STRUCTURAL AND THERMOCHEMICAL STUDIES OF PYRROLE BORANE BY QUANTUM CHEMICAL CALCULATIONS

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INTRODUCTION

- Finding safe and efficient hydrogen storage materials (HSMs) is very important to transition from using dirty fossil fuels to a cleaner hydrogen economy. Combustion of fossil fuels releases harmful greenhouse gases.[1]
- Hydrogen is seen as a cleaner, more efficient and cost-effective fuel for the next generation whilst meeting UN Sustainable Development Goals #7 (Affordable and Clean Energy) and #13 (Climate Change).[2]
- Amine boranes (ABs) can act as HSMs due to their high hydrogen content.[3] Dihydrogen bond formation across the B-N bond is important to facilitate the evolution of H_2.[4] N-substituted derivatives make dehydrogenation closer to thermoneutral.[5]
- BH_3-catalyzed dehydrogenation is favoured in saturated cyclic ABs.[6]
- This project is investigating the structural parameters, kinetics and thermochemistry of unsaturated pyrrole borane (**PB**) to evaluate its suitability for on-board vehicular applications (Figure 1).

Figure 1: Energy sources for vehicular use and their environmental impact

COMPUTATIONAL METHODS

- Bond dissociation energies and thermochemical parameters for the dehydrogenation of **PB** were predicted with MP2/cc-pVTZ and CBS-QB3.
- Transition-state structures of the dehydrogenation reaction of **PB** with and without the BH_3 catalyst were identified at CBS-QB3 level.

RESULTS

- *r*B-N is <u>much longer</u> in **PB** than in pyrrolidine borane.[6]
- The B-N_{BDE} is <u>much lower</u> in **PB** than in pyrrolidine borane (Table 2).
- ΔHr and ΔGr are <u>much larger</u> in **PB** than in pyrrolidine borane (Table 2).

*Table 1: Optimized structural parameters for **PB** (Figure2) at different levels of theory and basis set. All distances are in pm; angles and dihedral angels are in degrees.*

PB	rB-N	rN-C	∠C-N-B	ϕC-C-N-B
MP2/6-311G*	173.0	143.1	110.8	115.7
MP2/6-311+G*	173.1	143.1	111.0	116.2
M06-2X/6-31G*	173.7	143.0	111.0	116.1
M06-2X/Aug-cc-pVTZ	172.2	142.7	111.2	116.8

Table 2: Thermochemical parameters predicted at CBS-QB3 and MP2/cc-pVTZ level of theory at 298.15 K.

Property	**PB**		Pyrrolidine borane[6]
	MP2/cc-pVTZ	CBS-QB3	
B-N_{BDE}	+30.0	+11.3	+157.9
ΔHr	-103.4	-112.4	-11.1
ΔGr	-138.1	-146.2	-46.5
ΔS_r	+117.2	+113.0	+117.2

Units in kJ/mol except ΔS_r which is in J/K/mol.

*Figure 2: Structure of **PB** (M06-2X/6-31G*)*

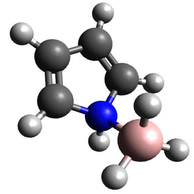


*Figure 3: Energy profile diagram for the dehydrogenation of **PB** without catalyst BH_3 at 298.15 K using CBS-QB3. Relative energies (in brackets) in kJ/mol.*

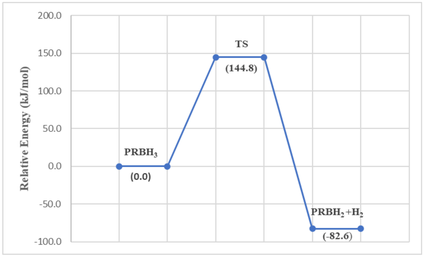
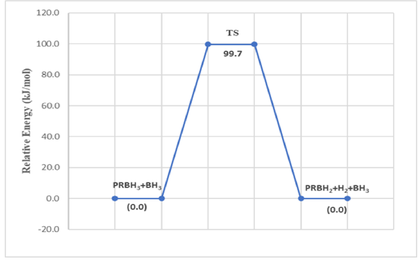


*Figure 4: Energy profile diagram for the dehydrogenation of **PB** with catalyst BH_3 at 298.15 K using CBS-QB3. Relative energies (in brackets) in kJ/mol.*



DISCUSSION

- **PB** has a longer dative B-N bond distance than pyrrolidine borane and is predicted to dissociate across the B-N bond rather than dehydrogenate to release H_2 due to the lower B-N bond dissociation energy.
- The predicted enthalpy of dehydrogenation shows that the H_2 release reaction of **PB** is more exothermic and not close to thermoneutrality.
- Transition-state structures for both the uncatalyzed and catalyzed dehydrogenation reaction pathways also reinforce the prediction that dissociation of **PB** will be favoured over the dehydrogenation process (Figures 3/4).

FUTURE PLANS

Future work will focus on extending this study to new cyclic amine borane complexes that are potential candidates for chemical hydrogen storage. For instance, imidazolidinebisborane, 4H-1,4thiazine borane, thiomorpholine borane and pyrazolidinebisborane. These new compounds will be synthesized and subjected to rigorous experimental and theoretical investigations to understand their structure and reactivity towards hydrogen evolution with the aim of meeting the UN Sustainable Development Goals and reducing dependency on fossil fuels.

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