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An In-Depth Mechanistic Study of Ru-Catalysed Aqueous Methanol Dehydrogenation and Prospects for Future Catalyst Design**

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Herein we provide mechanistic insights into the dehydrogenation of aqueous methanol catalysed by the [Ru(trop₂dae)] complex (which is *in-situ* generated from [Ru(trop₂dad)], trop₂dad = 1,4-bis(5H-dibenzo[a,d]cyclohepten-5-yl)-1,4-diazabuta-1,3-diene), established by density functional theory based molecular dynamics (DFT-MD) and static DFT calculations incorporating explicit solvent molecules. The aqueous solvent proved to participate actively in various stages of the catalytic cycle including the catalyst activation process, and the key reaction steps involving C–H activation and hydrogen production. The aqueous solvent forms an integral part of the reactive system for the C–H activation steps in the [Ru(trop₂dae)]

system, with strong hydrogen bond interactions with the anionic oxygen (RO[−], R=CH₃, CH₂OH, HCO) and hydride moieties formed along the reaction pathway. In contrast to the [Ru(trop₂dad)] catalyst, C–H activation and hydrogen production does not proceed via a metal-ligand cooperative pathway for the [Ru(trop₂dae)] system. The pK_a of the coordinated amine donors in these complexes provides a rationale for the divergent reactivity, and the obtained mechanistic information provides new guidelines for the rational design of active and additive free catalytic systems for aqueous methanol dehydrogenation.

Introduction

The energy infrastructure centred around renewable energy resources will be key to achieve a substantial reduction of greenhouse gas emission in the coming decades. Owing to the intermittent nature of energy production by renewable sources such as wind and solar energy, the development of better means to store and transport energy is required for a large scale

sustainable implementation of renewable energy technologies.^[1] Reversible storage of energy in the form of stable and easy to transport chemicals, driven by cheap electricity (produced by renewable sources) during peak hour production can address these challenges. Hydrogen equivalents stored in the form of aqueous methanol is one relevant example of chemically stored energy, which can also be transported using existing infrastructure. To actually use aqueous methanol as an energy storage vector, it is of importance to develop catalytic systems capable of generating hydrogen from aqueous methanol *on-demand* to enable hydrogen based electricity production in fuel cells.^[2,3] In this work, we focus on homogeneous molecular complexes that can generate three equivalents of hydrogen from aqueous methanol under mild conditions (1 atm, < 100 °C).^[4,5] A number of highly active and selective complexes have been reported in the literature for this transformation.^[4–11] For large scale industrial applications, it will be beneficial to develop highly active, additive-free and stable catalytic systems based on non-toxic elements (preferably abundant) that can operate under mild conditions.^[12] The discovery of such catalytic systems can benefit from a detailed mechanistic understanding of the catalysed aqueous methanol dehydrogenation. Here, we provide such mechanistic insights for the [Ru(trop₂dad)]/[Ru(trop₂dae)] catalytic system (trop = 5H-dibenzo[a,d]cyclohepten-5-yl; dad = 1, 4-diazabuta-1,3-diene; dae = 1,2-diaminoethane; see also Figure 1b), which is beside the related couple [Ru(trop₂dap)]/[Ru(trop₂ipa)] (dap = 1,3-diaminopropane; ipa = 3-iminoprop-1-en-1-amine)^[13] the only one to date that can achieve this transformation in the absence of any additives (acid, base or secondary catalyst) and under mild conditions.^[5]

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Figure 1. (a) Elementary steps in the dehydrogenation of methanol–water mixture to three equivalents of H_2 and CO_2 . (b) Complexes relevant for this study.

Dehydrogenation of aqueous methanol to CO_2 by the $[\text{Ru}(\text{trop}_2\text{dad})]$ catalyst occurs in four distinct steps, as shown in Figure 1a. In the first step, methanol is dehydrogenated to form formaldehyde, which subsequently undergoes hydration to form methanediol. The third step involves dehydrogenation of methanediol to produce formic acid (FA). In the final step, FA dehydrogenation results in the release of CO_2 . In total, three equivalents of hydrogen and one equivalent of CO_2 are produced. The catalysts for these transformations typically include a Lewis acidic site (metal centre) which accepts the hydride formed upon C–H bond activation. A Brønsted base is needed to deprotonate the OH moiety, which can be a part of the catalyst (internal Brønsted base, typically an amido ligand) or an external base.^[14,15] Such heterolytic bond cleavages involve formation of charge separated polar intermediates such as $\text{O}^{\delta-}$, $\text{H}^{\delta-}$ and $\text{H}^{\delta+}$ which are affected both by the dielectric constant and hydrogen bonding capabilities of the solvent environment. Therefore, one can anticipate that solvent effects can play an important role in these transformations and are expected to be more pronounced in a polar protic medium, where solvent molecules can participate actively and may be part of reaction intermediates. A realistic modelling study of these reactions therefore requires to include explicit solvent molecules.^[13–16] Previous studies from our group have uncovered the key aspects of methanol dehydrogenation catalysed by $[\text{Ru}(\text{trop}_2\text{dad})]$.^[19] Complex 1H^- is the precursor of the active catalyst complex $[\text{Ru}(\text{trop}_2\text{dad})](1)$ (see Scheme 1a). Complex 1 can also undergo hydrogenation of the dad ligand via a side reaction in the catalytic system to form the hydrogenated Ru^0 complex $[\text{Ru}(\text{trop}_2\text{dae})](2)$. Complex 2 exhibits similar catalytic

Scheme 1. a) Catalyst activation and *in-situ* generation of complex $2/2'$. b) Proposed mechanism for dehydrogenation of methanol to formaldehyde catalysed by complex $2'$. A similar mechanism underlies the dehydrogenation of methanediol and formic acid. Transient bonds are shown as red dashed lines.

activity to complex 1H^- in the aqueous methanol dehydrogenation reaction (TON = 426, 90 °C, ambient pressure). Complex **2** undergoes a solvent mediated rearrangement to form complex **2'** containing a Ru^{II} center.^[19–21] We used static DFT models with a small number of solvent molecules to demonstrate that solvent molecules participate directly in the dehydrogenation of methanol to formaldehyde catalysed by complex **2'**, involving several hydrogen bond interactions with the anionic oxygen and hydride moieties (in CH_3O^-). Interestingly, explicit solvent effects did not play an important role in the computed mechanism of aqueous methanol dehydrogenation by the $[\text{Ru}(\text{trop}_2\text{dad})]$ complex **1**.^[19] These observations indicated the need for an in-depth investigation of solvent effects on the mechanism of hydrogen production from aqueous methanol promoted by complex **2'**. The importance of an explicit description of the solvent had also been demonstrated for aqueous methanol dehydrogenation catalysed by the $[\text{Ru}(\text{PNP})]$ complex,^[15,22] in addition to a number of other catalytic systems including water oxidation^[23–26] and transfer hydrogenation of ketones.^[16,17,27]

In order to gain a detailed understanding of the effects of solvent on aqueous methanol dehydrogenation catalysed by complex **2'**, we performed extensive mechanistic studies employing a combination of density-functional theory based molecular dynamics (DFT-MD) simulations of fully explicitly solvated complexes incorporating explicit thermal motion, and static DFT calculations of explicit micro-solvated complexes. Our results reveal the active participation of solvent in various stages of the catalytic cycle. In particular, we show that an explicit description of the solvent environment is essential for an accurate modelling of the catalyst activation step (protonation of complex 1H^- to form complex **1**), and in modelling the dehydrogenation of methanol, methanediol and formic acid catalysed by complex **2'** (Scheme 1). Our results show, in marked contrast to complex **1**, that dehydrogenation of methanol catalysed by complex **2'** does not proceed via a Noyori-Morris type metal-ligand cooperative pathway. Rather it proceeds via a metal-centred pathway without the direct involvement of the ligand moiety. Moreover, we find divergent hydrogen production pathways for complex **1B** ($[\text{Ru}(\text{H})(\text{tropNH}-\text{CH}=\text{CH}-\text{Ntrop})]$) and complex **2'B** ($[\text{trans-Ru}(\text{H})_2(\text{tropNH}-\text{CH}_2-\text{CH}_2-\text{NHTrop})]$). See Figure 1. The former releases H_2 via a direct (unassisted) pathway,^[19] while the latter expels H_2 via a solvent enabled pathway leaving the ligand nitrogen (N_{dae}) in a protonated state throughout the entire process. Based on these detailed mechanistic insights, we propose principles that can enable rational design of highly active additive free catalytic systems for aqueous methanol dehydrogenation.

Results

Catalyst activation

Experimentally, the anionic hydride 1H^- (Figure 1b) was shown to react with a slight excess of water or an acid to produce the

active catalyst complex **1** and H_2 (Scheme 1a).^[5] Stoichiometric reaction of complexes 1H^- or **1** with an alcohol or alcohol/water mixtures leads to the full hydrogenation of the ligand, forming complex **2**. The protonation of complex 1H^- to produce the active catalytic complex **1** can be studied using the reaction as described by equation (1):

A previous computational study based on DFT and CCSD(T) calculations suggested that the formation of complex **1** is not feasible, and therefore an alternative reaction pathway based on anionic intermediates derived from complex 1H^- was considered.^[28] However, experimental data clearly indicated formation of complex **1** as the active species.^[5] In terms of electrostatics, the stoichiometric reaction in equation (1) results in transfer of a delocalised negative charge on complex 1H^- to the (solvated) hydroxide species $\text{OH}^- \cdot (\text{H}_2\text{O})_{n-1}$, in which the negative charge is more localised due to the small size of the resulting anion (especially for small values of n). Therefore, we studied the effect of increasing the number water molecules (increasing n) around OH^- on the relative Gibbs free energy ($\Delta G_{298\text{K}}$) and enthalpy ($\Delta H_{298\text{K}}$) of protonation of complex 1H^- . As expected, DFT calculations show that the free energy change upon protonation of complex 1H^- is strongly dependent on the number of solvent molecules considered (see Figure S1). While the process is calculated to be uphill by +32 kcal mol⁻¹ with one water molecule, the presence of six water molecules lowers the free energy difference to only +11.5 kcal mol⁻¹. These results clearly reveal the importance of considering an appropriate number of explicit solvent molecules to describe the catalyst activation step.

To gain deeper insights into the catalyst activation pathway, we performed DFT based molecular dynamics (DFT-MD) with an explicit description of the water solvent. We studied the protonation pathway of complex 1H^- by a solvent water molecule in an explicit solvent box using the method of constrained molecular dynamics (CMD), where the proton-transfer reaction coordinate (Q) involves the cleavage of the O–H bond of a water molecule with simultaneous formation of the $\text{N}_{\text{dad}}-\text{H}$ bond.^[29] The calculated barrier for this protonation is +9.3 kcal mol⁻¹, with the overall process being endergonic by only +5.1 kcal mol⁻¹ as shown in Figure 2a.

The protonation of N_{dad} by a solvent water molecule results in the formation of complex **1B** and an OH^- anion, that diffuses away into the solution via the Grotthuss mechanism (see Figure 1 and Figure 2b).^[30] Clearly, such a realistic picture of the protonation can only be captured by incorporating explicit solvent simulations and accounting for thermal fluctuations. Dehydrogenation of complex **1B** generates complex **1**, the active catalytic species in this catalytic system. A detailed mechanism including solvent effects for this transformation is discussed in the hydrogen production section (*vide infra*).

Figure 2. (a) Free energy profile for the protonation of the ligand moiety (N_{dad}) in complex $1H^+$ by a solvent molecule obtained from constrained DFT-MD simulations. The reaction coordinate (Q) is shown in the left inset. (b) Representative snapshots of the transition state ($Q = 0 \text{ \AA}$) and the product state ($Q = 0.67 \text{ \AA}$) formed upon protonation of the ligand nitrogen (N_{dad}) of complex $1H^+$ by a solvent molecule. The OH^- anion formed upon deprotonation of the solvent molecule (enlarged) diffuses away into the solution via the Grotthuss mechanism involving the highlighted solvent molecules.

C–H activation steps for methanol, methanediol and formic acid

Having established the catalyst activation pathway, we studied the C–H activation of methanol by complex $2'$ (which is generated *in-situ* by hydrogenation of complex 1) producing formaldehyde and complex $2'B$ (see Scheme 1a). Complex $2'$ binds methanol and undergoes internal proton transfer from the OH group of methanol to the amido moiety to form complex $2'A$ (Scheme 1b). The complex then rearranges to form the zwitterionic agostic methoxide adduct $2'A'$. We determined the free energy barrier for the C–H activation step in complex $2'A'$ using DFT-MD. The reaction pathway was determined with CMD, using the hydride-transfer reaction coordinate (Q) that involves the cleavage of a C–H bond with simultaneous formation of a Ru–H bond (inset in Figure 3), and which was varied between $-0.93 \text{ \AA}$ and $0.87 \text{ \AA}$. This reaction coordinate (Q) has also been used in our previous studies to investigate such hydride transfer processes.^[15,17] Analysis of the CMD snapshots along the reaction shows a number of important interactions of the solvent with the reaction intermediates. In particular, the anionic oxygen moiety of methoxide (CH_3O^-) has strong hydrogen bond interactions with solvent molecules in

Figure 3. (a) Free energy profile for C–H activation by hydride transfer from a methoxide anion to ruthenium, obtained by constrained DFT-MD simulations. The reaction coordinate (Q) is depicted in the left inset. The barrier obtained with a static DFT model is shown for comparison. (b) A representative configuration near the initial state ($Q = -0.73 \text{ \AA}$), showing the methoxide anion being stabilised by three hydrogen bonds, and the product state ($Q = 0.63 \text{ \AA}$) showing the formaldehyde and interactions of the solvent with the hydrides on the metal centre.

the reactant state as shown in Figure 3b. Closer to the product state, the solvent interacts with the C–H bond being cleaved and the hydrides on the Ru metal center (Figure 3b).

While DFT-MD simulations provide valuable insights into these solvent interactions, owing to their computational expense, we resorted to static DFT micro-solvation calculations using explicit water solvent molecules to study the C–H activation steps of methanediol and formic acid. To have a proper benchmark, it is important to verify that such micro-solvated models inspired by the DFT-MD simulations can capture the most important solvent interactions in a quantitative manner. To this end, we compared the free energy barrier for C–H activation in methanol obtained from static DFT micro-solvation calculations to the barrier obtained with constrained dynamics simulations (Figure 3a). The barrier obtained with the static micro-solvated DFT calculations proved to be in close agreement with that obtained with solvent-box DFT-MD simulations ($+17 \text{ kcal mol}^{-1}$ and $+18 \text{ kcal mol}^{-1}$ relative to complex $2'A'$, respectively) using the same XC functional (BP86//BLYP(Water)), thus showing that the micro-solvation DFT approach performs well in capturing the most important solvation effects for this catalytic system.

Next, we computed the C–H activation barriers for dehydrogenation of methanediol and formic acid using a similar micro-solvation based approach that takes the most important solvent

interactions into account. In Figure 4, the relative activation energy barriers obtained with BP86//B3LYP(Water) are reported with respect to the alkoxide/formate adduct **2'A** (Scheme 1b). C–H activation of methanol to formaldehyde is the rate-limiting step in the overall process, with a computed barrier of +26.2 kcal mol⁻¹. A common feature of all three activated complexes **2'TS-1-CH₃OH_{3w}**, **2'TS-1-(CH₂(OH))_{2sw}** and **2'TS-1-HCOOH_{5w}** at the corresponding transition states (TS) involving C–H activation of methanol, methanediol and formic acid is the strong interaction of the anionic oxygen moiety and the H_{trans} center with the solvent (Figure 4). Interestingly, the C–H bond being cleaved also shows strong interactions with the solvent, except for formic acid where such interactions are sterically hindered (see Section S4 in the ESI).

Hydrogen production

Hydrogen production in the catalytic system occurs via the dehydrogenation of hydride complexes **1B** and **2'B**, which are hydrogenated forms of complexes **1** (the [Ru(trop₂dad)] complex) and **2'** (the [Ru(trop₂dae)] complex) respectively (Figure 1b). We considered three possible pathways for hydrogen production from a hydrogenated metal-ligand complex (Scheme 2). The first possibility is a direct (unassisted) hydrogen production (Scheme 2a) where the metal hydride is protonated by the ligand and solvent does not play a direct role in the proton transfer process. Another possibility entails protonation of the metal hydride via a solvent molecule acting as a proton relay (solvent mediated pathway, Scheme 2b). The final possibility we considered involves a solvent molecule that directly protonates the metal hydride without a direct involvement of

the ligand (solvent enabled pathway, Scheme 2c). In the latter case the ligand could bear a proton (as in complexes [Ru(PNP)] or **2'**) or may contain another functionality such as a methyl group ([Ru(PN^{Me}P)]).^[19,31] We would like to note here that mechanisms in Scheme 2a and 2b can be seen as a Noyori-Morris type mechanisms, where the metal and ligand cooperate to produce hydrogen. In contrast, Scheme 2c is purely a metal-centred mechanism with no direct cooperation of the metal and the ligand during the hydrogen production step.

We investigated direct (unassisted) and solvent mediated/enabled pathways for H₂-release from complexes **1B** and **2'B** using DFT-MD, with the pathways determined with CMD simulations. For complex **1B**, the chosen reaction coordinate (Q) for the direct (unassisted) pathway is the distance between the proton on N_{dad} and the hydride on Ru (H_{dad}–H_{Ru}), and is varied between 2.6 Å and 0.85 Å. The free energy profile as a function of Q and a representative snapshot of the TS is shown in Figure 5a. The computed barrier is +16.2 kcal mol⁻¹ (Figure 6a). To compare this to the solvent mediated mechanism, we also computed the barrier for this pathway. In this case, Q is the proton transfer coordinate that involves the cleavage of the solvent O–H bond and the simultaneous protonation of the Ru–H bond. Q varies between –0.5 Å and +0.85 Å (Figure 5b). The TS involves deprotonation of the ligand nitrogen (N_{dad}), indicating that the process is solvent mediated, as shown in Scheme 2b. The computed barrier (+19.2 kcal mol⁻¹) is somewhat higher than the direct pathway, suggesting that the direct pathway is the main operating mechanism for hydrogen production in complex **1B**, in good agreement with our previous DFT calculations with a micro-solvation model.^[19] Note that in the presence of large amounts of formic acid in the catalytic system, the metal hydride could be directly protonated

Figure 4. Snapshots of the transition state structures (**2'TS-1-CH₃OH_{3w}**, **2'TS-1-(CH₂(OH))_{2sw}** and **2'TS-1-HCOOH_{5w}**) for the C–H activation step obtained from micro-solvation based DFT models along with the activation energy barriers (relative to complex **2'A**) obtained in kcal mol⁻¹ (BP86//B3LYP (Water)) for (a) methanol, (b) methanediol and (c) formic acid.

Scheme 2. (a) Direct (unassisted), (b) solvent mediated and (c) solvent enabled mechanisms for hydrogen production during methanol dehydrogenation reactions.

by formic acid, and a solvent/substrate mediated pathway will lead to hydrogen production under these conditions.^[5,19]

For complex **2'B**, DFT-MD in combination with CMD was used to compute the barrier for H₂-release via a solvent mediated/enabled pathway. A direct pathway for hydrogen production was also explored, but was found to have a much higher activation barrier (see Section S6 in the ESI). The chosen proton-transfer reaction coordinate (Q) involves the cleavage of a solvent O–H bond with simultaneous protonation of the Ru–H bond and was varied between $-0.5 \text{ \AA}$ and $+1.27 \text{ \AA}$. The free energy profile along with a representative snapshot of the product state ($Q = 1.27 \text{ \AA}$) is shown in Figure 6a, with a rather low barrier of $+8.2 \text{ kcal mol}^{-1}$. The product state still has a protonated ligand nitrogen (N_{dae}) as shown in Figure 6b, and the overall mechanism is clearly solvent enabled (Scheme 2c). It results in the formation of an OH[−] anion that diffuses away into solution. Dehydrogenation of complex **2'B** using static DFT calculations with explicit solvent molecules also shows a solvent enabled pathway with similar barriers.^[19] Such a hydrogen production pathway for complex **2'B** is reminiscent of Beller's [Ru(PNP)] complex, for which DFT-MD simulations indicated that it also operates via a solvent enabled mechanism where the ligand nitrogen moiety remains protonated throughout the reaction.^[15]

Based on the static DFT calculations we summarise the overall mechanism for methanol dehydrogenation and hydrogen production catalysed by complex **2'** along with the corresponding relative Gibbs free energy (ΔG_{298}) values (BP86//

B3LYP(Water)) in Scheme 3 (see also Section S5 in the ESI for MERP involving methanediol and formic acid dehydrogenation). The origin of different hydrogen production pathways in complexes **1B** and **2'B** and their implications for the overall catalytic mechanism is discussed in detail in the next section.

Discussion

We have studied the mechanism of catalytic dehydrogenation of aqueous methanol mediated by the [Ru(trop₂dad)] and [Ru(trop₂dae)] complexes, using a combination of DFT-MD simulations and static DFT calculations taking explicit solvation (DFT-MD/static DFT) and thermal (DFT-MD) effects into consideration. We found that explicit description of the bulk solvent environment is essential for an accurate description of the catalyst activation process, that involves the protonation of an N_{dad} moiety in complex **1H**[−] by a solvent water molecule to produce complex **1B**. H₂-loss from complex **1B** yields the active catalyst complex **1** ([Ru(trop₂dad)]). The mechanism of methanol dehydrogenation by catalyst **1** was investigated in detail in our previous studies,^[19] but in addition to complex **1**, another complex **2** ([Ru(trop₂dae)]) is experimentally known to be generated *in-situ* under catalytic conditions. We had shown that both are catalytically active.^[19,20] Complex **2** converts to complex **2'** to perform catalysed dehydrogenation of aqueous methanol. Our previous studies indicated that (unlike for [Ru(trop₂dad)]) complex **1**) explicit solvation effects are important to describe

Figure 5. Free energy profile for hydrogen production from complex **1B** obtained from DFT-MD simulations, via (a) direct pathway with the reaction coordinate (Q) depicted in the left inset. A representative configuration of the transition state at $Q = 1.25$ Å is shown in the right inset. (b) Solvent mediated pathway with the chosen Q depicted in the left inset, and a representative configuration of the activated complex at $Q = 0.6$ Å shown in the right inset. Here, the ligand nitrogen (N_{add}) is deprotonated along the reaction, resulting in a solvent mediated pathway.

correctly the mechanistic features of the catalytic methanol dehydrogenation by complex **2'**. Herein we investigated the mechanism for aqueous methanol dehydrogenation to CO_2 and three equivalents of dihydrogen by complex **2'** taking explicit solvation effects into consideration. DFT-MD simulations that include thermal motion of explicit solvent molecules show that the solvent is an integral part of the reactive system. The solvent actively participates in the reaction via hydrogen bond interactions. In fact, it was not possible to locate a TS for the hydride transfer process in the absence of explicit solvent molecules for the dehydrogenation of methanol to formaldehyde (see section S3 in the ESI). We observed two contrasting effects of explicit solvent molecules in modelling the C–H activation steps: (1) The solvent stabilises the anionic RO^- moiety in the reactant species ($\text{R} = \text{CH}_3, \text{CH}_2\text{OH}, \text{CHO}$) via hydrogen bonding interactions and thereby increases the barriers for the C–H activation step compared to isolated models without such hydrogen bonding interactions. (2) Similar

hydrogen bonding interactions of the solvent with the Ru-H-C bond (of the incoming hydride) stabilises $2'\text{TS-1-CH}_3\text{OH}_{3\text{sw}}$ and $2'\text{TS-1-(CH}_2(\text{OH})_2)_{5\text{sw}}$ thereby assisting the C–H activation process. For $2'\text{TS-1-HCOOH}_{5\text{sw}}$, we note that the steric hindrance caused by the O=C=O moiety prevents hydrogen bonding interactions between the hydride moiety and surrounding water molecules (see Section S4 in the ESI). Moreover, the repulsive interactions of the hydride moieties on the metal centre in complex **2'B** increases the energy penalty for hydride transfer to complex **2'**, thus resulting in higher TS barriers for the C–H activation steps.^[33] However, hydrogen bond interactions of the solvent with the H_{trans} moiety facilitates C–H activation by stabilizing $2'\text{TS-1-CH}_3\text{OH}_{3\text{sw}}$, $2'\text{TS-1-(CH}_2(\text{OH})_2)_{5\text{sw}}$ and $2'\text{TS-1-HCOOH}_{5\text{sw}}$. To summarise, in aqueous solution solvent molecules can assist and mitigate C–H activation via hydrogen bonding interactions as discussed above. Thus, the solvent molecules constitute an integral part of the reactive

Figure 6. (a) Free energy profile for hydrogen production from complex **2'B** obtained from DFT-MD simulations, via a solvent enabled pathway with the chosen Q depicted in the left inset and (b) a representative configuration of the transition state at $Q = 0.6$ Å and the product state at $Q = 1.27$ Å. The OH^- anion formed upon deprotonation of the solvent molecule (enlarged) diffuses away into the solution via the Grotthuss mechanism involving the highlighted solvent molecules. The ligand nitrogen (N_{dse}) remains protonated throughout the process.

system and must be included for an accurate description of this process.

Next, we compared the mechanisms for hydrogen production by complexes **1B**, **2'B** and Beller's $[\text{Ru}(\text{PNP})]$ complex,^[15] which proceed via distinctly different reaction steps. H_2 -loss from complex **1B** proceeds via the direct (unassisted) pathway (see Scheme 2), while complex **2'B** and Beller's $[\text{Ru}(\text{PNP})]$ complex both lose H_2 via a solvent enabled pathway without direct involvement of the ligand. The latter is a result of the high pK_a of the ligand NH moiety. Collectively, the pK_a of the NH moiety and the hydricity of the metal hydride are the key factors in determining the energetics, thermodynamics, activation barrier, and the underlying mechanism for hydrogen production. We anticipate that the natural charge on the hydride is a good measure of its hydricity. The higher the negative natural charge, the higher the hydricity. We show that ligand pK_a (computed using DFT-MD with explicit water solvent) and our measure of natural charge for the hydricity of the metal-hydride bond can be used to differentiate between the (direct) unassisted, solvent mediated, and solvent enabled mechanisms (Scheme 2) of different catalysts.

For a catalytic system with low hydricity and low ligand pK_a , the direct (unassisted) mechanism seems to be the most preferred pathway, as it is difficult for the hydride to be protonated by a protic solvent, while the ligand can be easily deprotonated and directly participate in the mechanism (Scheme 2). This is the case for complex **1B** where the hydride has a computed natural charge of +0.08 units, and the computed estimate of the ligand ($\text{N}_{\text{dad}}-\text{H}$ function) pK_a is ~10 units (Figure 7 and Section S7 in ESI). A catalytic system with high ligand pK_a and high hydricity seems to undergo a solvent enabled (metal-centered) H_2 -formation mechanism, as the hydride is easily protonated by a protic solvent (methanol/water) while the ligand remains protonated along the reaction and therefore cannot directly participate in the mechanism (Scheme 2c). This is the case for both complexes **2'B**, (natural charge on the hydride of -0.16, and a computed $\text{pK}_a(\text{NH})$ of ~23 (see Section S7 in the ESI)), and Beller's $[\text{Ru}(\text{PNP})]$ catalytic system (computed natural charge on hydride = -0.28, computed $\text{pK}_a(\text{NH})$ of ~25^[15]) as shown in Figure 7. Other possibilities include (1) a catalytic system with high hydricity and low pK_a that is most likely to operate via a solvent mediated

Scheme 3. Overall mechanism with an explicit solvation model for dehydrogenation of methanol to formaldehyde catalysed by complex **2'** along with the corresponding Gibbs free energy values (ΔG_{298}) in kcal mol⁻¹ (BP86//B3LYP (Water)).^[32]

mechanism, as the solvent can protonate the hydride while the ligand can be easily deprotonated and directly participate in the mechanism, and (2) a catalytic system with low hydricity and high pK_a that could also operate via a solvent enabled mechanism, as the ligand remains protonated throughout the reaction and cannot directly participate in the mechanism (Scheme 2). For a catalyst operating via a direct (unassisted) or a solvent mediated process, the metal and the ligand cooperate to evolve hydrogen, as in the case of complex **1B**, resulting in a Noyori-Morris type mechanism. For catalysts operating via a solvent enabled pathway, the NH moiety is not directly involved in the hydrogen production mechanism owing to its high pK_a . Instead, the ligand may be involved via supramolecular contributions, such as H-bonding stabilization. Such catalytic systems would typically require an additive (Brønsted base) to achieve high activity since the ligand cannot function as an internal acceptor base under the applied reaction conditions.^[15]

To summarise, our results show that the [Ru(trop₂dad)] catalytic system exhibits metal-ligand cooperativity, in marked contrast to the [Ru(trop₂dae)] catalytic system, that operates via a solvent enabled (metal-centred) pathway without the direct

involvement of the ligand. In this regard, accurate estimation of the ligand pK_a is important, as it determines the exact role of the ligand (either as an internal acceptor base or a hydrogen bond donor) in the overall mechanism for aqueous methanol dehydrogenation.

Based on these mechanistic insights, it is evident that the hydricity of the Ru-H bond in complex **2'B** and the ligand pK_a are the most important parameters that govern the mechanism and activation energy barrier for dehydrogenation of methanol.^[34] From a catalyst design perspective, selective functionalization of complex **2'** can help to influence these parameters. To tune the hydricity of the metal centre in **2'B**, we substituted the trans hydride moiety (H_{trans}) by (1) a fluoride group ($Y=F$) or (2) a SiH_3 group ($Y=SiH_3$), and computed the corresponding methanol C-H activation barriers (BP86//B3LYP (Water)). Additionally, we considered replacing the $X=CH_2$ in [Ru(tropHN-CH₂-X-NHtrop)] by $X=CO$. In order to determine the nature of the reaction mechanism during aqueous methanol dehydrogenation (Noyori-Morris or metal-centred), we examined the transition states of these catalytic systems.^[35] The results are presented in Figure 8. We expected that replacing

Figure 7. Computed pK_a of the NH moiety using DFT-MD simulations with explicit water solvent and the overall nature of the mechanism (Noyori-Morris/solvent enabled) during aqueous methanol dehydrogenation for the [Ru(trop₂dad)], [Ru(trop₂dae)] and [Ru(PNP)] catalytic systems.

Figure 8. Some examples to tune the activation energy barriers and the reaction mechanism for dehydrogenation of methanol by the [Ru(trop₂dae)] catalytic system by selective functionalization of the complex 2' (BP86//B3LYP(Water)).

Y=H by Y=F would increase the acidity of the metal centre due to strong electron-withdrawing effect of the fluoride group. Consistent with our expectations the overall C–H activation energy barrier reduced by about 50%. Interestingly substituting the H_{trans} moiety by an electron rich SiH₃ group also resulted in a lower TS barrier for C–H activation due to destabilization of the methoxide adduct 2'A, and switched the mechanism from metal-centred (Y=H) to a Noyori-Morris type mechanism. Furthermore, we expected that the X=CO substitution would decrease the pK_a of the N_{dae} <C–>H moiety due to the electron withdrawing nature of the CO moiety. While this substitution increased the TS barrier for C–H activation to ~34 kcal mol^{–1}, it changed the mechanism to a Noyori-Morris type mechanism reflecting the importance of the ligand pK_a , consistent with our

expectations. Note that the role of the ligand pK_a as an important characteristic has also been suggested in an earlier study of Ru-catalysed methanol dehydrogenation,^[15] and is clearly elucidated in the present work as well. All these observations show the possibility to tune the C–H activation barriers and the nature of the operating mechanism by modifying the hydricity of the metal center and the ligand pK_a via selective ligand functionalization of the [Ru(trop₂dae)] complex. This is by no means a comprehensive study of all possible substituents that can be incorporated, but we expect it to serve as a guideline for future high-throughput screening studies.^[36,37]

Conclusions

To summarise and conclude, we have investigated aqueous methanol dehydrogenation catalysed by the [Ru(trop₂dad)] and [Ru(trop₂dae)] catalytic systems, using a combination of DFT-MD simulations and static DFT models incorporating explicit solvent molecules. The results demonstrate the active participation of solvent in various stages of the catalytic cycle, including catalyst activation, C–H activation and hydrogen production. Additionally, for hydrogen production we find divergent pathways for the [Ru(trop₂dad)] and the [Ru(trop₂dae)] catalytic systems. Analysis of hydricity and ligand pK_a of these complexes can help to rationalise the origin of different hydrogen production pathways. We anticipate that these descriptors may have a generic use in identifying, and possibly tuning the operating mechanism for hydrogen production by other catalytic systems that operate in a protic solvent environment. The present study constitutes an interesting example of two active complexes in a catalytic system that exhibit divergent pathways for aqueous methanol dehydrogenation.

Computational Methods

The DFT-MD model consisted of the catalyst complexes with 108 explicit water molecules in a cubic periodic system (L = 16 Å) and the electronic structure was determined using the BLYP functional,^[38,39] supplemented with a dispersion correction (D3).^[40] The static DFT micro-solvation calculations using explicit water solvent molecules were performed at the RI-DFT-D3/BP86/def2-TZVP level of theory, including a dispersion contribution (disp3).^[38,41] In this paper, the representation “BP86//XC(Water)” stands for single-point SCF calculations performed using XC functional (XC = B3LYP or BLYP) with implicit solvent corrections (COSMO) for water on DFT optimised geometry using the BP86 functional, with a dispersion correction (disp3).^[42] An example for the naming convention for complexes in this study: **2**^{TS}-**1**-CH₃OH_{3w} indicates the transition state for dehydrogenation of CH₃OH in the presence of complex **2** with three explicit solvent water molecules considered in the static DFT model. Further details on the computational methods are provided in Section S1 in the ESI.

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Conflict of Interest

The authors declare no conflict of interest.

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- [34] Equivalently one can state that the Lewis acidity of the metal center and Bronsted basicity of the ligand in complex **2'** are the most important parameters that govern the mechanism and activation energy barrier for the dehydrogenation of methanol.
- [35] Noyori-Morris mechanism: Both Ru and N_{dae} participate directly in the mechanism with Ru receiving the hydride from C–H and N_{dae} receiving simultaneously the proton formed upon cleavage of the O–H bond in methanol/methanediol/formic acid. Metal-centered mechanism: The O–H bond in methanol/methanediol/formic acid is already deprotonated in a separated step. The transition state for C–H cleavage only involves transfer of a hydride moiety to the metal center. N_{dae} does not participate directly in the mechanism because it is protonated. See a.o.: a) C. A. Sandoval, T. Ohkuma, K. Muñiz, R. Noyori, *J. Am. Chem. Soc.* **2003**, *125*, 13490–13500; b) K. Abdur-Rashid, M. Faatz, A. J. Lough, R. H. Morris, *J. Am. Chem. Soc.* **2001**, *123*, 7473–7474.
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