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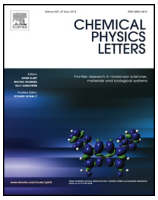

Borane and alane mediated hydrogen release from silane and methylsilane

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ABSTRACT

The dehydrogenations of silanes SiH_4 and CH_3SiH_3 in the presence of borane and alane were investigated using density functional (B3LYP) and coupled-cluster (CCSD(T)/aug-cc-pVnZ) theories. The calculated results showed that the hydrogen release reactions are more favorable in presence of BH_3. Our theoretical analyses have further revealed that the addition of an extra BH_3 can lead to several low energy barrier pathways. This observation is important to understand the catalytic role of BH_3 in such reactions (depending on its release mechanism). Overall, silane and its alkyl derivatives can be used as effective starting materials for H_2 production.

1. Introduction

Hydrogen is considered as the lightest, simplest, and cleanest alternative fuel for environment-friendly vehicles. However, efficient on-board storage of hydrogen remains a critical issue. Different strategies for hydrogen storage include conventional hydrogen storage in high-pressure tanks, hydrogen adsorption on materials with large surface areas, metal hydrides, complex hydrides, and chemical hydrogen storage (CHS) [1–5]. It is known that complex hydrides, which are complexes between more-covalent light-weight hydrides (e.g. BH_3 and AlH_3), with more-ionic hydrides (e.g. LiH and NaH) are good candidates for hydrogen storage [5–12]. However, these complex hydrides only release hydrogen at high temperature and high pressure conditions which are sometimes not suitable for practical usages. Milder conditions can be achieved by the CHS strategy, in which hydrogen is released (from hydrides, for instance) through various chemical reactions with minimal energy requirements. Dehydrogenation reaction of ammonia borane NH_3BH_3, for example, already occurs at the temperature range of ~80 to 130 °C [13], whereas the complex hydrides such as $LiAlH_4$ only decomposes to release H_2 at the temperature above 200 °C [5]. Therefore, the CHS could be considered as competitive alternative to other hydrogen storage systems.

The catalytic role of BH_3 and AlH_3 on the dehydrogenation barrier of several hydrides has been reported, and AlH_3 is slightly better in this respect [6,11]. H_2 release from BH_3NH_3 in the presence of BH_3 and AlH_3 are much more favorable with respect to the non-catalytic one due to the lower energy barriers (12.5 and 15.8 kcal/mol, respectively) [6,11]. BH_3 and AlH_3 are also known to induce a significant reduction in the dehydrogenation barriers of CH_3CH_3 (53.7 and 55.6 kcal/mol for the respective catalysts) [11].

High volatility of SiH_4 has made it an important gaseous precursor to generate various reactive species (like, SiH_3, SiH_2, etc.) through various chemical vapor deposition (CVD) techniques [14]. These reactions are important to deposit n-type active transistor layer with further processing [12]. SiH_4 is also used to generate boron-doped thin film (in the CVD process) through reactions with borane (BH_3), diborane (B_2H_6) and boron trichloride (BCl_3) [15,16]. SiH_4 has also importance in hydrogen storage and this property was investigated using high-level computational techniques to study the reactions between SiH_4 and BH_3/AlH_3 [9]. The results showed that BH_3 yields energetically favorable reaction channel during H_2 release from SiH_4.

In the present work, quantum chemical calculations are carried out to further investigate the role of BH_3/AlH_3 on the energetics and mechanisms of the hydrogen-release from SiH_4 and CH_3SiH_4. The catalytic effect of BH_3 is also explored for the reactions between SiH_4 and BH_3 in the presence of an extra BH_3 molecule.

2. Computational details

Density functional theory (DFT) [17] was used for geometry optimizations and vibrational analyses. The popular hybrid

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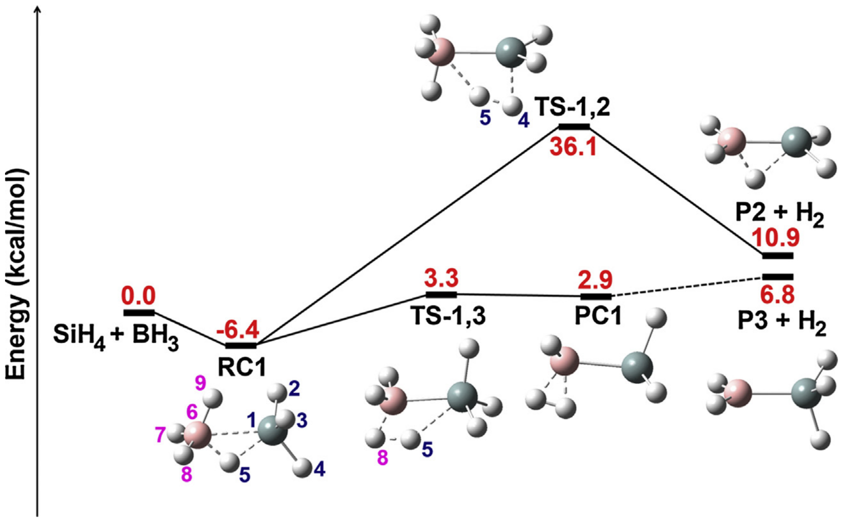

Figure 1. Schematic potential energy profile for the dehydrogenation from SiH_4 and BH_3. The labels of the hydrogen atoms connected to the Si and B atoms are indicated in dark blue and pink numbers, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

B3LYP exchange-correlation functional [18,19] was used in DFT calculations together with 6-311G(d,p) basis set. Single point electronic energy computations were performed using the coupled-cluster theory (including triple excitations, CCSD(T)) on the DFT-optimized structures to obtain more accurate energetics. Larger correlation consistent aug-cc-pVTZ (abbreviated as aVTZ) basis set of atoms was used in such calculations. Relative energies, reported in the manuscript, were calculated from these CCSD(T)/aVTZ energies and corrected for zero-point energies (ZPE) that were extracted from harmonic vibrational frequency calculations at the B3LYP/6-311G(d,p) level.

The computational strategy as discussed above has been gauged against the earlier results of computed geometries and interaction energies of the reactant complex **RC1** between SiH_4 and BH_3 (Figure 1) at the second-order Møller–Plesset perturbation level (MP2) [15,16]. In the present work these parameters were further computed using MP2/aVTZ, DFT/B3LYP/6-311(d,p) and CCSD(T)/aVTZ methods (Table S1 in the ESI). Single point CCSD(T)/aVTZ calculations were also carried out to compute the interaction energies using the optimized geometries from both MP2 and DFT/B3LYP methods and these interaction energies are corrected for basis set superposition (BSSE) error. The core electron correlation effects were further evaluated for the MP2 and CCSD(T) calculations. All the calculations were carried out using the GAUSSIAN 09 code [20].

For the complex **RC1**, the MP2 method yields the shortest bond distance while the DFT/B3LYP method yields the longest one (Table S1 in the ESI). The Si—B bond distance obtained from CCSD(T)/aVTZ calculation is slightly larger (by 0.02 Å) than that at the MP2 level. Inclusion the core-electron correlation into the MP2 calculation reduces the bond distance by 0.04 Å. This reduction is in agreement with the earlier results [16]. The effect of geometry change in different methods, on the other hand, has no marked effect on the computed interaction energies at the CCSD(T)/aVTZ level (Table S1 in the ESI). The same agreement is found for the interaction energies also (with ZPE corrections). In addition, the BSSE-corrected interaction energies of **RC1** at different levels of theory also show that the inclusion of the core-electron correlation is not necessary because it only results in larger BSSE values. The full-core and frozen core interaction energies are nearly equal after corrected for BSSE. These results thus justify the use of the computational strategy, as discussed above, to investigate the proposed H_2-eliminations reactions of SiH_4 and CH_3SiH_4.

Table 1
Interaction energies (ΔE), BSSE-corrected energies (ΔE^{BSSE}) and BSSE energies (kcal/mol) of different reactant complexes obtained at CCSD(T)/aVTZ level.

	$-\Delta E$	$-\Delta E^{\text{BSSE}}$	BSSE energies
RC1	6.4	5.5	1.1
RC4	3.8	3.4	0.4
RC7	9.0	7.9	1.1
RC10	8.0	7.0	1.0
RC12	6.0	5.5	0.5
RC14	18.1	15.5	2.6
RC16	12.6	10.9	1.7

The BSSE errors (of **RC1** and other reactant complexes) are calculated at CCSD(T)/aVTZ level using the counterpoise (CP) method [21] as implemented in GAUSSIAN 09 suite of program. The data listed in Table 1 show that the BSSE energies are in the range of 0.4–2.6 kcal/mol. Relatively large BSSE values are those of the reactant complexes between SiH_4 and 2 BH_3 molecules. Compared to the BSSE energy obtained with the same CCSD(T) method but smaller aVDZ basis set [15], the use of the larger aVTZ basis set significantly reduce the BSSE value for **RC1**, from 3 kcal/mol down to 1 kcal/mol.

3. Results and discussion

3.1. Reactions between SiH_4 and BH_3/AlH_3

The potential energy surface for the dehydrogenation of the reactant complex **RC1** is shown in Figure 1. The H^5 of SiH_4 (Figure 1) behaves as Lewis-base, while the B atom of BH_3 behaves as Lewis-acid. In the **RC1** complex they interact with each other ($B\cdots H^5$ interaction distance: 1.32 Å) through such acid–base interactions (similar to the previous report [9,15,16]). Because of this interaction, the Si^1—H^5 bond becomes much weaker as compared to the other Si—H bonds (bond distance elongation of >0.1 Å).

The removal of H^5 and H^8 atoms from **RC1** via **TS-1,3** has a small energy barrier (ΔE: 9.7 kcal/mol with respect to **RC1**) and yields a product complex **PC1** in which the H_2 molecule still attaches to the **P3** molecule. The structure of **PC1** is very similar to that of **TS-13** (cf., Figure 1). In addition, the natural charge distributions obtained from an NBO analysis (Table S2 of the ESI) also show a small change between the **TS-13** and **PC1**. These similarities result in the very small difference in their relative energies, being 0.4 kcal/mol. It