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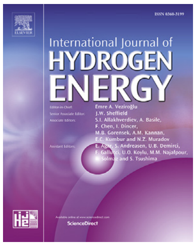

The mechanism of the chain-growth of ammoniaborane: A classic Lewis pairs catalysed by a Frustrated Lewis Pairs

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ABSTRACT

Ammonia borane (AB) is an outstanding hydrogen-storage material, which has been gained many attentions. It can be regenerated from polyborazylene based on the experimental study, but the uncontrollable B–N dehydro-coupling in the polymerization from AB to borazine is still a problem for the continuous application of AB. Frustrated Lewis Pairs (FLPs) is a landmark discovery to dissociate small molecules by activating strong nonpolar bonds reversibly, which is recently applied to directly polymerize three molecular AB to a cyclotriborazylene (CTB, $B_3N_3H_{12}$, which transforms into borazine after releasing 3 equiv. H_2). Here we analyse how a dimethylxanthene-derived FLPs catalyse AB to CTB. The cyclization experiences three steps by our calculation: the connection between FLPs and AB (1), the growth of B–N chain (2) and an intermolecular dehydrogenation between terminal N-$H^{\delta+}$ and $^{\delta-}$H–B (3), which gives us a clue of a possible reversibility of the dehydrogenation of AB and broadens the applicability of this concept in the relevant catalyst design.

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Introduction

Hydrogen energy resource is a kind of clean energy where hydrogen is stored in condensed materials by physisorption or chemisorption as atomic or ionic states [1,2]. Boron-nitrogen compounds always appear potential application in the field of the solid state hydrogen-storage materials. Ammonia borane (AB), with a molecular formula of H_3NBH_3, was a star compound in the area of hydrogen storage materials owing to its favourable stability and high hydrogen content (up to 19.5 wt%) [3–5]. Lots of people studied the decomposition pathway of AB and its derivate [6–8]. Dixon's results show –BH_3 group catalyse the dehydrogenation of AB very efficiently and decrease its energy gap of 6.1 kcal/mol after the formation of BH_3NH_3–BH_3 [9]. Based on the research of Shimoda and Fijalkowski, the major mechanism of decomposition is evolution of hydrogen by N-$H^{\delta+}$ … $^{\delta-}$H–B directly [10]. The strong dihydrogen bond also gives AB much higher volumetric density due to the classic intramolecular interaction between Lewis acid and Lewis base [11]. AB is proved to be regenerated from polyborazylene experimentally [12]. The redistribution of B–H bond of AB is demonstrated to be accomplished from

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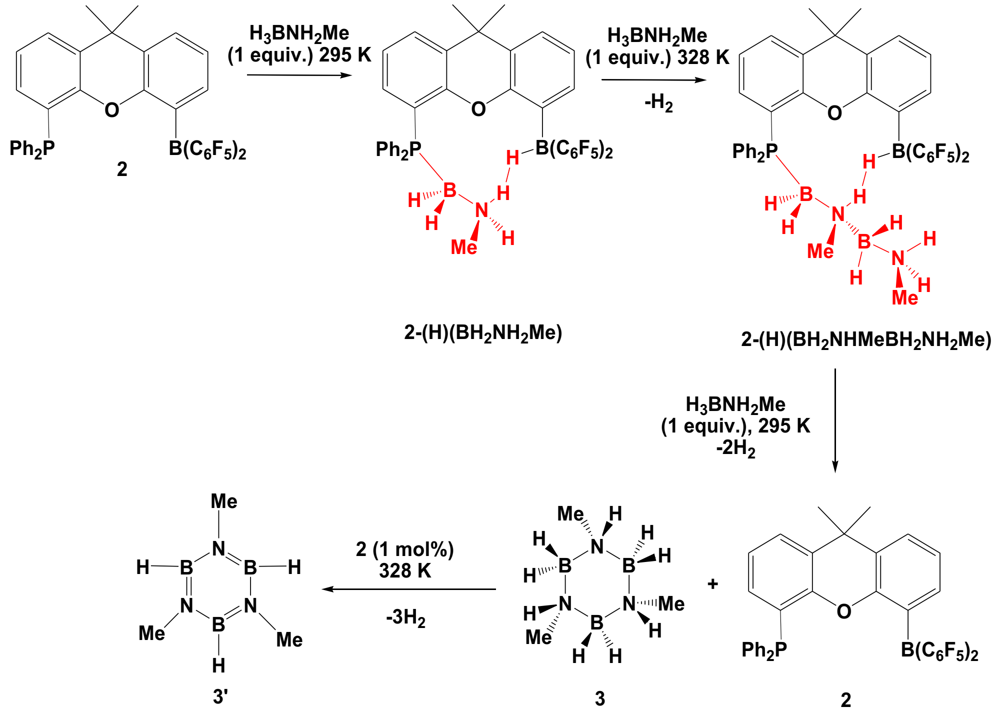
borazine theoretically [13]. Mckee and Nutt hypothesized a pathway to explain the cyclization of borazine from designed $NH_2BHNHBH_2$ and BH_2NH_2, where both the stepwise and synergetic pathway are based on the unsaturated bonds of B–N [14].

Here we hypothesize it is a key problem for the continuous application to avoid the spontaneous chaotic dehydrogenation in the oligomerization from AB to borazine. A lot of methods have been tried to solve the problem including tuning the characters of the dehydrocoupled products on the basis of Brønsted and Lewis theory [15,16]. Frustrated Lewis pairs (FLPs) is discovered by Stephen and Erker based on the Lewis acid-base theory [17–19]. The cooperative reactivities of Lewis acid and Lewis Base in FLPs are usually based on the steric hindrance in one molecule (or in two molecular fragments). The ultra-high activity is usually applied to activate small molecules, such as splitting H–H bond heterolytically [20–22]. Based on such characters, FLPs can be an excellent catalyst for the activation of the B–H (or N–H) bond of AB, which is just the key step for the dehydrogenation of AB.

Recently, a metal-free Frustrated Lewis Pairs (FLPs) show success in catalysing the cyclization of three molecular NH_2MeBH_3 to form a cyclic triborazane under a quite mild condition in Aldridge's experiments (showed in Scheme 1) [23,24]. From the cyclized products (**3** or **3′** in Scheme 1), it is possible to realize reversible formation of AB [13]. It is a clue for us to design a similar pathway for the generation of pure borazine from AB for the continuous regeneration, with avoiding the strong B–N coupling in the cyclization [25]. In this paper, we obtain the mechanism of the BN chain-growth and cyclization pathway from AB catalysed by dimethylxanthene-derived FLPs on the basis of Aldridge's experiments [23]. We also analyse the possible reversibility of each step in the process of cyclization.

Computational methods

The detailed mechanism of the cyclization catalysed by FLPs is predicted by using the gradient-corrected density functional theory with dunning basis set (M062x/cc-pVTZ) [26,27]. The reactions containing ions were calculated under the theoretical level of M062x/6–311++G(d,p). In order to simplify the model to accelerate the calculation, we substitute the $-CH_3$ and $-C_6F_5$ in the experimental structure [22] to –H and $-CF_3$ respectively. The optimized structures and the corresponding coordinates are provided in the supporting information (Section S1 and S3). We explain the complete catalytic process from the first B–H activation of AB to the formation of CTB including the possible four processes of B–N chain-growth. We confirmed all the transition states by applying the intrinsic reaction coordination (IRC) method. The parallel calculations performed by Møller-plesset perturbation theory (mp2/6–311++G(d,p)). The comparison of the total energy for each compound has been listed in the supporting information (Section S2 of SI). The results from both the two methods appear the same tendencies, which indicate our calculations are reasonable. The designed pathways are showed in Fig. 1. The enthalpies of each reaction under the same theoretical level are listed in supporting information (Table S1). We list the electronic enthalpies, Gibbs Free energies and Zero point energies (ZPE) of the stationary points and transition states including all the imaginary frequency of each transition state (Table S3).



Scheme 1 – The cyclization from Methyl substituted amine borane (NH_2MeBH_3) to cyclic triborazane (3) catalysed by dimethylxanthene-based FLPs (2) in Aldridge's experiments [23].

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