution, pH, or residual Co^{2+} concentrations were noted when compared with the standard experimental method of adding Co^{2+} ion solution to solid $NaBH_4$. Also, varying the $NaBH_4$ concentration by varying the amount of water holding the cobalt ions (maintaining a constant BH_4^-/Co^{2+}

Table II. Effects of the Dissolution of $NaBH_4$ on Reaction

BH_4^-/Co^{2+} [a,b]	H_2 evolved,[c] mmol	H_2 predicted by Scheme I, mmol	pH of filtrate	unreacted Co^{2+} ions, mmol
1	5.6 (10.1)	6	7.6	1.02
2	13.1 (15.2)	14	8.1	0.09
4	24.9 (27.4)	30	9.4	0.02
6	40.9 (46.3)	46	9.8	0.01

[a] 2.0 total mmol of $CoCl_2$ and total mmol of $NaBH_4$ varied from 2.0 to 12. [b] $NaBH_4$ dissolved in 50 mL of prepurged H_2O in a reaction vessel prior to addition of Co^{2+} solution. [c] Total amount of gas evolved given in parentheses.

Table III. Effect of $NaBH_4$ Concentration on Reaction

concentration of $NaBH_4$ solution,[a] M	H_2 evolved,[b] mmol	pH of filtrate	unreacted Co^{2+} ions, mmol
0.40	14.3 (15.5)	8.1	0.10
0.16	13.9 (15.4)	8.2	0.13
0.08	(15.2)	8.1	0.09
0.02	13.3 (15.7)	8.3	0.19

[a] BH_4^-/Co^{2+} ratio of 2 was maintained in all reactions by treating $NaBH_4$ (0.15 g, 4.0 mmol) dissolved in an appropriate volume of prepurged H_2O with 200 mL of 0.010 M Co^{2+} solution. [b] Total amount of gas evolved given in parentheses.

Table IV

(a) Effect of Varying the Volume of Co^{2+} Solution

BH_4^-/Co^{2+} [a]	reaction time,[c] min	pH of filtrate	wt of solid,[b] mg	gas evolved, mmol	unreacted Co^{2+} ions, mmol
2	~2	8.4	126	15.0	0.10
4	3	9.4	68	15.6	0.01
8	6	9.9	34	15.8	0.01
20	15	10.5	8.2	16.3	

(b) Effect of Co^{2+} Ion Concentration on Reaction

concentration of Co^{2+} solution,[d] M	gas evolved, mmol	pH of filtrate	unreacted Co^{2+} ions, mmol
0.01	15.0	8.4	0.10
0.025	36.2	7.8	0.27
0.05	69.8	8.2	0.79
0.10	137.6	8.4	0.64

[a] Sodium borohydride (0.15 g, 4.0 mmol) was treated with appropriate volume of 0.010 M Co^{2+} solution to give the desired ratio. [b] Solid isolated under ambient conditions. [c] Time includes addition time for Co^{2+} solution of 45 seconds or less. [d] All reactions carried out at BH_4^-/Co^{2+} ratio of 2 using 200 mL of the Co^{2+} solution and the appropriate weight of $NaBH_4$.

ratio) resulted in the same primary product Co_2B and without significant changes in other parameters (Table III).

Effects of Varying Volumes and Concentrations of Co^{2+} Solutions. The amount of solid $NaBH_4$ was held constant while the volume of Co^{2+} solution was varied. In all cases where 0.010 M Co^{2+} solution was added in different volumes, the primary solid product remained Co_2B. However, it was noted that the reaction times necessary to evolve all gases were longer as the volume of Co^{2+} solution decreased (Table IV).

With increases in the concentration of the Co^{2+} solution from 0.010 to 0.025, 0.050, and 0.10 M while maintaining a BH_4^-/Co^{2+} ratio of 2 and a fixed volume of 200 mL, the reaction time went from 120 s (0.010 M) to 30 s (0.10 M). Thus, more concentrated solutions reacted faster. And it was noted that the highly concentrated solutions yielded *more solid product* than was expected. In addition, after thermal processing, the XRD showed increasing amounts of metallic cobalt (see Figure 3).
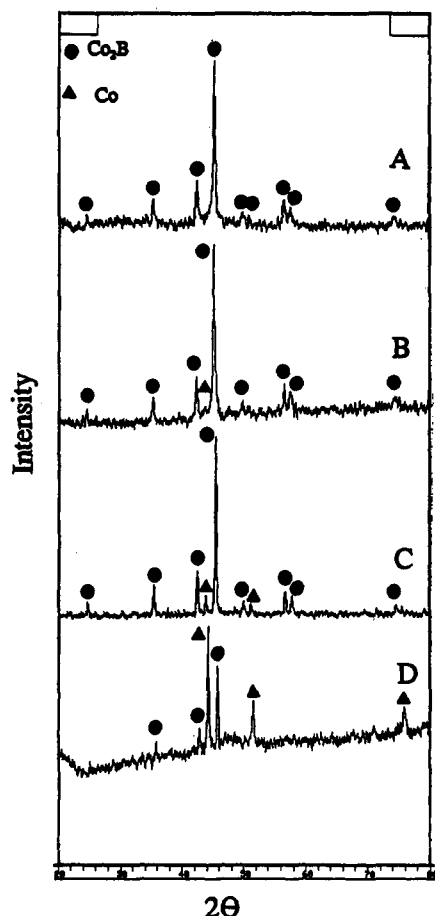
Figure 3. Dependence of product formed on Co^{2+} solution concentration at $BH_4^-:Co^{2+}$ ratio of 2.

Effects of Catalytic Decomposition of NaBH₄ by Particles Generated in the Reduction Process. It has been noted by earlier workers[7] that particles generated from borohydride–metal ion reductions are active catalysts for several hydrogenation processes as well as the dehydrogenation/decomposition of BH_4^-. The BH_4^- reaction/decomposition (eq 4) was shown to occur at different rates depending on the particular metal ion system under study.[8]

In the present study differing rates were also observed depending on the composition of the particles generated (i.e. Co metal, Co_2B, or $Co(BO_2)_2$; see later discussion and Table V and Figure 4).

The rate of reaction 4 was also shown to be pH dependent

$$BH_4^- + 2H_2O \xrightarrow{catalyst} BO_2^- + 4H_2 \qquad (4)$$

To encourage the dominance of reaction 4, a series of experiments were carried out where a small portion of the Co^{2+} solution was added to the solid NaBH₄, a desired time allowed to elapse, and the remainder of the Co^{2+} solution added. In this way, the catalytic reaction 4 was allowed to proceed to different stages of completion, thereby generating different concentrations of BO_2^-. In this way the time interval between eqs 6 and 7 would determine how much time eq 6 had to operate and thereby how much $NaBO_2(aq)$ was formed. As a result, the higher the $NaBO_2(aq)$ concentration became, the more eq 8 competes favorably with eq 7.

(7) (a) Brown, H. C.; Brown, C. A. *J. Am. Chem. Soc.* **1962**, *84*, 1493. (b) Brown, H. C.; Brown, C. A. *J. Am. Chem. Soc.* **1962**, *84*, 1494. (c) Brown, C. A.; Brown, H. C. *J. Org. Chem.* **1966**, *31*, 3989. (d) Brown, H. C.; Ichikawa, K. *J. Am. Chem. Soc.* **1961**, *83*, 4372.

(8) Schlesinger, H. I.; Brown, H. C.; Finholt, A. E.; Gilbreath, J. R.; Hockstrue, H. R.; Hyde, E. K. *J. Am. Chem. Soc.* **1953**, *75*, 215.
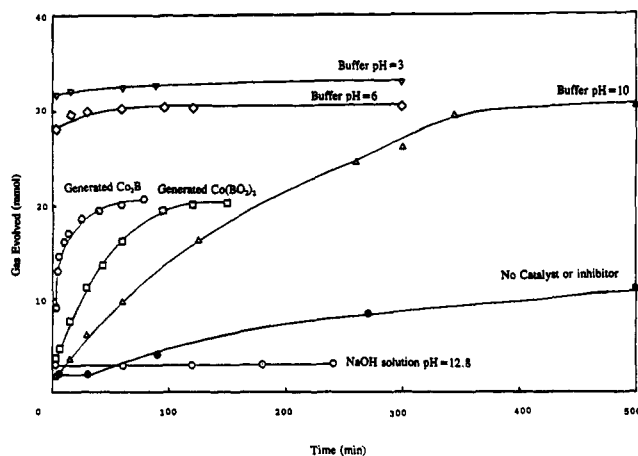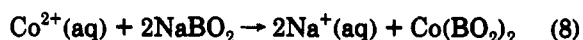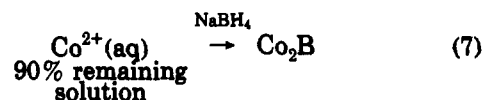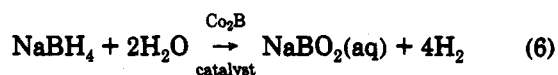

Figure 4. Gas evolution vs time for different catalysts/inhibitors.

$$\underset{\substack{10\% \text{ of} \\ \text{solution}}}{Co^{2+}(aq)} \xrightarrow{NaBH_4} Co_2B \qquad (5)$$

$$NaBH_4 + 2H_2O \xrightarrow[catalyst]{Co_2B} NaBO_2(aq) + 4H_2 \qquad (6)$$

$$\underset{\substack{90\% \text{ remaining} \\ \text{solution}}}{Co^{2+}(aq)} \xrightarrow{NaBH_4} Co_2B \qquad (7)$$

$$Co^{2+}(aq) + 2NaBO_2 \rightarrow 2Na^+(aq) + Co(BO_2)_2 \qquad (8)$$
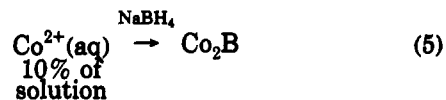
The resultant products were isolated under argon. The amounts of H_2 evolved were measured, and the pH and residual Co^{2+} concentration monitored. The trends shown in Table VI are that the amount of unreacted Co^{2+} increased and the weight of the solid product isolated increased as the time allowed for reaction 6 to proceed increased. Thermal processing of the solid products under argon followed by XRD analysis showed a progression from mostly Co_2B for short reaction times, to Co, and finally to $Co_3(BO_3)_2$ for longer reaction times. It is clear that such variations in experimental procedure that encourage reaction 6 have a dramatic effect on the identity of the solid product produced.

Discussion

Formation of the Primary Product Co₂B. As a starting point, we need to develop a rationale as to how Co_2B can be formed as the primary product. Indeed, Co_2B is not the primary product in nonaqueous borohydride reductions; instead it is metallic cobalt particles.[9] Therefore, the presence of water is crucial.

In Scheme I a reaction sequence is shown that may aid our understanding of this process. The equilibrium in step i is well established as the reason why aqueous solutions of transition metal ions are acidic. In step ii, H^+ and BH_4^- may react with the $[(H_2O)_5CoOH]^+$ species. This hydrated cobalt–borane adduct could then react with another $[(H_2O)_5CoOH]^+$ species. The resulting species 2 is triply charged. Reduction could occur by reaction with 3 more equiv of BH_4^- (step iv) with concomitant formation of more H_2 (step v). Finally, in step vi the adduct could yield Co_2B which forms Co_2B particles and precipitates. The addition of all these steps yields the overall equation (9) with the experimentally observed stoichiometry based on Co^{2+} and BH_4^- needed, and Co_2B. However, the 12.5

(9) Unpublished results from our laboratory.

Table V. Decomposition of NaBH₄ in H₂O under Differing Conditions*

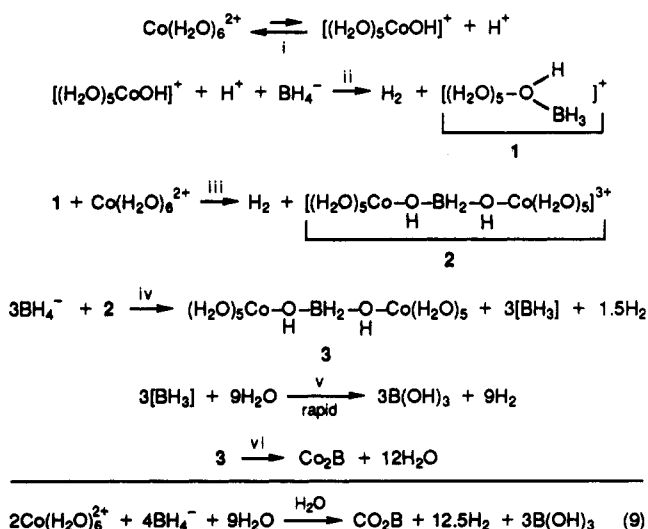| catalysts/inhibitor	react time, min	wt of NaBH₄, mg	pH of resulting solution	gas evolved,^{e} mmol	% gas liberated		
					5 min	10 min	30 min
no catalyst/or inhibitor		235	10.6	16.8^d (25)		8.0	8.9
generated Co₂B^b	90	154	10.5	20.5 (16)	71	80	93
generated Co(BO₂)₂^c	150	153	10.6	20.4 (16)	24		55
buffer pH = 3	30	297	4.9	33.0 (32)	97		100
buffer pH = 6	105	300	7.8	30.5 (32)	94		98
buffer pH = 10	1020	307	10.3	33.5 (32)	5.4		18
NaOH solution pH = 12.8		302	12.8	2.6^d (32)	8.1	8.1	8.1

^{a} A total volume of 200 mL was used in all cases. ^{b} 100 mg of solid used. ^{c} 60 mg of solid used. ^{d} Reaction incomplete after 16 h, expected amount of H₂ used in determining percentages. ^{e} Expected amount of H₂ that could be produced by the reaction NaBH₄ + 2H₂O → NaBO₂ + 4H₂ are given in parentheses.

Table VI. Effect of Catalytic Decomposition of NaBH₄ on Reaction*

time, min	gas evolved,^{b} mmol	pH of filtrate	unreacted Co²⁺ ions, mmol	wt of solid product,^{c} mg
5	15.3 (8.7)	8.0	0.15	110
8	15.8 (11.8)	8.3	0.17	132
9	16.5 (15.0)	8.3	0.25	145
12	16.5 (16.0)	8.6	0.22	150
15	16.5 (16.3)	8.3	0.28	169

^{a} Approximately 150 mg of NaBH₄ (4.0 mmol) and 200 mL 0.010 M Co²⁺ (2.0 mmol) solution were used in each experiment. Ten percent of the Co²⁺ solution was first added and after the noted time interval the remaining 90% of the solution was added. ^{b} Numbers in parentheses indicate amount of gas evolved at the time the remaining 90% of the Co²⁺ solution was added. Expected amount of H₂ according to the decomposition reaction is 16 mmol. ^{c} Product isolated using standard inert atmosphere conditions.

Scheme I. A Reaction Sequence Leading to Co₂B in Aqueous Solution

$$Co(H_2O)_6^{2+} \rightleftharpoons_i [(H_2O)_5CoOH]^+ + H^+$$

$$[(H_2O)_5CoOH]^+ + H^+ + BH_4^- \xrightarrow{ii} H_2 + [(H_2O)_5-O\langle^H_{BH_3}]^+$$

$$\underbrace{\qquad\qquad}_{\mathbf{1}}$$

$$\mathbf{1} + Co(H_2O)_6^{2+} \xrightarrow{iii} H_2 + [(H_2O)_5Co-O-BH_2-O-Co(H_2O)_5]^{3+}$$

$$\underbrace{\qquad\qquad\qquad H\qquad H\qquad\qquad}_{\mathbf{2}}$$

$$3BH_4^- + 2 \xrightarrow{iv} (H_2O)_5Co-O-BH_2-O-Co(H_2O)_5 + 3[BH_3] + 1.5H_2$$
$$H\qquad H$$

$$\mathbf{3}$$

$$3[BH_3] + 9H_2O \xrightarrow[rapid]{v} 3B(OH)_3 + 9H_2$$

$$\mathbf{3} \xrightarrow{vi} Co_2B + 12H_2O$$

$$2Co(H_2O)_6^{2+} + 4BH_4^- + 9H_2O \xrightarrow{H_2O} Co_2B + 12.5H_2 + 3B(OH)_3 \quad (9)$$

mol of H₂ predicted is a bit lower than we observed by experiment (see later discussion). These reaction steps do indicate a key role for water in the overall process.

If **1** is indeed an intermediate which must capture an additional Co²⁺(aq) species, this step may be rate determining since Co²⁺ concentration is lower than BH₄⁻ concentration. If it is rate determining, then it might be possible to stop subsequent steps by forming species analogous to **1** but with reagents that can only donate one H⁻. With this in mind we used NaBEt₃H instead of NaBH₄. Reaction of Co²⁺(aq) solution with NaBEt₃H in Et₂O yielded a sea-blue colloidal suspension that slowly turned pink. A white solid precipitated, and no Co₂B or metallic Co formed. Although other complications may enter into this system, these results could be taken as support for steps ii and iii in Scheme I.

After many duplicate experiments and many different ratios and experimental conditions, the amount of H₂ generated as according to eq 9 was always found to be very close to 14 rather than the predicted 12.5. Also, the rise in pH must be accounted for, and Scheme I as it stands does not do this.

A possible explanation for these observations deals with the reaction of BH₄⁻ with H₂O. This is a rather slow reaction in pure water, but, as mentioned earlier, can be catalyzed by Co₂B particles. It is also known that this reaction is sensitive to pH; lower pH increases the rate with or without catalyst.

$$BH_4^- + 2H_2O \underset{fast}{\overset{\substack{pure\ H_2O\\slow}}{\rightleftharpoons}}\ {}_{cat.} BO_2^- + 4H_2 \quad (10)$$
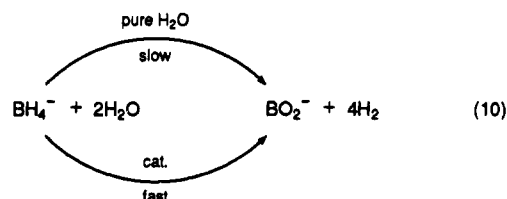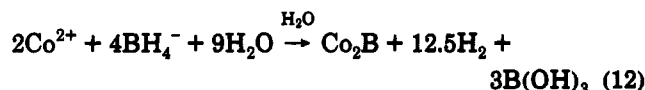
It can be noted from Tables I–III that the pH of the filtrate is sensitive to the BH₄⁻/Co²⁺ ratio. The larger this ratio is, the higher the pH becomes. It seems reasonable to assume that reaction 10 becomes more important with increased BH₄⁻ concentration. The rise in pH can be explained by equilibrium 11. Indeed, measurements we have made on the pH of NaBO₂(aq) showed that as the concentration of NaBO₂(aq) went up, the pH continuously increased from 9.11 to 11.09 (see Table VIII).

$$BO_2^- + H_2O \rightleftharpoons OH^- + BO_2H \quad (11)$$
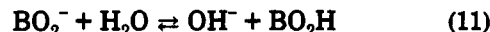
A rationale for these results would be that reaction 10 is important to a limited degree during, and especially after, the reduction of Co²⁺ to Co₂B. Some additional H₂ would be generated in this way, and the pH would rise. However, as the pH rises, reaction 10 slows down, and so the system is self-limiting. In this way, another 1–2 mol of H₂ is generated, explaining the excess H₂ generated. This reaction also pushes the pH up into the 10–11 range when adequate BH₄⁻ is available to carry out reaction 10, but the basicity of the solution then effectively stops reaction 10.

So through the combined reactions 9 and 11, the observed products are generated.

$$2Co^{2+} + 4BH_4^- + 9H_2O \xrightarrow{H_2O} Co_2B + 12.5H_2 + 3B(OH)_3 \quad (12)$$

$$\tfrac{1}{2}BH_4^- + H_2O \xrightarrow{cat.} \tfrac{1}{2}BO_2^- + 2H_2 \quad (13)$$

The BH₄⁻/H₂O reaction would proceed as approximately ¹/₂ mol BH₄⁻ so that only 2 mol of H₂ is generated. In fact,

Table VII

(A) Magnetic and Physical Properties of Co₂B Samples

sample	σ, emu/g (10 K)	Hc, Oe (10 K)	crystallite size, nm	surface area, m²/g
as prepared	48 (32)[a]	260 (55)	<2	15.9
heated at 350 °C for 2 h under Ar	60 (44)	365 (242)	13	10.1
heated at 500 °C for 2 h under Ar	63 (53)	325 (215)	19	3.5

(B) Magnetic and Physical Properties of Co Samples

sample	prepared from	σ, emu/g	Hc, Oe	crystallite size, nm	surface area, m²/g
fresh	[Co₂B/Co(BO₂)₂][b]	53 (29)[a]	333 (58)[a]	<2	9.1
	[Co₂B/O₂][c]	29 (9.8)	238 (40)		54.6
heat treated for 2 h at 350 °C under Ar	Co₂B/Co(BO₂)₂	94 (83)	553 (403)	15	8.6
	Co₂B/O₂	72 (60)	810 (483)	13	17.4
heated treated at 500 °C for 2 h under argon	Co₂B/O₂	92 (80)	87 (63)	37	1.2

[a] Number in parentheses measured at 300 K. Without parentheses at 10 K. [b] Sample isolated under inert conditions. [c] Sample isolated under ambient conditions.

Table VIII. NaBO₂(aq) pH Measurements

NaBO₂ concn, M	pH	NaBO₂ concn, M	pH
0.001	9.16	0.050	10.5
0.005	9.80	0.100	10.6
0.006	9.95	0.500	10.8
0.010	10.2	1.00	11.1

probably less than $1/2$ equiv BH_4^- reacts since experimentally we find 13.7 ± 0.6 mol of H_2 are actually formed.

The implications of these findings with regard to using the correct experimental conditions to encourage Co₂B formation are (1) to add all of the Co²⁺ solution quickly to solid NaBH₄ with good stirring or (2) to add Co²⁺ solution to *freshly prepared* BH_4^- solution by means of a Y-junction. These methods will ensure to the greatest degree possible that Co²⁺(aq) will be constantly in the presence of adequate amounts of BH_4^- in order to carry out the reactions as outlined in Scheme I. It should be noted that the required BH_4^-/Co²⁺ ratio is about 2, but that the reaction will be second order in Co²⁺. Therefore, the concentration of Co²⁺ should be reasonably high. (3) A third method, used earlier by Brown and co-workers[8] and more recently by Corrias and co-workers,[10] is the physical mixing of solid CoCl₂·6H₂O and solid NaBH₄. However, a large excess of NaBH₄ is required so that Co₂B is the major product.
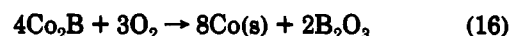
It becomes apparent that the physical state of the CoCl₂ or NaBH₄ (solids or fresh solutions) is less important than the mixing techniques. Reaction conditions must be used that encourage the immediate reduction of Co²⁺ to Co₂B before significant amounts of NaBO₂ are formed. This means that 2 mol of Co²⁺ must interact with 4 mol of BH_4^- relatively quickly.

Changing the Primary Product from Co₂B to Co(BO₂)₂. The formation of Co(BO₂)₂ instead of Co₂B is also possible. Of course this is usually an undesirable result. However, the change can be made by adding a small amount of Co²⁺ solution to a BH_4^- solution. A fast reaction forming a small amount of Co₂B takes place, followed by the onset of the catalytic decomposition of BH_4^- with water to form BO_2^- and H_2 (reaction 10). During this process all of the BH_4^- is available for this decomposition if adequate time is allowed. Table VI shows the results of experiments carried out where interval times of 5–15 min were used. Note that the hydrogen evolution is nearly complete after about 12 min in the absence of most of the Co²⁺ solution. The amount of unreacted Co²⁺ also increases with catalytic reaction time, and this is to be

(10) Corrias, A.; Ennas, G.; Licheri, G.; Marongiu, G.; Paschina, G. *Chem. Mater.* **1990**, *2*, 363.

expected since the further reaction 11 proceeds, the less reducing power remains in the solution. In fact the extent with which reaction 11 proceeds determines the solid product. If most of the NaBH₄ has been converted to NaBO₂, when the major portion of the Co²⁺ is finally added, the main reaction path available is simply the formation and precipitation of Co(BO₂)₂.[5]

$$Co^{2+}(aq) + 2NaBO_2 \rightarrow Co(BO_2)_2 + 2Na^+ \quad (14)$$

A Mixture of Primary Products Co₂B and Co(BO₂)₂. Metallic Co as a Secondary Product. As might be anticipated, if intermediate catalysis times are allowed, a mixture of products of Co₂B and Co(BO₂)₂ is formed. Interestingly, the pyrolysis of a mixture of Co₂B and Co(BO₂)₂ leads to the formation of *metallic Co* and B_2O_x (which is subsequently oxidized to B_2O_3 and washed away with water). This appears to be a major process by which metallic Co particles are formed. One other way is by sacrificial oxidation of Co₂B[5]

$$2Co_2B + Co(BO_2)_2 \xrightarrow{O_2} 5Co(s) + 2B_2O_x \rightarrow B_2O_3 \quad (15)$$

$$4Co_2B + 3O_2 \rightarrow 8Co(s) + 2B_2O_3 \quad (16)$$

There is no evidence that Co(s) is a primary product under any set of experimental conditions. This surprising result demonstrates that there is still much to be learned about these ubiquitous reducing reagents since most often metal particles are the desired products. Indeed, in the case of Co, the metallic form is obtained as a product, but it is a *secondary* product, only formed during sacrificial oxidation/reduction solid-state reactions (15 and 16).

An interesting trend was observed with regard to Co(s) formation where the concentration of the Co²⁺ was increased (while always maintaining a ratio of BH_4^-/Co²⁺ of 2). The proportion of Co(BO₂)₂/Co₂B formed went up and this subsequently yielded more Co(s) upon heat treatment (see Figure 3); that is, the Co(s) increased while Co₂B decreased in the final product. Of course increasing concentration would cause increased reaction rate for reactions 12, 13, and 14. However, it appears that the rate of (13) increases more relative to (12). This might be explained in the following way. A reaction that is obviously important, but has not yet been discussed, is the aggregation of Co₂B molecules to solid particles

$$Co_2B + nCo_2B \rightarrow \rightarrow Co_2B \text{ nanoscale particles}$$
$$\text{that precipitate} \quad (17)$$
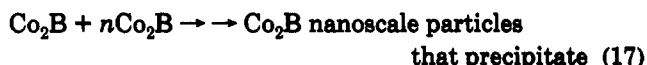
Since reaction 13 is catalyzed by Co₂B, the rate of this reaction would be dependent on the surface area of the
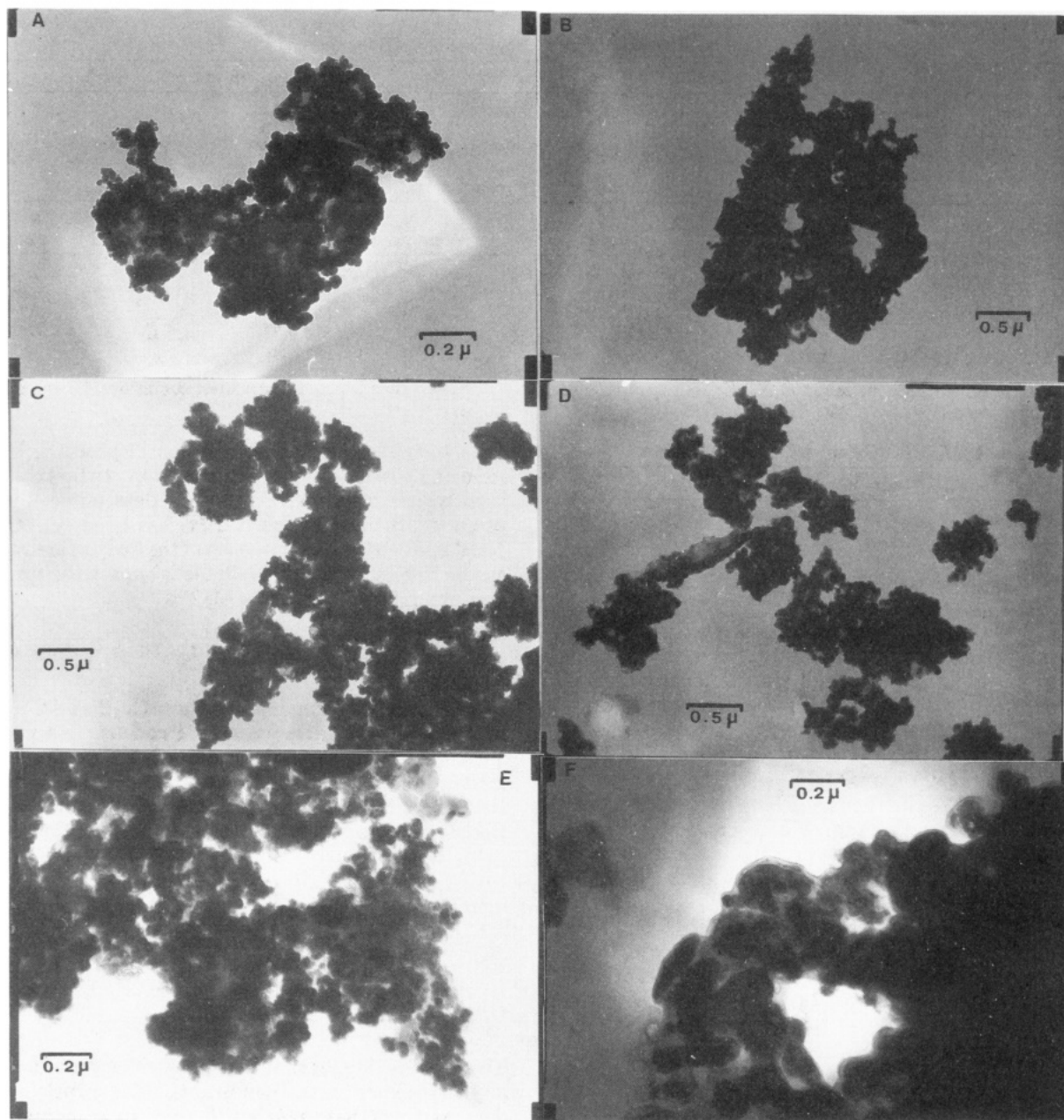
Figure 5. TEM photographs: A, Co_2B (fresh); B, Co_2B (350 °C); C, Co_2B/O_2 (fresh); D, Co_2B/O_2 (350 °C); E, $Co_2B/Co(BO_2)_2$ (fresh); F, $Co_2B/Co(BO_2)_2$ (350 °C).

Co_2B. In more concentrated solutions of Co^{2+} and BH_4^-, the formation of Co_2B (reaction 12) would increase, and so more very small particles of Co_2B would be formed in a short time. Subsequently, the rate of reaction 13 may increase tremendously because more catalysis sites are available. And so reactions 12 and 13 increase in rate, but the rate of (13) increases relatively more, essentially because the rate of aggregation of Co_2B (reaction 17) cannot "keep up".

A Mixture of Co_2B (Primary Product) and Co (Secondary Product). Generation of Co_3B. Samples of Co_2B filtered and washed under ambient conditions and subsequently dried and handled under inert atmosphere conditions yielded Co_3B along with metallic Co, and Co_2B on heat treatment. Regardless of reaction conditions Co_3B was not observed as a primary or sole product in any of the reactions. It was only observed when the reactions were carried out so as to yield Co_2B and the product handled so as to allow partial conversion of Co_2B to Co as illustrated by eq 16 prior to thermal processing,

suggesting that the reaction described by eq 18 gives rise to this product.

$$Co_2B + Co \xrightarrow{\Delta} Co_3B \qquad (18)$$
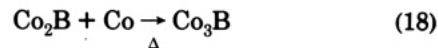
Corrias and co-workers[10] indicate that Co_3B is one of the thermal annealing products after generating powders using methods developed by Schlesinger and co-workers which are known to yield Co_2B. However, they do indicate that products were handled in air. Other publications[4a] which indicate the formation of Co_3B upon annealing also indicate product handling which will cause partial oxidation of the initially formed Co_2B.

Nature of Products. The primary product Co_2B is best prepared by rapid mixing of a 0.010 M Co^{2+} solution with solid $NaBH_4$ (see Experimental Section). Under conditions of rapid mixing of 0.010 M Co^{2+} solutions, the overall ratio of BH_4^-/Co^{2+} had little effect. Under all circumstances, the Co_2B product must be isolated and handled under airless conditions. Upon heat treatment

under argon larger crystals of Co_2B can be obtained. (See Table VIIA and Figure 5A,B). It should be noted that extremely small Co_2B crystallites are obtained initially, but that heat treatment causes rather significant sintering even as low at 350 °C.

The magnetic properties can be compared with bulk Co_2B. The σ values of 60 and 63 emu/g obtained for the thermally processed samples compares reasonably well with the bulk value of 65.8 emu/g.[11] The as prepared material yielded slightly lower values. The elemental analysis indicates that nearly 10% of this material is impurities.[12] The coercivities of the thermally processed material did not change greatly with changing crystallite size, suggesting that the crystallite sizes of these particles are near the single domain size of bulk Co_2B. The temperature dependence of the coercivity and magnetization is provided in Figure 6.

Cobalt metal particles can only be obtained as a secondary product by adjusting conditions so that a mixture of Co_2B and $Co(BO_2)_2$ is produced, and this solid mixture is forced to undergo a solid-state reaction to produce Co(s) and boron oxides (see Experimental Section). Metallic Co particles are also obtained when Co_2B initially generated is isolated under ambient conditions which results in the sacrificial oxidation of the boron to give metallic Co and boron oxide. The properties of the Co(s) produced in these ways are shown in Table VIIB. Magnetic properties of these small particles can be compared to bulk fcc Co metal (162 emu/g). The saturation magnetization (σ) value changes significantly as crystallite size increases with accompanying coercivity increase. Note the maximum coercivity displayed by crystallite sizes of about 13–14 nm and the drastic decrease upon further growth to 37 nm. The σ value of the latter material is significantly lower than the bulk value even though the XRD shows only fcc metallic Co. The analysis of the powder indicates the presence of boron which could exist in the form of B_2O_3 and/or $Co_3(BO_3)_2$. The temperature dependence of the magnetization and coercivity is given in Figure 6. The fresh $Co_2B/Co(BO_2)_2$ samples show significantly higher σ values than the Co_2B samples isolated under ambient conditions. These samples show similar coercivities and similar temperature dependence for the coercivities and saturation magnetization. However, while the ambient condition isolated Co_2B sample shows drastic change in coercivity upon heat treatment at 350 °C, only modest changes are observed in the $Co_2B/Co(BO_2)_2$ sample.

(11) (a) Hasegawa, R.; Ray, R. *J. Appl. Phys.* **1979**, *50*, 1586. (b) Livingston, L. D. *J. Appl. Phys.* **1981**, *52*, 2506.

(12) Wang, J.; Bartholomew, C. H. *Proc.-Int. Cong. Catal., 9th* **1988**, *2*, 813–20.
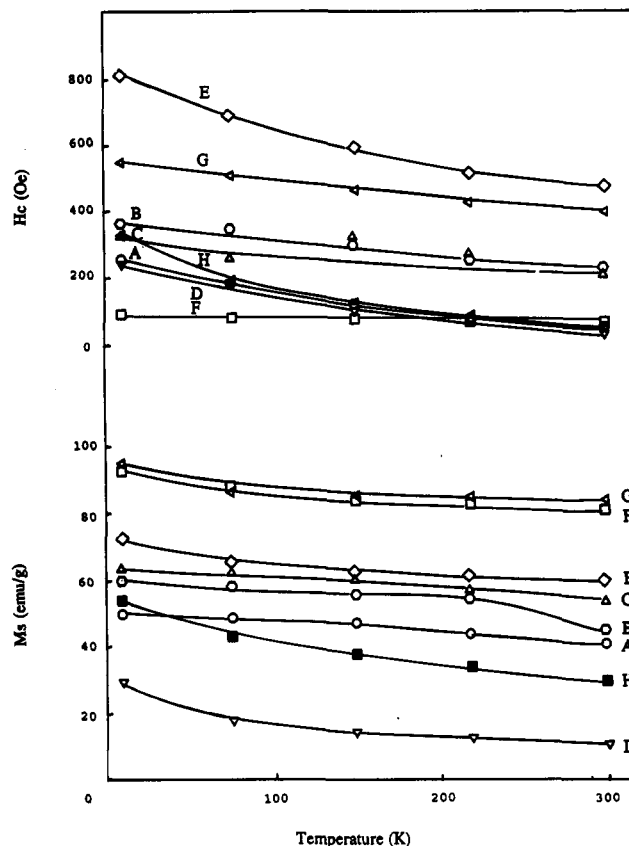

Figure 6. Saturation magnetization and coercivity of powders as a function of temperature: A, Co_2B (fresh); B, Co_2B (350 °C); C, Co_2B (500 °C); D, Co_2B/O_2 (fresh); E, Co_2B/O_2 (350 °C); F, Co_2B/O_2 (500 °C); G, $Co_2B/Co(BO_2)_2$ (fresh); H, $Co_2B/Co(BO_2)_2$ (350 °C).

Finally, $Co(BO)_2$ can be produced as a primary product under conditions where the majority of BH_4^- is converted to BO_2^- under catalytic conditions before the majority of Co^{2+} is added. This is generally an unwanted outcome, and to avoid it the $BH_4^- \rightarrow BO_2^-$ conversion must be avoided or at least controlled. Upon heat treatment, the fine particles of $Co(BO_2)_2$ can be converted to $Co_3(BO_3)_2$ and B_2O_3.[5]