Lawrence Berkeley National Laboratory
Lawrence Berkeley National Laboratory

Title
CATALYSIS BY PLATINUM SINGLE CRYSTAL SURFACES: LOW PRESSURE HYDROCARBON REACTIONS AND THE EFFECTS OF INTRODUCING STRONGLY BOUND OXYGEN AT THE SURFACE

Permalink
https://escholarship.org/uc/item/9nf953vv

Author
Smith, Carol Ellen

Publication Date
1978-07-01
CATALYSIS BY PLATINUM SINGLE CRYSTAL SURFACES:
LOW PRESSURE HYDROCARBON REACTIONS AND THE EFFECTS
OF INTRODUCING STRONGLY BOUND OXYGEN AT THE SURFACE

Carol Ellen Smith
(Ph.D. thesis)
July 1978

Prepared for the U. S. Department of Energy
under Contract W-7405-ENG-48

TWO-WEEK LOAN COPY
This is a Library Circulating Copy which may be borrowed for two weeks.
For a personal retention copy, call Tech. Info. Division, Ext. 6782
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.
CATALYSIS BY PLATINUM SINGLE CRYSTAL SURFACES:
LOW PRESSURE HYDROCARBON REACTIONS AND THE EFFECTS
OF INTRODUCING STRONGLY BOUND OXYGEN AT THE SURFACE

Carol Ellen Smith

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

This work was done with support from the U.S. Department of Energy
CATALYSIS BY PLATINUM SINGLE CRYSTAL SURFACES: LOW PRESSURE HYDROCARBON REACTIONS AND THE EFFECTS OF INTRODUCING STRONGLY BOUND OXYGEN AT THE SURFACE

Contents

Abstract ................................................................. v

I. Introduction ......................................................... 1

II. Experimental Procedures and Difficulties ................. 8

  2.1. Experimental Apparatus ................................. 8
  2.2. Platinum Single Crystal Catalysts .................. 14
  2.3. Experimental Procedure ................................. 17
  2.4. Determination of Oxygen Coverages ................. 23
  2.5. Experimental Difficulties ............................... 28
     2.5.1. Choosing the Reaction Conditions ............. 28
     2.5.2. Contribution of the Mass Spectrometer Ionizer to the System Reactivity ............. 48
     2.5.3. Constant Pressure Corrections ................. 50
     2.5.4. Cleaning Procedures ............................ 52
     2.5.5. Uncertainties in the Pumping Speed and Gain of the Electron Multiplier ........... 53

III. The Effect of Strongly Bound Oxygen on the Dehydrogenation and Hydrogenation Activity and Selectivity of Platinum Single Crystal Surfaces ......................... 55

  3.1. Introduction .................................................. 55
  3.2. Oxygen Treatment of Platinum Single Crystals .... 57
  3.3. Results ..................................................... 61
      3.3.1. LEED Studies of Nonreactive Oxygen Adsorbed on Platinum ..................... 61
3.3.2. The Dehydrogenation and Hydrogenation of Cyclohexane .................. 65
3.3.3. The Dehydrogenation of cyclohexane ................. 73
3.4. Discussion ............................................. 82
  3.4.1. AES and LEED Studies ............................ 82
  3.4.2. Reactivity Studies ............................... 85
3.5. Conclusions ............................................ 96
IV. Other Low-Pressure Reactivity Studies .................... 98
  4.1. Introduction .......................................... 98
  4.2. The Formation of Ordered Carbonaceous Overlays .... 99
  4.3. Dehydrocyclization of n-Heptane--Results and Discussion ..................... 105
  4.4. Isomerization Studies ................................ 106
Acknowledgements .......................................... 108
Appendix A. Stereographic Projection, Laue X-Ray Diffraction Techniques, and LEED, with Special Emphasis on Stepped and Kinked Surfaces .................. 109
Appendix B. Pumping Speed Calculations ....................... 162
Appendix C. Calculation on Reaction Rates and Turnover Numbers 173
References ............................................... 174
CATALYSIS BY PLATINUM SINGLE CRYSTAL SURFACES: LOW PRESSURE HYDROCARBON REACTIONS AND THE EFFECTS OF INTRODUCING STRONGLY BOUND OXYGEN AT THE SURFACE

Carol Ellen Smith

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
and
Department of Chemistry
University of California
Berkeley, California 94720

ABSTRACT

The dehydrogenation of cyclohexene and cyclohexane, and the hydrogenation of cyclohexene were studied on the clean and preoxidized surfaces of three platinum single crystals: a Pt(111), a stepped Pt(S) - [6(111) x (100)] and a kinked Pt(S) - [7(111) x (310)]. The choice of reaction conditions is discussed with respect to detection limits and the variation of the catalyst reactivity with reagent pressures and catalyst temperature; the reactions were carried out using flow conditions at low pressure (10^{-6} to 10^{-5} torr total pressure), at a platinum temperature of 150°C.

Oxygen coverages were monitored by Auger electron spectroscopy (AES), an Auger peak ratio of O_{510}/Pt_{237} = 0.5 having been determined to correspond to approximately 5 \times 10^{14} oxygen atoms/cm^2. The surface structures of the clean and oxidized platinum crystals were determined by low energy electron diffraction (LEED): after high temperature (800°C) oxygen treatment, the predominant oxygen structure observed on the Pt(111) was a (2 \times 2); the predominant oxygen structure observed on both the Pt(S) - [6(111) x (100)] and the Pt(S) - [7(111) x (310)] was a (\sqrt{3} \times \sqrt{3}) - R30°.
Low coverages of strongly bound oxygen enhanced the rates of the dehydrogenation and hydrogenation reactions, and changed the selectivity of cyclohexene dehydrogenation to benzene over hydrogenation to cyclohexane. These effects of preoxidation on catalytic rates and selectivity were found to be sensitive to the structure of the platinum surface, kink sites playing a particularly active role in the enhancement of dehydrogenation and hydrogenation activity by strongly bound oxygen. Three models are discussed which relate the oxidation of platinum surfaces to the observed effects on catalytic reactivity and the structure sensitivity. A change in the electronic structure of the platinum surface through oxidation provides the best general model for explaining the oxygen effects, though complex formation involving the adsorbed oxygen or surface reconstruction during oxidation may also be important.

In addition to the investigations of cyclohexene and cyclohexane dehydrogenation and cyclohexene hydrogenation, several preliminary studies of other low-pressure reactions are reported on. The dehydrocyclization of n-heptane to toluene and benzene was studied on the clean Pt(111), stepped, and kinked surfaces, and on these surfaces with ordered carbonaceous overlayers and with various coverages of strongly bound oxygen. No enhancement of this reaction was observed in the presence of strongly bound oxygen or ordered carbon structures. The studies of neo-pentane and iso-butane in the presence of excess hydrogen showed that under the low pressure conditions used in this investigation, hydrogenolysis reactivity was favored over isomerization reactivity on the kinked Pt(S) - [7(111) x (310)].
I. INTRODUCTION

Platinum is one of the most versatile and widely used catalysts known. Classes of reactions in which it plays a vital catalytic role include oxidation, reduction, hydrogenation, dehydrogenation, dehydrocyclization and isomerization. Such reactions lie at the heart of industrially important processes such as hydrocarbon reforming (where low octane hydrocarbons such as straight-chain paraffins are "reformed" into higher octane species, such as the aromatics or branched hydrocarbons) and automobile emission control. Because of the high cost of platinum, a practical catalyst typically contains only a small amount of metal (about 1% by weight) dispersed as small particles on a high surface area support such as alumina or silica. The metal particles typically range from 100 to 500Å in diameter; in the smaller particles, almost every platinum atom is exposed at the surface, providing a very efficient use of the metal. As the particle size changes from 10Å to about 50Å, there is a rapid change in the average coordination number of a metal atom at the surface (1,2), from low values characteristic of structural defects such as corner and edge sites to higher values characteristic of the perfect low index crystal faces.

Since changing the average platinum particle size causes a change in the surface structure of the exposed metal atoms, studying the effect of metal crystallite size on the catalytic activity of supported catalysts can provide information about the sensitivity of a given reaction to the presence of different structural sites. For example (3), if the specific catalytic activity for a reaction is independent of crystallite size (especially in the 10 to 50Å range), then it is probably
reasonable to assume that the active sites for the reaction are individual metal atoms, or very simple sites involving several metal atoms. If changing the crystallite size does affect the specific catalytic activity, then special, more specific surface sites are probably involved in some step of the reaction.

A number of reactions have been studied over a series of dispersed platinum catalysts in which the average metal crystallite size was varied. These reactions have been classified by Boudart, et al. (4), as "facile" or "demanding," depending on whether the specific catalytic activity of the reaction (i.e., the activity referred to unit surface area of the metal) changes with the mean particle size (demanding) or is independent of the mean particle size (facile). Among the reactions found to be facile on supported platinum catalysts at atmospheric pressures were the dehydrogenation of cyclohexane (2,5), the hydrogenation of cyclohexene (2,6), and the hydrogenolysis of cyclopentane (2).
The isomerization of neo-pentane to iso-butane was found to be a demanding reaction over supported platinum catalysts (4) and oxidation reactions involving O₂ also appear to be dependent on the average metal crystallite size (2,3,5).

It has been pointed out by Manogue and Katzer (7) that the specific catalytic activity of a reaction may appear sensitive to changes in the dispersed metal particle size due to factors which are not related purely to the geometrical or structural changes in the metal particles. These factors include, for example, impurity stabilized surface reconstruction, selective poisoning of specific sites or crystallites of certain sizes, and intrinsic activity changes associated with the
number of metal atoms present in very small crystallites, all of which may change with the average metal particle size. For this reason, Manogue and Katzer suggested that "demanding" reactions be further subclassified as "primary structure sensitive" (directly dependent on the metal surface structure), "secondary structure sensitive" (dependent on particle size, but not purely on the metal surface structure), and "primary size sensitive" (dependent on the number of metal atoms in very small metal particles). For example, Poltorak and Boronin (2) observed that the cyclohexane dehydrogenation reaction was independent of the average platinum particle size after thorough reduction of the catalyst; however, if the catalyst was oxidized at 400°C before reactions, the dehydrogenation reactivity of the highly dispersed catalysts increased significantly with respect to the catalysts with low dispersion. Thus, Manogue and Katzer would classify this as a case of secondary structure sensitivity.

In order to design supported catalysts for desired reactivity levels and product selectivity, it is clear that it would be very profitable to gain a fundamental knowledge of platinum catalytic activity as a function of atomic surface structure and surface composition. But it is difficult to precisely control the metal particle surface structure and composition on a supported catalyst, where only the average particle size can be determined. Even the simplest supported catalyst requires such a complex description for its full characterization, that it is as yet unattainable with today's surface characterization techniques. For example, the physical description of a platinum-alumina catalyst (8) would require: the definition of the sizes of
the metal particles and the atomic and electronic structure of their surfaces; the structure of the alumina, including the pore structure; a knowledge of where the metal particles are located on the base. The consideration of how these parameters change with time, as a function of temperature, pressure, poisons, or promoters further complicates the description.

The study of platinum single crystal surfaces was undertaken in this investigation so that reactive investigations could be made on catalysts with reproducibly well-characterized surface structures and surface compositions. As stated by Gwathmey and Cunningham (9) 20 years ago:

"If it can be demonstrated that certain faces of any one catalyst are areas of high activity while others are areas of low activity, and further that within any one face special structures, such as imperfections or kinks, may have special activity, some of the unnecessary mystery of catalysis will be removed. Attention can then be directed toward explaining why a particular structure has a certain activity. Attempts may even be profitably made to control the activity of the catalyst by controlling the faces exposed and the type and number of imperfections within any one face."

High densities of low coordination number defect sites such as steps and kinks (atoms in edge or corner positions respectively, as compared with the ideal surface positions of flat, low index planes) can be easily introduced into single crystal platinum surfaces by cutting samples at small angles to the low Miller index planes, the (111), (100), and (110). These stepped and kinked surfaces provide
a convenient model for highly dispersed supported catalysts, where most of the metal atoms in the small particles are exposed at the surface with low coordination number. The low Miller index planes are good models for the large metal crystallites on supported catalysts of low dispersion.

The reactive studies in this investigation were carried out in an ultrahigh vacuum (UHV) system at low pressure (10^-6 to 10^-5 torr total pressure). The advantage of low pressure conditions was that it allowed the characterization of the platinum catalyst surface structure by low energy electron diffraction (LEED) and characterization of the surface composition by Auger electron spectroscopy (AES) immediately before and after hydrocarbon reactions. Because the reagent pressures were orders of magnitude lower than those used in practical, high-pressure catalysis on platinum supported catalysts, it was not expected that the low pressure work would provide the values of physical parameters which prevail at high pressure. Rather it was hoped that this work would help identify platinum surface structures important in hydrocarbon reactions and suggest mechanisms or models that could be related to observations at high pressure.

In this investigation, the dehydrogenation of cyclohexene and cyclohexane, and the hydrogenation of cyclohexene were studied on the clean and oxidized surfaces of three platinum single crystal catalysts: a Pt(111), a stepped Pt(S) - [6(111) x (100)] and a kinked Pt(S) - [7(111) x (310)]. These three surfaces were chosen to model the variation in surface structure between a supported catalyst of low dispersion and one of high dispersion. The choice of the low
pressure reaction conditions is discussed in Chapter II, with respect to the detection limits of the system and the variation of the catalyst reactivity with reagent pressures and catalyst temperature. A careful optimization of conditions was necessary to achieve a balance between detection above the system reactivity and reproducibility of the specific reaction rates at a given set of conditions. The hydrocarbon reactions were studied using flow conditions at low pressure ($10^{-6}$ to $10^{-5}$ torr total pressure), at a platinum catalyst temperature of 1500°C.

Oxygen coverages were monitored by Auger electron spectroscopy (AES), an Auger peak ratio of $0_{510}/Pt_{237} = 0.5$ having been determined to correspond to approximately $5 \times 10^{14}$ oxygen atoms/cm$^2$. The surface structures of the clean and oxidized platinum crystals were determined by low energy electron diffraction (LEED): after high temperature (800°C) oxygen treatment, the predominant oxygen structure observed on the Pt(111) was a (2 x 2); the predominant oxygen structure observed on both the Pt(S) - [6(111) x (100)] and the Pt(S) - [7(111) x (310)] was a ($\sqrt{3} \times \sqrt{3}$) - R30°.

Low coverages of strongly bound oxygen enhanced the rates of the dehydrogenation and hydrogenation reactions, and changed the selectivity of cyclohexene dehydrogenation to benzene over hydrogenation to cyclohexane. These effects of preoxidation on catalytic rates and selectivity, discussed in Chapter III, were found to be sensitive to the structure of the platinum surface; for the clean surface reactivity, on the other hand, little structure sensitivity was observed, the Pt(111) being only a factor of two less reactive for cyclohexene dehydrogenation than the stepped and kinked surfaces,
and poisoning more rapidly for both cyclohexene and cyclohexane
dehydrogenation. Kink sites seemed to play a particularly active
role in the enhancement of dehydrogenation and hydrogenation activity
by strongly bound oxygen. Three models are discussed which relate
the oxidation of platinum surfaces to the observed effects on catalytic
reactivity and the structure sensitivity. A change in the electronic
structure of the platinum surface through oxidation provides the best
general model for explaining the oxygen effects, though complex for-
mation involving the adsorbed oxygen or surface reconstruction during
oxidation may also be important.

In addition to the investigations of cyclohexene and cyclohexane
dehydrogenation and cyclohexene hydrogenation, several preliminary
studies of other low pressure reactions are reported on in Chapter IV.
The dehydrocyclization of n-heptane to toluene and benzene was studied
on the clean Pt(111), stepped, and kinked surfaces, and on these surfaces
with ordered carbonaceous overlayers and with various coverages of
strongly bound oxygen. No enhancement of this reaction was observed
in the presence of strongly bound oxygen or ordered carbon structures.
The studies of neo-pentane and iso-butane in the presence of excess
hydrogen showed that under the low pressure conditions used in this
investigation, hydrogenolysis reactivity was favored over isomerization
reactivity on the kinked Pt(S) - [7(111) x (310)].
II. EXPERIMENTAL PROCEDURES AND DIFFICULTIES

2.1. Experimental Apparatus

The apparatus used in this experimental investigation was an ultrahigh vacuum (UHV) system centered with an early model Varian LEED chamber; a schematic of this UHV system is shown in Fig. 2.1. A platinum catalyst sample was mounted in the vacuum chamber by spot-welding short pieces of 0.38 mm wire (either tantalum or platinum) to the edge of the sample at one end and to stainless steel supports at the other. These stainless steel supports were suspended from the sample manipulator, the rotation of which allowed both sides of the catalyst to be cleaned and characterized. The sample was heated resistively by way of copper leads to the stainless steel supports and its temperature was monitored by a platinum/platinum-10% rhodium thermocouple (0.13 mm wire) spotwelded to the sample edge.

The UHV system was equipped with an ion bombardment gun (Physical Electronics Industries, model PHI-2000) for sputter cleaning of the catalyst surface, 4-grid Varian low energy electron diffraction optics for observing the catalyst surface structure, and a retarding grid Auger electron spectrometer (utilizing the LEED optics for detection) to determine the catalyst surface composition. A bariated nickel Phillips cold cathode electron source provided the well-collimated beam of electrons for LEED; the electrons were incident on the single crystal sample at energies ranging from 10 to 215 eV, and the back-scattered diffraction beams were displayed on a phosphorized (P-11) screen. The LEED patterns were photographed using a Crown Graphic camera with an 3.5 lens and Polaroid Type 57 (ASA 3000) sheet film.
Fig. 2.1. Schematic diagram of reaction chamber used for low pressure catalytic reaction studies.

- Ion Bombardment Gun
- Sample Manipulator
- LEED Optics
- Cold Trap
- Mass Spectrometer
- Auger Electron Gun
- Gas Inlets
- Single Crystal Catalyst Sample
- To Diffusion Pump
- To Ion Pump
An idealized schematic of the LEED process is shown in Fig. 2.2; for additional information on low energy electron diffraction, there are a number of good references (10-13). A 12B cathode ray tube gun fitted with a Varian tungsten ribbon filament was used as the source of primary electrons for Auger electron spectroscopy; the energy of the primary electrons for most spectra was 2.5 keV. A schematic diagram of the Auger process is shown in Fig. 2.3; for additional information on AES, there are a number of good reviews available in the literature (14-17).

The pumping system for the stainless steel chamber (approximately 15 liter volume) consisted of a 400 l/s Vac-Ion pump and a 2-in. NRC diffusion pump, equipped with a water baffle and a liquid nitrogen trap. Each pump could be independently isolated from the reaction chamber by a gate valve; the gate valve between the diffusion pump and the chamber was air-operated and interlocked to prevent oil contamination (DC 705) of the system in the event of vacuum loss, overheating, or water flow problems.

The reaction chamber was typically baked at about 200°C for 48 hr after bringing the system up to atmospheric pressure with a flow of dry nitrogen; this was accomplished by wrapping the chamber with heating tapes, then with aluminum foil. The ion pump was usually heated at about 150°C during the first 24 hr of the chamber bake-out. Background pressures with the ion pump alone and diffusion pump alone were typically $6 \times 10^{-10}$ and $5 \times 10^{-9}$ respectively after bake-out; these background pressures climbed to roughly $1 \times 10^{-9}$ and $1 \times 10^{-8}$ respectively after several hydrocarbon reactions had been run.
Fig. 2.2. Idealized schematic diagram of low energy electron diffraction from a single crystal surface.
\[ I_{\text{Auger}} = I_{W_0(Z)} = E_{X_P}(Z) - E_{Y_Q}(Z + \delta) - \phi_c \]

\[ 0.50 < \delta < 0.75 \]

**Fig. 2.3.** Schematic diagram of the Auger electron process. Electron bombardment creates a hole in the \( W_0 \) band which is filled by an electron from the \( X_P \) band; the energy released by this process causes ejection of an Auger electron from the \( Y_Q \) band. The kinetic energy of the Auger electron can be measured, and is characteristic of the element from which it was ejected.
A UTI 100C quadrupole mass spectrometer was mounted in direct line of sight of the platinum sample. The standard dual tungsten filaments were replaced by a single thoriated iridium filament which was run at low emission (0.30 ma); this kept the filament surface area and temperature low and helped reduce background reactivity.

Gases were introduced into the reaction chamber from a gas manifold through two Varian bakeable leak valves. The manifold had connections for four gas cylinders and one liquid-reagent container (for admitting the vapor above the liquid). It could be pumped down to a base pressure $<1 \times 10^{-3}$ torr by a liquid-nitrogen-cooled sorption pump before introducing gases and could be valved off in the middle to create two sections, from which two gases could be independently introduced into the vacuum chamber. Some experiments were run with hypodermic needles attached to the leak valves to admit gases directly onto the platinum sample. The tips of the needles were typically 1 cm from the crystal during a reaction and were not observed to have a significant effect on the measured reaction rates, either in this investigation or that of Blakely (18). The needles, however, did affect the measurement of pumping speeds for various gases; this effect will be discussed in Appendix B.

Roughly half of the experiments discussed in Chapter III were run by Dr. Jean-Paul Biberian* using a second UHV system very similar to the one just described. Background pressures in this system were

---

*On leave from Centre de Mecanisme de la Croissance Cristalline U. E. R. Scientifique de Luminy, 70 Route Léon Lachamp 13288 Marseille cédex 2, FRANCE.
approximately 3 x 10^{-9} \text{torr} \text{ when pumped only by a 140 l/s Vac-Ion pump and } 5 \times 10^{-8} \text{torr} \text{ when pumped only by a 2-in., liquid-nitrogen trapped diffusion pump.}

2.2. \textbf{Platinum Single Crystal Catalysts}

The catalysts used in this study were platinum wafers, approximately 1 mm thick, cut from 99.999\% pure single crystal rods. Each of the three samples reported on was cut from a different rod, two of which were obtained from Materials Research Corporation and the third from Research Organic/Inorganic Chemical Corporation. The single crystal rod was oriented using Laue back-reflection x-ray techniques. With the rod still held in the goniometer, a 1 to 2 mm thick slice was cut by an electrical discharge, or "spark cutting" process. Since the cutting process was only accurate to within several degrees, both sides of the platinum wafer were reoriented to within 1/2^\circ \text{ of the desired orientation using Laue techniques and then polished to this orientation using energy paper mounted on a facing wheel while the crystal was still held in the goniometer. Both sides of the wafer were then mechanically polished starting with four successively finer grades of emery paper, then 1 micron diamond paste on a rotating wheel, and finally a 0.05 micron alumina powder/water slurry in a vibrating bath. For these polishing steps, the platinum crystal was mounted in Koldmount, an epoxy resin soluble in acetone or methylethylketone, manufactured by Vernon-Benshoff Co., Albany, New York. The final accuracy of the polished surfaces was typically \pm 10^\circ.

The surface composition of the catalyst samples was determined by Auger electron spectroscopy. The impurities observed for all three
platinum crystals studied were calcium, carbon, phosphorous, and sulfur. The calcium was removed from the surface by sputtering with 500 eV argon ions, with the sample at 900°C; carbon, phosphorous and sulfur were removed by oxidation at 700 to 800°C in 1 x 10^{-7} torr of oxygen. Residual adsorbed oxygen from brief oxidation treatments could be removed by heating the sample to 1000°C in vacuum.

The clean surface structure of each platinum catalyst was determined by low energy electron diffraction. Shown in Fig. 2.4 are clean surface LEED patterns and surface schematics for the three samples studied. The first was a hexagonally close-packed Pt(111) surface. The second was a stepped surface, Pt(S) - [6(111) x (100)] - Pt(755), which was cut 9.50 ± 0.50° from the (111) plane in the direction of the (100) plane on the [011] zone. It has (111) terraces averaging 6 atoms wide and a step density of approximately 2.6 x 10^{14} step atoms/cm^2 or 17% of the surface atoms. The third sample was a kinked surface, Pt(S) - [7(111) x (310)] - Pt(10,8,7); it was cut 8.50 ± 0.50° from the (111) plane towards the (310) plane on the [132] zone, and is therefore rotated 19° ± 10° from the [011] zone. For this surface, the (111) terraces average 7 atoms wide. The orientation of the steps is now a high Miller Index plane, (310), and approximately every third atom along each step is in a kink position; this gives a kink density representing about 6% of the surface atoms. For additional discussion of stepped and kinked surface nomenclature, how this nomenclature and the Miller Indices can be determined from Laue and LEED photos for a given surface, and how to determine the cutting angles for a desired stepped or kinked surface, refer to Appendix A.
Fig. 2.4. Low energy electron diffraction patterns and schematic representations of the three platinum surfaces studied:
(A) Pt(111);
(B) Pt(S)-[6(111)x(100)] ↔ Pt(755);
(C) Pt(S)-[7(111)x(310)] ↔ Pt(10,8,7).
The clean surface structures, as determined by LEED, agreed well with those predicted by the crystal orientation as determined by Laue back-reflection x-ray diffraction patterns, assuming that surfaces close to the Pt(111) are stable in a configuration of (111) terraces separated by monatomic height steps (see Section A.5). The surface area of the Pt(111) and the Pt(S) - [7(111) x (310)] was 0.6 cm²; the surface area of the Pt(S) - [6(111) x (100)] was 1.1 cm². This does not include the unoriented circumferential area of the platinum wafers (about 0.15 cm² for the Pt(111) and kinked surfaces and about 0.3 cm² for the stepped surface); the presence of this unmasked surface area on each crystal that is not structurally well-defined will make experimentally observed differences in structure sensitivity less than if it were not present.

### 2.3. Experimental Procedure

The surface composition of the catalyst sample was determined immediately before reactions by Auger electron spectroscopy. It was particularly important to ascertain that all carbon, calcium, phosphorous and sulfur impurities had been removed by cleaning procedures before a reaction was started. In Fig. 2.5, an AES spectrum of a heavily contaminated (as when initially introduced into the UHV system) platinum surface is shown in (A), and the spectrum of a sample with only carbonaceous deposits (as after a hydrocarbon reaction) is shown in (B). The cleaning procedure for the surface illustrated in Fig. 2.5A would be sputtering of the surface with 500 eV argon ions for 15 to 30 min, followed by heating at 800°C in 1 x 10⁻⁷ torr of oxygen for 15-30 min, then heating the sample at 1000°C in vacuum for several minutes.
Fig. 2.5. Auger electron spectra of (A) a platinum surface heavily contaminated with phosphorous, sulfur, carbon, and calcium, and (B) a platinum sample contaminated only by carbonaceous deposits, as after a typical hydrocarbon reaction.
To clean the surface illustrated in Fig. 2.5B, 1 to 2 min at 800°C in 1 x 10^-7 torr of oxygen followed by brief flashing of the sample to 1000°C in vacuum would be sufficient. The AES spectrum of a clean platinum catalyst is shown in Fig. 2.6A. The AES was also used to monitor the oxygen coverage of the catalysts during studies of the effect of strongly bound oxygen on the reactivity and selectivity of the platinum (see Chapter III). The oxygen coverage is reported as a ratio of the oxygen 510 eV (O_510) Auger peak intensity to the platinum 237 eV (Pt_237) Auger peak intensity. It was determined that a ratio of O_510/Pt_237 = 0.5 represents approximately one monolayer coverage (see Section 2.4). The spectrum of a catalyst sample with an oxygen coverage greater than one monolayer is shown in Fig. 2.6B.

After surface characterization, hydrogen, then the hydrocarbon reactant were introduced into the reaction chamber independently by the use of two variable leak valves. The catalyst sample was brought to the reaction temperature, and residual background gases were monitored before introduction of the hydrocarbon. The largest background components (after hydrogen, which is masked by the introduction of this gas as a reactant) were normally carbon monoxide and water, with lesser amounts of carbon dioxide, light hydrocarbons (<C_5), oxygen, and benzene. The cyclohexene dehydrogenation experiments were carried out at 150°C with 1 x 10^-6 torr of hydrogen and 6 x 10^-8 torr of cyclohexene; the cyclohexane dehydrogenation experiments were carried out at 150°C using 1 x 10^-5 torr of hydrogen and 2 x 10^-6 torr of cyclohexane.

The standard conditions for these reactions, and for several others which are reported on briefly in Chapter IV, are listed in Table 2.1;
Fig. 2.6. Auger electron spectra of (A) a clean catalyst surface, and (B) a platinum catalyst surface with an oxygen coverage greater than $5 \times 10^{14}$ oxygen atoms/cm$^2$ after treatment at 800$^\circ$C in $1 \times 10^{-6}$ torr oxygen.
Table 2.1. Standard pressure and temperature conditions for hydrocarbon reactions studied.

<table>
<thead>
<tr>
<th>Hydrocarbon Reagent</th>
<th>Hydrocarbon Reagent Pressure (Torr)</th>
<th>Hydrogen Pressure (Torr)</th>
<th>Crystal Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexene</td>
<td>$6 \times 10^{-8}$</td>
<td>$1 \times 10^{-6}$</td>
<td>150</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>$2 \times 10^{-8}$</td>
<td>$1 \times 10^{-5}$</td>
<td>150</td>
</tr>
<tr>
<td>N-heptane</td>
<td>$2 \times 10^{-6}$</td>
<td>$1 \times 10^{-5}$</td>
<td>450</td>
</tr>
<tr>
<td>Neo-pentane</td>
<td>$1 \times 10^{-7}$</td>
<td>$1 \times 10^{-6}$</td>
<td>120</td>
</tr>
<tr>
<td>Iso-butane</td>
<td>$4 \times 10^{-7}$</td>
<td>$5 \times 10^{-6}$</td>
<td>120</td>
</tr>
</tbody>
</table>
the choice of the various standard conditions will be discussed in Section 2.5.1.

The liquid hydrocarbon reactants were Matheson "Spectroquality" chemicals. They were degassed by several cycles of cooling the reagent to liquid nitrogen temperature followed by pumping on the reagent container with a sorption pump. The gases (H₂, O₂, Ar, etc.) were research grade from Matheson, and were used directly from the gas cylinders. The UTI 100C quadrupole mass spectrometer was used to monitor the partial pressures of reactant and product gases as a function of time, having been first calibrated with a nude ionization gauge (the corrections were not made for the different ionization cross sections in the ion gauge of the reactants and products). These calibrations were made periodically, as they are sensitive to aging of the mass spectrometer filament (especially sagging), and to any change of the ionizer voltages or the resolution (which is determined by the ratio of the rf to dc voltages on the filtering rods). The cracking patterns of the reagent and product hydrocarbons were also measured when the gases were calibrated; the measured relative peak heights were used in analyzing reaction rate data rather than API values (19), though there was generally good agreement between the two sets of data. The UTI 100C is equipped with both a Faraday cup and an electron multiplier. All calibrations were done using the Faraday cup; the gain of the electron multiplier was measured during each experiment so that partial pressures could be consistently reported with respect to the Faraday cup calibrations.
The reactions were carried out under constant flow conditions by valving off the ion pump and pumping continuously on the chamber with the diffusion pump. The conductance-limited value of the pumping speed (measured with the valve to the chamber open fully) under these conditions was $10 \text{ l/s}$ for hydrogen, $0.8 \text{ l/s}$ for cyclohexane and $0.5 \text{ l/s}$ for cyclohexene and benzene. (For the second UHV system used in the platinum oxidation effect studies, the measured value of the pumping speed was $3.3 \text{ l/s}$ for hydrogen, $1.1 \text{ l/s}$ for cyclohexane and $0.7 \text{ l/s}$ for cyclohexene and benzene.) The pumping speed calculations are discussed in Appendix B. Under these flow conditions at low pressure, it is assumed that the gases in the reaction chamber (about 15 liters in volume) are well-mixed, since even at $1 \times 10^{-5}$ torr the mean free path (approximately 5 meters) is much larger than the dimensions of the chamber.

Reactions were typically run for 100 to 200 min, by which time the measured reactivity closely approached that of a blank, control reaction due to the poisoning of the platinum surface. Upon termination of an experiment, the reaction chamber was pumped down with the ion pump, and the catalyst surface once again characterized by AES and LEED.

2.4. Determination of Oxygen Coverages

The oxygen coverage was determined using a method reported recently by Biberian and Somorjai (20). It consists of plotting the Auger peak-to-peak signal intensity from the substrate against the similar signal from the adsorbate. The curve is composed of segments of straight lines, the first break indicating the completion of one monolayer.
of adsorbate. This method is more sensitive when utilizing an Auger transition of high energy for the adsorbate, and of low energy for the substrate.

This method was applied to the calibration of oxygen on a Pt(S) - [6(111) x (100)] surface. The 64 eV and 237 eV Auger peak-to-peak signal intensities of platinum were monitored as a function of the 510 eV Auger peak-to-peak signal intensity from the oxygen while heating the crystal at 800°C in 5 x 10^-7 torr of oxygen. This is plotted for the 64 eV platinum peak in Fig. 2.7; the position of the break as shown in the figure indicates that the formation of a monolayer of oxygen occurs at O_{510}/Pt_{64} = 0.11 and O_{510}/Pt_{237} = 0.5.

The LEED structure observed at the formation of an oxygen monolayer was (\sqrt{3} x \sqrt{3}) - R30°. A simple model giving rise to this structure will place one adsorbed oxygen atom on the surface for every three platinum surface atoms. Based on this model the ratio O_{510}/Pt_{237} = 0.5 corresponds to about 5 x 10^{14} atoms of oxygen/cm^2.

The Auger peak-to-peak signal intensity from the oxygen is proportional to the amount of adsorbed oxygen during the formation of the first monolayer, however the ratio O_{510}/Pt_{237} is no proportional to the coverage because of the attenuation of the platinum Auger peak-to-peak signal intensity by the adsorbed oxygen. The 237 eV platinum Auger transition is attenuated by 26% during the formation of a monolayer of oxygen. Taking this factor into consideration the following relation (20) is obtained: 

\theta = \left[ 0.26 + 0.37 \frac{Pt_{237}}{O_{510}} \right]^{-1},

where \theta = 1 corresponds to one oxygen atom for every three platinum surface atoms or 5 x 10^{14} oxygen atoms/cm^2. In Table 2.2 the oxygen
Fig. 2.7. The 64 eV Auger peak-to-peak signal intensity of platinum plotted as a function of the 510 eV Auger peak-to-peak signal intensity of adsorbed oxygen while heating the crystal at 800°C in 5x10^{-7} torr of oxygen. The position of the break indicates that the formation of a monolayer of oxygen (5x10^{14} oxygen atoms/cm^2) occurs at O_{510}/Pt_{64} = 0.11 and O_{510}/Pt_{237} = 0.5 (not shown).
Table 2.2. Oxygen coverages ($\theta$) and surface concentrations for various values of the $O_{510}/Pt_{237}$ Auger peak ratio, where $\theta = 1$ corresponds to one oxygen atom for every three platinum surface atoms, or $5 \times 10^{14}$ oxygen atoms/cm².

<table>
<thead>
<tr>
<th>$O_{510}/Pt_{237}$</th>
<th>0.05</th>
<th>0.10</th>
<th>0.15</th>
<th>0.20</th>
<th>0.25</th>
<th>0.30</th>
<th>0.35</th>
<th>0.40</th>
<th>0.45</th>
<th>0.50</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta$</td>
<td>0.13</td>
<td>0.25</td>
<td>0.37</td>
<td>0.47</td>
<td>0.57</td>
<td>0.67</td>
<td>0.76</td>
<td>0.84</td>
<td>0.92</td>
<td>1.0</td>
</tr>
<tr>
<td>oxygen atoms/cm² x $10^{-14}$</td>
<td>0.65</td>
<td>1.3</td>
<td>1.9</td>
<td>2.4</td>
<td>2.9</td>
<td>3.4</td>
<td>3.8</td>
<td>4.2</td>
<td>4.6</td>
<td>5.0</td>
</tr>
</tbody>
</table>
coverages and surface concentrations are listed for different values of the Os10/Pt237 Auger peak ratio.

This calibration is in fairly good agreement with others (21-24) considering that the orientation of the surfaces, the temperature of adsorption and the type of AES analyzer used were different. Bonzel and Ku (21) find a ratio Os10/Pt237 = 0.65 for one monolayer of oxygen adsorbed at about 300°C (7.5 x 10^{14} oxygen atoms/cm^2) on Pt(111) using a cylindrical mirror analyzer (CMA). Weber, et al. (22) obtain a ratio of 0.5 for one monolayer of oxygen (8 x 10^{14} oxygen atoms/cm^2) with polycrystalline platinum at room temperature. Wilf and Dawson (23) measure a ratio 0.55 for one monolayer of oxygen (3.5 x 10^{14} oxygen atoms/cm^2) on Pt(110) with a retarding grid analyzer (RGA) after adsorption at room temperature. Gland and Korchak (24) report a ratio of 0.5 for one monolayer of oxygen (4 x 10^{14} oxygen atoms/cm^2) with Pt(S) - [12(111) x (111)] using a CMA.

2.5. Experimental Difficulties

2.5.1. Choosing the Reaction Conditions

In choosing the reaction conditions for the experiments reported on in this investigation, there were three main variables: hydrocarbon pressure, hydrogen pressure and catalyst temperature. The important factors considered in determining the "optimum" conditions were the
ease of detection of catalyst reactivity above the inherent reactivity of the vacuum system (due to stainless steel walls, mass spectrometer filament, etc.) and the reproducibility of the product turnover numbers at a given set of conditions.

In Fig. 2.8, the maximum turnover numbers for the production of benzene from cyclohexane (the calculation of turnover numbers is discussed in Appendix C) are plotted as a function of cyclohexane pressure for the stepped Pt(S) - [6(111) x (100)] and the kinked Pt(S) - [7(111) x (310)] surfaces. It can be seen that for both surfaces, the benzene production increases linearly with increasing cyclohexane pressure over the pressure range studied; for the stepped surface, the hydrogen pressure was held constant at $1 \times 10^{-5}$ torr while the cyclohexane pressure was varied and for the kinked surface, the hydrogen pressure was varied with the cyclohexane pressure to maintain a hydrogen to cyclohexane ratio of about 10:1. Thus, increasing the cyclohexane pressure does increase the ease of detection of the catalyst reactivity above the system reactivity (which increased by only a factor of two between $4 \times 10^{-8}$ torr and $2 \times 10^{-6}$ torr cyclohexane); however, the change of the characteristics of turnover number as a function of time must also be considered to determine the optimum cyclohexane pressure for this experiment.

In Fig. 2.9, the trend for benzene production from cyclohexane as a function of time is shown for increasing cyclohexane pressure (system reactivity has been subtracted). At low cyclohexane pressure, $5 \times 10^{-7}$ torr, the reactivity is small, and there is not a well defined maximum in the turnover number as a function of time. In fact, in
Fig. 2.8. Maximum turnover numbers for benzene production from cyclohexane as a function of cyclohexane pressure for the clean Pt(S) - [6(111) x (100)] (■) - and the clean Pt(S) - [7(111) x (310)] (▲).
Fig. 2.9. The trend with increasing cyclohexane pressure for benzene production from cyclohexane as a function of time.
most cases at lower pressure, it is difficult to be confident that one is detecting any real platinum surface reactivity. For example, a typical run on the kinked surface at $3 \times 10^{-8}$ torr cyclohexane is plotted in Fig. 2.10, along with a blank run (with no platinum crystal in the chamber) at the same pressure. (To calculate "turnover numbers" in molecules/sec/"Pt atom" from a blank run, the reaction rates monitored as a function of time for the system alone are divided by the number of platinum atoms at the surface of the platinum catalyst sample under study. This yields the "excess" reactivity due to the system per platinum atom, that must be subtracted from each run on the catalyst under study. Thus, if the blank run shown in Fig. 2.10 were to be subtracted from a run on the stepped surface, each "turnover number" would first be divided by 2, because the surface area of the stepped surface was approximately twice that of the kinked surface.) It can be seen that subtraction of the system reactivity (i.e., the blank run data) from the kinked surface reactivity would yield a small, unreliable difference, especially in view of the fact that the entire curve for the experimental run on the platinum sample is within the fluctuation range of the blank, from run to run, and vice versa. Thus, it is this author's opinion, based on a large number of runs and blanks at these conditions, that the standard conditions used by Blakely (18,25) for the cyclohexane experiments ($4 \times 10^{-8}$ torr cyclohexane and $1 \times 10^{-6}$ torr hydrogen) are not likely to yield reliable dehydrogenation rates for cyclohexane to benzene. It appears that the data reported by Blakely was not corrected for system reactivity
Fig. 2.10. Benzene production from cyclohexane as a function of time for the clean Pt(S) - [7(111) x (310)] (150°C), uncorrected for system reactivity (☐) and for a blank run with no platinum crystal in the chamber (●). Reaction conditions: cyclohexane pressure, 3x10⁻⁸ torr; hydrogen pressure, 1x10⁻⁶ torr. No significant platinum reactivity is detected above system reactivity.
and the "steady state" turnover number of about $1 \times 10^{-5}$ molecules/sec obtained on all of the platinum surfaces studied (including the Pt(111) (26)) after an "induction period" of about 20 min probably represents the level of system reactivity under these conditions and not platinum reactivity.

At higher cyclohexane pressures, $1 \times 10^{-6}$ torr, it can be seen in Fig. 2.9 that the benzene production increases to levels readily observable above the system reactivity; the reactivity passes through a well-defined maximum, then decreases to the level of background reactivity over a period of several hours. The maximum turnover number as a function of time was found to vary roughly between $\pm 15\%$ from run to run at the conditions $P_{C_{6}H_{12}} = 2 \times 10^{-6}$ torr and $P_{H_{2}} = 1 \times 10^{-5}$ torr for a given UHV system. As the pressure of cyclohexane was increased from $1 \times 10^{-6}$ torr to $1 \times 10^{-5}$ torr, the maximum reactivity was reached in increasingly shorter times, and catalyst poisoning set in faster and occurred more rapidly. Thus, although the reactivity increases significantly over this pressure range, the experimental uncertainty also increases; this is largely due to (1) the overlap of the reactivity maximum with the initial period of several minutes required to introduce and stabilize the pressure of the hydrocarbon reagent (the variation of the cyclohexane pressure during this initial period can introduce large errors into the calculated turnover numbers) and (2) the difficulty in accurately determining the maximum of a sharp reactivity peak due to the scan time of 25 to 30 sec required to record the appropriate atomic mass unit range with the mass spectrometer.
In view of both detection ease and reproducibility, a pressure of $2 \times 10^{-6}$ torr of cyclohexane was chosen as the standard pressure of this reagent. Because of the day-to-day fluctuation of system reactivity (for example, this reactivity was sensitive to recent ion sputtering of the platinum sample), and the problems in accurately determining catalyst reactivity when the reactivity plots show a low, broad peak, conditions were sought under which the benzene production from cyclohexane went through a well-defined maximum, followed by poisoning. The assumption was made that the platinum catalyst poisons completely under low pressure conditions within several hours; when a constant level of reactivity was reached (or in some cases, a slowly increasing reactivity), this was assumed to arise totally from the system reactivity, and was hence subtracted before reporting the platinum surface reactivity. This data treatment would throw out any low, long-term steady state reactivity of the platinum; however, it does take into account the day-to-day fluctuation of the system reactivity, which would make accurate determination of a low steady reactivity extremely difficult, in any case.

The presence of hydrogen during a dehydrogenation reaction, such as the production of benzene from cyclohexane, is apparently necessary to slow down the poisoning of the platinum surface by the buildup of a carbonaceous deposit from the cracking of the hydrocarbon reagent. In the absence of hydrogen, the production of benzene from cyclohexane or cyclohexene was very low, and complete poisoning of the catalyst was rapid. Increasing the hydrogen pressure to high levels, however, increases the background pressures of residual gases (due to displacement
from the system walls, and increased backstreaming from the pumps) and also tended to increase the background reactivity of the system. Shown in Fig. 2.11 is a plot of maximum turnover numbers for benzene production from cyclohexane as a function of hydrogen pressure. The pressure of cyclohexane was kept constant at $2 \times 10^{-6}$ torr for each run; the total pressure was always kept $<1 \times 10^{-4}$ torr during experiments due to noise problems and high residual gas pressures in the $1 \times 10^{-4}$ to $1 \times 10^{-3}$ torr pressure range (pressures approaching $1 \times 10^{-3}$ torr would result in automatic shutdown of most of the UHV equipment, including the mass spectrometer).

It can be seen that increasing the hydrogen to cyclohexane ratio from 1:1 to 5:1 results in a significant improvement in the dehydrogenation reactivity; further increase of the hydrogen pressure (to a ratio of 30:1) did not lead to much additional increase in the maximum reactivity, or decrease in the poisoning rate. Thus, to keep residual gas pressures and system reactivity as low as possible while significantly slowing down the surface poisoning by carbonaceous deposit buildup, a standard pressure of $1 \times 10^{-5}$ torr of hydrogen (and hence a hydrogen to cyclohexane ratio of 5:1) was chosen as the standard pressure of this reagent.

Sets of experiments similar to those described above were run to determine the optimum pressures for cyclohexene and hydrogen in the study of cyclohexene dehydrogenation to benzene. The conversion of cyclohexene to benzene at low pressure was much higher than the conversion of cyclohexane to benzene, and the poisoning of the platinum surface correspondingly faster during the former reaction. Thus,
Fig. 2.11. Maximum turnover numbers for benzene production from cyclohexane as a function of hydrogen pressure for the clean Pt(S) - [6(111) x (100)].
to best meet the criteria of ease of detection and reproducibility, a lower pressure of cyclohexene was chosen, $4 \times 10^{-8}$ torr, along with a higher hydrogen to hydrocarbon ratio of 20:1 ($1 \times 10^{-6}$ torr hydrogen).

The third important experimental variable was platinum catalyst temperature. Plots of benzene production from cyclohexene and cyclohexane as a function of $1000/T$, where $T$ is the catalyst temperature (°K) are shown in Fig. 2.12. The benzene production in both cases goes through a maximum in the temperature range of 120° to 150°C (27). The dehydrogenation of cyclohexene and cyclohexane apparently have activation barriers; but the rate of platinum catalyst poisoning also increases with increasing temperature, and this latter effect starts to dominate at temperatures above 150°C. For this reason, the cyclohexene and cyclohexane experiments were run with a crystal temperature of 150°C.

The benzene production as a function of time from a typical cyclohexane run on the Pt(S) - [7(111) x (310)] at standard conditions (pressure of cyclohexene = $2 \times 10^{-6}$ torr, pressure of hydrogen = $1 \times 10^{-5}$ torr, catalyst temperature = 150°C) before correction for system reactivity is shown in Fig. 2.13, along with a cyclohexane blank run at standard conditions. The system reactivity curve was subtracted from each platinum crystal reactivity curve to arrive at the cyclohexane dehydrogenation reactivity vs time plots discussed in Section 3.3.3 (see Fig. 3.6).

The production of benzene as a function of time from a typical cyclohexene run on the Pt(111) at standard conditions (pressure of cyclohexene = $6 \times 10^{-8}$ torr, pressure of hydrogen = $1 \times 10^{-6}$ torr, catalyst temperature = 150°C) before correction for system reactivity
Fig. 2.12. Benzene production from cyclohexene (\(\Delta\)) and from cyclohexane (\(\square\)) as a function of \(1000/T\) (where \(T\) is the catalyst temperature in °K) showing the maximum in reactivity in the temperature range 120°C to 150°C.
[Diagram showing benzene production from cyclohexane as a function of time for the clean Pt(S)-[7(111)x(310)] (150°C), uncorrected for system reactivity (-●-), and for a blank run (-Δ-) at standard conditions.]
is shown in Fig. 2.14, along with a cyclohexene blank run at standard conditions. It can be noted that the system reactivity represented a much lower percentage of the total reactivity at the maximum of benzene production from cyclohexene, than at the maximum of benzene production from cyclohexane (compare Figs. 2.13 and 2.14); thus, the absolute values of the turnover numbers for cyclohexene dehydrogenation are reported with greater confidence than those for cyclohexane dehydrogenation. The system reactivity curve was subtracted from each platinum crystal reactivity curve to arrive at the cyclohexene dehydrogenation to benzene reactivity vs time plots discussed in Section 3.3.2 (see Fig. 3.2).

For both the cyclohexane and cyclohexene experiments, the only product readily detected on the clean platinum catalyst surfaces was the dehydrogenation product, benzene. Routine checks were made for other products, such as cyclohexene and n-hexane from cyclohexane, for cyclohexane and n-hexane from cyclohexene, but detection above the system reactivity was not possible. For example, the data (uncorrected for system reactivity) for cyclohexene production from cyclohexane at standard conditions from a typical run on the clean Pt(S) - [7(111) x (310)] is plotted in Fig. 2.15, along with data from a blank run at these conditions. There is obviously no detectable significant difference between the "crystal reactivity" and the system reactivity at these conditions. The data (uncorrected for system reactivity) for n-hexane production from cyclohexane at standard conditions from a typical run on the clean kinked surface is plotted in Fig. 2.16, along with data from a blank run at these conditions.
Fig. 2.14. Benzene production from cyclohexene as a function of time for the clean Pt(111) (150°C), uncorrected for system reactivity (—●—), and for a blank run (—Δ—) at standard conditions.
Fig. 2.15. Production of cyclohexene from cyclohexane as a function of time for the clean Pt(S)- [7(111)x(310)] (150°C), uncorrected for system reactivity (□) and for a blank run (●) at standard conditions. No significant platinum reactivity is detected above system reactivity.
C₆H₁₂ → nC₆H₁₄

P_H₂ = 1x10⁻⁵ torr; P_C₆H₁₂ = 2x10⁻⁶ torr

- Pt(S)-[7(111)x(310)]; 150°C
- Blank Run

Fig. 2.16. Production of n-hexane from cyclohexane as a function of time for the clean Pt(S)-[7(111)x(310)] (150°C), uncorrected for system reactivity (□) and for a blank run (○) at standard conditions. No significant platinum reactivity is detected above system reactivity.
Again, there is no significant difference between the two curves at the standard conditions.

The inability to detect the dehydrogenation product cyclohexene and the hydrogenolysis product n-hexane during the cyclohexane experiments on clean platinum surfaces (including a highly kinked surface) does not agree with the results of Blakely (18,25), who reported detecting both of these products using lower cyclohexane pressures (4 x 10^-8 torr cyclohexane, with a hydrogen to cyclohexane pressure ratio of 20:1 for cyclohexene and benzene production, and a ratio of 300:1 for n-hexane production) than the standard pressure in this work. In this investigation, neither cyclohexene nor n-hexane was detected above system reactivity at a cyclohexane pressure of 4 x 10^-8 torr and a hydrogen pressure of 8 x 10^-7 torr; increasing the hydrogen pressure to 1 x 10^-5 torr increased both "crystal reactivity" and system reactivity, but did not result in a significant difference that could be attributed to platinum catalytic activity. Certainly these results argue with the statement by Blakely and Somorjai (25) that "even though n-hexane is a minority hydrogenolysis product, it is a reliable measure of the degree of hydrogenolysis because of its ease of mass spectrometric detection and it is not formed in a background reaction with the walls of the reaction chamber."

Although the 86 amu peak (used by Blakely and this investigation for measuring n-hexane production) is easy to detect and deconvolute (besides n-hexane, the only other contribution to the 86 peak is the small isotope peak in the cracking pattern of cyclohexane) it was always a small peak in the mass spectrum, and as such, particularly
sensitive to fluctuations in the noise level of the mass spectrometer, the calibration factors, the cracking patterns, and the system reactivity. Thus, it is this author's opinion that the values of n-hexane production and cyclohexene production from cyclohexane reported by Blakely are likely to represent levels of system reactivity and not platinum reactivity. This conclusion is strengthened by the recent determination that the "Pt(S) - [3(111) x (100)]" (step density approximately $5 \times 10^{14}$ atoms/cm$^2$) reported on in Blakely's work (see Section 3.4.2) is actually a kinked Pt(S) - [2(111) x (610)] (kink density about $1.4 \times 10^{14}$ atoms/cm$^2$). The reported hydrogenolysis reactivity (cyclo-hexane to n-hexane) on this surface was about the same as that on the Pt(S) - [6(111) x (610)] (kink density about $4 \times 10^{13}$ atoms/cm$^2$); the higher rate observed on the Pt(S) - [7(111) x (310)] (kink density reported by Blakely as $7 \times 10^{13}$ atoms/cm$^2$) was probably due to a fluctuation of the system reactivity, rather than an enhancement of hydrogenolysis rates by the presence of kink sites. Lower molecular weight hydrogenolysis products from cyclohexane were also not detected above system reactivity in this investigation, unlike in the work of Blakely.

The data (uncorrected for system reactivity) for cyclohexane production from cyclohexene from typical runs on the clean Pt(S) - [7 (111) x (310)] and the clean Pt(111) are plotted in Fig. 2.17, along with data from a blank run at the same conditions. As reported in Chapter III, there was do detectable significant difference between the "crystal reactivity" and the system reactivity at the standard conditions until low levels of strongly bound oxygen
Fig. 2.17. Production of cyclohexane from cyclohexene as a function of time for the clean Pt(S)-[7(111)x(310)] (-Δ-) and the clean Pt(111) (---○---), and 150°C and uncorrected for system reactivity, and for a blank run (...□...) at standard conditions. No significant platinum reactivity is detected above system reactivity.
were introduced at the surface. No hydrogenolysis products from cyclohexene were detected above system reactivity levels at the standard conditions employed.

2.5.2. Contribution of the Mass Spectrometer Ionizer to the System Reactivity

It was determined that the mass spectrometer ionizer region was a major contributing factor to the production of benzene from cyclohexane and cyclohexene in blank runs; typical blank runs are plotted in Figs. 2.13 and 2.14 for cyclohexane to benzene and cyclohexene to benzene respectively. Two blank runs for benzene production from cyclohexane are plotted in Fig. 2.18 in which the mass spectrometer filament was turned off between periods of scanning the mass spectrum (periods when the filament was off are indicated by dashed lines); all other filaments were routinely turned off throughout all experiments, including blank runs. It can be seen that when the mass spectrometer filament was off, the benzene production fell off significantly, only to climb rapidly again when the filament was turned back on.

Initially this effect was thought due to dehydrogenation of cyclohexane (or cyclohexene) by the hot filament itself, even though only one thoriated iridium filament was being used at low emission (0.3 ma). However, dismantling the ionizer region and rigorously etching it (a solution of 25 parts H₂O, 1 part HNO₃ and 1 part HF for the ceramics and a solution of 50 parts H₂O₂, 15 parts HCl, 20 parts HF, and 15 parts H₂O for the metal pieces, including the grids, focus plate, and screws) resulted in a dramatic reduction in the system reactivity by about 80% (see "after etching ionizer" blank run in Fig. 2.18). Over a period of about 1 month, during which time the
Fig. 2.18. Two blank runs for benzene production from cyclohexane in which the mass spectrometer filament was turned off between periods of scanning the mass spectrum. Periods when the filament was off are indicated by dashed lines (----). One run was before etching the ionizer (-●-) and the other after etching the ionizer (-□-).
platinum crystal sample underwent numerous cleaning cycles and hydrocarbon experiments, the system reactivity increased back to the previous, higher level.

Thus, it would seem that the reactivity of the ionizer is associated with the buildup of some sort of deposit. It is not known if this deposit is carbonaceous in nature, arising from hydrocarbon cracking in the ionizer region, or metallic. If metallic, the deposit could arise from ion sputtering the platinum sample (the crystals were mounted midway between the ion bombardment gun and the mass spectrometer), from platinum vaporization during high temperature heating, from vapor transport of platinum as a volatile platinum oxide during oxygen treatments (at 800°C) or heating to 1000°C to remove strongly bound oxygen, or perhaps even from vaporization of iridium from the filament (although run at low temperature, it flashed to white-hot whenever initially turned on). Before etching, the ionizer region was largely coated with a gray/black film.

The reactivity of the ionizer region increases when the mass spectrometer filament is on. This is probably due to the heat radiated to the ionizer region by the hot filament--the focus plate, for example, heats up to about 150°C when the mass spectrometer is used with two tungsten filaments (28), and the filament mount would probably get hotter. The reactivity might also be affected by the presence of energetic electrons and positive ions in the ionizer region.

2.5.3. Constant Pressure Corrections

In order to achieve the desired steady state value of the hydrocarbon reagent within 1 to 3 min, it was necessary to open the
leak value initially to a relatively large aperture, then close it to the final aperture as the pressure approached the desired value. The uncertainty of this procedure resulted in a fluctuation of the steady state pressure around the standard pressure (2 x 10^{-6} \text{ torr cyclohexane} \text{ and } 6 \times 10^{-8} \text{ torr cyclohexene}). To minimize the effect of this random pressure fluctuation, all turnover numbers were corrected to the standard pressure by assuming that the reactivity was directly proportional to the hydrocarbon pressure (see Fig. 2.8), and thus multiplying the turnover numbers by standard pressure/actual pressure.

This correction should give reasonable results for small fluctuations around the standard pressure, where the hydrogen to hydrocarbon pressure ratio does not change much. The correction is most ineffective during the first several minutes of the experiment, as the hydrocarbon pressure increases through several orders of magnitude to reach the desired steady state value; thus, it is very important to achieve the steady state value before the reactivity passes through a maximum. Since the dehydrogenation reactivity of the clean platinum catalysts was not negligible at room temperature, this problem could not be circumvented by introducing the hydrocarbon reagent to a steady state value before heating the platinum sample.

The high conversion of cyclohexene to benzene at the standard conditions (about 40% at maximum on the kinked surface, for example) introduced a further problem for this experiment. As the platinum surface poisoned and the reactivity decreased, the pressure of the product, benzene, decreased and the pressure of the reagent, cyclohexene,
increased; this gradual increase in cyclohexene continued until a constant, low level of reactivity was reached. The correction of the turnover numbers to the standard cyclohexene pressure during this time is at best a first order approximation to what the turnover numbers would be if a true steady state pressure of cyclohexene could be maintained. Since the conversion of cyclohexane to benzene is much lower at the standard conditions (about 0.2% at maximum), this further problem was not encountered for the cyclohexane dehydrogenation experiments.

2.5.4. Cleaning Procedures

In order to obtain reproducible results from low pressure cyclohexane and cyclohexene experiments on the clean platinum surfaces, it was necessary that the surfaces be reproducibly free from contamination. Segregation of any of the bulk platinum impurities at the surface--calcium, carbon, sulfur or phosphorous--could significantly affect the catalytic activity of the platinum surface. However, the introduction of low levels of strongly bound oxygen at the surface during routine cleaning treatments to remove carbon produced the largest fluctuations in platinum reactivity.

The effect of strongly bound oxygen on the cyclohexane and cyclohexene experiments on the three platinum surfaces will be discussed in detail in Chapter III. Before this investigation was carried out, however, it was noticed that after relatively long oxygen treatments to remove carbon (much longer than the 1 to 2 min necessary to remove a monolayer of carbon, as was later determined), the length of time the platinum sample was heated at 1000°C, and whether or not it was flashed to 1000°C in hydrogen before introducing the hydrocarbon reagent
could make a significant, though not always predictable, difference in the dehydrogenation reactivity. It was then determined that these results could be reproduced by introducing various amounts of strongly bound oxygen onto the surface, even though the oxygen Auger peaks had not been detected before or after the earlier runs (low levels of oxygen not being checked for as rigorously in the early experiments). Thus, careful consideration of all possible surface contaminants and of all steps of the cleaning procedure is very important in obtaining reproducible catalytic activity results at low pressure.

2.5.5. Uncertainties in the Pumping Speed and Gain of the Electron Multiplier

As discussed in detail in Appendix B, the pumping speeds needed to make the turnover number calculations could be calculated by several different methods. Each method had inherent inaccuracies, due for instance to the inability to close the leak valve instantaneously, the desorption of molecules from the chamber walls as the chamber pressure was lowered, back streaming of molecules from the pumps, or the finite thickness of the aperture between the chamber and the pump. Thus, the absolute values of the pumping speeds used in the turnover number calculations are probably accurate only to within a factor of two or three. This imparts the same uncertainty to the absolute values of the turnover numbers, but should not affect the relative values of turnover numbers.

The UTI 100C quadrupole mass spectrometer was equipped with both a Faraday cup (FC) and an electron multiplier (EM). Due to its greater stability, the FC was used in making all pressure calibrations of the mass spectrometer. However, the product detection from cyclohexane
and cyclohexene at the standard conditions could only be conveniently monitored with the EM. This made it necessary to measure the gain of the EM during each experiment and convert EM signals to equivalent FC signals in order to make the partial pressure calculations. The gain of the EM was typically stable only to within 5% or 10% during an experiment that was run for several hours. Furthermore, calculation of the gain of the EM, especially for the low standard pressure of cyclohexene (6 x 10⁻⁸ torr) was made difficult by a relatively low signal to noise ratio for the small signals to the FC. These uncertainties in determining the gain of the electron multiplier added to the fluctuation of the calculated turnover numbers.
III. THE EFFECT OF STRONGLY BOUND OXYGEN ON THE DEHYDROGENATION AND HYDROGENATION ACTIVITY AND SELECTIVITY OF PLATINUM SINGLE CRYSTAL SURFACES

3.1. Introduction

In recent years there have been a number of studies of adsorption of oxygen on both polycrystalline and single crystal platinum surfaces (29-46). The oxygen adsorption is thought to be dissociative except at very low temperature (34-36). After low temperature exposures (<500°C), the oxygen which has chemisorbed ("reactive" oxygen) reacts readily with either hydrogen or carbon monoxide, even at room temperature, and can be desorbed at about 500°C. The second observed state of oxygen, which starts to form extensively with exposures at platinum temperatures above 500°C, is relatively nonreactive: this state is stable in vacuum to about 800°C (36,37), in hydrogen to about 500°C (36), and in carbon monoxide to about 700°C (34,35). Because of the strong interaction between the oxygen and platinum atoms, this state has been extensively referred to as platinum oxide in the literature, even though there are relatively few cases where workers have positively identified the epitaxial growth of a layer of stoichiometric PtO₂ (38,39) or PtO (34) on the surface. Although bulk platinum oxide is not stable at temperatures above 500°C (47,48), it has been noted (49-51) that a thin film of stable surface oxide might form under these conditions, due to the difference of energy states, and hence in the chemical bonding, at a surface as compared to the bulk material. Thus, the state of strongly bound, relatively nonreactive oxygen at the surface will henceforth be referred to interchangeably as platinum oxide. The oxide surface coverage obtained depends on the oxygen pressure,
the exposure time and the exposure temperature (35,36), and there is evidence that the oxide can be many layers thick, with significant diffusion of oxygen atoms into the bulk (36,37,52).

Our interest in the oxidation of platinum was to determine how the preadsorption of low coverages of strongly bound, nonreactive oxygen would affect the catalysis of hydrocarbon reactions by platinum. This question could be of considerable importance with respect to supported platinum catalysts, where strongly bound oxygen could be introduced by oxygen pretreatments or might arise naturally through interactions of platinum with the oxide support. The study of oxidized platinum as a catalyst is not new, but has not been extensive. It was reported by Adams and co-workers in 1922 (53,54) that platinum oxide is a better catalyst than ordinary platinum black for the hydrogenation of organic compounds. Poltork and co-workers (2,5) studied the dehydrogenation of cyclohexane and the hydrogenation of cyclohexene as a function of dispersion on supported platinum catalysts, and reported that preoxidation of the catalysts at 400°C resulted in a significant enhancement of activity on the highly dispersed catalysts, but that the catalysts with large platinum crystallites showed no effect.

A recent study by Voorhoeve, et al. (55) of the production of hydrogen cyanide during reduction of nitric oxide over platinum catalysts has demonstrated that incorporation of oxygen into the platinum surface layers during the reaction at 650°C to 750°C maintains the catalyst in a state where it is able to produce HCN even in the presence of SO₂ in the gas mixture. In the absence of oxygen, SO₂ strongly inhibits the HCN production; the effect of preoxidation of the platinum catalyst
at high temperature was not investigated. Regeneration of the catalyst after exposure to \( \text{SO}_2 \) by the introduction of oxygen is believed to involve the replacement of sulfur in the platinum surface layers by oxygen. It has been shown in other studies that a few monolayers of oxide on platinum foils passivates the surface towards the decomposition of sulfur and carbon containing species at room temperature (44) and that a thin film of surface oxide can protect platinum electrodes from corrosion (56).

In this chapter the catalytic effect of preoxidation is reported on three well-characterized platinum single crystal surfaces—a Pt(111), a stepped Pt(S) - \([6(111) \times (100)]\) and a kinked Pt(S) - \([7(111) \times (310)]\). It was observed that low coverages of strongly bound oxygen enhance the rates of cyclohexene and cyclohexane dehydrogenation to benzene at low pressure (10\(^{-6}\) to 10\(^{-5}\) torr total pressure) and change the selectivity of cyclohexene dehydrogenation over hydrogenation to cyclohexane. Furthermore, the effect of preoxidation on catalytic rates and selectivity was found to be sensitive to the presence of surface irregularity sites: kink sites were found to play a particularly active role in the dehydrogenation activity enhancement by strongly bound oxygen. Three models are discussed which relate the oxidation of the platinum surfaces to the observed effects on catalytic reactivity and the structure sensitivity.

3.2. Oxygen Treatment of Platinum Single Crystals

To adsorb oxygen onto the platinum, the single crystal samples in this study were treated at about 800°C, at pressures of oxygen ranging from 1 x 10\(^{-7}\) torr to 1 x 10\(^{-4}\) torr, with exposure times from
several minutes to many hours. Under these conditions, the oxygen should adsorb in the oxide state, as discussed in Section 3.1, and this was experimentally observed. Auger spectra of the oxygen-treated platinum (taken either at 800°C or after cooling the sample to room temperature) showed minima at 489 and 510 eV (see Fig. 2.68), a chemical shift of about 7 eV from the minima seen at 496 and 517 eV for reactive oxygen on platinum (35, 39, 57).

The adsorbed oxygen was observed to be very stable. The platinum samples could be left overnight at room temperature in a relatively high ambient background of both hydrogen and carbon monoxide with no significant decrease in the O_{510}/Pt_{237} Auger peak ratio. The oxygen could not be removed by heating the platinum in vacuum at temperatures below 800°C; to remove final traces of nonreactive oxygen, it was necessary to alternate argon ion sputtering with extended heating of the samples above 900°C. The adsorbed oxygen was also stable under reaction conditions of up to 1 x 10^{-5} torr of hydrogen at 150°C. The intensity of the O_{510} Auger peak did not change significantly during the course of the reactions. (Small changes, however, were not readily detectable because of the buildup of approximately 3/4 of a monolayer of carbon on the catalyst surface during a reaction—the attenuation by the carbon layer leads to an increase in the O_{510}/Pt_{237} Auger peak ratio during the reaction and thus makes comparison of this ratio before and after the reaction unreliable.)

It has already been noted that the oxygen coverage of the platinum surfaces depended on the oxygen pressure, the exposure time and the exposure temperature. At a given oxygen pressure and exposure
temperature, the increase in coverage was not always a reproducible function of time. Similar reproducibility problems were encountered by Conrad, et al. (51) during the oxidation of Ir(111) surfaces. It was particularly difficult to reproduce high coverages of oxygen (greater than one monolayer), most notably on the Pt(111) and the Pt(S) - [7(111) x (310)] after several months of experimentation.

Additional variables that seemed to be important were: (1) The pressure of residual background gases--relatively high pressures of hydrogen and carbon monoxide slowed down the uptake of oxygen by the platinum catalysts. (2) Previous oxygen and heat treatment of the sample--the increase of oxygen coverage with time was more rapid if the sample had previously undergone long oxygen exposures and only short periods of heating above 900°C than if the sample had been rigorously cleaned by ion sputtering and extended high temperature heating. The controlling factor here seems to be the concentration of oxygen remaining in the bulk from previous oxygen exposures. (3) The concentration of bulk and/or surface impurities--for each of the three platinum samples studied, it was possible to adsorb higher concentrations of oxygen in shorter exposure times when the sample was initially introduced into ultrahigh vacuum with all observed impurities (i.e., calcium, carbon, sulfur, and phosphorous) present in the bulk than at any later time after numerous cleaning cycles. This initial "advantage" did not require impurities present on the surface (within the detection limits of AES), nor was it regained by exposing the sample to atmospheric conditions, even for several days. Out observations rule out any enhancement of oxygen adsorption by carbon (which has been shown by
other experiments to be an inhibitor to oxygen adsorption (58-60)) or calcium (there was no correlation between the periodic fluctuations of this impurity at the surface and the concentration of adsorbed oxygen). One set of experimental results did seem to indicate that sulfur plays some role in enhancing oxygen adsorption. Midway through the reactivity studies on the Pt(111), the platinum support wires were replaced by tantalum support wires to check if there was significant dehydrogenation or hydrogenation activity due to the platinum wires. Immediately after changing the support wires, a large sulfur peak was detected on the Pt(111) surface by AES--this sulfur could have been picked up during spotwelding, or from surface diffusion from the tantalum wire, which has a large sulfur impurity, during annealing of the spotwelds in vacuum. During relatively short (30 to 60 min) high temperature (800°C) oxygen treatments to remove the sulfur (and carbon) from the surface, monolayer coverages of oxygen ($O_{510}/Pt_{237} = 0.5$) were readily attained, whereas several days previous, several hours of oxygen exposure at the same temperature and pressure led to saturation coverages of only 1/2 monolayer. These results are certainly not conclusive, and there is no obvious explanation for enhancement of oxygen adsorption by adsorbed sulfur; however, Lang, et al. (37) also noted that the presence of sulfur seems to favor the coadsorption of oxygen. There was no indication that surface roughness was an important factor in this change of the platinum samples with time, as good, sharp LEED patterns could be obtained from the surfaces during the initial stage when oxygen was more readily adsorbed, and later
roughening of the surface by argon ion sputtering could not reproduce this initial stage.

There are two ways to achieve a given oxygen coverage on a platinum sample: the sample can be exposed to oxygen until the desired coverage is attained, or the sample can be exposed until a coverage greater than that desired is reached, at which time the sample is heated above 900°C or argon ion sputtered to remove nonreactive oxygen until the desired coverage is reached. It was observed on the Pt(111) that the reactivity of a platinum sample was significantly different at a given oxygen coverage depending on which of these two approaches was used, the reactivity being higher when the first approach was taken (i.e., oxygen exposure to desired coverage). The reactions reported on below were all carried out after the platinum samples had been oxidized by this first, direct approach, unless noted otherwise. The results of experiments run on the Pt(111) after the crystal had been heated to high temperature or ion sputtered to reach the desired oxygen coverage will be reported at the end of Section 3.3.3 after other data on the dehydrogenation of cyclohexane.

3.3. Results

3.3.1. LEED Studies of Nonreactive Oxygen Adsorbed on Platinum

The low energy electron diffraction (LEED) of each platinum single crystal catalyst was studied before and after oxygen treatments and reactive studies. The clean surface LEED patterns are shown in Fig. 2.4. The onset of an ordered oxygen structure on the platinum surfaces was observed in each case at an oxygen coverage of about
$O_{510}/Pt_{237} = 0.2$ (somewhat less than one half monolayer). The ordered structures were initially observed on isolated parts of both faces of the crystals; at an oxygen coverage of about one monolayer ($O_{510}/Pt_{237} = 0.5$), the ordered structures were observed to be uniform over both sides of the crystals.

The oxygen structure observed on the Pt(111) was a $(2 \times 2)$, illustrated in Fig. 3.1A for an oxygen coverage of $O_{510}/Pt_{237} = 1.9$. Sometimes a faint $(\sqrt{3} \times \sqrt{3}) - R30^\circ$ oxygen structure was observed simultaneously with the $(2 \times 2)$ oxygen structure on the Pt(111), but it was not uniform over the surface. A $(\sqrt{3} \times \sqrt{3}) - R30^\circ$ oxygen structure was observed on both the Pt(S) - [6(111) x (100)] and the Pt(S) - [7(111) x (310)], as illustrated in Fig. 3.1B for the stepped surface at an oxygen coverage of $O_{510}/Pt_{237} = 0.65$, and in Fig. 3.1C for the kinked surface at an oxygen coverage of $O_{510}/Pt_{237} = 0.85$. A faint $(2 \times 2)$ oxygen structure was sometimes observed simultaneously with the $(\sqrt{3} \times \sqrt{3}) - R30^\circ$ oxygen structure on both the stepped and kinked surface (such a $(2 \times 2)$ oxygen structure appears very faintly in Fig. 3.1C of the kinked surface). In no case were the diffraction spots arising from the adsorbed oxygen observed as doublets, indicating that the diffraction from oxygen adsorbed on two adjacent terraces of the stepped or kinked surface was not coherent.

There are two additional observations to be made from the LEED patterns of oxygen adsorbed on the Pt(S) - [6(111) x (100)] and the Pt(S) - [7(111) x (310)]. On both of these surfaces, a single broad, diffuse spot was sometimes observed between the specular and first order spots of the platinum substrate, as seen in Fig. 3.1B on the
Fig. 3.1. Ordered oxygen structures observed by low energy electron diffraction on the three platinum surfaces studied: 
(A) (2x2)-0 on Pt(111); 
(B) ($\sqrt{3} \times \sqrt{3}$)-R30°-0 on Pt(S)-[6(111)x(100)]; 
(C) ($\sqrt{3} \times \sqrt{3}$)-R30°-0 on Pt(S)-[7(111)x(310)]; a faint (2x2)-0 is also present.
stepped surface. This spot appeared over a wide range of coverages (from less than half a monolayer to more than one monolayer), either in the absence of or presence of another oxygen ordered structure. It appears on the stepped surface at an angle of about 20° from the (00) doublet (this angle can be derived from measurements taken from the LEED photograph, as described elsewhere (12)) in a direction which is perpendicular to the step edges (as indicated by the doublet splitting). This would seem to indicate that this spot is centered at the specular reflection from the macroscopic plane of the surface, i.e., the Pt(755), which lies at an angle of about 9.5° from the terrace (111) planes in the appropriate direction (remembering that the angle measured from the photograph should be twice the angle between the reflecting planes).

The position of the diffuse spot on the kinked surface LEED pattern leads to the same interpretation, that it is centered at the specular reflection of the Pt(10,8,7) plane. Perhaps the ordering of the oxygen atoms along the step and kink edges leads to the beginnings of a registry between oxygen atoms on adjacent terraces, which would lead to coherent diffraction by the oxygen atoms in the specular direction of the macroscopic plane (which is determined by the step and kink platinum atoms).

A third spot was sometimes observed between the two spots of the platinum substrate doublets in the presence of a well-ordered oxygen structure on both the stepped and kinked crystals. These spots, as seen in Fig. 3.1C, are the (00) and second order spots due to the ordered oxygen adsorbate layer.

The surface structures of the platinum catalysts were also checked after a hydrocarbon reaction had been run. The ordered oxygen
structures were stable under reaction conditions, as were the clean platinum surface structures. The buildup of disordered carbon during a reaction (approximately 3/4 of a monolayer) resulted in a very high background intensity, but did not otherwise alter the LEED pattern observed before starting a run.

3.3.2. The Dehydrogenation and Hydrogenation of Cyclohexene

The reaction of cyclohexene in the presence of excess hydrogen was studied on the three platinum single crystal catalysts with clean surfaces and for a series of oxygen coverages. The standard conditions used for these experiments were 6 x 10^{-8} torr of cyclohexene and 1 x 10^{-6} torr of hydrogen, and a catalyst temperature of 1500°C. Turnover numbers, the number of product molecules per second per platinum surface atom, were calculated as a function of time from the mass spectrometer data using the following equation: \( T_i = \frac{21P_iS_i}{A} \), where \( T_i \) is the turnover number, \( P_i \) the partial pressure in torr and \( S_i \) the pumping speed in cm³/sec for the \( i \)th product and \( A \) is the surface area in cm² of the platinum sample (see Appendix C for the derivation of this equation).

On the clean platinum surfaces, the only detectable product from cyclohexene was the dehydrogenation product, benzene. A plot of turnover number for benzene production as a function of time for two clean surface experiments is shown in Fig. 3.2. One experiment shown was on the Pt(111) and the other on the Pt(S) - [7(111) x (310)]; the clean surface reactivity of cyclohexene on the Pt(S) - [6(111) x (100)] was very similar to that shown for the kinked surface. These curves have been corrected for any background partial pressure of benzene.
Fig. 3.2. Benzene production from cyclohexene as a function of time on the clean kinked Pt(S) - [7(111)x(310)] surface (●●●) and the clean Pt(111) surface (●△●).
in the reaction chamber (measured after introducing the hydrogen and heating the platinum sample to 150°C) and for the reactivity of the reaction chamber (this was measured by periodic "blank" control runs, with the platinum sample poisoned and at room temperature, or with no platinum sample in the chamber). The production of benzene from cyclohexene over the platinum catalysts typically passed through a maximum after 2 to 3 min, fell off rapidly during the next 5 to 10 min, then slowly approached the background reactivity level over the next 100 to 200 min. The maximum in the turnover number as a function of time varied by about ±15% during a series of experiments on a given platinum sample under standard reaction conditions in a given reaction chamber, and it is this maximum turnover number which will be reported as a function of oxygen coverage. For calibration purposes, clean surface reactivities were checked for all three platinum samples in both reaction chambers. For the cyclohexene reaction, the relative clean surface values agreed very well between the two systems, but the absolute values differed consistently by a factor of two. Rather than redo all calibrations for both systems, average absolute values have been reported.

The dehydrogenation reactivity of cyclohexene on the Pt(111) sample peaked at approximately 1/2 the maximum values observed for both the stepped and kinked samples. The maximum reactivity was achieved earlier on the Pt(111), and fell off more rapidly as well. By integrating the curves of turnover number as a function of time, it was determined that the total reactivity observed was 0.15 molecule/Pt surface atom on the clean Pt(111), 0.30 molecule/Pt
surface atom on the clean Pt(S) - [6(111) x (100)], and 0.35 molecule/Pt surface atom on the clean Pt(S) - [7(111) x (310)]. The buildup of approximately 0.8 monolayer of a carbonaceous deposit was observed on all three platinum samples during a cyclohexene reaction, whether or not there was oxygen on the surface. The carbon coverage was determined by measuring the C_{272}/Pt_{237} Auger peak intensity ratio; calibration showed that C_{272}/Pt_{237} = 3.2 represents one monolayer coverage (20).

On the oxygen covered surfaces, the hydrogenation product, cyclohexane, was observed as a product of the cyclohexene reaction, as well as the dehydrogenation product, benzene. The shape of the curves of turnover number as a function of time for benzene production did not change significantly with oxygen coverage for any of the three platinum samples studied. For cyclohexane production, the turnover numbers were an order of magnitude lower than for benzene production; the reactivity with time followed the same trends illustrated in Fig. 3.2 for the dehydrogenation product, but the maximum cyclohexane production was reached 1 to 2 min earlier than the maximum benzene production.

The maximum turnover numbers for benzene production from cyclohexene are plotted as a function of oxygen coverage in Fig. 3.3 for the three platinum samples. The largest effect on reactivity of the adsorbed oxygen was observed on the kinked Pt(S) - [7(111) x (310)] surface. On this surface, the benzene production exhibits a maximum at an oxygen coverage of about one half monolayer (O_{510}/Pt_{237} = 0.25) that represented an increase in reactivity of about six times over the
Fig. 3.3. Maximum turnover numbers from benzene production from cyclohexene as a function of oxygen coverage ($O_{510}/Pt_{237} = 0.5$ corresponds to about $5 \times 10^{14}$ oxygen atoms/cm$^2$) on Pt(S)-[7(111)x(310)] (---), Pt(S)-[6(111)x(100)] (----), and Pt(111) (...).
clean surface (the total reactivity increased to about 2 molecules/Pt surface atom at this maximum). At oxygen coverages greater than one monolayer, the benzene production fell off to a relatively constant value that was less than that observed for the clean kinked surface.

An enhancement of the benzene production with oxygen adsorption was also observed on the stepped Pt(S) - [6(111) x (100)] and the Pt(111) surfaces. In these two cases, the benzene production shows a maximum at a lower oxygen coverage, about 1/3 monolayer (0510/Pt237 = 0.15), and the increase in reactivity was about a factor of two over that of the clean surfaces. At higher oxygen coverages, the benzene production decreased to values lower than those observed for the clean surfaces.

The maximum turnover numbers for cyclohexane production from cyclohexene are plotted as a function of oxygen coverage in Fig. 3.4 for the three platinum samples. At the low pressure conditions under which these reactions were carried out, the dehydrogenation product is thermodynamically favored over cyclohexane production. Cyclohexane formation was below the level of detectability in all of the experiments over the clean platinum surfaces. With the addition of adsorbed oxygen, the product cyclohexane was observed with the kinked Pt(S) - [7(111) x (310)] and the stepped Pt(S) - [6(111) x (100)], but remained undetectable with the Pt(111). On both the kinked and stepped surfaces, the maximum hydrogenation activity occurred at about one third monolayer oxygen coverage (0510/Pt237 = 0.15), and was greater for the kinked surface. Hydrogenation activity on the kinked surface decreased to undetectable levels at oxygen coverages greater
Fig. 3.4. Maximum turnover numbers for cyclohexane production from cyclohexene as a function of oxygen coverage on Pt(S) - [7(111) x (310)] (-○-), Pt(S) - [6(111) x (100)] (-□-), and Pt(111) (...▲...).
Cyclohexene $\rightarrow$ Cyclohexane

- $\text{Pt(S-[7(III) x (310)]}$
- $\text{Pt(S-[6(III) x (100)]}$
- $\text{Pt(III)}$

$P_{H_2} = 1 \times 10^{-6} \text{ torr}$; $P_{C_6H_{10}} = 6 \times 10^{-8} \text{ torr}$

$150 \degree C$

**Fig. 3.4**

XBL 785-4956A
than one monolayer, but low levels of activity were observed on the stepped surface at high oxygen coverages. As the rate of cyclohexane production from cyclohexene was close to the detection limit of the systems, the turnover numbers reported for this reaction have greater uncertainty than those for benzene production under the same conditions.

The detection of two products (benzene and cyclohexane) from cyclohexene on oxygen covered platinum made it possible to consider the selectivity of dehydrogenation over hydrogenation as a function of oxygen coverage. The turnover numbers for benzene and cyclohexane production on the kinked Pt(S) - [7(111) x (310)] surface have been replotted together as a function of oxygen coverage in Fig. 3.5. It can be seen that the ratio of benzene to cyclohexane varies from greater than 40:1 on the clean surface (assuming that a turnover number of 1 \times 10^{-5} \text{ molecules/sec/Pt atom} could be detected) to about 10:1 at \( \theta_{510}/\theta_{237} = 0.13 \) to about 100:1 at \( \theta_{510}/\theta_{237} = 0.22 \). Thus, it can be seen that the selectivity of the kinked catalyst changes markedly with small changes in oxygen coverage during the buildup of half a monolayer of oxygen on the platinum. The selectivity of dehydrogenation over hydrogenation also decreases from greater than 40:1 on the clean surface to about 10:1 at \( \theta_{510}/\theta_{237} = 0.27 \) on the stepped Pt(S) - [6(111) x (100)], but does not seem to increase again at higher oxygen coverages. The selectivity cannot be discussed for the Pt(111), as the hydrogenation product was not detected with this surface.

3.3.3. The Dehydrogenation of Cyclohexane

The reaction of cyclohexane in the presence of excess hydrogen was also studied on the three platinum samples with clean surfaces and
Fig. 3.5. Maximum turnover numbers for benzene production from cyclohexene (- - -), and for cyclohexane production from cyclohexene (---) as a function of oxygen coverage on Pt(S) - [7(111) x (310)] showing the change in selectivity of cyclohexene dehydrogenation over hydrogenation.
for a series of oxygen coverages. The standard conditions used for these experiments were $2 \times 10^{-6}$ torr of cyclohexane and $1 \times 10^{-5}$ torr of hydrogen and a catalyst temperature of 150°C. The only detectable product from cyclohexane was the dehydrogenation product, benzene; though higher reagent pressures were used in the cyclohexane experiments than in the cyclohexene experiments, the rate of benzene production from cyclohexane was still an order of magnitude lower than from cyclohexene. Again, since this lower level of reactivity is close to the detection limit of the systems, the turnover numbers for benzene production from cyclohexane have a greater uncertainty than those for benzene production from cyclohexene.

A plot of benzene production from cyclohexane as a function of time for two clean surface experiments is shown in Fig. 3.6. One experiment shown was on the Pt(111) and the other on the Pt(S) - [6(111) x (100)]; the clean surface reactivity of cyclohexane on the Pt(S) - [7(111) x (310)] was very similar to that shown for the stepped surface. Again, these curves have been corrected for any background partial pressure of benzene and for the reactivity of the reaction chamber. The production of benzene from cyclohexane over the platinum catalysts typically passed through a maximum after 5 to 7 min, then approached the background reactivity level over 100 to 200 min. The maximum turnover number as a function of time was the same for all three clean platinum surfaces within the experimental error (absolute values from the two reactor systems have been averaged). The maximum benzene reactivity, however, was achieved earlier on the Pt(111), and decreased more rapidly than on either the stepped or
Fig. 3.6. Benzene production from cyclohexane as a function of time on the clean stepped Pt(S) - [6(111) x (100)] surface (---□---) and the clean Pt(111) surface (...▲…).
kinked surfaces. Buildup of approximately 0.7 monolayer of a carbonaceous deposit was observed on all three platinum samples during a cyclohexane experiment, whether or not there was oxygen on the surface. This was slightly less than the carbon buildup observed for the cyclohexene reactions, in spite of the greater hydrocarbon reagent pressure and lower hydrogen to hydrocarbon ratio.

It is appropriate to note at this point that the cyclohexane reaction was studied on the clean Pt(111) sample when it was mounted on the sample manipulator with short pieces of platinum wire and when mounted with short pieces of tantalum wire. No significant difference in reactivity was observed, leading to the conclusion that the platinum support wires, when used, did not add significant undesired reactivity to that of the platinum single crystal catalysts.

The maximum turnover numbers for benzene production from cyclohexane are plotted as a function of oxygen coverage in Fig. 3.7 for the three platinum samples. The effect of adsorbed oxygen on the cyclohexane dehydrogenation reactivity of the kinked Pt(5) - [7(111) x (310)] is similar to the effects previously observed for cyclohexene dehydrogenation and hydrogenation. The reactivity goes through a maximum at an oxygen coverage of about 0.12 (approximately 1/4 monolayer), then decreases again, starting to level off at a value which is, in this case, greater than that of the clean surface reactivity.

The effect of adsorbed oxygen on the benzene production from cyclohexane on the Pt(111) surface follows a different trend than those previously described. The reactivity increases from the clean
Fig. 3.7. Maximum turnover numbers for benzene production from cyclohexane as a function of oxygen coverage on 
Pt(S) - [7(111) x (310)] (---), Pt(S) - [6(111) x (100)] (---□---), and Pt(111) (...▲...).
Cyclohexane → Benzene

- \(\text{Pt(S)}-[7(\text{III}) \times (310)]\)
- \(\text{Pt(S)}-[6(\text{III}) \times (100)]\)
- \(\text{Pt (III)}\)

\(P_{H_2} = 1 \times 10^{-5}\) torr; \(P_{C_6H_2} = 2 \times 10^{-6}\) torr

150°C

Fig. 3.7
surface value to a maximum at a coverage of about $0_{510}/Pt_{237} = 0.15$; rather than decrease again, this maximum reactivity is maintained in the presence of higher oxygen coverages up to and greater than one monolayer. It is interesting to note that the reactivity of the kinked surface at high oxygen coverages starts to level off at a value close to this maximum reactivity maintained on the Pt(111) surface.

No oxygen coverage effects were observed on the stepped Pt(S) - [6(111) x (100)] sample for cyclohexane dehydrogenation, up to monolayer coverages. The benzene production from cyclohexane was checked for the clean surface and at various oxygen coverages in each of the reaction chambers with the same result.

As mentioned earlier, it was observed on the Pt(111) that the cyclohexane dehydrogenation to benzene reactivity was significantly lower if the crystal was heated to high temperature or ion sputtered to reach the desired oxygen coverage. In Fig. 3.8, the maximum turnover numbers for benzene production from cyclohexane are plotted as a function of oxygen coverage for both increasing oxygen coverage (the crystal was exposed to oxygen at 800°C until the desired coverage was reached) and decreasing oxygen coverage (the crystal was heated at 1000°C and/or ion sputtered after each experiment to produce a lower oxygen coverage, then treated in oxygen at 800°C for several minutes only, to remove residual carbon). It can be seen that the reactivity trend with decreasing coverage is roughly linear, with fairly large scatter in the data, and that the average reactivity is about 2/3 that on the clean Pt(111). With removal of the last traces of strongly bound oxygen (within AES detection limits), the clean surface reactivity
Fig. 3.8. Maximum turnover numbers for benzene production from cyclohexane as a function of oxygen coverage on the Pt(111) for both increasing oxygen coverage (\ldots \triangle \ldots) and decreasing oxygen coverage (--\square--). One point (\triangle) was obtained by flashing the Pt(111) briefly to 1000°C to remove carbon and some oxygen after the experiment at $O_{510}/Pt_{237} = 0.22$ on the increasing oxygen coverage curve.
level was regained and the increasing oxygen coverage trend could be reproduced by successive oxygen treatments. One point is shown in Fig. 3.8 at an oxygen coverage, \( \frac{O_{510}}{Pt_{237}} = 0.18 \), that was obtained by flashing the Pt(111) briefly to 1000ºC to remove carbon and some oxygen after the experiment at \( \frac{O_{510}}{Pt_{237}} = 0.22 \) on the increasing oxygen coverage curve. The dehydrogenation reactivity after this treatment was lowered, but was still about twice that observed for the decreasing oxygen coverage curve. Following this run, the Pt(111) was exposed to oxygen 800ºC until the oxygen coverage reached \( \frac{O_{510}}{Pt_{237}} = 0.35 \); it can be seen in Fig. 3.8 that the reactivity observed after this treatment was back up to the constant, maximum value observed on the Pt(111) at oxygen coverages above \( \frac{O_{510}}{Pt_{237}} = 0.15 \).

In each case for decreasing oxygen coverage, a hydrocarbon experiment was run before the crystal was heated to 1000ºC and/or ion sputtered to lower the oxygen coverage. Thus, these results do not rule out the possibility that the previous reaction itself is responsible for altering the surface, and hence the subsequent reactivity, and not the difference in treatment to obtain a given oxygen coverage. This could easily be checked by oxygen exposure at 800ºC to reach a given oxygen coverage, followed immediately by flashing to 1000ºC to remove oxygen before running the hydrocarbon reaction.

3.4. Discussion

3.4.1. AES and LEED Studies

The formation of a surface layer of stable platinum oxide on the three platinum samples studied was evidenced by the observed chemical shift of the oxygen Auger peaks to lower energy (510 eV vs 517 eV).
and by the stability of the adsorbed oxygen under vacuum and reducing conditions. Ordered oxygen structures were observed by LEED, but no attempt was made to determine the stoichiometry, PtO_x, of the oxide layer from the data. The O_{510}/Pt_{237} Auger peak intensity ratio was calibrated in conjunction with the LEED data on the Pt(S) - [6(111) x (100)], obtaining O_{510}/Pt_{237} = 0.5 at a coverage of approximately one monolayer, that was one oxygen atom for every three platinum surface atoms, or approximately 5 x 10^{14} oxygen atoms/cm^2. This is in reasonable agreement with previous calibrations of the Auger signal with coverage (21-24).

In oxygen treating these three platinum samples with a varied concentration of surface defects (step and kink sites), no structure dependence was noted; approximately the same oxygen surface coverages were obtained on each sample at a given oxygen pressure, exposure time, and exposure temperature. This question was not addressed in detail, however, and a small structure dependency could easily have been masked by other variables that were difficult to control (e.g., variation of residual H_2 or CO in the ambient background, or the concentration of bulk impurities) from one oxygen exposure to the next, or from crystal to crystal. The decrease in saturation coverages obtained on a platinum sample after many oxygen treatments and hydrocarbon reactions was especially difficult to control, and is a problem which has been reported by other groups (61,62).

There is no general agreement in the literature as to the ordered structures observed by LEED in the presence of an oxide layer on platinum single crystals. We observed a strong (2 x 2) oxygen structure on the
Pt(111) (Fig. 3.1A), sometimes accompanied by a faint ($\sqrt{3} \times \sqrt{3}$) - R30° oxygen structure. Merrill and co-workers (36,63) observed a strong ($\sqrt{3} \times \sqrt{3}$) - R30° oxygen structure, accompanied by a weak (3 x 15) oxygen structure on the oxidized Pt(111). There is, however, good agreement that chemisorption of oxygen at low temperature (i.e., "reactive" oxygen) gives rise to an ordered (2 x 2) oxygen structure on the Pt(111) (21,36,59,64-66) and on stepped surfaces close to the Pt(111) (24,65,67). Légaré and co-workers (38,39) observed complex LEED patterns on the Pt(111) at high oxide coverages that they relate to the growth of an epitaxial layer of PtO$_2$ with a slightly larger real unit cell than the substrate Pt(111); the interpretation of their results, however, is difficult because of their failure to remove a substantial concentration of surface calcium.

On both the Pt(S) - [6(111) x (100)] and Pt(S) - [7(111) x (310)] a ($\sqrt{3} \times \sqrt{3}$) - R30° oxygen structure (Fig. 3.1B,C) was observed, sometimes accompanied by a faint (2 x 2) oxygen structure. Légaré, et al. (39) have also investigated the oxidation of a Pt(S) - [6(111) x (100)] by LEED and AES; after high pressure oxygen adsorption at 500°C, they observe simultaneously (2 x 2) and ($\sqrt{3} \times \sqrt{3}$) - R30° oxygen structures, as well as spots they associate with the growth of an epitaxial layer of PtO$_2$. In our work, and in the work of Légaré, et al., the diffraction spots arising from the adsorbed oxygen were not observed as doublets; Gland and Korchak (24), however, observed splitting of the oxygen (2 x 2) structure on a Pt(S) - [12(111) x (111)] after adsorption of oxygen at low temperature.
These results on the stepped and kinked platinum surfaces seem to indicate that the presence of a high density of defect sites favors the formation of the $(\sqrt{3} \times \sqrt{3}) - R30^\circ$ oxygen structure over the $(2 \times 2)$ oxygen structure; perhaps the density of defect sites on a given Pt(111) surface determines which structure is observed. For each platinum surface studied, the oxygen structures observed after oxidation were very stable in vacuum and under the highly reducing conditions of the hydrocarbon reactions.

3.4.2. Reactivity Studies

The experimental results reported here lead to two important conclusions: (1) low coverages of strongly bound, nonreactive oxygen on platinum catalysts enhance the dehydrogenation rates of both cyclohexene and cyclohexane to benzene, and change the selectivity of dehydrogenation over hydrogenation for the cyclohexene reaction; and (2) the effect of preoxidation on the reactivity of the platinum surfaces is structure sensitive, the reactivity being most enhanced on the kinked surface. The role that oxygen plays in changing the reactivity and selectivity of platinum catalysts is as yet poorly understood, but there are three models that might explain the observed effects. These models have been previously discussed by McCabe and Schmidt (61,68) with respect to the enhanced bonding of H$_2$ and CO that they observed on oxidized platinum surfaces.

The first model postulates that the formation of a surface layer of oxide will result in a change in the electronic structure of the surface platinum atoms: in the oxide, the adsorbed oxygen atoms would tend to remove platinum valence electrons, and the surface platinum
atoms would become positively charged. This change in electronic structure could affect the binding of hydrogen and hydrocarbon reactants, intermediates, and products to the catalyst surface, which in turn could change the rates and selectivity of the observed reactions. Since the presence of high concentrations of step and kink defect sites has a large effect already on the electronic structure of the clean platinum surfaces (69) the formation of a surface oxide might change the electronic structure of each surface site differently, giving rise to the observed structure sensitivity of the preoxidation on the reactions. McCabe and Schmidt (61,68) have determined that oxide covered platinum surfaces have new binding sites for both hydrogen and carbon monoxide with significantly higher binding energies than on the clean surfaces; in addition, they observed that the initial sticking coefficient for hydrogen was higher by almost a factor of two on the oxidized surface, falling to a low value as soon as the higher binding energy state was populated. They observed the largest effects for low oxide coverage (just as the enhancement of dehydrogenation and hydrogenation activity was observed to be greatest at low oxygen coverage), with the creation of one to two higher energy binding sites per oxide atom at the expense of the lower energy clean surface binding sites. This enhanced bonding of hydrogen could explain the large increase in hydrogenation activity of cyclohexene to cyclohexane observed on two of the platinum catalysts that were studied. Upon low temperature adsorption of oxygen on platinum, the work function increases by about 1 eV (61,63,70,71); with high temperature oxidation, on the other hand, the work function has been shown to decrease by
about 1 eV (36,38,63). This decrease would seem to indicate that oxidation leads to adsorbed oxygen atoms beneath the surface platinum atoms; the positively charged surface metal atoms would thus be readily available for bonding with hydrogen and hydrocarbons.

The second model proposes that the strongly adsorbed oxygen atoms are active in compound formation with other adsorbates such as hydrogen and hydrocarbons; such oxygen containing compounds could provide alternate pathways for dehydrogenation or hydrogenation, thus changing observed reaction rates and selectivity. For example, the formation of hydroxyl groups on the surface might enhance the hydrogenation activity of cyclohexene to cyclohexane. An oxygen atom strongly adsorbed at a step or kink platinum site might show different activity for compound formation than an oxygen atom at a (111) terrace site; this could provide an explanation for the observed structure sensitivity of the reactivity and selectivity on oxidized platinum catalysts.

The third model is that the oxidation of the platinum surface results in a reconstruction or rearrangement of the surface atoms. The enhancement of dehydrogenation activity and the change in selectivity could then be postulated to arise from the creation of new active sites during this rearrangement; the structure sensitivity could arise from a variation in the ease of reconstruction from surface to surface. Platinum dispersed as small particles on oxide supports has been observed to exhibit increased mobility under oxidizing atmospheres (72,73) and LEED observations indicate that the Pt(110) surface reconstructs after extensive heating in oxygen (34,64,70). A similar surface rearrangement has been observed by Amariglio and co-workers (74) to
occur on platinum and nickel during the synthesis of water from oxygen and hydrogen, and they postulate that sites formed by this reaction are active for ethylene hydrogenation (75-77). The mechanism they propose cannot be used to explain our results, however, due to the nonreactivity of the strongly bound oxygen with hydrogen under our experimental conditions.

Consideration of the structure sensitivity of the observed oxidation effects on reactivity and selectivity will provide additional information for the critical appraisal of the three proposed models. Before discussing the effect of oxygen on the platinum structure sensitivity, a brief look at the clean surface structure sensitivity is in order. For the dehydrogenation of cyclohexene to benzene, the observed order of reactivity was

\[
\text{Pt(S)} - [7(111) \times (310)] \approx \text{Pt(S)} - [6(111) \times (100)] > \text{Pt(111)},
\]

where the Pt(111) was a factor of two less reactive than the stepped and kinked surfaces. This result is not in agreement with the work of Blakely and Somorjai (25), who reported that the dehydrogenation of cyclohexene to benzene requires the presence of step sites and does not occur on the Pt(111) surface. The Pt(111) surface was observed to poison more rapidly than the other two surfaces. The catalyst poisoning is believed to arise from the building of a carbonaceous deposit on the surface during the course of the reaction—carbon coverages of approximately 0.8 monolayer were observed on all three surfaces after a cyclohexene experiment. The poisoning mechanism was not studied in detail, however. Since the poisoning characteristics and carbon buildup did not change significantly with preoxidation
of the platinum catalysts, and since the strongly bound oxygen was nonreactive under the reaction conditions, the oxygen enhancement of dehydrogenation rates cannot be explained by a simple "clean-off" reaction with the adsorbed oxygen that would delay carbon buildup on the catalyst surface.

For the dehydrogenation of cyclohexane to benzene, all three platinum surfaces studied showed about the same level of reactivity. This result agrees well with studies on dispersed platinum catalysts at the high pressure which indicated that the dehydrogenation of cyclohexane to benzene is structure insensitive (2,4,78). Our result on the Pt(111) is not in agreement with the relatively low turnover number reported by Blakely and Somorjai (25) on a Pt(111) in comparison to several stepped and kinked surfaces under low pressure conditions. The Pt(111) surface was observed to poison more rapidly for cyclohexane dehydrogenation than the other two surfaces; Mitrofanova, et al. (5) observed that supported platinum catalysts with low dispersion (large metal crystallites) poisoned more rapidly than catalysts with very high dispersion for this same reaction under high pressure conditions.

Preoxidation of the platinum catalyst surfaces resulted in an enhancement of benzene production from cyclohexene on all three surfaces studied; however, the relative enhancement of reactivity on the kinked Pt(S) - [7(111) x (310)] surface was more than three times that on either the Pt(111) or stepped Pt(S) - [6(111) x (100)], and the maximum enhancement on the kinked surface occurred at an oxygen coverage (O_{510}/Pt_{237} = 0.25) significantly higher than on the other two surfaces (O_{510}/Pt_{237} = 0.15). Thus, although the presence of kink sites did
not significantly increase the clean surface reactivity of the kinked surface over that of the stepped surface, the presence of kink sites markedly affected the change in reactivity in the presence of low coverages of strongly bound oxygen. The relative enhancement of cyclohexene dehydrogenation to benzene on the stepped surface was very similar to that on the Pt(lll), the rates over the stepped surface being about twice the rates over the Pt(lll) surface at any oxygen coverage.

The enhancement of cyclohexene hydrogenation to cyclohexane was also greater (by about a factor of two) for the kinked surface than for the stepped surface, and the selectivity of dehydrogenation over hydrogenation as a function of oxygen coverage differed considerably for these two surfaces; the dehydrogenation reaction was not detected on the Pt(lll), even at low oxygen coverages. Poltorak and Boronin (2) observed that highly dispersed platinum catalysts showed an enhancement of cyclohexene hydrogenation after oxidation at 400°C, while the reactivity of supported catalysts with low dispersion was not significantly altered; our results are in good qualitative agreement with these high pressure experiments on supported catalysts if we assume that highly dispersed metal particles have a high concentration of low-coordination step and kink sites, while the larger particles on low dispersion catalysts are fairly representative of low index planes such as the Pt(lll).

The enhancement of cyclohexene dehydrogenation by low oxygen coverages seems too large, particularly on the kinked surface, to be explained by surface reconstruction with the creation of new active
sites, especially in view of the observation that the LEED pattern from the platinum substrate did not change significantly with oxygen coverage for any of the three surfaces studied. It seems that a change in the electronic structure of the platinum surface atoms due to the preoxidation and/or the formation of surface compounds involving oxygen must be largely responsible for the observed enhancement and change in selectivity. Apparently, the presence of platinum kink sites promotes particularly favorable surface electronic changes and/or enhances compound formation. Although the formation of hydroxyl groups might be important in the observed hydrogenation activity, the decrease in the work function observed with the strongly bound oxygen (36,38,63) leads to an interpretation that a significant proportion of the adsorbed oxygen is below the platinum surface atoms and prompts us to believe that compound formation is not the primary mechanism for enhancement of dehydrogenation activity.

For cyclohexane dehydrogenation to benzene, preoxidation of the platinum catalyst surfaces resulted in reactivity enhancement on only two of the surfaces, the kinked Pt(S) - [7(111) x (310)] and the Pt(111). The maximum enhancement on the kinked surface was about twice that for the Pt(111) and the observed variation of turnover number with oxygen coverage was markedly different for the two surfaces. On the kinked surface, the reactivity passes through a maximum, then decreases again, the same trend as observed for cyclohexene dehydrogenation and hydrogenation on all three surfaces; on the Pt(111), the reactivity increases to a maximum which is maintained in the presence of higher oxygen coverage. The reactivity of the kinked surface at high oxygen
coverages starts to level off at a value close to this maximum reactivity maintained on the Pt(111) surface. This observation lends itself to the interpretation that there are active sites for cyclohexane dehydrogenation associated with (111) terraces and with kink defects, and that these two types of active sites are "enhanced" in different ways by strongly bound oxygen (as predicted by the electronic surface structure model), only the terrace sites remaining active with relatively high oxygen coverages. Additional experiments at oxygen coverages greater than one monolayer (O$_{510}$/Pt$_{237} = 0.5$) would help clarify this interpretation.

It is interesting to note that cyclohexane dehydrogenation to benzene is maintained at a reactivity level above that of the clean surfaces at high oxygen coverages for both the kinked and Pt(111) surfaces whereas the rate of cyclohexene dehydrogenation to benzene fell off to values lower than on the clean surfaces for each platinum catalyst at high oxygen coverage. In the case of cyclohexane dehydrogenation it does not seem possible to interpret the decline of dehydrogenation reactivity at high oxygen coverages as a simple blocking of platinum sites by the adsorbed oxygen as the coverage increases. If one postulates that there are distinct terrace and kink active sites for cyclohexane dehydrogenation, the activities of which become different in the presence of strongly bound oxygen, then it would appear that only the kink sites are "blocked" or inactivated by high oxygen coverage, while the terrace sites maintain their enhanced reactivity up to at least monolayer coverages of oxygen.
If there are distinct terrace and kink sites for cyclohexene dehydrogenation, they are both inactivated by high oxygen coverage.

The benzene production from cyclohexane was significantly lower on the Pt(111) if the crystal was heated to high temperature or ion sputtered to reach the desired oxygen coverage; this trend is shown in Fig. 3.8. This makes it clear that the oxygen coverage alone, as determined from the Auger peak ratio $O_{510}/Pt_{237}$ is not sufficient to predict the platinum surface reactivity, and that the pretreatment history is also very important. Brief flashing at 1000°C to remove carbon and some oxygen after an experimental run decreased the observed reactivity by about 30% from the maximum reactivity observed for high oxygen coverages on the Pt(111); repeated heat treatments above 1000°C, combined with ion sputtering of the surface resulted in an average decrease of about 70% from this maximum reactivity, to a benzene production level less than that on the clean surface. Apparently both terrace and kink sites are affected adversely by the more severe pretreatments. These observations might be explained by a high temperature rearrangement of the surface (a reversal of a favorable surface reconstruction which occurred during the adsorption of the strongly bound oxygen) or by a depletion of oxygen at the surface (which would lessen electronic surface structure changes by the oxygen, or hamper surface compound formation). The ordered oxygen structures described in Section 3.3.1 typically disappeared after ion sputtering or prolonged heating at 1000°C, even though the $O_{510}$ Auger peak could still be readily detected. As mentioned in Section 3.3.3, these results do not rule out that an alteration of the surface by the hydrocarbon
reaction itself is partially responsible for the observed decrease in reactivity; the ordered oxygen structures, however, were stable under the reaction conditions, while they did not persist during ion sputtering or prolonged high temperature heating.

In any case it seems to be the kink sites that play the more important role in cyclohexane dehydrogenation activity enhancement at low oxygen coverages, even though they do not significantly increase this reactivity on the clean kinked surface. Our results are in qualitative agreement with those of Mitrofanova, et al. (5) at higher pressures; they observed that cyclohexane dehydrogenation to benzene was enhanced on highly dispersed platinum catalysts after oxidation at 400°C, while the reactivity of low dispersion catalysts was not significantly altered.

It is clear from the work of Poltorak and co-workers (2,5) that preoxidation of supported platinum catalysts can also significantly enhance dehydrogenation and hydrogenation rates over the platinum at higher pressures. The enhancement that they observed was a function of the platinum dispersion, the highly dispersed catalysts being most strongly affected by preoxidation. Strongly bound oxygen on supported platinum catalysts might arise through an interaction of the metal with the oxide support, or can be introduced by oxygen pretreatment. Although we produced the platinum surface oxide by high temperature treatment (800°C), low temperature studies of oxygen adsorption on platinum have shown that 1 to 5% strongly bound, nonreactive oxygen can be detected even after mild oxygen pretreatments (34,61,66,79,80).
The lack of any enhancement by strongly bound oxygen of cyclohexane dehydrogenation activity on the stepped Pt(S) - [6(111) x (100)] was unexpected and is still not understood. It cannot easily be explained by any of the three models that have been proposed to explain the effects of oxidation on the reactivity and selectivity of platinum catalysts. Possibly the Pt(S) - [6(111) x (100)] was contaminated by a low concentration of an impurity that we did not detect (through none of our AES data leads us to suspect impurity problems). The experiments should certainly be repeated on a second Pt(S) - [6(111) x (100)] to clarify this finding.

Although it is not yet clear how readily these results at low pressure can be extrapolated to higher pressures, it is interesting to compare the cyclohexane dehydrogenation experiments to those of Herz (81) at cyclohexane pressures of 15 torr (hydrogen pressure, 100 torr). Herz observed the following order of reactivity for cyclohexane dehydrogenation to benzene on the "clean" surfaces:
Pt(S) - [2(111) x (610)]* > Pt(111) > Pt(S) - [6(111) x (100)]. At low pressure, the clean surface reactivity for benzene production from cyclohexane was observed to be about equal on the stepped, kinked, and Pt(111)

*It has been determined by this author, using Laue x-ray diffraction, that the "Pt(S) - [3(111) x (100)]" reported on initially by Blakely (18,25), then Herz (81) is in actuality a kinked Pt(S) - [2(111) x (610)]. This kinked surface is cut about 280 ± 10° from the (111) plane towards the (610) plane on the [165] zone and is rotated 90 ± 10° from the [011] zone. The (111) terraces average 2 atoms wide and approximately every sixth atom along each step is in a kink position; this gives a kink density of approximately 9% of the surface atoms, or 1-1/2 times the kink density of the Pt(S) - [7(111) x (310)] reported on in this work.
surfaces. However, at low oxygen coverages, the observed order of reactivity was: \( \text{Pt(S)} - [7(111) \times (310)] > \text{Pt}(111) > \text{Pt(S)} - [6(111) \times (100)] \); moreover, the relative values of the maximum turnover numbers of the three crystals is about the same at \( \frac{0.510}{\text{Pt}237} = 0.08 \) as the relative values of the initial specific rates to benzene observed by Herz on the "clean" surfaces in his study. The Auger spectrometer used by Herz was admittedly not sensitive enough to detect oxygen, and his cleaning procedure to remove carbon (platinum samples heated at 925°C in \( 1 \times 10^{-6} \) torr oxygen for 120 min, followed by pump-down for 65 min, followed by brief heating above 900°C, hydrogen not being admitted until the crystal temperature was below 300°C) has subsequently been shown to be inadequate to remove all traces of strongly bound oxygen from the platinum surfaces. Thus, it is most probable that his "clean" surfaces were contaminated by low coverages of oxide; in this case, there is good agreement between the low and higher pressure data, even with respect to the relatively low reactivity of the stepped \( \text{Pt(S)} - [6(111) \times (100)] \).

3.5. Conclusions

Low coverages of strongly bound oxygen enhance the rates and change the selectivity for dehydrogenation and hydrogenation reactions on platinum catalysts. These oxygen effects are sensitive to the structure of the platinum surface, kink sites playing a particularly important role in the enhancement of dehydrogenation and hydrogenation activity by low coverages of oxygen. Analysis of our results indicate that a change of the electronic structure of the platinum surface through oxidation provides the best general model for explaining the
oxygen effects, though surface reconstruction during oxidation or complex formation involving the adsorbed oxygen may also be important.

Our results demonstrate that additives such as oxygen, in addition to surface irregularities, can play important roles in optimizing the rates and selectivity of hydrocarbon reactions over platinum catalysts. For supported catalysts, strongly bound oxygen could be introduced by oxygen pretreatments, or might arise naturally through interactions of platinum with the oxide support.
IV. OTHER LOW-PRESSURE REACTIVITY STUDIES

4.1. Introduction

In addition to the investigations of cyclohexene and cyclohexane dehydrogenation and cyclohexene hydrogenation reported on in Chapter III, the following preliminary investigations were made: the dehydrocyclization of n-heptane to toluene and benzene on the Pt(111), Pt(S) - [6(111) x (100)] and Pt(S) - [7(111) x (310)] surfaces; and the isomerization of neo-pentane and iso-butane on the Pt(S) - [7(111) x (310)] surface. The reaction conditions for these studies--hydrocarbon and hydrogen pressures, and catalyst temperature--are reported in Table 2.1; the reactions were run under flow conditions using the procedures described in Section 2.3.

Dehydrocyclization and isomerization are both important processes over platinum reforming catalysts, and it was desired in this investigation to study representative reactions--production of toluene and benzene from n-heptane, isomerization of neo-pentane to iso-pentane and n-pentane, and isomerization of iso-butane to n-butane--over platinum single crystal catalysts with well-characterized surface composition and surface structure. The dehydrocyclization of n-heptane was considered particularly interesting because it has been previously reported (18,82-84) that reaction rates for the production of toluene from n-heptane at low pressure are very sensitive to the formation of ordered carbonaceous overlayers on the platinum catalysts. The conditions for producing ordered carbonaceous overlayers were investigated, particularly the "(9 x 9)" carbon structure (pictured in Fig. 4.2A and B and described in Section 4.2). The n-heptane reaction was run on the clean Pt(111), stepped and kinked surfaces, on these
surfaces with ordered carbonaceous overlayers, and on these surfaces with various coverages of strongly bound oxygen (the adsorption of which is described in Chapter III). The results were difficult to interpret: most experiments showed no dehydrocyclization reactivity detectable above the system reactivity and the conditions that did enhance dehydrocyclization have not been well-defined due to the inability to systematically reproduce them. It seems likely that both carbonaceous deposits and strongly bound oxygen play a role under low pressure conditions, but nothing more definitive was learned.

The isomerization studies of neo-pentane and iso-butane showed that under the low pressure conditions used in this investigation, significant isomerization reactivity above the system reactivity could not be detected. Low levels of hydrogenolysis reactivity of neo-pentane to iso-butane and of iso-butane to propane could sometimes be detected.

4.2. The Formation of Ordered Carbonaceous Overlayers

It was reported by Baron, Blakely and Somorjai (83) that the rate of toluene production from n-heptane, studied at low pressure on a series of Pt(S) - [n(111) x (100)] surfaces, went through a maximum on the Pt(S) - [6(111) x (100)] surface (terraces averaging 6 atoms wide). It was felt that the rate of dehydrocyclization was high on this surface because of the formation of an ordered carbonaceous overlayer during the run, characterized by what they analyzed to be a (9 x 9) LEED pattern. Later experiments (85) could not reproduce these results. Several additional Pt(S) - [6(111) x (100)] catalyst samples were studied after the first one, but the rates of dehydrocyclization of n-heptane to toluene were observed to be low and no
ordered carbonaceous overlayers were detected by LEED after the experiments. It was undertaken as part of this investigation (86) to determine the conditions necessary for the formation of ordered carbon structures during reactions in order that their effect on the platinum catalytic reactivity could be systematically studied.

The surface structure of the platinum catalysts was routinely checked by LEED after each hydrocarbon reaction to determine if an ordered carbonaceous overlayer was present. The results were routinely negative: the LEED pattern after a run typically showed the platinum substrate spots and a high background due to the presence of a disordered carbonaceous overlayer (about 3/4 of a monolayer of carbon was typically detected by AES after a hydrocarbon reaction). Occasionally, a weak graphite ring was detected immediately after a reaction—as is illustrated in Fig. 4.1A, following a neo-pentane reaction on the Pt(S) - [7(111) x (310)]—this graphite was rotationally disordered, sometimes showing an increased intensity in directions of preferred orientation. Several times, very faint extra spots were also observed immediately following a hydrocarbon experiment, but these ordered structures were not uniform over the surface, deteriorated rapidly under the electron beam, were not readily identifiable, and were not correlated with enhanced platinum reactivity.

Heating the platinum catalyst to temperatures between 800° and 1000°C in vacuum after a run would significantly lower the high background intensity and in some cases an ordered overlayer structure could then be observed. In some cases, a graphite ring, such as that shown in Fig. 4.1A would form; in other cases, heating the crystal
Fig. 4.1. (A) Graphite ring on Pt(S) - [7(111) x (310)].
(B) Well-oriented graphite on Pt(S) - [7(111) x (310)].
would cause significant orientation of the graphite domains, as is illustrated in Fig. 4.1B on the Pt(S) - [7(111) x (310)]. However, in order to see the formation of an ordered structure resembling a (9 x 9), as reported by Baron, et al. (83,84), it was found necessary to deposit low concentrations of strongly bound oxygen on the surface before starting a reaction, by heating the platinum at 800°C in oxygen for some period of time longer than that required to remove any carbon surface impurity (as described in Section 3.2).

Such a structure formed on the Pt(111) after treating the catalyst sample in oxygen, running a cyclohexene experiment (similar results were obtained following n-heptane or cyclohexane experiments), then heating the crystal briefly to 1000°C in vacuum, as shown in Fig. 4.2A and B. This structure was characterized by a ring of six extra spots spaced hexagonally around each platinum substrate spot at a distance about 1/9 that between the platinum (111) spots. The extra spots were usually accompanied by graphite rings, which were usually oriented to some degree (this is seen clearly in Fig. 4.2A, where the platinum (00) spot is to the lower left and two platinum first order spots appear on the right side just inside the graphite ring). The complexity of the structure was revealed at higher electron beam energies, as shown in Fig. 4.2B (the platinum (00) spot has been rotated just off the edge of the screen to the left), where there seems to be an "extra" ring and spots adjacent to the second order diffraction features. The structure shown in Fig. 4.2A and B was not analyzed in detail, nor was it possible from this study to determine whether or not the observed diffraction features could all be accounted for by the simple
Fig. 4.2. (A) The "(9x9)" carbon structure on Pt(111); the platinum (0,0) spot is to the lower left, and two platinum first order spots can be seen, to the upper and lower right, inside the graphite ring. (B) The "(9x9)" carbon structure on Pt(111) at higher energy--the platinum (0,0) spot has been rotated just off the screen to the left. (C) A partially ordered carbon overlayer on Pt(111).
superposition of a graphite structure and a \((9 \times 9)\) ordered carbon structure. To express this uncertainty, the structure observed in this study will henceforth be referred to as a \"\((9 \times 9)\)\" carbon structure.

If the concentration of strongly bound oxygen was insufficient, heating the platinum sample above 800°C after a hydrocarbon experiment resulted in the formation of graphite rings alone, or the interesting partially ordered carbon structure shown on the Pt(111) in Fig. 4.2C. If the oxygen coverage was too high, heating the catalyst above 800°C after a run removed all of the carbon deposit leaving the surface clean, with perhaps some residual oxygen (in some cases on the Pt(111), very complex LEED patterns were observed with both oxygen and carbon). It is difficult to be precise about the conditions necessary to form the \"\((9 \times 9)\)\" structure--this same structure was observed after heating on the Pt(111) surface with very different surface compositions by AES, ranging from a monolayer coverage of carbon and an undetectable O510 Auger peak to a very small residual carbon peak and close to a monolayer of oxygen. Variables such as the length of time at high temperature, and the concentration of oxygen and carbon beneath the surface are probably important, but their exact influence has not yet been determined.

In any case, the relatively lengthy oxygen treatments at 800°C used by the previous investigator (18,82-84) to remove carbon contamination probably resulted in residual strongly bound oxygen on the platinum surfaces, and may well have influenced the formation of ordered carbonaceous structures reported. Greater care in removing this residual oxygen before experiments may explain the failure to
reproduce these results in later work on other platinum stepped surfaces.

4.3. Dehydrocyclization of n-Heptane--Results and Discussion

The dehydrocyclization of n-heptane was studied on the clean Pt(111), Pt(S) - [6(111) x (100)], and Pt(S) - [7(111) x (310)] surfaces, on these surfaces with ordered carbonaceous overlayers such as those shown in Figs. 4.1 and 4.2, and on these surfaces with various concentrations of strongly bound oxygen up to and greater than one monolayer coverage. The reaction conditions are reported in Table 2.1; both toluene and benzene production from n-heptane were monitored as a function of time during all reactions.

The clean surface reactivity on all three platinum samples was normally low--no significant production of benzene or toluene above the system reactivity level. The platinum catalysts were then treated at 800°C in oxygen for varying lengths of time to yield increasing coverages of strongly bound oxygen. The dehydrocyclization activity of n-heptane did not increase significantly with oxygen coverage within the detection limits of the experiments on any of the platinum samples studied. After each experiment, the catalyst sample was checked for ordered overlayers by LEED, heated above 800°C and checked by LEED again (if heating above 800°C did not initially result in an ordered overlayer, the crystal was heated again, to a somewhat higher temperature, then checked by LEED; this was repeated until an ordered overlayer formed or until the background intensity decreased to the level of a clean surface). If an ordered carbonaceous overlayer formed, an n-heptane reaction was run on this surface. However, none of the
ordered structures observed could be correlated with any significant increase in dehydrocyclization activity.

It should be noted that during several n-heptane experiments in the course of this investigation, significant production of benzene or toluene from n-heptane was observed. Interestingly, significant production of both toluene and benzene was never observed in the same experiment. In no case could the positive dehydrocyclization results be reproduced by repeating the successful experiments at the "same" conditions, nor was there any correlation with surface composition (before or after the reaction) or with surface structure (before or after the reaction). It would seem that at low pressure, a careful balance of variables—such as surface composition, surface structure, catalyst temperature, and reagent gas mixture—is necessary for efficient dehydrocyclization of n-heptane to toluene and benzene, but has not yet been well-characterized.

4.4. Isomerization Studies

The study of hydrocarbon isomerization reactions is relatively difficult using mass spectrometric techniques. Two isomers such as iso-butane and n-butane have all the same peaks in their mass spectrum cracking patterns, but the relative peak intensities do change. This makes it possible to detect isomerization products by monitoring the ratio of two peaks in the cracking pattern as a function of time: for example, the ratio of the 42 and 43 amu peak signals to the 57 amu peak signal should increase if significant isomerization of neo-pentane to iso-pentane or n-pentane occurs. But the analysis is complicated by the potential contribution to the peaks of interest from other
hydrocarbons—either in the background or resulting from competing reactions, such as hydrogenolysis. In the example above, the 42 and 43 amu peaks are both strong peaks in the cracking pattern of iso-butane, which is expected to be the primary hydrocracking product from neo-pentane. Thus, low levels of isomerization activity at low pressure are very difficult to detect.

Preliminary studies of the isomerization of neo-pentane and iso-butane in the presence of excess hydrogen were made on the clean Pt(S) - [7(111) x (310)] surface; the reactions were run under flow conditions, and the reaction conditions are reported in Table 2.1. A number of amu peaks were monitored as a function of time for each reaction. There was no evidence in any of the runs that significant isomerization of neo-pentane or iso-butane was taking place at low pressure over the platinum catalyst. This was in agreement with the previous results of Blakely (18) under similar conditions. Low levels of hydrogenolysis reactivity of neo-pentane to iso-butane and of iso-butane to propane were detected. The influence of low concentrations of strongly bound oxygen on the isomerization reactions was not studied, but would make an interesting investigation.
ACKNOWLEDGEMENTS

I would like to make the following acknowledgements: the National Science Foundation, for financial support my first 3 years at Berkeley in the form of a Graduate Fellowship; my research director, Gabor A. Somorjai, for introducing me to surface science and catalysis; my colleague, Jean Paul Biberian, for his collaboration in this investigation and for his never-failing optimism; my fiancé, John C. Hemminger, for his patience, encouragement, suggestions, proof-reading sessions, and moral support throughout the work that has gone into this thesis; my family, especially my parents, for their love and encouragement during this endeavor, as during all my others. This work was done, in part, under the U. S. Department of Energy.
A.1. General Properties of Stereographic Projection

In working with the various planes of a crystal lattice, there is an obvious advantage to developing a simple representation of the planes in two dimensions (2-D), where the prime requisite of a useful projection would be that it somehow preserve the angular relationships that exist in three dimensional (3-D) space and hence preserve the symmetry properties as well.

The first step toward developing a 2-D representation of a crystal lattice is the spherical projection. Pick an origin in the crystal lattice, say at the intersection of the crystal axes, and consider all the planes (hkl), using Miller index notation, which contain the origin (this will include one plane from each set of parallel planes designated (hkl)). The orientation of any one of these planes can be equally well represented by the normal to the plane, [hkl]; that is, one can equivalently measure angles between normals rather than between planes. (Note that it is only true in general for cubic systems that the vector [hkl] will be perpendicular to the plane (hkl); only cubic systems will be discussed in detail here.) Thus, all the planes in the crystal can be represented by a set of plane normals radiating from the chosen origin. If a reference sphere is now centered at this origin, the plane normals will intersect the surface of the sphere in a set of points called poles. The resulting collection of poles, each representing by its position on the sphere the orientation of a crystal plane, constitutes a spherical projection. The reference
sphere can be ruled, like a globe, with equally spaced great circles (meridians or longitude) and small circles (parallels or latitude) and the various poles referred to these coordinates. It is also possible to measure directly the angle between two planes by measuring the distance between the respective poles on the surface of the sphere along a great circle (by dividing the circumference of the great circle into 360 equal parts each of which corresponds to 1°). Remember that any two points on the surface of a sphere determine a great circle. The spherical projection of the faces of a cube is illustrated in Fig. A.1.

Now that the crystallographic planes are represented by a set of points in 3-D, we would like to project the spherical projection into 2D. To do this, we need to choose a suitable surface which will become the plane of projection and a viewpoint from which the projection is made (the viewpoint and a point on the sphere determine a line, the intersection of which with the plane of projection is the projection of that point on the plane of projection). Common surfaces chosen by mapmakers for making projections from 3-D into 2-D are cylinders, cones and planes. For use in crystallography, the stereographic projection has been found most useful. To make a stereographic projection, a projection plane is placed tangent to the sphere at a given point, the point of tangency, and the viewpoint is placed at the point of the sphere diametrically opposite to the point of tangency. This is illustrated in Fig. A.2A. Equivalently, the plane of projection can be placed so as to cut the sphere through the origin, perpendicular to the line determined by the viewpoint and the previous
Fig. A.1. Spherical projection of the faces of a cube.
Fig. A.2. (A) The stereographic projection: the plane of projection is placed tangent to the sphere and the viewpoint is the point on the sphere diametrically opposite to the point of tangency. (B) Relationship between radial distance on the stereographic projection and colatitude, $\theta$. 
point of tangency, without changing the nature of the stereographic projection. This is illustrated in Fig. A.2B; when the plane of projection cuts the sphere, the projection of the point P falls at P", whereas when the plane is tangent to the sphere, the projection of point P falls at P'. If the reference sphere (used in the spherical projection) is taken to be a unit sphere, then the stereographic projection provides a convenient way to represent the spherical projection within a unit circle. In any case, there is a simple relationship between the angle between a point P and the point diametrically opposite the viewpoint, θ, and the distance on the plane of projection between the projection of point P (P' or P") and the center of the plane of projection (the point of tangency, A, or the origin of the sphere, O); this is shown in Fig. A.2B.

Some of the most useful properties of the stereographic projection are: (1) the angular relations between the projected poles are preserved; (2) symmetry properties of the axis perpendicular to the plane of projection are preserved; (3) the angular relationships are not changed by rotation of the poles about the axis of projection; and (4) circles or circular arcs on the spherical projection are projected as true circles or arcs of true circles on the stereographic projection (great circles on the sphere appear on the projection as arcs of circles passing through two diametrically opposite points of the unit circle). It can be seen in Fig. A.2 that only the lower hemisphere is conveniently projected into the unit circle; if it is desired to represent the entire sphere, the convention is to "reflect" each point in the upper hemisphere to its diametrically opposite point.
on the lower hemisphere, then take the projection of this point. This convention removes ambiguity that may arise during rotation around the axis of projection. The angle between any two points on a stereographic projection can be measured using a stereographic "protractor" called a Wulff net which has the same diameter as the projection being used. The Wulff net is simply a meridian projection (stereographic projection with the point of tangency chosen on the "equator") of a sphere that has been ruled with parallels of latitude and longitude, usually every two degrees. The Wulff net is placed on the stereographic projection with the centers superimposed, then rotated until the two poles in question lie on a great circle (longitude line); the difference in latitude between the two points is the angle between the points (i.e., the angle between the two crystallographic planes represented by the points). A number of good references (87-89) give more detailed examples of how the Wulff net can be used in conjunction with stereographic projections.

A.2. Standard Projections and the Unit Stereographic Triangle

A stereographic projection showing the poles of all the important planes in a crystal is very useful, since it will show at a glance all the important relative orientations. When such a projection is prepared with the (hkl) plane as the plane of projection, that is, the [hkl] normal will be the axis of the projection and the (hkl) pole will be at the center of the projection, this is called the (hkl) standard projection. Such a projection can be drawn by calculating the angles between various planes (or there are tables available which tabulate the angles between planes) and plotting the poles with the
aid of a Wulff net; usually only the poles in one hemisphere are projected on a standard projection. The most useful standard projections are those for the low index, close-packed planes: the (111), (100), and (110) in a cubic system. A (100) standard projection showing the other low index poles is shown in Fig. A.3.

The preparation of standard projections can often be simplified by the use of zone relationships. Consider a set of planes with one direction in common—say \([uvw] = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}\)—that is, every plane in the set is parallel to the direction \([uvw]\). Then these planes are said to belong to the \([uvw]\) zone, and \([uvw]\) is the zone axis. If a plane \((hkl)\) belongs to the zone \([uvw]\), then

\[
[hkl] \cdot [uvw] = 0 = hu + kv + lw.
\]  

(A.1)

Also, if two planes intersect (i.e., have a direction in common), then they determine the zone:

\[
[uvw] = [h1k1l1] x [h2k2l2]
\]  

(A.2)

Using the above two relationships, given by Eqs. (A.1) and (A.2), one can determine any other plane which belongs to the zone.

Now, in the spherical projection, all the poles representing planes which belong to one zone will lie in a plane which passes through the origin of the sphere and thus cuts the reference sphere as a great circle; this great circle on the sphere will project onto the stereographic projection as a circular arc cutting diametrically opposite points of the unit circle. The axis of this zone will be represented by a pole which lies 90° from the great circle so projected. Repeated
application of the zone laws can greatly simplify placing the points on a standard projection--important planes usually belong to more than one zone and their poles are thus located at the intersection of zone lines. Also, important directions are usually the axes of important zones. Several zones are marked in Fig. A.3 on the (100) standard projection; the unit circle bounding the standard projection is the [100] zone.

Looking at the (100) standard projection, it will be noticed that the entire projection can be subdivided into triangles with one vertex from each of the forms (100), (111), and (110) (a form is a set of symmetry equivalent planes). Each of these triangles is equivalent and is known as a unit stereographic triangle; it is the smallest unit in which one plane from each cubic form is included. A unit stereographic triangle is shown in Fig. A.4. In addition to the vertices, a number of higher Miller index planes have been indicated on the triangle, including the three surfaces studied in this investigation--(111), (755), and (10,8,7). Stepped and kinked surface notation has been indicated where applicable.

A.3. Using the Principles of Stereographic Projection with Stepped and Kinked Surfaces

It has been determined experimentally by LEED that some high Miller index planes close to the low index planes are stable in a configuration with low index terraces separated by monatomic height steps. If the plane of the step is a low index plane, the surface is called a stepped surface; if the plane of the step is a high index plane, causing the step edge to include a high density of corner or kink positions, the surface is called a kinked surface. Schematics
Fig. A.3. The (100) standard projection—the low index poles of one hemisphere and some major zone lines are plotted.
Fig. A.4. The unit stereographic triangle. The surfaces studied in this investigation were the (111), (755), and (10,8,7).
of the stepped and kinked surfaces studied in this investigation are shown in Fig. 2.4. The nomenclature commonly used for stepped and kinked surfaces was developed to give more information about the surface configuration than the Miller index notation does. For example, the stepped surface designated as the Pt(S) - [6(111) x (100)] is noted to be a stepped surface by "(S)," has (111) terraces that are 6 atoms wide on the average, and has monatomic high steps with a (100) orientation (note that a comparable stepped surface with steps two atoms high would be designated Pt(S) - [6(111) x 2(100)]). Similarly, the Pt(S) - [7(111) x (310)] is noted to be a stepped surface by "(S)," has (111) terraces that are 7 atoms wide on the average and has monatomic high steps with a (310) orientation: it is the high Miller index orientation of the step edges that marks this surface as a kinked surface. A schematic of two stepped surfaces differing only by step orientation is shown in Fig. A.5; a schematic of a kinked surface is shown in Fig. A.6.

Looking at the unit stereographic triangle again in Fig. A.4, there are several immediate questions that might be asked. First, why do the stepped surfaces lie on the boundary zone lines of the triangle, while the kinked surfaces lie on the interior of the triangle? Second, how does one determine the correspondence between the Miller index notation and the stepped and kinked surface notation? The answer to the first question is simple, if one keeps the zone relationships in mind. For a stepped surface such as the 6(111) x (100), the terrace planes, (111), the step planes, (100), and the "macroscopic" plane, (755), all have a direction in common--this is the direction determined
Fig. A.5. Schematic diagram of two stepped surfaces differing only by stepped orientation.
Fig. A.6. Schematic diagram of a kinked surface. Note that the step edge itself is now a high Miller index plane.
by the step edges. But, in this case, the (111), (100), and (755) planes must all belong to a common zone, the [01\bar{1}]. Thus, the 6(111) x (100) must lie on the zone line between the (111) and the (100), which forms one side of the unit stereographic triangle. A similar argument can be used for any stepped surface, which by definition has low index terraces and steps. For a kinked surface such as the 7(111) x (310), the terrace (111) planes, the step (310) planes, and the macroscopic (10,8,7) plane all have a direction in common, again the direction determined by the step edges. Thus, the (111), (310), and (10,8,7) planes all belong to a common zone, the [\bar{1}32] zone; but this zone cuts through the center of the unit stereographic triangle, so that kinked surfaces in general will lie in the interior of the triangle.

To determine the correspondence between the Miller index notation and the stepped and kinked surface notation (i.e., given a stepped surface designation, how would one determine the Miller index, or vice versa), one must work with the geometry of the stepped and kinked surfaces and invoke the zone relationships. It should always be kept in mind, however, that stepped surface designations are meaningful only after there is experimental evidence, such as from LEED, that a given macroscopic plane is stable in such a configuration.

In the simplest case, one might wish to determine the Miller index of a pole which has already been carefully plotted on a (100) standard projection (this plot could be made directly from measurements taken from a Laue or LEED photograph, as will be discussed later in this appendix). This is shown in Fig. A.7. The pole P defines a
Fig. A.7. Determining the Miller index of a pole P. (A) The pole P defines a direction in space that makes the angles $\rho$, $\sigma$, and $\tau$ with the coordinate axes. (B) Measuring $\rho$, $\sigma$, and $\tau$ from the (001) standard projection. For a cubic system, $h:k:l = \cos\rho:\cos\sigma:\cos\tau$, where (hkl) is the plane normal to the direction defined by P.
direction in space (Fig. A.7A) normal to the plane (hkl) whose indices are required, and this direction makes angles $\rho$, $\sigma$, and $\tau$ with the coordinate axes $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$ which are represented in the standard projection by the poles (100), (010), and (001). These angles are measured on the projection as shown in Fig. A.7B. If the perpendicular distance between the origin and the (hkl) plane nearest the origin is $d$,

$$\cos \rho = \frac{d}{a/h} = \frac{dh}{a}$$  \hspace{1cm} (A.3)

$$\cos \sigma = \frac{d}{b/k} = \frac{dk}{b}$$  \hspace{1cm} (A.4)

$$\cos \tau = \frac{d}{c/l} = \frac{dl}{c}$$  \hspace{1cm} (A.5)

For the cubic system where $a = b = c$, taking the ratio of Eq. (A.3), Eq. (A.4) and Eq. (A.5) yields:

$$h:k:l = \cos \rho: \cos \sigma: \cos \tau$$  \hspace{1cm} (A.6)

It can be seen in Eq. (A.6) that the unknown Miller indices are in the same ratio as the measured direction cosines with the three crystal axes. Thus, one can determine the smallest prime integers with the required ratio. If the pole $P$ is known to lie on a zone $[uvw]$, as would be the case if the stepped surface notation of the pole were known, then a good check of the calculated Miller index is available: from Eq. (A.1), the determined (hkl) must satisfy $hu + kv + lw = 0$.

As a second case, let us say that we have decided to study a stepped surface, the $6(111)$ x (100), and wish to determine the Miller index of this surface. A schematic of a $6(111)$ x (100) surface is
shown in Fig. 2.4B. First, determine the angle, $\theta$, that the macroscopic plane makes with the terrace (111) plane:

$$\tan \theta = \frac{\text{step height}}{\text{terrace width}} \quad (4.7)$$

The step height and terrace width can be determined from geometric considerations. Referring to Fig. A.8, it is calculated that the "effective width" of one terrace atom is $\sqrt{3} \frac{d}{2}$ (due to the close packing of atoms in (111) planes), and the height of the step atom above the (111) terrace atoms is $\frac{\sqrt{2}}{3}d$. Substituting into Eq. (A.7),

$$\tan \theta = \frac{\sqrt{2}/3 \ d}{(n-1) \sqrt{3/2} \ d + \sqrt{3} \ d/3} = \frac{2\sqrt{2}}{3n-1} \quad (A.8)$$

where $d$ is the diameter of one atom (i.e., the nearest neighbor distance) and $n$ is the average number of atoms across one terrace. For the 6(111) x (100) surface, $n = 6$, and substitution in Eq. (A.8) yields that $\tan \theta = 0.257$, or that $\theta = 9.45^\circ$. To determine the Miller index, $(hkl)$, we now set up three equations in the unknowns, $h$, $k$, and $l$.

The angle between the (111) terrace and the 6(111) x (100) plane is $9.45^\circ$. Thus, taking the dot product yields:

$$(hkl) \cdot (111) = h + k + l = \sqrt{3} \sqrt{h^2 + k^2 + l^2} \ \cos 9.45^\circ \quad (A.9)$$

Rearranging gives:
Fig. A.8. Geometry of a threefold site on a (111) terrace. It is determined that \((\sqrt{3}/2) d\) is the effective width of a row of (111) atoms and that \(\sqrt{2}/3 \, d\) is the height of an atom occupying a threefold site.
In order to obtain two additional equations, we need to invoke the concept of zones. In this case, the \(6(111) \times (100)\) belongs to the zone determined by the (111) and (100) planes and lies between these two low index planes. This zone is \([111] \times [100] = [0\bar{1}1]\). Thus, from Eq. (A.1),

\[(hkl) \cdot [0\bar{1}1] = 0 = k - 1\]  \hspace{1cm} (A.11)

yielding that \(k = 1\). The angle between the (111) and (100) planes is 54.74° (this can be calculated by the dot product or looked up in a table). Thus, the angle that \((hkl)\) makes with (100) is 54.74° - 9.45° = 45.29°. This leads to the equation:

\[(hkl) \cdot (100) = h = \sqrt{h^2 + k^2 + l^2} \cos 45.29°\]  \hspace{1cm} (A.12)

Rearranging gives:

\[\frac{h}{\sqrt{h^2 + k^2 + l^2}} = 0.704\]  \hspace{1cm} (A.13)

Solving Eq. (A.10), Eq. (A.11), and Eq. (A.13) simultaneously:

\[\frac{h + 2k}{0.986\sqrt{3}} \cdot \frac{\sqrt{h^2 + 2k^2}}{\sqrt{h^2 + k^2 + l^2}} = \frac{h}{0.704}\]  \hspace{1cm} (A.14)

\[1.005 \, h = 1.407 \, k\]  \hspace{1cm} (A.15)

\[\frac{h}{k} = \frac{1.407}{1.005} = \frac{1.400}{1} = \frac{14}{5}\]  \hspace{1cm} (A.16)
Thus, from Eqs. (A.11) and (A.16), \((hkl) = (755)\).

From a \(n(111) \times (111)\) surface, which differs from the preceding example only in the orientation of the steps (see Fig. A.5), the equation for determining the angle, \(\theta\), between the macroscopic plane and the \((111)\) terraces becomes:

\[
\tan \theta = \frac{\sqrt{2/3} \ d}{(n - 1) \ \sqrt{3/2} \ d + \sqrt{3} \ d/6} = \frac{2\sqrt{2}}{3n - 2}
\]  

(A.17)

So, for the \(6(111) \times (111)\) surface, \(\theta = 10.02^\circ\) is calculated from Eq. (A.17). Three equations in the unknowns, \(h\), \(k\), and \(l\), can then be set up as in the preceding example, the \(6(111) \times (111)\) surface belonging to the \([\overline{2}20]\) zone determined by the \((111)\) and \((1\overline{1}1)\) planes, and it is determined that \((hkl) = (332)\).

In an analogous manner, by formulating the appropriate geometries, Miller indices can be calculated for stepped surfaces with \((100)\) or \((110)\) terraces. The Miller indices and the angles between the macroscopic plane and the terrace plane have been calculated for a number of stepped surfaces and are tabulated in Table A.1. General formulas are also indicated for calculating the Miller indices and angles in terms of \(n\), the average number of atoms in one terrace width. To confirm that the Miller index, \((hkl)\), calculated for a given stepped surface is correct, the angle, \(\theta\), between \((hkl)\) and the terrace plane should be calculated from the dot product of \((hkl)\) with the terrace plane and compared with the value of \(\theta\) calculated from the formula given in Table A.1.
Table A.1. Miller indices and angles between the macroscopic plane and the terrace plane for various stepped surfaces. The ratio a/b is measured from a LEED photograph (see Figs. A.18 and A.19), where a is the perpendicular distance between adjacent rows of doublets and b is the doublet splitting.

<table>
<thead>
<tr>
<th>Stepped Surface Designation</th>
<th>Miller Index</th>
<th>Angle of Cut from Terrace Along Zone Line Towards Step $\tan^{-1} \frac{2\sqrt{2}}{3n-2}$</th>
<th>a/b</th>
</tr>
</thead>
<tbody>
<tr>
<td>n(111) x (111)</td>
<td>(n,n,n-2)</td>
<td>$\tan^{-1} \frac{2\sqrt{2}}{3n-2}$</td>
<td></td>
</tr>
<tr>
<td>2(111) x (111)</td>
<td>(110)</td>
<td>35.26°</td>
<td>1.41</td>
</tr>
<tr>
<td>3(111) x (111)</td>
<td>(331)</td>
<td>22.00°</td>
<td>2.18</td>
</tr>
<tr>
<td>4(111) x (111)</td>
<td>(221)</td>
<td>15.79°</td>
<td>3.00</td>
</tr>
<tr>
<td>5(111) x (111)</td>
<td>(553)</td>
<td>12.28°</td>
<td>3.84</td>
</tr>
<tr>
<td>6(111) x (111)</td>
<td>(332)</td>
<td>10.02°</td>
<td>4.69</td>
</tr>
<tr>
<td>7(111) x (111)</td>
<td>(775)</td>
<td>8.47°</td>
<td>5.55</td>
</tr>
<tr>
<td>8(111) x (111)</td>
<td>(443)</td>
<td>7.33°</td>
<td>6.40</td>
</tr>
<tr>
<td>9(111) x (111)</td>
<td>(997)</td>
<td>6.45°</td>
<td>7.26</td>
</tr>
<tr>
<td>n(111) x (100)</td>
<td>(n+1,n-1,n-1)</td>
<td>$\tan^{-1} \frac{2\sqrt{2}}{3n-1}$</td>
<td></td>
</tr>
<tr>
<td>2(111) x (100)</td>
<td>(311)</td>
<td>29.50°</td>
<td>1.66</td>
</tr>
<tr>
<td>3(111) x (100)</td>
<td>(211)</td>
<td>19.47°</td>
<td>2.45</td>
</tr>
<tr>
<td>4(111) x (100)</td>
<td>(533)</td>
<td>14.42°</td>
<td>3.28</td>
</tr>
<tr>
<td>5(111) x (100)</td>
<td>(322)</td>
<td>11.42°</td>
<td>4.12</td>
</tr>
<tr>
<td>6(111) x (100)</td>
<td>(755)</td>
<td>9.45°</td>
<td>4.97</td>
</tr>
<tr>
<td>7(111) x (100)</td>
<td>(433)</td>
<td>8.05°</td>
<td>5.83</td>
</tr>
<tr>
<td>8(111) x (100)</td>
<td>(977)</td>
<td>7.01°</td>
<td>6.69</td>
</tr>
<tr>
<td>9(111) x (100)</td>
<td>(544)</td>
<td>6.21°</td>
<td>7.55</td>
</tr>
<tr>
<td>n(100) x (111)</td>
<td>(2n-1,1,1)</td>
<td>$\tan^{-1} \frac{\sqrt{2}}{2n-1}$</td>
<td></td>
</tr>
<tr>
<td>2(100) x (111)</td>
<td>(311)</td>
<td>25.24°</td>
<td>1.66</td>
</tr>
<tr>
<td>3(100) x (111)</td>
<td>(511)</td>
<td>15.79°</td>
<td>2.60</td>
</tr>
<tr>
<td>4(100) x (111)</td>
<td>(711)</td>
<td>11.42°</td>
<td>3.57</td>
</tr>
<tr>
<td>5(100) x (111)</td>
<td>(911)</td>
<td>8.93°</td>
<td>4.56</td>
</tr>
<tr>
<td>6(100) x (111)</td>
<td>(11,1,1)</td>
<td>7.33°</td>
<td>5.55</td>
</tr>
<tr>
<td>7(100) x (111)</td>
<td>(13,1,1)</td>
<td>6.21°</td>
<td>6.54</td>
</tr>
<tr>
<td>8(100) x (111)</td>
<td>(15,1,1)</td>
<td>5.39°</td>
<td>7.53</td>
</tr>
<tr>
<td>9(100) x (111)</td>
<td>(17,1,1)</td>
<td>4.76°</td>
<td>8.53</td>
</tr>
<tr>
<td>Stepped Surface Designation</td>
<td>Miller Index</td>
<td>Angle of Cut from Terrace Along Zone Line Towards Step</td>
<td>( \tan^{-1} \frac{1}{n} )</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>--------------</td>
<td>-------------------------------------------------------</td>
<td>----------------------------------</td>
</tr>
<tr>
<td>( n(100) \times (100) )</td>
<td>( (n,1,0) )</td>
<td>( \tan^{-1} \frac{1}{n} )</td>
<td>( 26.57^\circ )</td>
</tr>
<tr>
<td>( 2(100) \times (100) )</td>
<td>( (210) )</td>
<td>( 26.57^\circ )</td>
<td>1.58</td>
</tr>
<tr>
<td>( 3(100) \times (100) )</td>
<td>( (310) )</td>
<td>( 18.43^\circ )</td>
<td>2.24</td>
</tr>
<tr>
<td>( 4(100) \times (100) )</td>
<td>( (410) )</td>
<td>( 14.04^\circ )</td>
<td>2.92</td>
</tr>
<tr>
<td>( 5(100) \times (100) )</td>
<td>( (510) )</td>
<td>( 11.31^\circ )</td>
<td>3.61</td>
</tr>
<tr>
<td>( 6(100) \times (100) )</td>
<td>( (610) )</td>
<td>( 9.46^\circ )</td>
<td>4.30</td>
</tr>
<tr>
<td>( 7(100) \times (100) )</td>
<td>( (710) )</td>
<td>( 8.13^\circ )</td>
<td>5.00</td>
</tr>
<tr>
<td>( 8(100) \times (100) )</td>
<td>( (810) )</td>
<td>( 7.13^\circ )</td>
<td>5.70</td>
</tr>
<tr>
<td>( 9(100) \times (100) )</td>
<td>( (910) )</td>
<td>( 6.34^\circ )</td>
<td>6.40</td>
</tr>
<tr>
<td>( n(110) \times (111) )</td>
<td>( (2n-1,2n-1,1) )</td>
<td>( \tan^{-1} \frac{\sqrt{2}}{2n} )</td>
<td></td>
</tr>
<tr>
<td>( 2(110) \times (111) )</td>
<td>( (331) )</td>
<td>( 13.26^\circ )</td>
<td>1.45</td>
</tr>
<tr>
<td>( 3(110) \times (111) )</td>
<td>( (551) )</td>
<td>( 8.05^\circ )</td>
<td>2.14</td>
</tr>
<tr>
<td>( 4(110) \times (111) )</td>
<td>( (771) )</td>
<td>( 5.77^\circ )</td>
<td>2.84</td>
</tr>
<tr>
<td>( 5(110) \times (111) )</td>
<td>( (991) )</td>
<td>( 4.49^\circ )</td>
<td>3.55</td>
</tr>
<tr>
<td>( n(110) \times (100) )</td>
<td>( (n,n-1,0) )</td>
<td>( \tan^{-1} \frac{1}{2n-1} )</td>
<td></td>
</tr>
<tr>
<td>( 2(110) \times (100) )</td>
<td>( (210) )</td>
<td>( 18.43^\circ )</td>
<td>1.58</td>
</tr>
<tr>
<td>( 3(110) \times (100) )</td>
<td>( (320) )</td>
<td>( 11.31^\circ )</td>
<td>2.55</td>
</tr>
<tr>
<td>( 4(110) \times (100) )</td>
<td>( (430) )</td>
<td>( 8.13^\circ )</td>
<td>3.54</td>
</tr>
<tr>
<td>( 5(110) \times (100) )</td>
<td>( (540) )</td>
<td>( 6.34^\circ )</td>
<td>4.53</td>
</tr>
<tr>
<td>( 6(110) \times (100) )</td>
<td>( (650) )</td>
<td>( 5.19^\circ )</td>
<td>5.52</td>
</tr>
<tr>
<td>( 7(110) \times (100) )</td>
<td>( (760) )</td>
<td>( 4.40^\circ )</td>
<td>6.52</td>
</tr>
<tr>
<td>( 8(110) \times (100) )</td>
<td>( (870) )</td>
<td>( 3.81^\circ )</td>
<td>7.52</td>
</tr>
<tr>
<td>( 9(110) \times (100) )</td>
<td>( (980) )</td>
<td>( 3.37^\circ )</td>
<td>8.51</td>
</tr>
</tbody>
</table>
Calculation of the Miller index for a kinked surface (represented by a pole in the interior of the unit stereographic triangle) is also analogous to the example worked out in detail for the stepped 6(111) x (100) surface; only the geometry for determining the angle between the surface and the terrace plane becomes somewhat more complicated and harder to generalize in terms of the average terrace width as was done for the stepped surfaces in Table A.1. Once this angle has been determined (either by a good stereographic plot or by a geometric calculation) and the zone determined to which both the terrace and step edges belong (for example, for the 7(111) x (310) surface, the (111) and (310) planes determine the [132] zone) then the three equations in the unknowns h, k, and l can be set up and solved.

Given only a Miller index, how does one determine the stepped surface designation? First, plot the pole on a stereographic projection or unit stereographic triangle. This can be done with the aid of a Wulff net or by using the formulas:

\[
\begin{align*}
    x &= \frac{h'}{1 + l'} \\
    y &= \frac{k'}{1 + l'}
\end{align*}
\]

(A.18) (A.19)

where x and y are the coordinates on the stereographic projection which is based on the unit circle (i.e., the reference sphere of the spherical projection has radius = 1) and (hkl) has been normalized to fall on the unit sphere:
If the given plane lies on a boundary zone line of the unit stereographic triangle, then it is a stepped surface, and the stepped surface designation can be approximated by measuring the angle between the given pole and the nearest low index vertex of the triangle, then using Table A.1 to pick out the closest stepped surface designation. If the given plane lies in the interior of the unit stereographic triangle, it is a kinked surface. Here the first step is to determine the zone to which both the given plane and the nearest low index vertex (the terrace plane) belong. The intersection of this zone line with the side of the unit triangle opposite the terrace pole determines the pole which represents the orientation of the step edges (since the given plane is a kinked surface, the plane of the steps will itself be a high Miller index stepped surface). Now the average terrace width can be calculated for the given surface by measuring the angle between the pole and the terrace pole and comparing it to angles calculated for various terrace widths along the zone line determined by the terrace plane and the kinked surface (these angles will vary as the geometry of the surfaces is varied from zone to zone).

A.4. Laue X-Ray Diffraction

A.4.1. The Reciprocal Lattice

Let \( \vec{a}, \vec{b}, \) and \( \vec{c} \) be the primitive vectors or crystal axes defining the unit cell of a real space crystal lattice (for a cubic system, \( \vec{a}, \vec{b}, \) and \( \vec{c} \) are mutually perpendicular and \( a = b = c \)); then points in the real space lattice are given by

\[
(h', k', l') = \frac{(hk1)}{\sqrt{h^2 + k^2 + l^2}}
\]
\[ \tau_{mnp} = m \mathbf{a}^* + n \mathbf{b}^* + p \mathbf{c}^* \]  
(A.21)

where \( m, n, \) and \( p \) are integers. The reciprocal lattice is defined and developed to provide a solution to the diffraction conditions from the real space lattice. The fundamental reciprocal lattice vectors are defined in terms of the real space crystal axes as follows:

\[ \mathbf{a}^* = \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}} \]  
(A.22)

\[ \mathbf{b}^* = \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}} \]

\[ \mathbf{c}^* = \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}} \]

The points of the reciprocal lattice are then constructed using the reciprocal lattice vectors given by:

\[ \kappa_{hkl} = \mathbf{h} \mathbf{a}^* + \mathbf{k} \mathbf{b}^* + \mathbf{l} \mathbf{c}^* \]  
(A.23)

Whenever \( \Delta \mathbf{k} \), the change in the wavevector on scattering, is equal to any reciprocal lattice vector \( \kappa_{hkl} \), the conditions for diffraction from the real space lattice are satisfied.

An entirely equivalent development of the reciprocal lattice which lends itself to pictorial representation is given as follows:

1. From a common origin in the real space lattice (for example, the intersection of the crystal axes), draw a normal to each crystal plane.
2. Place a point on the normal to each plane, \( (hkl) \), at a distance from the origin equal to the interplanar spacing, \( 1/d_{hkl} \). Then each point preserves all the important characteristics of the parallel
stack of planes it represents: the direction of the point from the origin preserves the orientation of the plane and the distance of the point from the origin preserves the interplanar spacing. These points, then, represent the reciprocal lattice points and the reciprocal lattice vectors are defined as:

$$\mathbf{r}_{hk1} = \frac{1}{d_{hk1}} \mathbf{n}$$  \hspace{1cm} (A.24)

where $\mathbf{n}$ is a unit vector in the [hkl] direction. It can be shown mathematically that the reciprocal lattice points defined by the above construction do form a 3-D lattice and that they are equivalent to the points given by Eq. (A.23) for any h, k, and l (89). This construction of the reciprocal lattice is illustrated in Fig. A.9 for some planes belonging to the [002] zone; notice that the reciprocal lattice points of a zone lie in a plane that is perpendicular to the zone axis.

A.4.2. Relating the Reciprocal Lattice to X-Ray Diffraction

The diffraction of x-rays is controlled by the Bragg Law:

$$n\lambda = 2d_{hk1}\sin\theta_{hk1}$$  \hspace{1cm} (A.25)

where $\lambda$ is the wavelength of the incident x-rays, $d_{hk1}$ is the interplanar spacing for a set of (hk1) planes, and $\theta_{hk1}$ is the angle that the incident x-ray beam makes with the (hk1) planes. Equation (A.25) can be rearranged, neglecting values of $n > 1$ ($n$ must be an integer), to yield:
Fig. A.9. Geometrical construction of the reciprocal lattice. Each reciprocal lattice point is in a direction normal to the plane it represents, and its distance from the origin in proportional to $1/d_{\text{hkl}}$, the interplanar spacing.
The following geometrical construction of x-ray diffraction can now be made (see Fig. A.10A): (1) The crystal can be depicted as being located at the center, \( C \), of a circle (sphere) of radius \( 1/\lambda \). (2) The point, \( O \), where the x-ray beam leaves the circle (sphere) after passing through the crystal is the origin of the reciprocal lattice of the crystal. (3) Whenever a reciprocal lattice point lies on the circle (sphere), the Bragg Law is satisfied, and a diffracted x-ray beam passes through the reciprocal lattice point. (4) X-ray diffraction can occur only when a reciprocal lattice point lies on the circle (sphere), which in 3-D is called the Ewald sphere or sphere of reflection. It is in this sense that a diffraction experiment reveals the nature of the reciprocal lattice directly, whereas the real space lattice is revealed only indirectly.

An equivalent statement of the Bragg law is sometimes given in the form of the Laue Condition:

\[
\frac{\vec{S} - \vec{S}_0}{\lambda} = \vec{0}_{hk1} = ha^* + kb^* + lc^*
\]

(A.27)

where \( \vec{S} \) and \( \vec{S}_0 \) are unit vectors in the directions of the incident and diffracted x-ray beams respectively. The Laue Condition can be represented by a geometrical construction very similar to that used for the Bragg Law; this construction is shown in Fig. A-10B.
Fig. A.10. (A) Geometrical construction on the Bragg Law: 0 is the origin of the reciprocal lattice of the crystal and X-ray diffraction can occur only when a reciprocal lattice point lies on the circle (sphere). (B) Geometrical construction of the Laue Condition, showing that it is equivalent to the Bragg Law in interpretation.
A.4.3. The Laue X-Ray Technique

To satisfy the diffraction conditions for different values of $h$, $k$, and $l$ simultaneously, either $\vec{S}' - \vec{S}_0$ or $\lambda$ in Eq. (A.27) must be variable. In the Laue experiment, white x-rays are used to provide a continuous range in the value of $\lambda$. For a typical metal x-ray source, the wavelength varies from a short wavelength limit, $\lambda_{\text{sw1}}$, to some $\lambda_{\text{max}}$ (usually about $2\lambda_{\text{sw1}}$) beyond which the intensity of the x-rays are so weak that the diffracted beams cannot be conveniently detected. The effect of providing variable wavelength x-rays can be visualized by rewriting the Laue Condition (Eq. (A.27)) in the following way:

$$\vec{S}' - \vec{S}_0 = \lambda \vec{\sigma}_{\text{hkl}}$$  (A.28)

Now, if we let $\lambda$ vary from $\lambda_{\text{sw1}}$ to $\lambda_{\text{max}}$, and incorporate $\lambda$ into the reciprocal lattice itself (as suggested by Eq. (A.28)), each reciprocal lattice point becomes a line segment ranging from $\lambda_{\text{sw1}} \vec{\sigma}_{\text{hkl}}$ to $\lambda_{\text{max}} \vec{\sigma}_{\text{hkl}}$. The diffraction condition is satisfied whenever a reciprocal lattice "segment" intersects the sphere of reflection. This is illustrated in Fig. A.11.

A set of planes belonging to a common zone will have reciprocal lattice points that lie in a plane containing the reciprocal lattice origin (indicated by the point 0 in the geometrical constructions). Such a plane will cut the sphere of reflection along some circle. The diffraction beams passing through the reciprocal lattice points along this circle on the sphere of reflection form a circular cone. The axis of the cone is perpendicular to the reciprocal cutting plane and parallel to the zone axis. This is illustrated in Fig. A.12.
Fig. A.11. Geometrical construction of the Laue X-ray technique, where $\lambda$ is allowed to vary from $\lambda_{\text{min}}$ to $\lambda_{\text{max}}$, and is incorporated into the reciprocal lattice; the diffraction condition is satisfied whenever a reciprocal lattice "segment" intersects the sphere of reflection.
Fig. A.12. The diffracted beams from planes belonging to a common zone form a circular cone, the axis of which is parallel to the zone axis. The intersection of these cones of diffraction with the film are hyperbolae and ellipses for back-reflection Laue and front-reflection Laue, respectively.
It can be seen that changing the orientation of the crystal will change
the orientation of the zone axes with respect to the sphere of reflection
and hence will change the diffraction cones. In a Laue experiment,
the reflections are recorded by placing a sheet of film perpendicular
to the x-ray beam either in the front or back reflection region.
Thus, the Laue method will be sensitive to changes in orientation
of the crystal being studied.

In back reflection Laue, a photographic plate is placed perpendicular
to the x-ray beam, between the source and the crystal sample. It
can be seen from Fig. A.12 that the film in position for back reflection
Laue will only cut cones of diffraction whose axes make angles greater
than 45° with the incident beam and that it will cut these cones along
hyperbolae (in the limiting case when the angle is 90°, the intersection
of the "cone"--now become a plane--with the film will be a straight
line). Thus, the diffraction spots of crystal planes belonging to
a common zone will be detected belong a common hyperbola on the film;
since important planes usually along to more than one zone, their
diffraction spots will appear at the intersection of several hyperbolae.
The Laue back reflection pattern of an alumina crystal is shown in
Fig. A.13A--a number of zones can be seen cutting the film in hyperbolae,
and a low index pole can be seen in the upper right corner at the
intersection of a number of zones. In front reflection Laue, the
film is placed perpendicular to the x-ray beam, but with the crystal
sample between the incident beam and the film (also known as transmission
Laue, and useful only for samples with sufficiently low absorption
of x-rays). The film in position for front reflection Laue will only
Fig. A.13. Back-reflection Laue diffraction patterns of: (A) an alumina crystal, showing a number of zones which have intersected the film as hyperbolae; (B) a Pt(100) surface; and (C) a Pt(111) surface.
cut cones of diffraction whose axes make angles less than 45° with the incident beam; these cones will intersect the film in ellipses.

The photograph of a Laue diffraction pattern is a 2-D representation of a 3-D crystal lattice; however, it should be stressed that it is not a stereographic projection of that lattice. How can one take advantage, then, of the useful properties of the 2-D stereographic projection in analyzing Laue diffraction patterns? Since the diffracted x-ray beams in the Laue experiment are related to the normals to the crystallographic planes under study through the reciprocal lattice (remember that the reciprocal lattice vectors are constructed perpendicular to their respective planes) and it is the poles representing these normals that are projected in making the stereographic projection of the spherical projection, it is possible to relate the positions of individual diffraction spots directly to the orientation of the corresponding plane normals and hence to the stereographic projection of the corresponding poles. Measuring from the center of the film, the vertical displacement of the diffraction spot is proportional to $\gamma$, the longitude coordinate (which is related to the "tilt" or orientation of the great circle on which the pole lies); the horizontal displacement of the diffraction spot is proportional to $\delta$, the latitude coordinate (which is related to the position of a pole on a given great circle). For a fixed crystal to film distance it is possible to prepare a chart ruled in such a way that one can directly measure the $\gamma$ and $\delta$ values for every point on the film. Such a chart was first prepared by A. B. Greninger and is known as the Greninger chart; it is pictured in Fig. A.14. The mathematical equations have been
Fig. A.14. The top half is the Greninger chart, the bottom half is a protractor. On the Greninger chart, the hyperbolae running right to left are curves of constant $\gamma$ (longitude); the curves running top to bottom are curves of constant $\delta$ (latitude).
derived elsewhere (88) that are necessary for relating the vertical and horizontal coordinates of the film to the longitude and latitude coordinate of the stereographic projection. On the top half of the Greninger chart (the bottom half is simply a protractor), the hyperbolas running from left to right are curves of constant γ (graduated at 20° intervals) and the set of curves running from top to bottom are curves of constant δ (also graduated at 20° intervals).

To use the Greninger chart in the interpretation of Laue diffraction patterns, the chart is placed over the photograph with the centers coinciding and the sides parallel (it is important that the vertical and horizontal directions not be reversed); this is shown in Fig. A.15. Values of γ and δ can now be read directly off the chart and plotted on a stereographic projection. For example, a Fig. A.15 there is a prominent spot at γ = +15.50° and δ = +8.00° (note that the chart is read to the nearest half degree and that the film is divided in four quadrants with respect to the signs of γ and δ). Using a Wulff net, this point would be plotted on a stereographic projection at a longitude of +15.50° and a latitude of +8.00°.

In many cases it is not necessary to prepare a stereographic projection from a Laue diffraction pattern in order to identify the planes giving rise to the diffraction spots, and hence the orientation of the crystal sample. For instance, the symmetry properties of the low index poles can often be used to advantage; if close to the center of the diffraction pattern, it is usually easy to identify the four-fold symmetry of a (100) pole, the three-fold symmetry of a (111) pole, and the two-fold symmetry of a (110) pole (recall that these low index
Fig. A.15. Illustration of using the Greninger chart to measure the coordinates of diffraction spots from a back-reflection Laue photograph.
poles will be located at the intersection of several zone lines). The Laue diffraction pattern of a Pt(100) surface is shown in Fig. A.13B; the four-fold symmetry of the pattern immediately identifies the central spot (which cannot be seen because of the large bright spot in the center due to the incident x-ray beam) as a (100) diffraction spot. Identification of the other diffraction spots is now greatly simplified; with the use of the Greninger chart, a (100) standard projection, and a table of angles between various planes, this can be done quickly without plotting a stereographic projection. The angle between any two diffraction spots of a Laue diffraction pattern can be determined directly using the Greninger chart as follows: keeping the center of the chart superimposed over the center of the film, rotate the chart until the two spots in question line up on a hyperbola of constant $\gamma$ (remember that lines of constant $\gamma$ run from left to right on the chart); now take the difference in $\delta$ between the two spots and this is the angle between the two corresponding poles. This is equivalent to lining up two poles on a great circle (longitude line) and measuring the difference in latitude between them. For example, in Fig. A.15 there are two diffraction spots lined up on the $\gamma = 100^\circ$ curve, one at $\delta = +24.0^\circ$ and the other at $\delta = -19.0^\circ$; thus, the difference in $\delta$ is $43.0^\circ$ and the angle between the two corresponding poles is $43.0^\circ$. Using this technique, the angles between various diffraction spots and the (100) pole (placed at the intersection of the zone lines) can be measured and compared with a table that lists angles between the (100) and other (hkl) planes. Once tentative identification of several poles has been made (the (100) standard
projection is very helpful in doing this consistent), a cross check of the angles measured between these planes should be made (if a table of angles is not available, angles between planes can be quickly calculated from their dot products). All of the spots in Fig. A.13B could then be positively identified; because of the four-fold symmetry of the (100) pole, the spots only need to be identified in one quadrant of the film--all the others follow from the symmetry.

The Laue diffraction pattern of a Pt(III) surface is shown in Fig. A.13C; the three-fold symmetry of the pattern leads to the easy identification of the central spot as the (111) diffraction spot. The identification of the other poles could be made by the method described above, using a (111) standard projection for reference.

As was discussed in Section 2.2, the Laue back reflection x-ray technique was used to orient the stepped and kinked crystals studied in this investigation. To accomplish this orientation, the procedure followed is very similar to that described above for identifying the diffraction spots on the diffraction pattern from the low index (100) and (111) surfaces. For example, let us assume that we want to cut a Pt(S) - [8(111) x (100)] surface. The single crystal rod should first be oriented so that the terrace plane, (111), is close to being perpendicular to the incident x-ray beam; this would result in a Laue diffraction pattern such as the one shown in Fig. A.13C, where the (111) pole is very clearly indicated by its three-fold symmetry. Now, the 8(111) x (100) surface lies between the (111) and (100) planes on the [011] zone; from Table A.1, the Miller index of the stepped surface is (977) and the angle between this plane and the (111) terrace
plane is $7.0^\circ$. Thus, in order for the (977) plane to be perpendicular to the incident x-ray beam (as is necessary for cutting a slice of this orientation), the crystal rod must be reoriented from the position shown in Fig. A.13C so that the center of the film will coincide with the point on the $(01\bar{1})$ zone that is $7.0^\circ$ from the (111) pole in the direction of the (100) pole (many of the high Miller index stepped and kinked surfaces have diffraction spots that are too weak to be detected on film, so it is important to be able to make the desired orientation on the basis of the calculated angles and zones directly). It will be noticed on the diffraction pattern in Fig. A.13C that there are six prominent zones that intersect at the (111) pole; three of these zones indicate the directions towards the nearest (100) poles and the other three indicate the directions towards the nearest (110) poles. These directions can be differentiated by identifying several poles on each of two adjacent prominent zones (one in each important direction); this is done as described above by measuring the angles between these poles and the (111) pole. When the directions towards the (100) poles have been identified (for most purposes of orientation, the three directions will be equivalent) the rod is reoriented so that the center of the film coincides with a point on one of the appropriate zone lines that is $7.0^\circ$ from the (111) pole. This position is illustrated in Fig. A.14A. When measuring angles on a diffraction pattern such as that shown in Fig. A.16A, it is very important to remember to superimpose the center of the Greninger chart over the center of the film and not over the low index pole which lies at the intersection of many zone lines.
Fig. A.16. Back-reflection Laue photographs of (A) a stepped Pt(S)-[8(111)x(100)] ↔ Pt(977) surface; and (B) a kinked Pt(S)-[7(111)x(430)] ↔ Pt(13,12,9) surface.
To orient a kinked surface, the procedure is the same as just described for the stepped surface. For example, let us assume that we want to cut a \( \text{Pt}(S) - [7(111) \times (430)] \). This surface lies between the (111) and the (430) planes on the \([341]\) zone; the angle between this plane and the (111) terrace is about 8.5°. Because the \([341]\) zone is not a prominent one and will not show up on film, it is necessary to know the angle of rotation of this zone from the nearest prominent zone, in this case the \([110]\) zone determined by the (111) and (110) planes. This angle is calculated from the dot product of the \([110]\) and \([341]\) zones to be 13.9°. Once again, the crystal rod should first be oriented close to the (111) terrace plane in order to determine the directions toward the nearest (110) poles; then the rod is reoriented so that the center of the film coincides with a point that is 8.5° from the (111) pole and rotated 14° away from one of the zone lines determined by the (111) and a (110) pole (remember that this rotation is a simple plane angle on the film, and can be measured with the protractor on the bottom of the Greninger chart. This position is illustrated in Fig. A.16B.

Given an unknown crystal orientation, for instance, starting with one of the diffraction patterns in Fig. A.16, it is possible to work backwards and determine both the Miller index and stepped surface notation of the orientation. The first step is to locate and identify the nearest low index pole. Then measure the angle between the given orientation (center of film) and this pole, determine the zone line on which the undetermined pole lies (for a stepped surface) or measure the angle of rotation to the nearest prominent zone line
in the case of a kinked surface. Using the methods outlined in Section A.3 it should now be possible to calculate the Miller index and stepped or kinked surface notation for the surface in question. It is always helpful to be able to refer to the appropriate standard projections, a complete table of angles, a unit stereographic triangle, and a list of angles for various stepped surfaces such as the one given in Table A.1.

A.5. Indexing Surfaces Using LEED

The Laue diffraction pattern of a single crystal sample allows the complete determination of the orientation of the macroscopic plane of the surface; however, a surface sensitive technique such as LEED can give much additional information about the actual surface configuration. For example, the clean Pt(100) surface is reconstructed (90), and some of the high Miller index planes close to the low index planes have been observed to be stable in a configuration with low index terraces separated by monatomic height steps (91,92). It is desired in this section to discuss briefly the sort of information that can be gained about stepped and kinked surfaces from LEED patterns.

There are three pieces of information that can be readily extracted from a LEED pattern of a stepped or kinked surface without doing an extensive intensity analysis: (1) the average height of the steps; (2) the average width of the terrace; and (3) whether or not the surface is kinked, and, if so, what the angle of rotation is away from the nearest prominent zone line. The LEED pattern of a stepped or kinked surface is characterized by the appearance of doublets in place of the singlet diffraction beams seen for unreconstructed low index
surfaces (see Fig. 2.4). The average height of the steps can be determined by measuring the electron beam energies at which the diffraction beams of a doublet have equal intensity and the greatest difference in intensity, and then making some simple calculations that have been described elsewhere (91, 93). The average width of the terraces can be determined by measuring the doublet width. If the surface is stepped (i.e., lies on a boundary zone line of the unit stereographic triangle), all four diffraction beams of two adjacent doublets will be colinear if the two doublets are adjacent in the direction perpendicular to the step edges (the splitting of the doublet occurs perpendicular to the step edges). If the surface is kinked, the four diffraction beams of two adjacent doublets will not be colinear in any direction. In order to understand how to determine the average terrace width and the angle of rotation for a kinked surface, it is first necessary to consider how the doublets arise in the LEED pattern in the first place.

The LEED pattern of a stepped or kinked surface arises from the interference of two sets of diffraction beams: the first set of diffraction beams comes from the low index terrace planes; the second set of diffraction beams comes from the atoms of the periodic steps or kinks (these are the atoms which define the high Miller index or macroscopic surface). To calculate the expected positions of both sets of beams, it is necessary to first calculate the real space and reciprocal space lattices for the two sets of planes. Starting with the low index (111) terrace planes, the unit cell vectors for the surface can be defined as (refer to Fig. A.17A):
Fig. A.17. Real space and reciprocal space unit cell vectors for (A) the (111) plane; (B) the (755) plane; and (C) the (10,8,7) plane.
\[ \vec{a} = (1,0,0) \]
\[ \vec{b} = (1/2,-\sqrt{3}/2,0) \]
\[ \vec{c} = (0,0,1) \]  

(A.29)

where the components of the vectors \( \vec{a}, \vec{b}, \) and \( \vec{c} \), are given in units of \( d \), the nearest neighbor platinum atom distance. Using Eq. (A.22), the reciprocal lattice unit cell vectors are calculated to be:

\[ \vec{a}^* = (-1,-1/\sqrt{3},0) \]
\[ \vec{b}^* = (0,2/\sqrt{3},0) \]  
\[ \vec{c}^* = (0,0,-1) \]  

(A.30)

The position of the diffraction beams expected from the reciprocal lattice of the (111) terrace (shown in Fig. A.17A) are plotted as X's in Fig. A.18.

Now, for the high index (755) plane, the plane of the step atoms for a 6(111) x (100) surface, the unit cell vectors can be defined as (refer to Fig. A.17B):

\[ \vec{a} = (1,0,0) \]
\[ \vec{b} = (1/2,-4.97,0) \]  
\[ \vec{c} = (0,0,1) \]  

(A.31)

where the components of the vectors are given in units of \( d \). Using Eq. (A.22), the reciprocal lattice unit cell vectors are calculated to be:
Fig. A.18. The superposition of diffraction beams expected from the (111) plane (X's) and the (755) plane (O's) give rise to the doublets (circled) seen in the LEED pattern of a 6(111)x(100) surface. The ratio a/b is characteristic of the average terrace width.
\[
\begin{align*}
\mathbf{a}^* &= (-1, -0.101, 0) \\
\mathbf{b}^* &= (0, 0.201, 0) \\
\mathbf{c}^* &= (0, 0, -1)
\end{align*}
\]  

(refer to Fig. A.17B). The positions of the diffraction beams expected from the reciprocal lattice of the (755) plane are plotted as \( \circ \)'s in Fig. A.18 (note that the (00) spots of the (111) and (755) planes are not superimposed). The superposition of the two sets of diffraction beams in Fig. A.18 show clearly that the doublets seen in the LEED pattern of a stepped surface arise from the positive interference of a diffraction beam from the (111) terraces with a pair of adjacent diffraction beams from the (755) plane. The diffraction spots (\( \circ \)'s) that would appear in the LEED pattern are circled in Fig. A.18; the remaining diffraction beams from the (755) plane are sufficiently weakened by negative interference with the nodes in the (111) diffraction that they cannot be seen. The (111) diffraction beams are weakened by negative interference with the (755) diffraction.

It is now apparent why the doublet splitting is proportional to the average terrace width, since this distance in the reciprocal lattice is determined by the distance between step edges in real space. Thus, the ratio \( a/b \), where \( b \) is the doublet splitting and \( a \) is the perpendicular distance between adjacent "rows" of doublets (see Fig. A.18), is characteristic of a given average terrace width. Values of \( a/b \) are given in Table A.1 for all the stepped surfaces listed; these values can be calculated from the geometrical models discussed in Section A.3. For example, \( a/b = 4.97 \) for the 6(111) \( \times \) (100) surface.
For a kinked surface, the calculations are similar. Let us consider a kinked 7(111) x (310) surface for example. The real and reciprocal space lattice vectors have already been calculated for the terrace (111) planes in Eq. (A.29) and Eq. (A.30) (see Fig. A.17A). The position of the diffraction beams expected from the reciprocal lattice of the (111) terrace are plotted as X's in Fig. A.19. Now, for the high index (10,8,7) plane, the plane of the kink atoms for a 7(111) x (310) surface (see Fig. 2.4), the unit cell vectors can be defined as (refer to Fig. A.17C):

\[ \mathbf{a}^* = (2.50, 0.866, 0) \]
\[ \mathbf{b}^* = (1, -5.83, 0) \]
\[ \mathbf{c}^* = (0, 0, 1) \] (A.33)

where the components of the vectors are given in units of d. Using Eq. (A.22), the reciprocal lattice unit cell vectors are calculated to be:

\[ \mathbf{a}^* = (-0.378, -0.065, 0) \]
\[ \mathbf{b}^* = (-0.056, 0.162, 0) \]
\[ \mathbf{c}^* = (0, 0, -1) \] (A.34)

(refer to Fig. A.17C). The positions of the diffraction beams expected from the reciprocal lattice of the (10,8,7) plane are plotted as O's in Fig. A.19 (note that the (00) spots of the (111) and (10,8,7) planes are not superimposed). Again, doublets arise from the positive interference of a diffraction beam from the (111) terraces with a pair of adjacent diffraction beams from the (10,8,7) plane. The
Fig. A.19. The superposition of diffraction beams expected from the (111) plane (X's) and the (10,8,7) plane (O's) give rise to the rotated doublets (circled) seen in the LEED pattern of a 7(111)x(310) surface. The ratio a/b is characteristic of the average terrace width and kink atom configuration.
diffraction spots (●'s) that would appear in the LEED pattern are circled in Fig. A.19; the remaining diffraction beams from the (10,8,7) plane are sufficiently weakened by negative interference with the nodes in the (111) diffraction that they cannot be seen. The (111) diffraction beams are weakened by negative interference with the (10,8,7) diffraction.

It is now apparent why the four diffraction beams of two adjacent doublets will not be colinear in any direction if the surface is kinked. Since the unit cell of the kink atoms is rotated with respect to the unit cell of the terrace (111) atoms by the angle of rotation between the zone of the kinked step edges and the nearest prominent zone of the (111) pole (either in a (100) or (110) direction), this angle can be determined directly from the LEED pattern by measuring the rotation of the doublets with respect to the rows of doublets. As for the case of the stepped surface, the average terrace width is related to the doublet splitting. The ratio $a/b$, where $b$ is the doublet splitting and $a$ is the perpendicular distance between adjacent rows of doublets (see Fig. A.19), is characteristic of a given average terrace width and a given average configuration of the kink atoms (the latter configuration must be determined from the angle of rotation of the doublets before the average terrace width can be determined). Note that the ratio $a/b$ is somewhat approximate for the kinked surface case because the perpendicular distance between the rows of doublets no longer corresponds exactly to the length of the reciprocal lattice vector or to the average terrace width in reciprocal space. The error introduced is only a few percent, however. Another problem is the inability to determine the exact positions with respect to each other
of the kink atoms in adjacent step edges; this relationship determines
the unit cell of the macroscopic kinked surface. The calculations
above were done for one particular configuration; again the error
introduced is probably a few percent (theoretically it is possible to
determine the exact configuration of the kink atoms--on the average--
from the LEED pattern; it is difficult in actuality because of the
finite width of the diffraction spots as they are recorded).
APPENDIX B. PUMPING SPEED CALCULATIONS

The pumping speeds for various hydrocarbons used in the turnover number calculations (see Appendix C) were measured in the following way: after establishing a steady state pressure of gas in the reaction chamber with a constant leak rate in and pumping speed out, the leak valve was "instantaneously" closed and the decay of pressure of the gas recorded as a function of time using the mass spectrometer. This decay should be exponential. Let \( n \) be the number of molecules, \( V \) the chamber volume, \( P \) the pressure, \( T \) the temperature and \( S \) the pumping speed; then:

\[
\text{Rate In - Rate Out = Accumulation}
\]

\[
0 - \frac{n}{V} S = V \frac{d}{dt} \left( \frac{n}{V} \right) \quad \text{(B.1)}
\]

From the ideal gas law,

\[
\frac{n}{V} = \frac{P}{RT} \quad \text{(B.2)}
\]

Substituting Eq. (B.2) into Eq. (B.1),

\[
- \left( \frac{P}{RT} \right) S = V \frac{d}{dt} \left( \frac{P}{RT} \right) \quad \text{(B.3)}
\]

This leads to:

\[
\frac{dP}{dt} = - \frac{S}{V} P \quad \text{(B.4)}
\]

\[
\frac{dP}{P} = - \frac{S}{V} dt \quad \text{(B.5)}
\]
\begin{align*}
\ln\left(\frac{P}{P_0}\right) &= -\frac{S}{V} t \quad \text{(B.6)} \\
P &= P_0 e^{-St/V} \quad \text{(B.7)} \\
P &= P_0 e^{-t/\tau} \quad \text{(B.8)}
\end{align*}

where \( \tau = \frac{V}{S} \), and \( P_0 \) is the initial, steady state pressure. When \( P = \frac{P_0}{e} \), Eq. (B.8) yields that \( t = \tau \). Thus, to determine the pumping speed, \( S \), from the decay curve, one measures the time required to reach the pressure \( \frac{P_0}{e} \), where \( P_0 \) was the initial pressure. This is illustrated in Fig. B.1A. (Note that for gases with a finite residual pressure, \( P_0 \) must be corrected for this background level, \( P_\infty \).)

Alternatively, taking the slope of the decay curve at \( t = 0 \):

\begin{equation}
\left. \frac{dP}{dt} \right|_{t=0} = P_0 \left( -\frac{1}{\tau} \right) e^{-t/\tau} \bigg|_{t=0} = -\frac{P_0}{\tau} \quad \text{(B.9)}
\end{equation}

This determines the tangent to the curve at the point \((0, P_0)\):

\begin{equation}
P = -\frac{P_0}{\tau} t + P_0 \quad \text{(B.10)}
\end{equation}

when \( P = 0 \), Eq. (B.10) yields that \( \tau = t \). Thus, the pumping speed can also be determined by drawing the initial tangent to the decay curve and measuring the time at which it intercepts the \( t \)-axis (refer to Fig. B.1A).

For an ideal exponential decay curve, measuring the intercept of the initial tangent line and measuring the time required for the pressure to decay to \( 1/e \) of the initial value give identical values for the pumping speed. In the non-ideal case, however, one measurement
Fig. B.1. (A) Calculation of the pumping speed, $S$, from the exponential decay curve of the pressure as a function of time after an "instantaneous" closure of the leak valve. The decay parameter, $\tau = \frac{V}{S}$, can be measured as the time required for the pressure to drop to $1/e$ of the initial pressure, $P_0$, or as the intercept of the initial tangent to the decay curve with the $t$-axis. (B) After a small decrease in the aperture of the valve before the pump, the mass spectrometer signal is monitored as a function of time (this signal being directly proportional to $n$, the density of molecules), and this curve can be used to determine $n_0$, $n_\infty$, and $t$ in order to calculate $A_\infty$ from Eq. (B.24). The initial pumping speed, $S_0$, is then calculated using Eq. (B.11) and Eq. (B.21).
Fig. B.1

\[ P = P_0 e^{-t/\tau} \]

\[ \tau = \frac{V}{S} \]

\[ P = -\frac{P_0}{\tau} t + P_0 \]

Density of Molecules (n)

Time (t)
might be preferable to the other. For example, a variable leak valve cannot, in actuality, be closed instantaneously. The finite time required to shut the valve completely alters the initial shape of the decay curve, and makes the initial slope difficult to determine. The system parameter $\tau$ is not affected by this problem, and the time of decay method thus provides better calculation of $S$. One simply choses a point on the decay curve at $t = t'$ where $P = P_0'$, after the valve is firmly shut and the curve is truly exponential; then Eq. (B.8) yields that when $P = P_0'/e$, $t = t' + \tau$.

With hydrocarbons that adsorb strongly on the chamber walls, another problem is encountered. After the leak valve has been closed and the pressure in the chamber starts to drop, molecules on the walls will start to desorb. This results in a gas pressure higher than that expected from true exponential decay and may significantly increase the time required for the pressure to reach $P_0/e$. In this case, the initial slope determination may be more accurate for measuring $\tau$ and calculating the real pumping speed.

It was observed in this investigation that for gases with a fast pumping speed and relatively low sticking probability, such as hydrogen, the time required to decay to $P_0/e$ gave a more reliable measurement of $\tau$ than the initial tangent intercept with the $t$-axis. For very "sticky" gases, such as benzene and cyclohexene, it was necessary to rely on the tangent method if the walls were allowed to saturate with the hydrocarbon (i.e., more than a few minutes exposure). For gases between these two extremes, the two measurements gave fairly consistent values of $S$. 
One further observation is worth noting. When gases were directed onto the crystal sample by hypodermic needles leading from the leak valves (026 gauge needle for hydrogen and 014 gauge for the hydrocarbons), extremely low values were calculated for the pumping speeds by this decay method (low by a factor of 6 for hydrogen and a factor of 10 for the hydrocarbons). Apparently the needles retained enough gas to maintain a sizeable "leak" into the chamber for several minutes even after the valves were closed behind them. Thus, one must consider system parameters carefully when judging the reliability of pumping speed calculations.

In a situation where the use of the method described above is inadequate, because of the presence of directing needles, or because of desorption of molecules from the chamber walls during pump-down, another method for calculating the pumping speed is available. If the pumping speed is not conductance limited, and the pump is separated from the chamber by an ideal aperture (one that can be assumed to have infinitely thin walls), and it is reasonable to assume that every gas molecule striking the aperture passes through and is irreversibly pumped (i.e., no backstreaming), then the pumping speed of the $i$th component is,

$$S_i = \frac{v_i A}{d} \text{ (cm}^3/\text{sec)}$$

where $v_i$ is the velocity of the $i$th component in cm/sec and $A$ is the area of the aperture, in cm$^2$. To calculate $S_i$, then, the area of the aperture, $A$, must be determined. Let $n_i$ be the density of the
\( i \)th component in molecules/cm\(^3\), \( V \) be the chamber volume in cm\(^3\), and \( N_0 \) be the leak rate, in molecules/sec; then:

\[
\text{Rate In} - \text{Rate Out} = \text{Accumulation}
\]

\[
N_0 - n_iS_i = V \frac{dn_i}{dt} \quad . \tag{B.12}
\]

Dropping the subscript "\( i \)" for convenience, Eq. (B.12) yields the first order linear differential equation

\[
\frac{dn}{dt} + \left( \frac{S}{V} \right) n = \frac{N_0}{V} \quad . \tag{B.13}
\]

This is an equation of the general form

\[
\frac{dy}{dx} + P(x) y = Q(x) \quad . \tag{B.14}
\]

to which the general solution is

\[
y = e^{-\int Pdx} \left[ \int Qe^{\int Pdx} \ dx + c \right] \quad . \tag{B.15}
\]

Letting \( P(x) = (S/V) \) and \( Q(x) = (N_0/V) \) and substituting into Eq. (B.15) yields:

\[
n = ce^{-St/V} + \frac{N_0}{S} \tag{B.16}
\]

At \( t = 0 \), \( n_0 = \frac{N_0}{S_0} \); solving for \( c \) in Eq. (B.16) at \( t = 0 \) then yields:

\[
c = \frac{N_0}{S_0} - \frac{N_0}{S} \tag{B.17}
\]

and substitution back into Eq. (B.16) gives
\[ n = \frac{N_0}{S} + e^{-St/V} \left[ \frac{N_0}{S_0} - \frac{N_o}{S} \right] \quad (B.18) \]

Now assume that at \( t = 0 \), an "instantaneous" change in the aperture is made (as by slightly opening or closing the valve between the pump and the chamber). Before the change, at \( t = 0 \), \( A = A_0 \) and using Eq. (B.11).

\[ n_0 = \frac{N_0}{S_0} = \frac{4N_0}{VA_0} \quad (B.19) \]

After the change, at \( t = \infty \), \( A = A_\infty \) and

\[ n = \frac{N_0}{S_\infty} = \frac{4N_0}{VA_\infty} \quad (B.20) \]

Combining Eq. (B.19) and Eq. (B.20) yields:

\[ A_0 = \frac{n_\infty}{n_0} A_\infty \quad (B.21) \]

Since \( n \), the molecule density, is proportional to the mass spectrometer signal, which can be recorded as a function of time when the aperture is changed at \( t = 0 \), one need only determine \( A_\infty \) to calculate \( A_0 \) and hence \( S_0 \).

Using Equations (B.18), (B.19) and (B.20),

\[ n_\infty - n = \frac{N_0}{S} - \left[ \frac{N_0}{S_\infty} + e^{-S_\infty t/V} \left( n_0 - n_\infty \right) \right] \]

\[ = (n_\infty - n_0) e^{-S_\infty t/V} \quad (B.22) \]

Rearrangement of Eq. (B.22) yields:
Taking the logarithm of both sides of Eq. (B.23), substituting for $S$ from Eq. (B.11) and rearranging gives:

$$A_\infty = \frac{(4V)}{v} \ln \left( \frac{n_\infty - n_0}{n_\infty - n} \right) \quad . \quad (B.24)$$

Figure B.1B illustrates how the mass spectrometer signal monitored as a function of time for a small decrease in aperture can be used to determine $n_0$, $n_\infty$, and $t$ in order to calculate $A_\infty$ from Eq. (B.24) (since $n$ appears always as a ratio in Eq. (B.24), it is not necessary to convert the mass spectrometer signal numerically to a molecule density before doing the calculation). $A_0$ is then calculated from Eq. (B.21), and $S_0$ from Eq. (B.11). The velocity of the $i$th component is inversely proportional to the square root of $M_i$, the molecular weight of the $i$th component; thus, at room temperature,

$$S_i = \frac{6.3 \times 10^4 A_0}{\sqrt{M_i}} \quad . \quad (B.25)$$

For the experimental apparatus used in this investigation, the aperture method for calculating pumping speeds just described could be used with the ion pump by closing the gate valve to a small initial aperture (0.2 to 0.3 cm$^2$) to establish a steady state gas pressure in the chamber, then slightly opening or closing the valve while monitoring the mass spectrometer signal. Ideally, $A_0$ can be accurately calculated by either opening or closing the valve at $t = 0$; in actuality, closing the valve slightly is more reliable, as it avoids the problem of
desorption from the walls as the pressure starts to drop. For the diffusion pump, the pumping speed of which was conductance limited, an "effective aperture" could be calculated using the ion pump and gate valve: a steady state pressure was achieved with a constant leak rate in, with the ion pump valved off and the valve to the diffusion pump open fully; then, maintaining the same leak rate, the diffusion pump was valved off completely as the gate valve to the ion pump was opened slightly, until the original steady state pressure was achieved. The "effective aperture" of the diffusion pump was the aperture calculated for the ion pump gate valve at this steady state pressure, by slightly closing the valve and monitoring the pressure change.

A comparison of the pumping speeds calculated by the two methods described in this appendix--leak valve closure and pump aperture change--showed that for hydrogen, the two methods yielded the same pumping speed within experimental error, but for hydrocarbons the pump aperture change method yielded significantly higher values of the calculated pumping speed than the leak valve closure method (e.g., a factor of 3 higher for benzene and cyclohexene, and a factor of 2 higher for cyclohexane). This discrepancy probably arises from several problems. First, as discussed earlier, the desorption of hydrocarbon molecules from the chamber walls as the pressure drops after closing the leak valve would tend to yield calculated pumping speeds that are lower than the true pumping speeds in the leak valve closure method; this problem is hard to avoid by drawing the initial tangent line to the curve and determining the t-axis intercept because of the necessarily "non-instantaneous" closure of the leak valve. In the aperture change
method, backstreaming from the ion pump, while the pump is under load, is not taken into account; also, the assumption that the aperture has infinitely thin walls ignores the fact that some molecules do strike the edge of the aperture and bounce back or adsorb (especially in the case of hydrocarbons with a high sticking probability). In both of these cases, the aperture change method will tend to overestimate the pumping speed.

Thus, the true pumping speed for hydrocarbons is probably a value somewhere between the values calculated by the two methods discussed above. The pumping speeds used in the turnover number calculations reported in this investigation were those calculated by the leak valve closure method--this method was more direct for the diffusion pump, but the turnover numbers reported may thus be as much as a factor of two to three too low.
APPENDIX C.  CALCULATION OF REACTION RATES AND TURNOVER NUMBERS

In order to calculate $R_i$, the reaction rate of the $i$th product in molecules/sec at a given time, one needs to know the partial pressure, $P_i$, of the product at that time and the rate of removal, i.e., the pumping speed, $S_i$, of the $i$th product. If $300\text{K}$ is taken as room temperature, then

$$R_i = \frac{P_i(\text{torr}) S_i(\text{cm}^3/\text{sec})}{82.058 (\text{cm}^3 \text{ atm/mole } 0\text{K}) \times \frac{300(0\text{K})}{760(\text{torr/atm})}} \times 6.02 \times 10^{23} (\text{molecules/mole})$$

$$= 3.2 \times 10^{16} P_i S_i \text{ (molecules/sec)}$$

where $82.058 \text{ cm}^3 \text{ atm/mole } 0\text{K}$ is simply the gas constant, and $6.02 \times 10^{23}$ molecules/mole is Avogadro's number.

The turnover number of the $i$th product, $T_i$, in molecules/sec/Pt atom, is equal to $R_i$ divided by the total number of surface platinum atoms of the catalyst sample. The number of platinum atoms per square centimeter on a (111) face is about $1.5 \times 10^{15}$. Thus:

$$T_i = \frac{R_i(\text{molecules/sec})}{1.5 \times 10^{15} A (\text{cm}^2)}$$

where $A$ is the surface area of the catalyst sample in cm$^2$. Substituting Eq. (C.1) into Eq. (C.2), one obtains

$$T_i = \frac{3.2 \times 10^{16} P_i S_i(\text{molecules/sec})}{1.5 \times 10^{15} A (\text{cm}^2)}$$

$$= \frac{21 P_i S_i}{A} \text{ (molecules/sec/Pt atom)} \quad (C.3)$$
REFERENCES

27. Cyclohexene dehydrogenation data supplied by Mark Davis, University of California, Berkeley.
This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.