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Synthesis and Comparison of Reactivity of Amine-Borane Complexes

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ABSTRACT

The present study emphasizes on synthesis and characterization of three ABs: Aniline-Borane (AAB), Triethylamine-Borane (TAB), and N,N-Dimethylaniline-Borane (DMAB). The AB reagents were characterized by 11B-NMR spectra and new green procedure was developed to determine the active borane concentration by gasometer. Furthermore, the reactivity of AB complexes has been compared against 1-decene under microwave and ultrasound radiation for the first time. The outcome of gasometer and microwave, ultrasound reactions revealed that TAB is extremely stable and inert. Whereas AAB release borane species rapidly and complete the hydroboration of 1-decene.

Keywords: Amine-Borane, 11B-NMR, Gasometer, Microwave, Ultrasound, Hydroboration.

INTRODUCTION

Many of the borane reagents that Brown *et al.,* discovered which proved to be essential to overcome the challenges that occur when experimenting with diborane directly[1]. It is unstable and reactive gas at room temperature, and it usually needs to be generated in situ[2]. Diborane presents unique challenges because it reacts explosively with moist air and must be worked under an inert atmosphere[3,4]. Amine-Boranes (AB) are a highly beneficial class of boron reagents, and they are labile complexes of Lewis bases and been utilized in an extensive range of organic and material chemistry applications since Burg and Schlesinger (1937) first published data on their synthesis[5,6]. A range of Lewis bases can be used as electron donors when designing and synthesising the AB adducts in the laboratory[7-9].

Utility of Amine-borane complexes

In accordance with the recent study reports, transition metal catalysts have been utilised in an attempt to enhance their reactivity in hydrogenation reactions[10,11]. AB reagents have a dual function in direct amidation, whereby they may activate both aromatic and aliphatic carboxylic acids and then deliver amines to produce corresponding functionalized amides with a yield of 99% reported by PV Ramachandran *et al.,*[12,13] Apart from their uses in synthetic organic chemistry AB reagents have drawn a lot of interest in material chemistry as a potential ingredient for the synthesis of B-N polymers, a hydrogen storage medium, and rocket propellants[14]. Literature report revealed as AB complexes are utilized in hydrogen storage fuel cells, due to stability and has high gravimetric content of H_2[15-17]. According to a recent study, the synthesis of boron metal complexes composed of heterocyclic ligands, is employed as a catalyst in organic synthesis and agricultural waste management process[18]. The researchers found that various BN nanocomposite loaded with Pt, Pd, Ti, Si, and Al which enhanced the hydrogen storage[19]. Dimethylamine-Borane and Morpholine-Borane complexes are employed as reducing agents in electronics sector for the fabrication of circuit boards and electroplating applications[20,21].

Structure and reactivity of AB complexes

The reactivity of AB complexes depends on the bond strength of N-B bond and nature of the groups attached on nitrogen of amine group, stable AB reagents are inert, have a lower reactivity, and can be prepared more easily[22,23]. The opposite is true if the AB adduct is reactive, unstable and difficult to prepare. According to Brown *et al.,* less basic, alkyl substituted amines shall form a reactive AB adducts than simple unhindered alkyl amines[24,25]. The present investigation strives to establish an environmentally friendly, effective method to determine the concentration of active borane and to compare the reactivity of aliphatic and aromatic AB complexes under microwave radiation because there is not enough clear-cut evidence in the literature regarding the impact of groups on the reactivity of amine-borane complexes. Furthermore, the objective is to examine the reactivity of AAB and methyl substituted DMAB against 1-decene under microwave radiation, as well as to investigate the impact of steric enhancement of methyl groups on the reactivity of DMAB reagent.

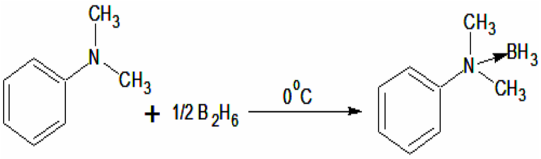
MATERIALS AND METHODS

The chemicals used for the experiment are procured from Fluka and Aldrich, and liquid substrates were distilled prior to use. ^{11}B-NMR (128 MHz) spectra of AB complexes were recorded on Bruker AVANCE III-400 spectrometer. The IR spectrum of AB complex is accomplished by using Perkin-Elmer instrument, the active borane concentration of AB complexes can be determined according to Sigma-Aldrich technical bulletin procedure[26].

EXPERIMENTAL

Preparation and characterization of AB complexes

The three AB reagents are prepared according to a standard protocol and kept in a nitrogen atmosphere and complexation tendency of an amine was monitored by using the ^{11}B-NMR technique, confirmed by the peak at -3ppm to -11ppm[27]. Scheme 1 illustrate the preparation of DMAB complex.



Scheme 1. Preparation of DMAB

Quantitative analysis of DMAB complex

The active hydride content of borane of AB complexes can be determined using a gasometer and the hydrogen evolution procedures. The results of the study can be used to calculate the number of hydrides available for hydroboration and for functional group reduction.

Procedure for the determination of hydride concentration of AB complex

In order to determine the active hydride concentration of AB complex, the literature reported procedure used 1.0M HCl in 50% aq. diglyme and 1.0M HCl in 50% aq. ethylene glycol. However, in the lab, we developed the following procedure to determine the active hydride concentration of AB stock solution. The gas burette is assembled as illustrated in Fig. 1 and the hydrolysis flask C is charged with 100 mL of water. Cooling water is circulated through the spiral condenser E and trap F is cooled in ice/salt. With stopcocks L and M both open to the atmosphere, the levelling bulb J is adjusted to give a zero reading for the level of distilled water in the gas burette. Stopcock L is then closed, and stopcock M is turned so that the hydrolysis flask and the gas burette form a closed system. 1 mL of the AB stock solution is added slowly through the septum followed by the addition of 20 mL of 3N-sulphuric acid in 50% aqueous ethanol solution using a hypodermic syringe. The solution was well stirred, hydrolysis of the AB reagent is observed, and the initial, final water level is noted. From this the total volume of water displaced is calculated with corrections as, PV=nRT and Concentration of borane=RT/PV.

Table 2 highlights the results of total hydrolysis time for three AB complexes, along with the literature reported values, and provides the appropriate discussion.

Comparison of reactivity of AB complexes through Hydroboration studies

Hydroboration experiment is conducted under microwave and ultrasound radiation, to compare the reactivity of three AB reagents. The reaction mixture consists of AB reagent stock solution (1 mmole) and 1-decene (3 mmoles) in 1:3 ratio and separately exposed to microwave and ultrasound radiation. The progress of hydroboration can be monitored by TLC with the solvent system (30% ethylacetate+hexane) as an eluant[28].

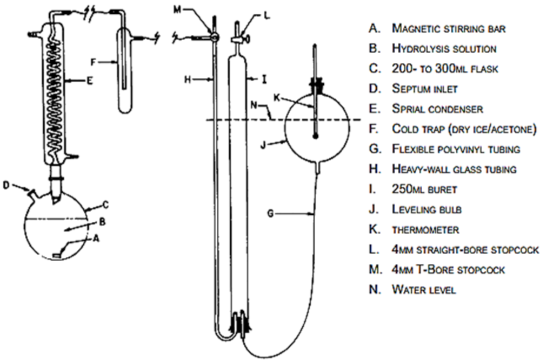


Fig. 1. Gasometer assembly (Adapted from Aldrich Technical Bulletin, AL-123, 1996)

Experimental procedure of Hydroboration-Oxidation

A 50 mL oven dried, three necked round bottom flask was placed under a microwave reactor and connected to a mercury bubbler with a take-off adapter. Afterwards, a sterile syringe was utilised to add 1 mL of 1-decene (6 mmol) and then the AB reagent stock solution (6 mL, 2 M solution) in dry THF (6 mL) under nitrogen atmosphere. Microwave irradiation was applied to the reaction mixture, TLC was used to monitor progress of the reaction. Afterwards, 2 millilitres of 20% sodium hydroxide were gradually added to the reaction mixture until it became alkaline. The reaction mixture of alkaline sodium hydroxide solution had been cooled before 2 millilitres of 35% hydrogen peroxide was added gradually. TLC was used to monitor the progress of the oxidation reaction. The reaction mixture was filtered, and the aqueous layer is extracted with diethyl ether (3X10 mL). The organic layers are combined, dried over anhydrous Na_2SO_4 and the solvent has been removed by vacuum distillation, Table 3 provided summary of the findings. The ultrasound mediated hydroboration-oxidation reaction is experimentally performed in the same manner as described above.

RESULTS AND DISCUSSION

Characterization of AB complex

It is essential to characterise the AB reagents in order to evaluate and comprehend the nature, which can be accomplished with the help of IR and ^{11}B-NMR spectroscopic techniques. Herewith the IR spectra values explained, and the ^{11}B-NMR values are illustrated in Table 1.

The IR spectra of AAB complex is explained as, FT-IR (KBr) (v wave number) cm^{-1}: the peak appears at 3416 broad peak which is due to water contamination, 2924 N-H stretch and 2360 B-H stretching vibrations, 1619 N-H bending vibration (strong), 1443 N-H bending vibration (weak), 1370 B-N bending vibration, 1153 B-H bending vibration, 1106 aromatic C-C bending vibration. From these values it is confirmed that the presence of N-H, B-H bonds and B-N bond in AAB complex.

Table 1: Typical ^{11}B-NMR spectral values for various AB reagents

No	Amine-Borane (AB) complex	^{11}B-NMR peak value (ppm)	Nature of the signal
1	Triethylamine-Borane (TAB)	-11 coupled-8 to -11 decoupled	Quatret
2	Aniline-Borane (AAB)	-12 coupled-9 to -12 decoupled	Quatret
3	N,N-Dimethyl Aniline-Borane (DMAB)	-4 coupled-4 to -9 decoupled	Quatret

The type of group bound to the N-gen atom of the amine group will determine the position of ^{11}B-NMR signal of AB complexes, and possible to confirm the stability and shelf life of AB reagents. Although the basicity of aliphatic and aromatic amines differs substantially, yet the chemical shift values are barely different is observed. The time required for the total hydrolysis of AB reagents can be determined through gasometer analysis and the results are compared with the literature values and highlighted in Table 2.

Table 2: Time for total hydrolysis of AB complexes at 25°C (Brown and Murray, 1984)

No	AB complex	Time for total hydrolysis (minutes) 1.0M HCl in 50% aq. Diglyme[§]	1.0M HCl in 50% aq. Ethylene glycol[§]	3N Sulphuric acid in 50% aq. Ethanol
1	Aniline-Borane (AAB)	15	20	10
2	N,N-Dimethylaniline-Borane (DMAB)	50	70	25
3	Triethylamine-borane (TAB)	390	410	180

[§]literature reported values

The TAB complex is stable and less reactive, while the AAB reagent is more reactive, the fact that it undergoes hydrolysis completely than other two AB complexes. TAB complex takes a more time to hydrolyse completely, and releases borane slow rate which suggest that it has strong N-B bond. It has been observed that AAB hydrolyses more quickly than DMAB reagent, releases borane gas faster and in compare with the previous methods, we developed the green, novel procedure which is accurate and consume less time. The differences in reactivity of AB complexes will be ascertained through the rate of hydroboration of 1-decene under microwave and ultrasound radiation. Table 3 provides a summary of the outcomes, and the TAB reagent seemed to be stable and innocuous as it failed to hydroborate the 1-decene even after more time exposed to microwave and ultrasound radiation. On the other hand, AAB performed the hydroboration and oxidation of 1-decene in short time, producing a mixture of 1- and 2-decanol with 95% yield.

Table 3: Comparison of reactivity of AB complexes with 1-Decene under MWI and Sonication

No	AB complex	Hydroboration under MWI (minutes)	Alcohol Yield(%)	Hydroboration under Ultrasound (minutes)	AlcoholYield(%)
1	TAB	No Hydroboration	Nil	No Hydroboration	Nil
2	DMAB	Hydroboration is completed by 3 min mixture of 1-Decanol and 2-Decanol	96%	Hydroboration is completed by 20 min mixture of 1-Decanol and 2-Decanol	94%
3	AAB	Hydroboration completed by 2 min mixture of 1-Decanol and 2-Decanol	95%	Hydroboration is completed by 18 min mixture of 1-Decanol and 2-Decanol	92%

DMAB demonstrated comparable efficiency in the hydroboration and oxidation of 1-decene, yielding a mixture of 1- and 2-decanol with 95% yield. The TAB have strong N-B bond which makes the complex stable, However, AAB and DMAB complexes possess moderately strong N-B bonds, when subjected to microwave and ultrasound radiation, allows the instant release of borane gas, and makes them as effective reagents. According to experimental observations, TAB is the least reactive reagent whereas AAB is the most reactive.

CONCLUSION

In the current study we developed an expedient novel, green procedure of gasometer analysis to determine the active borane concentration, and the comparison of reactivity of aliphatic, aromatic AB complexes by hydroboration of 1-decene first time reported under the microwave and ultrasound irradiation. We conclude that the TAB reagent is stable and inert whereas AAB complex is reactive and moderately stable. Further, the reaction kinetics, mechanism, synthetic utility are under progress and will be disclosed in near future.

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Conflicts of interest

The authors (s) declare (s) that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. Brown, H.C.; Singaram, S. Molecular addition compounds 7. Synthesis of addition compounds of boron trifluoride, borane, and alane., *Inorg. Chem.*, **1980**, *19*, 455-457.
2. Brown, H. C., *Organic Syntheses via Boranes.*, **2000**, Revised edition, *2*. Aldrich Chemical Co. Inc., Milwaukee, WI.
3. Pelter.; Smith, K.; Brown, H. C., *Borane Reagents.*, **1988**, Academic Press: San Diego, CA.

4. Reddy, D.O. A short chronological Review on the Synthesis of Amine-Boranes., *Chemical Review and Letters*., **2020**, *4*, 184-191. doi: https://doi.org/10.22034/crl.2020.238 849.1070
5. Marjorie, A.Y.; Marty, B.J.D.; Ciuculescu-Pradines, C.D. Chapter 6: Amines and Amine-boranes., *Series:Nanoscience and Nanotechnology*., **2021**, doi: https://doi.org/10.1039/978183 9163623-00130
6. Burnham, B. S. Amine-Boranes., *Encyclopaedia of Metalloproteins*., **2013**, Editors: Kretsinger RH, Uversky VN, Permyakov EA. Springer New York.
7. Colebatch, L. A.; Weller, S. A. Amine–Borane Dehydropolymerization: Challenges and Opportunities., *Chemistry - A European Journal*., **2019**, *25*(6), 1379-1390. ISSN 1521-3765.
8. Ramachandran, P.V.; Kulkarni, A.S.; Zhao, Y.; Mei, G. J. Amine–boranes bearing borane-incompatible functionalities., *Chemical Communication*., **2016**, *52*, 11885-11888.
9. Ramachandran, P. V.; Kulkarni, A. S. Open-Flask Synthesis of Amine–Boranes via Tandem Amine–Ammonium Salt Equilibration–Metathesis., *Inorganic Chemistry*., **2015**, *54*, 5618-5620.
10. Couturier, M.; Andresen, B.M.; Dubé. P.; Negri, J.T. The use of borane-amine adducts as versatile palladium catalysed hydrogen-transfer reagents in methanol., *Tet. Lett*., **2001**, *42*(1), 2763-2766.
11. Moigne, L. L.; Posenato, T.; Gajan, D.; Lacôte, E. Catalyst-Free Transfer Hydrogenation from Amine-Borane Small Oligomers., *Chemistry A European Journal*., **2024**, *30*(1), 15-22.
12. Ramachandran, P.V.; Alawaed, A. A. Titanium-Mediated Reduction of Carboxamides to Amines with Borane-Ammonia., *Molecules*., **2023**, *28*(12), 4575: 01-12.
13. Ramachandran, P.V.; Hamann, H.J.; Choudhary, S. Amine-Boranes as Dual-purpose reagents for direct Amidation of Carboxylic acids., *Organic Letters*., **2020**, *22*, 21, 8593-8597.
14. Lin, R.; Scherschel, N.F.; Zeller, M.; Snyder, M.; Son, S.; Ramachandran, P.V.; Piercey. D.G. Synthesis and Energetic Characterization of Borane-Amines on High-Nitrogen Heterocycles., *ACS Omega*., **2024**, *9*, 14241-14248. doi: https://doi.org/10.1021/acsomega.3c09934
15. Yu, J.; Lu, K.; Lei, W.; Hao, Q. Ammonia borane as an efficient direct fuel in alkaline fuel cells: mechanism, catalysts, applications, and challenges., *J. Mater. Chem.* A., **2022**, *10*, 16779-16794.
16. Hua, T. Q.; Ahluwalia, R. K. Off-board regeneration of ammonia-borane for use as a hydrogen carrier for automotive fuel cells., *Int. J. of Hydrogen Energy*., **2012**, *37*(19), 14382-14392.
17. Jayakumar, S. V.; Srinivas, K. A.; Hiriyanna, G.; Pati, H.N. Microwave accelerated hydroboration of alkenes with N,N-Dimethylaniline-Borane., *Rasayan Journal of Chemistry*., **2008**, *1*, 326-330.
18. Alam, M. Z.; Khan, S. A. Synthesis of Heteroatoms Including at Least One Boron Metal Complexes and Their Catalytic Applications. In: Jawaid, M., Khan, A. (eds) Multifunctional Boron-Nitride Composites. **2023**, *Composites Science and Technology*. Springer, Singapore. doi: https://doi. org/10.1007/978-981-99-2866-8_2
19. Mohasin, M.; Alam, M. Z.; Ullah, Q.; Khan, S.A. Boron Nitride Nanocomposites Used as Hydrogen Storage Material. In: Jawaid, M., Khan, A. (eds) Multifunctional Boron-Nitride Composites. **2023**, *Composites Science and Technology*. Springer, Singapore. doi: https://doi.org/10.1007/978-981-99-28 66-8_8
20. Mallory, G. O.; Hajdu, J. B. Electroless plating, Fundamentals and Applications., *Noyes Publications*, **1990**, William Andrew, Orlando, Florida. https://trove.nla.gov.au/work/6453483
21. Jayakumar, S. V.; Ahamed, M. F. A. Ultrasound Mediated Hydroboration of Alkenes, Alkynes Employing: N,N-Dimethylaniline.Borane (DMAB)., *Der Pharma Chemica*., **2018**, *10*(3), 90-93.
22. Brown, H. C.; Murray, L. T. Molecular Addition Compounds. 9. Effect of Structure on the Reactivities of Borane-Amine Complexes., *Inorganic Chemistry*., **1984**, *23*(18), 2746-2753.

23. Jayakumar, S. V.; Ahamed, M. F. A. Ultrasound Mediated Functional Group Reduction and Chemo-selective Studies by DMAB., *Chemical Science Transactions*., **2019**, *8*, 418-424.
24. Brown, H. C.; Kanth, J. V. B.; Zaidlewicz, M., Molecular Addition Compounds. 13. N,N-Diisopropyl-N-isobutylamine–Borane., *Organometallics*., **1999**, *18*(7), 1310-1317.
25. Jeyakumar, S. V.; Ganesh, S. K. Microwave Mediated Reduction of Selected Functional Groups Employing: N,N-Dimethylaniline. borane., *Orbital: Electronic Journal of Chemistry*., **2014**, *6*, 56-60.
26. Quantitative Analysis of Active Metals and Metal Hydrides via Gas Burette., *Aldrich Technical Bulletin* AL-123, revised 4/96, **1996**, Sigma-Aldrich, St. Louis, Missouri, USA. 01-04.
27. Brown, H. C.; Zaidlewicz, M.; Dalvi, P.V. Molecular Addition Compounds. 10. Borane adducts., *Organometallics*., **1998**, *17*(19), 4202-4205. DOI: https://doi.org/10.1021/om980418u
28. Jayakumar, S. V.; Saxena, A.; Tomar, D.R. Microwave Mediated Modification of Selected Limonoids with DMAB Reagent and Antibacterial Studies., *Macromolecular Symposia*., **2024**, *413*, 2300005-2315. doi: https://doi. org/10.1 002/masy.202300005