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DFT and ab initio direct dynamics study on the reaction of H_2 loss reaction from H_2BNH_2

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Abstract

DFT and ab initio molecular orbital calculations are carried out for the H_2 loss reaction from aminoborane (H_2BNH_2). The geometries of all the stationary points are optimized at the B3LYP and MP2 methods with a series of basis sets up to aug-cc-pVTZ. The harmonic vibrational frequencies are calculated at the same level of theory. One transition state is found at the B3LYP/(aug-)cc-pVTZ and MP2/(aug-)cc-pVTZ level of theory. The energies and enthalpies are refined at the G3, G3MP2, G3MP2B3, CBS-Q, CBS-QB3, and HL methods based on the geometries optimized using B3LYP/aug-cc-pVTZ method. The rate constants are evaluated using the conventional transition-state theory (TST), canonical variational transition-state theory (CVT), and canonical variational transition-state theory with small curvature tunneling correction (CVT/SCT) and conventional transition-state theory with Eckart tunneling correction (TST/Eckart).

Keywords: Aminoborane; Iminoborane; Unimolecular decomposition; Ab initio calculation; Vibrational transition state theory; Rate constant

1. Introduction

Aminoborane, H_2BNH_2, the B–N analogue of ethylene was first detected in a mass spectrometric study [1] and formed in the thermal decomposition of H_3BNH_3 [2,3]. It has received extensive experimental [4–8] and theoretical attentions [9–13] due to its importance as a basic unit for complex aminoborane. Carpenter presented the infrared matrix isolation characterization of aminoborane [8]. Ha [9] calculated the equilibrium geometries, rotational constants and vibrational frequencies of aminoborane, diaminoborane and aminodifluoroborane with ab initio SCF method and he found that the appreciable amount of the double bond character existed these molecules. Then, Mo [12] and Minyaev [13] reported the reaction paths and the theoretical analysis for the internal rotation in aminoborane. Gerry [14] measured its high-resolution infrared spectrum. Briggs [15] determined the microwave spectrum, the molecular structure and the quadrupole coupling constants of H_2BNH_2. Komm [16] reported the preparation and characterization about poly(aminoborane). Recently, Suresh [17] studied the conjugation involving nitrogen lone-pair electrons of some boron–nitrogen compounds.

It has been shown that H_3BNH_3 can be a potential chemical hydrogen (H_2) storage medium for fuel cell and other applications [18] since its moderate decomposition temperatures, the exothermic character of the decomposition process and the relatively high hydrogen content. Recently, the H_2 release process of the H_3BNH_3 has been concerned by many experimental [3,18–22] studies. In 1985, Geanangel and Wendlandt [20] described the process of three stepwise hydrogen loss from H_3BNH_3 to BN by thermogravimetry (TG) and differential scanning calorimetry (DSC) technologies. And then, they suggested the thermal dissociation of H_3BNH_3 by differential thermal analysis (DTA) curves and better defined the chemical steps in

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the decomposition reaction of H_3BNH_3 [3]. Carpenter and Ault studied the pyrolysis of the adduct H_3BNH_3 and observed the evidence of H_2BNH_2 [23]. Quite recently, the thermally activated decomposition of ammonia–borane has been investigated by using combined thermoanalytical methods by Baitalow et al. [18,19], which indicated that H_3BNH_3 underwent stepwise thermal decomposition in the temperature range up to 500 K and the decomposition reaction is accompanied by hydrogen evolution. Wolf assumed that the monomeric aminoborane might be a reactive intermediate during the formation of borazine at the thermal decomposition of H_3BNH_3 [18,19]. Eventually borazine is formed from H_2BNH_2 via a dehydrogenation to the highly reactive monomeric iminoborane HBNH [24] and the trimerization of HBNH.

Thus it can be seen that the reaction of H_2 loss from H_2BNH_2 is an important step during the decomposition of H_3BNH_3. In order to provide detailed dynamics information on the reaction and obtain the rate constants over a wide temperature range of the hydrogen elimination from the H_2BNH_2, high-level ab initio calculation and rate constants calculation are still required. The aim of the present work is to perform a theoretical calculation on the reaction of $H_2BNH_2 \rightarrow HBNH + H_2$ to provide reliable results for the reaction enthalpy, reaction potential energy surface (PES) and the gas phase rate constant.

2. Methodology

2.1. Electronic structure calculations

The geometries and frequencies of all stationary points (reactants, products, and the transition state) are optimized at the B3LYP [25] and MP2 [26–28] methods of theory with (aug-)cc-pVDZ [29–31] and (aug-)cc-pVTZ basis sets [29]. To yield more reliable reaction enthalpy and barrier, the higher-level energies calculations for all stationary points are further performed with the G3 [32], G3MP2 [33], G3MP2B3 [34], CBS-Q [35], CBS-QB3 [36,37], and a combination method [38,39] (denoted as HL) based on the optimized geometries at the B3LYP/aug-cc-pVTZ levels of theory. Here, the method employ a combination of quadratic configuration interaction calculations with perturbative inclusion of the triplet contribution, QCISD(T) [40], and second-order Møller–Plesset perturbation theory (MP2) [26–28]. And he estimate the infinite basis set limit via the extrapolation of results obtained for sequences of the correlation-consistent polarized-valence basis sets. The higher-level estimate, E_{HL} is obtained as the sum of the QCISD(T) extrapolations. The combination of extrapolations can be expressed as [38]:

$$\begin{aligned} E_{\mathrm{HL}} = {} & E[\mathrm{QCISD}(T)/\mathrm{cc-pVTZ}] + \{E[\mathrm{QCISD}(T)/\mathrm{cc} \\ & -\mathrm{pVTZ}] - E[\mathrm{QCISD}(T)/\mathrm{cc-pVDZ}]\} \times 0.46286 \\ & + E[\mathrm{MP2/cc-pVQZ}] \end{aligned}$$

$$\begin{aligned} & + \{E[\mathrm{MP2/cc-pVQZ}] - E[\mathrm{MP2/cc-pVTZ}]\} \times 0.69377 \\ & + E[\mathrm{MP2/cc-pVTZ}] + \{E[\mathrm{MP2/cc-pVTZ}] \\ & - E[\mathrm{MP2/cc-pVDZ}]\} \times 0.46286 \end{aligned}$$

In order to reduce computation cost, the minimum energy path (MEP) is obtained using the intrinsic reaction coordinate (IRC) method [41] at the B3LYP/aug-cc-pVTZ levels of theory. In the calculation of rate

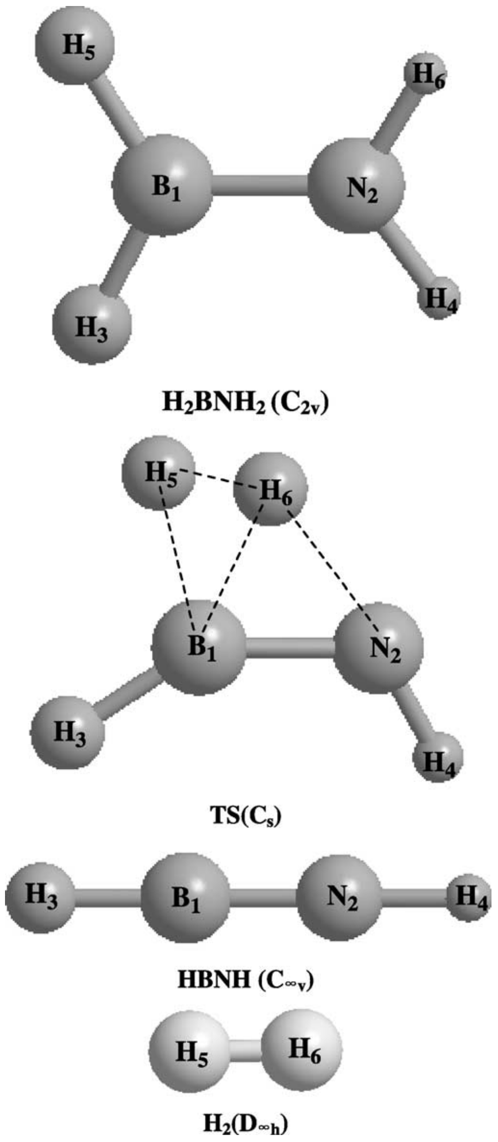

Fig. 1. Pictorial of optimized geometries of the stationary points.