

Thermochemistry for the Dehydrogenation of Alkylated Cyclodi-, Cyclotri-, and Cyclotetraborazane

Kevin Anderson

Department of Chemistry, University of Alabama, Tuscaloosa, AL 35487, USA

Borane amine compounds hold promise in a chemical hydrogen storage setting due to their high gravimetric and volumetric content of releasable hydrogen. The heats of formation and the thermodynamics of the dehydrogenation of N-methyl substituted cyclodi-, cyclotri- and cyclotetraborazane were predicted at the G3(MP2) level following B3LYP/DGDVZP2 level optimization. The dehydrogenation of the N-methyl substituted compounds was predicted to be more endothermic than the dehydrogenation of equivalent non-substituted compounds.

Introduction

There is a significant interest in the development of hydrogen fuel cells as a suitable power source for use in the transportation sector. Ideally, these fuel cells would be environmentally friendly and would be independent of petroleum as a feedstock. One critical issue with these hydrogen-based fuel cells in the transportation sector is the safe and efficient storage of hydrogen. Chemical hydrogen storage materials that have a ready release/uptake of H₂ provide a possible solution to this issue [1]. It is also necessary that these processes are near thermoneutral to reduce the heat needed for the release of hydrogen and to minimize the energy costs of the regeneration process.

Borane amine derivatives show promise as effective hydrogen storage materials due to their low molecular weight and high volumetric and gravimetric density of covalently bound hydrogen that can be released at low temperatures necessary for transportation applications. For example, Borazine (1), BH₃NH₃, has received attention for these reasons. Decomposition of Borazine in solution yields hydrogen and cyclotriborazane, c-B₃N₃H₁₂ [11]. Upon further heating, cyclotriborazane decomposes to borazine, c-B₃N₃H₆ [6,11]. This is outlined in equation 1 [9]. The production of c-B₃N₃H₁₂ from three molecules of Borazine may proceed through the dimer, cyclodiborazane. For this reason, the release of hydrogen from this structure is investigated, leading to c-B₂N₂H₄. The dehydrogenation of cyclotetraborazane to produce c-B₄N₄H₈ was studied

for similar reasons. The cyclic six-member ring is likely to be an intermediate in the formation of a graphite-type solid structure (Figure 1).

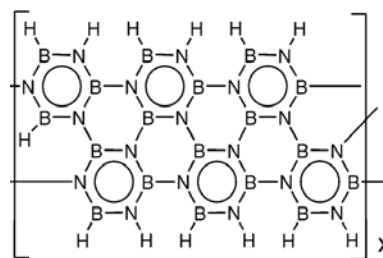
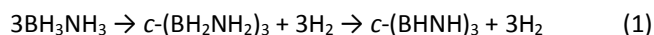


Figure 1: Graphitic Borane-Amine Structure [4]



One significant issue arises from the fact that ammonia borane is a solid at room temperature, making it less than ideal for the transportation sector because substantial changes to the infrastructure would be needed to accommodate non-liquid fuels. Alkyl substituted ammonia boranes have lower melting points, likely because there are fewer hydrogen bond interactions due to the substitution of alkyl groups for partially charged hydrogen atoms [2, 5]. Borane amine could be solubilized in methyl substituted ammonia borane. This would allow for the generation of liquid fuels that could allow portions of the current infrastructure to be utilized.

Due to the weight penalty associated with the heavier methyl-substituted compounds acting as a solvent, we wish to determine if these compounds could act as storage materials in their own right to

maximize weight percent storage. Amine boranes have a weight percent storage for hydrogen of 14.9% if 2 molecules of hydrogen are produced. The alkyl substituted analogues have a weight percent storage of 9.8% if 2 molecules of hydrogen is produced [4].

The heats of formation for these N-methylammonia and ammonia B-methylborane, as well as various molecules involved in the dehydrogenation processes, have been calculated at the CCSD(T)/CBS level [4]. In order to aid in the understanding of the effects of methylation on these molecules, N-methyl substituted cyclodi-, cyclotri-, and cyclotetrazaborazane were studied at the G3(MP2) level (Figure 2). N-methyl substituted borane amines are studied because it was found that B-substituted borane amines make the dehydrogenation process more exothermic and taking the reaction further away from thermoneutrality [4].

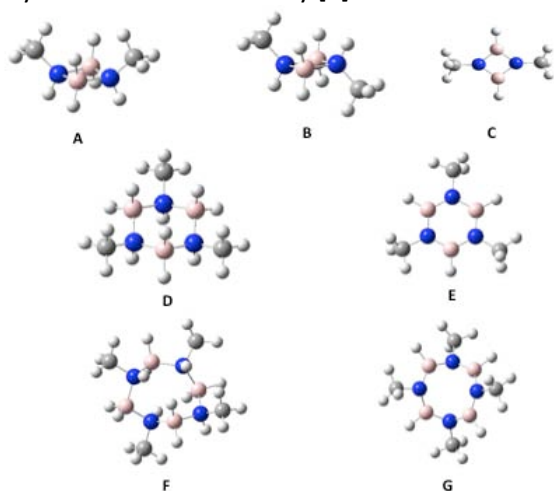


Figure 2: Structures of Methyl-Substituted Compounds.

- A) *cis*- $c\text{-B}_2\text{N}_2\text{H}_6(\text{CH}_3)_2$, B) *trans*- $c\text{-B}_2\text{N}_2\text{H}_6(\text{CH}_3)_2$,
 C) $c\text{-B}_2\text{N}_2\text{H}_2(\text{CH}_3)_2$, D) $c\text{-B}_3\text{N}_3\text{H}_9(\text{CH}_3)_3$, E) $c\text{-B}_3\text{N}_3\text{H}_3(\text{CH}_3)_3$,
 F) $c\text{-B}_4\text{N}_4\text{H}_{12}(\text{CH}_3)_4$, G) $c\text{-B}_4\text{N}_4\text{H}_4(\text{CH}_3)_4$.

The G3(MP2) heats of formation for the dehydrogenation products of the alkyl-substituted molecules are reported in order to allow the prediction of the effects of methylation on dehydrogenation of these larger borane amine-based structures.

Computational Methods

The thermodynamic properties of the smaller alkyl-substituted compounds have been predicted based on molecular orbital theory using coupled

cluster methods at the CCSD(T) level [4]. For large molecules, computation at this level is not feasible. To help counteract this, we look at the calculated heats of formation and dehydrogenation energies by utilizing a computationally less intensive method using the G3(MP2) level of theory. We have been testing the reliability of this method by comparing calculation results between the G3(MP2) and the more accurate CCSD(T) methods [4, 9].

All G3(MP2) calculations were run on the Cray XD-1, Altix, or DMC at the Alabama Supercomputer Center using the Gaussian 2003 software package. All structures were first optimized using Density Functional Theory at the B3LYP/DGDZVP2 level. These optimized geometries were then used as the input for the G3(MP2) calculations. Only the most thermally stable conformations for each molecule are reported.

The atomization method was used to calculate the heats of formation. $\Delta E_0[\text{G3(MP2)}]$ is the difference in the G3(MP2) calculated energy between the molecule and the isolated electrons and nuclei in the gas phase at 0 K (Equation 2). The heat of formation at 0 K is found by subtracting this $\Delta E^0[\text{G3(MP2)}]$ from the sum of the experimental heats of formation at 0K (Equation 3). From this value, the heat of formation at 298 K is found by subtracting the sum of the thermal corrections ($H^{298}-H^0$) for the individual atoms from the H^{298} of the molecule (Equation 4). The molecular H^{298} is found by adding the difference between the G3(MP2) calculated energies at 298 K and 0 K to the heat of formation at 0 K. The values for the atomic heats of formation and thermal corrections were taken from table values. The predicted heats of formation for the non alkyl-substituted borane amine structures were recalculated using the new value for the heat of formation for boron of 135.10 kcal/mol [9].

$$\Delta E^0[\text{G3(MP2)}] = \Sigma(\text{G3(MP2)})_{\text{atoms, 0 K}} - \text{G3(MP2)}_{\text{molecule, 0 K}} \quad (2)$$

$$\Delta H_f^0_{\text{G3(MP2)}} = \Sigma \Delta H_f^0_{\text{atoms}} - \Delta E^0[\text{G3(MP2)}] \quad (3)$$

$$\Delta H_f^{298}_{\text{G3(MP2)}} = \Delta H_f^0_{\text{G3(MP2)}} + (E^{298} - E^0)_{\text{G3(MP2), molecule}} - \Sigma(H^{298} - H^0)_{\text{atomic}} \quad (4)$$

The thermodynamics of dehydrogenation of these cyclic borane amine structures at 298K are predicted using Hess's law (Equation 5).

$$\Delta H_{\text{Reaction}}^{298} = \sum \Delta H_f^{298} \text{ Products} - \sum \Delta H_f^{298} \text{ Reactants} \quad (5)$$

Results and Discussion

Because the G3(MP2) method predicts reasonable BDEs and dehydrogenation energies, we can use this method on B-C-N compounds that are too large and computationally expensive to calculate at the CCSD(T) level. Heats of formation (Table 1) and dehydrogenation energies (Table 2) of the methylated cyclodi-, cyclotri- and cyclotetrazaboranes were predicted at the G3(MP2) level. The 298 K values are used in the discussion below. The reported experimental heat of formation of N-trimethyl cyclotriborazane was -217 ± 1 kcal/mol [8, 11]. This value is clearly incorrect because it varies from our predicted value by over 113 kcal/mol, which is well outside the range of error for these types of calculations.

The cis and trans isomers of N-dimethyl cyclodiborazane are calculated to be essentially equal at 298K, slightly preferring the trans isomer at 0K. Dehydrogenation of N-dimethyl cyclodiborazane resulting in $c\text{-B}_2\text{N}_2\text{H}_2(\text{CH}_3)_2$ and 2 H₂ is predicted to be 4.6 kcal/mol more endothermic than the equivalent reaction of the related non-methylated species, indicating an effect from alkyl substitution at the nitrogen sites of the compound [9]. Dehydrogenation of N-trimethyl cyclotriborazane to give 3 H₂ molecules is calculated to be 12.4 kcal/mol less exothermic than the equivalent reaction of the twist-boat conformation of $c\text{-B}_3\text{N}_3\text{H}_{12}$ demonstrating a larger substituent effect of the methyl groups decreasing the exothermicity of the dehydrogenation reaction. This trend continues with the dehydrogenation reaction of $c\text{-B}_4\text{N}_4\text{H}_{12}(\text{CH}_3)_4$ to give 4H₂+ $c\text{-B}_4\text{N}_4\text{H}_4(\text{CH}_3)_4$ [9]. The dehydrogenation of N-tetramethyl cyclotetrazaborazane is approximately thermoneutral and is -28.8 kcal/mol less exothermic than non-methylated cyclotetrazaborazane [9].

Table 1: Calculated G3(MP2) Heats of Formation (kcal/mol) [6]

Molecule	Theory (0 K)	Theory (298 K)
$c\text{-B}_2\text{N}_2\text{H}_4$ (D_{2h})	-23.6	-27.1
$c\text{-B}_2\text{N}_2\text{H}_8$ (D_{2h}) ^a	-43.9	-50.9
$c\text{-B}_3\text{N}_3\text{H}_6$ (D_{3h}) ^a	-106.5	-112.4
$c\text{-B}_3\text{N}_3\text{H}_{12}$ twist boat (C_3) ^a	-82.6	-93.5
$c\text{-B}_4\text{N}_4\text{H}_8$ (D_{4h})	-123.3	-131.0
$c\text{-B}_4\text{N}_4\text{H}_{16}$ (C_{4v})	-95.2	-110.0
$c\text{-B}_2\text{N}_2\text{H}_2(\text{CH}_3)_2$ trans (C_i)	-16.1	-21.6
$c\text{-B}_2\text{N}_2\text{H}_6(\text{CH}_3)_2$ trans (C_{2h})	-40.2	-50.0
$c\text{-B}_3\text{N}_3\text{H}_3(\text{CH}_3)_3$ (C_{3h})	-94.2	-103.5
$c\text{-B}_3\text{N}_3\text{H}_9(\text{CH}_3)_3$ (C_{3v})	-78.4	-93.6
$c\text{-B}_4\text{N}_4\text{H}_4(\text{CH}_3)_4$ (S_4)	-99.4	-111.8
$c\text{-B}_4\text{N}_4\text{H}_{12}(\text{CH}_3)_4$ (C_1)	-99.2	-119.6

^a Taken from Reference 9 and recalculated with new heat of formation of B of 135.1 ± 0.2 kcal/mol [7].

Table 2: Dehydrogenation Reactions at the G3(MP2) level (kcal/mol) [6]

1 st Dehydrogenation Step	(0 K)	(298 K)
$c\text{-B}_2\text{N}_2\text{H}_8 \rightarrow c\text{-B}_2\text{N}_2\text{H}_4 + 2\text{H}_2$	17.9	21.6
$c\text{-B}_3\text{N}_3\text{H}_{12}$ twist boat $\rightarrow c\text{-B}_3\text{N}_3\text{H}_6 + 3\text{H}_2$	-27.5 ^a	-22.2 ^a
$c\text{-B}_4\text{N}_4\text{H}_{16} \rightarrow c\text{-B}_4\text{N}_4\text{H}_8 + 4\text{H}_2$	-33.0	-25.4
$c\text{-B}_2\text{N}_2\text{H}_6(\text{CH}_3)_2 \rightarrow c\text{-B}_2\text{N}_2\text{H}_2(\text{CH}_3)_2 + 2\text{H}_2$	21.6	26.2
$c\text{-B}_3\text{N}_3\text{H}_9(\text{CH}_3)_3 \rightarrow c\text{-B}_3\text{N}_3\text{H}_3(\text{CH}_3)_3 + 3\text{H}_2$	-19.4	-13.0
$c\text{-B}_4\text{N}_4\text{H}_{12}(\text{CH}_3)_4 \rightarrow c\text{-B}_4\text{N}_4\text{H}_4(\text{CH}_3)_4 + 4\text{H}_2$	-7.3	3.4

^a Taken from Reference 9 and recalculated with new heat of formation of B of 135.1 ± 0.2 kcal/mol [7].

Conclusion

Methyl substitution at N in the cycloborazane rings decreases the exothermicity of the dehydrogenation reactions and in the case of N-tetramethyl cyclotetrazaborazane, the thermodynamics for dehydrogenation reaction become favorable as it is near thermoneutral. Similarly, the dehydrogenation of $c\text{-B}_3\text{N}_3\text{H}_9(\text{CH}_3)_3$ is closer to thermoneutrality than the equivalent non-methylated compound. Dehydrogenation of $c\text{-B}_2\text{N}_2\text{H}_6(\text{CH}_3)_2$, $c\text{-B}_3\text{N}_3\text{H}_9(\text{CH}_3)_3$, and $c\text{-B}_4\text{N}_4\text{H}_{12}(\text{CH}_3)_4$, resulting in the production of two, three, and four molecules of H₂, are 26.2, -13.0, and 3.4 kcal/mol at the G3(MP2) level at 298 K, respectively.

References

- [1] Dressalhaus M, Crabtree G, Buchanan M & Eds. (2003). Basic Energy Needs for the Hydrogen Economy. Office of Science, U.S. Department of Energy.

- [2] Framery E & Vaultier M. (2000). Efficient synthesis and NMR data of N-and B- substituted borazines. *Heteratom Chem*, 11:218.
- [3] Gaussian 03, Revision C.01. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb M A, Cheeseman JR, Montgomery JA, Vreven T, Kudin KN, Burant JC, et al. Gaussian, Inc., Wallingford CT, 2004.
- [4] Grant D, Matus M, Anderson K, Autrey S & Dixon D. (2009). Thermochemistry for the Dehydrogenation of Alkyl Substituted Ammonia Boranes. Manuscript.
- [5] Geanangel R & Shore S. (1966). Boron-Nitrogen Chemistry. *Preparative Inorganic Chemistry*, 3:123-238.
- [6] Jaska C, Temple K, Lough A & Manners I. (2003). Transition Metal-Catalyzed Formation of Boron-Nitrogen Bonds: Catalytic Dehydrocoupling of Amine-Borane Adducts to Form Aminoboranes and Borazines. *Journal of the American Chemical Society*, 125:9424.
- [7] Karton A & Martin J. (2007). Heats of Formation of Beryllium, Boron, Aluminum, and Silicon Re-examined by Means of W4 Theory. *J. Phys. Chem.* 111:5936.
- [8] Lias S, Bartmess J, Liebman J, Holmes J, Levin R, & Mallard W. (1988). Gas-Phase Ion and Neutral Thermochemistry. *J. Phys. Chem. Ref. Data*: 17, Supplement 1.
- [9] Matus M, Anderson K, Camaioni D, Autrey S & Dixon D. (2007). Reliable Predictions of the Thermochemistry of Boron-Nitrogen Hydrogen Storage Compounds: $B_xN_xH_y$, $x=2,3$. *J. Phys. Chem* 111:4411.
- [10] Tel'noi V, Rabinovich I. (1980). Thermochemistry of Organic Derivatives of Non-transition Elements. *Russ. Chem. Rev.*: 49, 603 (Engl. Translation: 49, 1134).
- [11] Wang J & Geanangel R. (1988). ^{11}B NMR Studies of the Thermal Decomposition of Ammonia-Borane in Solution. *Inorg. Chim. Acta*, 148:185.

Kevin Anderson is a senior majoring in Chemistry with a minor in Computer-Based Honors from Grapevine, Texas. He works for Dr. David Dixon in the Computational Chemistry Group and is a recipient of the Randall Undergraduate Research Award and the Outstanding Chemistry Undergraduate Student Award.