

การศึกษาเชิงทฤษฎีของการปลดปล่อยไฮโดรเจนจาก  $\text{BH}_3\text{NH}_3$ ,  $\text{AlH}_3\text{NH}_3$ ,  $\text{BH}_3\text{PH}_3$  และ  $\text{AlH}_3\text{PH}_3$

นางสาวพรพรรณ ชนาภิวัดน์

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THEORETICAL STUDY OF HYDROGEN RELEASE FROM  $\text{BH}_3\text{NH}_3$ ,  $\text{AlH}_3\text{NH}_3$ ,  
 $\text{BH}_3\text{PH}_3$  AND  $\text{AlH}_3\text{PH}_3$

Miss Pornpan Chanapiwat

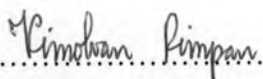
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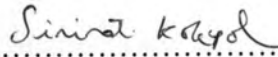
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**By** Miss Pornpan Chanapiwat  
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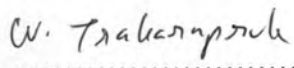
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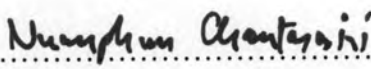
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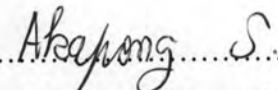
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พรพรรณ ชนาภิวัดน์ : การศึกษาเชิงทฤษฎีของการปลดปล่อยไฮโดรเจนจาก  $\text{BH}_3\text{NH}_3$ ,  $\text{AlH}_3\text{NH}_3$ ,  $\text{BH}_3\text{PH}_3$  และ  $\text{AlH}_3\text{PH}_3$ . (THEORETICAL STUDY OF HYDROGEN RELEASE FROM  $\text{BH}_3\text{NH}_3$ ,  $\text{AlH}_3\text{NH}_3$ ,  $\text{BH}_3\text{PH}_3$  AND  $\text{AlH}_3\text{PH}_3$ ) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: รศ.ดร.วิทยา เรืองพรวิสุทธิ, 100 หน้า.

การคำนวณโครงสร้างอิเล็กทรอนิกส์โดยการใช้วิธี B3LYP และ MP2 ด้วยเบซิสเซต 6-311++G(d,p) เพื่อทำนายกลไกของการปลดปล่อยไฮโดรเจนจาก โบเรนเอมีน ( $\text{BH}_3\text{NH}_3$ ), อัลเลนเอมีน ( $\text{AlH}_3\text{NH}_3$ ), โบเรนฟอสฟีน ( $\text{BH}_3\text{PH}_3$ ) และอัลเลนฟอสฟีน ( $\text{AlH}_3\text{PH}_3$ ) ในระบบที่ไม่มีและมีโมเลกุลโบเรน ( $\text{BH}_3$ ), แอมโมเนีย ( $\text{NH}_3$ ), อัลเลน ( $\text{AlH}_3$ ) หรือฟอสฟีน ( $\text{PH}_3$ ) จากผลการคำนวณพบว่า โมเลกุลโบเรน แอมโมเนีย และอัลเลนสามารถแสดงบทบาทของการเป็นตัวเร่งปฏิกิริยาที่มีประสิทธิภาพสำหรับการปลดปล่อยไฮโดรเจนจาก  $\text{BH}_3\text{NH}_3$ ,  $\text{AlH}_3\text{NH}_3$ ,  $\text{BH}_3\text{PH}_3$  และ  $\text{AlH}_3\text{PH}_3$  เมื่อเปรียบเทียบกับตัวเร่งปฏิกิริยาทั้งสามชนิดคือ สารประกอบโบเรน แอมโมเนีย และอัลเลน พบว่า แอมโมเนียเป็นตัวเร่งปฏิกิริยาที่มีประสิทธิภาพในระบบ  $\text{AlH}_3\text{NH}_3$  และ  $\text{AlH}_3\text{PH}_3$  ส่วน โบเรน และอัลเลนเป็นตัวเร่งที่มีประสิทธิภาพในระบบ  $\text{BH}_3\text{NH}_3$  และ  $\text{BH}_3\text{PH}_3$  ตามลำดับ ค่าพลังงานกระตุ้นที่ต่ำที่สุดสำหรับการปลดปล่อยไฮโดรเจนจาก  $\text{BH}_3\text{NH}_3$ ,  $\text{AlH}_3\text{NH}_3$ ,  $\text{BH}_3\text{PH}_3$  และ  $\text{AlH}_3\text{PH}_3$  มีค่าเท่ากับ 23.62, 24.52, 29.26 และ 28.26 กิโลแคลอรีต่อโมล ตามลำดับ นอกจากนี้มีการคำนวณหาค่าคงที่อัตราเร็วที่มีค่าสูงสุดในการเกิดปฏิกิริยาของการปลดปล่อยไฮโดรเจนจาก  $\text{BH}_3\text{NH}_3$ ,  $\text{AlH}_3\text{NH}_3$ ,  $\text{BH}_3\text{PH}_3$  และ  $\text{AlH}_3\text{PH}_3$  มีค่าเท่ากับ  $2.37 \times 10^{-5}$ ,  $6.87 \times 10^{-7}$ ,  $1.14 \times 10^{-9}$  และ  $4.17 \times 10^{-9}$  วินาที<sup>-1</sup> ตามลำดับ

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต.....พรพรรณ ชนาภิวัดน์  
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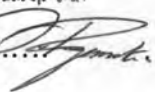
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 KEY WORD: BORANE AMINE/ ALANE AMINE/ BORANE PHOSPHINE/  
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 PROPERTIES

PORNPAN CHANAPIWAT: THEORETICAL STUDY OF HYDROGEN  
 RELEASE FROM  $\text{BH}_3\text{NH}_3$ ,  $\text{AlH}_3\text{NH}_3$ ,  $\text{BH}_3\text{PH}_3$  AND  $\text{AlH}_3\text{PH}_3$ . THESIS  
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The electronic structure calculations using the B3LYP and MP2 levels of theory with the 6-311++G(d,p) basis set have been used to predict the molecular mechanism of hydrogen release from borane amine ( $\text{BH}_3\text{NH}_3$ ), alane amine ( $\text{AlH}_3\text{NH}_3$ ), borane phosphine ( $\text{BH}_3\text{PH}_3$ ) and alane phosphine ( $\text{AlH}_3\text{PH}_3$ ) in systems without and with the borane ( $\text{BH}_3$ ), ammonia ( $\text{NH}_3$ ), alane ( $\text{AlH}_3$ ) or phosphine ( $\text{PH}_3$ ) molecules. The calculated results demonstrate that the  $\text{BH}_3$ ,  $\text{NH}_3$  and  $\text{AlH}_3$  compounds can play the role of an efficient catalyst for hydrogen release from the  $\text{BH}_3\text{NH}_3$ ,  $\text{AlH}_3\text{NH}_3$ ,  $\text{BH}_3\text{PH}_3$  and  $\text{AlH}_3\text{PH}_3$ . A comparison among the  $\text{BH}_3$ ,  $\text{NH}_3$  and  $\text{AlH}_3$  catalysts, it was found that the  $\text{NH}_3$  is the efficient catalyst in the  $\text{AlH}_3\text{NH}_3$  and  $\text{AlH}_3\text{PH}_3$  systems. The  $\text{BH}_3$  and  $\text{AlH}_3$  are the efficient catalysts in the  $\text{BH}_3\text{NH}_3$  and  $\text{BH}_3\text{PH}_3$  systems, respectively. The lowest activation energies for hydrogen release from the  $\text{BH}_3\text{NH}_3$ ,  $\text{AlH}_3\text{NH}_3$ ,  $\text{BH}_3\text{PH}_3$  and  $\text{AlH}_3\text{PH}_3$  are 23.62, 24.52, 29.26 and 28.26 kcal/mol, respectively. In addition, the highest calculated rate constants for hydrogen release from the  $\text{BH}_3\text{NH}_3$ ,  $\text{AlH}_3\text{NH}_3$ ,  $\text{BH}_3\text{PH}_3$  and  $\text{AlH}_3\text{PH}_3$  are  $2.37 \times 10^{-5}$ ,  $6.87 \times 10^{-7}$ ,  $1.14 \times 10^{-9}$  and  $4.17 \times 10^{-9} \text{ s}^{-1}$ , respectively.

Field of study: Petrochemistry and Polymer Science Student's signature: Pornpan Chanapiwat

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Principal Advisor's signature: 

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**LIST OF ABBREVIATIONS AND SYMBOLS**

Å	Angstrom
<i>A</i>	Pre-exponential factor
ala	Alane amine
alp	Alane phosphine
B3LYP	Beck 3 Lee–Yang–Parr
ba	Borane amine
bp	Borane phosphine
<i>c</i>	Speed of light
DFT	Density functional theory
<i>E</i>	Energy
<i>G</i>	Gibbs free energy
<i>H</i>	Enthalpy
$\hat{H}$	Hamiltonian operator
HF	Hartree–Fock
<i>h</i>	Plank’s constant
IRC	Intrinsic reaction coordinate
<i>k</i>	Rate constant
$k_B$	Boltzman’s constant
<i>K</i>	Equilibrium constant
MP2	Second-order Møller–Plesset perturbation theory
MO	Molecular orbital
<i>q</i>	Partition function
$q_{rot}$	Rotational partition function
$q_{trans}$	Translational partition function
$q_{vib}$	Vibrational partition function
$q_{elect}$	Electronic partition function
<i>R</i>	Gas constant
<i>S</i>	Entropy
STO	Slater type orbital
<i>T</i>	Absolute temperature

TS	Transition state
TST	Transition state theory
ZPE	Zero point energy
$\psi$	Wave function
$\chi$	Mulliken electronegativity
$\kappa$	Kappa
$\sigma$	Rotational symmetry number of the molecule
$\nu_i$	Imaginary frequency