Dipolar H_2 activation by H_2O

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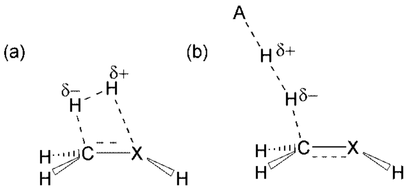
When a water molecule can act as a proton acceptor during the critical H–H bond heterolytic dissociation step of formaldehyde hydrogenation, the barrier drops—an observation which links dihydrogen activation chemistry to hydride transfer at a detailed molecular level.

The hardness of the H–H molecule is an obstacle to hydrogenation reactions, and consequently they usually require a catalyst, often in the form of a transition metal, in order to proceed. The reverse reaction type, H_2 eliminations, has been the subject of many gas phase studies. For example, detailed experimental and theoretical work has shown that loss of H_2 from protonated molecules of the type CH_3XH^+ (X = NH_2, OH, F, SH) take place *via* non-symmetrical 1,2-elimination mechanisms [Scheme 1(a)].[1–3] The resulting tight transition structures for these and similar H_2 eliminations give rise to substantial potential energy barriers. The dipolar nature of the emerging H_2 molecule during passage of the transition state has been noted.[4]

Very interestingly, it appears that intermolecular hydride transfer[5] is related to these hydrogenations/dehydrogenations. A special hydride transfer mechanism is found in superacid systems, particularily in the gas phase, where proton transfer may initiate H_2 elimination: $AH^+ + CH_3X \rightarrow CH_2X^+ + H_2 + A$. This reaction type has been reviewed in the context of chemical ionization mass spectrometry.[6] A reasonable transition structure for such a reaction is illustrated in Scheme 1(b). Although mechanisms of both unimolecular H_2 eliminations and hydride abstractions are reletively well known, the idea behind the present paper is to see how they are linked together at a detailed molecular level. We pursue this idea further by specifically asking if a third molecule, A, may change the reactivity in H_2 additions/eliminations.



Scheme 1

In order to do this we decided to perform quantum chemical calculations on a prototype system, hydrogenation of formaldehyde, using the methods MP2/6-31G(d,p)[7,8] and G2[9] with help of the program package GAUSSIAN 98.[10] Only the G2 values will be displayed in the following discussion.

According to our calculations hydrogenation of formaldehyde to give methanol [eqn. (1)]

$$CH_2O + H_2 \rightarrow CH_3OH \qquad (1)$$

is exoergic by $\Delta E = -78$ kJ mol^{-1} and has $\Delta G^o = -52$ kJ mol^{-1} which is in acceptable agreement with the experimentally known[11] exothermicity (at room temperature) of $\Delta H^o = -93$ kJ mol^{-1}. The reaction has a critical energy of $E_o = 301$ kJ mol^{-1} (Fig. 1, upper reaction path *via* the transition structure **TSa**).

Upon protonation [eqn. (2)],

$$CH_2OH^+ + H_2 \rightarrow CH_3OH_2^+ \qquad (2)$$

the critical energy is reduced to $E_0 = 122$ kJ mol^{-1} (Fig. 1, middle path *via* the transition structure **TSb**), which still is quite unfavourable for a direct gas phase reaction, but significantly below that of reaction (1). At the same time, as the result of the higher proton affinity of methanol, the overall reaction becomes somewhat more exoergic, with $\Delta E^o = -145$ kJ mol^{-1} and $\Delta G^o = -94$ kJ mol^{-1}. The corresponding experimental value[11] is $\Delta H^o = -142$ kJ mol^{-1}.

Upon providing the proton *inter*- rather than *intra*-molecularily a further, and substantial, drop in the critical energy is observed. The termolecular gas phase reaction [eqn. (3)]

$$CH_2O + H_2 (+ H_3O^+) \rightarrow CH_3OH (+ H_3O^+) \qquad (3)$$

has barriers (corresponding to **TSc** and **TSd**) for which the potential energies are below that of the reactants (these values are $E_0 = -36, -34$ kJ mol^{-1}, respectively). Water is seen to promote reaction strongly through either of these closely parallel mechanisms. In the first step a proton is donated from the hydronium ion **3** to the oxygen of formaldehyde. Protonated formaldehyde may then form one of the two complexes **6a** (a C–H···O complex) or **6b** (a O–H···O complex) with the water

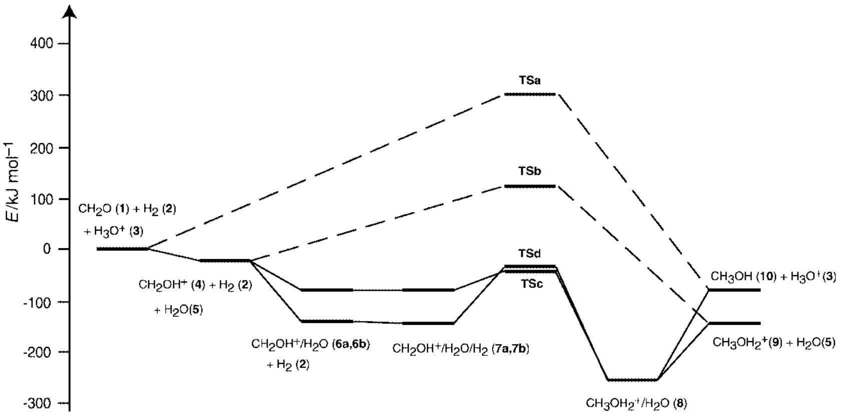


Fig. 1 Schematic potential energy diagram (G2) for the various routes for hydrogenation of formaldehyde. Potential energies are given in kJ mol^{-1}.

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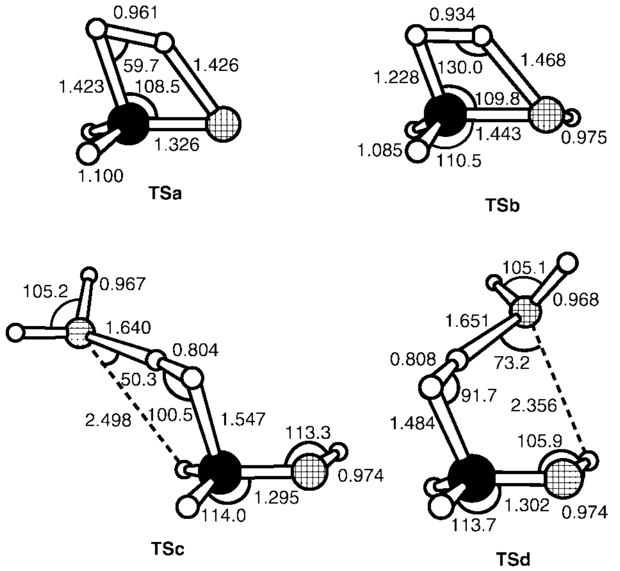

Fig. 2 Structures of the found transition structures (MP2/6-31G(d,p)) of the reactions studied. Black filled circles represent carbon, white open circles are hydrogen, while the patterned circles are oxygen. Bond lengths are given in Å and angles are in degrees. The connection between the transition structures and the minima indicated in Fig. 1 was verified through explicit calculation of minimum energy paths (intrinsic reaction coordinate).

molecule. In the next step of the parallel mechanisms, H_2 is associated with the corresponding complex (**6a** or **6b**). These new complexes are **7a** and **7b**, respectively. In the key step (*via* **TSc** or **TSd**) of the two parallel mechanisms, the H_2 molecule is split in a heterolytic process: the hydride ends up at the carbon and the proton ends up on water. All along the reaction the water is docked to the organic part through a hydrogen bond. The final products are obtained by breaking the hydrogen bonded complex **8**.

The transition structures **TSc** and **TSd**, are characterized by being cyclic. In contrast to **TSb** which has a tight four-membered ring, **TSc** and **TSd** form loose six-membered rings. While the H–H bond of **TSa** is 0.934 Å, it is only 0.804 Å in **TSc** and 0.808 Å in **TSd**, demonstrating that the latter transition structures are earlier along the reaction coordinate. These values should be compared to the MP2/6-31G(d,p) value of 0.734 Å for an intact H_2 molecule.

As indicated above, reaction (3), can be regarded from another perspective. When read from right to left (Fig. 1) **TSc** and **TSd** are the possible transition structures for the weakly endoergic hydride abstraction of methanol by H_3O^+.

We are not sure that the findings presented here may be of immediate practical use; a termolecular reaction through **TSc** or **TSd** is certainly difficult to achieve in the gas phase. This is illustrated by the fact that the free energies of these transition structures are +24 and +28 kJ mol^{-1}, respectively, compared to that of the reactants (**1** + **2** + **3**). In a strongly acidic water solution, in a suitable supercritical phase, or on an acidic surface (*e.g.* in a zeolite) the molecules are solvated, approximately corresponding to the situation in the complexes **7a** and **7b**. Despite this, the results presented here give an optimistic perspective on a non-transition metal hydrogenation catalysis chemistry.

We are aware of previous studies that illustrate the mediating effect of a water molecule in similar situations. As a good example we would mention that McKee *et al.*[12] showed that a water molecule slightly lowers the activation energy for the concerted dihydrogen exchange reaction (4).

$$CH_2O + CH_3OH \rightarrow CH_3OH + CH_2O \qquad (4)$$

In this reaction the two hydrogens are transferred through a one step cyclic relay type mechanism, which has several common features with reaction (3) above.

In summary we have shown (a) that protonation of formaldehyde lowers the energy barrier for hydrogenation, and (b) the barrier is further lowered upon inclusion of a water molecule.

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