Molecular hydrogen assisted transport of H atoms

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Transport of hydrogen atoms plays a key role in chemical and biological processes involving metabolism of molecular hydrogen. Several ‘gas-phase’ and more intricate organometallic models (mimics of the hydrogenase enzyme) are developed to show the intriguing role of the molecular hydrogen as a third party in the pass-on transfer of hydrogen atoms. This hydrogen assisted transport (HAT) mechanism is based on the current understanding of the hydrogen exchange reactions and it is believed to be applicable to certain H/D-isotope exchange processes and remote transport of H-atoms.

1. Introduction

Hydrogen atom transfer is one of the main concerns in the chemical and biological processes involving metabolism of molecular hydrogen. It is most essential in the storage of hydrogen [1–6] and the enzymatic catalysis [7–18]. The H/D-isotope exchange based on H-atom transfer is a potent experimental tool in identifying unknown reaction mechanisms, yet many elementary processes remain unknown, especially those in solid state and on heterosurfaces. Little is known about the role of molecular hydrogen itself in enzymatic processes.

Recently, a comprehensive potential energy surface for hydrazine, N2H4, has been developed in a collaborative effort [14] at the CCSD(T)/CBS and CBS-QB3 levels of theory to uncover chemical activation reactions of amidogen radicals (NH2), which reveals particularly a novel, assisted by molecular hydrogen, stereoselective reaction pathway (Eq. (1)). This reaction is important due to its association with the gas-phase decomposition of cis-diazene (cis-N2H2), the key intermediate in N2-fixation (enzymatic reduction) and heterogeneous catalytic transformations of elemental nitrogen and hydrogen. Remarkably, H2 inhibits the enzymatic turnover cycle of N2H2 and N2, while it does not affect N2H4, which is not yet explained properly [10–12,18].

The reaction (1) can be regarded as the simplest symmetric-synchronous double H-atom abstraction reaction from a diazene-like substrate [14].

\[
\begin{align*}
\text{D} + \text{H}_2\text{N} & \rightarrow \text{D} \cdots \text{H} \cdots \text{H} \cdots \text{N} \\
\text{D} + \text{H}_2\text{N} & \rightarrow \text{D} \cdots \text{H} \cdots \text{H} \cdots \text{N} \\
\text{net:} & \\
\text{D}_2 + \text{cis-N}_2\text{H}_2 & \rightarrow \text{HD} + \text{HD} + \text{N}_2
\end{align*}
\]

Eq. (1) supported by H2 (D2) decomposition of cis-diazene.

An analogous heterogeneous reaction scheme has also been proposed based on the iron-organic hydride models, which significantly facilitates dehydrogenation of cis-diazene [14,15].

In this report, several ‘gas-phase’ theoretical models are developed to show a potential role for dihydrogen as a mediator of H(D)-atom transport in diverse H/D-exchange processes. The molecular hydrogen assisted transfer (HAT) mechanism (hereafter abbreviated as HAT) is considered as a pass-on transfer of hydrogen atoms mediated by H2 which ultimately may lead to the remote transport of H-atoms.

Various hydrogenase based biomimics reactions are also developed to demonstrate the principal performance of HAT-mechanism in more complicated systems.

The remote hydrogen transport phenomenon is implicitly considered or hypothesized in several experimental works for diverse environments [1,2,6,17]. While biological processes are known to proceed mostly in a stereo-regulative manner, the interpretation of isotope exchange in solid state and heterosurfaces (interfaces) are further complicated by reagent accessibility problems caused by variable reaction fronts and mass-transfer processes. Dehydrogenation of LiNH2 and 2LiD mixture in metal-N-H based hydrogen storage materials is, for instance, accompanied by desorption of H2, HD, and D2 gases along with the formation of Li2NH(D) phase. Such a result was unexpected in view of the unfavored direct combination
of negatively charged N- and D-atoms in solid reagents [2]. Successive hydrogenation of Li2NH(D) by normal H2 results in the formation of Li2ND2, which also, according to Chen et al. [2], points out the possibility of new H/D exchange mechanism.

The remote transfer of hydrogen atoms from the catalyst surface toward the unsaturated bonds, located away from the surface at the polyhedral oligomeric silsesquioxane (POSS) site is proposed in [6] to explain unique experimental results on H-scavenging effect of Pd-catalysts coated by POSS.

H-atom transfer (via discrete or concurrent transfer and combination of protons and electrons or transfer of H-atoms) and related H/D-exchange plays a basic role in biological processes, particularly in N2-fixation and activation of hydrogen [7–13]. While high pressures and temperatures (200 atm and 500 °C) with iron-based catalysts are employed to hydrogenate nitrogen in the industrial Haber–Bosch process [3], the activation of N2 occurs at ambient conditions in biological media, supported by the nitrogenase enzyme [10–13]. Importantly, the hydrogen is always produced when N2-ase reduces nitrogen to NH3 (a turnover cycle) [18,10]. Most N2-fixing bacteria contain hydrogenase enzyme to recycle excessive hydrogen [7]. Hydrogenase is a relatively simple enzyme in structure and functions compared to the nitrogenase, which has been called ‘the Everest of enzyme-mountains’ [10] because of its intricacy. The turnover cycles in both enzymes are shown to be accompanied by H/D-exchange. To characterize nitrogenase catalyzed formation of HD, Sellmann et al. have particularly suggested an a priori model with three hydrogen atoms involved in the H/D-exchange reaction scheme [17].

While the Haber–Bosch process is also believed to proceed via the dissociation of H2 on catalyst surfaces, as comprehensively reviewed in [3], the reversible conversion of protons and electrons into H2 by hydrogenase is assumed to proceed via the following scheme (Fig. 1 [9]).

Hydrogenase converts protons and electrons into H2 reversibly and heterolytic cleavage of dihydrogen is a critical step in the catalytic cycle [8]. As shown by Cao and Hall using B3LYP calculations [16], transferring the proton to a CN-ligand has a much higher barrier of activation (37.8 kcal mol−1) than its transfer to the bridging S-atom (17.4 kcal mol−1) when propanedithiolate (PDT) is used as the bridging ligand. When more realistic di(thiomethyl)amine (DTN) bridging ligand is used, as suggested by Nicolet et al. [7] and utilized here (vide infra), the bridgehead N-atom serves as a suitable base and provides a kinetically and thermodynamically favored route to heterolytic cleavage or formation of hydrogen [5,8].

In all these processes, dihydrogen plays a certain mediator role. The mechanism is expected to be linked by some means to the H2-assisted H-transfer reactions depending critically on the varied reaction conditions. It is believed that outlined in this report HAT-mechanism would be a useful means to explain some of these H/D-exchange processes.

The underlying physical principles behind the dihydrogen mediated reactions considered here are Woodward–Hoffmann general rules: cycloaddition reactions involving 4n-electrons are forbidden as concerted processes while those involving 4n + 2 electrons are thermally allowed [19,20]. A six-center, termolecular reaction 3H2 is particularly allowed by the orbital correlations while the hydrogen exchange reaction of 2H2 is Woodward–Hoffmann-forbidden [20–28]. The last statement more strictly concerns the H4 exchange via a D4n transition state, while the exchange is considered as allowed through a C2n reaction coordinate and a rhombic transition state (D4n), as well as from the trans to the rhombic arrangements [4,28]. The H6 bond-exchange also obeys this rule only through configuration interaction, not by virtue of the typically utilized nodal properties [20,22].

More than three decades ago, the benchmark ab initio (DZPD + CI) calculations have been performed by Dixon, Stevens and Herschbach [20], which demonstrate that a termolecular hydrogen exchange reaction (3H2) is indeed accessible without breaking an H–H bond and proceeds through a symmetric hexagonal transition state D6h. The hexagonal minimum was found to be 68.7 kcal mol−1 above the 3H2 asymptote and ca.39 kcal mol−1 lower than 2H2 + 2H asymptote, i.e., a process involving dissociation of a hydrogen molecule.

Based on the substantial stability of H6 relative to dissociation of an H2 bond, LeSar and Herschbach suggested that solid molecular hydrogen might undergo a high pressure transition to form a new phase involving termolecular complexes before transition to the atomic or metallic phase [22].

Degenerate H6 system has been subject of several other theoretical studies motivated mainly by the inconclusive experimental results on activation energy of H/D-exchange [20–28]. The review of early works one can find in [22]. Improved by Taylor, Kormornicki, and Dixon H4+-exchange barrier is 67.4 kcal mol−1 at CASSCF level and 66.5 kcal mol−1 while employing the multireference Davidson's correction [21]. A somewhat higher value (68.8 kcal mol−1 for activation enthalpy at 0 K) was obtained later by Schleyer and co-workers at the QCISD(T)/6-311++G(d,p) level of theory using MP2 geometries [24]. The quite large 'enthalpy of concert' (the difference of 28–30 kcal mol−1 between the H–H bond enthalpy and the concerted-hydrogen exchange activation barrier) has been ascribed to the partial aromatic character of the benzene-like H6 ring [21,24–28].

Degenerate bond-exchange is also known to take place between (HF)6, (HCl)6 and different homoligand and mixed halogens via the more polarized hexagonal TS [29–31]. Some of these mainly low-barrier reactions have experimental evidences in liquid and gas-phases serving historically as the fundamentals for explanation of termolecular reactions of H2 [22,29–31]. Several examples of degenerate hydrogen exchange reactions have been considered by Schleyer and coworkers in conjunction with the ion-pair formation reactions assisted by Lewis acids (corresponding sites of zeolites, in particular) [27,30]. Along with the acidic catalyzed hydrogenation reactions, Radom and co-workers have considered, supported by dihydrogen the hydrogenation of benzene, ethylene and several other unsaturated substrates [32]. Quite recently, McKee and coworkers have thoroughly analyzed in-cage reactions of nH2 catalyzed by fullerene (C60) [4].

Reminiscent of the H2-assisted H-transfer processes considered here is also the isomerization reaction HOC+ + H2 → HCO+ + H2 assisted (catalyzed) by dihydrogen which is proven to take place in interstellar medium [33,34]. This process is due to the stabilization of the H3+ TS and the stepwise dissociation and formation of the H–OH and H–C bonds, respectively.

Theoretical models concerning the H2-mediated processes in biocatalysis to our knowledge are absent save early reports indicated above [14,15]. The H2-assisted H-transfer (HAT) mechanism highlighted here is based on the supporting role of dihydrogen as a third party in remote transfer of H-atoms and H/D-exchange processes. This phe-

Figure 1. The active site of Fe-only hydrogenase [9].
nomenon is the particular case of more general degenerate multi-hydrogen exchange reactions discussed above. The main idea of current work is that adding Hz can make allowed a 4-center 2 σ-bond (or a a/π) exchange reaction which is not allowed by Woodward-Hoffman rules. An isotopic (H/D) exchange may take place when D2 is used as a mediator-catalyst. A series of simple ‘gas-phase’ termolecular, bimolecular and more intricate organometallic models are developed using DFT and \textit{ab initio} methods.

2. Methods

The main calculations are performed using the B3LYP hybrid DFT functional [35,36] with different basis sets for simple ‘gas-phase’ models and the Los Alamos effective core potential (LANL2DZ) for Fe-atoms in conjunction with the Dunning-Hay double zeta basis set for the remaining atoms in metallicorganic systems [37,38], as implemented in GAUSSIAN-03 [39]. Stationary points are verified using vibration mode and IRC analysis.

Spinless and neutral systems are studied for small models and Q = −2 and S = 0 for Hz-ase models with protonated NH-bridgehead unless otherwise stated. While the iron ions in the N2-ase enzyme (FeMoco active center) are expected to be in the high-spin electronic state based on the ligand field considerations (weak-field sulfide donor set, coordination number less than five) [10], the CN- and CO-ligands maintain a low-spin configuration of transition metal in Hz-ase [8]. Synthetic hydride complexes also typically have strong-field organometallic or phosphine co-ligands, which enforce a low-spin electronic configuration with the hydride ligand itself being a quite strong-field ligand. Therefore, all bio-mimic calculations presented here are performed for low-spin states.

B3LYP functional is proven to demonstrate good general performance for hydrogen transfer reactions [4,14,40–42]. However, the dispersion interactions are somewhat underestimated in hydrogen models compared to the CCSD(T)/cc-pV(TZ) results when the same correlation consistent large basis set is used, as recently demonstrated by Lee and McKee [4]. Due to the inherent compensation effects, the difference is less expressed when moderate 6-31G(d,p) basis set is employed. Alternatively, MP2 method overestimates the H-exchange barrier. Calculated here zero point vibration energy corrected MP2 value using extended 6-311++G(3df,2p) basis set is 76.51 kcal mol \(^{-1}\), which is much higher than the indicated above benchmark value of Taylor et al. at 66.5 kcal mol \(^{-1}\) [21] or Jiao et all at 68.8 kcal mol \(^{-1}\) [24]. For comparison, our analogous data at B3LYP/aug-cc-pVDZ and B3LYP/6-31G(d,p) are 61.37 and 68.37 kcal mol \(^{-1}\), respectively, in agreement with the similar data from [4]. Corresponding enthalpies at 298 K are 57.98 and 64.58 kcal mol \(^{-1}\), respectively. The last value is included in Table 1 \textit{(vide infra)} along with all other moderate basis set enthalpy results at 298 K, and Hz-ase results calculated at B3LYP/LANL2DZ level [37,38]. Natural Bond Orbital (NBO) analysis of transition states is performed at B3LYP/6-311++G(2d,2p) level of theory using implemented in GAUSSIAN-03 procedure [39].

3. HAT mechanism in ‘gas-phase’ models

Dihydrogen mediated H-transfer reactions (HAT) are of special interest as they contain \textit{triple-hydrogen-bond} in transition states (Eq. (2) and Table 2). Such a combination is stabilized in TS with constituent atoms located at 1.1–1.2 Å distances from each other, and varied distances between terminal H and X,Y-atoms depending on the nature of heavy atoms (typically between 1.2 to 1.5 Å).

In conventional dihydrogen bonds A–H...H–B the H...H distance is known to be typically 1.7–1.9 Å, much shorter than the normal H–H contact of ca. 2.4 Å [44,45]. In the normal H-bond, a protonic hydrogen X–H (X = N,O) interacts with the basic

![Diagram](https://example.com/diagram.png)

**Table 1**

Molecular hydrogen (D_2) assisted reactions. Termolecular bond exchange models.*

<table>
<thead>
<tr>
<th>H_mXH + D_2 + HYH_m→ (TS)</th>
<th>H_mXD + HYH_m+ HD</th>
</tr>
</thead>
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<tr>
<td>H_2</td>
<td>2.20</td>
</tr>
<tr>
<td>HF</td>
<td>3.98</td>
</tr>
<tr>
<td>H_2O</td>
<td>3.44</td>
</tr>
<tr>
<td>NH_3</td>
<td>3.04</td>
</tr>
<tr>
<td>CH_4</td>
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</tr>
<tr>
<td>CH_4</td>
<td>2.55</td>
</tr>
<tr>
<td>CH_4</td>
<td>2.55</td>
</tr>
<tr>
<td>NH_3</td>
<td>3.04</td>
</tr>
<tr>
<td>CH_3NH_2</td>
<td>3.04</td>
</tr>
<tr>
<td>NH_2NH_2</td>
<td>3.04</td>
</tr>
<tr>
<td>MgH_2</td>
<td>1.66</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>H_mXH</th>
<th>χ</th>
<th>H_mXH</th>
<th>ΔH^e kcal mol (^{-1})</th>
<th>v_1 cm (^{-1})</th>
<th>θ Deg</th>
<th>q(D) e (^{-})</th>
<th>q(H) e (^{-})</th>
<th>q(X) e (^{-})</th>
<th>q(Y) e (^{-})</th>
</tr>
</thead>
<tbody>
<tr>
<td>H_2</td>
<td>2.20</td>
<td>H_2</td>
<td>2.20</td>
<td>64.5</td>
<td>-2537.3</td>
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<tr>
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<td>2.98</td>
<td>25.0</td>
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<td>0.372</td>
<td>-0.567</td>
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<td>H_2O</td>
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<td>H_2O</td>
<td>3.44</td>
<td>32.5</td>
<td>-2020.4</td>
<td>87.1</td>
<td>-0.326</td>
<td>0.375</td>
<td>-0.944</td>
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<tr>
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<td>3.04</td>
<td>NH_3</td>
<td>3.04</td>
<td>38.0</td>
<td>-1596.3</td>
<td>87.1</td>
<td>-0.471</td>
<td>0.362</td>
<td>-1.094</td>
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<td>CH_4</td>
<td>2.55</td>
<td>106.9</td>
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<td>90.9</td>
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<td>0.195</td>
<td>-0.945</td>
</tr>
<tr>
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<td>CH_4</td>
<td>2.55</td>
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<td>96.3</td>
<td>-0.084</td>
<td>0.168</td>
<td>-0.507</td>
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<td>CH_4</td>
<td>2.55</td>
<td>3.04</td>
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<td>CH_3NH_2</td>
<td>3.04</td>
<td>28.7</td>
<td>-1481.8</td>
<td>94.9</td>
<td>-0.247</td>
<td>0.333</td>
<td>-0.812</td>
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<tr>
<td>NH_2NH_2</td>
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<td>NH_2NH_2</td>
<td>3.04</td>
<td>29.3</td>
<td>-1453.0</td>
<td>94.9</td>
<td>-0.250</td>
<td>0.108</td>
<td>-0.638</td>
</tr>
<tr>
<td>MgH_2</td>
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<td>MgH_2</td>
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<td>53.5</td>
<td>-570.2</td>
<td>178.5</td>
<td>0.067</td>
<td>-0.405</td>
<td>1.407</td>
</tr>
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</table>

* Transition vectors are sketched only in one direction to show progress of H-atoms.

- Pauling Electronegativity of central atoms.
- Enthalpies at B3LYP/6-31G(d,p) and NBO analysis at B3LYP/6-311++G(2d,2p) levels.
- Imaginary frequencies for TS.
- NBO charges for two types of triple hydrogen atoms.
- \( q(D) = 0.11 e \) on the S-attached hydrogen atom.
- \( q(C_{\text{terminal}}) = -0.574 e \).
- \( q(C_{\text{terminal}}) = -0.315 e \).
lone-pair of an electronegative atom while HAT-mechanism includes attractive interactions and polarization of the H-H covalent bond by protic and hydridic H-atoms. The role of the proton acceptor center can play the electropositive transition metal or

### Table 2
Molecular hydrogen (D₂) assisted reactions. Bimolecular H-transport models (HAT-mechanism).

<table>
<thead>
<tr>
<th>(Substrate) XAYH</th>
<th>X</th>
<th>A</th>
<th>Y</th>
<th>ΔHₐ kcal mol⁻¹</th>
<th>v₁,ₑ⁻¹ cm⁻¹</th>
<th>Θ Deg.</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-Memberd Ring TS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl₃-MONO</td>
<td>O</td>
<td>N</td>
<td>O</td>
<td>45.60</td>
<td>112.82</td>
<td>76.17</td>
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<tr>
<td>HNNN</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>45.18</td>
<td>86.45</td>
<td>112.82</td>
</tr>
<tr>
<td>HOO(OH)</td>
<td>O</td>
<td>O(H)</td>
<td>O</td>
<td>41.78</td>
<td>112.82</td>
<td>86.45</td>
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<tr>
<td>HOOD</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>40.02</td>
<td>84.48</td>
<td>112.82</td>
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<tr>
<td>CH₂=CHOH</td>
<td>O</td>
<td>C(H)</td>
<td>C(H₂)</td>
<td>38.50</td>
<td>94.81</td>
<td>112.82</td>
</tr>
<tr>
<td>HOOCOH</td>
<td>O</td>
<td>C(H)</td>
<td>O</td>
<td>37.72</td>
<td>81.91</td>
<td>112.82</td>
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<tr>
<td>5-Memberd Ring TS</td>
<td></td>
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<tr>
<td>CyHN₅</td>
<td>O</td>
<td>N</td>
<td>N</td>
<td>65.24</td>
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<tr>
<td>H₂O₂ (trans)</td>
<td>O</td>
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<td>97.75</td>
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<tr>
<td>HNO</td>
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<td>N</td>
<td>N</td>
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<td>86.90</td>
<td>112.82</td>
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<tr>
<td>CH₄</td>
<td>C(H)</td>
<td>C(H)</td>
<td>C(H)</td>
<td>86.15</td>
<td>92.10</td>
<td>112.82</td>
</tr>
<tr>
<td>H₂O₂(cis)</td>
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<td>O</td>
<td>82.47</td>
<td>92.10</td>
<td>112.82</td>
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<td>HNO</td>
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<td>cis-N₂H₅</td>
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<td>92.10</td>
<td>112.82</td>
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<tr>
<td>Biocatalytic Model</td>
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<tr>
<td>H₂-ase</td>
<td>O</td>
<td>Fe</td>
<td>O</td>
<td>23.30</td>
<td>105.85</td>
<td>112.82</td>
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</table>

a TS vectors are sketched to show transfer of H-atoms.
b Imaginary frequencies for TS.
c Termolecular H/D-exchange reaction HO₂⁺ + HO⁺ + D₂ → HO₂⁺ + DO⁺ + HD.
d TS structure is presented in Figure 3.
e H/D exchange by only H-atom of pentazole cycle.
f Trans oriented in TS. Isomerization leads to the formation of water oxide, H₂O₂.
g H/D exchange accompanied by the isomerization to NNH₂.
h H/D exchange accompanied by inversion of O, N or C-centers.
i Some other biomimics are also calculated and will be reported separately [48].

### Table 3
Molecular hydrogen (D₂) assisted dehydrogenation reactions.

<table>
<thead>
<tr>
<th>(Substrate) HXYH</th>
<th>X</th>
<th>Y</th>
<th>ΔHₐ kcal mol⁻¹</th>
<th>v₁,ₑ⁻¹ cm⁻¹</th>
<th>Θ Deg.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂H₄</td>
<td>C(H)</td>
<td>C(H)</td>
<td>86.15</td>
<td>112.82</td>
<td>112.82</td>
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<tr>
<td>H₂O₂(cis)</td>
<td>O</td>
<td>O</td>
<td>82.47</td>
<td>112.82</td>
<td>112.82</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>C(H₂)</td>
<td>C(H₂)</td>
<td>74.62</td>
<td>112.82</td>
<td>112.82</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>C(H)</td>
<td>O</td>
<td>60.55</td>
<td>99.7</td>
<td>112.82</td>
</tr>
<tr>
<td>cis-N₂H₅</td>
<td>N</td>
<td>N</td>
<td>17.68</td>
<td>120.3</td>
<td>112.82</td>
</tr>
</tbody>
</table>

a TS vectors are sketched to show hydrogen elimination.
b Imaginary frequencies for TS.
c Hydrogenation of conjugated systems catalyzed by acids and dihydrogen is thoroughly considered by Radom and co-workers [32].
d Trans oriented in TS, leading to the elemental products O₂ + 2HD.
e TS is closure to the product set CH₃O + 2HD.
f To elemental products N₂ + 2HD (see Introduction and Ref. [14].
π-bonded carbon atom. This process may lead ultimately to the transfer of an H-atom between two ligand molecules or from one electronegative coordination center in a single molecule to another remote one (vide infra).

Three types of models are developed here to evaluate relevance of HAT-mechanism in different environments (Tables 1–3 and Figs. 2 and 3). A series of the termolecular bond-exchange reactions mediated by molecular hydrogen are listed in Table 1. Typical HAT and some dehydrogenation reactions catalyzed by H2 are presented in Tables 2 and Table 3, respectively. Activation enthalpies are calculated relative to the isolated reagents.

Almost all electronegative atoms readily form bond-exchange transition states (Table 1). TS structures are similar to those in degenerate 6-membered ring multiple hydrogen exchange reactions indicated above, e.g., 3H2, 3HCl, etc. They differ only by the prearranged presence of molecular hydrogen (denoted as D2 for clarity) as a third-party. The barrier heights vary substantially depending on the electronegativity of the reactive X- and Y-centers in bare, and type of substituents in mixed systems. There is a direct correlation between electronegativity of contacting to triple hydrogen bond heavy atoms of ligands and barrier heights in pure (homoligand) systems (top part of the Table 1). This effect in mixed systems can also be traced. 3H2 and H2 + 2MgH2 are the obvious exceptions (vide infra).

The analogous transition states for some neutral homoligand systems such as D2+(H2S)2, are unstable. More basic ammonia in a heteroligand system makes possible the reaction of H2S as well due likely to the additional polarization of TS (see, Table 1). The reaction NH3 + H2S + D2 forms mixed hydrogen isotope products NH2D and HD while molecular content remains unchanged (ΔH° = +32.5 kcal mol−1).

As expected, the barriers for all examined H2-promoted reactions vary substantially depending on the ionic and electronic states of the reagents. In general, HAT-transition states are formed readily by the electronegative atom based hydrides.

Triple hydrogen bond angle D–D–H (0, Table 1) in all cases is around 90 degrees except for the H2, which forms symmetric hexagonal TS structure with 120° internal angles. A particularly striking case is the neutral MgH2 based reaction with the similar TS and practically linear D–D–H angle (178.5 deg, see Table 1) and exceptionally low barrier of activation (as low as 5.35 kcal mol−1). HAT-type mechanism holds also for positively charged MgH2 systems (Q = +1 and +2) although via the more intricate TS structure and with the higher activation barriers (data not presented).

The search for TS structures in ionic systems of other first row elements reveals relevant transition states only for BeH2 (Q = +1 and +2) and BH3 (only when Q = +2). TS were unstable for ionic and neutral LiH containing systems.

The population analysis for transition state structures at B3LYP/6-311+G(2d,2p) level shows that triple-hydrogen-bonds are polarized. Natural charges on key atoms presented in Table 1 show an alternation of populations on ring-constituting atoms. A particularly striking case is the neutral MgH2 based reaction with the similar TS and practically linear D–D–H angle (178.5 deg, see Table 1) and exceptionally low barrier of activation (as low as 5.35 kcal mol−1). HAT-type mechanism holds also for positively charged MgH2 systems (Q = +1 and +2) although via the more intricate TS structure and with the higher activation barriers (data not presented).

Intriguingly, the central D atom in 2MgH2 + D2 system is almost electroneutral and the stabilization is achieved mainly due to the electrostatic interactions between Mg and connected hydrogen atoms. Terminal H-atoms in all TS structures as well as the bridged hydrogen atoms are also positive, except for MgH2 system.

As seen from Table 1, the barrier is exceptionally high for CH4 (106.9 kcal mol−1), which is higher than BDE in methane at 105 kcal mol−1. Even more difference holds in the next aliphatic homologue, C3H6 (107.4 kcal mol−1 vs. BDE 101 kcal mol−1). On the other hand, the barrier is reduced significantly in bond-exchange reaction between H2 and two ethylene molecules where ligand’s π-electrons are implicitly involved in the TS- interactions (81.2 kcal mol−1 vs. BDE at 111 kcal mol−1).

The substituent effect on barrier height from the electrondonating CH3-group is small in methane homologue (only by ca.0.5 kcal mol−1) but it is somewhat higher when the same group is attached to the electronegative N-atom as it occurs in CH3NH + H2S + H2 reaction (the barrier is reduced by 2.8 kcal mol−1). In contrast, it increases barrier by almost the same amount (2.7 kcal mol−1) when attached to H2S-ligand (see Table 1). π-electron withdrawing group NH2 in turn increases the barrier by 3.2 kcal mol−1 in H2-assisted reaction of hydrazine with H2S.

As mentioned above, all listed in Table 1 termolecular bond-exchange reactions occur via the 6-membered ring transition state structure [22–26]. However, the transition ring can be easily extended maintaining main features of TS by switching to a remote center when an alternative reaction center is available on ligands (reagents). Such a seven membered ring TS can be generated via the switching of reaction center to the sulfur atom instead of proximal N-atom, as it illustrated in Figure 2a. The forward reaction barrier is fairly low at 25.0 kcal mol−1 with the exothermicity being 14.1 kcal mol−1. The product NH3S has a zwitter-ionic character with all positive charges located on hydrogen atoms.

![Figure 2](image-url)  
Figure 2. (A) TS for 7-membered ring expansion reaction with switching from the proximal N- to remote S-center, (B) TS for H-transfer from O- to terminal C-center in vinyl alcohol (ethenol).
Mulliken charges are ca. 0.33 e\(^-\) on each H-atom and \(Q_N = +0.6\) e\(^-\) and \(Q_S = +0.4\) e\(^-\). All 3H\(_2\)-like termolecular reactions have also very unfavored entropic contributions. Alternatively, H-transfer can take place in a bimolecular manner. Several examples are collected in Table 2 with one of the H-exchange units replaced by a bifunctional (ambident) bulk ligand. Figure 2b illustrates a simple keto-enol transformation reaction via the H-transfer from O- (Y-center) to the \(sp^2\)-hybridized terminal C-atom (X-center) of the vinyl alcohol (ethanol). The \(\pi\)-electrons make this reaction allowed. Supported by the decreased ring-strain in TS, it reduces the barrier up to 38.5 kcal mol\(^{-1}\), as compared to the 4-electron center uncatalyzed H-transfer reaction at 53.4 kcal mol\(^{-1}\) at the same level (at higher G3SX level it is ca 60 kcal mol\(^{-1}\) [47]).

As a substrate that is acted upon by a H\(_2\)-catalyst, may serve cis-HONO, HCOOH, and HOOO\(^-\) (with the energy slightly below the O\(_2\) + HO\(^-\) asymptote); see Table 2. As a side note, these substrates may serve themselves as H-transfer catalysts [43]. Intriguingly, an addition of H-atom to HOOO\(^-\) radical in TS, does not appreciably change the barrier in closed-shell HOO(H)O (increases it only by 1.8 kcal mol\(^{-1}\)). Note that the system is unstable when catalyst is removed: it falls apart to HO\(_2\) and HO\(^-\). In overall, H-abstraction of H\(_2\) via a radical (HO\(^-\), HOOR, NH\(_2\); etc.) is significant, yet HAT-mechanism may occur supported by proper orientation of reagents.

The top part of Table 2 lists H\(_2\)-assisted H-transport reactions that occur via the six-membered ring TS. The HAT-process may occur also through the five and four member TS-ring structures with a tri-hydrogen 'hat' on central A-Y and Y-atoms, respectively as presented in the second and third parts of the Table 2. These bimolecular reactions retain all principal features of termolecular HAT-reactions.

The simplest bimolecular H-transfer reactions are H\(_2\)-mediated inversion of CH\(_4\), NH\(_3\), and H\(_2\)O, which occur via the 4-membered TS (the same holds for HF).

The barrier heights correlate with the electronegativity of central atoms (C, N, O, F). In overall, the barriers are increased substantially (by 15–20 kcal mol\(^{-1}\)) compared to the 6-membered ring-TS bimolecular processes (Table 2) due to the additional ring-strain energy in 4-membered TS. Note that the barrier in CH\(_4\) system is higher by more than 40 kcal mol\(^{-1}\) than other barriers which are placed close to each other at 58–65 kcal mol\(^{-1}\). H\(_2\)-mediated inversion of NH\(_3\) requires, for instance, ca. 39 kcal mol\(^{-1}\) lower activation energy than the dissociation energy of H-H bond and ca. 28 kcal mol\(^{-1}\) lower than the BDE of N-H.

The barrier in analogous O-centered reaction of HON is reduced by ca. 30 kcal mol\(^{-1}\) due to the involvement of N=O bond \(\pi\)-electrons. Triple-hydrogen-bond "hat", however, is pushed-back at distance 1.912 Å, with \(\Theta\) angle as wide as 140.5° (cf. MgH\(_2\), Table 1).

Analogous HAT-reactions via the 5-membered TS might require lower barriers again due to the less ring-strain. However, as it seen in a series of NH\(_3\), trans-N\(_2\)H\(_2\) and HNNN, increasing the ring-size changes barriers unequally (65 vs. 40 vs. 45 kcal mol\(^{-1}\)). Note, that TS for HNNNN is unstable while HN\(_5\) is converged to the cyclic pentazole with an attached 5-membered HAT-ring with somewhat higher barrier at ca. 54 kcal mol\(^{-1}\).

The stereoselective HAT-reaction of two in-ring nitrogen atom containing cis-N\(_2\)H\(_2\) somewhat differs (Table 3), as it mentioned in Introduction. In fact, it is not the regular H-transport-process.
but bond-exchange leading to the decomposition of diazene to elemental hydrogen and nitrogen. The same process holds in case of cis-oriented hydrogen peroxide, as well as ethene, ethane and methyl alcohol with significantly higher barriers (Table 3).

4. HAT mechanism in extended models (hydrogenase mimics)

The HAT ideology is further applied to the Fe-only model of the hydrogenase enzyme (Figure 3), which contains CO- and CN-ligands, dithiomethylamine (DTN) linker, μ-SCH₂NHCH₂S⁻ and SCH₄-group to model S[Fe₂S₃]-Cys ligand. Such a truncation is common in H₂-ase modeling literature [5,8]. Calculations have been performed for the Fe(II)/Fe(II) form of the H₂-ase model with protonated bridged DTN and/or CH₃S-groups (Q = 2, S = 0).

A schematic reaction is depicted at the bottom of the Figure 3 showing H-transport in the H₂-ase model with actual ligands, for completeness. As seen, the approaching H₂-molecule (D₂) mediates H-transfer of protonated bridge (NH₂-group) to the distal Fe-center. The dihydrogen forms a 7-membered semi-rigid ring transition state, transfers an atom to Fe and captures the H-atom from the amino group of DTN-linker, and releases back as isotopically mixed HD. Thus, dihydrogen plays the role of a pass-on agent in remote transfer of an H-atom of protonated DTN bridge (NH₂-group) to the distal Fe-center exactly in the same manner as it occurs in simple ‘gas-phase’ models. Altered coordination number of the iron center converts tetragonal polyhedron to the trigonal bipyramidal one (Figure 3).

The barrier is remarkably low (23 kcal mol⁻¹) compared to the gas-phase models presented in Table 2. The process is also favored thermodynamically (ΔHrxn = −24 kcal mol⁻¹).

Protonated at SCH₂-group model (Q = −1, S = 1/2) leads to the similar results with somewhat higher barrier of activation, 25.7 kcal mol⁻¹.

The system spin-state may drastically change and redirect the mechanism, according to our preliminary calculations [48]. Probably, further inclusion of the real electron supplier Fe₄S₄-cubane cluster in the H₂-ase model may alter the barrier as well, depending on the reaction conditions.

Importantly, H-transport (H-export) occurs even with further expansion of the TS-ring, to a ligand groups (e.g., to the C-atom of CO-group). These results along with the developed more complicated H-transport models based on nitrogenase mimics will be reported separately [48].

As a side note, some radicals such as HOOOC and HO₂⁺ may also play the role of H-transfer catalysts instead of H₂ (e.g., the analogous barrier for H₂-ase by HO₂⁺ is as low as 17.1 kcal mol⁻¹ [43]).

In addition, the quantum tunneling may play a principal supporting role in low temperature H₂-mediated H-transport processes (see, e.g., [49] concerning the tunneling splitting in water trimer).

5. Conclusions

In conclusion, several new models are developed on the intriguing role of hydrogen molecules in remote transport of H-atoms in various media. H₂ molecules are shown to assist H-transfer reactions (HAT-mechanism) in simple ‘gas-phase’ models as well as in more intricate organometallic analogues. It is believed that the developed mechanism may be of help in understanding of complex H/D-exchange processes. As barriers are varied depending on reaction type and conditions, one can expect further development of more feasible and selective HAT reactions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2010.09.003.

References