

CHAPTER III

DETAILS OF THE CALCULATIONS

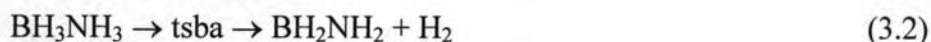
3.1 Computational method

All structures, geometries, vibrational frequencies and transition state (TS) were determined using Becke three parameters exchange functional combined the Lee, Yang and Parr correlation functional (B3LYP) and second-order perturbation theory (MP2) with the 6-311++G(d,p) basis set. The calculations were performed with the Gaussian 03 program [25]. The molecular graphics of all molecular structures were generated with the MOLEKEL 4.3 program [26].

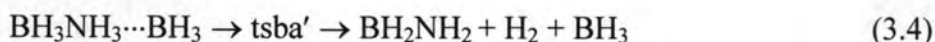
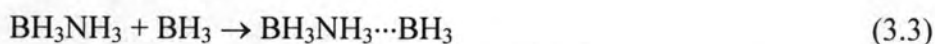
In this study, we use the quantum chemical method to predict the molecular mechanism of hydrogen release in the systems of borane amine [12-13], alane amine [14], borane phosphine and alane phosphine and the ability of borane, ammonia, alane and phosphine to serve as a catalyst for hydrogen release reaction. The B3LYP/6-311++G(d,p) optimized structures of studied molecules are shown in Figure 3.1. To ascertain the identity of the relevant transition structure (TS), intrinsic reaction coordinate (IRC) [28] calculations were also done at the same level. Mechanism of hydrogen release reactions of all studied compounds are listed as follows.

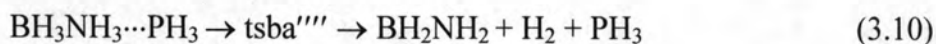
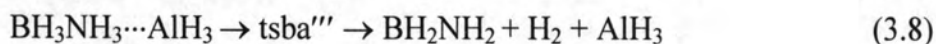
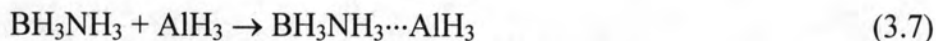
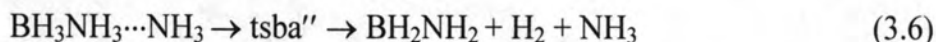
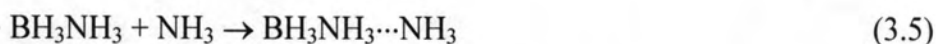
3.2 Synthetic and hydrogen release reactions of BH_3NH_3

System without catalyst:



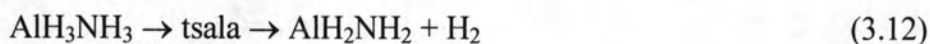
Systems with catalyst:



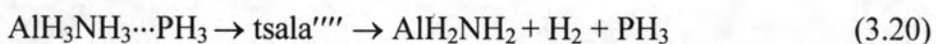
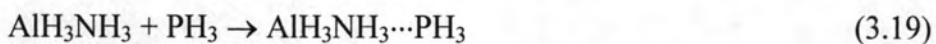
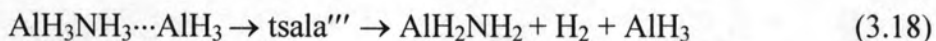
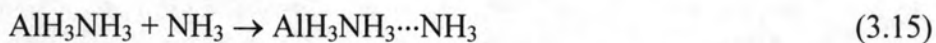
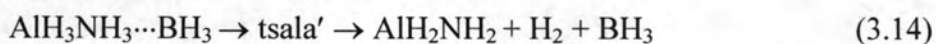
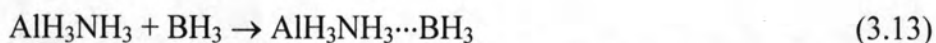


3.3 Synthetic and hydrogen release reactions of AlH_3NH_3

System without catalyst:



Systems with catalyst:

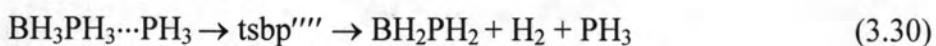
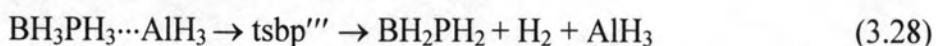
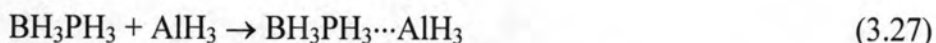
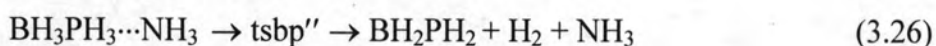
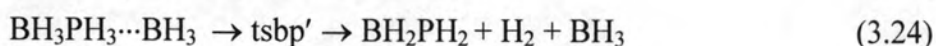


3.4 Synthetic and hydrogen release reactions of BH_3PH_3

System without catalyst:

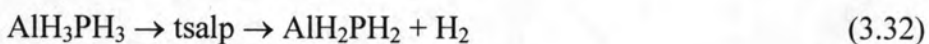


Systems with catalysts:

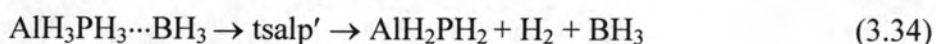
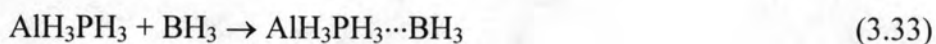


3.5 Synthetic and hydrogen release reactions of AlH_3PH_3

System without catalyst:



Systems with catalyst:



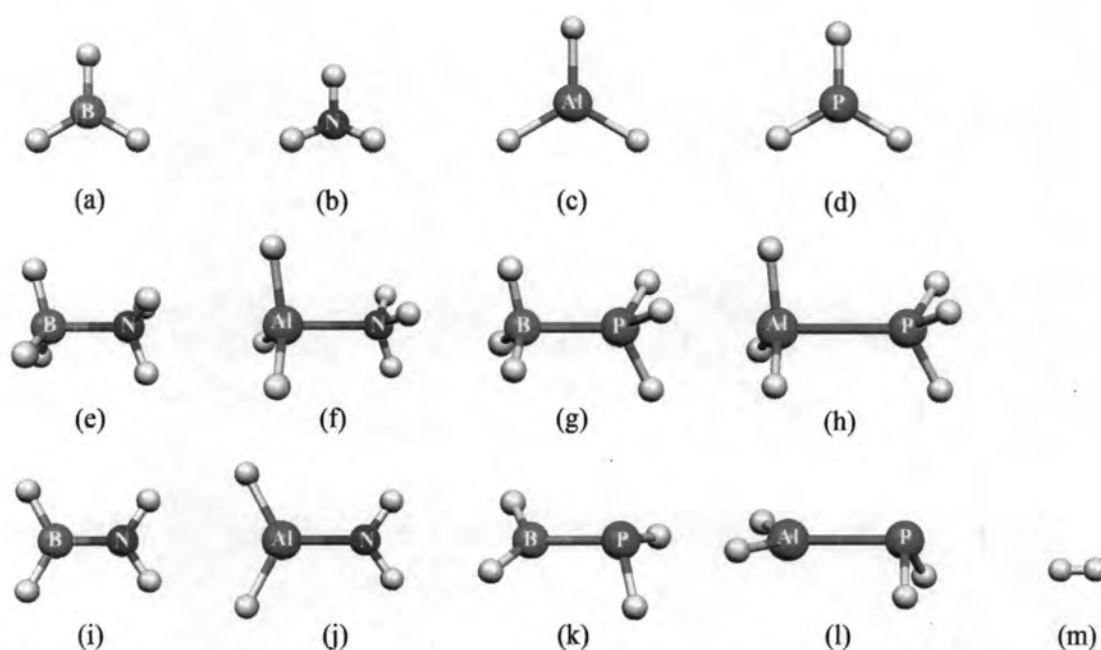
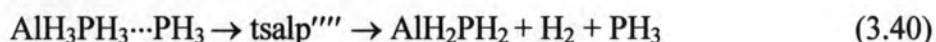
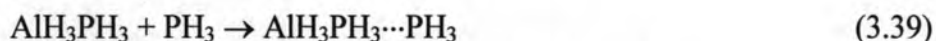
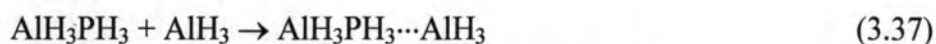
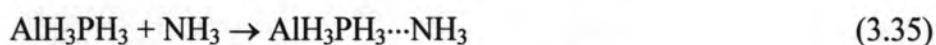


Figure 3.1 The reactant and product models: (a) BH_3 , (b) NH_3 , (c) AlH_3 , (d) PH_3 , (e) BH_3NH_3 , (f) AlH_3NH_3 , (g) BH_3PH_3 , (h) AlH_3PH_3 , (i) BH_2NH_2 , (j) AlH_2NH_2 , (k) BH_3PH_3 , (l) AlH_3PH_3 , (m) H_2 optimized with B3LYP/6-311++G(d,p).

3.6 Transition state and thermodynamic properties calculations

In this work, we have predicted the molecular mechanism of hydrogen release from borane amine, alane amine, borane phosphine and alane phosphine in systems without and with the borane, ammonia, alane and phosphine. Transition-state structures optimized at the B3LYP/6-311++G(d,p) and MP2/6-311++G(d,p) levels of

theory. Their thermodynamic properties were derived from the vibrational frequency calculations at their corresponding levels of theory. Frequency calculations were carried out to confirm the single imaginary mode for all transition-state structures.

3.6.1 Activation energies

The activation energy ($\Delta^\ddagger E$) is the energy difference between the reactants and the highest transition state barrier are shown in expression (3.41). In the catalysis reaction, the energy required to enter transition state decreases, thereby decreasing the energy required to initiate the reaction as shown in Figure 3.2.

$$\Delta^\ddagger E = E_{(TS)} - E_{(reactant)} \quad (3.41)$$

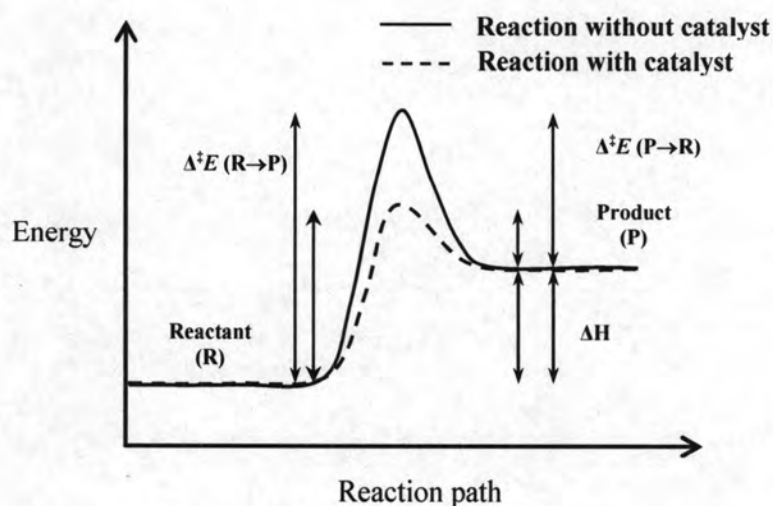


Figure 3.2 The relationship between activation energy ($\Delta^\ddagger E$) and enthalpy of reaction (ΔH) without and with a catalyst.

3.6.2 Rate constant and equilibrium constant

The rate constant $k(T)$, in term of partition function (Q) and equilibrium constant, K derived from transition state theory were calculated from activation free energy, $\Delta^\ddagger G^\circ$ by use of the following equation:

$$k(T) = \frac{k_B T}{hc^0} e^{-\Delta^\ddagger G^0 / RT} \quad (3.42)$$

$$k = \kappa \left[\frac{k_B T}{h} \right] \left[\frac{Q_{TS}}{Q_{Complex}} \right] e^{-\Delta^\ddagger E / RT} \quad (3.43)$$

$$k = \kappa A e^{-\Delta^\ddagger E / RT} \quad (3.44)$$

$$K = e^{-\Delta^\ddagger G / RT} \quad (3.45)$$

where $\kappa = 1 + (1/24)(h\nu_i c / k_B T)^2$, $A = (k_B T / h) / (Q_{TS} / Q_{Complex})$, k_B is Boltzman constant, T is absolute temperature, Q_{TS} and $Q_{Complex}$ are the partition functions of transition state and complex, respectively, h is Plank constant, c^0 is concentration factor, c is speed of light and ν_i is imaginary frequency of transition state.

3.6.3 Gibbs free energy and enthalpy

The energy difference between reactants and products is the enthalpy (ΔH) or the Gibbs free energy (ΔG) of the reaction as shown in equations (3.46) and (3.47). If the energy of the reactants is higher than the energy of the products, the reaction is exothermic. If the energy of the reactants is lower than the energy of the products, the reaction is endothermic.

$$\Delta H = H_{product} - H_{reactant} \quad (3.46)$$

$$\Delta G = G_{product} - G_{reactant} \quad (3.47)$$