

# Mechanisms of Initial Dissociative Chemisorption of Oxygen on Transition-Metal Surfaces

PETER D. NOLAN, M. CLAY WHEELER,  
JOHN E. DAVIS, AND C. BUDDIE MULLINS\*

*Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas 78712-1062*

Received November 22, 1996

## Introduction

Dissociative adsorption of oxygen on transition-metal surfaces has been studied extensively due to its importance as a fundamental step in many industrial catalytic processes.<sup>1</sup> Additionally, the relative simplicity of the oxygen molecule may allow generalization to studies of other adsorption systems as well. Efforts to develop a rudimentary understanding of these oxidation reactions have centered largely on surface chemical techniques that probe the chemical and physical interactions of gas-phase molecules and metal surfaces. Specifically, single-crystal metal samples under ultrahigh vacuum conditions ( $\sim 10^{-10}$  Torr) are typically employed, and the fairly recent application of supersonic molecular beam techniques has shown marked utility in simplifying and characterizing adsorption reaction pathways. In cooperation with several spectroscopic techniques, experiments designed to probe adsorption probabilities over a wide range of conditions have yielded much insight into the mechanisms by which gas-phase molecules interact with metal surfaces. In particular, fundamental studies investigating adsorption mechanisms in the limit of zero adsorbate coverage have

provided evidence of complex and seemingly numerous adsorption mechanisms.

Mechanistic details of oxygen adsorption on bare transition-metal surfaces are typically explained under two distinct regimes. Under certain conditions, indirect or precursor-mediated mechanisms are employed, while for others, a more direct process is thought to characterize adsorption. In general, if a thermally accommodated surface state precedes dissociative chemisorption (surface chemical bonding), substrate temperature may be paramount in dictating adsorption probability. Conversely, in the absence of a dissociation precursor, where an impinging molecule is considered to dissociate essentially upon impact with the surface, adsorption probabilities may be expected to be a stronger function of gas-phase properties than surface conditions.<sup>2</sup> This easily measurable trend has often been used as a defining criterion for labeling a system "direct" or "precursor-mediated".

Although direct and indirect mechanisms exhibit clearly distinct trends in experimental adsorption data, differences in the inherent physical properties that dictate which mechanisms manifest themselves in various systems may be much more subtle; indeed, strong similarities exist in the basis behind several mechanistic explanations. A universal concept of electron transfer likely underlies oxygen adsorption mechanisms, and the ease of transfer may dictate the lifetime of negative-ion intermediates and thus their putative existence. The ultimate formation of a chemical bond between oxygen and a metal surface implies an exchange of electrons, specifically donation from the surface into the antibonding orbitals of the oxygen molecule, and the rate of this transfer may vary considerably among systems. Furthermore, the facility of charge transfer is often experimentally manifested as an effective kinetic energy barrier to the dissociated final state.

In regimes exhibiting impeded electron transfer (due to low surface temperature, low incident kinetic energy, unfavorable surface configuration or electronic states, etc.), intermediate surface states have sufficient lifetimes to accommodate fully to the substrate temperature and serve as precursor states to dissociation. Kinetic competition between desorption and dissociation is often clearly observable as a change in adsorption probability with substrate temperature. Molecular intermediates are frequently used to rationalize data exhibiting such a dependence, and the existence of these states *as low coverage precursors* has indeed been supported over a wide range of experimental conditions.

In the opposite extreme, namely, systems displaying facile electron transfer, the surface intermediates have insufficient lifetimes to complete thermal accommodation, and other factors (lattice oscillations, incident translational energy, etc.) may contribute more strongly to trends in adsorption. Due to an observed surface temperature independence and increasing adsorption probability with kinetic energy, data from such studies have been ex-

Peter D. Nolan was born in Mankato, MN, in 1971 and received his B.S. degree in chemical engineering from North Carolina State University in 1994. He is currently pursuing his Ph.D. in chemical engineering at The University of Texas at Austin, studying molecular beam/transition-metal chemisorption systems.

M. Clay Wheeler was born in San Diego, CA, in 1963. He received his B.S. degree in 1992 in chemical engineering from The University of Texas at Austin, where he received his Ph.D. in chemical engineering in 1997 for his work on surface reactions on transition metals and semiconductors.

John E. Davis was born in Rutherfordton, NC, in 1968 and received his B.S. degree in chemical engineering from North Carolina State University in 1991. He received his Ph.D. in chemical engineering from The University of Texas at Austin in 1996 for his work in studying molecular intermediates in dissociative chemisorption mechanisms of gas–surface interactions.

C. Buddie Mullins was born in 1954 in Roswell, NM. He received his Ph.D. in chemical engineering from the California Institute of Technology in 1990 and joined the faculty of The University of Texas at Austin in 1991, where he is the Chevron Centennial Teaching Fellow. Mullins has interests in fundamental aspects of molecular and dissociative adsorption on solid surfaces.

plained under simple direct mechanisms. However, these results may be rationalized in a broader sense as occurring through essentially the same charge-transfer mechanism as precursor-mediated adsorption; since the electron transfer occurs more readily, the molecular species do not have the opportunity to accommodate appreciably, rendering kinetic precursor effects less important.

Much of the available literature focuses on the existence or absence of precursors in dissociation, but the distinction may not be so absolute. The lifetime of negative-ion intermediates, and hence the degree of thermal accommodation, influences the extent to which kinetic competition plays a role in adsorption probabilities over various conditions. The relative role of this competition in light of additional relevant explanations (several examples are delineated in the balance of this review) may justify experimental data trends on various surfaces and under various conditions. The charge-transfer basis for oxygen adsorption may help to clarify mechanistic details of dissociation by rationalizing ostensibly distinct explanations.

### Low Kinetic Energy Regime

The concept of dissociation precursors dates back to Langmuir,<sup>3,4</sup> as a mobile, molecular surface state could explain a coverage independence in the adsorption probability of cesium on a tungsten filament. Up to nearly saturation coverage, a unity adsorption coefficient was observed, necessitating a surface diffusion mechanism, as direct adsorption cannot explain high adsorption probabilities in high coverage regimes (with reduced available adsorption sites). Since then molecular precursors have been invoked widely to rationalize similar trends as well as surface temperature dependencies on adsorption for various systems.

Typically hypothesized for oxygen at low incident energies (less than  $\sim 0.1$  eV), a precursor-mediated mechanism is often characterized by an impinging molecule trapping into a physisorbed (physically adsorbed) state via weak van der Waals interactions. From this state, surface thermal energy drives a kinetic competition between one of two ultimate fates: (1) desorption from the surface to the gas phase or (2) dissociation into chemisorbed atomic species—likely through one or more molecularly chemisorbed states. Since successful trapping largely depends on efficient linear momentum dissipation, systems governed by such a process are likely to exhibit a strong inverse relation of incident kinetic energy with trapping probability—hence with dissociative chemisorption probability as well (Figure 1). However, an absence of such a dependence for at least two systems, Ag(110) and (100), suggests that a contribution from the physically adsorbed state may not always manifest itself strongly enough for experimental detection.<sup>5,6</sup> Additionally, surface temperature effects are often strong since the final dissociated state is accessed directly by a surface species with sufficient lifetime for appreciable thermal accommodation.

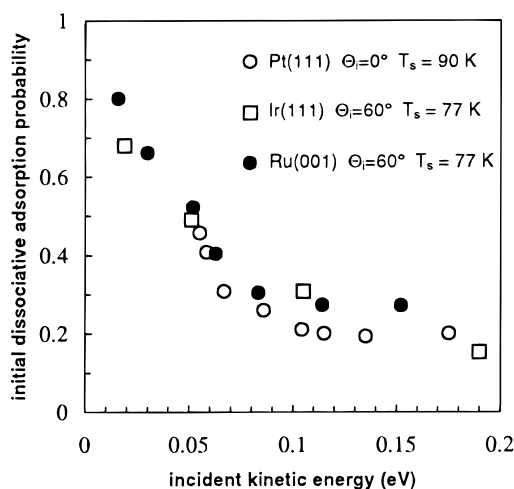


FIGURE 1. Figure shows initial dissociative adsorption probability versus incident kinetic energy for Ir(111),<sup>12</sup> Ru(001),<sup>13</sup> Pt(111).<sup>18</sup> In the low incident kinetic energy regime, initial adsorption probability falls with increasing kinetic energy for most transition-metal systems. The decrease in adsorption probability likely stems from a required dissipation of linear momentum necessary for “trapping” into a physically adsorbed state.

On transition-metal surfaces, short precursor lifetimes preclude the spectroscopic detection of chemisorbed molecular oxygen at high temperatures; the molecular species appears easiest to isolate on platinum and silver surfaces—substrate temperatures below only  $\sim 200$  K are required. However, the fact that measurable quantities of molecular oxygen have not been observed at these temperatures on other transition-metal surfaces does not abate the extent to which the molecular species influences the dissociation process. Although the lifetime, and hence the steady-state apparent concentration of such a precursor (whether it be physically or chemically adsorbed) is too short for detection, it may well be sufficient to equilibrate thermally to the surface and subsequently play a role in the mechanism and kinetics of dissociative adsorption.

A spectroscopic study on Al(111) by Hofmann et al.<sup>7</sup> showed early evidence that physically adsorbed molecular oxygen is the precursor to the dissociated state. Although the pathway leading to *low coverage* adsorption was not specifically considered, the formation of physically adsorbed oxygen and its conversion to an atomically chemisorbed species were investigated. The implication of molecular oxygen as a precursor to atomic oxygen manifested itself in UPS (ultraviolet photoelectron spectroscopy) measurements of the conversion from the molecular species to the atomic final state. Because the conversion through the molecular state occurs so rapidly, a surface temperature of 30 K and approximately half a monolayer of dissociated oxygen were required to first observe the physically adsorbed state. Further evidence supporting the precursor lies in the observed decrease in chemisorption probability from nearly unity at 30 K to less than 0.05 at 300 K.

Early studies of low kinetic energy chemisorption on W(110) and (100) by Kohrt and Gomer<sup>8</sup> and Wang and

Gomer<sup>9</sup> yielded additional evidence of precursor-mediated adsorption. An observed decrease in initial adsorption probability with increasing kinetic energy (up to 0.08 eV via an effusive beam) on both faces indicated the plausibility of a molecular dissociation precursor—a possibility corroborated by the initial insensitivity of adsorption probability to surface coverage. Wang and Gomer identified a weakly chemisorbed molecular species,  $\alpha$ -O<sub>2</sub>, which they believed to be the previously postulated molecular precursor,<sup>8</sup> but subsequent UPS and XPS (X-ray photoelectron spectroscopy) analysis furnished no evidence of molecular oxygen until after the formation of an atomic layer. However, this observation does not preclude a mobile precursor, as the lifetime of such a surface species may be too short to allow spectroscopic identification. In a nonactivated dissociation process, a nondesorbing molecular precursor may diffuse along the surface to a suitable site and dissociate;<sup>10</sup> since the time scale of such an event largely depends on substrate temperature, the precursor may not be practically isolatable until dissociation sites are filled and it can remain atop a covered surface. Further, the presence of surface oxygen adatoms increases the metal's work function, impeding electron transfer and rendering the formation of the molecular state more likely. Thus, the  $\alpha$ -O<sub>2</sub> species may indeed represent the molecular precursor to the final dissociated state, despite the fact that its existence has been verified only atop a saturated atomic monolayer.

Although examples of experimental data supporting a low coverage, low kinetic energy, precursor-mediated oxygen adsorption mechanism exist for several systems,<sup>5,11–15</sup> it is perhaps most instructive to consider the Pt(111) surface since a very large body of research has been conducted recently on this system. High coverage studies, similar to those discussed on tungsten and aluminum, have implicated the presence of a low-coverage molecular dissociation precursor on this surface.<sup>16,17</sup> While the best true evidence of a precursor to *initial* adsorption most assuredly lies in spectroscopic verification in the low coverage limit, short precursor lifetimes render this analysis difficult. Because low coverage precursor evidence inferred through high coverage experiments is largely circumstantial (nothing mandates the same mechanisms need apply in the two different coverage regimes), various kinetic measurements have been employed to discern adsorption mechanisms. The recent development of molecular beam techniques has helped to provide strong kinetic evidence of a molecular precursor to dissociatively chemisorbed oxygen and allowed the construction of simple, one or two-dimensional potential energy surfaces characterizing the adsorption process.

Dissociative chemisorption measurements of O<sub>2</sub> on Pt(111) by Luntz et al.<sup>18,19</sup> via the reflective method described by King and Wells<sup>20</sup> clearly show a trend of decreasing adsorption probability with increasing surface temperature and incident kinetic energy in the low-energy regime (see Figure 2). Both inverse trends are justified using a kinetic scheme with physically and chemically adsorbed molecular dissociation precursors. This simpli-

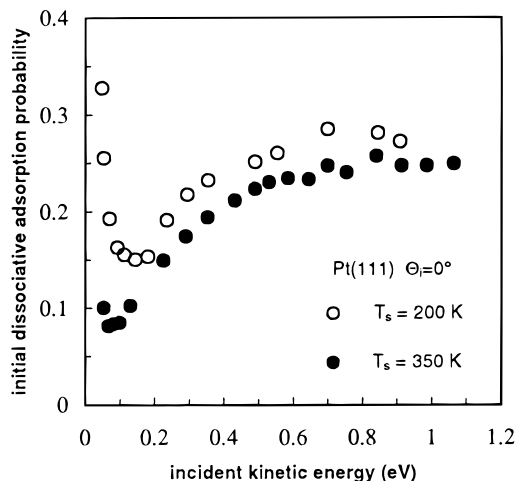


FIGURE 2. The O<sub>2</sub>/Pt(111) system<sup>18</sup> exhibits a marked surface temperature dependence over the entire energy range studied; clearly increasing adsorption probability with increasing surface temperature trend extends well into the high energy regime. A kinetic model based on direct molecular chemisorption has been most convincingly used to explain such an effect for this surface as well as for Ag(110),<sup>5</sup> Ir(111),<sup>12</sup> and Ir(110).<sup>14</sup>

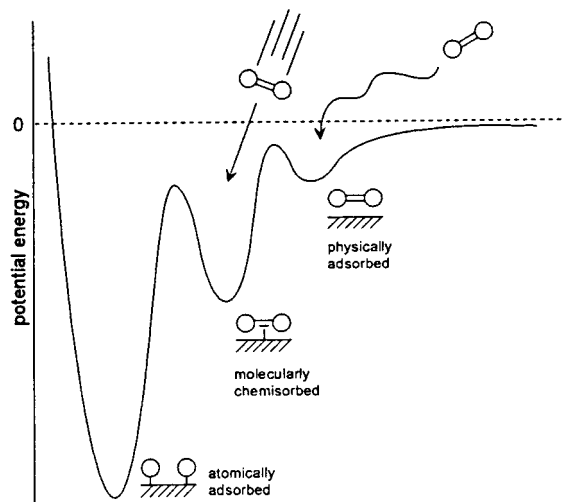


FIGURE 3. A one-dimensional potential energy schematic showing qualitative aspects of oxygen adsorption. Relative barrier heights to dissociation and desorption from the molecularly chemisorbed and physisorption wells may dictate the observed surface temperature dependence in various systems. Low incident energy molecules initially sample the physically adsorbed state, while hyperthermal molecules may adsorb directly as a molecularly chemisorbed species.

fied model may be visualized most easily as a one-dimensional potential energy surface featuring a shallow molecularly chemisorbed well prior to the dissociation well (Figure 3). The initial energy dependence may be attributed to a decreasing trapping probability into the physically adsorbed state with increasing incident energy, and the inverse temperature dependence arises from the positive difference in barrier heights for desorption and dissociation (for both molecular states). If the molecular precursor accommodates thermally to the substrate, kinetic competition dictates rate enhancement to the state with the larger apparent activation barrier as surface temperature increases. Similar simplistic kinetic models

have been discussed in the literature.<sup>21</sup> Much recent debate has centered on characterizing the molecular precursor itself; various studies employing TDS (thermal desorption spectroscopy),<sup>22–24</sup> UPS,<sup>22,23,25–27</sup> EELS (electron energy-loss spectroscopy),<sup>22,24,26,27</sup> and NEXAFS (near-edge X-ray adsorption fine structure)<sup>28–30</sup> have resolved atomic, molecularly physisorbed, and molecularly chemisorbed states. However, separate EELS and NEXAFS experiments have identified different surface species (namely a peroxy-like  $O_2^{2-}$  phase and a superoxy-like  $O_2^-$  phase) as the molecularly chemisorbed state. Perhaps the most compelling description of this adsorbed precursor state is the concept of sequential precursors first developed by Avery et al.<sup>24</sup> and recently characterized as both peroxy-like and superoxy-like species by Puglia et al.<sup>31</sup> This successive precursor mechanism makes intuitive sense when the chemisorption process is viewed as a consecutive addition of electronic charge into the molecular antibonding orbitals.

## High Kinetic Energy Regime

Much of the research focused on high kinetic energy adsorption of oxygen on transition metals has transpired in the past decade, due to the recent establishment of molecular beam techniques. High nozzle temperatures and inert gas seeding have allowed the development of well-characterized, nearly monoenergetic beams with high translational energies (up to  $\sim 1.5$  eV) and permitted the study of dissociative adsorption in the high-energy regime. Although precursor-mediated mechanisms are widely used to explain trends in low kinetic energy adsorption data, the question remains over whether such indirect mechanisms apply for high translational energies as well.

In general, oxygen/transition-metal systems in the high incident energy regime exhibit a common trend of increasing adsorption probability with increasing translational energies. Often depicted one-dimensionally as an effective potential energy barrier, the underlying impetus to dissociation likely lies in the ability of the substrate to donate charge to an impinging oxygen molecule. Metals with higher work functions may necessitate smaller molecule/surface separations for successful electron donation, requiring higher incident energies to overcome the dissociation barrier. However, the cumulative picture is considerably more complicated, as adsorption probabilities cannot be correlated directly with work function magnitudes. Effects such as surface geometry and others not considered in an electron-sea depiction of the metal likely contribute to reaction kinetics and dynamics as well.

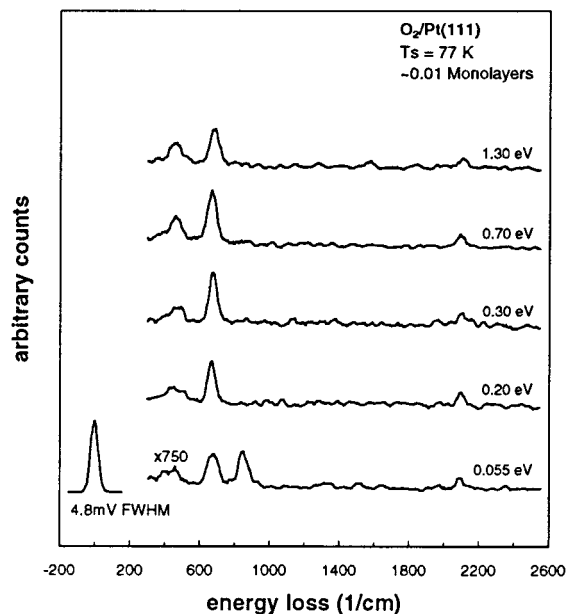
An insensitivity of adsorption probability to surface temperature of several systems under certain conditions has led to the assignment of “direct” mechanisms, where the impinging molecule is thought to essentially dissociate upon impact. In such a picture, no intermediate surface state is present, and the thermal properties of the surface will not drive the temperature dependent kinetic branching observed in “indirect” (precursor-mediated) mecha-

nisms. Recently, observed substrate temperature dependences of certain systems have been explained through either direct or indirect mechanisms, and a closer look at this debate may prove instructive, as the explanations for presumably opposing viewpoints may well be compatible.

A re-examination of oxygen adsorption on W(110) using high-energy molecular beams by Rettner et al.<sup>32</sup> proved interesting in light of the previously accepted precursor model for the system. While experimental findings supported earlier assertions<sup>8,9</sup> of precursor-mediated adsorption for energies below  $\sim 0.05$  eV, behavior consistent with a direct adsorption mechanism was observed in the high-energy regime. The initial sticking probability was found to rise markedly with increasing incident energy, indicating that trapping into a physically adsorbed molecular state is negligible. The observance of a decreasing trend in adsorption probability with increasing surface coverage (even for near zero coverages) further substantiates this implication by precluding a dominant *mobile* precursor state. Further, over a range of incident kinetic energies, incident angles, and substrate temperatures, adsorption probability measurements were determined to scale reasonably well with “normal energy” (i.e., the effective translational energy due to the normal component of an impinging molecule’s velocity,  $E_n = E_i \cos^2 \theta$ ). Although normal energy scaling merely suggests the presence of a normal translational energy dissociation barrier along the reaction coordinate (between the initial gas-phase and final dissociated states), such a trend is often used as rationale for an activated, direct process.

Similar behavior has been observed on Cu(110) by Hodgson et al.,<sup>15</sup> normal energy scaling, increasing initial sticking with increasing translational energy, and a relative insensitivity of initial sticking to surface temperature indicated a direct mechanism for high translational energies. The results from such studies suggest coexisting dissociation channels—namely a precursor-mediated channel present at low kinetic energies and a direct mechanism predominating at high energies.

In contrast to systems exhibiting evidence of simple, direct mechanisms, the  $O_2$ /Pt(111) system has featured temperature dependencies consistent with a regime in which an incoming molecule responds to thermal effects from the surface. Luntz et al.<sup>18</sup> observed a significant temperature dependence throughout the kinetic energy range studied—even at translational energies as high as 1.2 eV (Figure 2). The authors suggest a “quasi-direct” mechanism in which the incident species briefly accesses the molecular precursor potential en route to dissociation; the lifetime in this well may be sufficient for parallel and perpendicular momentum scrambling but not so long that the species completely “forgets” its incident state. This mechanism retains the direct mechanism characteristic of enhanced adsorption probability for increasing incident energy and may also explain the absence of normal energy scaling. Phonon interaction upon entrance or exit from the molecular resonance well was offered as possible explanations for the temperature dependence, but neither convincing evidence nor a quantitative model existed.



**FIGURE 4.** EEL spectra indicate different initial adsorption states for high and low translational energies.<sup>34</sup> High-energy oxygen adsorption features exclusive population of a peroxo-like molecular species ( $690\text{ cm}^{-1}$ ), while both peroxo-like and superoxo-like ( $870\text{ cm}^{-1}$ ) states are observed after exposure to a low kinetic energy oxygen beam. Atomic oxygen ( $490\text{ cm}^{-1}$ ) likely arises from dissociation of the molecular state over the time of the experiment.

A follow-up study by Rettner and Mullins<sup>33</sup> provided a novel explanation for the mechanism of high-energy adsorption of oxygen on Pt(111). The authors considered a purely indirect, precursor-mediated mechanism more likely at high incident energies; since high kinetic energy adsorption does not increase saturation coverage, it appears unlikely that the final dissociated state is accessed directly from the gas-phase molecular state. Specifically, this “direct molecular chemisorption” model suggested that dissociative chemisorption for this system occurs via direct access of an accommodated molecular precursor followed by thermally dictated kinetic branching between desorption and dissociation (Figure 3). Through a kinetic treatment much like that for low-energy, precursor-mediated adsorption, the direct molecular chemisorption interpretation accounts for the relatively strong temperature dependence in adsorption probabilities observed for the system.

Only recently, however, was direct verification of this high-energy molecular chemisorption mechanism realized.<sup>34</sup> Figure 4 displays EEL spectra of small beam doses of oxygen on a clean, Pt(111) surface at 77 K. Peaks at  $490$ ,  $690$ , and  $870\text{ cm}^{-1}$  correspond to atomic oxygen, peroxo-like molecular oxygen ( $\text{O}_2^{2-}$ ), and superoxo-like molecular oxygen ( $\text{O}_2^-$ ), respectively; the loss feature at  $2100\text{ cm}^{-1}$  signifies background CO adsorption. For the entire range of energies studied ( $0.055\text{--}1.30\text{ eV}$ ), molecular oxygen is indeed observed on the surface; the small atomic oxygen features result from dissociation from the molecular species over the time of the experiment. Simple direct dissociation (from the gas phase) appears negligible.

Interestingly, high incident energies ( $0.2\text{--}1.3\text{ eV}$ ) populate the peroxo-like state exclusively, while low-energy ( $0.055\text{ eV}$ ) adsorption exhibits filling of both molecular states. Given that the peroxo-like state is characterized by a higher degree of charge transfer than the superoxo-like state, the nature of the translational energy effect on the adsorption reaction appears to be tied closely to electron transfer facility. Perhaps hyperthermal incident molecules penetrate the surface “deeper” and are more receptive to initial electron donation than molecules approaching the surface slowly.

Observations of high-energy inverse dependencies of initial adsorption probabilities on surface temperature have prompted assignment of direct molecular chemisorption as an adsorption model describing oxygen adsorption on several surfaces. A similar high-energy, surface temperature dependence on Ag(110)<sup>5</sup> has been ascribed to direct access of a molecularly bound precursor state, an explanation substantiated by the observed absence of dissociated oxygen on the surface at low surface temperature. EELS measurements of surface states at 83 K following dosing with beam energies up to  $0.62\text{ eV}$  yielded only molecularly bound oxygen, indicating the plausibility of a low coverage intrinsic dissociation precursor. Likewise, the model has been implicated in describing oxygen adsorption on Ir(110);<sup>14</sup> although spectroscopic evidence of a molecularly chemisorbed species has not been realized, the stability of such a state at 90 K has been inferred from CPD (contact potential difference) measurements.<sup>35</sup> Finally, recent adsorption data on Ir(111)<sup>12</sup> have been attributed to direct access of the molecular well. EEL spectra yield no molecular oxygen state at 70 K (at the lowest oxygen coverages investigated) but identify two molecularly chemisorbed states at coverages of approximately 0.25 monolayers of atomic oxygen for both  $1.4\text{ eV}$  and ambient adsorption; lower temperatures are likely necessary to isolate the presumed low coverage precursor.

Although direct access of a one-dimensional potential energy well quantitatively accounts for the kinetic competition observed between dissociation and desorption, clear insufficiencies arise when considering dynamical aspects as well. In particular, the increase in dissociation probability with increasing translational energy implies the presence of an activation barrier prior to the molecular well. Further, if the molecular state serves as a necessary precursor (within the energy ranges studied) to the atomic state, it follows that the potential barrier to dissociation must be greater than that to molecular adsorption. This positive difference between dissociation and desorption barrier heights clearly contrasts the negative difference required to explain desorption enhancement with increasing surface temperature. A similar barrier height paradox has been delineated by Artsyukhovich et al.<sup>36</sup> in considering high- and low-temperature adsorption and desorption from Pt(111). A one-dimensional potential energy surface adsorption depiction appears useful for rationalizing temperature-dependent trends in experimental data, but multidimensional models are clearly needed to provide rigorous treatment.

While a direct molecular chemisorption precursor model readily accounts for a surface temperature dependence in the adsorption probability, such behavior has been accounted for under a purely direct explanation as well. Guo et al. observe this surface temperature trend for oxygen adsorption on the reconstructed Pt{100}-hex-R0.7° surface.<sup>37,38</sup> The authors rule out a precursor-mediated regime, citing normal energy scaling of initial adsorption probabilities and no observed dissociation (only desorption) from a molecularly adsorbed species. Rather, a previously described surface oscillation model<sup>39</sup> was invoked to explain the temperature dependence. Under this hard cube calculation, increased surface temperature is expected to enhance low adsorption probabilities (less than ~0.5) and suppress high probabilities (greater than ~0.5). Initial sticking coefficients on the low free energy, reconstructed Pt{100}-hex-R0.7° surface are very small (less than 0.006 for all beam energies and surface temperatures considered) and are thus in qualitative agreement with the enhancement predicted by the surface oscillator model. However, much of the observed experimental adsorption data appears consistent with precursor-mediated adsorption; such an explanation may hold for this system if the potential barrier for dissociation from a molecularly bound state is positive with respect to the vacuum zero. An informative addendum to this study could be realized in comparing the form of the dissociative adsorption profile to that of molecular adsorption (at sufficiently low substrate temperature); resulting self-similar curves would, at the very least, suggest that the initial adsorption stages of each are governed by a common process of molecular adsorption. Surface oscillations undoubtedly play a role in adsorption trends in this and other systems, but molecular intermediates may contribute as well.

Observations of temperature-enhanced adsorption for a facile adsorption system by Wheeler et al.<sup>13</sup> have prompted assignment of a different plausible mechanism. Initial chemisorption probabilities of O<sub>2</sub> on Ru(001) were found to increase slightly with increasing temperature in the high-energy, high adsorption probability regime. Clearly this effect is difficult to reconcile under models considering only accommodated molecular intermediates or surface oscillations. Further, normal energy scaling of initial sticking probabilities supports the notion that thermal branching from an accommodated molecular state is not likely the most important dissociation mechanism. Hence, a mechanism was proposed which suggests that the dominant dissociation mechanism is dictated by the ease of electron donation from the surface to the oxygen molecule; at increased substrate temperature, the increased population of electronic states above the Fermi level allows more rapid electron transfer and thus increased adsorption probability. This effect may contribute to adsorption on the Pt{100}-hex-R0.7° surface in a similar manner.

An explicit coupling of charge exchange to the nature of the dissociation barrier in the high incident energy regime may explain the experimental behavior observed

in the Ru(001) study as well as in the aforementioned studies on W(110)<sup>32</sup> and Cu(110).<sup>15</sup> Incident kinetic energy appears instrumental in the adsorption reaction coordinate, as dissociation probability increases with increasing energy in such systems exhibiting apparent direct regimes. In fact, high incident kinetic energies may correspond to close physical proximity and thus facile charge transfer and high reaction probability.

Recently, a thermally-assisted tunneling mechanism has gained popularity in high incident energy adsorption regimes on silver surfaces. Raukema et al.<sup>11</sup> report a surface temperature trend in dissociative adsorption similar to that observed on Ru(001) but reject an electronic transfer enhancement explanation because they detect no increase in *molecular* adsorption with increasing temperature for high translational energy beams. The authors suggest that increased substrate temperature decreases the energy difference between the dissociation barrier and the translational energy of the incident molecule, thus enhancing the tunneling probability to the final dissociated state. Since tunneling rates are very mass sensitive, the observed isotope effect between <sup>16</sup>O<sub>2</sub> and <sup>18</sup>O<sub>2</sub> corroborates a tunneling assertion.<sup>40,41</sup> Furthermore, calculations of a nonadiabatic thermal tunneling mechanism for oxygen on silver surfaces in general have been performed to demonstrate agreement with experimental kinetic observations and hence the feasibility of such an event.<sup>42</sup> Unlike systems exhibiting facile adsorption, dissociative adsorption probabilities on Ag(111) are low (<10<sup>-3</sup>), and a tunneling mechanism may predominate as a special case for such a system.

While differing mechanisms have been proposed for several systems under various conditions, clearly the final dissociatively chemisorbed state for all oxygen/transition-metal systems is a product of electron transfer to the incident oxygen molecule. In fact, electron-induced dissociation of a single oxygen molecule on Pt(111) was demonstrated recently using tunneling current from an STM tip.<sup>43</sup> A useful explanation of the electronic mechanism of adsorption was offered by Haochang et al.<sup>44</sup> in describing oxygen adsorption on a Ag(111) surface. In brief, the oxygen molecule undergoes successive electron harpooning events by the metal surface, and the resulting, unstable peroxide ion dissociates due to antibonding orbital occupancy as well as Coulombic repulsion between the negative charges within the species. Although it refers to a specific adsorption system, this depiction may prove useful in understanding various dissociation phenomena.

## Conclusion

Despite extensive research, the mechanistic details of oxygen chemisorption on transition metals remain difficult to characterize accurately. For adsorption in the low kinetic energy regime, substantial agreement appears to exist on a trapping-mediated mechanism involving a physically and/or chemically adsorbed species acting as a precursor to dissociative chemisorption. In fact the concept of electron donation in the formation of chemical

bonds between an adsorbate and surface supports the likelihood of molecularly chemisorbed intermediates whether or not appreciable physisorption effects exist.

Differing adsorption probability trends involving surface temperature have fueled recent debate over dissociative adsorption at high incident energies. An absolute distinction between direct and indirect mechanisms, however, may be somewhat unnecessary, as the underlying basis of molecular intermediate formation seems likely under all typical dissociation scenarios. Addition of charge from the transition metal to the incident molecule implies the formation of negative ion, intermediate species; the resulting perturbation in dissociative kinetics is governed not by the mere presence but by the lifetime and consequent degree of thermal accommodation of a potential precursor. Surfaces and conditions exhibiting facile electron transfer may not be conducive to accommodated intermediates and appear purely direct—or solely dependent on gas-phase conditions—while less reactive systems may feature kinetically important precursor states.

Certainly molecular intermediate lifetime is not the only important variable in a kinetic and dynamic treatment of dissociative adsorption. Additional variables such as surface oscillations and surface electronic state populations are surely present in all systems, and current models are somewhat simplistic in that they address only those which appear to manifest themselves most strongly in experimental observations. This treatment, while reasonable as certain effects predominate and others are negligible under particular conditions, arises from a lack of a comprehensive physical and chemical understanding, and a more complete knowledge of dissociation systems is necessary before meaningful construction of a unifying theory of dissociative adsorption can be realized.

## References

- (1) Bielanski, A.; Haber, J. *Oxygen in Catalysis*; Marcel Decker, Inc.: New York, 1991.
- (2) Weinberg, W. H. In *Kinetics of Interface Reactions*; Grunze, M., Kreuzer, H. J., Eds.; Springer: Berlin, Heidelberg, 1987; p 94.
- (3) Langmuir, I. *Chem. Rev.* **1929**, *6*, 451.
- (4) Taylor, J. B.; Langmuir, I. *Phys. Rev.* **1933**, *44*, 423.
- (5) Vattuone, L.; Rocca, M.; Boragno, C.; Valbusa, U. *J. Chem. Phys.* **1994**, *101*, 713.
- (6) Buatier de Mongeot, F.; Rocca, M.; Valbusa, U. *Surf. Sci.* **1996**, *363*, 68.
- (7) Hofmann, P.; Horn, K.; Bradshaw, A. M.; Jacobi, K. *Surf. Sci.* **1979**, *82*, L610.
- (8) Kohrt, C.; Gomer, R. *J. Chem. Phys.* **1969**, *52*, 3283.
- (9) Wang, C.; Gomer, R. *Surf. Sci.* **1979**, *84*, 329.
- (10) Brundle, C. R.; Broughton, J. Q. In *The Chemistry and Physics of Solid Surfaces and Heterogeneous Catalysis*; King, D. A., Woodruff, D. P., Eds.; North-Holland: Amsterdam, The Netherlands, 1985; p 131.
- (11) Raukema, A.; Butler, D. A.; Box, F. M. A.; Kleyn, A. W. *Surf. Sci.* **1996**, *357*, 151.
- (12) Davis, J. E.; Nolan, P. D.; Karseboom, S. K.; Mullins, C. B. *J. Chem. Phys.* **1997**, *107*, 943.
- (13) Wheeler, M. C.; Seets, D. C.; Mullins, C. B. *J. Chem. Phys.* **1996**, *105*, 1572.
- (14) Kelly, D.; Verhoef, R. W.; Weinberg, W. H. *J. Chem. Phys.* **1995**, *102*, 1.
- (15) Hodgson, A.; Lewin, A. K.; Nesbitt, A. *Surf. Sci.* **1993**, *293*, 211.
- (16) Gland, J. L. *Surf. Sci.* **1980**, *93*, 487.
- (17) Gland, J. L.; Korchak, V. N. *Surf. Sci.* **1978**, *75*, 733.
- (18) Luntz, A. C.; Williams, M. D.; Bethune, D. S. *J. Chem. Phys.* **1988**, *89*, 4381.
- (19) Luntz, A. C.; Grimblot, J.; Fowler, D. E. *Phys. Rev. B* **1989**, *39*, 12903.
- (20) King, D. A.; Wells, M. G. *Surf. Sci.* **1972**, *29*, 454.
- (21) King, D. A. *CRC Crit. Rev. Solid State Mat. Sci.* **1978**, *7*, 167.
- (22) Gland, J. L.; Sexton, B. A.; Fisher, G. B. *Surf. Sci.* **1980**, *95*, 587.
- (23) Grimblot, J.; Luntz, A. C.; Fowler, D. E. *J. Electron Spectrosc. Relat. Phenom.* **1990**, *52*, 161.
- (24) Avery, N. R. *Chem Phys. Lett.* **1983**, *96*, 371.
- (25) Collins, D. M.; Spicer, W. E. *Surf. Sci.* **1977**, *69*, 114.
- (26) Steininger, H.; Lehwald, S.; Ibach, H. *Surf. Sci.* **1982**, *183*, 1.
- (27) Lehwald, S.; Ibach, H.; Steininger, H. *Surf. Sci.* **1982**, *117*, 342.
- (28) Stohr, J.; Gland, J. L.; Eberhardt, W.; Outka, D.; Madix, R. J.; Sette, F.; Koestner, R. S.; Doebler, U. *Phys. Rev. Lett.* **1983**, *51*, 2414.
- (29) Outka, D.; Stohr, J.; Jark, W.; Stevens, P.; Soloman, P.; Madix, R. *J. Phys. Rev. B* **1987**, *35*, 4119.
- (30) Wurth, W.; Stohr, J.; Feulner, P.; Pan, X.; Bauchspiess, K. R.; Baba, Y.; Hudel, E.; Rocker, G.; Menzel, D. *Phys. Rev. Lett.* **1990**, *65*, 2426.
- (31) Puglia, C.; Nilsson, A.; Hernnas, B.; Karis, O.; Ben-nich, P.; Martensson, N. *Surf. Sci.* **1995**, *342*, 119.
- (32) Rettner, C. T.; DeLouise, L. A.; Auerbach, D. J. *J. Chem. Phys.* **1986**, *85*, 1131.
- (33) Rettner, C. T.; Mullins, C. B. *J. Chem. Phys.* **1991**, *94*, 1626.
- (34) Nolan, P. D.; Lutz, B. R.; Tanaka, P. L.; Davis, J. E.; Mullins, C. B. *Phys. Rev. Lett.*, in press.
- (35) Taylor, J. L.; Ibbotson, D. E.; Weinberg, W. H. *Surf. Sci.* **1979**, *79*, 349.
- (36) Artsyukhovich, A. N.; Ukraintsev, V. A.; Harrison, I. *Surf. Sci.* **1995**, *347*, 303.
- (37) Guo, X.-C.; Bradley, J. M.; Hopkinson, A.; King, D. A. *Surf. Sci.* **1994**, *310*, 163.
- (38) Guo, X.-C.; Bradley, J. M.; Hopkinson, A.; King, D. A. *Surf. Sci. Lett.* **1993**, *292*, L786.
- (39) Hand, M.; Harris, J. *J. Chem. Phys.* **1990**, *92*, 7610.
- (40) Reijnen, P. H. F.; Raukema, A.; van Slooten, U.; Kleyn, A. W. *J. Chem. Phys.* **1991**, *94*, 2368.
- (41) Reijnen, P. H. F.; Raukema, A.; van Slooten, U.; Kleyn, A. W. *Surf. Sci.* **1991**, *253*, 24.
- (42) Citri, O.; Baer, R.; Kosloff, R. *Surf. Sci.* **1996**, *351*, 24.
- (43) Stipe, B. C.; Rezaei, M. A.; Ho, W.; Gao, S.; Persson, M.; Lundqvist, B. I. *Phys. Rev. Lett.* **1997**, *78*, 4411.
- (44) Haochang, P.; Horn, T. C. M.; Kleyn, A. W. *Phys. Rev. Lett.* **1986**, *57*, 3035.

AR960278P