

THE ORGANOMETALLIC CHEMISTRY OF METAL SURFACES

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Abstract - The organometallic chemistry of metal surfaces is defined as a function of surface crystallography and of surface composition for a set of cyclic hydrocarbons that include benzene, toluene, cyclohexadienes, cyclohexene, cyclohexane, cyclooctatetraene, cyclooctadienes, cyclooctadiene, cycloheptatriene and cyclobutane.

INTRODUCTION

The coordination chemistry of molecules chemisorbed on metal surfaces is a subject of substantial technological importance and scientific challenge (Ref. 1-4). Adhesion, lubrication, corrosion, catalysis, electrolysis and ablation are some of the basic processes in surface chemistry. Because of the intrinsic difficulties in the study of surface chemistry, few basic phenomena or processes have been elucidated at the molecular level. Nevertheless, the possibility of characterization of surface chemistry at the molecular level has been substantially enhanced by the development by surface physicists of various electron spectroscopies and diffraction techniques to the specific problems of surface chemistry (Ref. 3). These, in conjunction (Ref. 5) with conventional chemical and physical techniques, can effectively probe the molecular features of surface science.

Few metal surface reactions occur on the collisional time scale. Generally, a molecule must first form a surface coordinate bond before reactions, either intramolecular or intermolecular in character, occur. *Surface chemistry is coordination chemistry. If the molecule or molecules in question are organic, then the surface chemistry is organometallic chemistry.* A perspective in coordination and organometallic chemistry is not only useful to a study of metal surfaces, it is, in my view, essential. Thus, although surface science is not a conventional subject in organometallic symposia, the scientific content of metal surface chemistry of organic molecules is by definition, organometallic chemistry.

Presently, our surface science research is focused on the chemistry of unsaturated organic molecules—acetylenes, olefins and aromatic hydrocarbons—at the surface of transition metals especially those of the nickel, cobalt and iron groups. The objective is the establishment of the molecular details of the surface chemistry of these organic molecules as a function of d-level occupancy of the metal, surface crystallography or topography, and surface composition. To define the chemistry as a function of surface crystallography and surface composition, i.e., clean surfaces and surfaces "contaminated" with carbon, sulfur and oxygen atoms, and to exploit the surface spectroscopic and diffraction techniques, the experimental regime is that of the ultra high vacuum (10^{-10} to 10^{-11} torr) chamber. However, this regime of single crystal planes with clean or relatively clean surfaces under extremely low pressures is not the regime of ordinary real world surface chemistry. The most serious limitations in the ultra high vacuum studies are (1) thermodynamic changes due to the low ambient pressures, particularly for hydrogenation-dehydrogenation reactions where the equilibrium is shifted toward dehydrogenation because of the low thermodynamic activity of the hydrogen atoms on the surface at these pressures, and (2) kinetic changes whereby the dominant reaction mechanism may change in the ca. 10^{10} to 10^{12} change in pressure between the two regimes. Nevertheless, the control of surface topography and composition does enable delineation of chemistry at the molecular level. Extrapolation from the low to the "high" pressure regimes is feasible, provided that adequate account is made of thermodynamic, kinetic and surface composition changes that may ensue. An experimental modification that can be used to bridge the two pressure regimes is an ultra high vacuum system equipped with an isolation cell so that the surface characterization techniques can be employed under ultra high vacuum conditions and the chemical reactions run, with the crystal enclosed by the isolation cell, at high temperatures. This modification does not fully circumvent all problems, however. For example, surface composition will change substantially simply in going from a high vacuum condition to higher pressures.

GENERAL EXPERIMENTAL PROCEDURE

All experiments were performed in an all-metal bakeable ultra high vacuum system with a base pressure of 10^{-10} to 10^{-11} torr. Nickel, palladium and platinum single crystal rods of $\sim 99.999\%$ purity were spark cut at appropriate angles to generate a disk of ~ 6 mm diameter and 2.3 mm thickness with faces of desired crystallography (checked by Laue X-ray patterns). These faces were first chemically and then mechanically polished. These crystal faces are not perfect at the atomic level. For example, a close-packed plane such as the (111) plane of a cubic close-packed metal will have step and kink imperfections. These deviations from ideality are not generally a problem in assessing chemistry as a function of crystallography. Most of the surface atoms will be in the environment of the selected crystal plane — hence, the observed chemistry will be largely that of the selected plane. In some cases, chemistry associated with, for example, the ubiquitous step or step imperfections of an atomically flat plane can be pinpointed by comparing carefully the spectroscopic features and the chemistry for the (111) plane with those of stepped faces and of stepped-kinked faces of varying periods (for an illustration, see the specific discussion by Friend *et al* of carbon monoxide chemistry on platinum (Ref. 6).

The crystal is affixed to some metal support (typically tantalum) and then mounted on the crystal manipulator, a device that has rotational and translational degrees of freedom for proper positioning of the crystal within the vacuum chamber. Accessory attachments to the crystal are a button heater for heating the crystal and thermocouple leads for temperature measurements of the crystal. At this point, the manipulator with attached crystal is emplaced in the chamber and an extended — 24 to 48 hour — bakeout of the chamber at 230 to 280°C follows. Then the crystal is cleaned.

The crystal is not only contaminated on the surface but also internally and these trace bulk impurities are potential surface contaminants. Very low initial bulk impurities can lead to low surface purities if there is any tendency for segregation of impurities at the surface when the crystal is heated. The number of surface atoms in a metal crystal is about 10^{15} per cm^2 as compared to a bulk density of about 10^{22} atoms per cm^3 . If there were 0.0001% carbon impurity in the bulk and if there was a high degree of segregation at the surface, then the metal crystal could have a full monolayer of carbon on the surface after an annealing treatment. Thus, the metal crystal must be subjected to a stringent purification procedure.

Crystal cleaning procedures are based on the crystal chemistry, the chemistry and the impurity segregation features peculiar to each metal. A conventional cleaning procedure consists of ion (charged argon or neon ion) sputtering of the surface at some temperature whose upper limit is set by phase transitions or the melting point of the metal and impurity segregation characteristics and whose lower limit is set by impurity atom mobility. For example, the major impurities in nickel are sulfur, phosphorus and carbon. Carbon may be removed by oxidation at 350°C. Essentially, all the sulfur and phosphorus atoms can be removed by argon ion bombardment.

Surface purity is established by an Auger analysis in which high energy electrons (1-5keV) are directed at the metal crystal at grazing incidence angles or a normal incident angle. The ejected electrons in this experiment have a relatively short mean escape depth, ca. 5-20 Å, so that the analysis is largely a surface elemental analysis. The Auger analysis for many elements can be very sensitive but is only semiquantitative (factor of two at best) as commonly applied (Ref. 7).

Low energy electron diffraction is a basic surface characterization technique for sensing the ordering of surface metal atoms and of chemisorbed species at a surface. In principle, this diffraction technique can structurally define a chemisorption state but this is a very complicated experimental and theoretical problem (Ref. 8-10). In fact, this technique has been successful structurally only for atoms chemisorbed on a regular surface. By itself, the technique cannot resolve the *full* structural features of multi-atom molecules or molecular fragments, particularly those containing hydrocarbon atoms, chemisorbed on a surface. Angle-resolved photoemission studies (Ref. 11) can assess the orientation of atoms or simple molecules or radicals like CO, CN or NO chemisorbed on flat surfaces but extension to larger and more complicated species obviously is much more difficult. This form of photoemission spectroscopy is complementary to low energy electron diffraction. Information concerning the vibrationally excited states of species chemisorbed on metal surfaces can be obtained by infrared reflection, by high resolution electron energy loss spectroscopy and by other techniques such as ellipsometry and Raman but presently the most sensitive and generally applicable technique is energy loss spectroscopy (Ref. 12). For the studies reported herein, the essential physical techniques were (1) Auger electron spectroscopy for the elemental analysis of the exposed surface, (2) low energy electron diffraction for characterization of the clean metal surface crystallography and of ordered chemisorption states' unit cell size and rotational orientation *vis-a-vis* the metal surface unit cell, and (3) high resolution electron energy loss spectroscopy for

information about vibrationally excited states of the chemisorbed species.

Chemical techniques provide very important information about chemisorbed molecules and surface mediated reactions. Here, the most generally useful, complementary physical technique is mass spectrometry for characterization of the gas phase above the crystal surface. One classic surface science technique is the so-called thermal desorption spectroscopy. In this experiment, the crystal with the chemisorbed species is heated rapidly (at a linear rate of 15 to 50° per second) and with the crystal face aligned with the inlet of a multiplexed mass spectrometer which then senses the molecules released from the crystal face to provide a measure of specific molecules in terms of number and temperature. If, for example, a molecule reversibly chemisorbs, the thermal desorption spectrum characterizes, as a function of initial coverage and of specific heating rate, the temperature at which the rate of desorption is a maximum. In principle, such experiments can establish the order of the desorption process—zero order for physisorbed molecules, first order for chemisorbed molecules, second order for fragments that must combine as for hydrogen where the surface chemisorption state consists of atoms which combine to give gaseous H₂. In principle, the activation energy for desorption can be established—which in the case of reversible chemisorption sets a maximum value for the heat of chemisorption. However, the analysis is subject to assumptions based on an idealized construct of a kinetic model, to an unknown frequency factor, and to experimental constraints including the major one of pumping capability (Ref. 13). For chemisorbed species that decompose partially or wholly, the mass desorption profile can be suggestive of molecular details of the molecular process; four general cases are outlined in Fig. 1.

One of our approaches to chemical characterization of molecular details of surface chemistry is borrowed directly from molecular coordination chemistry—it is the displacement reaction: Molecule A is chemisorbed on a metal surface. Then molecule B, which is or is presumed to be more strongly chemisorbed on the metal surface than A, is introduced. In the ideal case, if A is present on the surface as a molecule, then B will displace A from the surface, provided that the displacement is effected at temperatures where the activation temperature for displacement is exceeded. Because the temperature demands in the displacement reaction are generally less than for thermal desorption reactions, the displacement reaction can be a very sensitive probe of molecular chemisorption states. On the other hand, if molecule A chemisorbs with fragmentation to radical species, then displacement of A by B is a less likely process.

The technique of isotopic labelling and cross labelling that has been so effective for mechanistic studies in solution state chemistry is just as invaluable for surface chemistry—but it has been a rarely employed technique in surface science. It can provide, in an unequivocal fashion, a characterization of the molecular details of surface chemistry.

The Surface Scenario

The prime objective of our surface science studies to date has been the elucidation of the molecular details of hydrocarbon chemisorption and reactions at the surfaces of transition metals as a function of surface crystallography and composition. The metals studied to date have included ruthenium, nickel, palladium and platinum. The last three are face-centered cubic and the primary surfaces of interest have been the (111), (110) and (100) planes and the stepped and stepped-kinked surfaces illustrated in Figs. 2-6. Ruthenium is a hexagonal close-packed metal and to date, only the basal or close-packed (0001) plane has been studied. The hydrocarbons that have been most extensively studied and that have been most informative of molecular features have been benzene and its derivative, toluene, the related 1,3- and 1,4-cyclohexadienes, cyclohexene and cyclohexane. Also informative in a qualitative fashion has been the surface chemistry of other cycloalkenes and cyclopolyenes of the C₈, C₇ and C₄ systems.

Benzene

Benzene chemisorption on the atomically flat Ni(111) and Ni(100) surfaces is fully molecular in character (Ref. 14). Benzene is quantitatively displaced from these surfaces by trimethylphosphine at 25°C. No reversible C-H bond breaking occurs under these conditions as evidenced by the displacement of only C₆H₆ and C₆D₆ by trimethylphosphine from an initial surface state formed from C₆H₆ and C₆D₆. Thermal desorption experiments show competing reactions of benzene desorption and decomposition (to give hydrogen gas and carbon-contaminated surfaces) on these surfaces. Displacement reactions effected as a function of temperature established the temperatures for fast, irreversible C-H bond breaking on these surfaces of ~100-115°C for Ni(111) and ~150-200°C for Ni(100) (Ref. 14). Stepped and stepped-kinked nickel surfaces, 9(111)x(111) and 7(111)x(310) respectively, showed an analogous benzene chemistry to that of Ni(111). However, phosphine displacement of benzene from these surfaces was only ~95 and 90% complete, respectively (Ref. 14).

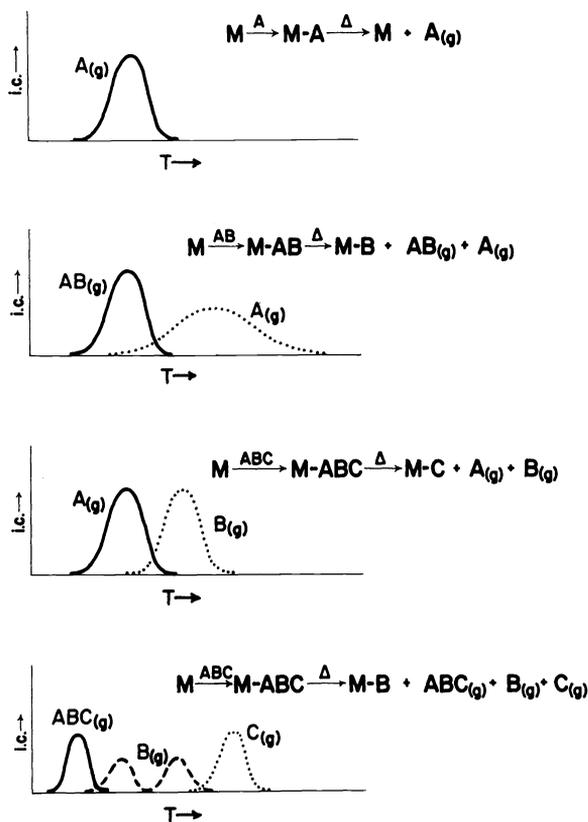


Fig. 1. Illustrative but hypothetical desorption spectra for molecules chemisorbed on a metal surface. Plotted is the ion current for the parent mass ion derived from the gaseous species desorbed from the surface as a function of temperature (line shapes are a function of crystal heating rates among other factors). The top spectrum is the idealized fully reversible adsorption, a situation rarely encountered except for hydrogen, nitrogen, carbon monoxide (electronegative metals), and some saturated hydrocarbons. Following is the desorption spectrum for a system in which the adsorption is only partially reversible; a common example found in surface chemistry is that for hydrocarbons where A represents carbon and $A(g)$ would represent $H_2(g)$. The third spectrum comprises fully irreversible chemisorption; an example is $Ni(111)-CNCH_3$ which primarily yields H_2 at low temperatures and N_2 at high temperatures to leave a $Ni(111)-C$ surface. The last spectrum illustrates competing reversible thermal desorption and thermal decomposition. Note that in the last spectrum $B(g)$ shows two thermal desorption maxima. This type of spectrum with two $B(g)$ desorption maxima is sometimes observed for hydrocarbons on metal surfaces where $B(g)$ is $H_2(g)$; a specific example discussed in the text is the decomposition of toluene on atomically flat metal surfaces.

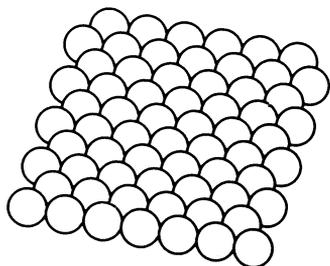


Fig. 2

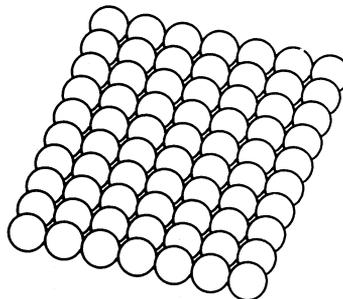


Fig. 3

Fig. 2. A perspective of the (111) plane of a face-centered cubic metal or a (0001) plane of a hexagonal close-packed metal. All metal atoms in the surface plane have a coordination number of nine compared to twelve for those in the bulk.

Fig. 3. This is a representation of the other atomically flat surface, (100), of a face-centered cubic metal. All surface metal atoms have a coordination number of eight.

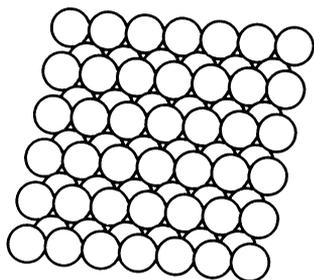


Fig. 4

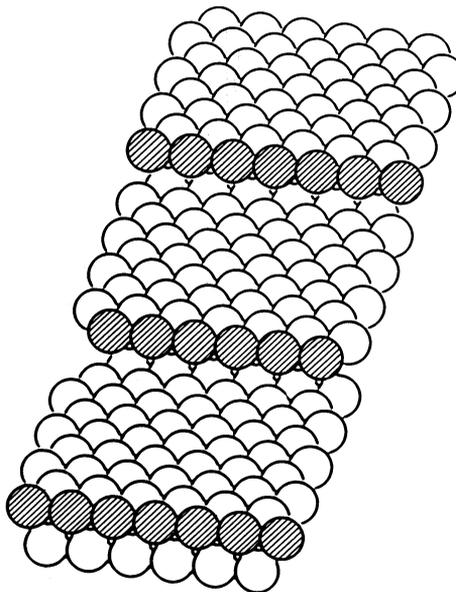


Fig. 5

Fig. 4. The remaining low Miller index plane, the (110) of a face-centered cubic metal is in effect a super stepped surface—every other row is a step. An alternative notation for this surface is $2(111) \times (111)$. The step atoms here have a coordination number of seven and those recessed in the troughs, a coordination number of eleven.

Fig. 5. This is a stepped surface for a face-centered cubic metal. One notation used for this surface is $9(111) \times (111)$: the surface is generated basically from the (111) plane but every ninth row is a step and the steps are one atom high. The step atoms shown as black circles have a coordination number of seven. All atoms of this surface represented here by unshaded circles are in (111) environments.

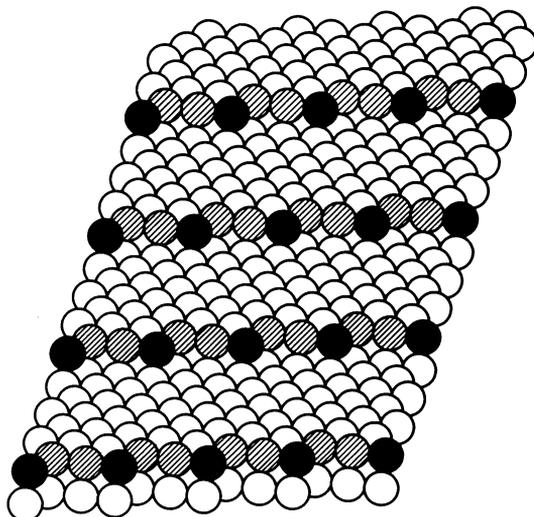


Fig. 6. Related to the stepped surface illustrated in Fig. 4 is the stepped-kinked surface shown above. This has the notation $7(111) \times (310)$. The clear circles represent the so-called terrace or (111) type planes. Every seventh row a one atom step is encountered but this row is uneven with every third (dark shaded circles) atom a kink atom. Kink atoms have a coordination number of six.

All these data (Ref. 14) and earlier low energy electron diffraction (Ref. 15) and vibrational (Ref. 16) studies strongly implicate a benzene chemisorption state (Fig. 7) on the atomically flat nickel surfaces in which the C_6 plane is normal to the surface plane—a feature that is intuitively plausible on purely molecular coordination principles. A similar benzene chemisorption stereochemistry should prevail for the stepped and stepped-kinked surfaces. However, here some C-H hydrogen atoms can closely approach step or kink atoms—a stereochemical feature that could and should lead to C-H bond breaking (Fig. 8). Hence the qualitative differentiation between $Ni(111)$ and its derivative stepped $9(111) \times (111)$ and stepped-kinked $7(111) \times (310)$ surfaces can be readily rationalized.

Similar to nickel(111) in the stereochemistry of chemisorbed benzene was $Ru(0001)$, $Pd(110)$ and $Pt(111)$ —similar in the sense that chemisorption was largely or wholly molecular in character and that reversible C-H bond breaking was not evident at least at moderate temperatures. None of the benzene chemisorption states on atomically flat surfaces was fully thermally reversible. In these cases, thermally excited states for the chemisorbed benzene apparently provide for close approach of C-H hydrogen atoms to the surface which then leads to irreversible (under ultra high vacuum conditions) C-H bond breaking. There were, however, significant differences among these metals in the chemisorption behavior of benzene.

Benzene chemisorption on $Ni(111)$ was characterized by a partial thermal benzene desorption at $\sim 115^\circ C$ and by a quantitative displacement by trimethylphosphine. In contrast, benzene chemisorbed on $Pt(111)$ was partially ($\sim 90\%$) displaced by trimethylphosphine and a relatively complex thermal desorption behavior was observed. There appears to be differentiable benzene chemisorption states. Up to 0.1 of a monolayer benzene adsorption, the majority of the benzene appears to be irreversibly bound (only traces of benzene were thermally desorbed or chemically displaced). This fraction of the benzene may be associated with surface imperfections, e.g., steps and kinks. With coverages between 0.1 and 0.65, a benzene thermal desorption peak at $200-220^\circ C$ was first evident and the intensity was directly related to coverage. At the higher coverages, a second benzene thermal desorption maximum appeared at $\sim 100-130^\circ C$. The presence of these two benzene desorption peaks does not in itself necessarily imply that there are two structurally or stereochemically different benzene chemisorption states (it is possible for a molecular chemisorption state of structural and stereochemical singularity to yield two or more molecular thermal

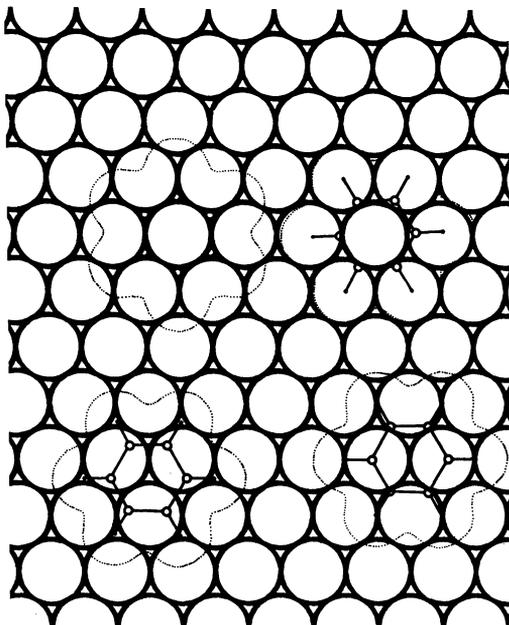


Fig. 7. An infinite array of registries for Ni(111)-C₆H₆ are consistent with the low energy electron diffraction study of the ordered chemisorption state. Shown above are four idealized possibilities with the C₆ centroid centered over a single nickel atom, over two-fold sites and over three-fold sites. Each of the possible registries are consistent with the $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ unit cell established by low energy electron diffraction studies and vibrational (high resolution electron energy loss) data. The benzene bond distances were derived from X-ray and neutron diffraction study of C₆H₆Cr(CO)₃; the dotted lines define the van der Waals outline of the benzene molecule. Because the distance between hydrogen atoms at para positions in the benzene molecule is virtually identical to twice the nickel atom diameter, the registry with the C₆ centroid atop a single nickel atom is precise (upper left and right). Overlaps with the π and π^* benzene orbitals and metal surface orbitals should be excellent. In one rotational form (upper right) the hydrogen atoms of the benzene lie directly over single nickel atoms so as to generate multicenter C-H-Ni bonds. The van der Waals extension of the benzene molecule (dotted line) is virtually identical with the space occupied by the central nickel atoms and the surrounding six nickel atoms. Another form generated from the above by a rotation of 30° has the C-H hydrogen atoms lying nearly above the two-fold sites (upper left). Either of these may be the most stable registry for benzene on this surface.

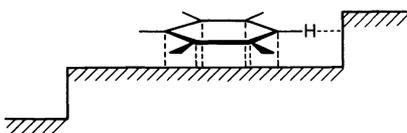


Fig. 8. This schematic representation for π bound benzene on a stepped or stepped-kinked surface illustrates the potential close approach of C-H hydrogen atoms to surface step atoms.

desorption maxima because of cooperativity effects).

There is an intriguing relationship among these apparently differentiable benzene chemisorption states on Pt(111) as shown in experiments wherein C_6D_6 was first adsorbed to a coverage of about 0.5 and then C_6H_6 was adsorbed to a final coverage of about 0.65. In the thermal desorption experiment, the C_6D_6 largely appeared in the high temperature range of 200–220°C; very little was detected in the low temperature peak range of 100–130°C. Thus, there appeared to be little interchange of benzene between the two differentiable states. However, when this experiment was repeated with C_6H_6 adsorption to a final saturation coverage of about 0.9, the C_6D_6 appeared in both desorption ranges. Under these conditions, there was an interchange. Finally, if C_6D_6 was adsorbed to saturation coverage and then the crystal was exposed to a C_6H_6 flux for an extended time period, the thermal desorption spectrum was largely composed of C_6H_6 molecules—the C_6D_6 molecules had been largely displaced (HD and D_2 were also detected, indicating that some or most of the irreversibly chemisorbed benzene molecules were derived from C_6D_6).

Benzene chemisorption on a stepped Pt 6(111)x(111) surface at less than ~ 0.33 of a monolayer was fully irreversible thermally and no benzene molecules were displaced by trimethylphosphine. Above a third of a monolayer coverage, benzene desorption was detected with a primary maximum at $\sim 175^\circ C$ and at higher coverage with a second maximum at $\sim 100^\circ C$. Chemisorption of C_6H_6 and C_6D_6 on the stepped surface gave at high coverages thermal desorption maxima at ~ 175 and $100^\circ C$ with the lower one composed solely of C_6H_6 and C_6D_6 molecules and the higher one composed of all possible $C_6H_{6-x}D_x$ molecules. This experiment unequivocally established two features of the benzene chemisorption state on the stepped surface:

- (i) There are at least two different benzene chemisorption states on this surface: one that is strongly bound and the other relatively weakly bound. There is no fast interchange of benzene molecules between these two states. Vibrational data for Pt(111)- C_6H_6 reported by Lehwald, Ibach and Demuth have been interpreted in terms of two co-existing states with the C_6 centroid over a single platinum atom and over a three-fold site (see Fig. 7 & Ref. 16).
- (ii) Reversible C-H bond breaking occurs only in the more strongly bound state and does not occur at $25^\circ C$ as shown in $P(CH_3)_3$ displacement reactions for Pt 6(111)x(111)- C_6H_6 - C_6D_6 . This effective H-D exchange process is unique to the stepped surface; the flat (111) platinum surface did not effect H-D exchange between C_6H_6 and C_6D_6 . None of the nickel surfaces, including the stepped and stepped-kinked surfaces effected reversible C-H bond breaking but this is probably reflective of a thermodynamic constraint for nickel under ultra high vacuum conditions. In any case, there is a topographical or electronic feature (or both features) intrinsic to the stepped surface that allows a more facile C-H bond breaking process for chemisorbed benzene (nickel and platinum) and that also allows reversible C-H bond breaking on the platinum surface. Benzene is primarily bound on atomically flat or largely flat metal surfaces in a π fashion with the C_6 ring plane (see Fig. 7) nearly parallel to the surface plane. In this configuration, C-H bond breaking is not favorable—thermal excitation is required before significant bond breaking occurs ($\sim 100^\circ C$ and $180^\circ C$ for Ni(111) and Ni(100), respectively). With stepped and stepped-kinked surfaces, some benzene C-H hydrogen atoms can closely approach surface metal atoms (see Fig. 8). Hence the distinction in benzene chemistry between the (111) and the stepped surfaces may be largely topographical rather than electronic in character.

One further comment regarding the benzene system is that the platinum surface chemistry appears more complicated than that for nickel. This is not an uncommon facet of platinum surface chemistry—often there appear to be more than one chemisorption state at $20^\circ C$ on a well-defined platinum surface like the (111) whereas there typically appears to be only one such state for the analogous nickel surface. One experimental difficulty that may account for a small part of the differential behavior is that it is more difficult to prepare specific crystal surfaces largely free of imperfections for platinum than for the harder nickel metal.

Toluene

Toluene irreversibly chemisorbs on all the nickel surfaces. On heating, hydrogen was evolved with two discrete desorption maxima: at ~ 130 and $185^\circ C$ on Ni(111), Ni 9(111)x(111) and Ni 7(111)x(310) and at 110 and $230^\circ C$ on Ni(100). On the ruffled Ni(110) surface, toluene decomposition gave rise to a single H_2 desorption maximum at $\sim 150^\circ C$ (Ref. 14). These results implied that different types of C-H bonds were broken at different temperatures. Accordingly, the thermal decomposition of the isomeric molecules, $C_6H_5CD_3$ and $C_6D_5CH_3$ was examined on these surfaces. For the Ni(100)-toluene surface, a single D_2 desorption curve was observed for $C_6H_5CD_3$ and for $C_6D_5CH_3$ with desorption maxima at ~ 110 and $230^\circ C$, respectively. A fully analogous behavior was extant for the Ni(111), Ni 9(111)x(111), and Ni 7(111)x(310) surfaces: for each surface there was a single D_2 desorption peak for $C_6H_5CD_3$ and for $C_6D_5CH_3$ with desorption maxima at ~ 130 and $185^\circ C$, respectively. Toluene thermal decomposition on Ni(110) showed no differentiation in D_2 desorption between $C_6H_5CD_3$ and $C_6D_5CH_3$.

These labelled toluene studies established that for the flat surfaces, aliphatic C-H bond breaking proceeds before aromatic C-H bond breaking. No aromatic C-H bonds were broken below temperatures of ~ 160 and $\sim 200^\circ\text{C}$, respectively, for the Ni(111) and Ni(100) surfaces. Conversely, all aliphatic C-H bonds in chemisorbed toluene were broken *below* or at temperatures of ~ 130 and $\sim 100^\circ\text{C}$ for the Ni(111) and Ni(100) surfaces, respectively. Because hydrogen desorption from these surfaces is an activated process, temperatures of 70 and 120°C are required before hydrogen atoms on the surface recombine and desorb as H_2 (or D_2) from the Ni(100) and Ni(111) surfaces, respectively, at saturation coverages. Thus, some C-H bonds in toluene *could* be cleaved at temperatures as low as 25°C . Our experiments do not define the temperature at which C-H bond cleavage *first* occurs for toluene (whereas this temperature was defined for the benzene case). We tentatively suggest that toluene is bound near room temperature on the flat (111) and (100) surfaces not as the toluene molecule but as a planar benzyl radical. Toluene should initially chemisorb in a fashion analogous to that proposed for benzene, but this necessarily places methyl group hydrogen atoms in close proximity to the surface metal atoms whereby aliphatic C-H bond cleavage of these C-H bonds should be facilitated and a planar C_7 benzyl species may be generated. The latter species can optimally bond with metal surface orbitals through all seven carbon atom donor and acceptor orbitals and all seven hydrogen $1s$ orbitals. All the labelling studies support this representation. None of the data allow such mechanistic interpretations for the (110) surface but here too the toluene chemisorption state probably does not comprise an intact toluene molecule.

Cyclohexene, Cyclohexadiene and Cyclohexane

The surface chemistry of simple olefins and acetylenes is seemingly complex and a fully definitive characterization of ethylene and acetylene chemisorption states on nickel group metals has not been achieved yet. For an atomically flat surface, the initial interaction of an olefin with the surface atoms should primarily involve the π and π^* orbitals of the unsaturated molecule such that the unsaturated C-C bond should be nearly parallel to the surface plane. If the olefin is cyclohexene, there will be saturated C-H hydrogen atoms very close to the surface and these will be susceptible to facile bond breaking (see Fig. 9). In fact, a common reaction of cyclohexene at a metal surface is dehydrogenation to give benzene; cyclohexadienes show this same dehydrogenation behavior.

Cyclohexene was found to chemisorb on Ni(111), Ni(110) and Ni(100) and to undergo dehydrogenation to benzene at 20 – 60°C —as established by trimethylphosphine displacement of benzene from these surfaces. When $c\text{-C}_6\text{H}_{10}$ and $c\text{-C}_6\text{D}_{10}$ mixtures were employed, only C_6H_6 and C_6D_6 were formed. Carbon contamination greatly increased the effectiveness of the (110) surface for the cyclohexene dehydrogenation. Analogous results were observed for the nickel surface chemistry of 1,3- and 1,4-cyclohexadiene.

Cyclohexene reactions on the platinum (111) surface were analogous to those on nickel but the dehydrogenation temperature was higher for platinum. Thus on Pt(111), chemisorbed cyclohexene dehydrogenated to benzene above $\sim 80^\circ\text{C}$; reaction rate was moderate at 100°C and fast at 130°C . These temperatures were established by heating Pt(111)- $c\text{-C}_6\text{H}_{10}$ to a set temperature, introducing trimethylphosphine, and monitoring by mass spectrometry the gas phase above the crystal for the appearance of benzene. Dehydrogenation of $c\text{-C}_6\text{H}_{10}$ and $c\text{-C}_6\text{D}_{10}$ on Pt(111) at 100 – 130°C yielded all possible $\text{C}_6\text{H}_6\text{-xD}_x$ species.

In contrast to Pt(111), the stepped Pt 6(111)x(111) surface effected dehydrogenation of cyclohexene to benzene at 20°C as evidenced by benzene displacement from Pt 6(111)x(111)- $c\text{-C}_6\text{H}_{10}$ on exposure to trimethylphosphine. When Pt 6(111)x(111)- $c\text{-C}_6\text{H}_{10}$ - $c\text{-C}_6\text{D}_{10}$ was simply heated, C_6H_6 and C_6D_6 desorbed at 90 – 115°C and all possible $\text{C}_6\text{H}_x\text{D}_{6-x}$ benzene molecules desorbed at $\sim 175^\circ\text{C}$. The temperature at which C-H H-D exchange occurred on this surface was above 20°C but the precise temperature has not been defined.

Cyclohexadiene, either isomer, chemisorbed and underwent dehydrogenation on Pt(111) even at 0°C . Clearly, the benzene formation occurs on this surface much more readily from cyclohexadiene than from cyclohexene. For the diene, the stepped platinum surface effected benzene formation at 20°C and lower.

Demuth, Ibach and Lehwald (Ref. 16) have shown that cyclohexane chemisorbed on Ni(111) at low temperatures desorbs at $\sim 100^\circ\text{C}$ in a quantitative fashion. Consistent with this report, we found no evidence of cyclohexane reaction with Ni(111) at 0 – 70°C , Ni(110) at 25 – 90°C , and Ni(100) at 25 – 200°C . Hence the residence time for cyclohexane on these surfaces within these temperature ranges and under the ultra high vacuum conditions was short relative to the rate of any dehydrogenation process.

Cyclohexane chemisorption on Pt(111) has been reported as partially reversible at the 0°C temperature of maximum desorption rate. We found that Pt(111)- $c\text{-C}_6\text{H}_{12}$, formed at -15 to -35°C , gave a cyclohexane thermal desorption maximum at $\sim 0^\circ\text{C}$. The desorption was nearly quantitative although a small amount of hydrogen was desorbed from the surface at much higher temperatures, a weak broad desorption between 200 and 400°C . No benzene was detected

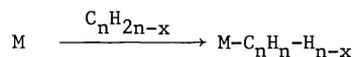
in the thermal desorption experiment; however, a small amount of cyclohexane could have been converted to benzene and gone undetected in the thermal desorption experiment. Treatment of Pt(111) with cyclohexane at 134°C gave a state that yielded only hydrogen, no benzene, in a thermal desorption experiment and left about a tenth of a monolayer of carbon on the surface.

Cyclohexane has a much higher sticking coefficient on Pt 6(111)x(111) than on Pt(111) and appeared to saturate at a coverage of about 0.20 to 0.25 of a monolayer. For this surface, the thermal desorption and displacement reactions established that dehydrogenation to benzene had occurred. (In assessing the experimental results, it is essential to keep in mind that benzene chemisorbed at below one-third monolayer coverage on this stepped platinum surface cannot be thermally desorbed or displaced by trimethylphosphine at 30°C as intact benzene). No benzene was detected in thermal desorption or chemical displacement reactions with the stepped surface treated with cyclohexane (~0.25 monolayer). In the thermal desorption experiment, there were three H₂ desorption maxima at ~110, 169 and 314°C which corresponded precisely to the desorption maxima of ~110 to 130°C for free H on this surface and to the benzene decomposition—hydrogen maxima of ~169 and 314°C—on this stepped surface. Thus the chemisorption state generated in the cyclohexane reaction with the stepped surface appears to be best characterized as Pt 6(111)x(111)-C₆H₆-H with all the benzene molecules residing in the most strongly bound state as established in the benzene experiments with the stepped platinum surface. Remaining open sites on this Pt 6(111)x(111)-C₆H₆-H surface were incapable of effecting cyclohexane dehydrogenation and coverages above 0.25 could not be realized at moderate temperatures and the low pressures of the ultra high vacuum system. However, treatment of this saturated state with trimethylphosphine followed by thermal desorption did yield some gaseous benzene at a desorption maximum of 164°C.

These experiments establish for the platinum system at least a quantitative difference between the atomically flat (111) and the stepped 6(111)x(111) surfaces in the dehydrogenation of cyclohexane. If the extent of the cyclohexane reaction on the Pt(111) surface is largely due to surface imperfections, e.g., steps, then the difference between the two surfaces in this cyclohexane chemistry is a qualitative one.

Cycloalkene and Cyclopolyene Chemistry

In principle, it should be possible to extend the cyclohexene and cyclohexadiene surface chemistry to other hydrocarbon ring systems. Possibly, the general and favorable end state after dehydrogenation would be M_{surface}-C_nH_n with a delocalized planar C_n ring system largely π bound to the surface. Certainly, in molecular coordination chemistry, these species are well-defined for n = 3 through 8. Definitive characterization of a surface process comprising dehydrogenation of a cycloalkene or cyclopolyene to C_nH_n species:



is most readily achieved if the C_nH_n species can be thermally desorbed or displaced by another molecule and then characterized by mass spectrometry. However if n is odd, C_nH_n is a radical and is not desorbable, as such, into the gas phase. Spectroscopy is the only alternative to a study of odd numbered C_nH_n surface species.

Cyclooctatetraene chemisorbed in a partially reversible fashion on Pt(111); on heating, cyclooctatetraene desorbed at ~150°C. Trimethylphosphine displaced the tetraene from these surfaces at 20°C but not quantitatively. Cyclooctadienes and cyclooctene reacted with Pt(111) with at least partial conversion to cyclooctatetraene at temperatures above 20°C. For example, adsorption of 1,3-cyclooctadiene on Pt(111) (0.6 of a monolayer) yielded a state from which no cyclooctatetraene could be displaced by trimethylphosphine at 20°C. However, if the crystal was heated to 100°C, and then the trimethylphosphine was introduced, cyclooctatetraene was displaced. Similar results were obtained with cyclooctene but only at very high coverages, ~1.0 monolayer.

Although the conversions for the cyclooctadiene and cyclooctene dehydrogenations apparently are not high, the analogy to the C₆ system is established. These studies do not define the stereochemistry of the Pt(111)-C₈H₈ state; the tetraene could be planar and parallel with the surface plane or it could be bound as a diene. Spectroscopic studies in progress may resolve this stereochemical issue.

Cyclobutene surface chemistry is now under study. Cyclobutane did not have a significant sticking coefficient on Pt(111) at 0°C or at 90°C. No cyclobutadiene was detectably desorbed from these surfaces in thermal desorption experiments. However, small amounts of cyclobutadiene appeared to be displaced by trimethylphosphine from a Pt(111) surface on which cyclobutane had been adsorbed at 20°C. Monosilacyclobutane did not react detectably with Pt(111) at ~20°C.

Cycloheptatriene surprisingly was readily desorbed thermally from Ni(100) after adsorption at 20°C. The thermal desorption maximum was ~100°C. Two competing thermal reactions were:

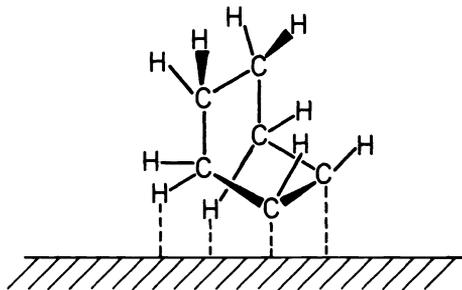


Fig. 9

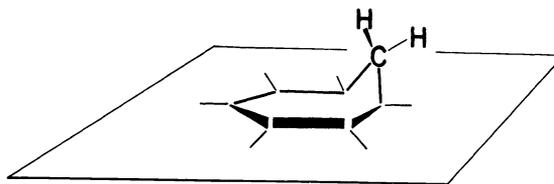
CYCLOHEPTATRIENE

Fig. 10

Fig. 9. The presumed initial chemisorption state of cyclohexene on a flat metal surface is shown here. Initial bonding should largely involve the π and π^* orbitals of the olefinic function so that the olefinic C-C bond vector should be parallel, or nearly so, to the surface plane. Irrespective of the conformation of the C_6 ring, some aliphatic C-H hydrogen atoms should be near to the surface plane and these C-H bonds should be susceptible to facile cleavage.

Fig. 10. Illustrated above for cycloheptatriene chemisorbed on an atomically flat surface plane is one possible stereochemistry in which none of the C-H hydrogen atoms can closely approach the surface metal atoms—a feature that would seem to be required for Ni(100)- C_7H_8 because a significant fraction of cycloheptatriene chemisorbed on Ni(100) can be thermally desorbed.

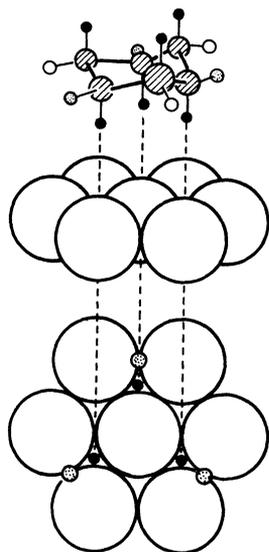


Fig. 11

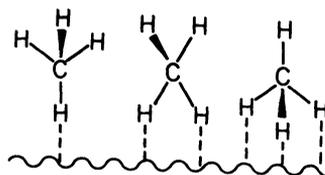


Fig. 12

Fig. 11. A representation of the interaction of cyclohexane (chair form) with Ru(0001) as suggested by Madey and Yates (Ref. 18) in their classic study of hydrocarbon chemisorption on this basal plane of ruthenium. Three Ru-H-C three-center bonds are formed with three of the axial hydrogen atoms on one side of the chair form of cyclohexane. Weaker three-center Ru-H-C bonds may also be present with equatorial C-H hydrogen atoms.

Fig. 12. Three idealized representations of possible structures for chemisorbed methane. The representation on the right is not far removed from representations of transition states in SN_2 nucleophilic substitution reactions of tetrahedral carbon except for the (presumed) multicenter C-H-M interactions.

(1). degradation to give H_2 and $Ni(100)-C$, a reaction that was inhibited if the $Ni(100)$ surface was partially carbided prior to cycloheptatriene adsorption and (2). formation of benzene. On $Ni(110)$, cycloheptatriene adsorbed in a largely irreversible fashion although some cycloheptatriene desorbed thermally at $\sim 100^\circ C$. No hydrocarbons thermally desorbed from $Pt(111)$ -cycloheptatriene.

Chemisorption of cycloheptatriene was expected to be accompanied by dehydrogenation to give $Ni(100)-C_7H_7$ which should simply decompose in a thermal desorption experiment to give H_2 and $Ni(100)-C$. This decomposition reaction could be accompanied by a rearrangement to toluene or benzyl but the hydrogen desorption profile for these species on $Ni(100)$ are very characteristic and there was no correspondence here: cycloheptatriene does not rearrange in any significant fashion to toluene or benzyl. The observed cycloheptatriene degradation may simply be representative of the sequence $Ni(100)-C_7H_8 \rightarrow Ni(100)-C_7H_7-H$ several steps $Ni(100)-C + H_2(g)$. There were two unexpected features to the $Ni(100)$ -cycloheptatriene thermal desorption behavior. Firstly, the desorption of a substantial fraction of cycloheptatriene as cycloheptatriene requires that the chemisorption state precursor to thermal desorption have all the C-H hydrogen atoms relatively far removed from the vicinity of the surface atoms. A speculative representation is shown in Fig. 10. Secondly, the formation of benzene as a decomposition product was not anticipated. However, it is notable that molecular transition metal coordination complexes of cycloheptatriene do show conversion to $M-\eta^6-C_6H_6$ complexes.

Norbornadiene is the other isolable C_7H_8 isomer to toluene and cycloheptatriene. This diene showed a high sticking coefficient on $Pt(111)$ at $20^\circ C$. At high coverages of the diene on this platinum surface, thermal desorption led to the desorption of hydrogen and of benzene (at $250^\circ C$)—at low coverages, no hydrocarbon molecules could be thermally desorbed.

The absence of a significant norbornadiene desorption peak is somewhat surprising. If the norbornadiene is bound as a diene, the only C-H hydrogen atoms that might closely approach the surface metal atoms (and consequently undergo C-H bond fission) are the olefinic hydrogen atoms.

Clearly, the metal surface chemistry of cycloalkenes and cyclopolyenes is relatively complex but is interpretable. The key stereochemical issue is the placement of C-H hydrogen atoms relative to the surface metal atoms. If the placement is close, then dehydrogenation is the favored process. If the C_nH_x surface species is a radical then neither thermal desorption nor chemical displacement will yield a gaseous C_nH_x species. A C_nH_x molecular species will be displaced, thermally or chemically, provided that all C-H hydrogen atoms are relatively far removed from the surface metal atoms.

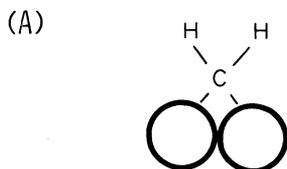
Chemisorption of Saturated Hydrocarbons.

Saturated hydrocarbons typically chemisorb on clean metal surfaces only at low temperatures. The nature of the surface chemical bond has not been definitively established for these saturated hydrocarbons. Methane, for example, does not react with metal surfaces at $20^\circ C$ or moderately higher temperatures; its desorption temperature for most metal surfaces is well below $20^\circ C$. Three plausible representations of a methane chemisorption state are illustrated in Fig. 11. In these representations, the bonding comprises C-H-M multicenter interactions. In principle, the tridentate form should be more stable than bidentate, etc. However, the ionization potential of methane is so high that it is not clear from purely qualitative considerations which of these forms should be the most stable one. It is important to note that the monodentate form is not an intermediate directly productive to methane reaction at a surface to give, initially, $M_{surf.}-CH_3$ and $M_{surf.}-H$ species whereas the other forms should be productive: C-H bond stretching so as to ultimately generate $M_{surf.}-H$ bonds would also provide a reasonable pathway for the formation of $M_{surf.}-C\sigma$ bonds from the initially bidentate or tridentate forms. To gain some structural insight to this methane question, we plan low temperature studies of methane chemisorption states using photoemission and high resolution electron energy loss spectroscopy. Interestingly, a photochemically excited higher energy state for copper atoms reacts with methane at low temperatures to form CuH and CH_3 species presumably through a CH_3CuH intermediate (Ref. 17). Of interest here is the stereochemical nature of the $Cu-CH_4$ precursor state.

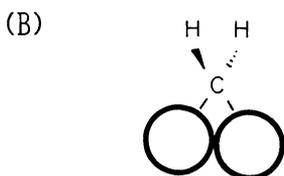
Higher hydrocarbons whether cyclic or acyclic should have and do have a tighter bonding on metal surfaces—the ionization potentials are lower than for methane and the number of individual carbon atom C-H- $M_{surf.}$ multicenter bonds can be greater. Madey and Yates (Ref. 18) have suggested that cyclohexane is chemisorbed on close-packed metal surfaces, e.g., $Ru(0001)$, through multicenter C-H-M bonds as shown in Fig. 12.

Derivative of methane chemisorption is the surface chemistry of methyl, methylene, and methylidyne fragments. Although these fragments undoubtedly are intermediates in many surface reactions, the synthesis of a metal surface chemisorption state based wholly or largely on any one of the three radicals has not been demonstrated—the intrinsic surface reactivity of such fragments complicates the synthesis problem. While seeking a solution to this experimental problem, we have sought insight from a theoretical analysis (Ref. 19).

Any theoretical analysis of surface chemisorption states or surface reactions presently is at best a crude approximation of the real surface state. Our analysis is based on the extended Hückel molecular orbital method—not because it is superior to other methods but because of our familiarity with this method in molecular structure and with its deficiencies or limitations. Chosen for a reference surface was the Ni(111) plane. Of the three fragments, methylene was initially the most informative in the calculations (Ref. 19). These suggested that the most stable surface site was the carbon atom located at a two fold site and bonded to nickel atoms— and with the CH₂ plane normal to the surface plane. Interestingly, the calculations suggested that the most stable conformer was with the CH₂ plane enclosing the Ni-Ni bond vector of the two nickel atoms bonded to the carbon atom:



rather than the conventional conformer observed for bridging methylene groups in molecular complexes:



The reason that the former appeared to be more stable was the more effective C-H-Ni multicenter interaction.

Consistent with the CH₂ calculations, the most stable surface configurations for CH₃ (A) and CH (B) were (A) with the CH₃ carbon atom bonded symmetrically to three nickel atoms and the three hydrogen atoms lying above these three nickel atoms (again with some degree of C-H-Ni multicenter bonding) and (B) with the CH carbon atom primarily bonded to two nickel atoms and with the C-H bond vector tipped so as to generate a multicenter C-H-Ni interaction.

Because of the crude character of these largely topological calculations, no substantial reliability can be assigned to them—but they are suggestive in a general context. The significance of the calculational results is not in the relative ordering (energy) of possible stereochemical form for a given CH_x species but in the incisive identification of C-H-M multicenter bonding as a secondary bonding interaction and an interaction that may be stereochemically determinant. Given the relatively high coordination unsaturation of surface metal atoms, multicenter C-H-M_{surf} bonds will probably tend to form, especially if the metal is relatively electropositive and if the C-H hydrogen atoms can closely approach the surface metal atoms. In the molecular chemisorbed state of olefins, alkynes, and arenes wherein the primary bonding involves the π and π^* orbitals associated with the carbon atoms, secondary C-H-M multicenter bonding may or may not be significant, depending upon the surface topography—i.e., the ease with which the C-H hydrogen atoms can approach the surface metal atoms. For saturated hydrocarbons, multicenter C-H-M interactions probably will provide the major bonding contributions for the chemisorption state (Ref. 19).

Most importantly, a surface C-H-M multicenter interaction resembles a way point in the basic hydrocarbon process of carbon-hydrogen bond breaking. This process is the most dominant hydrocarbon surface reaction at moderate temperatures—carbon-carbon bond breaking generally requires relatively high temperatures. Allow D₂ and a hydrocarbon to coreact on a metal surface at even 20°C, and the hydrocarbon will become rapidly enriched in deuterium. In order to selectively break and reform carbon-hydrogen bonds on a metal surface, the surface topography must be tailored to the stereochemical features of the initial C-H-M interaction and of the scission state of C-M and H-M. Our nickel surface studies of toluene incisively demonstrate a selective scission of the aliphatic C-H bonds at temperatures characteristic of the specific metal surface. Selectivity here requires an atomically flat surface. These idealized studies are related to real world catalysis: an irregular nickel surface shows no selectivity in the H-D exchange reaction between D₂ and C₆H₅CH₃; however nickel crystallites, probably largely in the form of cube octahedra which have flat (111) and (100) surface planes do show selective deuterium introduction into the aliphatic position of toluene.

Molecular organometallic chemistry has provided many examples in which there is multicenter C-H-M bonding. A significant fraction of these have been crystallographically defined either from X-ray or neutron diffraction data—these structural data show a wide range of hydrogen-metal atom distances (1.74 Å is the shortest presently established) and that the C-H-M array is always bent, never linear. If a large collection of such structures with very accurate hydrogen positions could be obtained (Ref. 20 & 21), then the set could be used to approximately map out part of the geometric reaction pathway, i.e., the distances and angles for C-H-M, in the carbon-hydrogen bond breaking reaction. To a first approximation, such a shape analysis from the molecular organometallic regime would be useful in better understanding geometric features of the surface regime.

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