Eley−Rideal Surface Chemistry: Direct Reactivity of Gas Phase Atomic Hydrogen with Adsorbed Species

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Introduction

There have been a number of recent theoretical and experimental investigations of the reaction between gas-phase atomic hydrogen and various adsorbates on transition metal surfaces.[1−29] These studies have been carried out in an effort both to observe the occurrence of and to characterize direct, or Eley−Rideal, surface reactions.[30] Most surface reactions have historically been found to proceed via a Langmuir-Hinshelwood mechanism where two species, which have thermally equilibrated with the surface, react to form a product which eventually desorbs from the surface. In the Langmuir−Hinshelwood reaction mechanism (Figure 1A), the characteristics of the reaction are governed, therefore, by the temperature of the surface. In the Eley−Rideal mechanism (Figure 1B), on the other hand, a gas-phase reagent reacts directly with an adsorbed species (adspecies), the product of the reaction either desorbing or else remaining adsorbed on the surface depending on the particular chemical reaction. The defining characteristic of an Eley−Rideal reaction is that one of the reactants is not chemisorbed locally and, hence, not in equilibrium with the surface temperature. The gas-phase reagent may react directly in one step or may sample several surface sites before reacting, as in the so-called "hot" precursor model, which describes a dynamically trapped intermediate.[31] A "direct" reaction obeying either of

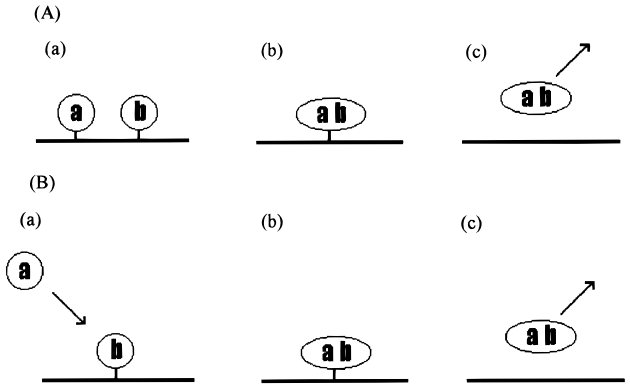

Figure 1. (A) Diagram of the Langmuir−Hinshelwood (LH) reaction a + b → ab. The distinguishing feature of a LH reaction is that both a and b are adsorbed on the surface (a) prior to reacting to form ab, which may remain on the surface (b) or desorb (c). (B) Diagram of the Eley−Rideal (ER) reaction (a + b → ab). The distinguishing feature of an ER reaction is that one species (here it is species a) does not chemisorb locally prior to reaction (a), and hence is not in equilibrium with the surface temperature. The resulting ab species may remain on the surface (b) or desorb (c).

W. Henry Weinberg obtained a B.S. degree in chemical engineering from the University of South Carolina, and a Ph.D. degree in chemical engineering from the University of California, Berkeley, in 1971. After a postdoctoral year at the University of Cambridge, he joined the faculty of the California Institute of Technology in 1972. He was promoted to Associate Professor with tenure in 1974, and to Professor of Chemical Engineering and Chemical Physics in 1977. He was the first Chevron Professor of Chemical Engineering from 1981 to 1986. He was a Visiting Professor of Chemistry at Harvard University in 1980, a Visiting Professor of Chemistry at the University of Munich in 1982, a Visiting Professor of Chemistry at the University of Pittsburgh in 1987–88, and a Visiting Professor of Materials at the University of Oxford in 1991. He assumed his present position as Professor of Chemical Engineering, Materials Engineering, and Chemistry at the University of California, Santa Barbara (UCSB), in 1989. Weinberg was a Principal Investigator in the US-USSR Exchange Program in Chemical Catalysis between 1974 and 1980. He has served on numerous review panels for industrial and academic organizations, and for various governmental agencies (particularly, the Department of Energy and the National Science Foundation). Currently, he is on the Advisory Editorial Board of three journals: *Applied Surface Science*, *Surface Science*, and *Langmuir*. In addition, he is the General Editor of the prestigious review journal *Surface Science Reports*. Weinberg has received numerous awards and honors, including the following: Wayne B. Nottingham Prize of the American Physical Society, Victor K. Lamer Award of the American Chemical Society, Alfred P. Sloan Foundation Fellowship, Camille and Henry Dreyfus Foundation Teacher-Scholar Award, Creativity Award of the National Science Foundation, Allan P. Colburn Award of the American Institute of Chemical Engineers, Alexander von Humboldt Foundation Senior U.S. Scientist Award, Giuseppe Parravano Award of the Michigan Catalysis Society, Colloid or Surface Chemistry (Kendall) Award of the American Chemical Society, and, most recently, the 1995 Arthur W. Adamson Award for the Advancement of Surface Chemistry of the American Chemical Society and the 1995 Distinguished Teaching Award of the College of Engineering at UCSB. He is a Fellow of the American Association for the Advancement of Science, the American Physical Society, and the American Vacuum Society, and a member of the National Academy of Engineering. Weinberg has presented over 350 invited lectures or seminars at various academic, industrial, and governmental organizations around the world during the past 25 years including the 1994 Distinguished Foreign Lectureship of the College of Engineering of the Hong Kong University of Science and Technology, the 1995 American Chemical Society Distinguished Lectureship of the Chemical Engineering Department of the University of Wisconsin at Madison, and the 1996 Astor Distinguished Lectureship of the University of Oxford. During that same period of time, he has presented over 200 invited or contributed talks at various national and international conferences. He has authored or coauthored over 450 scientific papers that have appeared in refereed journals, as well as the book *Low-Energy Electron Diffraction: Experiment, Theory, and Surface Structural Determination* (Springer-Verlag: Heidelberg, 1986; 608 pp) (with M. A. van Hove and C.-M. Chan). All of these publications are related to various aspects of surface chemistry and physics, or heterogeneous catalysis.

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these two detailed mechanisms would be expected to occur only when there is a rather small activation barrier to the reaction, a situation which might be expected for a gas-phase radical reactant which undergoes an exothermic reaction, and this reasoning has motivated the recent work with atomic hydrogen. If the reaction product does not accommodate to the surface temperature, it desorbs with high translational and internal energy, dependent on the exothermicity of the elementary reaction.

We will review here four specific examples, taken from our laboratory, which illustrate most of the important concepts of Eley−Rideal surface chemistry. The discussion will be limited to the chemistry of the Ru(001) surface which was studied under ultrahigh vacuum (UHV) using standard surface characterization methods and atomic hydrogen produced with either a hot filament source or a microwave discharge. These four specific examples are the abstraction of chemisorbed hydrogen, forming dihydrogen, which desorbs at least 150 K below the threshold temperature for recombinative desorption of two hydrogen adatoms; the hydrogenation of chemisorbed CO, forming η^1- and η^2-formyls and η^2-formaldehyde; the selective hydrogenation of chemisorbed formate, forming a formyl and a hydroxyl; and the hydrogenation of oxygen adatoms to form water.

Atomic Hydrogen Adsorption on and Abstraction from Ru(001)

Molecular hydrogen adsorbs dissociatively on the hexagonally close-packed Ru(001) surface.[32] Under typical ultrahigh-vacuum conditions, no molecular hydrogen is stabilized on the surface at temperatures as low as 20 K and at a pressure of hydrogen as high as 10^{-6} Torr.[33] The saturation coverage of the dissociatively adsorbed hydrogen is one adsorbed atom (adatom) per unit cell ($\theta_H = 1$), and all adatoms reside in 3-fold hollow sites.[32,34] At $\theta_H = 1$ the heat of dissociative chemisorption of the hydrogen is exothermic by 23 kcal/mol, varying from 29.5 kcal/mol in the low-coverage limit to this value at $\theta_H = 1$, due to the presence of repulsive near-neighbor interactions of 0.4 kcal/mol and repulsive next-near-neighbor interactions of 0.17 kcal/mol.[22]

Since there are two different 3-fold hollow sites per primitive unit cell, one of which is a hexagonally close-packed (hcp) site and the other of which is a face-centered cubic (fcc) site, and since there is very little difference in the binding energy of hydrogen to these two types of sites, one is faced with the question of why the dissociative chemisorption of H_2 saturates at $\theta_H = 1$. Since the dissociative chemisorption of the H_2 is still exothermic by 1 eV/molecule at this coverage, the answer must be that there is a kinetic barrier, above the gas-phase energy zero, which separates the short-lived physically adsorbed molecular precursor state from the chemisorbed state. If this is true, then it should be possible to achieve considerably higher coverages of hydrogen adatom overlayers if one adsorbs atomic rather than molecular hydrogen. Indeed, one might intuitively expect that the saturation coverage of hydrogen in this case would be $\theta_H = 2$ since there are two 3-fold sites per primitive unit cell, and interadsorbate repulsive interactions would certainly not be expected to cause the Ru−H binding energy to decrease below 52.3 kcal/mol at $\theta_H = 2$. The latter would render the adsorption reaction endothermic with respect to molecular hydrogen in the gas phase, but the Ru−H bond strength at $\theta_H = 1$ is considerably larger than this, namely, 63.8 kcal/mol.

As it turned out, this intuitive reasoning was only half right. Temperature-programmed desorption measurements revealed that the saturation coverage of hydrogen following exposure of the surface to atomic hydrogen is $\theta_H = 1.42$, which is obviously considerably less than the anticipated value of $\theta_H = 2$.[22] On the other hand, as expected, the heat of adsorption of the hydrogen only decreased from 23 to 21.5 kcal/mol in going from $\theta_H = 1$ to $\theta_H = 1.42$, which could be explained quantitatively in a mean field picture with an additional interadsorbate repulsive interaction energy of 3 kcal/mol for $\theta_H > 1$.[22] The experimentally measured temperature-programmed desorption spectra of H_2 for four coverages between $\theta_H = 1$ and $\theta_H = 1.42$, with an adsorption temperature of 100 K and a heating rate of 5 K s^{-1}, are shown in Figure 2A. Simulated temperature-programmed desorption spectra of the same overlayer, with the lattice gas model supplemented by mean field interactions which was alluded to above, are shown in Figure 2B. The simulations agree quantitatively with the experimentally measured data. It is also important to note that high-resolution electron energy spectroscopy (HREELS) showed that all hydrogen adatoms reside in 3-fold hollow sites at all coverages, as judged by frustrated translational modes observed at 1135 and 815 cm^{-1} for chemisorbed hydrogen which downshift by a factor of approximately 0.7 for chemisorbed deuterium (for which the saturation coverage was also found to be $\theta_D = 1.42$).

Although we have a detailed understanding of the binding sites and the energetics of hydrogen adsorption on Ru(001) from the low-coverage limit up to saturation coverage of $\theta_H = 1.42$, the key question we must address concerns what limits the saturation coverage to $\theta_H = 1.42$ (as opposed to $\theta_H = 2$, for example). The answer to this question is that the saturation coverage of hydrogen is dictated by a steady-state balance of adsorption of atomic hydrogen and a direct (Eley−Rideal) abstraction reaction, i.e.,

$$H(g) + H(a) \rightarrow H_2(g) \qquad (1)$$

which occurs at a surface temperature that is at least 150 K below the threshold temperature for the recom-

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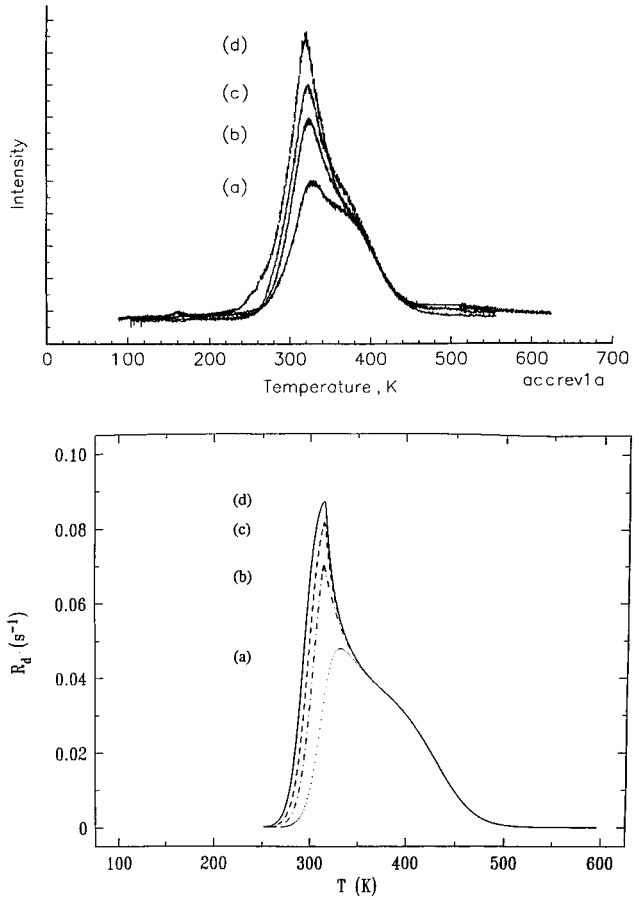

Figure 2. (A, top) Experimental hydrogen thermal desorption spectra at coverages of (a) 1.0, (b) 1.21, (c) 1.32, and (d) 1.42 hydrogen adatoms per primitive Ru(001) unit cell created using gas-phase atomic hydrogen. The adsorption temperature is 100 K, and the heating rate is 5 K s^{-1}. (B, bottom) Simulated hydrogen thermal desorption spectra at surface coverages of (a) 1.0, (b) 1.21, (c) 1.32, and (d) 1.42 hydrogen adatoms per primitive Ru(001) unit cell. For coverages greater than 1, a mean field approximation is used to describe the repulsions between the adatoms. For surface coverages less than 1, the quasichemical approximation is used to describe the near-neighbor repulsions and a mean field approximation is used to describe the next-near-neighbor repulsions. The heating rate is 5 K s^{-1}.

binative thermal desorption of hydrogen, namely, 100 K versus 250 K; cf. Figure 2A. In order to validate this assertion and to quantify the governing kinetics, an overlayer of deuterium adatoms with an initial coverage of $\theta_D = 1$ was exposed to various fluences of atomic hydrogen, and the surface coverages of hydrogen and deuterium were determined by temperature-programmed desorption (of H_2, HD, and D_2) after a number of different exposures of atomic hydrogen.[20] These data are shown in Figure 3 where the fractional surface coverages of deuterium (◆) and hydrogen (●) are plotted as a function of atomic hydrogen exposure (in units of 10^{14} hydrogen atoms cm^{-2}). The statistical uncertainty associated with each datum point is shown explicitly in Figure 3, and we also verified that the results for abstraction of adsorbed deuterium by gas-phase atomic hydrogen and abstraction of adsorbed hydrogen by gas-phase atomic deuterium are identical within these experimental uncertainties.

In order to attempt to understand the experimental data of Figure 3 (ignoring the solid curves for the moment), let us adopt the point of view that there is indeed a direct abstraction reaction channel, as indicated in eq 1, and see where this leads us. If the abstraction reaction is direct *and* if the adsorption of atomic hydrogen obeys first-order Langmuirian kinetics (with a rate which is proportional to the fraction of vacant sites), then we may write

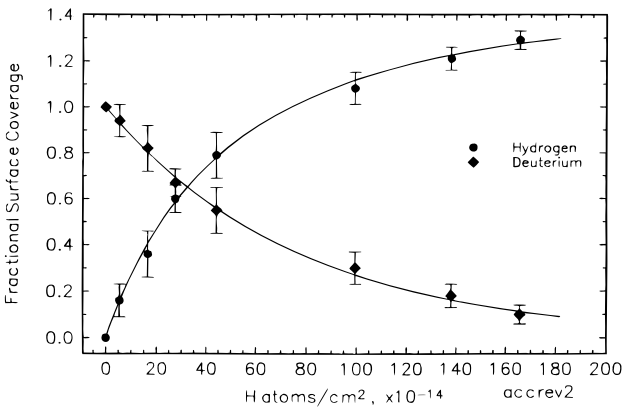

Figure 3. Hydrogen and deuterium surface coverages on Ru(001) as a function of gas-phase atomic hydrogen exposure. The initial deuterium surface coverage is 1 adatom per primitive unit cell, and the surface temperature is 100 K. The solid lines are calculated on the basis of the model described in the text.

$$d\theta_D/dt = -P_r F_H \theta_D \quad (2)$$

and

$$d\theta_H/dt = P_a F_H(\theta_s - \theta_H - \theta_D) - P_r F_H \theta_H \quad (3)$$

in order to describe the experimental data of Figure 3, the abstraction of D(a) by H(g). Here, P_r is the coverage-independent probability of the assumed first-order abstraction reaction, P_a is the coverage-independent probability of the assumed Langmuirian adsorption mechanism, F_H is the impingement flux of the gas-phase atomic hydrogen, and θ_s represents what the saturation coverage of the atomic hydrogen would be in the absence of any direct abstraction. The data of Figure 3 allow an immediate assessment of the *ratio* of the initial rate of deuterium removal from the surface, i.e., $d\theta_D/dt)|_{\theta_H=0,\theta_D=1}$, to the initial rate of hydrogen adsorption on the surface, i.e., $d\theta_H/dt)|_{\theta_H=0,\theta_D=1}$. The magnitude of this measured ratio is found to be 0.4 at $\theta_H = 0$ and $\theta_D = 1$. With these initial conditions the ratio of eq 2 to eq 3 is simply

$$P_r/P_a(\theta_s - 1) = 0.4 \quad (4)$$

which may be considered to be one equation with two unknowns, namely, P_r/P_a and θ_s; i.e., we suppress completely our preconceived conviction that θ_s should be 2. A second equation is obtained from the long-time, steady-state result, namely, $d\theta_H/dt = 0$. In this case with $\theta_H = 1.42$ and $\theta_D = 0$, eq 3 becomes

$$1.42P_r = (\theta_s - 1.42)P_a \quad (5)$$

Solving eqs 4 and 5 simultaneously yields the following:

$$\theta_s = 1.97 \cong 2 \quad (6)$$

and

$$P_r/P_a = 0.4 \quad (7)$$

The result of eq 6 for θ_s is very pleasing indeed and verifies our intuition that the saturation coverage of atomic hydrogen on Ru(001) would be two adatoms per primitive unit cell in the absence of an abstraction reaction. Equation 7 quantifies the ratio of the coverage-independent factors of the probabilities of first-order reaction and adsorption.

Our best estimate of our atomic flux suggests that the probability of adsorption of atomic hydrogen in the low-coverage limit is essentially unity. This implies that the coverage-dependent probabilities of adsorption and reaction are given by

$$P_a(\theta) = 0.5\,(2 - \theta) \tag{8}$$

and

$$P_r(\theta) = 0.2\theta \tag{9}$$

respectively. The form of eq 8 emphasizes the fact that the initial probability of adsorption of the atomic hydrogen is unity, with half the hydrogen initially occupying 3-fold hcp sites and the other half initially occupying 3-fold fcc sites. If one substitutes eqs 8 and 9 into eqs 2 and 3, together with the experimentally employed atomic impingement flux of 6×10^{12} cm^{-2} s^{-1}, the solution of eqs 2 and 3 leads to the solid curves shown in Figure 3. Obviously, there is essentially perfect agreement between the measured data and the calculated curves, which validates our original assumption that the abstraction reaction is a direct first-order reaction and the adsorption kinetics are of a first-order (in vacant surface sites) Langmuirian form.

The form of eq 8 immediately implies that the coverage-independent cross section for atomic hydrogen adsorption is simply half the area of a primitive surface unit cell, namely,

$$\sigma_a = 3.2 \times 10^{-16}\ \text{cm}^2 \tag{10}$$

and

$$\sigma_a(\theta) = (2 - \theta)\sigma_a \tag{11}$$

Equation 7 then implies that the coverage-independent cross section for the direct Eley−Rideal reaction is given by

$$\sigma_r = 1.3 \times 10^{-16}\ \text{cm}^2 \tag{12}$$

and

$$\sigma_r(\theta) = \theta\sigma_r \tag{13}$$

We should emphasize that these values of the probabilities and cross sections for adsorption and reaction are identical for hydrogen and deuterium, and we should also mention that the experimental results of Figure 3 are independent of surface temperature, at least for surface temperatures between 100 and 220 K.

In order to verify that we have a complete understanding of the interactions between gas-phase atomic hydrogen and the Ru(001) surface, data like those of Figure 3 were measured with an initial deuterium coverage of $\theta_D = 1.42$, rather than $\theta_D = 1$. These results are presented in Figure 4. The solid curves,

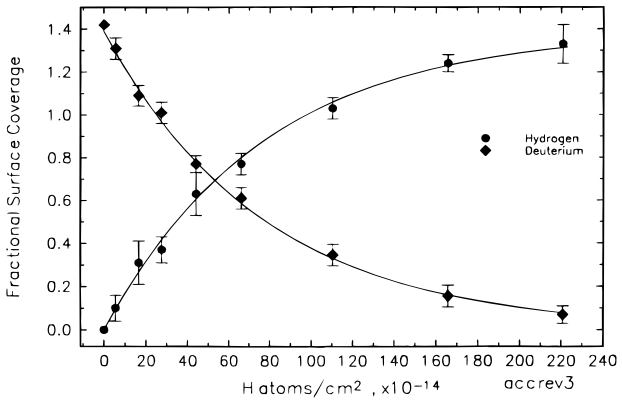

Figure 4. Hydrogen and deuterium surface coverages on Ru(001) as a function of gas-phase atomic hydrogen exposure. The initial coverage of deuterium is 1.42 adatoms per primitive unit cell and the surface temperature is 100 K. The solid lines are calculated on the basis of the model described in the text.

which describe the measured data quantitatively, employ the same probabilities of adsorption and reaction [cf. eqs 8 and 9] which were deduced in connection with the data of Figure 3. This result supplies independent confirmation that our quantitative picture of this surface chemistry is correct. Notice that the curves in Figure 4 have a mirror plane of symmetry through $\theta = 0.71$ since the rate of the abstraction reaction is rate limiting at all coverages for this initial coverage.

The most important lesson to be learned from the discussion to this point is that gas-phase atomic hydrogen is an extremely reactive reagent for the purpose of effecting direct surface chemistry. The probability of the hydrogen abstraction reaction by hydrogen is very high indeed: it would be 0.4 *per collision* at the hypothetical saturation coverage on the surface of $\theta_H = 2$. At a fractional coverage of $\theta_H = 1.42$, the exothermicity of the adsorption reaction is 63 kcal/mol, whereas the exothermicity of the abstraction reaction is 41.5 kcal/mol. The fact that the rate of the abstraction reaction is equal to the barrierless rate of adsorption at this coverage suggests that the barrier for the abstraction reaction is at most on the order of k_BT of the (thermal) hydrogen atoms. This, in turn, suggests that the atomic hydrogen might very well be reactive in a variety of *synthesis* reactions on single-crystalline surfaces at low surface temperatures in UHV, potentially opening up the possibility of isolating, and characterizing spectroscopically, intermediates not heretofore observed under these conditions. These exciting possibilities are the topic of the remainder of this Account.

Fischer−Tropsch Chemistry on Ru(001) in UHV at 100 K

Fischer−Tropsch synthesis, the reaction of carbon monoxide and hydrogen at high temperatures and pressures over a suitable catalyst, is a well-established technological process.[35−51] Two different general mech-

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anisms are thought to occur, depending on the operating conditions and the catalyst, namely, CO dissociation followed by hydrogenation, and carbonyl insertion into the metal−hydrogen bond. The products of the reaction are hydrocarbons and oxygenated hydrocarbons. The details of neither of these general mechanisms are understood, however, due to the reaction conditions which are required for them to occur. For example, the initial step of both general mechanisms—CO dissociation and carbonyl insertion to form (presumably) a formyl—are endothermic reactions compared to chemisorbed CO and hydrogen, and this means that all intermediates in the reaction will have short surface lifetimes (i.e., be present in low concentrations). This makes spectroscopic identification and characterization of the surface intermediates all but impossible.

The hydrogenation of CO on single-crystalline surfaces of Fe, Ni, and Ru has, in fact, been studied at "high" pressures, on the order of 10−100 Torr.[52−56] The major reaction product under these conditions was found to be methane, and *ex situ* characterization of the catalytic surfaces was effected by Auger electron spectroscopy and X-ray photoelectron spectroscopy. This *ex situ* characterization, however, gave no insight into the details of the reaction mechanism. Much work under UHV conditions involving the coadsorption of CO and hydrogen has also been carried out on various single-crystalline surfaces of several group VIII transition metals.[57−65] In general CO−H repulsive interactions are observed, occasionally resulting in phase separation, especially on close-packed surfaces. In no case has a chemical reaction been observed for coadsorbed CO and hydrogen under these UHV conditions. The totality of this research has provided no insight whatsoever into Fischer−Tropsch chemistry.

In view of the very high reactivity of gas-phase atomic hydrogen, we were encouraged to attempt to hydrogenate chemisorbed CO on Ru(001) at a surface

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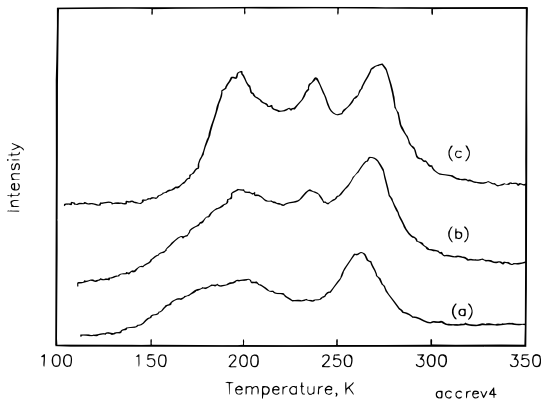


Figure 5. Temperature-programmed desorption spectra showing the evolution of D_2 following approximate atomic deuterium exposures of (a) 3, (b) 12, and (c) 27 ML on a saturated overlayer of CO on the Ru(001) surface at 110−130 K. The heating rate is 5 K s^{-1}.

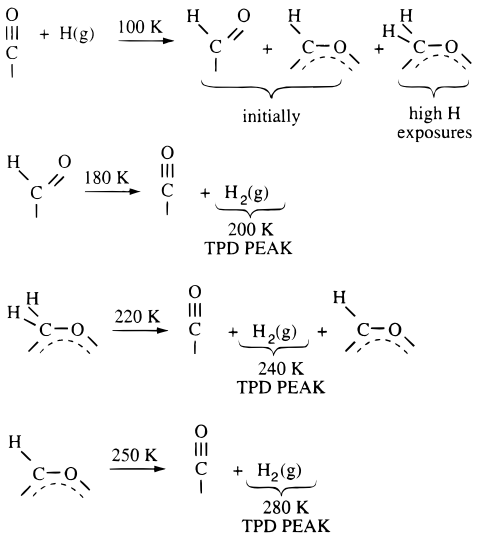
temperature of 100 K by making use of direct Eley−Rideal chemistry.[13,14,23] Although the energetics of removing a chemisorbed formyl from Ru(001) into the gas phase are not known with great certainty, our crude estimates suggested that the reaction

$$CO(a) + H(g) \rightarrow HCO(a) \qquad (14)$$

is exothermic by about 0.5 eV. If correct, this would suggest that there may be only a small barrier to this radical−molecule reaction. Figure 5 shows temperature-programmed desorption spectra of D_2 after exposure of a Ru(001) surface which is saturated with CO ($\theta_{CO} \cong 0.65$) to various fluences of atomic hydrogen, ∼3 ML in spectrum a, ∼12 ML in spectrum b, and ∼27 ML in spectrum c. Here 1 ML corresponds to a fluence of one effective monolayer, i.e., 1.56×10^{15} cm^{-2}. The effective coverages of hydrogen which desorb in these three spectra are $\theta_H \cong 0.5$, $\theta_H \cong 0.75$, and $\theta_H \cong 1.1$; i.e., a very considerable amount of hydrogen has been stabilized on this surface, which is completely poisoned with respect to the dissociative chemisorption of H_2. The key question, of course, concerns whether the gas-phase atomic hydrogen has reacted with the chemisorbed CO to produce stable surface intermediates or whether the hydrogen has simply coadsorbed with the CO on the Ru(001) surface. Although this issue can only be resolved unambiguously by spectroscopy, the fact that the middle (240 K) peak fills in last in the temperature-programmed desorption spectra of Figure 5 suggests the "reaction scenario".

High-resolution EELS spectra were measured after exposing chemisorbed CO on Ru(001) to various fluences of gas-phase atomic hydrogen and deuterium at 100 K; HREELS spectra were also measured after momentary annealing of the overlayers to various temperatures (to clarify the stability of the surface intermediates which are formed). The surface chemistry which we observed, as judged by HREELS, is summarized in Scheme 1. At low exposures of atomic hydrogen, a mixture of η^1(C)- and η^2(C,O)-formyls are formed, and the concentration of η^2(C,O)-HCO saturates prior to that of the η^1(C)-HCO. At higher exposures of atomic hydrogen, side-on bonded formaldehyde, η^2(C,O)-H_2CO, is formed. The η^1(C)-HCO is the least stable surface species, and it largely decomposes to CO and hydrogen (which desorbs as the

Scheme 1



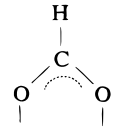
peak near 200 K in the temperature-programmed desorption spectra of Figure 5) and partly converts to η^2(C,O)-HCO. The η^2(C,O)-H_2CO is of intermediate stability between the two types of formyls. Upon heating, it largely decomposes to CO and hydrogen (which desorbs as the 240 K peak in Figure 5) and partly converts to η^2(C,O)-HCO. The η^2(C,O)-HCO is the most stable reaction product which decomposes also to CO and hydrogen (which desorbs as the 280 K peak in Figure 5). The positions of the three peaks in Figure 5 give a rather reasonable estimation of the activation energies of decomposition of the three surface species and, hence, quantify their thermal stability. In the case of η^1(C)-HCO, η^2(C,O)-H_2CO, and η^2(C,O)-HCO, these activation energies are approximately 11.5, 14, and 16.5 kcal/mol. For an initial CO coverage of 0.15 (rather than the saturation coverage of 0.65), the decomposition temperatures are each lowered by about 30 K, reflecting a decrease in each activation energy of about 1.5 kcal/mol; i.e., there is some "self-retardation" of the decomposition reactions by virtue of their high surface concentration.

These results are quite important since they demonstrate that it is possible to isolate, identify, and characterize the thermal stability of surface intermediates which are relevant to Fischer−Tropsch chemistry in UHV at a temperature of 100 K.

Reaction of Atomic Hydrogen with Chemisorbed Formate on Ru(001)

The decomposition of formic acid on transition metal surfaces is a very useful model system for studying the kinetics and mechanism of a branching reaction. In other words, the formic acid can undergo either dehydrogenation to CO_2 and H_2 or dehydration to CO and H_2O.[66−76] On the Ru(001) surface, formic acid

Chart 1



chemisorbs dissociatively at a surface temperature as low as 80 K by cleavage of the O−H bond to yield a formate and a hydrogen adatom, via a short-lived molecularly adsorbed formic acid molecule, i.e.,

$$HCOOH(g) \rightarrow HCOOH(a) \rightarrow HCOO(a) + H(a) \quad (15)$$

On Ru(001) the chemisorbed formate has been shown by HREELS to be a symmetrical bidentate bridging species, as shown in Chart 1.[74,76] The saturation fractional coverage of chemisorbed formate is approximately 0.33 following adsorption at 80 K with an equal surface coverage of hydrogen adatoms, and it is approximately 0.5 following adsorption at 300 K, a temperature at which all hydrogen has recombinatively desorbed; i.e., only formate is present on the surface in this case.[74]

Sun and Weinberg[76] observed that the formate decomposes by both dehydrogenation and dehydration, and the yields of CO and CO_2 have a ratio of 1:1 at all formate coverages on the Ru(001) surface. Furthermore, they made the very important observation that CO_2 and H_2O desorbed at the same temperature, which varied between approximately 310 and 400 K, depending on the initial formate coverage. The importance of this observation is that it provided putative evidence for a seemingly exotic reaction mechanism. Let us understand what is meant by this. If the formates *independently* undergo dehydrogenation and dehydration, then one expects C−H bond cleavage leading to CO_2 and recombinative desorption of H_2 for the dehydrogenation channel, and C−O bond cleavage leading initially to adsorbed formyl and an oxygen adatom for the dehydration channel. The formyl decomposes to CO and hydrogen, and the hydrogen is oxidized by the oxygen adatoms to form water. The only trouble with this scenario is that the Langmuir−Hinshelwood (surface) reaction between hydrogen and oxygen adatoms (the rate-limiting step in the water synthesis reaction) *does not occur* on the Ru(001) surface under these conditions.[77,78] The issue of water synthesis is discussed more fully later. In view of the fact that reaction-limited desorption of water and CO_2 was observed at the same temperature, the branching ratio for CO and CO_2 was 1:1, and the Langmuir−Hinshelwood production of H_2O from adsorbed oxygen and hydrogen does not occur, Sun and Weinberg proposed the following "coupled channels mechanism" for formate decomposition on Ru(001):[76]

$$HCOO(a) \rightarrow CO_2(g) + H^*$$

$$H^* + HCOO(a) \rightarrow HCO(a) + OH(a) \quad (16)$$

In this mechanism the "hot" hydrogen atom, H*, is dynamically trapped at the surface but neither accommodated to the surface temperature nor chemi-

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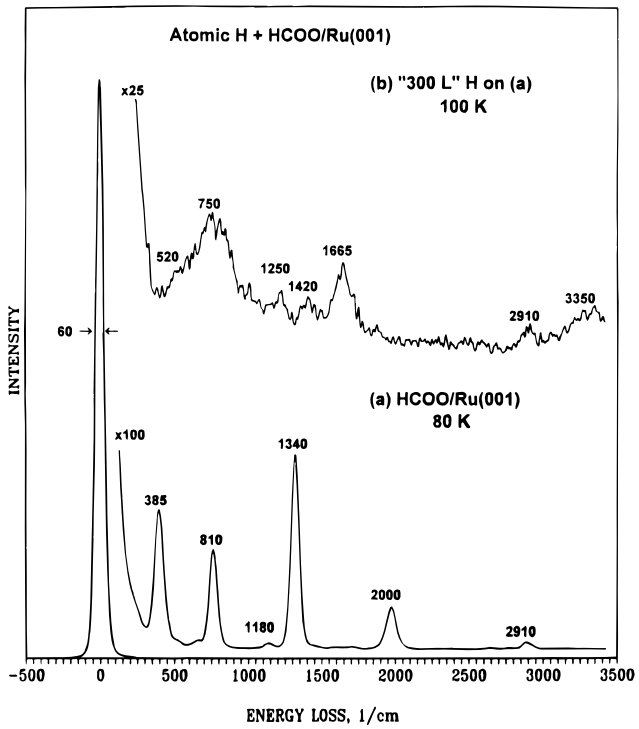

Figure 6. High-resolution electron energy loss spectra recorded at 80 K: (a) after exposure of a clean Ru(001) surface to 6 L of formic acid followed by annealing to 305 K; (b) after exposure of the surface of (a) to ~15 ML of atomic hydrogen at 100 K.

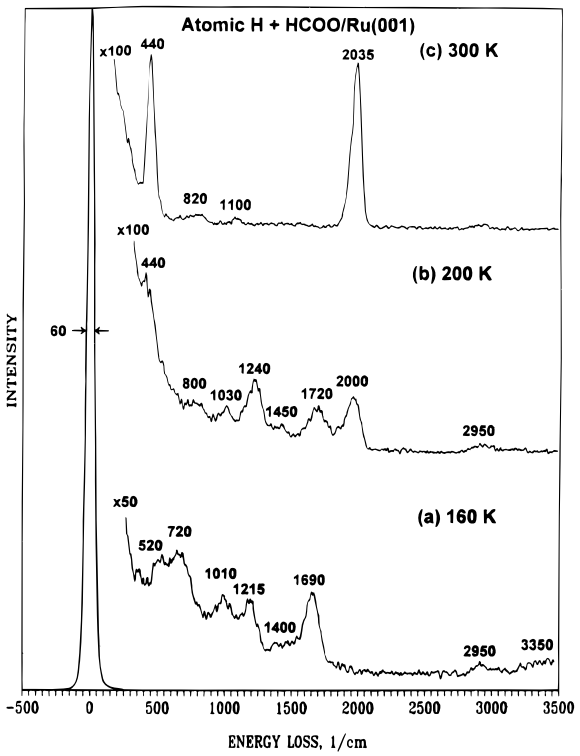

Figure 7. High-resolution electron energy loss spectra recorded after annealing the surface of Figure 5b to the indicated temperatures: (a) 160 K, (b) 200 K, and (c) 300 K.

sorbed locally. The proposal then is that this hot hydrogen can insert into the C−O bond of a neighboring formate, and there are always neighboring formates due to strongly attractive formate−formate interactions,[79] to form a formyl and a hydroxyl. These intermediates lead to the production of CO and water since the Langmuir−Hinshelwood reaction between hydroxyls and hydrogen adatoms does occur under these conditions.[27]

How does all of this relate to the topic of this Account? The connection is through the *postulated* hot hydrogen atom in the mechanism of eq 16. If the mechanism of eq 16 is correct, one would predict that the reaction of gas-phase atomic hydrogen with formate at low surface temperatures would form hydroxyls and formyls which would be further hydrogenated to water and formaldehyde, totally and partially, respectively, by the impinging atomic hydrogen. One also must be mindful, however, of the possibility of competing abstraction of hydrogen from the formate to produce CO_2 and H_2, both of which would desorb at 100 K, for example.

The HREELS of chemisorbed formate on Ru(001) at 80 K with a fractional coverage of 0.33 is shown in Figure 6a, and the expected modes are resolved: the frustrated translation of the formate perpendicular to the surface at 385 cm^{-1}, the OCO symmetric deformation ("scissoring") mode at 810 cm^{-1}, a C−H deformation mode at 1180 cm^{-1}, the symmetric OCO stretching mode at 1340 cm^{-1}, and the C−H stretching mode at 2910 cm^{-1}. There is a small (<0.01 ML) amount of CO also present as judged by the intensity of the mode near 2000 cm^{-1}. Figure 6b shows the HREEL spectrum of this overlayer after an exposure to 15 ML of atomic hydrogen at a surface temperature of 100 K. The observed loss peaks show that the atomic hydrogen has reacted with *all* of the chemisorbed formate, and the reaction products which remain on the surface are η^1(C)- and η^2(C,O)-formyls, η^2(C,O)-formaldehyde, and water. This is just what would be predicted from the addition of additional atomic hydrogen to the products of the second reaction of eq 16 and, thus, provides very strong support indeed to the proposed coupled channels mechanism of formate decomposition on Ru(001).

The HREEL spectra obtained after annealing the surface of Figure 6b to various temperatures are shown in Figure 7. Annealing to 160 K results in the desorption of some of the adsorbed water, and annealing to 200 K results in the desorption of all water and the decomposition of much of the η^1(C)-HCO. Annealing to 300 K results in the decomposition of all η^1(C)- and η^2(C,O)-formyls and η^2(C,O)-formaldehyde, with only CO and hydrogen remaining on the surface. Indeed, the fractional surface coverage of CO in Figure 7c is $\theta_{CO} \cong 0.33$, which demonstrates there is no measurable contribution from the reaction

$$H(g) + HCOO(a) \rightarrow H_2(g) + CO_2(g) \qquad (17)$$

during exposure of the formate to atomic hydrogen. This is also in complete agreement with the mechanism of eq 16 and the observed 1:1 branching ratio of CO_2 to CO in the formate decomposition on Ru(001).

This is yet another example of the ability of gas-phase atomic hydrogen to effect direct surface reactivity, and in this case to do so selectively when more than one reaction channel is potentially available.

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Reaction of Gas-Phase Atomic Hydrogen with Dissociatively Chemisorbed Oxygen on Ru(001)

As noted in passing above, the Langmuir−Hinshelwood reaction between coadsorbed hydrogen and oxygen adatoms does not occur on the Ru(001) surface under UHV conditions. The reason for this is simple. The activation energy for recombinative desorption of molecular hydrogen is approximately 6.5 kcal/mol less than that for the reaction[80]

$$\mathrm{H(a) + O(a) \rightarrow OH(a)} \qquad (18)$$

The respective barriers are approximately 16 and 22.5 kcal/mol.[27] However, the reaction

$$\mathrm{H(g) + O(a) \rightarrow OH(a)} \qquad (19)$$

on Ru(001) is estimated to be exothermic by approximately 55−65 kcal/mol (depending on the precise value of the Ru−OH bond energy) and would be expected to have only a small barrier. This encouraged us to attempt to hydrogenate chemisorbed oxygen with a beam of atomic hydrogen.[27] As detailed next, we were successful in this enterprise and verified that the Langmuir−Hinshelwood reaction

$$\mathrm{OH(a) + H(a) \rightarrow H_2O(a)} \qquad (20)$$

occurs on Ru(001) under UHV conditions with an activation energy of approximately 9 kcal/mol. Most of the work was carried out with atomic deuterium rather than hydrogen (for technical reasons), but we verified that both deuterium and hydrogen produced identical results within experimental uncertainties.[19] The flux of the atomic deuterium beam was maintained at the constant value of 1.2×10^{13} cm^{-2} s^{-1}, and the initial surface was Ru(001) with an ordered p(1 × 2) oxygen adatom overlayer corresponding to a fractional coverage of $\theta_O = 0.5$. The area of this primitive unit cell is approximately 12.8 Å^2.

In the earlier discussion of hydrogen abstraction by hydrogen, our analysis was couched in the language of probabilities. Here, we talk in terms of reaction cross sections, σ, to illustrate how either (inherently equivalent) approach may be taken. The elementary reactions of concern to us are the following:

$$\mathrm{O(a) + D(g) \xrightarrow{\sigma_{OD}} OD(a)}$$

$$\mathrm{OD(a) + D(g) \xrightarrow{\sigma_{D_2O}} D_2O(a)} \qquad (21)$$

$$\mathrm{OD(a) + D(a) \xrightarrow{k_{LH}} D_2O(a)}$$

where k_{LH} is the competing Langmuir−Hinshelwood reaction rate coefficient, which is negligible at the surface temperature of 90 K that was employed in the results to be discussed. The time dependence of the surface coverages of oxygen, hydroxyls, and water, according to the mechanism of eq 21, is given by

$$d\theta_O/dt = -\sigma_{OD}F_D\theta_O \qquad (22)$$

$$d\theta_{OD}/dt = \sigma_{OD}F_D\theta_O - \sigma_{D_2O}F_D\theta_{OD} - k_{LH}\theta_{OD}\theta_D \qquad (23)$$

$$d\theta_{D_2O}/dt = \sigma_{D_2O}F_D\theta_{OD} + k_{LH}\theta_{OD}\theta_D \qquad (24)$$

and the terms involving k_{LH} in eqs 23 and 24 may be neglected. A combination of HREELS and temperature-programmed reaction showed that the maximum observed (pseudo-steady-state) value of θ_{OD} during the early stages of reaction is approximately 0.015. We may thus write

$$\sigma_{OD}F_D\theta_O \cong \sigma_{D_2O}F_D\theta_{OD} \qquad (25)$$

and we find

$$\sigma_{D_2O}/\sigma_{OD} = \theta_O/\theta_{OD} \cong 0.485/0.015 \cong 32 \qquad (26)$$

In order to quantify σ_{OD}, we may again make use of the pseudo-steady-state approximation and write

$$d\theta_{D_2O}/dt \cong -d\theta_O/dt = \sigma_{OD}F_D\theta_O = \sigma_{OD}F_D[\theta_O(0) - \theta_{D_2O}] \qquad (27)$$

which leads to

$$\theta_{D_2O}(t) = \theta_O(0)[1 - e^{-\sigma_{OD}F_Dt}] \qquad (28)$$

Since $\theta_O(0)$ is known to be 0.5, F_D is known to be 1.2×10^{13} cm^{-2} s^{-1}, and $\theta_{D_2O}(t)$ is measured with temperature-programmed desorption experiments, a plot of $\theta_{D_2O}(t)$ can be constructed, and the measured data can be fitted to determine σ_{OD}. Such a construction is shown in Figure 8 in which the solid curve corresponds to a value of

$$\sigma_{OD} = 6.8 \times 10^{-17}\ \mathrm{cm}^2 \qquad (29)$$

which leads directly, via eq 26, to

$$\sigma_{D_2O} = 2.2 \times 10^{-15}\ \mathrm{cm}^2 \qquad (30)$$

The fact that the datum point at the highest exposure time in Figure 8 lies below the solid curve is a

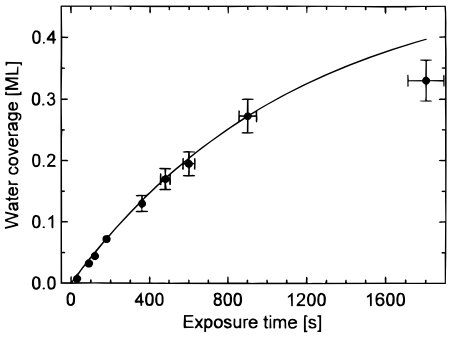

Figure 8. Surface coverage of water on Ru(001) as a function of gas-phase atomic deuterium exposure time. The flux of atomic deuterium is maintained at 1.2×10^{13} cm^{-2} s^{-1}, and the initial oxygen coverage is 0.5 ML. The adsorption temperature is 90 K. The solid line is calculated on the basis of the model described in the text.

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consequence of the fact that the product water remains adsorbed at the reaction temperature and acts to poison the direct reaction for $\theta_{D_2O} \gtrsim 0.3$, an effect which is not considered in eqs 22−24. When the reaction is carried out at a surface temperature of 200 K or greater, no such poisoning is observed since water desorbs upon formation. We close by noting that the rate-limiting step in the reaction of chemisorbed oxygen with hydrogen to form water on Ru(001) is the first step, the formation of hydroxyls, in the case of both Langmuir−Hinshelwood kinetics and direct Eley−Rideal kinetics. The barriers are much lower, however, in the case of Eley−Rideal kinetics, which allows the reaction to proceed at a surface temperature of 90 K. The intermediate and product of the reaction can be characterized conveniently by HREELS, which allows a decisive articulation of the mechanism and a determination of the rates of both elementary reactions which embody it.

Summary

We have discussed the use of gas-phase atomic hydrogen to effect surface reactions via Eley−Rideal kinetics under UHV conditions and at low surface temperatures. The Eley−Rideal mechanism describes a reaction between a reactant which has chemisorbed and one which has not; i.e., the impinging hydrogen may or may not have been dynamically trapped at the surface, but it has not chemisorbed locally and accommodated to the surface temperature. This protocol realizes that the rate of many hydrogenation reactions which obey Langmuir−Hinshelwood kinetics is limited by the strength of the metal−H bond, which is on the order of 65 kcal/mol in the low-coverage limit. The reactant atoms being produced in the gas phase, and not by dissociative chemisorption, the metal−H bond does not form and, hence, does not need to be activated for reaction to occur.

We have illustrated these ideas with four specific examples, taken from our laboratory, involving the Ru(001) surface, namely, the abstraction of chemisorbed hydrogen, forming dihydrogen, which desorbs at least 150 K below the threshold temperature for recombinative desorption of two hydrogen adatoms; the hydrogenation of chemisorbed CO, forming η^1- and η^2-formyls and η^2-formaldehyde; the selective hydrogenation of chemisorbed formate, forming a formyl and a hydroxyl; and the hydrogenation of oxygen adatoms to form water.

We anticipate that this powerful experimental technique will continue to provide deep insights into the mechanisms of surface reactions that have not heretofore been possible to examine. We anticipate also that other radical beams will be employed in the future, such as atomic oxygen, atomic nitrogen, and molecular radicals. This is certainly one of a number of extremely exciting current research activities in the broad and rich field of surface chemistry.

I acknowledge the stimulation and indispensable contributions of my entire research group, past and present, and, in particular, Tom Jachimowski, Kevin Lyons, Bill Mitchell, Matthias Schick, and Jun Xie, on whose work this Account was based. I also acknowledge many enjoyable and stimulating conversations with Professor Brian Bent, Dr. John Harris, Professor Bret Jackson, Professor Bengt Kasemo, Dr. Bruce Kay, and Dr. Charlie Rettner. Primary support of this work was provided by the National Science Foundation (Grant CHE-9626338) with additional support from the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant 28189-AC5), and the Royal Shell Laboratories, Amsterdam.

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