Chemistry of Borohydride Reduction of Iron(II) and Iron(III) Ions in Aqueous and Nonaqueous Media. Formation of Nanocapsule Fe, Fe₃B, and Fe₆B Powders

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The reduction of Fe(II), Fe₃B, and Fe₆B by NaBH₄ 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 upon the solution Fe⁷⁺ yields mainly nanocrystalline, nanoscale Fe₃B, while in dry diglyme the product is nanocrystalline Fe₆B. In the case of Fe(II) the primary product again is Fe₃B, but in diglyme it is Fe₆B. An unexpected finding was that, in dry diglyme, iron borohydride coordination compounds are indefinitely stable and only solid yield Fe(II) (or Fe) upon heating. These compounds are probably [{Fe₆B₄}(μ₄-H)₂] and [{Fe₆B₄}(μ₆-H)] where L = diglyme. Treatment of these complexes in DI water causes the precipitation of Fe₆B.

Introduction

Understanding the chemistry of BN₄⁺ reduction of transition metal ions takes on increasing importance as more and more scientists use this approach to prepare "nanomaterials," a nanocrystalline material,² and catalysts.³ It has become clear that boron is incorporated into the solid products, but the metallic boron ratio varies widely according to literature reports. These 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 Co₃B, CoB₅, metallic Co, and Co₆B₁₈ by the borohydride reduction of cobalt ions in aqueous and nonaqueous media.⁴ As part of our continuing effort to understand and control the formation of nanocrystalline magnetic materials, we have studied the reduction of Fe²⁺ and Fe⁷⁺ in aqueous and nonaqueous media. Herein are reported experiments leading to different nanocrystalline iron compounds.


The tissue was discolored and showed no signs of degeneration.

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Table 1. Nonaqueous Solvent Reactio...
FeBr₂ + 2NaH₂PO₄ → (H₂O)(Fe₂(PO₄)₂)₂ + 2NaBr

This compound is indefinitely stable at room temperature. This is in contrast to an earlier report where Fe(OMe)₃ in ethanol is an unstable colorless solid that decomposes at 10°C.² In our case, only upon heating to 65–70°C did decomposition cease with the vigorous evolution of gas.³ A nanocrystalline product precipitated. After collection of this solid and drying, elemental analysis showed an Fe:Br ratio of slightly less than 1. This anhydrous material showed no XRD peaks, as expected. The microanalyzer spectra showed two overlapping broad peaks with isomer shifts of 0.20 and 0.94 mm/s with quadrupole splittings of 0.13 and 2.16 mm/s, respectively. These peaks were not well resolved even at 77 K, but these results are similar to those observed for other iron boride nanocrystalline materials.⁴

Heat treatment of the sample yielded Fe₇B₃ nanocrystallites along with a small amount of Fe₃C, according to XRD and Microanalyzer (Figures 1 and 2). The Mössbauer showed a hyperfine field of 257 kOe and an isomer shift of 0.08 mm/s, values that are consistent with those reported for Fe₇B₃. Exposure of the fresh nanocrystalline powder to air resulted in its turning red hot and slowly oxidizing. X-ray powder diffraction analysis indicated that this air-exposed sample was composed to boron exists, iron oxides, and α-Fe, probably as shown by eq. 2. Evidence was also found for the presence of small amounts of nanocrystalline Fe₇B₃ (Figures 1C and Figure 2D).

Fe₇B₃ + 1.5O₂ → 7FeO + 1.5B₂O₃

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. Mössbauer and X-ray powder diffraction analysis of this powder are given by Figure 3A of Figure 3E and Figure 3F and indicates that mainly iron oxides were present. This shows that slow, continuous exposure to oxygen did cause complete oxidation (Fe₇B₃ + O₂ → 7FeO + 1.5B₂O₃).[2]

The formation of 3 and its thermal decomposition to Fe₇B₃ are independent of both the concentration of the reagents and the Fe₇B₃/Fe₇O₃ ratio (Table 1). The yields of raw materials were quite high, and the amount of H₂ released was very close to that predicted by reaction 1.

(4) Unsuccessful attempts were made to crystallize both pyrolyzed compounds [Li₂Fe(P₂O₇)₄] and [Zn₂Fe(P₂O₇)₄]. In these cases, 1-3 phase as fleeting intermediates. Although solid states reactions,
(5) 2H₂O + 2FeBr₂ → Fe₂Br₄ + 4H₂O

Studies are continuing. Our primary interest here is in the decompomposition process.

(9) The unreacted component of a ν₉₅₀⁺ resonance is usually observed in spectra of nanocrystalline Fe₇B₃ (Glave et al., 1991). This component is due to the presence of iron hexabromide in the sample at low temperature. The characteristic peaks of the hexabromide component are reappear at t = 450°C, which is expected to be the transition temperature for this material. The transition temperature for the hexabromide component is 180°C, which is the expected transition temperature for this material.
(10) Reaction of iron with liquids of FeBr₂/FeBr₃ is probably the major reaction leading to the evolution of the iron...
Figure 2. Most transient species of Fe(II) bromide (Nonaqueous, in Pure Diglyme, L = Diglyme),

\[2\text{FeBr}_2 + 4\text{Br}^- \rightarrow 2\text{Fe} + 6\text{Br}_2\]

than an intimate mixture of Fe(II) and Br(II) from FeBr₂ upon heat treatment. It should also be pointed out, in this regard, that heat treatment as low as 400 °C causes no ionic crystals of FeBr₂ to form, a temperature that would probably be too low for a solid state Fe(II)/Br⁻ reaction to occur. The stability of Fe in diglyme at room temperature allows other chemical decomposition pathways to be investigated. 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 FeBr₂, and H₂ evolution was 15–16 mmol (see Table 2). According to

Table 2. Behavior of Diglyme/FeBr₂/Br⁻ and

\[\text{Diglyme}/\text{FeBr}_2/\text{Br}^- \text{Intermediates in the Presence of H}_2\text{O}\]

<table>
<thead>
<tr>
<th>vol of H₂O mL</th>
<th>weight of gas evolved, mmol</th>
<th>% yield</th>
<th>time, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>15.0</td>
<td>96</td>
<td>10</td>
</tr>
<tr>
<td>100</td>
<td>14.4</td>
<td>95</td>
<td>10</td>
</tr>
<tr>
<td>1000</td>
<td>14.1</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>10000</td>
<td>14.0</td>
<td>15</td>
<td>10</td>
</tr>
</tbody>
</table>

* A Nonaqueous, rate of 2 was used. \(\text{Diglyme}/\text{FeBr}_2/\text{Br}^-\) rate of 2 was used. Total of 6.0 mL of Nonaqueous, and 2.0 mL of FeBr₂ were used. A Nonaqueous, rate of 2 was used. \(\text{Diglyme}/\text{FeBr}_2/\text{Br}^-\) rate of 2 was used. Total of 6.0 mL of Nonaqueous, and 2.0 mL of FeBr₂ were used. A Nonaqueous, rate of 2 was used. Total of 6.0 mL of Nonaqueous, and 2.0 mL of FeBr₂ were used.

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

\[2\text{FeBr}_2 + 4\text{Br}^- \rightarrow 2\text{Fe} + 6\text{Br}_2\]

Scheme 2 (1/2L/FeBr₂ plus Water)

\[2\text{FeBr}_2 + 4\text{Br}^- + \text{H}_2\text{O} \rightarrow 2\text{FeBr}_3 + 3\text{Br}_2 + \text{H}_2\]

The amount of water (1 or 10 mL) made little difference in product amounts. The formation of FeBr₃ was quantitative, with no FeBr₂ in heat-treated powder. It is interesting that the solid product is the same, FeBr₃, whether completely aqueous conditions are used or where water is added later. This is particularly surprising since FeBr₃ 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 FeBr₃ 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 FeBr₂ was dissolved in water, the FeBr₂/Br⁻ aqueous complex was formed. When this solution was mixed rapidly with solid NaBH₄, 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 FeBr₂ also present (Figure 3). Examination by transmission electron microscopy confirmed the presence of α-Fe and FeBr₂ (Figure 4). The product mix in this reaction was found to be independent of the BH₄⁻/Fe²⁺ ratio. If the black gel-like suspension was isolated under ambient conditions, a yellow-brown emulsion powder was found. XRD analysis indicated that a mixture of iron (II) hydroxide was present. Thus, oxidation of the FeBr₂ mixture proceeded vigorously to completion. In the Fe²⁺/water mixture, product compositions change. For example, Figure 1 shows that a small amount of water added to the FeBr₂/diglyme solution prior to NaBH₄/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, FeBr₂, and FeBr₃, and NaBH₄ crystals were present and that there are changes in the amount of water added. The Fe³⁺/BH₄⁻ reaction is quite complex and not as clear-cut as the Co³⁺/BH₄⁻ system. In attempting to rationalize these results in aqueous media, we offer Scheme 3.
This reaction sequence attempts to account for the products and amounts formed (Table 3). For 3 mmol of PbO, 14 mmol of H₂ 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 H₂, by electron transfer. Indeed, if 3 has a significant lifetime, it could dimerize, eventually resulting in Pb₃O₇ formation (this is what is proposed in the case of Co₃O₅ formation in aqueous media). In fact, a small amount of Pb₃O₇ was formed along with the major product of Pb₂O₃. Thus, the fate of 3, dimerization or reduction, may be the key to understanding the disposition towards metallic iron or iron oxide formation.

IL, Et₄N(O)₂A, a. In Pure Dihydrate and with Subsequent Water Additions. The addition of solutions of Fe(III)–dihydrate or Na₂H₂O₂–dihydrate produced a bright red color. This red solution was indefinitely stable under inert atmosphere. Upon heating of this solution to 95–110 °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 propylene glycol and acetone under Ar, followed by vacuum drying, yielded a noncrystalline pyrogenic solid. Elemental analysis of this solid yielded a FeO stoichiometry of 0.92. As expected, XRD of the fresh powder gave no distinguishable signal. Monobeur at 300 and 77 K yielded a broad unresolved

Figure 5. X-ray powder diffraction spectra showing the changes in the product for the nonaqueous Fe(III) and NaHClO₄ reaction in the presence of H₂O: A, 0.22 ml of H₂O added; B, 1.0 ml of H₂O added; C, 5.0 ml of H₂O added; D, 10 ml of H₂O added; E, 15 ml of H₂O added; F, 20 ml of H₂O added; G, 30 ml of H₂O added; H, 100 ml of H₂O added. Samples were heat-treated at 400°C.

Table 3. Aqueous Sodium Bromide Reduction of Iron(III) and Iron(II) ions

<table>
<thead>
<tr>
<th>NaHClO₄/iron ratio</th>
<th>onset of gas evolution, min</th>
<th>pH of filtrate</th>
<th>traces, min</th>
<th>% yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15.5</td>
<td>6.8</td>
<td>15</td>
<td>96</td>
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<tr>
<td>2</td>
<td>24.6</td>
<td>9.0</td>
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<td>94</td>
</tr>
<tr>
<td>3</td>
<td>15.4</td>
<td>6.2</td>
<td>15</td>
<td>95</td>
</tr>
<tr>
<td>3</td>
<td>15.0</td>
<td>7.9</td>
<td>60</td>
<td>90</td>
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<td>3</td>
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<tr>
<td>3</td>
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<td>7.0</td>
<td>1.3</td>
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</tr>
<tr>
<td>3</td>
<td>23.0</td>
<td>7.0</td>
<td>1.3</td>
<td>98</td>
</tr>
</tbody>
</table>

Iron(III) reduction reaction. 1 Iron(II) reduction reaction. 1 All reactions carried out by adding 100 ml of 0.1 M iron salt solution to the appropriate weight of NaHClO₄ solid. 2 Sample isolated under ambient conditions. 3 The 200 ml iron salt solution was added to the solid NaHClO₄ in two 100 ml portions, mixing for all gases to be evolved before washing of the second portion. 4 Phs of starting iron(III) and iron(II) complexes were 3.6 and 2.2, respectively. 5 Based on major product at Fe/P, except in case of isolation under ambient conditions.

Scheme 4. Iron(II) Bromide (Aquaposs)

FeBr₂(aq) + 2H₂O(aq) → FeBr₂(OH)₂(aq) + 2H₃O⁺

H₂O(aq) + H₃O⁺ → H₂O(l) + H⁺ + 2H₂O(l)

H₂O(aq) + H⁺ → H₂O(l) + H⁺ + 2H₂O(l)

FeBr₂(OH)₂(aq) + 2H₂O(aq) → Fe(aq) + 3H₂O(l) + 2Br⁻

In another set of experiments, the workup and isolation of the fresh Fe(II) product was carried out as above. A brown-black air-stable powder was collected. Upon heat treatment under...
Scheme 4. 

\[ \text{Fe}^{2+} + 2 \text{ClO}_3^- \rightarrow \text{FeCl}_3 + 3 \text{Cl}_2 \]  

\[ \text{Fe}^{2+} + 2 \text{ClO}_3^- \rightarrow \text{FeCl}_3 + 2 \text{Cl}_2 \]

Table 4. Nonaqueous Felli Reactions with NaNH₄ under Different Conditions

<table>
<thead>
<tr>
<th>NaNH₄/Fel ratio</th>
<th>out of gas evolved, mmHg</th>
<th>mean time, min</th>
<th>yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>6:1</td>
<td>66</td>
<td>92</td>
<td></td>
</tr>
<tr>
<td>10:1</td>
<td>100</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td>2:1</td>
<td>125</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>1:1</td>
<td>490</td>
<td>113</td>
<td></td>
</tr>
<tr>
<td>5:1</td>
<td>70</td>
<td>113</td>
<td></td>
</tr>
</tbody>
</table>

* A total of 6.0 mmol of NaNH₄ was reacted with 1.0 mmol of Fel. In all other cases 2.0 mmol of Fel was reacted with the appropriate number of millimoles of NaNH₄. * Diploidal solutions of FeCl₃ concentration was 0.0. 2.0 M. * Diploidal solutions of FeCl₃ concentration was 0.0. 2.0 M.

Figure 7. X-ray powder diffraction patterns of powders prepared by decomposition of (dimethyl)Fe(II)(H₂O)₃ and (dimethyl)Fe(II)(H₂O)₃ in water (samples A and C) at 650 °C. A. Sample from FeCl₃ reaction B. Sample from FeCl₃ reaction C. Samples are crystalline FeCl₃.

Additional information on amounts of water to the room-temperature dimerization reduction of (FeCl₃)₃ in rapid gas evolution with the precipitation of a black powder. After heat treatment under Ar, O₂, and N₂ ambient (Figures 7 and B) spectra confirmed as product to be FeCl₃. Thus, the decomposition of 4 was driven by the reaction of FeCl₃ during thermal decomposition of 4 to identify the product to be FeCl₃. Here again, the driving force may be the formation of the p-bridging-iron 2 plus B(FeCl₃). A speculative reaction sequence is shown in Scheme 5. A great deal of FeCl₃ should be released, and experimentally this was found to be true (Table 2). The yields of FeCl₃ and H₂O were very high, which suggests the overall stoichiometry suggested in Scheme 5. Note that a common intermediate (FeCl₃)₃ 2 (D) has been proposed in Scheme 2 and 3. However, the reaction of FeCl₃ and H₂O was not pursued. Further investigations is ongoing.

Figure 8. Houben spectra of powders prepared by water decomposition of (dimethyl)Fe(II)(H₂O)₃ and (dimethyl)Fe(II)(H₂O)₃ in the presence of FeCl₃ at 650 °C. A, sample from FeCl₃ reaction. B, sample from FeCl₃ reaction. Both samples are crystalline FeCl₃.

Scheme 5. (FeCl₃)₃ plus Water

\[ 3\text{FeCl}_3 + 3\text{H}_2\text{O} \rightarrow 3\text{FeCl}_3 \cdot 3\text{H}_2\text{O} + 3\text{HCl} \]

\[ 3\text{FeCl}_3 \cdot 3\text{H}_2\text{O} \rightarrow 3\text{FeCl}_3 + 3\text{H}_2\text{O} \]

Additional information on amounts of water to the room-temperature dimerization reduction of (FeCl₃)₃ in rapid gas evolution with the precipitation of a black powder. After heat treatment under Ar, O₂, and N₂ ambient (Figures 7 and B) spectra confirmed as product to be FeCl₃. Thus, the decomposition of 4 was driven by the reaction of FeCl₃ during thermal decomposition of 4 to identify the product to be FeCl₃. Here again, the driving force may be the formation of the p-bridging-iron 2 plus B(FeCl₃). A speculative reaction sequence is shown in Scheme 5. A great deal of FeCl₃ should be released, and experimentally this was found to be true (Table 2). The yields of FeCl₃ and H₂O were very high, which suggests the overall stoichiometry suggested in Scheme 5. Note that a common intermediate (FeCl₃)₃ 2 (D) has been proposed in Scheme 2 and 3. However, the reaction of FeCl₃ and H₂O was not pursued. Further investigations is ongoing.
Scheme 6. Iron(III) Bromide (Aqueous)

\[
\text{FeBr}_3^{2+} + \frac{1}{2} \text{H}_2 \text{O} \rightarrow \text{Fe}^{3+} + 3 \text{Br}^- + \frac{1}{2} \text{O}_2
\]

\[
\text{FeBr}_3^{2+} + \frac{1}{2} \text{H}_2 \text{O} \rightarrow \text{Fe}^{3+} + 3 \text{Br}^- + \frac{1}{2} \text{O}_2
\]

The lifetime of species 3, 5, or 6 in an aqueous solution of NaHBrO would depend on the rate of the next reaction, which could be electron transfer reduction by Fe(II). However, if this reaction is relatively slow, as in the case of 6, then disproportionation could result, eventually leading to reduction and Cu(II) or Fe(II) formation. However, if electron transfer reduction is relatively fast, then Fe(II) or Fe(II) 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 chemistry of intermediates species to accept electrons, or disperse and then accept electrons, can change the product from Fe(II), Fe(II), Fe(II), etc.

Due to these subtleties, it is understandable that the method of Fe(II) and Br reduction is important. We have found that, for aqueous reactions, the most reproducible results are found when Fe(II) is added to solid NaHBrO, with rapid stirring under N2. By using this approach, the side reaction of Br2 hydrolysis by water (that is catalyzed by the forming Fe(II)Br2 particles) can be minimized. Aqueous media reactions are very rapid at room temperature.

In the case of heterogeneous catalysts, 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(II)-diglyme solution with the NaHBrO-diglyme solution in sealed T-joint.

One of the surprising results of this study is the fact that Fe(II)Br2 and NaHBrO coordination compounds were found to be stable in diglyme at room temperature. Only upon heating or water addition does reaction to form Fe(III)Br2 occur.

This study has attempted to elucidate the chemistry of Fe(II) and Fe(III) under three sets of conditions: (1) aqueous, (2) heterogeneous, and (3) heterogeneous followed by water addition. The reaction schemes presented fit the dihalogen chemistry well. However, further work on elucidation of the true intermediates is necessary, and is ongoing.

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