5). Similar, stable acyloxy carbene complexes are formed by reaction of the anionic acyl complexes **3** with acid chlorides blocking a potential synthesis of α-diketones.[33]
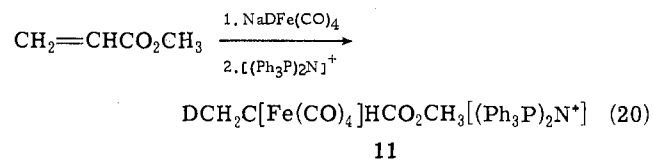
The mechanisms for paths g, h, i, and j (Figure 1) have not been studied. It seems probable that these involve oxidation of **2** or **3**, affording very reactive iron(III) acyl complexes. Oxidative enhancement of migratory insertion and solvolysis of oxidized acyls have precedents.[34]

Mechanisms for the reducing reactions (eq 11 and 12, Figure 2) are poorly understood. The coordinatively saturated hydride slowly adds to α,β-unsaturated esters, affording the kinetically determined product **11** (eq 20) which is reduced by protonation (step k, Figure 1),[5] but the first step in eq 20 is too

slow to account for the rate of reductions in reactions such as eq 11 and 12 (Figure 2).

$$CH_2 \!\!=\!\! CHCO_2CH_3 \xrightarrow[\text{2.}[(Ph_3P)_2N]^+]{\text{1. NaDFe(CO)}_4}$$

$$DCH_2C[Fe(CO)_4]HCO_2CH_3[(Ph_3P)_2N^+] \quad (20)$$

11

We are still investigating mechanisms for the reduction reactions (eq 11, 12) and oxidatively induced migration.[34] These may bring to a close our studies of this reagent.

This Account is based on the experimental and intellectual efforts of my students and associates: J. Cawse, D. R. Clark, M. P. Cooke, R. Finke, N. W. Hoffman, R. G. Komoto, P. L. Matlock, W. O. Siegl, R. Wahren, and S. R. Winter; support was provided by the National Science Foundation (MPS70-01722-A03) and the Center for Materials Research (N00014-67-A-0112-0056 and DAHC15-73-G15). I am also indebted to my colleague J. I. Brauman for collaboration in the mechanistic studies discussed herein.

(33) Low yields of α-diketone have been found after destructive distillation mixtures formed from acid chlorides and the acyl complex: Y. Sawa, M. Ryang, and S. Tsutsumi, *J. Org. Chem.*, **35**, 4183 (1970).

(34) (a) K. M. Nicholas and M. Rosenblum, *J. Am. Chem. Soc.*, **95**, 4449 (1973); (b) M. Rosenblum, *Acc. Chem. Res.*, **7**, 122 (1974).

Crystallographic Dependence in the Surface Chemistry of Tungsten

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One of the most intriguing aspects of modern studies of the chemistry of solid surfaces (especially metals) is that their chemistry can be strongly dependent on the specific crystal face exposed. Beginning with the work of Cunningham and Gwathmey on the interaction of ethylene with single-crystal surfaces of nickel[1] and the more recent work of Delchar and Ehrlich on the interaction of nitrogen with single-crystal planes of tungsten,[2] it has become obvious that different planes of the same metal can have entirely different chemistry. In fact, the work of Schmidt and his coworkers[3,4] suggests that different planes of the same metal can exhibit a greater difference in chemistry than the same planes of different but closely related metals.

The realization that such diversity can exist explains to some extent why areas such as catalysis are characterized by a *lack of understanding on a fundamental level*, an observation which becomes obvious on reading reviews such as the books by Bond[5] and Thomas and Thomas.[6] A normal polycrystalline material of the type used for catalytic studies will expose a distribution of crystal faces, as well as an array of

high-energy sites such as grain boundaries and defects of various types. As a result, measurements obtained on such a sample could yield results which are composites of contributions from all such sources. For such materials one cannot, as has been the usual case, treat the surface as a uniform reactant.

Despite this intriguing diversity with crystal face, the majority of single crystal work in the past has been conducted on a single crystal face. Moreover, until recently this field has been dominated by studies on tungsten surfaces, mainly for experimental reasons. The ability to clean and characterize surfaces has been so central to the renaissance that has occurred in this area that tungsten, considered the easiest metal to clean, has occupied a central position. The ability to clean and characterize surfaces, and thus eliminate the problem of foreign species at the surface, stems directly from the development of techniques for the production and measurement of ultrahigh vacuum ($<10^{-9}$ Torr).[7,8] Pressures of this order

(1) A. T. Gwathmey and R. E. Cunningham, *Adv. Catal.*, **10**, 57 (1958).

(2) T. A. Delchar and G. Ehrlich, *J. Chem. Phys.*, **42**, 2686 (1965).

(3) H. R. Han and L. D. Schmidt, *J. Phys. Chem.*, **75**, 227 (1971).

(4) M. Mahnig and L. D. Schmidt, *Z. Phys. Chem. (Frankfurt am Main)*, **80**, 71 (1972).

(5) G. C. Bond, "Catalysis by Metals", Academic Press, New York, N.Y., 1962.

(6) J. M. Thomas and W. J. Thomas, "Introduction to the Principles of Heterogeneous Catalysis", Academic Press, New York, N.Y., 1967.

(7) G. Ehrlich, *Adv. Catal.*, **14**, 255 (1963).

(8) P. A. Redhead, J. P. Hobson, and E. V. Kornelson, "The Physical Basis of Ultrahigh Vacuum", Chapman and Hall, London, 1968.
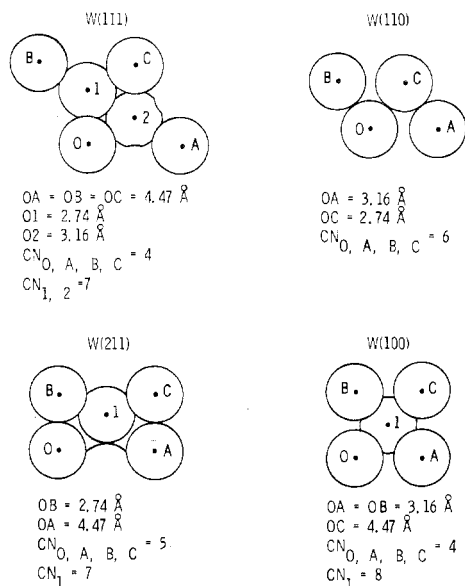
Figure 1. Schematic representations of the unit cells of the four lowest index planes of tungsten. The distances are those between the designated atoms, and the coordination numbers, CN, are the number of nearest neighbors around each designated atom.

are necessary to allow one to maintain a surface free of contaminants for a period sufficiently long to allow experiments to be performed. As a "rule of thumb" one can expect complete contamination of a surface from adsorption of background gases in times of the order of 1 sec at pressures of 10^{-6} Torr. Since contamination times vary inversely with the pressure, the need for reduced background pressures is obvious. With the development of ultra-high-vacuum techniques, numerous new experimental techniques have developed over the past 10 to 15 years, specifically for the study of solid surfaces, and the rate of technique development has accelerated in the past few years. This is not the correct forum to consider these experimental techniques, and the interested reader should consult several recent reviews for details.[9-11]

Most studies of adsorption on "clean surfaces" have been concerned mainly with diatomic absorbates such as H_2, O_2, N_2, and CO. Very little work has been done with the more complicated hydrocarbon molecules, a major reason being concern over possible contamination by carbon residues. In addition, there has been an apparent general feeling among the workers in this area, mainly physicists, that the surface interaction would be more easily understood through the use of relatively simple adsorbates. However, when one considers that, in contrast to the case of a metal surface, our knowledge of adsorbates is essentially exact, the difference in complexity between nitrogen and a small polyatomic molecule is negligible. Moreover, by systematic variation of the adsorbate of which our knowledge is essentially exact, it should be possible to gain knowledge about the adsorbate.

This Account will be concerned with two main

themes: (1) the extension of "clean surface" type studies to more complex adsorbates and reactions, and (2) the systematic study of the same interaction or reaction on a coherent set of crystal faces of the same metal, tungsten. In order of decreasing surface density these are the (110), (100), (211), and (111) planes. For reference, Figure 1 contains representations of their surface unit cells as given by Nicholas.[12] In each case the atoms marked by letters are the atoms which define the surface unit cell, and the atoms marked by the numbers 1 and 2 are partially exposed metal atoms, respectively, in the first and second layers from the outermost layer. Also noted in the figure is the coordination number, or number of nearest neighbors, for each surface tungsten atom. For these planes the definition of "surface" will vary with the adsorbate system. In general, one would consider any metal atom in the surface region that is missing its full complement of nearest neighbors (8 for bccub metals) to be a surface atom. With this definition both the (211) and (111) planes have considerable three-dimensional character. Hydrogen is small compared to the characteristic dimensions of the surface, and as a result the "surface" for hydrogen adsorption is this total three-dimensional surface. However, the steric restrictions on ethylene are such that only the outermost layer of tungsten atoms are available for adsorption, and in contrast to the case for hydrogen the surface for ethylene adsorption is more nearly two dimensional.

Hydrogen

The complexity that can exist in even a simple interaction as the crystal face is varied is well illustrated by the case of hydrogen on tungsten, one of the most extensively studied adsorption systems.[13-15] Despite this large amount of work, however, there are basic and important questions unanswered. Moreover, no correlations exist for organization of the large amount of data available. The thermal desorption spectra contained in Figure 2 are illustrious of the complexity that does exist. The (100), (110), and (111) spectra are taken from a paper by Tamm and Schmidt,[16] and the (211) spectrum from Rye et al.[17] Equivalent results have been obtained by several different groups for the (100),[16,18-20] (111),[16,18,21] and (110)[16,18] faces of tungsten. Thermal desorption is conceptually a simple experiment. The surface is dosed to a given coverage with the desired gas, and the temperature of the sample then rapidly raised. By following the gas-phase pressure and the substrate temperature as a function of time, one can generate a spectrum of the desorbing gas vs. tempera-

(9) J. M. Blakely, "Introduction to the Properties of Crystal Surfaces", Pergamon Press, New York, N.Y., 1973.

(10) R. B. Anderson, Ed., "Experimental Methods in Catalytic Research", Vol. 1 and 2, Academic Press, New York, N.Y., 1968.

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(15) L. D. Schmidt, *Catal. Rev.*, **9**, 115 (1974).

(16) P. W. Tamm and L. D. Schmidt, *J. Chem. Phys.*, **54**, 4775 (1971).

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(19) D. L. Adams and L. H. Germer, *Surf. Sci.*, **23**, 419 (1970).

(20) T. E. Madey and J. T. Yates, Jr., "Structure et Proprietes de Surfaces des Solides", Editions du Centre national de la Recherche Scientifique, Paris, 1970, No. 187, p 155.

(21) T. E. Madey, *Surf. Sci.*, **29**, 571 (1972).

ture. Analysis of such data is complicated by the dynamics of the vacuum system which must also be considered along with the dynamics of the desorption process.[7,22] Data obtained in a rapidly pumped system, as for the data in Figure 2, are normally analyzed by Redhead's methods[22] or by computer simulation.[15] The activation energies for desorption and the order for desorption, x, given for each of the peaks in Figure 2 were obtained by such techniques. The reader should see ref 16 and 17 for details. The designation β_i used in Figure 2 is the standard method used for labeling peaks of this type.

As can be seen from Figure 2, desorption is quite complex with at least 11 peaks from the four planes representing at least 11 desorption processes with activation energies ranging from 14 to 35 kcal/mol. With the exception of the β_1 peak from W(100), all the β states desorb with second-order kinetics, and all the β states, including the β_1 on W(100), exchange H_2 and D_2.[16,17] These observations have been taken to indicate that absorption of hydrogen is dissociative with the adsorbed species being atomic hydrogen. The nature of the processes leading to these multiple peaks, however, has been somewhat in question. The obvious initial interpretation of this multiplicity of peaks is that they result from site heterogeneity or hydrogen atoms adsorbed in different binding sites on the surface, a model consistent with the observation that the most complex spectrum results from hydrogen adsorption on the most complex surface, W(111).

However, only in the case of the desorption spectra is such evidence for multiple states seen for all the planes. Results from both work-function[20] and field-emission tunneling[23] experiments on W(100) and W(110) indicate a single form of hydrogen on the surface. This has led to the suggestion that multiple peaks in the desorption spectra may result from an *induced heterogeneity* due to lateral interactions between adatoms on adjacent, identical sites. When treated statistically such a model is capable of yielding a qualitative,[24] but not quantitative,[25] description of the desorption spectrum from W(100). Thus, there is a question as to whether the desorption spectra reflect induced or site heterogeneity.

No general indication of multiple states, equivalent to that observed for the desorption kinetics, is seen in the adsorption kinetics. Adsorption kinetics can be derived from a series of desorption spectra obtained as a function of exposure (exposure, defined as the integral of the dosing pressure with respect to time, is proportional to the total number of impacts per cm² of surface). Redhead has shown that the area under the desorption spectrum is proportional to the amount of material desorbed from the surface,[22] and the coverage, θ, can therefore be determined by dividing the area under a given desorption spectrum by the area under a spectrum obtained for saturation. Thus, by obtaining a series of spectra at various exposures, one can determine the relationship between coverage and exposure. This relationship is given in
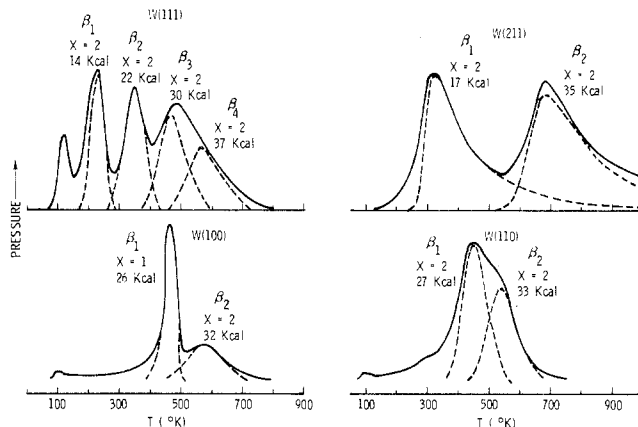
(22) P. A. Redhead, *Vacuum*, **12**, 203 (1962).
(23) E. W. Plummer and A. E. Bell, *J. Vac. Sci. Technol.*, **9**, 583 (1972).
(24) T. Toya, presented at the Fifth International Conference on Solid Surfaces, Boston, 1971; *J. Vac. Sci. Technol.*, **9**, 890 (1972), abstract only.
(25) D. L. Adams, *Surf. Sci.*, **42**, 12 (1974).

Figure 2. Hydrogen flash desorption spectra from W(111),[16] W(100),[16] W(110),[16] and W(211).[17] The notation β_i is the standard designation for peaks in spectra of this type. x is the order for the hydrogen desorption reaction, and the energy beside each peak is the activation energy for the desorption reaction represented by each peak.

general by the integrated form of the adsorption rate expression[18]

$$\int \frac{d\theta}{f(\theta)} = \frac{\alpha}{n^\circ} \frac{1}{\sqrt{2\pi mkT}} \int P dt \qquad (1)$$

where α is the sticking probability or the probability of an impact on a free site leading to adsorption, n° is the saturation coverage in molecules/cm², the square root term is from the kinetic theory treatment of the rate of impact of molecules with the surface, and $f(\theta)$ gives the general dependence on surface coverage. Plots of the left side of eq 1 vs. exposure will generate, for the correct form of $f(\theta)$, a straight line, the slope of which yields the ratio of the sticking probability to the saturation coverage, α/n°. Provided n° is known for one plane, values for other planes can be obtained from the ratios of the areas under saturation spectra on different planes obtained under identical conditions. The adsorption parameters obtained in our laboratory by such procedures are given in Table I. The saturation coverages given in the first row are based on Madey's absolute value for the (100) plane.[26] These results are in excellent agreement with those of several groups for the (100)[26-28] and (111)[29] planes, although we disagree slightly with Tamm and Schmidt[29] as to the form of the adsorption kinetics of W(110).

In the case of W(211), where the resolution between peaks is sufficiently large, we are able to determine the adsorption kinetics for the individual states. In the case of the (111) plane, our resolution is insufficient to determine the kinetics for the individual states, but Tamm and Schmidt report a slight break for their sticking coefficient s ($s = \alpha f(\theta)$) vs. coverage data at half-coverage indicating at least two forms of adsorption kinetics. In the case of (100) and (110), adsorption is characterized by a single set of parameters over the entire coverage range. Thus, interpretation of the adsorption kinetics in terms of site heterogeneity is clearly possible only for the (211) plane and possibly for the (111) plane.

The gross difference in kinetics for the two states

(26) T. E. Madey, *Surf. Sci.*, **36**, 281 (1973).
(27) J. A. Becker, *Actes Congr. Int. Catal. 2nd, 1960*, 1771 (1961).
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Rye Accounts of Chemical Research

Table I
Summary of Experimental and Derived Values for Hydrogen Adsorption[a,18]

	(110)	(100)	(211) β_1	(211) β_2	(111)
$n°$, molecules/cm^2	9.1×10^{14}	1×10^{15} [b]	4.5×10^{14}	4×10^{14}	9.4×10^{14}
α	0.22	0.56	0.05	0.57	~1
$f(\theta)$	$(1 - \theta)^2$	$(1 - \theta)$	$(1 - \theta)$	1	~1
$n°$ calcd	7.1×10^{14}	1×10^{15}	8.2×10^{14}		8.7×10^{14}
μ, D	0.15	0.25	0.08	0.20	Complex

[a] Row 1, monolayer coverages in molecules/cm^2; row 2, sticking probabilities for adsorption (see eq 1); row 3, coverage dependence for adsorption kinetics (eq 1); row 4, calculated saturation coverages assuming one hydrogen atom adsorbed for each two missing nearest-neighbor tungsten atoms; row 5, surface dipole moments per hydrogen atom obtained from the experimental data using eq 2. [b] Reference 26.
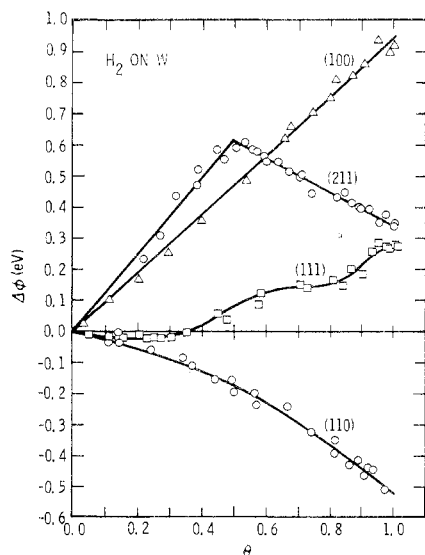

Figure 3. Work function change vs. coverage for hydrogen adsorption at ~110 K on the (110), (100), (111), and (211) planes of tungsten.[18]

on W(211) and the row and trough nature of this surface (see Figure 1) allow an assignment for the general location of the sites.[17] The critical feature is that adsorption into the β_2 state is independent of coverage ($f(\theta) = 1$). The most straightforward interpretation for kinetics of this form is that the initial impacts from the gas phase occur with the outermost rows (identified with the β_1 sites) followed by a rapid transfer to the troughs (identified with the β_2 sites). Such a process would give kinetics independent of coverage until the β_2 states are filled, and subsequent kinetics determined by filling of the β_1 states. Since ethylene is restricted on steric grounds to interaction with the rows, deuterium in the β_2 state and ethylene were predicted and confirmed to adsorb completely independently.[17] No similar assignment of sites can be made as yet for the more complex case of W(111).

Changes in work function, $\Delta\varphi$, can serve as an additional method of distinguishing between induced and site heterogeneity. In the simplest interpretation the change in work function is linearly proportional to both the coverage and the dipole moment of the adsorbate bond,[30,31] or more correctly the normal component of the dipole moment, $\mu_\perp$.[18]

(30) J. C. Tracy, Ph.D. Thesis, Materials Science Center Report No. 1017, Cornell University, Ithaca, N.Y., 14850.
(31) P. M. Gundry and F. C. Tomphins in "Experimental Methods in Catalytic Research", R. B. Anderson, Ed., Academic Press, New York, N.Y., 1968, pp 100–168.

$$\Delta\varphi = 4\pi n° \theta \mu_\perp \qquad (2)$$

In terms of this model a dipole layer polarized positively outwards would yield a work function decrease and one polarized negatively would yield a work function increase. As Madey and Yates have pointed out,[20] one would expect different dipole moments for different forms of adsorbed hydrogen, or site heterogeneity. As a result, changes in slope would be expected in work function vs. total coverage data. Such data obtained in our laboratory using the Kelvin vibrating capacitor method[30,31] are given in Figure 3. No such breaks appear in the case of the (100)[20] and (110)[28] planes, planes where other evidence suggests induced heterogeneity. For W(211) and W(111), where site heterogeneity is strongly suggested, large breaks do occur, and at coverages corresponding exactly to sequential filling of the various states observed in the flash desorption spectra.

Thus, it would appear that the question of site vs. induced heterogeneity does not have a unique answer but depends on the specific crystal plane, or type of plane. Of the planes we have investigated, the (211) and (111) planes show site heterogeneity while the (100) and (110) planes are cases of induced heterogeneity.

One would expect that chemisorption would be sensitive to the degree of unsaturation of surface metal atoms. As a measure of unsaturation, we will take the number of missing nearest-neighbor tungsten atoms, i.e., the deviation of the coordination numbers given in Figure 1 from eight. If we assume that multiple sites with different binding energies require multiple types of surface atom unsaturation, the agreement for the four planes we have studied is excellent. For both the (100) and (110) planes where a single site apparently exists, the surfaces are characterized by surface tungsten atoms with a single degree of unsaturation: two missing nearest neighbors for W(110) and four missing nearest neighbors for W(100). For W(211) and W(111) multiple sites exist and the surfaces of these planes have multiple types of unsaturated tungsten atoms.

The saturation coverages of hydrogen can also be correlated with the degree of unsaturation of surface tungsten atoms. For example, each unit cell of 17.3 $Å^2$ on the (111) plane contains a total of three tungsten atoms missing a total of six nearest neighbors. If we assume that one hydrogen atom is chemisorbed for each two missing nearest neighbors, a saturation coverage of 8.7×10^{14} molecules/cm^2 is calculated.

"Trans" Di-Adsorbed Ethylene

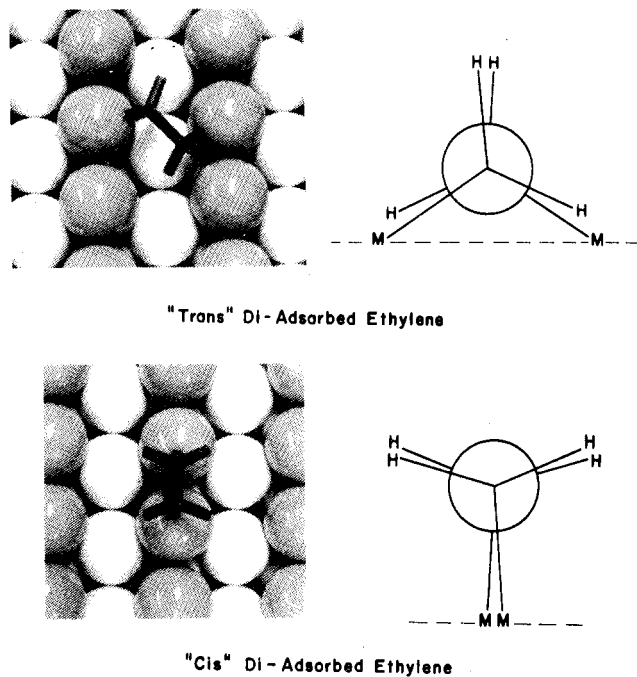
"Cis" Di-Adsorbed Ethylene

Figure 4. Structures for di-σ-adsorbed ethylene. The models shown at the left were constructed to a scale consistent with metallic and covalent radii, and the Newman projections at the right show the orientation about the C–C axis.

This calculated value and similar values for the three remaining planes based on the same assumption are given in Table I. Given the probable error in the experimental determinations of the saturation coverage, the agreement between the experimental and calculated values is exceptionally good. In two cases, W(111) and W(110), there are slight differences, but differences which probably reflect experimental error. In the case of the (110) plane, literature values[16] differ from the calculated value by no more than 7%, and values for the (111) plane[16,26] fall in the range of $(6.0–17.5) \times 10^{14}$ molecules/cm^2.

Ethylene

The correlations given above for hydrogen are essentially electronic in nature in that their basis is in the chemical unsaturation of the surface tungsten atoms. Our understanding of the chemistry of ethylene, on the other hand, results from restrictions on the interaction due to the size and structure of the ethylene molecule. These structural considerations, which form the basis for the major portion of our interpretation of the ethylene results, can be illustrated by the structures shown in Figure 4 for the two possible interactions of ethylene with the (211) plane.[32] Ethylene chemisorbs by opening of the double bond and formation of carbon–metal σ bonds to two adjacent metal atoms to form a 1,2-diadsorbed ethane complex with the surface.[33–36] The photoelectron spectroscopy results of Plummer et al. on W(110) are in general agreement with the results presented here, but they believe that partial dehydrogenation occurs during *room temperature adsorption*, leading to a chemisorbed acetylene like species;[37] in our case the
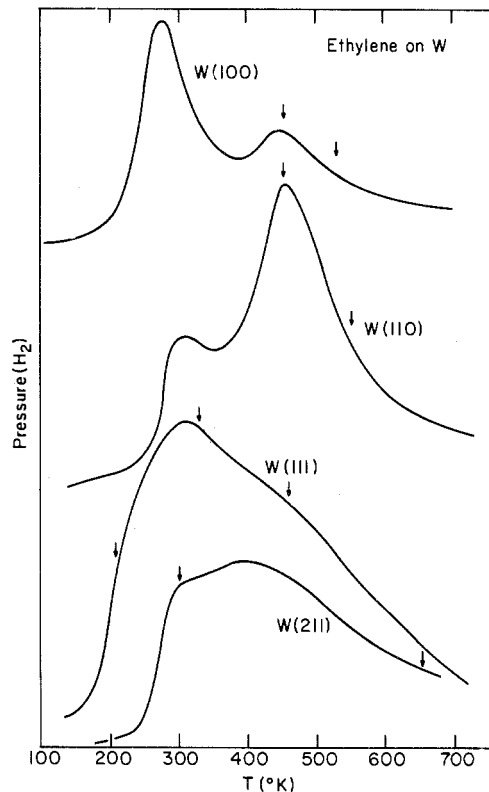

Figure 5. Flash decomposition spectra for saturation coverages of ethylene adsorbed at ~110 K on four faces of tungsten.[32] The arrows above each spectrum indicate the temperature of the peak maxima observed for hydrogen desorption.

substrate was held at ~110 K during adsorption in order to assure that only chemisorption occurred. For strain-free adsorption, chemisorbed ethylene can adjust to metal–metal spacings ranging from ~2.8 Å to ~4.7 Å by rotation around the carbon–carbon bond. This rotation is seen better in the Newman projections shown in the right side of the figure. It should be noted that interaction with the unsaturated trough atoms is sterically restricted.[17]

Both decomposition to hydrogen and a carbon residue and hydrogenation are available reaction paths for ethylene chemisorbed on tungsten. Above 200 K decomposition is the predominant reaction, resulting in tungsten being a poor catalyst for hydrogenation. The temperature profile of the decomposition reaction is given by the thermal decomposition spectra collected in Figure 5.[32] In all cases, decomposition is the major reaction (≳98%).[38] The arrows in Figure 5 indicate the temperatures at which the peak maxima occur in hydrogen desorption. Since hydrogen is the major gas-phase product, one needs to distinguish between hydrogen desorption and ethylene decomposition as rate limiting for appearance of hydrogen in the gas phase. Although hydrogen from ethylene decomposition is first transferred to the surface and then to the gas phase,[39,40] the rate-limiting step is apparently decomposition.[17]

With the assumption of concerted decomposition and consideration of the chemical implications of structures such as in Figure 4, one can explain the

(32) B. D. Barford and R. R. Rye, *J. Vac. Sci. Tech.*, **9**, 673 (1971).
(33) G. H. Twigg and E. K. Rideal, *Trans. Faraday Soc.*, **36**, 533 (1940).
(34) R. P. Eischens and W. A. Pliskin, *Adv. Catal.*, **10**, 1 (1958).
(35) P. W. Selwood, *J. Am. Chem. Soc.*, **83**, 2853 (1961).
(36) R. L. Burwell, Jr., *Acc. Chem. Res.*, **2**, 289 (1969).

(37) E. W. Plummer, B. J. Waclawski, and T. V. Vorburger, *Chem. Phys. Lett.*, **28**, 510 (1974).
(38) P. G. Cartier and R. R. Rye, *J. Catal.*, **32**, 88 (1974).
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(40) P. G. Cartier and R. R. Rye, *J. Chem. Phys.*, **59**, 4602 (1973).

Table II
Sequential Adsorption of D_2 and C_2H_4 on Tungsten[a]

	(110)	(211)	Polycrystaline	(100)	(111)
θ_{D_2}	0.98	0.96	0.86	0.67	0.36
$\theta_{C_2H_4}$	0.24	0.37	0.41	0.52	0.86
$N_{H_2}/N_{C_2H_4}$	6.5	5.4	4.1	2.4	0.76
$Kf_s (\times 10^3)$	0.4 ± 0.1	3.8 ± 1	1.5	4.5 ± 0.9	7.5 ± 2
$Kf_h (\times 10^3)$	3.4 ± 0.3	24.6 ± 4.3	10.3	11.9 ± 3.4	13.1 ± 0.9

[a] Rows 1 and 2, coverages of D_2 and C_2H_4 obtained by saturating each surface with D_2 followed by an identical dose of C_2H_4;[39,40] row 3, ratio of chemisorbed hydrogen to chemisorbed ethylene; rows 4 and 5, fractions of chemisorbed ethylene converted to ethane during a flash for the case, f_s, where no hydrogen is preadsorbed, and the case, f_h, where the hydrogen and ethylene coverages are those given in rows 1 and 2.[38]

spectra in Figure 5. With decomposition of ethylene occurring through transfer of hydrogen to the surface, the transition state for decomposition involves interaction of the ethylenic hydrogen with the surface. The "trans" form of ethylene adsorbed on the 4.47-Å spacings of the (211) plane has two of the ethylenic hydrogens forced into close proximity with the surface, and the "cis" form on the 2.74-Å spacings has all four hydrogens equally far removed from the surface. As the transition state for decomposition should be favored for short ethylenic hydrogen-surface distances, the "cis" form should be relatively the most stable toward decomposition and produce a hydrogen peak at higher temperature. The densities of these two sites are in a ratio of 1:1, and the decomposition spectrum is composed of two poorly resolved peaks in approximately a 1:1 ratio. From the above discussion and assuming no bias toward occupation of one site over the other, we would assign the low-temperature peak to decomposition on the 4.47-Å spacing and the high-temperature peak to decomposition on the 2.74-Å spacing. Similar considerations for the remaining three faces yield a qualitative explanation for the *number and relative size of the decomposition peaks, and the relative temperature at which these peaks occur.*

Both the adsorption kinetics and the work function change associated with adsorption are consistent with the above picture of ethylene adsorption. The major feature in understanding both these effects is that ethylene, being constrained to interact with the outermost layer of surface metal atoms, is restricted to be above the surface; the full three-dimensional character of the surface region, which apparently is a major source of the complexity in hydrogen adsorption kinetics, is not available to ethylene. In contrast with the case of hydrogen, the adsorption kinetics of ethylene are identical. On each plane the rate of adsorption is proportional to the fraction of unoccupied sites, $f(\theta) = 1 - \theta$, with sticking coefficients of essentially unity.[18]
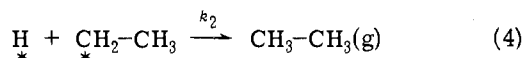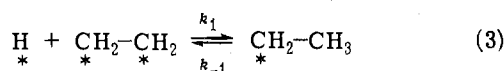
Again in contrast with the case of hydrogen, ethylene adsorption leads to a work function decrease on all four planes;[18] such invariance in the sign of $\Delta\varphi$ would be expected for an adsorbate constrained to be above the surface. The variation in sign of $\Delta\varphi$ for hydrogen may not be the result of surface-hydrogen bonds of opposite polarity, but to the position of the hydrogen nucleus either above or below the average electron surface. However, the magnitude of the work

function change per adsorbed ethylene varies with crystal plane in the order: (110) > (100) > (211) > (100). This is exactly the same as the order for the density of surface tungsten atoms that are available for ethylene adsorption: (110) > (100) > (211) > (111). A more instructive way to view this latter trend is in terms of the average distance between adjacent surface tungsten atoms, a quantity which increases as the density decreases. Increasing distance between surface tungsten atoms would, considering the structure of adsorbed ethylene in Figure 4, mean a decreasing normal component of the carbon–surface bond dipole moment, and, since the work function is linearly related to this normal component (eq 2), these structural considerations would predict, as observed, a maximum work function change which decreases with decreasing density of surface tungsten atoms. This same argument can be made semiquantitative by calculating the angle between the normal and the carbon–surface bond.[18]

The fact that ethylene is restricted to be above the plane of the surface while hydrogen is capable of interacting with the full three-dimensional character of the surface places strong restrictions on the interaction when both are present. If the surface is first saturated with ethylene and then hydrogen admitted, no hydrogen is adsorbed.[39,40] However, if hydrogen is preadsorbed, ethylene does adsorb, with the process being one of displacement or coadsorption depending on the crystal plane.[40] The effect of this crystallographic dependence can be seen in the isotope spectra given in Figure 6 for sequential adsorption of deuterium and ethylene on polycrystalline tungsten. D_2 is used to distinguish between surface hydrogen (D_2 + ½HD) and ethylenic hydrogen (H_2 + ½HD). In this case 14% of the preadsorbed deuterium was displaced while 41% of an ethylene monolayer was adsorbed. Table II contains the coverages and the deuterium to ethylene ratios obtained for identical experiments on each of the surfaces. The crystallographic dependence clearly shows in the different shapes of the hydrogen isotope spectra from polycrystalline tungsten, Figure 6. Similar experiments with the individual crystal planes yield isotope spectra which are identical in shape and differ only by scaling factors. However, in the polycrystalline case the separate crystal planes have different ratios of D_2 to C_2H_4 and contribute to different regions of the polycrystalline spectrum. From knowledge of the decomposition spectra (Figure 5), we predicted that this distribution

of isotopes on polycrystalline tungsten resulted from a high ratio of D_2 to C_2H_4 on the (10) and (211) planes and a low ratio on the (100) and (111) planes,[39] a prediction in agreement with the subsequent single-crystal data given in Table II.[40] The ability to see contributions from the individual crystal faces in polycrystalline results means that there is little interplanar communication on polycrystalline tungsten despite high hydrogen mobility,[41] and each of the separate faces can be treated as a separate reacting entity. The coverage data in Table II can, in fact, be used to calculate the distribution of crystal planes on the polycrystalline sample.[40]

Although decomposition is the main reaction that occurs during a flash decomposition experiment, small amounts of ethane (<2%) are also produced. The fraction of the chemisorbed ethylene that is converted to ethane (Table II) can be obtained from the ratio of the area under the mass 30 spectrum (unique to ethane) to the area under the mass 2 spectrum;[38] f_s refers to the case of a monolayer of C_2H_4 and f_h to the case where the H_2 and C_2H_4 coverages are those given in rows 1 and 2 of Table II. The order of hydrogenation activity $[(110) < (100) < (211) < (111)]$ is again exactly the inverse of the order of the densities of surface tungsten atoms. There is an apparent reversal of order in the case of the (211) and (111) planes when hydrogen is preadsorbed, but this is due to a concentration effect; if the different ratios of H_2 to C_2H_4 are considered, the activity of the (111) plane is especially pronounced. To explain this trend in activity, the critical feature is again the distance between adjacent metal atoms, the average value of which should decrease as the density increases. This observation forms the basis for the explanation of the crystallographic effects in terms of the Horiuti-Polanyi mechanism[42] (eq 3 and 4). The asterisks in

$$\underset{*}{H} + \underset{*}{CH_2}-\underset{*}{CH_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{*}{CH_2}-CH_3 \qquad (3)$$

$$\underset{*}{H} + \underset{*}{CH_2}-CH_3 \overset{k_2}{\longrightarrow} CH_3-CH_3(g) \qquad (4)$$

these expressions represent bonds to the surface. The step of major importance is the reverse step in eq 3, the conversion of the half-hydrogenated state back to chemisorbed ethylene. This step should occur through a transition state of the form[38]

$$\underset{d}{\underset{*\rule{2cm}{0.4pt}*}{\overset{\displaystyle CH_2 \rule{1cm}{0.4pt} CH_3}{\diagup \quad \overset{r}{} \quad \diagdown}}}$$
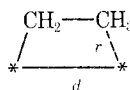
The probability of formation of this transition state decreases as the distance r increases. Since r is directly related to the metal–metal spacing d, the result is a low value for k_{-1} on long spacings and a longer lifetime of the half-hydrogenated state for production of ethane via reaction k_2. As a result, the most active plane should be the one with the longest metal–metal spacings, and the least active for hydrogenation should be the plane with the shortest metal–metal spacings. In general, the order of hydrogena-

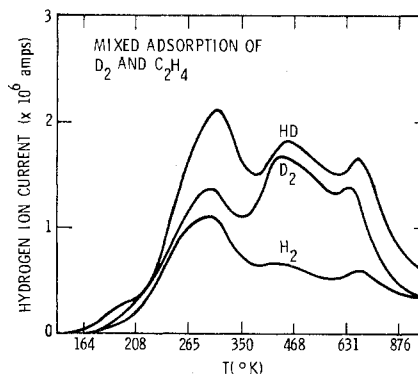(41) R. Gomer, R. Wortman, and R. Lundy, *J. Chem. Phys.*, **26**, 1147 (1957).
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Figure 6. Hydrogen isotope spectra resulting from the sequential adsorption of D_2 and C_2H_4.[39] The surface was first saturated with D_2 and then exposed to C_2H_4 for 3 min at 2.5×10^{-8} Torr.

tion activity should be the inverse of the density of surface metal atoms, as we observe. This explanation would predict exactly the opposite trend for incorporation of deuterium in the product ethane, since such incorporation would require k_{-1} to be a rapid process; short metal–metal spacings which favor rapid conversion of the half-hydrogenated state back to chemisorbed ethylene while unfavorable for the production of ethane are necessary for extensive incorporation of deuterium in the ethane that is produced. Experimentally, preadsorption of deuterium leads to the complete range of deuterated ethanes from ethane-d_0 to ethane-d_6 with the order of activity for incorporation of deuterium, as measured by the ratio of $d_6:d_2$ $[(111) < (100) < (211) < (100)]$, approximately the inverse of the hydrogenation activity.[38]

Conclusions

Modern ultra-high investigations into the interaction of molecules with solid surfaces have progressed from the use of polycrystalline samples to the point where interactions with a single crystal face can be studied. From these latter studies, the single most intriguing point that has resulted is the diversity that can and does exist in the chemistry of different crystal faces of the same metal. From a practical standpoint, this diversity in chemistry requires that one systematically study sets of crystal planes if results from this area are ever to connect with the practical world of polycrystalline materials. In addition to this practical question, systematic studies of the crystallographic dependence can determine trends leading to the development of models that systematize the diverse observations.

Throughout this Account, I have stressed the case of tungsten, a bccub metal. This is partly because of past personal interest, but also because tungsten has been the most extensively studied metal. The face-centered cubic (fccub) metals, in general, have received much less attention. Because of the greater practical importance of fccub metals such as platinum in the area of catalysis, however, fccub metals are now receiving more attention. From the evidence now available it appears that there may not be as much diversity in the single-crystal chemistry of the fccub metals as there is in the bccub metals. Ertl and coworkers in a recent study of the interaction of hydrogen with single crystal faces of Ni^{43} pointed out that this system, as well as the $CO-Ni,^{44,45}$ $H_2-Pd,^{46}$

and $CO-Pd^{47}$ systems, are examples of cases where the "structural" factor is of only minor importance. However, the equilibration of H_2 and D_2 on Pt is dependent on crystal face,[48] and preliminary evidence indicates that the interaction of ethylene with single crystal faces of platinum can be quite complex.[49] In contrast to the case of tungsten, where ethylene decomposition is concerted, similar decomposition on platinum occurs both by a concerted process and by a two-step process involving an acetylenic intermediate.[49]

Thus, it is clear in the case of tungsten that extensive crystal face dependence exists, and one may speculate that the face dependence may not be as extensive in the case of the fccub metals. However, there is just not enough evidence at the moment to make clear correlations of this type.

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What Makes Proton Transfer Fast?

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Proton transfer is an elementary chemical reaction of undeniable importance. It must occur, for example, in all changes which are catalyzed by Brønsted acids or bases, and acid–base catalysis of this sort is probably the most common means by which a chemical or biological reaction may be facilitated.

A central issue in the study of proton transfer concerns its rate: just what is it that makes some proton transfers fast while others are slow? This question has occupied the minds of a number of chemists for many years, and much insight into the matter has been obtained.

We, ourselves, have been especially interested in the effect of charge delocalization on the rate of proton transfer and the relationship which this bears to the identity of the atoms between which the transfer is taking place. Factors such as these may be classified as purely kinetic, but, before their importance can be assessed, thermodynamic effects must also be taken into account, i.e., allowance must be made for the extra drive a reaction might receive because it is exothermic or the impediment it suffers when it is endothermic.
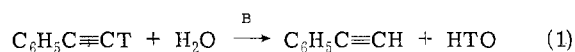
Fast Proton Transfer to Carbon

It is common experience that proton transfer between electronegative atoms such as oxygen or nitrogen is very fast whereas that involving carbon is usu-

ally quite slow. This would seem to be related to the fact that the electron pair which receives the proton onto an oxygen or nitrogen base is generally localized on a single atom, as in ammonia or amines. The corresponding pair of a carbon base, on the other hand, except in unusual circumstances, is strongly delocalized away from the atom to which the proton becomes attached; this is so, for example, in nitronate and enolate ions, the reprotonations of which are classic examples of slow proton transfer.

If delocalization is indeed responsible for this striking difference in behavior, then confining an electron pair to a single carbon atom should produce a base which behaves like a nitrogen or oxygen species, i.e., which protonates very rapidly. Unfortunately, substances with which this hypothesis can be tested are rare, but some do exist, among them the acetylide ion. When an acetylenic carbon–hydrogen bond ionizes as an acid, the electron pair is left behind in an sp hybrid orbital which is orthogonal to the π system of the carbon–carbon triple bond; in this circumstance charge delocalization cannot take place, and the electron pair remains localized on a single carbon atom.

We began our search for fast proton transfer to carbon by studying the acid–base behavior of acetylenes, choosing phenylacetylene as a representative substrate. This material is an easily handled liquid which reacts with ordinary bases in aqueous solution at convenient rates;[1] these rates, moreover, can be measured readily by using tritium as a tracer (eq 1).

$$C_6H_5C{\equiv}CT + H_2O \xrightarrow{B} C_6H_5C{\equiv}CH + HTO \qquad (1)$$

In our hands this hydrogen-exchange reaction proved

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