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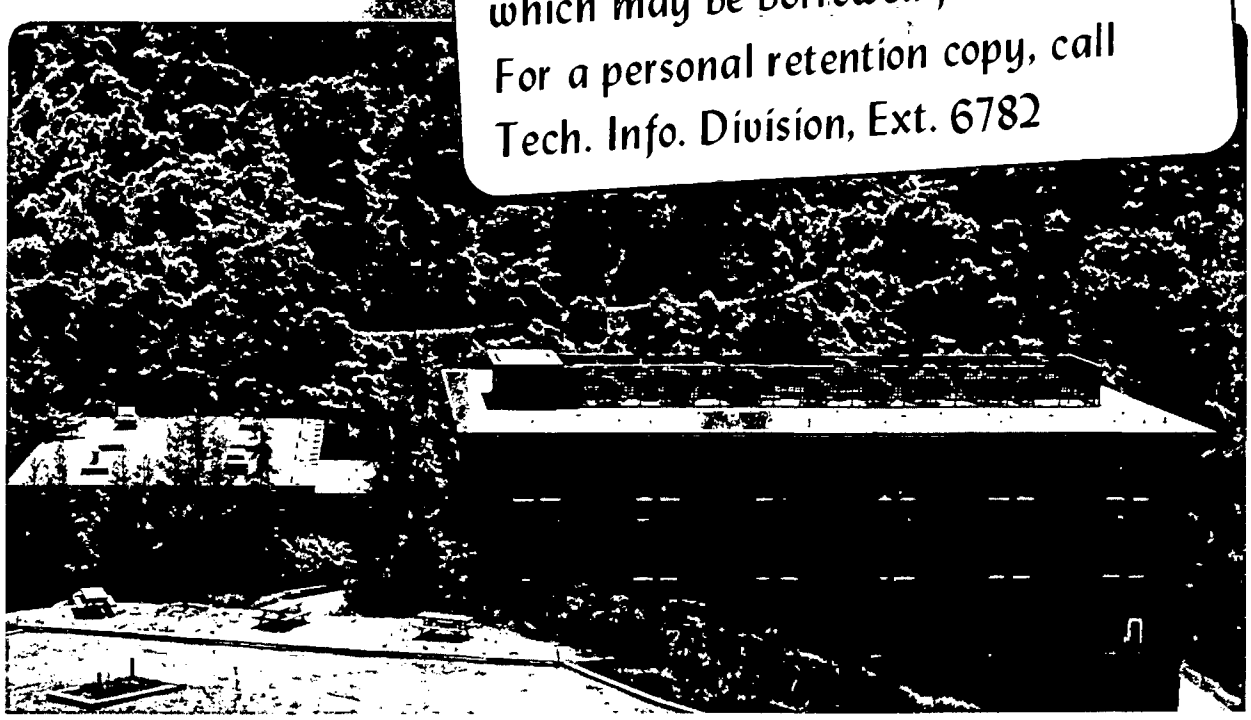

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THE DESORPTION, DECOMPOSITION, AND DEUTERIUM EXCHANGE REACTIONS OF UNSATURATED HYDROCARBONS (ETHYLENE, ACETYLENE, PROPYLENE, AND BUTENES) ON THE Pt(111) CRYSTAL FACE

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Abstract

The adsorption and thermal desorption of C_2H_2, C_2H_4, C_3H_6, and C_4H_8 (cis- and trans-) on Pt(111) has been studied as a function of coverage. The undissociated olefin molecules, in the monolayer coverage range, desorb at 285 ± 4°K, 280 ± 5°K, and 261 ± 6°K for C_2H_4, C_3H_6, and C_4H_8, respectively. At high exposures, multilayers of C_3H_6 and C_4H_8 formed while the Pt(111) crystal was maintained at 110°K. The desorption temperatures of these multilayers are 139 ± 5°K and 150 ± 8°K for C_3H_6 and C_4H_8, respectively. After the partial desorption of the undissociated molecules, the remaining adsorbed hydrocarbons decompose to yield desorbing H_2 and partially dehydrogenated surface species. The three olefins give rise to a sharp H_2-desorption peak at 297 ± 4, 296 ± 4, and 294 ± 5°K for C_2H_4, C_3H_6, and C_4H_8, respectively. The remaining surface species undergo a further dehydrogenation reaction that gives rise to another sharp desorption peak at 492 ± 6, 436 ± 5, and 381 ± 5°K, respectively. At even higher temperatures a series of three more H_2 peaks, at similar temperatures for all the hydrocarbons, appear at ~ 550, 640, and 710°K. These H_2 peaks represent the final and complete dehydrogenation of the hydrocarbon fragments on the Pt(111) surface. The H_2 desorption spectrum of C_2H_2 is very similar to that of C_2H_4 except for the absence of the first H_2 peak at 297°K. D_2 coadsorption produces changes in the binding of the hydrocarbon molecules on the Pt surface. Limited D incorporation into the undissociated hydrocarbon molecules has been observed to occur through H-D exchange in the coadsorption experiments. At higher temperatures, the stable room temperature phase of all these hydrocarbons undergoes extensive H-D exchange when exposed to D_2 without decomposition.

Introduction

Thermal desorption spectroscopy (TDS) is a useful technique to obtain information on the bonding properties of molecules adsorbed on solid surfaces. Reaction orders and kinetic parameters can be obtained for the various surface reactions that give rise to the observed desorption peaks. We have sued this technique to obtian information o the activation energies and preexponential factors that determine the desorption and decomposition reactions of C_2H_2, C_2H_4, C_3H_6, and C_4H_8 adsorbed on the Pt(111) surface. The first two hydrocarbons have received much interest recently, and various models have been proposed for the stable room temperature phase that is formed upon heating the adsorbed hydrocarbons to about 300°K. Low energy electron diffraction (LEED) and high resolution electron energy loss spectroscopy (HREELS) techniques were used in this laboratory[1] which led to the conclusion that the stable surface species is ethylidine ($\equiv C-CH_3$) with a verticle C-C axis. Another model was proposed also by use of HREELS to be ethylidene ($=CH-CH_3$)[2,3] with an inclined axis. Other techniques have also been used, including ultraviolet photoelectron spectroscopy (UPS)[4] and TDS[5] which led to the proposal of still another model, namely vinyl group species ($CH-CH_2$) for the stable surface species. However, some consensus seem to have been reached lately as to the nature of the surface species at room temperatue.[6] It appears that ethylidine ($C-CH_3$) is the correct model as deduced from a careful comparison of the observed HREELS vibration frequencies and the infrared absorption spectrum of the organometallic compound $CH_3CCo(CO)_9$).[7]

Our TDS data provides further confirmation to this assignment and also extends this result to other similar surface species that form upon adsorption of C_3H_6 and C_4H_8 on the Pt(111) surface after heating to room temperature. The

formation of propylidyne and butylidyne in the latter molecules is also confirmed by recent LEED studies in our laboratory.[8]

The alkylidyne species are not the exclusive property of the Pt(111) surfaces but appear to form as well on the metal surfaces like Pt(100)[9], Pd(111),[10], and Rh(111)[11].

We have also investigated the possibility of exchange between H, in the alkylidine surface species, and D. This exchange is observed to occur extensively without dissociation of the surface species. These results will provide new information as to the reaction mechanisms that take place on the Pt surface layers. The interaction of preadsorbed D_2 and the hydrocarbon molecules, prior to the formation of the stable alkylidynes, is also investigated.

Experimental

The experiments were performed in an ultrahigh vacuum chamber evacuated with ion and diffusion pumps. The Pt(111) single crystal samples were in the form of thin discs of approximately 1 cm diameter and thickness of ~ 1 mm. The crystal was mounted on a U-shaped Pt wire of 0.020 inch diameter, spot welded around the edges. Temperatures were measured by means of a chromel-alumel thermocouple spotwelded to the top edge of the crystal. Heat was carried to and from the crystal through the Pt wires. These wires were firmly fastened to two copper blocks that could be cooled to liquid nitrogen temperatures. The crystal could also be rotated to allow positioning for Auger electron spectroscopy (AES), low energy electron diffraction (LEED) and thermal desorption experiments (TDS). Detection of the various desorption products was performed with a UTI-mass spectrometer with the ionizer placed at approximately 10 cm from the Pt crystal face. A linear temperature ramp was achieved in the range of 110-800° K by suddenly passing a high current of the order of 15 amps through the supporting Pt wires. The heating rates were always in the range of 7-14° K/sec, with a constancy of ± 0.5°K/sec in the temperature range studied. Pumping times for the different gases used were of the order of 0.5 seconds or less.

The different hydrocarbons used in this work were introduced into the vacuum chamber via a leak valve with a capillary tube to dose the crystal from ~ 1 cm distance from the surface while the platinum sample was held at 110 K. Pressures and exposures were measured with a Bayard-Alpert ion gauge without correction for inhomogeneous pressure distributions and differences in sensitivity, especially with hydrocarbons. The values of all the exposures in Langmuirs (1 L = 10^{-6} torr x sec) given in this work are thus only qualitative.

The cleanliness of the surface was monitored by Auger electron spectroscopy with a retarding field analizer. After the TDS experiments with the unsaturated hydrocarbons, the crystal surface was covered with carbon, typically with a ratio of Auger peak heights C(275 eV)/Pt(237 eV) <1. This carbon could be easily removed by heating in $2x10^{-7}$ torr of O_2 for 5-10 minutes at a crystal temperature of ~ 1000° K. Subsequently, the crystal was flashed to above 1300°K and then cooled to 110°K in a period of ~ 5 minutes. Background pressures in the range of 10^{-10} torr were usually obtained but increased during the course of the hydrocarbon experiments and O_2 cleaning to reach a final value between 1 and $2x10^{-9}$ torr. It is possible, however, that this background pressure is inhomogeneous as the liquid nitrogen cooling device near the crystal acted as a very effective cryopump.

When desorbing the hydrocarbons, in the course of the TDS experiments, desorption of hydrocarbons adsorbed on the cooling device occurred that gave rise to a very sharp peak at the beginning of the flash and then to a slowly rising background. The first peak corresponds to desorption from the Pt wire that served to cool and heat the Pt crystal and the slowly increasing background is due to the Cu-blocks that heat slowly in the course of the TDS experiment.

Results

The adsorption and subsequent desorption of the unsaturated hydrocarbons on Pt(111) were studied as a function of exposure. The hydrocarbons studied were acetylene, ethylene, propylene, cis-butene and trans-butene. When the crystal was heated, after the low temperature adsorption (110)°K) of the

hydrocarbon, a series of reactions occurred that led to partial desorption of undissociated molecules first and then, at a slightly higher temperature, to H_2 evolution from the sequential dehydrogenation of the remaining surface species. The H_2-TDS spectra obtained for the various adsorbed olefins is summarized in Fig.1. For all of the olefins that were studied, the primary dehydrogenation process gave rise to a sharp H_2 desorption peak at approximately the same temperature of 296°K (within 3°K) for the three olefins. This peak will be referred to as peak A in the following. At still higher temperatures, a second dehydrogenation reaction takes place, that gives rise to a second H_2 desorption peak (referred to as peak B) at a temperature that decreases with increasing molecule weight of the hydrocarbon, as shwon in Fig.1. Finally, a series of three more H_2 desorption peaks (peaks C) appear at temperatures above 500°K which represent the final and complete dehydrogenation of the remaining partially dehydrogenated layer on the Pt(111) surface. These high temperature H_2-TDS peaks are very similar for all the unsaturated hydrocarbons studied, indicating nearly equivalent decomposition mechanisms.

Acetylene has a H_2-TDS spectrum similar to that of ethylene, with the exception of peak A that is missing in acetylene, as seen in Fig. 4.

In Table I we list the temperatures of the desorption peaks for all the adsorbed hydrocarbons that were studied.

The exchange of hydrogen and deuterium in the adsorbed hydrocarbons was also studied in two different temperatures regimes. At low temperatures we investigated the H-D exchange in the undissociated molecules by coadsorbing D_2 and the hydrocarbon. At higher temperatures (above 300°K), the exchange of H in the stable surface species is studied as a function of exposure to D_2

at various temperatures.

Kinetic parameters for the processes giving rise to the various desorption peaks can be extracted from the observed peak position and width in the TDS curves. A simple method to obtain activation energies and preexponential factors was used for the first order process that occurred in the present study. The values obtained using this method are summarized in Tables II and III. The details of the method are exposed in the appendix at the end of this paper.

We describe now the adsorption and thermal desorption behavior of each hydrocarbon on the Pt(111) surface separately.

Ethylene: In Fig.2 we show the TDS curves after various exposures of the Pt(111) surface to C_2H_4. Undissociated molecules desorb with a main peak at 285 ± 4°K. At temperatures that are only slightly above this desorption peak, decomposition of the remaining adsorbed C_2H_4 molecules occurs which gives rise to H_2 evolution. Two major peaks, A and B, appear in the H_2-TDS curves at 297 ± °K and 492 ± 6°K, respectively. Peak B is accompanied by two shoulders at temperatures of approxmately 435 and 550°K. The intensity of these two shoulders is not always constant in the different experiments and may be the result of the decomposition of other hydrocarbon fragments that are present in the surface in small amounts. In fact, the 550°K shoulder lies in the region that we call C, where similar H_2 desorption peaks are observed with the other unsaturated hydrocarbons.

The area under the H_2-TDS curves increases linearly as a function of exposure, as shown in the insert of Fig.2, up to about 0.4 L where saturation occurs.

The contribution of the three different regions (peaks A, B, and C) to the total area has been measured. Essentially, peak A alone accounts for

33 ± 3% of all desorbed H_2. Peak B accounts for 52 ± 3%, while the two peaks at 641 and 704°K of region C account for 15 ± 3%. We have included the contribution of the shoulder at 550°K in peak B due to its strong overlap.

The temperature of the various desorption peaks does not change as a function of hydrocarbon exposure, indicating that first order processes govern the desorption and dehydrogenation reactions in each case.

If D_2 is preadsorbed on the surface at 110°K, and then is exposed to the hydrocarbons, the following changes in the TDS curves are observed: (1) The undissociated molecules show a broad distribution instead of the well defined peak at 287°K. This is shown in curve C of Fig.2, corresponding to a preadsorption of 6 L of D_2 followed by exposure to 0.2 L of C_2H_4. (2) The H_2-TDS curves show a change in the relative areas of peaks A and B, the latter peak being less intense than in the absence of preadsorbed D_2. Also, the total area of the H_2-TDS curve is less than that corresponding to the same hydrocarbon exposure in the absence of D_2. Desorption of HD is observed in this coadsorption experiments. The HD-TDS curves are similar to the H_2-TDS curves, but the relative area of peak B is still smaller than in the H_2-TDS curves. The order in which D_2 and C_2H_4 are adsorbed is unimportant for low C_2H_4 exposures (<0.1 L), but at higher exposures of ethylene (>0.4 L) D_2 can no longer be adsorbed. The D_2-TDS curves show a main peak between 200 and 300°K, depending on the exposures to both D_2 and C_2H_4. Also, a small D_2 peak is observed at the position of peak A that overlaps the main D_2 peak. Examples of these results are shown in Fig.3. For comparison the D_2 and H_2-TDS curves obtained after exposure of the clean surface to D_2 or C_2H_4 alone are also given. The shoulder below peak A in one of the HD-TDS curves corresponds to H-D recombination from adsorbed background H_2. All these results show that only a little amount of exchange between the hydrocarbon and the D-atoms takes

place at these low temperatures.

Acetylene. Acetylene gives a H_2-TDS spectrum similar to that of ethylene except for the absence of peak A, as can be seen in Fig.4. The tempeature of peak B is again 492 ± 5°K. The small peak at approximately 230°K that is present in the figure is due to background H_2 adsorption. A plot of the area under the H_2-TDS curves versus C_2H_2 exposure shows a linear increase up to about 0.4 L where saturation is observed. If D_2 is preadsorbed at 110°K prior to C_2H_2 adsorption, the H_2-TDS curve is similar but less intense thant that obtained after the same C_2H_2 exposure of the clean Pt surface, as shown in Fig.5. The extent of H-D exchange and D incorporation under these conditions is very small, as shown by the small intensity of peak B in the HD and D_2-TDS curves. The D_2-TDS curves show only one large peak at about 230°K which corresponds to the desorption of unreacted D_2. The other peaks of H_2 and HD in the curves of Fig.5, at temperatures between 200 and 300°K, are due to adsorbed H_2 from the background.

Propylene. In Fig.6 we show the TDS curves from adsorbed C_3H_6 obtained after an exposure of the Pt surface to 0.5 L of hydrocarbon. The undissociated molecules desorb with maximum rate at 280 ± 5°K at low exposures (0.2 L). At higher exposures other smaller peaks appear at 245, 200, and 139 ± 6°K. The 245°K peak overlaps strongly with the 280°K peak, and the 139°K peak corresponds to the formation of multilayers as shown by its rapid increase at high exposures (see Fig. 7a). After desorption of undissociated molecules the dehydrogenation of the remaining adsorbed C_3H_6 molecules gives rise to the H_2-TDS curve of Fig.6. Peak A is found at 296 ± 4°K, peak B at 436 ± 5°K and at higher temperatures (C region), three more peaks at 524 ± 4, 637 ± 4 and 712 ± 4°K. The shoulder at 328°K is due to hydrocarbon adsorption from the background that occurs during the cooling of the crystal after high

temperature cleaning in O_2. Similar shoulders were observed in some cases also for C_2H_4. An example of this background adsorption is shown in Fig.13. The relative areas under the peaks A, B, and C were measured to be 26 ± 3, 41 ± 3, and 33 ± 3%, respectively. The contribution of peak A may be overestimated due to the shoulder at 328°K. A plot of the area under the H_2-TDS curve versus exposure gives a linear increase up to about 0.4 L where saturation occurs. In the D_2 precovered surface, the saturation is observed to occur at lower exposures of hydrocarbon (depending on the D_2 exposure). The peak at 280°K from the undissociated C_3H_6 is substituted by a broad distribution, as shown in Fig. 7b. The formation of multilayers in this case occurs also at lower exposures than in the absence of D_2. The H_2, HD, and D_2-TDS curves from coadsorption experiments are shown in Fig.8a. The same general observations as for C_2H_4 can be repeated here. The H_2-TDS curves show a decrease in the intensity of peak B relative to peak A. The HD-TDS curves are similar, but with a still less intensive peak B and the D_2-TDS curves show still smaller peaks A and B. Most of the D_2 desorbs at temperatures below that of peak A which, in the example of Fig.8a, overlaps strongly with peak A. Incorporation of the coadsorbed D into the undissociated molecule, through H-D exchange prior to desorption, is observed to occur. This is shown in Fig.8b, where the TDS curves correspondening to atomic mass units 42, 43, 44, and 46 are shown for a surface exposed to 12 L of D_2 at 110°K followed by 0.5 L of C_3H_6. For reference, the gas phase mass spectrum of C_3H_6 is shown in the insert. As we can see, no desorption at mass 44 is observed when D_2 is not preadsorbed. The absence of peaks at mass 46 indicates that exchange of more than 3 H atoms is negligible under these conditions.

Cis- and trans-2-butene. Although both isomeric forms of 2-butene were studied, no differences were observed in the TDS curves of both undissociated C_4H_8 and H_2 molecules. Consequently, we will not distinguish between these two forms in describing their adsorption and desorption behavior. In Fig.9 we show the TDS curves from a Pt(111) surface saturated with C_4H_8 which occurs after 0.3 L exposure. The H_2-TDS curves show peak A at 294 ± 5°K, peak B at 381 ± 5°K, and the group of C peaks at ~ 583, 634 ± 6 and 705 ± 4°K. Background adsorption of residual C_4H_8 while the crystal was above 300°K was usually more severe than with the lighter hydrocarbons. This background adsorption resulted in the filling of the valley between peaks A and B, particularly at the lower exposures. For this reason, exposures below 0.1 L are not considered here. The relative areas of peaks A, B, and C are 24 ± 3, 50 ± 3, and 25 ± 3% in that case.

The undissociated molecules desorb with a main peak at 261 ± 6°K, i.e. 34°K below peak A. At high exposures another peak is observed at 150 ± 8°K that corresponds to the formation of multilayers, as shown in Fig.10a. If D_2 is preadsorbed at 110°K, the 261°K peak is substituted by a broad distribution with increasing D coverage, as shown in Fig.10b. Also, the formation of multilayers is enhanced by the presence of deuterium. These results are in the same line as those from the other hydrocarbons.

The H_2-TDS curves are also affected by D_2 preadsorption in much the same way as in the other hydrocarbons. The H_2-TDS curves show a relatively smaller peak B, as seen in Fig.9. This peak becomes even smaller in the HD-TDS curves and in the D_2-TDS curves, the D_2 peak appears at temperatures lower than that of peak A.

H-D Exchange in the Stable Room Temperature Hydrocarbon Monolayer

When heating the adsorbed hydrocarbon at temperatures above that corresponding to peak A, but less than that corresponding to peak B, it is known that adsorbed C_2H_2 and C_2H_4 give rise to a stable species which has been identified as ethylidyne. Exchange between H in this species and D was investigated by exposing the Pt surface covered with C_2H_2 and C_2H_4 to gas phase D_2 at various temperatures and D_2 pressures. The extent of the exchange is indicated by the intensity of the H_2, HD, and D_2-TDS curves after such an experiment. It is found to increase with increasing surface temperature and D_2 exposure. It also depends on the initial hydrocarbon coverage being larger for the lower surface coverages. In Fig.11 we show some examples of these experiments. In Fig.11a we show H_2, HD, and D_2-TDS curves following a 12 L D_2 exposure of a Pt surface previously exposed to 0.1 L of C_2H_2 at 110°K. During the D_2 exposure the surface was maintained at 400°K. The top curve is a H_2-TDS curve from C_2H_2 which has not been exposed to D_2. The second curve corresponds to a surface exposed to 0.1 L of C_2H_2 and heated in vacuum at 400°K for 60 seconds. As we can see, no modification occurs in that case. If the same surface is exposed to $2x10^{-7}$ torr of D_2 for 60 seconds at 400°K, appreciable exchange occurs as shown by the three lower TDS curves corresponding to H_2, HD, and D_2. From the relative areas under these three curves, an average composition of 2-H and 1-D atoms per molecule can be estimated. In another example shown in Fig.11b, the Pt surface was initially exposed to 0.1 L of C_2H_4 at 110°K. Again no loss of H_2 from the ethylidyne species is observed if the surface is heated in vacuum to the reaction temperature (388°K in this case), and for the same length of time. If, while the crystal is maintained at 388°K, D_2 is admitted into the chamber for a total exposure of 30 L, extensive exchange takes place

as shown in the figure by the H_2 and D_2-TDS curves. In this example the average H:D atom ratio per molecule is found to be approximately 1:2. It is interesting to note that the temperature of peak B after these exchange experiments is found to be somewhat greater than in the absence of exchange. The temperature of the peak is now 502 $\pm$ 8°K, i.e., 10°K approxmately greater than in C_2H_2 and C_2H_4 alone.

D_2 exchange with the stable proplylidyne surface species also occurs readily. In the example of Fig.12, curve a corresponds to H_2 thermal desorption after exposure of the Pt surface to 0.3L of C_3H_6. Curve b is the result of heating this surface layer to the reaction temperature of 363°K for 2 minutes in vacuum and then allowing it to cool to 110°K prior to desorption. In curve c the surface layer of C_3H_6 was heated to 363°K for 2 min. in vacuum, followed by exposure to $2x10^{-7}$ torr of D_2 for another 2 min. at the same temperature of 363°K. As in the case of C_2H_2, the extent of exchange increases with increasing surface temperature and D_2 exposure. It also depends on the hydrocarbon coverage being larger at the lower C_3H_6 coverages. In the case of C_3H_6 the amount of exchange, as measured by intensity of peak B in the HD-TDS curves is limited, for a given exposure, by the lower temperature that can be used in the exchange experiments, as peak B occurs at 56°K lower temperature than in the case of C_2H_2. This limitation is still more severe in the case of butene. For this reason the exchange in the stable form of butene was not studied in detail.

C_2H_4 Adsorption on Pt(111) with C Layers

A final set of experiments was performed to study the adsorption of C_2H_4 on a Pt(111) surface that was covered with dehydrogenated carbon residues.

We exposed the surface to 0.1 L of ethylene successively after each TDS experiment without removing the C deposit left from the preceding experiments. Essentially, the same shape of H_2-TDS curve was obtained. The relative area of peak A, however, was smaller than that of peak B, the difference increasing with increasing C coverage. In Fig. 13a, we show the H_2-TDS curves corresponding to C coverages of 0 and 1. The coverage of 1 corresponds to a C(275)/Pt(237) Auger peak ratio of ~ 2, according to a recent absolute determination using C^{14} labeled hydrocarbons.[16] The dashed curve in the figure corresponds to background adsorption of residual hydrocarbons in the process of cooling the crystal. This background adsorption gives rise to shoulders in the high temperature side of peak A. A plot of the intensitites of peaks A and B, as a function of the C(275)/Pt(237) Auger peak ratio, is shown in Fig.13b

Discussion

Ethylene. The desorption of undissociated C_2H_4 molecules occurs with maximum rate at 285°K, i.e. 12°K before the maximum desorption rate for the decomposition reaction giving rise to peak A. From the observed low temperature half-width (19 ± 3°K) and peak temperature, the following values for the activation energy E and preexponential factor ν were obtained as discussed in the appendix section:

$$E = 12.0 \pm 3.2 \text{ kcal/mol} \qquad \nu = 10^{9.2 \pm 2.8} \text{ sec}^{-1}$$

Formation of multilayers was not observed with C_2H_4 at 110°K.

Following the desorption of undissociated C_2H_4, partial dehydrogenation of the remaining surface species occurred with maximum rate at 297°K. The species resulting from this first dehydrogenation has been shown by LEED and HREELS[1,6] to be ethylidyne ($\equiv C - CH_3$). The corresonding reaction is then

$$(C_2H_4)_{ads} \longrightarrow (C_2H_3)_{ads} + 1/2\ H_2 \qquad (1)$$

Since the desorption of H_2 is observed to be first order, we can assume that the rate limiting step in reaction (1) is the breaking of C-H bonds. The desorption of H_2 occurs then by H recombination in the Pt surface. This second reaction must be fast to account for the observed order of the reaction. This is, in fact, the case as demonstrated by the much lower desorption temperature of the coadsorbed D_2 in the example of Fig.5 where the D_2 peak appears at ~ 230°K.

The large shift of the D_2 peak when coadsorbed with hydrocarbons as compared to the desorption from the clean Pt surface (at ~ 300°K), can be explained by the repulsive interactions between the D atoms and the hydrocarbon molecules. This repulsion explains also the desorption of undissociated hydrocarbon molecules at lower temperatures in the presence of preadsorbed D_2. Similar effects that were observed during D_2 coadsorption experiments with C_4H_{10} and C_5H_{12} are reported elsewhere.[17]

From the observed low temperature half-width (13 ± 1°K) and the temperature of peak A, the following values for the activation energy E, and preexponential factor ν were obtained (see appendix) for the reaction (1):

$$E = 18.4 \pm 1.7 \text{ kcal/mole} \qquad \nu = 10^{13.6 \pm 1.4}\ \text{sec}^{-1}$$

Reaction (1) implies that the area of peak A should be 25% of the total area under the H_2-TDS curve. This value is not far from our measured 33 ± 3% contribution of peak A. The discrepancy is probably due to the observed sensitivity of the relative areas of peaks A and B to the presence of coadsorbed H_2 (or D_2). This was demonstrated in our coadsorption experiments with D_2, where the area of peak A was found to increase, relative to that of peak B,

when D_2 was preadsorbed on the surface. A possible explanation to this effect might be that some C_2H_4 (or C_2H_6) desorbs from the surface after the desorption of peak A. This desorption could then be the result of the rehydrogenation of C_2H_3 intermediates in the presence of adsorbed H (or D) to yield C_2H_4 (C_2H_3D) or C_2H_6 ($C_2H_3D_3$) instead of forming ethylidyne. Another possibility is the occurance of reactions similar to (1) but with loss of two H atoms which would leave C_2H_2 species on the surface similar to those formed with acetylene.

At higher temperatures, the stable ethylidyne species decomposes giving rise to H_2 desorption (peak B) with maximum rate at 492°K. Recent HREELS studies[3] indicate that at temperatures above this decomposition reaction the remaining surface species are CH groups.[xx] We propose then the following reactions:

$$(C_2H_3)_{ads} \longrightarrow C_nH + H_2 \qquad n < 2 \qquad (2)$$

At present it is not possible to conclude which of these reactions (n=1,2) occurs, although the existence of three peaks in region C (at 550, 641, and 704°K) seem to indicate that more than one type of CH groups exists on the surface after the decomposition of ethylidyne.

The activation energy E, and preexponential factor ν for this decomposition reaction (2) were obtained from the observed low temperature half-width (29 ± 5°K) and peak temperature (see appendix), the results are

$$E = 22.0 \pm 4.1 \text{ kcal/mol}$$

$$\nu = 10^{9.5+2.0} \text{sec}^{-1}$$

Finally, the complete dehydrogenation of the CH type residues yields peaks C at temperatures of ~ 550, 641 ± 4, and 704 ± 4°K. Since these peaks overlap strongly with each other, it is not possible to use the method of the peak width to obtain the kinetic parameters. An estimate of the activation energies for these decomposition reactions can be obtained by assuming a

of formula (2) of the appendix: 33, 39, and 43 kcal/mol, respectively, for the processes giving rise to the 550, 641, and 704°K peaks.

Acetylene

It has been shown by LEED and HREELS[1,6] that the stable room temperature phase formed upon adsorption of C_2H_2 on the Pt(111) surface in the presence of H_2 is also ethylidyne. The formation of this species, however, requires the incorporation of one H atom per molecule, a process that does not occur efficiently in the short time of our desorption experiments. This is shown in the results of Fig.5, where negligible incorporation of D was observed in the coadsorption experiments. HREELS experiments by Ibach et al.[2] have shown that the stable species formed after heating the adsorbed C_2H_2 to room temperature in vacuum is different from ethylidyne. A possible candidate for this species is vinilidyne ($=C=CH_2$)). The decomposition pattern of this species is remarkably similar to that of ethylidyne, as shown in the H_2-TDS curves of Fig.4. The decomposition reaction can be written as:

$$(C_2H_2)_{ads} \longrightarrow (C_nH)_{ads} + 1/2H_2 \qquad n < 2$$

with similar fragments left on the surface as in the C_2H_4 case. The activation energy, E, and preexponential factor ν were calculated following the procedure outlined in the appendix using the measured low temperature half-width (31 ± 3°K) and peak temperature (492 ± 5°K). The following values were obtained:

$$E = 20.6 \pm 2.2 \text{ kcal/mol}$$

$$\nu = 10^{8.8+1.2} \text{ sec}^{-1}$$

Propylene

The desorption of undissociated C_3H_6 molecules proceeds at maximum rate at

280°K at submonolayer coverages. This desorption proceeds by 16°K the onset of dehydrogenation reactions at its maximum rate. Using the method of the appendix, the following values of E and ν were obtained from the low temperature half-width at low coverage (17 ± 2°K) and the peak temperature:

$$E = 12.2 \pm 1.7 \text{ kcal/mol}$$

$$\nu = 10^{9.4+1.5} \text{sec}^{-1}$$

At higher exposures, other peaks appear at 245, 200, and 139°K ± 6°K. The widths of these peaks could not be measured as a result of their strong overlap. The last one corresponds to the multilayer desorption. Estimates of the activation energies are obtained by assuming $\nu = 10^{13}$ and by use of formula (2) in the appendix. The following values are thus obtained: 15, 12, and 8 kcal/mol, respectively.

The dehydrogenation behavior of C_3H_6 is similar to that of C_2H_4. The first reaction, that results in the formation of peak A, gives rise to a stable species of a similar nature to that obtained with C_2H_4, i.e. propylidyne ($\equiv C-CH_2-CH_3$). This has been demonstrated by recent LEED studies in this laboratory.[8] The following reaction is then proposed:

$$(C_3H_6)_{ads} \longrightarrow (C_3H_5)_{ads} + 1/2H_2 \qquad (4)$$

The arguments used in the case of C_2H_4 can be repeated here regarding the H recombination step in the Pt surface. The measured low temperature half-width (12 ± 2°K) and the peak temperature (296 ± °K) are used to measure the activation energy E and preexponential factor ν , as explained in the appendix. The following values of E and ν are found for this C-H bond breaking reaction:

$$E = 19.9 \pm 3.6 \text{ kcal/mol}$$

$$\nu = 10^{14.8+2.9} \text{sec}^{-1}$$

The area under peak A, according to the reaction (4) should be 17% of the total area under the H_2 TDS curve. The discrepancy between this value and our measured 26 ± 3% is due probably to the mentioned increase in the relative area of peak A as a result of small background H_2 coadsorption and also to the presence of the shoulder at 328°K that increases the relative area of the peak.

The decomposition of propylidyne to yield desorbed H_2 and CH residues may be written as

$$(C_3H_5)_{ads} \longrightarrow C_nH_1 + 2H_2 \qquad n < 3 \qquad (5)$$

Since the CH species gives three H_2 desorption peaks in the C region similar to those from C_2H_2 and C_2H_4, it seems that the same type of residues are found in that case. From the low temperature half-width of peak B (20 ± 2°K) and the peak temperature, the following values for E and ν are obtained as explained in the appendix:

$$E = 25.7 \pm 2.9 \text{ kcal/mol}$$

$$\nu = 10^{12.7 \pm 1.6} \text{ sec}^{-1}$$

As in the case of C_2H_4, the values of the activation energies for the peaks in the C region can be estimated by assuming $\nu = 10^{13} \text{sec}^{-1}$ which gives the following values of E for the 524, 637, and 712°K peaks, respectively: 32, 39, and 43 kcal/mol.

The effect of D_2 preadsorption is much the same as for the other hydrocarbons. The possibility of exchange in these experiments between the C_3H_6 molecules and the D atoms has been demonstrated. Since the maximum number of H atoms exchanged with D atoms did not exceed 3, it seems tempting to conclude that the methyl group did not participate in the exchange.

2-Butenes

Recent LEED studies in this laboratory[8] with 2-butene adsorbed on Pt(111) have also shown that here again the stable room temperature species after, adsorption of C_4H_8 on this surface is butylidyne ($\equiv C-CH_2-CH_2-CH_3$). This requires a shift of the double bond from the second to the first C atoms. Our H_2 TDS results also support this assignment in view of the similar spectra obtained with C_2H_4 and C_3H_6. The decomposition pattern of the adsorbed C_4H_8 can thus be interpreted in a similar way, with the following reactions:

$$(C_4H_8)_{ads} \longrightarrow (C_4H_7)_{ads} + 1/2\ H_2 \qquad (6)$$

$$(C_4H_7)_{ads} \longrightarrow (C_nH)_{ads} + 3H_2 \qquad n < 4 \qquad (7)$$

Reaction (6) with a C-H bond braking step as rate limiting gives rise to peak A at 294 ± 6°K and a low temperature half-width of 21 ± 3°K. With these values the following values of E and ν are obtained in the manner indicated in the appendix:

$$E = 10.7 \pm 1.8 \text{ kcal/mol}$$

$$\nu = 10^{7.8 \pm 1.5} \text{ sec}^{-1}$$

The low value of ν obtained in this case (as compared to the corresponding values for C_2H_4 and C_3H_6) is somewhat surprising if one considers the similarity of the C-H bond breaking processes involved in each case. This low value of ν could be a spurious result from the existence of two or more strongly overlapping peaks at the position of peak A in C_4H_8. This overlap would give rise to a wide peak and a consequent low value of ν . In that case, one could not use the method of the appendix to obtain E and ν . An estimate of E is possible by assuming $\nu = 10^{13} \text{sec}^{-1}$, which would give a value of E=17.7 kcal/mol, according to formula (2) of the appendix.

The area under peak A predicted by reaction (6) is 13% to be compared with our measured 24 $\pm$ 3%. The reasons for discrepancy are most probably the same as those given in the case of C_3H_6 and will not be repeated here.

The kinetic parameters for reaction (7), E and ν , can be obtained from the low temperature half-width (24 ± 3°K) and peak temperature as explained in the appendix. The results are

$$E = 16.0 \pm 2.2 \text{ kcal/mol}$$

$$\nu = 10^{9.0 \pm 1.5} \text{ sec}^{-1}$$

A similar treatment to the C region peaks which represent the dehydrogenation of the CH residues gives the following estimated values of E (assuming $\nu = 10^{13}$ sec^{-7}): 36, 39, and 43 kcal/mol for the processes fiving rise to the 583, 634, and 705°K H_2 peaks, respectively.

Partial desorption of undissociated molecules preceeds by 33°K, at the maximum rates, the decomposition reaction (6). Using the method of the appendix the kinetic parameters E and ν for the desorption process were calculated using the low temperature half-width (17 ± 3°K) of the 261°K peak. The result is

$$E = 10.5 \pm 1.7 \text{ kcal/mol}$$

$$\nu = 10^{8.7 \pm 1.2} \text{ sec}^{-1}$$

At high exposures multilayers of butene formed that desorbed with maximum rate at 150°K. Application of the same method using the measured low temperature half-width (11 ± 2°K) gives

$$E = 5.2 \pm 1.1 \text{ kcal/mol}$$

and

$$\nu = 10^{7.7 \mp 1.1} \text{sec}^{-1}$$

H-D exchange in stable alkylidyne species

We have shown in the experimental section that exchange of H and D in the ethylidyne and propylidyne species occurs readily. The process is an activated one as seen by the increase in the area under the HD TDS curves as a function of temperature. An important observation also is the invariance of the area and shape of the H_2-TDS curves after heating in vacuum the ethylidyne and propylidyne covered Pt surface (see Figs. 11 and 12). Since the temperature was the same as that in the exchange experiments, we must conclude that the intermediate species in the surface reaction must not contain a smaller number of hydrogen atoms. If hydrogen was removed from the hydrocarbon and adsorbed on the Pt surface in the exchange process, it would readily desorb and hence the area under the H_2 TDS curves after heating in vacuum would decrease. In view of these results we propose the formation of ethylidine ($=CD-CH_3$) by α incorporation of D followed by β abstraction of H according to the reactions

$$\equiv C-CH_3+D \longleftrightarrow =CD-CH_3 \qquad (8)$$

$$=CD-CH_3 \longleftrightarrow =CD-CH_2- +1/2H_2 \qquad (9)$$

$$=CD=CH_2- \longleftrightarrow \equiv C-CH_2D \qquad (10)$$

And similar reactions for the C_3H_5 propylidyne. In these reactions the alkylidine species is only an unstable intermediate that converts rapidly into the stable alkylidyne through dehydrogeantion.

C_2H_4 adsorption on C-covered Pt(111)

The similarity of the H_2 TDS curves from C_2H_4 adsorbed on clean and C-covered Pt(111), particularly in the region of peak B, indicates that the

presence of C does not prevent the formation of ethylidyne on the Pt surface. This results indicate that even with a total C coverage of (1) as judged from AES, the C layer does not uniformly cover the Pt surface. Clean islands of Pt atoms are present even in highly C-covered surfaces. The decrease in the relative area of peak A might indicate that the H atoms resulting from reaction (1) may attach to C atoms and desorb at higher temperatures than that of peak A.

Conclusion

1. The olefins C_2-C_4 adsorb readily on the Pt(111) surface without decomposition in the range of 110°K to 260°K.

2. Desorption of the undissociated olefins preceeds the dehydrogenation reactions by 12, 16, and 33°K at the maximum rates for C_2H_4, C_3H_6, and C_4H_8, respectively. Activation energies E and preexponential factors ν were calculated from the observed low temperature half-widths and peak temperatures in each case. The values of these parameters are summarized in Table II.

3. Multilayer formation is observed at 110°K for high exposures of C_3H_6 and C_4H_8. They desorb at temperatures of 139 and 150°K, respectively.

4. After partial desorption, C_2H_4, C_3H_6, and C_4H_8 decompose to yield desorbed hydrogen in three main reaction steps. In the first step, one hydrogen atom is lost per molecule that results in the formation of alkylidyne species on the Pt(111) surface. Kinetic parameters E and ν were calculated for these reactions which are summarized in Table III. The second dehydrogenation step corresponds to the decomposition of the alkilidyne species and gives rise to a large H_2 desorption peak at temperatures of 492, 436, and 381°K for

C_2H_4, C_3H_6, and C_4H_8, respectively. The activation energies and preexponential factors, E and ν , are also summarized in Table III. The third dehydrogenation step involves the complete dehydrogenation of CH residues and gives rise to three H_2 desorption peaks similar for all the hydrocarbons studied. Only carbon residues are left on the surface after these reactions.

5. The dehydrogenation of C_2H_2 is similar to that of C_2H_4 although different species are involved in the two cases. This species is probably vinilidyne in the case of C_2H_2 when heated in the absence of hydrogen.

6. Preadsorption of D_2 causes a broadening of the desorption spectrum of undissociated olefins extending to the lowest temperatures. In these coadsorption experiments, D_2 desorbs at substantially lower temperatures than on the clean Pt(111) surface at the same coverage. These results indicate the existence of repulsive interactions between the adsorbed D atoms and the hydrocarbons molecules.

7. Incorporation of D into the undissociated hydrocarbon molecule by H-D exchange occurs also at low temperatures. In the case of C_3H_6, exchange of up to 3 hydrogen atoms has been observed.

8. Exchange of H-D in the stable alkylidyne species occurs readily. The extent of this exchange increases with increasing temperatues and D_2 exposure, indicating that the process is activated.

9. In a Pt(111) surface covered with monolayer amounts of carbon, adsorption of C_2H_4 still produces the stable ethylidyne species, indicating the nonuniformity of the carbon layer.

TABLE I: Desorption Peak Temperatures

Adsorbate on Pt(111)	Undissociated Molecules: Multilayer desorption peak (°K)	Undissociated Molecules: Monolayer desorption peak (°K)	H_2 Desorption Peaks: Peak A °k	H_2 Desorption Peaks: Peak B °K	H_2 Desorption Peaks: Peak C °K
C_2H_2	—	—	—	492 ± 5	~ 550,639+4,713+4
C_2H_4	—	285 ± 4	297 ± 4	492 ± 6	~ 550,641+4,704+4
C_3H_6	139 ± 5	280 ± 5	296 ± 4	436 ± 5	~ 524+4,637+4,712+4
C_4H_8	150 ± 8	261 ± 6	294 ± 5	381 ± 5	~ 583,634+6,705+4

TABLE II. Activation energies E and preexponential factors ν for desorption of undissociated hydrocarbon molecules on Pt(111)

Absorbate	Multilayer		Monolayer	
	E(kcal/mol)	ν (sec^{-1})	E(kcal/mol)	ν (sec^{-1})
C_2H_4	—		12.0 ± 3.2	$10^{9.2 \pm 2.8}$
C_3H_6	~ 8	~ 10^{13}	12.2 ± 1.7	$10^{9.4 \pm 1.5}$
C_4H_8	5.2 ± 1.1	$10^{7.7+1.8}$	10.5 ± 1.7	$10^{8.7+1.2}$

TABLE III. Activation energies, E, and preexponential factors, ν , for the dehydrogenation reactions of unsaturated hydrocarbons on Pt(111)

Reaction	H_2-TDS peaks	E (kcal/mol)	ν (sec^{-1})
ACETYLENE:			
$(C_2H_2)_{ads} \rightarrow (C_nH)_{ads} + 1/2H_2$	B	20.6 ± 2.2	$10^{8.8 \pm 1.2}$
$(C_nH)_{ads} \rightarrow (C_n)_{ads} + 1/2H_2$	C	~ 33	~ 10^{13}
	C	~ 39	~ 10^{13}
	C	~ 44	~ 10^{13}
ETHYLENE:			
$(C_2H_4)_{ads} \rightarrow (C_2H_3)_{ads} + 1/2H_2$	A	18.4 ± 1.7	$10^{13.6 \pm 1.4}$
$(C_2H_3)_{ads} \rightarrow (C_nH)_{ads} + H_2$	B	22.0 ± 4.1	$10^{9.5 \pm 2.0}$
$(C_nH)_{ads} \rightarrow nC_{ads} + 1/2H_2$	C	± 33	~ 10^{13}
	C	∓ 39	~ 10^{13}
	C	± 43	~ 10^{13}

Continued

PROPYLENE:

$(C_3H_6)_{ads} \rightarrow (C_3H_5)_{ads} + 1/2H_2$	A	19.9 ± 3.6	$10^{14.8 \pm 2.9}$
$(C_3H_5)_{ads} \rightarrow (C_nH)_{ads} + 2H_2$	B	25.7 ± 2.9	$10^{12.7 \pm 1.6}$
$(C_nH)_{ads} \rightarrow (nC)_{ads} + 1/2H_2$	C	~ 32	~ 10^{13}
	C	~ 39	~ 10^{13}
	C	~ 43	~ 10^{13}

2-BUTENES:

$(C_4H_8)_{ads} \rightarrow (C_4H_7)_{ads} + 1/2H_2$	A	10.7 ± 1.8	$10^{7.8 \pm 1.5}$
$(C_4H_7)_{ads} \rightarrow (C_nH)_{ads} + 3H_2$	B	16.0 ± 2.2	$10^{9.0 \pm 1.5}$
$(C_nH)_{ads} \rightarrow nC_{ads} + 1/2H_2$	C	~ 36	~ 10^{13}
	C	~ 39	~ 10^{13}
	C	~ 43	± 10^{13}

Appendix

We have used the classical treatment of thermal desorption[13-15] to obtain the kinetic parameters E (activation energy) and ν (preexponential factor) of the various desorption and decomposition reactions studied in this paper. Under the conditions of high pumping speed and low heating rates used here,[12] the increase in the partial pressure of the desorbing product is proportional to the reaction rate. For our first order reactions then,

$$\Delta P = -C\frac{dn}{dt} = C\,\nu\,n\,\exp\left(\frac{-E}{RT}\right)$$

where C is a constant that contains the pumping speed, volume of the chamber, and area of the crystal; n is the concentration of surface species, and ν and E the preexponential and activation energies, respectively, for the rate limiting step. This equation can be solved to yield,

$$\Delta P = C n_o\,\nu\,\exp\left(-\frac{E}{RT} - \frac{\nu}{\beta}\int_{T_o}^{T}\exp\left(-\frac{E}{RT'}\right)dT'\right) \qquad (1)$$

with n_o being the initial surface concentration of adsorbed hydrocarbons and T_o and β the initial temperature and heating rate, respectively. From this equation and the condition of peak maximum T_m,

$$\frac{E}{RT_m^2} = \frac{\nu}{\beta}\exp\left(-\frac{E}{RT_m}\right) \qquad (2)$$

The values of E and ν can be obtained by fitting the width calculated from (1) by numerical integration to the experimental peak widths. The shape of the desorption peaks predicted by (1) and observed experimentally, is asymmetric for the first order processes with the low temperature tail extending in a

wider temperatures range than the high temperature tail. We have observed always a higher sensitivity for broadening of the high temperature tail. This broadening arises from inhomogenous temperature distribution across the crystal as well as from surface heterogeneities that might give rise to a distribution of binding energies of the adsorbed molecule. For that reason we have taken as a criterium for best fit the condition of equality between the calculated and experimental widths, w, measured from the low temperature tail at half height, T_1, to the peak temperature T_m ($w=T_m-T_1$). The desorption curves calculated with the E and ν parameters determined in that way show a good fit with the experimental ones.[17] The calculated high temperatue tail falls somewhat more sharply than the experimental one.

The errors in the calculated values of E and ν can be obtained from the measured standard deviations in T_m and w by use of the formulae:

$$\frac{\partial \ln \nu}{\partial \ln w} = \frac{\partial \ln E}{\partial \ln w} \left(1+\frac{E}{RT_m}\right)$$

and

$$\frac{\partial \ln \nu}{\partial \ln T_m} = \frac{\partial \ln E}{\partial \ln T_m} \left(1+\frac{E}{RT_m}\right)$$

where $\frac{\partial \ln E}{\partial \ln T_m}$ and $\frac{\partial \ln E}{\partial \ln w}$ are numbers of the order of unity (<1).

These formulae can be deduced from (1) and (2) and the definition of T_1 by differentiation. They are expressed in a convenient form to allow a simple correlation between the measured percentage errors of T_m and w and the corresponding errors in E and ν.

Finally, we should point out that an important requirement in this

width of the desorption peaks. This width plays a decisive role in the determination of E and ν values in this method in such a way that variations in w that may arise from unwanted broadening or peak overlapping can result in important variations in E and ν . For these reasons, when the absence of overlap could not be avoided, we used the simple approximate method of assuming a $10^{13}sec^{-1}$ value for ν and using formula (2) to estimate E.

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Figure Captions

Fig.1 H_2-TDS curves corresponding to the decomposition of C_2H_4, C_3H_6, and C_4H_8 adsorbed on the Pt(111) surface at 110°K. In each case, the exposure was ~ 0.5 L (1 L=10^{-6} torr x sec). Heating rate 10°K sec^{-1}.

Fig.2 TDS curves corresponding to various exposures of Pt(111) to C_2H_4. The continuous trace corresponds to the measured partial pressure of H_2 resulting from the decomposition of C_2H_4. Dashed lines correspond to the desorption of undissociated molecules (m/e=27): (a) 0.3 L exposure; (b) 0.2 L exposure; (c) 6 L D_2 at 110°K + 0.2 L C_2H_4. In the insert is plotted the area under the H_2-TDS curves versus exposure. Heating rate 10°K sec^{-1}.

Fig.3 Decomposition TDS curves from C_2H_4 with and without D_2 preadsorption. The top curve corresponds to adsorption of D_2 alone at 110°K and is included for comparison. Heating rate 10°K sec^{-1}.

Fig.4 H_2-TDS curves form the decomposition of C_2H_2 (upper curve) and C_2H_4 (lower curve). The two spectra are very similar above 300°K. Peak A (297°K) is absent in C_2H_2. The small peak above 200°K in C_2H_2 is due to adsorbed background H_2. Heating rate 10°K sec^{-1}.

Fig.5 H_2-, HD-, and D_2-TDS curves from a Pt(111) surface precovered wth 6 L of D_2 and subsequently exposed to C_2H_2 at 110°K. Very limited exchange occurs, as shown by the small peak of the HD-TDS curve at about 500°K. The H_2 and HD peaks below 300°K in the three upper curves are due to adsorbed background hydrogen.

Fig.6 TDS curves from Pt(111) exposed to 0.5 L of C_3H_6 at 110°K. The continuous line is due to H_2-decomposition from the adsorbed propylene. Dashed line corresponds to desorption of undissociated C_3H_6 (m/e=42). Heating rate 10°K sec^{-1}.

Fig.7 TDS curves of undissociated C_3H_6 after adsorption on Pt(111) at 110°K for various exposures fo the hydrocarbon, (a) clean surface, (b) Pt surface precovered wtih 12 L of D_2.

Fig.8 (a) H_2-, HD-, and D_2-TDS curves from a Pt(111) surface exposed to 12 L of D_2 at 110°K followed by 0.1 L of C_3H_6; (b) TDS curves from undissociated C_3H_6 in a surface precovered with 12 L of D_2 and then exposed to 0.5 L of C_3H_6. The mass spectrometer was tuned successively to m/e=42, 43, 44, and 46. The intensity of the various peaks in the gas phase C_3H_6 mass spectrum is also shown for comparison.

Fig.9 TDS curves from C_4H_8 adsorbed on Pt(111) after 0.3 L exposure at 110°K. Curve A, H_2-TDS from the dissociation of C_4H_8 adsorbed on the clean Pt surface. Curves B, H_2, HD, and D_2 after C_4H_8 adsorption on a Pt surface preexposed to 6 L of D_2 at 110°K. Dashed curve corresponds to the desorption of undissociated C_4H_8 molecules (m/e=56).

Fig.10 TDS curves from undissociated C_4H_8 molecules adsorbed on a Pt(111) surface at 110°K. (a) clean Pt surface at various C_4H_8 exposures, (b) Pt surface preexposed to various amounts of D_2 followed by 0.5 L exposure to C_4H_8.

Fig.11 (a) H_2-, HD-, and D_2-TDS from the decomposition of the ethylidyne surface species. After 0.1 L exposure at 110°K, the H_2-TDS curve on the top is obtained. The second curve from the top corresponds to the same exposure followed by 60 sec heating at 400°K in vacuum. The three lower curves are the result of exposing the surface species at 400°K to 12 L of D_2.

(b) Similar experiment with C_2H_4. The D_2 exposure is now 30 L. The peaks observed below 400°K are due to background adsorption of H_2 and unreacted D_2.

Fig.12 H_2- and HD-TDS curves from C_3H_6 adsorbed on Pt(111) at 110°K. Curve a corresponds to adsorption of 0.3 L of C_3H_6 on the clean Pt surface. Curve b coresponds to the same exposure of C_3H_6 after heating the crystal to 363°K in vacuum for 2 min. Curve c is the HD-TDS curve after exposing the same surface species to 2×10^{-7} torr of D_2 for 2 min. at 363°K.

Fig.13 (a) H_2-TDS curve from the decomposition of C_2H_4 adsorbed on the clean Pt(111) surface (top curve). The dashed curve is the result of adsorption of residual background hydrocarbons while the crystal temperature was above 300°K. Lower curve corresponds to the adsorption of C_2H_4 on a C-covered Pt surface with a coverage of ~ 1.

(b) Intensity of the H_2-TDS peaks A and B as a function of C/Pt(237) Auger peak-to-peak ratio. θ_c=1 corresponds to a C/Pt(237) ratio of approximately 2.

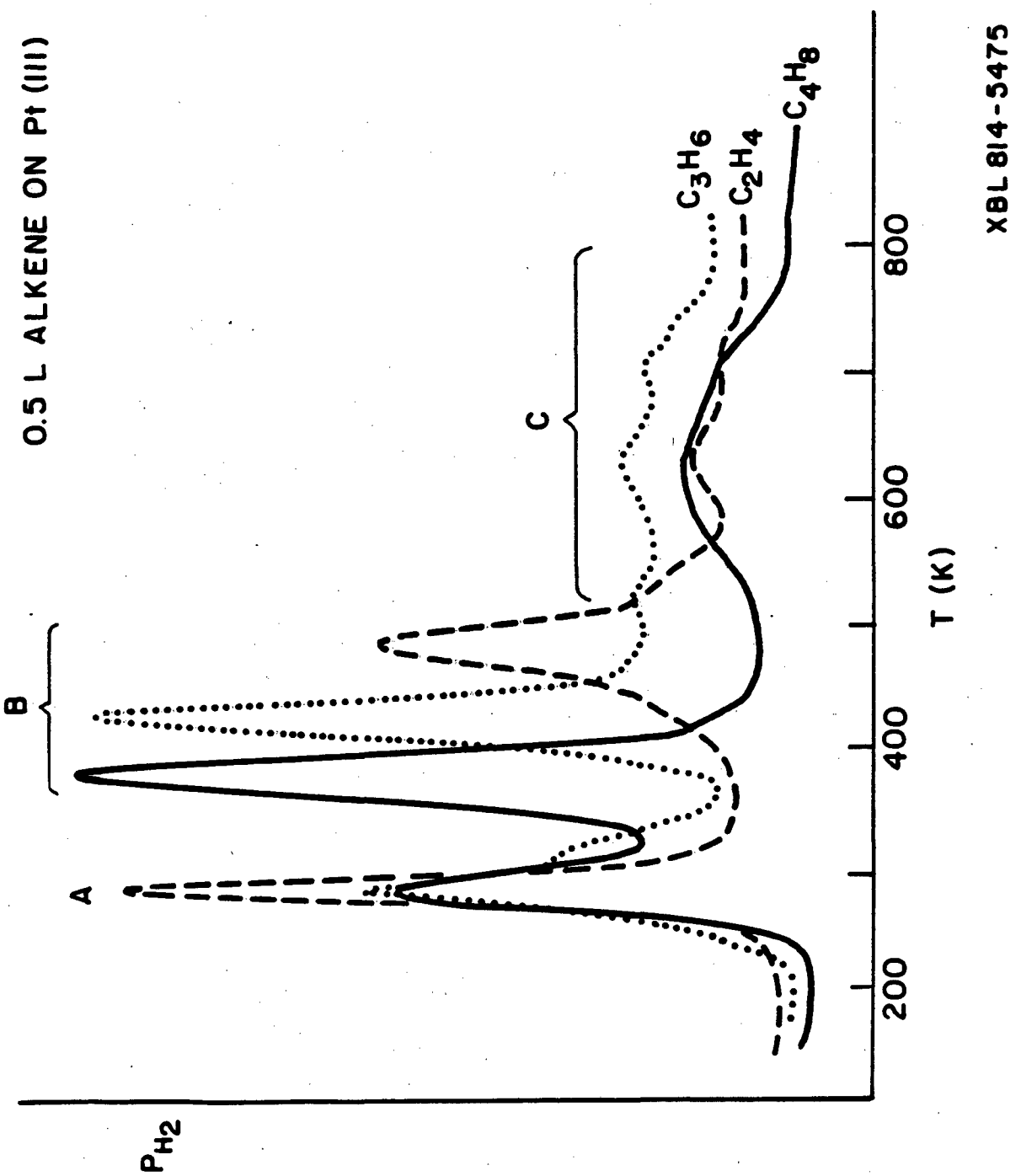
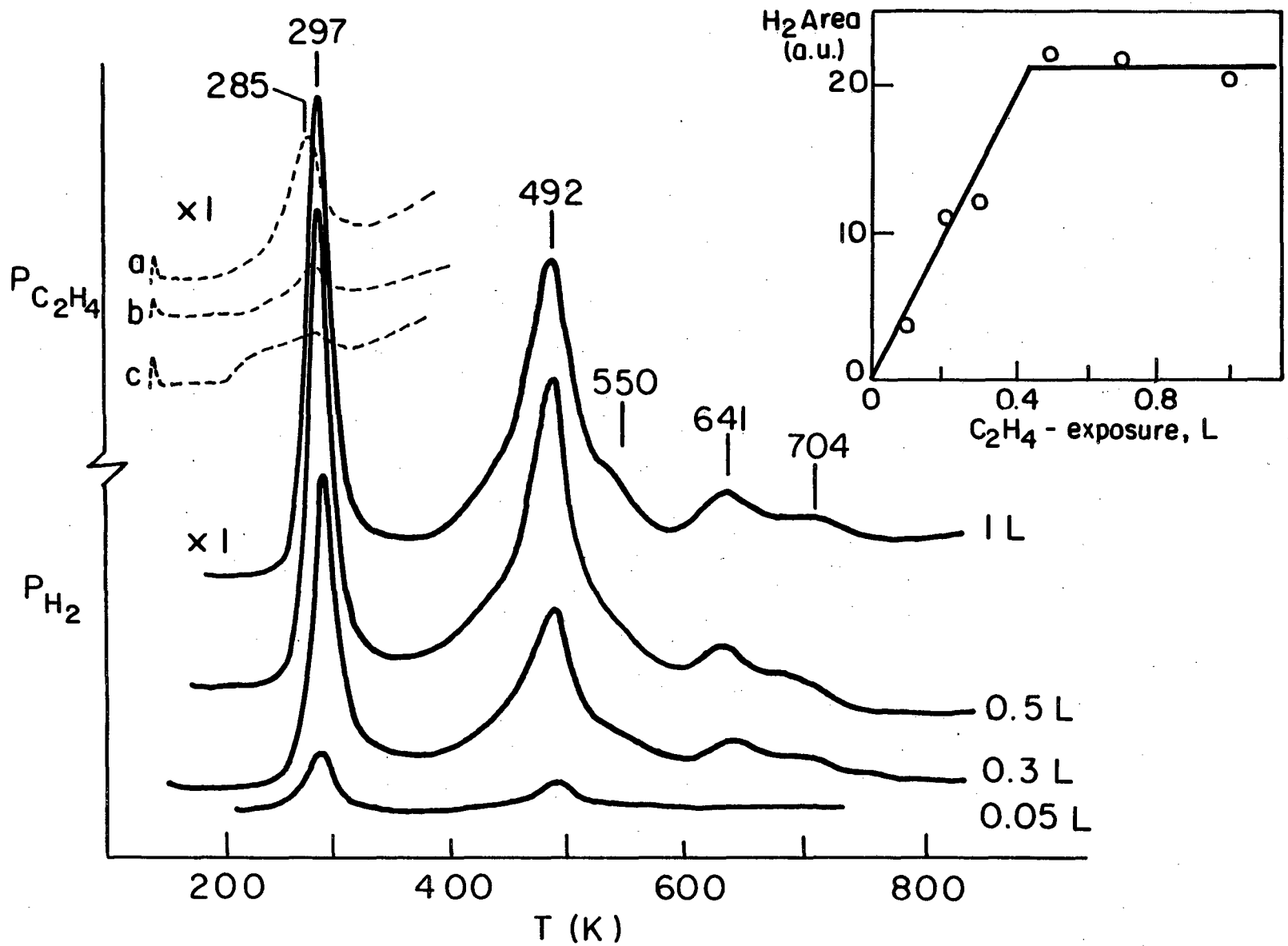
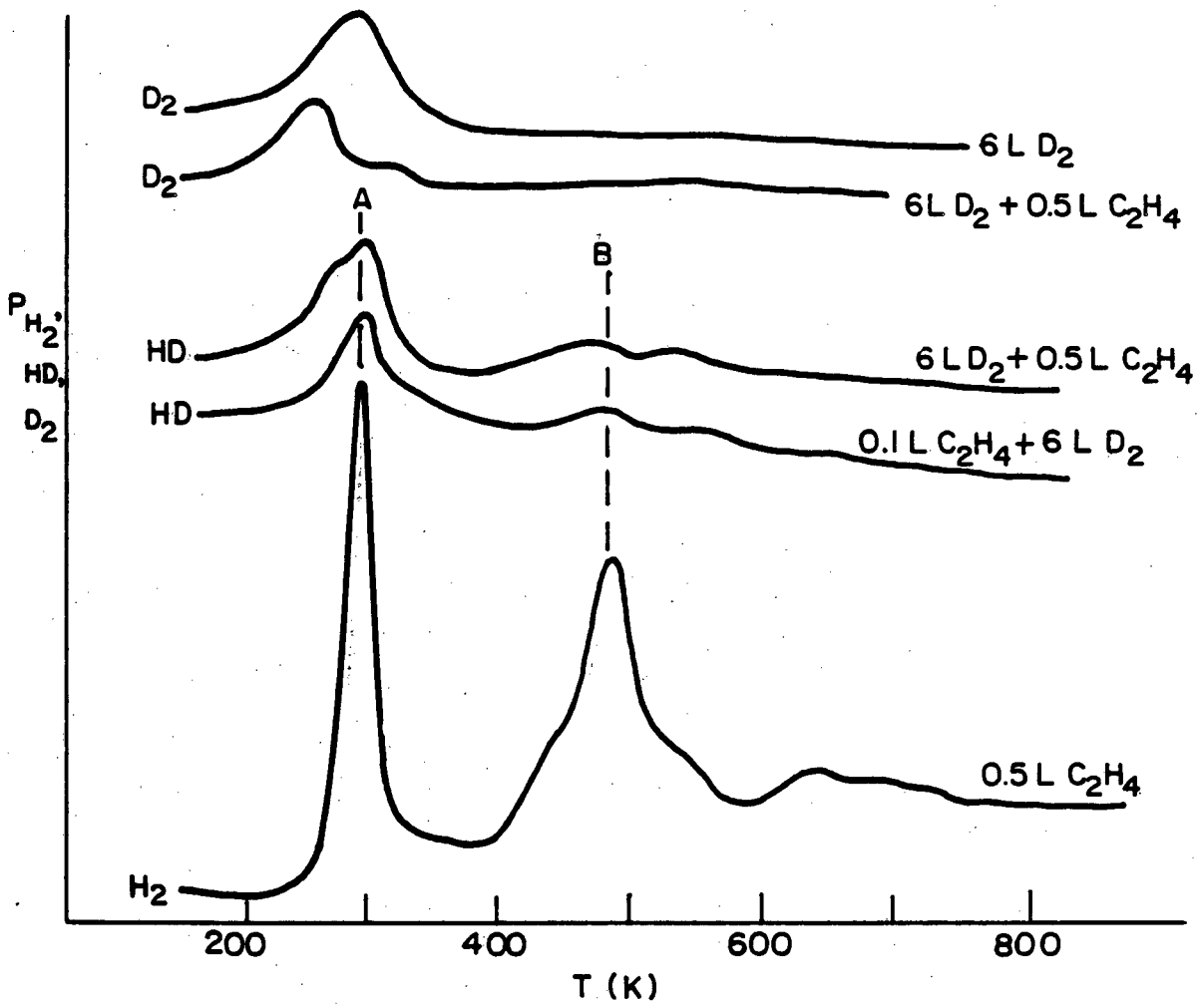

0.5 L ALKENE ON Pt (111)
A
B
C
C_3H_6
C_2H_4
C_4H_8
P_{H_2}
200
400
600
800
T (K)
XBL 814-5475

Fig.1



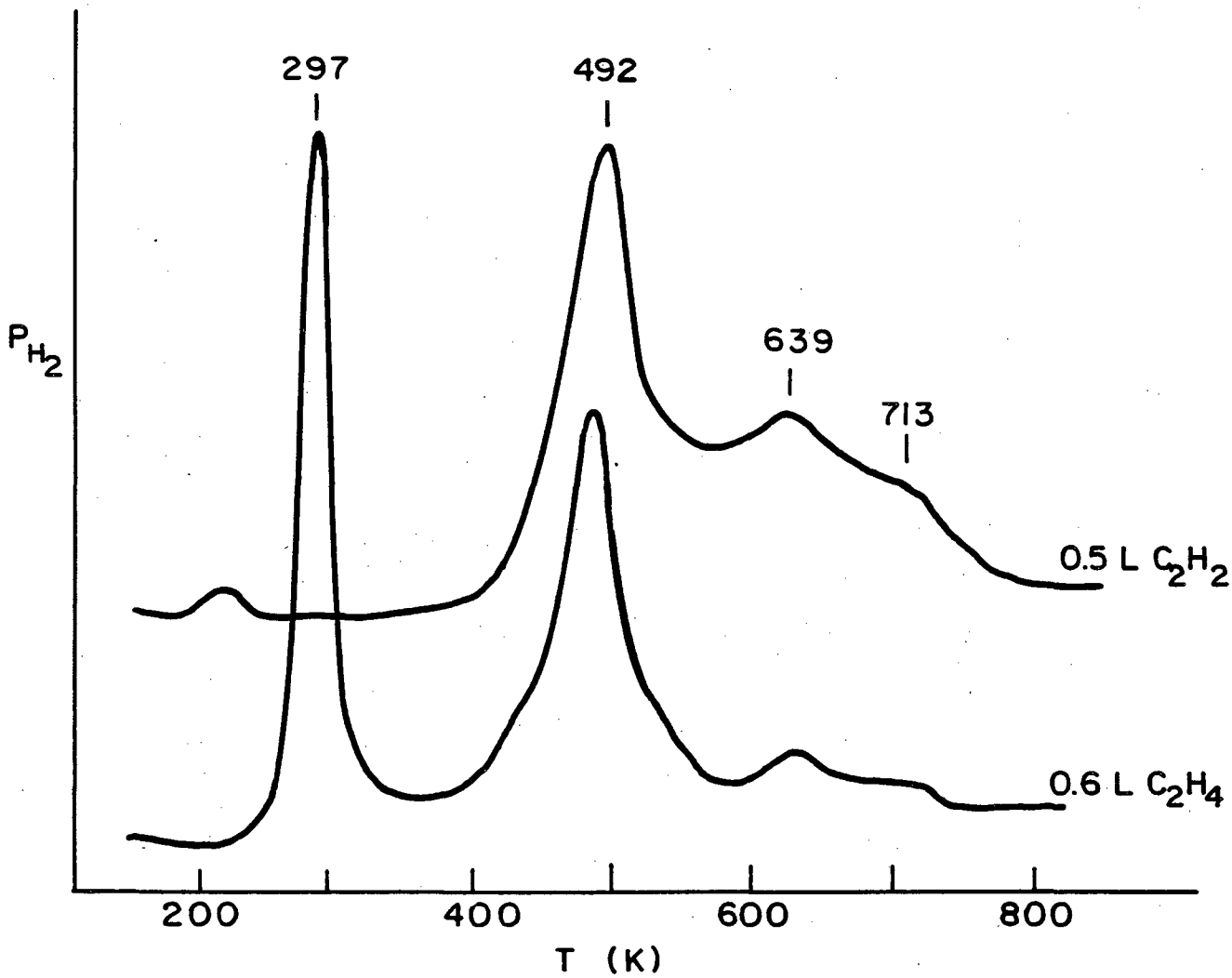
XBL 814-5476

Fig.2



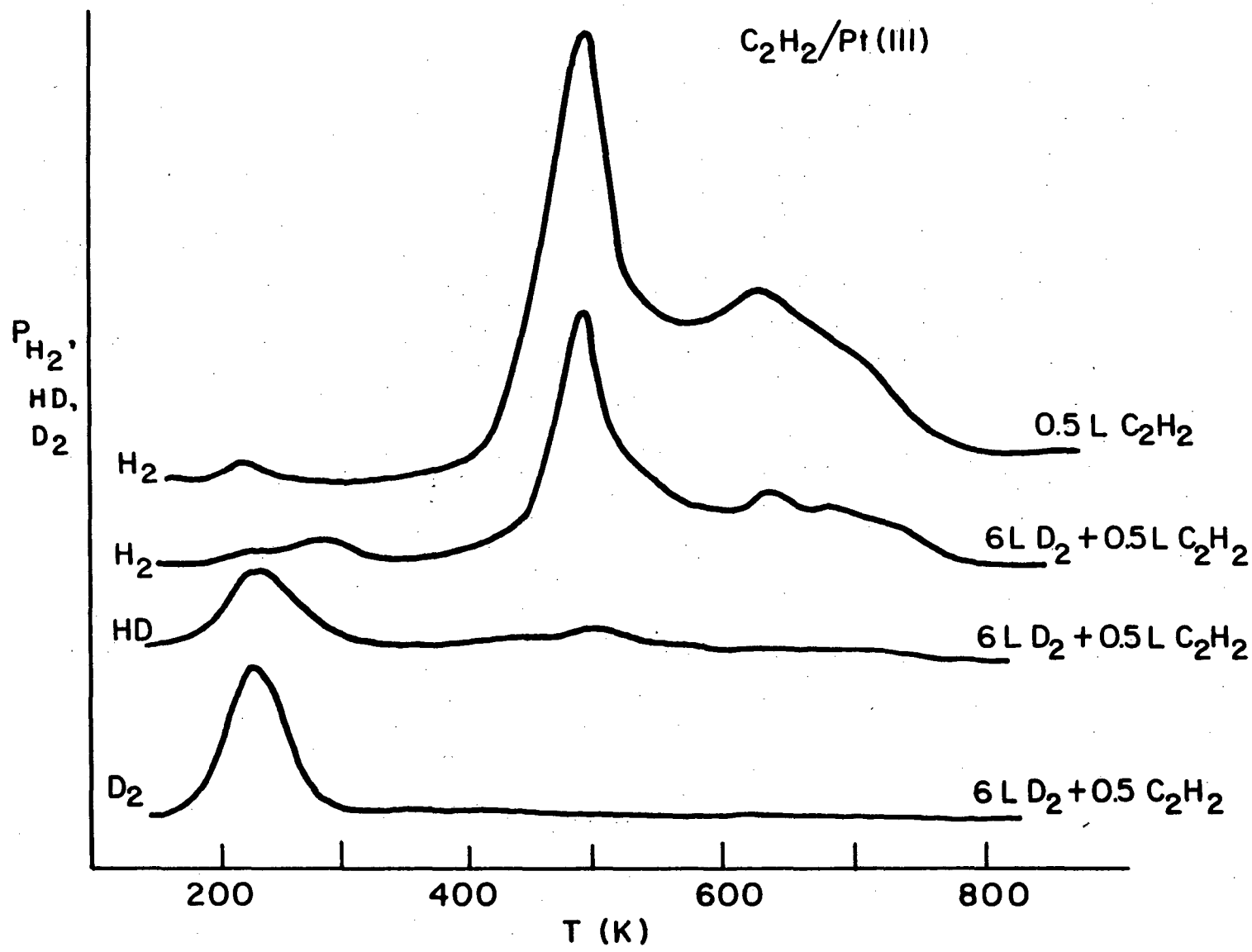
XBL 814 - 5477

Fig.3



XBL814-5478

Fig.4



X BL 814-5479

Fig. 5

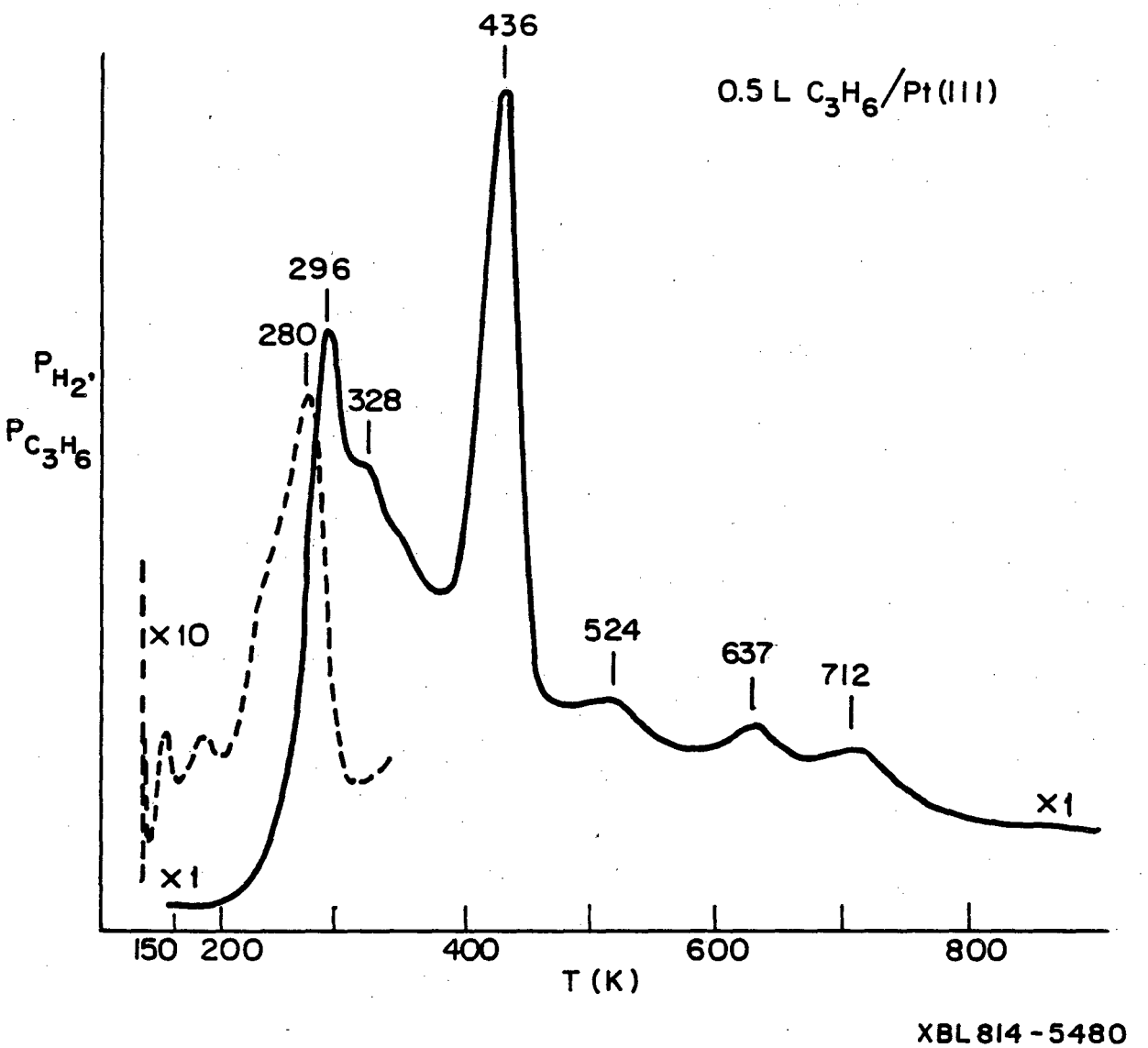

436
0.5 L C_3H_6/Pt(111)
296
280
328
P_{H_2},
$P_{C_3H_6}$
×10
524
637
712
×1
×1
150
200
400
600
800
T (K)
XBL 814-5480

Fig.6

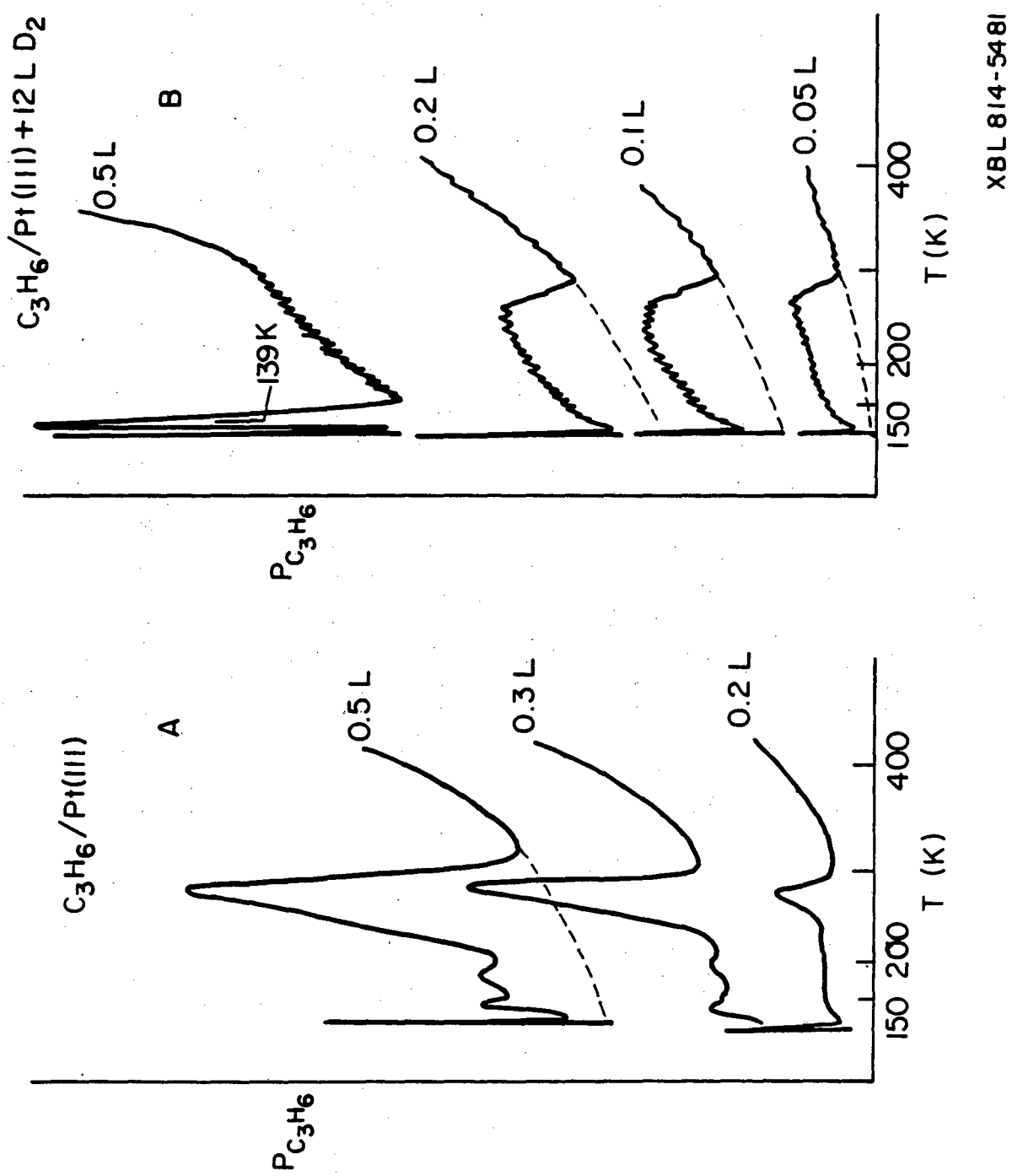

C_3H_6/Pt(111)+12 L D_2
B
0.5 L
139 K
0.2 L
0.1 L
0.05 L
$P_{C_3H_6}$
150
200
400
T (K)
XBL 814-5481
C_3H_6/Pt(111)
A
0.5 L
0.3 L
0.2 L
$P_{C_3H_6}$
150
200
400
T (K)

Fig.7

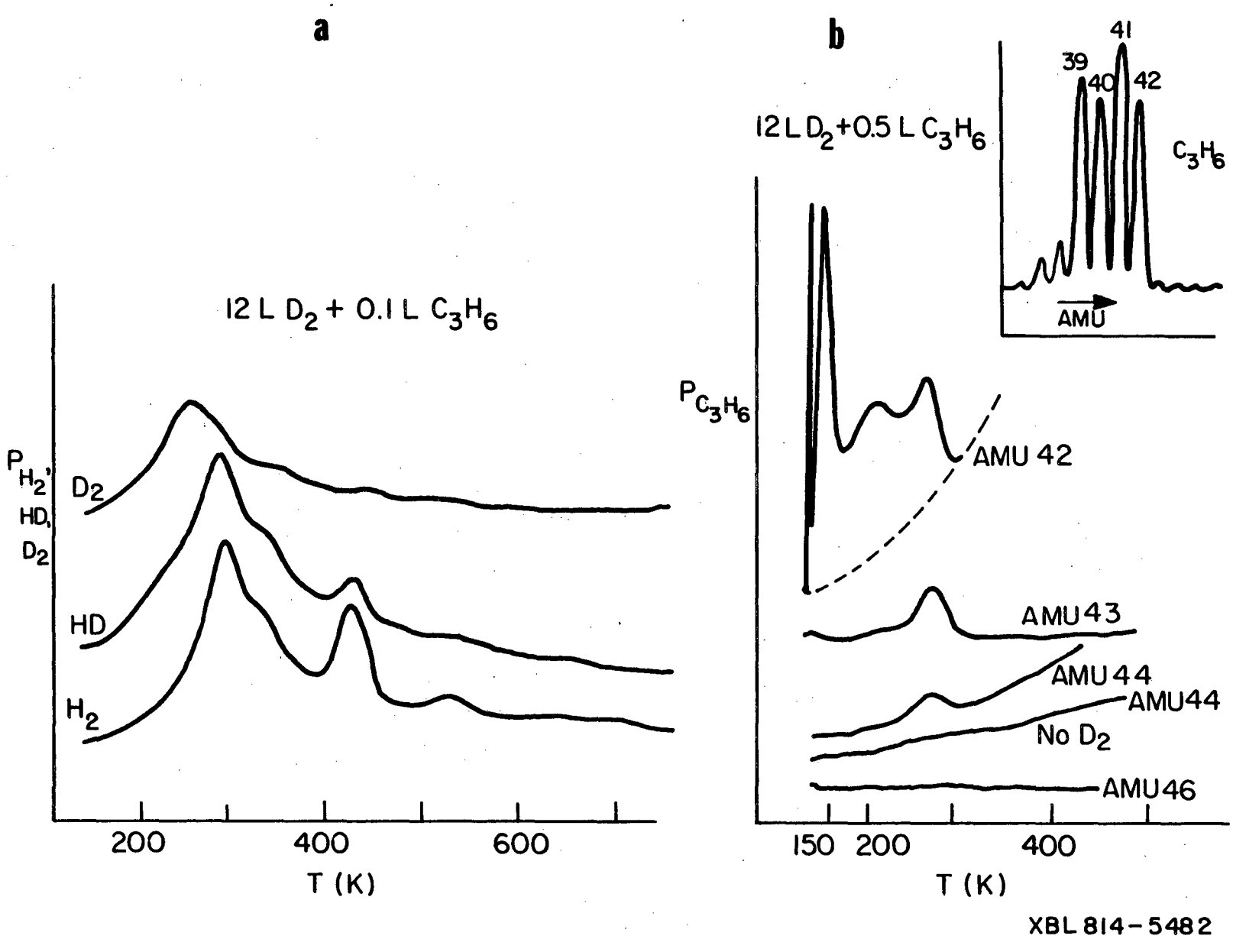
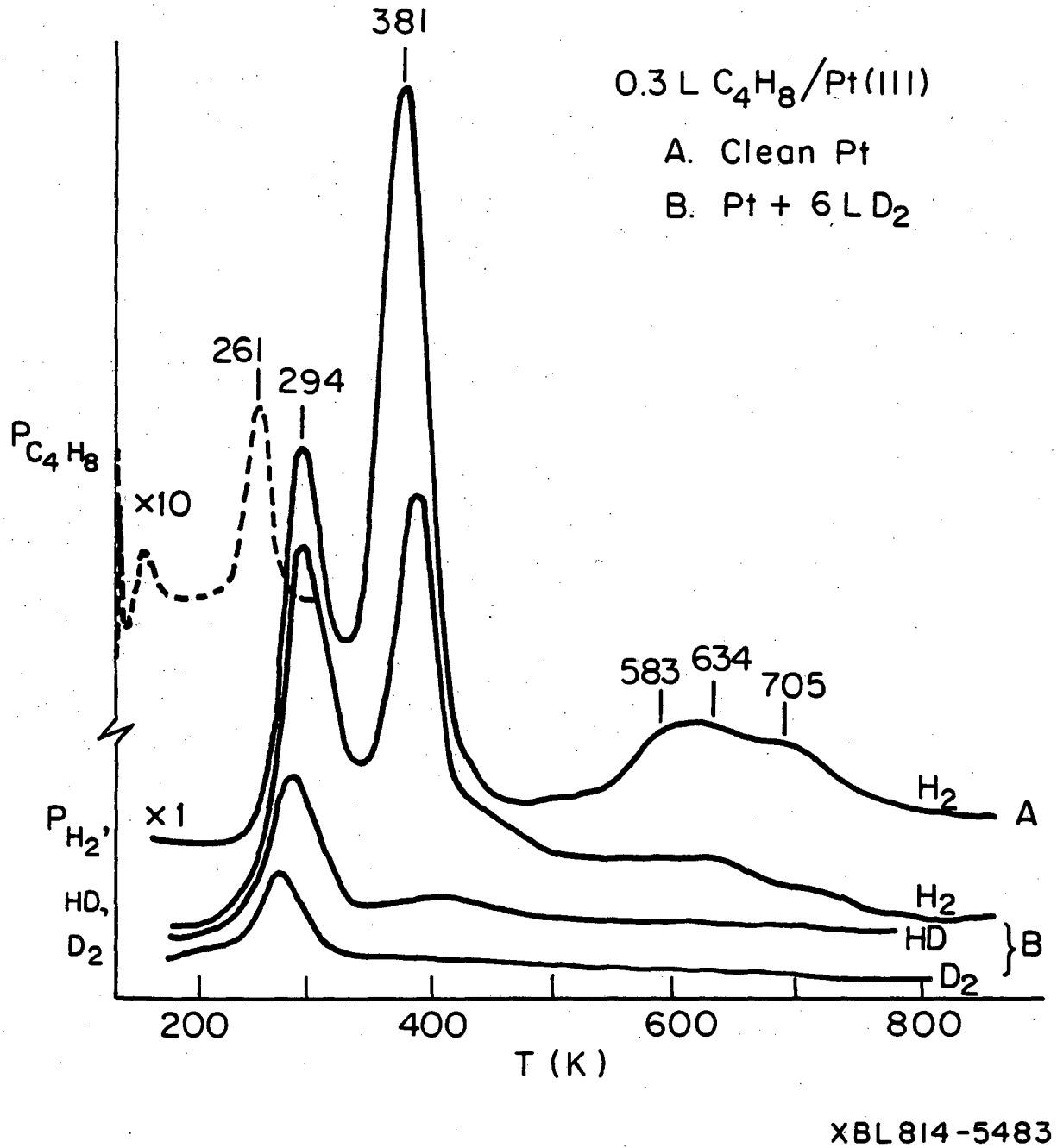

a
12 L D2 + 0.1 L C3H6
PH2, HD, D2
D2
HD
H2
200
400
600
T (K)
b
12 L D2+0.5 L C3H6
39
40
41
42
C3H6
AMU
PC3H6
AMU 42
AMU43
AMU44
AMU44
No D2
AMU46
150
200
400
T (K)
XBL 814-5482

Fig.8



XBL814-5483

Fig.9

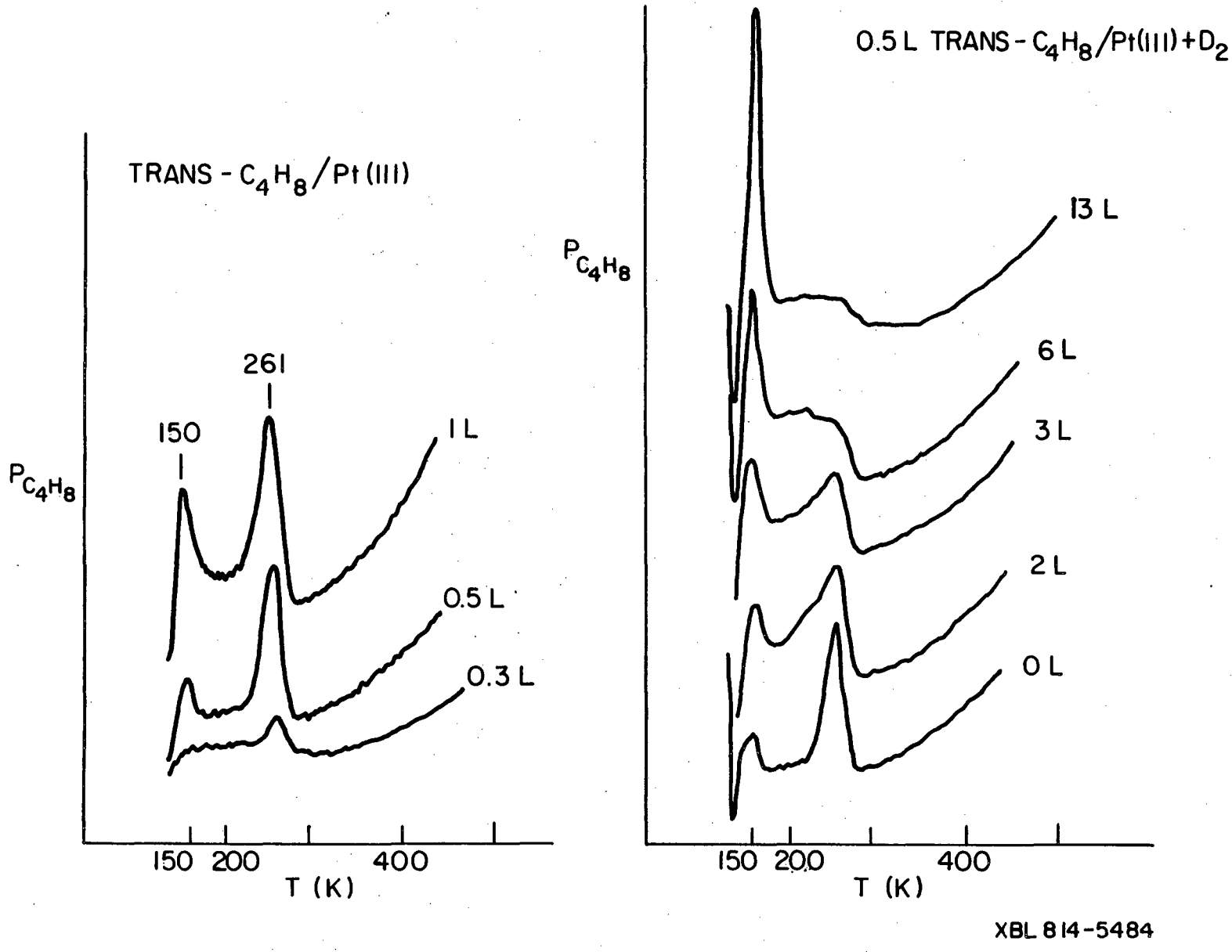

TRANS - C_4H_8/Pt(111)
$P_{C_4H_8}$
150
261
1 L
0.5 L
0.3 L
150 200 400
T (K)
0.5 L TRANS - C_4H_8/Pt(111)+D_2
$P_{C_4H_8}$
13 L
6 L
3 L
2 L
0 L
150 200 400
T (K)
XBL 814-5484

Fig.10

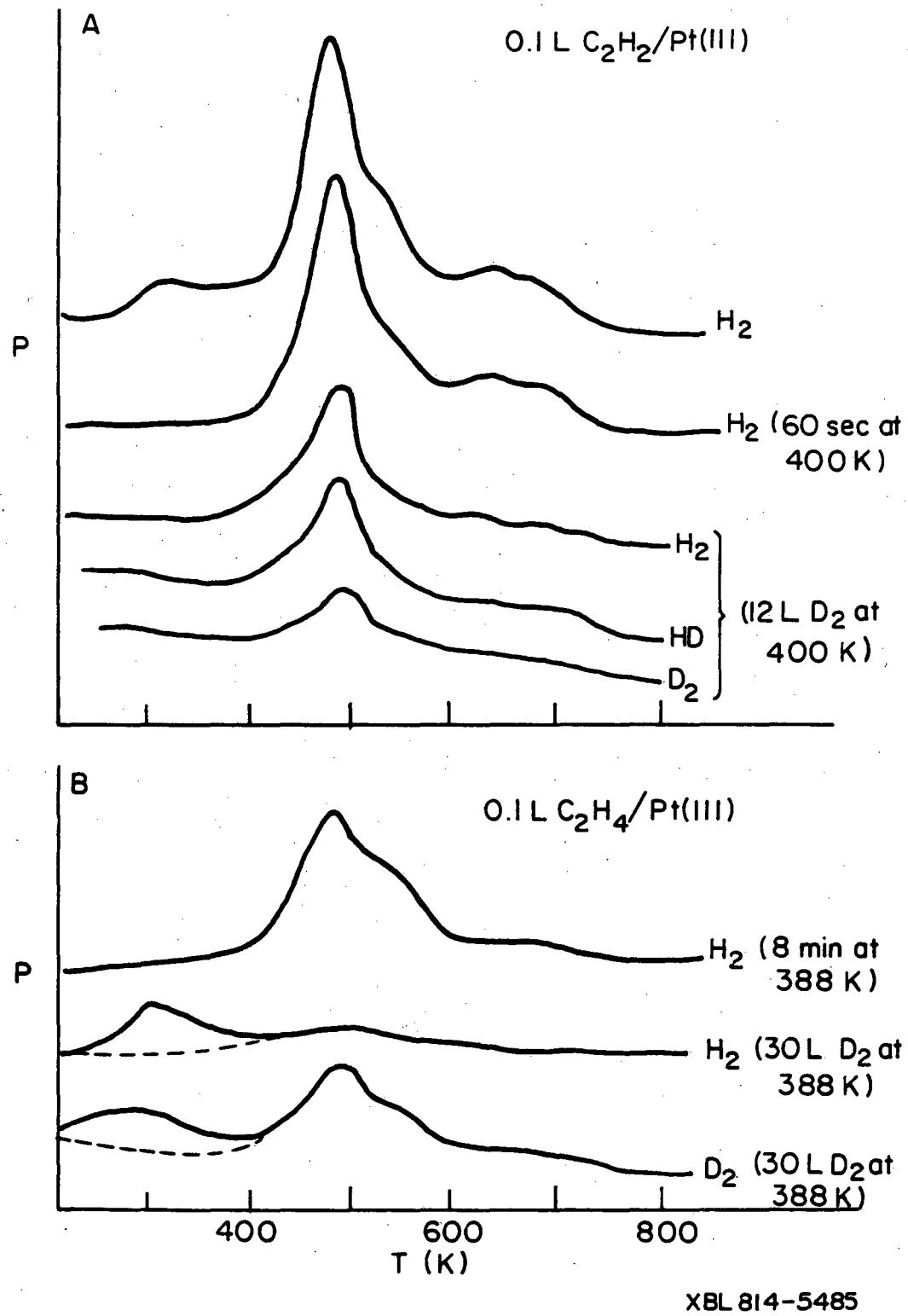

A
0.1 L C_2H_2/Pt(111)
P
H_2
H_2 (60 sec at 400 K)
H_2
HD
D_2
(12 L D_2 at 400 K)
B
0.1 L C_2H_4/Pt(111)
P
H_2 (8 min at 388 K)
H_2 (30 L D_2 at 388 K)
D_2 (30 L D_2 at 388 K)
400
600
800
T (K)
XBL 814-5485

Fig.11

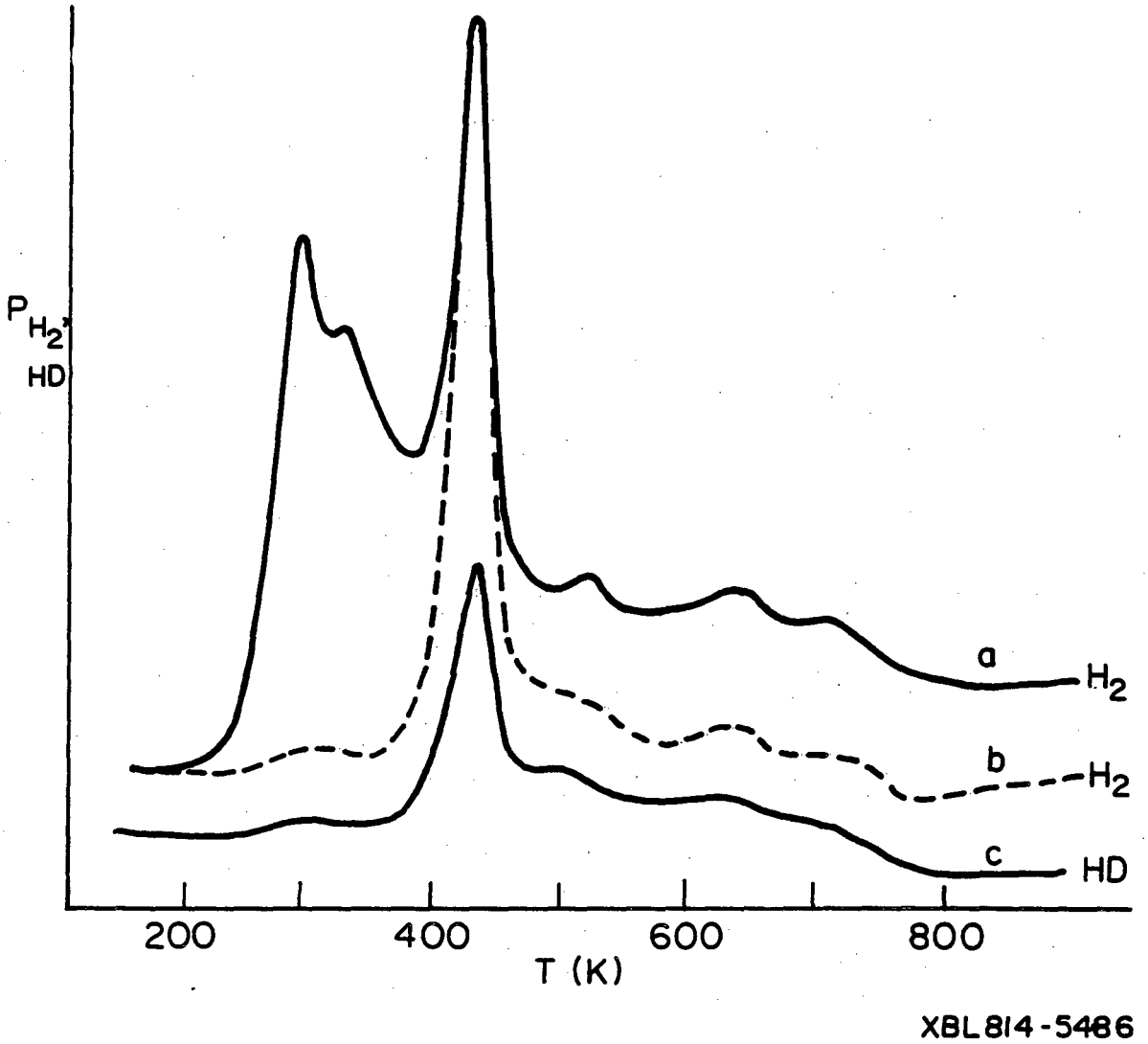


Fig.12

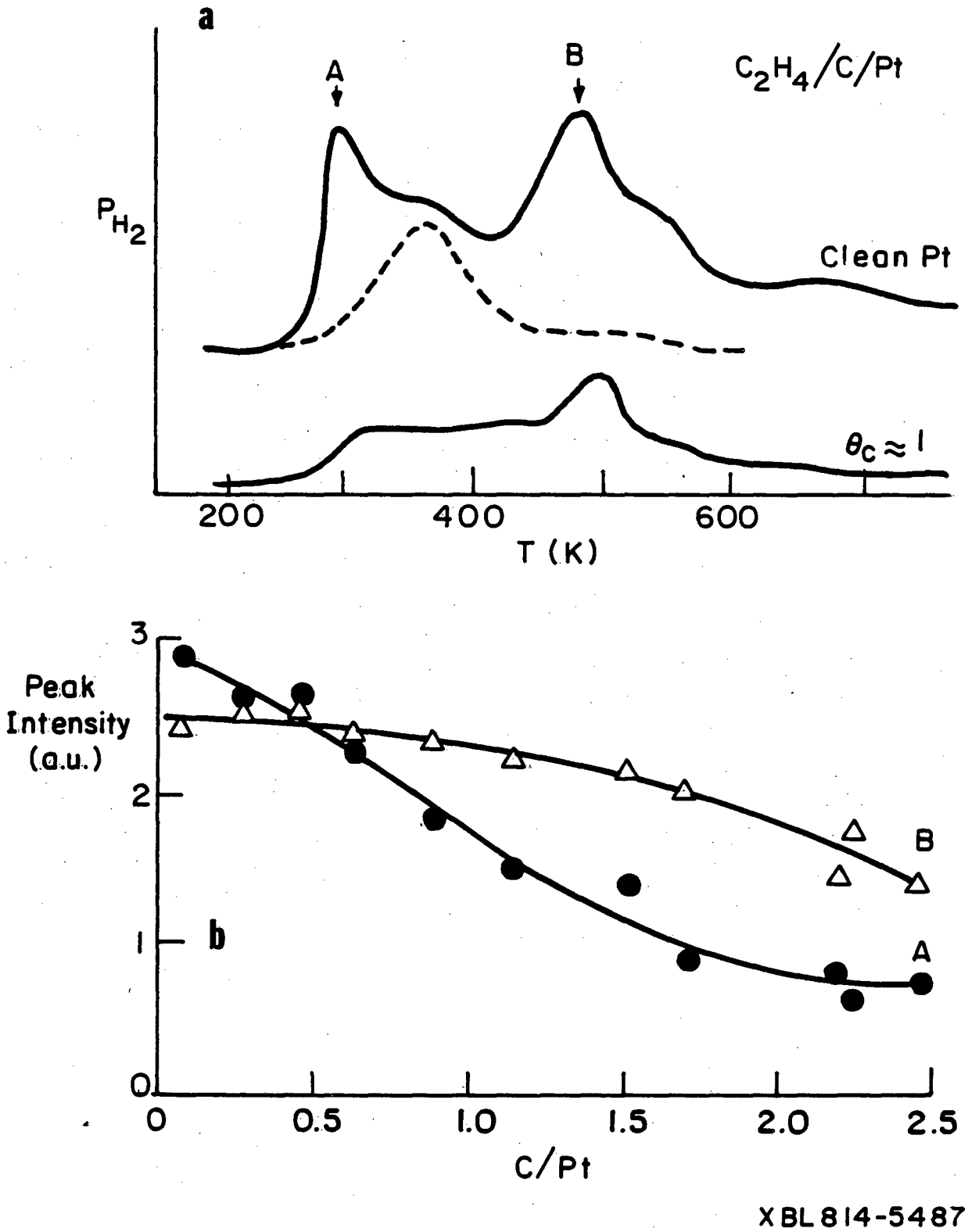

a
A
B
$C_2H_4/C/Pt$
P_{H_2}
Clean Pt
$\theta_C \approx 1$
200
400
600
T (K)
3
Peak
Intensity
(a.u.)
2
1
0
b
B
A
0
0.5
1.0
1.5
2.0
2.5
C/Pt
XBL 814-5487

Fig.13

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