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LEED, A.E.S and THERMAL DESORPTION STUDIES OF CHEMISORBED HYDROGEN and HYDROCARBONS (C2H2, C2H4, C6H12) ON THE (111) and STEPPED [6(lll)x(l00)] IRIDIUM CRYSTAL SURFACES COMPARISON WITH PLATINUM

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LEED, A.E.S AND THERMAL DESORPTION STUDIES OF CHEMISORBED HYDROGEN AND HYDROCARBONS (C₂H₂, C₂H₄, C₆H₆, C₆H₁₂) ON THE (111) AND STEPPED [6(111)X(100)] IRIDIUM CRYSTAL SURFACES
COMPARISON WITH PLATINUM

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ABSTRACT

The adsorption of hydrogen, ethylene, acetylene, cyclohexane and benzene was studied on both the (111) and stepped [6(111)X(100)] crystal surfaces of iridium. The techniques used were low energy electron diffraction, Auger electron spectroscopy, and thermal desorption mass spectrometry. At 30°C, acetylene, ethylene and benzene are adsorbed with a sticking probability near unity. The sticking probability of cyclohexane is less than 0.1 on both surfaces. Heating the (111) surface above 800°C, in the presence of the hydrocarbons, results in the formation of an ordered carbonaceous overlayer with a diffraction pattern corresponding to a (9X9) surface structure. No indication for ordering of the carbonaceous residue was found on the stepped iridium surface in these experimental conditions. The hydrocarbon molecules form only poorly ordered surface structures on both iridium surfaces when the adsorption is carried out at 30°C. Benzene is the only gas that can be desorbed

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from the surfaces in large amounts by heating. Ethylene remains largely on the surface, only a few percent is removed by heating while acetylene and cyclohexane cannot be desorbed at all. When adsorption is carried out at 30°C and the surface is subsequently flashed to high temperature, hydrogen is liberated from the surface. The hydrogen desorption spectra from the iridium surfaces exposed to \( \text{C}_2\text{H}_4, \text{C}_2\text{H}_2, \) or \( \text{C}_6\text{H}_6 \) exhibit two hydrogen desorption peaks, one around 200°C and the second around 350°C. The temperatures where these peaks appear vary slightly with the type of hydrocarbon. The relative intensities of these two peaks depend strongly on the surface used. Arguments are presented that decomposition of the hydrocarbon molecules (C-H bond breaking and possibly also C-C bond breaking) occurs easier on the stepped iridium surface than on the \((111)\) surface. The results are compared with those obtained previously on similar crystal surfaces of platinum. It appears that C-H bond breaking occurs more easily on iridium than on platinum.
Introduction

Hydrocarbons with their diversity of molecular and electronic structures are excellent probes of the nature of chemisorption. Their surface structures and other adsorption characteristics have been studied on both low and high Miller Index surfaces of platinum.\(^1\)\(^-\)\(^4\) It was found that many of the hydrocarbon molecules form well ordered surface structures on the platinum (111) crystal face while ordering was much poorer on the (100) face. Nevertheless work function change and other measurements have indicated that the adsorbed molecules stay largely intact on the low Miller Index platinum surfaces up to 200-250°C surface temperature where thermal cracking commences with an appreciable rate. On stepped, high Miller Index platinum surfaces, however, the hydrocarbon molecules appear to decompose rapidly even at 25°C and the carbonaceous partially dehydrogenated residue that forms is either disordered or ordered depending on the surface structure of platinum and on the type of adsorbate used.

In this paper we report on the chemisorption of selected hydrocarbon molecules and that of hydrogen on two types of iridium surfaces—one with low Miller Index (111) and one with high Miller Index (775), or stepped \([6(111)X(100)]\). These studies permit the determination of the effect of large concentrations of atomic steps on the surface on the chemisorption. Also these results can be directly compared with those on platinum surfaces of the same surface structure to relate variations in bonding characteristics with position in the periodic table. The study of hydrogen chemisorption is important in its own right. In addition hydrogen is also a product of the decomposition of hydrocarbons. Thus \(\text{H}_2\) must always be present during reactive chemisorption of organic molecules.
Experimental

The two iridium samples used in this study were cut from a single crystal of 99.99% nominal purity, purchased from Materials Research Corporation. The main impurities were Ru (100 ppm), W (40 ppm), Pt (30 ppm) and Fe (15 ppm). Other impurities were stated to have concentrations less than 10 ppm. The samples were cut to within 1° of the desired orientation and their surfaces were polished and etched. The samples are discs of about 7mm diameter with a thickness of about 0.8 mm for the Ir(S)-[6(lll)X(100)] sample and 0.4 mm for the Ir (111) sample.

The two samples were installed in two separate LEED-Auger ultra-high vacuum apparatus. Both systems contained four-grid electron optics and were equipped with quadrupole mass spectrometers and ion bombardment attachments. Typical ambient pressures for the systems are $1 \times 10^{-9}$ Torr (Mainly $H_2$, $H_2O$, CO, Ar and $CH_4$).

The main surface impurity was found to be carbon that could be removed by heating to 500-600° in an oxygen ambient of $5 \times 10^{-7}$ Torr for several minutes followed by flashing to 1200°C in order to remove oxygen from the surface. The surfaces produced in this way were clean within the limits detectable by Auger Electron Spectroscopy and showed the characteristic Low Energy Electron Diffraction patterns: (1 X 1) for the Ir (111) surface and the same pattern for the Ir(S)-[6(lll)X(100)] surface but with the doublets features characteristic for an ordered stepped [6(lll)X(100)] surface.

A capillary tube was used to introduce the hydrocarbons directly onto the crystal surface from a distance of about 1 cm. In this way the effective pressure of $C_2H_2$ and $C_2H_4$ was about three times the pressure
as recorded by the ionization gauge. For C₆H₆ and C₆H₁₂ the correction factor was about 3.5

The temperature of the samples was measured by means of thermocouples spotwelded near the edge of the crystals. Measurements made with infrared and optical pyrometers indicated that the temperature gradient across the surface of the samples was not more than about 5%, also when the temperature was rapidly increased during flash desorption experiments. In flash desorption experiments the crystal was heated and the intensities of the relevant masses were recorded versus the thermocouple voltages. The heating rate used was 20-25 degrees/sec in all thermal desorption experiments.

Results

First we shall describe the results of hydrogen chemisorption studies, then we shall describe the chemisorption characteristics of each hydrocarbon molecule (ethylene, acetylene, benzene and cyclohexane) on the Ir (111) and the stepped Ir [6(111) X (100)] surfaces.

1) Adsorption of hydrogen

A Ir(111) face

Exposure of the clean crystal to 10⁻⁶ Torr hydrogen at room temperature does not alter the LEED pattern. Heating the crystal up to 1000°C in this hydrogen atmosphere does not bring about any detectable change in the pattern.

Thermal desorption of hydrogen, shown in figure 1A, indicated that the amount of hydrogen atoms adsorbed on this face at a temperature of
40°C and a hydrogen equilibrium pressure of about $2 \times 10^{-9}$ Torr is less than 10% of the number of CO molecules which can be adsorbed on this surface at room temperature and a CO pressure of $2 \times 10^{-9}$ Torr. The peak maximum of the desorption peak shifts to a lower temperature when the substrate temperature is lowered (see Figure 1A), from 140°C upon adsorption at 40°C to 120°C upon adsorption at 0°C. The amount of hydrogen adsorbed on the surface at $2 \times 10^{-9}$ Torr H$_2$ increases significantly when the temperature of the iridium crystal is lowered. This observation indicates that hydrogen adsorbed under these conditions is in equilibrium with the hydrogen pressure. A lower temperature or a higher hydrogen pressure is required for obtaining a higher coverage.

b. Ir(S)-[6(111) X (100)]face

Just as on the (111) surface exposure of the crystal to hydrogen ($10^{-6}$ Torr) does not bring about any detectable change in the LEED pattern up to exposures of several hundred Langmuirs, neither at room temperature nor at elevated temperatures up to 1000°C.

The thermal desorption spectrum is shown in Figure 1B. The temperature where the maximum in the desorption peak appears is nearly equal to that on Ir (111). The shape of the desorption peak is, however, different, the tail of the peak at higher temperature is much more extended on the stepped surface than on the (111) face. This suggests that part of the hydrogen is bound more strongly than on (111). The total amount of hydrogen adsorbed at 40°C at a pressure smaller than $5 \times 10^{-9}$ Torr is 10 to 20% the maximum amount of CO which can be adsorbed under these circumstances. This amount increases when the temperature of the crystal is lowered.
2. Adsorption of ethylene

a. The Ir (111) surface.

Room temperature exposure of the clean surface at a pressure of $5 \times 10^{-8}$ Torr $\text{C}_2\text{H}_4$ causes the appearance of weak extra diffraction features. They consist of doublets of very diffuse spots near the $(1/3, 1/3)$ positions. The surface structure is thus similar to a poorly ordered $(\sqrt{3} \times \sqrt{3}) R 30^\circ$ structure.

The initial sticking probability at room temperature is close to 1 as indicated by the increase in the carbon $272 \text{eV}$ Auger peak as a function of exposure, shown in Figure 2.

Flash desorption spectra are shown in Figure 3. The main desorption peak is due to hydrogen. Also a small amount of gas with masses 28, 27 and 26 were detected, desorbing around $125^\circ\text{C}$. The desorption curves for masses 26 and 27 are identical, indicating that the desorbing species is merely ethylene and not acetylene. Most of the hydrocarbon remains on the surface as indicated by the carbon Auger peak height. Thus, it appears that much of the adsorbed ethylene is dissociated to fragments that are held tenaciously and cannot be removed by flashing. The total amount of desorbing $\text{C}_2\text{H}_4$ is not more than a few percent of the amount of adsorbing hydrogen. Two hydrogen peaks are resolved, one around $210^\circ\text{C}$ and the second around $360^\circ\text{C}$. The amount of desorbing hydrogen around $360^\circ\text{C}$ is much smaller than that desorbing around $210^\circ\text{C}$.

After heating the crystal above $360^\circ\text{C}$ in vacuum additional $\text{C}_2\text{H}_4$ can be adsorbed on the surface as indicated by the increase in the carbon Auger peak and by subsequent flash desorption. The hydrogen desorption spectra are equal to those shown in Figure 3, but the total amount of
desorbing hydrogen is smaller than after the first heating. This heating—adsorption process can be repeated several times before the surface is completely saturated with a carbonaceous residue.

The additional diffraction spots observed when a clean Ir (111) surface is exposed to C₂H₄ at room temperature disappear when the crystal is heated to about 150°C. No indication for ordering is found then. Heating at a temperature of 200°C, or better directly exposing the crystal at 200°C to C₂H₄, causes the appearance of very faint and diffuse 1/2-order spots indicating the formation of a poorly ordered (2 X 2) surface structure. This structure is related to the 2nd hydrogen desorption peak around 360°C. Heating the crystal above 360°C causes the disappearance of the (2 X 2) structure and results in a further disordering of the adsorbed layer as indicated by the very high uniform background intensity. Heating the crystal covered with the carbonaceous residue to 750-800°C causes a drastic change in the LEED pattern. A well ordered surface structure is formed as indicated by the LEED pattern which is shown in figure 4. This process starts around 750°C but a temperature of 800°C is required for complete ordering. The new structure corresponds roughly to a (9 X 9) structure but not all of the fractional order spots could be observed. The structure is stable up to 1500°C.

b. The Ir (S)-[6(111) X 100] surface

Exposure of the Ir(S)-[6 (111) X (100)] clean surface to C₂H₄ at a pressure of 5 X 10⁻⁸ Torr causes the appearance of weak additional spots corresponding to a (2 X 2) structure. The background of the diffraction pattern is high indicating that much of the adsorbed layer is disordered. The increase of the carbon Auger peak versus exposure is similar to that
on (111) which was shown in Figure 2.

Thermal desorption mass spectrometry reveals desorption of hydrogen and ethylene. Ethylene is desorbed around 150°C. The amount of desorbing ethylene is a few percent of the amount of desorbing hydrogen, just as on Ir (111). The main desorption product is hydrogen which desorption spectrum is shown in figure 5. Two desorption peaks are detected just as on Ir (111) but their relative intensities appear to be different from that observed on Ir (111). The relative contribution of desorbing hydrogen appearing in the 2nd peak is more important on the stepped surface than on the (111) plane. When hydrogen is desorbed from the surface the (2 X 2) structure disappears. Additional C₂H₄ can be adsorbed after desorption of hydrogen as appears from the intensity of the carbon Auger peak. When this second exposure is carried out at room temperature the (2 X 2) structure is regenerated. Heating results again in liberation of hydrogen. Two peaks are again resolved but the relative magnitudes of the peaks have been changed (See Figure 5b). The size of the low temperature peak is relatively larger in the second run. The hydrogen desorption spectrum exhibits a more Ir (111)—like behaviour. The total amount of desorbing hydrogen is smaller than the first time. This flash desorption-adsorption process can be repeated several times. The carbon Auger peak increases during this process, and so does the background intensity in the LEED pattern. The amount of desorbing hydrogen decreases, successively, both in the first and the second peak and both hydrogen desorption peaks shift to a somewhat higher temperature, especially the high temperature peak. The contribution of desorbing hydrogen appearing in the high temperature peak to the total amount of desorbing hydrogen decreases.
We shall now describe the LEED observations that have been obtained by increasing the temperature stepwise in a \( \text{C}_2\text{H}_4 \) ambient of \( 5 \times 10^{-7} \) Torr. The \((2 \times 2)\) structure disappears at a temperature where hydrogen is liberated from the surface. No diffraction spots in addition to those due to the metal have been observed after the disappearance of the \((2 \times 2)\) structure. Heating results in a higher background intensity which is caused by the increasing amount of disordered carbon accumulating on the surface as found by A.E.S. No ordering of the carbonaceous residue was found at high temperature, contrary to that found on \( \text{Ir}(111) \). A pattern characteristic of an \( \text{Ir}(S)-[6 \text{(111)} \times \text{(100)}] \) surface heated to \( 800^\circ\text{C} \) in the presence of \( \text{C}_2\text{H}_4 \) is shown in Figure 6b.

3. Adsorption of \( \text{C}_2\text{H}_2 \)

LEED observations during exposure at room temperature and during increasing crystal temperature are similar to those described for \( \text{C}_2\text{H}_4 \) for both iridium surfaces. The increase of the carbon Auger peak as a function of exposure is shown in Figure 7 for two different adsorption temperatures viz. 30°C and 200°C. The plots shown were measured for the \( \text{Ir}(111) \) surface but the plots for the \( \text{Ir}(S)-[6 \text{(111)} \times \text{(100)}] \) are nearly identical. Figure 7 is almost the same as the corresponding figure for \( \text{C}_2\text{H}_4 \) adsorption (Figure 2), indicating that the sticking probabilities of both gases are equally high, near unity. The only significant difference between \( \text{C}_2\text{H}_2 \) and \( \text{C}_2\text{H}_4 \) adsorption can be found in the desorption spectra which are shown in Figure 3 for the \( \text{Ir}(111) \) surface and in Figure 8 for the \( \text{Ir}(S)-[6\text{(111)} \times \text{(100)}] \) surface. While a small part of adsorbed \( \text{C}_2\text{H}_4 \) can be removed from the surface by heating, no indication
was found for the desorption of any \( \text{C}_2\text{H}_2 \) or other hydrocarbon. Hydrogen is the only gas that can be desorbed. The total amount of desorbing hydrogen after \( \text{C}_2\text{H}_4 \) adsorption is almost twice that found after adsorption of \( \text{C}_2\text{H}_2 \).

4. Adsorption of benzene

a. The Ir (111) surface

Exposure of the clean surface at room temperature to \( \text{C}_6\text{H}_6 \) yields extra diffraction features as shown in Figure 9. The extra features are faint and diffuse but yet better defined than those after adsorption of \( \text{C}_2\text{H}_4 \) and \( \text{C}_2\text{H}_2 \) at room temperature due to a lower background intensity. The surface structure corresponds to a poorly ordered \((3 \times 3)\) structure. When the surface is heated to about 200°C in vacuum or in the presence of \( 5 \times 10^{-8} \) Torr \( \text{C}_6\text{H}_6 \) the additional features disappear. Heating the (111) surface in the presence of \( 5 \times 10^{-8} \) Torr \( \text{C}_6\text{H}_6 \) to \( \sim 800°C \) causes the same complex diffraction pattern characteristic of a \((9 \times 9)\) surface structure as was observed after heating the crystal to this temperature in the presence of \( \text{C}_2\text{H}_4 \) or \( \text{C}_2\text{H}_2 \). (Figure 4)

In Figure 10, the relative increase of the carbon Auger peak is shown as a function of exposure with the crystal at room temperature. Comparable results obtained for the crystal at 200°C have been included in this figure. Comparing Figure 10 with the corresponding Figures for \( \text{C}_2\text{H}_4 \) and \( \text{C}_2\text{H}_2 \) adsorption (Figures 2 and 7) it may be concluded that the initial sticking probabilities of the three gases are roughly the same, near unity.

Thermal desorption spectra reveal that the main desorption products from the (111) surface which has been exposed previously to \( \text{C}_6\text{H}_6 \) at room temperature are benzene and hydrogen. The desorption spectra are shown in Figure 11. The desorption spectrum for benzene consists of a single
peak around 150°C. The spectrum for hydrogen consists of two peaks, one peak around 200°C and a second smaller peak around 380°C. The amount of desorbing benzene is of the same order of magnitude as the amount of desorbing hydrogen.

b. The Ir(S)-[6(111) X (100)] surface.

Adsorption of C₆H₆ at room temperature on the stepped surface results in increased intensity of the background but no ordered structures were found. The background intensity increases further when the crystal is heated in the presence of C₆H₆. The increase in the carbon Auger peak versus exposure is identical to that found on Ir(111).

Heating results in desorption of benzene and of hydrogen. The desorption spectra are shown in Figure 12. Two desorption peaks of hydrogen have been detected just as on Ir(111). The high temperature peak is relatively more important than for the (111) plane.

5. Adsorption of cyclohexane

a. The Ir(111) surface.

Adsorption of cyclohexane at room temperature does not yield diffraction spots in addition to those due to the metal substrate. Subsequent heating in the presence of 5 X 10⁻⁸ Torr C₆H₁₂ to 700°C does not change the LEED pattern either except for an increasing background intensity. When the surface is heated to higher temperatures (about 800°C and higher) a new complex diffraction pattern appears which is identical to the pattern shown in Figure 4 corresponding to the (9 X 9) surface structure.

The increase in the carbon Auger peak versus exposure which is shown in Figure 10 for two different crystal temperatures (30°C and 200°C)
reveals that the sticking probability of \( \text{C}_6\text{H}_{12} \) on the surface is much lower than that of \( \text{C}_2\text{H}_2 \), \( \text{C}_2\text{H}_4 \) and \( \text{C}_6\text{H}_6 \). Also the maximum amount of carbon on the surface after exposure at 30°C is much lower than after exposure to \( \text{C}_2\text{H}_4 \), \( \text{C}_2\text{H}_2 \) or \( \text{C}_6\text{H}_6 \). This amount is higher when the adsorption is carried out with the crystal at 200°C, as is also shown in Figure 10.

Heating the crystal which has been exposed to \( \text{C}_6\text{H}_{12} \) results in the production of some hydrogen. No indication was found for any desorption of hydrocarbon. The hydrogen desorption spectrum is shown in Figure 11. Comparable desorption for hydrogen from a surface exposed to \( \text{C}_6\text{H}_6 \) have been included in this Figure. The sensitivity of the mass spectrometer was the same in these experiments. Clearly, the amount of desorbing hydrogen is much lower from the surface previously exposed to \( \text{C}_6\text{H}_{12} \) than from the same surface which was exposed to \( \text{C}_6\text{H}_6 \) under exactly identical experimental conditions. The desorption spectrum for hydrogen from the surface previously exposed to \( \text{C}_6\text{H}_{12} \) at room temperature reveals three maxima: one around 130°C coinciding with the desorption peak of hydrogen from a \((111)\) surface exposed to pure hydrogen, a second one around 200°C and a third peak around 310°C. Heating the crystal previously exposed to \( \text{C}_6\text{H}_{12} \) at 200°C results in a single hydrogen desorption peak around 350°C.

b. The Ir(S)-[\(6(111)\times(100)\)] surface.

Admission of \( \text{C}_6\text{H}_{12} \) with the crystal at 30°C causes the appearance of faint and diffuse extra spots corresponding to a \((2 \times 2)\) surface structure. These spots disappear upon heating at 200°C. The main effect of heating in the presence of \( \text{C}_6\text{H}_{12} \) \((5-50 \times 10^{-8} \text{ Torr})\) on the LEED pattern is an increase of the background intensity.

Results obtained by means of AES are nearly similar to those described
for the Ir(lll) surface. The initial sticking probability is about 1/10 of that of benzene. The maximum amount of carbon on the surface after exposure at room temperature is less than 1/3 of the amount of carbon after adsorption of C₂H₄, C₂H₂ and C₆H₆ under identical experimental condition. The carbon Auger peak increases when the crystal is heated in the presence of C₆H₁₂.

The only product which is liberated from the surface by heating, is hydrogen. Its desorption spectrum is shown in Figure 13.

Discussion

Exposure of clean metal surfaces to acetylene, ethylene, benzene and cyclohexane can lead to the formation of a variety of adsorbates. The molecules can be adsorbed by means of breaking C-H bonds resulting in the production of adsorbed hydrogen and partly dehydrogenated hydrocarbons. The unsaturated and aromatic hydrocarbons can also be adsorbed intact without breaking of C-H bonds. Dissociatively adsorbed species can react with undissociated hydrocarbons leading to selfhydrogenation reactions. Adsorption of C₂H₄, e.g., may thus also produce partially hydrogenated species on the surface. Breaking of the C-C bonds may also occur, especially at higher temperature. All these different processes depend strongly on the type of hydrocarbon, the type of metal and on the experimental conditions used, such as the temperature. Recently it has been found in this laboratory that the surface structure may have a large additional influence on the extent of dehydrogenation and C-C bond breaking of the hydrocarbon, and on the ordering of the adsorbed species on Pt surfaces.¹⁻⁴) In brief, the unsaturated
hydrocarbons adsorbed on Pt(111) and (100) planes at room temperature and at low pressures are largely bound undissociatively, and they form an ordered layer at this temperature. On a Pt(S)-[6 (111) X (100)] surface dehydrogenation (C-H bond breaking) occurs readily even at low temperature. Ordered carbonaceous layers are produced at higher temperature (∼800°C). On the Pt(S)-[7(111) X (310)]* surface or (976) face, a surface with a high concentration of kinks in each step, the rate of hydrocarbon decomposition (C-C bond breaking) appears to be much higher than on the other faces. In this discussion we shall compare the behaviour of iridium in hydrocarbon adsorption with that of platinum.

Table I and II list the surface structures of all of the molecules studied on the two iridium surfaces and compares them with the surface structure found on platinum crystal faces. The chemisorption characteristics are markedly different on the Ir(111) and stepped Ir-[6(111) X (100)] surface for each of the molecules that were studied. Hydrogen while not producing ordered surface structures with unit cells different from the substrate unit cell show different flash desorption characteristics on the two iridium surfaces. The high temperature tail of the desorption peak that is detectable on the stepped surface may be associated with an adsorption on sites of higher binding energy than that present on the (111) crystal face. The results of hydrogen adsorption studies on palladium stepped surface would certainly support this contention.6) The temperature where hydrogen was found to be desorbed (around 140°C) is in line with literature data of hydrogen desorption from a polycrystalline iridium filament7) and from iridium tips8,9).

The hydrocarbon molecules form only very poorly ordered surface

*For a description of this notation see e.g. Ref. 3.
structures on either the (111) or stepped Iridium surfaces at low temperatures. C\textsubscript{2}H\textsubscript{4} and C\textsubscript{2}H\textsubscript{2} form surface structures that are somewhat better ordered on the stepped than on the (111) metal surface. C\textsubscript{2}H\textsubscript{2} forms a well-ordered surface structure on platinum (111) and yields the same surface structure for adsorbed C\textsubscript{2}H\textsubscript{4} that has been proven to be also due to C\textsubscript{2}H\textsubscript{2} that forms after the dehydrogenation. The lack of ordering on iridium indicates either a lack of mobility of hydrocarbon molecules necessary for ordering at these temperatures or a chemical reaction, i.e., decomposition. The observation that C\textsubscript{2}H\textsubscript{2}, C\textsubscript{2}H\textsubscript{4} and C\textsubscript{6}H\textsubscript{12} all yield the same diffraction pattern on the stepped surface regardless of molecular size would suggest that decomposition occurs even at 30\textdegree{}C on stepped iridium surfaces. The degree of decomposition is certainly different on the two crystal faces, at room temperature being higher on the stepped surface than on the (111) surface, as the differences in surface structural behaviour and flash desorption indicate. The weak (2 X 2) structure which has been observed on the Ir (S)-[6(111) X (100)] surface after adsorption of C\textsubscript{2}H\textsubscript{2} and C\textsubscript{2}H\textsubscript{4} at 30\textdegree{}C is not formed on Ir(111) surfaces until about 200\textdegree{}C. This could be indicative of a higher degree of dehydrogenation of 30\textdegree{}C on the stepped surface than on the Ir(111) surface. The (2 X 2) surface structure may be attributed to partly dehydrogenated hydrocarbon molecules on the surface. The hydrogen desorption spectra from iridium previously exposed to hydrocarbons at 30\textdegree{}C exhibit two peaks on both surfaces. The temperature where these peaks occur vary slightly with the type of hydrocarbon. The slightly different temperatures of the corresponding hydrogen desorption peaks on the two surfaces could be
caused partly by errors in the temperature calibrations. (The studies on the two crystals were carried out in two different vacuum systems). It is, however, worth mentioning that the contribution of desorbing hydrogen appearing in the high temperature peak appears to be relatively more important on the stepped surface than on the (111) surface. When, adsorption is carried out on the stepped surface partly covered with a carbonaceous residue however, (see Figures 5b, 8b) the hydrogen desorption spectrum resembles the spectrum found on (111). This could indicate that the steps do not contribute any more to the desorption of hydrogen, they are apparently already saturated with the carbonaceous residue.

The difference between Ir(111) and Pt(111) surfaces in their ability for C-H bond breaking, as indicated by flash desorption spectra, is striking. On Pt(111) C₂H₄, C₂H₂ and C₆H₆ can be desorbed, in large part, by heating. On Ir(111), however, C₆H₆ is the only gas that can be desorbed in large amounts, by heating. C₂H₄ remains largely on the surface, only a few percent is removed by heating, while C₂H₂ cannot be desorbed at all.

The differences between platinum and iridium surfaces after heating to high temperature (above 800°C) following hydrocarbon adsorption are marked. Ir(111) yields an ordered (9 X 9) coincidence carbon surface structure. This structure can be attributed to a hexagonal overlayer of carbon similar to the structure of the basal plane of graphite deposited on the (111) surface. A similar structure was found on a Pt(S)-[6(111) X (100)] surface when this surface was heated to 800°C in the presence of various hydrocarbons. Using a Pt(111) surface under similar experimental conditions would, however, produce a ringlike diffraction pattern characteristic of a graphitic overlayer with rotationally disordered domains. This
observation can be rationalized by again considering stronger metal-carbon interaction on Ir that imposes the periodicity on the carbon atoms in the overlayer on the Ir(111) crystal face while the structure of the graphitic overlayer on Pt(111) face is independent of the substrate periodicity and rotational symmetry.

Ordering of the dehydrogenated carbonaceous residue on the stepped iridium surface is absent when the surface is heated to above 800°C. Atomic steps of (100) orientation appear to prevent the formation of ordered domains, large enough to be detectable by LEED. The reasons for this are not clear since coincidence lattices due to carbon residue have been observed on stepped platinum surfaces of the same atomic structure. Perhaps the rate of carbon-carbon bond breaking on account of the steps is too rapid to allow nucleation and growth of the ordered overlayer. The surface resembles in this respect\(^3\) the Pt(S)-[7(111) X (310)] surface, exhibiting a large concentration of kinks in each step, where ordering of the carbon residue is also absent. On the Ir(111) face slower dehydrogenation allows ordering as observed.

It is tempting to list the stepped and (111) iridium and platinum surfaces according to their ability to break C-H and C-C bonds as

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

The surfaces at the beginning and at the end of this series are not likely to be versatile catalysts in reactions where C-H and C-C bond dissociations are necessary. The stepped iridium surface would decompose the reactants too rapidly and the residue that forms would black the surface rather well to further chemical reactions. The platinum (111) surface interacts with the reactants too mildly and would not efficiently break the chemical bonds.
The surfaces in the middle of the series would likely be very versatile catalysts. This contention will be subjected to experimental scrutiny in the near future.

The present and our previous study of adsorption on Ir(111) and Ir(S)-[6(111) × (100)] surfaces reveal a significant influence of the surface structure on the bonding of the adsorbed molecules: heat of adsorption, ordering of the adsorbed species and degree of decomposition of the molecules are in many cases markedly different on the two iridium surfaces. Similar observations were made on platinum. It is, however, striking that iridium and platinum differ significantly in their behaviour upon adsorption of hydrocarbons: Ordering of the adsorbed species at low temperatures is much poorer on iridium than on platinum, C-H and possibly also C-C bond breaking appears to occur more easily on iridium than on platinum. A marked difference between iridium and platinum has also been reported in the weak adsorption of nitrogen; not only the heat of adsorption and the dipole moment are different on these metals but also the anisotropy of heat of adsorption and dipole moment on the various crystal faces. The noble metals iridium and platinum are neighbors in the periodic system of elements. Arguments based on surface geometry cannot be the cause of the differences in adsorption properties since both metals have the face centered cubic crystal structure with lattice constants varying only by 2%. Hence, it appears that small differences in electronic structure of Group VIII metals can result in significant variation of chemical properties. One fewer d-electron for iridium permits greater electron donation from the hydrocarbon adsorbate to the metal atom thereby weakening the C-C or C-H bonds. When seen in this
light it is hoped that a systematic investigation of adsorption of various gases on well-defined single crystal surfaces on the different Group VIII metals will help to understand the basic principles of chemisorption and catalysis.
Acknowledgment

This work was supported by the U.S. Energy Research and Development Administration and the office of Naval Research (N00014-75-C-0890).
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### TABLE II
SURFACE STRUCTURES FORMED ON STEPPED SURFACES OF IRIDIUM AND PLATINUM

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<th></th>
<th>Ir(S)-[6(111) X (100)]</th>
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| 850°C | Disorder (this paper)  | \(
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\end{array} \) (ref. 3) | C ring (ref. 3, 11) |
| \(C_2H_2\) | Poorly ordered(2X2) (this paper) | --                     | --                     |
| 200°C | Disorder (this paper)  | --                     | --                     |
| 350°C | Disorder (this paper)  | --                     | --                     |
| 850°C | Disorder (this paper)  | C ring                 | (ref. 11)              |
| \(C_6H_6\) | Disorder (this paper)  | 3(1d)-C (ref. 3)       | complex (ref. 11)      |
| 200°C | Disorder (this paper)  | --                     | --                     |
| 350°C | Disorder (this paper)  | disorder (ref. 11)     | disorder (ref. 11)     |
| 850°C | Disorder (this paper)  | (9X9) (ref. 3)         | C ring                 (ref. 11) |
| \(C_6H_{12}\) | Poorly ordered(2X2) (this paper) | 2(1d)-C (ref. 3)       | disorder (ref. 11)     |
| 200°C | Disorder (this paper)  | --                     | disorder (ref. 11)     |
| 350°C | Disorder (this paper)  | disorder (ref. 3)      | disorder (ref. 11)     |
| 850°C | Disorder (this paper)  | complex (ref. 3)       | C ring                 (ref. 11) |
REFERENCES


Legends to the Figures

Figure 1. Hydrogen desorption from Ir(111) (Figure A) and Ir(S)-[6(111) X (100)] (Figure B) surfaces after exposure of the crystals being at a temperature of 40°C (I), 20°C (II) or 0°C (III) to hydrogen.

Figure 2. Increase in the ratio \( \rho = \frac{\text{intensity of the C 272 eV Auger peak}}{\text{intensity of the Ir 230 eV Auger peak of the clean surface}} \) when an Ir(111) surface is exposed to \( \text{C}_2\text{H}_4 \) at 30°C.

Figure 3. Desorption of \( \text{H}_2 \) and \( \text{C}_2\text{H}_4 \) from Ir(111) exposed to \( \text{C}_2\text{H}_4 \) or \( \text{C}_2\text{H}_2 \).
- \( \text{H}_2 \) from the surface previously exposed to \( \text{C}_2\text{H}_2 \)
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Figure 7. Increase in the ratio $\rho = \frac{\text{intensity of the C 272 eV Auger peak}}{\text{intensity of the Ir 230 eV Auger peak of the clean surface}}$

when the Ir (111) surface is exposed to $\text{C}_2\text{H}_2$
A: sample temperature is $30^\circ\text{C}$
B: sample temperature is $200^\circ\text{C}$

Figure 8. Hydrogen desorption from Ir(5)-(6111) X (100)) previously exposed to $\text{C}_2\text{H}_2$ at room temperature
A: after exposure of the clean surface
B: after reexposure the surface which has been heated to $600^\circ\text{C}$ in vacuum after the first exposure to $\text{C}_2\text{H}_2$.

Figure 9. LEED pattern of benzene adsorbed on Ir(111) at room temperature.
Electron energy 52 eV.

Figure 10. Increase in the ratio $\rho = \frac{\text{intensity of the 272 eV Auger peak}}{\text{intensity of the Ir 230 eV Auger peak of the clean surface}}$

when the Ir(111) surface is exposed to benzene (-----) and cyclohexane (----)
A: adsorption temperature is $30^\circ\text{C}$
B: adsorption temperature is $200^\circ\text{C}$

Figure 11. Desorption of $\text{H}_2$ and $\text{C}_6\text{H}_6$ from Ir(111) previously exposed to $\text{C}_6\text{H}_6$ (-----) or $\text{C}_6\text{H}_{12}$ (----)
A: adsorption temperature is $30^\circ\text{C}$
B: adsorption temperature is $200^\circ\text{C}$

Figure 12. Desorption of benzene (Fig. A) and hydrogen (Fig. B) from (Ir(5)-(6111) X (100)) previously exposed to benzene at $30^\circ\text{C}$.

Figure 13. Desorption of hydrogen from an Ir(5)-(6111) X (100) surface previously exposed to cyclohexane at $30^\circ\text{C}$. 
Fig. 1
Fig. 2
Fig. 3
Fig. 5
Fig. 7
Fig. 10
Fig. 11
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