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DETERMINING POTENTIAL DEPENDENT ACTIVATION BARRIERS FOR  
ELEMENTARY ELECTROCATALYTIC REACTIONS USING DENSITY  
FUNCTIONAL THEORY

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## ABSTRACT

A method for calculating potential dependent activation barriers for elementary electrocatalytic reactions was studied using density functional theory (DFT) calculations. Reactions involving C-H and O-H bond formation and dissociation and the effects of water solvation on O-H bond formation and dissociation were investigated. Computational methods currently available for calculating electrochemical activation barriers either depend on severe approximations and/or are not transferable to general ion/electron transfer reactions. The proposed method uses a thermochemical approach that determines potential dependent activation barriers for elementary, electrochemical reactions by modeling electrochemical reactions as a two-step mechanism, locating the transition states for analogous non-electrochemical surface reactions, and extrapolating to the solvated, potential dependent system using Butler-Volmer kinetics. Comparing the activation barriers calculated using the proposed method with experimental data suggests that the method is valid. A transferable method for determining potential dependent activation barriers will allow for more educated computational and experimental electrochemical studies, which can potentially improve the efficiency of electrochemical conversion devices.

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## Chapter 1

### Introduction

Designing efficient electrochemical devices in order to reduce human reliance on fossil fuels while also meeting the increasing demand for energy is one of the greatest challenges of the 21<sup>st</sup> century. Atomistic modeling has been extensively employed to propose improvements to battery, fuel cell, electrolysis, and photoelectrolysis devices; for example, novel binary metal catalysts, which are cheaper than platinum, have been recommended for use for oxygen reduction<sup>1</sup>, hydrogen evolution<sup>2</sup>, methanol oxidation<sup>3</sup>, and borohydride oxidation<sup>4</sup>. The thermodynamics of elementary electrocatalytic steps with these reactions have been studied extensively using density functional theory (DFT) methods, especially over the last decade. The kinetics of these elementary electrochemical reactions, however, have been either neglected or approximated. By developing a transferable method to determine activation barriers that are dependent on electrode potential, more educated computational and experimental studies can be conducted to improve the efficiency of electrochemical conversion devices.

There are many challenges associated with DFT calculation of activation barriers for elementary electrochemical steps. For one, if a reactant or product is an ion in an electrolyte, current DFT methods require making severe approximations when modeling electrode-electrolyte interfacial structures. Correctly representing an ion as it transfers from the bulk electrolyte to the interfacial region challenges the length and time scales available to DFT methods. As the transfer is also coupled with electron transfer from the metal, it also becomes challenging to control or even measure the electrode potential with the DFT model.

While multi-step electrocatalytic reactions involve elementary steps with ion and electron transfer and non-electrochemical bond dissociation or formation, the majority of DFT-based studies for electrocatalysis only focus on electrochemical step reaction energies or activation

barriers for non-electrochemical reactions steps. A method to calculate potential dependent reaction free energies was proposed by Nørskov et al. in 2004.<sup>5</sup> The method outlined in Nørskov's study was based off of previous work conducted by the Anderson group at Case Western Reserve University.<sup>6</sup> The Anderson method was able to translate standard metal-adsorbate-vacuum interface calculations into their electrochemical equivalent through a simple reference electrode approach, described in more detail below. Other more intricate methods for calculating potential dependent reaction free energies include Neurock and co-workers' "double-reference method"<sup>7,8</sup> and the continuum solvation models of Goddard<sup>9,10</sup> and Anderson.<sup>11</sup> The methods of Goddard and Anderson have been developed to include charge separation either by adding explicit charges<sup>7-12</sup> or an external electric field.<sup>13-15</sup> These methods allow for the inclusion of solvation effects and electrode-electrolyte charge separation, but do not allow for the straight forward calculation of electrochemical reaction activation barriers.

While there are examples in the literature of potential dependent activation barriers calculated using DFT, each method either requires severe approximations and/or is not transferable to other ion/electron transfer reactions. The Anderson group, for example, developed a method that uses metal clusters of 1-2 atoms and evaluates the electron affinity/ionization potential as a function of adsorbate potential to calculate activation barriers, known as the "local reaction center model."<sup>16-19</sup> This method produces divergent results as more atoms are added to the metal cluster, requiring a trade-off in being able to define electron affinity/ion potential versus having a better electronic structure representation of the extended metal surface. Janik et. al used the "double-reference method" to calculate the potential dependent activation barrier for the reduction of  $O_2^*$  on a Pt(111) surface to  $OOH^*$ ,<sup>20</sup> but difficulties in establishing the first of the "double" reference potentials when an explicit ion is added to the periodic model cell unit make this approach generally impractical. Skulason et al. studied the activation barriers of the hydrogen oxidation/evolution reaction, included an  $H^+$  species in the unit cell and extrapolated results to a



low concentration.<sup>21</sup> Developing a realistic solvation environment for transferring the ion is a requirement for this method, which is impractical for more complex reactions.

The method outlined in this paper uses a thermochemical approach that determines potential dependent activation barriers for elementary, electrochemical reactions by modeling electrochemical reactions as a two-step mechanism, locating the transition states for analogous non-electrochemical surface reactions, and extrapolating to the solvated, potential dependent system using Butler-Volmer kinetics. The method has been used in a previously published paper by the Janik group to calculate potential dependent barriers within the borohydride oxidation reaction, arriving at overall kinetics that matched experiment.<sup>4</sup> This thesis will expand this method to include reactions involving C-H and O-H bond formation and dissociation and the effects of solvation. Recommended future work would involve directly evaluating the symmetry factor or each elementary reaction.

## Chapter 2

### Methods

The Vienna Ab Initio Simulation Package<sup>22-24</sup> was used to carry out gradient-corrected periodic density functional theory calculations of the potential dependent reaction energies and activation barriers for each of the elementary electrochemical reactions studied. The Perdew-Wang (PW91) form of the generalized gradient approximation determined the exchange and correlation energies.<sup>25</sup> A 3 x 3 x 1 Monkhorst-Pack grid was used to generate a k-point grid.<sup>26</sup> The forces on the reactant atoms were minimized to values lower than 0.05 eV Å<sup>-1</sup>. The climbing image nudged elastic band method (CI-NEB) was used to isolate the transition states of elementary reactions on the surface.<sup>27,28</sup> Four images with equal spacing were used between the initial and the final state. The transition state was the image with the highest energy and a tangent force of less than 0.05 eV Å<sup>-1</sup>. Transition states also had one imaginary vibrational frequency. The Pt(111) surface was represented using a 3 x 3 unit cell and three metal layers, for a total of 27 Pt atoms in the unit cell.

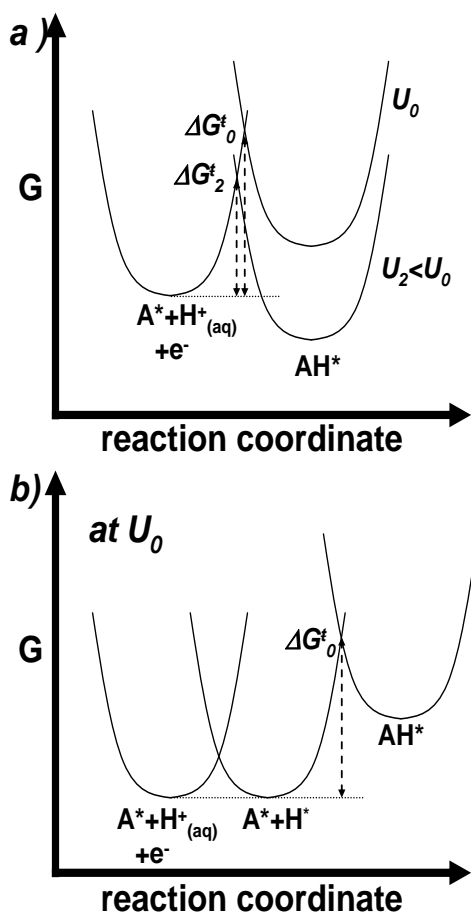
Elementary electrochemical reactions typically involve the transfer of an ion/electron pair to an adsorbate or from an adsorbate. The chemical potential of the reactant ion being transferred is given by its value in the electrolyte. The electrochemical reaction for this transfer can be written as:



where “\*” represents a surface site and “A\*” represents a surface-adsorbed species. The activation free energy of reaction (1) in the forward direction is dependent upon the electrode potential ( $U_2$ ), which can be calculated based on Butler-Volmer theory using the following equation:

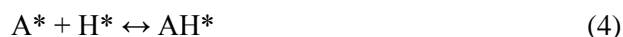
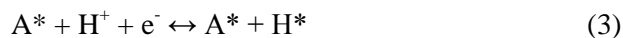
$$\Delta G_2^t = \Delta G_0^t + \beta F(U_2 - U_0) \quad (2)$$

where  $F$  is Faraday's constant,  $F(U_2-U_0)$  represents the change in free energy of the reaction due to the change in potential from  $U_0$  to  $U_2$ , and  $\beta$  represents the symmetry factor. The symmetry factor characterizes the relationship between the activation barrier change and the reaction energy change. The symmetry factor typically has a value between 0.3 and 0.7.<sup>29</sup> Figure 2-1 illustrates how an activation barrier at any electrode potential  $U_2$  can be calculated once a barrier is calculated at a reference potential  $U_0$  and a symmetry factor is determined.



**Figure 2-1.** Idealized reaction energy diagram for a) an electroreduction reaction of an adsorbate  $A^*$ . b) schematic reaction energy diagram illustrating the proposed method, where the activation barrier at potential  $U_0$  is determined for the analogous non-electrochemical hydrogenation reaction.

This thesis proposes that for an elementary electrochemical reaction in which ion/electron transfer occurs, the barrier at the equilibrium potential for ion adsorption can be approximated as the non-electrochemical barrier for an equivalent surface reaction. This method uses a two-step mechanism to model ion/electron transfer, which can be written as:



where reaction (4) is a non-electrochemical step. The activation barrier for this non-electrochemical step can be calculated using standard methods. The barrier computed for this non-electrochemical surface reaction is then assigned to the equilibrium potential for reaction (3) ( $\Delta G_0^t$  at  $U_0$ ). The equilibrium electrode potential  $U_0$  for reaction (3) can then be determined by setting the free energy of the  $H^+ + e^-$  pair equal to that of a  $\frac{1}{2}$   $H_2$  gas molecule at a normal hydrogen electrode and the electron chemical potential varied linearly with electrode potential, written as:

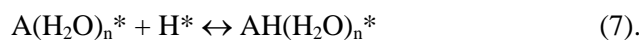
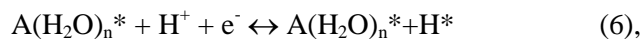
$$\Delta G_{rxn,3} = G_{A^*+H^*} - G_{A^*} - \frac{1}{2}G_{H_2} - e^-U_0 = 0 \quad (5)$$

where  $G_{A^*+H^*}$  represents the free energy of the adsorbed species and  $G_{H_2}$  represents the free energy of gas phase  $H_2$  species, both of which are calculated using DFT with statistical mechanics corrections for thermal and entropic terms. The equilibrium electrode potential for reaction (3),  $U_0$ , is found by setting  $\Delta G_{rxn,3}$  to zero and solving for  $U_0$ . The activation barrier for reaction 4 is then assigned to  $U_0$ , i.e. it is assigned as  $\Delta G_0^t$  in equation (2). The electrode potential  $U_0$  is in reference to a relative hydrogen electrode (RHE) and  $e^-$  represents the charge of an electron (negative number). Equation (2) then describes the potential dependent activation barrier, where  $\beta$  represents the symmetry factor and is at first approximated as 0.5. Future work will involve exploring possible corrections for the symmetry factor. This method also assumes that the Born-Oppenheimer approximation is valid, such that the rate of attainment of the transition state nuclei

configuration for the formation of the A-H bond limits the reaction rate. While this study looked at reactions taking place in an acidic, aqueous solution, the proposed method is also transferable to elementary electrochemical reactions involving the transfer of other ions and in other solvents.

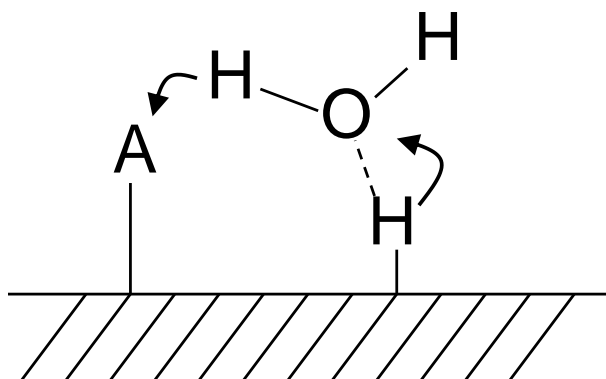
Solvating water molecules are known to have an effect on hydrogenation activation barriers and it is expected that they also affect H reduction barriers. Water molecules may solvate an adsorbate in two ways: by hydrogen bonding with the adsorbate and by shuttling hydrogen from solution or the metal surface to the adsorbate. Desai et al. have illustrated that solvating water molecules lower the barriers of the dehydrogenation/hydrogenation of acetic acid on Pd(111).<sup>30</sup> Hydrogenation/dehydrogenation reactions can progress through transition states with greater ionic character in the presence of water because A-H bond formation/dissociation may be more heterolytic in character. These transition states typically involve the shuttling of an H atom from the solution or surface to an adsorbate A\* through the Grotthuss mechanism. Figure 2-2 illustrates an H atom shuttling through two water molecules with another water molecule directly solvating the adsorbate.

Water solvating and shuttling can be explicitly included in the framework of the proposed method. Reactions 3 and 4 would be replaced by:



In reaction (6), H\* is co-adsorbed with  $n$  H<sub>2</sub>O molecules and the A\* adsorbate. The activation barrier is calculated in the same manner as the non-solvated system, where the barrier for the solvent-assisted ion transfer reaction (7) is assigned the equilibrium potential for reaction (6). As water molecules are added, the activation barrier is expected to converge. When enough water molecules are present to solvate the ion, the ion may originate far away from the electrode surface and, thus, the initial state will resemble a state in which the ion is located in the bulk

electrolyte. It is hypothesized that convergence would be achieved in 1-3 water molecules. A complication of applying the proposed method with added water molecules is the occurrence of multiple local energy minimum structures and reaction trajectories.



**Figure 2-2.** The Grotthuss mechanism for a proton being transfer through two water molecules with another water molecule solvating the adsorbate, in this case  $O_2$ .

## Chapter 3

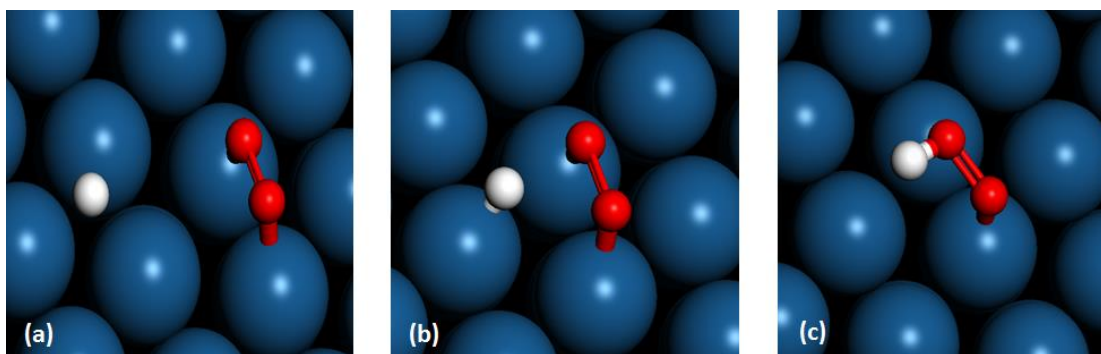
### Results and Discussion

Elementary electrochemical reactions involving the transfer of a proton and an electron to an adsorbate were studied. The adsorbates that were used in this study include  $O_2$ , OH,  $CH_2$ , and  $CH_3$ . The oxygen reduction reaction is one of the most studied electrochemical reactions, mainly because of its role in fuel cells. The reactions  $O_2 + H$  and  $OH + H$  are thought to be possible rate limiting steps in the oxygen reduction reaction. The reactions  $CH_2 + H$  and  $CH_3 + H$  are prevalent in the hydrogenolysis of ethane and the reduction of  $CO/CO_2$  to  $CH_4$ , as well as their reverse occurring in methane oxidation. The non-polar C-H bond formation in the  $CH_2 + H$  and  $CH_3 + H$  offered a good contrast with the polar O-H bond formation in the  $O_2 + H$  and  $OH + H$  reactions. The effects of water solvation on the  $O_2 + H$  reaction were also studied. The activation barrier at an electrode potential  $U_0$ , which is referenced to a relative hydrogen electrode (RDE), is given for each reaction.

#### 3.1 $O_2 + H \rightarrow OOH$

The initial state for the reaction of  $O_2 + H$  reaction is shown in Figure 3-1a. Oxygen forms a bridge between two Pt atoms with a bond distance of 1.36 Å. The H atom sits in an fcc 3-fold hollow site. At the transition state, shown in Figure 3-1b, the H atom shifts to the H-atop site of the Pt atom neighboring an oxygen atom. The O-O bond length increases to 1.53 Å at the transition state. Once the H atom binds to the adsorbate, the adsorbate bends back into a position similar to that of the initial state, as shown in Figure 3-1c. The oxygen bond distance at the final state is 1.43 Å. The bond angles between the OOH, the surface and O-O, and the surface and O-H are 101.9°, 113.0°, and 92.6°, respectively.

The activation energy calculated for the  $\text{O}_2 + \text{H}$  reaction was calculated to be 0.63 eV ( $\Delta G^{\ddagger}_0$ ) at the equilibrium potential for adsorption of  $\text{H}^+$  to the initial state ( $U_0$ ) of 0.26 V-RHE. The experimentally determined activation barrier for the overall oxygen reduction reaction at its equilibrium potential (1.23 V-RHE) is 0.44 eV.<sup>31</sup> Clearly, the extrapolated value for the barrier using equation (2) with  $\beta = 0.5$  is 1.12 eV. Though we do not expect exact agreement as the experimental value itself has a sizeable uncertainty, this value is higher than the experimental value when no water is included in the DFT model to aid proton transfer. The Anderson method calculated a value of 0.60 eV at the equilibrium potential and included water in the  $\text{H}^+$  transfer reaction, suggesting that representation of the reaction as a purely surface hydrogenation reaction is not accurate.<sup>32</sup>



**Figure 3-1.** The initial (a), transition (b), and final (c) states for the reaction of  $\text{O}_2$  and  $\text{H}$  on Pt(111).

### 3.2 $\text{O}_2 + \text{H} \rightarrow \text{OOH} + 1$ water solvate

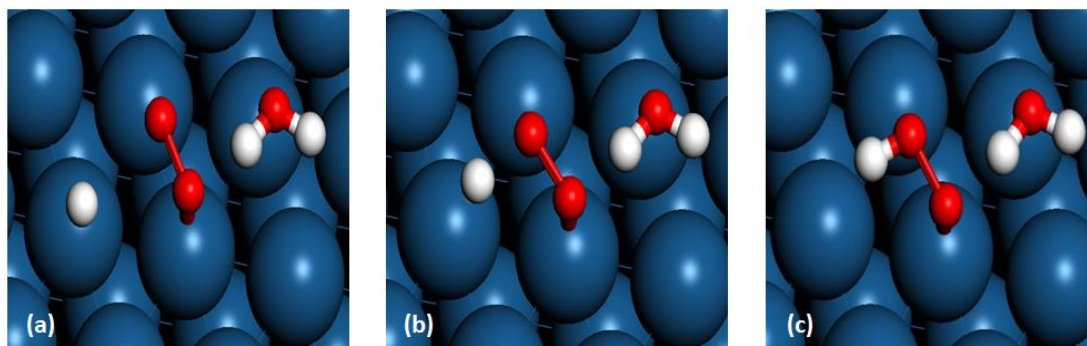
The initial state for the reaction of  $\text{O}_2^* + \text{H}^*$  with one water molecule solvating the oxygen adsorbate is shown in Figure 3-2a. Oxygen forms a bridge between two Pt atoms with a bond distance of 1.43 Å. This distance is significantly longer than the oxygen bond distance without a solvating water molecule (1.36 Å). Hydrogen bonding to one of the oxygen adsorbate atoms causes additional electron donation from the metal to the  $\text{O}_2 \pi^*$  orbital, which increases the bond distance between the two oxygen adsorbate atoms. The H atom sits in an atop site on one of the Pt atoms neighboring the oxygen adsorbate. The transition state, shown in Figure 3-2b, has



similar qualitative characteristics as the transition state for the  $\text{O}_2 + \text{H}$  reaction without a solvating water molecule. One of the oxygen atoms of the adsorbate bends at an angle of  $71.1^\circ$  relative to the surface to pick up the H atom from the atop site. Once the H atom binds to the adsorbate, the adsorbate bends back into a position similar to that of the initial state, as shown in Figure 3-2c. The bond angles between OOH, the oxygen of the adsorbate and the Pt surface, and the surface and the O-H bond in the final state are  $108.7^\circ$ ,  $100.7^\circ$ , and  $78.3^\circ$ , respectively. It is unclear why the O-H bond bends downward with the addition of a water molecule, while without water, the bond bend upward. The oxygen bond length changes by about  $0.06 \text{ \AA}$  from the initial and final state as a result of the reaction.

The activation barrier calculated for  $\text{O}_2 + \text{H}$  reaction with a water molecule solvating the oxygen adsorbate was calculated to be 0.19 eV at 0.17 V-RHE, a significant decrease from the non-solvated system. The  $U_0$  for H addition with one water molecule present is 0.09 V lower than with no water co-adsorbed, indicating the presence of water slightly destabilizes proton adsorption. This would suggest that hydrogen bonding between the adsorbate and the water molecules plays a significant role in the kinetics of the reduction of oxygen. Another DFT study calculated the value of the activation barrier for the solvated  $\text{O}_2 + \text{H}$  reaction to be 0.28 eV, which is reasonably close to the value calculated using the proposed method.<sup>33</sup> This study used the Poisson-Boltzmann implicit continuum model to estimate solvent effects, the same method employed by Goddard<sup>9,10</sup> and Anderson<sup>11</sup>, which is not accurate of calculating potential dependent activation barriers. The value for the activation barrier at 1.23 V-RHE with a solvating

water molecule is 0.72 eV, still higher than the experimental value, but much closer.



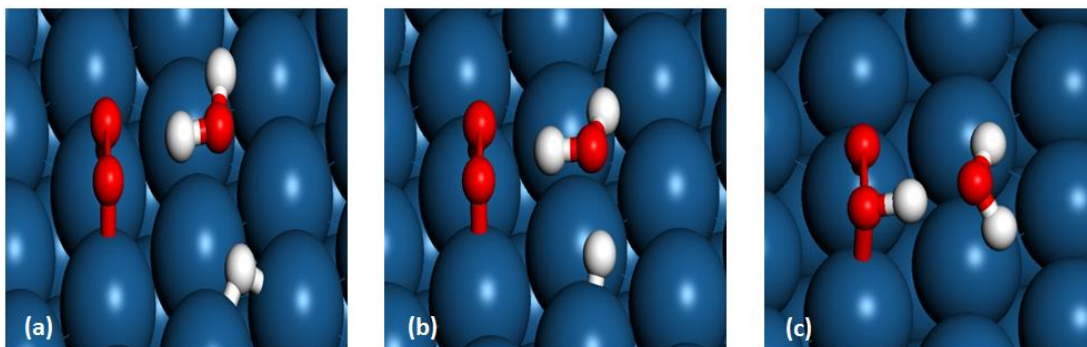
**Figure 3-2.** The initial (a), transition (b), and final (c) states for the reaction of  $O_2$  and H with one water solvating the adsorbate on Pt(111).

### 3.3 $O_2 + H \rightarrow OOH + 1$ water shuttle

The initial state for the reaction of  $O_2 + H$  reaction with one water molecule acting as a H atom shuttle is shown in Figure 3-3a. Oxygen forms a bridge between two Pt atoms with a bond distance of 1.391 Å. Like in the reaction with one water molecule solvating the adsorbate, hydrogen bonding causes the O-O bond distance to increase compared to the initial state without water. The H atom sits in a bridge on two of the Pt atoms neighboring Pt atoms. The transition state, shown in Figure 3-3b, involved the H atom moving to the atop site of the Pt atom closest to the adsorbate. The water molecule rotates in order to form a bond with the surface-bound H atom, forming a hydronium ion with O-H bond distances longer than water. The O-H bond closest to the oxygen molecule adsorbate breaks and reforms on the adsorbate, as shown in Figure 3-3c. The O-O bond distance changes by 0.104 Å from the initial and final state with the addition of an H atom. Hydrogen bonding with the newly formed O-H bond on the adsorbate causes a build-up of negative charge on the oxygen atoms, which increases the O-O bond distance. The bond angles between OOH and the surface and the O-H bond are 98.1° and 100.1°.

The activation barrier calculated for  $O_2 + H$  reaction with a water molecule solvating the oxygen adsorbate was calculated to be 0.01 eV at an electrode potential of -0.02 V-RHE. This

lower potential indicated hydrogen adsorbed is significantly destabilized relative to no H<sub>2</sub>O molecule being present. The reaction is nearly barrierless, though the transition state found does demonstrate a single imaginary frequency and does suggest a slight barrier. This result suggests that a single water molecule involved in proton shuttling drastically lowers the barrier, though our approach has led to barrier determination at a large oxygen reduction overpotential, where this reaction is nearly barrierless. Extrapolating with  $\beta = 0.5$ , the activation barrier at 1.23 V-RHE is 0.64 eV, similar to the experimental result and the computational result of Anderson (determined with a more complex approach).<sup>32</sup>

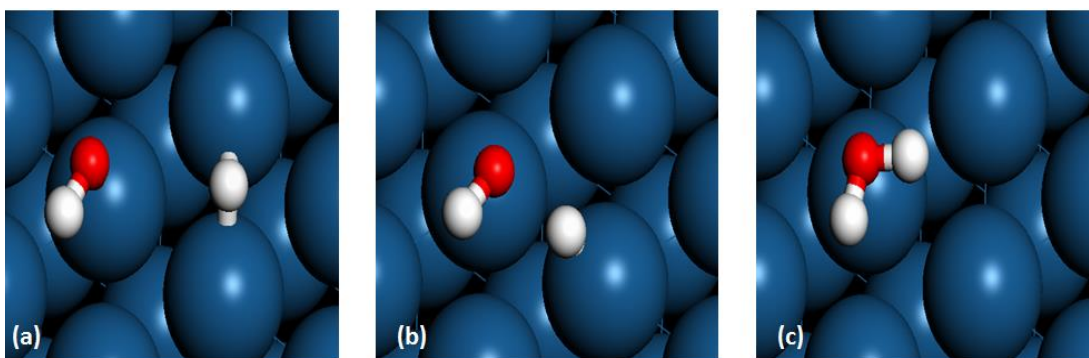


**Figure 3-3.** The initial (a), transition (b), and final (c) states for the reaction of O<sub>2</sub> and H with one water shuttling the adsorbed hydrogen to the adsorbate on Pt(111).

### 3.4 OH + H → H<sub>2</sub>O

The initial state for the reaction of OH + H is shown in Figure 3-4a. The hydroxyl group is bound at the atop site of one Pt atom while the H atom is bonded at a neighboring bridge site. The O-H bond distance is 0.98 Å and the bond angle between the surface and the hydroxyl group is 106.3°. At the transition state, shown in Figure 3-4b, the adsorbed H atom moves to the atop site and points toward the hydroxyl adsorbate. The angle between the surface, the H atom, and the oxygen of the hydroxyl group is 138.4°. At the final state, the O-H bond distance is 0.98 Å and the H-O-H bond angle is 105.5°. The adsorbed H atom then binds to the hydroxyl group, forming H<sub>2</sub>O on an atop site, as shown in Figure 3-4c.

The activation barrier calculated for OH + H reaction was calculated to be 0.05 eV at a standardized potential of 0.27 eV. This value can be compared to activation barrier of 0.17 eV as calculated by Michaelides and Hu.<sup>34</sup> Differences in simulation conditions may contribute to the difference. In Hu's study, a four-layer Pt slab and a 2 x 2 unit cell was used to calculate the barrier, whereas a three-layer Pt slab and a 3 x 3 unit cell were used in this study. Nonetheless, the barrier for this reaction is quite low. Adding water molecules would likely make the reaction barrierless.



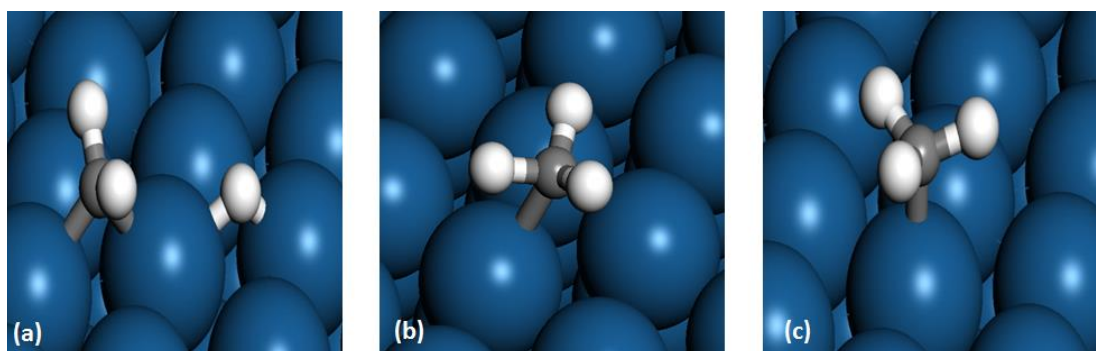
**Figure 3-4.** The initial (a), transition (b), and final (c) states for the reaction of OH and H on Pt(111).

### 3.5 $\text{CH}_2 + \text{H} \rightarrow \text{CH}_3$

The initial state for the reaction of  $\text{CH}_2 + \text{H}$  reaction is shown in Figure 3-5a. Both the adsorbed  $\text{CH}_2$  group and the adsorbed H atom bind in a bridge site of the Pt surface. The C-H bond length is 1.097 Å and the Pt-C bond length is 2.07 Å. The H-C-H bond angle is 112.8°. At the transition state, shown in Figure 3-5b,  $\text{CH}_3$  is substantially formed. The distance and the angle between the surface and the carbon atoms are 2.231 Å and 56.5°. The C-H bond distances at the transition state are not all equal length: two are 1.09 Å and the forming bond is elongated at 1.12 Å. As the reaction moves toward the final state, the newly formed methyl group migrates from the bridge site to the atop site. The Pt-C bond length and angle are 2.07 Å and 97.0°. All three C-H bonds are 1.10 Å long and have bond angles around 111°. The final state of the reaction is shown in Figure 3-5c.

The activation barrier calculated for  $\text{CH}_2 + \text{H}$  reaction was calculated to be 0.62 eV at an electrode potential of 0.20 V-RHE. This value is comparable to the activation barrier of 0.76 V calculated by Chen and Vlachos.<sup>35</sup> These conditions were similar to that of Hu's study of  $\text{OH} + \text{H}$  detailed in the previous section, which is likely the reason for the difference in calculated values. The calculated barrier suggests that  $\text{CH}_3$  formation should be rapid at reduction potentials below  $\sim 0$  V-RHE, which are relevant for  $\text{CO}_2$  electroreduction.

For C-H bonds, we do not expect water solvation or proton shuttling to lower the activation barriers. C-H bonds are relatively non-polar. Bond formation will require direct C and H interaction with the Pt surface. Nie et al. found that water does not lower the barrier for C-H formation and that C-H bonds form electrochemically through surface hydrogenation reactions.<sup>36</sup>



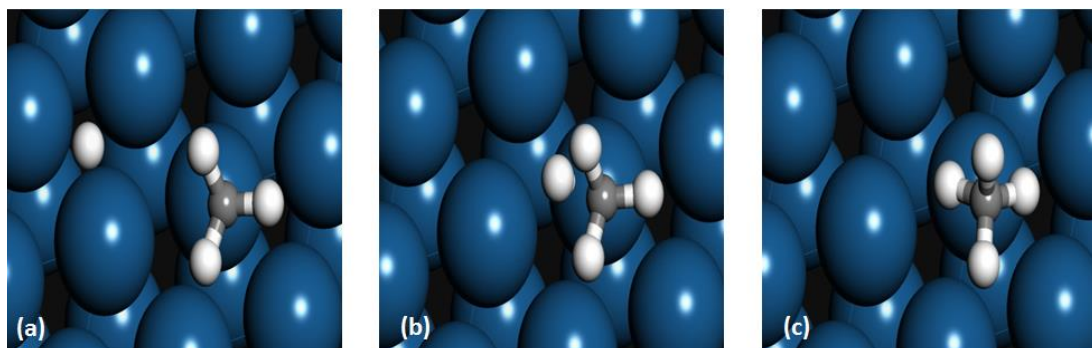
**Figure 3-5.** The initial (a), transition (b), and final (c) states for the reaction of  $\text{CH}_2$  and  $\text{H}$  on Pt(111).

### 3.6 $\text{CH}_3 + \text{H} \rightarrow \text{CH}_4$

The initial state for the reaction of  $\text{CH}_3 + \text{H}$  reaction is shown in Figure 3-6a. The adsorbed methyl group is bound to the Pt surface at an atop site, while the adsorbed H atom is bound in an fcc 3-fold hollow site. The C-H bond lengths are 1.10 Å and the Pt-C bond length is 2.07 Å. The bond angle between the surface and the carbon is approximately 90°. At the transition state, shown in Figure 3-6b, the adsorbed H atom migrates onto the same Pt atom as the methyl group. The H atom bonds to the surface at an angle of 56.9°. The bond length between

the surface and the carbon atom increased to 2.22 Å. The final state shown in Figure 3-6c, is an unbound methane molecule, having C-H bond lengths of about 1.10 Å and bond angles of 109.5°.

The activation barrier calculated for  $\text{CH}_3 + \text{H}$  reaction was calculated to be 0.88 eV at an electrode potential of 0.29 V-RHE. Chen and Vlachos used DFT to calculate the activation barrier to be 0.92 eV, which is reasonably close to the calculated value.<sup>35</sup> This result further supports that the proposed method can be used for reactions involving C-H bond formation and dissociation. For the reverse, oxidation reaction, the activation barrier at 0.29 V-RHE was calculated to be 0.63 eV, which is also comparable to the value calculate by Chen and Vlachos.<sup>35</sup> This activation barrier indicates that this reaction is a slow step in the methane oxidation reaction. Because methane is a very stable molecule, the C-H bonds on methane are difficult to break, which contributes to the high activation barrier.



**Figure 3-6.** The initial (a), transition (b), and final (c) states for the reaction of  $\text{CH}_3$  and  $\text{H}$  on  $\text{Pt}(111)$ .

## Chapter 4

### Conclusions

The calculated potential dependent activation barriers for the elementary electrochemical reactions studied and their corresponding standard potentials are shown in Table 4-1. The potential dependent activation barriers calculated using the proposed method were similar to values calculated in the literature, supporting the validity of the method. The results indicate that the method is transferable for reactions involving O-H and C-H bond formation and dissociation. Water solvation and shuttling was also shown to have a significant impact on the  $O_2 + H$  reaction, suggesting that hydrogen bonding plays a role in governing the kinetics of this reaction. Convergence of the potential dependent activation barrier was achieved with one water molecule for the  $O_2 + H$  reaction. Other elementary electrochemical reactions involving O-H and C-H bond formation and dissociation and water solvation will be studied to further validate the method. Direct evaluation of the symmetry factor,  $\beta$ , using dipole corrections will also be studied to determine the exact position of the transition state along the electrochemical reaction coordinate for each elementary electrochemical reaction.

**Table 4-1.** The Electrode Potential  $U_0$ , the Reaction Activation Barrier for the Studied Hydrogenation Reactions, and the Activation Barrier at the Equilibrium Potential for the overall reaction

Reaction	# of H <sub>2</sub> O (Mode)	$U^0$ (V-RHE)	$G_{act}^0$ (eV)	$G_{act}^0$ at $E^0$ (eV (V-RHE))
$O_2 + H \rightarrow OOH$	0	0.26	0.63	1.12 (1.23)
$O_2 + H \rightarrow OOH$	1 (solvate)	0.17	0.19	0.72 (1.23)
$O_2 + H \rightarrow OOH$	1 (shuttle)	-0.02	0.01	0.64 (1.23)
$O_2 + 4H^+ + 4e^- \rightarrow 2 H_2O$	experimental <sup>31</sup>			0.44 (1.23)
$OH + H \rightarrow H_2O$	0	0.27	0.05	
$CH_2 + H \rightarrow CH_3$	0	0.20	0.62	
$CH_3 + H \rightarrow CH_4$	0	0.29	0.88	

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