

Borohydride Reduction of Nickel and Copper Ions in Aqueous and Nonaqueous Media. Controllable Chemistry Leading to Nanoscale Metal and Metal Boride Particles

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The reduction of $\text{Ni}^{2+}(\text{aq})$, $\text{Ni}^{2+}(\text{diglyme})$, $\text{Cu}^{2+}(\text{aq})$, and $\text{Cu}^{2+}(\text{diglyme})$ by NaBH_4 has been studied with mechanistic and stoichiometric factors as the focus. The approximate balanced equations were for copper, $\text{Cu}^{2+}(\text{aq}) + 2\text{BH}_4^-(\text{aq}) + 6\text{H}_2\text{O} \rightarrow \text{Cu}(\text{s}) + 7\text{H}_2 + 2\text{B}(\text{OH})_3$, in the diglyme case a colorless, soluble $\text{Cu}(\text{BH}_4)_2$ complex was formed first that upon pyrolysis at 90 °C yielded $\text{Cu}(\text{s})$, $\text{Cu}^{2+}(\text{diglyme}) + 2\text{BH}_4^-(\text{diglyme}) \rightarrow \text{Cu}(\text{BH}_4)_2(\text{diglyme}) (90\text{ }^\circ\text{C}) \rightarrow \text{Cu}(\text{s}) + \text{H}_2 + \text{B}_2\text{H}_6$; nickel, $2\text{Ni}^{2+}(\text{aq}) + 4\text{BH}_4^-(\text{aq}) + 9\text{H}_2\text{O} \rightarrow \text{Ni}_2\text{B}(\text{s}) + 12.5\text{H}_2 + 3\text{B}(\text{OH})_3$, upon air exposure the nanoscale Ni_2B was converted to $\text{Ni}(\text{s}) + \text{B}_2\text{O}_3$ probably by the equation $4\text{Ni}_2\text{B} + 3\text{O}_2 \rightarrow 8\text{Ni}(\text{s}) + 2\text{B}_2\text{O}_3$, in the diglyme solution a mixture of products was formed by the approximate reaction $2\text{Ni}^{2+}(\text{diglyme}) + 4\text{BH}_4^-(\text{diglyme}) \rightarrow \text{Ni}_2\text{B}(\text{s}) + \text{Ni}(\text{s}) + 3\frac{1}{2}\text{H}_2 + 1\frac{1}{2}\text{B}_2\text{H}_6$. A summary of findings for the aqueous and nonaqueous reduction of Fe^{3+} , Fe^{2+} , Co^{2+} , Ni^{2+} , and Cu^{2+} is presented.

Introduction

Borohydride reduction of metal ions is currently used extensively for the production of nanoscale metal and metal boride particles.¹⁻³ The chemistry of the process is however not well understood. As a result, the literature is replete with various recipes for powder preparation given rise to products of varying nature and composition.^{2,3} As part of our continuing effort to understand this process and thus control the nature of ultrafine powders formed, we have studied the reduction of nickel and copper ions in aqueous and nonaqueous media. In this report reaction steps leading to the formation of fine powders of copper, nickel, and nickel borides are reported.

Experimental Section

General Procedures. All reactions were carried out in a 1-L three-necked round-bottom flask attached to a vacuum line of known volume using standard inert atmosphere and Schlenk techniques unless otherwise stated.⁴ The reaction vessel had

two sidearms arranged so that solution could be added in vacuo. Gas evolution in the setup was monitored using a Hg-manometer connected to the vacuum line. Acetone (Fisher Scientific) and distilled water were purged with argon for several hours prior to use. Diglyme (Aldrich Chemical) was dried by refluxing over Na metal under Ar for several days. Anhydrous NiCl_2 (Strem Chemicals), CuBr_2 (Strem), and NaBH_4 (Aldrich) were stored in an inert atmosphere box and used without further purification. Aqueous solutions of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (Fisher) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Mallinckrodt) were prepared using prepurged water.

Heat treatments of isolated powders were carried out under Ar in either a quartz tube or a sealed Pyrex tube using heating tape. Generally, samples were brought to the desired temperature within 2 min and kept at that temperature for 2 h, after which they were allowed to cool to room temperature (5–10 min). X-ray powder diffraction (XRD) data were obtained on a SCINTAG 3000 machine with $\text{Cu K}\alpha$ Ni filtered radiation. Powder diffraction studies on pyrophoric materials were quickly carried out on samples protected from rapid oxidation with mineral oil. Elemental analyses were obtained from Galbraith Laboratories in Knoxville, TN.

Reaction of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and NaBH_4 in Water. The 1000-mL round bottom designed for direct connection to a vacuum line and adapted with a sidearm to allow for addition of solution in vacuo was charged with NaBH_4 (0.15 g, 4.0 mmol) in an inert atmosphere box. The reaction vessel was then connected to the vacuum line, evacuated to $\sim 10^{-3}$ Torr and isolated from the diffusion pumps. A water solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.01 M, 200 mL, 2.0 mmol) was added in ~ 45 s. The light green Cu^{2+} solution first yielded on contact with NaBH_4 a yellow-brown solution and then a brown-black gelatinous precipitate with gas evolution. The reaction was visually complete within 2 min. A total of 14.9 mmol of gas was evolved (Table 1). The precipitate was filtered and washed with three 20-mL portions of prepurged water and then acetone (~ 20 mL) and dried in vacuo yielding a filmy coppery material (0.10 g, 79%). X-ray powder diffraction analysis of the powder indicated metallic copper with crystallite size ~ 30 nm. This powder was not pyrophoric in air but upon extended exposure to ambient conditions some oxidation to Cu_2O was observed.

If the material generated as described above was isolated under ambient conditions, a brown filmy material (0.11 g, 87%) was obtained which upon X-ray powder diffraction analysis showed Cu (dominant) and Cu_2O .

Reactions in which 50% of the Cu^{2+} solution was first added to the NaBH_4 , and the remaining 50% of solution added after gas evolution was complete, also yielded on isolation under ambient conditions a brown powder (0.09 g, 71% based on Cu). Powder diffraction studies indicated a mixture of Cu_2O and metallic Cu.

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Table 1. Copper(II) Ion Reaction with NaBH₄ under Differing Conditions

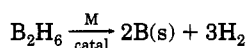
BH ₄ ⁻ /Cu ²⁺ ratio	gas evolved, mmol found (expected)	reaction time, min	% yield of Cu(s)
2 ^a	14.9 (14.0)	10	79
2 ^b	14.9 (14.0)	10	87 ^d
2 ^c	5.9 (4.0)	45	94

^a An aqueous solution of Cu²⁺ was allowed to react with solid NaBH₄. Product isolated using standard inert atmosphere techniques. ^b An aqueous solution of Cu²⁺ was allowed to react with solid NaBH₄. Product isolated under ambient conditions. ^c Reaction carried out in pure diglyme. ^d % yield calculated in the assumption that the product was only metallic copper.

Table 2. Nickel(II) Ion Reaction with NaBH₄ under Differing Conditions

BH ₄ ⁻ /Ni ²⁺ ratio	gas evolved, mmol found (expected)	reaction time, min	wt of product (mg)
2 ^a	14.8 (12.5)	5	132 ^c (Ni ₂ B)
2 ^a	14.7 (12.5)	5	140 ^d (Ni ₂ B)
4 ^a	28.6 (25.0) ^e	30	141 ^c (Ni ₂ B)
2 ^b	6.3 (5.0) ^f	360	110 ^c (Ni(s), Ni ₂ B)
2 ^b	6.0 (5.0) ^f	360	190 ^d (Ni(s), Ni ₂ B)

^a Reaction carried out in water. ^b Reaction carried out in diglyme. ^c Sample isolated under inert conditions. ^d Sample isolated under ambient conditions. ^e Excess BH₄⁻ is hydrolyzed eventually according to the equation BH₄⁻ + 2H₂O → BO₂⁻ + 4 H₂. ^f Usually B₂H₆ decomposes in the presence of small metal particles to give boron or metal boride plus hydrogen by the equation



and this accounts for some of the extra gas generated.

Reaction of CuBr₂ and NaBH₄ in Diglyme. The reaction vessel described above was charged with CuBr₂ (0.43 g, 2.0 mmol) in an inert atmosphere box connected to a vacuum line and evacuated to ~10⁻³ Torr. Diglyme (100 mL) was added with stirring. A 50 mL diglyme solution of NaBH₄ (0.15 g, 4.0 mmol) was then added to the CuBr₂ suspension. All the CuBr₂ slowly dissolved over a period of 1 h as it reacted with the NaBH₄, and the brownish solution turned colorless with minimal gas evolution. A white residue (NaBr) was also apparent. Filtration of the white suspension yielded a colorless solution which was stable indefinitely at room temperature. The solution was heat treated at ~90 °C using a water bath. Vigorous gas evolution was observed with precipitation of a coppery film on the walls of the reaction vessel. Heating was discontinued when gas evolution ceased (45 min). The powder was isolated and washed with prepurged water and acetone using standard inert atmosphere techniques yielding upon vacuum drying a brown powder (0.12 g, 94%). X-ray diffraction studies showed metallic copper with crystallite size of 24 nm.

Reaction NiCl₂·6H₂O and NaBH₄ in Water. The reaction vessel described above was charged with NaBH₄ (0.15 g, 4.0 mmol) in an inert atmosphere box connected to a vacuum line and evacuated to 10⁻³ Torr. The setup was then isolated from the diffusion pumps and 200 mL of NiCl₂·6H₂O (0.010 M, 2.0 mmol) solution was added over 45 s. Instantaneous gas evolution was observed with the precipitation of a black powder (Table 2). Gas evolution virtually ceased within 5 min. The suspension was filtered, washed using prepurged H₂O and then acetone, and dried in vacuo yielding 0.13 g of a black pyrophoric powder. Elemental analysis of the dried powder yielded the following: Calcd for Ni₂B: Ni, 91.6; B, 8.40. Found: Ni, 83.2; B, 6.90; Ni/B ratio, 2.22. After heat treatment in a sealed tube (Ar atmosphere) at 400 °C for 2 h, the analysis indicated the following: Ni, 88.1; B, 7.78; Ni/B ratio, 2.08. The heat-treated product was examined by X-ray powder diffraction which showed Ni₂B and small quantities of metallic Ni and Ni₃B. The crude powder was also examined using XRD, which indicated a noncrystalline product.

Table 3. Behavior of NiCl₂/NaBH₄ Reaction in the Presence of H₂O^a

H ₂ O added (mmol) ^b	gas evolved, mmol found (expected)	reaction time, min	wt of product ^d (mg)
0	6.3 (5.0)	360	109
6 ^c	13.8 (14.0)	1440	70
56	14.4 (14.0)	30	123
278	15.1 (14.0)	5	127
556	15.9 (14.0)	5	121
2778	15.5 (14.0)	5	124

^a 2.0 total mmol of NiCl₂ in diglyme reacted with 4.0 total mmol of NaBH₄ in diglyme. ^b Appropriate volume of H₂O added to dissolve the NiCl₂ and then 50 mL of diglyme added prior to reaction. ^c Reaction carried out in diglyme using NiCl₂·6H₂O. ^d Mixture of Ni₂B, Ni₃B, and Ni(s).

If the black suspension from the above reaction was isolated under ambient conditions, an air-stable black powder (0.14 g) which upon heat treatment and examination by XRD showed metallic Ni.

Reactions of NiCl₂ and NaBH₄ in Diglyme. The reaction vessel described in the general procedure was charged with NiCl₂ (0.26 g, 2.0 mmol) in an inert atmosphere box connected to a vacuum line and evacuated to ~10⁻³ Torr. Diglyme (100 mL) was added and then a 50 mL solution of NaBH₄ (0.15 g, 4.0 mmol) was added with stirring. A slow dissolution of the NiCl₂ ensued as reaction with the NaBH₄ occurred. A slow gas evolution was observed within ~5 min after the start of the reaction and continued for 6 h. During this time a black precipitate slowly formed. A total of 6.3 mmol of gas was evolved. The suspension was filtered, washed with prepurged H₂O and acetone, and dried in vacuo yielding 0.11 g of a black pyrophoric powder. Elemental analysis of the crude powder yielded the following: Ni, 76.6; B, 5.75; Ni/B ratio, 2.45. Analysis of sample heat treated at 400 °C for 2 h in a sealed Pyrex tube showed the following: Ni, 81.4; B, 6.12; Ni/B ratio, 2.45. The XRD analysis of the heated powder indicated a mixture Ni, Ni₂B, and Ni₃B.

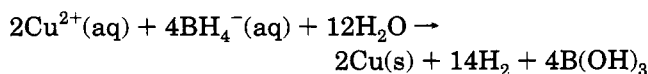
Reaction of NiCl₂ and NaBH₄ in Diglyme in the Presence of Water. A series of reactions were carried out using a BH₄⁻/Ni²⁺ ratio of 2 in which the anhydrous NiCl₂ was dissolved in a known volume of water (Table 3) prior to addition of diglyme solution. The NiCl₂/water/diglyme solution was added simultaneously with the NaBH₄-diglyme solution to the reaction vessel as previously described. Instantaneous reaction yielding a black precipitate and gas evolution was observed. Samples were filtered, washed, and dried using standard inert atmosphere techniques.

Results and Discussion

I. Copper(II). (a) *In water.* The reaction of Cu²⁺ ions with NaBH₄ in water first yields a yellow-brown solution. This is followed by immediate gas evolution with the precipitation of a brown-black gel-like solid. Isolation of the solid under inert conditions yielded an air-stable copper-like film which based on XRD analysis indicated metallic copper with crystallite size of ~30 nm, in near quantitative yields.

Chemical reactions that help explain the formation of metallic copper are summarized in Scheme 1.

Scheme 1. Reactions of Cu²⁺(aq) with Borohydride Starting with 2 mmol of Copper Ion in Water



Because of the positive redox potential of copper, metallic

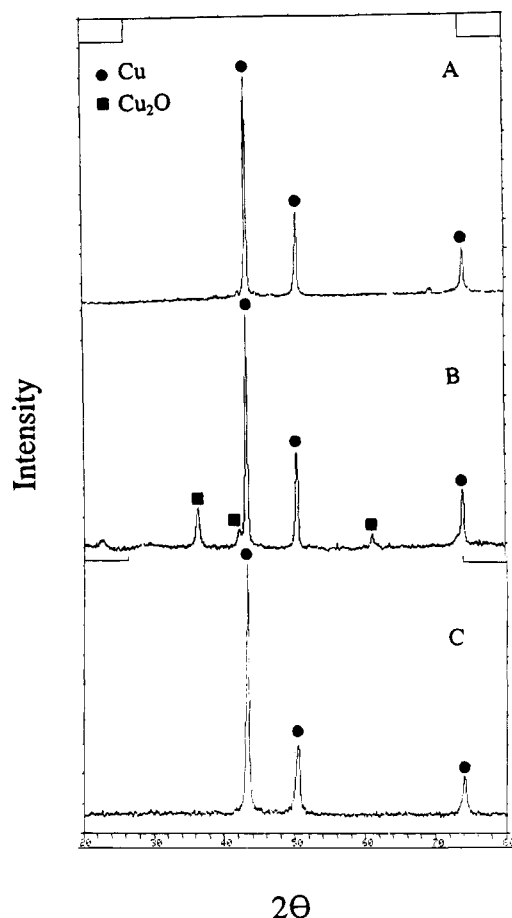


Figure 1. X-ray powder diffraction spectra of crude powders from Cu^{2+} ions and NaBH_4 reactions: A, aqueous reaction, sample isolated under inert conditions; B, aqueous reaction sample isolated under ambient conditions; C, reaction carried out in nonaqueous medium, sample isolated under inert condition.

copper is formed in its reaction with NaBH_4 instead of the boride, in contrast to what is observed for cobalt and nickel (see later discussion) which have more negative redox potentials and follow a different reaction path.

A total of 14.9 mmol of gas was observed in comparison with the expected 14.0 mmol of H_2 . The difference of 0.9 mmol is probably due to the partial pressure of water vapor. The powder obtained is not pyrophoric in air; however, upon extended exposure to air, slow oxidation to Cu_2O was observed. Isolation of the suspension from the above reaction under ambient conditions yielded a mixture of Cu and Cu_2O in contrast to metallic Co⁵ and Ni (see later discussion) which were formed in the analogous nickel and cobalt reactions.

(b) *In Pure Diglyme.* The reaction of Cu^{2+} and sodium borohydride in diglyme yielded a colorless complex, presumably $\text{L}_n\text{Cu}(\text{BH}_4)_2$ ($\text{L} = \text{diglyme}$), **1**, which is stable indefinitely at room temperature. Thermal decomposition of this complex at 90 °C yielded a brown-black precipitate with gas evolution. Isolation of the suspension under inert conditions yielded air-stable brown black copper powder in 94% yield. X-ray powder diffraction analysis of this powder indicated that it was indeed metallic copper with average crystallite size of 24 nm. A total of 5.9 mmol of gas was evolved.

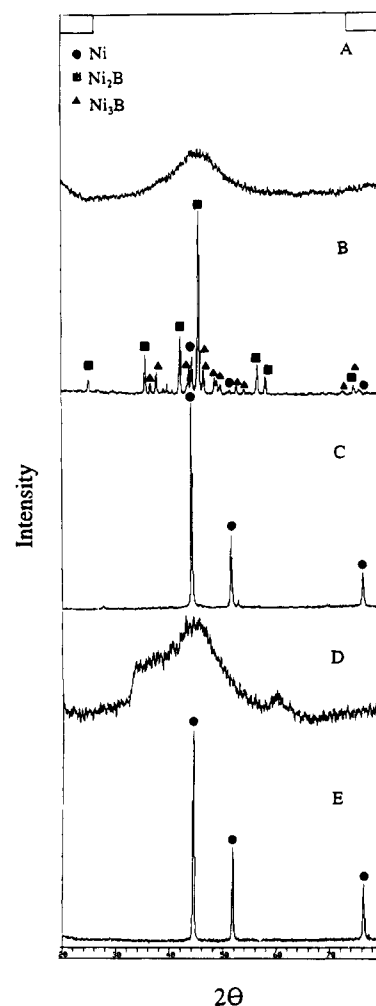
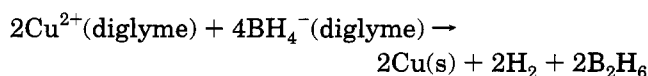
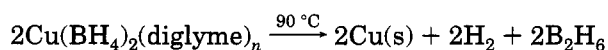
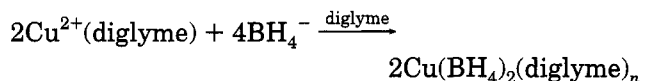


Figure 2. X-ray powder diffraction data on powders from Ni^{2+} ions and NaBH_4 reaction in aqueous media: A, fresh powder isolated under inert conditions; B, sample isolated under inert conditions and heat processed under Ar at 500 °C; C, fresh powder exposed to ambient conditions; D, sample isolated under ambient conditions; E, sample isolated under ambient condition and heat processed at 500 °C under Ar.

The formation of metallic copper in this nonaqueous reaction is described by Scheme 2.

Scheme 2. Reactions of Cu^{2+} (diglyme) with Borohydride Starting with 2 mmol of Copper(II) in Diglyme



The stability of complex **1** suggests that in diglyme solution there is a kinetic barrier to the reduction process as a whole. The scheme indicates that a total of 4.0 mol of gas should be generated in contrast to the 5.9 mmol observed. It has however been demonstrated that fine particles of some metals or metal borides will catalytically

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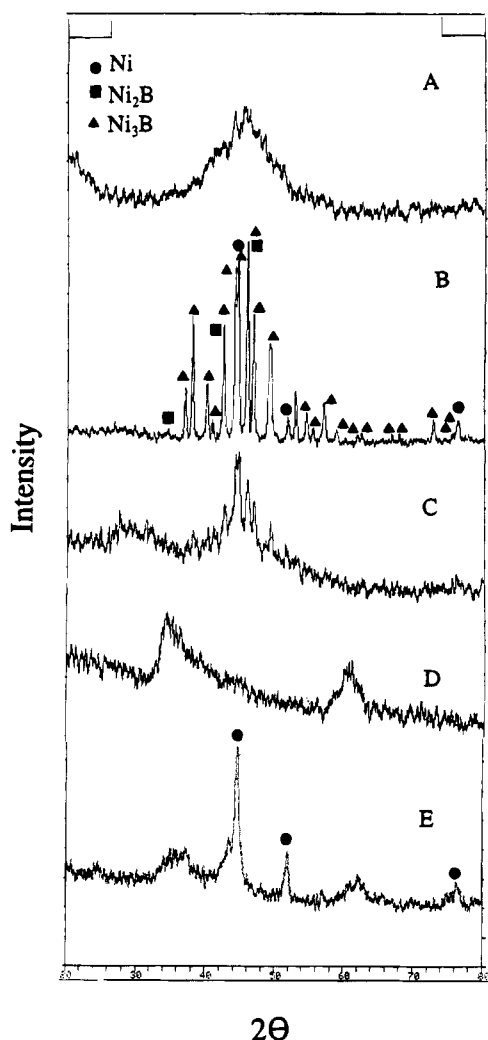
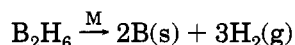


Figure 3. X-ray powder diffraction data on powders from Ni^{2+} ions and NaBH_4 reaction in diglyme: A, crude sample isolated under inert conditions and protected with Nujol; B, sample isolated under inert condition and heat processed at 400°C under Ar; C, dried, fresh powder exposed to air; D, crude sample isolated under ambient conditions to yield air stable powder; E, sample isolated under ambient conditions and heat treated under Ar at 500°C .

decompose B_2H_6 to give B(s) and H_2 .⁶ This reaction



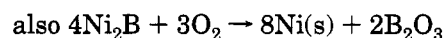
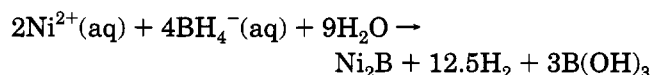
is probably responsible for the generation of the additional gas observed.

II. Nickel(II). (a) *In Water.* The reaction of Ni^{2+} ions and sodium borohydride in water resulted in the instantaneous precipitation of a black powder with vigorous gas evolution. Isolation of the black suspension under completely inert conditions yielded a noncrystalline, black pyrophoric powder which upon thermal processing and XRD analysis showed the presence of mainly Ni_2B (Figure 2A,B). The XRD of the dried fresh powder after exposure to air gave sharp lines corresponding to metallic Ni (Figure 2C). Also, work-up and isolation of the black precipitate from the above reaction under ambient conditions yielded an air-stable powder which upon heat treatment showed metallic Ni in the powder diffraction spectrum (Figure 2D,E). A total of 14.8 mmol of gas was evolved in a typical

reaction starting with 2 mmol of Ni^{2+} and 4 mmol of BH_4^- . In the reaction with BH_4^- in water, nickel behaves very similarly to cobalt and identical balanced equations may be written for Ni^{2+} as previously shown for Co^{2+} .⁵ However, the experiments did differ in some aspects. For example, the Co_2B was readily isolated as a pure material under inert conditions whereas in the Ni^{2+} reaction even after very careful work-up under Ar, trace amounts of metallic Ni were present along with the main Ni_2B product. Secondly, no $\text{Ni(BO}_2)_2$ was formed under the same conditions where $\text{Co(BO}_2)_2$ was produced.⁵

(b) *In Pure Diglyme and Diglyme–Water Mixtures.* The reaction of a yellow suspension of NiCl_2 in diglyme with a diglyme solution of NaBH_4 first yielded a colorless solution which slowly decomposed at room temperature, yielding a black precipitate with steady gas evolution. A total of 6.3 mmol of gas evolved over a period of 6 h. A reaction carried out at 70°C also took 6 h to go to completion, suggesting that the reaction rate was limited by the solubility of the NiCl_2 in diglyme. Isolation of the suspension under inert conditions yielded 0.11 g of a black pyrophoric powder. The XRD analysis of the crude powder showed a broad line (Figure 3A). The heat-treated powder was air stable and showed a mixture of Ni, Ni_3B , and Ni_2B on X-ray diffraction analysis. Exposure of the fresh dry powder to air caused it to burn giving rise to crystallites of Ni, Ni_2B , and Ni_3B (Figure 3C). If the precipitate from the reaction was isolated under ambient conditions, a stable light green powder was obtained which upon heat processing and XRD analysis indicated a mixture of metallic Ni and nickel oxide (Figure 3 D,E and Schemes 3 and 4).

Scheme 3. Reaction of $\text{Ni}^{2+}(\text{aq})$ with Borohydride Starting with 2 mmol of Nickel Ion in Water



Scheme 4. Reaction of $\text{Ni}^{2+}(\text{diglyme})$ with Borohydride Starting with 2 mmol of Nickel(II) in diglyme

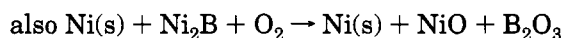
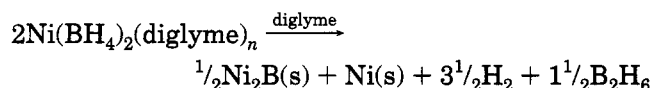
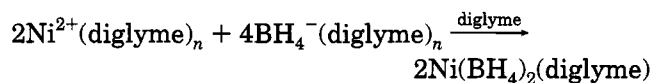


Figure 4 shows the XRD of heat-treated samples from a series of reactions in which differing amounts of H_2O were added to the NiCl_2 –diglyme solution prior to mixing with the NaBH_4 –diglyme solution. Again these reactions all gave a mixture of Ni, Ni_3B , and Ni_2B products with very little variation. These are in contrast to the Co^{2+} reactions in diglyme⁶ which yielded metallic Co upon work up and showed a steady gradation of metallic Co to Co_2B as increasing amounts of water were added to the reaction mixtures.

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Table 4. General Trends in Borohydride Reduction of First Row Transition-Metal Ions

metal ion	reduction potential, E^a	metal containing products of borohydride reduction			refs
		in water under argon	in diglyme under argon	in water under air	
Fe^{3+}	-0.036 ^b	Fe	FeB	Fe, FeO_x	7
Fe^{2+}	-0.41	Fe	Fe_2B^c	Fe, FeO_x	7
Co^{2+}	-0.28	Co_2B	Co^e	$\text{Co}_3(\text{BO}_3)_2$, Co	5, 6
Ni^{2+}	-0.23	Ni_2B	Ni, Ni_2B , Ni_3B^c	Ni, NiO	f
Cu^{2+}	+0.34	Cu	Cu^d	Cu, Cu_2O	f

^a Standard condition $\text{M}^{2+} + 2\text{e}^- \rightarrow \text{M}(\text{s})$. ^b $\text{Fe}^{3+} + 3\text{e}^- \rightarrow \text{Fe}(\text{s})$. ^c $\text{Ni}(\text{BH}_4)_2$ formed first; slow decomposition at 25 °C yielded a mixture of solid Ni, Ni_2B , and Ni_3B . $\text{Fe}(\text{BH}_4)_2(\text{diglyme})$ and $\text{Fe}(\text{BH}_4)_3(\text{diglyme})$ are stable in diglyme, and upon heating to 70 °C the precipitation of FeB or Fe_2B takes place. ^d $\text{Cu}(\text{BH}_4)_2$ formed first; thermal decomposition at 90 °C yielded Cu(s). ^e $\text{Co}(\text{BH}_4)_2$ is not stable. ^f This work.

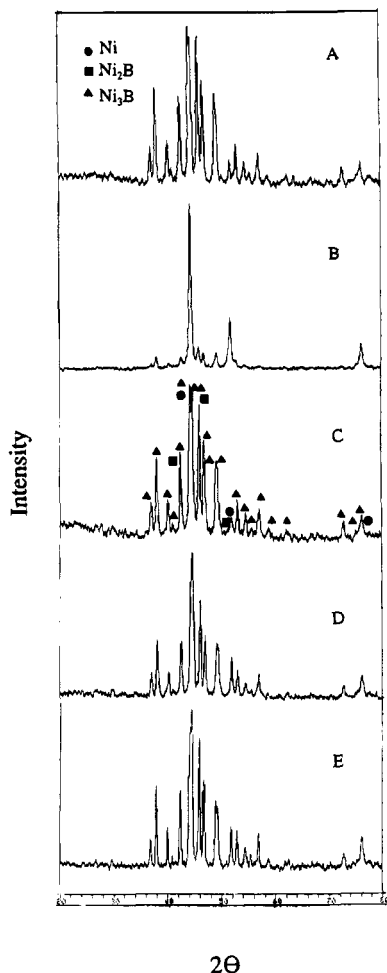


Figure 4. Sample obtained from $\text{Ni}^{2+}/\text{BH}_4^-$ reactions in which the noted amount of water was added to reaction mixture, sample isolated under inert conditions and heat treated at 400 °C under Ar: A, 0.0 mmol of H_2O ; B, 56 mmol of H_2O ; C, 279 mmol of H_2O ; D, 556 mmol of H_2O ; E, 2778 mmol of H_2O .

Reaction and Summary of Borohydride Reduction of Fe^{3+} , Fe^{2+} , Co^{2+} , Ni^{2+} , and Cu^{2+} in Water and

in Dry Diglyme. The borohydride reduction of these metal ions is a valuable way to produce nanoscale metal, metal boride, and sometimes metal borate particles. After several years of investigation of these as well as other metal ions, we can draw some useful conclusions and generalizations.

(a) *Reduction Potential of the Metal Ion.* As we move from left to right in the transition-metal series, metal ion reduction becomes easier (see Table 4). The most favorable reduction potential is for Cu^{2+} and nanoscale Cu(s) is the product in both water and diglyme solutions. However, with iron, cobalt, and nickel, often metal borides are formed (see Table IV), and this is probably due in part to their less favorable reduction potentials. However, predictions as to whether metals or metal borides will form are not really possible, based only on thermodynamic considerations. Indeed, predictions based on $\Delta H^\circ_{\text{rxn}}$ are not very reliable, especially since ΔH°_f for metal borides are small values and solvation energies of reactants and products are difficult to evaluate. And of course kinetic parameters are just as important as thermodynamics. Thus, in such complex systems it becomes necessary to study each ion in some detail.

(b) *Primary Products.* The predominant primary products are shown in Table 4. Note that cobalt and nickel behave quite similarly giving M_2B in aqueous media, but Co(s) and Ni(s), Ni_2B , and Ni_3B in diglyme. Iron, on the other hand, behaves somewhat differently.

(c) *Secondary Products.* An important point to make is that the presence of air during the reduction process can change the outcome. Usually a mixture of metal (formed by $\text{M}_2\text{B} + \text{O}_2 \rightarrow \text{M}(\text{s}) + \text{B}_2\text{O}_3$) and metal oxides is formed.

(d) *Metal Borohydride Intermediates.* A surprising result was that in the cases of iron and copper, rather stable $\text{M}(\text{BH}_4)_{2,3}$ complexes were generated in diglyme. Only by heating did solid products precipitate. These stable coordination compounds are certainly of interest and await further work.

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(7) Glavee, G. N.; Klabunde, K. J.; Sorensen, C. M.; Hadjipanayis, G. C. *Inorg. Chem.*, in press.