

STUDIES OF HYDROCARBON REACTIONS ON LOW-INDEX
IRIDIUM AND PLATINUM SURFACES

Thesis by
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To my Mom and Dad

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ABSTRACT

The interaction of hydrocarbons with the (110)-(1x2) and (111) surfaces of iridium and the (110)-(1x2) surface of platinum has been studied under ultrahigh vacuum conditions. The principle experimental techniques employed were thermal desorption mass spectrometry and low energy electron diffraction.

Chapter 2 describes the extension of previous studies of the adsorption and reaction of ethane and propane on the Ir(110)-(1x2) surface to the normal isomers of butane, pentane, hexane and heptane. At low coverages, each of these alkanes undergoes dissociative chemisorption at 130 K. At higher coverages, molecular adsorption occurs as well. Thermal desorption spectra of hydrogen are similar in many respects for the dissociatively adsorbed overlayers of all six of these paraffins. Both desorption-limited and reaction-limited adstates of hydrogen are observed, the latter being associated with the dehydrogenation of hydrocarbon fragments on the surface. Ethane, butane and hexane form high temperature adstates, the associated fragments of which are low in hydrogen content, while those for propane, pentane and heptane contain relatively more hydrogen. This difference may be explained by extending a model for dehydrogenation which has been proposed previously [T. S. Wittrig, P. D. Szuromi and W. H. Weinberg, *J. Chem. Phys.* **(76)**, 3305 (1982)] for understanding the dissociative adsorption of other saturated hydrocarbons on this surface.

Chapter 3 discusses cyclopropane, propylene, propyne and allene on the reconstructed Ir(110)-(1x2) surface. Annealing adlayers of these hydrocarbons (at low coverages) leads to the formation of surface hydrogen and hydrocarbon fragments of approximate stoichiometry C_3H_2 . The importance of the β'_2 adsite of hydrogen on this surface of iridium has been demonstrated further by inhibition studies with hydrogen, CO and surface carbon. The close-packed Ir(111)

surface dehydrogenates propylene, but neither propane nor cyclopropane adsorb dissociately under the same reaction conditions, indicating a strong effect for the activation of carbon-hydrogen bonds of alkanes.

Chapter 4 describes the investigation of this strong effect of surface geometry on the dissociative adsorption of alkanes on surfaces of platinum. Previous work (L. E. Firment, Ph. D. Thesis, Univ. of California, Berkeley, 1976) shows that the close-packed Pt(111) surface does not dehydrogenate the normal alkanes through octane under ultrahigh vacuum conditions. On the reconstructed Pt(110)-(1x2) surface, low coverages of n-butane and n-pentane adsorb dissociatively at approximately 200 K to form surface hydrogen and hydrocarbon fragments, whereas only molecular adsorption is observed for ethane and propane. Inhibition of this reaction by precoverages of hydrogen suggests strongly that carbon-hydrogen bond activation is the initial reaction step, and occurs at the same adsite as for the adsorption of hydrogen at lower coverages. Thus for both iridium and platinum the availability of high coordination adsites on the (110)-(1x2) surface appears to lower the kinetic barriers that must be overcome to activate carbon-hydrogen bonds in alkanes. Differences in the electronic structure of the two metals manifest themselves in such details as the magnitude of that kinetic barrier.

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CHAPTER 1

INTRODUCTION

The activation of alkanes is an important area of current interest in the field of catalysis. A high proportion of our basic chemical feedstocks is in the form of alkanes. In the absence of suitable catalysts, alkane activation is often nonselective and energy intensive. In their presence, useful reactions of alkanes such as reforming, hydrogenolysis and dehydrogenation can occur. Hence the study of the activation of alkanes by platinum metals in both homogeneous (1) and heterogeneous (2) systems, and an understanding of the mechanisms involved, is of both fundamental and applied interest.

The first step in the activation of an alkane at a surface is a process involving cleavage of a σ bond, usually dehydrogenation. Subsequent reactions can include formation of dehydrogenation products (such as alkenes, alkynes, and aromatics), and formation of hydrogenolysis products (cleavage of carbon-carbon bonds followed by hydrogenation, e.g., ethane and methane from cyclopropane). In heterogeneous systems the rate of hydrogenolysis of alkanes is usually surface sensitive (2), meaning that the activity of the catalyst depends on the manner of its surface preparation. Classical studies, conducted at pressures on the order of 100 Torr on supported catalysts, have determined macroscopic details of catalytic reactions such as product distributions and kinetic rate parameters. However, from such data the nature of the active surface species is not determined directly but can only be inferred. In order to understand these phenomena at a microscopic level, comparative model studies of the adsorption and reaction of several hydrocarbons, mainly alkanes, on different low index surfaces of iridium and platinum under ultrahigh vacuum conditions have been undertaken.

These experimental conditions are particularly suited for acquiring fundamental data for these reactions. Ultrahigh vacuum conditions (base pressures below 2×10^{-10} Torr) allow clean, well-ordered surfaces to be prepared and

characterized, and also minimize the adsorption of background contaminants. In this manner the interaction of selected adsorbates with the surface can be controlled. By employing metal single crystals of known crystallographic orientation, reproducible surfaces of differing geometries are available. Diffraction techniques can be used to ascertain these surface geometries and establish the type of sites available on the surface for adsorption, reaction and desorption.

The experimental techniques that are available in the particular system in which these studies were conducted included thermal desorption mass spectrometry (TDMS), low energy electron diffraction (LEED), Auger electron spectroscopy (AES), X-ray and ultraviolet photoelectron spectroscopies and contact potential difference measurements. The techniques of TDMS, AES and LEED were used to obtain the data presented in this thesis and are described below.

In the TDMS experiment, the crystal is heated at a constant rate while the mass spectrometric signals characteristic of the desorbing gases are monitored. At the pumping speeds achieved in our system the partial pressures which are measured are proportional to the rate of desorption. Surface coverages can be determined by integration of the desorption signals. TDMS can be used to determine exposure-coverage relationships, to obtain kinetic data such as Arrhenius parameters for desorption, and to characterize gas phase products from the reaction of surface species. LEED can be used to determine the translational symmetry of the surface and of overlayers. In the studies presented its primary use was to monitor the presence of the (1x2) reconstruction of the Ir and Pt(110) surfaces. Ordered overlayers of hydrocarbons were not detected in any of these studies. In AES high energy electrons bombard the surface, causing ejection of electrons from the core levels of atoms. A second electron in such atoms can fall into the remaining core hole from a higher shell, causing ejection of the third electron. This is the Auger electron, and its energy can be used to

determine the atomic environment from which it was ejected. AES was used to verify carbon deposition from hydrocarbon reactions, and to monitor the level of possible surface impurities, such as silicon.

The Ir(110)-(1x2) surface was chosen for the initial studies for the following reasons. Information from classical studies of the interaction of hydrocarbons such as cyclopropane with iridium catalysts is available (3). This particular surface has been shown to be highly corrugated at the microscopic level, and may be pictured as a series of two-layer deep troughs, the sides of which are (111) microfacets (4). The presence of steps is believed to enhance certain catalytic reactions. The interaction of some simpler molecules (e.g., O₂, CO, H₂, H₂O) has been studied previously under ultrahigh vacuum conditions (5). Hence many key aspects of the reactivity of this surface were known previous to the investigations involving hydrocarbons. This motivated the work which appears as appendices to this thesis, of which a brief overview is provided here.

It was shown that alkanes (cyclopropane, ethane, propane, isobutane and neopentane) can dissociate on the Ir(110)-(1x2) surface at low coverages and temperatures below 130 K. These reactions are limited by the availability of high coordination β'_2 adsites, whose activity is inhibited by the hydrogen that is liberated from dissociation of carbon-hydrogen bonds. Saturation coverages of the dissociatively adsorbed overlayers is approximately 1×10^{14} molecules-cm⁻². There is no evidence that hydrogenation or hydrogenolysis reactions occurred under these experimental conditions, or that the surface reconstruction was affected by the dissociation reactions. Features appear in the thermal desorption spectra of hydrogen characteristic both of desorption-limited (β'_2) and reaction-limited (α, γ) processes. From these spectra the formation of hydrocarbon species which are stable in the presence of the reactive β'_2 adsites can be inferred. The stoichiometry of these fragments can be understood in terms of a

model for their structure which involves the formation of metallacycles containing three carbon atoms.

Chapter 2 concerns the further study of the reactions of alkanes with the Ir(110)-(1x2) surface. The investigation of the normal alkanes is extended to butane, pentane, hexane and heptane. At low coverages these hydrocarbons dissociate at temperatures of 130 K and above, giving rise to the characteristic desorption-limited (β_2') and reaction-limited (α,γ) states of hydrogen. The fragments associated with the high temperature γ desorption states are relatively more rich in hydrogen for the alkanes which contain an odd number of carbon atoms. The metallacycle model proposed earlier **(6)** has been extended to explain these results. Comparison to the previous results for isobutane and neopentane demonstrates that the dissociation reactions precede possible rearrangements of the carbon atom skeletons to a more stable structure.

Chapter 3 reports the results of the interaction of saturated and unsaturated hydrocarbons which contain three carbon atoms with the reconstructed Ir(110)-(1x2) and the close-packed Ir(111) surfaces. At surface coverages such that reactive β_2' adsites were still available, the reactions of the unsaturated hydrocarbons propylene, propyne and allene were found to be similar to those of propane and cyclopropane. This suggests that the reactions of these alkenes and alkynes are dominated by the strong dehydrogenating ability of these adsites, as opposed to the particular electronic and geometric structures of the molecules. On the Ir(111) surface, propane and cyclopropane dehydrogenate only at defect sites, while the saturation coverages of dissociatively adsorbed propylene are approximately the same on both iridium surfaces.

These results show that the geometry of the (110)-(1x2) surface is a critical factor in the ability of iridium to activate alkanes under such conditions.

Previous work (7) shows that the normal alkanes through octane do not adsorb dissociatively on the close-packed Pt(111) surface under ultrahigh vacuum conditions. This suggested that a study of the interaction of normal alkanes with the reconstructed Pt(110)-(1x2) could yield a greater understanding of the effect of surface structure on alkane activation. This work is presented in Chapter 4. On this surface, low coverages of n-butane and n-pentane dissociate at approximately 200 K to form surface hydrogen and hydrocarbon fragments, whereas only molecular adsorption is observed for ethane and propane. Carbon-hydrogen bond activation appears to be the initial step, as the reaction is inhibited by precovering the surface with hydrogen. Thus for both iridium and platinum the availability of high coordination adsites appears to lower the activation barriers that must be overcome to activate carbon-hydrogen bonds in alkanes. The formation of hydrocarbon fragments which are richer in hydrogen than those on the corresponding iridium surface and the higher kinetic barrier to dissociative adsorption of alkanes indicate that differences can be observed which are due to the different electronic structure of the two metals.

References

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CHAPTER 2

THE ADSORPTION AND REACTION OF NORMAL
ALKANES ON THE IR(110)-(1x2) SURFACE

(The text of Chapter 2 consists of an article coauthored with W. H. Weinberg which has been accepted for publication in Surface Science.)

Abstract

Previous studies of the adsorption and reaction of ethane and propane on the Ir(110)-(1x2) surface have been extended to the normal isomers of butane, pentane, hexane and heptane. At low coverages, each of these alkanes undergoes dissociative chemisorption at 125-130 K. At higher coverages, molecular adsorption occurs as well. Thermal desorption spectra of hydrogen are similar in many respects for the dissociative adsorption of all six of these paraffins, and both desorption-limited and reaction-limited adstates are observed. The latter are associated with the dehydrogenation of hydrocarbon fragments on the surface. Ethane, butane and hexane form high temperature adstates, the associated fragments of which are low in hydrogen content, while those for propane, pentane and heptane contain relatively more hydrogen. This difference may be explained in terms of a model for dehydrogenation which has been proposed previously [T. S. Wittrig, P. D. Szuromi and W. H. Weinberg, *J. Chem. Phys.* **76**, 3305 (1982)] in understanding the reaction of other hydrocarbons on this surface.

1. Introduction

The reactive interaction of hydrocarbons with well-characterized transition metal surfaces under ultrahigh vacuum (UHV) conditions has been investigated frequently with unsaturated species, such as alkenes (1). These molecules chemisorb strongly to transition metal surfaces, initially through their π electrons. The reaction of alkanes, however, requires that σ bonds undergo activation. Goodman has examined the products of ethane and cyclopropane hydrogenolysis at high pressures over nickel surfaces (2), while Muetterties and coworkers have observed the dehydrogenation of cyclohexane to benzene on nickel and platinum surfaces (3). However, under UHV conditions usually only molecular adsorption, as opposed to bond cleavage, has been observed for smaller alkanes. In recent investigations in our laboratory, the interaction of alkanes with the reconstructed Ir(110)-(1x2) surface has been studied (4-6). Ethane, cyclopropane, propane, isobutane and neopentane have been observed to adsorb dissociatively at low coverages and temperatures (< 130 K) and to dehydrogenate upon heating. Here the earlier results reported for ethane and propane have been extended to the next four normal alkanes, namely butane, pentane, hexane and heptane. It will be shown that these hydrocarbons undergo dissociative adsorption and dehydrogenation in a manner similar to the alkanes studied previously. Moreover, the stoichiometries of certain thermal desorption adstates of hydrogen resulting from adsorption of these normal alkanes can be correlated with whether the molecules contain an even or an odd number of carbon atoms. This extends a model, proposed earlier (6), which has helped explain the stoichiometries of such fragments for other hydrocarbons.

The results reported for ethane and propane are germane and will be reviewed briefly here (6). It has been shown that for adsorption at 130 K, dissociative adsorption occurs initially. By "dissociative," we mean that desorption of the parent alkane does not take place upon heating of the surface. As this adlayer saturates, a nondissociative,

molecularly adsorbed adlayer forms. No evidence of multilayer formation has been observed under our experimental conditions ($T \geq 100$ K and $p \leq 10^{-9}$ Torr). Upon heating, the dissociatively adsorbed overlayer undergoes stepwise dehydrogenation to form hydrocarbon fragments on the surface and ultimately surface carbon after complete dehydrogenation and hydrogen desorption. No hydrocarbons are observed to desorb from the *dissociatively* adsorbed overlayer, i.e., there is no evidence of self-hydrogenolysis, and the initial C-H bond cleavage is irreversible.

To help interpret the thermal desorption spectra of hydrogen from these dissociatively adsorbed overlayers, the adstates of hydrogen after exposures of (a) 0.5 L, (b) 2 L and (c) 300 L to the clean surface are shown in Fig. 1. The high temperature or β_2 adstate saturates after an exposure of 0.5 L, while the low temperature or β_1 adstate saturates after an exposure of 300 L at an adsorption temperature of 100 K (7). Thermal desorption spectra of hydrogen from saturation coverages of the dissociatively adsorbed alkanes are shown as solid lines in Fig. 2A for ethane and in Fig. 2B for propane, and these can be compared directly with the β_2 adstate of hydrogen, which is shown in both cases as the dashed lines. The features at 400 K for these hydrocarbons are very similar to the β_2 adstate of hydrogen on the clean surface, and are designated the β_2' adstates. This similarity suggests that the β_2' adstate arises from desorption-limited hydrogen evolution from the metallic surface. For propane the high temperature edge of the β_2' adstate is virtually identical to that of the β_2 adstate of hydrogen, while for ethane the high temperature edge of its β_2' adstate shows slightly greater intensity. Propane exhibits a well defined higher temperature feature at approximately 550 K, which has been labeled the γ adstate. It has been shown that desorption occurring from the γ adstate is due to the dehydrogenation of (relatively) stable hydrocarbon fragments. At higher coverages, a third reaction-limited adstate is observed for propane. This α adstate appears as a low temperature shoulder on the β_2' adstate as may be seen in Fig. 2B. Previously, the stoichiometry of the γ fragment was measured

by determining the ratio R of the integrated intensities of the β_2' and the α adstates to that of the γ adstate (6). For propane this value, 3.2 ± 0.3 , indicates that the stoichiometry of the γ fragment is approximately C_3H_2 at all coverages. Ethane, however, displays no well defined desorption feature at higher temperatures, although there may be slight mass spectral intensity due to reaction-limited desorption of hydrogen. Using the known surface coverage of hydrogen, the saturation coverages of the dissociatively adsorbed overlayers have been shown to be 1.1×10^{14} molecules-cm $^{-2}$ for both ethane and propane.

It was found that postadsorption of hydrogen at 100 K on saturated overlayers of these two hydrocarbons caused an increase in the amount of desorption of the molecular hydrocarbon and a decrease in the amount of desorption of hydrogen due to dissociative adsorption demonstrating that dissociative chemisorption is not complete at 100 K. This increase in the amount of molecular desorption is caused by poisoning of the β_2' adsite. Reversal of a surface reaction (C-H bond formation) was excluded by experiments involving the postadsorption of deuterium: no incorporation of deuterium into the parent hydrocarbons was observed. After annealing these adlayers to 130 K, the postadsorption of hydrogen has no effect on the concentration of the dissociatively adsorbed alkane present, indicating that the reaction goes to completion at this temperature. Preadsorption of hydrogen poisoned the β_2' adsites on the surface and, in turn, the dissociative adsorption of these hydrocarbons.

2. Experimental Procedures

The experiments were performed in an ion pumped stainless steel bell jar that has been described previously (8). The base pressure of the bell jar was below 4×10^{-11} Torr of reactive contaminants. The hydrocarbon exposures were carried out with a directional beam doser consisting of a multichannel array of capillaries (9). During adsorption the crystal was positioned approximately 3 mm from the doser face. This provided

a beam pressure to background pressure ratio of greater than 100:1. These exposures were calibrated in Langmuir (L) units by comparison of thermal desorption spectra obtained by backfilling the bell jar and by employing the doser. All the gases used in this study were examined mass spectrometrically for purity, and no extraneous gases were detected. The crystal was cleaned of surface carbon by exposure to 10^{-7} Torr of O_2 for 2-2.5 min at 900 K, followed by annealing the surface to 1600 K. The concentrations of hydrocarbons that are adsorbed dissociatively on this surface are determined easily since the absolute coverage of adsorbed hydrogen is known and used as a reference. Following an exposure of 0.5 L of hydrogen to the clean surface, the resulting coverage of hydrogen is $(7.3 \pm 1.0) \times 10^{14}$ atoms-cm $^{-2}$ (7).

3. Results

3.1 Thermal Desorption of Hydrogen from Hydrocarbon Overlayers

At low coverages, the four larger straight-chain alkanes adsorb dissociatively on the surface below 130 K. This is due to their reaction with the β_2 adsites, which is manifest as the β_2' peak. The resulting thermal desorption spectra of hydrogen show significant variations as a function of coverage, which are due in part to the self-poisoning nature of the dissociative adsorption of these alkanes. Thermal desorption spectra of hydrogen from saturated coverages of the dissociatively adsorbed alkanes are shown as solid lines in Fig. 2C for butane, Fig. 2D for pentane, Fig. 2E for hexane and Fig. 2F for heptane; and they can be compared with the saturated β_2 adstate of hydrogen, which is shown as a dashed line in each figure. Spectral features common to all of the hydrocarbons will be discussed first. All spectra exhibit a desorption peak at 400 K at all coverages which is similar to the β_2 adstate for hydrogen on the clean surface and is labeled the β_2' adstate. Also occurring at all coverages is an adstate at approximately 550 K, labeled the γ adstate. It arises from dehydrogenation of surface hydrocarbon fragments, since after the thermal desorption spectra are measured, adsorption of

hydrogen causes repopulation of only adstates which resemble the β_2' adstate. Furthermore, the γ fragments are stable with respect to vacant β_2' adsites on the surface. If a dissociatively adsorbed overlayer of any of these hydrocarbons is annealed to 375 K for times on the order of one minute, then the β_2' adstate will desorb completely. If the surface is then cooled and a thermal desorption spectrum of hydrogen is measured, the γ adstate is still observed with the same intensity as for adsorption without annealing. This is shown in Fig. 3 for a saturated, dissociatively adsorbed overlayer of pentane. Prior to measuring the spectra, in (a) the surface was annealed to 375 K for one minute, while in (b) the surface was not annealed. It is clear that no decrease occurs in the intensity of the γ adstate.

At higher coverages, a third adstate develops at temperatures below 400 K, and this is labeled the α adstate. This may be seen clearly in Fig. 2. While this adstate occurs in the same temperature regime as the β_1 adstate for hydrogen on the clean surface, it does not arise from the desorption of hydrogen bound to the metal substrate, since the peak shapes deviate considerably from that of the β_1 adstate for comparable coverages. Moreover, if a dissociatively adsorbed overlayer of sufficient coverage is annealed so that the α adstate desorbs, it cannot be repopulated by exposure to hydrogen. As in the case of the γ adstate, this indicates that this adstate results from reaction-limited desorption of hydrogen, as opposed to the formation or modification of surface adsites.

Figures 2C through 2F show that the β_2' adstate is less intense than the β_2 adstate of hydrogen on the clean surface for each of these alkanes: by approximately 5% for butane, 10% for pentane, 15% for hexane and 20% for heptane. Furthermore, the intensity of the γ adstates for butane and hexane are not so intense as those observed for correspondingly smaller hydrocarbons such as propane or pentane, respectively. As defined previously (6), the ratio R for butane was determined to be 9.0 ± 0.1 , implying a fragment stoichiometry of approximately C_4H_1 , while for hexane R was determined to

be 7.0 ± 0.8 , implying a fragment stoichiometry of approximately C_6H_2 . For pentane and heptane, however, the ratio R was determined to be 2.3 ± 0.1 and 1.8 ± 0.1 , implying fragment stoichiometries of approximately C_5H_4 and C_7H_6 , respectively. Previously, the stoichiometries C_2H_0 for ethane and C_3H_2 for propane were observed (6). Evidently, the hydrogen content of the fragments resulting from the dehydrogenation of normal alkanes containing an odd number of carbon atoms is higher than that for hydrocarbons containing an even number of carbon atoms. At saturation, the lower temperature α adstates show their intensity maxima at approximately 330 K for butane, 320 K for pentane, 310 K for hexane, and 300 K for heptane. These adstates are *much* more prominent than that observed for propane, which developed as a shoulder of the β_2' adstate. The absolute coverages of the dissociatively adsorbed hydrocarbon overlayers can be measured from the hydrogen thermal desorption spectra. In units of 10^{14} molecules-cm⁻², the coverages are the following: butane, 1.0; pentane, 0.9; hexane, 0.8; and heptane, 1.0. In each case the error is approximately 1.0×10^{13} molecules-cm⁻².

For saturation coverages, the β_2' adstates of butane, hexane and heptane exhibit greater intensity than the β_2 adstate of hydrogen for temperatures above 400 K, as was observed with ethane. The intensity of the saturated β_2' adstate for pentane at temperatures above 400 K is essentially the same as that of the β_2 adstate of hydrogen up to the onset of the desorption of the γ adstate at approximately 440 K, as has been observed for propane. We propose that a broadening observed for ethane, butane and hexane is due to reaction-limited desorption from the dehydrogenation of relatively unstable (compared to the γ adstate) hydrocarbon fragments by β_2' adsites. These adsites become available due to desorption of hydrogen from the metal surface at temperatures below approximately 400 K and thus are available for reaction at higher temperatures. For heptane, the following series of annealing and coadsorption experiments has demonstrated that this is an apparent effect due the greater intensity of the γ adstate for heptane. In each case a dissociatively adsorbed overlayer of the alkane is

annealed to 375 K so that surface hydrogen desorbs, leaving the relatively stable γ fragments. The coverages were chosen to be sufficiently high to observe broadening of the β_2' adstate, but not so high to limit adsorption of hydrogen after annealing due to a high coverage of hydrocarbon fragments on the surface. The surface is cooled and exposed to sufficient hydrogen to saturate the β_2 adstate (5 L). The thermal desorption spectra of hydrogen for the surfaces prepared in this manner are shown as solid lines for hexane (1.25 L exposure, followed by 5 L of hydrogen after annealing to 375 K) in Fig. 4A, and for heptane (1 L exposure, followed by 5 L of hydrogen after annealing to 375 K) in Fig. 4B. Dashed lines in Figs. 4A and 4B are 0.5 L exposures of hydrogen to the clean surface. For hexane the β_2' adstate is now essentially within an envelope formed by the β_2 adstate of hydrogen, while for heptane the β_2' adstate still exceeds the β_2 adstate in intensity above 400 K. It can be concluded that the broadening observed initially for hexane is due to dehydrogenation of relatively unstable hydrocarbon fragments, while the broadening for heptane is due to simultaneous desorption from both the β_2' and γ adstates. The high hydrogen content of the γ adstate for heptane, relative to the other hydrocarbons that have been studied, appears to be the cause of this broadening. Hence heptane is similar to propane and pentane in that the hydrocarbon fragments which decompose above 400 K are stable in the presence of vacant β_2' adsites. Ethane, butane and hexane, however, form fragments which appear to decompose, at least partially, in the presence of vacant β_2' adsites.

The thermal desorption spectra of hydrogen for the four larger alkanes are shown as a function of coverage in Fig. 5. In each case, a 2.5 L exposure resulted in saturation of the dissociatively adsorbed overlayer, and in the initial population of the molecularly adsorbed overlayer. For each hydrocarbon it can be seen that the α adstate begins to populate at exposures of approximately 1 L. The α adstates become relatively more intense as the chain length of the parent hydrocarbon increases.

3.2 Thermal Desorption of Hydrocarbons from Hydrocarbon Overlayers

The dissociative adsorption of the normal alkanes on the Ir(110)-(1x2) surface at 100 K has been shown to saturate. Just below the exposures necessary to cause this saturation, a molecularly adsorbed overlayer of the hydrocarbon begins to populate. No hydrocarbons other than the one adsorbed initially were observed to desorb under these conditions.

Thermal desorption spectra of the molecularly adsorbed overlayers as a function of exposure are shown for butane, pentane, hexane and heptane in Fig. 6. The chemisorbed adstates, which are indicated as spectra (a), have their intensity maxima for low coverages at approximately 170 K for butane, 190 K for pentane, 210 K for hexane and 230 K for heptane. These temperature maxima decrease approximately 15 K at saturation coverages, as can be seen in the spectra labeled (b). In contrast to the results obtained for the adsorption of ethane and propane at 100 K, multilayers are formed at large exposures for each of the hydrocarbons. Multilayer desorption is observed at progressively higher temperatures with increasing hydrocarbon chain length, and occurs at approximately 120, 135, 150 and 165 K, respectively, for butane through heptane.

3.3 Coadsorption of Hydrogen with Hydrocarbon Overlayers

The coadsorption of hydrogen has been employed previously to understand the nature of the reactive adsite for these dehydrogenation reactions and to investigate the extent of these reactions at the adsorption temperature. For ethane and propane, it was shown that poisoning of the dehydrogenation reaction can be accomplished by preadsorption of hydrogen (5,6). This poisoning is complete when the β_2 adstate of the clean surface is saturated. Thermal desorption spectra of hydrogen are shown in Fig. 7 for (a) exposure of the clean surface to 0.5 L of hydrogen followed by exposure to 5 L of pentane at 100 K, and for (b) exposure of the clean surface to 0.5 L of hydrogen. The

formation of the γ adstate is completely poisoned by the preadsorption of hydrogen. The initial population of the β_1 adstate is due to background hydrogen adsorption. Similar spectra were observed both for butane and hexane. Since the desorption of β_2 hydrogen begins in a temperature regime in which heptane is still adsorbed molecularly on the surface, hydrogen did not poison completely the formation of the γ adstate of this alkane.

In previous investigations of the postadsorption of hydrogen on ethane and propane adlayers at 100 K, it has been shown that the adsorption of hydrogen decreased the intensity of the γ adstates and caused a corresponding increase in the intensity of the molecularly desorbing parent hydrocarbons. However, annealing the hydrocarbon adlayers to 130 K caused the postadsorption of hydrogen to have no effect on the intensity of either the γ or the molecularly adsorbed adstates. Similar results have been observed for the four higher alkanes. Thermal desorption spectra of hydrogen are shown in Fig. 8A for (a) 1.5 L of hexane exposed to the clean surface and (b) 2 L of hydrogen postadsorbed on the above surface at 100 K. In Fig. 8B the corresponding molecular hexane desorption spectra are shown. Both effects discussed above are observed. However, if the hydrocarbon adlayer is annealed to 130 K prior to the adsorption of hydrogen, then no increase in the amount of molecular desorption and no decrease in the intensity of the γ adstate is observed.

4. Discussion

In studying the adsorption of normal paraffins on the Ir(110)-(1x2) surface, it has been shown that in all cases the β_2' adsites are the most reactive toward dehydrogenation. Poisoning of these adsites decreases the reactivity completely. An investigation of propane adsorption on the close-packed Ir(111) surface has shown that dehydrogenation, which occurs only at defect sites, is negligible compared to molecular desorption (10). This supports the view that a particular adsite of the more "open" surface is

involved in these reactions. With the exception of ethane, dehydrogenation by the β_2' adsites is incomplete, and leads to the formation of γ and α adstates. Saturation coverage of the γ adstate correlates with the size of the hydrocarbon and with the number of carbon atoms in the hydrocarbon, i.e., an "odd-even" effect is present. The saturation coverage of the α adstate tends to increase with the size of molecule.

Previously, a model was developed to explain the stoichiometry of the γ adstate for a number of hydrocarbons, including propane, studied on the Ir(110)-(1x2) surface (6). For propane, it was proposed that three-carbon-atom metallacycles are formed by the complete dehydrogenation of the first and third carbon atoms, leaving a bridging methylene group that is not bound directly to the surface. At low temperatures, the hydrogen atoms of the methylene do not react with surface adsites. At higher temperatures, carbon-carbon bond scission results in decomposition of the methylenes and rapid desorption of hydrogen. This model predicts that no γ adstate would exist for ethane (as observed experimentally), since no three-carbon-atom metallacycle could be formed in this case, while the C_3H_2 stoichiometry was explained correctly for propane. Since the exchange of hydrogen atoms between the surface adstates and the hydrocarbon fragments is rapid when the surface is heated to temperatures on the order of 400 K (6), direct verification of this model could not be obtained by thermal desorption studies of deuterium-labeled hydrocarbons. The metallacycle model can be extended to the cases of pentane and heptane. The stoichiometries C_5H_4 and C_7H_6 can be explained by assuming that every "odd number" carbon atom dehydrogenates completely, leaving a chain of three-carbon-atom metallacycles, which has two units for pentane and three units for heptane.

Butane and hexane, however, do not appear to adhere to such a simple model. Butane could form one metallacycle unit, while hexane could form two. In each case a methyl group would not be bonded directly to the metallic surface. Such a group could contribute from three to zero hydrogen atoms to the γ adstate fragment, depending on

the extent of dehydrogenation below 400 K. The expected stoichiometries would range from C_4H_5 and C_6H_7 if the methyl group were stable, to C_4H_2 and C_6H_4 if the methyl group dehydrogenated completely. The observed stoichiometries of C_4H_1 and C_6H_2 indicate that a metallacycle structure, as proposed above, is not formed, and that the fragments which are formed are almost completely dehydrogenated by the metallic surface.

The formation of α adstates at higher coverages has been observed previously for other alkanes (6). It was proposed that these adstates were formed at higher surface coverages due to a lack of accessible β_2' adsites. Dehydrogenation of the remaining species could occur through other adsites, which would normally be less reactive. Partial reaction at available β_2' adsites could pin molecular fragments at the surface. In the absence of β_2' adsites, other adsites dehydrogenate the fragments, giving rise to the α adstates. Increasing the molecular size would tend to limit the probability of a molecule reacting with sufficient β_2' adsites, causing the α adstate to become more intense with increasing chain length. This is the observed effect.

The importance of the β_2' adsites has been demonstrated by the ability of hydrogen to poison the dehydrogenation reaction. Exposure of the clean surface to 0.5 L of hydrogen results in a complete poisoning of the β_2' dehydrogenation reaction in the case of pentane. This is indicated by the absence of the γ adstate in this experiment. In the case of heptane, a residual activity of the surface is observed in such an experiment due to desorption of β_2 hydrogen beginning before the molecular desorption of heptane is complete.

Postadsorption of hydrogen on adlayers of these normal paraffins at 100 K retards dissociative adsorption (with a concomitant enhancement in molecular adsorption). Annealing the alkane overlayers to 130 K for 30 seconds prior to the postadsorption of the hydrogen leads to no change in the intensities of the γ adstate or the molecularly

adsorbed states. This establishes that the dehydrogenation reaction is at most only partially completed at 100 K, or has virtually not occurred. The latter seems reasonable in light of the following simple calculation. Assuming a preexponential factor of the reaction rate coefficient of 10^{12}s^{-1} , and assuming that the reaction is completed at 130 K in approximately one second, then an activation barrier of 7.1 kcal/mole may be estimated. Using these same values at 100 K implies that the reaction would require approximately one hour to go to completion. This estimate would increase further if more than one second were required for the reaction to go to completion at 130 K.

It is interesting to note the differences between the thermal desorption spectra of hydrogen from butane and isobutane, and from pentane and neopentane. While butane exhibits a fragment stoichiometry of C_4H_1 , isobutane exhibits a stoichiometry of C_4H_4 , i.e., the latter retains considerably more hydrogen. The only significant difference between these two adsorbates is that isobutane has three-carbon-atom chains while butane has four-carbon-atom chains. Hence, the formation of γ adstates with high hydrogen content is correlated with the possibility of forming metallacycles containing three carbon atoms. While both n-pentane and neopentane form fragments of stoichiometry C_5H_4 , their thermal desorption spectra of hydrogen show differences in the formation of the α adstates. For example, at saturation the maximum intensity of the α adstate of neopentane is approximately 100 K higher than that of n-pentane. This would suggest that these alkanes largely retain their carbon-carbon bond frameworks after the initial steps of dehydrogenation prior to carbon-carbon bond scission above 400 K, and that isomerization of those frameworks to the most thermodynamically stable one is not occurring readily under our experimental conditions.

5. Conclusions

It has been shown that n-butane, n-pentane, n-hexane and n-heptane undergo dissociative chemisorption at low coverages at 130 K on the Ir(110)-(1x2) surface, while at

higher coverages molecular adsorption occurs as well. The presence of vacant β_2' adsites facilitates dehydrogenation, since preadsorption of hydrogen on the surface poisons the reaction completely. Thermal desorption spectra of hydrogen are similar in many respects for dissociatively adsorbed overlayers of these paraffins, and both desorption-limited (β_2') and reaction-limited (α and γ) adstates are observed. The latter are associated with the dehydrogenation of surface hydrocarbon fragments. Ethane, n-butane and n-hexane form γ adstates, the associated fragments of which are low in hydrogen content, while those for propane, n-pentane and n-heptane are relatively richer in hydrogen.

Acknowledgment

This research was supported by the National Science Foundation under Grant Number CHE-8206487.

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Figure Captions

- Figure 1. Thermal desorption spectra of hydrogen resulting from exposure of the clean surface to (a) 0.5 L, (b) 2 L and (c) 300 L of hydrogen.
- Figure 2. Thermal desorption spectra of hydrogen, shown as solid lines, resulting from saturation exposures of the clean surface to: A, ethane (0.7 L); B, propane (2 L); C, n-butane (2.5 L); D, n-pentane (2.5 L); E, n-hexane (2.5 L); and F, n-heptane (2.5 L). The spectra in dashed lines result from an exposure of the clean surface to 0.5 L of hydrogen.
- Figure 3. Thermal desorption spectra of hydrogen resulting from exposure of the clean surface to (a) 2.5 L of n-pentane; and (b) from the surface in (a) annealed to 375 K for 60 s.
- Figure 4. Thermal desorption spectra of hydrogen, shown as solid lines, after exposure of: A, 1.25 L of hexane annealed to 375 K, followed by exposure at 100 K to 5 L of hydrogen; and B, 1 L of heptane annealed to 375 K, followed by exposure at 100 K to 5 L of hydrogen. The spectra in dashed lines result from an exposure of the clean surface to 0.5 L of hydrogen.
- Figure 5. Thermal desorption spectra of hydrogen as a function of exposure for: A, n-butane; B, n-pentane; C, n-hexane; and D, n-heptane. Exposures are shown adjacent to the corresponding spectra.
- Figure 6. Thermal desorption spectra of parent hydrocarbons (monitoring mass 27) for: A, n-butane; B, n-pentane; C, n-hexane; and D, n-heptane. Exposures are shown adjacent to the corresponding spectra.
- Figure 7. Thermal desorption spectra of hydrogen after exposure of the clean surface to (a) 0.5 L of hydrogen followed by 5 L of pentane; and (b) 0.5 L of hydrogen.

Figure 8. Thermal desorption spectra of (A) hydrogen and (B) molecular hexane (mass 27) after (a) exposure of the clean surface to 1.25 L of hexane; and (b) exposure of the surface to 1.25 L of hexane followed by 0.5 L of hydrogen.

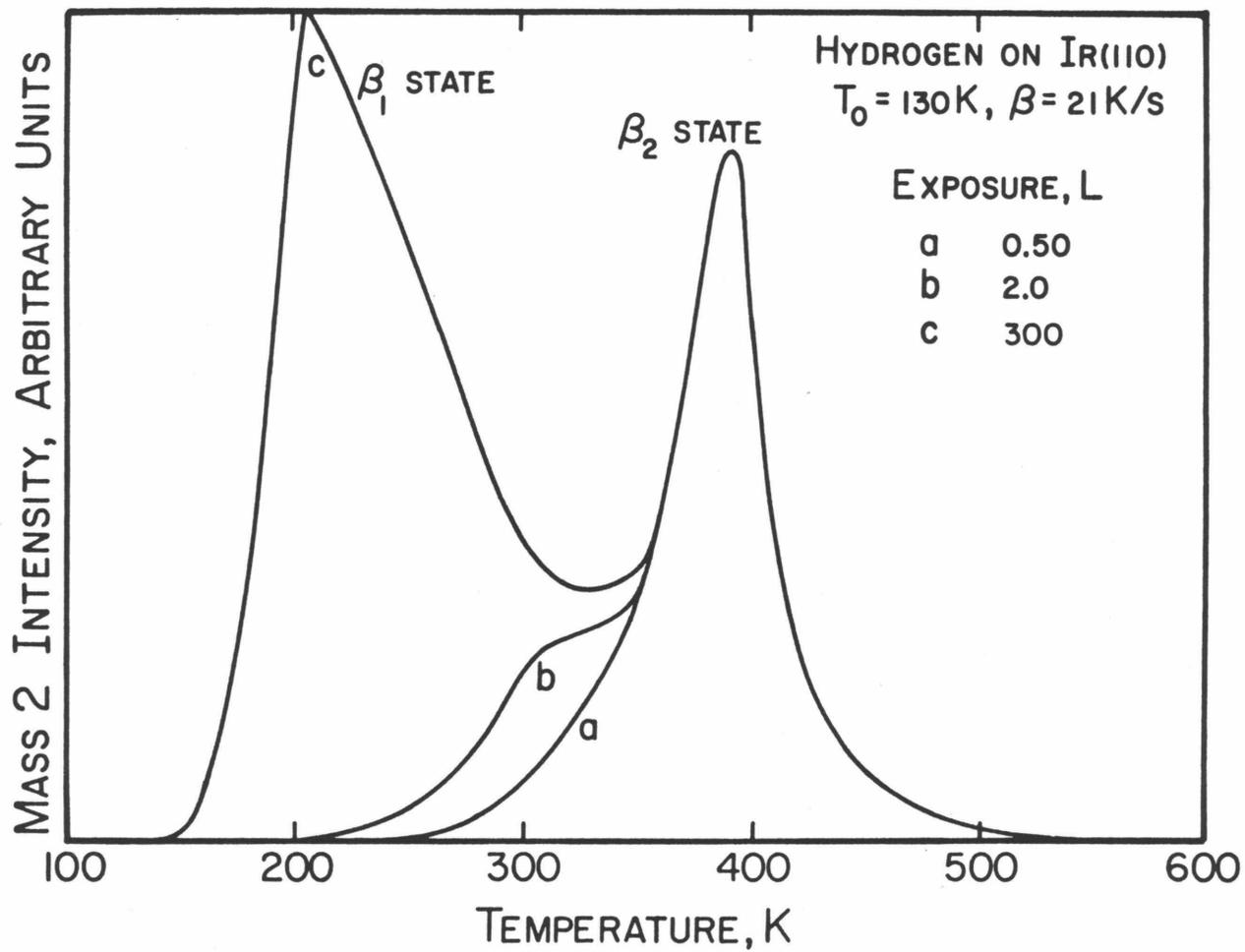


Figure 1

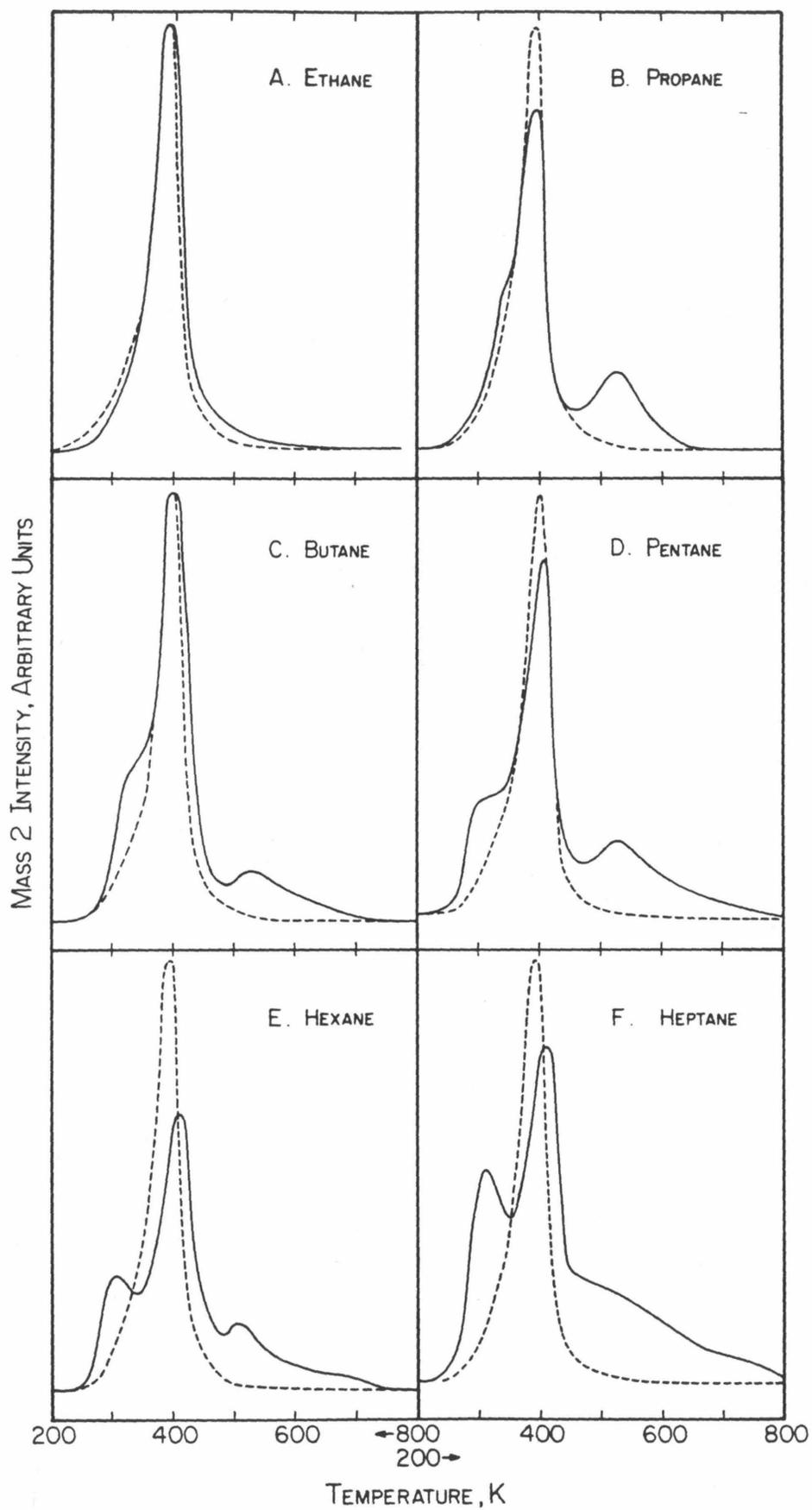


Figure 2

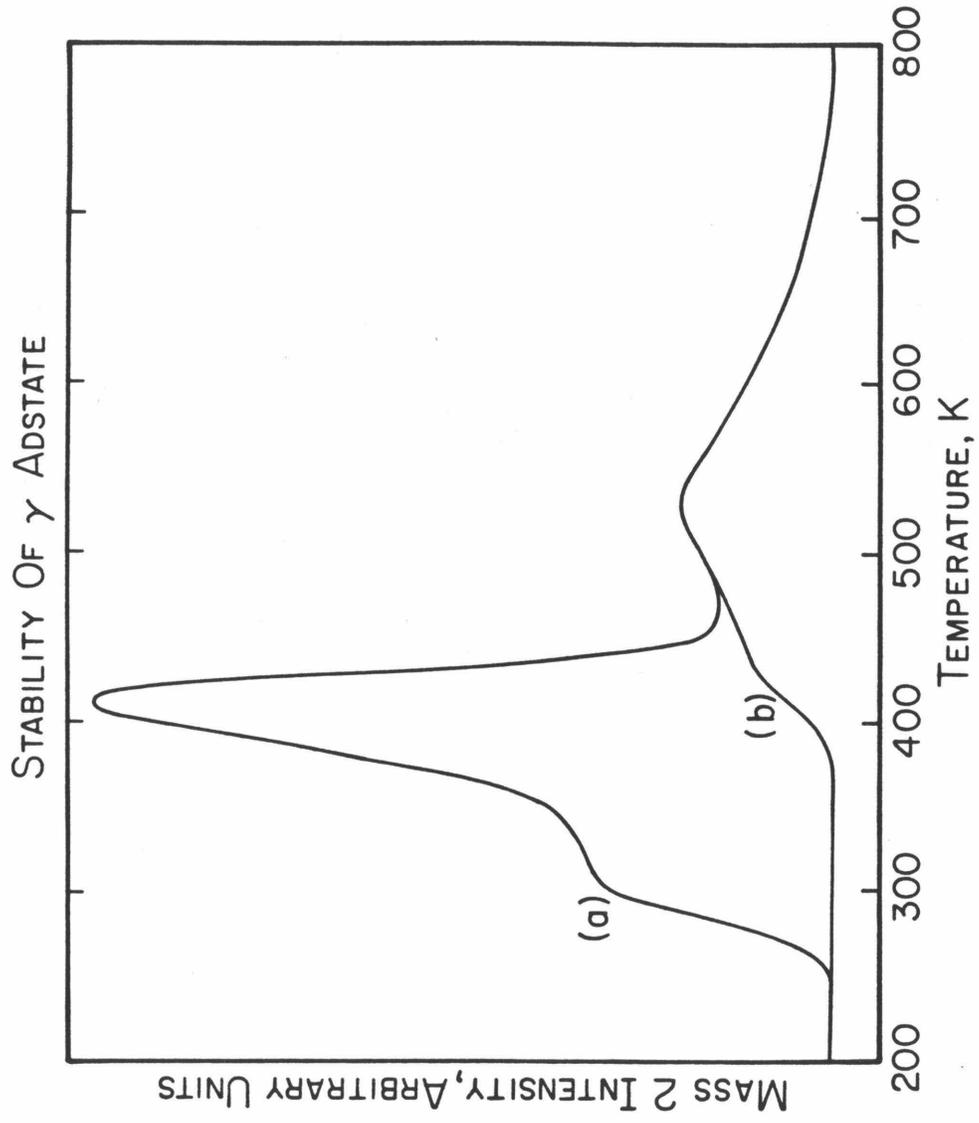


Figure 3

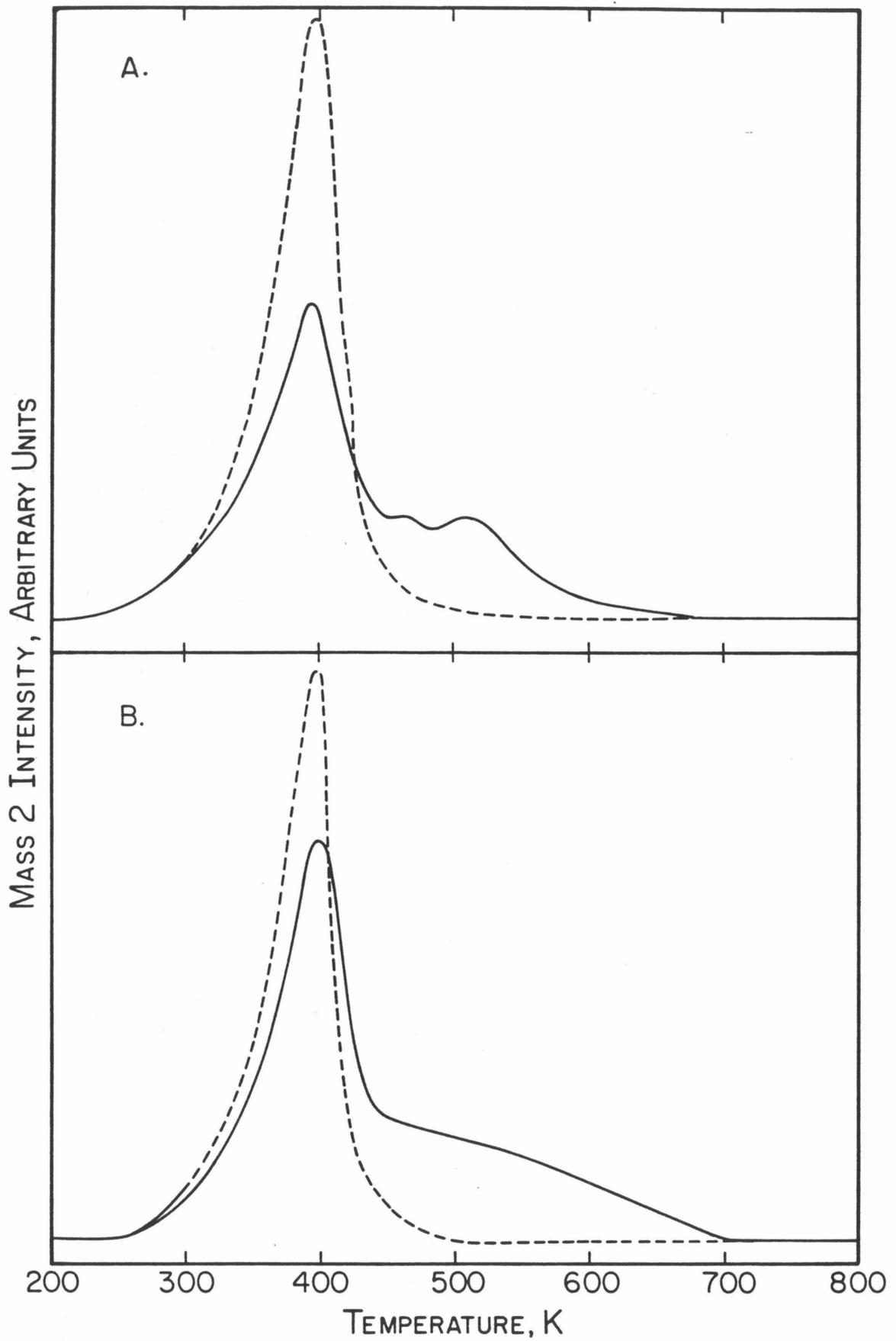


Figure 4

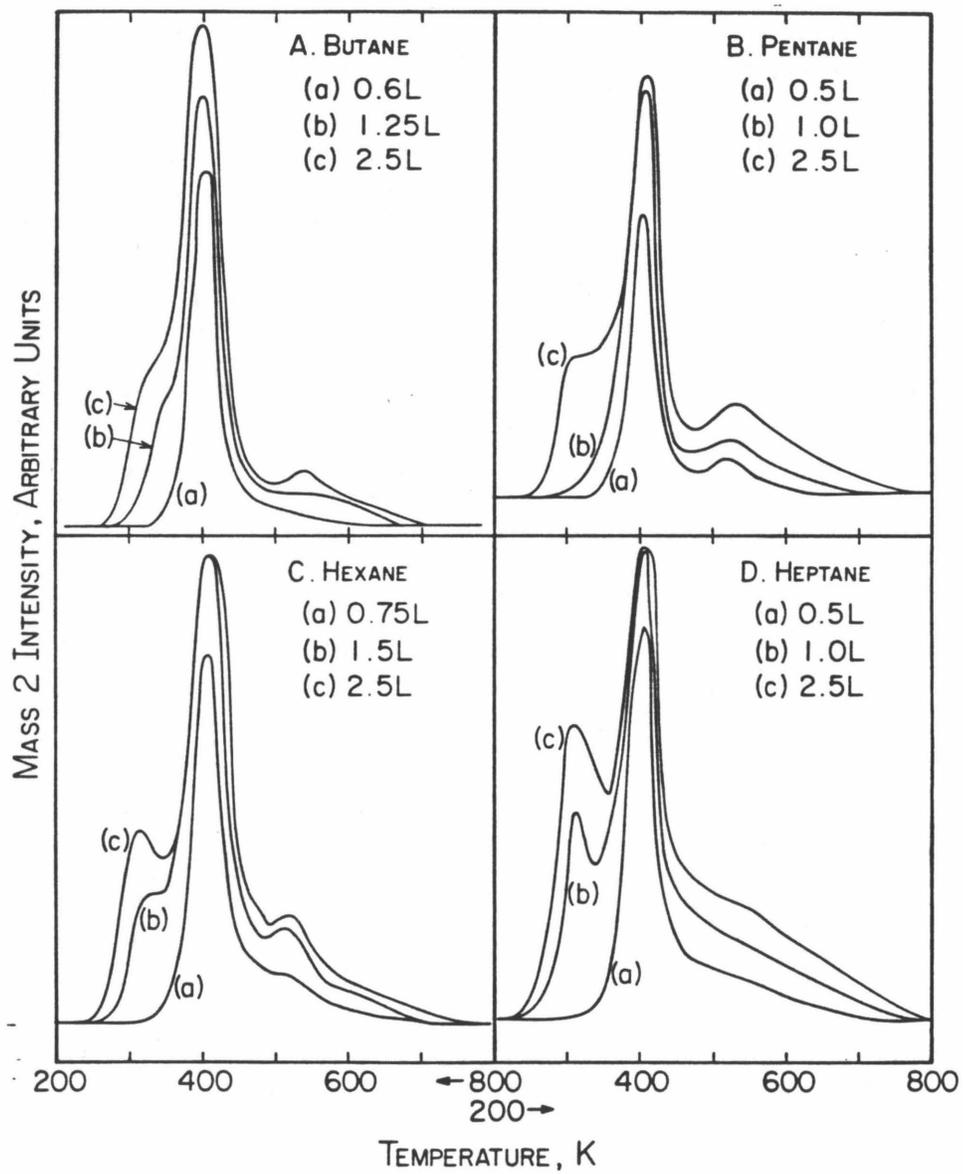


Figure 5

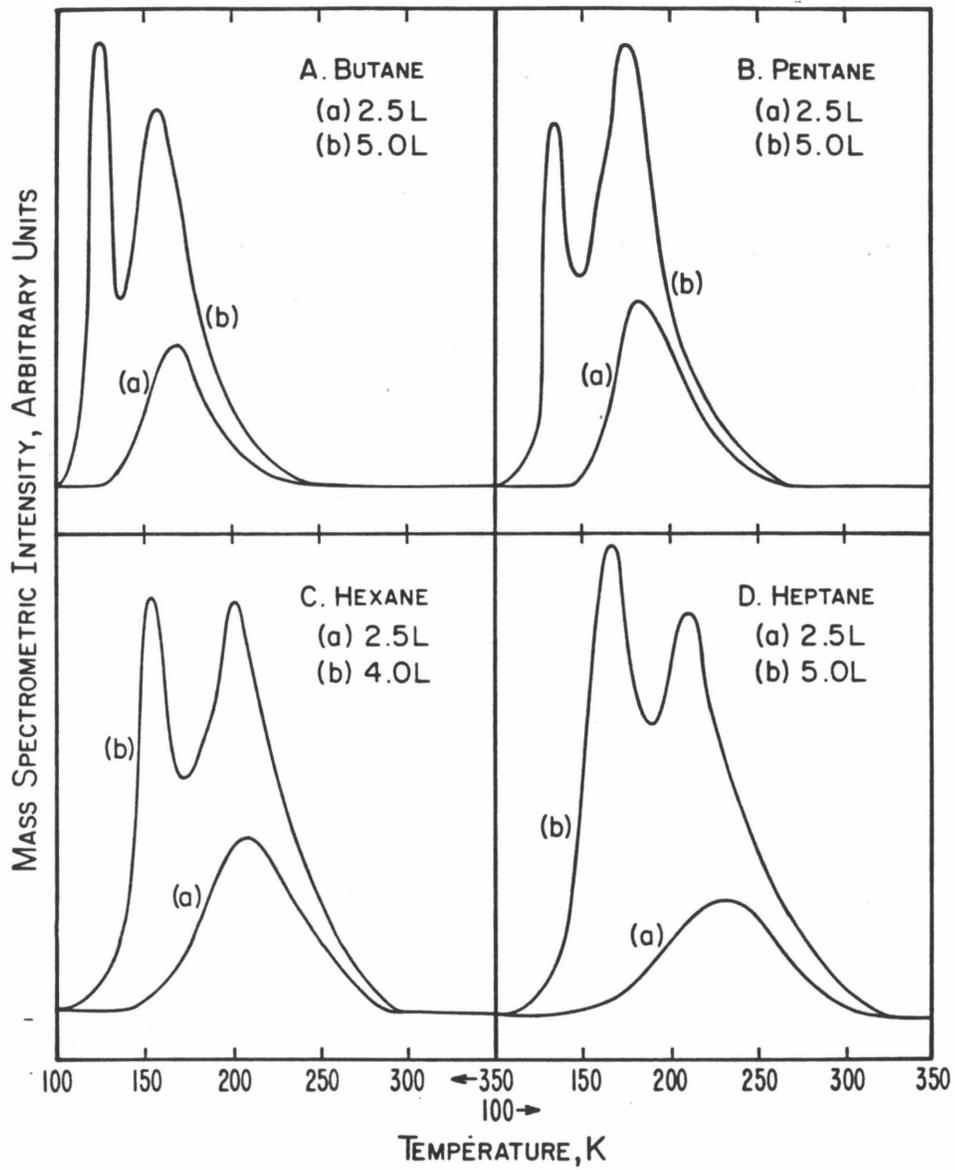


Figure 6

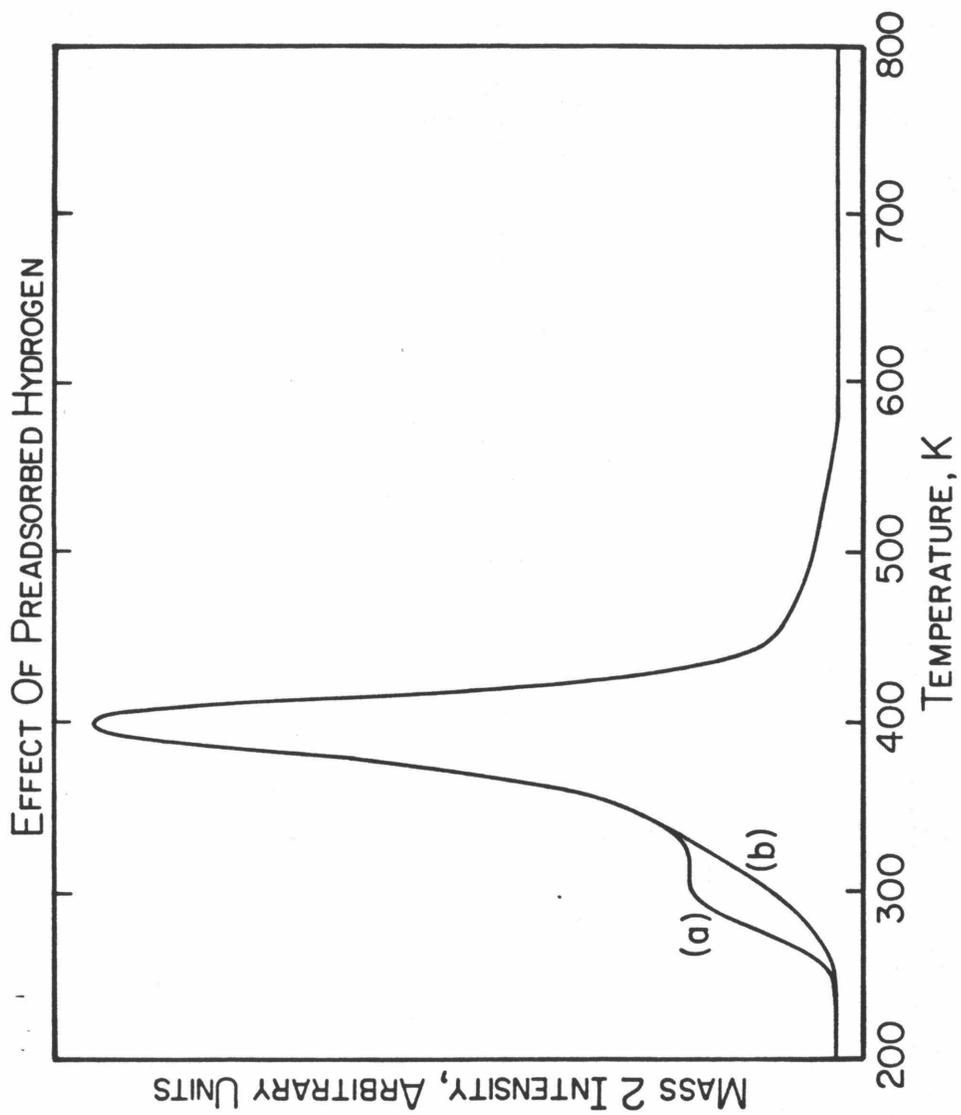


Figure 7

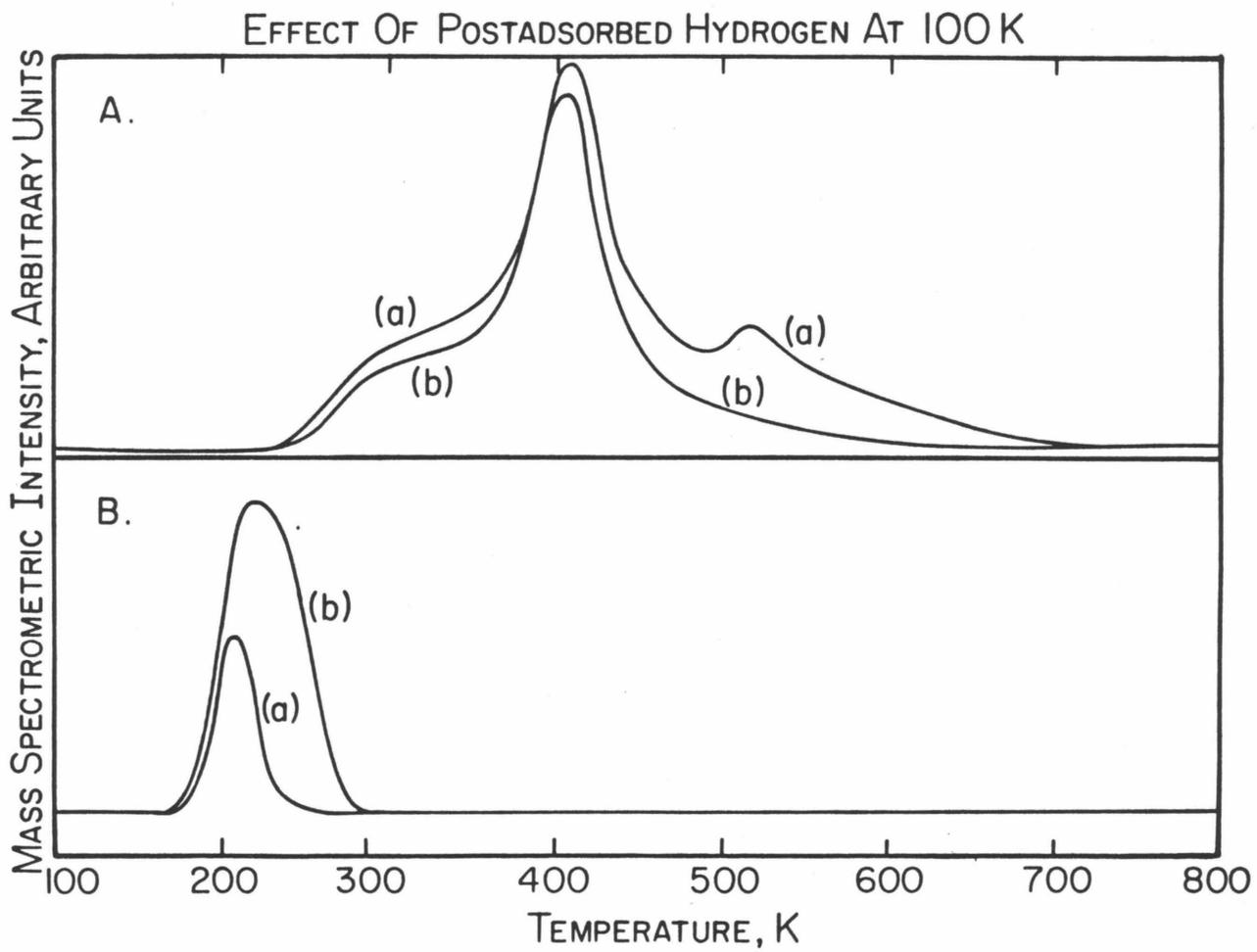


Figure 8

CHAPTER 3

THE REACTION OF SATURATED AND UNSATURATED
HYDROCARBONS WITH THE (110)-(1x2)
AND (111) SURFACES OF IRIDIUM

(The text of Chapter 3 consists of an article coauthored with J. R. Engstrom and W. H. Weinberg which has appeared in The Journal of Chemical Physics 80, 508 (1984).)

The reaction of saturated and unsaturated hydrocarbons with the (110)-(1×2) and (111) surfaces of iridium^{a)}

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The dehydrogenation of propane, cyclopropane, propylene, propyne, and allene has been investigated on the reconstructed Ir(110)-(1×2) surface. Annealing adlayers of these hydrocarbons (at low coverages) leads to the formation of surface hydrogen and hydrocarbon fragments of approximate stoichiometry C₃H₂. The importance of the β₂ adsite of hydrogen on this surface of Ir has been demonstrated further by poisoning studies with hydrogen, CO and surface carbon. The Ir(111) surface was found to dehydrogenate propylene but neither propane nor cyclopropane under the same reaction conditions, indicating a strong effect of surface geometry for the C-H bond activation of alkanes.

I. INTRODUCTION

A fundamental study of the interaction of hydrocarbon molecules with well-characterized transition metal surfaces is important as a means of gaining insight into the more general mechanisms of various reactions of hydrocarbons on transition metal catalyst surfaces. The relationship of particular adsites to various reaction pathways can be understood better by studying the reactions on different orientations of single crystals. In turn, if hydrocarbons which vary widely in electronic and geometric structure dehydrogenate in a very similar manner on a surface, then the presence of a particularly reactive adsite on that surface is implicated.

The adsorption and decomposition (dehydrogenation) of ethane, propane, cyclopropane, isobutane, and neopentane have been studied on the reconstructed Ir(110)-(1×2) surface primarily by thermal desorption mass spectrometry (TDMS).¹⁻³ Dynamic low-energy electron diffraction (LEED) calculations indicate that the clean surface reconstructs to form (111) microfacets which are three atomic rows in width, and which are inclined at an angle of 109.4° with respect to one another.⁴ While previous studies of the interaction of saturated hydrocarbons with other single crystalline surfaces of group VIII metals under UHV conditions have observed generally nondissociative chemisorption,⁵⁻⁷ the adsorption of alkanes on the Ir(110)-(1×2) surface is dissociative even at low temperatures (≤ 130 K) and leads to dehydrogenation due to a particularly reactive (β₂) adsite.¹⁻³

Here the interaction of cyclopropane and propane with Ir(110)-(1×2) is compared with that of three unsaturated hydrocarbons which also contain three carbon atoms, namely, propylene, propyne, and allene. On the Pt(111) surface, the dehydrogenation of a number of alkenes, including propylene, was found to vary markedly with the particular hydrocarbon molecule.⁸ It will be shown that despite the wide variation in electronic and geometric structure of these five hydrocarbons, their dehydrogenation in the presence of va-

cant β₂ adsites is remarkably similar. The importance of this adsite will be demonstrated both by its selective poisoning on the Ir(110)-(1×2) surface and by comparison with the close-packed Ir(111) surface. In both cases, the absence of the β₂ adsite causes the dehydrogenation of the hydrocarbons to be correlated to the geometric and electronic structure of the individual adsorbates. This is a further indication that the unusual ability of the Ir(110)-(1×2) surface to activate C-H bonds in alkanes is primarily either a geometric effect, or an electronic effect induced by its particular surface geometry.

II. EXPERIMENTAL PROCEDURES

The experiments were performed in an ion-pumped stainless steel bell jar which has been described in detail previously.⁹ The base pressure of the bell jar was below 4×10⁻¹¹ Torr of reactive contaminants. The hydrocarbon exposures were carried out with a directional beam doser consisting of a multichannel array of capillaries.¹⁰ During dosing, the crystal was positioned ~3 mm from the face of the doser. This provides a beam pressure-to-background pressure ratio of over 100:1. The unit of exposure that is employed for the beam doser is the Torr s and refers to the product of the time of exposure and the pressure in the storage bulb of the doser. The storage bulb supplies gas through a capillary to the doser head leading into the vacuum system. Therefore, the flux of gas into the vacuum system is proportional to the pressure in the storage bulb. For the gases employed in this study, an exposure of 1 L is approximately equivalent to 3 Torr s for propane, 2.5 Torr s for cyclopropane, and 3.5 Torr s for propylene. Although the proportionality factor was not measured for propyne and allene, by assuming reasonable ion gauge sensitivities it is estimated to be between 3 and 4 Torr s. The temperature of adsorption was in all cases between 90 and 100 K. Heating rates between 10 and 15 K s⁻¹ were used in performing thermal desorption experiments on this surface. The crystals were cleaned of surface carbon produced by the dehydrogenation of the hydrocarbons in the following manner. The Ir(110)-(1×2) surface was exposed to 1×10⁻⁷ Torr of O₂ for 2-2.5 min at a

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crystal temperature of 900 K, and then heated to 1600 K to desorb the oxygen. The Ir(111) surface was exposed to 5×10^{-8} Torr of O_2 for 2–2.5 min at a crystal temperature of 1100 K, and then heated to 1600 K to desorb the oxygen.

The hydrogen coverage calibration that is used to determine the concentration of dissociatively adsorbed hydrocarbon molecules on the Ir(110)-(1×2) surface involves a titration of the hydrogen with adsorbed oxygen as described previously.¹¹ The hydrogen concentration on this surface following an exposure of 0.5 L of H_2 is $(7.3 \pm 1.0) \times 10^{14}$ atoms cm^{-2} .

The hydrocarbon gases used in this study were purified by cryogenic distillation, and all gases were checked for purity mass spectrometrically after admission into the ultrahigh vacuum system.

III. EXPERIMENTAL RESULTS

A. Adsorption on Ir(110)-(1×2)

1. Thermal desorption of hydrogen from hydrocarbon overlayers

The dehydrogenation of cyclopropane and propane overlayers on Ir(110)-(1×2) has been studied previously in this laboratory by thermal desorption mass spectrometry.¹⁻³ Thermal desorption spectra of hydrogen obtained from saturated overlayers of these dissociatively adsorbed hydrocar-

bons are shown in Figs. 1(A) and 1(B). From the absolute hydrogen coverage calibration obtained for this surface, the absolute coverages of dissociatively adsorbed cyclopropane and propane were found to be $(2.1 \pm 0.2) \times 10^{14}$ and $(1.1 \pm 0.3) \times 10^{14}$ molecules cm^{-2} , respectively. In Fig. 1(C) thermal desorption spectra of hydrogen are shown resulting from an exposure of the clean surface (a) to 0.5 L of hydrogen, which saturates the β_2 adstate, (b) to 2 L of hydrogen, and (c) to 300 L of hydrogen, which saturates both the β_1 and β_2 adstates.¹¹

The thermal desorption of hydrogen from dissociatively adsorbed cyclopropane and propane both exhibit features which we have defined previously as the β'_2 and γ adstates. The β'_2 adstate is similar in intensity and temperature maximum to the β_2 adstate of hydrogen on the clean surface, suggesting that the β'_2 adstate arises from the desorption of hydrogen from metallic sites similar to the β_2 adsite. The high temperature γ adstate arises from hydrogen which is more strongly bound than any hydrogen which is adsorbed on the Ir substrate. This implies that the desorption of hydrogen from the γ adstate is limited by the dehydrogenation of hydrocarbon fragments on the surface (i.e., the cleavage of C–H bonds). This is not surprising since the formation of surface fragments by the adsorption of unsaturated hydro-

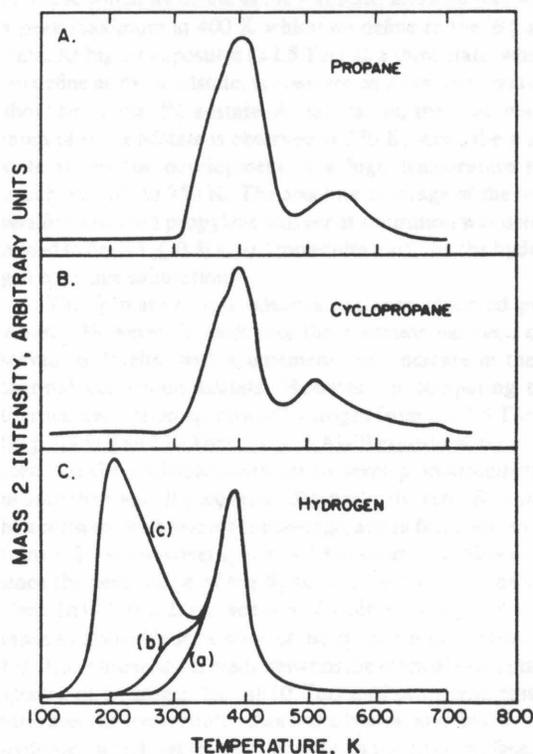


FIG. 1. Thermal desorption of hydrogen resulting from exposure of the Ir(110)-(1×2) surface to: A. 6 Torr s of propane (saturation). B. 4 Torr s of cyclopropane (saturation). C. (a) 0.5 L of hydrogen (saturation of β_2 adstate), (b) 2 L of hydrogen, (c) 300 L of hydrogen (saturation of β_1 and β_2 adstates).

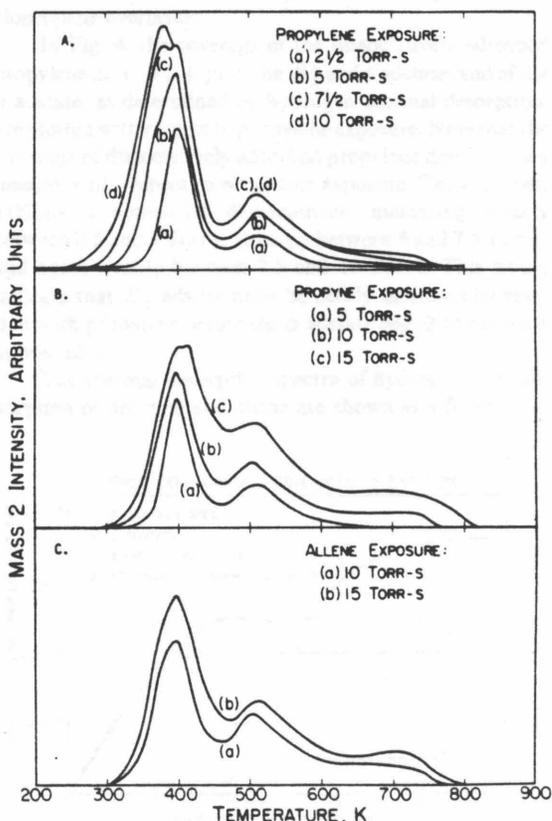


FIG. 2. Thermal desorption of hydrogen as a function of exposure of the Ir(110)-(1×2) surface to: A. Propylene, B. Propyne, C. Allene. Exposures are shown adjacent to the corresponding spectra.

carbons has been observed spectroscopically on other metals.¹²⁻¹⁴ The thermal desorption of hydrogen from a saturated, dissociatively adsorbed adlayer of propane exhibits, in addition, a low temperature shoulder on the β_2' peak, which has been defined as the α adstate.³ As has been discussed previously, this adstate is due to the dehydrogenation of relatively less stable hydrocarbon fragments on the surface.³

It has been shown that the low temperature (α , β_2') and high temperature (γ) adstates for both propane and cyclopropane develop at the same rate with increasing coverage. The quantity R has been defined as the ratio of the peak areas of the α and β_2' adstates to that of the γ adstate.³ For propane, R has the value 3.2 ± 0.3 , while for cyclopropane the value is 2.1 ± 0.3 . These ratios indicate that the fragment(s) associated with the γ adstate have an average composition of C_3H_2 . The γ adstate is stable if the surface on which it is present is annealed to 400 K for times on the order of one minute, i.e., it is stable in the presence of vacant β_2' adsites.¹ It was also shown that the coverage-exposure relationship for the dissociative adsorption of cyclopropane is linear.¹

Thermal desorption spectra of hydrogen after exposures of (a) 2.5, (b) 5, (c) 7.5, and (d) 10 Torr s of propylene to the clean surface are shown in Fig. 2(A). The thermal desorption spectra of hydrogen, and hence, of the irreversibly adsorbed adlayer of propylene are observed to saturate after an exposure of 10 Torr s. At low exposures, only two thermal desorption features are observed: one with a peak maximum at 550 K which we define as the γ adstate, and a second with a peak maximum at 400 K which we define as the β_2' adstate. At higher exposures (>2.5 Torr s), a third state, which we define as the α adstate, is observed as a low temperature shoulder of the β_2' adstate. At saturation, the peak maximum of the α adstate is observed at 370 K. Also, the γ adstate shows the development of a high temperature tail which extends to 750 K. The absolute coverage of the irreversibly adsorbed propylene adlayer at saturation was determined to be $(2.5 \pm 0.3) \times 10^{14}$ molecules cm^{-2} by the hydrogen coverage calibration.

The formation of α adstates has been observed previously. However, in each case the α adstate has been observed to develop with a commensurate increase in the γ thermal desorption adstate. However, in comparing the thermal desorption spectra of hydrogen from the 7.5 Torr s [Fig. 2(A)(c)] and 10 Torr s [Fig. 2(A)(d)] exposures, it can be seen that the α adstate continues to develop, independently of both the γ and β_2' adstates. Obviously, the ratio R cannot be a constant with respect to coverage, and in fact it increases from ~ 2.0 at low coverages to ~ 2.8 at saturation. However, since the peak shape of the β_2' adstate for hydrogen on the clean Ir(110)-(1 \times 2) surface is well defined, it is possible to make a reasonable separation of the β_2' and α peak areas. In Fig. 3, a comparison is made between the thermal desorption spectra of hydrogen for (a) 10 Torr s of propylene which saturates the irreversibly adsorbed adstates, and (b) 0.5 L of hydrogen which saturates β_2' adstate on the clean surface. If the α and β_2' adstates are separated by comparing the peak to the appropriate β_2' feature of the clean surface (i.e., the area outside the β_2' envelope on the low temperature side is

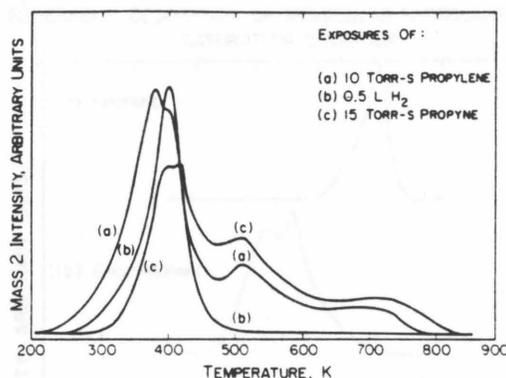


FIG. 3. Thermal desorption of hydrogen resulting from exposure of the Ir(110) surface to: (a) 10 Torr s of propylene. (b) 0.5 L of hydrogen. (c) 15 Torr s of propyne.

the α adstate area), then it can be shown that the ratio of the β_2' peak area to the γ peak area, defined as R' , is to within 5% a constant with respect to coverage, and has the value 2.0 ± 0.2 . If the α adstates of the thermal desorption spectra of hydrogen from propylene are subtracted, the resulting spectra (for equivalent coverages) appear to be identical (to within $<5\%$) in both peak maximum temperature and intensity to thermal desorption spectra of hydrogen from cyclopropane overlayers.

In Fig. 4, the coverage of the dissociatively adsorbed propylene ($\alpha + \beta_2' + \gamma$), of the β_2' and γ adstates and of the α adstate, as determined by hydrogen thermal desorption, are plotted with respect to propylene exposure. Note that the coverage of dissociatively adsorbed propylene does not vary linearly with respect to propylene exposure. The α adstate exhibits a sinusoidal development, increasing weakly between 0.5 and 5 Torr s, strongly between 5 and 7.5 Torr s, and again weakly between 7.5 and 10 Torr s. This would indicate that β_2' adsites must be nearly saturated by reaction with propylene before the α adstate begins to populate appreciably.

The thermal desorption spectra of hydrogen after adsorption of propylene and allene are shown as a function of

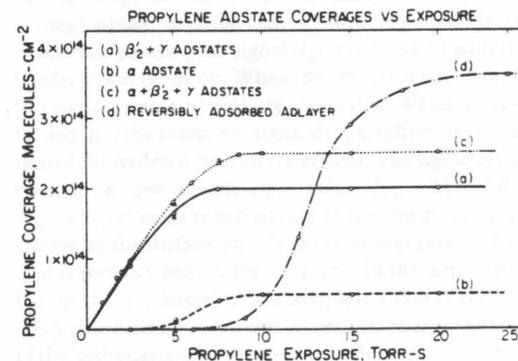


FIG. 4. Surface coverages of propylene adstates as a function of exposure to the Ir(110)-(1 \times 2) surface.

exposure in Figs. 2(B) and 2(C), respectively, with exposures of propyne of (a) 5, (b) 10, and (c) 15 Torr s, and with exposures of allene of (a) 10 and (b) 15 Torr s. Since their thermal desorption spectra were found to be very similar, the results will be discussed together. At low coverages, both exhibit a γ and a β_2 thermal desorption adstate. At exposures up to 10 Torr s, R for these hydrocarbons is 1.0 ± 0.1 , and thus the stoichiometry of the γ adstate is approximately C_3H_2 .

At high coverages, the β_2 and γ adstates show a broad trailing edge extending to ~ 800 K. This can be observed by comparing Fig. 3(c), 15 Torr s of propyne, which saturates the irreversibly adsorbed adlayer, with Fig. 3(b), 0.5 L of hydrogen, which saturates the β_2 adstate on the clean surface. Note that the intensity of the β_2 peak maximum is not so fully developed at saturation as it had been for propane, cyclopropane, and propylene. Also, note that in this case no low temperature broadening is observed. Beyond an exposure of 10 Torr s, the apparent value of R ceases to remain a constant, falling to 0.75 ± 0.1 , or an apparent stoichiometry of $C_3H_{2.3}$. However, it is possible that propyne and allene can be adsorbed at low temperatures and high coverages without dehydrogenation, due to the lack of vacant β_2 adsites. As the temperature of the surface is increased, hydrogen in the β_2 adsites desorbs, making these adsites available. The molecularly adsorbed hydrocarbon can then dehydrogenate, causing the evolution of reaction-limited hydrogen to appear as a high temperature broadening of the β_2 desorption feature. This mechanism also results in the formation of fragments which dehydrogenate in the same temperature regime as the γ adstate. This conjecture is supported by considering the ratio of the area of the β_2 adstate to the area of the γ adstate while including the high temperature broadening of the β_2 adstate. In this case, R maintains a constant value of 1.0 ± 0.1 . It appears that additional propyne or allene can adsorb on the surface after the β_2 adsites have been poisoned and that the fragments formed by their partial dehydrogenation have a stoichiometry of $\sim C_3H_2$. The absolute coverages of the irreversibly adsorbed propyne and allene adlayers, as determined by the hydrogen coverage calibration, are $(4.0 \pm 0.4) \times 10^{14}$ and $(3.6 \pm 0.4) \times 10^{14}$ molecules cm^{-2} , respectively.

2. Thermal desorption of molecular hydrocarbons

For each of the hydrocarbon molecules that has been studied, no hydrocarbon other than the one originally adsorbed was observed in the thermal desorption mass spectra. Parent peak spectra for each hydrocarbon adsorbed *molecularly* at saturation coverage are shown in Fig. 5. No desorption peaks of the molecular hydrocarbons were observed above 170 K. For propylene, propyne, and allene, only a single peak structure is observed with desorption maxima at saturation coverage between 115 and 120 K. The coverage-exposure relationship for molecularly adsorbed propylene is shown in Fig. 4(d). Note that almost no propylene is adsorbed molecularly until the *irreversibly* adsorbed adlayer approaches saturation coverage. It has also been shown that cyclopropane and propane exhibit little or no formation of

REVERSIBLE DESORPTION OF MOLECULAR HYDROCARBONS, SATURATION COVERAGE

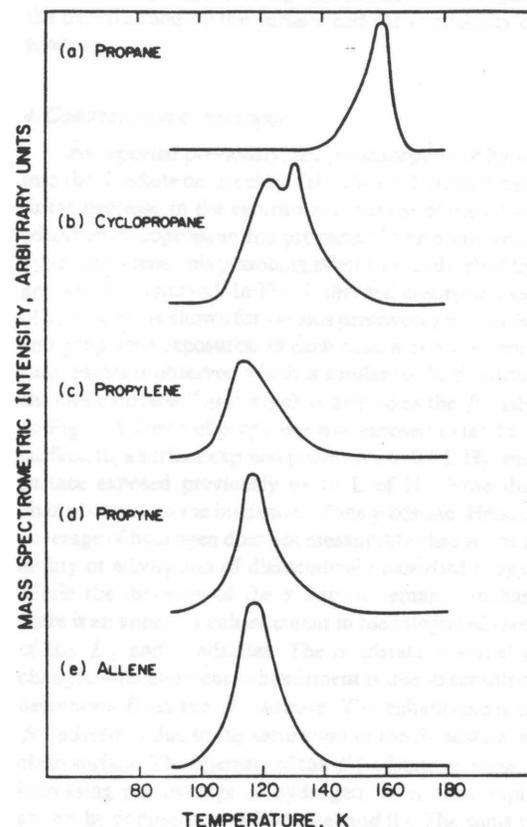


FIG. 5. Thermal desorption spectra of saturated molecular adstates on the Ir(110)-(1 \times 2) surface: (a) Propane (mass 43). (b) Cyclopropane (mass 42). (c) Propylene (mass 42). (d) Propyne (mass 40). (e) Allene (mass 40).

the molecular adlayer until saturation of the dissociatively adsorbed adlayer is completed.^{1,3}

This separation of the regimes of dissociative and molecular adsorption, coupled with the hydrogen coverage calibration which has been measured for this surface, permits the coverage of the molecular adlayer to be measured through uptake experiments.¹ In these experiments, the hydrocarbon parent peak signal (I_p) is monitored with the molecular beam doser on. When the crystal is out of the beam, this signal maintains a steady state value. When the crystal is turned into the beam, the signal drops, reflecting the adsorption of the hydrocarbon on the crystal. The signal eventually rises to a new steady-state value $I_{p,\infty}$. The difference $I_{p,\infty} - I_p$ reflects the probability of adsorption of the hydrocarbon by the surface, and the integral over time of this function is proportional to the coverage. In the initial phases of the uptake, the adsorption is completely that of the *dissociatively* adsorbed hydrocarbon molecules. Hence, the coverage of the hydrocarbon on the surface in this regime can be determined from thermal desorption spectra of hydrogen. This measurement determines the constant of proportionality

between the relative and absolute coverages for both dissociative and molecular adsorption. Using this technique, it was determined previously that the saturation coverage of molecularly adsorbed cyclopropane was $(6.6 \pm 1) \times 10^{14}$ molecules cm^{-2} . Saturation coverages of the molecular adlayers have been determined for propane to be $(4.2 \pm 0.7) \times 10^{14}$ molecules cm^{-2} , and for propylene $(3.6 \pm 0.6) \times 10^{14}$ molecules cm^{-2} .

3. Postadsorption of hydrogen and propylene on annealed propylene adlayers

A saturated adlayer of propylene annealed to 800 K retains no hydrogen. This surface retains some reactivity for subsequent dehydrogenation of propylene, but its activity is poisoned by the presence of surface carbon. This is illustrated in Fig. 6. In Fig. 6(a), the hydrogen thermal desorption spectrum after a 10 Torr s exposure of propylene on the clean surface is shown. In Fig. 6(b), the thermal desorption spectrum of hydrogen is shown after a 10 Torr s exposure of propylene to the surface which remained after the measurement of Fig. 6(a). In Fig. 6(c), the thermal desorption spectrum of hydrogen is shown after a 10 Torr s exposure of propylene to the surface which remained after the measurement of Fig. 6(b). A comparison of the integrated intensities of the thermal desorption peaks indicates that the activity of the surface is poisoned successively by $\sim 60\%$ after each exposure. The poisoning of β_2' adsites causes the decomposition of the hydrocarbon to shift to relatively higher temperatures. In Figs. 6(d) and 6(e), hydrogen thermal desorption spectra are shown for hydrogen adsorption on the surface after the measurement of Fig. 6(a), the exposures being 0.5 and 5 L of H_2 , respectively. The adsorption of hydrogen is poisoned by the carbon on the surface as well, and for the exposure of 0.5 L [which normally saturates the β_2 adstate on the clean Ir(110)-(1 \times 2) surface], the poisoning is again 60%. This is in agreement with the strong link that has

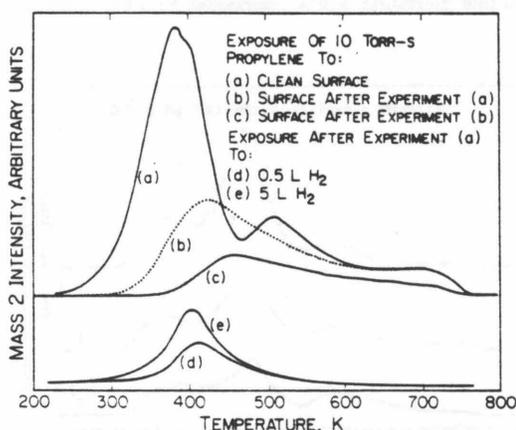


FIG. 6. Thermal desorption spectra of hydrogen resulting from exposure of 10 Torr s of propylene to: (a) The clean Ir(110) surface. (b) The surface after experiment (a). (c) The surface after experiment (b); and resulting from exposure of the surface after experiment (a); (d) 0.5 L of hydrogen. (e) 5 L of hydrogen.

already been established between surface activity for propylene dehydrogenation through abstraction of hydrogen from the hydrocarbon by the surface and the availability of β_2' adsites.

4. Coadsorption of hydrogen

As reported previously, the preadsorption of hydrogen into the β_2 adsite on the clean Ir(110)-(1 \times 2) surface causes a linear decrease in the saturation coverage of dissociatively adsorbed cyclopropane and propane.^{2,3} For propylene, propyne, and allene, this poisoning effect by preadsorbed hydrogen was not observed. In Fig. 7, thermal desorption spectra of hydrogen are shown for various precoverages of hydrogen and propylene exposures. In each case, a new low temperature feature is observed which is similar to the β_1 adstate on the clean surface,¹¹ and which is defined as the β_1' adstate. In Fig. 7, 5 Torr s of propylene was exposed to (a) the clean surface, (b) a surface exposed previously to 0.5 L H_2 , and (c) a surface exposed previously to 10 L of H_2 . Note that no changes occur in the intensities of the γ adstate. Hence, precoverage of hydrogen does not measurably change the probability of adsorption of dissociatively adsorbed propylene. While the intensity of the γ adstate remains unchanged, there is an apparent enhancement in the integrated intensity of the β_2' and α adstates. The α adstate is actually unchanged—its apparent enhancement is due to simultaneous desorption from the β_1' adstate. The enhancement of the β_2' adstate is due to the saturation of the β_2 adstate on the clean surface. The intensity of the β_1' adstate increases with increasing precoverage of hydrogen, as is most explicitly shown by comparison of Figs. 7(a) and (b). The sums of the thermal desorption areas for the separate exposures are in each case equal within experimental uncertainty to the areas obtained in the coadsorption measurements. This indicates

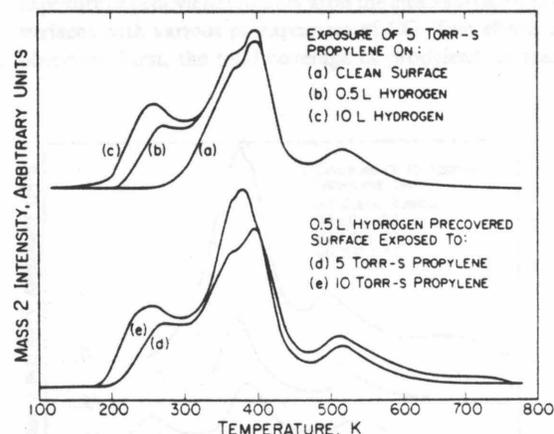


FIG. 7. Thermal desorption spectra of hydrogen resulting from exposure of 5 Torr of propylene to the following: (a) The clean Ir(110)-(1 \times 2) surface. (b) Surface (a) exposed to 0.5 L of hydrogen. (c) Surface (a) exposed to 10 L of hydrogen; and from exposure of the Ir(110)-(1 \times 2) surface to 0.5 L of hydrogen followed by exposure to: (d) 5 Torr s of propylene. (e) 10 Torr s of propylene.

that little if any preadsorbed hydrogen is desorbed during the exposure to propylene at 100 K.

In Figs. 7(d) and 7(e), 5 and 10 Torr s of propylene were exposed to a surface previously exposed to 0.5 L H₂. In both cases, the intensity of the γ adstates is unchanged compared to exposures of propylene on the clean surface. The β_1' and α adstates appear to be enhanced, again due to the previous saturation of the β_2 adstate and the concurrent desorption from the β_1' adstate, respectively. The intensity of the β_2' adstate increases with increasing propylene postexposure as well.

Similar reactivity has been observed for the adsorption of propyne and allene on surfaces preexposed to hydrogen, i.e., the formation of a β_1' adstate. Not surprisingly, the unsaturated hydrocarbon molecules react more readily with the surface than do the saturated hydrocarbons studied previously.

The formation of the β_1' adstate by postexposure of propylene to the surface precovered with hydrogen could arise from two sources. One is that hydrogen from the irreversible adsorption of propylene shifts hydrogen adsorbed in the β_2 adstate to the β_1' adstate. Another is that preadsorbed hydrogen remains unshifted, and that propylene reacts to yield β_1' hydrogen, presumably through a different mechanism. Both possibilities would cause the intensity of the β_1' adstate to increase with both increasing hydrogen and propylene exposures. The former explanation is more likely since the γ adstates observed for a given exposure of propylene are the same on both the clean and on the hydrogen precovered surfaces, suggesting that a similar reaction occurs in both cases. Moreover, such shifting of hydrogen from the β_2 to the β_1' adstate has been observed previously on this surface with the coadsorption of hydrogen and CO.¹⁵

Isotopic labeling cannot distinguish between these two possibilities. As shown in Fig. 8, isotopic exchange occurs readily among adstates during the thermal desorption experiment. Thermal desorption spectra of H₂, HD, and D₂ are shown for 10 Torr s of propylene exposed to a surface preexposed to 0.5 L of deuterium. While deuterium was initially

adsorbed only in the β_2 adstate, it appears in all adstates (β_1' , α , β_2' , and γ) in the desorption measurement. This result is similar to that reported previously for isobutane.³ The appearance of deuterium in the γ adstate indicates that exchange must occur below 400 K between the hydrocarbon fragments and the hydrogen adsorbed on the metal surface.

Previously, it was shown that the *postadsorption* of hydrogen on propane adlayers at 100 K causes an increase in the amount of propane that desorbs molecularly and a decrease in the amount of hydrogen that desorbs from the γ adstate.³ Less than 40% of the dehydrogenation reactivity remained after 4 L of hydrogen was postadsorbed on a saturated propane adlayer at 100 K. This reactivity is probably due to the fact that hydrogen is not a completely effective poison under these conditions, rather than a residual reactivity of the surface at 100 K. For cyclopropane and propylene, this effect was not observed. No increases were observed in the concentration of the molecularly adsorbed hydrocarbons when hydrogen was postadsorbed, i.e., both cyclopropane and propylene are chemisorbed strongly at 100 K. At saturation coverages of the dissociatively adsorbed adlayers of cyclopropane and propylene, no additional hydrogen was observed to adsorb (i.e., $< 10^{13}$ molecules cm⁻²).

5. Coadsorption of CO

The coadsorption of CO can be used to determine the relative energetics of chemisorption of surface species. On the Ir(110)-(1 × 2) surface, it can be used to help differentiate between reaction-limited and desorption-limited hydrogen that is observed in thermal desorption spectra. The coadsorption of CO has been carried out with propane, cyclopropane, and propylene. In all cases investigated, the preadsorption of CO causes the dissociative adsorption of these three hydrocarbon molecules to be poisoned, i.e., no hydrogen desorbs when 2.5 L of CO is preadsorbed. Thermal desorption spectra of hydrogen are shown in Fig. 9 for a saturation exposure of propylene (10 Torr s) on the clean surface and on surfaces with various preexposures of CO. Two effects are observed. First, the total coverage of propylene decreases

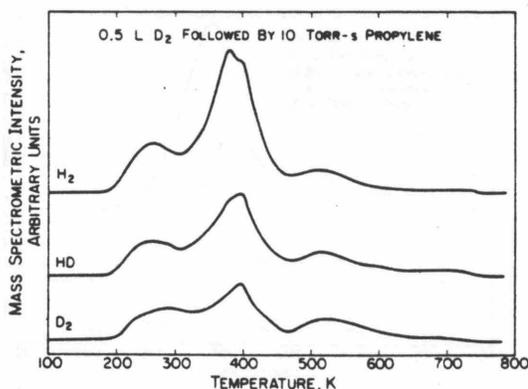


FIG. 8. Thermal desorption spectra of H₂, HD, and D₂ following exposure of the Ir(110)-(1 × 2) surface to 0.5 L of deuterium followed by 10 Torr s of propylene.

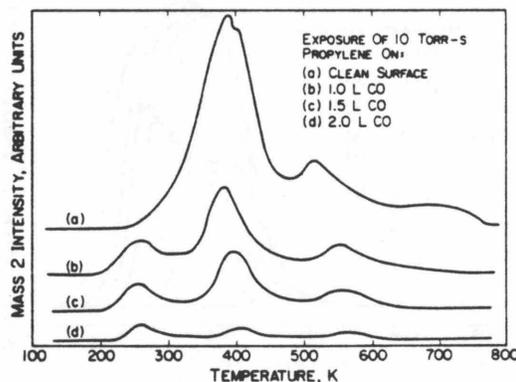


FIG. 9. Thermal desorption spectra of hydrogen following exposure of 10 Torr s of propylene to the clean and CO-precovered surfaces as shown.

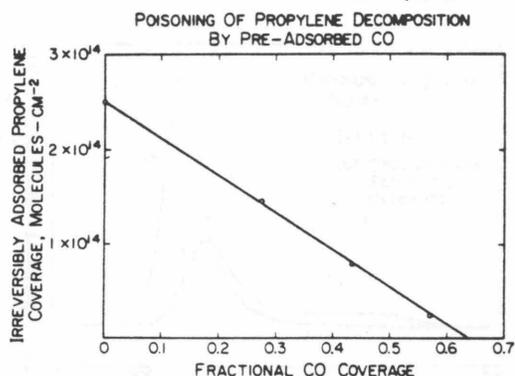


FIG. 10. Irreversibly adsorbed adlayer coverage as a function of precoverage of CO.

with increasing preexposure to CO and second, the presence of CO on the surface induces the desorption of hydrogen from the β'_1 adstate. The latter has been observed previously for the coadsorption of hydrogen and CO on the clean surface, and for the exposure of other hydrocarbons on surfaces which were preexposed to CO.^{3,15} The total saturation coverage of dissociatively adsorbed propylene decreases linearly in precoverage of CO, as shown in Fig. 10.

The postadsorption of CO on surfaces preexposed to propane at 100 K has been shown to cause two effects.³ As with the postadsorption of hydrogen, a decrease in the amount of dissociatively adsorbed propane and an increase in the amount of molecularly adsorbed propane are observed. In addition, the postadsorption of CO can cause a shifting of hydrogen from the β_2 adstate to the β'_1 adstate. The former is not observed for the postadsorption of CO on surfaces preexposed to cyclopropane and propylene. However, the shifting of hydrogen from the β_2 adstate to the β'_1 adstate has been observed for both of these hydrocarbons as well. Thermal desorption spectra of hydrogen are shown in Fig. 11 after the postexposure of 2 L of CO on surfaces with preexposures of propylene of (a) 2.5, (b) 6 and (c) 10 Torr s.

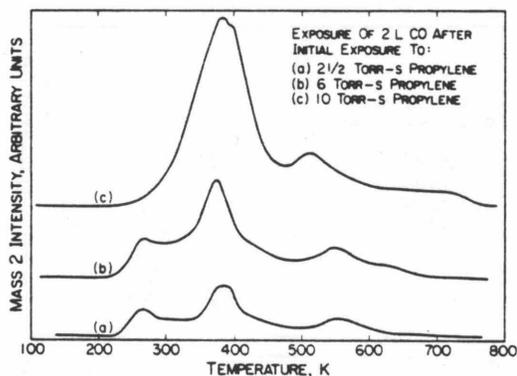


FIG. 11. Thermal desorption spectra of hydrogen after exposure of 2 L of CO to the Ir(110)-(1 × 2) surface preexposed to: (a) 2.5, (b) 6, (c) 10 Torr s of propylene.

Figure 11(c) is identical to that which would be observed in the absence of the postexposure to CO. Corresponding thermal desorption spectra of CO show that almost no CO desorbs from the surface preexposed to 10 Torr s of propylene. Similar thermal desorption spectra of CO from surfaces with other preexposures to propylene indicate that the irreversibly adsorbed propylene poisons the postadsorption of CO. The thermal desorption spectra in Figs. 11(a) and 11(b) show the shifting of hydrogen from the β_2 adstate to the β'_1 adstate. However, desorption of the α adstate occurs in the same temperature regime (along with some hydrogen which has not been shifted from the β_2 adstate) as in the absence of postadsorbed CO. This is a further indication that the α adstate is a reaction-limited as opposed to a desorption-limited adstate.

B. Adsorption on Ir(111)

Clearly, the β_2 adsites cause a characteristic dehydrogenation reaction to occur for a variety of hydrocarbons adsorbed on the Ir(110)-(1 × 2) surface. For comparison, the adsorption of hydrogen, propane, cyclopropane, and propylene has been investigated on the close-packed Ir(111) surface. The fourfold hollow sites of the Ir(110)-(1 × 2) surface, which are apparently related to the reactive β_2 adsite, are not present on the (111) surface, except possibly at defect and step sites. The LEED pattern of the clean crystal did not exhibit any spot splitting, which would be indicative of a regularly stepped surface. However, the kinetics of both adsorption and desorption of hydrogen indicate the presence of defects, the concentration of which is ~2.5%–5% of the concentration of surface sites.¹⁶

In order to quantify the coverages of dissociatively adsorbed hydrocarbons on the Ir(111) surface, it was necessary to measure the coverage–exposure relationship for hydrogen. The thermal desorption spectra resulting from the adsorption of hydrogen on the clean surface are shown in Fig. 12 for exposures ranging from 0.5 to 250 L. At saturation coverage, it is assumed that the number of adsorbed hydrogen atoms is equal to the number of exposed iridium atoms at

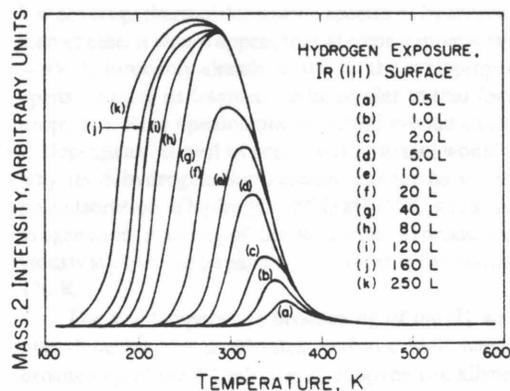


FIG. 12. Thermal desorption spectra of hydrogen as a function of exposure of hydrogen to the Ir(111) surface.

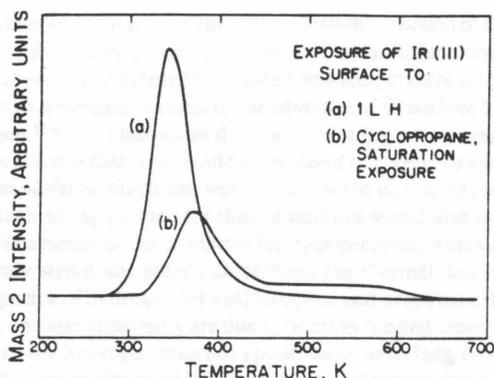


FIG. 13. Thermal desorption spectra of hydrogen resulting from exposure of the Ir(111) surface to: (a) 1.0 L of hydrogen. (b) 10 Torr s of cyclopropane (saturation).

the surface. If the adsorption of hydrogen on the Ir(111) surface is similar to that observed on the Pt(111) surface by Christmann and Ertl, then this estimate should be correct to within $\sim 10\%$.¹⁷

The dissociative adsorption of propane and cyclopropane on this surface was similar. In both cases, the thermal desorption spectra of hydrogen for saturation coverages of these alkanes were very similar and revealed that little hydrogen desorption occurred. In Fig. 13 thermal desorption spectra of hydrogen are shown for (a) 1 L exposure of hydrogen, and (b) saturation exposure of cyclopropane. Since the irreversible adsorption of one cyclopropane molecule results in the desorption of three hydrogen molecules, $\sim 1 \times 10^{13}$ molecules cm^{-2} adsorb dissociatively. For propane, the corresponding value is less than 5×10^{12} molecules cm^{-2} . Both of these estimates are approximately a factor of 20 less than the similar values for dissociative adsorption on the Ir(110)-(1 \times 2) surface,^{1,3} and indicate that the reaction occurs at defect sites.

The dissociative adsorption of propylene on the Ir(111) surface resulted in considerably different thermal desorption

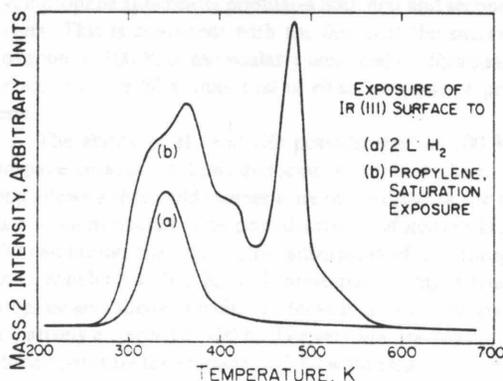


FIG. 14. Thermal desorption spectra of hydrogen resulting from exposure of the Ir(111) surface to: (a) 10 Torr s of propylene (saturation). (b) 2 L of hydrogen.

spectra of hydrogen than were observed for the alkanes. In Fig. 14 spectra are shown for (a) an exposure of 10 Torr s of propylene, which saturates the irreversibly adsorbed adlayer, and (b) an exposure of 2 L of hydrogen to the clean surface. No attempt has been made at a detailed interpretation of the dehydrogenation reactions associated with the propylene adlayer. The saturation coverage of the dissociatively adsorbed adlayer of propylene is estimated to be 3.9×10^{14} molecules cm^{-2} . It is apparent that the chemistry of dehydrogenation of hydrocarbons on the Ir(111) surface is very much a function of the particular molecule adsorbed.

IV. DISCUSSION

The five hydrocarbon molecules investigated are structurally similar as a group only in that each one has a three-carbon atom framework. Yet certain aspects of their chemistry on the Ir(110)-(1 \times 2) surface are quite similar. All undergo dissociative adsorption to form surface hydrogen and stable hydrocarbon fragments. Dehydrogenation occurs preferentially at the β_2' adsite when it is vacant. In each case, the (relatively) stable γ fragments that are formed have a stoichiometry of approximately C_3H_2 . Hydrocarbons with the same initial stoichiometry, i.e., cyclopropane and propylene, or propyne and allene, show very similar thermal desorption spectra of hydrogen for the same coverages. Sufficiently strong adsorbates poison the β_2' adsite, limiting the dehydrogenation reactivity of the surface.

It has been proposed previously that the hydrocarbon fragment corresponding to the γ adstate of hydrogen may be formed from the parent molecule by total dehydrogenation of the first and third carbon atoms leaving a bridging methylene group which is stable so long as carbon-carbon bonding is thermally stable.³ Such an argument explains easily the stoichiometry of the fragments formed in the case of propane and cyclopropane. In the case of the other three hydrocarbons, hydrogen from the first and third carbon atoms migrates to the second carbon atom by 1,2 shifts. Such shifts are certainly facile, as has been indicated by the rapid hydrogen-deuterium exchange into the γ adstates. This would explain how such differing pairs of molecules as cyclopropane and propylene, and propyne and allene could have such similar low coverage thermal desorption spectra of hydrogen. In the former case, it would appear that at some temperature below ~ 450 K (probably already at 100 K) the cyclopropane ring opens, causing its fragment to be similar to that formed by propylene. Ring opening due to partial π -bond character of cyclopropane (as well as possibly ring strain) would explain why its dehydrogenation reaction cannot be inhibited by postadsorption of hydrogen or CO at 100 K, while the dehydrogenation reaction of the saturated hydrocarbons previously studied can be partially inhibited in this fashion up to 130 K.

The low temperature broadening of the β_2' adstate of propylene (or the α adstate), and the high temperature broadening of the β_2' adstates of propyne and allene which occurs after the β_2' adsites have been saturated have not been observed with the saturated hydrocarbons studied previously. These are the hydrocarbons that might be expected to

chemisorb strongly to the surface through reaction of their π bonds to form strong metal-carbon bonds. Recent work has shown that ethylene also shows a low temperature α state at high coverages, outside of the envelope of β_2 surface hydrogen.¹⁸ Since these states develop only at higher coverages, it is possible that they would correspond to reversible adstates on surfaces which are less active toward dehydrogenation. Such an explanation for these α adstates would also explain the absence of the α adstate for cyclopropane, which is the only significant difference between the thermal desorption spectra of hydrogen for cyclopropane and propylene. These α adstates apparently are due to reaction-limited desorption, i.e., the hydrogen does not appear to be desorbing from β_1 -like adsites. On Pt(111), Salmeron *et al.* observed that propylene has two reversible adstates: one at 140 K and one at 280 K.⁸ On the Ir(110)-(1 \times 2) surface only an adstate corresponding to the lower temperature one on the platinum surface is observed. Such a species presumably chemisorbs through its π bond to the surface, and on the Ir(110)-(1 \times 2) surface dehydrogenation occurs as opposed to desorption. On the Pt(111) surface, fragments formed from acetylene have greater high temperature stability than fragments formed from ethylene.⁸ Hence, the high temperature (rather than low temperature) dehydrogenation of the high coverage adstates of propyne and allene appears to be reasonable. The formation of these adstates accounts for most of the increase in the coverage of the dissociatively adsorbed adlayers for the unsaturated hydrocarbons as compared to the saturated hydrocarbons.

The temperatures of the intensity maxima of desorption of the molecular adlayers appear to correlate inversely with the saturation coverages of the corresponding dissociatively adsorbed adlayers. The indication is that these states still interact with the metal surface, and that this interaction weakens with increasing dissociative adlayer coverage due to some combination of site blocking and electronic effects. The molecular adstate of propane interacts strongly with the metallic substrate, and it is probably a part of the first adlayer. The molecular states of propylene, propyne, and allene interact much more weakly, and they appear to constitute a second adlayer. The molecular overlayer of cyclopropane apparently populates both first and second adlayers. This is consistent with the fact that the saturation coverage at 100 K of molecularly adsorbed cyclopropane is greater by over 50% than that of either propane or propylene.

The ability of H₂ and CO postadsorbed at 100 K on propane adlayers to limit dissociative propane chemisorption allows a threshold temperature of the dissociation reaction to be measured. The postadsorption of neither H₂ nor CO can inhibit the dissociative adsorption of cyclopropane and propylene at 100 K, and, presumably, this is true for propyne and allene as well, i.e., these hydrocarbons are dissociatively adsorbed at 100 K. The very low reaction threshold temperature for propane (130 K) would lead us to believe that a reaction threshold temperature of below 100 K for these less saturated hydrocarbons is not unreasonable. For cyclopropane, such a conclusion is in agreement with pre-

vious UPS results which show little or no indication of molecular cyclopropane until the dissociatively adsorbed overlayer is saturated.¹

The relative poisoning ability of hydrogen toward the irreversible adsorption of cyclopropane and propylene apparently would indicate that the ability to form a strong surface bond without necessarily breaking a carbon-hydrogen bond is the crucial difference. Hence, cyclopropane acquires the character of a molecule containing a π bond, i.e., reactivity at 100 K and high coverage of the irreversible adlayer, only in the presence of vacant β_2 adsites. When these sites are poisoned, cyclopropane acts like a fully saturated hydrocarbon. Hence, the dissociative adsorption of cyclopropane is poisoned by the preadsorption of hydrogen, and cyclopropane does not show broadening of the β_2 adstate with increasing coverage of the dissociatively adsorbed overlayer.

Stronger poisons, such as surface carbon and CO, limit the dissociative adsorption of all five hydrocarbons. On the carbon-covered surface formed by the dehydrogenation of the dissociated adlayers, the relative decrease in the saturation coverage of the dissociatively adsorbed adlayer is the same as that for hydrogen adsorbed in the β_2 adstate. This shows directly the importance of the β_2 adsite for this dehydrogenation reaction. The shifting of hydrogen adsorbed in the β_2 adstate to the β_1 adstate by the coadsorption of CO made such a direct measurement difficult for this poison. However, it was demonstrated that the poisoning ability of CO toward this reaction was linear in its coverage.

The adsorption measurements on the Ir(111) surface indicate clearly the importance of the β_2 adsites for the dehydrogenation of propane and cyclopropane under our reaction conditions. The small extent of irreversible adsorption was certainly caused by defect sites on the surface. The reactivity of the unsaturated hydrocarbons was more clearly related to individual differences in molecular electronic and geometric structure than to the dominance of any surface adsite. Apparently the reactivity of saturated hydrocarbons with the Ir(110)-(1 \times 2) surface is due to some combination of a geometric effect and an electronic effect induced by its particular surface geometry.

V. CONCLUSIONS

On the Ir(110)-(1 \times 2) surface, all five hydrocarbons investigated exhibit irreversible adsorption initially, leading to the formation of surface fragments of approximate stoichiometry C₃H₂. This occurs in spite of the differences in their electronic and geometric structure. Upon saturation of the β_2 adsites, these structural differences are reflected in that the unsaturated hydrocarbons exhibit dissociatively adsorbed adstates which appear to be formed through the reaction of π electrons. All five hydrocarbons form molecularly adsorbed adstates at low temperatures. In all cases, surface carbon and CO were found to act as poisons to the β_2 adsite of hydrogen and toward its particular dehydrogenation reaction. The poisoning ability of hydrogen varied inversely with the π -bond character of the molecule. Similar studies on the Ir(111) surface demonstrated the importance of the β_2 adsite

on the Ir(110)-(1×2) surface, since reactivity on the close-packed surface varied with the structure of the hydrocarbon and was not dominated by any particular surface adsite.

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CHAPTER 4

THE ADSORPTION AND REACTION OF NORMAL

ALKANES ON THE PT(110)-(1x2) SURFACE

(The text of Chapter 4 consists of an article coauthored with J. R. Engstrom and W. H. Weinberg which has been submitted to The Journal of Physical Chemistry.)

Abstract

The interaction of ethane, propane, n-butane and n-pentane with the reconstructed Pt(110)-(1x2) surface has been investigated, principally using mass spectrometry. Ethane and propane exhibit only weak molecular chemisorption, whereas low coverages of n-butane and n-pentane undergo dissociative adsorption at approximately 200 K to form surface hydrogen and hydrocarbon fragments. The surface site required for dissociation is similar to that for the adsorption of hydrogen at lower coverages, since dissociative adsorption is inhibited strongly by surface hydrogen. Similar activation of alkanes has been observed previously for the Ir(110)-(1x2) surface, but on the close-packed Pt(111) and Ir(111) surfaces dissociative adsorption of these alkanes is either not observed or occurs only at defect sites. Thus surface geometry exhibits a strong influence on C-H bond activation in alkanes.

1. Introduction

The interaction of saturated hydrocarbon molecules with the Pt(110)-(1x2) surface has been studied by thermal desorption mass spectrometry and low-energy electron diffraction (LEED). This work was motivated by previous results concerning the interaction of saturated hydrocarbons with the Ir(110)-(1x2) surface and the (111) surfaces of Ir and Pt (1-6). On the Ir(110)-(1x2) surface all alkanes except methane adsorb dissociatively at low surface coverages and at temperatures below 130 K (1-4). These reactions are limited by the availability of high coordination β_2' adsites (1). The activation of carbon-hydrogen bonds liberates hydrogen, which eventually saturates these sites. For the normal alkanes from C₂ through C₇ saturation coverages of the dissociatively adsorbed overlayers is on the order of 1×10^{14} molecules-cm⁻². No evidence was found for hydrogenolysis products arising from reaction of the hydrocarbons with surface hydrogen. On the Ir(111) surface, similar dissociation reactions are observed only at defect sites (2,3). Saturation coverages of the dissociatively adsorbed overlayers are at least twenty times less than the corresponding coverages on the (110)-(1x2) surface. Furthermore, the normal alkanes from ethane through octane exhibit no significant reactivity with the Pt(111) surface under ultrahigh vacuum conditions (5,6). These results suggest that the availability of high coordination adsites is critical in lowering the activation barriers that must be overcome in cleaving carbon-hydrogen bonds in alkanes.

The results presented here concerning the interaction of alkanes with the (110)-(1x2) surface of platinum extend further the understanding of the effect of surface geometry and electronic structure on the activation of alkanes. Although the exchange of deuterium into benzene adsorbed on the Pt(110) surface has been observed(7), to our knowledge the interaction of saturated hydrocarbons under ultrahigh vacuum conditions has not been investigated

previously on this surface of platinum. The alkanes studied include ethane, propane, n-butane and n-pentane. Neither molecular nor dissociative adsorption of methane could be observed under our experimental conditions, namely surface temperatures above 100 K.

2. Experimental Procedures

The experiments were performed in an ion-pumped stainless steel bell jar which has been described in detail previously (8). The base pressure of the bell jar was below 2×10^{-10} Torr of reactive contaminants. The Pt(110) crystal was cut from a single crystal of platinum and was polished to within 1° of the (110) orientation using standard metallographic techniques. The crystal was etched in aqua regia and cleaned by argon ion sputtering at high temperatures (1200 K), high temperature annealing (1400 K) and heating in oxygen at 800 K and 5×10^{-7} Torr. Auger electron spectroscopy was used to verify surface cleanliness. The determination of the presence of silicon by Auger spectroscopy is complicated by the overlap of its LMM transition at 92 eV with the platinum ONN transition. On Pt(111) both surface and subsurface silicon can be oxidized and the presence of silicon inferred from the oxygen transition of its oxide (9). Silicon was present in our sample, and was removed by several cycles of oxidation and argon ion bombardment. The formation of silicon oxide species was minimized subsequent to this treatment by cleaning the crystal of carbidic carbon with oxygen at 5×10^{-8} Torr for five minutes at temperatures less than 600 K, followed by annealing to 1000 K to ensure desorption of surface oxygen (10). The Auger electron spectrum of the clean surface is in good agreement with that published recently by Mundschau and Vanselow (11) for a surface from which impurities such as sulfur, phosphorous and silicon have been removed. After cleaning and annealing, the (1x2) LEED pattern characteristic of the surface

reconstruction of the clean surface could be observed. Streaking was observed at times in the fractional-order beams, indicating that some disorder was present across the close-packed rows. This has been observed in other investigations of the Pt(110)-(1x2) surface (12). The missing row model of the surface reconstruction accounts for data obtained by Rutherford backscattering (12) and by helium atom diffraction (13), and is the only model of the several that have been proposed which is in agreement with recent results from low energy alkali impact collision ion spectroscopy (14).

The adsorption temperature was 100 K for ethane and propane and 150 K for n-butane and n-pentane. The higher adsorption temperatures for the latter were employed to minimize the adsorption of hydrogen from the background, since these two alkanes adsorb dissociatively. The hydrocarbons used were purified cryogenically, and the purity was verified by mass spectrometry.

3. Results

3.1 Thermal Desorption of Hydrogen

A knowledge of the thermal desorption spectra of hydrogen adsorbed on the clean surface as a function of coverage is necessary to interpret the desorption spectra of hydrogen resulting from the dissociative adsorption of these hydrocarbons. In Fig. 1 the thermal desorption spectra are shown for exposures of hydrogen of (a) 0.02 L, (b) .05 L, (c) 0.5 L, (d) 2.0 L, (e) 20 L and (f) 50 L. In assigning the absolute surface coverage, we have used the value of Jackman *et al.* (12) from nuclear microanalysis, namely a saturation coverage of 1.1×10^{15} atoms-cm⁻² at 170 K. A study of the adsorption and desorption kinetics as a function of hydrogen coverage will be published separately (15). These spectra are in good agreement with those published previously by Ferrer and Bonzel (16). The state that desorbs above 300 K has a considerably higher probability of

adsorption than does the state which desorbs at lower temperatures. We label these two adstates β_2 and β_1 , respectively. The coverage-exposure relation suggests that there are two consecutive regimes obeying second order adsorption kinetics which have different "initial" probabilities of adsorption, which we estimate to be unity and 5×10^{-3} , respectively. The saturation coverage of the β_2 adstate appears to be half that estimated for the β_1 adstate, based on an extrapolation of the coverage-exposure curve. On the Ir(110)-(1x2) surface, the β_2 adstate, which has its desorption maximum at 400 K, exhibits first order adsorption kinetics with an initial probability of adsorption of unity, while the lower temperature β_1 adstate exhibits second order adsorption kinetics with a much lower "initial" probability of adsorption, namely 7×10^{-3} (17). The β_2 adstate accounts for one-third of the adsorbed hydrogen. These differences were attributed to the differences in coordination at the two adsites. Apparently the two desorption states on the Pt(110)-(1x2) surface arise also from desorption from two different sites.

3.2 Thermal Desorption of Hydrogen and Alkanes from Alkane Overlayers

The interaction of ethane, propane, n-butane and n-pentane with the Pt(110)-(1x2) surface has been characterized by thermal desorption mass spectrometry. In all cases the only hydrocarbon that is observed to desorb is the parent alkane. For ethane and propane only desorption of the molecularly adsorbed alkane is observed. As shown in Fig. 2A and 2B, this occurs at 140 K and 175 K respectively. For n-butane and n-pentane only the desorption of hydrogen is observed after such low exposures to the surface. The thermal desorption spectra of hydrogen are shown as a function of exposure in Fig. 3A for n-butane and in Fig. 3B for n-pentane. Both desorption-limited and reaction-limited evolution of hydrogen occurs. The hydrogen desorption peak

near 320 K is due to desorption from the metal surface (cf. Fig. 1), whereas the peaks at approximately 400 and 550 K are due to decomposition of hydrocarbon fragments adsorbed on the surface. The surface coverage of dissociatively adsorbed molecules at saturation in units of 10^{19} molecules-cm⁻² is 6.0 ± 0.6 for n-butane and 7.5 ± 0.8 for n-pentane, based on the hydrogen coverage data of Jackman *et al.* (12). The amount of surface hydrogen which results from a saturation coverage of n-butane is 55% of that required to saturate the β_2 adstate, while for n-pentane the corresponding value is 70%. The ratios of the areas of the peaks at 320, 400 and 550 K are estimated to be 5:3:2 for n-butane and 5:5:2 for n-pentane. Overlap of these desorption peaks introduces an error of at least 20% to these values. Molecular desorption of the parent hydrocarbon accompanies dissociative adsorption at higher exposures, as may be seen in Fig. 2C for n-butane and 2D for n-pentane. At lower coverages desorption occurs at 210 and 245K respectively, while at higher coverages a second desorption state is observed at 160 and 190 K. Desorption of multilayers should occur at the same temperatures as observed on the Ir(110)-(1x2) surface, at 110 and 140 K, respectively (4). After the thermal desorption experiments, surface carbon is readily detectable by Auger spectroscopy. The fractional-order LEED beams, which are characteristic of the surface reconstruction, do not appear to have changed in relative intensity compared to the clean surface.

3.3 Thermal Desorption from Annealed Alkane Overlayers

Several experiments were conducted to investigate the stability of the hydrocarbon fragments, the presence of which are evident from the reaction-limited desorption of hydrogen. If an adlayer of n-butane or n-pentane is annealed to 320 K for times on the order of one minute, and then cooled to 150 K, a thermal desorption spectrum of the resulting surface reveals that no

change in intensity occurs for the reaction-limited desorption of hydrogen. This is shown in Fig 4, in which the thermal desorption spectrum of hydrogen in (a) results from exposure of the clean surface to 1.0 L of n-pentane, while that shown in (b) results from the same exposure of n-pentane annealed, as described above, for 30 s. Above 400 K the spectra are identical, indicating that the hydrocarbon fragments on the surface, which are manifest by the high temperature desorption states, are stable in the presence of the vacant surface sites at which hydrogen may be adsorbed.

The adsites which give rise to the thermal desorption peak of hydrogen at 320 K are apparently the sites responsible for dissociative adsorption of n-butane and n-pentane. The dissociative adsorption of these alkanes saturates upon exposure of 1.0 L at 150 K. However, if these overlayers are annealed to 320 K, so that surface hydrogen desorbs, and are then cooled to 150 K and reexposed to the alkane, the intensity of the reaction-limited high temperature desorption of hydrogen increases. In Fig. 4(c) the thermal desorption of hydrogen is shown which results from an exposure of 1.0 L of n-pentane at 150 K, annealing the surface to 320 K for 30 s, cooling to 150 K, and then reexposing the surface to 1.0 L of n-pentane. An increase in intensity of approximately 70% in the reaction-limited desorption of hydrogen at 400 and 550 K occurs. This indicates that the dissociative adsorption of alkanes requires the same site as that for the high temperature desorption state of hydrogen on the clean surface.

A saturated overlayer of n-pentane annealed to 700 K retains no hydrogen, and results in the formation of surface carbon. This surface retains approximately 90% of its initial activity toward dissociative adsorption of n-pentane. In Fig. 5(a), the hydrogen thermal desorption spectrum is shown after an exposure of 1.0 L of n-pentane to the clean surface, whereas in 5(b) the corresponding

spectrum is shown for an exposure of 1.0 L of n-pentane to the surface which resulted after the measurement of 5(a). The shifting of the reaction-limited desorption states to higher temperatures is evidently caused by the presence of surface carbon. The LEED pattern observed after this experiment possesses all the beams characteristic of the (1x2) reconstruction. After five cycles of exposure of 1.0 L of n-pentane, annealing to 700 K and cooling to 150 K, the saturation coverage of the dissociatively adsorbed n-pentane has decreased by 50%. The desorption temperature for low coverages of the molecularly adsorbed n-pentane shifts to approximately 200 K from 245 K. The fractional-order LEED beams are almost completely extinguished at this point, resulting in a (1x1) pattern which has high background intensity. Thus high carbon concentrations can remove the surface reconstruction. An ultimate reactivity of n-pentane of 4.0×10^{14} molecules-cm⁻² can be estimated from these experiments.

3.4 Coadsorption of Hydrogen and Alkanes

The strong dependence of dissociative adsorption of alkanes on the availability of the high temperature hydrogen adsorption site on the Pt(110)-(1x2) surface suggests that preadsorption of hydrogen would inhibit activation of C-H bonds in alkanes by this surface. In Fig. 6(a) the thermal desorption spectrum of hydrogen is shown for an exposure of 1.0 L of n-butane to a surface previously exposed to (a) 0.02 L of hydrogen (background exposure); (b) 0.05 L of hydrogen; and (c) 0.5 L of hydrogen. The reaction-limited desorption of hydrogen at 400 and 550 K is absent in spectrum (c), indicating that no dissociative adsorption of n-butane occurs. Similar results have been obtained for n-pentane. This inhibition in dissociatively adsorbed alkanes is related linearly to the precoverage of hydrogen. The inhibition is complete after an exposure of only 0.5 L of hydrogen, which corresponds to approximately one-third of the

amount of hydrogen that can be adsorbed on the clean surface (cf. Fig. 1). As adsorption of hydrogen from the background could not be avoided in our experiments due to the high adsorption probability of hydrogen at low coverages, the saturation coverages of n-butane and n-pentane quoted above were obtained by linear extrapolation to zero hydrogen precoverage.

The effect of postadsorption of hydrogen on overlayers of n-butane and n-pentane depends on the thermal history of the alkane overlayer, due to the activated and irreversible nature of the dissociative adsorption of these alkanes. If either n-butane or n-pentane is adsorbed at 150 K and 0.5 L of hydrogen is then exposed to the surface while it is still at 150 K, the dissociative adsorption of the alkane is inhibited completely. However, if the alkane overlayer is annealed to higher temperatures, the inhibition effect can be suppressed. In Fig. 7 thermal desorption spectra of hydrogen are shown for an exposure of 0.5 L of hydrogen on a surface exposed previously to 1.0 L of n-pentane which had been annealed for 30 s to (a) 150 K, (b) 180 K and (c) 200 K. The desorption of hydrogen from the high temperature states in spectrum (c), and the desorption from the molecular state are identical to that which results for exposure of the clean surface to 1.0 L of n-pentane at 150 K, indicating that dissociation has gone to completion after 30 s at 200 K. The desorption of molecular n-pentane which occurs in experiment (a) is approximately equal to that for adsorption of 1.5 L of n-pentane at 150 K, due to the complete inhibition of dissociation by surface hydrogen. The increase in the reaction-limited desorption of hydrogen and the decrease in desorption of the molecularly adsorbed alkanes with increasing annealing temperatures demonstrates that the dissociation of these alkanes is activated, and will go to completion in under one minute by approximately 200 K.

The coadsorption of deuterium was investigated to determine if exchange could occur between hydrogen in the hydrocarbon fragments and hydrogen adsorbed on the surface of the metal. If such exchange occurs, the use of deuterium labeling of these alkanes to reveal structural information in thermal desorption studies is complicated by mixing between states. In Fig. 8 the thermal desorption spectra of masses 2 and 3 are shown for exposure of the surface to 0.02 L of deuterium followed by 1.0 L of n-pentane. Some coadsorption of background hydrogen occurs as well. The desorption of HD from the reaction-limited high temperature desorption states proves that exchange of surface deuterium into the hydrocarbon fragments occurs. Such exchange is incomplete, however, since the relative intensity of the features at 400 and 550 K compared to that at 320 K is approximately half as much in the HD spectrum compared to the H₂ spectrum. The partial exchange observed here is in qualitative agreement with the rates measured by Surman *et al.* (7) for the exchange of deuterium into benzene adsorbed on this surface.

4. Discussion

The dissociative adsorption of alkanes on the Pt(110)-(1x2) surface is an activated process, which at 200 K occurs at a sufficiently high rate that it competes effectively with desorption from the molecularly chemisorbed states of these alkanes. Thus the dissociative adsorption of methane, ethane and propane could not be observed under our (low pressure) experimental conditions, since desorption of the molecularly adsorbed state occurs below this temperature. For n-butane and n-pentane the higher desorption temperature of molecular chemisorption allows their dissociation to be observed. The surface site which is critical to the initial step of carbon-hydrogen bond activation appears to be the same one at which dissociatively adsorbed hydrogen (from molecular hydrogen)

is bound and which has been defined as the β_2 adstate. The saturation of this site by hydrogen prevents dissociative adsorption of n-butane and n-pentane. This accounts for the following aspects of the dissociative adsorption of alkanes on this surface: (1) The dissociatively adsorbed overlayer saturates at an adsorption temperature of 150 K; (2) The surface is reactivated for further dissociative adsorption by the desorption of surface hydrogen; (3) Dissociative adsorption is inhibited both by the preadsorption of hydrogen into the β_2 adstate and by the postadsorption of hydrogen onto non-dissociated alkane overlayers at low temperatures. The studies involving the postadsorption of hydrogen demonstrate further the existence of a kinetic barrier to dissociation which can be overcome near 200 K.

The activity of the Pt(110)-(1x2) surface toward dissociative adsorption of alkanes can be compared to that exhibited by the Ir(110)-(1x2) surface (1-4). The kinetic barrier to dissociative adsorption is not so great on iridium, since on that surface the activation of carbon-hydrogen bonds occurs readily near 130 K. Thus ethane and propane adsorb dissociatively on the Ir(110)-(1x2) surface under our experimental conditions (1). Their desorption temperatures of 140 K and 175 K on the platinum surface, which should be similar to the values on iridium if the dissociative adsorption did not occur, are in accord with such a temperature for overcoming the activation barrier. Molecular desorption of ethane and propane on the Ir(110)-(1x2) surface occurs at 120 and 155 K, respectively. This difference in kinetic barriers correlates with the estimated energetic differences in the two product states. Whereas the metal-hydrogen bond strengths are probably equal, the metal-carbon bonds formed on the iridium surface should be stronger than those formed on the platinum surface, since metal-carbon bond strengths for diatomic metal carbides are greater for iridium than for platinum [150 compared to 145 (+- 1) kcal/mole (18)].

The hydrocarbon fragments formed on the platinum surface, which are manifest as the reaction-limited thermal desorption states of hydrogen, have a higher hydrogen content than those formed on the iridium surface. The greater dehydrogenation activity of iridium is reflected not only in the higher desorption temperature of hydrogen from the clean surface, but also in the activation of ethane and propane by this surface. While a simple model involving metallacycles was proposed to explain fragment stoichiometries on the iridium surface (1), it is apparent that such a model does not readily explain the stoichiometries observed on platinum. The higher desorption temperature for surface hydrogen on iridium also accounts for the complete exchange of surface deuterium into the hydrocarbon fragments formed on that surface, while on platinum such exchange occurs but is kinetically limited and incomplete. In both cases deuterium labeling of the hydrocarbon does not reveal structural information directly in thermal desorption mass spectrometry due to the exchange reaction.

The molecular desorption of these alkanes at low coverages occurs at temperatures approximately 30 K higher on the Pt(110)-(1x2) compared to same surface of iridium. At higher coverages the desorption temperatures of n-butane and n-pentane shift to values similar to those observed on iridium. Such a shift is also observed for adsorption onto the carbon residue. Since the coverages of dissociatively adsorbed alkanes are lower on the platinum surface, this suggests that the higher desorption temperatures represent desorption of the alkane from a metal surface site, while the lower desorption temperatures represent desorption from a site where surface carbon or hydrocarbon fragments screen the interaction between the alkane and the metal.

While high concentrations of surface carbon did not relax the reconstruction of the Ir(110)-(1x2) surface, the fractional-order LEED beams characteristic of the surface reconstruction are virtually extinguished under similar

conditions for platinum. Stabilization of the unreconstructed Pt(110) surface by carbon has also been noted by Ferrer and Bonzel (16). Relaxation of the surface reconstruction for the (110) surface of platinum, but not for iridium, occurs under certain conditions for the adsorption of CO and NO (19,20).

Whereas activity toward dissociative adsorption on the Ir(110) surface is inhibited readily by the presence of surface carbon or hydrocarbon fragments which result from the adsorption of a saturation coverage of an alkane overlayer on the clean surface (21), this is not observed on the Pt(110) surface. In this case approximately 1.5×10^{14} molecules-cm⁻² of n-pentane must adsorb dissociatively and dehydrogenate to surface carbon before an inhibition of 50% is observed. Several aspects of the relative reactivities may contribute to this, namely: (1) the higher saturation coverages of the dissociatively adsorbed overlayers on the clean surface of iridium compared to platinum; (2) the inhibition of dissociative adsorption of alkanes due to the presence of surface hydrogen which adsorbs from the background; (3) the loss of the reconstruction of the platinum surface due to the presence of surface carbon, which generates a surface with twice as many high coordination adsites; and (4) the possibility that the surface carbon remaining on the platinum surface may enter the subsurface layer as the surface reconstruction relaxes, diminishing its effectiveness as an inhibitor. The coverage of carbon atoms estimated to inhibit fully the dissociation of alkanes on the Pt(110)-(1x2) surface, 2×10^{15} cm⁻², is approximately twice the coverage required on the same surface of iridium (21).

The activation of n-butane and n-pentane on the reconstructed Pt(110)-(1x2) surface contrasts sharply with the adsorption of these alkanes on the close-packed Pt(111) surface. No dissociative adsorption of alkanes through n-octane was observed under similar experimental conditions (5). Similar results were observed for the adsorption of n-heptane on the corresponding Ir(111)

surface, except for the observation of a small reactivity ($< 1 \times 10^{13}$ molecules- cm^{-2}) which could be associated with defect sites (22). These results suggest that the activation barrier on these close-packed surfaces is in excess of 17 kcal/mole, compared to approximately 8 kcal/mole on the Ir(110)-(1x2) surface and 12 kcal/mole on the Pt(110)-(1x2) surface, assuming preexponential factors of 10^{13} . Clearly the enhanced reactivity of alkanes on the (110)-(1x2) surfaces of iridium and platinum as compared to the close-packed surfaces is due to some combination of geometric and electronic effects induced by its particular surface geometry.

5. Conclusions

The interaction of ethane, propane, n-butane and n-pentane with the reconstructed Pt(110)-(1x2) surface has been investigated at low temperatures and pressures, principally employing mass spectrometry. Ethane and propane exhibit only molecular chemisorption, whereas low coverages of n-butane and n-pentane undergo dissociative adsorption at approximately 200 K to form surface hydrogen and hydrocarbon fragments. The availability of unoccupied β_2 adsites of hydrogen is critical for the dissociative adsorption of these alkanes. PreadSORPTION of hydrogen into this adstate inhibits dissociation, and this inhibition is complete upon saturation of the β_2 adstate. Both postadsorption of hydrogen on n-butane and n-pentane overlayers and the absence of dissociative adsorption for ethane and propane indicate that the kinetic barrier to carbon-hydrogen bond activation is overcome at approximately 200 K. The surface carbon formed in these reactions can, at sufficiently high concentrations, cause the lifting of the surface reconstruction.

Similar activation of alkanes has been observed previously for the Ir(110)-(1x2) surface, but on this surface the activation barrier to dissociative adsorp-

tion corresponds to a surface temperature of 130 K. On the close-packed Pt(111) and Ir(111) surfaces, dissociative adsorption of these alkanes is either not observed or occurs only at defect sites in the low coverage limit. This confirms a strong influence of surface geometry on C-H bond activation in alkanes.

Acknowledgment

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Figure Captions

- Figure 1. Thermal desorption spectra of hydrogen after exposures of H_2 of (a) 0.02 L, (b) 0.05 L, (c) 0.5 L, (d) 2.0 L, (e) 20 L and (f) 50 L.
- Figure 2. Thermal desorption spectra molecularly adsorbed alkanes (monitoring mass 27) for adsorption of (A) ethane; (B) propane; (C) n-butane; and (D) n-pentane. Exposures are shown next to the corresponding spectra.
- Figure 3. Thermal desorption spectra of hydrogen resulting from exposure to (A) n-butane; and (B) n-pentane. Exposures are shown next to the corresponding spectra.
- Figure 4. Thermal desorption spectra of hydrogen after exposure of (a) the clean surface to 1.0 L of n-pentane; (b) the clean surface to 1.0 L of pentane, annealing to 320 K for 30 s and cooling to 150 K; and (c) the surface in experiment (b) to an additional 1.0 L of n-pentane.
- Figure 5. Thermal desorption spectra of hydrogen after exposure of (a) 1.0 L of n-pentane; and (b) 1.0 L of n-pentane to the surface after the experiment in (a).
- Figure 6. Thermal desorption spectra of hydrogen after exposure of 1.0 L of n-butane to (a) the clean surface; (b) the surface in (a) exposed to 0.05 L of hydrogen; and (c) the surface in (a) exposed to 0.5 L of hydrogen.
- Figure 7. Thermal desorption spectra of hydrogen after the adsorption of 0.5 L of hydrogen on a surface exposed previously to 1.0 L of n-pentane which had been annealed for 30 s to (a) 150 K; (b) 180 K; and (c) 200 K.
- Figure 8. Thermal desorption spectra of masses 2 and 3 after exposure of the surface to 0.02 L of deuterium followed by 1.0 L of n-pentane.

THERMAL DESORPTION OF HYDROGEN

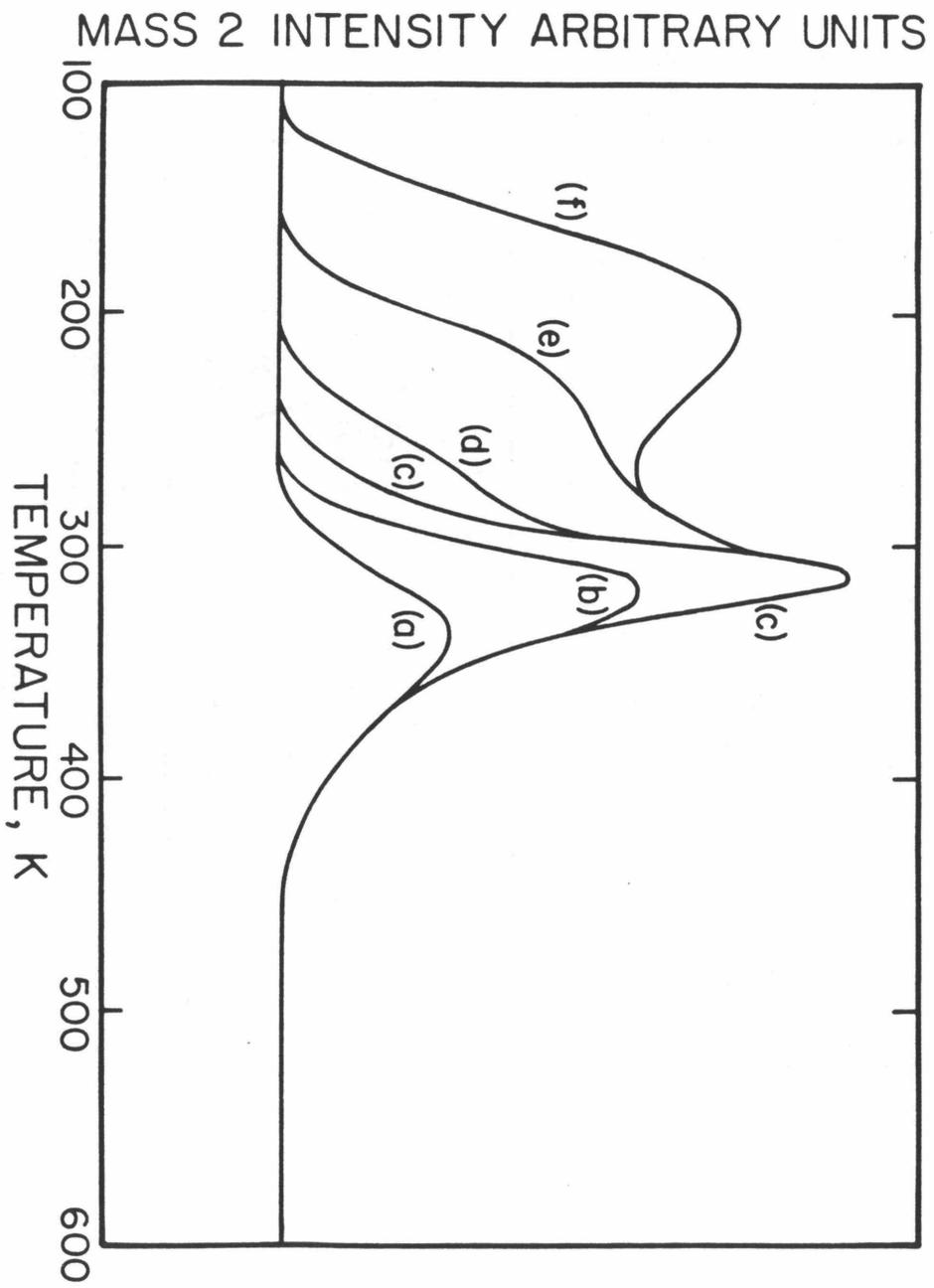


Figure 1

DESORPTION OF MOLECULAR ALKANES

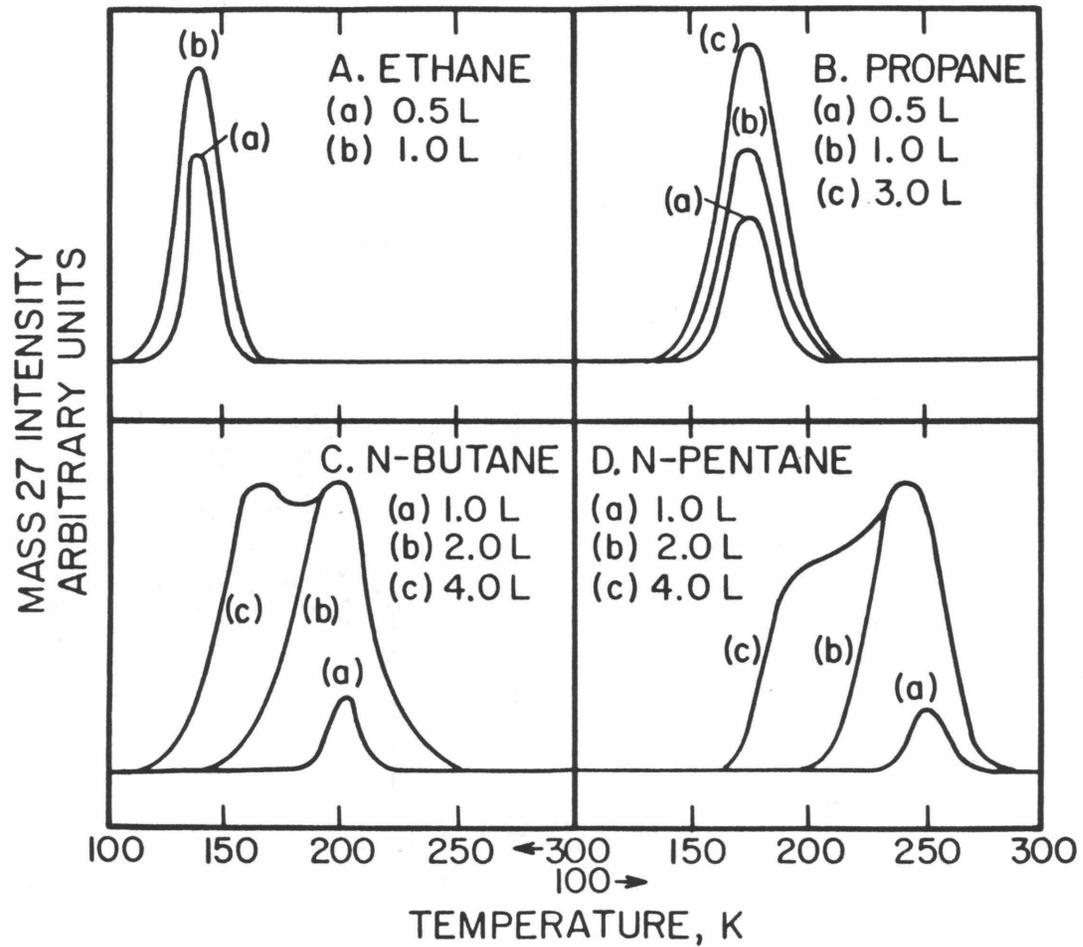


Figure 2

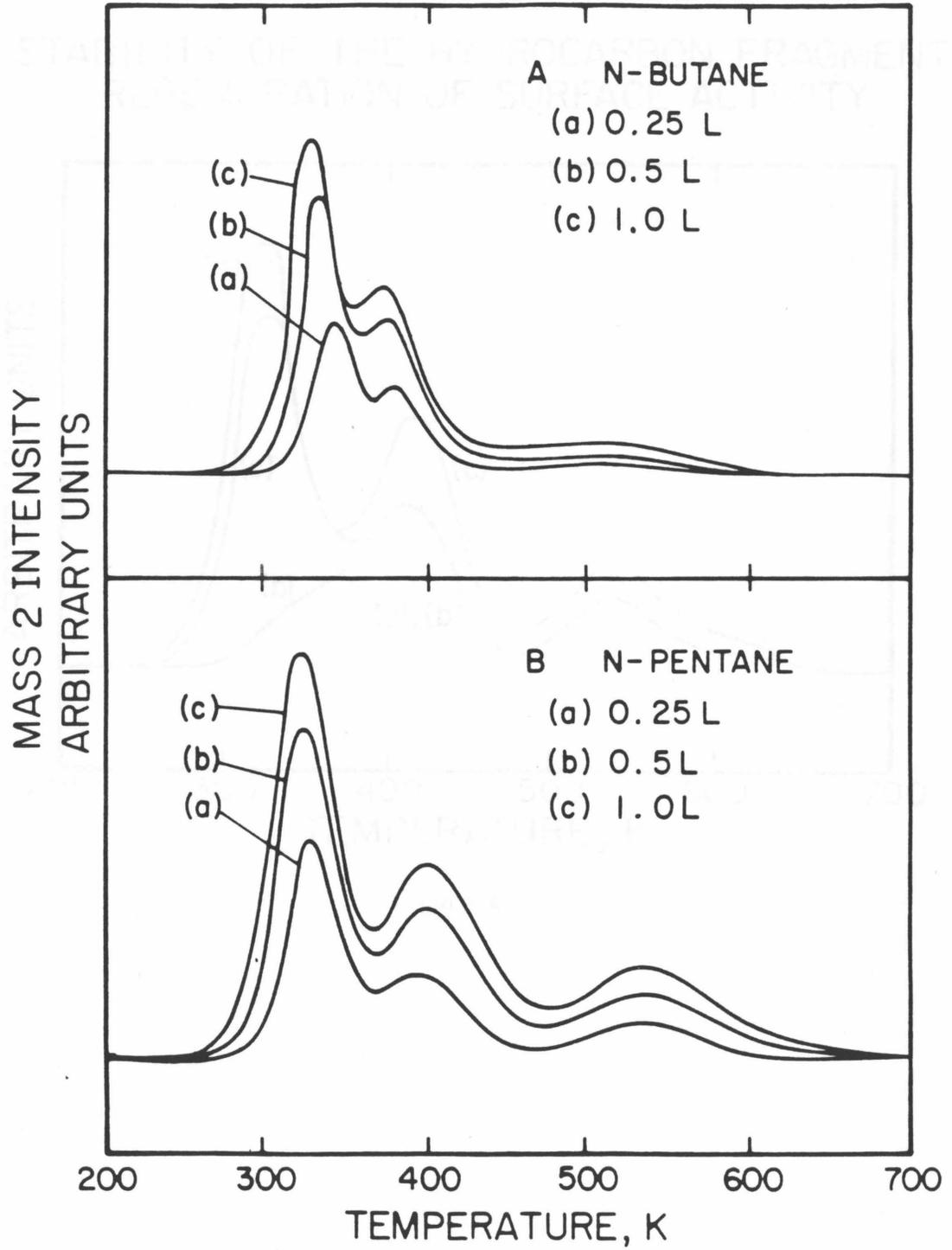
DESORPTION OF HYDROGEN
FROM ALKANE ADLAYERS

Figure 3

STABILITY OF THE HYDROCARBON FRAGMENTS
REGENERATION OF SURFACE ACTIVITY

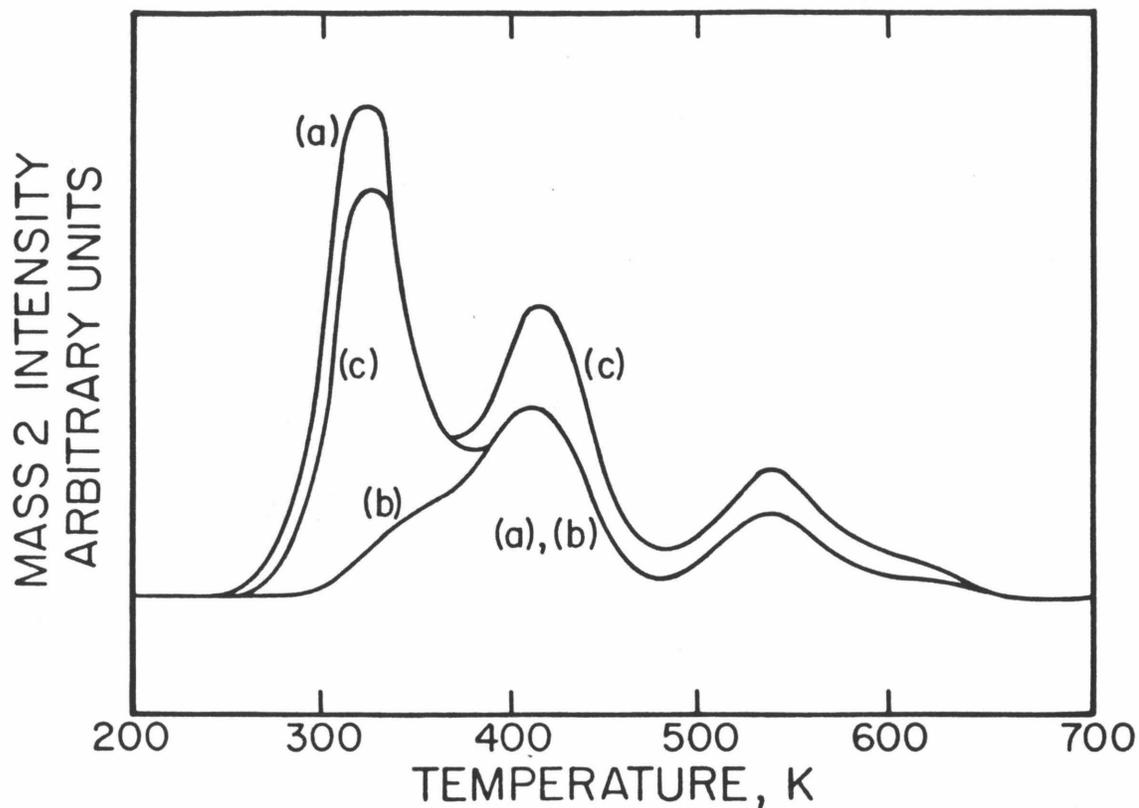


Figure 4

ADSORPTION ON CARBON RESIDUE

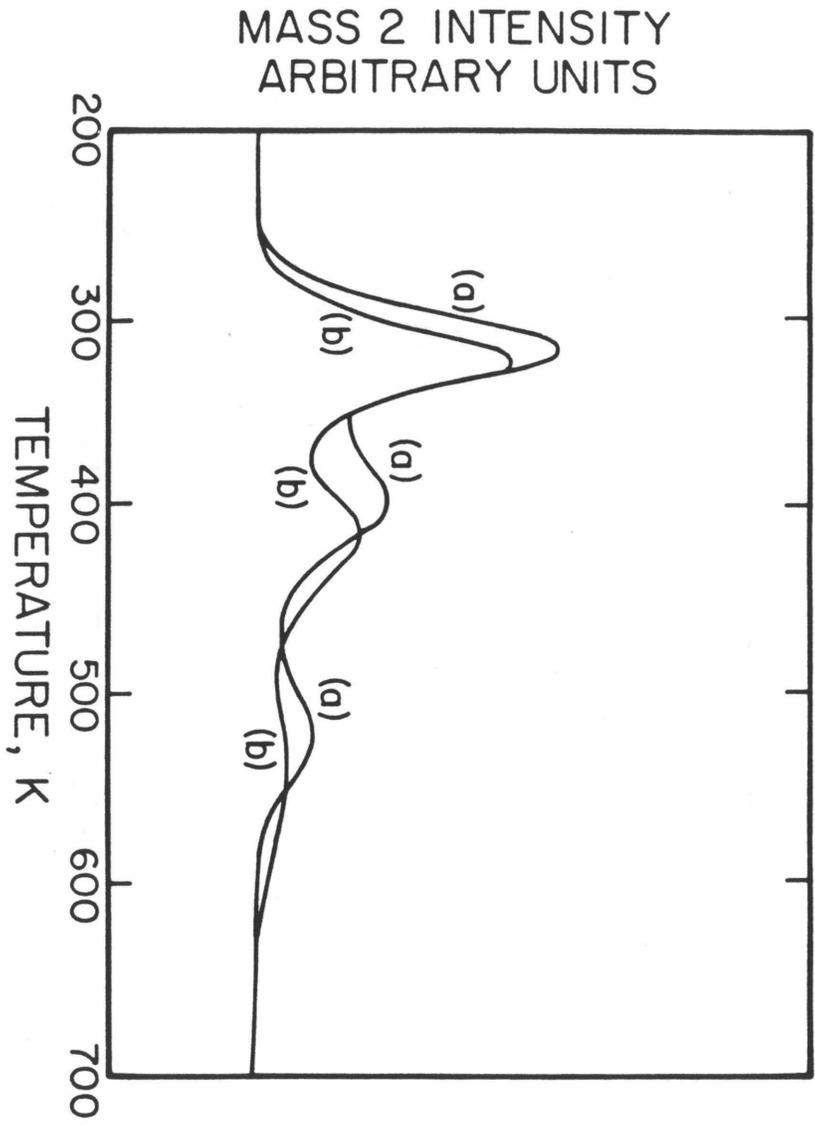


Figure 5

EFFECT OF PREADSORBED HYDROGEN ON N-BUTANE DISSOCIATION

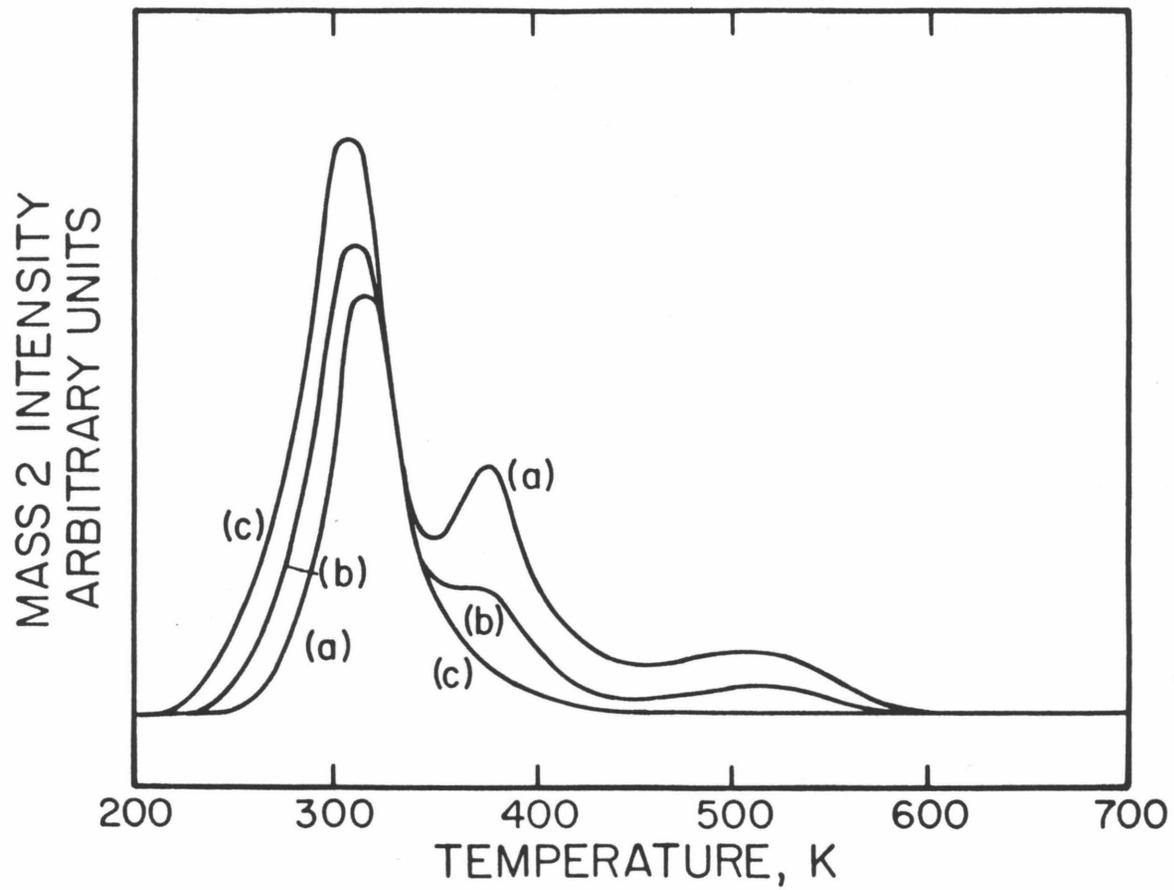


Figure 6

POSTADSORPTION OF HYDROGEN
ON ANNEALED N-PENTANE ADLAYERS

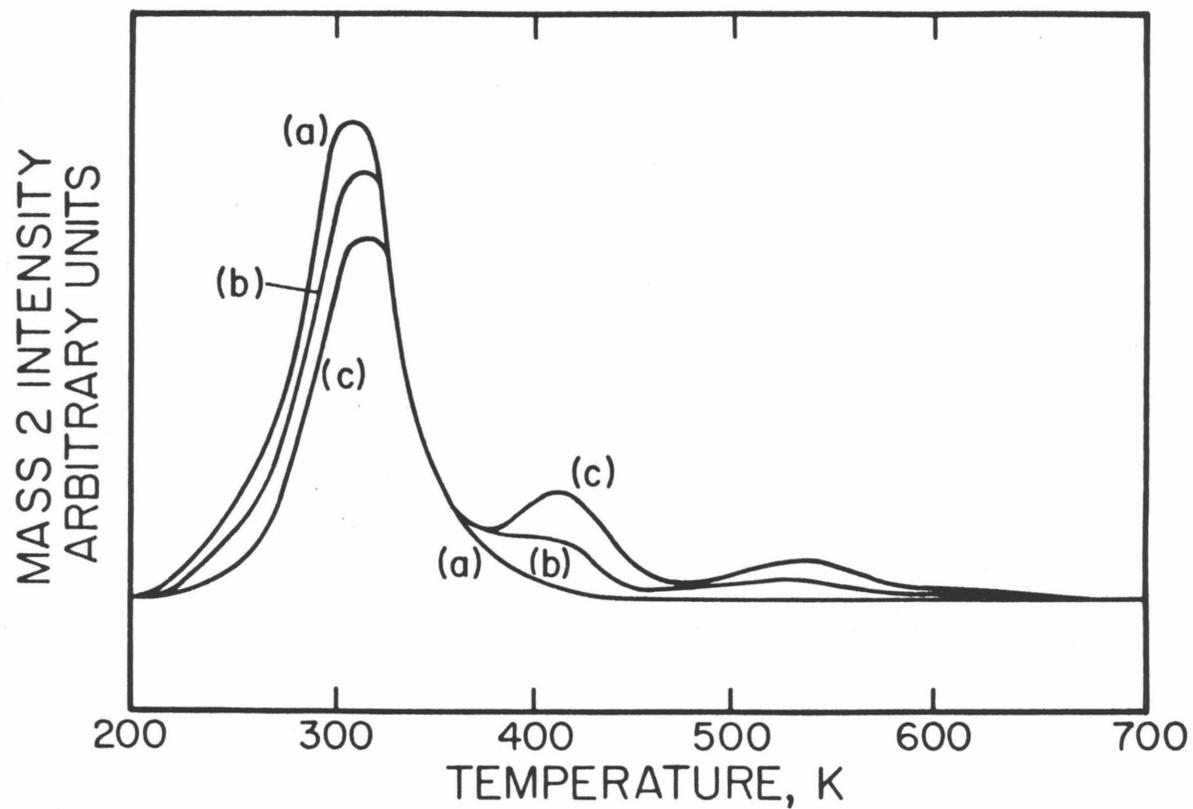


Figure 7

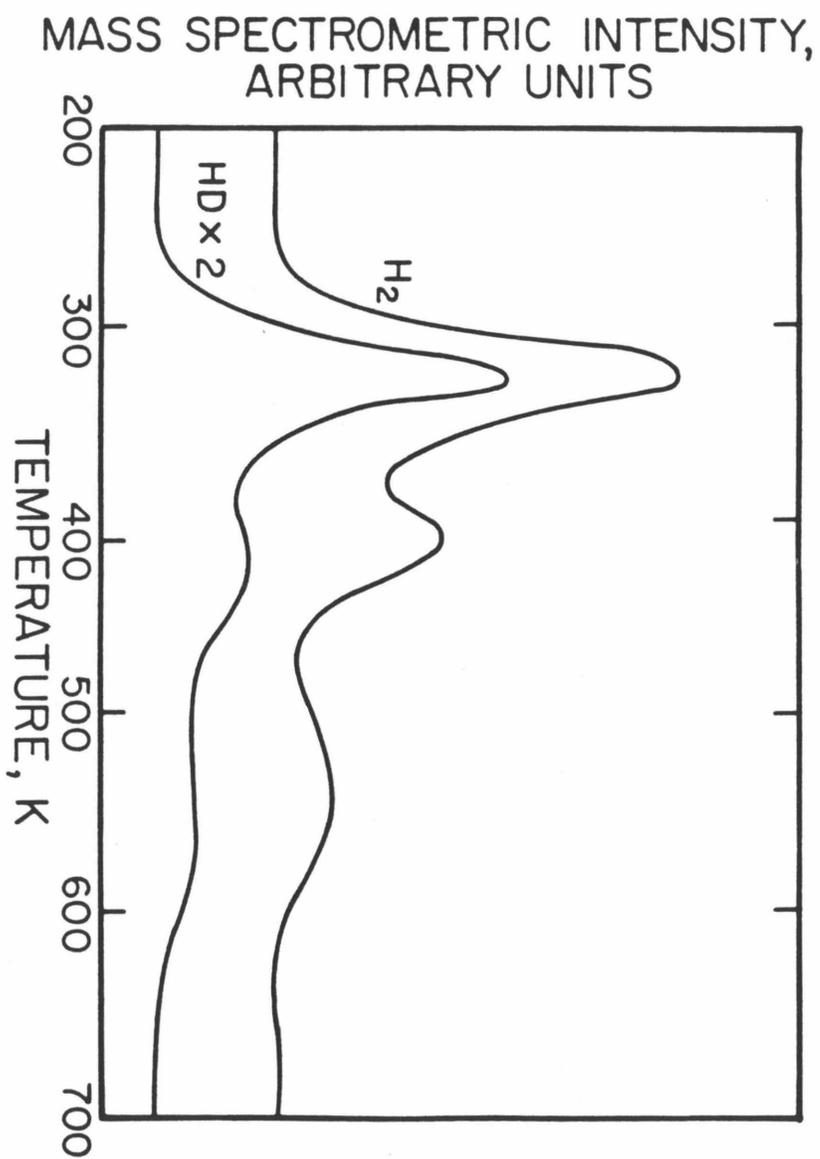
COADSORPTION OF DEUTERIUM
AND N-PENTANE

Figure 8

CHAPTER 5
CONCLUSIONS

The interaction of hydrocarbons with the (110)-(1x2) and (111) surfaces of iridium and the (110)-(1x2) surface of platinum has been studied under ultrahigh vacuum conditions. Techniques employed included thermal desorption mass spectrometry and low energy electron diffraction (LEED).

On the reconstructed Ir(110)-(1x2) surface, low coverages of the normal alkanes from ethane to heptane undergo dissociative chemisorption below 130 K. Inhibition of such adsorption by hydrogen indicates that this process proceeds by activation of carbon-hydrogen bonds. Saturation coverages of the dissociatively adsorbed layers are approximately 1×10^{14} molecules-cm⁻². At higher exposures, molecular adsorption occurs as well. Both desorption-limited (β_2) and reaction-limited thermal desorption states (α, γ) of hydrogen are observed, the latter being associated with the dehydrogenation of hydrocarbon species on the surface. Ethane, butane and hexane form high temperature adstates with stoichiometries of C₂H₀, C₄H₁ and C₆H₂, respectively, while the corresponding stoichiometries for propane, pentane and heptane are C₃H₂, C₅H₄ and C₇H₆. The fragment stoichiometries for this latter group of alkanes may be explained by extending a model for dehydrogenation which has been proposed previously [T. S. Wittrig, P. D. Szuromi and W. H. Weinberg, *J. Chem. Phys.* (76), 3305 (1982)], in which metallacycles are formed that have units of three carbon atoms and two surface metal atoms. Differences between the thermal desorption spectra of hydrogen from n-butane and isobutane, and from n-pentane and neopentane suggest that these alkanes largely retain the carbon-carbon bond frameworks after the initial steps of dehydrogenation prior to carbon-carbon bond scission above 400 K.

The strong dehydrogenating nature of this surface is apparent in the thermal desorption spectra of propane, cyclopropane, propylene, propyne and allene on the reconstructed Ir(110)-(1x2) surface. Annealing low coverages of these

hydrocarbons leads to the formation of surface hydrogen and of hydrocarbon fragments of approximate stoichiometry C_3H_2 . This occurs in spite of the differences in the electronic and geometric structure of these molecules. Upon saturation of the β'_2 adsites, these structural differences are reflected in the formation of additional dissociatively adsorbed adstates for the unsaturated hydrocarbons, which result from the dehydrogenation of molecules which are chemisorbed strongly through their π electrons. All five hydrocarbons form molecularly adsorbed adstates at high exposures. The importance of the β'_2 adsite of hydrogen on this surface of iridium has been demonstrated further by inhibition studies with hydrogen, CO and surface carbon. Under the same conditions on the close-packed Ir(111) surface propane, cyclopropane and n-heptane undergo dissociative adsorption only at defect sites. Saturation coverages of the dissociatively adsorbed adlayers are a factor of twenty less than on the Ir(110)-(1x2) surface. However, the extent of reaction of propylene is approximately the same on both surfaces. For iridium surfaces surface geometry has a strong effect on the activation of carbon-hydrogen bonds of alkanes.

This strong effect of surface geometry on the dissociative adsorption of alkanes also occurs for surfaces of platinum. Previous work (L. E. Firment, Ph. D. Thesis, Univ. of California, Berkeley, 1976) has demonstrated that the close-packed Pt(111) surface does not dehydrogenate the normal alkanes through octane under ultrahigh vacuum conditions. On the reconstructed Pt(110)-(1x2) surface n-butane and n-pentane dehydrogenate at approximately 200 K to form surface hydrogen and hydrocarbon fragments, whereas adlayers of ethane and propane undergo only molecular adsorption. Saturation coverages of the dissociative adlayers in units of 10^{13} molecules-cm⁻² are 5.0 +- 0.5 for n-butane and 7.0 +- 0.7 for n-pentane. Dehydrogenation by the surface leaves fragments which are relatively more rich in hydrogen than on the Ir(110)-(1x2) surface.

Inhibition of this reaction by precoverages of hydrogen suggests that carbon-hydrogen bond activation is the initial reaction step. Studies involving the post-adsorption of hydrogen on annealed adlayers of n-butane and n-pentane reveal that the kinetic barrier to dissociative adsorption is overcome at approximately 200 K, as is suggested by the lack of reactivity of ethane and propane. High coverages of the surface carbon formed by the dehydrogenation of the hydrocarbon fragments relax the surface reconstruction. Thus on the (110)-(1x2) surfaces of iridium and platinum pathways exist which have lower barriers to carbon-hydrogen bond activation than do the close-packed surfaces. However, the different electronic structures of the (110)-(1x2) surfaces manifest themselves in details such as the size of the kinetic barrier to dissociative adsorption.

APPENDIX A

THE CHEMISORPTION AND REACTION OF CYCLOPROPANE
ON THE (110) SURFACE OF IRIDIUM

(The text of Appendix A consists of an article coauthored with T. S. Wittrig and W. H. Weinberg which has appeared in The Journal of Chemical Physics 76, 716 (1982).)

Chemisorption and reaction of cyclopropane on the (110) surface of iridium^{a)}

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Thermal desorption mass spectrometry (TDMS), UV photoelectron spectroscopy (UPS), low-energy electron diffraction (LEED), and contact potential difference measurements have been employed to study the interaction of cyclopropane with the reconstructed Ir(110)-(1×2) surface. At an adsorption temperature of 100 K cyclopropane dissociates on the surface with a reaction probability of 0.87 ± 0.1 . This overlayer saturates at a coverage of cyclopropane of $(2.1 \pm 0.2) \times 10^{14} \text{ cm}^{-2}$. Upon further exposure, cyclopropane adsorbs molecularly into two different adsorption sites up to a saturation coverage of $6.6 \times 10^{14} \text{ cm}^{-2}$. The parameters of the desorption rate coefficients based upon Arrhenius constructions for low coverages of the two desorption states are $E_d = 6.4 \pm 1 \text{ kcal mol}^{-1}$ and $\nu_d = 1.0 \times 10^{13} \text{ s}^{-1}$, $E_d = 8.3 \pm 1 \text{ kcal mol}^{-1}$ and $\nu_d = 4.5 \times 10^{10} \text{ s}^{-1}$. The work function decreases by 0.5 eV during formation of the dissociated hydrocarbon residue at 100 K and decreases further (a total decrease of 0.7 eV) during the adsorption of molecular cyclopropane.

I. INTRODUCTION

The study of the interaction of cyclopropane with transition metal catalysts has long been utilized as a probe of the general nature of hydrocarbon catalysis.¹⁻¹⁰ These classical studies over dispersed supported catalysts have addressed such issues as the identity of surface species in hydrocarbon reactions, the role of kinks and steps as active sites, the nature of the hydrocarbon residue that is formed and its role in the mechanism of hydrogenolysis, and the product distribution in the hydrogenolysis reaction. A recent study of cyclopropane adsorption on Ru(001) in ultrahigh vacuum found that cyclopropane adsorbs and desorbs molecularly on this surface and undergoes no further reaction.¹¹ The purpose of this study is to establish a model system for the reaction of a simple hydrocarbon on a well characterized single crystal transition metal surface under ultrahigh vacuum conditions. This model system should make it possible to address some of the issues mentioned above from a fundamental point of view, making use of the array of techniques available in the ultrahigh vacuum environment. Here we consider the dissociative adsorption of cyclopropane on the Ir(110)-(1×2) surface.

II. EXPERIMENTAL PROCEDURES

The experiments were performed in an ion pumped stainless steel bell jar that has been described previously.^{12,13} The base pressure for these experiments was below 2×10^{-10} Torr of reactive contaminants. The cyclopropane exposures for most of the experiments were carried out with a directional beam doser.¹⁴ During dosing, the crystal is approximately 3 mm from the doser face. This provides a beam pressure-to-background pressure ratio of over 100:1. The exposure unit that is employed for the beam doser is Torr s and refers

to the product of the time of exposure and the pressure in the storage bulb of the doser. For cyclopropane in this system, 2.5 Torr s are approximately equivalent to 1 L.

III. LOW-ENERGY ELECTRON DIFFRACTION

It is well known that the clean surface of Ir(110) reconstructs to form a (1×2) LEED pattern.¹⁵ The structure that gives rise to this pattern has been shown to be a surface with every other row of surface atoms missing in the [001] direction.¹⁶ Thus, the surface may be pictured as a series of two-layer deep troughs, the sides of which are (111) microfacets as is shown in Fig. 1. A

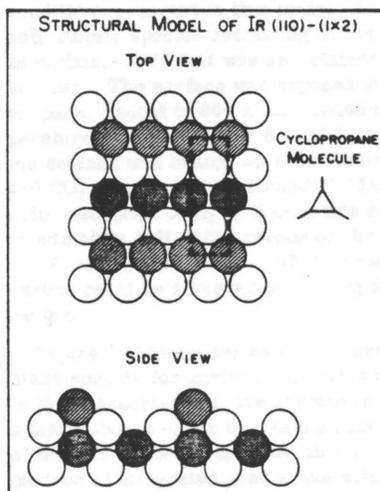


FIG. 1. Schematic view of the missing-row model of the Ir(110)-(1×2) surface. Cross-hatched circles represent top-layer atoms, open circles represent second-layer atoms, and dotted circles represent third-layer atoms. The scale of the cyclopropane molecule is shown also. The carbon atoms would lie at the vertices of the triangle and the projection of the hydrogen pairs onto the plane is shown as the three radiating lines.

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reconstructed unit cell is shown as a dashed rectangle in the top view. In addition, the comparative scale of the cyclopropane molecule is shown to the right of the top view.

For all the conditions reported in this study, no long-range ordering of either the cyclopropane or its decomposition products was observed with LEED. Additionally, the (1×2) substrate beams were always present, indicating the stability of the surface reconstruction under these conditions.

IV. ULTRAVIOLET PHOTOELECTRON SPECTROSCOPY

Figure 2 illustrates a series of UP spectra for various exposures of cyclopropane to Ir(110) at 100 K. For a 4 Torr s exposure, there is a broad background in the region of binding energy below 4 eV. On this background, there are observable peaks at approximately 6 eV and 9 eV. The intensity of these peaks corresponds to approximately 2% of the total intensity. Adsorbate peak intensity is defined here as the height of the peak above the background on which the peak appears. For higher exposures, the two peaks observed in the 4 Torr s spectrum as well as one near 4 eV become much more intense. At an exposure of 6 Torr s, they constitute approximately 10% of the total intensity, and at 15 Torr s exposure, they make up fully one third of the intensity. Exposures greater than 15 Torr s cause no further change in the UP spectrum.

The electronic levels of gas phase cyclopropane¹⁷ are indicated [as (e)] above spectrum (d) in Fig. 2 with a

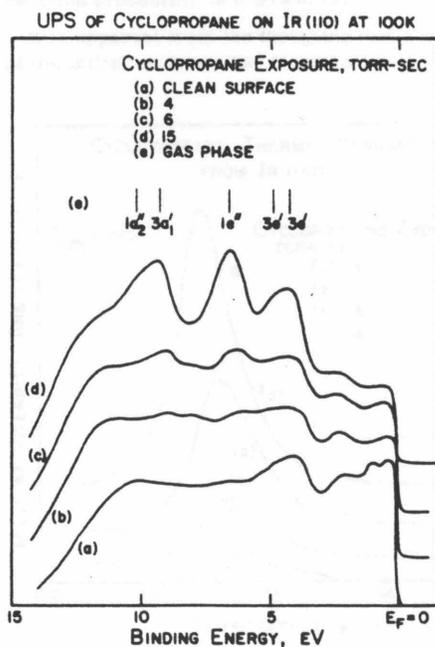


FIG. 2. He I UPS as a function of cyclopropane exposure to the Ir(110)-(1 × 2) surface.

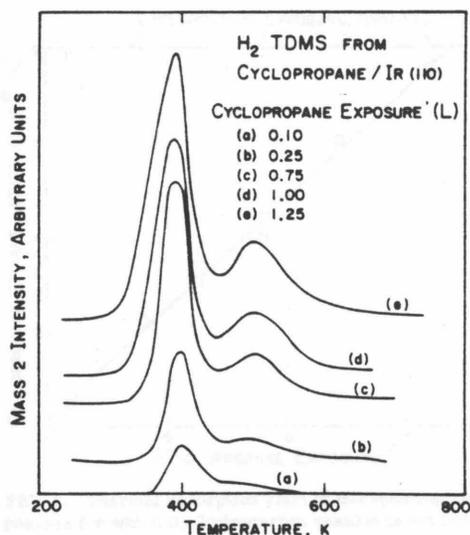


FIG. 3. Hydrogen thermal desorption as a function of cyclopropane exposure with $T_{\text{sub}} = 100$ K and $\beta = 20$ K s⁻¹.

static shift to account for relaxation effects. This illustrates that at saturation the predominant species on the surface is molecular cyclopropane.

V. THERMAL DESORPTION MASS SPECTROMETRY

For cyclopropane exposures below 5 Torr s, hydrogen and cyclopropane both appear in the thermal desorption mass spectrum. No other hydrocarbons appear in observable quantities as desorption products for any of the conditions reported in this study. Furthermore, the only atomic species remaining on the surface at 800 K is carbon. This fact was ascertained in the following manner. The surface was exposed to 10 Torr s of cyclopropane, heated to 800 K and cooled to below room temperature. Subsequently, 5 L of O₂ was adsorbed, and the surface was heated while monitoring H₂, H₂O, CO, and CO₂ mass spectrometrically. There was no detectable desorption of H₂ or H₂O in this experiment. Approximately half of the carbon on the surface desorbed as CO and approximately 10% desorbed as CO₂. All the carbon could be removed by heating the surface in oxygen.

Figure 3 shows a series of H₂ thermal desorption mass spectra for various exposures of cyclopropane. In these experiments, the exposures were made through a leak valve in order to obtain an accurate calibration of the flux of the beam doser as well as a reliable comparison of integrated peak areas with peak areas of H₂ thermal desorption from a hydrogen-covered surface. Since an accurate coverage calibration for hydrogen on Ir(110) is known,¹² it is possible to obtain an accurate absolute measure of the number of cyclopropane molecules that decompose as a function of cyclopropane exposure. If we define the reaction probability as the probability that any molecule that encounters the surface will eventually dissociate into H₂(g) and C(a) upon heat-

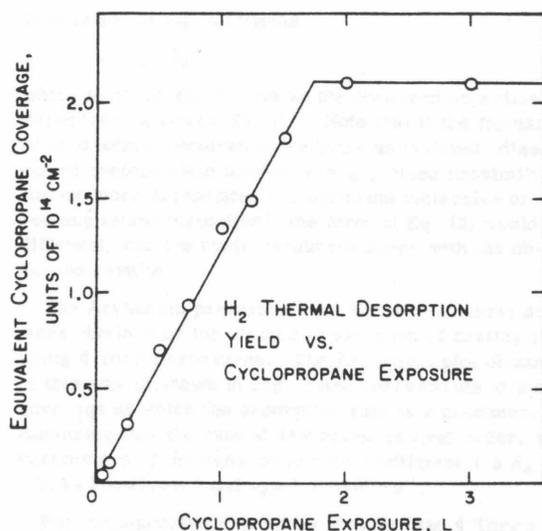


FIG. 4. Thermal desorption yield of hydrogen from cyclopropane adsorbed on Ir (110)-(1 × 2).

ing, the hydrogen thermal desorption yield is proportional to the cyclopropane reaction probability. As shown in Fig. 4, the reaction probability for a cyclopropane molecule is constant up to a saturation coverage equivalent to $(2.1 \pm 0.2) \times 10^{14}$ molecules cm^{-2} . This coverage corresponds approximately to one dissociated cyclopropane molecule per 2.5 reconstructed unit cells. Saturation occurs at an exposure of 1.7 L or about 4 Torr s. The slope of the line in Fig. 4 indicates that the reaction probability is 0.87 ± 0.10 .

It is apparent from the foregoing that a large fraction of the initial cyclopropane to encounter the surface dis-

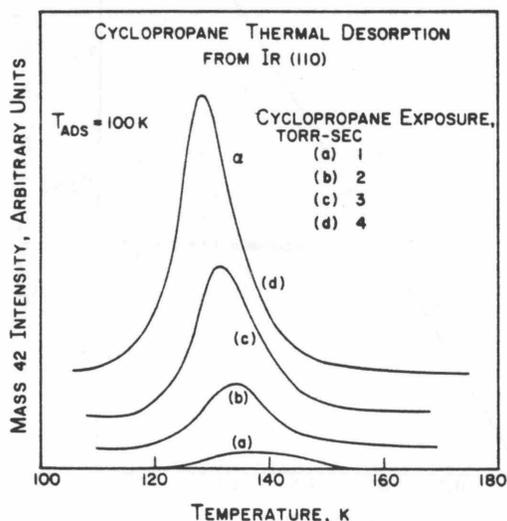


FIG. 5. Cyclopropane thermal desorption from Ir (110)-(1 × 2). The hydrocarbon residue is not saturated for these exposures, and $\beta = 4 \text{ K s}^{-1}$.

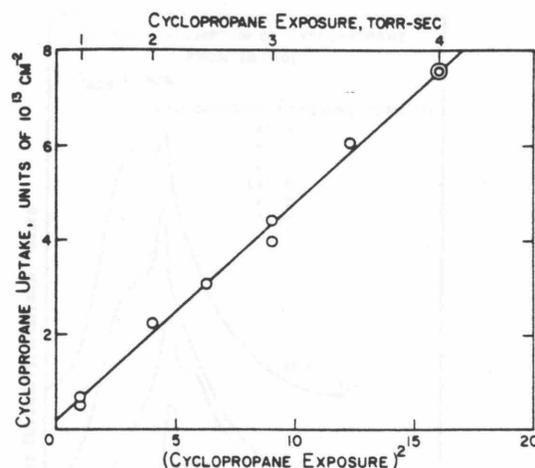


FIG. 6. Thermal desorption yield of α -cyclopropane for exposures for which the hydrocarbon residue is not complete.

sociates. The UPS results suggest that the dissociation occurs even at temperatures as low as 100 K. In any case, the dissociation must be complete below 150 K because no molecular cyclopropane remains on the surface above 150 K. The layer of dissociated cyclopropane will hereafter be referred to as the hydrocarbon residue.

Thermal desorption of small amounts of cyclopropane is also observed in this exposure regime (≤ 4 Torr s) as is illustrated in Fig. 5. In this adsorption regime, the total desorbed cyclopropane represents less than 15% of the adsorbed cyclopropane. This thermal desorption feature will be referred to as the α thermal desorption state. The relationship between cyclopropane coverage and exposure is shown in Fig. 6. The solid line represents the function

$$\Theta_{\Delta} = C_1 \epsilon_{\Delta}^2 + C_2, \quad (1)$$

where Θ_{Δ} is the coverage of cyclopropane in cm^{-2} , ϵ_{Δ} is the exposure in Torr s, $C_1 = 4.62 \times 10^{12} (\text{Torr s})^{-2}$, and $C_2 = 2.0 \times 10^{12} \text{ cm}^{-2}$. The nonzero intercept is equivalent to less than 0.3% of saturation coverage of cyclopropane on this surface.

This rather unusual variation of coverage with exposure for nondissociative adsorption might be explained in the following way. If the sites onto which the " α cyclopropane molecules" adsorb are formed by the dissociation of an isolated cyclopropane molecule and if the probability of adsorption of cyclopropane on these sites is a constant, then the rate of increase in the population of the α state should be proportional to the amount of residue, i.e.,

$$\frac{d\Theta_{\Delta}}{d\epsilon_{\Delta}} \propto \Theta, \quad (2)$$

where Θ is residue coverage. It has already been shown in Fig. 4 that Θ is proportional to ϵ_{Δ} . Thus,

$$\frac{d\Theta_{\Delta}}{d\epsilon_{\Delta}} \propto \epsilon_{\Delta}. \quad (3)$$

Integration of Eq. (3) yields

$$\Theta_{\Delta} = k_1 \epsilon_{\Delta}^2 + k_2, \quad (4)$$

which is of the same form as the observed experimental dependence given by Eq. (1). Note that if the formation of an α adsite required more than one isolated, dissociated cyclopropane molecule (e.g., close proximity of two or more dissociated cyclopropane molecules or residue island formation), the form of Eq. (2) would be different, and the model would not agree with the observed results.

The Arrhenius parameters for the α -desorption state were obtained by the method of variation of heating rate¹⁸ using 4 Torr s exposures. The Arrhenius plot obtained in this way is shown in Fig. 7 and corresponds to the coverage at which the desorption rate is a maximum. Assuming that the rate of desorption is first order, the parameters of the desorption rate coefficient are $E_d = 6.4 \pm 1 \text{ kcal mol}^{-1}$ and $\nu_d = 1.0 \times 10^{23} \text{ s}^{-1}$.

For cyclopropane exposures greater than 4 Torr s, a new thermal desorption state begins to populate in addition to the α state. As shown in spectrum (b) of Fig. 8, this state is labeled the β state. Two-state thermal desorption mass spectra occur for all exposures between 5 and 20 Torr s, which is saturation at 100 K. As shown in Fig. 8, for exposures of 10 Torr s or less, the temperature of the desorption maximum of the β state decreases with increasing coverage, whereas the desorption maximum of the α state remains constant at approximately 130 K. For exposures greater than 10

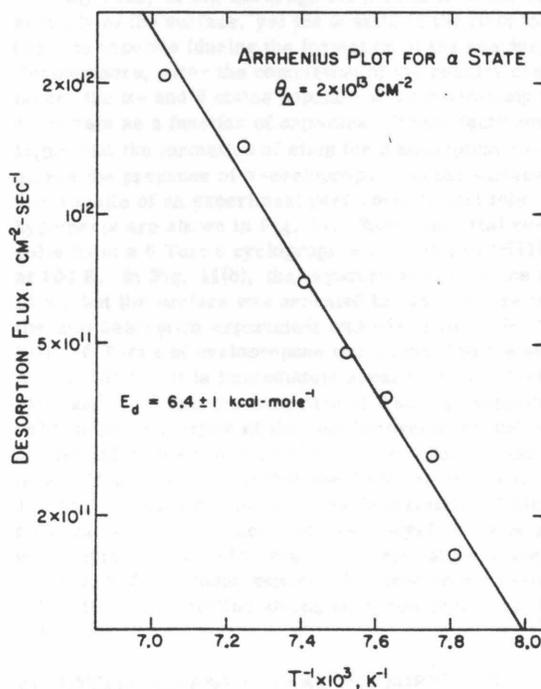


FIG. 7. Arrhenius plot for α state of cyclopropane determined by the method of variation of heating rate. See Table I.

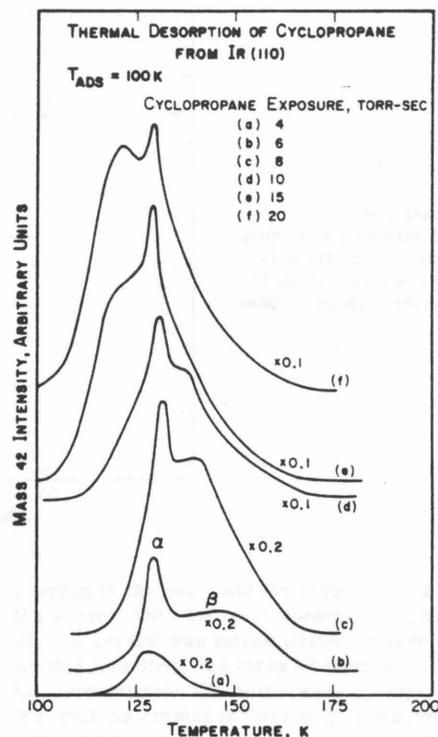


FIG. 8. Cyclopropane thermal desorption from Ir (110)—(1 \times 2). For this exposure regime, the hydrocarbon residue is saturated, and $\beta = 4 \text{ K s}^{-1}$.

Torr s, there are still two distinct features in the thermal desorption mass spectrum. However, the feature with a peak maximum of 130 K appears at a higher temperature than the other peak. The low temperature thermal desorption feature which is evident in Figs. 8(e) and 8(f) appears to represent a structure other than adsorption into the β adsites based on experiments concerning the adsorption of cyclopropane on the hydrocarbon residue after annealing to 200 K.¹⁹

The coverage-exposure relationship obtained from integrated mass 42 peak areas is shown in Fig. 9. After the initial formation of the residue, the cyclopropane coverage increases linearly with exposure up to at least two thirds of saturation. The saturation coverage is $(6.6 \pm 1.0) \times 10^{14} \text{ cm}^{-2}$ as will be demonstrated in the next section. This implies a density of three cyclopropane molecules for every two reconstructed unit cells on the surface. Saturation at an adsorption temperature of 100 K occurs at an exposure of approximately 20 Torr s.

The Arrhenius parameters for a low coverage of the β state of adsorbed cyclopropane were obtained by the variation of heating rate method using a 6 Torr s exposure. The resulting Arrhenius plots are presented in Fig. 10 for two different coverages. The coverage for line (a) corresponds to a temperature of approximately 155 K in Fig. 8(b), and for line (b), the corresponding temperature is 145 K. The parameters of the desorp-

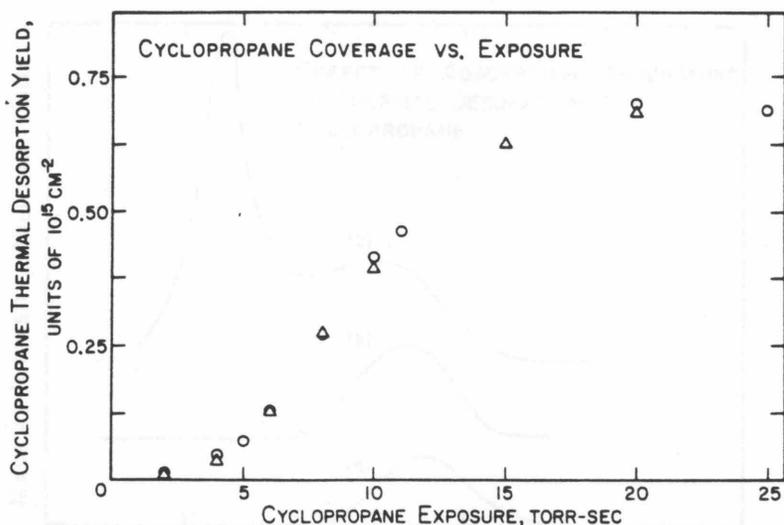


FIG. 9. Thermal desorption yield of cyclopropane from Ir (110)-(1 × 2). Triangles and circles represent data obtained on different days.

tion rate coefficient for the low coverage β state are (a) $E_d = 8.1 \pm 2 \text{ kcal mol}^{-1}$, and $\nu_d = 4.7 \times 10^{10} \text{ s}^{-1}$; and (b) $E_d = 8.5 \pm 1 \text{ kcal mol}^{-1}$, and $\nu_d = 4.4 \times 10^{10} \text{ s}^{-1}$. Since the desorption temperature of the β state of cyclopropane decreases by at least 20 K with increasing coverage, one would expect that E_d and possibly ν_d depend strongly on surface coverage. This conjecture, however, is not subject to experimental verification due to the overlap of the α - and β -desorption states at higher coverages.

In any case, at low coverage the β state is bound more strongly to the surface, yet the α state is the first to begin to populate (during the formation of the residue). Furthermore, after the completion of the residue overlayer, the α - and β states populate at approximately the same rate as a function of exposure. These facts could imply that the formation of sites for β adsorption requires the presence of α -cyclopropane on the surface. The results of an experiment performed to test this hypothesis are shown in Fig. 11. Spectrum 11(a) results from a 6 Torr s cyclopropane exposure to Ir(110) at 100 K. In Fig. 11(b), the exposure was the same as 11(a), but the surface was annealed to 125 K before the thermal desorption experiment was performed. In Fig. 11(c), 6 Torr s of cyclopropane was exposed to the surface at 135 K. It is immediately apparent from spectra 11(b) and 11(c) that the formation of β adsites depends only on the completion of the residue overlayer and does not depend on the presence of α -cyclopropane on the surface. This may indicate that the β adsites are formed by residue island formation or polymerization. This observation demonstrates also that α -cyclopropane and β -cyclopropane are adsorbed at different sites on the surface, and that these separate features do not result solely from interactions among adsorbed cyclopropane molecules.

VI. CYCLOPROPANE UPTAKE MEASUREMENT

The curve shown in Fig. 12 was obtained in the following manner. The beam doser was turned on with cyclo-

propane in the beam and the crystal facing away from the doser. With the mass spectrometer monitoring mass 42, the crystal was turned immediately to face the doser. As this was done, the mass 42 intensity (I_{42}) decreased to approximately 30% of its original value reflecting the fact that the crystal is "pumping" cyclopropane. As the crystal becomes saturated, I_{42} rises to some equilibrium value $I_{42, \infty}$. The difference $I_{42, \infty} - I_{42}$ is proportional to the probability of adsorption of cyclopropane on the sur-

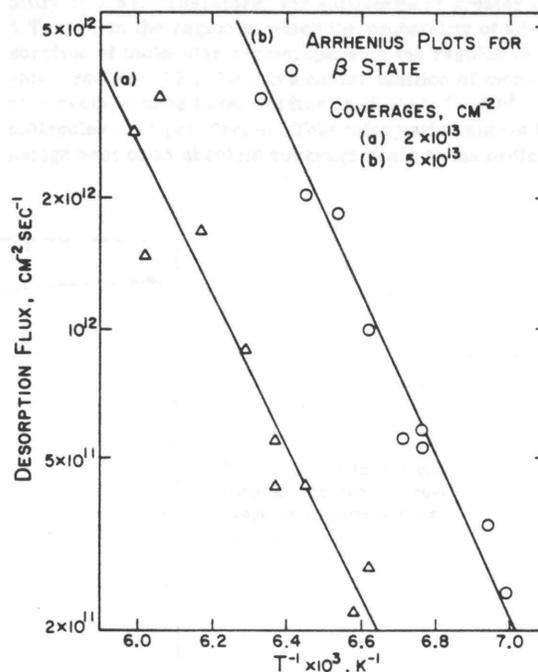


FIG. 10. Arrhenius plots for the β state of cyclopropane determined by the method of variation of heating rate. See Table I.

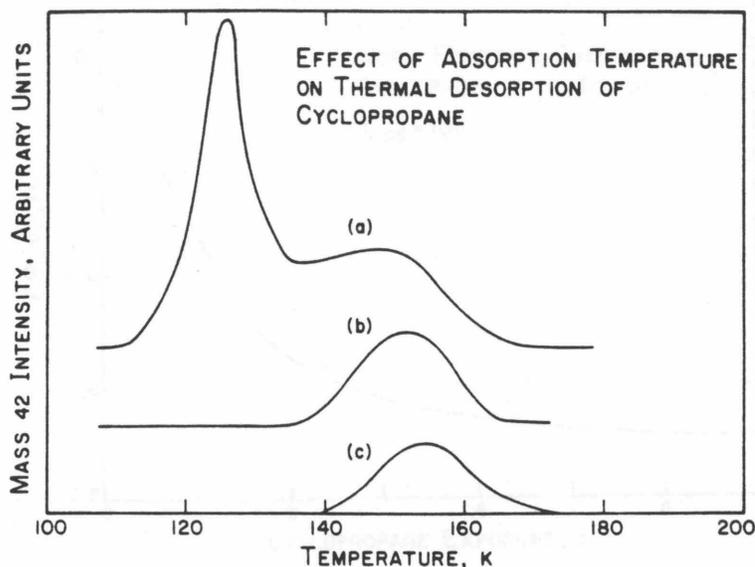


FIG. 11. Thermal desorption of cyclopropane after adsorption of 6 Torr s under different conditions. Spectrum (a)—adsorb at 100 K; spectrum (b)—adsorb at 100 K and anneal to 130 K for 30 s; spectrum (c)—adsorb at 135 K.

face as a function of time. It follows that the integral over time of $I_{42,0} - I_{42}$ is proportional to the coverage of cyclopropane (dissociated and nondissociated) on the surface at any time.

A comparison of Figs. 4 and 12 permits an approximate determination of the surface coverage of cyclopropane. The rate of adsorption (either dissociative or nondissociative) of cyclopropane onto the clean Ir(110) surface is 85% of the rate of adsorption onto the residue-covered surface. This fact is evident from a comparison of the initial slope of the curve in Fig. 12 with the slope for exposures of greater than 5 Torr s and was observed in numerous experiments of this type. The prob-

ability of dissociative adsorption for exposures of less than 4 Torr s has already been shown to be 0.87 ± 0.1 (cf. Fig. 4 and the associated text). It was also shown that this reaction probability resulted in a coverage of 2.1×10^{14} dissociated molecules cm^{-2} after an exposure of 4 Torr s. This is equivalent to 5.2×10^{13} molecules cm^{-2} per Torr s of exposure for a reaction probability of 0.87. Therefore, for exposures of greater than 4 Torr s, in the region in which the probability of adsorption of molecular cyclopropane on the residue is unity (see Fig. 12), the incremental addition of molecular cyclopropane to the surface is $(6.0 \pm 1.0) \times 10^{13}$ molecules cm^{-2} per Torr s. This information allows the assignment of an absolute coverage scale to the ordinates

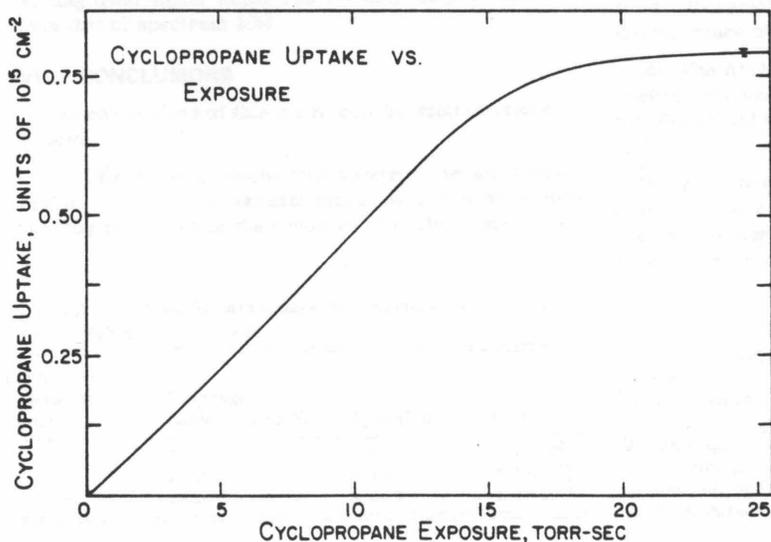


FIG. 12. Continuous measure of cyclopropane coverage as a function of exposure.

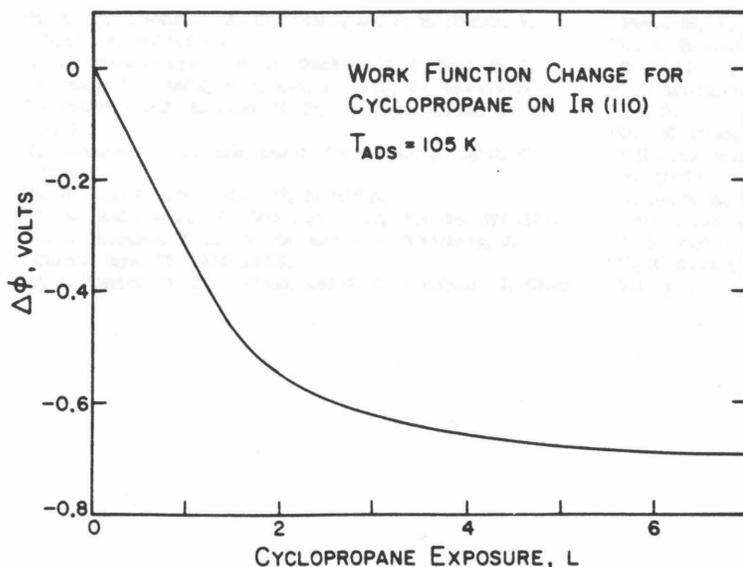


FIG. 13. Work function change as a function of cyclopropane exposure to Ir (110)-(1×2).

of Figs. 9 and 12. In particular, the saturation coverage of molecular cyclopropane on Ir(110) is $(6.6 \pm 1.0) \times 10^{14}$ molecules cm^{-2} (see Fig. 9).

VII. WORK FUNCTION

The work function change for cyclopropane adsorbed on Ir(110) as a function of exposure is shown in Fig. 13. There is a sharp linear decrease to about -0.5 eV over the range of residue formation (0–1.7 L), and then a more gradual decrease to a plateau of -0.7 eV as the overlayer saturates. The fact that most of the change in contact potential difference occurs during residue formation is borne out by the UPS results. In Fig. 2(b) (an exposure of 4 Torr s), the spectrum is approximately 0.5 eV wider than the spectrum of the clean surface, reflecting a change in work function. The spectra resulting from higher exposures are only slightly wider than that of spectrum 2(b).

VIII. CONCLUSIONS

The conclusions of this study may be summarized as follows:

(1) Ultraviolet photoelectron spectroscopy and thermal desorption of H_2 indicate that a layer of hydrocarbon residue results from the exposure of cyclopropane to an

Ir(110)-(1×2) reconstructed surface at 100 K. This layer is saturated at $(2.1 \pm 0.2) \times 10^{14}$ molecules cm^{-2} for a cyclopropane exposure of 1.7 L. The reaction probability is 0.87 ± 0.1 .

(2) For exposures of 1.7 L or less, small amounts of molecular cyclopropane adsorb into the α -thermal desorption state. The variation of cyclopropane coverage with exposure suggests that an α adsite is formed by the decomposition of an isolated cyclopropane molecule.

(3) For cyclopropane exposures greater than 1.7 L molecular cyclopropane adsorbs on the residue-covered surface with an initial probability of adsorption of unity. The molecular overlayer saturates at a coverage of $(6.6 \pm 1) \times 10^{14}$ molecules cm^{-2} . Saturation was obtained at 100 K by exposure of the surface to 8 L of cyclopropane. Ultraviolet photoelectron spectroscopy confirmed the existence of molecular cyclopropane on the surface.

(4) The Arrhenius parameters of the desorption rate coefficients were measured for low coverages of the α - and β -thermal desorption states. The results are shown in Table I.

(5) The work function decreases linearly during formation of the residue by -0.5 eV. Adsorption of molecular cyclopropane onto the residue results in a further decrease of the work function by -0.2 eV.

TABLE I. Arrhenius parameters for thermal desorption of cyclopropane from Ir (110)

Thermal desorption state	Coverage (molecules cm^{-2})	E_d kcal/mol	ν_d s^{-1}
α	2×10^{13}	6.4 ± 1	$1 \times 10^{16 \pm 1}$
β	2×10^{13}	8.1 ± 2	$4.7 \times 10^{16 \pm 2}$
β	5×10^{13}	8.5 ± 1	$4.7 \times 10^{16 \pm 2}$

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APPENDIX B

THE INTERACTION OF HYDROGEN AND CYCLOPROPANE

WITH THE (110) SURFACE OF IRIDIUM

(The text of Appendix B consists of an article coauthored with T. S. Wittrig and W. H. Weinberg which has appeared in Surface Science 116, 414 (1982).)

**THE INTERACTION OF HYDROGEN AND CYCLOPROPANE WITH
THE (110) SURFACE OF IRIIDIUM ***

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The interaction of cyclopropane with hydrogen and the residue resulting from the decomposition of the former on the reconstructed Ir(110)-(1×2) surface has been studied with thermal desorption mass spectrometry. Although hydrogen will not adsorb onto the saturated overlayer of dissociatively adsorbed cyclopropane, the preadsorption of hydrogen into the β_2 adstate inhibits the decomposition of cyclopropane on the surface. Desorption of the hydrogen from the saturated overlayer of the dissociatively adsorbed cyclopropane partially regenerates the reactivity of the surface.

1. Introduction

The study of the interactions of saturated hydrocarbons with transition metal surfaces is important because of the insight it may provide into the general mechanisms of hydrocarbon reactions on metal surfaces that may be of industrial importance. There have been several recent ultrahigh vacuum studies of the dehydrogenation of cyclohexane to form benzene [1-3]. Other studies of the *nonreactive* interaction of saturated hydrocarbons with surfaces of transition metals include LEED studies of the *nondissociative* adsorption of straight-chain paraffins on Pt(111) and Ag(111) [4], EELS and UPS studies of cyclopropane and cyclohexane adsorbed molecularly on Ru(001) [5], and an ESDIAD study of the *nondissociative* adsorption of ethane, cyclopropane and cyclohexane on Ru(001) [6].

In a recently completed study in this laboratory, it was shown that exposure of the clean Ir(110)-(1×2) surface to cyclopropane at 100 K results in the formation of an overlayer of hydrocarbon fragments on the surface [7]. A surface prepared in this manner yields the hydrogen thermal desorption

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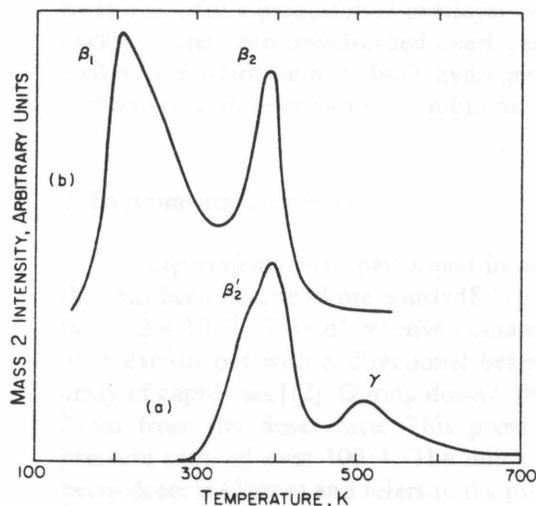


Fig. 1. (a) Hydrogen thermal desorption resulting from 1.7 L exposure of cyclopropane to the clean Ir(110)-(1 \times 2) surface. (b) Hydrogen thermal desorption resulting from 300 L exposure of H₂ to the clean Ir(110)-(1 \times 2) surface.

spectrum shown in fig. 1a. The only hydrocarbon that desorbs is molecular cyclopropane below 150 K. The thermal desorption spectrum of a saturation coverage of hydrogen on the clean Ir(110)-(1 \times 2) surface is shown in fig. 1b for comparison [8]. As indicated in this figure, there are two peaks referred to as the β_1 (low temperature) and β_2 (high temperature) thermal desorption states. The β_2 state populates according to first-order adsorption kinetics with an initial probability of adsorption of unity. Saturation of the β_2 state occurs after an exposure of 0.35 L of H₂.

The low temperature hydrogen desorption state from the cyclopropane residue has been labelled the β_2' state as indicated in fig. 1a. The similarity in intensity and temperature of desorption of this thermal desorption peak compared to the β_2 peak of hydrogen after adsorption of H₂ is taken as evidence to support the proposition that hydrogen desorbing from the β_2' state is bonded in hydrogen-iridium sites that are closely related to the β_2 adsorption sites of hydrogen on the clean surface. The γ thermal desorption state represents hydrogen that is more strongly bound to the surface than hydrogen on clean Ir(110). It is well known from spectroscopic studies of unsaturated hydrocarbons on transition metals that hydrocarbon fragments exist on these surfaces even after partial dehydrogenation [9,10]. The γ thermal desorption state represents hydrogen evolution from such fragments on the Ir(110) surface.

This paper describes measurements concerning the interaction of cyclopropane, the hydrocarbon residue derived from the dissociative chemisorption of cyclopropane, and hydrogen on the Ir(110)-(1 \times 2) surface. The adsorption of

hydrogen onto a preadsorbed overlayer of cyclopropane and the adsorption of cyclopropane onto preadsorbed overlayers of hydrogen were investigated, as well as the adsorption of both hydrogen and cyclopropane onto the hydrocarbon residue under various conditions.

2. Experimental procedures

The experiments were performed in an ion pumped stainless steel bell jar that has been described previously [8,11]. The base pressure of the bell jar was below 2×10^{-10} Torr of reactive contaminants. The cyclopropane exposures were carried out with a directional beam doser consisting of a multichannel array of capillaries [12]. During dosing, the crystal is positioned approximately 3 mm from the doser face. This provides a beam pressure-to-background pressure ratio of over 100:1. The unit of exposure that is employed for the beam doser is (Torr s) and refers to the product of the time of exposure and the pressure in the storage bulb of the doser. The storage bulb supplies gas through a capillary to the doser head leading into the vacuum system. Therefore, the flux of gas into the vacuum system is proportional to the pressure in the storage bulb. For cyclopropane in this system, 2.5 Torr s are approximately equivalent to an exposure of 1 L in the ultrahigh vacuum system, and this proportionality factor should be noted throughout the remainder of this paper.

The crystal was cleaned between thermal desorption experiments by exposure to 10^{-7} Torr of O₂ for 2 min at a crystal temperature of 900 K, followed by flashing to 1600 K to desorb the oxygen. Auger electron spectroscopy was used to verify that neither carbon nor oxygen nor any other impurity was present within detection limits after this cleaning procedure. This procedure reproducibly yielded a reconstructed Ir(110)-(1 × 2) surface, a structure which is maintained after a saturation coverage of cyclopropane at 100 K as well as after annealing this overlayer to 700 K (at which point a disordered carbonaceous residue remains on the reconstructed Ir surface).

The hydrogen used in this investigation was Matheson research purity (99.9999%). The cyclopropane was obtained from Linde, and the minimum purity was 99%. The cyclopropane was purified further by cryogenic distillation. Both gases were checked mass spectrometrically for purity after admission into the ultrahigh vacuum system.

3. Results and discussion

3.1. Adsorption of H₂ and the cyclopropane residue

The results of one of several experiments to determine the kinetics of adsorption of H₂ onto the saturated residue of cyclopropane are shown in

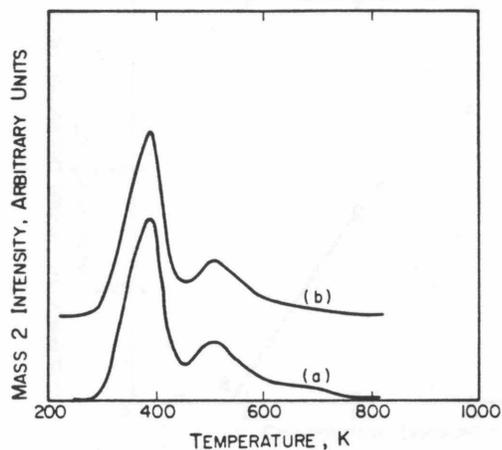


Fig. 2. (a) Hydrogen thermal desorption from a saturated residue of cyclopropane. (b) Hydrogen thermal desorption from a saturated residue of cyclopropane exposed to 2 L H₂.

fig. 2. A saturated overlayer of the hydrocarbon residue was prepared by exposing the clean surface to 10 Torr s of cyclopropane (equivalent to approximately 4 L as discussed in section 2) at 100 K, and subsequently annealing the surface to 200 K. An exposure of 10 Torr s ensured that the residue state was saturated, and the anneal cycle desorbed all reversibly adsorbed molecular cyclopropane. The thermal desorption spectrum shown in fig. 2b results from exposing 2 L of H₂ to a saturated overlayer of the hydrocarbon residue. The two spectra are identical, indicating that the probability of adsorption of H₂ on the saturated hydrocarbon residue is below 10⁻³. In particular, the β_1 adsorption sites of hydrogen available on the clean surface are poisoned by the presence of the hydrocarbon residue (cf. fig. 1b).

3.2. Cyclopropane adsorbed on preadsorbed hydrogen

On the other hand, if hydrogen is adsorbed prior to the adsorption of cyclopropane, the reactivity of the surface for the dissociation of cyclopropane is decreased. Here, the reactivity of the surface is defined as the total amount of cyclopropane that is adsorbed dissociatively on the surface, and it was measured by the following procedure. The thermal desorption yield of molecular cyclopropane (mass 42) is shown in fig. 3 as a function of cyclopropane exposure to the clean surface [7]. After an induction period of 4 Torr s, the yield exhibits a linear rise with increasing exposure. The magnitude of the induction period (defined here as the magnitude of the x-intercept of the line shown in fig. 3) can be used as a measure of the amount of cyclopropane that dissociates on the surface. For example, if no cyclopropane were to dissociate

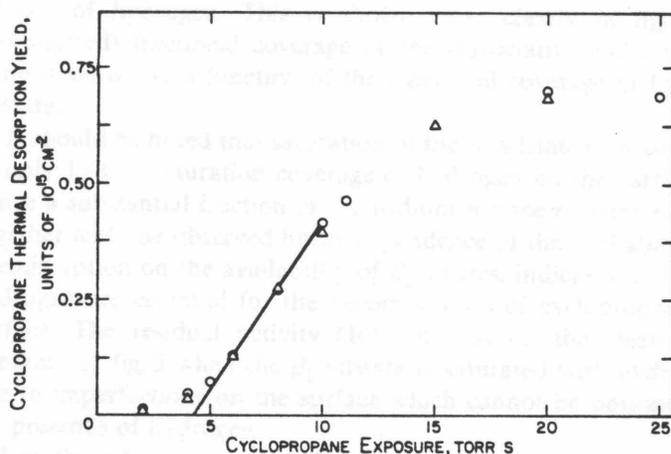


Fig. 3. Yield of cyclopropane as a function of exposure of cyclopropane.

on the surface, the x -intercept would be the origin. The reactivity of the surface for the dissociative chemisorption of cyclopropane was measured for various precoverages of hydrogen in the β_2 state. The results of these measurements are presented in fig. 4. The probability of adsorption of molecular cyclopropane on the residue (proportional to the slopes of the lines in fig. 4) remains constant for the various precoverages of hydrogen. However, the reactivity of the surface for the dissociation of cyclopropane (proportional to the x -intercepts of the lines in fig. 4) decreases linearly with increasing population of the β_2

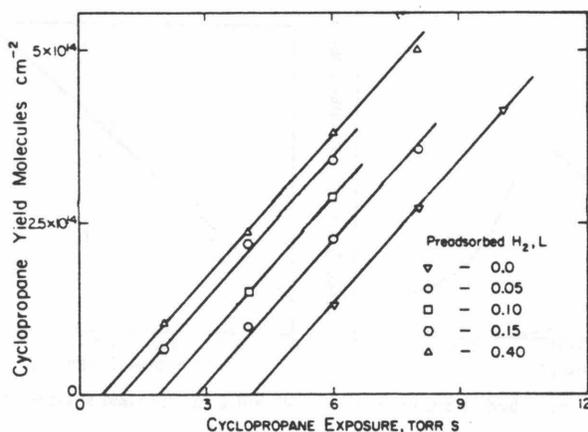


Fig. 4. Yield of cyclopropane as a function of exposure to cyclopropane parametric in the preexposure of the surface to hydrogen.

adstate of hydrogen. This is shown more clearly in fig. 5, in which the (normalized) fractional coverage of the dissociatively chemisorbed cyclopropane is shown as a function of the fractional coverage of hydrogen in the β_2 adstate.

It should be noted that saturation of the β_2 adstate of hydrogen corresponds to only 1/3 of saturation coverage of hydrogen on the surface at 100 K, and hence a substantial fraction of the iridium surface remains exposed. This fact, together with the observed linear dependence of the probability of dissociative chemisorption on the availability of β_2 adsites, indicates that the β_2 adsites of hydrogen are essential for the decomposition of cyclopropane on the Ir(110) surface. The residual activity (10% of that on the clean surface) that is apparent in fig. 5 when the β_2 adstate is saturated with hydrogen is probably due to imperfections on the surface which cannot be poisoned completely by the presence of hydrogen.

For the adsorption of cyclopropane onto surfaces with small fractional precoverages of deuterium, there was no observed desorption of mass 43 in the region of molecular cyclopropane desorption. Thus, there is no exchange between deuterium in the β_2 adstate and hydrogen in molecularly adsorbed cyclopropane. This is a further indication that the surface is not effective for C-H bond activation after the residue state is saturated.

3.3. Adsorption of hydrogen on the dehydrogenated residue

In previous work, it was determined that heating a surface on which cyclopropane was adsorbed to 700 K resulted in complete desorption of the

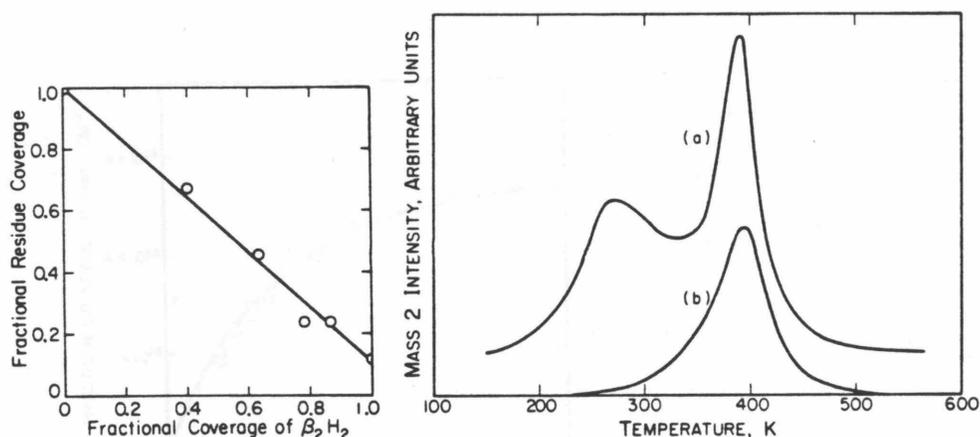


Fig. 5. Surface reactivity as a function of preexposure to hydrogen.

Fig. 6. (a) Hydrogen thermal desorption resulting from an exposure of 20 L of H_2 to the clean surface. (b) Hydrogen thermal desorption resulting from an exposure of 20 L of H_2 to the DHR.

hydrogen with no removal of the carbon from the surface [7]. A surface prepared in this manner (with a saturation coverage of the dissociated cyclopropane present initially, i.e. a surface on which no further cyclopropane will dissociate and on which the β'_2 and γ thermal desorption peaks of hydrogen are saturated) will henceforth be referred to as the dehydrogenated residue (DHR). If the DHR is exposed to 20 L of H₂, the thermal desorption spectrum of H₂ exhibits one peak in the range of temperature suggestive of the β_2 adstate as shown in fig. 6b. The thermal desorption spectrum resulting from an exposure of 20 L of H₂ to the clean Ir(110) surface is shown for comparison in fig. 6a.

Saturation of the β'_2 sites (cf. fig. 1a) available in the presence of the DHR corresponds to 60% of the saturation level of β_2 hydrogen on the clean surface as determined by a comparison of fig. 6a with fig. 6b. This indicates that 40% of the sites are poisoned by carbon on the surface. In addition, as is clear from fig. 6b, no β_1 adsorption sites are available on the DHR.

The DHR becomes saturated with hydrogen after an exposure of 1 L. Such a surface will be referred to as the hydrogen-treated carbon residue (HTCR). As may be seen in fig. 7, the hydrogen obeys first-order adsorption kinetics rather than the second-order kinetics usually associated with dissociative adsorption. This unusual behavior is also observed for the adsorption of H₂ into the β_2 adstate on the clean Ir(110) surface. This information is a further indication that the hydrogen adsorbed onto the DHR is adsorbed into sites very similar to the β_2 sites occupied by hydrogen on the clean surface. It should be mentioned, however, that the data of fig. 7 imply an initial probability of adsorption of H₂ on the DHR of 0.5 ± 0.1 as opposed to a value of unity on the clean surface. However, if the part of the surface that is poisoned for

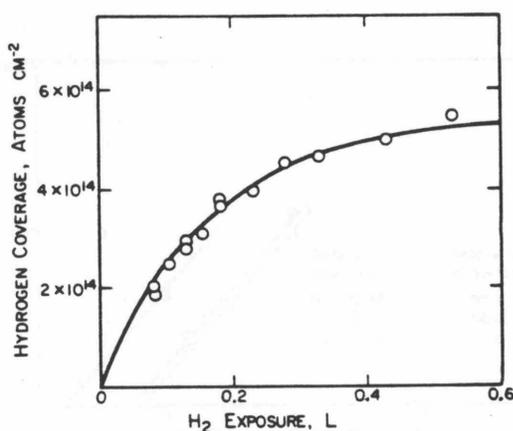


Fig. 7. Hydrogen coverage as a function of exposure to the DHR. The solid line represents first-order adsorption kinetics.

hydrogen adsorption by adsorbed carbon is taken into account, this lower probability for the adsorption of hydrogen is the expected result.

The absence of a γ peak near 500 K in fig. 6b indicates that C-H bonds are not reformed by adsorbing hydrogen onto the DHR. Further evidence of the lack of reactivity of the adsorbed carbon with hydrogen was obtained by exposing the DHR to 5×10^{-8} Torr of H₂ at 700 K for 4 min. Upon cooling and reexposure of this surface to 1.5 L of H₂, the surface exhibited exactly the same thermal desorption spectrum of H₂ as that shown in fig. 6b. If any appreciable ($\geq 5\%$) reaction of the chemisorbed carbon had taken place, it would have been observed as an increase in the intensity of the β'_2 thermal desorption state near 400 K. Therefore, the availability of β'_2 adsorption sites for hydrogen does not promote the reaction between hydrogen atoms and the adsorbed carbon under the experimental conditions investigated here.

3.4. Reactivity of cyclopropane on treated surfaces

However, the β'_2 sites can act as active centers for the dissociative adsorption of cyclopropane. The probability of dissociative chemisorption of cyclopropane was measured for the DHR, the HTCR, and the partially dehydrogenated residue (PDHR). The PDHR was formed by saturating the residue state at 100 K followed by annealing the surface to 425 K. This procedure desorbed the hydrogen from the β'_2 sites but left the γ C-H bonds intact (cf. fig. 1). As mentioned previously, the formation of the DHR left an adsorption state of hydrogen that would accommodate 60% as much β'_2 hydrogen as the clean surface. Exposure of the DHR to H₂ to create the HTCR, of course, rendered the β'_2 sites unavailable for reaction.

The reactivity of these surfaces for the dissociative adsorption of cyclopropane was measured in the manner described previously. The results are

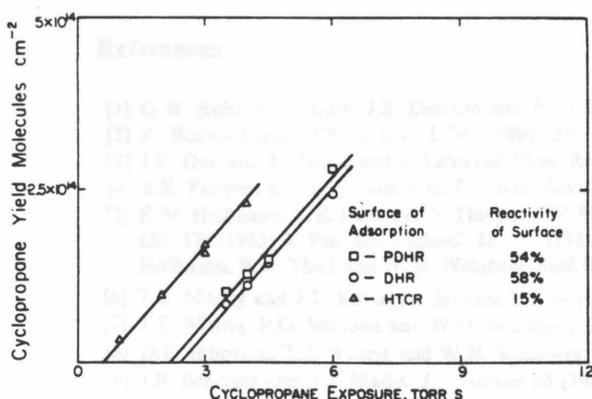


Fig. 8. Yield of cyclopropane as a function of surface pretreatment and exposure to cyclopropane.

presented in fig. 8. As shown in this figure, the DHR is 58% as reactive as the clean surface for the dissociation of cyclopropane. This is indistinguishably close to the measured availability of β_2' hydrogen adsorption sites (i.e. 60%). The presence of the C-H bonds in the PDHR does not affect the reactivity greatly. However, the presence of hydrogen atoms in the β_2' sites in the HPCR decreases the reactivity to 15% of the reactivity of the clean surface. This compares well with the 10% reactivity observed for a surface saturated with β_2 hydrogen (cf. fig. 5). Thus, the reactivity of the surface under these circumstances is again limited by the availability of β_2 hydrogen adsorption sites as active reaction centers.

4. Summary

The results of this study may be summarized as follows:

- (1) The reactivity of the Ir(110)-(1×2) surface for the dissociation of cyclopropane is determined by the number of β_2 hydrogen adsorption sites available. This implies that H-C bond rupture is the initial step in the dissociation of cyclopropane on the surface.
- (2) The β_1 adsorption state of hydrogen is poisoned by the presence of the cyclopropane residue on the DHR.
- (3) Exposure of the DHR to H₂ results in the adsorption of hydrogen into a state very similar to the β_2 hydrogen adsorption state observed on clean Ir(110). This state contains 60% as much hydrogen at saturation as the saturated β_2 state on the clean surface.
- (4) The chemisorbed carbon in the DHR is not reactive to hydrogen, even at temperatures as high as 700 K. The C-H bonds observed in the γ -state in thermal desorption spectra from a cyclopropane residue are not regenerated upon exposure of the DHR to H₂.

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APPENDIX C

THE INTERACTION OF ETHANE, PROPANE, ISOBUTANE
AND NEOPENTANE WITH THE (110) SURFACE OF IRIDIUM

(The text of Appendix C consists of an article coauthored with T. S. Wittrig and W. H. Weinberg that has appeared in The Journal of Chemical Physics 76, 3305 (1982).)

The interaction of ethane, propane, isobutane, and neopentane with the (110) surface of iridium^{a)}

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The adsorption and reaction of ethane, propane, isobutane, and neopentane with the reconstructed Ir (110)-(1×2) surface have been studied with the thermal desorption mass spectrometry. As the surface is heated, these hydrocarbons decompose to yield gaseous hydrogen and adsorbed carbon. No hydrocarbons other than the hydrocarbon initially adsorbed was observed to desorb under any of the conditions described in this investigation. The reactivity of the surface for the dissociation of the saturated hydrocarbons is linearly related to the availability of vacant β_2 hydrogen adsites on the surface. Three thermal desorption states of hydrogen, identified as the α , β_1 , and γ thermal desorption states, were observed following the dissociation of propane, isobutane, and neopentane. The α and γ thermal desorption states are hydrogen molecules desorbing from the surface following the dehydrogenation of hydrocarbon fragments on the surface, and the β_1 thermal desorption state represents hydrogen atoms that are bound to the metal surface in sites that are similar to the β_2 adsites of hydrogen on the clean surface. The thermal desorption of hydrogen following exposure of the surface to ethane exhibits only a β_2 thermal desorption peak.

I. INTRODUCTION

A fundamental investigation of the reactions of saturated hydrocarbons on transition metal surfaces is important because it may provide insight into the mechanism of hydrocarbon hydrogenolysis reactions in practical catalytic systems. There have been several recent studies carried out under ultrahigh vacuum conditions concerning the dehydrogenation of cyclohexane to form benzene.¹⁻⁴ Ultrahigh vacuum investigations of the non-reactive interaction of saturated hydrocarbons with metallic surfaces have included LEED studies of the nondissociative adsorption of straight-chain paraffins on Pt (111) and Ag (111),⁵ EELS, and UPS studies of cyclopropane and cyclohexane adsorbed molecularly on Ru (001),⁶ and an ESDIAD study of the nondissociative adsorption of ethane, cyclopropane, and cyclohexane on Ru (001).⁷

In a recently completed investigation in this laboratory, the adsorption and decomposition of cyclopropane on the reconstructed Ir(110)-(1×2) surface were examined.^{8,9} It has since been found that Ir(110)-(1×2) will promote the dissociation of a wide range of saturated hydrocarbons. Of the saturated hydrocarbons that have been investigated (including methane, cyclopropane, and those reported in this paper), only methane shows no indication of dissociation on the surface under the conditions that are described in this paper. This paper reports a study of the interactions of a series of hydrocarbons with Ir(110) to ascertain both the similarities and the differences, insofar as their interaction with this surface is concerned. These observations may be useful in deducing a more general understanding

of the interaction between saturated hydrocarbons and transition metal surfaces.

II. EXPERIMENTAL PROCEDURES

The experiments were performed in an ion-pumped stainless steel belljar that has been described previously.^{10,11} The base pressure of the belljar was below 2×10^{-10} Torr of reactive contaminants. The hydrocarbon exposures were carried out with a directional beam doser consisting of a multichannel array of capillaries.¹² During dosing, the crystal was positioned approximately 3 mm from the doser face. This provides a beam pressure-to-background pressure ratio of over 100:1. The unit of exposure that is employed for the beam doser is the Torr second (Torr s) and refers to the product of the time of exposure and the pressure in the storage bulb of the doser. The storage bulb supplies gas through a capillary to the doser head leading into the vacuum system. Therefore, the flux of gas into the vacuum system is proportional to the pressure in the storage bulb. For the gases employed in this study, an exposure of 1 L is approximately equivalent to an exposure of 7 Torr s for ethane, 3 Torr s for propane, 4 Torr s for isobutane, and 4 Torr s for neopentane.

The crystal was cleaned between thermal desorption experiments by exposure to 10^{-7} Torr of O₂ for 1.5–2 min at a crystal temperature of 900 K. This was followed by heating the crystal to 1600 K to desorb the oxygen.

The hydrogen coverage calibration that is used to determine the amount of dissociated hydrocarbon on the surface was determined by titration with oxygen.¹⁰ The hydrogen concentration on the surface following an exposure of 0.5 L of H₂ is $(7.3 \pm 1.0) \times 10^{14}$ molecules cm⁻².¹⁰

With the exception of neopentane, the gases used in this study were obtained from Matheson. The minimum purities quoted were 99.9999% for the hydrogen, 99.0% for the ethane, and 99.5% for the propane and isobutane. The neopentane was obtained from Chemtech, and the

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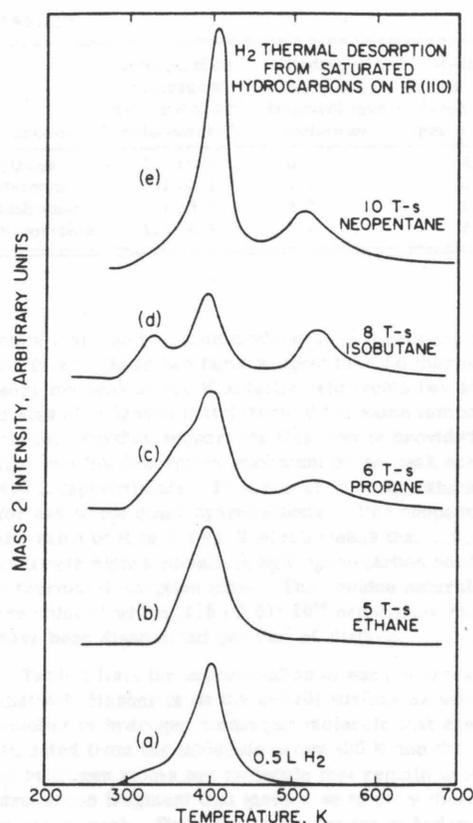


FIG. 1. Thermal desorption of hydrogen resulting from exposure of the Ir(110) surface to: (a) 0.5 L of H_2 ; (b) 5 Torr-s of ethane (saturation); (c) 6 Torr-s of propane (saturation); (d) 8 Torr-s of isobutane (saturation); and (e) 10 Torr-s of neopentane (saturation).

purity was greater than 99%. Each of the gases was checked mass spectrometrically for purity and no extraneous gases were detected by this method.

III. RESULTS

A. Thermal desorption of hydrogen from hydrocarbon overlayers

The thermal desorption mass spectra of hydrogen from saturated overlayers of each of the four hydrocarbons are shown in Fig. 1. Saturation refers here only to the dissociatively adsorbed hydrocarbon and not to the reversibly adsorbed molecular overlayer that desorbs at a lower temperature, as discussed later. The thermal desorption mass spectrum resulting from an exposure of 0.5 L of H_2 to the clean surface is shown in Fig. 1(a) for comparison. An exposure of 0.5 L of H_2 saturates the β_2 adstate of hydrogen on the clean surface.¹⁰ The temperature of adsorption for all exposures was 100 K and all spectra are drawn to the same scale to permit a direct comparison of the amount of hydrogen which desorbs in each case.

The thermal desorption of H_2 , resulting from saturation of the residue overlayer after the irreversible adsorption of ethane, exhibits a one-peak structure with a maximum rate of desorption at approximately 400 K as shown in Fig. 1(b). The area of the peak corresponds to $(1.1 \pm 0.3) \times 10^{14}$ dissociated ethane molecules per cm^2 .

In contrast to the single peak resulting from the decomposition of ethane, the thermal desorption of H_2 from the saturated overlayer of the decomposition products of propane, shown in Fig. 1(c), displays a more complicated three-peak structure. Once again, there is a peak in the temperature range (~ 400 K) that is suggestive of desorption of hydrogen from the β_2 adstate of hydrogen on the clean surface. This thermal desorption state (which appears for all the hydrocarbons investigated in this work) will be referred to as the β_2' thermal desorption state. Also evident in Fig. 1(c) is a low-temperature shoulder on the β_2' peak. This state will be defined as the α thermal desorption state. In the region of temperature near 520 K, there is a peak which will be referred to as the γ thermal desorption state. The temperature range of the γ state indicates that there are hydrogen atoms present on the surface that are more strongly bound than any hydrogen atoms on the clean surface [cf. Fig. 1(a)]. Therefore, the γ state evidently represents hydrogen atoms in highly unsaturated hydrocarbon fragments. This is consistent with the spectroscopic observation of partially dehydrogenated fragments in studies of the interactions of unsaturated hydrocarbons with other transition metals.¹³⁻¹⁵ The ratio of the combined areas of the α and β_2' peaks to the area of the γ peak is 3.2 ± 0.3 . This ratio will be referred to hereafter as R . This value of R indicates that 1.9 ± 0.2 hydrogen atoms in each propane molecule remain in hydrogen-carbon bonds until desorption occurs from the high temperature γ state. The total area of the thermal desorption of hydrogen from the residue overlayer resulting from the irreversible adsorption of propane indicates that $(1.1 \pm 0.3) \times 10^{14}$ propane molecules dissociate per cm^2 of surface.

The hydrogen thermal desorption from a saturated residue of isobutane, shown in Fig. 1(d), again exhibits three thermal desorption states. The α state is much more well resolved from the β_2' state than it was in the case of propane. The γ thermal desorption state has increased in intensity, signifying the presence of more hydrogen in the hydrocarbon matrix. The value of R for isobutane is 1.7 ± 0.2 which indicates that 3.7 ± 0.2 hydrogen atoms per molecule remain in hydrogen-carbon bonds on the surface. A saturation coverage of $(1.1 \pm 0.3) \times 10^{14}$ dissociated molecules per cm^2 was determined from the total area under the three thermal desorption peaks of hydrogen.

A saturated overlayer of the decomposition products of neopentane produces the hydrogen thermal desorption spectrum shown in Fig. 1(e). The most striking features of this spectrum are that no α state is observed and that the peak at 410 K has approximately twice the intensity as the β_2 thermal desorption state of hydrogen at saturation on the clean surface [cf. Fig. 1(a)]. This indicates that there are more hydrogen atoms in that

TABLE I.

Species	Hydrocarbon coverage at saturation (10^{14} molecule cm^{-2})	Hydrogen atoms in γ fragment (per molecule)	Hydrogen atoms desorbed below 420 K (per molecule)
Ethane	1.1 ± 0.3	0	6
Propane	1.1 ± 0.3	1.9	6.1
Isobutane	1.1 ± 0.3	3.7	6.3
Neopentane	1.5 ± 0.3	3.9	8.1

state than can be accommodated in β_2 -like sites on the surface. These two facts suggest that the thermal desorption peak at 410 K actually represents two adsorbed states of hydrogen that desorb in the same temperature range. Further support for this idea is provided by the fact that the desorption maximum of the peak occurs at 410 K (approximately 10 K higher in temperature than for any of the other hydrocarbons). For neopentane, the value of R is 2.1 ± 0.2 which means that 3.9 ± 0.2 hydrogen atoms remain in hydrogen-carbon bonds in the γ thermal desorption state. The residue saturates at the point at which $(1.5 \pm 0.3) \times 10^{14}$ neopentane molecules have been dissociated per cm^2 of surface.

Table I lists the concentration of each hydrocarbon that will dissociate on the Ir(110) surface as well as the number of hydrogen atoms per molecule that are abstracted from the molecule below 420 K and the number of hydrogen atoms per molecule that remain in the hydrocarbon fragment that gives rise to the γ thermal desorption peak. Since the concentration of hydrocarbon molecules that will dissociate on the surface is relatively independent of the molecule, it is apparently not strongly related to the size of the molecule. The number of hydrogen atoms per molecule that are removed from the molecule below 420 K is also relatively constant. Thus, the concentration of active centers for C-H bond cleavage on the surface to form the hydrocarbon fragment that corresponds to the γ thermal desorption peak is the factor that determines the concentration of dissociated molecules on the surface at saturation.

The development of the thermal desorption spectra as a function of hydrocarbon exposure is shown in Fig. 2. Each quadrant is drawn with a different mass spectrometric intensity scale to facilitate the presentation. As shown in Fig. 2, an exposure of 1 Torr s of ethane [III(a)] produces a thermal desorption peak with the same shape and peak temperature as a saturation exposure of 7.5 Torr s [III(b)]. The β_2' peak temperature for propane, shown in quadrant I of Fig. 2, remains constant at 400 K. However, comparison of the spectra resulting from a 2 Torr s exposure [I(a)] and a 5 Torr s saturation exposure [I(b)] indicates that the α shoulder on the β_2' peak does not populate until the β_2' adsite is saturated. For isobutane, in quadrant IV of Fig. 2, this point is illustrated more clearly. The β_2' and γ states are the only states that are populated after an exposure of 2 Torr s [IV(a)]. Following an exposure of 4 Torr s [IV(b)], the β_2' state is fully populated, and the α state is beginning to develop. For a saturation exposure of 6 Torr s

[IV(c)], the α state is fully developed, and the γ state has increased in intensity as well. Note that the peak temperature of the β_2' thermal desorption state remains constant at 395 K. The two thermal desorption peaks of neopentane, quadrant II of Fig. 2, develop simultaneously throughout the entire range of coverage. Following an exposure of 2 Torr s [II(a)], the β_2' peak temperature is 400 K, which is in the range of the β_2' peak temperatures of ethane, propane, and isobutane. However, for the two higher exposures of 5 Torr s [II(b)] and 8 Torr s [II(c)], the β_2' peak temperature increases to a value of 410 K. Since it has been observed that the α states of propane and isobutane develop subsequent to saturation of the β_2' state, this observation is consistent with the suggestion that the peak at 410 K for neopentane is composed of contributions from a β_2' adstate and an α adstate.

One observation that is not apparent from visual inspection of Fig. 2 is the fact that the value of R for both isobutane and neopentane is a constant (within $\pm 5\%$) as a function of coverage. Hence, on average, the number of hydrogen atoms per hydrocarbon molecule that desorb in the γ thermal desorption state remains constant regardless of the surface coverage. This implies that each hydrocarbon molecule undergoes dehydrogenation to form a stable hydrocarbon fragment of a definite stoichiometry that is stable at surface temperatures be-

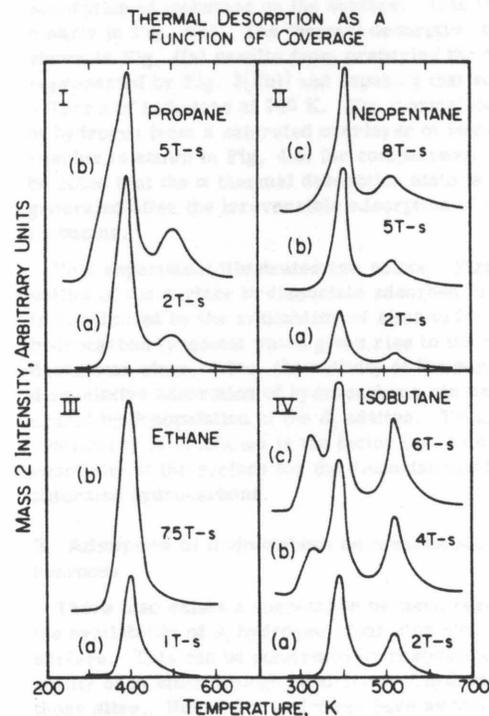


FIG. 2. Thermal desorption of hydrogen as a function of exposure for: I. Propane; II. Neopentane; III. Ethane; and IV. Isobutane. Exposures are shown adjacent to the corresponding spectrum.

low approximately 400 K.

Further proof of this proposition can be gained by the following experiment. If a surface with a saturated overlayer of hydrocarbon residue is annealed to 400 K, then both the α adsites and the β_2' adsites are depopulated. As will be shown later in this section, the β_2' adsites are thus rendered active centers for the dissociation of additional hydrocarbon molecules (i.e., they regain their ability to break C-H bonds). Thus, if the C-H bonds in the hydrocarbon entity corresponding to the γ adstate were unstable to the presence of these active centers, annealing a saturated overlayer of hydrocarbon residue to 400 K should induce a reduction in the γ peak area. This measurement was performed for isobutane and neopentane, and the results are presented in Fig. 3. Thermal desorption spectra of hydrogen resulting from saturation coverages of isobutane and neopentane are shown in I(a) and II(a), respectively, of Fig. 3. The thermal desorption spectra corresponding to the annealed surfaces are shown in I(b) for isobutane and II(b) for neopentane in Fig. 3. The saturated isobutane residue was annealed for 90 s at 400 K, and the saturated neopentane residue was annealed for 10 s at 400 K. Thus, the γ hydrocarbon fragment is stable at 400 K even in the presence of vacant β_2' hydrogen adsorption sites.

When a surface with a saturated overlayer of hydrocarbon residue is annealed to 400 K, the β_2' sites again become available as active centers for dissociation of

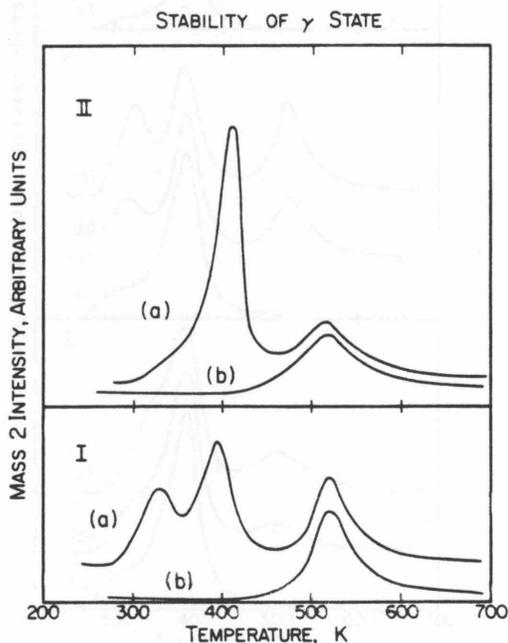


FIG. 3. Thermal desorption of hydrogen resulting from: I(a). Exposure of 8 Torr s of isobutane to the Ir(110) surface at 100 K; I(b). Surface of I(a) annealed to 400 K for 90 s; II(a). Exposure of 10 Torr s of neopentane to the Ir(110) surface at 100 K; and II(b). Surface of II(a) annealed to 400 K for 10 s.

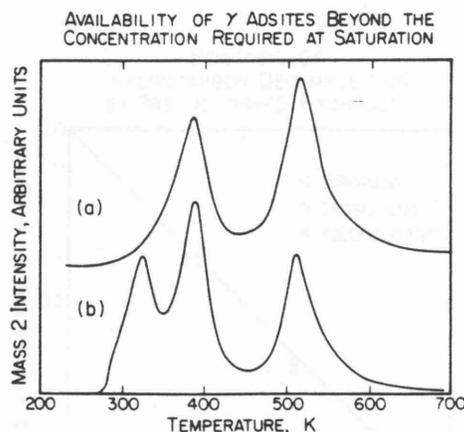


FIG. 4. Thermal desorption of hydrogen resulting from: (a) Exposure of the Ir(110) surface to 8 Torr s of isobutane at 100 K, followed by heating the surface to 400 K, recoiling to 100 K, and re-exposure to 8 Torr s of isobutane; and (b) Exposure of the Ir(110) surface to 8 Torr s of isobutane.

hydrocarbon molecules. If such a surface (prepared with isobutane) is cooled to 100 K and re-exposed to 8 Torr s of isobutane, the β_2' thermal desorption state is repopulated, and there is an increased intensity in the γ thermal desorption state due to additional dissociative adsorption of isobutane on the surface. This is shown clearly in Fig. 4(a). The thermal desorption spectrum shown in Fig. 4(a) results from preparing the surface represented by Fig. 3[I(b)] and exposing that surface to 8 Torr s of isobutane at 100 K. The thermal desorption of hydrogen from a saturated overlayer of isobutane residue is shown in Fig. 4(b) for comparison. It should be noted that the α thermal desorption state is not regenerated after the irreversible adsorption of additional isobutane.

This experiment illustrates two points. First, the ability of the surface to dissociate adsorbed isobutane is not limited by the availability of sites to form the hydrocarbon fragment which gives rise to the γ thermal desorption state. Also, the activity of the surface for dissociative adsorption of hydrocarbons can be regenerated by depopulation of the β_2' adsites. Thus, the availability of β_2' adsites is the factor that determines the reactivity of the surface for the dissociation of these saturated hydrocarbons.

B. Adsorption of hydrocarbons on preadsorbed β_2 hydrogen

There also exists a correlation between reactivity and the availability of β_2 hydrogen adsorption sites on the surface. This can be confirmed by restricting the availability of β_2 sites through adsorption of hydrogen into those sites. Reactivity is defined here as the total amount of hydrocarbon that will dissociate on the surface. Since, as discussed in Sec. III A, the ratio R is constant regardless of coverage, the number of hydrogen atoms per molecule retained in the γ adstate is constant

with coverage. Thus, the area of the γ thermal desorption peak is proportional to the number of dissociated molecules on the surface. Therefore, the area of the γ peak at saturation is proportional to the reactivity of the surface. The area of the γ thermal desorption peak is used as a measure of hydrocarbon coverage because the preadsorbed hydrogen adds to the intensity in the temperature range of the α and β'_2 thermal desorption peaks.

Representative thermal desorption spectra of hydrogen resulting from saturation exposures of neopentane, isobutane and propane adsorbed on various precoverages of β_2 hydrogen are shown in Figs. 5(I), 5(II), and 5(III), respectively. The adsorption of any one of these hydrocarbon molecules onto a surface saturated with β_2 hydrogen [shown as spectrum (c) in each section of Fig. 5], results in a spectrum that corresponds exactly to

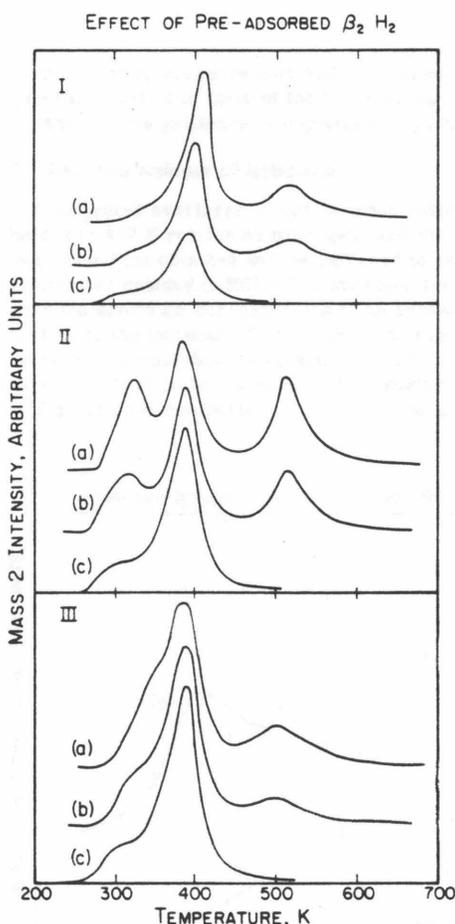


FIG. 5. Thermal desorption of hydrogen resulting from adsorption of: I. 10 Torr s of neopentane; II. 8 Torr s of isobutane; and III. 6 Torr s of propane onto surfaces prepared in the following manner: (a) Clean Ir(110) surface; (b) Ir(110) surface exposed to 0.05 L of H_2 ; and (c) Ir(110) surface exposed to 0.50 L of H_2 .

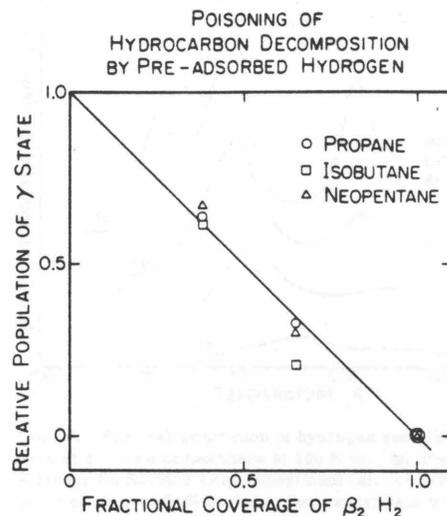


FIG. 6. Reactivity of surface for hydrocarbon decomposition as a function of the availability of β_2 hydrogen adsorption sites.

thermal desorption from a surface saturated with β_2 hydrogen (note that each section of Fig. 5 is drawn with a different mass spectrometric intensity scale). In particular, no desorption from the γ state is observed for these spectra, indicating no dissociative adsorption of these saturated hydrocarbons occurs on the surface when the β_2 adstate is saturated with hydrogen. Spectrum (b) in each section of Fig. 5 corresponds to hydrogen thermal desorption after a saturation exposure of each hydrocarbon to a surface that was previously exposed to 0.05 L of H_2 (corresponding to 38% of saturation of the β_2 adstate). A γ thermal desorption peak is observed under these conditions, but it is less intense than those measured after the corresponding exposure of hydrocarbon to the clean surface shown in spectrum (a) of each section of Fig. 5.

The reactivity of the surface for hydrocarbon decomposition (plotted as the normalized population of the γ adstate at saturation) is shown in Fig. 6 as a function of the fractional precoverage of hydrogen in the β_2 adsites. This figure indicates clearly that the ability of the surface to dissociate saturated hydrocarbon molecules is linearly related to the number of β_2 hydrogen adsorption sites available on the surface. This provides further evidence that the β'_2 thermal desorption state, observed for all of these hydrocarbons adsorbed on Ir(110) represents hydrogen atoms that have been abstracted from C-H bonds and are bonded to metal-hydrogen sites similar to the β_2 adsites of hydrogen on the clean surface.

If 0.05 L of deuterium is adsorbed into the β_2 adsites prior to the adsorption of a saturation exposure of isobutane, the subsequent thermal desorption spectrum of HD, shown in Fig. 7, indicates intensity in all three thermal desorption states (i. e., α , β'_2 , and γ). This result proves decisively that the hydrogen atoms in the hydrocarbon fragment, represented by the γ thermal de-

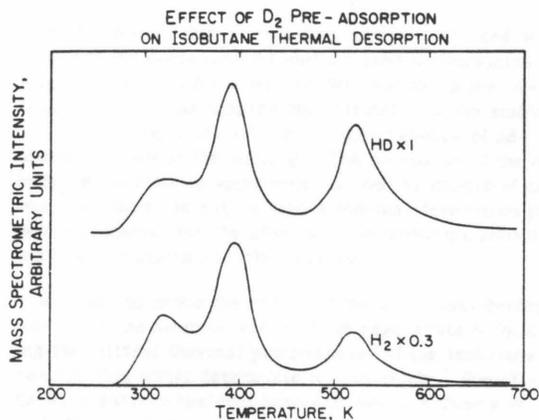


FIG. 7. Thermal desorption of H_2 and HD following the exposure of 8 Torr s of isobutane onto a surface that was pre-exposed to 0.05 L of D_2 .

sorption state, exchange with hydrogen atoms in the β_2 adstate. This is in spite of the fact that the γ adstate is stable in the presence of unpopulated β_2 adsites.

C. Annealed residues of isobutane

A saturated overlayer of hydrocarbon residue that is heated to 800 K retains no hydrogen, and the carbon overlayer thus obtained will be referred to as the dehydrogenated residue (DHR). The hydrogen thermal desorption spectrum corresponding to an exposure of 20 L of H_2 to the isobutane DHR is shown in Fig. 8(b). The hydrogen thermal desorption spectrum after an exposure of 20 L of H_2 to the clean Ir(110) surface is shown in Fig. 8(a) for comparison. Note that the adsorption

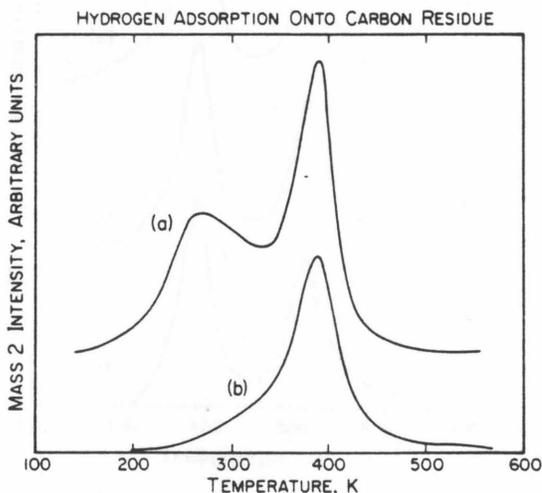


FIG. 8. Thermal desorption of hydrogen resulting from exposure of 20 L of H_2 to: (a) The clean Ir(110) surface, and (b) The dehydrogenated isobutane residue.

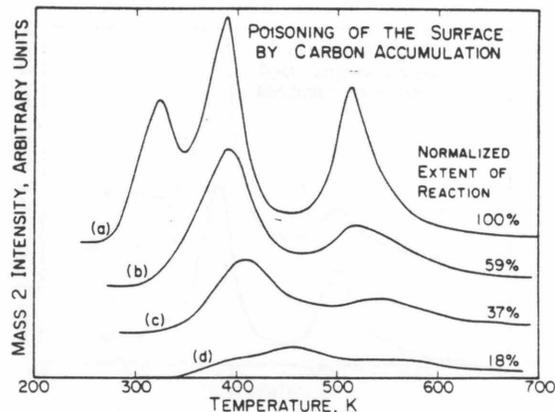


FIG. 9. Thermal desorption of hydrogen resulting from exposure of 8 Torr s of isobutane at 100 K to: (a) The clean Ir(110) surface; (b) Surface after experiment (a); (c) Surface after experiment (b); and (d) Surface after experiment (c).

of hydrogen into β_1 adsites is blocked by the presence of the carbon residue. Furthermore, the γ adstates (corresponding to the formation of C-H bonds) are not repopulated by exposure to hydrogen. This indicates that the dehydrogenation of the stable hydrocarbon fragments represented by the γ thermal desorption state is irreversible.

A series of experiments was performed in which a saturation exposure of isobutane was adsorbed on the surface, the surface was subsequently heated to 200 K, and then cooled to 100 K. This procedure was repeated a total of four times, and the results are shown in Fig. 9. The thermal desorption spectrum of hydrogen that follows an exposure of 8 Torr s of isobutane to the clean Ir(110) surface is shown in Fig. 9(a). The thermal desorption spectrum of hydrogen following an exposure of 8 Torr s of isobutane to the DHR formed in the experiment of Fig. 9(a) is shown in Fig. 9(b). Figures 9(c) and 9(d) follow in the same manner. The active centers for dissociation of isobutane molecules are progressively blocked by the accumulation of adsorbed carbon on the surface. The (normalized) extent of reaction of isobutane (proportional to the H_2 thermal desorption intensity) is tabulated for each experiment in Fig. 9. The amount of isobutane that dissociates on the surface is reduced by approximately 40% for each iteration. If the assumption is made that this trend will persist, an estimate of the total number of isobutane molecules that it is possible to dissociate on the surface can be obtained from the product of the infinite series $\sum_{n=0}^{\infty} (0.6 \pm 0.03)^n$ and the concentration of isobutane represented by Fig. 9(a) [i.e., $(1.1 \pm 0.3) \times 10^{14} \text{ cm}^{-2}$]. This number is $(2.8 \pm 0.8) \times 10^{14} \text{ cm}^{-2}$. Thus, a coverage of approximately $(1.1 \pm 0.3) \times 10^{15}$ carbon atoms per cm^2 of surface is sufficient to poison the dissociation of isobutane on the surface.

The number of hydrogen atoms per molecule in the γ hydrocarbon fragment (as computed from the ratio R)

remains in the range 3.7 ± 0.2 for spectra 9(b) and 9(c). Although the deconvolution method used to determine R was not practical for spectrum 9(d) due to its low intensity, it is clear that the stoichiometry of the stable γ intermediate is not affected by the presence of adsorbed carbon on the surface. The formation of the α hydrogen adstate is apparently blocked by adsorbed carbon. As shown in Fig. 9, the α thermal desorption peak does not appear for the adsorption of isobutane onto a surface containing adsorbed carbon.

In order to probe the nature of the α thermal desorption state, an attempt was made to regenerate it following the mildest thermal pretreatment of the isobutane residue that would depopulate it completely. Specifically, a surface that had been exposed to 8 Torr s of isobutane (saturation exposure) was heated to 320 K. This creates an overlayer that yields the hydrogen thermal desorption spectrum shown in Fig. 10(a). This surface will be referred to in this paper as the partially dehydrogenated residue (PDR). Exposure of the PDR to 6 Torr s of isobutane at 100 K results in the thermal desorption spectrum of hydrogen shown in Fig. 10(b). This spectrum is identical to the spectrum of Fig. 10(a), indicating that no further dissociative adsorption occurs upon exposure of isobutane to the PDR. Thus, the α adstate does not serve as an active center for dissociative adsorption of isobutane under these conditions.

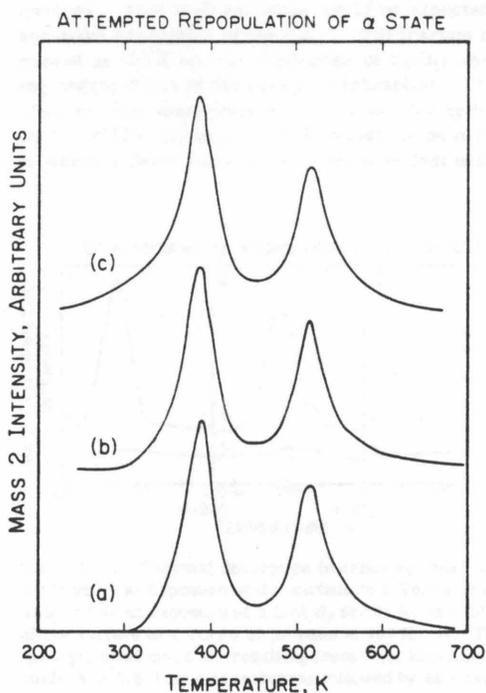


FIG. 10. Thermal desorption of hydrogen resulting from: (a) Exposure of the clean Ir(110) surface to 8 Torr s of isobutane, followed by heating to 320 K (i.e., formation of PDR); (b) Exposure of the PDR to 6 Torr s of isobutane; and (c) Exposure of the PDR to 5 L of H_2 .

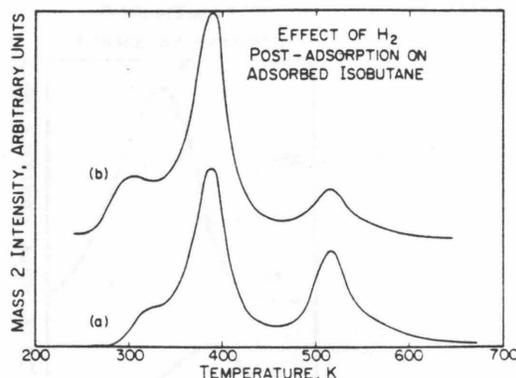


FIG. 11. Thermal desorption of hydrogen resulting from: (a) Exposure of 3.5 Torr s of isobutane to the Ir(110) surface followed by an exposure of 4 L of H_2 at 100 K; and (b) Exposure of 3.5 Torr s of isobutane to the Ir(110) surface at 100 K.

The thermal desorption spectrum of hydrogen following an exposure of 5 L of H_2 to the PDR is shown in Fig. 10(c). A slight broadening on the low-temperature side of the β_2' peak has occurred. This is due to the adsorption of hydrogen into a small concentration of β_1 hydrogen adsites ($< 5\%$ of the concentration of β_1 adsites on the clean surface). However, as before, there is no peak near 320 K which would be expected for desorption from the α adstate. Thus, the α adsite is not repopulated by exposure of H_2 to the PDR.

An attempt was made to adsorb hydrogen into the α adstate on a surface on which the α adstate was not saturated. Such a surface was prepared by the adsorption of 3.5 Torr s of isobutane at 100 K. The thermal desorption spectrum of hydrogen from this surface is shown in Fig. 11(a). It is apparent from inspection of this thermal desorption spectrum that the α thermal desorption peak has just begun to develop at this exposure. The thermal desorption spectrum that results from an exposure of 4 L of H_2 to the surface following an exposure to 3.5 Torr s of isobutane is shown in Fig. 11(b). There is some additional intensity in the region of desorption of the α state, but the peak temperature is 300 K, which is indicative of hydrogen adsorbed in β_1 hydrogen adsites. By comparison, the peak temperature of the α thermal desorption state is 320 K. Indeed, on a surface that is not saturated with hydrocarbon residue, it would be expected that some β_1 adsites would be available. Thus, it appears that the α thermal desorption state is not populated by postexposure to hydrogen in this case either.

D. Postadsorption of hydrogen on the hydrocarbon overlayers

A far more interesting feature of Fig. 11(b) is the loss of approximately 60% of the intensity in the γ thermal desorption state relative to Fig. 11(a). This result indicates that exposing the surface to hydrogen at 100 K has caused hydrogen that would otherwise have been evolved from the γ adstate to desorb as hydrogen in a

hydrocarbon molecule.

This proposition is proved incisively by the experiment represented in Fig. 12. The thermal desorption spectra in sections I, II, and III of Fig. 12 correspond to a major cracking fragment of propane, isobutane, and neopentane, respectively. Although the mass spectrometric intensity scale is consistent in each section of Fig. 12, the intensity scales are not consistent for separate sections. Spectra (b) are "blank" measurements for which a hydrocarbon overlayer corresponding to a coverage less than saturation was heated, and the amount of hydrocarbon that desorbed was monitored. Spectra (a) are the result of exposing hydrogen to the hydrocarbon overlayer represented by the corresponding spectra (b). Inspection of Fig. 12 shows clearly that postadsorption of hydrogen at 100 K induces the desorption of the molecular hydrocarbon from the surface upon heating. The analogous experiment for ethane is shown on a different temperature scale in Fig. 13. The mass spectrometric cracking patterns of the desorbing hydrocarbons match the cracking patterns of the hydrocarbon initially adsorbed in each case. The sensitivity of this analysis is sufficiently high to establish that at least 90% (and possibly all) of the desorbing hydrocarbon molecules correspond in each case to that hydrocarbon adsorbed initially.

If deuterium is postadsorbed onto the hydrocarbon overlayers rather than hydrogen, there is no exchange of deuterium into the C-H bonds of the desorbing hydrocarbons. This H-D exchange would be expected if dissociative adsorption of the parent hydrocarbon had occurred at 100 K and the adsorption of $H_2(D_2)$ were causing regeneration of the parent hydrocarbon. Thus, it is apparent that adsorption of these saturated hydrocarbons on the Ir(110) surface at 100 K results in an overlayer in which at least some of the molecules that will undergo

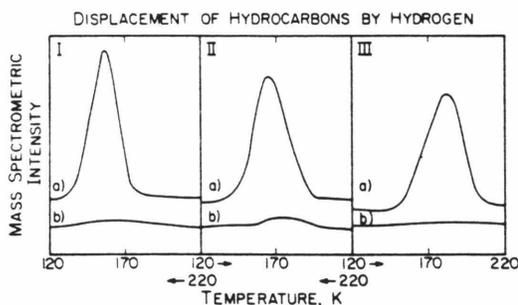


FIG. 12. I. Thermal desorption (monitoring mass 43) resulting from: (a) Exposure of the surface to 2 Torr s of propane followed by an exposure of 2 L of H_2 at 100 K; and (b) Exposure of the surface to 2 Torr s of propane at 100 K. II. Thermal desorption (of mass 43) resulting from: (a) Exposure of the surface to 3.5 Torr s of isobutane followed by an exposure of 0.25 L of H_2 at 100 K; and (b) Exposure of the surface to 3.5 Torr s of isobutane at 100 K. III. Thermal desorption (of mass 41) resulting from: (a) Exposure of the surface to 2 Torr s of neopentane followed by an exposure of 2 L of H_2 at 100 K; and (b) Exposure of the surface to 2 Torr s of neopentane at 100 K.

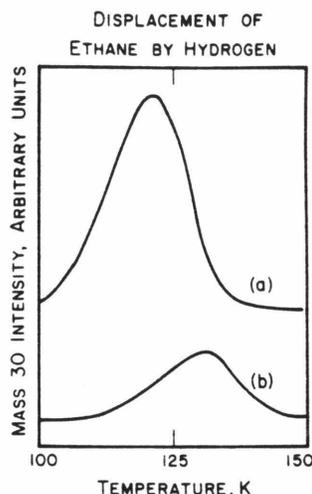


FIG. 13. Thermal desorption (of mass 30) resulting from: (a) Exposure of the surface to 2 Torr s of ethane followed by an exposure of 2 L of H_2 at 100 K; and (b) Exposure of the surface to 2 Torr s of ethane at 100 K.

dissociation retain their molecular identity. The post-adsorbed hydrogen is displacing these associatively adsorbed molecules from the vicinity of active centers on which they would otherwise dissociate at slightly higher temperatures.

The temperatures at which the dissociation takes place are below the temperatures at which reversibly adsorbed molecules desorb from the surface. All reversibly adsorbed ethane is desorbed upon heating the surface to 130 K. The corresponding temperatures for propane, isobutane, and neopentane are 160, 170, and 180 K, respectively. If, for propane, isobutane or neopentane, the adsorbed overlayer is heated to 130 K, recooled and then exposed to hydrogen, the amount of hydrocarbon that is dissociated on the surface is the same as if there were no postadsorption of hydrogen. Thus, at some temperature between 100 and 130 K, the adsorbed hydrocarbon molecules undergo a transformation (partial dehydrogenation) which renders them irreversibly adsorbed. The same result holds for ethane since all the molecular ethane has desorbed from the surface at a temperature of 130 K.

E. The effect of postadsorbed CO on adsorbed isobutane and neopentane

It was established in an earlier investigation of the coadsorption of H_2 and CO on Ir(110) that CO, which is adsorbed onto an overlayer of β_2 hydrogen, displaces the hydrogen atoms from β_2 to β_1 adsites.¹⁶ Thus, it would be expected that CO would also be effective in displacing associatively adsorbed hydrocarbon molecules from the vicinity of β_2 dissociation sites on the surface. This expectation is borne out, as shown explicitly for isobutane and neopentane in Fig. 14. Thermal desorption spectra I(b) and II(b) in Fig. 14 correspond to the

desorption of hydrogen from overlayers of isobutane and neopentane, respectively, onto which CO was adsorbed at 100 K. Spectra I(a) and II(a) in Fig. 14 represent hydrogen, which desorbs from the corresponding hydrocarbon overlayers that were not exposed to CO.

The nature of the lower temperature thermal desorption states is also clarified by these experiments. The displacement by CO of hydrogen adsorbed in the β_2' adstate to a β_1 adstate, analogous to the β_2 to β_1 displacement on the clean surface, occurs for both isobutane and neopentane. Thus, for isobutane [Fig. 14(I)], the thermal desorption peak at 400 K is no longer present, and a peak that desorbs in the range of temperatures (~270 K) suggestive of β_1 desorption appears in the spectrum. Note that this thermal desorption peak is

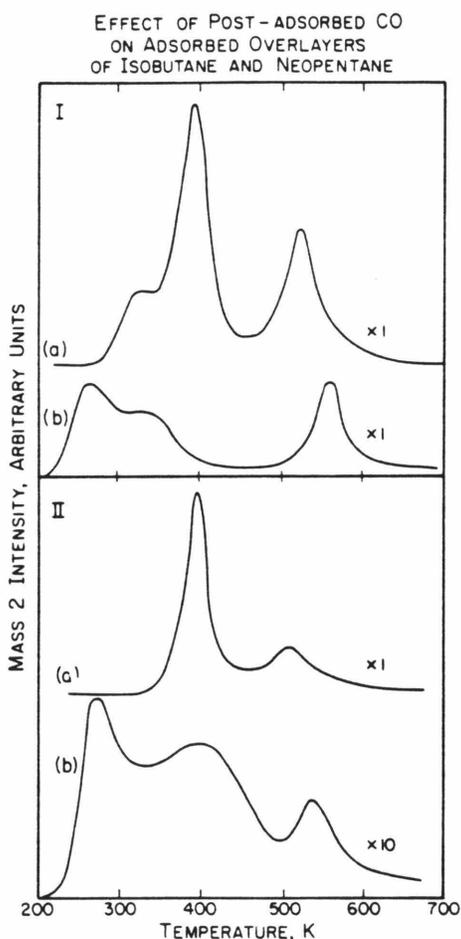


FIG. 14. I. Thermal desorption of hydrogen resulting from: (a) Exposure of the surface to 3.5 Torr s of isobutane at 100 K; and (b) Exposure of the surface to 3.5 Torr s of isobutane followed by an exposure of 2 L of CO at 100 K. II. Thermal desorption of hydrogen resulting from: (a) Exposure of the surface to 4 Torr s of neopentane at 100 K; and (b) Exposure of the surface to 4 Torr s of neopentane followed by an exposure of 2 L of CO at 100 K.

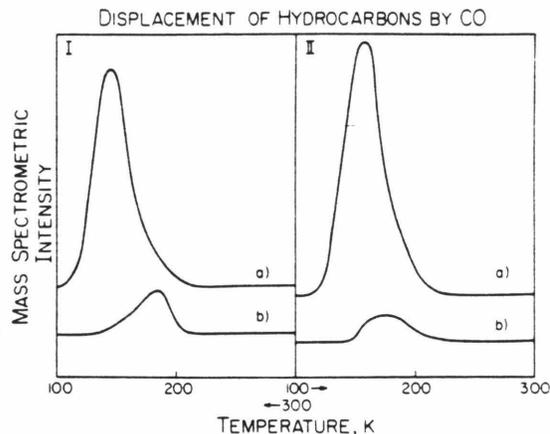


FIG. 15. I. Thermal desorption (monitoring mass 41) resulting from: (a) Exposure of the surface to 4 Torr s of isobutane followed by an exposure of 2 L of CO at 100 K; and (b) Exposure of the surface to 4 Torr s of isobutane at 100 K. II. Thermal desorption (monitoring mass 41) resulting from: (a) Exposure of the surface to 4 Torr s of neopentane followed by an exposure of 2 L CO at 100 K; and (b) Exposure of the surface to 4 Torr s of neopentane at 100 K.

distinguishable from the α peak, which has retained its peak temperature at 320 K. This observation illustrates that the α thermal desorption peak does not represent hydrogen adsorbed in β_1 -type hydrogen-metal bonds.

For neopentane [Fig. 14(II)], a peak at 270 K again appears in the thermal desorption spectrum of hydrogen following postadsorption of CO at 100 K. The fact that a thermal desorption peak is observed at 400 K is further evidence to support the idea put forward in Sec. IIIA that the peak at 410 K, in the thermal desorption spectrum of hydrogen subsequent to the adsorption and dissociation of neopentane, consists of contributions from an α adstate and a β_2' adstate.

The complementary thermal desorption measurements for isobutane and neopentane are shown in Secs. I and II of Fig. 15, respectively. Spectra (a) result from exposing CO to an overlayer of each hydrocarbon at a coverage at which the hydrogen thermal desorption is not saturated. Spectra (b) are "blank" measurements for the same hydrocarbon exposure with no postexposure of CO. A comparison of these spectra shows that the postexposure of CO induces the desorption of the parent molecular hydrocarbon. This indicates that CO displaces associatively adsorbed hydrocarbon molecules from the vicinity of the active centers for dissociation.

IV. DISCUSSION

A recent series of articles by Muetterties *et al.* has explored the concept of C-H-metal three-center two-electron bonds as precursors to C-H bond cleavage in hydrocarbon-metal surface interactions.^{4,17-19} This type of bonding interaction has been observed in organometallic chemistry (see Ref. 17, and references therein). Though this type of bonding may occur on many

metal surfaces, resulting in a weak chemisorption bond, it appears that the further reaction (C-H bond cleavage) is facilitated on stepped surfaces.^{4,17-19}

If a simple termination of the bulk is considered, the Ir(110) surface is a series of rows and troughs. However, the clean surface is reconstructed to form a (1 × 2) superstructure.²⁰ The structure of this reconstructed surface has been determined to be a surface with every other row of surface atoms missing in the [001] direction.²¹ Thus, not only are second layer Ir atoms exposed, but third layer atoms under the locations of the missing rows are exposed as well. The surface may be thought of as a series of two-atom wide (111) terraces inclined at a 90° angle to each other to form two-layer deep troughs. Consequently, this surface has a high concentration of surface steps.

As shown in Secs. III B and D, the β_2 hydrogen adsorption site on the Ir(110) surface acts as a hydrogen-acceptor site to enable hydrogen abstraction from C-H-metal bonds present on the surface. If these sites are blocked by hydrogen adsorption (either before or after adsorption of the hydrocarbon at 100 K), the extent of C-H bond cleavage is reduced.

In Sec. III A, it was shown that the area of the γ thermal desorption peak for propane, isobutane, and neopentane represents a constant number of hydrogen atoms per hydrocarbon molecule remaining in C-H bonds at a surface temperature of 400 K, regardless of the surface coverage. It was further shown that these C-H bonds are stable at 400 K, despite the presence of active C-H bondbreaking sites on the surface. These facts prove the existence of stable hydrocarbon fragments on the surface at temperatures above 500 K. The average stoichiometry of these fragments is approximately C₃H₂ for propane, C₄H₄ for isobutane, and C₅H₄ for neopentane. No γ hydrocarbon fragment was observed after the irreversible adsorption of ethane. There are, of course, many geometrical arrangements that are consistent with these stoichiometries, so any detailed structure of the γ fragments must await spectroscopic measurements. However, the absence of a γ hydrocarbon fragment for ethane may suggest that the γ fragments for propane, isobutane (2-methylpropane), and neopentane (2,2-dimethylpropane) involve dehydrogenation and bonding of the 1 and 3 carbons of the propane skeleton to the metal in a way that affords some stabilization to the other C-H bonds in the molecule. According to the stoichiometry, these C-H bonds would be fully "protected" in the case of propane and isobutane, but only partially protected in the neopentane γ fragment (the stoichiometry is C₅H₄ rather than the predicted C₅H₆). This apparent incongruity could be due to steric crowding between the two methyl groups, forcing one of them close enough to the surface to be dehydrogenated partially.

Any explanation of the nature of the α thermal desorption state must account for the following experimental observations:

(1) The α state has not begun to be populated until after the β_2 state has reached 80% of its saturation

coverage [see Figs. 2(I) and 2(IV)].

(2) For a saturated overlayer of isobutane annealed to 320 K to form the PDR, the α adstate is not repopulated upon exposure to H₂ or upon further exposure to isobutane at 100 K (see Fig. 10).

(3) It does not appear possible to adsorb H₂ into the α adstate of a nonsaturated overlayer of isobutane (see Fig. 11).

(4) The α adstate is distinct from the β_1 hydrogen-metal bonding state that exists on the clean surface (see Fig. 14).

(5) The stability of the α adstate (i. e., the temperature at which desorption from it occurs) depends on the hydrocarbon from which it is formed (see Figs. 1 and 2).

(6) The α adstate is not formed upon exposure of isobutane to the DHR (see Fig. 9) or upon exposure of isobutane to a surface previously saturated with isobutane and annealed to 400 K.

Observations (2)–(5) indicate that the α adsite is not a H-metal bond, but rather a C-H bond. It is apparent from observation (1) that as the density of the hydrocarbon overlayer increases, sites are created on the surface that possess only enough β_2 hydrogen abstraction sites to complete partially the transformation of the hydrocarbon molecule to the stable γ fragment. Thus, at some temperature below 130 K, a hydrocarbon fragment can be formed that is intermediate in hydrogen content between the parent molecule and the stable γ fragment. Sites apparently exist on the surfaces which will facilitate the transformation of these metastable fragments to the γ fragments, but only at temperatures higher than 130 K. These sites may be, for example, bare Ir sites that do not have the geometry of the β_2 (or β_2') hydrogen adsorption sites; or, in the case of neopentane, they could be β_2' sites that are vacated at 400 K. Upon dehydrogenation of the metastable fragment, the hydrogen recombines and desorbs as the α thermal desorption peak.

Observation (6) indicates that the presence of adsorbed carbon (or hydrocarbon fragments) on the surface interferes with the mechanism for the formation of the α adstate for hydrogen in adsorbed overlayers of isobutane. It may be that the chemisorbed carbon (or hydrocarbon fragment) poisons the sites which dehydrogenate the metastable α fragment, and the transformation to the γ fragment must await the depopulation of the β_2' adsites at 400 K. As was pointed out in Sec. III C, the stoichiometry of the γ fragment does remain the same, even for adsorption onto the carbon-poisoned surfaces. Thus, the dehydrogenation, to form the stable γ hydrocarbon fragment, must be completed at some temperature below 450 K.

V. SYNOPSIS

The results of this study may be summarized as follows:

(1) The β_2 hydrogen adsorption sites on the clean Ir(110)-(1 × 2) surface act as active centers for the dissociation of adsorbed, saturated hydrocarbons. Al-

though dissociative adsorption may occur to some extent at 100 K, experiments concerning the coadsorption of H_2 and CO with hydrocarbons indicate that molecular adsorption, followed by dissociation at slightly higher surface temperatures, occurs as well. The dissociation reaction is complete at surface temperatures below 130 K.

(2) The γ thermal desorption state, observed for propane, isobutane, and neopentane, represents hydrogen desorbing from hydrocarbon fragments that remain stable in the presence of active centers for C-H bond breaking (i. e., vacant β'_2 hydrogen adsites). Deuterium exchange into these C-H bonds does take place. The hydrocarbon fragments have a definite average stoichiometry for each species that does not depend on surface coverage. The stoichiometry of the fragment for propane is approximately C_3H_2 , for isobutane is C_4H_4 , and for neopentane is C_5H_4 .

(3) The α thermal desorption state represents hydrocarbon fragments that, although partially dehydrogenated, are not in the vicinity of a sufficient number of vacant β'_2 sites to be able to dehydrogenate fully to stable γ hydrocarbon fragments below 130 K. The completion of the dehydrogenation to stable γ fragments may occur at higher temperatures on metal sites which are less active sites for C-H bond cleavage. The atomic hydrogen which is formed during this dehydrogenation recombines and desorbs as the α thermal desorption peak of hydrogen.

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