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Concerted Dehydrogenation

Breaking the Myth of the Recalcitrant Chemisorbed Hydrogens on Boron Niride Nanotubes: A Theoretical Perspective**

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Hydrogen storage has emerged as one of the foremost challenges in the pursuit of a hydrogen-based renewable energy economy.[1] Ammonia borane (AB) is being investigated intensely for its potential to develop into a chemical hydrogen storage media[2] because of its high gravimetric capacity of hydrogen (19.6 wt %) and low molecular weight (30.7 $g\,mol^{-1}$). In the last few years several catalysts have been devised by experimentalists that are known to effectuate release of hydrogen from AB at controlled temperature.[2,3] However, hydrogenation of the spent fuel generated from dehydrogenation of AB is burdened with many obstacles.[2] In recent times there has been considerable progress in recovering AB from spent fuel but sustainability is still a question which plagues chemical hydrogen storage through AB.[4]

Other related materials, also based on B and N atoms, which have been implicated as a potential hydrogen storage media are boron nitride nanotubes (BNNTs).[5–9] BNNTs are multi-walled or single-walled nanounits which have networks of BN hexagons layered in cylindrical geometry, analogous to carbon nanotubes (CNTs) and are isostructural and isoelectronic with graphite.[9] BNNTS are profoundly interesting in terms of both physical and chemical properties which distinguish them from their carbon counterparts.[8,9] It is significant that despite of their chemical and thermal stabilities, unlike CNTs BNNTs can chemisorb hydrogen under milder conditions.[5–7] Ma et al. were the first to demonstrate that multi-walled bamboolike BNNT samples could store hydrogen up to 2.6 wt % at room temperature.[5] Furthermore it was realized that hydrogen was retained in the BN nanostructures mostly in chemisorbed form. Subsequently, Tang et al. discovered that collapsed BNNTs store hydrogen upto 4.2 wt % at room temperature.[6] Moreover, Chen et al. were able to chemisorb hydrogen on BNNTs through electrochemical routes.[10] Theoretical studies have suggested the capability of BNNTs to chemically adsorb H atoms favorably up to 50 % coverage in an *exo*-hydrogenated fashion in zigzag (8,0) and (10,0) BNNTs which correspond to 4 wt % storage.[11] However, experiments showed that chemisorbed hydrogen is released on heating the hydrogenated BN nanotubes above 350–450 °C[5–8] suggesting the existence of strong B−H and N−H bonds. The deep kinetic trap for the chemisorbed hydrogen atoms on BNNTs is also supported by periodic density functional studies. If the chemisorbed hydrogen can be released at ambient temperatures then BNNTs could become a viable media for hydrogen storage.

Of late there has been renewed interest in use of carbon materials like graphene and single-walled nanotubes for hydrogen storage through chemisorption.[12] Hydrogenation of graphene and CNTs have been achieved by using atomic hydrogen and Birch reduction.[12,13] On heating the hydrogenated graphene or CNTs, desorption of dihydrogen initiates at temperatures above 500 °C for graphane and 350 °C for hydrogneated CNTs. X-ray absorption fine structure (XAFS) studies show that the parent structure of these materials are restored on desorption of hydrogen.[12] The high desorption temperatures have established the notion of an energy-intensive dehydrogenation process and have become a stumbling block in realization of viable hydrogen storage in carbon- and BN-based nanomaterials. Though there are numerous theoretical studies on hydrogen chemisorption on BNNTS and BN fullerenes and corresponding metal-decorated analogs and changes in magnetic and electronic properties of hydrogenated BNNTs,[14] none has focused on the feasibility of low-temperature removal or release of hydrogen atoms through dehydrocoupling/dehydrogenation from hydrogenated BNNTs, which indeed is a challenging prospect. Can the dihydrogen molecules be released at room temperature to moderately elevated temperatures from hydrogenated BNNTs? The secret lies in low-barrier dehydrocoupling processes, which are integral steps for catalytic release of dihydrogen from such materials.

We propose here to explore the consequences of the hypothesis that hydrogenated BNNTs (HBNNTs) and hydrogenated BN fullerenes are likely to be chemically equivalent to ammonia borane or generally to amine boranes. Our quantum chemical studies demystify the chemical signatures of chemisorbed hydrogen atoms on BNNTs and BN fullerenes and discloses the unique trait that optimal proton and hydride acceptors can induce concerted dehydrocoupling/dehydrogenation of chemisorbed hydrogen atoms on BN nanotubes and fullerenes at low activation barriers surmountable at room temperatures (Figure 1).

Experimental and theoretical studies have shown that the hydrogen atoms on AB are distinctively bipolar, where the hydridic and protic characters are displayed by the B−H and N−H hydrogen atoms, respectively. This unique attribute is exploited to release H_2 from AB or dehydrogenate AB by

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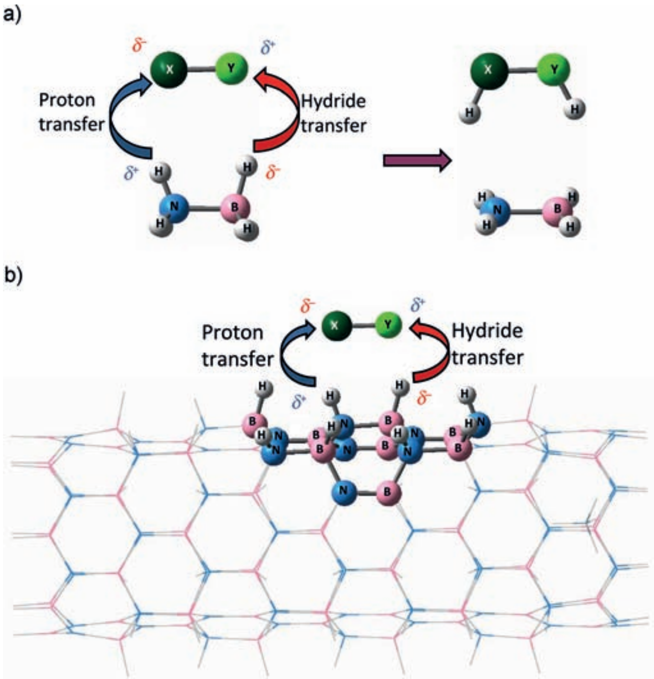

Figure 1. Concerted proton and hydride transfer from a) AB and b) hydrogenated BNNT (chemisorbed hydrogens on BNNT) to a bifunctional substrate.

diverse catalysts and reagents.[3] Interestingly the neighboring or geminal presence of the bifunctional property of protic and hydridic acceptance in a molecule can trigger dehydrocoupling/dehydrogenation of AB at low activation barriers involving concerted proton and hydride transfer from AB to the reagent forming NH_2BH_2 in a single step (Figure 1) through five- or six-membered transition states.[15] Similar dehydrocoupling reactions if viable for hydrogenated BN nanomaterials would imply that chemisorbed H_2 molecules can be released at ambient temperatures by the use of suitable catalysts.

The hybrid functional, B3LYP is employed to optimize the molecular geometries for all relevant intermediates and transition states in conjunction with Pople's basis sets. Single-point gas-phase computations are carried out using M05-2X, M06-2X and ωB97x-D functionals[16] employing 6-31++G(d, p) basis functions on the atoms which are directly involved in the reaction and on those directly in the vicinity of the reaction centers and 6-31G(d, p) on the rest of the atoms. The CPCM model is employed to compute single-point energies with THF as solvent.[17] The ensuing text discusses activation barriers computed with M05-2X, until and unless mentioned otherwise.

Natural bond orbital (NBO) charge analysis and molecular electrostatic potential (MEP) plot ascertained the protic and hydridic character of N−H and B−H hydrogen atoms on a 50 % hydrogenated (8,0) zigzag BNNT of approximate 2 nm in length.[17] The presence of heteropolarity on B−H and N−H hydrogen atoms suggests that chemisorbed hydrogen atoms on BNNTs can chemically emulate those on AB or in general amine boranes. This underlying premise was put to test with a range of molecules, a 50 % hydrogenated zigzag BNNT (with hydrogen capping at the ends) of (8,0) chirality of approximate lengths of around 1 nm and around 2 nm (hereafter referred to as 1-HBNNT and 2-HBNNT, respectively), fully hydrogenated BN fullerenes, $B_{16}N_{16}H_{32}$ and $B_{12}N_{12}H_{24}$,[14] and an armchair (3,3) H-terminated BNNT with 50 % chemisorbed hydrogens of 1 nm length[17] with hydrogen capping at the ends, taking three different reagents which have been predicted to undergo reactions with AB through acceptance of a proton and a hydride. For the nanotube models dehydrogenation was studied for a saturated BN bond in the middle of a tube (along the tube axis).

N-heterocyclic Enders' carbene (NHC) is an ideal choice as a test reagent as it has the distinctive bifunctional trait of acting as proton and hydride acceptor by the virtue of geminal presence of a lone pair and a low lying unoccupied orbital on the carbene carbon atom. Smaller carbenes are expected to interact with BNNTs or CNTs[18] but the NHC interacts much less favorably with the pristine BNNTs as compared to that of CH_2 because of enhanced steric encumbrance. No minimum is identifiable on optimization, which corresponds to a cycloaddition product of a carbene along a BN bond in BNNT for NHC reacting with a pristine (8,0) BNNT. However, for CH_2 interacting with BNNT we obtained a minimum which is a cycloaddition product along a BN bond. Another minimum corresponding to an adduct between the NHC carbene carbon and a boron atom on pristine BNNT was obtained, the formation of which is predicted to be slightly endothermic and endergonic. The NHC does not form cycloaddition adducts with 1-HBNNT or 2-HBNNT. However, a physisorbed state is observed for the NHC interacting with 2-HBNNT. Earlier it has been shown theoretically that NHC does interact with AB and can dehydrogenate AB through a concerted pathway.[15c] A transition state ($\mathrm{TS}^{\mathrm{NHC\text{-}2HBNNT}}$) for the concerted transfer of proton and hydride from the hydrogenated nanotube is identified for 2-HBNNT (Figure 2) with an imaginary frequency of $i678\ \mathrm{cm}^{-1}$. Similar transition states are obtained for 1-HBNNT, $B_{16}N_{16}H_{32}$, and $B_{12}N_{12}H_{24}$. The optimized interatomic distances between the carbene carbon, the protic and the hydridic hydrogen atoms, and the B and N atoms of $\mathrm{TS}^{\mathrm{NHC\text{-}2HBNNT}}$ at B3LYP level of theory show very similar bond distances as observed for those in the TS for simultaneous dehydrocoupling in AB with NHC.[15c] The gas-phase zero-point corrected total energy barrier, $\Delta E^{\neq}(\mathrm{g})_{\mathrm{M05\text{-}2X}}$ for concerted dehydrocoupling from 2-HBNNT is predicted to be $9.7\ \mathrm{kcal\,mol^{-1}}$, which is $4.9\ \mathrm{kcal\,mol^{-1}}$ lower compared to that of dehydrocoupling of AB by NHC. For 1-HBNNT the corresponding $\Delta E^{\neq}(\mathrm{g})_{\mathrm{M05\text{-}2X}}$ is predicted to be only $9.6\ \mathrm{kcal\,mol^{-1}}$. However, the entropic costs for bimolecular reactions are significantly high in the gas phase as the transition state through which a bimolecular reaction propagates is an unimolecular entity. The Gibbs free-energy of the activation barrier, $\Delta G^{\neq}(\mathrm{g})_{\mathrm{M05\text{-}2x}}$, is estimated to be $15.4\ \mathrm{kcal\,mol^{-1}}$. Alternatively, in the solvent phase the entropic costs for a bimolecular reaction are significantly lower than in the gas phase because of the considerable quenching in translational and rotational entropies of the participating entities. This in turn drives down the free-energy of the activation barrier. Necessary adjustments to the gas-phase thermodynamic corrections are incorporated for computing the free-energy

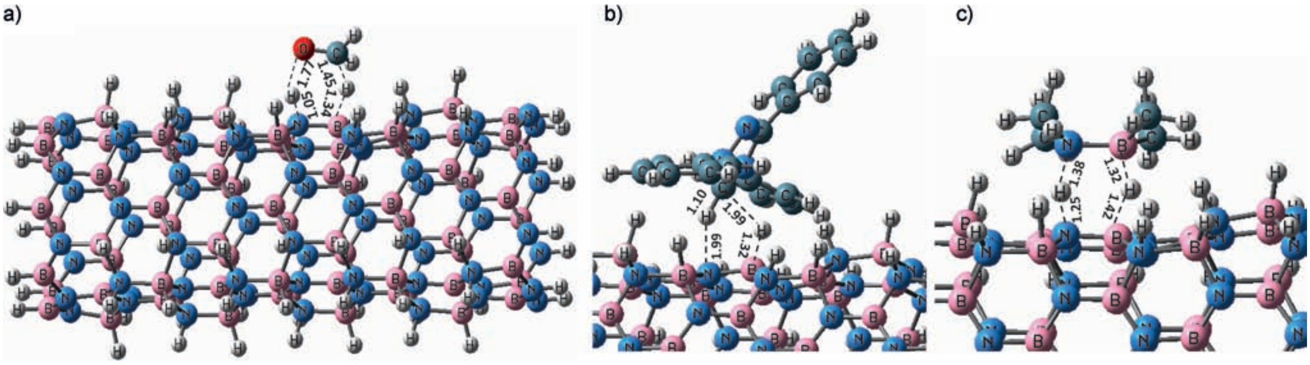

Figure 2. a) Optimized geometry of the transition state of 2-HBNNT with formaldehyde. Partial view of the optimized geometries of the transition state of 2-HBNNT with b) NHC and c) NMe_2BMe_2. (Full optimized geometries are present in the Supporting Information).

of activation in the solution phase following Wertz and others.[17,19] Though the solubility trends of hydrogenated nanotubes are not known, we expect that hydrogenation of BNNTs would make them soluble in THF as most of the hydrogenated BN materials are soluble in THF. Additionally, it is known that BNNTs can be dissolved in many different organic solvents after covalent functionalization.[20] Continuum solvent models are also employed to study heterogeneous chemical phenomena.[21] For truncated systems the CPCM model is expected to give reliable estimates. The solvent-phase free-energy of the activation barrier, $\Delta G^{\neq}(s)_{\text{SPC-M05-2X}}$, where the SPC suffix denotes the solvent-phase entropic correction, is predicted to be 10.1 kcal mol^{-1} for 2-HBNNT (Figure 3). However, the $\Delta G^{\neq}(s)_{\text{SPC-M05-2X}}$ for 1-HBNNT reacting with NHC turns out to be 20.2 kcal mol^{-1}. The difference may arise because of subtle variations in the geometry of the respective transition states.[17] The calculated barriers are expected to be surmountable at room temperature and pressure. This finding unambiguously suggests that properly equipped reagents can elicit dehydrocoupling in chemisorbed hydrogen atoms on BNNTs and casts doubt on the assumed insurmountable kinetic trap at room temperature.

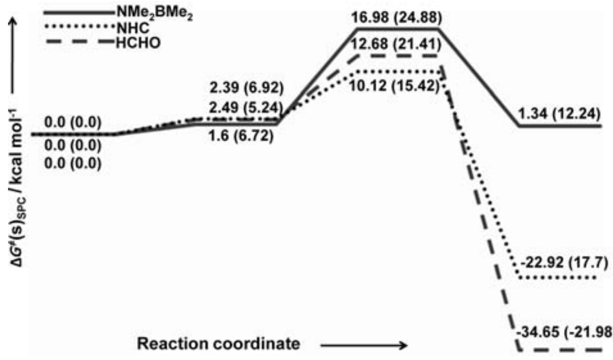

Figure 3. Solvent-phase corrected free-energy profile diagram for 2-HBNNT with NMe_2BMe_2, NHC, and HCHO. The corresponding gas-phase values are given in parentheses.

As CNTs and graphene are being intensely investigated as media for hydrogen storage through chemisorption,[13] the barrier for abstraction of hydrogen by an NHC from a 50% hydrogenated (8,0) analogous CNT has also been examined. The predicted $\Delta E^{\neq}(g)_{\text{M05-2X}}$ is 46.2 kcal mol^{-1} for this reaction, which is prohibitively high. Indeed the chemisorbed hydrogen atoms on hydrogenated CNTs are "recalcitrant". Nevertheless, the computed $\Delta E^{\neq}(g)_{\text{M05-2X}}$ of abstraction of hydrogen atoms from ethane (which is isoelectronic to AB) is predicted to be 55.0 kcal mol^{-1}. The much higher barrier of abstraction of hydrogen atoms by NHC of chemisorbed hydrogen from CNTS as compared to those on BNNTs certainly suggests that chemisorbed hydrogen atoms on CNTs are more robustly kinetically trapped than those on BNNTs. The stronger kinetic barrier is because of the difficulty of C−H activation. Hence, as a hydrogen storage material, BNNTs are plausibly more attractive species than CNTs. Certainly the comparison for catalytic dehydrogenation of AB to ethane can be extended for the case of chemisorbed hydrogen atoms on BNNTs to those on CNTs.[15a]

To investigate whether the vulnerability to dehydrocoupling is a more universal property for chemisorbed hydrogen on BNNTs, it is examined if proton and hydride can be transferred to a bifunctional acceptor of hydride and proton, NH_2BH_2. NH_2BH_2 is a very reactive species, as it oligomerizes to $(NH_2BH_2)_n$ oligomers rapidly.[2] However, theoretically it has been shown by Zimmerman et al. that a competing identity reaction between AB and NH_2BH_2 can operate which propagates through the intriguing simultaneous proton and hydride transfer.[15d] Moreover, Manners and co-workers have recently provided experimental evidence that aminoboranes can indeed abstract hydrogen from amine boranes.[22] This identity reaction provided the motivation to investigate if exchange of proton and hydride transfer can happen between hydrogenated BNNT and NH_2BH_2. Transition states have been identified for concomitant transfer of proton and hydride from 1-HBNNT, 2-HBNNT, and (3,3)-HBNNT. For 1-HBNNT the total energy activation barrier, $\Delta E^{\neq}(g)_{\text{M05-2X}}$ is predicted to be 11.7 kcal mol^{-1}. The optimized geometry of the TS for 1-HBNNT exhibits partially cleaved B−H and N−H bonds of the 1-HBNNT and developing B−H and N−H bonds with the reactant NH_2BH_2 species.[17] The corresponding barrier in the identity reaction between NH_2BH_2 and AB is predicted to be 7.5 kcal mol^{-1}. Additionally, the possibility of using a similar reaction to devise a transfer catalyst is explored. It is hypothesized that a NR_2BR_2 (R = alkyl) species which does not oligomerize or dimerize unlike NH_2BH_2 and NMe_2BH_2 can be potentially employed as a transfer catalyst for dehydrogenation of hydrogenated BN nanostructures and fullerenes. The NR_2BR_2 species can abstract hydrogen atoms from the hydrogenated BN framework through a similar concerted pathway (see Figure 2) and gets converted to NR_2HBR_2H, which can be dehydrogenated using a less sterically hindered dehydrogenation catalyst for AB or amine boranes.[3b] Interestingly it is found that NMe_2BMe_2 is a species for which dimerization and trimerization is thermodynamically and kinetically unfavorable in the gas phase.[17] Formation of the dimer or higher oligomers is not favored because of the increased steric requirement at the N and B centers. However, in THF the monomeric form is expected to be in equilibrium with the cyclic dimer.[17] The overall $\Delta E^{\ddagger}(g)_{M05\text{-}2X}$ for the dehydrogenation of 2-HBNNT by NMe_2BMe_2, is predicted to be 19.7 kcal mol^{-1}.[17] The corresponding barrier for 1-HBNNT reacting with NMe_2BMe_2 turns out to be 17.2 kcal mol^{-1}. The $\Delta G^{\ddagger}(g)_{M05\text{-}2x}$ for 2-HBNNT is found to be 24.9 kcal mol^{-1}. The dispersion-corrected ωB97x-D functional predicts a lower $\Delta G^{\ddagger}(g)_{\omega B97x\text{-}D}$ for abstraction of hydrogen by NMe_2BMe_2 from 2-HBNNT, 1-HBNNT, $B_{16}N_{16}H_{32}$, and $B_{12}N_{12}H_{24}$ which are as follows: 17.4, 17.7, 25.0, and 25.2 kcal mol^{-1}. The corresponding $\Delta G^{\ddagger}(g)_{M06\text{-}2X}$ estimates computed with M06-2X are 20.8, 24.2, 28.9, 24.7 kcal mol^{-1}. It is observed that for the abstraction of hydrogen atoms by NMe_2BMe_2 from hydrogenated BN materials the predicted free-energy barriers follow the trend: ωB97x-D < M06-2X < M05-2X. Hence, it appears that the functional which is more well-equipped to account for dispersion corrections, predicts lower barriers for this dehydrocoupling process. The corresponding solvent-phase free-energy activation barrier, $\Delta G^{\ddagger}(s)_{SPC\text{-}M05\text{-}2X}$, is estimated to be 17.0 and 23.1 kcal mol^{-1} for 2-HBNNT (Figure 3) and 1-HBNNT, respectively. The predicted barriers suggest that appreciable rates are likely to be observed for this reaction with (8,0) BNNT in THF from room temperature to moderately elevated temperatures (50 °C–70 °C). The free-energy change, $\Delta G(s)_{SPC\text{-}M05\text{-}2X}$, for the forward reaction in Equation (1)

$$NMe_2BMe_2 + 2\text{-HBNNT} \rightarrow NMe_2HBMe_2H + (2\text{-HBNNT})\text{-}H_2 \quad (1)$$

is 1.3 kcal mol^{-1}, which is very close to zero. Hence, in THF it is likely that NMe_2BMe_2 can act as a fairly efficient dehydrogenation transfer catalyst.[17] However, in THF the $\Delta G(s)_{SPC\text{-}M05\text{-}2X}$ for the equivalent reaction of NMe_2BMe_2 with $B_{12}N_{12}H_{24}$ and $B_{16}N_{16}H_{32}$ is predicted to be higher, with the estimates being 10 and 17.1 kcal mol^{-1}, respectively. The transfer catalyst is not likely to be that effective for the BN fullerenes, as the backward reaction is significantly more favorable. Such transfer catalysis can also be elicited by using $i\mathrm{Pr}_2N{=}BH_2$, a model aminoborane, which has been discovered recently.[22]

NHC and NH_2BH_2 are both very reactive species, but formaldehyde is a stable entity, which again shares their unique bifunctional trait. Ammine boranes are known to hydrogenate aldehydes and ketones.[23] Theoretical studies on AB reacting with HCHO had previously shown that a concerted hydrogenation pathway can exist. In concert with our earlier findings TSs are located for coincident proton and hydride transfer from hydrogenated nanotubes and fullerenes to HCHO, and these TSs (see Figure 2) correspond to the dehydrogenation of a hydrogenated BN bond in the corresponding hydrogenated BNNTs or fullerenes by HCHO leading to the formation of methanol. The predicted total energy barriers are found to be reasonably low for all the species examined. For instance, the $\Delta E^{\ddagger}(g)_{M05\text{-}2x}$ is estimated to be 13.9 kcal mol^{-1} for the dehydrogenation of 2-HBNNT by HCHO. For 1-HBNNT the $\Delta E^{\ddagger}(g)_{M05\text{-}2x}$ turns out to be 13.2 kcal mol^{-1}. For 2-HBNNT the $\Delta G^{\ddagger}(g)_{M05\text{-}2x}$ is only 21.4 kcal mol^{-1}. The corresponding gas-phase free-energy barrier for activation computed with the dispersion-corrected ωB97x-D functional is predicted to be 14.4 kcal mol^{-1} and the same with Truhlar's M06-2X variant is 21.0 kcal mol^{-1}. In THF solvent the $\Delta E^{\ddagger}(s)_{M05\text{-}2x}$ for 2-HBNNT and 1-HBNNT are as follows: 10.3 and 10.7 kcal mol^{-1}. All the hydrogenation reactions of formaldehyde investigated in this work are exothermic.[17] For 2-HBNNT and 1-HBNNT the $\Delta G^{\ddagger}(s)_{SPC\text{-}M05\text{-}2x}$ values are 12.7 and 15.2 kcal mol^{-1} (Figure 3), respectively. Low-barrier concomitant proton and hydride transfer to a bifunctional substrate is a general property of chemisorbed hydrogen atoms on BNNTs of different chirality and curvature. For instance, with the (3,3)-HBNNT model the $\Delta G^{\ddagger}(s)_{SPC\text{-}M05\text{-}2x}$ is 6.7 kcal mol^{-1} for the reduction of formaldehyde. The theoretical exploratory study certainly suggests that formaldehyde is reduced to methanol through a concerted transfer of a hydride ion and a proton ion from the HBNNT surface at an appreciable rate under moderate conditions in the gas phase. Significant reaction rates are expected for the same reaction in THF at room temperature and pressure. The present quantum mechanical study envisages a unique and intriguing possibility that chemisorbed hydrogen on BN nanotubes can reduce formaldehyde to methanol, a hydrogenation reaction occurring under ambient to moderate reaction conditions without the use of any metal catalyst. At 5–6 MPa applied pressure and significant room-temperature chemisorption of hydrogen is observed in collapsed BN nanotubes.[6] This chemisorbed hydrogen can plausibly reduce formaldehyde to methanol. Remarkably, the current findings suggest that BN nanotubes (a molecular species without transition metals) can potentially be used as a hydrogenation catalyst to convert formaldehyde to methanol at room temperature and at pressures which are prevalent for hydrogenation processes. All the known processes for such a transformation employ heterolytic or homolytic transition metal catalysis.[24]

Our computational study unearths the untapped reactive traits of chemisorbed hydrogen atoms on BN nanotubes and fullerenes. Behind the adamant reluctance to thermal desorption of dihydrogen from the chemisorbed state of hydrogen molecules on BN nanostructures we unfurl a vulnerability, which mimics the behavior of hydrogen atoms in AB and can be exploited to chemically desorb hydrogen at room temperature to moderate temperatures from BN nanotubes and fullerenes.

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