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Chemistry of Borohydride Reduction of Iron(II) and Iron(III) Ions in Aqueous and Nonaqueous Media. Formation of Nanoscale Fe, FeB, and Fe$_2$B Powders

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The reduction of FeBr$_2$(aq), FeBr$_3$(aq), FeBr$_2$(diglyme), and FeBr$_3$(diglyme) by NaBH$_4$ has been investigated with mechanistic and stoichiometric factors in mind. The bewildering complexity of such reactions has been partly alleviated. We find that the primary products are different depending on the reaction medium. In aqueous solution Fe^{2+} yields mainly noncrystalline, nanoscale Fe(s), while in dry diglyme the product is nanoscale Fe$_2$B. In the case of Fe^{3+}(aq) the primary product again is Fe(s), but in diglyme it is FeB. An unexpected finding was that, in dry diglyme, iron borohydride coordination compounds are indefinitely stable and only yield solid Fe$_2$B (or FeB) upon heating. These compounds are probably (L)$_n$Fe(BH$_4$)$_2$ and (L)$_n$Fe(BH$_4$)$_3$ where L = diglyme. Treatment of these complexes in-situ with water causes the precipitation of Fe$_2$B.

Introduction

Understanding the chemistry of BH$_4^-$ reduction of transition metal ions takes on increasing importance as more and more scientists use this approach to prepare "amorphous metals,"[2] nanocrystalline magnetic materials,[3] and catalysts.[4] It has become clear that boron is incorporated into the solid products, but the metal/boron ratios vary widely according to literature reports. This variations could be due to mixing procedures, solvent media, temperature, or other factors.

We described in recent publications the reaction steps involved in the formation of ultrafine Co$_2$B, Co$_3$B, metallic Co, and Co(BO$_2$)$_2$ by the borohydride reduction of cobalt ions in aqueous and nonaqueous media.[5,6] As part of our continuing effort to understand and control the formation of nanoscale magnetic materials, we have studied the reduction of Fe^{2+} and Fe^{3+} in aqueous and nonaqueous media. Herein are reported experiments leading to different nanoscale iron compounds. Again it has been found that the solvent medium (water or diglyme) is important in determining the final product. Likewise, subtle changes in reaction conditions can have unusual outcomes.

Experimental Section

General Procedure. Reactions were carried out in a 1-L three-necked round-bottom flask attached to a vacuum line of known volume unless otherwise stated. The line was equipped with a mercury manometer, and the reaction vessel had two side arms arranged so that solutions could be added in vacuo. Acetone (Fisher Scientific) and distilled water were purged with argon for several hours prior to use. Diglyme was refluxed over sodium metal for several days and distilled under Ar. Anhydrous FeBr$_3$ (Strem Chemicals), FeBr$_2$ (Strem Chemicals) and NaBH$_4$ (Aldrich Chemicals) were stored in an inert-atmosphere box and used as received. Aqueous solutions of FeCl$_2$·4H$_2$O (Aldrich Chemicals) and FeCl$_3$·6H$_2$O (Fisher Scientific) were prepared immediately before use using prepurged water. All reactions and product isolations were carried out using standard inert-atmosphere techniques unless otherwise stated.[7] The amount of gas formed was determined by pressure measurement in known volume and the identity of gas evolved determined using GC.

Heat treatment of powders was carried out either in a quartz tube under Ar or in a sealed Pyrex tube under low Ar pressure. 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 rapidly cool to room temperature. For samples isolated under inert-conditions, there were no weight losses upon heat treatment. X-ray powder diffraction data were obtained on a SCINTAG 3000 machine with Cu Kα radiation. Powder diffraction studies on pyrophoric samples were carried out on samples protected with mineral oil (Nujol), and Mossbauer data were obtained on a Ranger Scientific Inc MS-1200 using a cryostat designed by Cryo Industries of America Inc. Elemental analyses were obtained from Galbraith Labs, Knoxville, TN.

Reaction of NaBH$_4$ and FeBr$_2$ in Diglyme. To a Schlenk tube charged with anhydrous FeBr$_2$ (0.43 g, 2.0 mmol) was added diglyme (75 mL) with stirring. An orange solution resulted after stirring for about 2 h. A second tube was charged with NaBH$_4$ (0.15 g, 4.0 mmol) in an inert-atmosphere box and 50 mL of diglyme added with stirring to dissolve the solid, yielding a colorless solution. The reaction vessel described under General Procedure was connected to a vacuum line,

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Table 1. Nonaqueous $FeBr_2$ Reaction with $NaBH_4$ under Differing Conditions[a,b,c]

$NaBH_4/FeBr_2$ ratio	amt of gas evolved,[c] mmol (expected)	reacn time, min	% yield[d]	tot. vol of diglyme, mL
5	7.7 (8.0)	95		125
3	8.6 (8.0)	70	80	125
2	8.2 (8.0)	60	100	125
2	8.4 (8.0)	60	81	140
2	8.2 (8.0)	90	105	200

[a] The $NaBH_4$ used was dissolved in 50 mL of diglyme for all the reactions. [b] A total of 2.0 mmol of $FeBr_2$ was used in all the reactions. [c] All decompositions were carried out thermally at about 70 °C. [d] Based on major product as Fe_2B.

evacuated to about 10^{-3} Torr, and isolated from the pumps, and syringes were used to simultaneously transfer the diglyme solutions of $FeBr_2$ and $NaBH_4$ into the vessel at ambient temperature with stirring. A pale yellow solution resulted with the precipitation of a white solid (NaBr) and minimal gas evolution. The reaction vessel was placed in a water bath and warmed to 65−70 °C. The solution became colorless (still containing the white NaBr precipitate), and vigorous gas evolution which continued for about 30 min was observed with the precipitation of a black solid. The reaction mixture was allowed to cool to room temperature. The suspension was filtered through a fine glass frit, the residue was washed with three 25 mL portions of deoxygenated water followed by two 20 mL portions of deoxygenated acetone, and the filter cake was dried in vacuo. The filter frit with the black powder was transferred into an inert-atmosphere box and the weight of the pyrophoric powder determined to be 0.12 g (0.98 mmol 98%) based on Fe_2B as the only product. An average of 8.8 ± 0.2 mmol of gas was evolved during experiments carried out under these conditions.

Reactions were also carried out using different $FeBr_2/NaBH_4$ ratios as well as different concentrations of reagents (Table 1). It should be noted that if the black suspension generated from the above reaction was filtered and the residue washed and dried under ambient conditions, a yellow-brown air-stable powder was obtained.

Reaction of $FeBr_2$ and $NaBH_4$ in Diglyme in the Presence of Water. A number of reactions were carried out as described above using a BH_4^-/Fe^{2+} ratio of 2 in which the diglyme solution of $FeBr_2$ (0.43 g, 2.0 mmol) was treated with varying volumes of H_2O to give a desired H_2O/Fe^{2+} ratio prior to mixing with the $NaBH_4$−diglyme solution.

Reaction of $FeCl_2$ and $NaBH_4$ in Water. The 1000 mL reaction vessel described above was charged with $NaBH_4$ (0.15 g, 4.0 mmol) in an inert-atmosphere box, connected to a vacuum system, evacuated, and maintained at a static pressure of about 10^{-3} Torr. A freshly prepared aqueous solution of $FeCl_2{\cdot}4H_2O$ (0.01 M, 200 mL) was added to the vessel using four 60 mL syringes over a 45−60 s period. Immediate gas evolution was observed with the precipitation of a jellylike black solid. The reaction chamber was isolated and disconnected from the vacuum line after gas evolution had ceased (15 min). The solid was filtered off and washed with prepurged H_2O and acetone using standard inert-atmosphere techniques and the resulting powder dried in vacuo. A black, amorphous, pyrophoric powder (0.11 g) was collected in an inert-atmosphere box. Anal. Found for the crude dry powder; Fe, 82.9; B, 3.95; Fe/B ratio, 4.07. Calcd for Fe_2B: Fe, 91.2; B, 8.82. Found after thermal processing at 450 °C in a sealed Pyrex tube for 2 h: Fe, 92.2; B, 4.3; Fe/B ratio, 4.04.

The reaction described above was repeated, and the resulting black jellylike solid was isolated under ambient conditions yielding a yellow-brown air-stable powder (0.16 g).

Decomposition of $(Diglyme)_nFe(BH_4)_2$ by Reaction with Water. The complex $(diglyme)_nFe(BH_4)_2$ was prepared by reacting diglyme solutions of $FeBr_2$ (0.43 g, 2.0 mmol) and $NaBH_4$ (0.15, 4.0 mmol) in the 1.0-L reaction vessel as described above at ambient temperature. Addition of 1.0 mL of water (55.6 mmol) led to vigorous gas evolution with immediate precipitation of a black solid. After gas evolution had ceased (15 min), the black precipitate was isolated as described above, yielding 0.12 g of an amorphous pyrophoric powder. Analysis of samples heat processed at 450 °C using XRD and Mossbauer showed that Fe_2B (98%) was the only product. A total of 15.0 mmol of gas was evolved. The reaction was repeated using a BH_4^-/Fe^{2+} ratio of 2 and 10 mL (556 mmol) of H_2O, yielding the same results.

Decomposition of $(Diglyme)_nFe(BH_4)_2$ in Air. The $(diglyme)_nFe(BH_4)_2$ complex prepared by reacting diglyme solutions of $FeBr_2$ (0.43 g, 2.0 mmol) and $NaBH_4$ (0.15 g, 4.0 mmol) in the previously described reaction vessel under inert-atmosphere conditions, was exposed to ambient laboratory conditions. A slow precipitation of a light yellowish-green solid ensued with gas evolution. After gas evolution had stopped (~2 h), the solid was filtered off, washed, and dried under ambient conditions, yielding 0.22 g of yellow-brown air-stable powder.

Reaction of $FeBr_3$ and $NaBH_4$ in Diglyme. Diglyme (50 mL) solutions of $FeBr_3$ (0.59 g, 2.0 mmol) (red-brown) and $NaBH_4$ (0.23 g, 6.0 mmol), prepared as described for $FeBr_2$ above, were added to the 1.0-L reaction vessel with stirring at ambient temperature as previously described. A reddish-orange solution resulted with the precipitation of a white residue. The reddish-orange $(diglyme)_nFe(BH_4)_3$ was stable indefinitely at ambient temperature. The reaction vessel was heated to 95−100 °C using a water bath. The solution became orange, pale yellow, and then colorless, at which time vigorous gas evolution started with the precipitation of a black solid. The reaction mixture was allowed to cool to ambient temperature and the total amount of gas evolved determined (9.3 ± 0.2 mmol). The black suspension was isolated as described for $FeBr_2$ above, yielding 0.12 g of a black pyrophoric FeB powder (86%). Anal. Found for the crude powder before heat treatment: Fe, 64.5; B, 14.1; Fe/B ratio, 0.92. Found for the powder after heat treatment: Fe, 74.7; B, 14.0; Fe/B ratio, 1.03. Isolation of the black suspension generated in the above reaction under ambient conditions yielded a brown-black air-stable powder.

Reaction of $FeBr_3$ and $NaBH_4$ in Diglyme in the Presence of Water. A series of reactions were carried out as described above using a BH_4^-/Fe^{3+} ratio of 3 in which the diglyme solution of $FeBr_3$ (0.59 g, 2.0 mmol) was treated with varying volumes of H_2O to give a desired H_2O/Fe^{3+} ratio prior to mixing with $NaBH_4$−diglyme solution. Product isolation was done as previously described.

Reaction of $FeCl_3$ and $NaBH_4$ in Water. A freshly prepared 0.01 M solution of $FeCl_3{\cdot}6H_2O$ (200 mL) was added to solid $NaBH_4$ (0.23 g, 6.0 mmol) in a 1.0-L reaction vessel under a static vacuum, described in the general procedure, using four 60-mL syringes. Vigorous gas evolution was observed with the precipitation of a black jellylike solid. The reaction was complete in 90 s. The black suspension was isolated as described above for $FeCl_2$. A black amorphous, pyrophoric powder (0.11 g) was obtained. Anal. Found for the crude powder: Fe, 82.48; B, 3.58; Fe/B ratio, 4.46. After thermal processing at 450 °C in sealed Pyrex tube for 2 h analysis showed 3.70% B. If the resulting suspension from the above reaction was isolated under ambient conditions, a grayish-brown air-stable powder (0.17 g) was obtained.

Reaction of $(Diglyme)_nFe(BH_4)_3$ with Water. The complex $(diglyme)_nFe(BH_4)_3$, prepared by reacting diglyme solutions of $FeBr_3$ (0.59 g, 2.0 mmol) and $NaBH_4$ (0.23 g, 6.0 mmol) as described for $FeBr_2$, was treated with H_2O (1.0 mL, 55.6 mmol). This resulted in vigorous gas evolution and the generation of a black suspension over 30 min. Isolation of the black solid using standard inert-atmosphere techniques yielded a noncrystalline powder (0.12 g, 98%) which upon heat processing, XRD analysis, and MS analysis indicated Fe_2B.

A total of 20.5 mmol of gas was evolved. When the decomposition of the precursor was carried out using 10.0 mL of H_2O (556 mmol), the reaction was complete within 1 min, yielding the same total amount of gas and solid product.

Decomposition of $(Diglyme)_nFe(BH_4)_3$ in Air. Reaction of diglyme solutions of $FeBr_3$ (0.59 g, 2.0 mmol) and $NaBH_4$ (0.23 g, 6.0 mmol) yielded $(diglyme)_nFe(BH_4)_3$ as previously described. Exposure of the resulting solution to ambient conditions led to gas evolution, with the reddish-orange solution becoming colorless prior to the precipitation of yellow solid. A yellow-brown air-stable powder (0.18 g) was obtained after isolation and drying in air.

Results and Discussion

I. Iron(II). a. In Pure Diglyme and with Subsequent Water Additions.

The interaction of iron(II) bromide and sodium borohydride in diglyme at room temperature yielded a coordination compound which we propose as **1**, a pale yellow compound in solution (eq 1).

$$FeBr_2 + 2NaBH_4 \xrightarrow{L = \text{diglyme}} \underset{\mathbf{1}}{(L)_nFe(BH_4)_2} + 2NaBr \quad (1)$$

This compound is indefinitely stable at room temperature. This result is in contrast to an earlier report where $Fe(BH_4)_2$ in diethyl ether is an unstable colorless solid that decomposes at −10 °C.[8] In our case, only upon heating to 65−70 °C did decomposition ensue with the vigorous evolution of gas.[9] A noncrystalline product precipitated. After collection of this solid and drying, elemental analysis showed an Fe/B ratio of slightly less than 2. This noncrystalline material showed no XRD peaks, as expected. The Mossbauer spectra showed two overlapping broad peaks with isomer shifts of 0.20 and 0.94 mm/s with quadrupole splittings of 0.83 and 2.36 mm/s, respectively. The peaks were not well resolved even at 77 K, but these results are similar to those observed for other iron boride noncrystalline materials.[10]

Heat treatment of the sample yielded Fe_2B nanocrystallites along with a small amount of FeB, according to XRD and Mossbauer (Figures 1 and 2). The Mossbauer showed a hyperfine field of 237 kOe and an isomer shift of 0.08 mm/s, values that are consistent with those reported for Fe_2B.[11]

Exposure of the fresh noncrystalline powder to air resulted in its turning red hot and slowly smoldering. X-ray powder diffraction analysis indicated that this air-exposed sample was converted to boron oxide, iron oxides, and α-Fe, probably as shown by eq 2. Evidence was also found for the presence of small amounts of nanocrystalline Fe_2B (Figure 1C,D and Figure 2C,D).

$$Fe_2B + {}^3/_4O_2 \rightarrow 2Fe + {}^1/_2B_2O_3 \quad (2)$$

If the black suspension generated by the airless, *thermal* decomposition of **1** was isolated and dried under ambient conditions, a yellow-brown air-stable powder was obtained. Mossbauer and X-ray powder diffraction analyses of this powder are given by Figure 1E,F and Figure 2E,F and indicate that mainly iron oxides were present. This shows that slow, continuous exposure to oxygen did cause complete oxidation ($Fe_2B + O_2 \rightarrow FeO_x + B_2O_3$).

The formation of **1** and its thermal decomposition to Fe_2B are independent of both the concentration of the reagents and the BH_4^-/Fe^{2+} ratio (Table 1). The yields of Fe_2B were quite high, and the amount of H_2 released was very close to that expected. These results are summarized by Scheme 1, where it is proposed that, upon heating, compound **1**[9] decomposed with the formation of the dimer intermediate **2**. The presence of this intermediate has not been confirmed; however it does have the required Fe/B ratio.

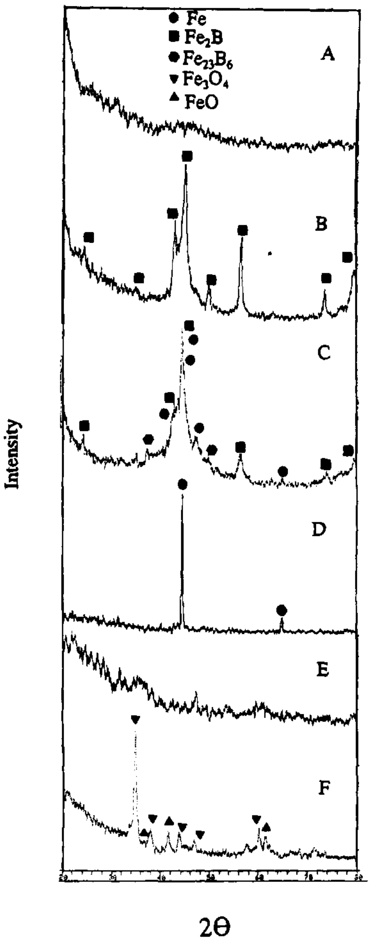

Figure 1. X-ray powder diffraction spectra of Fe_2B samples formed in nonaqueous solution: A, fresh sample protected in mineral oil; B, sample heat-treated at 550 °C; C, air-exposed sample; D, air-exposed sample heat-treated at 500 °C under Ar; E, sample isolated in air, fresh; F, sample isolated in air and heat-treated at 500 °C under Ar.

Note that B_2H_6 is a primary product but that it can be catalytically decomposed in the presence of ultrafine particles of metals or metal borides[6,13] to give the expected amounts of H_2.

Thus, in the noncrystalline solid products both Fe_2B and B(s) should be present. After washing of the filtrate with deoxygenated water and acetone, the solid still contained a slight excess of boron. But upon heat treatment, the major nanocrystalline product was only Fe_2B. Thus, we believe most of the excess noncrystalline boron was removed by the water/acetone washing, which would be encouraged by any adventitious oxygen present as well.[14]

To summarize, then, these results do not *prove* that the primary product is noncrystalline Fe_2B (plus a small amount of FeB), but there is no doubt that after heat treatment nanocrystalline Fe_2B is the major product. It would seem reasonable to assume therefore, that the primary product is indeed Fe_2B, rather

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(9) Unsuccessful attempts were made to crystallize both proposed compounds $(L)_nFe(BH_4)_2$ (**1**) and $(L)_nFe(BH_4)_3$ (**4**). In these cases L = diglyme or triphenylphosphine. Although solids were obtained, spectral studies (IR and NMR) have still not allowed characterization. Studies are continuing. Our primary interest here is in the decomposition products.

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(12) The unexpected phenomenon of a vigorous, exothermic oxidation leading to protected α-Fe crystallites has been observed in several other systems, namely Fe−Li bimetallic particles (Glavee, G. N.; Kernizan, C. F.; Klabunde, K. J.; Sorensen, C. M.; Hadjipanayis, G. C. *Chem. Mater.* **1991**, *3*, 967), Fe−Mg bimetallic particles (Klabunde, K. J.; Zhang, D.; Glavee, G. N.; Sorensen, C. M.; Hadjipanayis, G. C. *Chem. Mater.* **1994**, *6*, 784), and Co_2B nanoparticles.[5b] Although such protection from oxidation originally seemed inconceivable to us as well as one of the reviewers, it is indeed what we find experimentally over and over again. This unusual phenomenon is due to the properties of the second component being both a sacrifical agent and, after oxidation, a protective agent, i.e. Li → Li_2O, Mg → MgO, B → B_2O_3.

(13) Reaction of isolated fine powders with $BH_3{\cdot}THF$ in THF in the previously described reaction setup led to the evolution of the expected amounts of H_2.

(14) Although crystalline elemental boron is chemically unreactive, nanoscale particles should be quite reactive with water (and certainly adventitious oxygen). In fact, ΔH_{reacn} for $2B(s) + 6H_2O \rightarrow 2B(OH)_3 + 3H_2$ is −445 kJ.

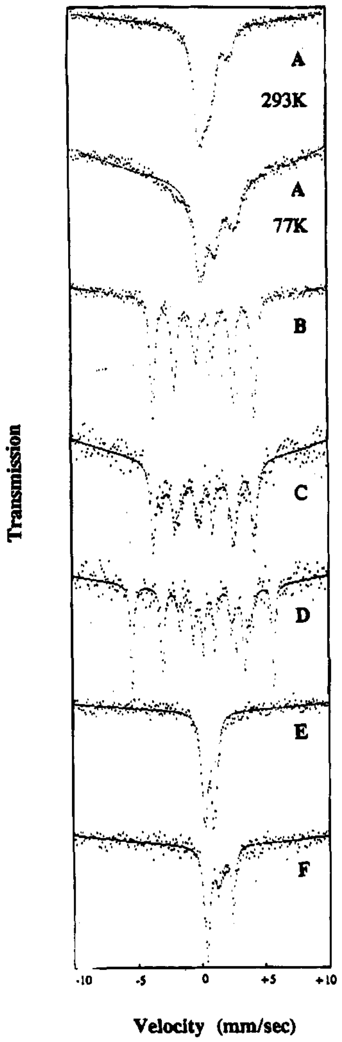

Figure 2. Mossbauer spectra of Fe_2B samples formed in nonaqueous solution: A, fresh sample protected in mineral oil (amorphous Fe_2B); B, sample heat-treated at 550 °C under argon (crystalline Fe_2B); C, crystalline Fe_2B exposed to air at 25 °C (beginning to oxidize); D, sample C heated to 500 °C forming Fe(s) and B_2O_3; E, sample isolated in air, fresh (amorphous); F, sample E heat-treated to 500 °C under Ar (crystalline Fe_3O_4 and FeO).

Scheme 1. Sodium Borohydride with Iron(II) Bromide (Nonaqueous, in Pure Diglyme, L = Diglyme)

$$2(\mathrm{L})_n\mathrm{Fe}^{2+} + 4\mathrm{BH_4}^- \longrightarrow \underset{\mathbf{1}}{2(\mathrm{L})_n\mathrm{Fe(BH_4)_2}}$$

$$2\ \mathbf{1} \xrightarrow{65-70\ ^\circ\mathrm{C}} \underset{\mathbf{2}}{[(\mathrm{L})_n\mathrm{Fe_2}(\mu\text{-}\mathrm{BH_4})]} + {}^3/_2\mathrm{H_2} + {}^3/_2\mathrm{B_2H_6} + n\mathrm{L}$$

$$\mathbf{2} \longrightarrow \mathrm{Fe_2B(s)} + 2\mathrm{H_2} + n\mathrm{L}$$

$${}^3/_2\mathrm{B_2H_6} \xrightarrow[\text{catalysis}]{\mathrm{Fe_2B}} 3\mathrm{B(s)} + {}^9/_2\mathrm{H_2}$$

$$2(\mathrm{L})_n\mathrm{Fe}^{2+} + 4\mathrm{BH_4}^- \longrightarrow \mathrm{Fe_2B} + 3\mathrm{B} + 8\mathrm{H_2} + 2n\mathrm{L}$$

than an intimate mixture of Fe(s) + B(s) that form Fe_2B upon heat treatment. It should also be pointed out, in this regard, that heat treatment as low as 400 °C causes nanocrystals of Fe_2B to form, a temperature that would probably be too low for a solid state Fe(s)/B(s) reaction to occur.

The stability of **1** in diglyme at room temperature allows other chemical decomposition pathways to be investigated.[9] In this regard, we added water in varying amounts. A precipitate formed immediately with vigorous gas evolution at room temperature. The solid product again proved to be Fe_2B, and H_2 evolution was 15–16 mmol (see Table 2). According to Scheme 2 about $12^1/_2$ mmol would be expected. Although the mechanism is not known, it is possible that the addition of water causes the formation of intermediate **2**, which again decomposes to the observed products. This sequence of reactions would be thermodynamically very favorable since 3 mol of $B(OH)_3$ would be formed.

Table 2. Behavior of $(\mathrm{Diglyme})_n\mathrm{Fe(BH_4)_2}$[a] and $(\mathrm{Diglyme})_n\mathrm{Fe(BH_4)_3}$[b] Intermediates in the Presence of H_2O

vol of H_2O, mL	amt of gas evolved, mmol	% yield[e]	reacn time, min
1.0[c]	15.0	100	40
10[c]	15.8	98	12
1.0[d]	21.4	96	90
10[d]	20.9	98	15

[a] A $NaBH_4/FeBr_2$ ratio of 2 was used. Totals of 4.0 mmol of $NaBH_4$ and 2.0 mmol of $FeBr_2$ were used. [b] A $NaBH_4/FeBr_3$ ratio of 3 was used. Totals of 6.0 mmol of $NaBH_4$ and 2.0 mmol of $FeBr_3$ were used. [c] Reaction of $(\mathrm{diglyme})_n\mathrm{Fe(BH_4)_2}$. [d] Reaction of $(\mathrm{diglyme})_n\mathrm{Fe(BH_4)_3}$. [e] Based on major product as Fe_2B for both $(\mathrm{diglyme})_n\mathrm{Fe(BH_4)_2}$ and $(\mathrm{diglyme})_n\mathrm{Fe(BH_4)_3}$.

Scheme 2. $(\mathrm{L})_n\mathrm{Fe(BH_4)_2}$ plus Water

$$2(\mathrm{L})_n\mathrm{Fe(BH_4)_2} + 9\mathrm{H_2O} \longrightarrow \underset{\mathbf{2}}{[(\mathrm{L})_n\mathrm{Fe_2}(\mu\text{-}\mathrm{BH_4})]} + 2^1/_2\mathrm{H_2} + 3\mathrm{B(OH)_3}$$

$$\mathbf{2} \longrightarrow \mathrm{Fe_2B} + 2\mathrm{H_2} + n\mathrm{L}$$

$$2(\mathrm{L})_n\mathrm{Fe(BH_4)_2} + 9\mathrm{H_2O} \longrightarrow \mathrm{Fe_2B(s)} + 12^1/_2\mathrm{H_2} + 3\mathrm{B(OH)_3}$$

The amount of water (1 or 10 mL) made little difference in product amounts. The formation of Fe_2B was quantitative, with no FeB in heat-treated powder. It is interesting that the solid product is the same, Fe_2B, whether completely nonaqueous conditions are used or where *water is added later.* This is particularly intriguing since Fe_2B is not the product under purely aqueous conditions (see later discussion). Because of this fact, we favor a reaction scheme that has a common intermediate such as **2**, even though other reaction schemes for formations of Fe_2B can be envisioned. Further work will be necessary in order to prove if Schemes 1 and 2 are indeed valid, but at this time they form a useful working hypothesis.

b. In Aqueous Media (Pure Water and Water–Diglyme Mixtures). Of course, when $FeBr_2$ was dissolved in water, the $Fe(H_2O)_6^{2+}$ aqua complex was formed. When this solution was mixed rapidly with solid $NaBH_4$, an instantaneous reaction took place with vigorous gas evolution. A gel-like black suspension was formed which upon filtration under inert-atmosphere conditions yielded a powder that according to XRD was mainly α-Fe. Upon heat treatment under Ar, the lines sharpened with α-Fe as the main component but with some Fe_2B also present (Figure 3). Examination by Mossbauer confirmed the presence of α-Fe and Fe_2B (Figure 4). The product mix in this reaction was found to be independent of the BH_4^-/Fe^{2+} ratio. If the black gel-like suspension was isolated under ambient conditions, a yellow-brown air-stable powder was found. XRD analysis indicated that a mixture of iron oxides and borates was present. Thus, oxidation of the Fe/Fe_2B mixture proceeded vigorously to completion. In the Fe^{2+} system, it is clear that there are many differences between aqueous and nonaqueous media. In the diglyme–water mixtures, product compositions change. For example, Figure 5 shows that a small amount of water added to the $FeBr_2$·diglyme solution *prior to* $NaBH_4$–diglyme addition can have a significant effect. A series of XRD spectra, recorded after heat treatment of the product at 400 °C under Ar, showed that mixtures of α-Fe, Fe_2B, and $Fe_{23}B_6$ crystallites were present and that their ratios changed with variation in the amount of water added. The Fe^{2+}/BH_4^- reaction is quite complex and not as clear-cut as the Co^{2+}/BH_4^- system.[5,6] In attempting to rationalize these results in aqueous media, we offer Scheme 3.

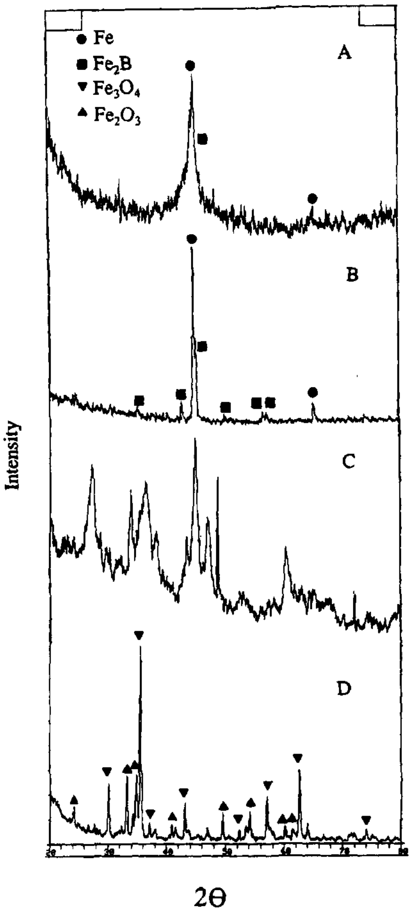

Figure 3. X-ray powder diffraction spectra of samples from the Fe^{2+} and borohydride reaction in aqueous solution; A, fresh sample isolated under inert-conditions; B, sample isolated under inert-conditions and heated at 500 °C under Ar; C, sample isolated under ambient conditions, fresh (a complex mixture of iron oxides and borates); D, sample isolated under ambient conditions and heated at 500 °C under Ar.

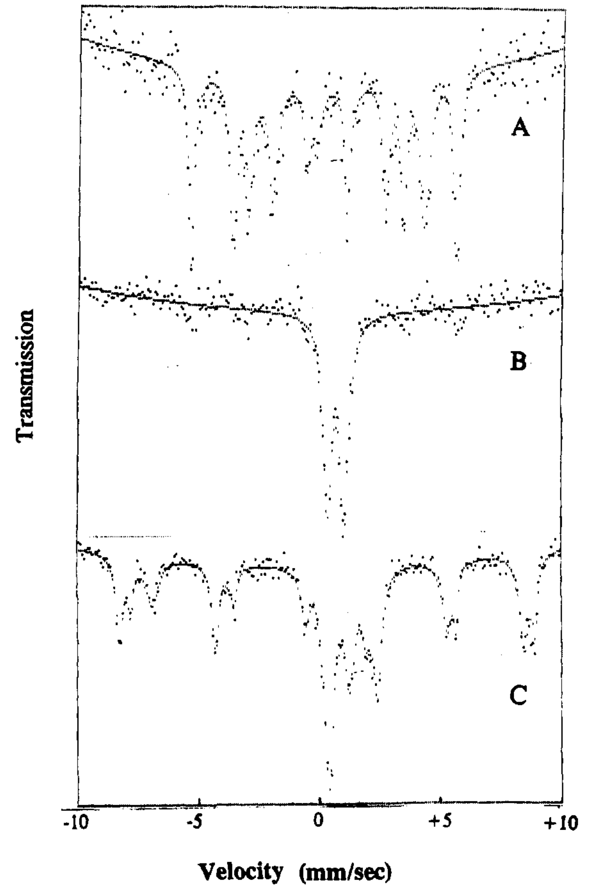

Figure 4. Mossbauer spectra of samples from the Fe^{2+} and borohydride reaction in aqueous solution: A, sample isolated under inert-conditions and heated at 500 °C under Ar (mainly Fe(s) with some Fe_2B); B, sample isolated under ambient conditions, fresh (mainly iron oxides); C, sample isolated under ambient conditions and heated at 500 °C under Ar (mainly iron oxides).

This reaction sequence attempts to account for the products and amounts formed (Table 3). For 2 mmol of Fe^{2+} 14 mmol of H_2 would be expected; about 15.5 was observed. This scheme attempts to show that the initial intermediate (structure 3 in Scheme 3) is apparently very susceptible to attack by a second BH_4^- by electron transfer.[15] Indeed, if 3 has a significant lifetime, it could dimerize, eventually resulting in Fe_2B formation (this is what is proposed in the case of Co_2B formation in aqueous media[5]). In fact, a small amount of Fe_2B was formed along with the major product α-Fe. Thus, the fate of 3, dimerization or reduction, may be the key to understanding the disposition toward metallic iron or iron boride formation.

II. Iron (III). a. In Pure Diglyme and with Subsequent Water Additions. The addition of solutions of $FeBr_3$–diglyme to $NaBH_4$–diglyme produced a bright red color. This red solution was indefinitely stable under inert atmosphere. Upon heating of this solution to 95–100 °C, the color changed from red to orange to yellow to colorless, at which point vigorous gas evolution started and continued over a period of 45 min, and a black powder precipitated. Isolation by filtration and washing with prepurged H_2O and acetone under Ar, followed by vacuum drying, yielded a noncrystalline pyrophoric solid. Elemental analysis of this solid yielded an Fe/B ratio of 0.92. As expected, XRD of the fresh powder gave no distinguishable signal. Mossbauer at 300 and 77 K yielded a broad unresolved single line similar to that reported for noncrystalline FeB films.[16]

Heat treatment under Ar gave nanocrystallites of FeB (Figure 6B). Also, the analysis of this sample yielded an Fe/B ratio of 1.03. The Mossbauer spectrum of the heat-processed sample showed a complicated set of lines suggestive of two overlapping sextets with a hyperfine field of 103 kOe corresponding to the α- and β-phases of FeB.[10] Thus, in the Fe^{3+} system, FeB is the primary product.

Again, as a working hypothesis, we suggest Scheme 4 as a reaction sequence leading to FeB. The formation of a stable $(L)_nFe(BH_4)_3$ (**4**)[9] is a key component. Further work on this interesting complex is needed.

Note that for 2 mmol of Fe^{3+} there should be 12 mmol of H_2 released and that the required ratio of Fe^{3+}/BH_4^- is 2/6 (rather than 2/4 for Fe^{2+}/BH_4^-). If Scheme 4 is correct, this suggests that some of the B_2H_6 formed (Scheme 4) is not completely decomposed. Control experiments have shown that nanoscale particles of α-Fe, FeB, Fe_2B, Co, and Co_2B all can serve as catalysts for the decomposition of B_2H_6 to boron and hydrogen.[6,13] However, residual B_2H_6 was detected by MS in the product mix. So it is possible that the amount of H_2 released by Scheme 4 was not quantitative (see Table 4).

When the fresh noncrystalline FeB solid product was quickly exposed to air, it spontaneously began to smolder with a red-hot heat. XRD and Mossbauer analysis of crystalline products showed the presence of α-Fe, Fe_2B, $Fe_{23}B_6$, and FeB. Presum-

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[15] BH_4^- can readily serve as both a hydride and electron transfer agent in organic and inorganic reactions. See: Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; New York, 1988; pp 190–192.

[16] (a) Blum, N. A.; Moorjani, K.; Poehler, J. O.; Satkiewicz, F. G. *J. Appl. Phys.* **1982**, *53*, 2074. (b) Blum, N. A.; Moorjani, K.; Poehler, J. O.; Satkiewicz, F. G. *J. Appl. Phys.* **1981**, *52*, 1808.

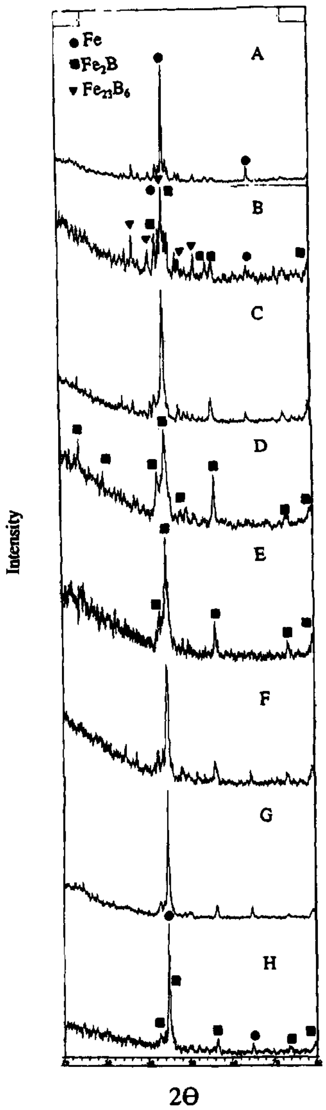
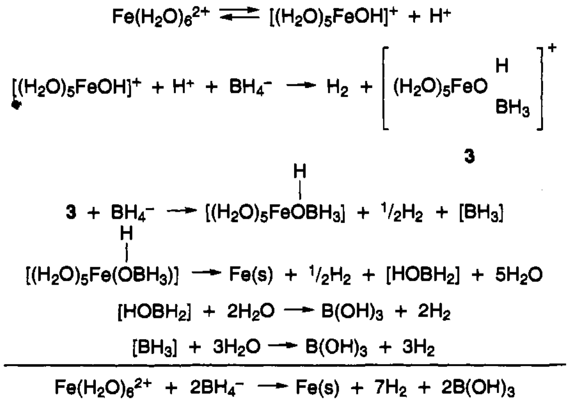


Figure 5. X-ray powder diffraction spectra showing the changes in the product for the nonaqueous $FeBr_2$ and $NaBH_4$ reaction in the presence of H_2O; A, 0.22 mL of H_2O added; B, 1.0 mL of H_2O added; C, 5 mL of H_2O added; D, 10 mL of H_2O added; E, 15 mL of H_2O added; F, 30 mL of H_2O added; G, 50 mL of H_2O added; H, 100 mL of H_2O added. Samples were heat-treated at 400 °C.

Scheme 3. Iron(II) Bromide (Aqueous)



$$Fe(H_2O)_6^{2+} \rightleftharpoons [(H_2O)_5FeOH]^+ + H^+$$

$$[(H_2O)_5FeOH]^+ + H^+ + BH_4^- \longrightarrow H_2 + \left[(H_2O)_5Fe\overset{H}{\underset{BH_3}{O}}\right]^+ \quad \mathbf{3}$$

$$\mathbf{3} + BH_4^- \longrightarrow [(H_2O)_5Fe\overset{H}{O}BH_3] + {}^1/_2H_2 + [BH_3]$$

$$[(H_2O)_5Fe(\overset{H}{O}BH_3)] \longrightarrow Fe(s) + {}^1/_2H_2 + [HOBH_2] + 5H_2O$$

$$[HOBH_2] + 2H_2O \longrightarrow B(OH)_3 + 2H_2$$

$$[BH_3] + 3H_2O \longrightarrow B(OH)_3 + 3H_2$$

$$Fe(H_2O)_6^{2+} + 2BH_4^- \longrightarrow Fe(s) + 7H_2 + 2B(OH)_3$$

Table 3. Aqueous Sodium Borohydride Reduction of Iron(II) and Iron(III) Ions

$NaBH_4$/iron ratio[c]	amt of gas evolved, mmol	pH of filtrate[f]	reacn time, min	% yield[g]
2[a]	15.5	6.8	15	98
3[a]	24.6	9.0	60	94
2[a,d]	15.4	6.2	15	
2[a,e]	15.0	7.9	60	90
3[b]	23.0	5.6	1.5	98
3[b,d]	23.0	7.0	1.5	
3[b,d,e]	22.0	5.2	5.0	

[a] Iron(II) reduction reaction. [b] Iron(III) reduction reaction. [c] All reactions carried out by adding 200 mL of 0.01 M iron salt solution to the appropriate weight of $NaBH_4$ solid. [d] Sample isolated under ambient conditions. [e] The 200 mL iron salt solution was added to the solid $NaBH_4$ in two 100 mL portions, waiting for all gases to be evolved before addition of the second portion. [f] pHs of starting iron(II) and iron(III) solutions were 3.6 and 2.2, respectively. [g] Based on major product as α-Fe, except in cases of isolation under ambient conditions.

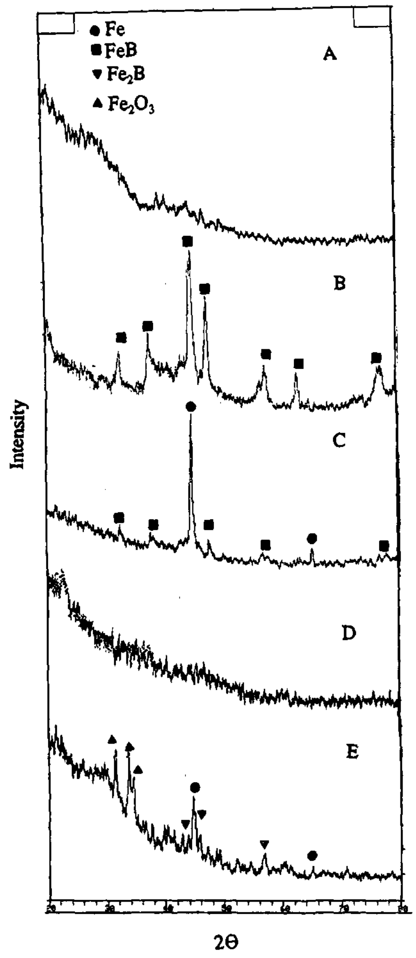


Figure 6. X-ray powder diffraction spectra of FeB samples generated in nonaqueous solution: A, fresh sample protected in mineral oil; B, sample heat-treated at 400 °C under Ar; C, sample exposed to air; D, sample isolated under ambient conditions; E, sample isolated under ambient conditions and heat-treated at 500 °C under Ar.

ably, noncrystalline B_2O_3 was also formed. This example shows again that oxidation reactions can be deceiving and often allow metal and metal boride particles to be formed and protected from further oxidation by a B_2O_3 coating.[5] The formation of B_2O_3 from FeB is extremely exothermic, and so the oxidation-process can generate enough heat to encapsulate nonoxidized materials.

$$2FeB + {}^3/_2O_2 \longrightarrow 2Fe + B_2O_3$$

$$\Delta H^\circ_{reacn} \approx -2400\ kJ$$

In another set of experiments, the workup and isolation of the fresh FeB product were carried out in air. A brown-black air-stable powder was collected. Upon heat treatment under

Scheme 4. Iron(III) Bromide (Nonaqueous, in Pure Diglyme, L = Diglyme)

$$(L)_nFe^{3+} + 3BH_4^- \longrightarrow \underset{\mathbf{4}}{(L)_nFe(BH_4)_3}$$

$$\mathbf{4} \xrightarrow{95-100\ ^\circ C} FeB + 3H_2 + B_2H_6$$

$$B_2H_6 \xrightarrow[\text{catalysis}]{FeB} 2B(s) + 3H_2$$

$$(L)_nFe^{3+} + 3BH_4^- \longrightarrow FeB(s) + 2B + 6H_2 + nL$$

Table 4. Nonaqueous $FeBr_3$ Reactions with $NaBH_4$ under Different Conditions

$NaBH_4/FeBr_3$ ratio	amt of gas evolved, mmol	reacn time, min	% yield[e]
6.0[a]	4.8	180	
3.0[b]	9.3	65	92
2.5	7.9	100	63
2.0	6.1	125	
1.5	4.8	170	23
1.0	3.8	450	
3[c]	9.5	90	113[e]
3[d]	9.2	70	116[e]

[a] A total of 6.0 mmol of $NaBH_4$ was reacted with 1.0 mmol of $FeBr_3$. In all other cases 2.0 mmol of $FeBr_3$ was reacted with the appropriate number of millimoles of $NaBH_4$. [b] Diglyme solution of $FeBr_3$ concentration was 4.0×10^{-2} M. [c] Diglyme solution of $FeBr_3$ concentration was 8.0×10^{-2} M. [d] Diglyme solution of $FeBr_3$ concentration was 5.0×10^{-2} M. [e] Calculation based on the crude product being only FeB, but Scheme 4 shows that free boron was generated and, despite water washing, evidence in the literature, supported by our analysis, shows that some free boron was incorporated into the lattice.

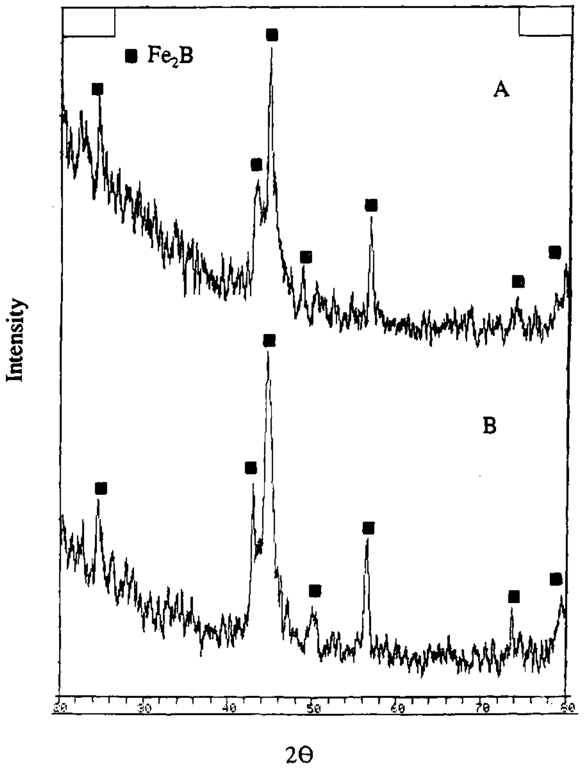


Figure 7. X-ray powder diffraction spectra of powders generated by decomposition of $(diglyme)_nFe(BH_4)_2$ and $(diglyme)_nFe(BH_4)_3$ in water (samples heat-treated at 450 °C): A, sample from Fe^{2+} reaction; B, sample from Fe^{3+} reaction. Both samples are crystalline Fe_2B.

Ar at 550 °C, α-Fe and Fe_2B were detected by XRD. These results amply demonstrate that workup of samples in air can change the product in unanticipated ways. Analysis by XRD and Mossbauer showed only the presence of "reduced" products α-Fe, Fe_2B, and other borides; again B_2O_3 was presumably formed.

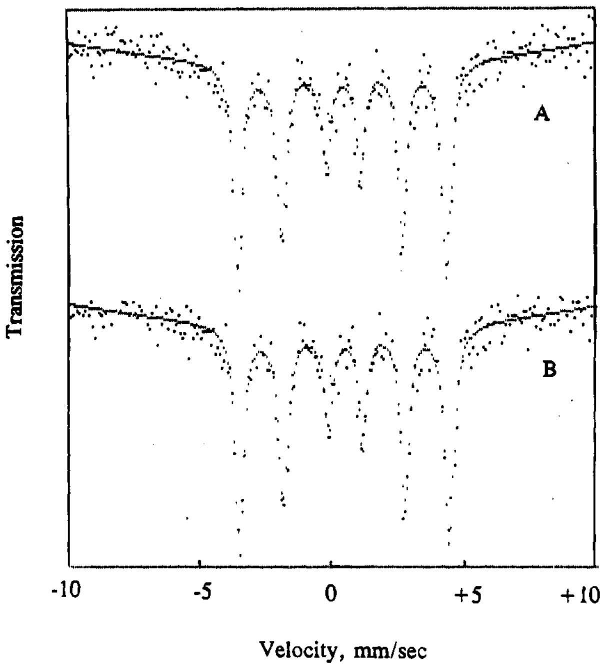


Figure 8. Mossbauer spectra of powders generated by water decomposition of $(diglyme)_nFe(BH_4)_2$ and $(diglyme)_nFe(BH_4)_3$ (samples heat-treated at 450 °C): A, sample from Fe^{2+} reaction; B, sample from Fe^{3+} reaction. Both samples are crystalline Fe_2B.

Scheme 5. $(L)_nFe(BH_4)_3$ plus Water

$$2(L)_nFe(BH_4)_3 + 15H_2O \longrightarrow \underset{\mathbf{2}}{[(L)_nFe_2(\mu\text{-}BH_4)]} + 17^1/_2H_2 + 5B(OH)_3 + nL$$

$$\mathbf{2} \longrightarrow Fe_2B + 2H_2 + nL$$

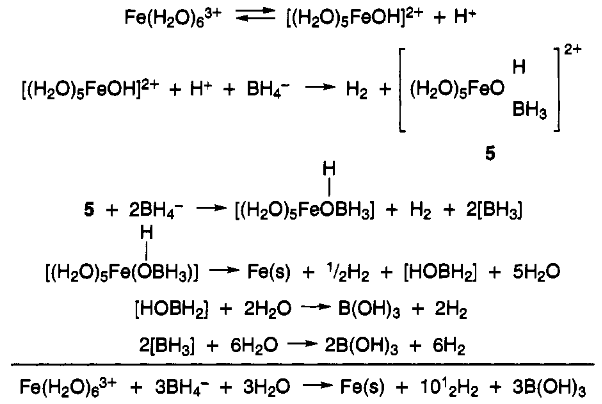
$$2(L)_nFe(BH_4)_3 + 15H_2O \longrightarrow Fe_2B + 19^1/_2H_2 + 5B(OH)_3 + 2nL$$

Addition of small amounts of water to the room-temperature diglyme solution of $(L)_nFe(BH_4)_3$ (**4**) resulted in rapid gas evolution with the precipitation of a black powder. After heat treatment under Ar, XRD and Mossbauer (Figures 7 and 8) spectra confirmed the product to be Fe_2B. Thus, the decomposition of **4** by water drives the reaction to Fe_2B, while thermal decomposition of **4** causes the product to be FeB. Here again, the driving force may be the formation of the μ-bridged dimer **2** plus $B(OH)_3$. A speculative reaction sequence is shown in Scheme 5. A great deal of H_2 should be released, and experimentally this was found to be true (Table 2). The yields of Fe_2B and H_2 were very high, which supports the overall stoichiometry suggested in Scheme 5. Note that a common intermediate $(L)_nFe_2(\mu\text{-}BH_4)$ (**2**) has been proposed in Schemes 2 and 5, resulting from the treatment of the surprisingly stable nonaqueous $(L)_nFe(BH_4)_2$ and $(L)_nFe(BH_4)_3$ species with water. Further investigation is ongoing.

b. In Aqueous Media (Pure Water and Water–Diglyme Mixtures). In pure, deoxygenated water the $Fe(H_2O)_6^{3+}$ aqua complex is formed. Addition of this solution to solid $NaBH_4$ resulted in an instantaneous reaction with gas evolution. The major product was α-Fe. Using rationale similar to that used in Scheme 3, Scheme 6 is proposed. Note the structure **5** is very similar to that of **3** in Scheme 3, except with a higher charge. Rapid attack of **5** by BH_4^- through electron transfer could yield α-Fe as shown. The stoichiometry requires an Fe^{3+}/BH_4^- ratio of 1/3, and for 2 mmol of Fe^{3+}, 21 mmol of H_2 should be released, and the data in Table 3 are in reasonably good agreement.

When water was added to the $FeBr_3$–diglyme solution *prior* to reaction with $NaBH_4$–diglyme, powders that were increasingly rich in α-Fe were produced (Figure 9). It would appear

Scheme 6. Iron(III) Bromide (Aqueous)



$Fe(H_2O)_6^{3+} \rightleftharpoons [(H_2O)_5FeOH]^{2+} + H^+$

$[(H_2O)_5FeOH]^{2+} + H^+ + BH_4^- \rightarrow H_2 + \left[(H_2O)_5Fe\overset{H}{O}BH_3\right]^{2+}$ **5**

$5 + 2BH_4^- \rightarrow [(H_2O)_5Fe\overset{H}{O}BH_3] + H_2 + 2[BH_3]$

$[(H_2O)_5Fe(\overset{H}{O}BH_3)] \rightarrow Fe(s) + \frac{1}{2}H_2 + [HOBH_2] + 5H_2O$

$[HOBH_2] + 2H_2O \rightarrow B(OH)_3 + 2H_2$

$2[BH_3] + 6H_2O \rightarrow 2B(OH)_3 + 6H_2$

$Fe(H_2O)_6^{3+} + 3BH_4^- + 3H_2O \rightarrow Fe(s) + 10\frac{1}{2}H_2 + 3B(OH)_3$

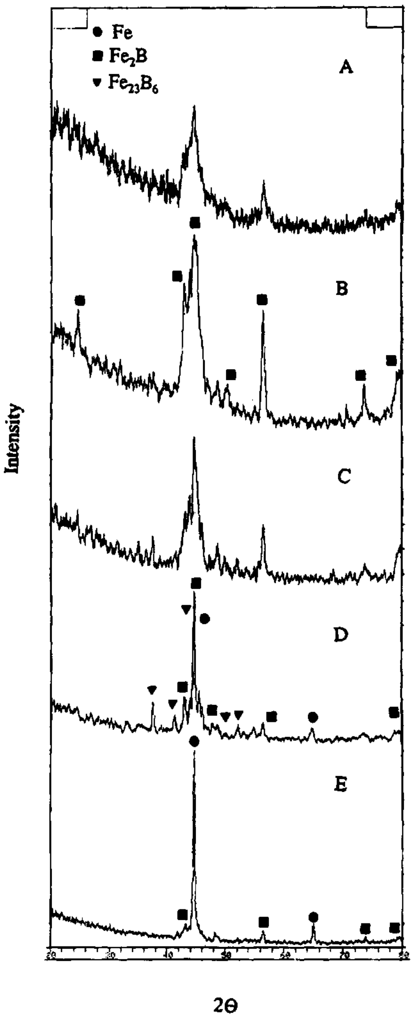


Figure 9. X-ray powder diffraction spectra showing the changes in the product for the nonaqueous $FeBr_3$ and $NaBH_4$ reaction in the presence of H_2O: A, 0.11 mL of H_2O added; B, 0.22 mL of H_2O added; C, 1.0 mL of H_2O added; D, 10.0 mL of H_2O added; E, 50 mL of H_2O added. Samples were heat-treated at 400 °C.

that small amounts of water change the product from FeB to Fe_2B and further increases in water progressively change the product to α-Fe.

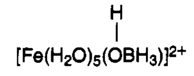
Rationale for this behavior might be given with regard to the ability of aqua complexes **3** or **5** and the cobalt analog[5] to accept electrons from BH_4^-. If we consider the equilibria below, (3)–(5) it would be expected that eq 3 would proceed furthest

$$Fe(H_2O)_6^{3+} \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+} + H^+ \quad (3)$$

$$Fe(H_2O)_6^{2+} \rightleftharpoons [Fe(H_2O)_5(OH)]^{+} + H^+ \quad (4)$$

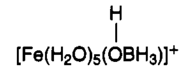
$$Co(H_2O)_6^{2+} \rightleftharpoons [Co(H_2O)_5(OH)]^{+} + H^+ \quad (5)$$

to the right, and a lower pH would result.[17] Reaction with 1 mol of BH_4^- could produce the proposed aqua complexes:



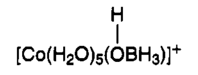
$[Fe(H_2O)_5(\overset{H}{O}BH_3)]^{2+}$

5



$[Fe(H_2O)_5(\overset{H}{O}BH_3)]^{+}$

3



$[Co(H_2O)_5(\overset{H}{O}BH_3)]^{+}$

6

The lifetime of species 3, 5, or 6 in an aqueous solution of $NaBH_4$ would depend on the rate of the next reaction, which could be electron transfer reduction by BH_4^-. However, if this reaction is relatively slow, as in the case of 6,[5] then dimerization could result, eventually leading to reduction and Co_2B (or Fe_2B) formation. However, if electron transfer reduction is relatively fast, then Fe(s) or FeB could be produced. In fact, **5**, because of the higher charge, would be expected to be reduced faster, as proposed in Scheme 6.

A Summary of Reaction Schemes

It is obvious that subtle changes in the tendency of intermediate species to accept electrons, or dimerize and then accept electrons, can change the product from Fe(s), FeB, Fe_2B, etc.

Due to these subtleties, it is understandable that the *method of $Fe^{3+/2+}$ and BH_4^- mixing is important.* We have found that, for aqueous reactions, the most reproducible results are found when the $Fe^{3+/2+}(aq)$ solution is added quickly to solid $NaBH_4$ with rapid stirring under Ar. By using this approach, the side reaction of BH_4^- hydrolysis by water (that is catalyzed by the forming Fe/Fe_2B particles) can be minimized. Aqueous media *reactions are very rapid at room temperatures.*

In the case of nonaqueous chemistry, the solvents must be very pure and dry, and again an inert-atmosphere is necessary. In this chemistry, it is best to mix the $Fe^{3+/2+}$–diglyme solution quickly with the $NaBH_4$–diglyme solution by means of a T-joint.

One of the surprising results of this study is that $(L)_nFe(BH_4)_2$ and $(L)_nFe(BH_4)_3$ coordination compounds were found to be stable in diglyme at room temperature. Only upon heating or water addition does reaction to form $Fe/FeB/Fe_2B$ occur.

This study has attempted to elucidate the chemistry of Fe^{3+} and Fe^{2+} under three sets of conditions: (1) aqueous, (2) nonaqueous, and (3) nonaqueous followed by water addition. The reaction schemes presented fit the stoichiometric data quite well. However, further work on elucidation of the true intermediates is necessary, and is ongoing.

Acknowledgment. The support of the National Science Foundation and the Office of Naval Research is acknowledged with gratitude.

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[17] $[Fe(H_2O)_6]^{3+} \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+} + H^+$, $K = 10^{-3.05}$; $[Fe(H_2O)_5(OH)]^{2+} \rightleftharpoons [Fe(H_2O)_4(OH)_2]^{+} + H^+$, $K = 10^{-6.31}$; $2[Fe(H_2O)_6]^{3+} \rightleftharpoons [Fe(H_2O)_4(OH)_2Fe(H_2O)_4]^{4+} + 2H^+$, $K = 10^{-2.91}$. See: Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry—A Comprehensive Text*, 4th ed.; Wiley: New York, 1980; p 758.