

An Improved Synthesis of Borazine with Aluminum Chloride as Catalyst

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Keywords: Boron / Heterocycles / Aluminum / Synthetic methods / Nitrides

Borazine is an excellent precursor for boron nitride. However the existing synthetic methods for the preparation of borazine have drawbacks such as relatively high reaction temperatures, side reactions, long reaction times, and low yields. An improved synthesis procedure was disclosed, which involved the use of aluminum chloride as a catalyst in the reaction of sodium borohydride with ammonium sulfate. The aluminum chloride catalyst brought the reaction temperature down

from 120–140 °C to 45 °C. Improved yields of borazine were obtained in comparison to the reaction without a catalyst. In addition, the reaction process was investigated in detail by ¹¹B NMR spectroscopy and Fourier transform infrared spectroscopy (FTIR). It was found that aluminum borohydride formed in very small quantity when aluminum chloride was introduced, which plays an important role in the reaction.

Introduction

Boron nitride (BN) has a number of unique properties, including high temperature stability and strength, excellent chemical, thermal shock, corrosion, and oxidation resistances, low dielectric constant and loss, high electrical resistivity, and large thermal conductivity, leading to a lot of potential applications as high-temperature structural and functional materials.^[1,2] Although BN is easy to obtain as a powder,^[3] it is not feasible to be prepared in the form of fibers, coatings, and complicated body shapes. Precursor-derived ceramic routes provide an approach to this issue.^[4–6] Borazine is proved to be an excellent precursor for boron nitride.^[7–9]

Borazine was originally discovered by Alfred Stock in 1926.^[10] Later, several other procedures for the synthesis of borazine were reported.^[11–13] However, practical applications of borazine continue to be held back by the absence of efficient, economical synthesis routes. Thomas Wideman et al. reported a convenient procedure for the laboratory preparation of borazine by treating ammonium sulfate with sodium borohydride in tetraglyme at 120–140 °C.^[14] Borazine readily undergoes dehydropolymerization above 70 °C.^[7] Therefore, the reaction temperature of 120–140 °C was so high that the formed borazine dehydropolymerized during the reaction. Consequently, it was desirable to find a suitable catalyst for the reaction to reduce the reaction temperature and to bring the reaction to completion in a shorter period of time. In this paper we describe the use of aluminum chloride as a catalyst in the reaction of ammo-

num sulfate with sodium borohydride for preparing borazine. The reaction process was investigated by ¹¹B NMR and FTIR spectroscopy.

Results and Discussion

Reaction of Sodium Borohydride and Ammonium Sulfate without Catalyst

Repeating experiments without catalyst at 140 °C gave about 30% yield of borazine and took about 6 h for completion. In addition, the reaction mixture became more and more viscous as the reaction proceeded. This may be the result of thermally induced dehydropolymerization of borazine, which was confirmed by ¹¹B NMR spectroscopic analysis of the reaction mixture after completion (Figure 1). The spectrum showed a very broad featureless resonance around 30 ppm.^[14] Increased viscosity of the reaction mixture also restrained efficient contact between (NH₄)₂SO₄ powder and the NaBH₄ solution. Accordingly, the reaction rate was reduced, which further promoted the polymerization of borazine.

Hence, it was desired to lower the reaction temperature to avoid polymerization of borazine. In another experiment, reaction of NaBH₄ with (NH₄)₂SO₄ was performed at 45 °C. The mixture continued to evolve gases slowly even after 40 h, indicating an incomplete reaction. Figure 2 shows the ¹¹B NMR spectrum of the reaction mixture after 40 h. Only weak resonances of borazine [δ = 30.2 ppm (d, $J_{B,H}$ = 139.4 Hz)] was observed.^[15] The disappearance of the peaks of NaBH₄ indicated that NaBH₄ was consumed completely.^[16] The strong peaks were identified as ammonia–borane [δ = –23.8 ppm (q, $J_{B,H}$ = 91 Hz)] and (μ -NH₂)-B₂H₅ (δ = –26.7 ppm).^[17,18] The weak resonances (δ = –11.9 ppm) were attributed to cyclotriborazane [H₂B–

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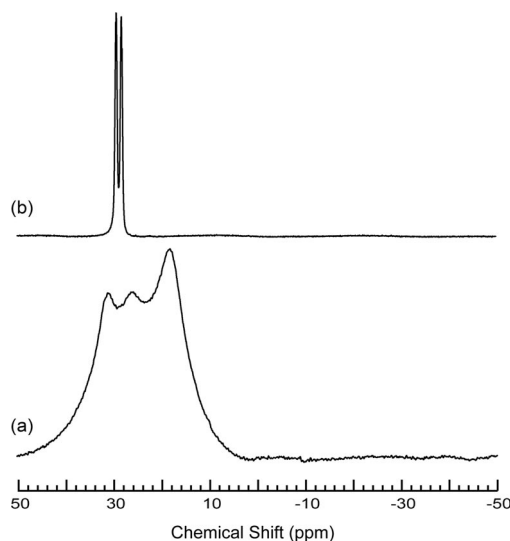


Figure 1. ^{11}B NMR spectra of the reaction mixture of NaBH_4 and $(\text{NH}_4)_2\text{SO}_4$ at 140°C after completion of the reaction (a) and purified borazine (b). The spectra indicate that borazine formed in the reaction had undergone polymerization.

$\text{NH}_2)_3$ which is an intermediate during the formation of borazine.^[19,20] Thus, it was shown that ammonia–borane rather than borazine was the predominant product when NaBH_4 was treated with $(\text{NH}_4)_2\text{SO}_4$ at temperatures as low as 45°C .

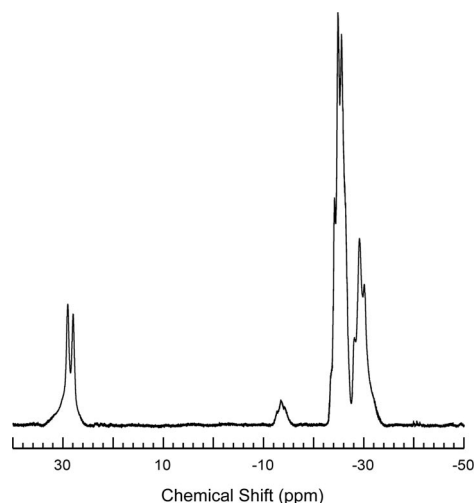


Figure 2. ^{11}B NMR spectrum of the reaction mixture of NaBH_4 and $(\text{NH}_4)_2\text{SO}_4$ at 45°C after 40 h. Byproducts ammonia–borane ($\delta = -23.8$ ppm), cyclotriborazane $[\text{H}_2\text{B}-\text{NH}_2]_3$ ($\delta = -11.9$ ppm), and $(\mu\text{-NH}_2)\text{B}_2\text{H}_5$ ($\delta = -26.7$ ppm) were observed in predominant quantities.

Reaction of Sodium Borohydride with Ammonium Sulfate Catalyzed by Aluminum Chloride

The reaction of NaBH_4 with $(\text{NH}_4)_2\text{SO}_4$ was found to proceed vigorously at low temperature (45°C) when the AlCl_3 catalyst was introduced. It took 3 h to complete the reaction at 45°C with the catalyst. Borazine was obtained

in 67% yield after purification, which is a substantial improvement over the yield obtained when the reaction was performed without a catalyst at 140°C (30% yield). The reaction catalyzed by AlCl_3 was investigated by ^{11}B NMR and FTIR spectroscopy.

Figure 3 shows the ^{11}B NMR spectra of the reaction mixture before the introduction of NaBH_4 solution and after. The quintet at -39.3 ppm ($J = 80.7$ Hz) suggests the presence of NaBH_4 . As the reaction proceeded, the peaks of NaBH_4 decreased. After 1 h a strong doublet at $\delta = 30.2$ ppm ($J_{\text{B,H}} = 139.4$ Hz) of borazine was observed and weak resonances at $\delta = -23.7$ ppm appeared. These resonances resulted from ammonia–borane, which is the intermediate during the formation of borazine.^[19]

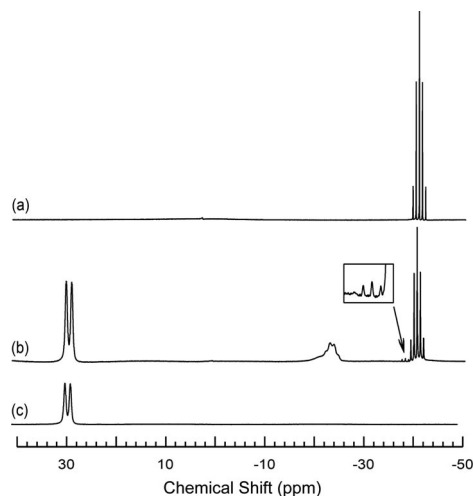
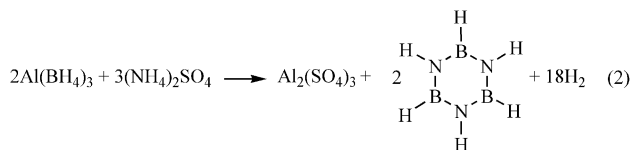
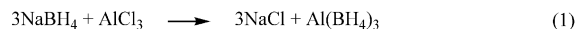


Figure 3. ^{11}B NMR spectra of the reaction mixture with AlCl_3 (1 mol-%) at 45°C : (a) after 0 h, (b) after 1 h; the NaBH_4 peaks decreased and the borazine peaks appeared; weak peaks of $\text{Al}(\text{BH}_4)_3$ were also observed; (c) after 3 h; there is only a weak peak of borazine left in the residual, indicating completion of the reaction and no polymerization of borazine.

The weak resonances at $\delta = -36.9$ ppm could be assigned to $\text{Al}(\text{BH}_4)_3$.^[21,22] A catalytic mechanism of AlCl_3 for the reaction of NaBH_4 with $(\text{NH}_4)_2\text{SO}_4$ was proposed on the basis of the observed presence of $\text{Al}(\text{BH}_4)_3$ (Scheme 1).



Scheme 1.

Early experiments showed that $\text{Al}(\text{BH}_4)_3$ was formed in trace amounts when the NaBH_4 and AlCl_3 solutions in tetraglyme were mixed together in a mol ratio of $3\text{NaBH}_4/\text{AlCl}_3$. When the NaBH_4 and $\text{Al}_2(\text{SO}_4)_3$ solutions in tetraglyme were mixed together in a mol ratio of $6\text{NaBH}_4/\text{Al}_2(\text{SO}_4)_3$, $\text{Al}(\text{BH}_4)_3$ was also formed in trace amounts. However the trace amounts of $\text{Al}(\text{BH}_4)_3$ could be expected

to play an important role in the reaction of NaBH_4 with $(\text{NH}_4)_2\text{SO}_4$. The reactivity and reducibility of metal borohydrides increases as the electronegativity of the metal decreases.^[23] It was experimentally found that both LiBH_4 and NaBH_4 could react with $(\text{NH}_4)_2\text{SO}_4$ to produce borazine,^[11–14] whereas KBH_4 does not react with $(\text{NH}_4)_2\text{SO}_4$ even at temperatures as high as 160 °C. This fact will be detailed in a later paper. The reducibility and reactivity of $\text{Al}(\text{BH}_4)_3$ was much stronger than that of NaBH_4 . As AlCl_3 was introduced, it first reacted with NaBH_4 to form $\text{Al}(\text{BH}_4)_3$.^[24] $\text{Al}(\text{BH}_4)_3$ reacted with $(\text{NH}_4)_2\text{SO}_4$ more readily and rapidly than NaBH_4 . Consequently, when AlCl_3 was introduced, the reaction proceeded vigorously even at 45 °C. The reaction with the AlCl_3 catalyst went to completion in a short time at low temperature (45 °C), and in addition, borazine did not dehydropolymerize during the reaction period as shown by the ^{11}B NMR spectra. After completion of the reaction, there was only a weak resonance of borazine left in the spectrum of the residue (Figure 3c).

It could be predicted that the reaction of NaBH_4 with $(\text{NH}_4)_2\text{SO}_4$ would also be catalyzed by $\text{Al}_2(\text{SO}_4)_3$. Further experiments showed that the reaction of NaBH_4 with $(\text{NH}_4)_2\text{SO}_4$ can be catalyzed by $\text{Al}_2(\text{SO}_4)_3$. The reaction at 45 °C with catalyst $\text{Al}_2(\text{SO}_4)_3$ gave 48% yield of borazine, which is lower than that for the AlCl_3 catalyst, but it is an improvement over the reaction without a catalyst at 140 °C. The reaction of NaBH_4 with $(\text{NH}_4)_2\text{SO}_4$ could be catalyzed by AlCl_3 or $\text{Al}_2(\text{SO}_4)_3$. However, the understanding of the mechanism of the catalyzed reaction is still immature and needs to be further investigated.

Figure 4 shows the FTIR spectra of the reaction mixture before the introduction of the NaBH_4 solution and after. The absorption peaks at 2875 (–CH₃– and –CH₂–) and 1110 cm^{–1} (C–O–C) are typical of tetraglyme. The absorption peaks of borazine were observed at 3475 (N–H stretch), 2525 (B–H stretch), and 1464/916/718 cm^{–1} (B–N six-membered rings).^[9] After 1 h, the absorption peaks of borazine at 3475 (N–H) and 2525 cm^{–1} (B–H) were ob-

served. The absorption peaks at 2281 and 2218 cm^{–1} of NaBH_4 decreased as the reaction proceeded.^[25] After 3 h, the absorption peaks of NaBH_4 disappeared, which indicated completion of the reaction. The absorption peaks of $\text{Al}(\text{BH}_4)_3$ overlaid those of tetraglyme and borazine. In addition, the amount of AlCl_3 introduced was small, and thus the absorptions of $\text{Al}(\text{BH}_4)_3$ could not be observed.

Conclusions

In conclusion, an improved procedure for preparation of borazine in large quantities with AlCl_3 as the catalyst has been established. With the addition of AlCl_3 (1 mol-%), the temperature for the reaction of NaBH_4 with $(\text{NH}_4)_2\text{SO}_4$ for preparing borazine was lowered from 140 to 45 °C, and an improved yield was obtained, which is in opposition to the reaction performed without a catalyst. These results can promote the applications of borazine, especially as a precursor for boron nitride. Aluminum borohydride was spectroscopically detected in minor quantities in the reaction mixtures catalyzed by AlCl_3 . It can be expected to play an important role in the process of borazine formation. Future work will involve further mechanistic investigations of the catalyzed reaction of NaBH_4 with $(\text{NH}_4)_2\text{SO}_4$.

Experimental Section

Preparation of Borazine Catalyzed by Aluminum Chloride: Powdered ammonium sulfate (1000 g, 7.6 mol) and aluminum chloride (14 g, 0.1 mol) were added to a 10-L, three-necked, round-bottom flask fitted with a thermometer, a reflux condenser, and an additional funnel filled with sodium borohydride (400 g, 10.6 mol) dissolved in tetraglyme (2000 mL). The exit of the condenser was connected through a series of liquid-nitrogen traps. The system was evacuated and filled with nitrogen gas several times. The solution of sodium borohydride in tetraglyme was added to the flask, and the contents were magnetically stirred at 45 °C for 3 h, until the reaction was complete (as indicated by ^{11}B NMR spectroscopy). Borazine and other volatile condensable compounds were trapped in the liquid-nitrogen traps. Syringes were used to sample the reaction mixture for ^{11}B NMR and FTIR spectroscopy during the reaction. The liquid-nitrogen traps were connected to a standard vacuum distillation line for purification after the reaction was complete. Borazine (190 g, 67% yield) was obtained after purification.

Blank Reaction: The procedure for the preparation of borazine with the use of NaBH_4 and $(\text{NH}_4)_2\text{SO}_4$ without a catalyst was similar to that of the catalyzed preparation.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (No. 50902150).

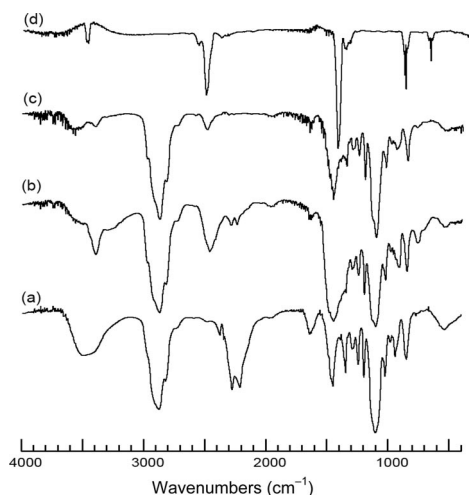


Figure 4. FTIR spectra of the reaction mixture with AlCl_3 (1 mol-%) at 45 °C (a) after 0 h, (b) after 1 h, and (c) after 3 h; (d) purified borazine.

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Received: October 7, 2009

Published Online: March 15, 2010