

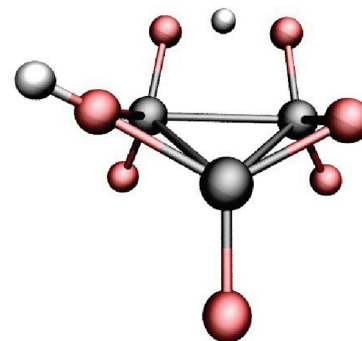
Proton Hop Paving the Way for Hydroxyl Migration: Theoretical Elucidation of Fluxionality in Transition-Metal Oxide Clusters

Raghunath O. Ramabhadran, Nicholas J. Mayhall, and Krishnan Raghavachari*

Department of Chemistry, Indiana University, Bloomington, Indiana 47405, United States

ABSTRACT The reactions of chemisorbed water on $W_3O_6^-$ and $Mo_3O_6^-$ clusters have been investigated to explore the phenomenon of fluxionality in transition-metal oxide clusters. The net observed phenomenon here is a hydroxyl migration. However, mechanistic studies using electronic structure theory reveal that the hydroxyl migration occurs by a synergistic pathway led by a proton hop and assisted by an interconversion between a bridging oxygen and a terminal oxygen. The proton hop provides access to two isomers, which differ in the relative position and orientation of the hydroxyl groups, thereby generating the scope for an enhanced catalytic activity in important processes such as hydrogen evolution from water.

SECTION Dynamics, Clusters, Excited States



Catalytic applications of transition-metal oxides (TMOs) are innumerable.¹ Small clusters of TMOs have been used as model systems to investigate the reactivity of low-coordinate and defective surface sites on these materials. For instance, hydrogen evolution from water and activation of inert chemical bonds (e.g., C–H) are important areas where these systems have been investigated recently in our group.^{2–4} Potential catalytic applications have driven the scientific community to probe these TMOs for unraveling interesting chemical features^{5–9} that could further assist in opening newer avenues in research. The electronic structures of the TMO clusters have been investigated by many research groups.^{10–21} A significant number of contemporary theoretical and experimental studies on these TMO clusters have been focused on their reactions with small molecules.^{22–35} A deeper understanding of the physical and chemical factors affecting the reactivity of the TMO clusters is extremely useful in furthering their catalytic applications.

One such major factor, fluxionality, is a key aspect in cluster science.³⁶ Historically, it is well-known that fluxionality can significantly affect the reaction sites in a molecule.³⁷ Proper exploitation of fluxionality can therefore have a significant impact on the alteration of the reaction site of a molecule and hence can be invaluable in catalysis, a point strikingly illustrated by the dexterous utility of fluxionality in purely metallic clusters.^{36,38} However, to the best of our knowledge, there have not been many studies on the fluxionality of TMO clusters. While Dixon and co-workers in 2006 have reported that larger rings of certain TMO clusters exhibit structural fluxionality,²⁰ the effect of chemical reactivity on fluxionality and the scope for catalysis have hitherto not been explored.

The first step toward utilizing fluxionality in TMO clusters involves the elucidation of structural fluxionality in TMO

clusters when they react with small molecules. In this letter, we theoretically demonstrate the phenomenon of proton-assisted fluxionality in TMO clusters. On the basis of our current interest in the catalytic applications of molybdenum and tungsten oxide clusters toward hydrogen evolution from water,^{4,23,24} chemisorbed water on the surface of $W_3O_6^-$ and $Mo_3O_6^-$ clusters has been chosen to study this phenomenon of proton-assisted fluxionality. The “proton hop” effectively results in a hydroxide group migration, whereas the actual process occurring here is a proton migration resulting in the swapping of positions between a terminal oxygen and a bridging oxygen. Such a chemical rearrangement results in two isomers which differ in the position as well as relative orientation of the hydroxide groups. This creates an alteration in the reactive site of the TMO clusters before and after the proton hop, thereby influencing their catalytic activity.

The equivalence of different types of oxygens in the TMO clusters and the fact that oxygens (one of which belongs to chemisorbed water and the rest to the TMO clusters) and hydrogens (of chemisorbed water) are the atoms most actively involved in the fluxionality of the TMO clusters warrant a simplified notation for the atoms involved to avoid confusion in the following discussion. In this study, the oxygen of water is denoted as O^W (inset, Figure 1). Irrespective of the TMO cluster under study ($W_3O_6^-$ or $Mo_3O_6^-$), it is observed that water dissociates as H and O^{WH} , and the H adds to a bridging oxygen attached to W^1 and W^2 (or Mo^1 and Mo^2). The remaining metal center (tungsten or molybdenum) is denoted as W^3 .

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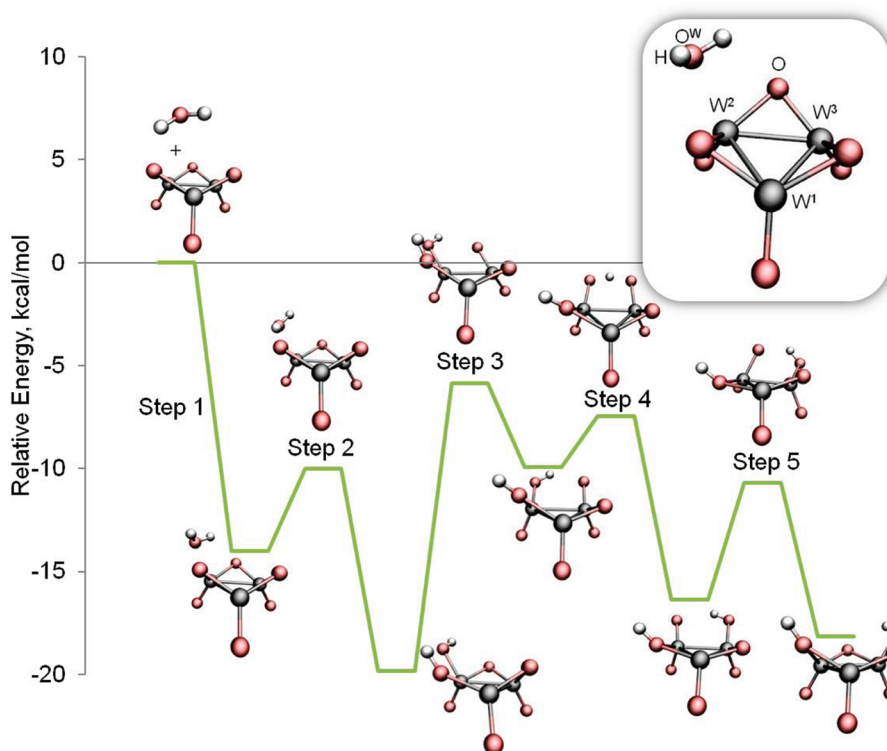


Figure 1. Reaction energy profile (kcal/mol) for the reaction of $W_3O_6^-$ (doublet) with water. The inset indicates the labels used to denote the relevant atoms on water and the metal oxide cluster. The metal oxide clusters have been oriented identically in both the inset and the reaction profile.

The oxygen bridging W^2 and W^3 (or Mo^2 and Mo^3), simply denoted as O (inset, Figure 1), plays a key role in the reactive chemistry leading to the fluxional behavior. Next, for the purposes of bookkeeping and a better understanding of this work, the entire reaction scheme under study has been classified in five steps (Figure 1). Again, irrespective of the TMO cluster under study ($W_3O_6^-$ or $Mo_3O_6^-$), step 1 is the barrierless formation of a complex between the TMO cluster and water. Step 2 is the formation of the initial adduct. Step 3 is the “preparation” step prior to the proton hop. Step 4 is the proton hop itself, and the final step 5 is the formation of the rearranged adduct.

The lowest-energy isomer of $W_3O_6^-$ (inset, Figure 1) has C_{3v} symmetry and a doublet electronic state. This is more stable than the lowest quartet state by 4 kcal/mol. Both isomers have three bridging oxygens and three terminal oxygens. The bridging oxygens are more reactive than the terminal oxygens in such oxygen-deficient electron-rich anionic clusters due to their larger partial charge and additional angle strain.⁴ Chemisorption of water initially results in the formation of a complex stabilized by 14 kcal/mol due to strong electrostatic interactions (step 1, Figure 1). Following this, hydrogen from water adds on to an electron-rich bridging oxygen center of the cluster, while the hydroxyl group ($O^W H$) adds to the relatively electron deficient tungsten center. The resulting adduct is stabilized relative to the starting reactants (water and $W_3O_6^-$) by 20 kcal/mol (step 2, Figure 1). We note that the addition of hydrogen to the bridging oxygen (between W^1 and W^2) results in an asymmetric bridging

environment involving the presence of a covalent W^1-OH bond and a partially broken W^2-O bridging oxygen bond. The remaining two bridging oxygens are intact, one of which plays a vital role in the manifestation of fluxionality. The next step (step 3, Figure 1) essentially acts as a precursor to the key proton hop. In this step, the bridging oxygen between W^2 and W^3 opens up to go to a terminal position on W^3 , and the W^2-W^3 distance shortens significantly. This step has the highest barrier in the entire reaction scheme. The resulting intermediate is more stable than the starting reactants by 10 kcal/mol. At this juncture, the intermediate is in the appropriate conformation to assist the key proton migration. The stage is set for the proton to hop across from $O^W H$ to the newly formed terminal oxygen on W^3 .

The very high propensity for the proton hop to occur is clearly illustrated by the low barrier (step 4, Figure 1) for the process. However, much of the preparation energy to assist the proton hop is actually spent to get the intermediate (formed in step 3) in the right conformation with the H of $O^W H$ (attached to W^2) facing the terminal oxygen (attached to W^3). The proton hop now becomes a highly favored process, partly due to the stabilization enjoyed by the transition state (TS) (step 4, Figure 1) via hydrogen bonding. The $O^W \cdots H$ distance in the TS is 1.186 Å, and the $O \cdots H$ distance is 1.275 Å (Table S1, Supporting Information). Also, the $O^W H O$ angle in this TS is 157°. Thus, the proton is very tightly sandwiched between the two oxygens in this TS for the proton hop. Hence, it does not come across as a big surprise that the barrier for this process is low.

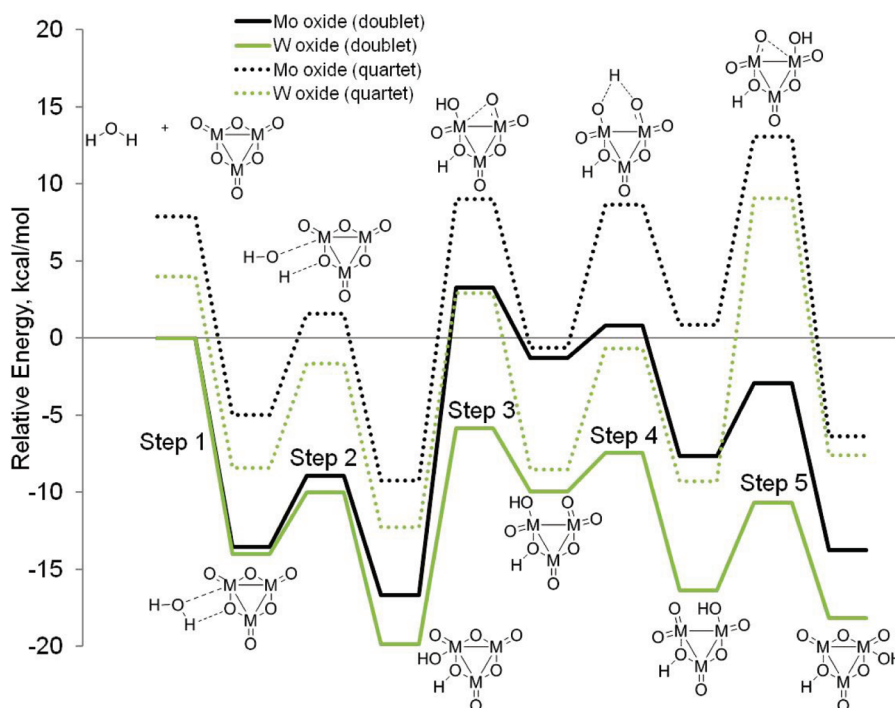


Figure 2. Comparison of the reaction energy profiles for the reaction of water with the Mo (black line) and W (green line) oxides in their doublet (solid line) and quartet (dotted line) states. M refers to either Mo or W, as indicated in the legend. The doublet states have been chosen as the origin along the relative energy coordinate.

The intermediate obtained immediately following the proton hop (step 4, Figure 1) is significantly stabilized relative to the starting materials by 16 kcal/mol. Compared with the intermediate immediately preceding the proton hop in step 3, it is more stable by approximately 6 kcal/mol. Structurally, the only significant difference between the two intermediates is the relative orientation of the two hydroxyl groups in the cluster. Prior to the proton hop, both of the hydroxyl groups are closer to each other, but after the proton hop, the hydroxyl groups are farther from each other. Since electron-rich groups such as the hydroxyl tend to stay away from each other to minimize electrostatic repulsion,³⁹ the lower energy of the intermediate following the proton hop is readily explained.

The next and the final step in the reaction scheme (step 5) is the conversion of the terminal O^W (attached to W^2) to a position bridging W^2 and W^3 . This is in contrast to that seen earlier in step 3, where it was a cluster oxygen that occupied a position bridging W^2 and W^3 . A comparison of the barriers between steps 3 (bridging cluster O) and 5 (bridging O^W) in Figure 1 clearly reveals that the latter has a lower barrier. The same chemical principle, that is, the inclination of electron-rich hydroxyl groups to stay away from each other to minimize electrostatic repulsion, readily explains the magnitude of the relative barriers. In the TS for step 3, the two hydroxyl groups are much closer than the two hydroxyl groups in step 5, resulting in lesser electrostatic repulsion in the latter. Hence, the TS for step 5 is destabilized less relative to the TS for step 3. Besides, the initial adduct formed in step 2 is more stable than the intermediate formed after the proton hop in step 4. Thus, greater stabilization of the reactant (the initial adduct,

in this case) in step 3 and lesser destabilization of the TS in step 5 both account for the magnitude of the relative barriers observed here.

The rearranged adduct obtained in step 5 (Figure 1) is observed to be slightly higher in energy (by 2 kcal/mol) than the initial adduct formed in step 2 (Figure 1). This may appear contradictory as the two hydroxyl groups in the initial adduct are much closer relative to the hydroxyl groups in the rearranged adduct. A closer observation, however, reveals a relatively short $H \cdots O^W$ distance (2.513 Å) in the initially formed adduct (Table S2, Supporting Information), indicating a weak but stabilizing hydrogen-bonding-type interaction. In the rearranged adduct, the $H \cdots O^W$ distance is 4.092 Å (Table S2, Supporting Information), implying that there is no significant interaction between H and O^W . Due to this, the rearranged adduct lacks a stabilizing factor present in the initially formed adducts. Hence, it is slightly higher in energy. The manifestation of fluxionality is complete at this stage. The net effect of all of these steps is a hydroxyl group migration from W^2 to W^3 . However, mechanistically, it is evident that it is a proton hop from O^W to a bridging cluster oxygen that triggers fluxionality here.

In Figure 2, the fluxionality reaction profiles for both spin states (doublet and quartet) of molybdenum and tungsten oxide clusters are given. It is seen immediately that, qualitatively, the same mechanistic pattern is seen for both spin states for both metal oxides. As expected (vide supra), the reactant, intermediates, TSs, and products for the quartet spin state are slightly higher in energy relative to those in the doublet. Quantitatively, we observe that there are two small

differences between the reaction profiles of the quartet states and the doublet states for both Mo and W. The first difference is in the location of the overall highest-energy barrier. On both doublet surfaces, step 3 acts as the rate-determining step, while step 5 acts as the rate-determining step on both quartet surfaces. This is a result of the significantly larger doublet–quartet energy separations of the step 5 TSs. The second difference is in step 4, i.e., the proton hop. For both doublet states, the proton hop is clearly exothermic. However, in the quartet state, the reactants and products of the proton hop are nearly isoenergetic. Again, this arises from the significantly smaller doublet–quartet energy separation for the reactants with respect to the products obtained in the proton hop step.

To elucidate the role played by the identity of the transition-metal center, we compare the reaction profiles for molybdenum oxides and the tungsten oxides. Upon reaction with water, both the doublet state of Mo_3O_6^- and the quartet state (less stable by 8 kcal/mol) show similar qualitative reactivity trends as their tungsten analogues. In addition, the quantitative differences in step 4 (proton hop) between the doublet and the quartet states of W_3O_6^- are reproduced for Mo_3O_6^- as well. The differences in the W_3O_6^- and Mo_3O_6^- reaction pathways are most significantly pronounced in the step immediately preceding the proton walk (step 3). This is the step in which a metal–oxygen σ -bond is broken and a metal–oxygen π -bond is formed. The energetics of this step mirrors the relatively stronger tungsten–oxygen π -bond strength. We observe that the energy difference for this process between W_3O_6^- and Mo_3O_6^- is consistent with the bond energies obtained by Dixon and Peterson.²¹ Thus, the metal–oxygen bond strengths contribute significantly to the differences in the W_3O_6^- and Mo_3O_6^- reaction pathways.

A key observation in this study has been that for all of the reactions shown in Figure 2, the key step, i.e., proton hop, always has a lower barrier than the step preceding it. The inference drawn from this observation is that, irrespective of the spin state or the nature of the metal, a lot of the energy needed for the proton hop to occur is in the form of preparation energy, i.e., to get the molecule in the right conformation, following which the proton hop occurs most readily. Another observation, consistent with all of the systems studied here, is that the proton hop is essential to connect the initially formed adduct and the final rearranged adduct, i.e., in the absence of the proton hop, there is no energetic drive for the TMO clusters to rearrange. In our previous study on hydrogen evolution from water,⁴ we had shown that to liberate hydrogen from a tungsten oxide cluster, a hydride and a hydroxide should lie in close proximity. Further, hydrogen atom mobility was found to be critical in bringing the two groups close enough for H_2 elimination. The apparent hydroxyl group mobility discussed in this work, induced because of fluxionality, adds another dimension of complexity that creates more possible scenarios for hydrogen elimination. Thus, fluxionality is another aspect that needs to be taken into account for studying the catalytic role of these TMO clusters in hydrogen evolution. Finally, we note that our study is valid for isolated gas-phase ions where there is no dissipation of energy and that the behavior in condensed media may be different due to the possibility of the intermediates being trapped.

In conclusion, we have theoretically demonstrated for the first time the manifestation of fluxionality in TMO clusters during the course of their reaction with small molecules. Using the reactions of W_3O_6^- and Mo_3O_6^- with water as model systems, we observe that a proton hop across two oxygens in these TMO clusters mediates fluxionality. The net effect of the proton hop, resulting in an interchange between a bridging oxygen and a terminal oxygen, is the migration of a hydroxyl group from one metal to another. The relative positions and orientations of the two hydroxide groups before and after the proton hop are different, and this generates the scope for different catalytic activity. Novel applications of this proton-hop-mediated fluxionality are currently underway in our laboratory.

COMPUTATIONAL DETAILS

The Gaussian suite of programs has been used for all of our calculations.⁴⁰ All of the geometries were optimized with the unrestricted version of the B3LYP hybrid density functional.^{41,42} The 60 core electrons of tungsten and 28 core electrons of molybdenum were replaced with the Stuttgart–Dresden relativistic pseudopotentials. The remaining 14 valence electrons on both of these metal centers have been treated with an augmented version of the associated double- ζ basis sets including diffuse and polarization functions on all of the atomic centers.⁴³ The D95 basis set including diffuse and polarization functions was used to treat hydrogen and oxygen (see Supporting Information). Single-point calculations were then carried out using larger augmented triple- ζ basis sets. At the triple- ζ level, hydrogens and oxygens were treated using Dunning's correlation-consistent basis sets (aug-cc-pVTZ; see Supporting Information). The additional exponents used in both the double- ζ and the triple- ζ basis sets are provided in the Supporting Information. Vibrational analyses were carried out at the double- ζ level to confirm the nature of the minimum-energy structures and TSs. The associated zero-point energies and thermal corrections have been included in all of the energies obtained. Finally, intrinsic reaction coordinate calculations were carried out to verify that the TSs obtained connect to the minima on either side.

SUPPORTING INFORMATION AVAILABLE A list of relevant computed distances, the exponents used in the polarization and diffuse functions added on all of the atomic centers, and the Cartesian coordinates of all of the optimized structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author:

*To whom correspondence should be addressed. E-mail: kraghava@indiana.edu.

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