Water Dissociation on α_1-Hafnium and Ytterbium Substituted Dawson Polyoxotungstates: A Density Functional Theory Study[†]

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Density functional theory (DFT) calculations were devised to get insight into Lewis acidic catalysis by POMs, especially on the intriguing activation of complexed water molecules that was observed in some experimental cases. Computationally, it appears that deprotonation is feasible with $[\alpha_1\text{-Hf}(H_2O)P_2W_{17}O_{61}]^{6-}$, but not with $[\alpha_1\text{-Yb}(H_2O)P_2W_{17}O_{61}]^{7-}$. This reflects the difference of the electronic structures (diamagnetic for hafnium POM, paramagnetic for ytterbium POM). From a mechanistical point of view, indirect Brønsted catalysis cannot be excluded in the hafnium case, especially for Mannich reactions. But our calculations show that catalysis by $[\alpha_1\text{-Yb}(H_2O)P_2W_{17}O_{61}]^{7-}$ (and presumably all the lanthanide series) proceeds through direct complexation of the substrates to the POM.

Introduction

Catalysis by polyoxometalates (POMs) has been greatly expanding these last years.[1] POMs are clusters of early transition metals in high oxidation states (generally W^{VI}, Mo^{VI}, V^{V}) and oxo ligands.[2] They can be composed of only one type of metal oxide, as is the case for the Lindqvist structure (Figure 1a), or they can include heteroelements, e.g., the Keggin and Dawson polyanions (Figure 1b,c). This versatility leads to varied structures and fine-tuning of the properties that dictate POM reactivities, such as redox potentials, acidities, etc.

As part of our program devoted to building functional hybrid POMs for targeted applications,[3] we have introduced Lewis acidic polyoxoanions as recyclable catalysts for organic transformations.[4] This constitute to date a new avenue for catalysis by POMs. For example, we have shown that $(TBA)_5K[\alpha_1\text{-Hf}(H_2O)_4P_2W_{17}O_{61}]$ is an efficient, air stable, and chemoselective catalyst that promotes Mannich-type reactions (Scheme 1). Mizuno followed on our findings and has recently introduced new Hf and Zr sandwich silicotungstates.[5] He confirmed that incorporating Lewis acidic cations made the POMs suitable for this particular catalysis.

When taken from a water containing solution, the mass spectrum of the initial Hf-POM complex featured peaks attributed to hydroxo-containing fragments. Thus, under the analysis conditions, a water molecule was activated by the Hf-POM, generating a proton, and a hydroxo ligand on the Hf.

That this deprotonation was triggered by complexation of water to the Lewis acidic corner of the POM seemed probable (Scheme 2). Yet this could not unambiguously be inferred from MS analysis. This O−H activation is all the more relevant to our work that the corresponding hydroxo-complex $(TBA)_7[\alpha_1\text{-Hf}(OH)P_2W_{17}O_{61}]$ did not lead to Lewis acid catalysis. In addition, we had only circumstantial evidence for the exact mechanism of the reaction. Indeed, Mannich additions could be catalyzed via a direct Lewis acid−substrate interaction, or they could derive from the aforementioned proton.[6] To get a clearer mechanistic picture, we decided to probe this issue deeper, and to do that by seeking answers from modeling.

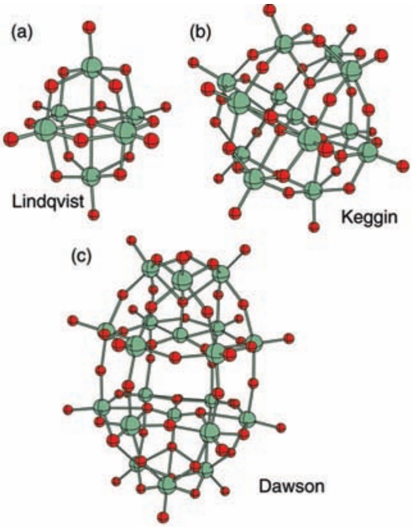
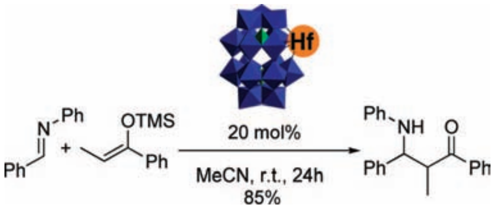


Figure 1. Examples of polyoxometallic structures.

SCHEME 1: POM-Catalyzed Mannich Reaction of Diphenylimine



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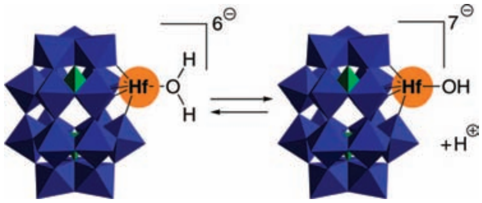
SCHEME 2: Lewis Acid-Mediated Activation of a Water Molecule on $[\alpha_1\text{-Hf(OH)P}_2\text{W}_{17}\text{O}_{61}]^{7-}$



Former modeling studies on POMs have proven to be useful to understand structures[7] or reactivities,[8] and we believe such an approach can help design more efficient Lewis acid catalysts.

Here we examine the deprotonation of a water molecule complexed to substituted Dawson POMs $[\alpha_1\text{-HfP}_2\text{W}_{17}\text{O}_{61}]^{6-}$ and $[\alpha_1\text{-YbP}_2\text{W}_{17}\text{O}_{61}]^{7-}$.

Computational Details

The TURBOMOLE[9] software was used to perform the QM (DFT) calculations by using the B-P86 functional, within the framework of the RI-J approximation.[10] The SV(P) basis set developed by Ahlrichs[11] was used for geometry optimization. Due to the large size of the α_1-Dawson cluster, frequency calculations were not performed. We recently used this level of calculation to study the regioselective activation of tin substituted Dawson POMs.[3a] The description of the latter systems correlated well with their observed behaviors and should thus be considered accurate enough for our purpose. Solvent effects induced by acetonitrile (dielectric constant was set to 36.64) were taken into accound by turning on the COSMO implementation. A previous study by Poblet showed that it is necessary to include at least nonspecific solvent effects (through COSMO or PCM models) when the ratio (charge/number of metal centers) is superior to 0.8.[12] This is not the case here, but we check to confirm there is no strong effect.

Results and Discussion

Water deprotonation of $[\alpha_1\text{-Hf(H}_2\text{O)P}_2\text{W}_{17}\text{O}_{61}]^{6-}$ **1-Hf** was examined first (Figure 2a). Optimization of the energy of **1-Hf** suggested a conformation in which the Hf−OH$_2$ distance is 2.428 Å. The two protons of the water molecule were found to point toward Hf−O−W bridging oxygens. One interacted with a ligand from the cap (calc H−O distance: 1.683 Å), and the other pointed toward the belt (calc H−O distance: 2.14 Å). This was in agreement with our previous report, which indicated the similar Sn−O−W bridges in $[\alpha_1\text{-Sn(R)P}_2\text{W}_{17}\text{O}_{61}]^{7-}$ to have increased electron density and nucleophilicity.[3a] When more molecules of water added in the vicinity of hafnium, they reorganized to create a network at the surface of the POM with only one directly connected to Hf (see Supporting Information for structure).

As was anticipated from the prearrangement of the water molecule in **1-Hf**, proton transfer to the POM (on bridging Hf−O−W) was calculated to proceed with only a small barrier (**TS1/2-Hf** 2.59 kcal/mol), leading to product **2-Hf**. Implicit solvent effects, as calculated with the COSMO implementation, are rather small. The water molecule in **2-Hf** was fully dissociated and the Hf−OH distance was reduced to 2.037 Å. Because the reaction was exothermic (**2-Hf** is 11.67 kcal/mol more stable), we could expect **1-Hf** to be rather acidic, which correlated well with its observed behavior in solution.[4a] The dissociation process involving the other water proton, which leads to **3-Hf** (−14.35 kcal/mol stabilization) was also calculated. This process was less favorable because the barrier associated was found to be 6.29 kcal/mol (**TS1/3-Hf**). The difference between the two processes is large enough to exclude direct deprotonation of **1-Hf** to **3-Hf**.

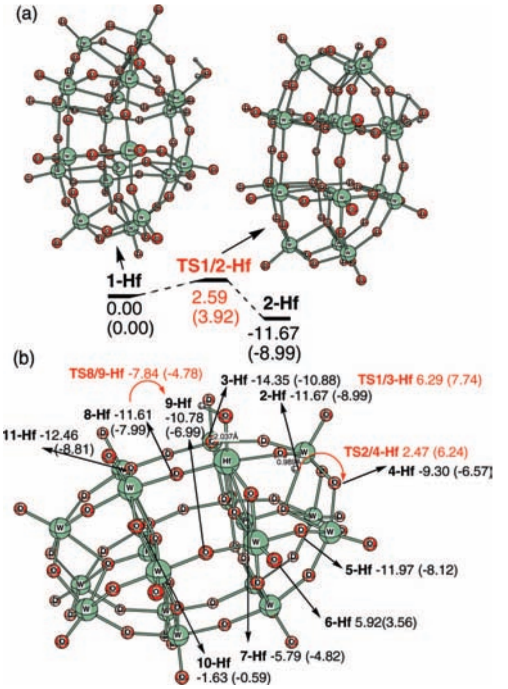


Figure 2. (a) Structures of the POM complexes **1-Hf** and **TS1/2-Hf**, calculated at the BP86/SV(P) level. (b) Structure of the POM complex **2-Hf**, at the same level. The energetic data for the other complexes and transition states are also given. In parenthesis are the values obtained with COSMO.

The proton bound to the POM framework after deprotonation might hop from one oxo to the other. For this to happen, two conditions are required: (i) the stability of the newly protonated species should be increased and (ii) the barrier for the transformation should be low enough. To ascertain this, we first calculated the energies of protonation on several representative external oxo ligands (Figure 2b, items printed in black). Most of the different forms had approximately the same stability when protonation occurred on bridging oxo ligands, which agrees with known data on protonated POMs.[13] The cases of **8-Hf** and **9-Hf** provide us with an interesting insight into Dawson protonation. In our abovementioned previous study related to the regioselective activation of Sn substituted POM, acylation of the belt−belt bridging oxos was detrimental.[3a] In the present case, capture of the proton results in hydrogen-bond mediated proton delocalization between the two oxygens and this can explain the relative stability of these two regioisomers. A small barrier was found for this proton exchange (3.77 kcal/mol). Finally, with **10-Hf**, one can get an estimate of the stabilization brought by the Hf(IV)-triggered increase of the electron-density on the neighboring oxo ligands.[3a,14] Indeed, protonation on **10-Hf** is 4 kcal/mol less stabilizing than protonation of **7-Hf** (−5.79 kcal/mol vs −1.63 kcal/mol).

We next tried to get an idea of the activation barriers involved (Figure 2b, red ink). Proton hopping from **2-Hf** to **4-Hf** led to a 14.1 kcal/mol barrier. This is much higher than the initial water deprotonation but still feasible, maybe through solvent molecules (not included in this work).

Overall, the Hf-substituted Lewis acidic POMs are also quite Brønsted acidic, and the proton can migrate onto the POM surface relatively easily.

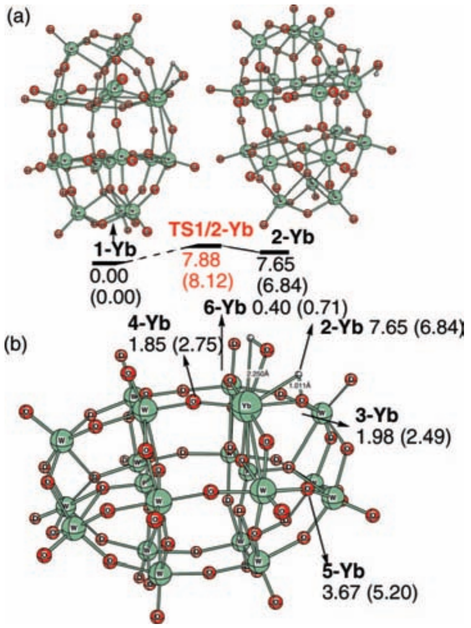


Figure 3. (a) Structures of the POM complex **1-Yb** and **TS1/3-Yb**, calculated at the BP86/SV(P) level. (b) Structure of the POM complex **2-Yb**, at the same level. The energetic data for the other complexes are also given. In parenthesis are the values obtained with COSMO.

We next examined the ytterbium derivative [α_1-Yb(H_2O)$P_2W_{17}O_{61}$]$^{7-}$. The optimized aqua complex geometry **1-Yb** is similar to the one found for **1-Hf**. The Yb−OH_2 distance is longer (2.57 Å vs 2.43 Å, Figure 3) which reflects the ionic radius increase (99 pm vs 83 pm[15]). An interaction with the same oxo ligand as before is observed. Yet, the proton transfer was not favorable. The associated barrier is higher than with Hf, yet still within reach (7.88 kcal/mol). The process is endothermic (7.65 kcal/mol). Furthermore, the first minimum obtained [α_1-Yb(OH)$P_2W_{17}HO_{61}$]$^{7-}$ (**2-Yb**) has the proton pointing outward (7.65 kcal/mol) rather than toward another oxo (as is the case with **2-Hf**). That said, this latter conformation (see **3-Yb**, 2 kcal/mol) has also a lower energy, but still in the endothermic range.

Overall, none of the protonated Yb hydroxo complexes is more stable than the water complex (see in particular **4-Yb** at 1.85 kcal/mol and **5-Yb** at 3.67 kcal/mol). It thus appears that deprotonation in the Yb compound is unfavorable.

We wondered what was the origin of such a difference between Hf and Yb. The immediate factor that came to our mind was that both metals were electronically different. **1-Hf** is a diamagnetic closed-shell polyanion, and **1-Yb** is paramagnetic. This was at the origin of great difference in their NMR patterns,[4] and we surmised that it could also play a predominant role for the reactivity.

The spin density isosurfaces for **1-Yb** and **2-Yb** have been calculated (Figure 4). For **1-Yb** the ground state is triplet. One single electron is localized on the ytterbium in a f orbital and the second one is delocalized all over the oxygens binding the ytterbium *but not on the water molecule*. In the case of **2-Yb**, one single electron is still localized on the metal but the second is now mainly localized on the oxygen atom of the remaining hydroxo. Therefore, this ytterbium−oxygen bond is best described as a 3e$^-$ electron bond with a repulsive character[16] and thus less stabilizing than in the case of the hafnium derivative, which confirmed our hypothesis.

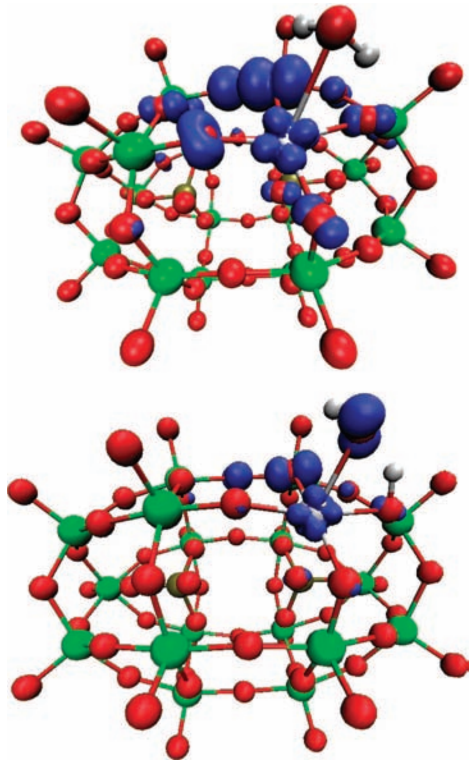


Figure 4. Spin density (show in blue) in **1Yb** (top) and **2Yb** (bottom), in green tungsten atoms, in red oxygen.

Conclusion

DFT calculations were devised to get insight into Lewis acidic catalysis by POMs, especially on the intriguing activation of complexed water molecules that was observed in some cases. It appears that spontaneous intramolecular deprotonation is feasible with [α_1-Hf(H_2O)$P_2W_{17}O_{61}$]$^{7-}$, but not with [α_1-Yb(H_2O)$P_2W_{17}O_{61}$]$^{7-}$. This reflects the difference of the electronic structures. From a mechanistical point of view, indirect Brønsted catalysis cannot be excluded in the hafnium case (it should be pointed out that Mizuno could exclude this mechanism for POM-catalyzed cyclization of citronellal). But our calculations show that catalysis by [α_1-Yb$P_2W_{17}O_{61}$]$^{7-}$ (and presumably all the lanthanide series) proceeds through direct complexation of the substrates to the POM.

Work to further assess the exact mechanism for [α_1-Hf(H_2O)$_n$$P_2W_{17}O_{61}$]$^{7-}$, and to understand the origin of the excellent chemoselectivity that POMs exhibit toward imines is underway. We will report our results in due course.

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Supporting Information Available: Energetics and Cartesian coordinates for all the calculated species. This information is available free of charge via the Internet at http://pubs.acs.org.

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