Catalytic Water Formation on Platinum: A First-Principles Study

A. Michaelides and P. Hu*

Contribution from the School of Chemistry, The Queen's University of Belfast, Belfast BT9 5AG, U.K.

Received October 3, 2000. Revised Manuscript Received January 10, 2001

Abstract: The study of catalytic behavior begins with one seemingly simple process, namely the hydrogenation of O to H_2O on platinum. Despite the apparent simplicity its mechanism has been much debated. We have used density functional theory with gradient corrections to examine microscopic reaction pathways for several elementary steps implicated in this fundamental catalytic process. We find that H_2O formation from chemisorbed O and H atoms is a highly activated process. The largest barrier along this route, with a value of ∼1 eV, is the addition of the first H to O to produce OH. Once formed, however, OH groups are easily hydrogenated to H_2O with a barrier of ∼0.2 eV. Disproportionation reactions with 1:1 and 2:1 stoichiometries of H_2O and O have been examined as alternative routes for OH formation. Both stoichiometries of reaction produce OH groups with barriers that are much lower than that associated with the O + H reaction. H_2O, therefore, acts as an autocatalyst in the overall H_2O formation process. Disproportionation with a 2:1 stoichiometry is thermodynamically and kinetically favored over disproportionation with a 1:1 stoichiometry. This highlights an additional (promotional) role of the second H_2O molecule in this process. In support of our previous suggestion that the key intermediate in the low-temperature H_2O formation reaction is a mixed OH and H_2O overlayer we find that there is a very large barrier for the dissociation of the second H_2O molecule in the 2:1 disproportionation process. We suggest that the proposed intermediate is then hydrogenated to H_2O through a very facile proton-transfer mechanism.

1. Introduction

The hydrogen oxidation reaction has been studied since the time of Faraday.[1] On contact with Pt hydrogen and oxygen react at room temperature and below to produce water. The remarkable ease with which this reaction proceeds prompted the introduction of the term "catalysis" and so it is in this reaction that the study of catalytic phenomena finds its roots.[2] Aside from the fundamental importance, the adsorption and reaction of adsorbates such as O, H, OH, and H_2O on Pt group metals is of great significance to electrochemistry, corrosion, and heterogeneous catalysis. In addition, individual steps in this reaction are common to all catalytic combustion processes involving H containing fuels over Pt. Consequently, the water formation reaction has been extensively studied.

Despite the apparent simplicity of this reaction and the substantial quantity of publications in this area, conflicting models have rendered its mechanism unclear.[3−15] Recently, Ertl

and co-workers[16] observed this reaction in progress with the scanning tunneling microscope (STM). This, together with high-resolution electron energy loss (HREELS) spectra, allowed them to clarify many of the existing controversies. Two distinct temperature-dependent mechanisms to H_2O formation were observed. Above the H_2O desorption temperature (∼180 K on Pt(111) under ultrahigh vacuum (UHV) conditions), when H_2O does not remain upon the surface, H_2O was formed via the simple successive addition of adsorbed H ($H_{(ads)}$) atoms to adsorbed O ($O_{(ads)}$):

$$O_{(ads)} + H_{(ads)} \rightarrow OH_{(ads)} \tag{1}$$

$$OH_{(ads)} + H_{(ads)} \rightarrow H_2O_{(ads)} \rightarrow H_2O_{(gas)} \tag{2}$$

When H_2O remains on the surface, at <180 K, the authors observed that the reaction proceeds through fronts. This prompted the proposal of an alternative mechanism for H_2O formation. It was suggested that H_2O and O disproportionation reactions,

$$H_2O_{(ads)} + O_{(ads)} \rightarrow 2OH_{(ads)} \tag{3}$$

were operable within this temperature regime. They proposed that reactions 1 and 2 initiate the process and the bulk of the H_2O is formed by cyclic repetition of disproportionation (reaction 3) and hydrogenation (reaction 2) steps. This autocatalytic process is very facile and can occur at temperatures as low as 120 K. If there is sufficient O and H present, it will continue until the surface becomes completely H_2O covered.

* Address correspondence to this author. E-mail: p.hu@qub.ac.uk.
 (1) Faraday, M. *Experimental Researches in Electricity*, 1844; or in *Great Books of the Western World*; Encyclopaedia Brit., Inc.: Chicago 1952, Vol. 145.
 (2) Berzelius J. J. *Jber. Chem.* **1837**, *15*, 237.
 (3) Norton P. R. *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis*; King, D. A., Woodruff, D. P., Eds.; Elsevier: Amsterdam, 1982; Vol. 4.
 (4) Thiel, P. A.; Madey, T. E. *Surf. Sci. Rep.* **1987**, *7*, 211.
 (5) Fisher, G. B.; Gland, J. L.; Schmieg, S. J. *J. Vac. Sci. Technol.* **1982**, *20*, 518.
 (6) Gland, J. L.; Fisher, G. B.; Kollin, E. B. *J. Catal.* **1982**, *77*, 263.
 (7) Anton, A. B.; Cadogan, D. C. *Surf. Sci.* **1990**, *239*, L548.
 (8) Ogle, K. M.; White, J. M. *Surf. Sci.* **1984**, *139*, 43.
 (9) Mitchell, G. E.; Akhter, S.; White, J. M. *Surf. Sci.* **1986**, *166*, 283.
 (10) Mitchell, G. E.; White, J. M. *Chem. Phys. Lett.* **1987**, *135*, 84.
 (11) Germer, T. A.; Ho, W. *Chem. Phys. Lett*. **1989**, *163*, 449.
 (12) Hellsing, B.; Kasemo, B.; Zhdanov, V. P. *J. Catal.* **1991**, *132*, 210.
 (13) Verheij, L. K.; Freitag, M.; Hugenschmidt, M. B.; Kempf, I.; Poelsema, B.; Comsa, G. *Surf. Sci.* **1992**, *272*, 276.

 (14) Verheij, L. K. *Surf. Sci.* **1997**, *371*, 100.
 (15) Verheij, L. K.; Hugenschmidt, M. B. *Surf. Sci.* **1998**, *416*, 37.
 (16) Volkening, S.; Bedurftig, K.; Jacobi, K.; Wintterlin, J.; Ertl, G. *Phys. Rev. Lett.* **1999**, *83*, 2672.

In a subsequent study[17] by repeating coadsorption experiments of Creighton and White,[18] Ertl and co-workers confirmed that the stoichiometry of the H_2O and O disproportionation on Pt-(111) was $2H_2O$ to 1O. The following equation

$$2H_2O_{(ads)} + O_{(ads)} \rightarrow 3OH_{(ads)} + H_{(ads)} \qquad (4)$$

was proposed to explain this process. The authors suggested that this was the OH producing reaction which occurred during H_2O formation at low temperatures on Pt(111). In addition, they assigned the observed intermediate in this process as the product of this disproportionation reaction, i.e., $3OH + H$, although the H atoms were never observed.

Theoretical work in this area has focused on the chemisorption of the pertinent atomic and molecular fragments involved.[19−31] The only occasions on which attempts have been made to calculate the energetics of any of these reactions on Pt are an atom superposition and electron delocalization technique (ASED) study by Anderson[19] many years ago and a more recent DFT study by Wilke et al.[20] Wilke et al. have, in fact, examined reactions 1 and 2 on Rh(111) and Pt(111). On Pt(111) they found that for a specific reaction coordinate reactions 1 and 2 had barriers of 0.8 and 0.7 eV, respectively. They suggested that barriers of this magnitude were not compatible with water formation at low temperatures (<180 K) and speculated, as has been done before,[13−15] that reactions at defect sites on the substrate may account for facile H_2O formation at low temperatures. The STM experiments of Ertl and co-workers,[16] however, did not detect any evidence to suggest that substrate defects played a significant role in H_2O formation.

Despite the recent developments, many important issues remain unresolved. Crucially, estimates from kinetic experiments on the energetics of the various elementary steps are conflicting[3,7,12] and the structures of certain intermediate and coadsorbed states have not been characterized. In particular, the microscopic reaction pathways of the various elementary steps are not known. For example, it is not known how the H_2O and O disproportionation reactions proceed and it is unclear why they should produce hydroxyl groups more readily than the reaction of adsorbed O and H. Furthermore, it has been established that on Pt(111) disproportionation with a 2:1 stoichiometry of H_2O and O is favored over disproportionation with a 1:1 stoichiometry, but why is this so? This question adopts a greater contemporary relevance given that disproportionation with a 2:1 stoichiometry of H_2O and O is now believed to be the main OH producing reaction at low temperatures. Could an understanding of this unusual stoichiometry reveal why H_2O formation is so facile on Pt(111)? Recently, in fact, we suggested that the product of the 2:1 disproportionation process may not be pure OH or OH

+ H coadsorbed as previously believed but rather a mixed $2OH + H_2O$ overlayer.[31] This is an important issue to consider since it goes to the heart of the mechanism of H_2O formation on Pt. Of equal interest is the way in which this observed intermediate is ultimately hydrogenated to H_2O.

In this study we use DFT to investigate this fascinating water formation reaction on Pt. Having determined energies of initial, transition, and final states for many possible elementary steps implicated in this process, we arrive at coherent mechanisms for the hydrogen-oxidation reaction on Pt(111). Briefly, we find that the successive addition of H to O and then to OH has a barrier of ~1 eV. Disproportionation reactions of H_2O and O have much lower activation energies, indicating that these will provide viable routes to H_2O formation at low temperatures. Disproportionation with a 2:1 ratio of H_2O and O is favored over disproportionation with a 1:1 ratio so long as one of the two H_2O molecules remains intact throughout the reaction. Indeed, the presence of the additional H_2O molecule in the 2:1 disproportionation reaction considerably improves the energetics of OH formation. We outline some details of our first-principle total energy calculations below. Following this we present energy profiles and reaction pathways for oxygen hydrogenation and H_2O and O disproportionation reactions. In the final section our results are summarized and the qualitative pictures which emerge for H_2O formation on Pt(111) are discussed.

2. Calculation Details

First-principle total energy calculations within the DFT framework were performed.[32] Ionic cores are described by ultra-soft pseudo-potentials[33] and the Kohn−Sham one-electron states are expanded in a plane wave basis set up to 300 eV. A Fermi smearing of 0.1 eV was utilized and the corrected energy extrapolated to 0 K. The generalized gradient approximation of Perdew and Wang[34] was used throughout. Periodic geometries were modeled for the most part with a three-layer Pt slab fixed at bulk truncated positions (calculated lattice constant = 3.9711 Å, experimental = 3.9239 Å). Calculations were also performed using a four-layer Pt slab in which the top layer of Pt atoms was allowed to relax. These calculations verify the accuracy of those performed with three layers. In certain cases we present results obtained using both the three- and four-layer models. The vacuum region between slabs was in excess of 11 Å. Previous calculations using this[35] and similar models[36,37] have shown that this approach provides an accurate description of the adsorbate−substrate interface. To investigate each reaction at experimental coverages, $\sqrt{3} \times \sqrt{3} - R30°$ and p(2×2) unit cells were used. Monkhorst Pack meshs[38] with $5 \times 5 \times 1$ and $4 \times 4 \times 1$ **k**-point sampling in the surface Brillouin zone were used for the $\sqrt{3} \times \sqrt{3} - R30°$ and p(2×2) unit cells, respectively.

Reaction pathways were searched with a constrained minimization technique.[39−42] In this approach we constrain the distance between the reactants in each reaction and minimize the total energy with respect to all remaining degrees of freedom. This method allows the transition complex to rotate and translate subject to the above constraint. By varying the distance between the reactants we obtain an energy profile for the reaction. The transition state is identified when (i) the forces on the atoms vanish and (ii) the energy is a maximum along the reaction

(17) Bedurftig, K.; Volkening, S.; Wang, Y.; Wintterlin, J.; Jacobi, K.; Ertl, G. *J. Phys. Chem. B* **1999**, *103*, 1084.
(18) Creighton, J. R.; White, J. M. *Surf. Sci.* **1982**, *122*, L648.
(19) Anderson, A. B. *Surf. Sci.* **1981**, *105*, 159.
(20) Wilke, S.; Natoli, V.; Cohen, H. *J. Chem. Phys.* **2000**, *112*, 9986.
(21) Lynch, M.; Hu, P. *Surf. Sci.* **2000**, *458*, 1 and references therein.
(22) Papoian, G.; Norskov, J. K.; Hoffmann, R. *J. Am. Chem. Soc.* **2000**, *17*, 4129.
(23) Feibelman, P. J. *Surf. Sci.* **1987**, *182*, 411.
(24) Koper, M. T. M.; van Santen, R. A. *J. Electroanal. Chem.* **1999**, *472*, 126.
(25) Fahmi, A.; van Santen, R. A. *J. Res. Phys. Chem. Phys.* **1996**, *197*, 203.
(26) Yang, H.; Whitten, J. L. *Surf. Sci.* **1997**, *370*, 136.
(27) Whitten, J. L.; Yang, H. *Surf. Sci. Rep.* **1996**, *218*, 55.
(28) Patrito, E. M.; Paredes Olivera, P.; Sellers, H. *Surf. Sci.* **1994**, *306*, 447.
(29) Muller, J. E. *Phys. Rev. Lett.* **1990**, *65*, 3021.
(30) Kua, J.; Goddard, W. A., III *J. Am. Chem. Soc.* **1999**, *121*, 10928.
(31) Michaelides, A.; Hu, P. *J. Chem. Phys.* **2001**, *114*, 513.

(32) Payne, M. C.; Teter, M. P.; Allan, D. C.; Arias, T. A.; Joannopoulos, J. D. *Rev. Mod. Phys.* **1992**, *64*, 1045.
(33) Vanderbilt, D. *Phys. Rev. B* **1990**, *41*, 7892.
(34) Perdew, J. P.; Chevary, V. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* **1992**, *46*, 6671.
(35) Bleakley, K.; Hu, P. *J. Am. Chem. Soc.* **1999**, *121*, 7644.
(36) Michaelides, A.; Hu, P. *Surf. Sci.* **1999**, *437*, 362.
(37) Michaelides, A.; Hu, P. *J. Chem. Phys.* **2000**, *112*, 6006.
(38) Monkhorst, H. J.; Pack, J. D. *Phys. Rev. B* **1976**, *13*, 5188.
(39) Michaelides, A.; Hu, P.; Alavi, A. *J. Chem. Phys.* **1999**, *111*, 1343.
(40) Michaelides, A.; Hu, P. *J. Chem. Phys.* **2000**, *112*, 8120.
(41) Zhang, C. J.; Hu, P.; Alavi, A. *J. Am. Chem. Soc.* **1999**, *121*, 7931.
(42) Alavi, A.; Hu, P.; Deutsch, T.; Silvestrelli, P. L.; Hutter, J. *Phys. Rev. Lett.* **1998**, *80*, 3650.
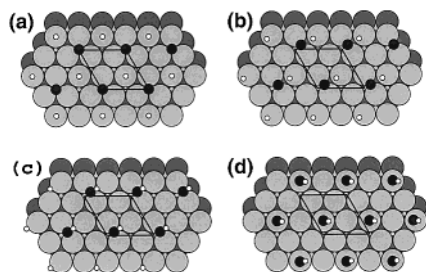
Figure 1. Selected points along the O + H reaction pathway on Pt-(111) in a p(2×2) unit cell: (a) the initial state is the most stable coadsorption of a single O and a single H in a p(2×2) unit cell; (b) the transition state of the reaction; (c) OH chemisorbed on a bridge site that is a local minimum; and (d) the final state of the reaction, which is OH adsorbed at a top site. Only two layers of Pt atoms are shown for clarity. The solid lines designate the surface unit cell. The gray, black, and white circles correspond to Pt, O, and H atoms, respectively. This coloring protocol is used throughout.

Figure 2. Top view of initial (a), transition (b), and final (c) states for the reaction of OH and H on Pt(111) in a p(2×2) unit cell.

coordinate but a minimum with respect to all remaining degrees of freedom. For each reaction several possible reaction channels were searched. Only the results of the lowest energy pathway, i.e., that which accesses the lowest energy transition state, are presented here.

3. Results and Discussion

(1) Hydrogenation Reactions. (a) O + H → OH. Oxygen on Pt(111) is well-known to absorb at 3-fold fcc sites and form an ordered p(2×2) overlayer, which saturates at $^1/_4$ monolayer (ML).[21,43,44] We have calculated a chemisorption energy for $^1/_4$ ML O at the fcc sites of 4.03 eV and an equilibrium O−Pt bond length of 2.06 Å. The diffusion barrier for O from fcc to bridge sites is ca. 0.5 eV.

Hydrogen on Pt(111) is less well characterized.[45−48] At monolayer coverage the 3-fold fcc sites have been suggested for H adsorption. At submonolyer coverage, however, H does not readily form an ordered overlayer and the potential energy surface for H diffusion appears to be very flat.[46] Consistent with these findings and the recent DFT calculations of Hoffmann and co-workers,[22] we find that at $^1/_4$ ML H binds at each of the four high-symmetry sites of Pt(111) with a similar energy, exhibiting only a slight preference (∼0.1 eV) for fcc 3-fold hollow sites. Chemisorption energies at each site were calculated to be ca. 2.9 eV and a H−Pt bond length at the fcc site of 1.85 Å was obtained.

When H adsorbs upon the p(2×2) oxygen covered surface a top site becomes the preferred chemisorption site. The structure of this coadsorption system is shown in Figure 1a. O atoms are at fcc sites and H atoms at the top sites of the fourth atom of each surface cell. This is the initial state for the reaction which is 0.06 eV less stable than that when O and H are chemisorbed in separate p(2×2) unit cells, indicating a very slight repulsive interaction between coadsorbed O and H. At the transition state (Figure 1b) of the reaction, the O−H distance is 1.56 Å. Oxygen is close to a bridge site and H is in a plane perpendicular to the Pt−Pt bond of the bridge site ($[\bar{1}\bar{1}2]$). The activation energy is 0.96 eV. After the transition state, O and H combine to produce OH chemisorbed at the bridge site (Figure 1c). Hydroxyl can then diffuse from the bridge site toward a top site, where it
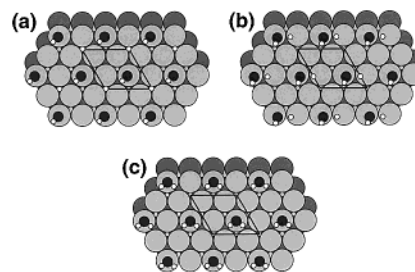
binds slightly more strongly (0.04 eV) to the surface (Figure 1d). This elementary step is 0.06 eV endothermic. The barrier for diffusion of OH between bridge and top sites has previously been determined to be just 0.1 eV.[31]

The most stable pure OH overlayer has, in fact, a surface coverage of $^2/_3$ ML with a $\sqrt{3} \times \sqrt{3} - R30°$ periodicity. This overlayer is approximately 0.25 eV per OH more stable than the p(2×2) overlayer shown in Figure 1d, mainly because of H-bonding between adjacent hydroxyls in the $\sqrt{3} \times \sqrt{3} - R30°$ overlayer.[31] In light of this increased stability and the low diffusion barrier of isolated hydroxyls it is likely that once formed OH groups will cluster and form $\sqrt{3} \times \sqrt{3} - R30°$ OH domains. Such clustering would lower the energy of the final state by approximately 0.25 eV, thus rendering the O + H elementary step slightly (ca. 0.2 eV) exothermic.

Allowing the substrate to relax has a rather small effect on the energetics of this reaction. Using a four-layer Pt slab with a p(2×2) unit cell, in which the top layer of Pt atoms is allowed to relax, the activation energy is 0.94 eV and the heat of reaction is 0.02 eV exothermic.

(b) OH + H → H₂O. To be consistent with the O + H reaction, the OH + H reaction was also investigated in a p(2×2) unit cell. The initial state for this reaction, i.e., the most stable coadsorption of OH and H within the p(2×2) unit cell, is illustrated in Figure 2a. Hydroxyls are at top sites and H atoms are at fcc 3-fold hollow sites. As with the coadsorption of O and H, there is a very slight repulsive interaction between OH and H with the coadsorbed state being 0.02 eV less stable than that when OH and H are adsorbed in separate p(2×2) unit cells. The reaction is initiated by the diffusion of $H_{(ads)}$ toward OH. As the $H_{(ads)}$−OH distance decreases, OH remains close to the top site. At an $H_{(ads)}$−OH separation of 1.60 Å, the transition state is accessed (Figure 2b). The activation energy for this reaction is only 0.21 eV. Thus, this elementary step proceeds much more readily than the O + H step. After the transition state the $H_{(ads)}$−OH distance decreases further, along with the total energy, yielding H₂O chemisorbed at a top site (Figure 2c). This reaction is 0.47 eV exothermic. Using the four-layer Pt slab in which the top layer of Pt atoms are allowed to relax yields an activation energy and exothermicity of 0.17 and 0.60 eV, respectively.

At $^1/_4$ ML coverage the top site, with an adsorption energy of 0.34 eV, is the preferred adsorption site for H₂O. Structure optimizations of H₂O at all four high symmetry sites on Pt-(111) revealed that the bridge site was the only other minimum in the potential energy landscape. H₂O binds to this site with an adsorption energy of 0.21 eV. The difference in binding energy of just 0.13 eV between bridge and top sites indicates that H₂O will diffuse easily along close packed rows of Pt atoms.

Experimental structure characterization of OH + H coadsorption is still lacking. As discussed, however, the most stable pure OH overlayer has $\sqrt{3} \times \sqrt{3} - R30°$ periodicity. If, when

(43) Steininger, H.; Lehwald, S.; Ibach, H. *Surf. Sci.* **1982**, *123*, 1.

(44) Starke, U.; Materer, N.; Barbieri, A.; Doll, R.; Heinz, K.; van Hove, M. A.; Somorjai, G. A. *Surf. Sci.* **1993**, *287*, 432.

(45) Christmann, K.; Ertl, G.; Pignet, T. *Surf. Sci.* **1976**, *54*, 365.

(46) Richter, L. J.; Ho, W. *Phys. Rev. B* **1987**, *36*, 9797.

(47) Koelman, B. J. J.; de Zwart, S. T.; Boers, A. L.; Poelsema, B.; Verheij, L. K. *Phys. Rev. Lett.* **1986**, *56*, 1152.

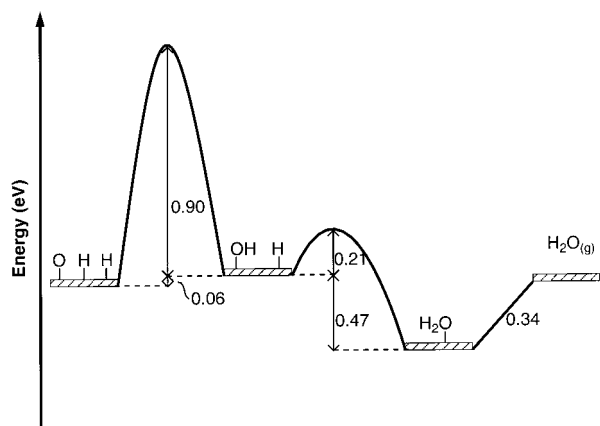(48) Christmann, K. *Surf. Sci. Rep.* **1988**, *9*, 1.

Figure 3. Relative energy diagram in eV for gas-phase H_2O ($H_2O_{(g)}$) formation from adsorbed O and H on Pt(111) in a p(2×2) unit cell.

coadsorbed with H, OH groups maintain a $\sqrt{3}\times\sqrt{3}-R30°$ periodicity, the initial state of the OH + H will be more stable and the barrier is likely to increase to ca. 0.5 eV. In addition, H_2O does not in reality form a p(2×2) overlayer. Instead, even at very low coverages, isolated H_2O molecules are stablized in H-bonded clusters and overlayers.[4] Thus, H-bonding is likely to lower the energy of the final state.

Our DFT computed barrier for the reverse of this elementary step, i.e., H_2O dissociation, is 0.68 eV (0.77 eV including substrate relaxation). The barrier to dissociation is, therefore, higher than the H_2O adsorption energy at this coverage. This is consistent with the fact that upon heating a H_2O covered Pt surface H_2O does not dissociate but instead desorbs.[4]

(c) Discussion of Reactions 1 and 2. Figure 3 displays the complete energy profile for the formation of H_2O from $O_{(ads)}$ and $H_{(ads)}$ at $^1/_4$ ML coverage. As we have seen, the first hydrogenation reaction, O + H → OH, is highly activated with a barrier of ∼1 eV. This barrier is incompatible with low temperature (<180 K) H_2O formation and crucially it indicates that significant H_2O formation at low temperatures *will not* proceed through this elementary step. H_2O formation via this step will be restricted to an appropriately high surface temperature: room temperature and above. The second elementary step, OH + H → H_2O, however, has a low barrier of ∼0.2 eV. This barrier *will* be surmountable in the low-temperature regime and is compatible with low-temperature H_2O formation. It is clear that once formed OH is easily hydrogenated to H_2O.

The fact that the barrier for the O + H reaction is so much higher than that for the OH + H reaction has major implications for the overall H_2O formation process. When we analyze the microscopic pathways of each reaction the reason for this difference becomes clear. To gain a qualitative understanding of each reaction barrier (E_a) we decompose it into the following terms:

$$E_a = \Delta E_{O(OH)} + \Delta E_H + \Delta E_{int} \qquad (5)$$

where $\Delta E_{O(OH)}$ is the energy difference between O (or OH) in the initial state (IS) and transition state (TS) in the absence of H ($E_{O(OH)}^{TS} - E_{O(OH)}^{IS}$). Likewise, ΔE_H is the energy difference between H in the initial and transition states in the absence of O (or OH) ($E_H^{TS} - E_H^{IS}$). ΔE_{int} is the interaction energy difference, $\Delta E_{int} = E_{int}^{TS} - E_{int}^{IS}$. E_{int} can be calculated from

$$E_{int} = E_{O(OH)+H} - (E_{O(OH)} + E_H) \qquad (6)$$

where $E_{O(OH)+H}$ is the total chemisorption energy of O + H or

Table 1. Reaction Barrier Decomposition for the O + H and OH + H Reactions on Pt(111)[a]

reaction	E_a (eV)	ΔE_O (eV)	ΔE_{OH} (eV)	ΔE_H (eV)	ΔE_{int} (eV)
O + H → OH	0.96	0.66		0.10	0.20
OH + H → H_2O	0.21		0.06	0.10	0.05

[a] ΔE_O, ΔE_{OH}, ΔE_H, and ΔE_{int} are as described in the text, all of which have been determined from self-consistent DFT calculations.

OH + H coadsorption and $E_{O(OH)}$ and E_H are the chemisorption energies of separate O (or OH) and H species.

Table 1 lists ΔE_O, ΔE_{OH}, ΔE_H, and ΔE_{int} for each reaction, all of which have been determined from self-consistent DFT calculations. From Table 1 it is clear that the largest component of each reaction barrier is the energy required to move the reactants from their initial locations to their transition state locations, i.e., ΔE_O, ΔE_{OH}, and ΔE_H. In fact, in both the O + H and OH + H reactions $\Delta E_O + \Delta E_H$ and $\Delta E_{OH} + \Delta E_H$ are equivalent to approximately $^3/_4$ (76%) of the total activation energy. The ΔE_H component, however, makes only a 0.10 eV contribution to each activation energy. This implies that the energy cost to move H from its initial location to its transition state location is relatively small in both the O + H and OH + H reactions. The difference between $\Delta E_O + \Delta E_H$ and $\Delta E_{OH} + \Delta E_H$ and ultimately the E_a for each reaction lies, therefore, in the energy required to move the O containing species (O or OH) from their respective initial to their respective transition states. The barrier for the O + H reaction is much larger than the barrier for the OH + H reaction because ΔE_O is 0.66 eV while ΔE_{OH} is only 0.06 eV. This is reasonable since O has to be activated from its preferred 3-fold fcc site to a bridge site to react, while OH requires no such activation to react. The inertness of chemisorbed O atoms at 3-fold hollow sites on the (111) facets of transition metal surfaces has recently been explained by Zhang and Hu.[49]

Wilke et al.[20] have recently used DFT to study the above reactions on Pt(111). They obtained barriers of 0.8 and 0.7 eV for the O + H and OH + H reactions, respectively. Their calculated barrier for the O + H reaction is quite similar to ours. Their barrier for the OH + H reaction, however, is more than three times as high as our value. We attribute this difference to the different approaches used to search reaction pathways. Wilke et al. performed a highly constrained search with points along the reaction pathway restricted to being symmetric along a single [$\bar{1}$12] surface plane. In our approach the only constraint is the distance between the reactants and thus the transition complex is not restricted to a particular plane or symmetry, being free to rotate and translate across the entire surface unit cell. Since in the O + H reaction the lowest energy transition state that we have identified is along the [$\bar{1}$12] plane, agreement between the two sets of calculations is quite good. In the OH + H reaction, however, the lowest energy transition state that we identified is not in the [$\bar{1}$12] plane. Therefore, it is not surprising that our calculated barrier for this reaction is lower than that obtained by Wilke et al.

(2) Disproportionation Reactions. Since OH formation by the addition of H to O is highly activated, some other mechanism must account for its formation and ultimately the formation of H_2O at low temperatures. The disproportionation of H_2O and O is believed to provide an alternative route to hydroxyls.[16] Reactions with 1:1 and 2:1 stoichiometries of H_2O and O have been suggested. Both stoichiometries of reaction have been examined and are discussed in turn below. To the best of our

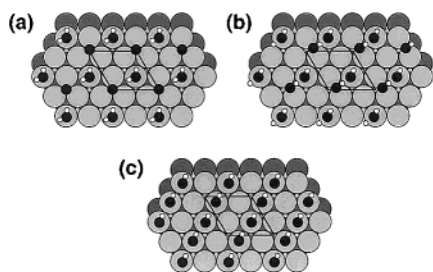(49) Zhang, C. J.; Hu, P. *J. Am. Chem. Soc.* **2000**, *122*, 2134.

Figure 4. Top view of initial (a), transition (b), and final (c) states of the 1:1 disproportionation of H_2O and O to form a $(2\times1)-$OH phase on Pt(111) in a p(2×2) unit cell.
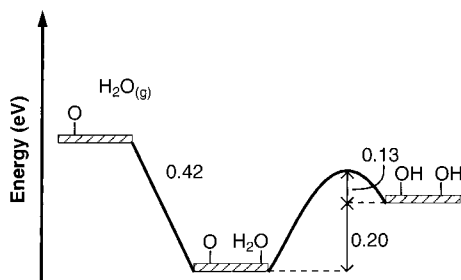

Figure 5. Relative energy diagram for the 1:1 disproportionation of H_2O and O to form a $(2\times1)-$OH phase on Pt(111) in a p(2×2) unit cell.

knowledge this is the first time that DFT has been applied to the determination of microscopic reaction pathways for H_2O and O disproportionation reactions on a metal surface.

(a) $H_2O + O \rightarrow 2OH$. The most stable coadsorption of a $^1/_4$ ML H_2O upon the O p(2×2) covered surface is shown in Figure 4a. As with the coadsorption of O and H, O atoms are at fcc sites and the counter-adsorbate, this time H_2O, is at top sites. This coadsorbed phase is 0.08 eV more stable than that when H_2O and O are chemisorbed in separate unit cells, indicating an attractive interaction between coadsorbed H_2O and O. The transition state (Figure 4b) for the reaction occurs rather close to the final state. It essentially consists of two pseudo-OH groups, one close to a top site and the other to a bridge site. After the transition state the pseudo-OH that is near to the bridge site diffuses toward a top site to produce a $(2\times1)-$OH phase (Figure 4c). This is the most stable OH phase at $^1/_2$ ML coverage, which is of a very similar stability to the $\sqrt{3}\times\sqrt{3}-$R30° OH phase.[31] The overall reaction is endothermic by 0.20 eV with an activation energy of 0.33 eV.

Having determined activation energies for OH formation by both the addition of H to O and the disproportionation of H_2O and O, we see that OH is indeed more easily produced through disproportionation. Figure 5 shows the energy profile for the reaction $H_2O + O \rightarrow 2OH$. On comparing Figure 5 and Figure 3 we glean important information related to the role played by O in modifying the reactivity of the Pt surface. First, the barrier to cleave an O−H bond of H_2O on an O covered Pt surface (0.33 eV) is lower than that on a clean Pt surface (0.68 eV). Thus, H_2O is more inclined to dissociate on an O covered Pt surface than on a clean Pt surface. Second, due to the presence of O the H_2O chemisorption energy increases (0.34 to 0.42 eV). Consequently, on the O covered surface the barrier to OH bond breakage in H_2O (0.33 eV) is less than the H_2O chemisorption energy (0.42 eV). This concurs with the experimental observations that when H_2O adsorbs upon an O covered Pt(111) surface it dissociates rather than desorbs.[4,50] As we have seen the opposite is true on a clean Pt(111) surface (Section 3.1).
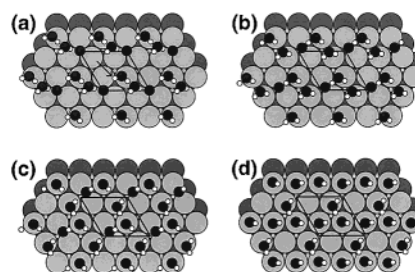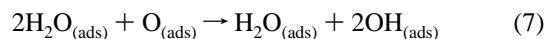
(50) Fisher, G. B.; Sexton, B. A. *Phys. Rev. Lett.* **1980**, *44*, 683.

Figure 6. Selected points along the $2H_2O + O \rightarrow 2OH + H_2O$ reaction pathway on Pt(111): (a) the initial state, (b) the transition state. (c) a $2OH + H_2O$ phase that is a local minimum, and (d) the final state, i.e., the p$(2\times2)-(2OH+H_2O)$ phase.

(b) $2H_2O + O \rightarrow 3OH + H$. Temperature-programmed desorption and isotope labeling studies have revealed that when a coadsorbed layer of O and H_2O is annealed from 95 K, H_2O and O react with a 2:1 stoichiometry.[17,18] The following reaction has been proposed to describe this process:

$$2H_2O_{(ads)} + O_{(ads)} \rightarrow 3OH_{(ads)} + H_{(ads)} \qquad (4)$$

The intermediate in the H_2O formation reaction, which propagates across the surface in the reaction fronts, has been assigned as the product of this 2:1 disproportionation process. Reaction 4, however, does not describe a single elementary step and must involve at least two individual steps. The only feasible sequence, at $^1/_4$ ML O coverage, to get from $2H_2O$ and O to $3OH$ and H is the *disproportionation* of one H_2O and O followed by the *dissociation* of the second H_2O:

$$2H_2O_{(ads)} + O_{(ads)} \rightarrow H_2O_{(ads)} + 2OH_{(ads)} \qquad (7)$$

$$H_2O_{(ads)} + 2OH_{(ads)} \rightarrow 3OH_{(ads)} + H_{(ads)} \qquad (8)$$

Recently, we suggested that the 2:1 disproportionation reaction on Pt(111) may not go to completion as reaction 4 indicates. Instead it stops after reaction 7 at a mixed $2OH + H_2O$ phase,[31] and this mixed $2OH + H_2O$ phase may be the observed intermediate. Here we tackle this issue thoroughly by determining reaction pathways and energetics for the two-step process of going from $2H_2O$ and O to $3OH$ and H.

(i) $2H_2O + O \rightarrow H_2O + 2OH$. Since experimentally H_2O reacts with a p(2×2) O overlayer, we have studied this reaction in a p(2×2) unit cell. Figure 6a displays the most stable adsorption of two H_2O molecules upon the p(2×2) O covered surface. It can be seen in Figure 6a that the H_2O molecules cluster to form H_2O dimers. One of the H_2O molecules in the dimer is at an off-top site and it is connected through a H bond to the other which is above a bridge site. Many possible reaction mechanisms for the transfer of a proton from the H_2O dimer to O have been considered. We find that the lowest energy route involves the removal of the H indicated by the arrow in Figure 6a. The pathway for this reaction is quite similar to that for the disproportionation of a single H_2O and O. As the $O_{(ads)}-$H (the H indicated by the arrow in Figure 6a) distance decreases, $O_{(ads)}$ begins to diffuse toward a bridge site. With $O_{(ads)}$ quite close to the bridge site the transition state (Figure 6b) is reached. This state then relaxes to a local minimum (Figure 6c), producing an OH chemisorbed at a bridge site. During the course of this process the second H_2O molecule of the H_2O dimer, which was originally quite high above the surface, moves toward a top site. The newly formed OH at the bridge site then diffuses toward a top site to produce a mixed $2OH + H_2O$ phase (Figure 6d). The activation energy for this elementary step is just 0.12

√3×√3−R30°−(OH+H₂O)+(1×1)−OH

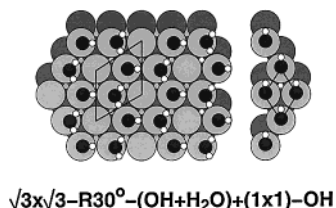**Figure 7.** Structure of the $\sqrt{3}\times\sqrt{3}-R30°-(OH+H_2O)+(1\times1)-OH$ overlayer. In the $\sqrt{3}\times\sqrt{3}-R30°-(OH+H_2O)$ regions there is 1:1 ratio of OH and H_2O with a surface coverage of $^2/_3$ ML of O containing adsorbates. The $(1\times1)-OH$ domains are pure OH. The overall experimental surface coverage of $^3/_4$ ML of O containing species is maintained if $^2/_3$ and $^1/_3$ of all adsorbed species are contained within the $\sqrt{3}\times\sqrt{3}-R30°$ and (1×1) domains, respectively.

eV and the reaction is 0.39 eV exothermic. The product of this reaction, which we shall refer to as $p(2\times2)-(2OH+H_2O)$, has a coverage of $^3/_4$ ML of O containing species. The structure of this phase can be viewed as linear OH chains which are cross linked through H bonding by adsorbed H_2O molecules.

(ii) $H_2O + 2OH \rightarrow 3OH + H$. In the preceding reaction a H_2O molecule that was part of a H_2O dimer reacted with a $p(2\times2)$ O overlayer. It was clear that this reaction was best investigated in a $p(2\times2)$ unit cell. For the present reaction the choice of unit cell is not as clear-cut. This is because the experimentally observed intermediate in the H_2O formation reaction, which is believed to be the product of this reaction, i.e., 3OH + H, has a rather unusual periodicity. STM and LEED have revealed a partitioned overlayer with an overall surface coverage of $^3/_4$ ML consisting of majority $^2/_3$ ML $\sqrt{3}\times\sqrt{3}-R30°$ and/or (3×3) domains and minority (1×1) domains.[17] It is possible, therefore, that once formed through reaction 7 the $p(2 \times 2)-(2OH+H_2O)$ phase undergoes reaction 8 to produce a $p(2\times2)-(3OH+H)$ phase which then rearranges into $\sqrt{3}\times\sqrt{3}-R30°$ and/or (3×3) domains and (1×1) domains. To model this scenario reaction 8 was examined in a $p(2\times2)$ unit cell, with the initial state merely the final state of the previous reaction, i.e., the $p(2\times2)-(2OH+H_2O)$ phase. Alternatively, the $p(2\times2)-(2OH+H_2O)$ phase rearranges into $\sqrt{3}\times\sqrt{3}-R30°$ and/or (3×3) domains and (1×1) domains and then reaction 8 occurs. To model this scenario we investigated reaction 8 in a $\sqrt{3}\times\sqrt{3}-R30°$ unit cell. The experimentally observed $^2/_3$ ML coverage of the $\sqrt{3}\times\sqrt{3}-R30°$ domains is reproduced by placing 1OH and 1H₂O in the $\sqrt{3}\times\sqrt{3}-R30°$ unit cell. Furthermore, as in the observed overlayer, if additional OH groups are located in (1×1) domains then the macroscopic surface coverage of $^3/_4$ ML of O containing species is maintained.[51] A schematic diagram of such a partitioned overlayer, which is of a similar stability[51] to the product of reaction 7, is shown in Figure 7. Reaction 8 was not examined in the (1×1) or (3×3) domains because the former are pure OH domains[17,31] and the later would be computationally too demanding with any results obtained likely to be similar to those obtained using a $\sqrt{3}\times\sqrt{3}-R30°$ unit cell (also see the comparison between reaction in the $p(2\times2)$ and $\sqrt{3}\times\sqrt{3}-R30°$ unit cells below).

---

(51) An overall surface coverage of $^3/_4$ ML of O containing species and a 2:1 ratio of OH and H_2O is maintained if $^2/_3$ and $^1/_3$ of all adsorbed species are in the $\sqrt{3}\times\sqrt{3}-R30°-(OH+H_2O)$ and $(1\times1)-OH$ domains, respectively. Accounting for $(1\times1)-OH$ domains also allows us to compare the relative stability of the $p(2\times2)-(2OH+H_2O)$ phase and the $\sqrt{3}x\sqrt{3}-R30°-(OH+H_2O)+(1\times1)-OH$ overlayer. Summation of the chemisorption energies of the adsorbates in each phase yields a total chemisorption energy in the $p(2\times2)-(2OH+H_2O)$ phase of 6.29 eV and a total chemisorption energy in the $\sqrt{3}\times\sqrt{3}-R30°-(OH+H_2O)+(1\times1)-OH$ overlayer of 6.20 eV (3.70 eV for 1 OH and H_2O in the $\sqrt{3}\times\sqrt{3}-R30°-(OH+H_2O)$ domain and 2.50 eV for l OH in the (1×1) domain). From this it can be seen that both phases are of a similar stability.
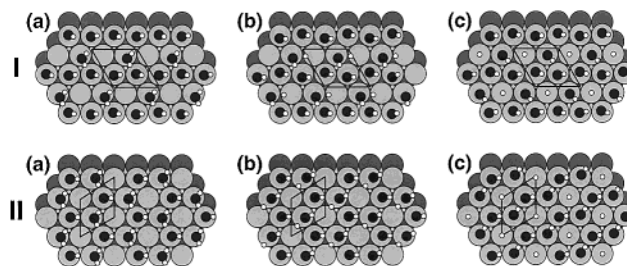

Figure 8. Top view of initial (a), transition (b), and final (c) states for the $2OH + H_2O \rightarrow 3OH + H$ reaction (reaction 8) on Pt(111): (I) reaction 8 in a $p(2\times2)$ unit cell with the $p(2\times2)-(2OH+H_2O)$ phase as the initial state and (II) reaction 8 in a $\sqrt{3}\times\sqrt{3}-R30°$ unit cell with the $\sqrt{3}\times\sqrt{3}-R30°-(OH+H_2O)$ phase as the initial state.

Initial, final, and transition states for reaction 8 in both the $p(2\times2)$ and $\sqrt{3}\times\sqrt{3}-R30°$ unit cells are shown in Figure 8. The energetics of this elementary step in both unit cells are qualitatively similar. The activation energy and heat of reaction for H_2O dissocation in the $p(2\times2)$ unit cell are 1.70 and 1.52 eV, respectively. In the $\sqrt{3}\times\sqrt{3}-R30°$ unit cell these values are 1.75 and 1.18 eV, respectively. Clearly, regardless of which unit cell is used, this elementary step is highly activated and highly endothermic. Contrary to the assumption in the literature, our calculations indicate that this reaction could not occur until high surface temperatures and it certainly will not proceed in the low-temperature (<180 K) regime.

By comparing the barriers for the dissociation of isolated H_2O molecules (0.68 eV in a $p(2\times2)$ unit cell) and H_2O molecules that are incorporated in the mixed OH and H_2O overlayers (1.70−1.75 eV) we see that it is much more difficult to dissociate the H_2O molecules that are incorporated into the OH and H_2O overlayers. This is because there is extensive H bonding in the OH and H_2O overlayers which affects the energetics of H_2O dissociation. In the $\sqrt{3}\times\sqrt{3}-R30°$ unit cell (Figure 7), for example, each O atom is coordinated to three H atoms with every OH moiety acting as both a H bond acceptor and donor. After dissociation of the H_2O molecule in this cell, however, there is less H bonding, with each O atom coordinated to just two hydrogens. This loss of H bonding upon dissociation increases the endothermicity and also the activation energy for dissociation of H_2O molecules in the mixed OH and H_2O overlayers.

(c) Discussion of Disproportionation Reactions. Figure 9 illustrates the complete energy profile going from $2H_2O$ and O to 3OH and H, i.e., reactions 7 and 8. The **two-step** process is >1 eV endothermic with a barrier of at least 1.7 eV. It is clear, therefore, that the two step process will be unfeasible in the low temperature regime. The problem with the overall process is the very high energy barrier to the second reaction (reaction 8). The first reaction (reaction 7), however, in this two-step process has a small barrier of just 0.12 eV and is exothermic by 0.39 eV. Such an elementary step could readily occur at low surface temperatures. The small barrier of reaction 7 and the very large barrier of reaction 8 substantiate our previous suggestion[31] that the 2:1 disproportionation reaction does not proceed to 3OH + H, as suggested by reaction 4. Instead it stops after reaction 7 at a mixed 2OH + H_2O phase. We suggest, therefore, that when H_2O and O react on Pt(111) reaction 7 describes the process more appropriately than reaction 4. The most significant implication of this in the present context is that it is the product of reaction 7, i.e., a mixed OH and H_2O overlayer, which is the observed low-temperature intermediate in the water formation reaction.

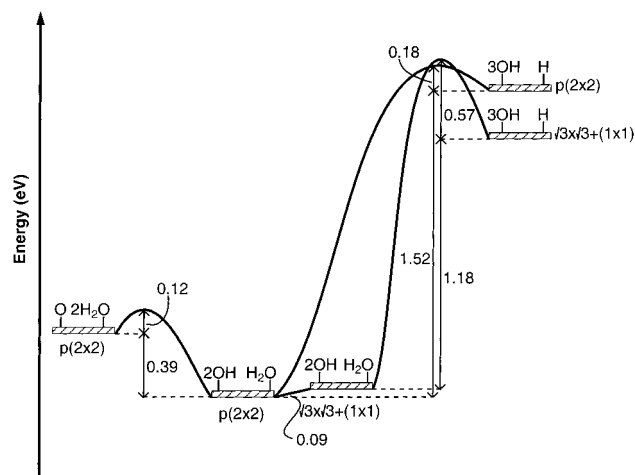As shown in Figures 6 and 7 we have identified two distinct

Catalytic Water Formation on Platinum

J. Am. Chem. Soc., Vol. 123, No. 18, 2001 4241

Figure 9. Relative energy diagram of the 2:1 disproportionation reaction of H_2O and O on Pt(111). The energetics for two elementary steps, i.e., $2H_2O + O \rightarrow 2OH + H_2O \rightarrow 3OH + H$, are displayed. The first reaction (reaction 7), as illustrated in Figure 6, has been examined in a p(2×2) unit cell. The second reaction (reaction 8), $2OH + H_2O \rightarrow 3OH + H$, has been examined in both p(2×2) and $\sqrt{3} \times \sqrt{3}$−R30° unit cells as illustrated in Figure 8. The initial state of reaction 8 in the $\sqrt{3} \times \sqrt{3}$−R30° unit cell is 0.09 eV less stable than the initial state of this reaction in the p(2×2) unit cell when the (1×1)−OH domains are accounted for.

$2OH + H_2O$ overlayers, namely p(2×2)−($2OH+H_2O$) and $\sqrt{3} \times \sqrt{3}$−R30°−($OH+H_2O$)+(1×1)−OH. Both phases are of a similar stability[51] and so either one is conceivably the observed intermediate. The periodicity of the $\sqrt{3} \times \sqrt{3}$−R30°−($OH+H_2O$)+(1×1)-OH overlayer (Figure 7), however, matches the STM images and LEED patterns of ref 17 and so it is this overlayer that is likely to be the true intermediate. The picture that emerges, therefore, for the 2:1 disproportionation process is that once formed through reaction 7 the p(2×2)−($2OH+H_2O$) phase rearranges into OH and H_2O overlayers of $\sqrt{3} \times \sqrt{3}$−R30° (and/or (3×3)) and (1×1) periodicity and that the H_2O molecules in the $\sqrt{3} \times \sqrt{3}$−R30° domains (and also the (3×3) domains) of this overlayer *do not* undergo further dissociation.

Our calculations clearly indicate that disproportionation reactions with 1:1 and 2:1 stoichiometries of H_2O and O proceed to OH with lower barriers (0.33 and 0.12 eV, respectively) than that associated with the O + H reaction (0.96 eV). Thus, H_2O does indeed facilitate an elementary step in the H_2O formation process on Pt(111). H_2O is, therefore, playing an autocatalytic role. Experimentally, disproportionation reactions with 1:1 and 2:1 stoichiometries of H_2O and O have been suggested. Isotopically labeled thermal desorption experiments have revealed, however, that the 2:1 stoichiometry is always favored.[17,18] The reason for this preference can be seen in our DFT calculations. The activation energy for the reaction with the 2:1 stoichiometry (0.12 eV) is lower than that in the reaction with the 1:1 stoichiometry (0.33 eV). In addition, the reaction with the 2:1 stoichiometry is *exothermic* by 0.39 eV while that with the 1:1 stoichiometry is *endothermic* by 0.20 eV. It is, therefore, for both kinetic and thermodynamic reasons that the disproportionation reaction with the 2:1 stoichiometry is more favorable than that with the 1:1 stoichiometry. The reaction with the 2:1 stoichiometry is, in fact, the only one studied that produces OH with an appreciable energy gain. On examination of the microscopic reaction pathway for the 2:1 disproportionation reaction we are able to identify the physical origin of its preference. As the first H_2O molecule in the H_2O dimer disproportionates with O, the second H_2O molecule is not merely
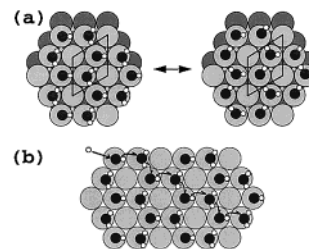
a spectator. Instead, through H bonding with the first H_2O molecule it is actively involved in the disproportionation process. Such H bonding interactions lower the barrier to disproportionation and also lower the energy of the final state. The high relative stability of the $2OH + H_2O$ overlayers and the ease with which they are formed is, we believe, the key to facile H_2O formation on Pt. The second H_2O molecule in the 2:1 disproportionation process is of critical importance, acting, in fact, as a very effective catalytic promoter. Since H_2O is often present in catalytic systems, especially at low temperatures, it is possible that this observation may have far reaching implications with H_2O exhibiting similar promotional abilities in other catalytic reactions.

(3) Hydrogenation of the $\sqrt{3} \times \sqrt{3}$−R30°−($OH+H_2O$) Phase. It was demonstrated in Section 3.1 that isolated OH groups are easily hydrogenated to H_2O. However, having established that the most thermodynamically favorable route to OH produces a mixed OH and H_2O overlayer and not pure OH, it remains to investigate how the OH and H_2O overlayer, which is the key intermediate in the H_2O formation process, is hydrogenated. Under the STM this intermediate phase appears as rings, with a width typically of 100−1000 Å, which grow and propagate across the surface, the motion of which transforms O covered areas into H_2O regions. As this phase propagates, it is not hydrogenated uniformly throughout. Instead H_2O formation is observed at the interior of the reaction fronts.[16] A process like this over such a long range is difficult for us to examine directly.

We have, however, investigated one hydrogenation mechanism that may be operable and could account for the experimental observation. It is possible that hydrogenation of this phase takes place by means of proton transfers. Proton-transfer mechanisms in the $\sqrt{3} \times \sqrt{3}$−R30°−($OH+H_2O$) phase and in other OH and H_2O phases have been examined. In each case the barrier to transfer a proton from H_2O to an OH within these phases is extremely low. In the $\sqrt{3} \times \sqrt{3}$−R30°−($OH+H_2O$) phase (Figure 10a), for example, the barrier is <0.01 eV. This indicates that, at a finite temperature, H atoms within the $\sqrt{3} \times \sqrt{3}$−R30°−($OH+H_2O$) phase will be constantly exchanging between OH and H_2O. It is possible, therefore, that conversion of an OH into H_2O could, for example, initiate a series of proton transfers which results in the formation of H_2O elsewhere in the OH and H_2O overlayer. A schematic diagram of such a process is illustrated in Figure 10b. We suggest that OH groups at the leading edge of the OH and H_2O fronts are hydrogenated by H atoms and that protons are transferred from the leading edge to the interior of the fronts where pure H_2O domains form.

Figure 10. (a) Schematic diagram illustrating proton transfer in the $\sqrt{3} \times \sqrt{3}$−R30°−($OH+H_2O$) phase, which we believe is the intermediate in the low-temperature H_2O formation reaction. (b) Illustration depicting a possible hydrogenation mechanism in the $\sqrt{3} \times \sqrt{3}$−R30°−($OH+H_2O$) phase.

4. Conclusions

Having performed extensive DFT calculations to determine the pathways and energetics of many reactions implicated in the oxygen−hydrogenation reaction on Pt(111) we now have a deeper understanding of this fundamental catalytic process. Largely in agreement with the recent experiments of Ertl and co-workers,[16,17] the energetics obtained from our first-principle calculations point to two distinct mechanisms for H_2O formation:

(a) When H_2O does not adsorb upon the surface (>180 K), H_2O must be formed via the successive addition of chemisorbed H to chemisorbed O and then to OH. The most highly activated step in this process, with a barrier of ∼1 eV, is the addition of the first H to chemisorbed O. This barrier is high because it is necessary to activate O from its favored fcc site to a bridge site to have a reaction. The hydrogenation of OH to H_2O proceeds much more readily with a barrier of ∼0.2 eV. The ∼1 eV barrier of the first step indicates that H_2O formation at low temperatures will not proceed through this elementary step. This route to H_2O formation is clearly not autocatalytic and is likely to be the dominant mechanism by which H_2O is formed at room temperature and above.

(b) When H_2O is present on the surface disproportionation reactions provide low-energy routes to the formation of adsorbed OH groups and ultimately H_2O. Disproportionation reactions involving a single H_2O and O as well as two H_2O and one O are possible with barriers of 0.33 and 0.12 eV, respectively. Disproportionation with a 2:1 stoichiometry of H_2O and O is kinetically and thermodynamically favored over disproportionation with a 1:1 stoichiometry. In the 2:1 disproportionation process the second H_2O molecule, although not directly involved in the disproportionation reaction itself, plays an additional catalytic role. This second H_2O molecule considerably improves the energetics of H_2O and O disproportionation. The reaction with the 2:1 stoichiometry represents, in fact, the only occasion that OH is formed with an appreciable energy gain, which explains the experimentally observed 2:1 stoichiometry for H_2O and O disproportionation on Pt(111). In support of our previous suggestion that the observed intermediate in the low-temperature H_2O formation reaction is a mixed OH and H_2O overlayer we find that the second H_2O molecule in the 2:1 disproportionation process is very difficult to dissociate. We suggest that once formed through the 2:1 disproportionation reaction the mixed OH and H_2O overlayer is hydrogenated by means of proton transfers to H_2O.

Appendix

The energetics of OH chemisorption on Pt is an issue of considerable interest. Experimental determinations of the OH chemisorption energy on Pt vary substantially, ranging from 1 to 2.6 eV. Depending upon the coverage, our calculated chemisorption energies of pure OH on Pt(111) are between 2.2 and 2.6 eV, which places our calculated values at the higher end of the experimentally determined energy range. It is difficult to directly measure the metal−OH bond strength experimentally and therefore experimental determinations are merely estimates. Of the experimental estimates, we find that our values agree best with those obtained under high vacuum conditions and when no coadsorbates are present. Indeed, OH adsorption is known to be very sensitive to the presence of coadsorbates. Sellers and co-workers (*Surf. Sci.* **1994**, *306*, 447) have, in fact, reviewed the energetics of OH adsorption on Pt. They concluded that at high coadsorbed O conditions OH chemisorption energies of about 1 eV are observed. On the other hand, under O depleted conditions OH chemisorption energies seem to reach a limiting value of 2.6 eV. Therefore, we believe that our value for the OH chemisorption energy is a good estimate of the bond strength between pure OH and Pt.