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THE ROLE OF HYDROGEN IN LOW AND HIGH PRESSURE HYDROCARBON REACTRIONS OVER METAL SINGLE CRYSTAL SURFACES

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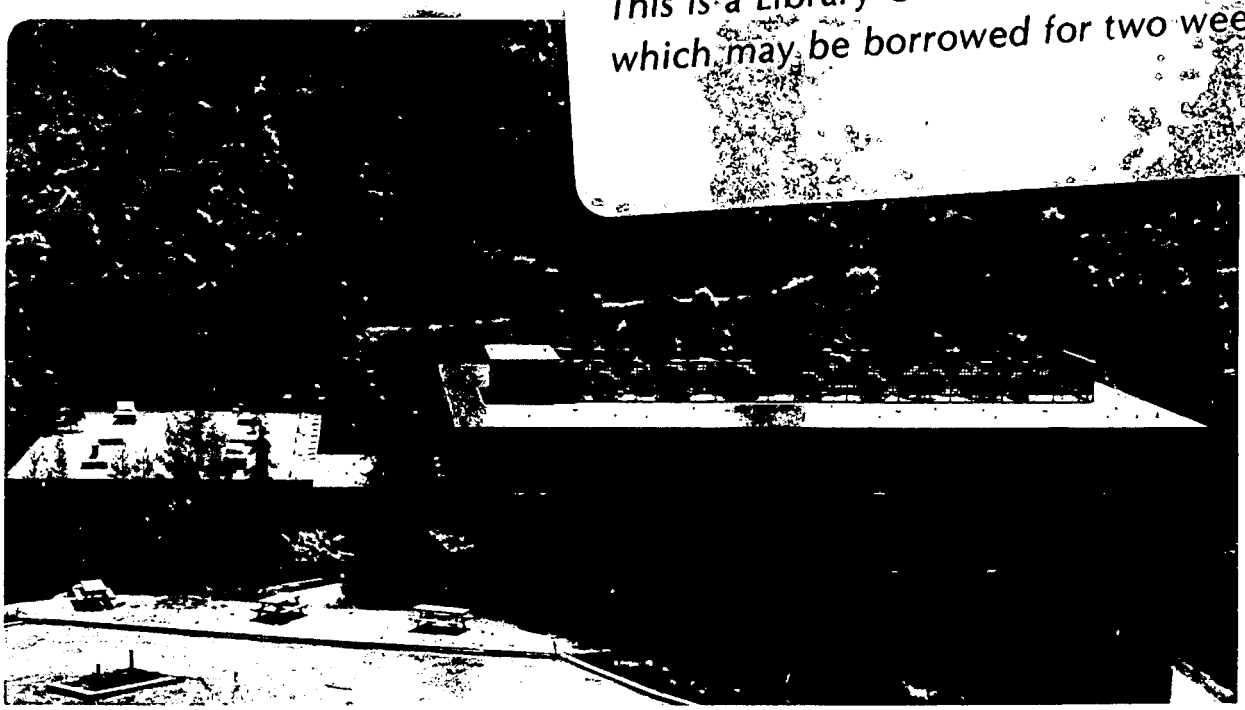

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1. INTRODUCTION

The chemisorption and surface reactions of hydrocarbons on metal surfaces have been investigated intensively from the viewpoint of heterogeneous catalysis. Hydrogenation, dehydrogenation and skeletal rearrangement reactions are of particular importance for the catalytic reforming of petroleum feedstocks. These reactions are selectively catalyzed by only a small group of transition metals and alloys, most notably platinum and platinum based alloys. The chemisorption of hydrocarbons over well defined surfaces of these metals and under controlled environments, generally ultra-high vacuum (UHV), has been widely studied since the development of new surface sensitive analytical techniques over the last two decades. A better understanding of the organic-metallic interface at the atomic scale has emerged from these investigations. The next step towards the comprehension of catalytic reactions requires bridging the gap between surface science studies under UHV and catalytic kinetic investigations at atmospheric

pressures. These types of investigations have been initiated in our laboratory over the past ten years.

Most experiments have been performed in standard ultra-high vacuum chambers equipped with several surface sensitive techniques such as Auger electron spectroscopy (AES), low energy electron diffraction (LEED), high resolution electron energy loss spectroscopy (HREELS), and mass spectrometry for thermal desorption studies (TDS). Additionally, these systems include an environmental cell for catalytic reaction studies, as described in more detail later. The samples used consist mainly of metal single crystals cut at different angles in order to expose particular crystallographic phases. Most work has been done on close packed surfaces, such as (111) and (100) faces of face center cubic metals. In few instances reactions have been performed on surfaces with controlled amount of defects (steps and kinks) in order to determine the dependence of activity on surface structure.

The present review presents a summary of the research that was carried out in this field, with emphasis on the extrapolation of knowledge obtained under UHV to high pressure conditions and on studies of well characterized model single crystal catalyst systems. The role of hydrogen as a unique reactant is also emphasized.

2. CHEMISORPTION STUDIES

2.a H_2 Chemisorption

A detailed description of H_2 chemisorption over metal surfaces have been already given in previous chapters, and therefore only its most relevant aspects will be mentioned here. H_2 chemisorption over

metals is generally dissociative and it is not activated. Several adsorption states have been observed even over smooth single crystal surfaces. Activation energies for desorption range from 15 to 30 Kcal/mol, with no clear trend across the periodic table [1,2]. A weakly chemisorbed state has also been observed in several cases, but the nature of such hydrogen and its importance to catalysis are not clear.

The results reported for hydrogen chemisorption on platinum single crystals are typical of those obtained for other metals, and will be used here to illustrate the main features of the process. This system has been studied using a wide variety of techniques by many groups [3-10]. Thermal desorption spectra reveal the existence of more than one adsorption state even over flat (111) surfaces. Additional stronger bonded states appear when steps and kinks are present (Fig. 1) [11]. The values for the activation energies of desorption are estimated to range from 5 and 9 Kcal/mol at low coverages over (111) terraces, to about 20 and 30 Kcal/mol on the steps and kinks respectively [3,10]. The heats of adsorption also change with coverage due to lateral interactions between adsorbed atoms. The main peak in the thermal desorption spectra (TDS) for H_2 on Pt(111) indicates a change in activation energy from 9.1 Kcal/mol at low coverages to 6.6 Kcal/mol at near saturation [3]. The area under the TDS can also be used to estimate the saturation coverage; Ertl and coworkers estimated $\theta_{sat} \sim 1$ using this procedure [3]. Unity saturation coverage was independently measured by Lee et al. [12] using He diffraction. They

determined that hydrogen forms a (1 x 1) structure where the H atoms sit on top of the three-fold hollow sites of the Pt(111) surface. Low energy electron diffraction (LEED), high resolution electron energy loss spectroscopy (HREELS), ultraviolet photoelectron spectroscopy (UPS), electron energy loss spectroscopy (ELS) and work function measurements have also been used to study this system [3,5,10]. Extensive theoretical work has also been published. More comprehensive reviews can be found elsewhere [2,13,14].

2.b Hydrocarbon chemisorption

Studies on the chemisorption of hydrocarbons on metal single crystals are extensive, and a complete review of the subject is beyond the scope of this article. Here we will only mention representative examples in order to present the relevant information needed for subsequent discussions.

The chemisorption of saturated low molecular weight alkanes (methane, ethane, propane) is activated, and therefore is generally not observed at room temperature. Physisorption of heavier alkanes can be attained at close to liquid nitrogen temperature, but such adsorption is followed only by molecular desorption as the metal is warmed up [15]. Chemisorption under UHV may occur at higher temperatures, and it generally starts with an initial C-H bond breaking step. Further heating of the system in such cases leads to full decomposition of the hydrocarbon fragments with simultaneous hydrogen desorption, while carbon is left behind on the surface [16].

Unsaturated hydrocarbons, on the other hand, can be easily adsorbed; they have sticking coefficients close to one at either

liquid nitrogen or room temperatures. Chemisorption is followed by stepwise decomposition as the temperature of the metal is increased. Studies for olefins, alkynes, cyclic olefins and aromatic compounds have been reported on many surfaces [17-24]. The chemisorption of ethylene and acetylene over Pt, Rh and Pd (111) surfaces have received special attention, since they form an ordered structure at room temperature that has been identified to be composed of ethylidyne moieties, with a structure that is shown schematically in Fig. 2 [25-35]. Ethylidyne then further decomposes above 400K to form C_2H and CH fragments, and the final dehydrogenation product is graphite, that is left on the surface at higher temperatures [32,36-38]. Chemisorption of ethylene over Ni(100), on the other hand, is followed by stepwise decomposition and the successive formation of a vinyl group, an acetylene like fragment, and a C_2H moiety [86].

Adsorption studies of other heavier alkenes have been performed as well [35,36,39,40]. H_2 TDS for ethylene, propylene and butene over Pt(111) are shown in Fig. 3. It can be seen that for all three olefins three decomposition regimes can be identified. At room temperature the first H_2 peak is observed, associated with the formation of ethylidyne or the corresponding alkylidyne analog [39,40]. Between 350 and 500K further decomposition takes place, with formation of smaller hydrocarbon fragments like CH and C_2H. Finally, total dehydrogenation above 600K leads to the formation of a graphitic overlayer on the Pt(111) surface.

Aromatic molecules follow a similar decomposition process as a function of temperature. HREELS and LEED studies of benzene adsorption

over Rh(111) indicate that the molecule adsorbs molecularly at low temperatures with the ring parallel to the surface [22,41]. H_2 TDS show that the first major decomposition peak occurs at 470K, with formation of surface species that are believed to consist of CCH and CH fragments from HREELS studies [42]. Further gradual decomposition occurs until graphite is formed at 800K. Similar results have been reported for other surfaces [21].

3. SURFACE REACTIONS AT LOW PRESSURES (10^{-8} - 10^{-5} torr)

In addition to thermal decomposition studies like those reported in the previous section, a few hydrocarbon reactions have been investigated under UHV as well. Two kinds of experiments can be differentiated: those where gas coadsorption is followed by thermal desorption of products, and a second kind where reactions are carried out under steady state conditions, generally by using molecular beams. In this section we will report results published for H_2-D_2 exchange, ethylene hydrogenation and cyclohexene reactions over platinum single crystal surfaces.

3.a <u>H_2-D_2 Exchange</u>

H_2-D_2 exchange is probably one of the simplest reaction that involves formation and breakage of chemical bonds, and therefore it has been studied extensively by several research groups [43-48]. Engel and Ertl have recently published a review on the subject [49]. The first step for the overall reaction involves the dissociative chemisorption of both H_2 and D_2. It appears that once atomic hydrogen is present on the surface, the reaction proceeds through a Langmuir-Hinshelwood

mechanism where the limiting step is the recombination of H and D atoms, followed by molecular desorption [43]. The process is more complicated over platinum surfaces, where two different kinds of sites are believed to coexist, and where the limiting step could be the migration of H atoms from one site to the other [50].

The rate of exchange increases rapidly as the catalyst temperature is raised, until it reaches a maximum value above 500-600K. This behavior has been attributed to a coverage dependence of the sticking coefficient, $s(\theta)$, for hydrogen. The rate of HD production is proportional to this sticking probability under the molecular beam experimental conditions [43], and since the steady state coverage changes with temperature, so does $s(\theta)$.

H_2-D_2 exchange have also shown a strong dependence on surface topography. Several research groups have proven that steps are at least an order of magnitude more active than flat (111) terraces on platinum [44,45,50]. Somorjai et al. have studied the angular dependence of HD production on Pt(s) - [6(111) x (111)] by using molecular beams, and proved that the reaction at the bottom of the steps is about seven times faster than on the terraces (Fig. 4). This results also suggest that the existence of a precursor state is not important for the reaction mechanism.

Finally, the angular and velocity distributions of the outgoing HD from molecular beam experiments have cosine and Maxwell-Boltzman distributions over Pt(111) and Pd(111), but deviation from such behavior have been reported for Cu(110) and Ni(111) [43,44,51,52].

3.b Ethylene hydrogenation and H-D exchange

Ethylene self-hydrogenation has been observed over several supported metals [53]. The same phenomenon has been reported on Ni(111) [54], Ni(100) [86] and Pt(111) [55-57] under UHV. Thermal desorption experiments revealed the formation of ethane at around room temperature after ethylene saturation of Pt(111). The activation energy was estimated to be 18 Kcal/mol, and a C-H bond breaking was proposed to be the limiting step [57]. If hydrogen is adsorbed prior to ethylene, the activation energy for ethane production drops to a value of 6 Kcal/mol, and its yield increases by about an order of magnitude (Fig. 5). Based on the experimental results, the following mechanism was proposed:

$$H_2(g) \longrightarrow 2H(a) \quad (1)$$

$$C_2H_4(g) \longrightarrow C_2H_4(a) \quad (2)$$

$$C_2H_4(a) \longrightarrow C_2H_3(a) + H(a) \quad (3)$$

$$C_2H_4(a) + H(a) \Longleftrightarrow C_2H_5(a) \quad (4)$$

$$C_2H_5(a) + H(a) \longrightarrow C_2H_6(g) \quad (5)$$

where (g) and (a) stands for gas and adsorbed respectively. A step was included in this scheme to account for the formation of ethylidyne, CCH_3 (Fig. 2). A computer simulation using this model gave results that were in excellent agreement with the experiments for both self-hydrogenation and hydrogen preadsorbed cases.

H-D exchange is a related reaction that takes place simultaneously with hydrogenation. If deuterium is preadsorbed on Pt(111), deuterated ethane and ethylene are produced from ethylene TDS [57]. Ethylidyne

can also exchange hydrogen atoms in the methyl group. Exchange has been observed by using TDS, HREELS and secondary ion mass spectroscopy (SIMS) at submonolayer ethylidyne coverages over Pt(111) and Rh(111) [36,58-60], but once saturation is reached, atmospheric pressures of deuterium are needed for the exchange to occur.

3.c Cyclohexene reactions

The reaction of cyclohexene with hydrogen over several platinum single crystal surfaces was studied at total pressures of 10^{-8} to 10^{-5} torr [61-64]. Typical experimental results are shown in Fig. 6. The carbon build-up, as followed by Auger electron spectroscopy (AES), is also presented. The rate for benzene production shows a maximum after an induction period of 3-4 minutes, followed by a decay due to poisoning from the irreversibly adsorbed carbonaceous residues left on the surface. Little cyclohexane formation was also detected. These results clearly show that the reaction probability for cyclohexene conversion under vacuum is close to one over the clean platinum surface, but it is reduced quickly by poisoning. Total turnover numbers of about 0.2 reacted molecules per platinum atom were obtained, so this reaction can not be considered catalytic.

Benzene production from cyclohexene at 10^{-5} torr total pressures displayed little structure sensitivity over Pt(111), Pt(557) and Pt(10,8,7) [63]. The activation energy for the dehydrogenation was calculated to be less than 4 kcal/mol for all three surfaces, and the rates were first order in cyclohexene and positive fractional order in hydrogen. Some n-hexane production was detected as well, with rates

comparable to benzene production over Pt(10,8,7) but an order of magnitude slower over Pt(111).

The effect of gold deposition over Pt(100) have also been investigated [62]. Surprisingly, the activity for benzene formation increases by a factor of four at one monolayer of gold. Further gold deposition leads to slow poisoning and reaction rate reduction. If platinum is deposited over Au(100), a broad maximum in rate is observed at 1-5 platinum layers, followed by an asymptotic decrease to the activity of pure platinum. There is not yet a clear explanation for this activity enhancement observed.

4. ATMOSPHERIC PRESSURE REACTIONS OVER SINGLE CRYSTAL SURFACES

Although UHV reaction studies are relevant to catalysis, their results cannot always be directly extended to high pressure conditions like those existing in most industrial processes. In fact, most surface reactions under vacuum are not catalytic in nature. Atmospheric pressures of reactants allow for existence of steady state concentrations of weakly bonded species that cannot be easily studied under vacuum. In some cases the presence of such new chemisorbed states open new pathways for reaction mechanisms. Two main approaches have been taken in order to link the two reaction regimes: 1) Surface sensitive techniques have been developed that can be used in situ to characterize the catalytic system while the reactions are taking place; and 2) A low pressure-high pressure apparatus was constructed that permits the transfer of the catalytic sample from UHV to atmospheric pressures and back so standard vacuum techniques can be used

to study changes occurring in the surface before and after exposure to reaction conditions.

Most work that has been carried out on single crystals have been performed using the second approach, and the following section will focus on reviewing their results. A typical experimental apparatus is shown schematically in Fig. 7 [65]. It consists of a standard UHV chamber equipped with several surface analytical techniques such as LEED, AES, TDS and HREELS, and a retractable environmental cell that can be used to isolate the sample from vacuum and to insert it in a loop that can be pressurized up to 100 atm with reactant gases. The reaction kinetics can then be studied by circulating the gases and periodically analyzing small amounts of the gas mixture using either gas chromatography or mass spectrometry. After reactions the loop is pumped and the cell opened so the catalyst is returned to UHV for further analysis. Several hydrocarbon reactions have been studied this way, including hydrogenation of olefins and aromatic compounds, H-D exchange and reforming reactions of several model hydrocarbon molecules.

4.a Reactions involving ethylidyne

It was mentioned in the previous section that when ethylene is chemisorbed at room temperature under UHV over Pt(111), Pt(100), Rh(111) or Pd(111), ethylidyne is formed (Fig. 2) [25,66,67,33]. This moiety is stable upon hydrogen treatment even at atmospheric pressures, as revealed by the use of ^{14}C ethylene and a radiotracer technique [37], and it can only be rehydrogenated at temperatures above 350K.

On the other hand, CH fragments formed from ethylene decomposition at 470K under UHV cannot be completely removed from the platinum surface even with high H_2 pressures. If ethylene adsorption is carried at above 600K, irreversibly chemisorbed carbon with little or no hydrogen content is left on the surface. Hydrogen to carbon ratios for the different fragments formed during ethylene chemisorption and their ability to be rehydrogenated are shown as a function of adsorption temperature in Fig. 8.

If ethylidyne is exposed to atmospheric deuterium, not only hydrogenation reactions are seen, but H-D exchange is observed as well. The exchange is possible under UHV only with submonolayer coverages of ethylidyne, but at saturation high pressures of D_2 are required for this reaction to occur. HREELS and TDS have been used to determine that the exchange occurs in a stepwise fashion, one hydrogen atom exchanged at a time, and at comparable rates to ethylidyne hydrogenation [59,60,68,69]. An example of such results is presented in Fig 9 for Rh(111). After 5 min. exposure of ethylidyne to 1 atm. D_2, new peaks appear in the vibrational spectrum, corresponding to Pt_3C-CH_2D.

Hydrogen can also be coadsorbed with ethylidyne. However, after ethylidyne saturation, H_2 chemisorption is observed only after exposures at pressures above 10^{-5} torr at 150K [57]. Furthermore, the exposure of ethylidyne to high H_2 pressures at 320K results in the formation of a new specie, probably ethylidene ($=CH-CH_3$), as identified by TDS (Fig. 10).

4.b Ethylene hydrogenation

Few studies of ethylene hydrogenation over single crystal surfaces have been published to date [54,68-71]. The activity over single crystals has been found to be comparable to that of supported metal particles in all cases [68-70], suggesting that similar reaction mechanisms take place over both kind of catalysts. Dalmai-Imelik and Massadier [70] have reported a structure dependence of the reaction rates as a function of crystallographic orientation of the exposed surface for nickel crystals. While the (100) surface is practically inactive for hydrogenation, activities for the (111) and (110) faces were much higher and differ by about a factor of two between themselves. These differences were explained in terms of the cracking of C_2H_4 observed over the (100) face. Self-hydrogenation at pressures of up to 0.1 torr has also been reported over nickel in the absence of H_2 [54].

The reaction over Pt(111) and Rh(111) crystals has been studied using several surface sensitive techniques [68,69,72]. Ethylidyne was found to be present on the surfaces after high pressure reactions, as confirmed by LEED, TDS and HREELS results (Fig. 11). All three techniques yielded similar results for Pt(111) saturated with ethylidyne and after high pressure ethylene hydrogenation reactions. Furthermore, reactions over ethylidyne saturated surfaces had identical kinetic parameters to those performed over clean platinum. However, rates for hydrogenation of ethylidyne are several orders of magnitude lower than for ethylene hydrogenation. Turnover frequencies for the relevant

processes are presented in Table I. Therefore, ethylene hydrogenation must take place in the presence of the strongly bonded hydrocarbon fragments. Furthermore, TDS and HREELS have shown that direct chemisorption of new ethylene molecules over the metal is sterically hindered, so the hydrogen incorporation need to occur on a second layer of weakly chemisorbed ethylene molecules. A mechanism involving hydrogen transfer from the surface through the ethylidyne fragments has been proposed to explain these results [68]. It includes the reversible interconversion of ethylidyne into ethylidene and vice versa, as illustrated in Fig. 12. Further proof for the model awaits for the unequivocal identification of ethylidene moieties on the surface.

4.c Other hydrogenation and dehydrogenation reactions

The hydrogenation of benzene over nickel single crystal surfaces has been studied by Dalmai-Imelik and Massadier [70]. They found no structure dependence for this reaction, contrary to what was observed for ethylene hydrogenation. The rates for dehydrogenation of cyclohexane over platinum, on the other hand, depend on the atomic structure of the catalytic surface [73]. Product accumulation curves for four different platinum surfaces are shown in Fig. 13. The stepped Pt(557) surface is about twice as active as Pt(111), and both kinked surfaces are appreciably more active than the stepped surface. The effect of gold deposited over Pt(111) or alloyed with it is to increase the turnover frequency for benzene formation, up to a maximum at a gold coverage of about half a monolayer, followed by a monotonic decrease at higher Au coverages [74]. The bimetallic results have

been explained in terms of a competitive mechanism where the chemisorbed species either dehydrogenate and desorb as products or decompose and deactivate the catalyst. If this second pathway requires big ensembles of platinum atoms, it would then be inhibited by the addition of gold, which would favor the desorption of products.

The reaction of cyclohexene with hydrogen has also been studied over platinum surfaces in the 10^{-7} to 10^{-2} torr pressure range [61]. The selectivity for hydrogenation over dehydrogenation changes drastically with changing pressures (Fig. 14): benzene is predominantly produced at low pressures ($\sim 10^{-7}$ torr) while cyclohexane is mainly observed at high pressures ($\sim 10^{2}$ torr). The low pressure reactions are structure sensitive and proceed over the clean metal surface. At high pressures such reactions are structure insensitive due to the continuous presence of near a monolayer of carbonaceous species, similar to the case for ethylene. Widely differing coverages of reactive, weakly adsorbed hydrogen could be crucial in the product selectivity reversal between high and low pressures.

4.d <u>Deuterium exchange reactions</u>

H-D exchange of ethane has been studied over Pt(111) surfaces [69,75]. The activation energy and pressure dependences with respect to deuterium and hydrogen were similar to those reported for supported catalysts. The resulting ethane product distribution was U-shaped, peaking at one and six deuterium atoms per ethane molecule (Fig. 15). A competitive mechanism with two branches was proposed. It included multiple sequential hydrogenation-dehydrogenation equilibria on one of

the ethene carbon atoms after adsorption. The presence of ethylidyne and ethylidene as intermediates were proposed.

Exchange reactions for isobutane, n-hexane and n-heptane have been reported as well [76]. As for ethane, the exchange product distributions were V-shaped for n-hexane and h-heptane, but it also had local maxima at d_4 and d_6 for isobutane. This difference is easily explainable, since ethane, n-hexane and n-heptane are all linear molecules, while isobutane has a tertiary carbon atom with three methyl groups attached to it. In addition, the exchange reactions were all shown to be structure insensitive and at least one order of magnitude faster than any other conversion process.

4.e Hydrocarbon skeletal rearrangement

There is a marked structure sensitivity in the rates for hydrogenolysis for ethane, n-butane and cyclopropane over nickel surfaces, as reported by Goodman [77,78]. Hydrogenolysis over (111) faces is about one order of magnitude slower than over (100) crystals. This trend parallels that reported for ethylene hydrogenation [70], but in this case the differences in rate were established to be intrinsic to the surface topography and not due to selective poisoning by carbon.

Hydrogenolysis and isomerization reactions over several platinum crystals have been reported for many hydrocarbons, including ethane, isobutane, n-butane, neopentane, methylcyclopentane, n-hexane and n-heptane [75,79-83]. Changes in reaction rates with differences in surface structure have been observed for most cases. Examples of initial isomerization turnover frequencies for different hydrocarbons and

platinum surfaces are shown in Fig. 16. For light alkanes there is an increase in activity when going from (111) to (100) terraces. Faster rates are also obtained when defects are present on the surface (as is the case for Pt(10,8,7), Pt(557) and Pt(332) as compared to Pt(111)). These changes are not observed for methylcyclopentane or n-hexane. Total conversion rates also decrease with molecular weight of the reactant molecule.

For n-hexane and n-heptane, cyclization and aromatization products are also obtained. Benzene formation from n-hexane is about four times faster on (111) terraces than (100) surfaces [82]. However, no significant differences in rates occur when steps and kinks are present, and the activities for Pt(111), Pt(557), Pt(332) and Pt(10,8,7) are all comparable. The same insensitivity to the presence of low coordination platinum atoms is seen for toluene formation from n-heptane, where the rates are within a factor of two for the four platinum surfaces studied, all having (111) terraces but different defect concentrations [83].

The formation of carbonaceous deposits over the catalyst surfaces is always detected after all hydrocarbon reactions. These deposits have been characterized by using several techniques, including AES, LEED, TDS, CO titration and ^{14}C radiotracer detection [37,84]. It was found that such fragments are mainly irreversibly adsorbed during reactions, covering most of the surface area. There are, however, a small fraction of platinum atoms uncovered that are the responsible for catalytic activity. The amount and kind of these metal atoms can

be measured by CO titration experiments [84]. Steps and kinks can be differentiated because CO chemisorbs more strongly on those defects as compared to (111) terraces, a difference that becomes evident by the presence of a high temperature peak in the thermal desorption spectra of CO. This is shown in Fig. 17 for Pt(557) [85]. It can be seen that the high temperature peak is observed in titrations after cyclohexane, neopentane, and isobutane reactions, but not after methylcyclopentane or n-hexane reactions. These results correlate well with those from kinetic studies, where surfaces with defects displayed higher activity for light alkanes than (111) terraces, while no difference was noticed for methylcyclopentane or n-hexane conversion.

Quantitative hydrogen thermal desorption studies were carried out as a function of surface structure and reaction temperature. The most important chemical properties of the carbonaceous deposits are their ability to store and exchange hydrogen with reactant surface species and to provide desorption sites for product molecules. A model was proposed where dehydrogenation of hydrocarbons occurred over the deposits, followed by surface migration to the base platinum sites, skeletal rearrangement and migration back to the carbonaceous fragments for rehydrogenation and desorption [84]. The hydrogenation-dehydrogenation role of the strongly bonded hydrocarbon fragments is consistent with the model proposed previously for ethylene hydrogenation.

5. CONCLUSIONS

The preceeding are representative studies of hydrocarbon reactions over metal single crystal surfaces, performed under controlled

environments. They show that high pressure experiments are recently being added to the vast knowledge available on chemisorption under ultrahigh vacuum using well characterized single crystal catalyst surfaces in order to bridge the gap between the two pressure regimes. One of the conclusions to be reached from these new results is that, although the information obtained under UHV is useful for the understanding of gas-solid interactions, they are in general noncatalytic processes, and extrapolation to high pressure catalytic reactions has to be done with caution. While chemisorption of hydrocarbons under vacuum generally leads to decomposition and hydrogen desorption, catalytic reactions take place at atmospheric pressures, including those where hydrogen-carbon bonds are formed. A good example of these differences was illustrated for the cyclohexene reactions in Fig. 14: there is a marked inversion in selectivity from almost total dehydrogenation to benzene in vacuum to hydrogenation and cyclohexane formation in the 10^2 torr range. High pressures of H_2 is also indispensable for most skeletal rearrangement processes. A second main difference between the two pressure regimes, also illustrated in Fig. 14, is the change in reaction probabilities, from almost unity under UHV down to less than 10^{-4} at one atmosphere. This change is explained in part by the formation of carbonaceous deposits over the catalyst surface under atmospheric reactant pressures, leading to changes in the reaction mechanisms. For example, while ethylene hydrogenation takes place over clean platinum in UHV with an activation energy of 6 kcal/mole, the same reaction is catalytic and takes

place in the presence of an ethylidyne layer at atmospheric pressures with an activation energy of 11 kcal/mol. Similar differences exist in other hydrogenation reactions. Hydrogenolysis and isomerization processes take place at higher temperatures and do occur over the metal atoms, but again hydrogenation and dehydrogenation steps are necessary to make these reactions catalytic, and hydrogen transfer through strongly bonded hydrocabon residues makes the difference between high pressure and vacuum.

In summary, the combination of surface science techniques with transfer devices that allow catalyst samples to be transported from UHV to high pressures and back is helping to obtain a better overall picture of catalytic reactions. It has become evident that hydrogen plays a vital role in hydrocarbon conversion. Hydrogen transfer mechanisms are also being better understood. They may not always proceed directly from the metal surface to the reactant molecule but may sometimes involve intermediate states where the strongly bonded hydrocarbon fragments may be key components. In situ spectroscopies together with studies over well characterized surfaces are still needed to further clarify the mechanistic details of these reactions on the atomic scale.

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Table I

Comparison of hydrogenation and exchange rates over Pt(111) single crystal surfaces at near room temperatures.

Process	Estimated Turnover Rate (reactions/metal atom · sec.)	Reference
H,D exchange in saturation CCH_3 methyl group	10^{-5}	68,69,72
Hydrogenation and removal of saturation CCH_3 from surface	6×10^{-5}	37,69
C_2H_4 hydrogenation $P_{E,0}$ = 20 torr P_{H2} = 100 torr	25	68,69

FIGURE CAPTIONS

Fig. 1 Thermal desorption spectra for hydrogen chemisorbed on the flat (111), stepped (557), and kinked (12,9,8) platinum single crystal surfaces.

Fig. 2 Atomic surface structure for ethylidyne species chemisorbed on Pt(111).

Fig. 3 Hydrogen thermal desorption spectra illustrating the sequential dehydrogenation of ethylene, propylene, and cis-2-butene chemisorbed on Pt(111) at about 120 K (β = 12 K/sec).

Fig. 4 HD production as a function of angle of incidence, θ, of the molecular beam, normalized to the incident D_2 intensity. (a) Pt(332) surface with the step edges perpendicular to the incident beam ($\phi = 90^\circ$); (b) Pt(332) where the projection of the beam on the surface is parallel to the step edges ($\phi = 9^\circ$); (c) Pt(111).

Fig. 5 C_2H_4 (27 amu) and C_2H_6 (30 amu) TDS curves corresponding to the decomposition of C_2H_4 adsorbed over clean (dashed lines) and hydrogen predosed Pt(111) surfaces at 150 K. Exposures were 6 L for C_2H_4 and 30 L for hydrogen.

Fig. 6 A comparison at 150°C of the cyclohexene dehydrogenation rate over Pt(223) at low pressures with the simultaneous build-up of the irreversibly chemisorbed carbonaceous overlayer. A C_{273}/Pt_{237} ratio of 2.8 corresponds to monolayer coverage.

Fig. 7 Schematic diagram of the low pressure-high apparatus for combined surface analysis and catalysis studies.

Fig. 8 Composition and reactivity of ^{14}C-ethylene chemisorbed on Pt(111) at 320-670K. The irreversibly adsorbed fraction determined by radiotracer analysis displays an excellent correlation with the average hydrogen content (H/C) of the strongly bound surface species.

Fig. 9 Vibrational spectra of ethylidyne on Rh(111) spectra illustrating the deuterium exchange in the methyl group. Spectra B and C were obtained from ethylidyne after exposure to 1 atm H_2 and D_2, respectively. CCH_3 and CCD_3 spectra are shown for comparison.

Fig. 10 Thermal desorption (amu = 2) spectra from H_2-ethylidyne coadsorption experiments.

a) 6L C_2H_4 dosed at 320K (saturated ethylidyne). Followed by

b) 1200 L H_2, 10^{-5} torr at 150K

c) 1200 L H_2, 10^{-5} torr at 320K, then cooled immediately to 150K

d) $\sim 10^{10}$ L H_2, 1 atmosphere at 240K

e) $\sim 10^{10}$ L D_2, 1 atmosphere at 240K, 4 amu TDS.

Fig. 11 Evidence for the presence of ethylidyne on the Pt(111) surface after hydrogenation of gas phase ethylene at atmospheric pressures over this surface. Temperature programmed desorption, low energy electron diffraction, and high-resolution electron energy loss spectroscopy data for ethylidyne are compared with the results of these techniques on Pt(111)

after ethylene hydrogenation at atmospheric pressure and return of the crystal to vacuum.

Fig. 12 Schematic representation of the mechanism for ethylene hydrogenation over Pt and Rh(111) single crystal surfaces.

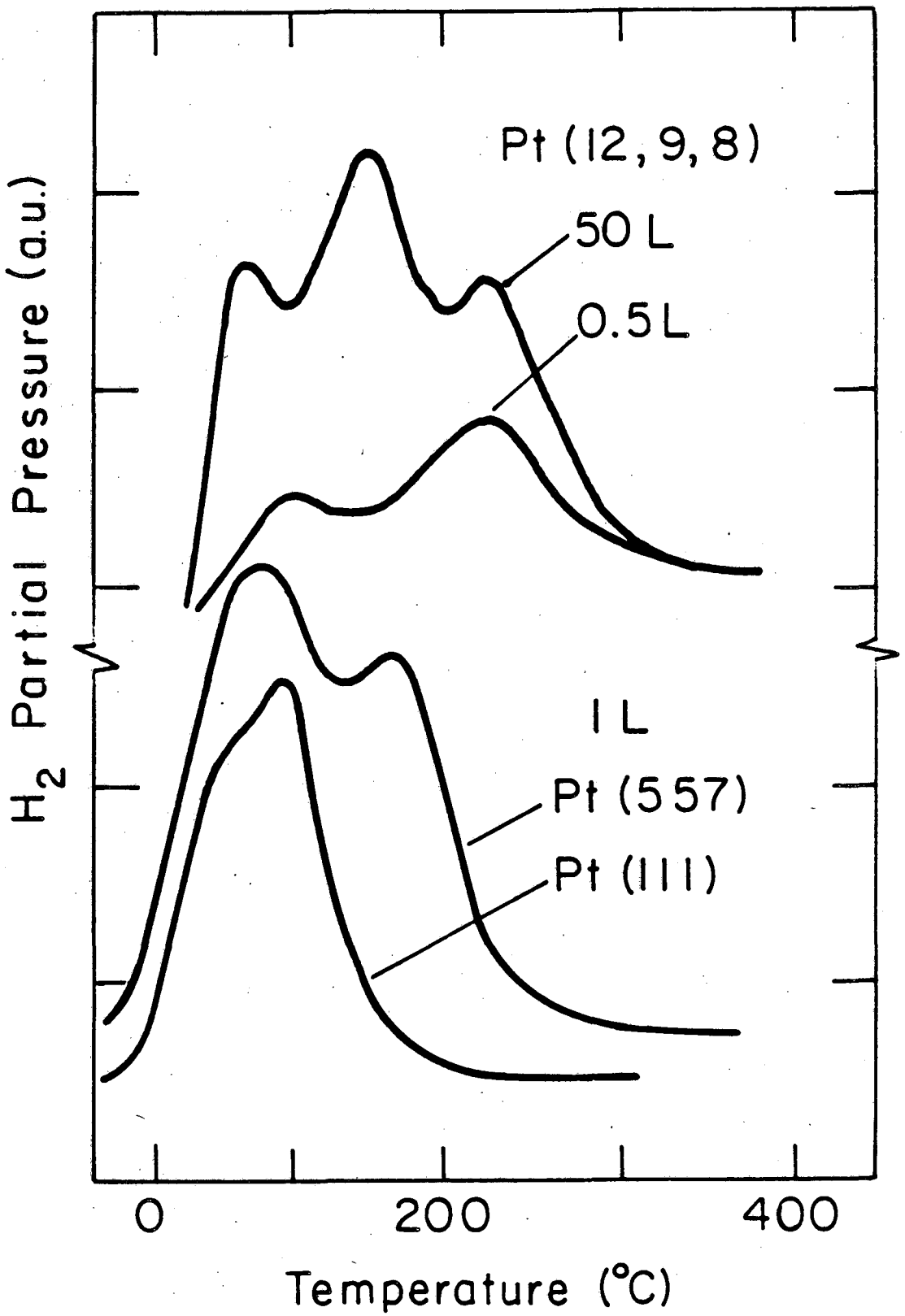
Fig. 13 Benzene production accumulation curves over platinum single crystals as a function of surface structure.

Fig. 14 Correlation of cyclohexene reaction rates and reaction probabilities over 10-orders of magnitude pressure range. The reactions were performed at 425K over the stepped Pt(223) crystal surface with $H_2/HC = 10$.

Fig. 15 Deuterium atom distribution in the resulting ethane from the exchange with deuterium over Pt(111). $P_{C_2H_6} = 10$ torr, $P_{D_2} = 100$ torr, T = 550K.

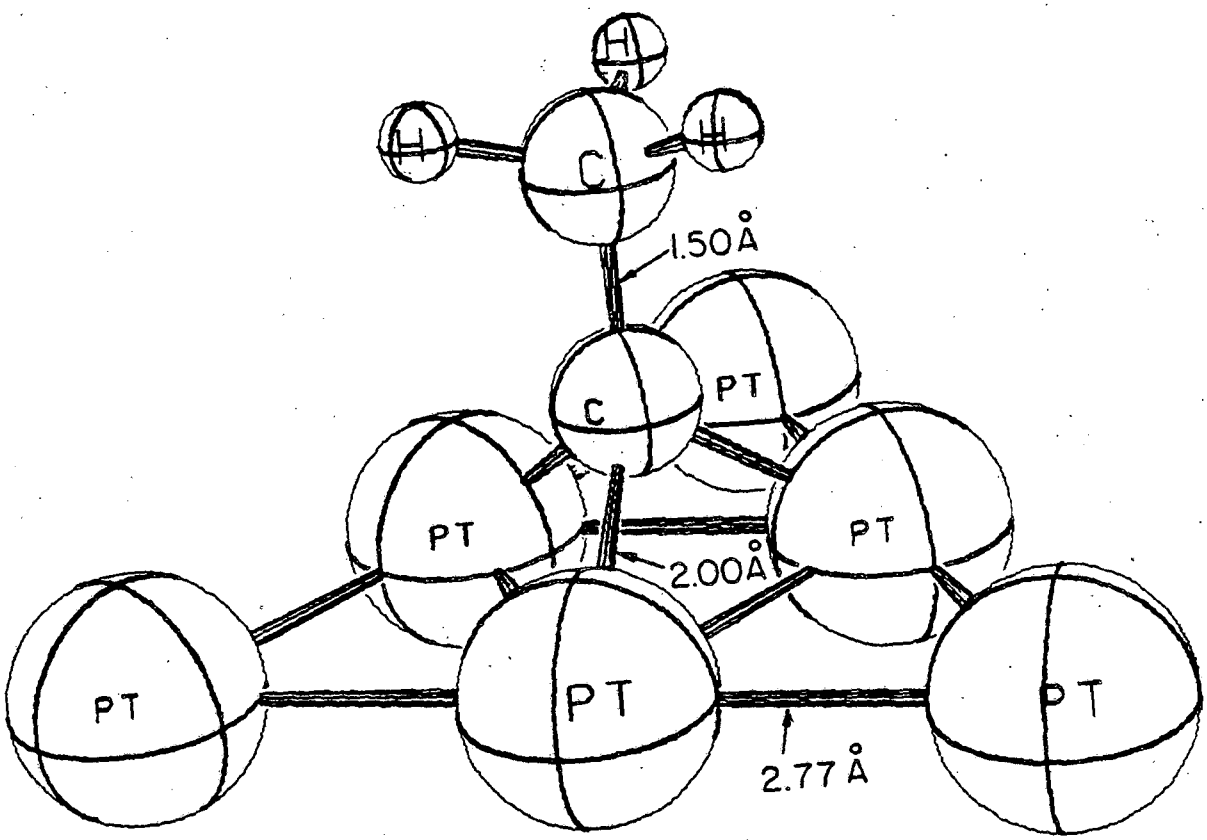
Fig. 16 Structure sensitivities for alkane isomerization reactions over platinum single crystal surfaces. Shown are the initial reaction rates as a function of crystallographic orientation.

Fig. 17 Comparison between CO thermal desorption from the clean (557) platinum surface and Pt(557) following hydrocarbon reactions. The adsorption temperature was 310-315K, 80 K/sec, and CO exposure = 36 L.



XBL 792-5816

Fig. 1



Pt (III) + ethylidyne

XBL794-6167

Fig. 2

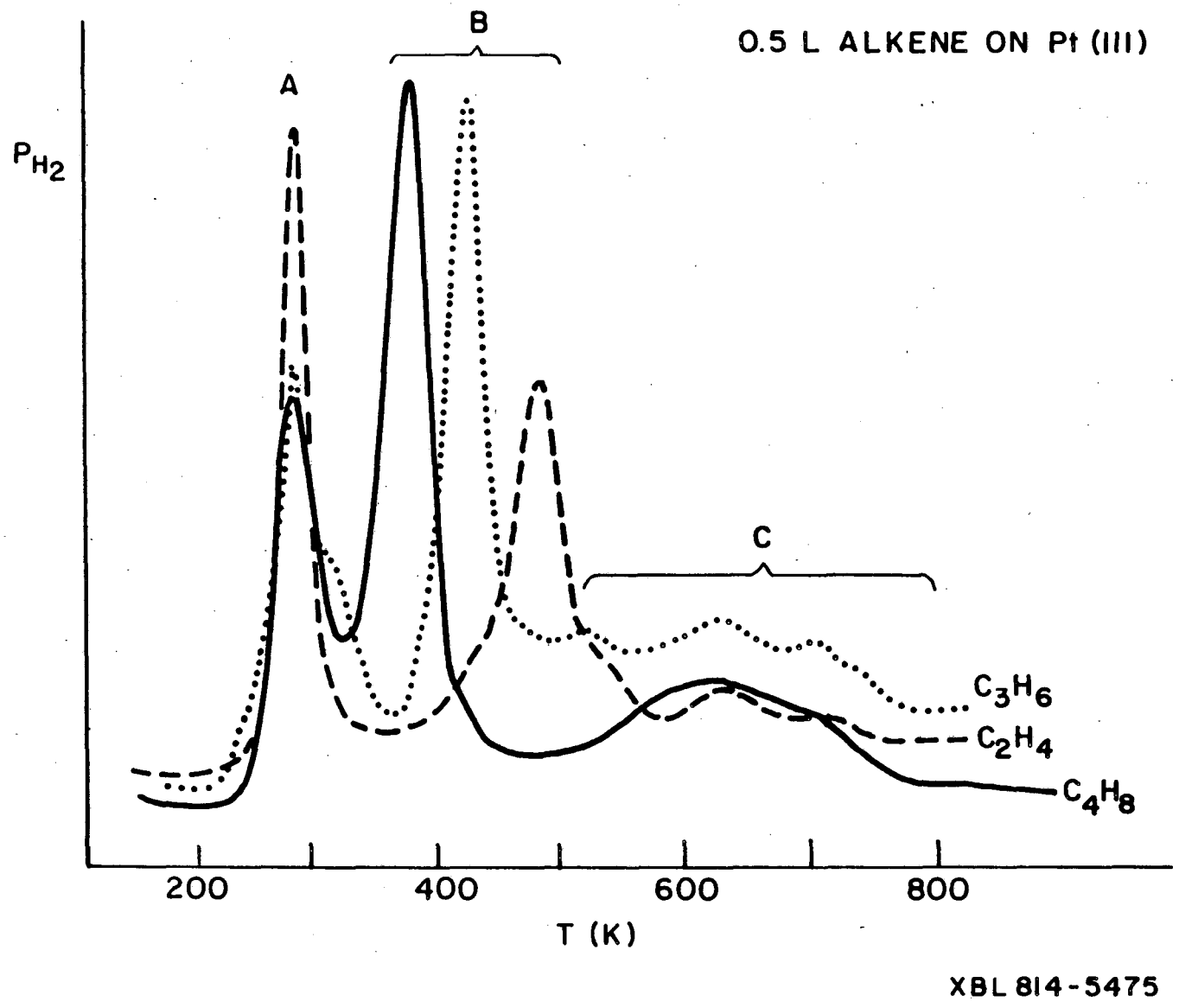
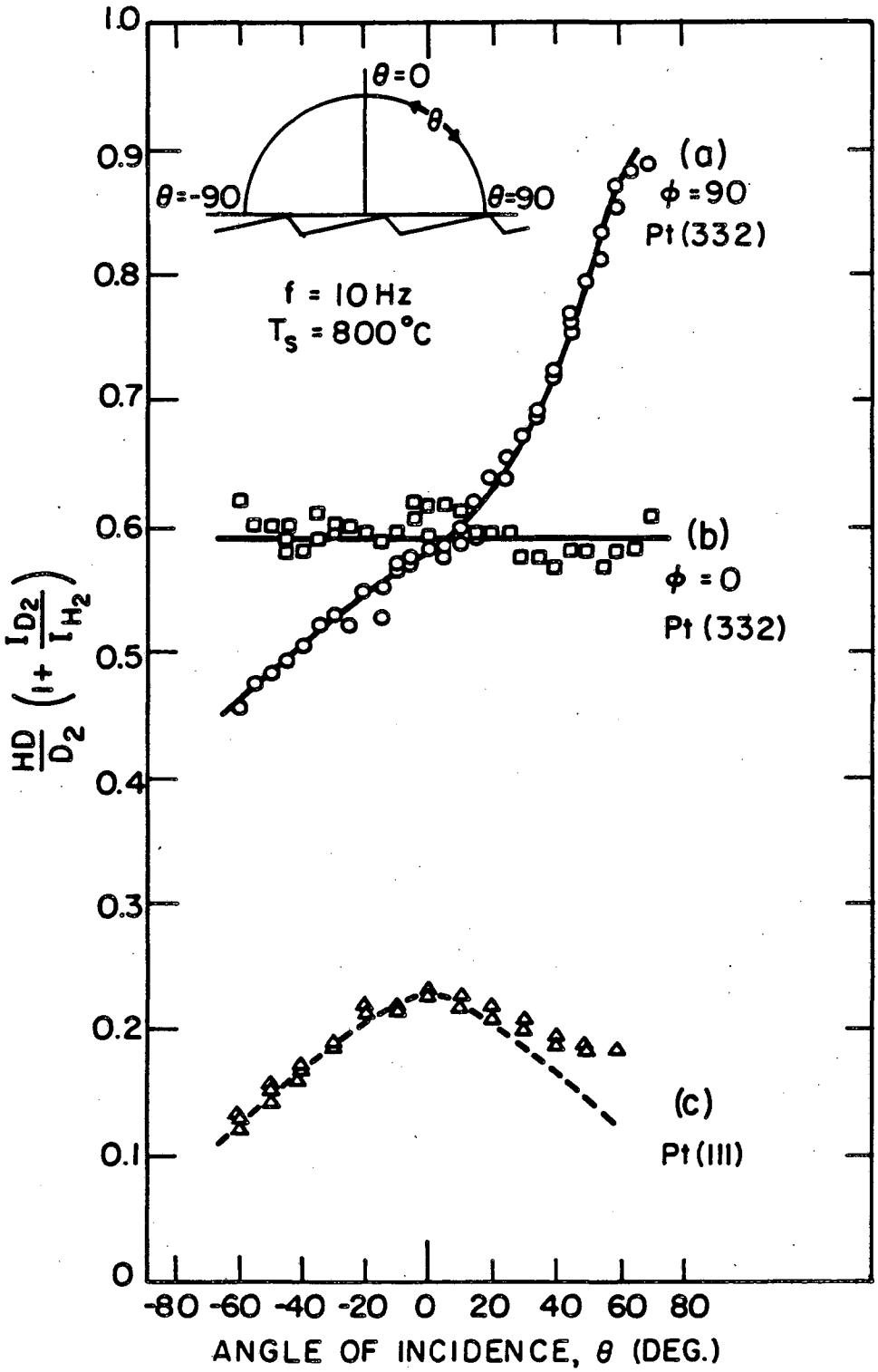

0.5 L ALKENE ON Pt (111)
A
B
C
P_{H_2}
C_3H_6
C_2H_4
C_4H_8
200
400
600
800
T (K)
XBL 814-5475

Fig. 3



XBL772-5084A

Fig. 4

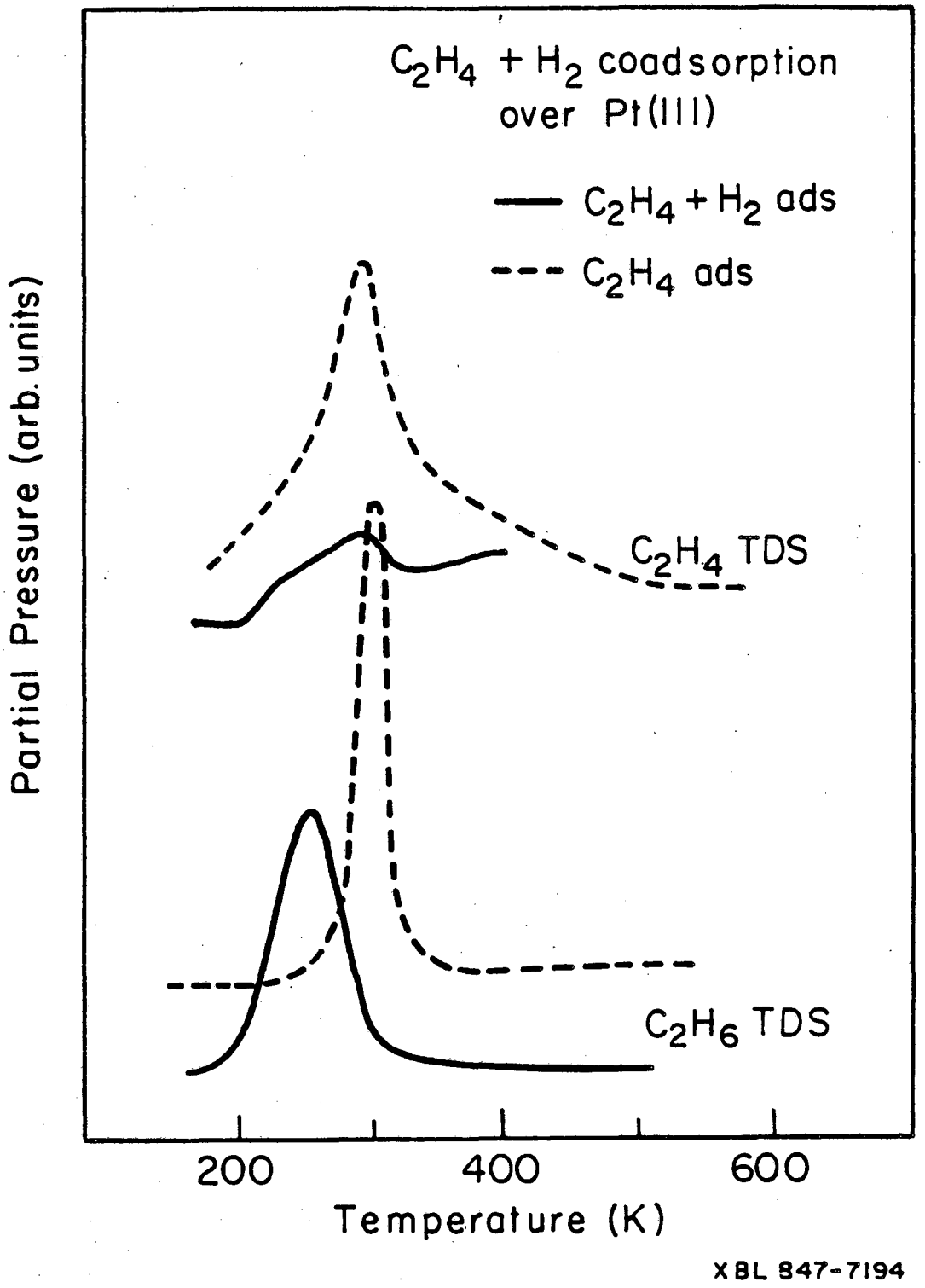
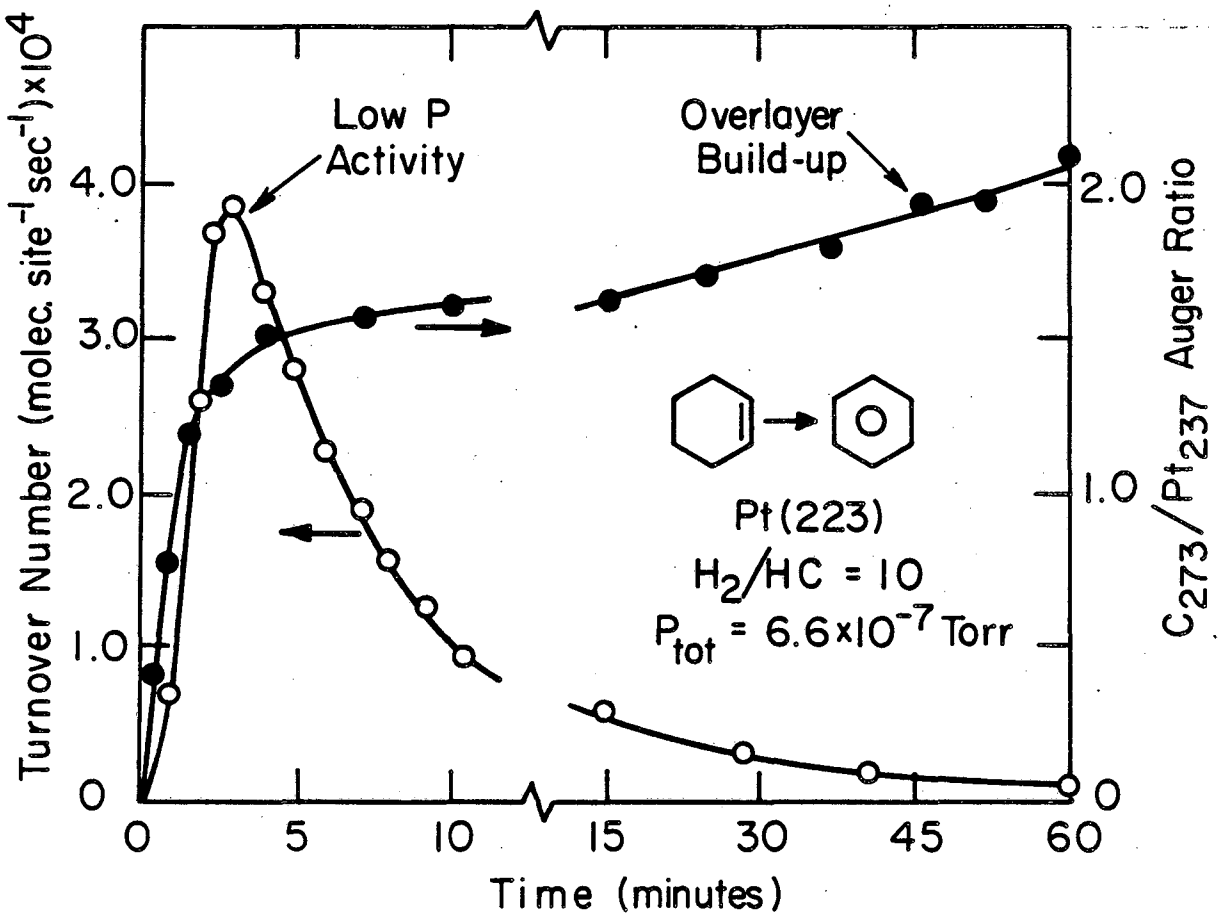

C_2H_4 + H_2 coadsorption over Pt(111)
C_2H_4 + H_2 ads
C_2H_4 ads
C_2H_4 TDS
C_2H_6 TDS
Partial Pressure (arb. units)
200
400
600
Temperature (K)
XBL 847-7194

Fig. 5



XBL 798-6750

Fig. 6

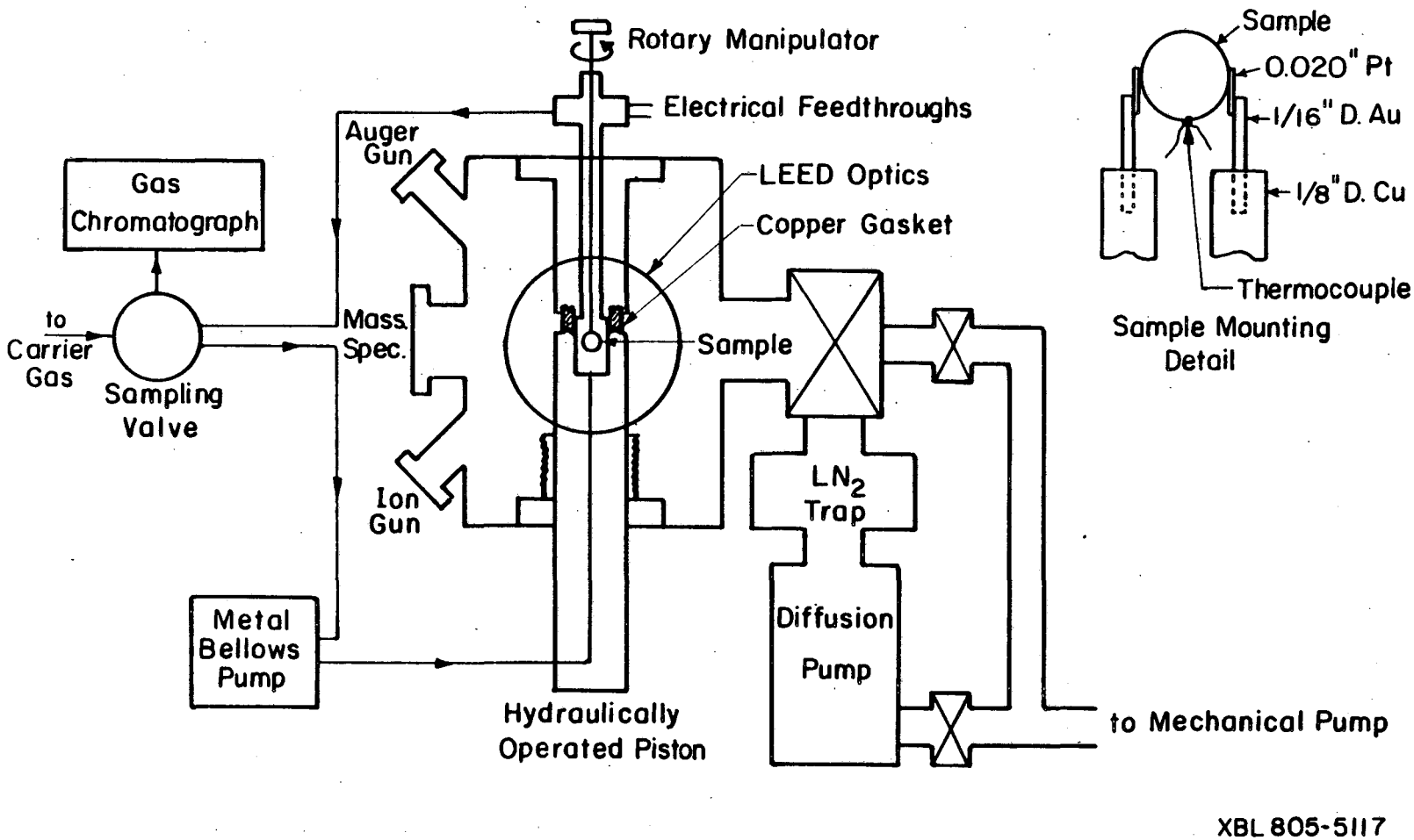
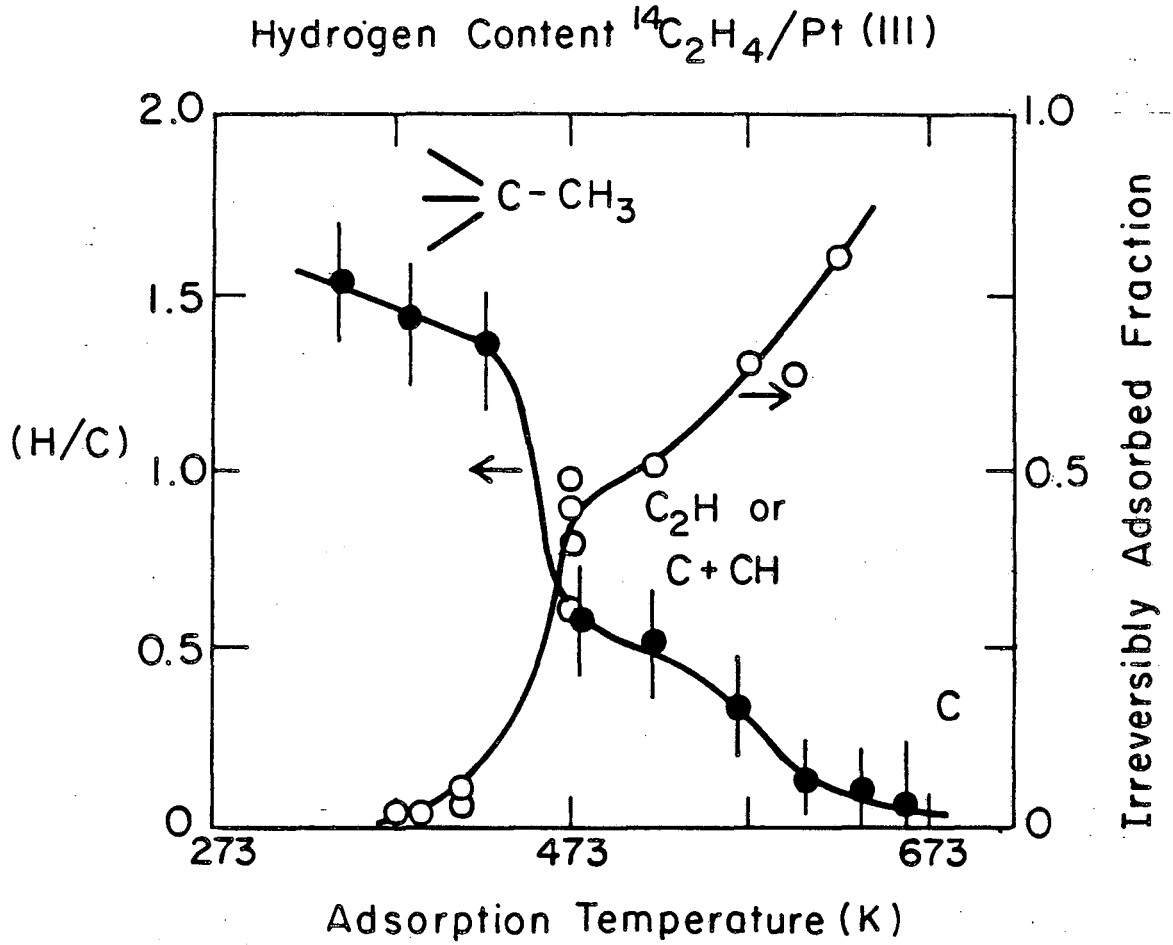

Rotary Manipulator
Electrical Feedthroughs
Auger Gun
LEED Optics
Copper Gasket
Gas Chromatograph
to Carrier Gas
Sampling Valve
Mass Spec.
Sample
Ion Gun
LN_2 Trap
Metal Bellows Pump
Diffusion Pump
Hydraulically Operated Piston
to Mechanical Pump
Sample
0.020" Pt
1/16" D. Au
1/8" D. Cu
Thermocouple
Sample Mounting Detail
XBL 805-5117

Fig. 7



XBL 812-5151A

Fig. 8

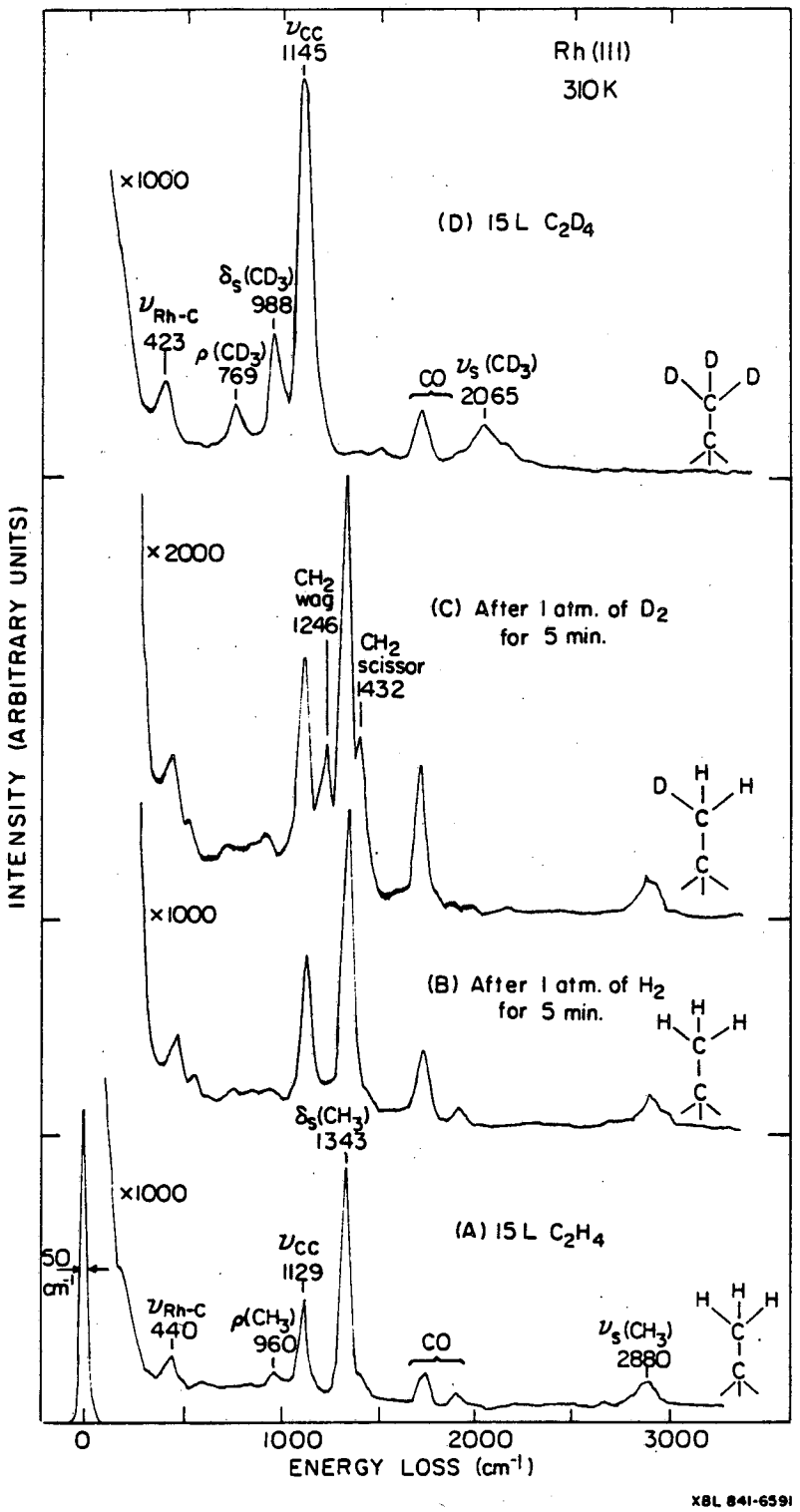

Rh (111)
310K
(D) 15 L C_2D_4
(C) After 1 atm. of D_2 for 5 min.
(B) After 1 atm. of H_2 for 5 min.
(A) 15 L C_2H_4
ν_{CC} 1145
×1000
$\delta_s(CD_3)$ 988
ν_{Rh-C} 423
$\rho(CD_3)$ 769
CO
$\nu_s(CD_3)$ 2065
×2000
CH_2 wag 1246
CH_2 scissor 1432
×1000
$\delta_s(CH_3)$ 1343
×1000
50 cm^{-1}
ν_{CC} 1129
ν_{Rh-C} 440
$\rho(CH_3)$ 960
CO
$\nu_s(CH_3)$ 2880
INTENSITY (ARBITRARY UNITS)
0
1000
2000
3000
ENERGY LOSS (cm^{-1})
XBL 841-6591

Fig. 9

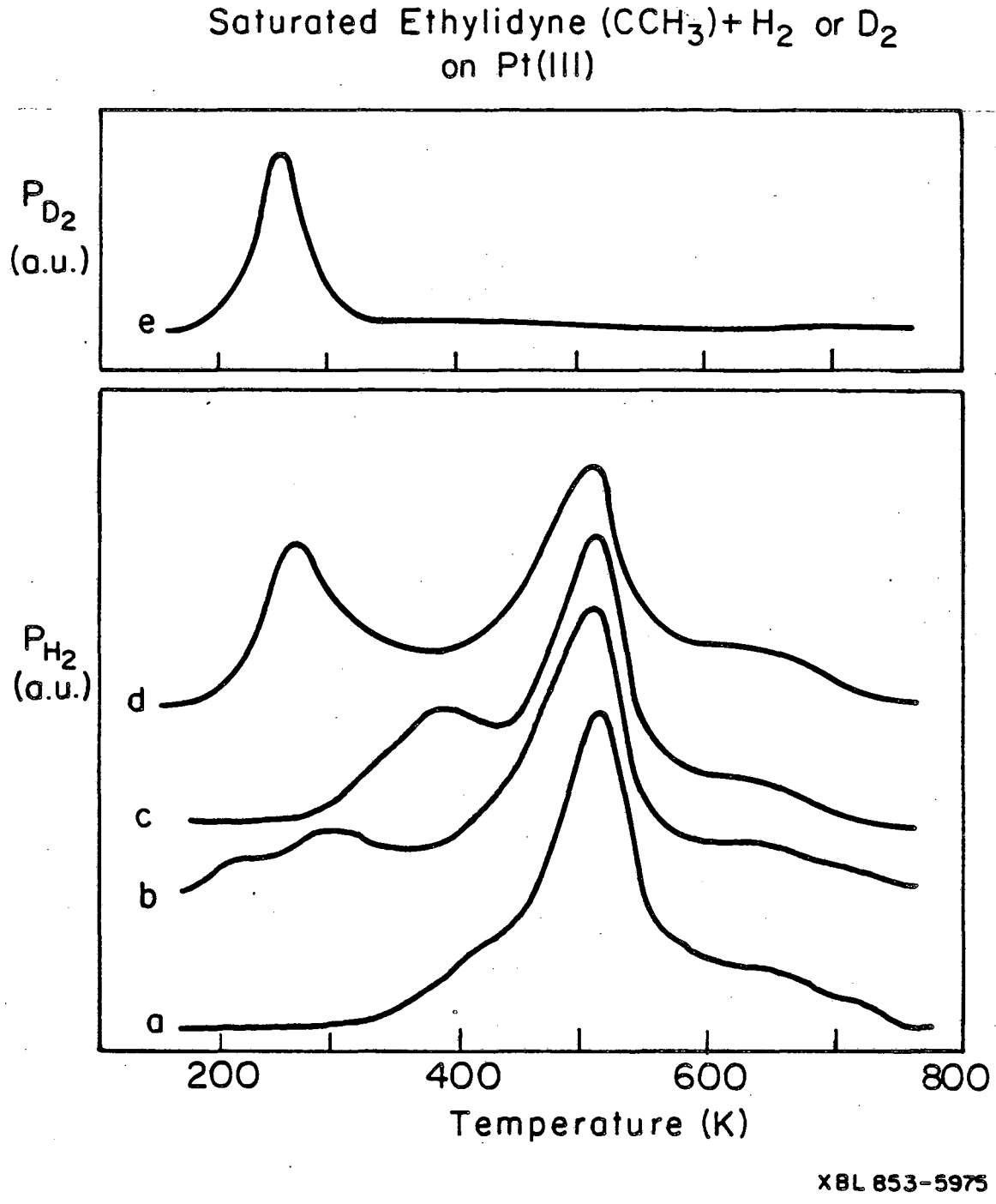

Saturated Ethylidyne (CCH_3)+ H_2 or D_2
on Pt(111)
P_{D_2}
(a.u.)
e
P_{H_2}
(a.u.)
d
c
b
a
200
400
600
800
Temperature (K)
XBL 853-5975

Fig. 10

Evidence for the Presence of Ethylidyne after Atmospheric Hydrogenation of Ethylene over Pt (111)

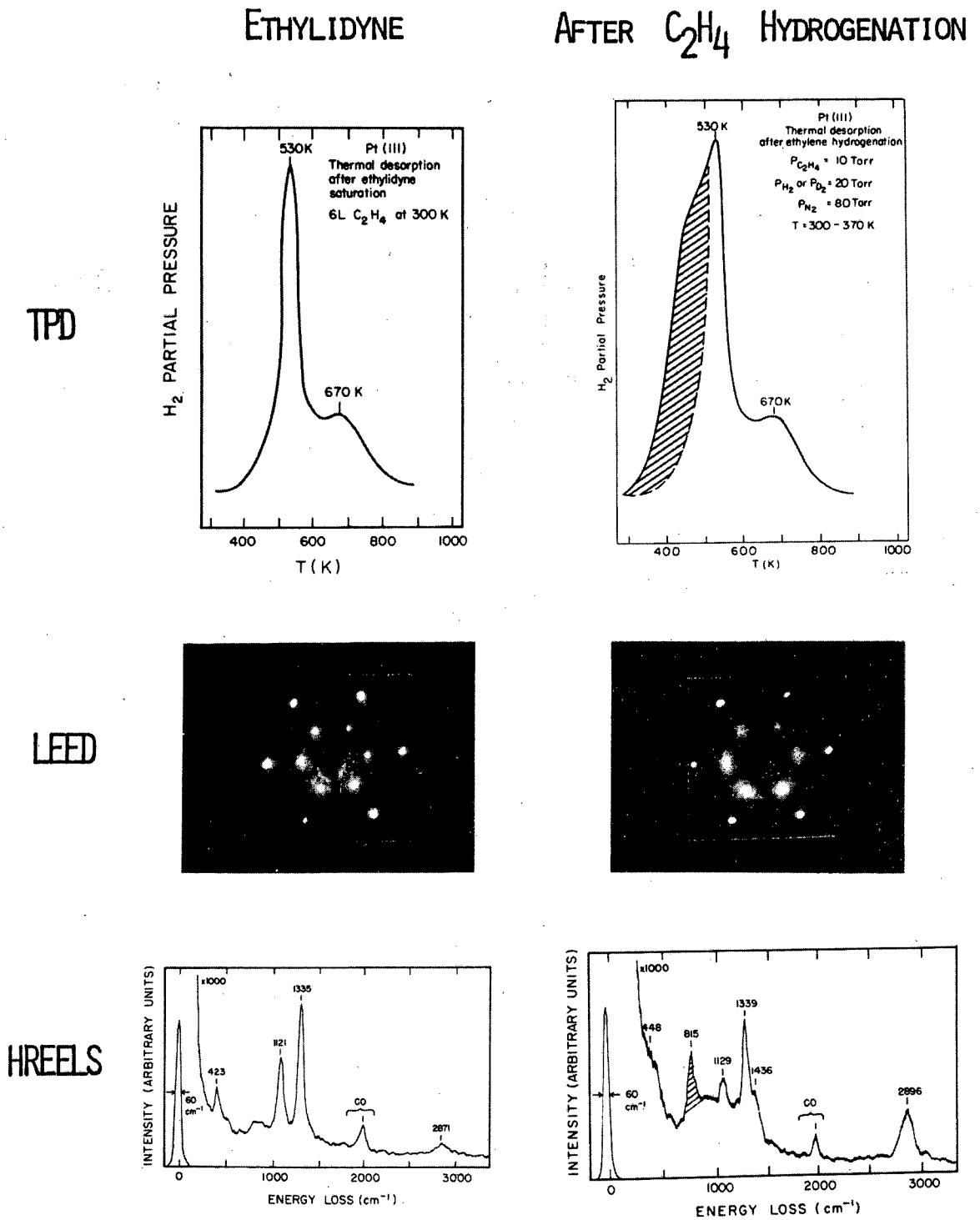
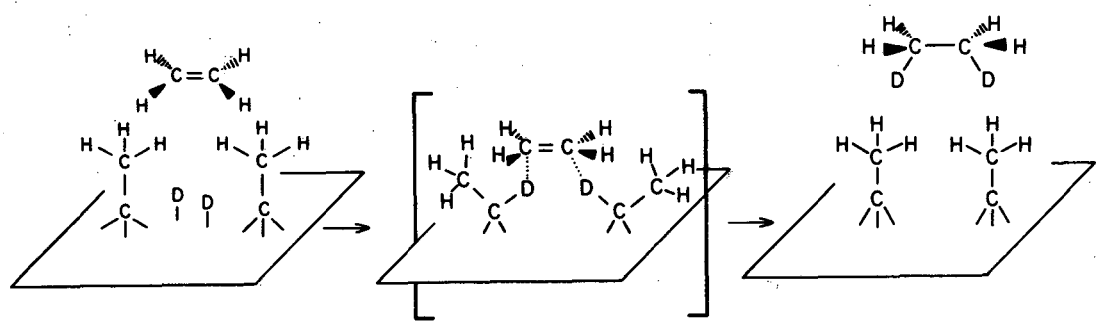


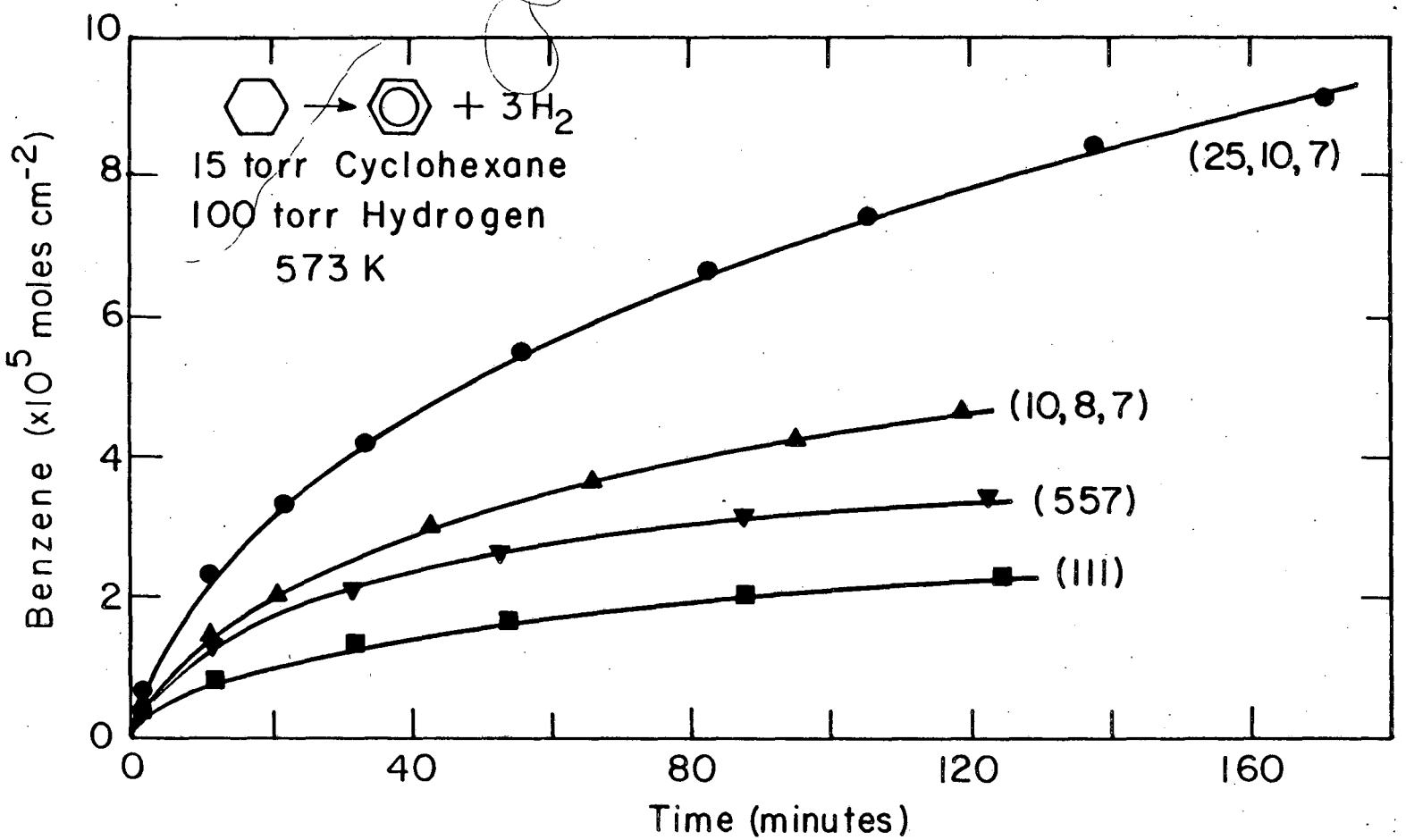
Fig. 11

PROPOSED MECHANISM FOR ETHYLENE HYDROGENATION



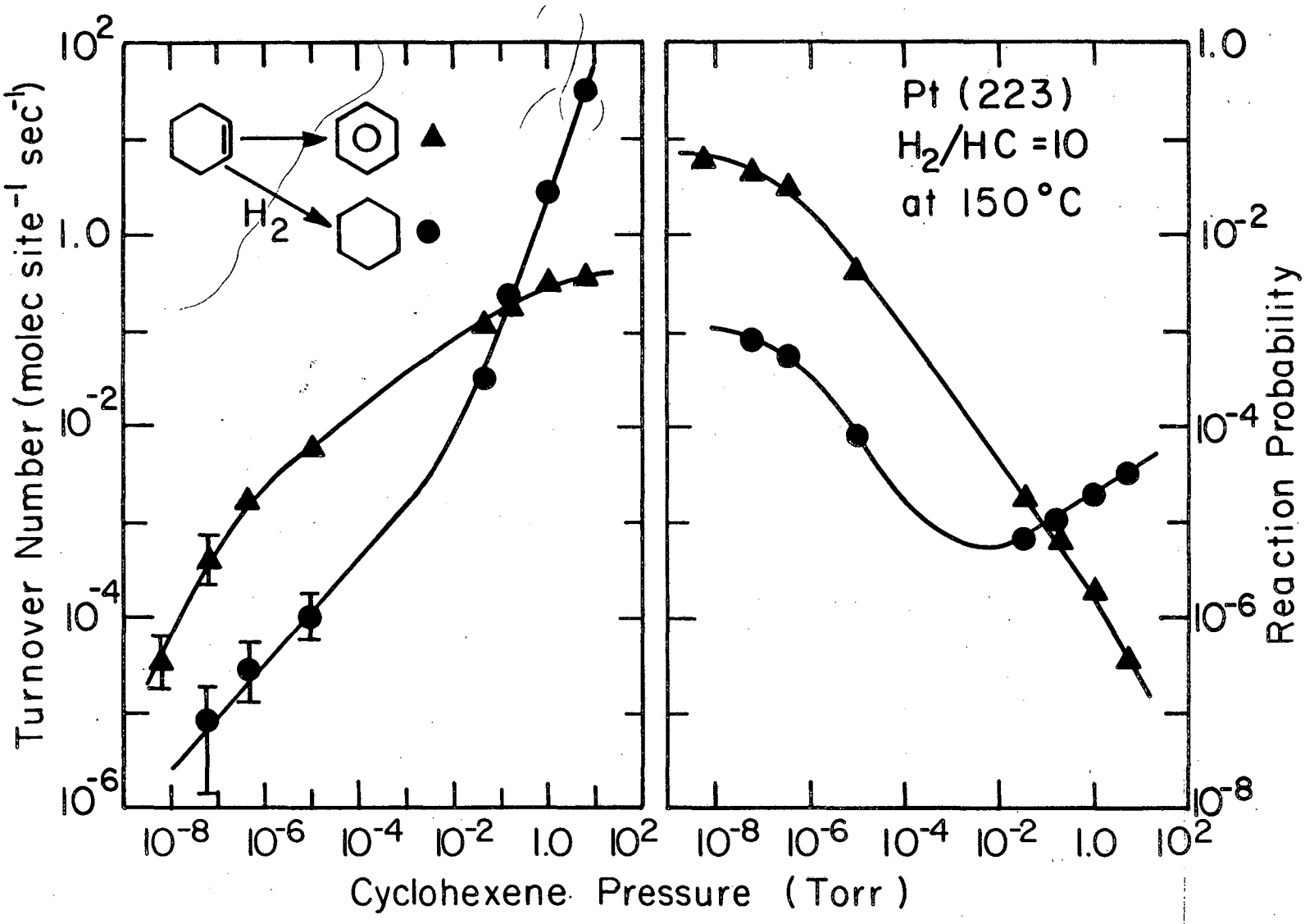
XBL 846-2494

Fig. 12



XBL7910-7266

Fig. 13



XBL 797-6698

Fig. 14

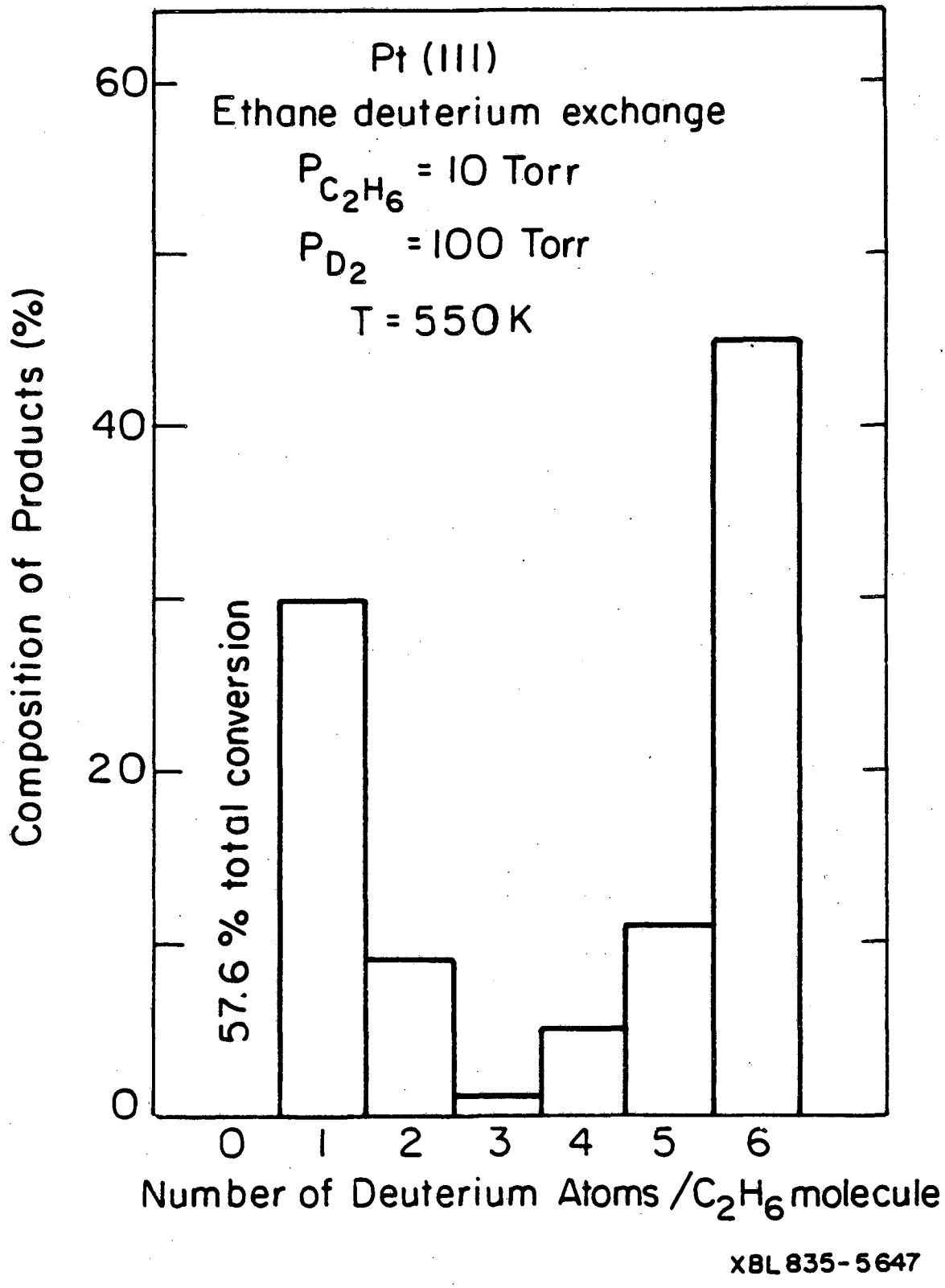
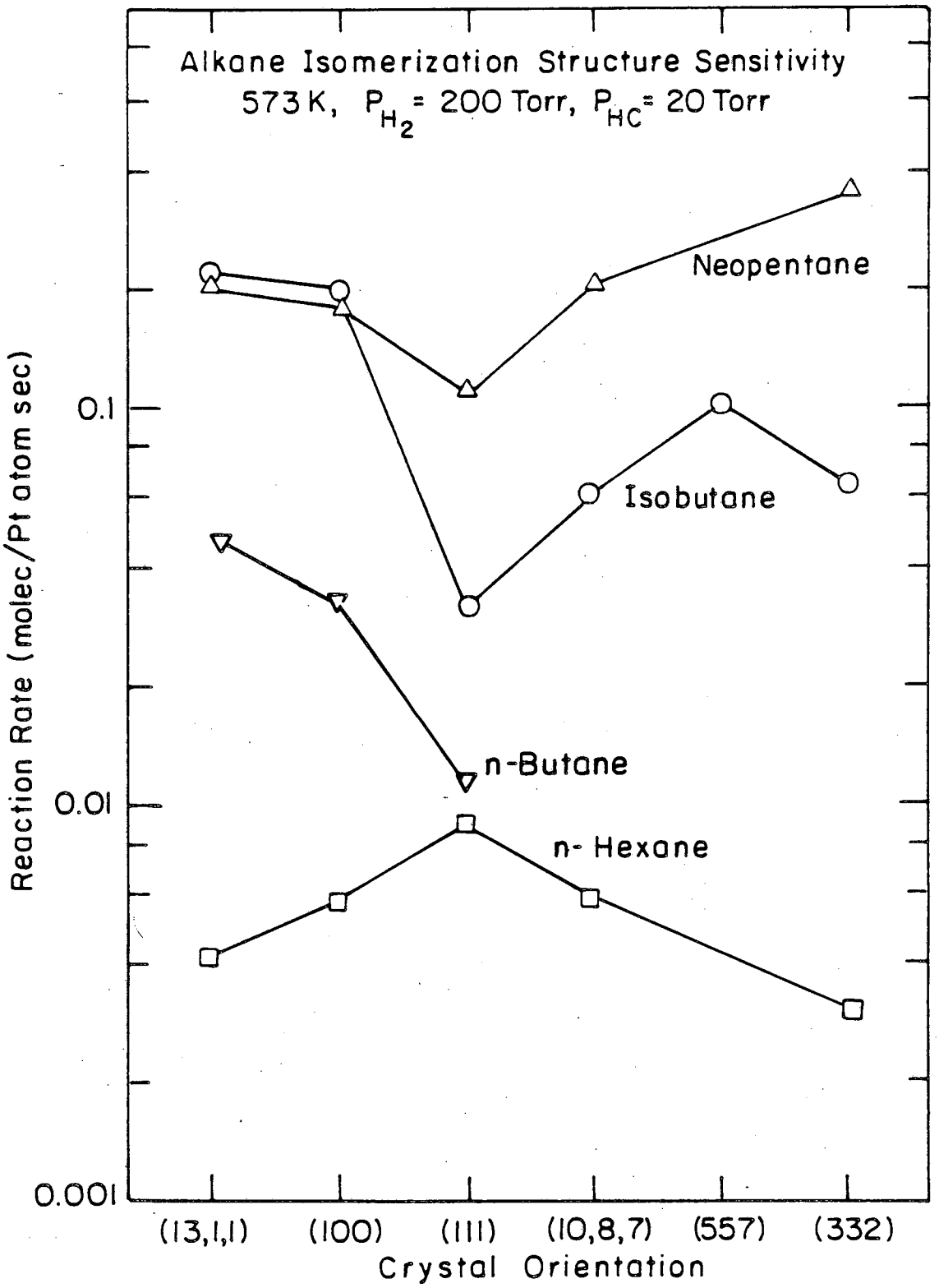

Pt (111)
Ethane deuterium exchange
$P_{C_2H_6}$ = 10 Torr
P_{D_2} = 100 Torr
T = 550 K
57.6 % total conversion
Composition of Products (%)
60
40
20
0
0
1
2
3
4
5
6
Number of Deuterium Atoms / C_2H_6 molecule
XBL 835-5647

Fig. 15



XBL 819-6633A

Fig. 16

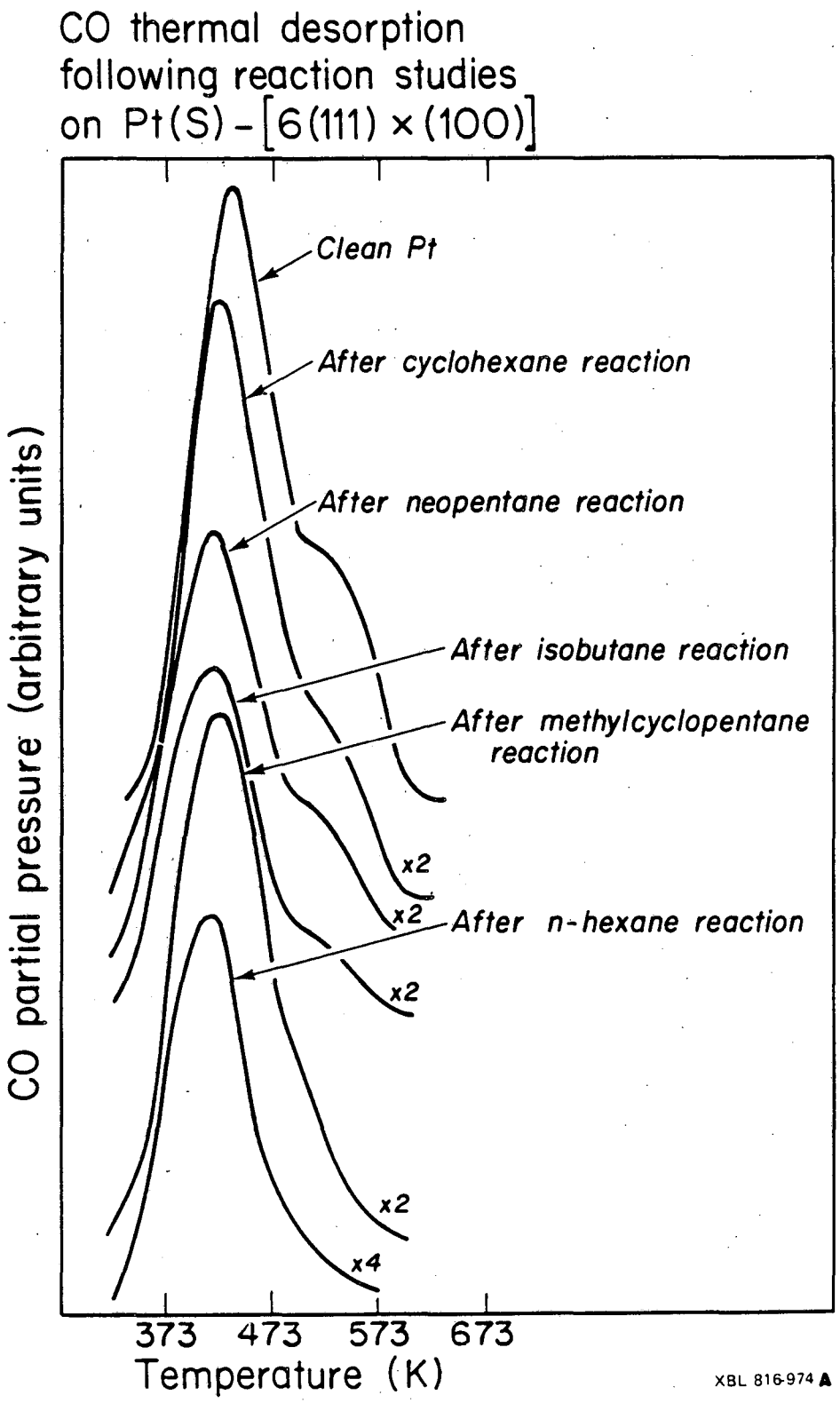

CO thermal desorption
following reaction studies
on Pt(S)-[6(111) × (100)]
Clean Pt
After cyclohexane reaction
After neopentane reaction
After isobutane reaction
After methylcyclopentane reaction
After n-hexane reaction
x2
x2
x2
x2
x4
CO partial pressure (arbitrary units)
373
473
573
673
Temperature (K)
XBL 816-974 A

Fig. 17

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