Title
LOW-ENERGY ELECTRON DIFFRACTION AND WORK FUNCTION STUDIES OF ADSORBED ORGANIC MONOLAYERS ON THE (100) AND (111) CRYSTAL FACE OF PLATINUM

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DISCLAIMER

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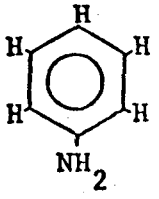
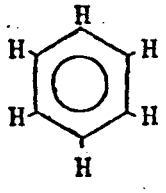
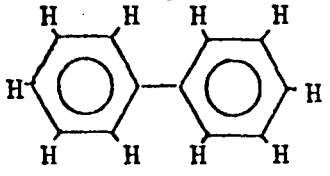
ABSTRACT

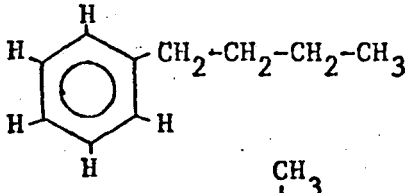
The adsorption and ordering characteristics of a large group of organic compounds has been studied on the platinum (100) and (111) single crystal surfaces. Low-energy electron diffraction has been used to determine surface structures. Work function change measurements have been made to determine the charge redistribution which occurs on adsorption. The molecules which have been studied are acetylene, aniline, benzene, biphenyl, n-butylbenzene, t-butylbenzene, cyanobenzene, 1,3-cyclohexadiene, cyclohexane, cyclohexene, cyclopentane, ethylene, n-hexane, mesitylene, 2-methylnaphtnalene, napthalene, nitrobenzene, propylene, pyridine, toluene, and m-xylene. All molecules studied adsorb on both the Pt(111) and Pt(100)-(5x1) surfaces and act as electron donors to the metal surface. The adsorbed layers are more ordered on the hexagonally symmetric Pt(111) surface than on the square symmetric Pt(100) surface. Unsaturated molecules generally adsorb on these crystal faces of platinum by forming π-bonds with the metal surface.

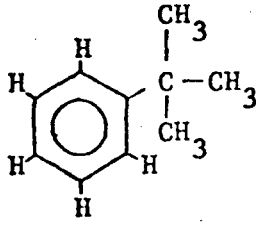
acetylene $H-C \equiv C-H$

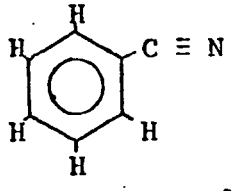
aniline 

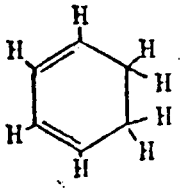
benzene 

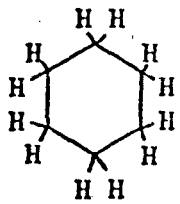
biphenyl 

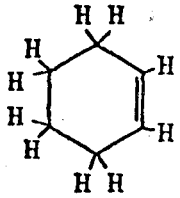
n-butybenzene 

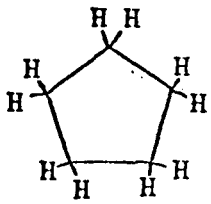
t-butylbenzene 

cyanobenzene 

1,3-cyclohexadiene 

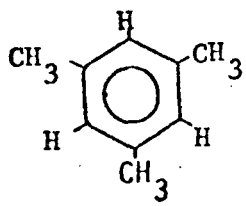
cyclohexane 

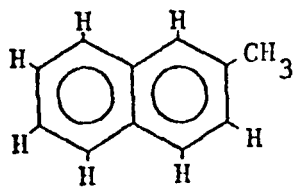
cyclohexene 

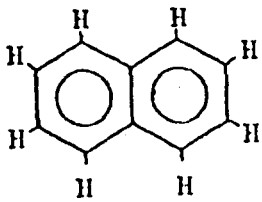
cyclopentane 

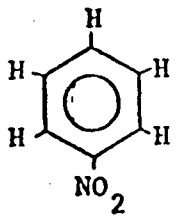
ethylene $CH_2 = CH_2$

n-hexane $CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$

mesitylene 

2-metylnaphthalene 

naphthalene 

nitrobenzene 

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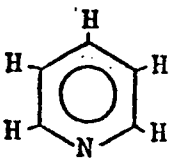
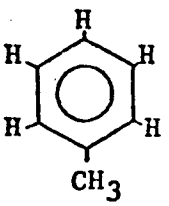
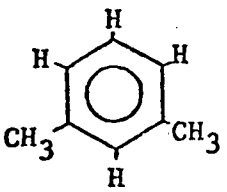
pyridine 

toluene 

m-xylene 

Introduction

The adsorption characteristics of organic molecules on metal surfaces is important in several areas of surface science. The nature of the chemical bond between the substrate and the adsorbate and the ordering of the adsorbed organic molecules play important roles in adhesion, lubrication, and hydrocarbon catalysis. Therefore, we have undertaken a study of the molecular structure, ordering and interaction of monolayers of several groups of organic compounds under ultra-high vacuum conditions on low Miller Index platinum crystal surfaces. The shape and the bonding characteristics of the organic molecules have been varied systematically so that correlations can be made between these properties and their interaction with the metal surface.

The two platinum crystal faces, (111) and (100), that were used as substrates in this study have six-fold and four-fold rotational symmetry, respectively. Thus, we can find out how the atomic surface structure of the metal influences the nature of chemisorption of the various organic molecules. Low-energy electron diffraction has been used to monitor the structure of the adsorbed layers on the platinum (111) and platinum (100) crystal surfaces. Work function changes (WFC) on adsorption have been used to determine the charge transfer that occurs on adsorption. Using these techniques, we can obtain answers to the following questions. Are the adsorbed hydrocarbon monolayers ordered? How does the ordering, if any, depend on the symmetry of the substrate? How does ordering depend on the shape of the adsorbed molecules? Finally, does work function change (WFC), that measures the net charge transfer between substrate and adsorbate layers, correlate with the nature of bonding? The adsorption of molecules with molecular dimensions smaller than substrate interatomic distances usually gives rise to the formation of ordered adsorbed structures with the rotational symmetry of the

substrate such that the unit vectors of the overlayer are closely related to the substrate unit cell vectors.[1,2] Thus in most cases local interactions between substrate and adsorbate seems to play a dominant role in determining their adsorption characteristics. However, as the surface density of small molecules is increased adsorbate-adsorbate interactions often become increasingly important as evidenced by continuous two dimensional compressions in the unit cell size[3,4] for some of the adsorbates.

Studies of the adsorption of large molecules where the molecular size is larger than the interatomic distances in the substrate is especially interesting because of the possibility that localized surface atom-adsorbed molecule interaction may not play a dominant role in the interaction between the substrate and the adsorbate. Large molecules may interact simultaneously with several surface atoms upon adsorption so that the characteristics of the adsorbed layers may be less controlled by the local substrate bond while the adsorbate-adsorbate interaction becomes more predominant. In the extreme, the interaction of these large molecules with metal substrates may be similar to the interaction of large polarizable rare gas atoms, such as xenon with metal substrates.[5,6,7,8] The surface structure of adsorbed xenon at high coverage is independent of the atomic structure of the substrate.

We have found that most of the monolayers of organic molecules that were studied did not undergo chemical change on these low Millex index platinum surfaces during the adsorption studies, but remained intact so that their ordering characteristics and surface structure could readily be studied. Although our investigations were restricted to adsorption on platinum surfaces, it is hoped that many of our conclusions will be applicable to describe the adsorption characteristics of organic molecules on other low Miller Index

metal surfaces.

Experimental

A. Techniques

A modified Varian LEED apparatus was used for these studies. It is equipped with an isolatable 240 l/sec ion pump, a water cooled titanium sublimatron pump and an auxiliary isolatable 8 l/sec ion pump. Typical ambient pressures for the system are 2×10^{-9} Torr during periods of daily use. A schematic diagram of the vacuum system used is shown in Figure 1.

A rotatable capillary was used to introduce all gases onto the crystal surface from a distance of 5 mm. This system was used so that the introduced gases would have a higher incident flux on the sample surface than the background gases. This was possible since the system is operated as a flow system during adsorption experiments. Work function changes (WFC,$\Delta\phi$) caused by adsorption were measured by the retarding field method using the LEED gun as the electron beam source. The retarding potentials were used as an internal voltage standards for the work function change measurements. The apparatus was equipped with four grid hemispherical electron optics. Diffraction information was taken using the post-acceleration LEED method. Auger measurements used to verify the cleaning procedures used were taken using the retarding field method. The details of the apparatus used have been described in detail elsewhere.[9, 10]

B. Procedure

Prior to each adsorption experiment the platinum samples were treated with flowing oxygen at pressures of $1\text{-}3\times10^{-5}$ Torr for 60 minutes at 1000°C to remove carbon impurities on the surface. After termination of the gas

flow, the system was pumped down and the electron guns were out-gassed and warmed up before the samples were cooled. Thus, the samples remained at 1000°C for a period of 30-45 minutes in vacuum. Measurements of work function changes made 5 hours stabilization period for the LEED gun mandatory. Following gun stabilization, the crystals were heated to 1000°C for 5 minutes in vacuum. The crystal surface produced in this manner were clean within the limits detectable by Auger electron spectroscopy. They displayed the characteristic Pt(111)-(1x1) and Pt(100)-(5x1) diffraction patterns. The crystal were then cooled for 20-40 minutes in a background pressure of $1x10^{-9}$ Torr to a temperature of 25-40°C. The organic vapor was then introduced through the capillary at the desired pressure. The actual pressure at the surface is approximately 6 times the recorded ion gauge reading since the ion gauge used was in the mouth of the ion pump. The WFC and LEED data data reported at elevated temperatures were taken by heating the samples for 10 minutes in flux, then cooling the sample to 20-40°C in flux and taking the WFC and LEED measurements. This procedure was used to assure the saturation of the surface with the adsorbate.

C. The Low Miller Index Platinum Crystal Surfaces

The two platinum crystal surfaces, (111) and (100), have six-fold and four-fold symmetry respectively. In the (111) crystal surface of platinum, each atom has six nearest neighbors and the structure is that expected from the projection of the X-ray unit cell onto the (111) plane. The low-energy electron diffraction pattern from this crystal face along with the schematic representation of its atomic surface structure is shown in Figure 2. The clean (100) crystal surface of platinum is reconstructed, i.e., the surface structure is not the one expected from the projection of the X-ray

unit cell onto the (100) plane. This surface reconstruction has been studied in several laboratories and appears to be due to hexagonal distortion of the surface layer in the (100) crystal face.[11,12] The accurate location of the atoms in the reconstructed surface awaits surface structure analysis using low-energy electron diffraction beam intensities. On adsorption of hydrocarbons, the reconstructed Pt(100)-(5x1) surface often relaxes to the Pt(100)-(1x1) surface. However, during several of the experiments, Pt(100)-(5x1) surface structure relaxed to the (1x1) surface structure only after adsorption was complete. The relaxation of the (5x1) surface structure had no apparent cause. Usually it occurred slowly with exposure at some constant pressure or more rapidly with gentle heating to 100°C. The important observation is that during relaxation of the (5x1) surface structure, no change occurred in the work function of the surface. Thus, it appears that no marked change in the charge transfer occurred with relaxation of the (5x1) structure. In any event, one may assume the the hydrocarbon molecule sees four-fold rotational summetry surface on the (100) crystal face and six-fold rotational symmetry on the (111) crystal face. The low-energy electron diffraction patterns of both the clean reconstructed (100) surface that exhibits the (5x1) surface structure and the relaxed (100) surface with the (1x1) unit cell are shown in Figure 3 along with schematic representations of their atomic surface structure.

The LEED results have been reproduced on three different sets ((111) and (100) orientation) of single crystal samples cut from different rods for benzene, napthalene, pyridine, toluene, t-butybenzene, aniline, nitrobenzene, cyanobenzene, ethylene, and acetylene. LEED observations have been made on two sets of single crystal samples. No significant variations have been observed if comparisons are made between adsorption experiments carried out under similar conditions, e.g. pressure, temperature. All other adsorbates

have been studied on a single set of single crystal samples.

It has been shown that stepped surfaces (cut at some angle with respect to the (111) or (100) crystal faces) have chemical reactivities that are very different from those exhibited by the low Miller index (111) and (100) crystal faces. These stepped surfaces will readily dehydrogenate many of the organic molecules studied here. Even slight misalignment ($\pm 2^{o}$) of the low index surface results in dramatic changes in magnitude of the work function change observed on adsorption and dramatically different LEED patterns are also observed on adsorption. Thus, extreme care should be taken to cut the crystals as accurately as possible to obtain the desired low Miller index surface.

D. Surface Contamination

The LEED patterns and the work function change observations vary with contamination of the surfaces. Results were difficult to reproduce without titanium sublimation pumping because of carbon monoxide contamination of the platinum surfaces at room temperature. The question of the effect of hydrogen contamination remains unfortunately unanswered since Auger spectroscopy is not sensitive to hydrogen and the system used was not equipped with a mass spectrometer. We do know that the introduction of 5:1 hydrogen:hydrocarbon mixture in similar adsorption studies leads to formation of equivalent LEED patterns for several adsorbates.[13] In fact ion pumping of hydrocarbons has been shown to produce a substantial amoung of hydrogen.[14] Therefore, these adsorption studies may have been carried out in the presence of some hydrogen in the ambient. However, the pumping system was arranged so that severe conductance limitation would minimize regurgitation effects. If the single crystal surfaces are not heated efficiently in vacuum to remove oxygen which is used for removing carbon the results are not reproducible. Even

slight carbon contamination of the surface leads to irreproducible results and the work function change observed on adsorption decreases drastically in magnitude.

E. Data Analysis

Analysis of the diffraction information yields only the translational unit vectors of the adsorbed surface layer. The position of the unit vector in the adsorbed layer relative to the underlying unit vectors has not been uniquely determined. Likewise, the number of adsorbate molecules per unit cell has not been determined uniquely. Rigorous answers for both of these questions await the application of structure analysis techniques utilizing LEED intensity data. The number of adsorbate molecules per unit cell has been approximated using available crystallographic and structural information. Three additional criteria have been employed to facilitate the deduction of surface structure. The first is that change in the number of equivalent adsorbate molecules per unit cell should not lead to a reduction in the unit cell size of our proposed structure. The second criteria is that the adsorbed layer should be close-packed over the surface, in particular, the surface should not contain large unoccupied areas. Studies of the ordering of small molecules on crystal surfaces clearly indicates that close-packing in the adsorbed layer generally occurs. In addition, large reductions of surface free energy usually result from uniform spreading of the organic layers on metal surfaces. The third criteria is that the adsorbed layers should be homogeneous. Thus, in determining the surface structures we have assumed that the adsorbed species is predominatly one adsorption type. That is, the adsorbed layer is not made up of patches with varying composition and/or bonding between substrate and adsorbate. This assumption appears reasonable in light of the reproducibility of our data, but exceptions cannot be ruled out.

RESULTS AND DISCUSSION

1. Summary of Experimental Findings

All the organic molecules studied adsorb on both the Pt(111) and Pt(100)-(5x1) surface. The results of adsorption experiments are shown in Tables 1 and 2. Ordering in the adsorbed layer was more pronounced on the Pt(111) surface than on the Pt(100)-(5x1) surface. In general, the adsorbed layer is more ordered and causes a larger work function change (WFC, $\Delta\phi$) on adsorption is the incident flux is lower. The work function decreases with adsorption for all the organic molecules studied. This implies that the adsorbed molecules are acting as electron donors to the metal surface. This might be expected since the metal has a high work function ($\sim$5.7 V)[15] and all of the molecules studied are polarizable.[16]

The magnitude of the work function change associated with the adsorption of unsaturated hydrocarbons where π-electrons make major contributions to the bonding is in the range of -1.3 to -2.0 volts. Saturated hydrocarbons that were studied produce much smaller work function changes, in the range of -0.9 to -1.2 volts. The largest work function change was observed during the adsorption of pyridine (-2.7 volt) and reflects the large contribution of the nitrogen lone electron pair and/or the permanent dipole moment to the charge transfer.

The work function change on adsorption for most of the molecules studied varies approximately inversely with the first ionization potential of the adsorbate as shown in Figure 4 and in Figure 5. The data is scattered, however there many types of molecules represented, some in fact have sizable permanent dipole moments.

Several compounds undergo pressure dependent transformations (usually above 10^{-6} Torr surface pressure) on the platinum surfaces studied; in fact the transformations occur over unexpectedly long time periods. For instance,

at a surface pressure of 10^{-6} torr typical transformation times involve several thousand seconds of exposure. The compound studied which undergoes transition at 20°C as indicated by changes in WFC and diffraction information are benzene, 1,3-cyclohexadiene (benzene on the surface), cyclohexane, n-hexane, cyclopentane, and mesitylene. We feel certain that these transitions are changes in the chemistry of the adsorbate-surface interaction since they occur with only a few of the molecules studied. The driving force for these chemical changes with increased surface coverage may be adsorbate-adsorbate repulsive interactions.

Below, we shall discuss the adsorption and ordering characteristics of the various hydrocarbon molecules on the low Miller index platinum surfaces separately and in some detail. We shall discuss the properties of groups of molecules together where the similarity of adsorption behavior warrants such classification.

2. The Adsorption of Benzene

a) Benzene on the Pt(111) Surface

On the Pt(111) surface benzene initially forms a poorly ordered adsorbed layer; the WFC on adsorption is -1.8 V. With further exposure the Pt(111)-$\begin{vmatrix} -2 & 2 \\ 4 & 4 \end{vmatrix}$-Benzene structure forms and the magnitude of the WFC decreases (-1.4 V). With further exposure the $\begin{vmatrix} -2 & 2 \\ 5 & 5 \end{vmatrix}$ structure forms and the magnitude of the WFC decreases until it reaches a steady state value of -0.7 V. The $\begin{vmatrix} -2 & 2 \\ 5 & 5 \end{vmatrix}$ structure forms when the WFC is approximately -1.1 V.

This correlation between the transformation of the benzene surface structure and the change in work function suggests that the orientation of the adsorbed benzene molecules is changing markedly as a function of increased exposure. Another possibility for such a correlated change in work function and structure might involve adsorption of a second layer of benzene. However, for the case of ethylene adsorption where second layer adsorption has been

reported previously[17] we find the magnitude of the WFC increases with addition of a second layer. Since the change in the WFC measured here is in the opposite direction, it seems unlikely that double layer adsorption is occurring.

The diffraction information indicates a change in the packing of the adsorbed benzene layer. A decrease in the density (number of benzenes per unit surface area) of the adsorbed layer during the transformation is not possible because of the high flux (0.5 L/sec) incident on the crystal throughout some of these experiments. In fact the observation that higher incident benzene fluxes cause the transformation to occur more rapidly indicates that the density of the adsorbed layer is increasing. The work function change during the transformation indicates that there is a decrease in the magnitude of the charge transfer occurring as the density of the adsorbed layer increases. If the adsorbed species retained the same bonding characteristics during the transformation and the coverage is increased, the magnitude of the WFC would increase. Thus, the increased density accompanied by a decrease in the magnitude of the WFC can only be explained by assuming the area per adsorbed molecule must be decreasing. The criteria for the transition are then:

(1) The area of the adsorbed species must decrease, and

(2) The charge transfer must decrease,

Keeping these criteria in mind a comparison of the WFC observed for benzene with other WFC data is valuable. With initial adsorption of benzene a WFC of -1.8V occurs. This WFC is slightly larger than the WFC on adsorption of mesitylene (-1.7V) a compound which is sterically hindered from interaction in any manner other than π-bonding. Indeed the WFC on adsorption for benzene is similar to the WFC observed on adsorption of most

of the simple substituted aromatics studies. (Table 1). These facts support the contention that π-bonding is occurring between benzene and the platinum surface in the initial disordered adsorbed state. That is, the aromatic π electrons are extensively involved in the transfer of charge between the substrate and adsorbate.

The final value of the WFC, -0.7 V, corresponds with the WFC observed at the same pressure for cyclohexane and cyclopentane (-0.7 V) adsorption. This indicates that the binding for these two cases (benzene in its final adsorbed state and cyclohexane or cyclopentane) is similar. For cyclopentane or cyclohexane adsorbed on platinum the binding appears to involve single dehydrogenation and subsequent binding of the adsorbate to the substrate through the dehydrogenated site.

A likely model consistent with these criteria and the comparisons made with the WFC observed on adsorption of other similar compounds is that the initial adsorbed state involves a benzene adsorbed with its ring at some small angle or parallel to the surface. The final adsorbed state with a $\begin{vmatrix} -2 & 2 \\ 5 & 5 \end{vmatrix}$ surface structure involves reoriented benzene molecules adsorbed with their rings at some large angle or perpendicular to the surface.

The initial adsorbed species would be held on the surface by a π-bond through the aromatic ring similar to the binds in the so-called "sandwich compounds."[18] Since the metal surface is highly electron deficient (ϕ_{Pt} = 5.7 v) a large induced dipole would be expected in the adsorbed layer. In fact, recent UPS studies have shown that benzene adsorbed on the Ni(111) surface interacts via the formation of a π-d bond.[19] The final adsorbed state with a $\begin{vmatrix} -2 & 2 \\ 5 & 5 \end{vmatrix}$ surface structure involves benzene molecules covalently bonded to the surface with their rings perpendicular or nearly perpendicular to the surface. For this type of adsorption to occur, the benzene must

either lose a hydrogen or its aromaticity. Recent exchange studies between perdeuterobenzene and benzene of Pt films have shown rapid exchange of hydrogen and deuterium between these species. These workers postulate a dissociation of the benzene (without loss of aromaticity) and loss of hydrogen atoms to form a single bonded intermediate.[20] Thus the adsorbed specie which gives the $\begin{vmatrix} -2 & 2 \\ 5 & 5 \end{vmatrix}$ structure is most likely a singly dehydrogenated benzene molecule covalently bonded to the surface through its dehydrogenated site.

This type of reorientation satisfies all the criteria for the transformation. That is, the initial adsorbed state involves π-bonding. The surface area occupied by the adsorbed species decreases and the charge transfer decreases through the transformation. The final adsorbed benzene specie interacts with the surface in a manner similar to interaction postulated for cyclohexane and cyclopentane, i.e., σ-binding. Using the criteria mentioned in the experimental section and the fact that the area per benzene molecule should decrease through the transition we postulate the benzene structures shown in Figures 6 and 7. The $\begin{vmatrix} -2 & 2 \\ 4 & 4 \end{vmatrix}$ structure contains three benzene molecules per unit cell (approximately 35.6 Å^2 per benzene molecule). The $\begin{vmatrix} -2 & 2 \\ 5 & 5 \end{vmatrix}$ structure contains four benzene molecules per unit cell (approximately 33.3 Å^2 per benzene molecule). The position of the adsorbate unit cell relative to the substrate unit cell is uncertain. However, there is sufficient evidence to indicate that the postulated number of benzene molecules per unit cell is correct.

The intermediate $\begin{vmatrix} -2 & 2 \\ 4 & 4 \end{vmatrix}$ structure shown in Figure 6 may involve either a homogeneous intermediate layer as shown with the benzene rings at some angle to the surface and partially dehydrogenated. However the apparent $\begin{vmatrix} -2 & 2 \\ 4 & 4 \end{vmatrix}$ diffraction pattern may also be due to the a mixture of patches of the $\begin{vmatrix} -2 & 2 \\ 5 & 5 \end{vmatrix}$ structure and some other unknown structure.

With gentle heating in flux the benzene structures and the WFC results suggest that the transformation from π to σ bonding may be reversible; however, the adsorbed layer becomes disordered so that structural corroboration of this result by LEED is not possible.

(b) Benzene on the Pt(100)-(5x1) Surface

Benzene adsorbed on the Pt(100)-(5x1) surface causes a WFC of -1.6 V and diffuse 1/2 order ring-like diffraction features to appear. With exposure the magnitude of the WFC decreases (-1.3 V), however, the diffraction pattern remains largely unchanged. The initial WFC suggests π-bonding. The value of the WFC is only slightly lower than the WFC on adsorption for several other simple substituted aromatics on the (100) surfaces. Initial adsorption may involve π-bonding between the aromatic ring and the surface while the final state may involve dehydrogenation and σ-bonding in combination with some π-bonding. The LEED results suggest that benzene may be singly dehydrogenated since a singly dehydrogenated specie adsorbed via the dehydrogenated site has a size which correlates well with the formation of 1/2 order diffraction feature. The apparent contradiction between these results may be caused by incomplete diffraction information since the diffraction information is diffuse and higher order features may be missing. However, the WFC data indicates that some sort of transition is occurring on the (100) surface similar to the transition on the (111) surface. Detailed interpretation must await further experimentation.

3. Naphthalene Adsorption

(a) Naphthalene on the Pt(111) Surface

The adsorption of naphthalene on the Pt(111) surface at 150^{o}C causes the formation of a (6x6) structure. The large WFC on adsorption (-2.0 V) indicates that a large amount of charge transfer occurs between substrate and adsorbate. It seems likely that the naphthalene ring system is involved in the formation

of a π-bond, that is the ring system is parallel or nearly parallel to the metal surface. Adsorption of naphthalene at 25°C causes the formation of a poorly ordered structure (WFC = -1.8 v±0.1 V). The degree of ordering and WFC depend on the exposure rate; the lower the exposure rate the better the order and the larger the magnitude of the WFC. However, heating any of these poorly ordered structures to 150°C causes the appearance of the (6x6) structure and causes the WFC to approach -2.0 V. These phenomena seem to indicate that naphthalene has low mobility on the surface. The adsorbed layer may order on heating to 150°C because the mobility of the adsorbed species increases; that is, the poorly ordered surface structure may be annealed at higher temperatures. The fact that better order results from low initial exposure rates seems to indicate that better ordering on the surface is also aided by slow crystallite growth, e.g., the growth of ordered domains of naphthalene. The transition required for the formation of a (6x6) diffraction pattern may be either an increase in domain size or an actual change in the adsorbed structure involving reorientation of the naphthalenes on the surface. The structure shown in Figure 8 was constructed with half of the naphthalenes arbitratily rotated by 90°. In fact we are certain only that the two scattering centers per unit cell cannot be equivalent. The structure proposed in Figure 6 is based on our best estimate of the number of naphthalenes per unit cell. The position of the adsorbed unit cell relative to the substrate is uncertain.

The adsorption of 2-methylnaphthalene was carried out to test the hypothesis that naphthalene was adsorbed parallel to the surface. If 2-methylnaphthalene gave the same structure as naphthalene, adsorption parallel to the surface would have been ruled out. However, 2-methylnaphthalene gave a disordered adsorbed layer on adsorption therefore the parallel adsorption model was not disproved. The WFC on adsorption of 2-methylnaphthalene

(-2.0 V) indicates that this substance is bound to the surface in a manner similar to naphthalene.

(b) Naphthalene on the Pt(100)-(5x1) Surface

Naphthalene adsorbed on the Pt(100) surface causes a WFC on adsorption of -1.7 V. Adsorption of 2-methylnaphthalene causes a WFC of -1.6 V. Apparently both of the compounds interact primarily by forming π-bonds with the surface. Diffraction information is completely lacking so that this interpretation is large speculative.

4. Pyridine and Dimethylpyridine Adsorption

(a) Pryidine and Dimethylpridines on the Pt(111) Surface

Pryidine adsorbed on the Pt(111) surface at 25°C forms a poorly ordered structure with a characteristic distance two times the size of the underlying lattice.

Pyridine adsorbed through its nitrogen with the aromatic ring perpendicular to the metal surface fits nicely into at Pt(111)-(2x2) unit all as shown in Figure 9. With this adsorption geometry and a (2x2) structure the WFC expected from a molecule with a 2.2 D permanent dipole moment would be $\Delta\phi$ = 3.1 V using the simple Helmholtz formation $\Delta\phi = (4\pi\sigma\mu \times 3 \times 10^{-16})$ volts where σ is the coverage in molecules/cm^2 and μ is the dipole moment in debye. The WFC observed on adsorption is -2.7 V, this agreement is remarkable since the simple form above does not include any mutual depolarization effects. This agreement implies that the molecules are adsorbed with their basic nitrogens down toward the surface. The hypothesis that the nitrogen lone electron pair was extensively involved in bonding between pyridine and the metal surface was tested by adsorbing 2,6-dimethylpyridine;[21, 22] 3,5-dimethylpyridine was used to check for the influence of other effects od dimethyl substitution such as the increased size of the molecule and electron density changes with methyl substitution.

Adsorption of 3,5-dimethylpyridine on the Pt(111) surface causes a WFC of -2.3 V. This value implies involvement of the nitrogen lone electron pair in the bonding. 3,5-Dimethylpryidine causes the appearance of diffuse 1/2 order diffraction features; however, the molecule is too large to fit in a Pt(111)-(2x2) unit cell, thus the diffraction information appears to be incomplete because of poor ordering.

Adsorption of 2,6-dimethylpyridine causes a WFC of -1.6 V on the Pt(111) surface. This value of the WFC is significantly smaller than the WFC on adsorption of 3,5-dimethylpyridine and is similar to the WFC observed for most of the simple substituted aromatics (Table 1). This implies that the nitrogen lone electron pair is not extensively involved in bonding and that π-bonding is the primary type of interaction which is occurring. The diffraction pattern was observed for toluene, m-xylene, and mesitylene compounds which are approximately the same size and which form π-bonds with the surface.

The adsorption of these two dimethylpyridines has shown that if a pyridine type nitrogen is not sterically hindered it interacts strongly with the surface through its basic nitrogen.

If the adsorbed pyridine is heated to 250^{o}C, a new structure forms characterized by one-dimensional order with the unit vector in the overlayer being three times as long as the unit vectors in the substrate lattice. The proposed structures are shown in Figure 9. The diffraction information seems to indicate an increase in the area per molecule since the unit cell size increases. The magnitude of the WFC decreases with heating (-1.7 V) indicating a less favorable geometry for the nitrogen lone electron pair interaction or less favorable orientation of the permanent dipole. Exchange studies with pyridine have indicated that the ortho position (next to the nitrogen(is very

susceptible to exchange.[23] Therefore, it is probably that pyridine at high temperature is singly dehydrogenated and is doubly adsorbed on the surface through the nitrogen and a dehydrogenated ortho-carbon as shown in Figure 7. The cross-section of such a species is three by one and one-half in terms of the Pt(111) unit vectors, thus this adsorbed orientation of pyridine could give rise to the observed diffraction pattern. The decrease in the magnitude of the WFC is easily explained using this pyridine orientation since the nitrogen has a less favorable geometry for interaction with the surface and the permanent dipole is no longer aligned perpendicular to the substrate surface.

(b) Pyridine and Dimethylpyridine on the Pt(100)-(5x1) Surface

Adsorption of pyridine on the Pt(100)-(5x1) surface causes a WFC of -2.4 V indicating that the nitrogen's lone electron pair is extensively involved in the interaction between substrate and adsorbate. This hypothesis is confirmed by experiments done with 2,6-dimethylpyridine and 3,5-dimethylpyridine. The WFC on adsorption of 2,6-dimethylpyridine is -1.5 V indicating little involvement of the nitrogen lone electron pair. Thus it appears that pyridine on the Pt(100) is adsorbed with its ring perpendicular or nearly perpendicular to the surface.

With heating the disordered pyridine layer causes a diffuse diffraction pattern characteristic of a $(\sqrt{2} \times \sqrt{2})R45^{o}$ structure to form. Pyridine is too large to fit in this unit cell, therefore it appears that the diffraction information is incomplete because of poor order.

5. Cyclohexane, Cyclohexene, 1,3-Cyclohexadiene and Benzene Adsorption

A paper dealing with adsorption of cyclohexane, cyclohexene, 1,3-cyclohexadiene, benzene, and the dehydrogenation reactions of the first three compounds on the Pt(111) surface has recently been published.[10] We include

a more complete description of the adsorption characteristics of these molecules here so that comparisons can be made between their adsorption and ordering behavior on the Pt(111) and Pt(100)-(5x1) surface.

(a) Cyclohexane and Cyclohexene Adsorbed on the Pt(111) Surface

Cyclohexane adsorbed on the Pt(111) surface at low pressure (6×10^{-9} Torr recorded pressure) causes a WFC of -1.2 V. With increased pressure (4×10^{-7} Torr recorded pressure) the magnitude of WFC decreases to -0.7 V and a disordered adsorbed layer forms. Cyclohexene adsorbed on the Pt(111) surface causes a WFC of -1.7 V and forms a $\begin{vmatrix} -2 & 2 \\ 4 & 4 \end{vmatrix}$ structure. Thus it seems apparent that cyclohexane is not adsorbed in the same manner as cyclohexene. This is, cyclohexane is not doubly dehydrogenated and adsorbed as an olefin at 20°C. Single dehydrogenation followed by interaction with the surface through the dehydrogenated site seems to be the most likely possibility. Using this type of bonding the transition which occurs at high pressure can be easily explained by examining the availability of several ring orientations relative to the surface. It appears that with increased pressure the adsorbed cyclohexanes "stand up" with respect to the surface. This transition may be caused by the repulsive interaction of the adsorbate molecules as the number of adsorbate molecules per unit surface area increases with increased organic vapor pressure. Cyclohexene forms a $\begin{vmatrix} -2 & 2 \\ 4 & 4 \end{vmatrix}$ structure and causes a WFC of -1.7 V on adsorption. The large WFC on adsorption indicates interaction of the π-electrons with the metal surface. A possible configuration for the $\begin{vmatrix} -2 & 2 \\ 4 & 4 \end{vmatrix}$ structure is shown in Figure 10. The structure has been constructed using the criteria and assumptions discussed in the experimental section. Note that cyclohexene has several possible ring conformations; we have used the one with the smallest projected area without allowing dehydrogenation. The structure allows fairly close approach of the unsaturated carbon-carbon bond to the metal surface. However, it may be possible for double dehydrogenation of the cyclohexene to occur and allow even

closer approach of the unsaturated bond to the surface. This would allow further reorientation and even smaller surface area per adsorbate molecules. It would also allow σ-bonding between substrate and adsorbate. (In this case the formation of an acetylenic π-bonded surface species seems unlikely without ring rupture since a six-membered ring cannot remain intact with four linear carbon atoms.) The behavior of the WFC with exposure (a slight slow decrease in magnitude of the WFC at high pressure) indicates that slight reorientation of the ring system is occurring without major chemical changes. Ethylene, a case for which dehydrogenation of adsorption at 20°C seems likely, displays a slow increase in magnitude of the WFC with exposure. However, it may be possible for double dehydrogenation of the cyclohexene to occur and allow even closer approach of the double bond to the surface as well as allowing σ-bonding between substrate and adsorbate.

With heating to 150°C in flux, cyclohexane and cyclohexene both cause an apparent (2x2) surface structure with diffuse diffraction features. The magnitude of the WFC increases to -1.4 V for cyclohexane and decreases for cyclohexene to -1.5 V. Both adsorbed layers are disordered at 300°C.

The marked increase in the magnitude of the WFC for cyclohexane for -1.7 V at 20°C to -1.4 V at 300°C indicates that dehydrogenation is occurring with heating. The fact that the magnitude of the WFC does not increase even more is probably caused by partial decomposition of the adsorbed layer to small fragments or amorphous carbon with heating. The identical diffraction patterns at 150°C are further evidence that dehydrogenation of the cyclohexane is occurring with heating. The small change in WFC value for cyclohexene with heating from 20°C to 150°C implies that little change is occurring in the bonding between the adsorbed layer and the substrate for cyclohexene. Thus it appears that the apparent (2x2) cyclohexene structure may be a disordered $\begin{vmatrix} -2 & 2 \\ 4 & 4 \end{vmatrix}$ surface structure or a $\begin{vmatrix} -2 & 2 \\ 4 & 4 \end{vmatrix}$ surface structure which is unresolved

by LEED because of small domain size. The apparent (2x2) cyclohexane structure may be due to the same sort of disordered structure. The difference in WFC values observed at 150° could be explained in assuming that the cyclohexane structure is made up of approximately one-half cyclohexane (high pressure form) and one-half cyclohexene; that is, at 150°C the dehydrogenation was not complete.

(b) 1,3-Cyclohexadiene and Benzene on the Pt(111) Surface

1,3-Cyclohexadiene on the Pt(111) surface apparently loses two hydrogens and is converted to benzene on the surface. 1,3-Cyclohexadiene causes the same sequence of surface structures as benzene. Initially the adsorbed layer is disordered, then the $\begin{vmatrix} -2 & 2 \\ 4 & 4 \end{vmatrix}$ forms and with further exposure the $\begin{vmatrix} -2 & 2 \\ 5 & 5 \end{vmatrix}$ structure forms. The WFC values for these three structures are similar to those observed for benzene adsorption (±0.1 V). The deviations in the WFC value can be easily explained by considering that part of the surface may be covered with hydrogen from the dehydrogenation of 1,3-cyclohexadiene. In fact, the transformation takes a significantly longer time for 1,3-cyclohexadiene than for benzene. This may also be a result of increased surface hydrogen concentration for the 1,3-cycloxadiene case. For a detailed explanation of the benzene structures see benzene section of the discussion. In brief, the benzene first forms a π-bond with the surface (disordered surface structure, WFC = -1.8 V) and the final adsorbed state involves a singly dehydrogenated benzene σ-bonded to the surface ($\begin{vmatrix} -2 & 2 \\ 5 & 5 \end{vmatrix}$ surface structure, WFC = -0.7 V).

(c) The Pt(111) Surface and the Mechanism of Cyclohexane Conversion to Benzene

The Pt(111) surface seems capable of catalyzing the conversion of cyclohexane to cyclohexene at elevated temperatures but not cyclohexane or cyclohexene to benzene. However, 1,3-cyclohexadiene converts to benzene at room

temperature. The primary difference between cyclohexane, cyclohexene, and 1,3-cyclohexadiene is adsorption geometry. Both cyclohexane and cyclohexene adsorbed on the Pt(111) surface may have little "contact" with the surface since they may adsorb in a "standing up" position. That is, several of the carbons are far removed spatially from the metal surface because of the conformations of the ring systems. Cyclohexadiene on the other hand is locked in a planar configuration so that all carbons are in intimate contact with the surface. In essence the activation barrier for dehydrogenation may be reduced dramatically for 1,3-cyclohexadiene because the metal can interact with the portions of the molecule where dehydrogenation must occur. This comes about because the ring system is rigid and the molecule is π-bonded parallel to the surface. For cyclohexane and cyclohexene the activation barrier is increased at high pressure (10^{-6} Torr surface pressure) since the molecules "stand up" on the surface because of repulsive interaction between adsorbate molecules.

(d) Cyclohexane and Cyclohexene on the Pt(100)-(5x1) Surface

Cyclohexane adsorbed on the Pt(100) surface goes through a transition with increasing organic pressure similar to that observed on the Pt(111) surface. Adsorption ot low pressure ($6x10^{-9}$ Torr record pressure) causes a WFC of -0.75 V while the (5x1) surface structure remains. Increasing the cyclohexane pressue (to $4x10^{-7}$ Torr recorded pressure) causes the magnitude of the WFC to decrease and also causes the (5x1) surface structure to disappear and a diffuse (2x1) diffraction pattern to form. Cyclohexene adsorbed on the Pt(100)-(5x1) surface causes the disappearance of the (5x1) and the appearance of a diffuse (2x1) surface structure; the WFC on adsorption is -1.6 V. Even though the diffraction patterns are similar, the large

difference in the WFC indicates a marked difference in the bonding characteristics between substrate and adsorbate for the two cases. The similar diffraction patterns may indicate similar geometries of adsorption for the two adsorbates, however, cyclohexane is not adsorbed as a doubly dehydrogenated olefinic species at room temperature. Single dehydrogenation followed by interaction with the surface through the dehydrogenated site seems to be the most likely possibility. The transition which occurs with cyclohexane adsorption may be rationalized by considering possible ring orientations relative to the metal surface. It appears that with increased pressure the adsorbed cyclohexane molecules "stand up" with respect to the metal surface. This transition may be caused by repulsive interaction between adsorbates as the density (number of adsorbates per unit surface area) in the adsorbed layer increases with increasing organic vapor pressure. The large WFC on adsorption (-1.6 V) of cyclohexene implies that π-bonding is occurring between substrate and adsorbate.

With heating in flux to 150°C both cyclohexane and cyclohexene cause the formation of a streaked (2x1) diffraction pattern. The magnitude of the WFC increases to -1.2 V (from -0.4 V) for cyclohexane and decreases slightly for cyclohexene to -1.5 V. With further heating to 300°C the magnitude of the WFC increases slightly for both cyclohexane (-1.5 V) and cyclohexene (-1.6 V).

The marked increase in the magnitude of the WFC for cyclohexane from -0.4 V to -1.5 V at 300°C indicates that dehydrogenation in occurring with heating. The fact that the WFC values are very similar at 300°C indicates that a large portion of the adsorbed cyclohexane layer is adsorbed in the same manner as cyclohexene at 300°C. In fact the identical ordered structures observed at 150°C indicate that the adsorption geometry is similar for these two compounds at 150°C. Thus it seems that at elevated temperatures cyclohexane

may be converted to cyclohexene.

(e) Adsorption of 1,3-Cyclohexadiene and Benzene on the Pt(100)-(5x1) Surface

Adsorption of 1,3-cyclohexadiene on the Pt(100)-(5x1) surface causes a WFC and diffraction pattern very similar to those caused by benzene adsorption on this surface. Benzene causes an initial WFC of -1.6 V which decreases to -1.3 V with exposure. 1,3-Cyclohexadiene causes an initial WFC of -1.7 V which decreases to -1.4 V with exposure. Both adsorbates cause surface structures with a periodicity twice the underlying lattice. Thus, it appears that 1,3-cyclohexadiene is converted to benzene on the Pt(100)-(5x1) although the evidence is certainly not as detailed as the data on the Pt(111) surface.

(f) The Pt(100) Surface and the Mechanism of Conversion of Cyclohexane to Benzene

The Pt(100) surface seems capable of catalyzing the conversion of cyclohexane to cyclohexene at elevated temperature but not the conversion of cyclohexane or cyclohexene to benzene. However, 1,3-cyclohexadiene is converted to benzene at room temperature. The primary difference between cyclohexane, cyclohexene, and 1,3-cyclohexadiene appears to be adsorption geometry. 1,3-Cyclohexadiene adsorbes parallel to the surface because the ring is rigid and π-bonding occurs. The ease with which conversion of 1,3-cyclohexadiene to benzene takes place may be explained because the portion of the molecule which must be dehydrogenated is in close proximity of the metal surface. The activation barrier for cyclohexane and cyclohexene appears to be high because the molecules "stand up" with high pressure (10^{-6} Torr surface pressure) and the part of the molecule which must be dehydrogenated is some distance from the surface.

Judging solely from WFC results it appears that the Pt(100) surface is a better catalyst for the reaction cyclohexane → cyclohexene than the Pt(111) surface. The (111) surface may be less selective and more reactive (leading

to decomposition of the reactant) or simply less reactive since the WFC results indicate only that the Pt(100) surface is covered by a larger portion of cyclohexene than the Pt(111) surface at 150°C and 300°C.

6. Adsorption of Substituted Aromatic Molecules

The surface structures formed on adsorption of substituted aromatic molecules are more ordered on the Pt(111) surface than on the Pt(100)-(5x1) surface. The aromatic molecules which have small substituent groups or high rotational symmetry form more ordered overlayers under the experimental conditions employed. Thus, the shape of the adsorbate molecules and the rotational symmetry of the substrate determines the degree of ordering which occurs in the adsorbed layer.

We have also found that the WFC on adsorption and the degree of ordering in the overlayer varies with the initial rate of growth of the adsorbed layer which can be varied by changing the incident vapor flux. The slower the rate of growth (smaller the incident flux), the larger the WFC change and the more ordered the overlayer for substituted aromatics. These observations seem to indicate that with low incident vapor flux the density of the adsorbed layer may be increased because of more efficient packing in the ordered overlayer. With slow growth rates, the size of the ordered domains is being increased in the adsorbed layer, leading to an increase in the density of surface sites occupied by the adsorbate.

Both of these observations, (1. High symmetry promotes ordered surface structure formation, and 2. Slow growth of the adsorbed layer promotes ordered structure formation), can be explained by a simple model of ordering for adsorbed aromatic systems on Pt surfaces. Ordered adsorption for these large molecules may proceed by a two-step mechanism. Initially the aromatic molecules may adsorb on the surface in a disordered fashion. The second step

involves ordering of the adsorbed layer and indicates the importance of surface diffusion (either translational or rotational) in this ordering process. If the adsorbate has a shape which approximates a circular cross-section, the reorientation into ordered layers is less difficult than reorientation of adsorbates with bulk side groups. Slow deposition of the overlayer allows adsorbed molecules more reorientation time before they become locked into place by a large number of neighbors. This type of ordering should be distinguished from ordering caused by site adsorption. Site adsorption involves adsorption into a specific surface site in a specific orientation. Ordering results because the surface sites are ordered. During site adsorption, adsorption and ordering occur simultaneously.

The WFC observed on adsorption ranges from -1.4 V for nitrobenzene to -1.8 V for aniline. Charge transfer of such magnitude indicates extensive interactions of the aromatic π systems with the substrate.

The interpretation of the diffraction information in these studies has been complicated by the absence of well-defined diffraction features. The diffraction features may be characteristic of the size and orientation of the unit cell in the ordered adsorbed layer or they may be characteristic of a coincidence distance between the adsorbed layer or they may be characteristic of a coincidence distance between the adsorbed lattice and the substrate lattice. Studies involving ordered adsorption of organic molecules on single crystal platinum surfaces have indicated that either situation may occur. Specifically, benzene forms coincidence lattices on the Pt(111) surface while naphthalene forms a structure for which molecular size is easily related to the unit mesh determined from the diffraction pattern. With these facts in mind, we have used the available chemical information, molecular dimensions, the observed WFC and the diffraction information to analyze the nature of the interaction between adsorbate and substrate.

a. Toluene m-xylene, Mesitylene, t-Butylbenzene, and n-Butylbenzene Adsorption on the Pt(111) Surface

Work function change. The maximum WFC observed on adsorption for these compounds range from -1.5 V for n-butylbenzene to -1.8 V for m-xylene. This large electron transfer from the adsorbed molecules to the metal substrate implies that the polarizable π electrons are involved extensively in the interaction between adsorbate and substrate. The similarity of the WFC on adsorption for this family of compounds also indicates that the primary interaction occurs beterrn the aromatic π system and the substrate surface since the benzene ring is the only structural entity common to all molecules. in the series. If the aromatic π system is the primary interaction center, it follows that the adsorption geometry should be similar for this family of compounds. In the absence of dehydrogenation the aromatic systems would be expected to adsorb parallel or nearly parallel to the substrate surface so that the aromatic π system could efficiently interact with the substrate surface.

That these aromatic systems are adsorbed parallel or nearly parallel to the surface is further supported by the results of the mesitylene adsorption studies carried out at low pressure (10^{-9} Torr). Each aromatic hydrogen in mesitylene has adjacent methyl groups. Since methyl groups are known to deactivate the exchange of adjacent hydrogens in hydrogen-deuterium exchange studies, there should be little chance for dehydrogenation of the aromatic hydrogens and for subsequent interaction of the dehydeogenated site with the surface to form σ (electron pair) bonds. Excluding demethylation, the only alternative for interaction appears to be π-bonding with the substrate surface. That is, mesitylene should be fairly inactive toward any type of interaction except π-bonding. The fact that its WFC on adsorption is similar to the WFC

of other aromatic adsorbates supports our contention that the primary interaction occurs via π-bonding.

n-Butylbenzene induces the smallest WFC on adsorption; the WFC on adsorption also depends markedly on the growth rate of the adsorbed layer. Both of these effects are caused by the presence of the long side chain which makes efficient packing in the surface plane difficult.

Diffraction studies. The diffraction patterns observed for this family of compounds indicate poor ordering of the adsorbed layer. For the series toluene, m-xylene, mesitylene adsorbed at room temperature, streaked diffraction features appear at 1/3. 1/2.6. 1/3.4 of the distance between the (00) beam and the first order platinum features. The unit cell size implied by these streaked features does not correlate with the molecular size of the adsorbed species since they are listed in order of increasing size above (the distance to the first order diffraction should vary inversely with the size of the unit cell). However, the diffraction patterns become better ordered in the series toluene, m-xylene, mesitylene. t-Butylbenzene and n-butylbenzene on the other hand form disordered adsorbed layers. Thus, it appears that large π-bonded adsorbed molecules of the same rotational multiplicity order more easily in the absence of long side-chains.

Detailed information concerning molecular orientation cannot be extracted from the diffraction patterns since poorly ordered layers are formed. However, it seems worthwhile to point out that toluene adsorbed parallel to the surface fits into the (3x3) unit cell observed while m-xylene and mesitylene do not fit into the (2.6x2.6) and (3.4x3.4) unit cells, respectively, which can be deduced from the diffraction features. The Pt(111)-(4x2)-toluene structure which forms at 150°C does not have a large enough unit cell to accommodate

toluene adsorbed parallel to the surface even though the WFC observed seems to support this adsorption geometry. However, for all cases mentioned above the diffraction features are diffuse since the layers were poorly ordered; therefore, caution must be exercised in attempting to deduce much structural information.

b. Toluene, b-Xylene, Mesitylene, t-Butylbenzene, and n-Butylbenzene Adsorption on the Pt(100)-(5x1) Surface

Work function change. The maximum WFC observed on adsorption for these compounds range from -1.5 V for n-butylbenzene and mesitylene to -1.75 V for t-butylbenzene. Again, the large amount of electron transfer, the similarity of the WFC for mesitylene adsorbed at low pressures is similar to the WFC observed for the other compounds in the series indicates that the interaction occurs prediminantly between the metal and the π electron cloud of the adsorbate.

The WFC on adsorption of n-butylbenzene depends markedly on the growth rate of the adsorbed overlayer. It appears that this is due to the long side chain which makes reorientation of the adsorbed molecules difficult.

Diffraction studies. Ordered adsorption on the Pt(100)-(5x1) surface seems to be correlated with the persistence of the (5x1) surface structure for these large π-bonded adsorbates. That is, if the (5x1) surface structure remains detectable after adsorption the adsorbed layer will be fairly well-ordered. On adsorption of toluene, m-xylene, and mesitylene, streaked 1/3 order diffraction features appear which co-exist with the diffraction features due to the (5x1) surface structure. Upon gentle heat treatment, both the (5x1) surface structure and 1/3 order streaks disappear leaving a (1x1) pattern with increased background intensity. On adsorption n-butylbenzene initially causes the appearance of diffuse streaked 1/3 order features along with a decrease in the intensity of the diffraction beams due to the presence of the

the (5x1) surface structure. With continued exposure both the (5x1) surface structure and the 1/3 order streaks are replaced by a (1x1) pattern with increased background intensity indicating disordered adsorption. t-Butylbenzene forms a disordered overlayer on adsorption and the (5x1) surface structure reverts to a (1x1) structure with high background intensity. During this order-disorder transformation in the adsorbed layer while the substrate surface structure is also changing from (5x1) to (1x1), no significant work function change takes place.

The (5x1) surface structure may be due to the formation of a hexagonal platinum overlayer on top of the square surface unit cell expected by projecting the bulk structure onto the surface plane.[11,12] This model explains the observed order-disorder transformation upon changes of substrate structure since a hexagonal surface (even one formed by reconstruction) might be expected to yield more ordered overlayers. It should be noted that several ordered surface structures have been observed on the Pt(100)-(1x1) surface even though the (5x1) structure has relaxed. We have observed structures for CO, ethylene, acetylene, benzene, and pyridine on the Pt(100)-(1x1) surface structure. These molecules appear to order via the one-step site mechanism. That is, the adsorption occurs with the molecules in a specific orientation at a specific surface site. The bonding arguments made for CO, ethylene and acetylene by other authors[24, 25, 26] supports this contention. Benzene and pyridine appear to interact with the (100) via the formation of an electron pair bond to the Pt(100) surface.

During the adsorption of mesitylene at high pressure (4×10^{-7} Torr), a pressure induced transition occurs on both low index platinum surfaces. The WFC decreases, and the LEED pattern becomes markedly different (on the Pt(111) a disordered layer forms; on the (100) surface the (5x1) structure converts

to the (1x1)). A change in the nature of interaction between the substrate and adsorbate is occurring which depends on the incident vapor flux. A comparison with the results obtained for benzene seems to indicate that a $\pi \rightarrow \sigma$ bond transition may be occurring. This may be due to demethylation of the aromatic ring and subsequent interaction with the surface through the demethylated carbon site or dehydrogenation of a methyl group and interaction of the substrate with the dehydrogenated site.

c. Aniline, Nitrobenzene and Cyanobenzene Adsorption on the Pt(111) Surface

Work function change. The WFC observed on adsorption of aniline, nitrobenzene, and cyanobenzene are -1.8 V, -1.5 V and -1.6 V, respectively. The similarity of WFC within the series and also the similarity to the WFC on adsorption of the other hydrocarbons studied supports the contention that these molecules also interact primarily by forming a π bond with the substrate surface. That is, they adsorb with the benzene ring parallel or nearly parallel to the surface. Nitrobenzene appears to decompose in the electron beam when adsorbed on the Pt(111) surface since the WFC and diffraction pattern both change with electron beam exposure at moderate voltages (30 V).

Diffraction studies. The diffraction patterns observed on adsorption are poorly ordered for this group of compounds. All three molecules cause the appearance of 1/3 order features in the diffraction pattern. Aniline adsorption gives rise to streaked diffraction features at 1/3 order along with streaks extending radially to (1/2 0) positions. This diffraction pattern seems to be the result of a poorly ordered complex structure. Adsorption of nitrobenzene and cyanobenzene cause the formation of diffuse 1/3 order diffraction features. Both of these molecules, adsorbed with their benzene ring parallel to the metal surface, fit into a (3x3) unit cell. However, the diffraction patterns indicate a great deal of disorder in the

adsorbed layer and the diffuse diffraction features might obscure much information necessary to interpret the surface structures.

d. Aniline, Nitrobenzene and Cyanobenzene on the Pt(100)-(5x1) Surface

Work function change. The WFCs on adsorption of aniline, nitrobenzene and cyanobenzene are -1.75 V, -1.4 V and -1.5 V, respectively. The similarity of the WFC within the series and the similarity to the WFC on adsorption of the other hydrocarbons studied supports the contention that these molecules also interact primarily by forming a π bond with the substrate surface. We expect the molecules to be adsorbed with their benzene ring parallel or nearly parallel to the substrate surface. Nitrobenzene adsorbed on the Pt(100)-(5x1) surface is not as sensitive to electron beam exposure as the overlayer on the Pt(111) surface. Apparently small changes in the interaction between substrate and adsorbate can markedly affect the electron beam sensitivity of the adsorbed layer.

Diffraction studies. These compounds form disordered overlayers on adsorption.

7. Acetylene, Ethylene, and Propylene Adsorption

(a) Acetylene, Ethylene, and Propylene on the Pt(111) Surface

A substantial body of experimental data exists concerning ethylene and acetylene adsorption on the Pt(111) surface.[24,25,26] A recent paper by Weinberg, Deans, and Merrill[25] reviews the relevant data and proposes a detailed adsorption model for ethylene and acetylene on the Pt(111) surface. In short, they conclude that ethylene is adsorbed dissociatively, while acetylene remains intact on adsorption and that both form a (2x2) surface structure. There is a second layer of reversibly adsorbed ethylene on top of the dissociatively adsorbed first layer. This reversibly adsorbed ethylene desorbs at 100°C. The hydrogen resulting from ethylene dissociation

desorbs at 200°C and the adsorbed layer of acetylenic residue consolidates above this temperature, They also conclude that the adsorbed acetylene (2x2) structure is not stable with respect to further acetylene exposure since more acetylene may adsorb in vacant interstitial sites and cause the adsorbed layer to become disordered. However the (2x2) structure that forms upon the adsorption of ethylene is stable to acetylene exposure since the dissociated hydrogens block the interstitial sites.

We have been able to reproduce these findings in our studies of acetylene adsorption. The adsorption of acetylene on the Pt(111) surface induces the formation of a (2x2) sturface structure. The acetylene (2x2) structure rapidly becomes disordered with further exposure to acetylene flux (completely disordered with ~40L). Our studies of the adsorption of ethylene yield somewhat different results. We have found that ethylene adsorbs on the Pt(111) face at 25°C in a disordered manner. Ordering occurs readily, however, upon impact by the incident electron beam and a (2x2) surface structure forms with the same properties as described by other workers. The (2x2) surface structure was not affected by further exposure to ethylene flux. The WFC observed for the acetylene (2x2) structure is -1.5 V and the WFC observed with adsorbed ethylene that was ordered by the incident electron beam is -1.5 V. The similarity of the WFC on adsorption and the I_{oo} vs eV curves are clear indications that in the adsorbed state these surface structures are identical. That is, on electron impact, the adsorbed ethylene dissociates into acetylene and two adsorbed hydrogens while acetylene adsorbs without dissociation. The two adsorbed structures may behave in a different manner with exposure to flux because the hydrogen on the surface from dissociation of the ethylene may inhibit further adsorption of ethylene which might cause the adsorbed layer to become disordered. This hypothesis is born out by the

WFC results. As the (2x2) acethylene structure is exposed to further acetylene flux, the pattern becomes that expected from a disordered layer and the magnitude of the WFC slowly increases to -1.65 V indicating an increase in the density of adsorbed species on the surface. Further exposure of the (2x2) structure obtained by electron impact dissociation of ethylene to ethylene flux results in no change in the work function indicating no change in the density of the adsorbed layer. With heating in vacuum the density of the adsorbed acetylene layer remains essentially constant up to 150°C (the highest temperature used) as indicated by no variation of the WFC. However, the density of the adsorbed ethylene layer decreases markedly with heating in vacuum above 100°C as indicated by a marked decrease in the magnitude of the WFC. Weinberg, Deans, and Merrill[25] attribute this low temperature desorption to a second layer of reversibly adsorbed ethylene which is adsorbed on top of the acetylene first layer.

Heating the adsorbed acetylene layer in flux up to approximately 150°C causes a maximum to occur in the magnitude of the WFC (-1.8 V) indicating an increase in density of the adsorbed layer. Heating the adsorbed ethylene layer in flux casuses a maximum in the magnitude of the WFC of -1.7 V at approximately 250°C indicating an increase in the density of the adsorbed layer. These increases in density may be caused by increased surface mobility which may result in increased packing efficiency. Hydrogen is known to desorb from ethylene covered Pt(111) surfaces at approximately 200°C.[22, 23] Thus the presence of surface hydrogen for the adsorbed ethylene case appears to limit the adsorbate surface density until substantial hydrogen desorption has occurred. Propylene adsorbed on the Pt(111) surface causes the formation of a (2x2) structure; the WFC on adsorption is -1.3 V. The I_{oo} vs eV curves suggest that propylene is dissociated to acetylene upon adsorption at 20°C.

The discrepancy between the WFC results found by Morgan and Somorjai[24] and those found in the current study can be explained by considering the differences in experimental procedures and equipment used. The work of Morgan and Somorjai was often performed on samples which were cleaned only by heating between adsorption experiments. This procedure produces carbon contaminated surfaces which do not adsorb as much gas as clean surfaces therefore the magnitude of the WFC observed on adsorption would be expected to be smaller than the WFC observed with adsorption on a clean surface. The system used had a high CO background since Ti sublimation pumping was not employed and in these early studies Auger electron spectroscopy, to check surface cleanliness, was also not available. Carbon monoxide is known to displace adsorbed olefins,[24] displacement would also lead to a reduction in the WFC observed.

(b) Acetylene, Ethylene, and Propylene Adsorbed on the Pt(100)-(5x1) Surface

The adsorption of ethylene or acetylene on the Pt(100)-(5x1) surface causes the formation of a $(\sqrt{2} \times \sqrt{2})R45^{o}$ surface structure. The WFC on adsorption is -1.65 V for acetylene and -1.2 C for ethylene. The WFC values seem to indicate that these molecules adsorb as distinct chemical species. That is, it appears that ethylene adsorbs associatively at $20^{o}C$ on the Pt(100)-(5x1) surface.

The diffraction pattern resulting from the $(\sqrt{2} \times \sqrt{2})R45^{o}$ surface structures have diffuse (1/2. 1/2) diffraction features but well-defined (10) features. The broadening of diffraction features results from the existence of adsorbate domain boundaries.[24] The structure of certain types of antiphase domain boundaries can be simply related to the symmetry of the adsorption sites occupied by adsorbate molecules on the surface.[25] The type of broadening observed for ethylene and acetylene implies that adsorption is occurring in

a four-fold symmetry site. An analysis for $(\sqrt{2} \times \sqrt{2})R45^{o}$ structures on square symmetric substrate unit cells has been reported by R. L. Park.[27]

Heating the adsorbed acetylene layer in flux to approximate 150°C causes a slight maximum to occur in the magnitude of the WFC (-1.7 V) indicating a slight increase in the density of the adsorbed layer and/or partial dehydrogenation of the adsorbed layer. Hydrogen is known to desorb from ethylene covered Pt(100)-(5x1) surfaces at approximately 200°C;[12] the desorption of hydrogen implies partial dehydrogenation of the adsorbed ethylene. Since desorption of hydrogen is occurring, an increase in the density of the adsorbed layer could be easily accomplished by further ethylene adsorption from the gas phase. The similarity of the WFC values at 250°C (-1.65 for acetylene and -1.5 V for ethylene) seems to indicate that the adsorbed layers are similar after heat treatment.

Propylene adsorbed on the Pt(100)-(5x1) surface causes the appearance of diffuse 1/2 order streaks and a WFC of -1.2 V. This seems to imply partial dissociation of propylene since the WFC results are identical with those observed for ethylene adsorption.

The discrepancy between the WFC reported here and those reported by Morgan and Somorjai[24] may be due to the fact that in earlier work cleaning was carried out between adsorption runs by heating the surface in vacuum, which is now known to produce carbon contaminated surfaces. Carbon monoxide displacement of adsorbed olefins may also have occurred. Again, in these early studies Auger electron spectroscopy was not available to test the cleanliness of the surface prior to adsorption.

8. Adsorption of Aliphatic Molecules on the Pt(111) and Pt(100)-(5x1) Surfaces

Cyclohexane, n-hexane, and cyclopentane adsorb on the Pt(111) surface at 20°C with organic vapor fluxes in the range 10^{-8} Torr to 10^{-6} Torr. All

three compounds undergo an organic vapor pressure induced transitions during which the magnitude of the WFC decreases. Comparison of the WFC data on adsorption of similar olefins (cyclohexene, and cyclopentene) at 20°C shows that the adsorbed state of these aliphatic molecules is certainly different than the adsorbed state of the olefins. That is, these compounds do not become doubly dehydrogenated and adsorb as olefins. With increased temperature cyclohexane and hexane (cyclopentane was not studied) apparently become at least partially dehydrogenated as evidenced by the fact that the magnitude of the WFC increases and goes through a maximum above 200°C.

Experiments below room temperature should be carried out to ascertain the presence of a complete monolayer[28] in case of the predominance of weak dispersion force interactions between adsorbate and the metal surface.[28] Monolayer or near monolayer coverage is necessary to interpret the observed work function changes in terms of net charge transfer since WFC is not only dependent on the nature of the surface chemical bond but also on the coverage. Also, the low surface temperature experiments reduce the possibility of dehydrogenation since many of the saturated hydrocarbons are known to dehydrogenate on platinum at elevated temperatures.

Several explanations of the transition which occurs with pressure are possible. It seems likely that the final state involves a molecule adsorbed perpendicular or nearly perpendicular to the metal surface. The low pressure adsorbed state may involve either a physisorbed molecule adsorbed parallel to the surface or singly dehydrogenated molecules covalently bound to the surface but adsorbed parallel or nearly parallel to the metal surface.

ACKNOWLEDGMENT

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FIGURE CAPTIONS

Figure 1. A schematic diagram of the ultra-high vacuum system and gas manifold used in the adsorption studies.

Figure 2. Low-energy electron diffraction pattern and schematic representation of the Pt(111) face.

Figure 3. (a) Diffraction pattern from the Pt(100)-(5x1) structure.

(b) Schematic representation of the (100) surface with a hexagonal overlayer.

(c) Diffraction pattern from the Pt(100)-(1x1) surface.

(d) Schematic representation of the (100) surface.

Figure 4. The maximum work function change on adsorption versus the first ionization potential of organic molecules adsorbed on the Pt(111) surface.

Figure 5. The maximum work function change on adsorption versus the first ionization potential of organic molecules adsorbed on the Pt(111)-(5x1) surface.

Figure 6. A diffraction pattern resulting from the Pt(111)-$\begin{vmatrix} -2 & 2 \\ 4 & 4 \end{vmatrix}$-benzene structure with a schematic diagram of the unit cell divided into areas containing a single benzene molecule. The relative position of the adsorbate and substrate unit cell is uncertain. The benzene is shown parallel to the surface for convenience; it may be rotated by some angle relative to the surface. All dimensions are in Angstroms.

Figure 7. Diffraction patterns taken at several voltages for the Pt(111)-$\begin{vmatrix} -2 & 2 \\ 5 & 5 \end{vmatrix}$-benzene structure (pattern A contains the first-order platinum diffraction features) and a schematic diagram of the unit

FIGURE CAPTIONS (contd.)

cell divided into areas which contain a single benzene molecule. The benzene is shown in several orientations; the most likely is shown in the top left corner. The position of the unit cell relative to the substrate unit cell is uncertain. All dimensions are in Ångstroms.

Figure 8. A diffraction pattern and schematic diagram of the Pt(111)-(6x6)-naphthalene structure with a probably arrangement of naphthalene molecules in the unit cell. The angle of rotation of one set of parallel naphthalene molecules with respect to the other set is uncertain. The position of the unit cell relative to the substrate unit cell is also uncertain. All dimensions are in Ångstroms.

Figure 9. A schematic diagram indicating the orientation of adsorbed pyridine on the Pt(111) surface. The orientation shown for the Pt(111)-(2x2) structure correlates with the adsorption data at 20°C. The orientation shown for the Pt(111)-(3x1.5) structure correlates with the adsorption data at 250°C and corresponds to a single dehydrogenated pyridine adsorbed through both its nitrogen and the dehydrogenated ortho site.

Figure 10. A schematic diagram indicating a possible orientation of cyclohexene on the Pt(111) surface. The carbon-carbon double bond is near the surface.

Table 1

Work Function Changes and Structural Information for Adsorption of Organic Compounds on the Pt(111) and Pt(100)-(5×1) Surfaces

Adsorbate	Temp °C	Pt(111)			Pt(100)-(5×1)			
		Work Function Change		Adsorbate Diffraction Features or Surface Structure	Work Function Change		Substrate Structure after Adsorption	Adsorbate Diffraction Features or Surface Structures
		Press (Torr)	WFC (Volts)		Press (Torr)	WFC (Volts)		
Acetylene	20°	1×10^{-8}	- 1.5	(2×2)	4×10^{-7}	- 1.65	(1×1)	$(\sqrt{2}\times\sqrt{2})R45°$
	20°	1×10^{-8} (10 min)	- 1.65	disordered				
	150°	4×10^{-7}	- 1.8	disordered	4×10^{-7}	- 1.7	(1×1)	$(\sqrt{2}\times\sqrt{2})R45°$
Aniline	20°	1×10^{-8}	- 1.8	Streaks at 1/3 order diffuse (1/2 0) features	1×10^{-8}	- 1.75	(1×1)	disordered
Benzene	20°	4×10^{-7}	- 1.8	poorly ordered	3×10^{-7}	- 1.6	(1×1)	diffuse ring-like 1/2 order streak
	20°	4×10^{-7} (5 min)	- 1.4	$\begin{vmatrix}-2 & 2\\ 4 & 4\end{vmatrix}$				
	20°	4×10^{-7} (40 min)	- .7	$\begin{vmatrix}-2 & 2\\ 5 & 5\end{vmatrix}$	3×10^{-7} (2 hrs)	- 1.3	(1×1)	diffuse 1/2 order streak
Biphenyl	20°	2×10^{-9}	- 1.85	very poorly ordered	2×10^{-9}	- 1.8	(1×1)	disordered
n-Butylbenzene	20°	8×10^{-9}	- 1.5	disordered	8×10^{-9}	- 1.5	(1×1)	disordered
t-Butylbenzene	20°	5×10^{-8}	- 1.7	disordered	5×10^{-8}	- 1.75	(1×1)	disordered
Cyanobenzene	20°	1×10^{-8}	- 1.6	diffuse (1/3 0) features	1×10^{-8}	- 1.5	faint (5×1)	disordered
1,3-Cyclohexadiene	20°	2×10^{-8}	- 1.75	poorly ordered	2×10^{-8}	- 1.7	(1×1)	diffuse 1/2 order streak
	20°C	2×10^{-8} (1 hr)	- 1.3	$\begin{vmatrix}-2 & 2\\ 4 & 4\end{vmatrix}$	2×10^{-8} (1 hr)	- 1.6	(1×1)	diffuse 1/2 order streak
	20°C	3×10^{-7} (5 hrs)	- .8	$\begin{vmatrix}-2 & 2\\ 5 & 5\end{vmatrix}$	2×10^{-8} (5 hrs)	- 1.4	(1×1)	diffuse 1/2 order streak
Cyclohexane	20°	6×10^{-9}	- 1.2	(1×1) low background	6×10^{-9}	- .75	(5×1)	low background
	20°	4×10^{-7}	- .7	very poorly ordered	4×10^{-7}	- .4	(1×1)	diffuse streaked (2×1) pattern
	150°	4×10^{-7}	- 1.1	apparent (2×2)	4×10^{-7}	- 1.2	(1×1)	streaked (2×1) pattern
	300°	4×10^{-7}	- 1.4	disordered	4×10^{-7}	- 1.5	(1×1)	disordered
Cyclohexene	20°	6×10^{-7}	- 1.7	$\begin{vmatrix}2 & 2\\ 4 & -2\end{vmatrix}$	6×10^{-7}	- 1.6	(1×1)	diffuse (1/2 0) features
	150°	6×10^{-7}	- 1.6	apparent (2×2)	6×10^{-7}	- 1.5	(1×1)	streaked (2×1) pattern
Cyclopentane	20°	7×10^{-9}	- .95	(1×1) low background	7×10^{-9}	- .4	(5×1)	low background
	20°	4×10^{-7}	- .7	disordered	4×10^{-7}	- .3	(1×1)	diffuse features at 1/2 order

Table 2

Work Function Changes and Structural Information for Adsorption of Organic Compounds on the Pt(111) and Pt(100)-(5×1) Surfaces

		Pt(111)			Pt(100)-(5×1)			
Adsorbate	Temp °C	Work Function Change		Adsorbate Diffraction Features or Surface Structure	Work Function Change		Substrate Structure after Adsorption	Adsorbate Diffraction Features or Surface Structures
		Press (Torr)	WFC (Volts)		Press (Torr)	WFC (Volts)		
Ethylene	20°	1×10^{-8}	- 1.5	diffuse (1/2 0) features	1×10^{-8}	- 1.2	(1×1)	$(\sqrt{2}\times\sqrt{2})R45°$
	250°	1×10^{-8}	- 1.7	disordered	1×10^{-8}	- 1.5	(1×1)	disordered
Graphitic Overlayer	950°		- 1.1	ringlike diffraction features		- 1.0	(1×1)	ringlike diffraction features
n-Hexane	20°	5×10^{-8}	- 1.1	disordered	5×10^{-8}	- .8	(1×1)	disordered
	20°	5×10^{-8} (5 hrs)	- .9	disordered	5×10^{-8} (5 hrs)	- .6	(1×1)	disordered
	250°	5×10^{-8}	- 1.5	disordered	5×10^{-8}	- 1.2	(1×1)	disordered
Mesitylene	20°	4×10^{-8}	- 1.7	Streaks at 1/3.4 order diffuse (2/3.4 0) features	4×10^{-8}	- 1.7	(5×1)	1/3 order streaks
	20°	4×10^{-7}	- 1.35	disordered	4×10^{-7}	- 1.2	(1×1)	disordered
2-Methyl-naphthalene	20°	6×10^{-8}	- 2.0	very poorly ordered	4×10^{-9}	- 1.6	faint (5×1)	disordered
Naphthalene	20°	9×10^{-9}	- 1.95	apparent (3×1)	9×10^{-9}	- 1.7	(1×1)	disordered
	150°	9×10^{-9}	- 2.0	(6×6)	9×10^{-9}	- 1.65	(1×1)	disordered
Nitrobenzene	20°	9×10^{-9}	- 1.5	diffuse (1/3 0) features (pattern electron beam sensitive)	9×10^{-9}	- 1.4	(1×1)	disordered
Propylene	20°	2×10^{-8}	- 1.3	(2×2) (pattern electron beam sensitive)	2×10^{-8}	- 1.2	(1×1)	1/2 order streaks (pattern electron beam sensitive)
Pyridine	20°	1×10^{-8}	- 2.7	diffuse (1/2 0) features	1×10^{-8}	- 2.4	(1×1)	disordered
	250°	1×10^{-8}	- 1.7	well defined streaks at 1/3, 2/3, 3/3 order	1×10^{-8}	-	(1×1)	$(\sqrt{2}\times\sqrt{2})R45°$
Toluene	20°	1×10^{-9}	- 1.7	streaks at 1/3 order	1×10^{-9}	- 1.55	(5×1)	streaks at 1/3 order
	150°	1×10^{-9}	- 1.65	(4×2)	1×10^{-9}	- 1.5	(1×1)	disordered
m-Xylene	20°	1×10^{-8}	- 1.8	streaks at 1/2.6 order	1×10^{-8}	- 1.65	(5×1)	streaks at 1/3 order

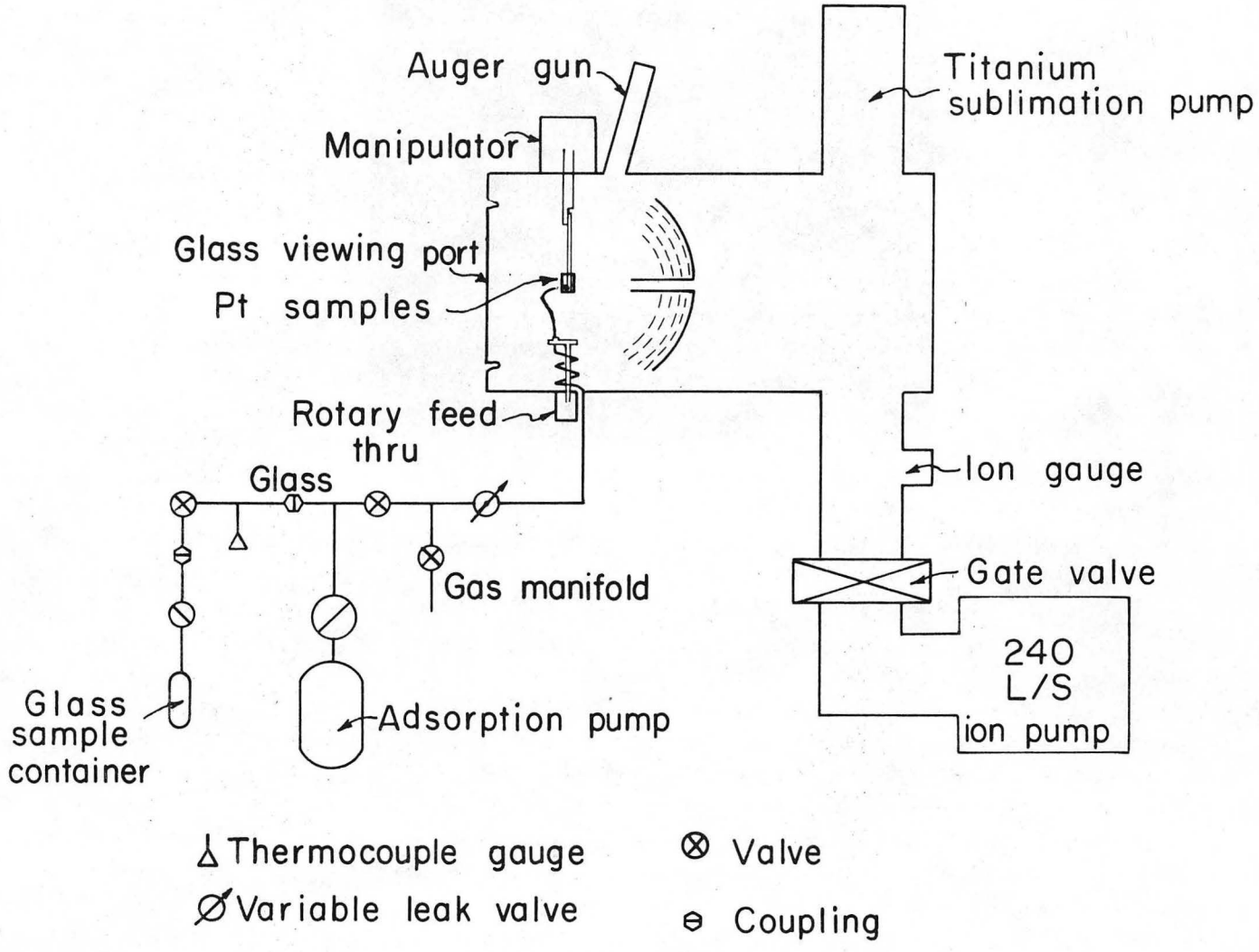
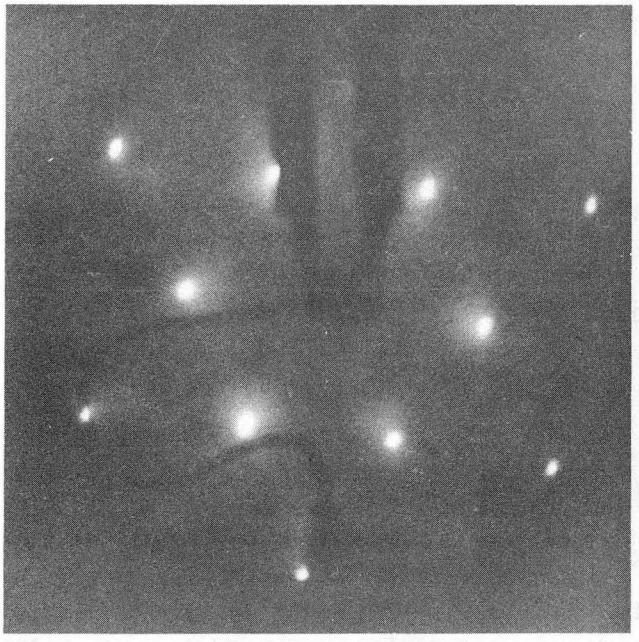
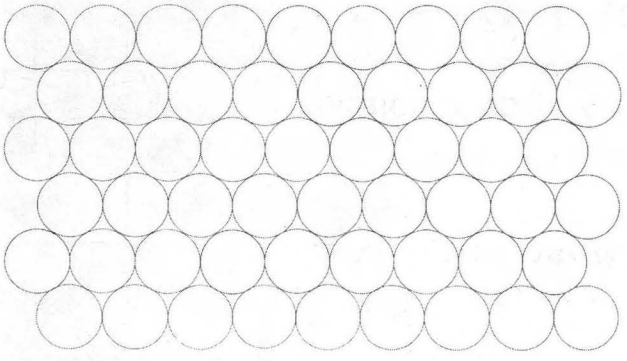


Fig. 1.





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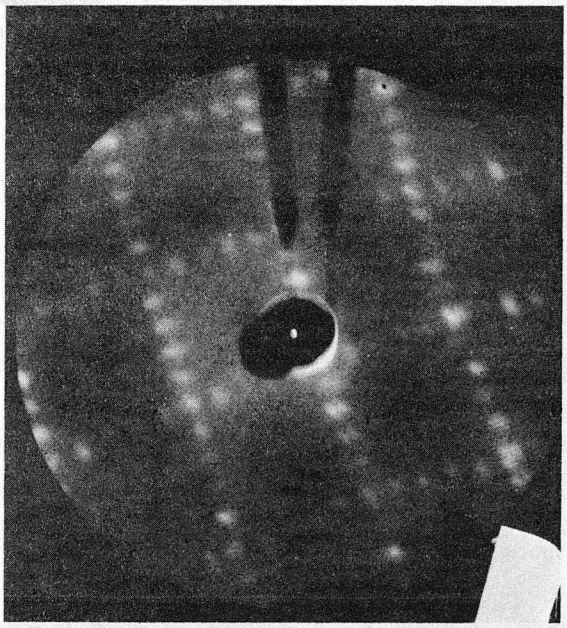

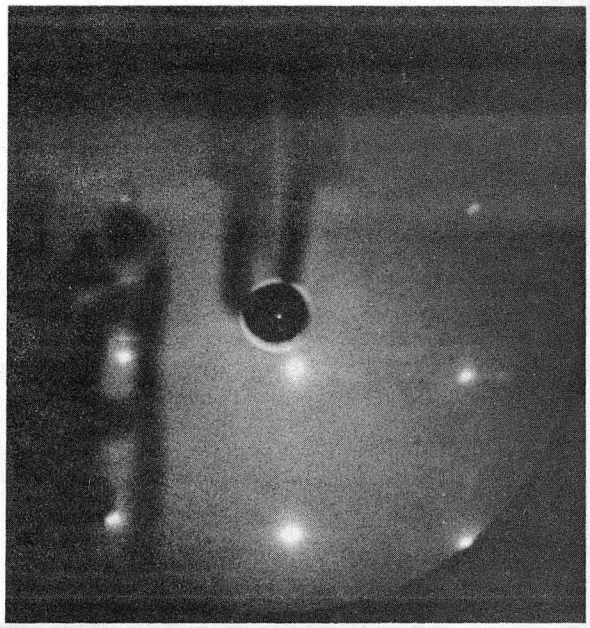

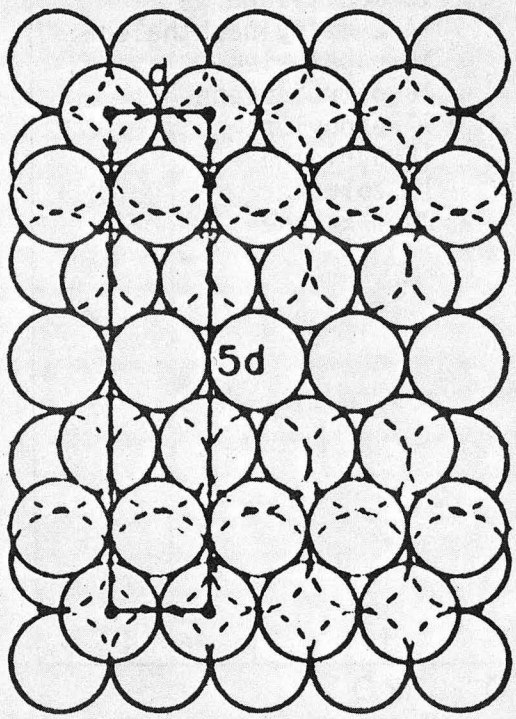

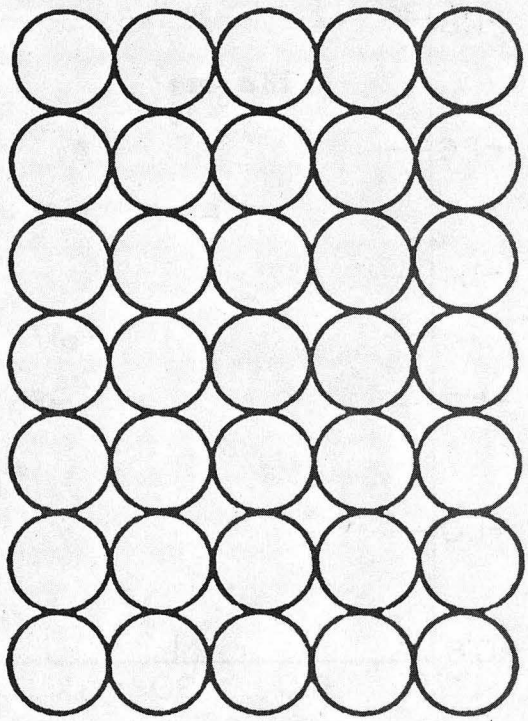

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Fig. 3.

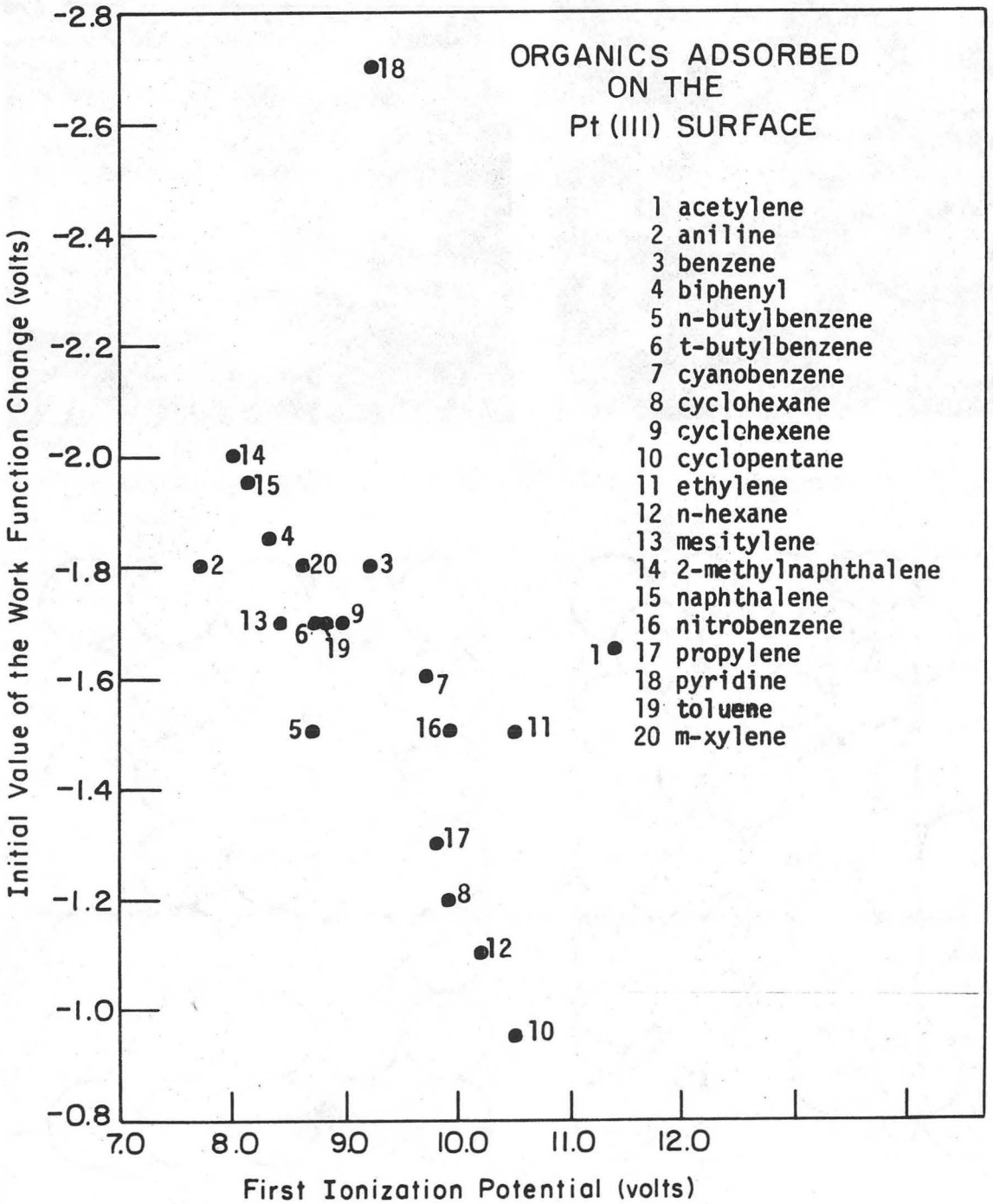

ORGANICS ADSORBED
ON THE
Pt (III) SURFACE
1 acetylene
2 aniline
3 benzene
4 biphenyl
5 n-butylbenzene
6 t-butylbenzene
7 cyanobenzene
8 cyclohexane
9 cyclohexene
10 cyclopentane
11 ethylene
12 n-hexane
13 mesitylene
14 2-methylnaphthalene
15 naphthalene
16 nitrobenzene
17 propylene
18 pyridine
19 toluene
20 m-xylene
Initial Value of the Work Function Change (volts)
-2.8
-2.6
-2.4
-2.2
-2.0
-1.8
-1.6
-1.4
-1.2
-1.0
-0.8
7.0
8.0
9.0
10.0
11.0
12.0
First Ionization Potential (volts)
XBL 737-1528

Fig. 4.

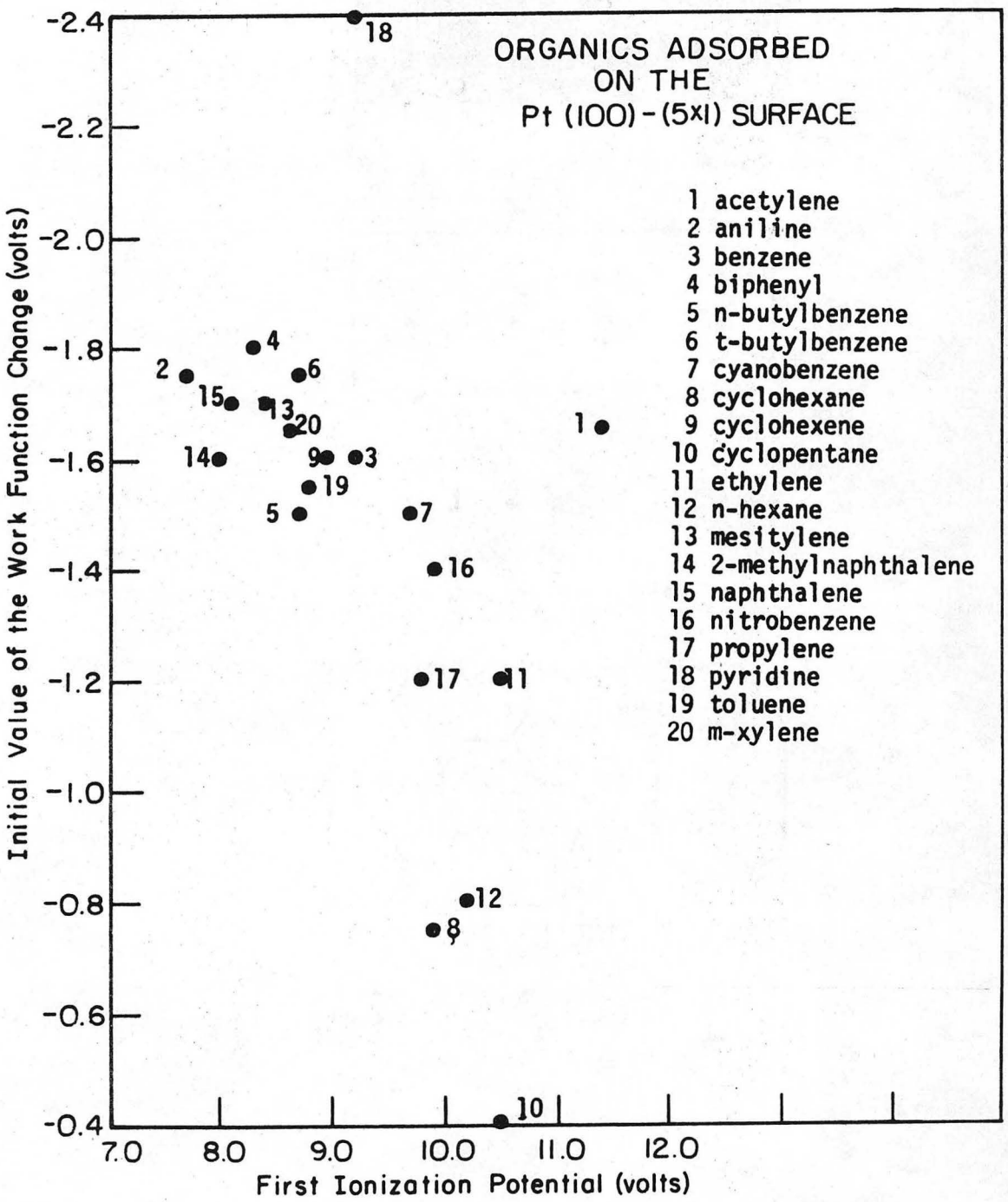
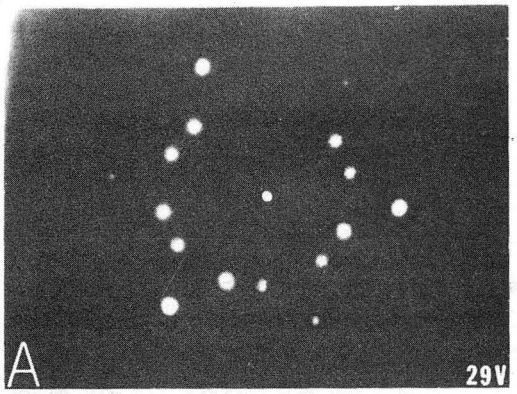
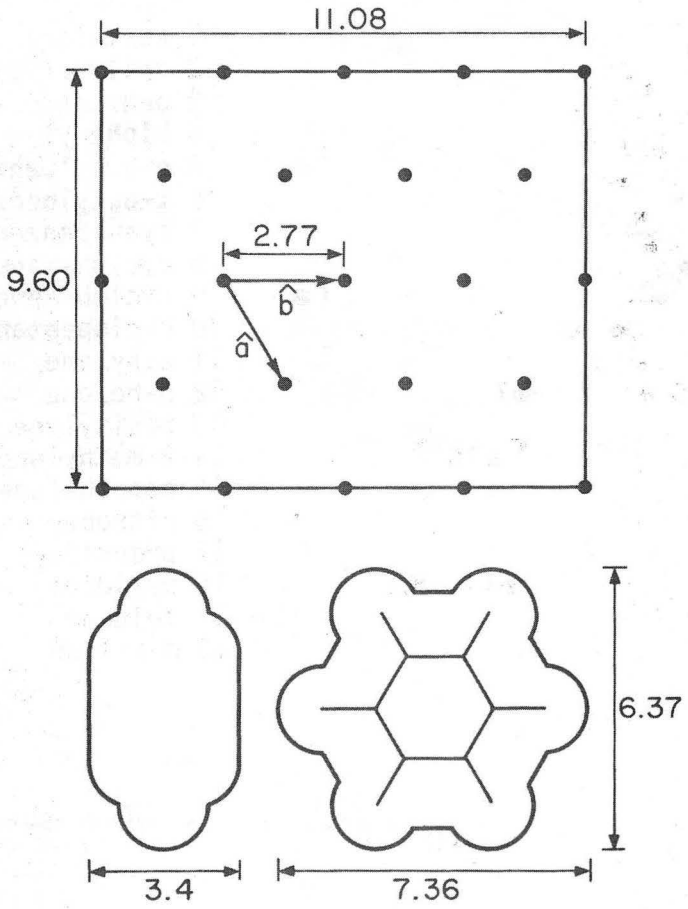


Fig. 5.





$$\text{Pt(111)} - \begin{vmatrix} 4\hat{a} & -2\hat{b} \\ 0 & 4\hat{b} \end{vmatrix} - \text{Benzene}$$

XBB 732-667A

Fig. 6.

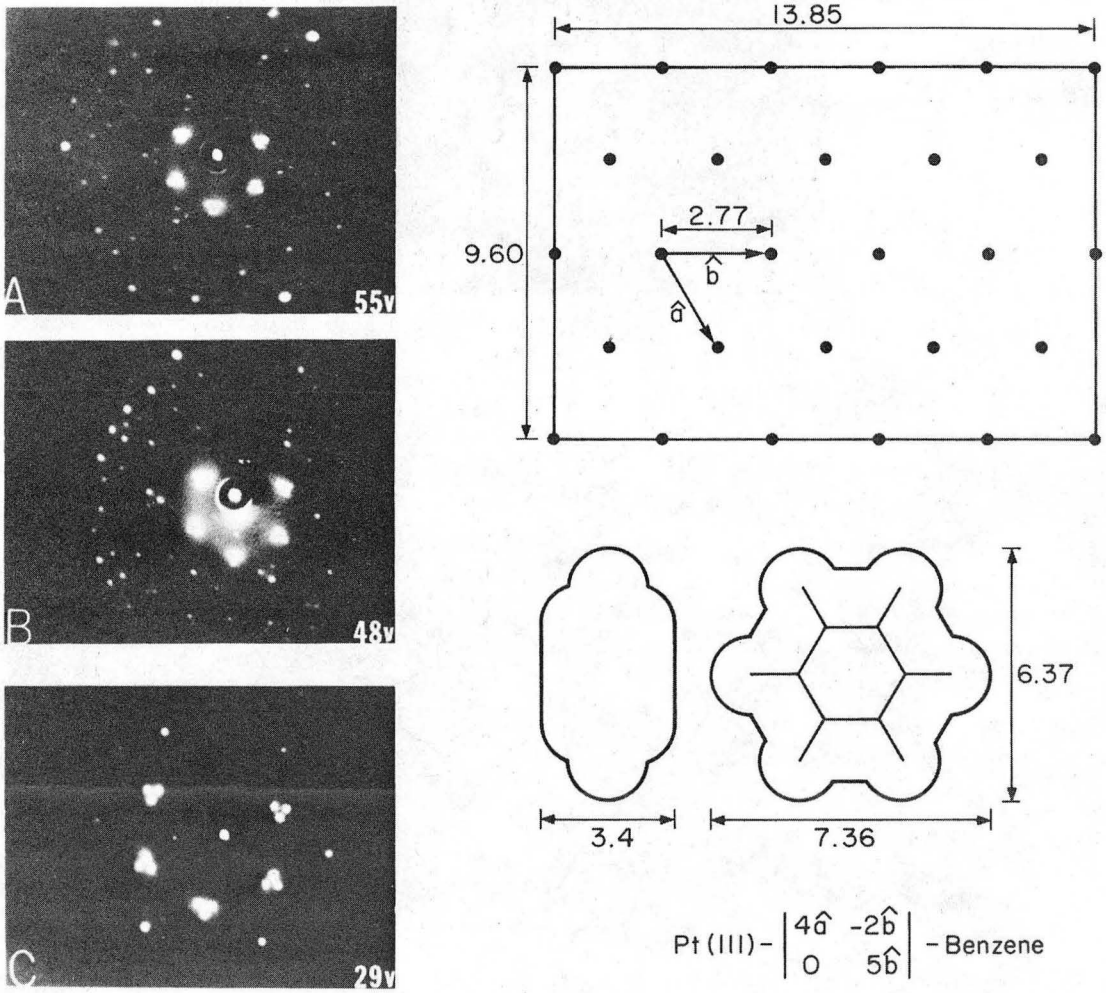
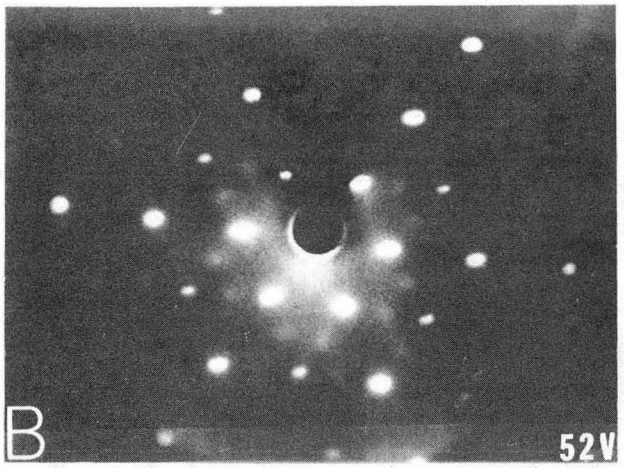
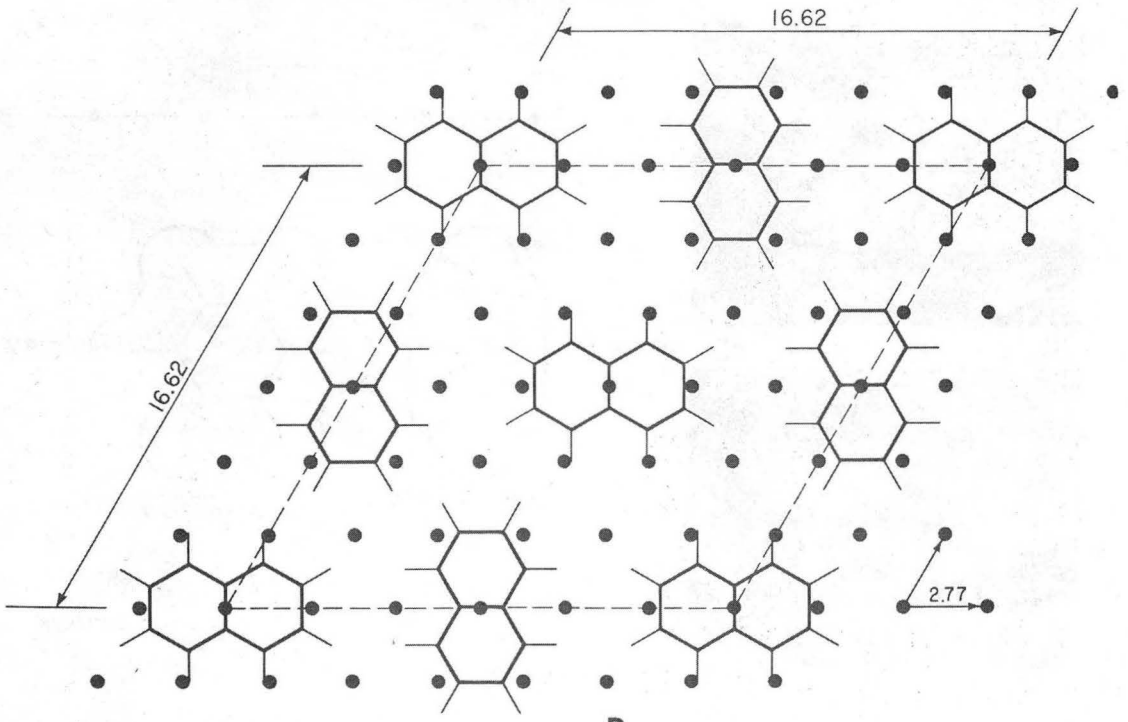


Fig. 7.

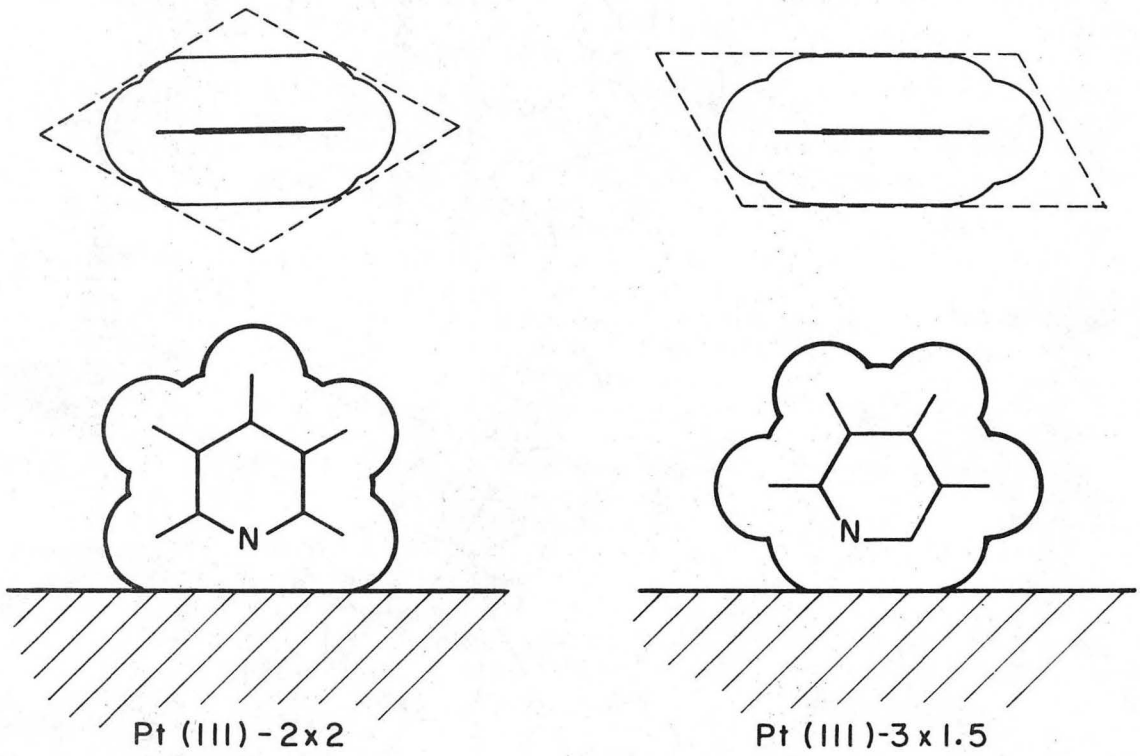




Pt(111) - (6×6) - Naphthalene

XBB 732-0670

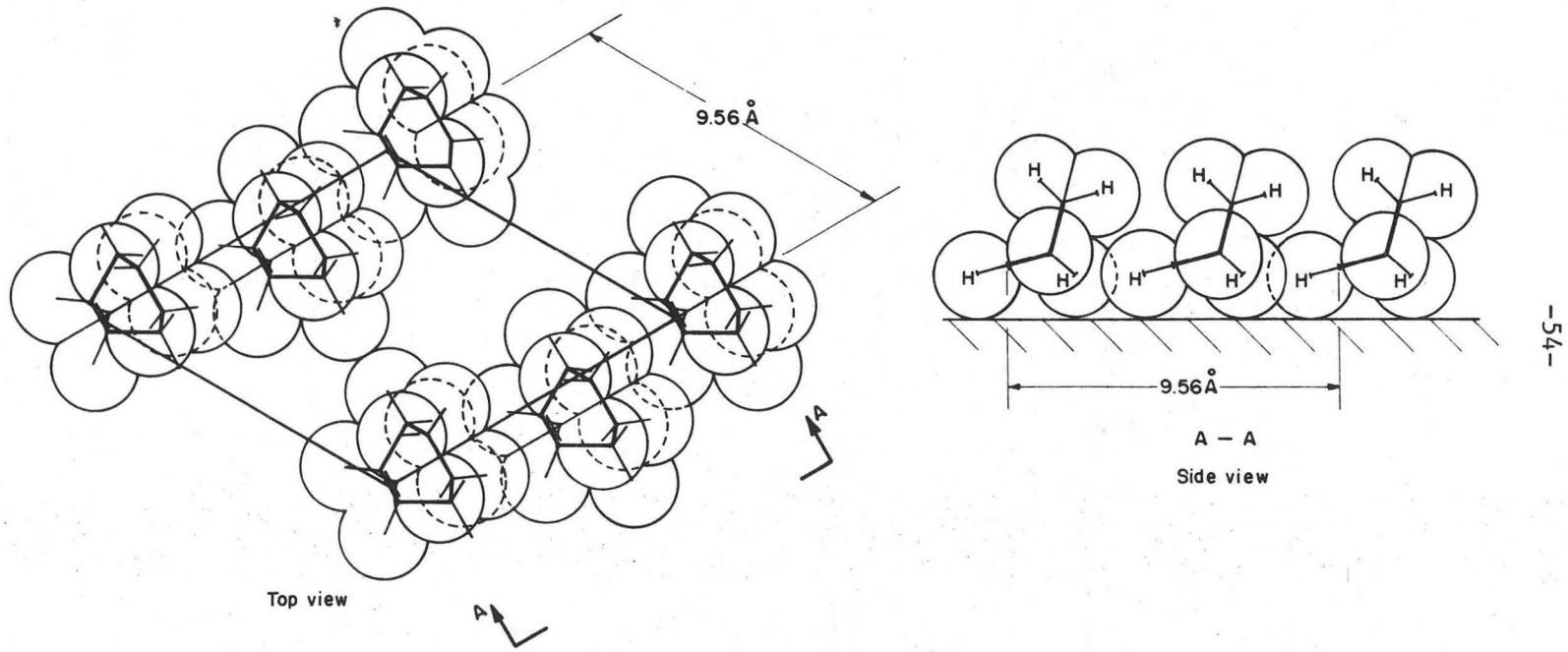
Fig. 8.



Pyridine

XBL737-3431

Fig. 9



Pt (111)-$\begin{vmatrix} 2 & 2 \\ 4 & -2 \end{vmatrix}$ - Cyclohexene

XBL737-1530

Fig. 10.

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