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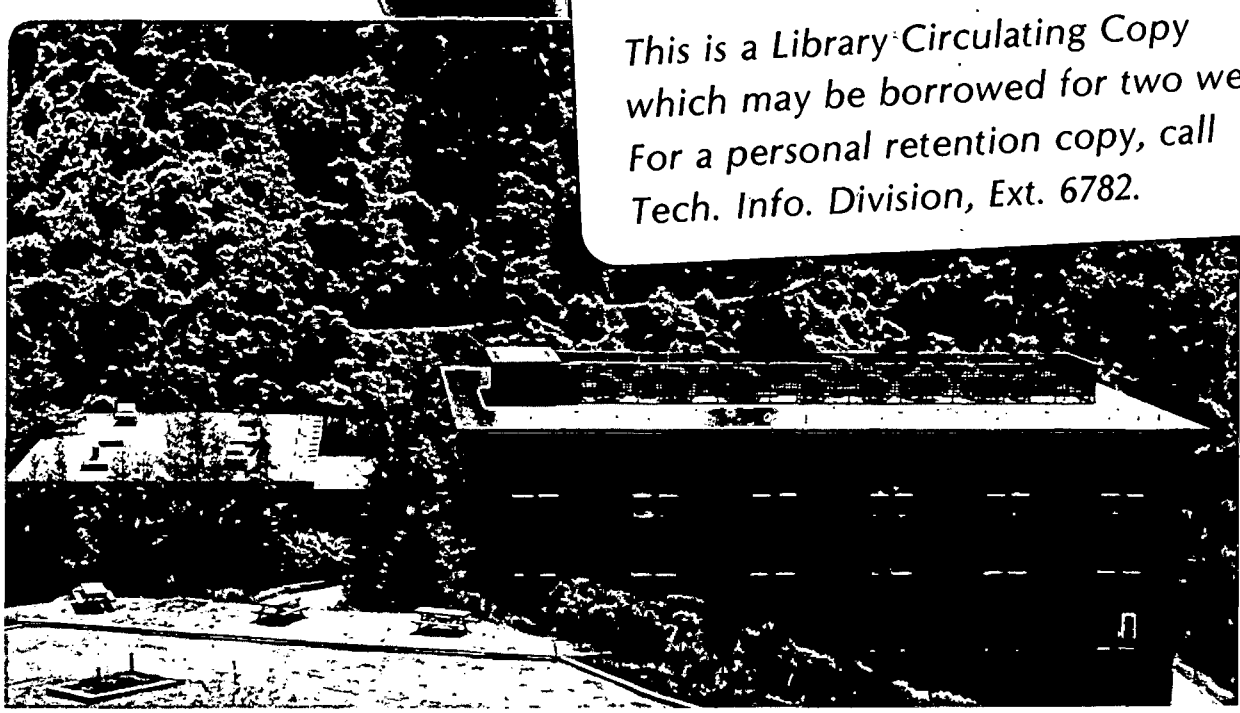

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ENERGETICS AND REVERSIBILITY OF HYDROCARBON SEQUENTIAL DEHYDROGENATION ON PLATINUM SINGLE CRYSTAL SURFACES: THERMAL DESORPTION AND CARBON-14 RADIOTRACER STUDIES

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ABSTRACT

The energetics and reversibility of hydrocarbon sequential dehydrogenation on the (100), (111) and (10,8,7) platinum single crystal surfaces has been investigated at 200-700K using carbon-14 radiotracer studies and hydrogen thermal desorption mass spectrometry (TDS). Propylene, cis-2-butene, n-hexane, ^{14}C-ethylene, and ^{14}C-benzene all displayed similar sequential dehydrogenation energetics with activation energies in the range 18-45 kcal/mole. Radiotracer studies revealed "active" and "inactive" forms of partially dehydrogenated carbon on the platinum surfaces which differ greatly in their reactivity for hydrogenation and hydrogen transfer reactions with H_2 or unlabelled hydrocarbons. The inactive fraction increased with increasing adsorption temperature as the surface species became more hydrogen deficient. Removal of the active ^{14}C-containing species by hydrogen transfer occurred more slowly than direct hydrogenation. The C-H bond breaking processes are discussed in connection with recent LEED, photoemission and vibrational spectroscopy studies that revealed atomic structures for the surface species.

INTRODUCTION

The chemistry of hydrocarbons adsorbed on platinum surfaces at temperatures of 300-800K is dominated by dissociative chemisorption involving the scission of one or more C-H bonds.[1] A detailed understanding of these elementary C-H bond breaking processes is essential for establishing meaningful reaction pathways for important hydrocarbon skeletal rearrangement reactions such as isomerization and aromatization, that can be catalyzed only at high temperatures (> 500K), where C-H bond breaking occurs very easily. Of particular importance is the energetics and reversibility of the sequential C-H bond breaking processes.

Thermal desorption and carbon-14 radiotracer studies have been applied here to investigate the energetics and reversibility of hydrocarbon sequential dehydrogenation on platinum single crystal surfaces possessing well defined atomic structure. The evolution of hydrogen from ethylene, propylene, cis-2-butene, benzene and n-hexane chemisorbed as a function of temperature on the flat (100) and (111) and kinked (10,8,7) platinum surfaces was monitored to determine the activation energies for sequential C-H bond breaking and the average (H/C) composition of the adsorbed species. Radiotracer studies were employed to explore the adsorption reversibility. Reactivity studies carried out near atmospheric pressures revealed two distinct types of carbonaceous species on the platinum surfaces:

(1) an active form consisting of partially dehydrogenated molecules (and/or fragments) which readily undergo hydrogenation and hydrogen transfer reactions under mild conditions, and

(2) an inactive form that displays little reactivity over the entire range of temperature (300-700K) and pressure (10^{-10} - 1 atm) investigated.

Removal of the active ^{14}C-containing species by hydrogen transfer reactions with

unlabelled hydrocarbons, viz.,

$$^{14}CH_x\ (ads) + {}^{12}CH_y\ (gas) \longrightarrow {}^{14}CH_{x+z}\ (gas) + {}^{12}CH_{y-z}\ (ads) \qquad (1)$$

displayed significant reaction rates at 520-570K. The proportion of the total surface carbon which exists in the active form decreases with increasing adsorption temperature as the surface species become more hydrogen deficient. The formation of inactive surface carbon has been associated with the formation of polymeric residues with very low hydrogen content (H/C < 0.5).

EXPERIMENTAL

Experiments were carried out in two ultra-high vacuum systems (base pressure < 10^{-9} Torr) equipped with 4-grid electron optics for low energy electron diffraction (LEED) and Auger electron spectroscopy (AES), an ion gun for crystal cleaning, precision leak valves for introducing gases at low pressures, a nude ion gauge for pressure measurement and a quadrupole mass spectrometer for thermal desorption studies. The mass spectrometer ionizers were mounted in direct line of sight to the single crystal samples at a distance of 8-15 cm. Both vacuum systems were also equipped with an internal isolation cell[2] that could be closed around the samples and pressurized to 1-10 atm. to function as a microbatch reactor. The reation cells were connected to external gas recirculation systems and to gas chromatograph sampling valves as described previosly.[3]

The counting system for in situ carbon-14 radiotracer studies that was detailed in a separate report[4] is diagrammed schematically in Figure 1. The counting system uses a solid state surface barrier detector which is mounted on a rotatable feedthru in the center of the UHV chamber. The detector could be reproducibly positioned directly in front of the single crystal surface

(within 1 cm) for counting adsorbed species, or rotated away for background corrections, high pressure reactions, or LEED and AES studies. The detector was interfaced to conventional counting electronics and to a pulse height analyzer where N(E) beta spectra could be stored and integrated to obtain the total radioactivity present on the surface. The absolute detection efficiency (in the range 2.4-3.2%) was calibrated for the experimental counting geometry by depositing thin films of ^{14}C-polymethylmethacrylate onto the single crystals and by monitoring the ^{14}C-count rate as a function of the amount deposited.(4) Using this system ^{14}C-containing species could be easily detected at surface concentrations of 10^{12}-10^{13} molec/cm^2.

The (100), (111) and (10,8,7) platinum single crystal samples used in this research were deliberately cut very thin (< 0.4 mm) so that the polycrystalline edges would contribute only 8-15% of the total platinum surfce area. The square (100) and hexagonal (111) platinum surfaces are the two flat crystal faces with highest atomic density. The kinked (10,8,7) crystal face has hexagonal terraces of (111) orientation that are periodically displaced by atomic steps, one atom in height, of (310) orientation. The samples were carefully spotwelded to gold or copper supports fixed to rotatable manipulators that enabled the sample temperature to be varied continuously between 100K (300K) and 1500K by a combination of liquid nitrogen cooling and resistive heating. The crystal temperature was monitored with a chromel-alumel thermocouple spotwelded to the edge of the sample. Linear temperature programs in the range 12-98K/sec were employed for all thermal desorption measurements.

Unlabelled hydrocarbon reagents were of the highest obtainable research purity: n-hexane (Phillips, > 99.96%), benzene (Baker, > 99.94%), ethylene (Matheson, > 99.92%), propylene (Phillips, > 99.6%) and cis-2-butene (Phillips, > 99.5%). The liquid hydrocarbons were outgassed by repeated freeze pumping

cycles at 77-210K prior to use. All reported exposures are uncorrected for ion gauge sensitivity (1L = 10^{-6} Torr sec).

Carbon-14 labelled ethylene (Amersham, 128 mc/mmole, radiochemical purity > 99.5%) and benzene (New England Nuclear, 16 mc/mmole, radiochemical purity > 98%) were used as supplied after several cycles of freeze pumping at 77K. Counting times for adsorbed species ranged from 3-10 minutes for $^{14}C-C_2H_4$ to 10-40 minutes for $^{14}C-C_6H_6$. Count rates for adsorbed species and background were in the range of 10-1600 and 2-5 counts per minute (cpm), respectively.

RESULTS AND DISCUSSION

1) ^{14}C-Ethylene and ^{14}C-Benzene Chemisorption on Pt(111)

Isotherms obtained for ^{14}C-ethylene chemisorption on Pt(111) at 330-570K are shown in Figure 2. For temperatures below about 450K, the initial sticking coefficient S_o and saturation coverage $C_s = 4 \times 10^{14}$ molec/cm^2 were constant. At higher temperatures a slow adsorption process was apparent which continued for exposures > 20L (1L = 10^{-6} Torr sec. uncorrectd for ion gauge sensitivity). As demonstrated below the slow adsorption process was accompanied by extensive dehydrogenation and rearrangement of the surface species.

Ethylene chemisorption on Pt(111) at 300-430K leads to the formation of surface "ethylidyne" species which display a (2x2) overlayer structure.[5-8] Dynamical LEED intensity analysis,[5] high resolution ELS[5,6] and TDS[7] studies have revealed that the ethylidyne species occupy 3-fold hollow adsorption sites with the C-C internuclear axis directed normal to the platinum surface with a C-C bond distance of 1.5Å. The α-carbon atom is bonded equivalently to three platinum atoms with a Pt-C bond length of 2.0Å. The radiotracer studies (Fig. 1) show that this species forms according to 1st-order Langmuir adsorption kinetics, i.e.,

$$\frac{d\theta}{de} = \frac{S_o}{C_s(2\pi mkT)^{1/2}} (1 - \theta) \quad (1)$$

where e was the gas exposure and S_o was constant at 0.9 ± 0.2 over the temperature range 330-420K.

The adsorption behavior of ^{14}C-benzene on Pt(100) and Pt(111) was similar to that shown for ^{14}C-C_2H_4 on Pt(111). Surface coverages by adsorbed species increased with increasing temperature and exposure.[4,8] Figure 3 compares the behavior for ^{14}C-C_6H_6 chemisorbed on Pt(111) with results reported by Tetenyi and Barbernics[9] for ^{14}C-benzene chemisorbed on platinum films. Since the surface coverages measured for ^{14}C-C_6H_6 chemisorption on Pt(111) (and Pt(100)) were always much higher than those noted for the films, it is likely that surface impurities were present on the films that could strongly suppress the chemisorption of benzene.

2) Thermal Desorption Studies of Sequential C-H Bond Breaking

Hydrogen thermal desorption spectra representing the sequential dehydrogenation and decomposition of ethylene, propylene and cis-2-butene chemisorbed at about 110K on the (111) platinum surface are shown in Figure 4. All three alkenes displayed similar behavior characterized by three sets of desorption peaks denoted by the regions A, B and C. The initial C-H bond breaking reaction (peak A) produced a sharp H_2 desorption peak at 295 ± 5K for all three alkenes. This peak occurred at a temperature that was just 10-30K higher than that required for molecular desorption.[7] It should be remembered from our previous previous studies[7] that only a small fraction (< 10-25%) of the surface species desorbed in the molecular form; most of the adsorbed species underwent sequential dehydrogenation and decomposition upon heating to 700K.

A second dehydrogenation reaction (region B) occurred at temperatures of 380-500K. The temperature required for this C-H bond breaking process was

highly sensitive to the structure of the original hydrocarbon. A final series of dehydrogenation reactions (region C) occurred at temperatures between 500 and 715K. These peaks occurred at similar temperatures for all three hydrocarbons and correspond to the complete dehydrogenation of the initially intact molecules.

Hydrogen thermal desorption spectra representing the sequential dehydrogenation and decomposition of benzene and n-hexane chemisorbed on Pt(100) and Pt(10,8,7) at a series of increasing temperatures in the range 315-700K are compared in Figures 5-7. Very similar spectra were obtained for ethylene, neopentane, benzene and cyclohexene chemisorption on Pt(111) and Pt(332).[8] Under these conditions only the desorption peaks in regions B and C can be detected (these are the only peaks for benzene). These peaks occurred at similar temperatures for all hydrocarbons over all surfaces investigated. Temperatures corresponding to the desorption peak maxima are summarized together with the relative areas of the peaks for all hydrocarbons studied in Table 1.

3) Energetics of C-H Bond Breaking

Activation energies for the C-H bond breaking processes that produced the different hydrogen desorption peaks were estimated by assuming that all such processes were unimolecular reactions. In this case, the rate of the dehydrogenation reaction

$$C_nH_x \text{ (ads)} \longrightarrow C_nH_{x-a} \text{ (ads)} + \frac{a}{2} H_2 \text{ (gas)}$$

is given by

$$-\frac{d\theta_{C_nH_x}}{dt} = \nu\theta_{C_nH_x} \exp(-E_a/RT) \qquad (1)$$

where ν and E_a are the pre-exponential factor and activation energy for dehydrogenation (or rearrangement with dehydrogenation), and $\theta_{C_nH_x}$ is the surface

coverage by species with composition C_nH_x. Since hydrogen recombination and desorption are very rapid at the temperatures (> 425K) where rearrangement and dehydrogenation take place[10], hydrogen desorption spectra resulting from the dehydrogenation of chemisorbed hydrocarbons can be used to directly monitor the decomposition rate. Kinetic analysis of the rearrangement process is then identical to that for first order molecular desorption. If, under these conditions, E_a is independent of temperature, Redhead has shown that[11]

$$E_a = RT_p^2 \, \nu/\beta \, \exp(-E_a/RT_p) \qquad (2)$$

where β is the sample heating rate and T_p is the temperature of a desorption peak maximum. Baetzold,[12] Benson[13] and others[14] have tabulated preexponential factors for unimolecular surface and gas phase reactions that are always in the range 10^{12}–10^{15} sec^{-1}. An average value of $\nu = 10^{13}$ sec^{-1} was used in this work. The assumption of first order reaction kinetics was justified by the fact that the desorption peak temperatures were invariant to changes in initial surface coverage. When possible, activation energies were also estimated from full widths of the desorption peaks at half maximum, ΔW, using the Edward's formula[15]

$$E_a = RT_p^2 \, \frac{2.4464}{\Delta W} \, (1 - 0.5725) \, \frac{\Delta W}{T_p} + 0.2625 \, \frac{\Delta W}{T_p}^{2} + \ldots \qquad (3)$$

which requires no assumptions for the magnitude of ν.

Activation energies for the sequential dehydrogenation of all hydrocarbons investigated are summarized in Table 2. The activation energies for C-H bond breaking varied widely from about 18 kcal/mole for the desorption peaks in region A to 22-30 kcal/mole for the desorption peaks in region B to 32-44 kcal/mole for the final, complete dehydrogenation steps that correspond to region C.

4) Temperature Dependent Composition of the Strongly Bound Surface Species

The average (H/C) stoichiometry of the adsorbed hydrocarbon species, expressed as hydrogen atoms per surface carbon atom, was determined as a function of adsorption temperature from the total areas under the hydrogen thermal desorption spectra. The desorption peak area was assumed to be proportional to the amount of hydrogen originally retained by the adsorbed species. Comparison of this peak area, A, with the C_{273}/Pt_{237} AES peak to peak height ratio, I, provided a relative measure of the initial (H/C) composition, i.e. $(H/C) = \alpha(A/I)$. The constant α was determined before and/or after each series of experiments by chemisorbing benzene on clean platinum at 300-315K and executing the same hdyrogen thermal desorption experiment. A standard ratio (H/C) = 1.0 was assumed under these conditions yielding $\alpha = (I/A)_{Bz}$. This assumption is readily justified by the fact that benzene chemisorbs on platinum in a molecular form for adsorption temperatures below 350-380K.[8,16,17]

The temperature dependent composition of the strongly adsorbed species resulting from benzene and n-hexane chemisorption on Pt(100), Pt(111) and Pt(10,8,7) is shown in Figure 8. The hydrogen content of the surface species decreased with increasing adsorption temperature and appraoched zero at temperatures just higher than 670K.

5) Reversibility of Sequential Dehydrogenation: Radiotracer Studies of Ethylene and Benzene Rehydrogenation and Hydrogen Transfer Reactions on Pt(111) and Pt(100)

Radiotracer decay curves representing the rehydrogenation of ethylidyne species chemisorbed on the (111) platinum surface are shown in Figure 9. The ethylidyne species were prepared by chemisorbing ^{14}C-ethylene at 335-345K and 10^{-7} Torr using a constant exposure of 6L. The rehydrogenation reactions were carried out at 300-470K in the presence of 1 atm of flowing hydrogen. The reac-

tions were interrupted at intervals of 1-10 min so that the residual coverage ($\theta(t)/\theta(t = 0) = \theta/\theta_o = cpm/cpm_o$) by radioactive surface species could be determined as a function of the total reaction time. Two points are significant: (1) the ethylidyne species became highly reactive only at temperatures higher than about 340K, and (2) the rehydrogenation reaction was not a simple first-order (or second order) process.[18] At 300K only about 25 percent of the surface species were removed by rehydrogenation in 30 min reaction time. By contrast, at 370K or higher temperatures, the same surface species underwent essentially complete rehydrogenation in just 2-5 min. From the initial slopes of the decay curves the activation energy for ethylidyne hydrogenation can be very roughly estimated as 5-10 kcal/mole. It appears clear that ethylidyne species and related reaction intermediates with the alkylidyne surface structure[19] should be exceedingly reactive under typical alkane reaction conditions at 500-800K.

A similar series of rehydrogenation reactions was carried out following the chemisorption of ^{14}C-ethylene on Pt(111) at 473 and 600K. Ethylene adsorption at these temperatures produced surface species with avearge composition "C_2H" (473K) and "C" (600K). Representative results of these reaction studies are shown in Fiugre 10. Rehydrogenation of these more strongly adsorbed species at 370-640K proceeded in at least two distinct stages. A very rapid initial reaction ($R_h > 10^{-2}$ molec/Pt atom sec) which was complete within about 2 min was always followed by a very slow rehydrogenation reaction ($R_h < 10^{-5}$ molec/Pt atom sec) which continued for hours without reaching completion. The rapid initial reaction appears to represent the hydrogenation of small C, C_2, CH and C_2H fragments that are present following ethylene chemisorption at 470-650K.[6,7] The very slow later stages of reaction appear to represent the gasification of polymerized surface species with very low hydrogen content. Similar catalytic

behavior characterized by a two stage rehydrogenation reaction was recently reported by Krebs and Bonzel[20] for the hydrogenation of surface carbon deposited on iron foils at 560K.

These results show that for temperatures higher than about 470K, ethylene chemisorption on Pt(111) is always partially irreversible The proportion of the total surface carbon which existed in the inactive form increased with increasing adsorption temperature. In Figure 11 the irreversibly adsorbed fraction is shown as a function of temperature along with the (H/C) stoichiometry of the adsorbed layer as determined from thermal desorption studies. Irreversibly adsorbed fraction is defined as the proportion of preadsorbed ^{14}C-ethylene which could not be removed by rehydrogenation (40-80 min reaction time) at the same temperature at which the initial adsorption was carried out. The (H/C) ratio displayed a striking correlation with the adsorption reversibility. Sequential dehydrogenation of ethylidyne to "C_2H" like species at 450-470K was accompanied by a marked decrease in reversibility from 95-100 percent to about 50-70 percent. The reversibility approached zero as the hydrogen content decreased further at higher adsorption temperatures.

The fact that the amount of inactive carbon deposited at 473K was highly dependent upon the temperature of subsequent rehydrogenation reactions indicates that the process responsible for the formation of the inactive carbon involves two independent pathways. Initial polymerization responsible for the overall shape of Figure 10 appears to occur during adsorption. Further polymerization, which competes with direct hydrogenation, appears to occur during the initial stages of the rehydrogenation reactions. Provided that the activation energy for inactivation is smaller than that for hydrogenation, the irreversibly adsorbed fraction should decrease with increasng reaction temperature as observed experimentally.

The formation of inactive metal-organic surface species derived from ^{14}C-ethylene on alumina supported Ni,[21] Pd,[21] Rh,[21,22] Ir[23] and Pt[21] catalysts was investigated by Thomson and Webb and co-workers. Inactive carbonaceous species were detected under all conditions of direct hydrogenation and hydrogen transfer with unlabelled ethylene and acetylene at 290-470K. At 290K, the irreversibly adsorbed fraction decreased in the sequence Pd (63%) > Ni (20%) > Ir (6-13%) > Pt (4-7%). The inactive fraction retained by the platinum catalyst increased to 40-60% at 470K. These results appear to be in excellent agreement with those reported here for the small area (111) platinum single crystal surface.

The strongly adsorbed "C_2H" fragments resulting from ^{14}C-ethylene chemisorption on Pt(111) at 470K were active for intermolecular hydrogen transfer reactions with unlabelled hydrocarbons. Radiotracer decay curves illustrating hydrogen transfer between "C_2H" and n-hexane and cyclohexane at 523-573K are shown in Figure 12. An interesting feature of the hydrogen transfer reactions is the ease with which they occurred. Initial removal of the active ^{14}C-containing species by hydrogen transfer with 20 Torr of n-hexane or cyclohexene displayed initial reaction rates (10^{-2} - 10^{-3} molec/Pt atom sec) that appear to be within about an order of magnitude to those determined for direct hydrogenation in 1 atm of hydrogen. Hexenes and benzene were detected as byproducts of the hydrogen transfer reactions. Cyclohexene (a good hydrogen donor) underwent hydrogen transfer with "C_2H" more rapidly than n-hexane (a poor hydrogen donor). In the absence of hydrogen, the hydrogen transfer reactions were accompanied by the deposition of carbonaceous deposits on the platinum surface (C_{273}/Pt_{237} = 5-8) that could be detected by AES.

It should be noted that no hydrogenation or hydrogen transfer could be detected at low reactant pressures (10^{-8} - 10^{-6} Torr). High surface concentra-

tions of adsorbed species that can be produced at atmospheric pressures appears to be an essential requirement for activity in these chemical reactions.

Radiotracer decay curves representing the rehydrogenation and hydrogen transfer reactions of ^{14}C-benzene preadsorbed on Pt(100) and Pt(111), respectively, are displayed in Figures 13 and 14. Results for ^{14}C-C_6H_6 rehydrogenation on Pt(111) were reported previously.(4) The adsorbed species derived from benzene chemisorption at 330 and 570K displayed similar reactivities on both platinum surfaces, and these reactivities were much like those just described for ^{14}C-C_2H_4 chemisorbed on Pt(111). The weakly adsorbed species resulting from benzene chemisorption at 330K underwent essentially complete hydrogenation under mild conditions (300-360K, 1 atm. H_2) in minutes. By contrast, the more strongly adsorbed surface species produced by benzene chemisorption at 570K could only be partially hydrogenated in two hours even at temperatures as high as 670K. In this case a rapid initial reaction was always followed by a very slow gasification reaction. The fraction of the total surface carbon which existed in the inactive form increased with increasing adsorption temperature and decreasing reaction temperature. The strongly adsorbed species displayed significant reactivity in hydrogen transfer reactions with unlabelled benzene and n-hexane.

6) Significance of Hydrogen Transfer Reactions

The radiotracer studies clearly demonstrate that hydrogen transfer reactions take place readily between hydrocarbon species strongly chemisorbed on the (111) platinum single crystal surface. Previous studies of cyclohexene hydrogenation and disproportionation catalyzed at 425K over Pt(322) revealed that direct hydrogenation was ten times faster than hydrogen transfer.(1,8) Because the activation energy for disproportionation (~ 16 kcal/mole) was larger than that for direct hydrogenation (5-6 kcal/mole), the importance of

the hydrogen transfer pathway is expected to increase with increasing reaction temperature. Overall, our results[1,24] clearly suggest that many important types of hydrocarbon conversion reactions may be influenced by hydrogen transfer reactions between the adsorbed species that always cover the platinum surface. Under steady state reaction conditions at 600-800K only a small concentration (1-20 percent) of uncovered platinum surface sites exists for dissociative chemisorption of hydrogen molecules.[24] Under these conditions hydrogen transfer may become favored over direct hydrogenation since the latter process is strongly suppressed in the absence of uncovered platinum surface sites.[25]

The notion that hydrogen transfer reactions may be important in reforming catalysis is not new. Thomson and Webb[26] have argued that a hydrogen transfer mechanism provides a general explanation for the patterns of catalytic activity displayed by metal catalysts in olefin hydrogenation reactions. Gardner and Hansen[27] reached a similar conclusion in connection with studies of ethylene hydrogenation over tungsten catalysts. Unfortunately, the crucial experiments required to distinguish the kinetics of hydrogenation and hydrogen transfer were not reported in these studies. Our results certainly tend to confirm that hydrogen transfer reactions could be important, especially at higher reaction temperatures. Further experiments are warranted to determine exactly how important these processes may be.

7) Nature of the Sequential C-H Bond Breaking Processes

The hydrogen thermal desorption clearly indicate that the dehydrogenation of hydrocarbons chemisorbed on platinum always occurs in a sequential manner. Each dehydrogenation reaction produced a surface species that was stable from room temperature to the temperature of the next higher C-H bond breaking process. Complete dehydrogenation occurred only after adsorption at temperatures that were higher than about 670K.

Recent dynamical LEED intensity analysis[5,19] and high resolution ELS[5,6,28] studies of ethylene, propylene and butenes chemisorbed on Pt(111) have revealed surface structures for the adsorbed species that can be used for an analysis of the hydrogen desorption peaks that were displayed in regions A, B and C. Chemisorption of these unsaturated hydrocarbons at 300-400K produces stable surface species with the alkylidyne surface structure, i.e.,

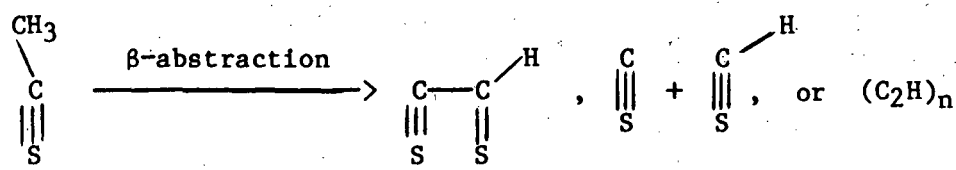
$$\begin{array}{l} H_2C{=}CH_2 \\ H_2C{=}CHCH_3 \\ H_2C{=}CHCH_2CH_3 \end{array} \xrightarrow[300\text{-}400K]{Pt(111)} Pt_3{\equiv}CR + 1/2\ H_2 \qquad (R = CH_3,\ C_2H_5,\ C_3H_8) \qquad (2)$$

Formation of these species requires scission of a single C-H bond corresponding to the sharp hydrogen desorption peak displayed in region A. The activation energy for this process was about 18 kcal/mole independent of the structure of the initial hydrocarbon.

Further dehydrogenation of the alkylidyne surface species occurred in region B at temperatures between 380 and 500K. These reactions yielded strongly bound species with average composition "C_2H", "C_3H_2" and "C_4H_3". The activation energy for this rearrangement decreased from about 29 kcal/mole for ethylidyne to 22-25 kcal/mole for propylidyne and butylidyne. Vibrational spectroscopy studies[16] suggest that CH fragments are the most abundant species resulting from ethylidyne dehydrogenation on Pt(111). However, the appearance of several hydrogen desorption peaks in region C clearly indicates that more than one type of "CH" fragment must exist on the surface. The radiotracer studies also demonstrate that at least two types of species are present, active and inactive forms of surface carbon that differ greatly in their reactivity for hydrogenation and hydrogen transfer reactions.

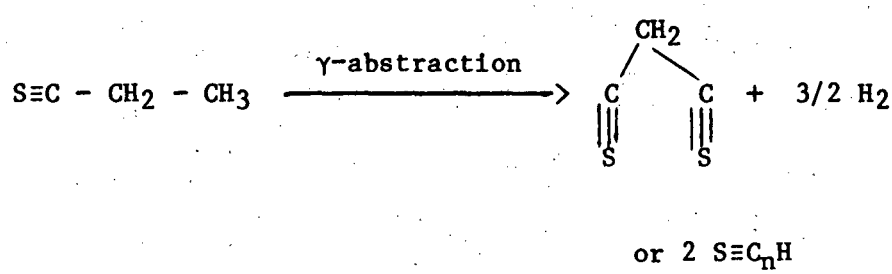
Ethylidyne dehydrogenation represents an important example of β-hydrogen

abstraction from a multiply bonded surface species. Two hydrogens are lost in this process, i.e.,



(3)

where S is a surface site composed of one or more platinum atoms. Similar rearrangements occur during the sequential dehydrogenation of propylidyne and butylidyne. Since in these cases the activation energies were lowered substantially relative to that for ethylidyne dehydrogenation, it appears likely that γ-hydrogen abstraction may become favored over β-abstraction, i.e.,



(4)

Regardless of the exact structure of the resulting fragments (which is presently not known), it is clear that these species were exceedingly stable. Further dehydrogenation represented by the hydrogen desorption peaks in region C required activation energies in the range 34-44 kcal/mole. These high activation energies indicate that the remaining C-H bonds were not provided easy access to platinum surface sites. Careful vibrational spectroscopy studies are needed to clarify the structure and bonding of the stable fragments with low hydrogen content.

The sequential dehydrogenation of benzene and n-hexane chemisorbed on Pt(100), Pt(111) and Pt(10,8,7) appeared to occur by a similar series of reaction steps. With benzene, no dehydrogenation was detected until temperatures

near 420K, and then rearrangement was accompanied by scission of 3 C-H bonds (on average). The activation energy for this process (about 27 kcal/mole) was similar to that for alkylidyne decomposition and corresponds reasonably well with the resonance stabilization energy for the benzene molecule (36 kcal/mole).

Rearrangement and sequential dehydrogenation of adsorbed hydrocarbons must be accompanied by an increase in metal-organic bond multiplicity polymerization of the adsorbed species, or a combination of both these processes. As detailed above, the average composition displayed at tempeartures between 300 and 600K was that expected for the formation of carbyne (Pt≡CR), "CH" and $(C_2H)_n$ type species on the surfaces. Polymerization becomes feasible only if these species have considerable mobility. The growth of graphitic carbon islands, that become detectable by LEED at temperatures above 700K, clearly requires extensive polymerization of the adsorbed species. Auger spectroscopy studies carried out before and after the thermal desorption studies indicated that little or no carbon is dissolved into the near surface region.[8] With this in mind, it is likely that sequential dehydrogenation at 500-700K is accompanied by polymerization of the adsorbed species by a mechanism that involves the growth of graphitic carbon islands or precursors thereof. This viewpoint is supported by recent high resolution AES studies by Chesters et al.[29] which revealed that the sequential dehydrogenation of ethylene and acetylene on Pt(111) at 450-590K is accompanied by polymerization of the surface species. Ultraviolet photoemission spectroscopy (UPS) studies for benzene and cyclohexene chemisorbed on Pt(100) also tend to confirm that polymeriztion takes place readily.[8] A continuous transition of the adsorbate UPS spectral features from aromatic to graphitic character has been observed at temperatures beginning as low as 450-500K. This temperature range corresponds closely with that for the formation of inactive surface carbon in radiotracer studies.

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TABLE 1: Hydrogen Desorption Peak Temperatures and Peak Areas For the Sequential Dehydrogenation of Hydrocarbons Chemisorbed on Platinum

System	H_2 Desorption Peak Temperature (±15K)					Peak Area (% of Total)		
	A	B	C			A	B	C
C_2H_4/Pt(111)[a]	295	490	540	640	710	30	50	20
C_3H_6/Pt(111)[a]	296	430	530	640	710	20	45	35
C_4H_8/Pt(111)[a]	293	380	---	630	700	20	55	25
C_6H_6/Pt(100)[b]	---	480	590	---	690	—	50	50
C_6H_6/Pt(111)[b]	---	465	---	630	(broad)	—	50	50
C_6H_6/Pt(10,8,7)[b]	---	470	590	640	700	—	50	50
n-C_6H_{14}/Pt(10,8,7)[b]	---	445	590	640	725	—	55	45

(a) β = 12 K/sec

(b) β = 69-98 K/sec

TABLE 2: Activation Energies For the Sequential Dehydrogenation of Hydrocarbons Chemisorbed on Platinum[a]

Adsorption System	Activation Energies for Sequential Dehydrogenation (kcal/mole)				
	A	B	C		
C_2H_4/Pt(111)	18 (18)[b]	30 (23)[b]	32	39	44
C_3H_6/Pt(111)	18 (17)[b]	26 (25)[b]	32	39	44
C_4H_8/Pt(111)	18 (17)[b]	23 (20)[b]	—	38	43
C_6H_6/Pt(111)	----	26	—	30-40	—
C_6H_6/Pt(100)	----	27	34	--	41
C_6H_6/Pt(10,8,7)	----	27	34	38	42
n-C_6H_{14}/Pt(10,8,7)	----	25	34	38	43

(a) calculated by the Redhead method with $\nu = 10^{13}$ sec^{-1}

(b) calculated by the Edwards method

FIGURE CAPTIONS

Figure 1: Schematic diagram of the radiotracer counting system for adsorption and catalysis studies using small area surfaces in ultra-high vacuum.

Figure 2: Adsorption isotherms (left frame) for ^{14}C-C_2H_4 chemisorption on Pt(111) at 330-570K. The adsorption behavior at 330-420K is well described by a first order Langmuir model (right frame).

Figure 3: Comparison between results for ^{14}C-benzene chemisorption on Pt(111) (70-80L gas exposure) and Pt-films as reported by Tetenyi and Barbernics.[9]

Figure 4: Hydrogen thermal desorption spectra illustrating the sequential dehydrogenation of ethylene, propylene and cis-2-butene chemisorbed on Pt(111) at 110K (β = 12 K/sec).

Figure 5: Hydrogen thermal desorption spectra representing the sequential dehydrogenation of benzene chemisorbed on Pt(100) at 340-500K. The gas exposure was 36L and β = 98 K/sec.

Figure 6: Hydrogen thermal desorption spectra illustrating the sequential dehydrogenation of benzene chemisorbed on Pt(10,8,7) at a series of temperatures in the range 340-680K. The gas exposure was 36L and β = 69 K/sec.

Figure 7: Hydrogen thermal desorption spectra representing the sequential dehydrogenation of n-hexane chemisorbed on Pt(10,8,7) at a series of temperatures in the range 330-700K. The gas exposure was 36L and β = 69 K/sec.

Figure 8: Temperature dependent (H/C) composition of the surface species resulting from n-hexane and benzene chemisorption on Pt(100), Pt(111) and Pt(10,8,7).

Figure 9: Radiotracer decay curves illustrating the rehydrogenation of ^{14}C-ethylidyne species chemisorbed on Pt(111).

Figure 10: Radiotracer decay curves illustrating the partial rehydrogenation of ethylene decomposition products with average composition "C_2H" (left frame) and "C" (right frame). These species were prepared by chemisorbing ^{14}C-C_2H_4 on Pt(111) at 470 and 600K.

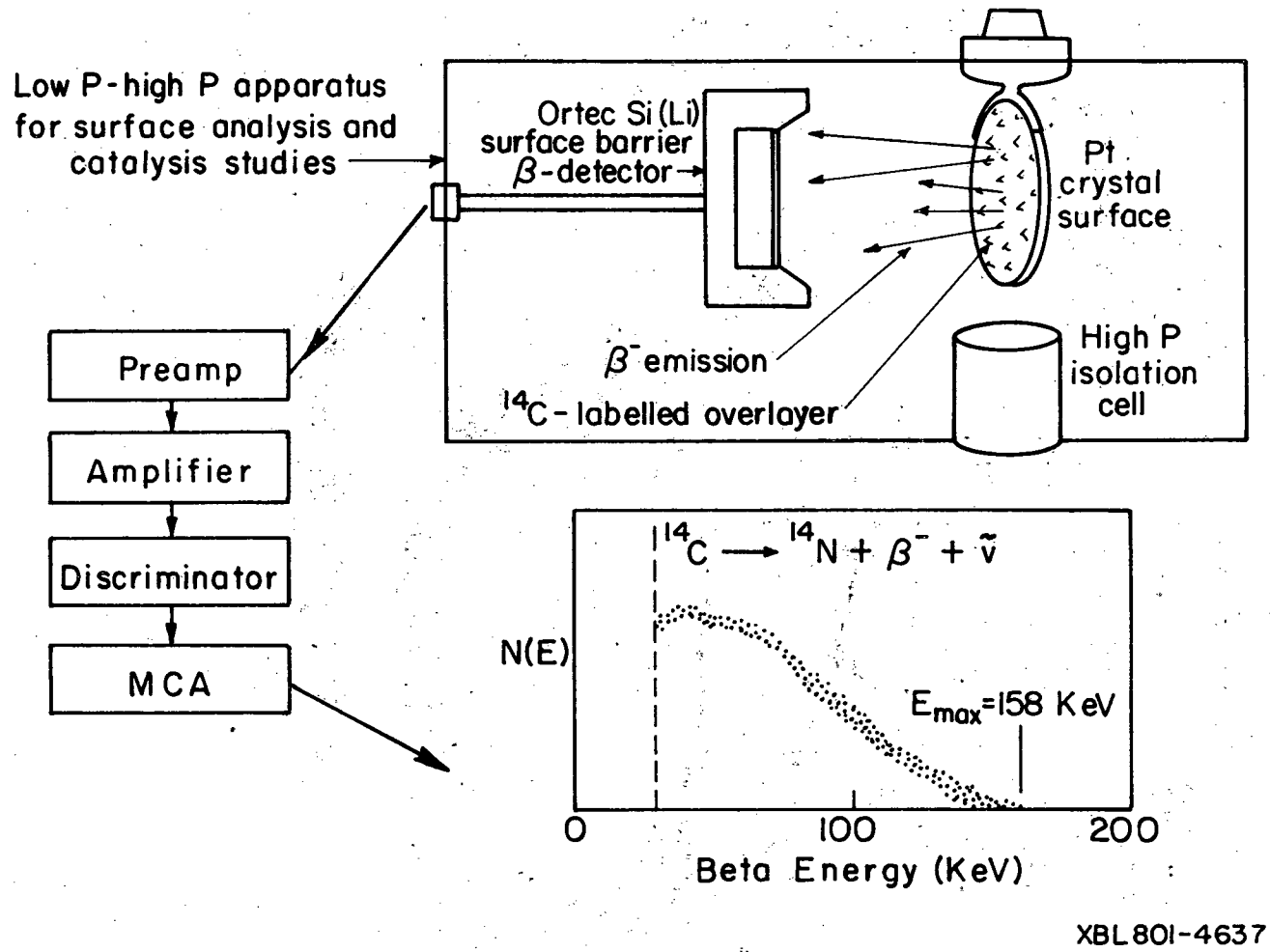
Figure 11: Composition and reactivity of ^{14}C-ethylene chemisorbed on Pt(111) at 320-670K. The irreversibly adsorbed fraction determined by radiotracer analysis displays an excellent correlation with the average hydrogen content (H/C) of the strongly bound surface species.

Figure 12: Radiotracer decay curves illustrating hydrogen transfer reactions between n-hexane (left frame) or cyclohexene (right frame) with "C_2H" surface species that were produced from ^{14}C-ethylene chemisorption on Pt(111) at 470K.

Figure 13: Radiotracer decay curves illustrating the hydrogenation of surface species produced from ^{14}C-benzene chemisorption on Pt(100) at 330 and 570K.

Figure 14: Radiotracer decay curves illustrating hydrogen transfer reactions between n-hexane or benzene with surface species produced from ^{14}C-benzene chemisorption on Pt(111) at 570K.

^{14}C - Radiotracer Studies of Carbonaceous Layers on Platinum



XBL801-4637

Fig. 1

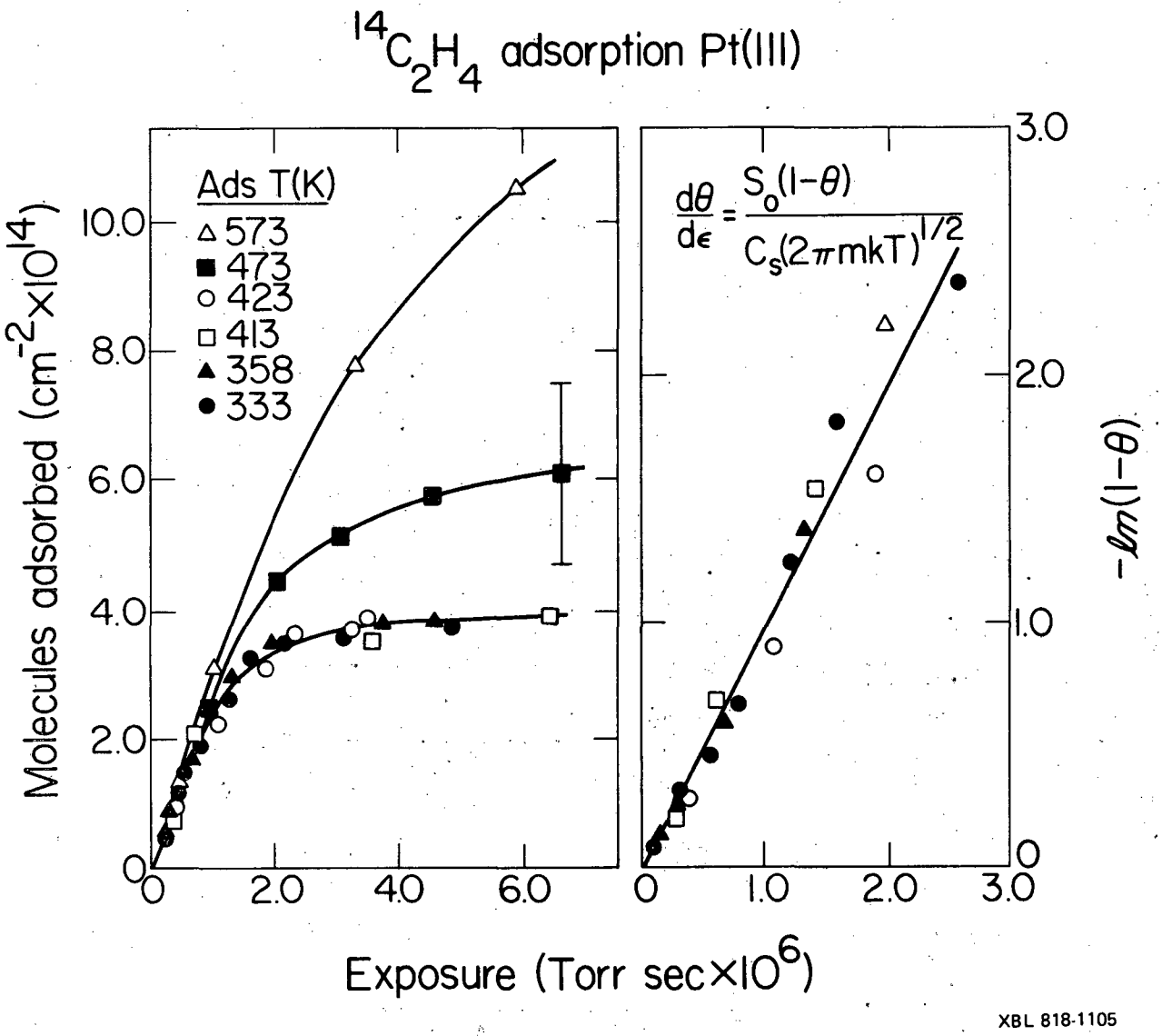
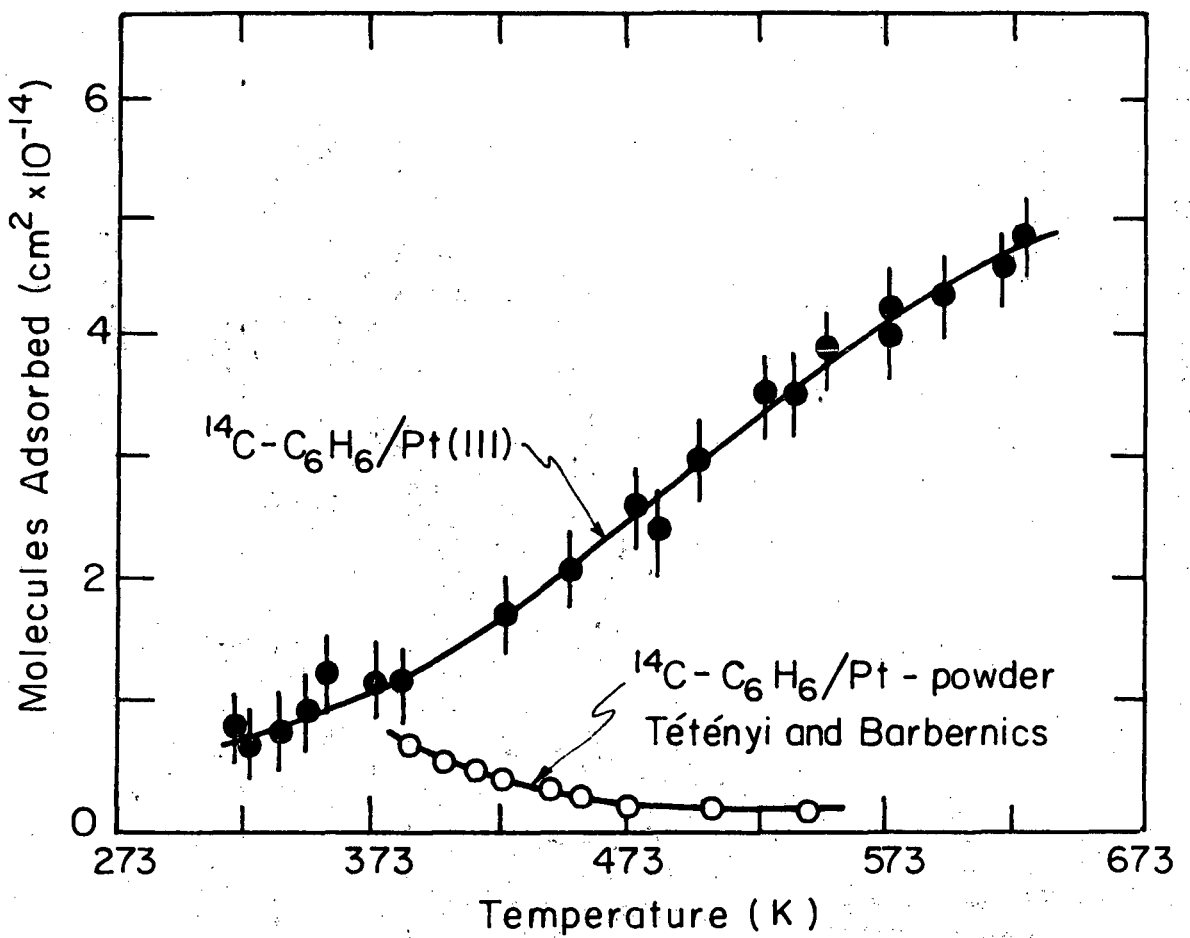

$^{14}C_2H_4$ adsorption Pt(111)
Ads T(K)
573
473
423
413
358
333
Molecules adsorbed ($cm^{-2} \times 10^{14}$)
10.0
8.0
6.0
4.0
2.0
0
2.0
4.0
6.0
$\frac{d\theta}{d\epsilon} = \frac{S_o(1-\theta)}{C_s(2\pi mkT)^{1/2}}$
3.0
2.0
1.0
0
1.0
2.0
3.0
$-\ln(1-\theta)$
Exposure (Torr sec$\times 10^6$)
XBL 818-1105

Fig. 2

Comparison between Model and Practical Catalysts



XBL 808-5687A

Fig. 3

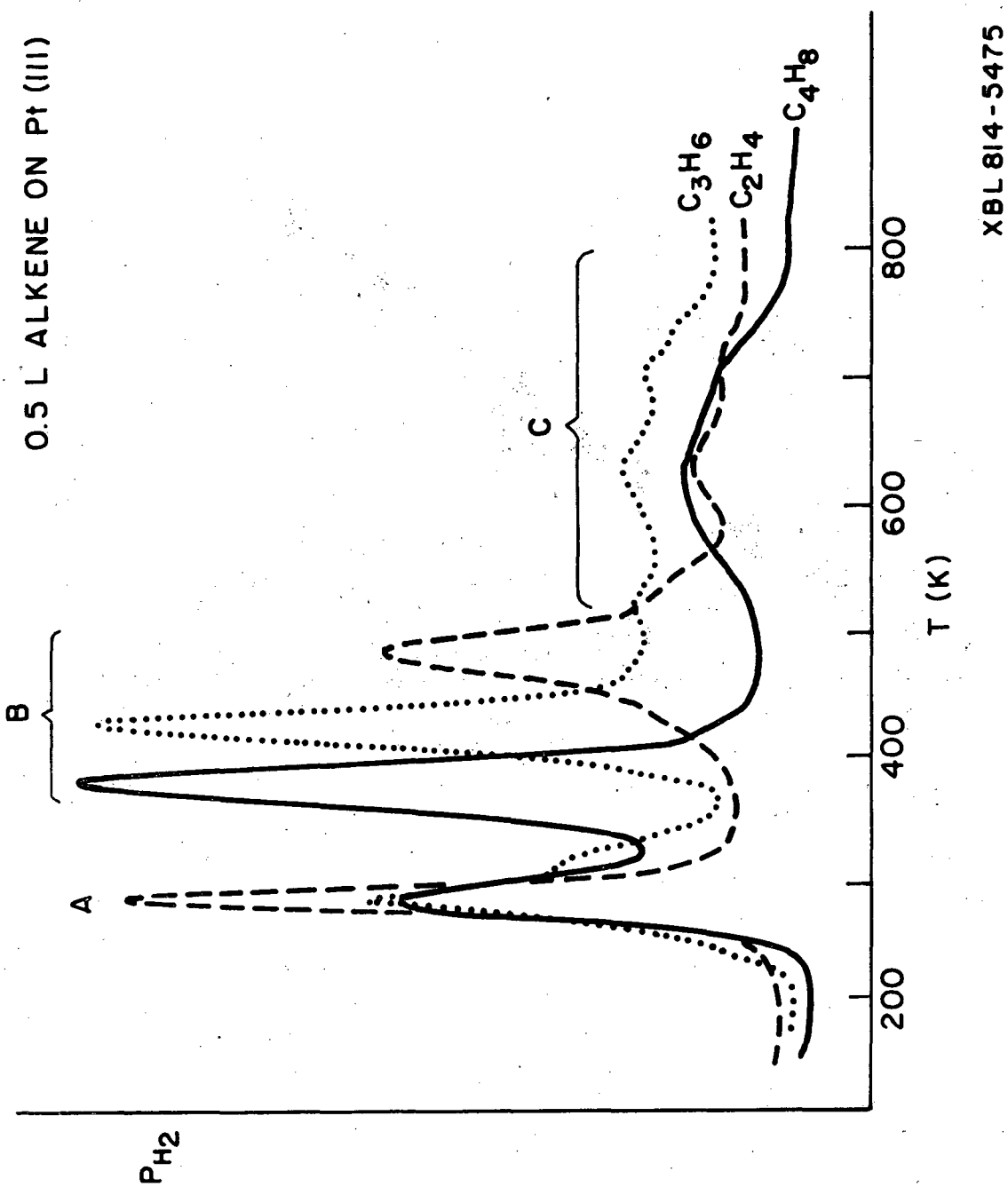
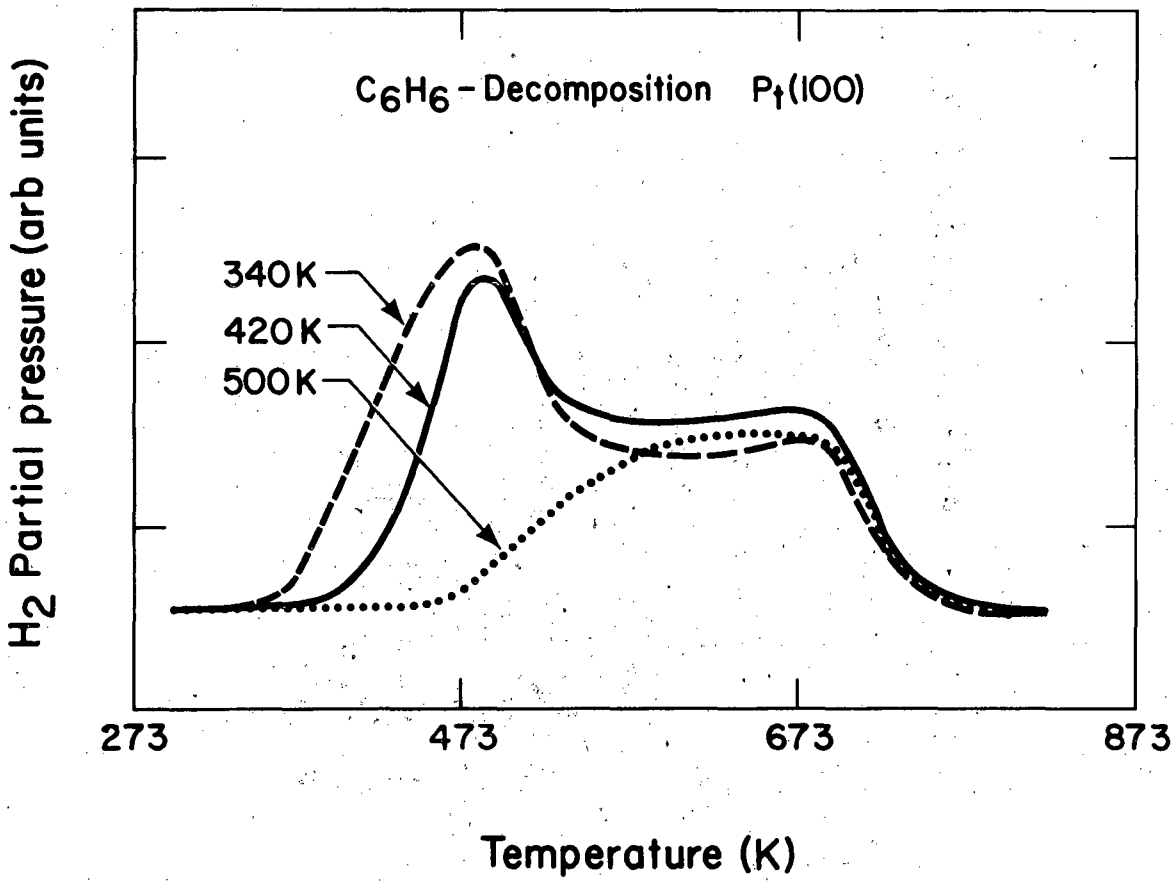

0.5 L ALKENE ON Pt (111)
B
A
C
C_3H_6
C_2H_4
C_4H_8
P_{H_2}
200
400
600
800
T (K)
XBL 814-5475

Fig. 4



XBL 818-1100

Fig. 5

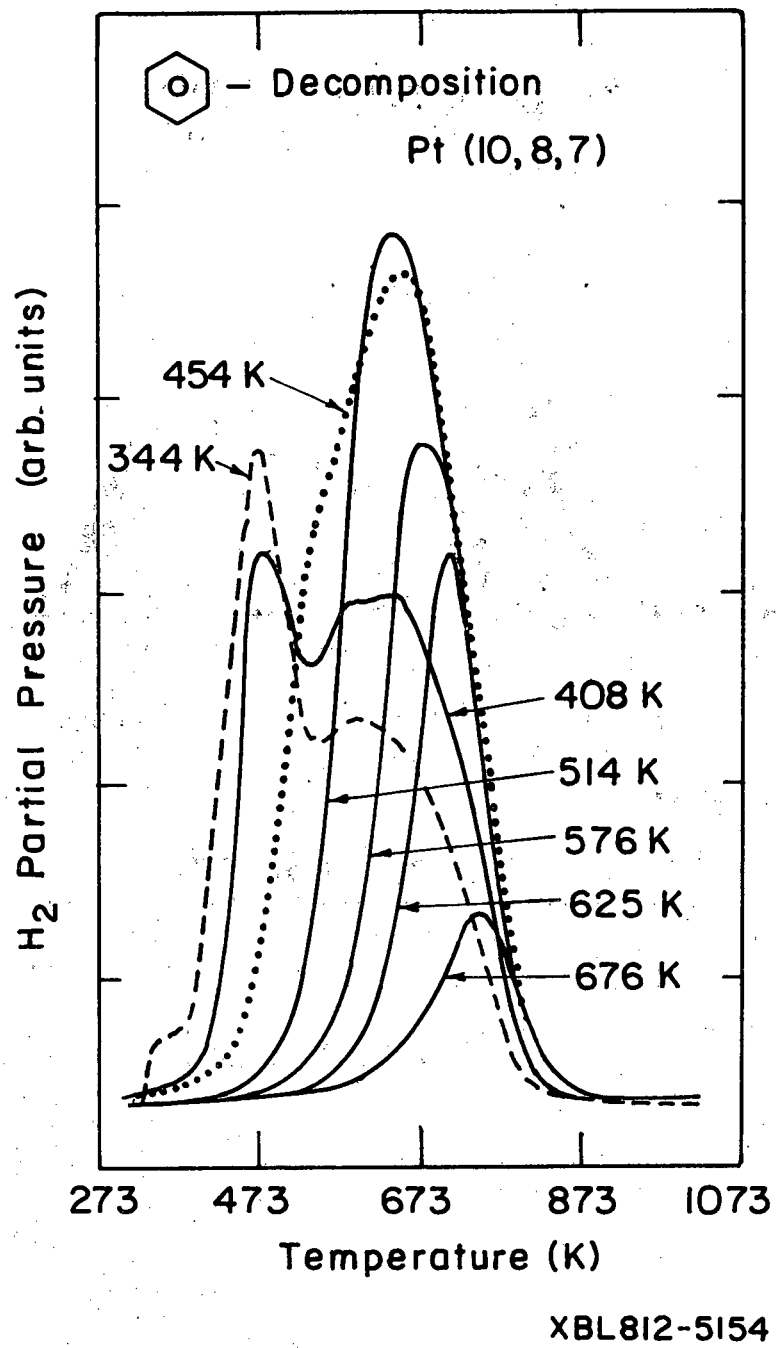
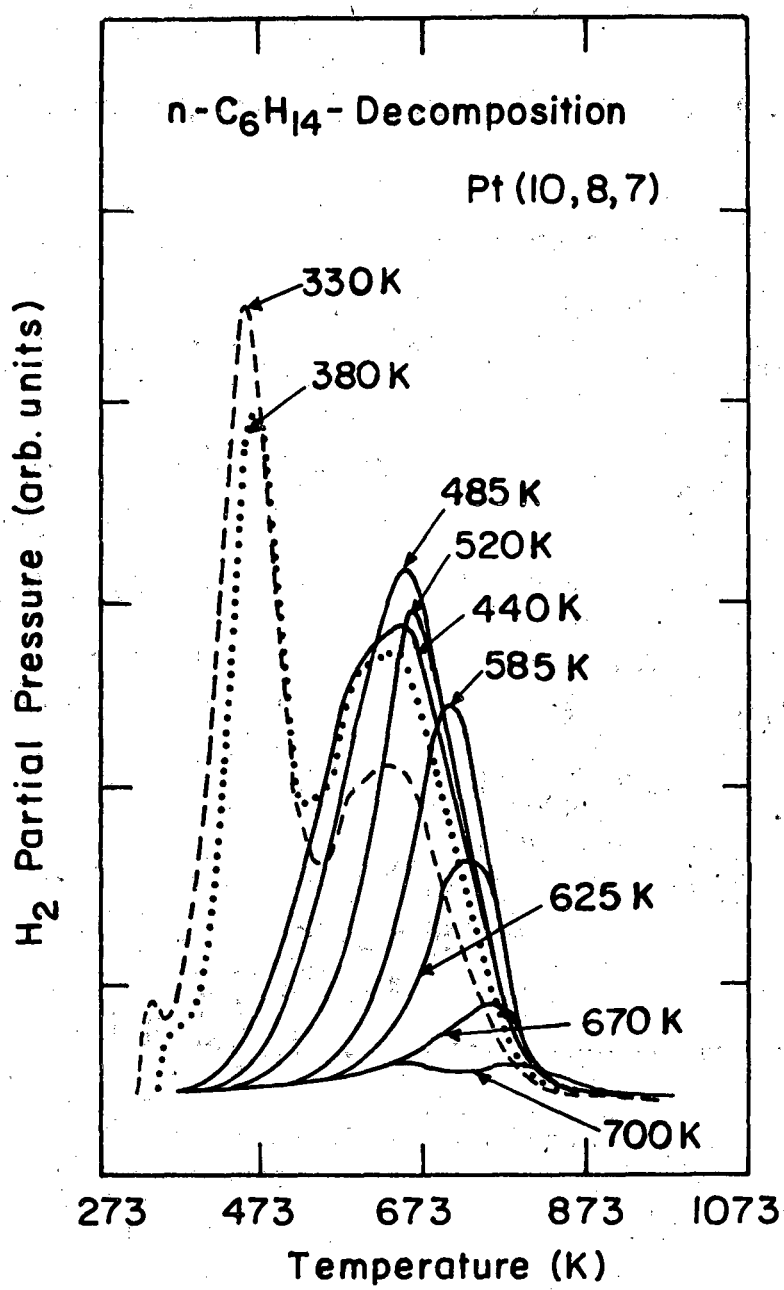

– Decomposition
Pt (10, 8, 7)
454 K
344 K
408 K
514 K
576 K
625 K
676 K
H_2 Partial Pressure (arb. units)
273
473
673
873
1073
Temperature (K)
XBL812-5154

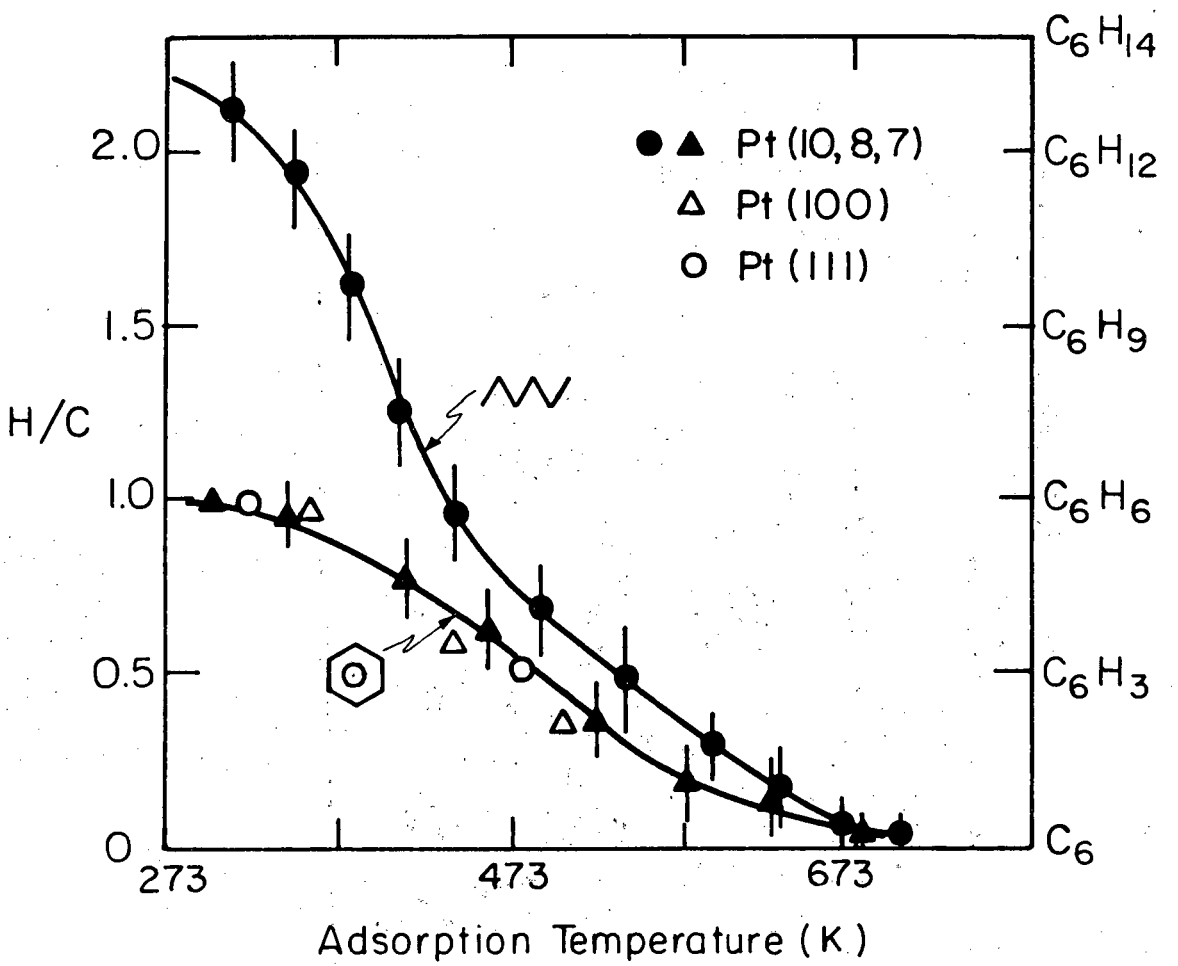
Fig. 6



XBL 812-5155A

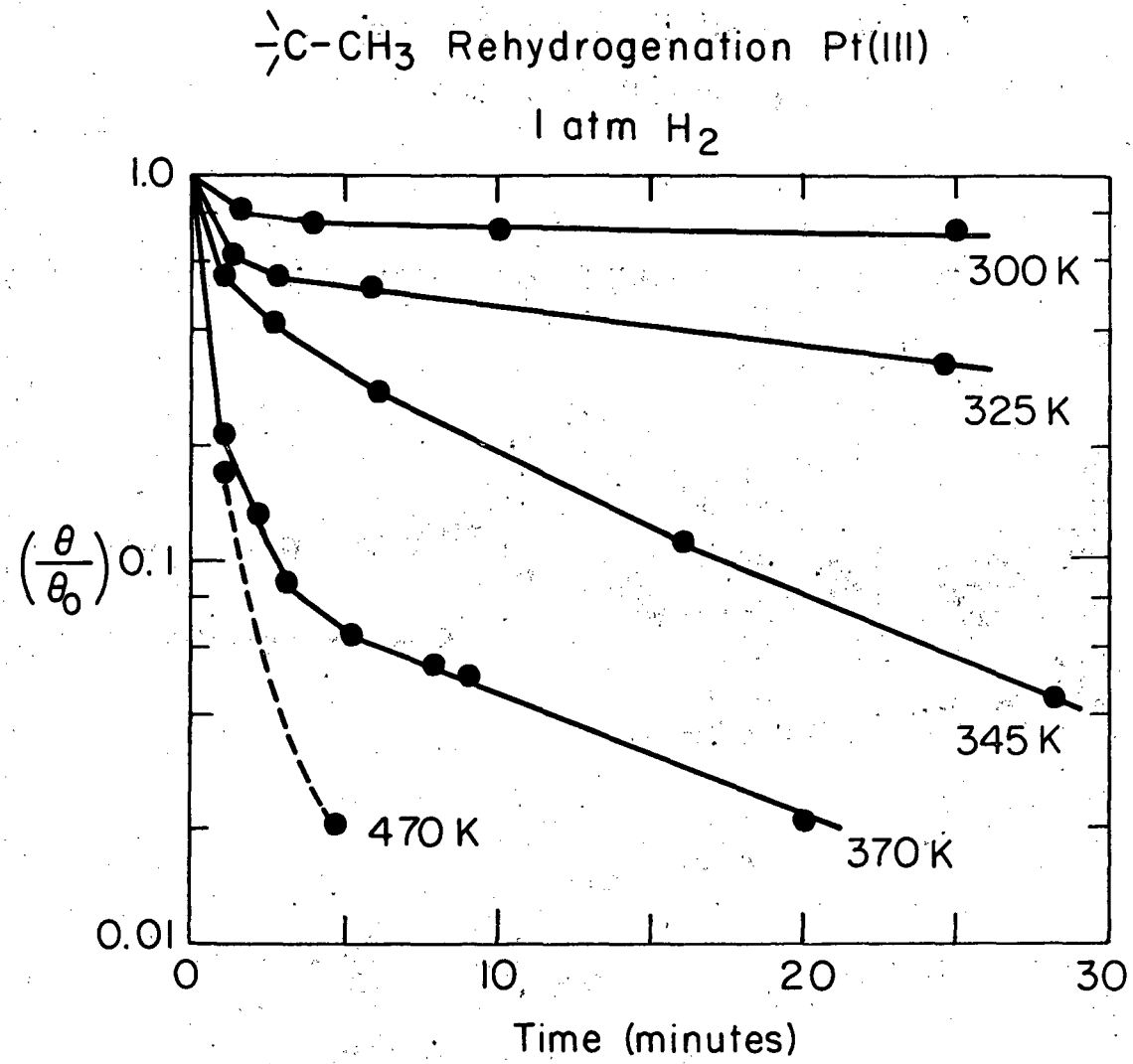
Fig. 7

Hydrogen Content of the Adsorbed Layer



XBL 808-5684A

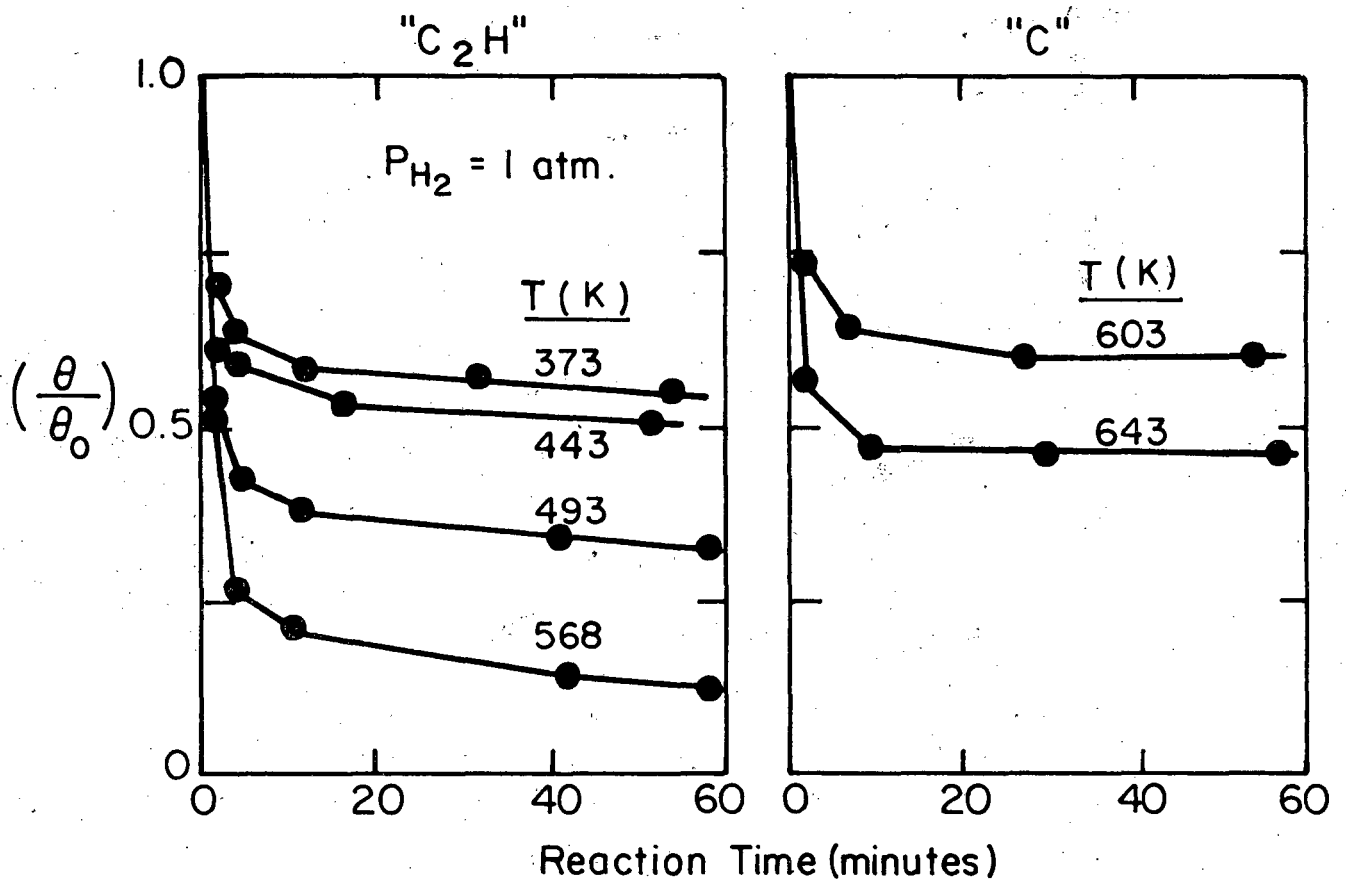
Fig. 8



XBL813-5385

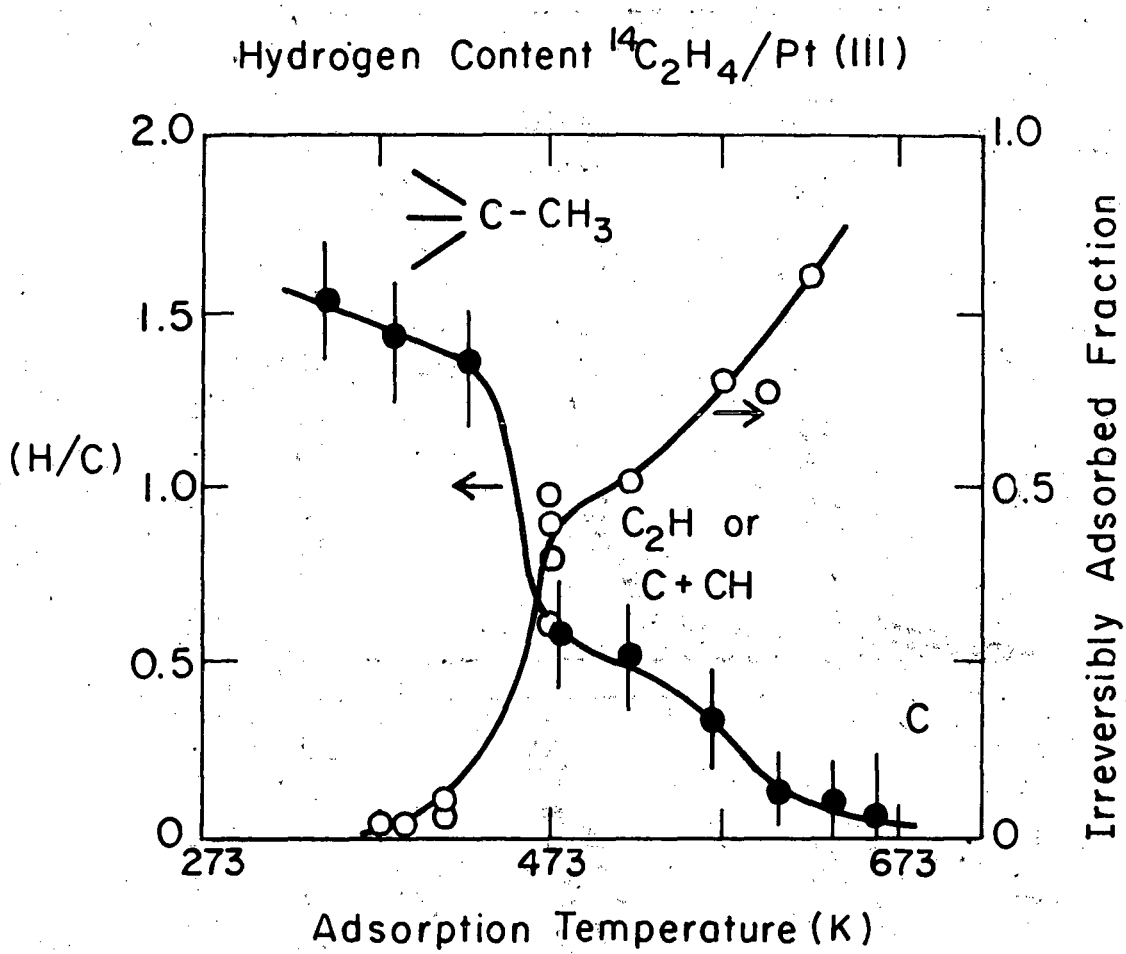
Fig. 9

Rehydrogenation of Ethylene Decomposition Products-Pt(III)



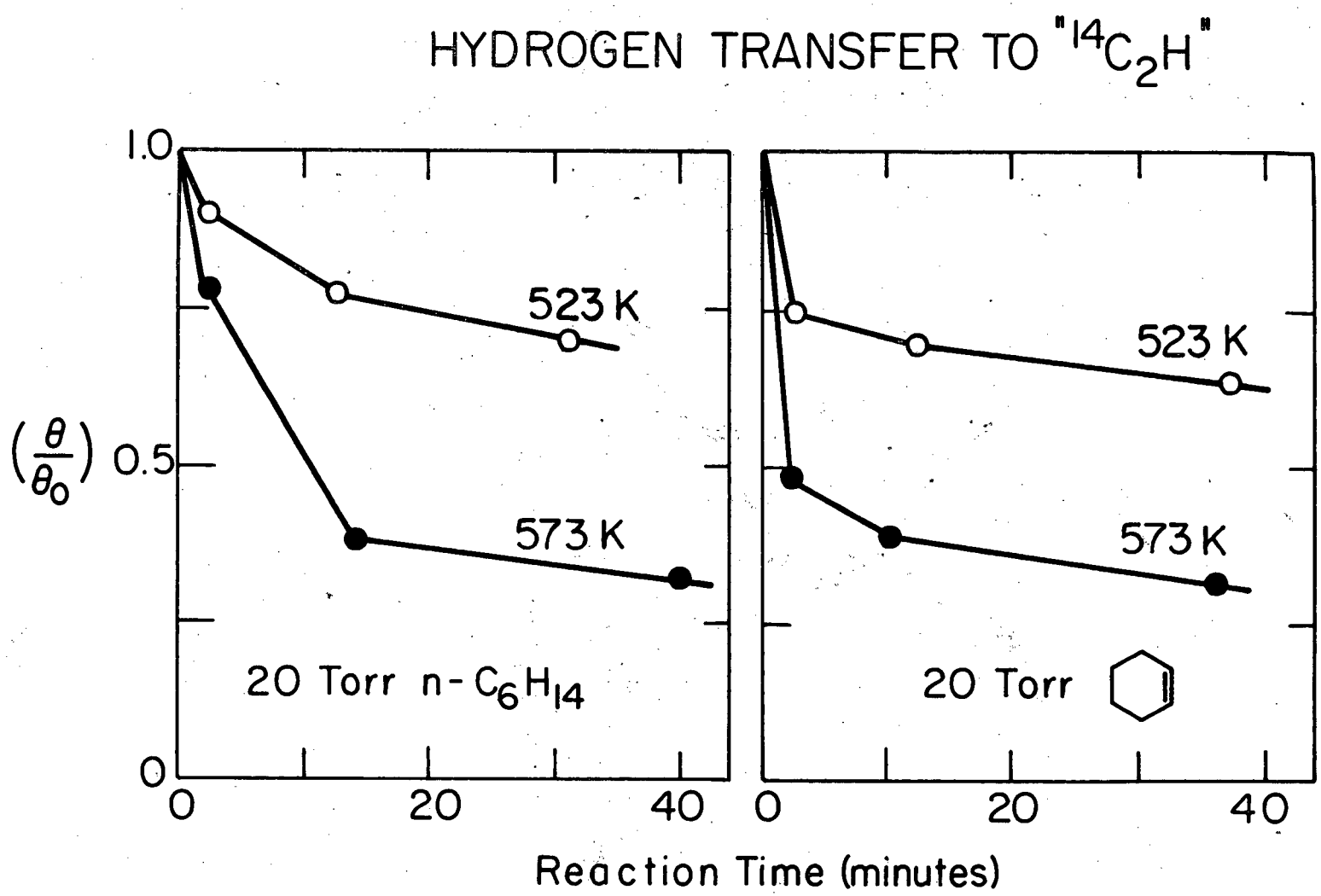
XBL 817-6083A

Fig. 10



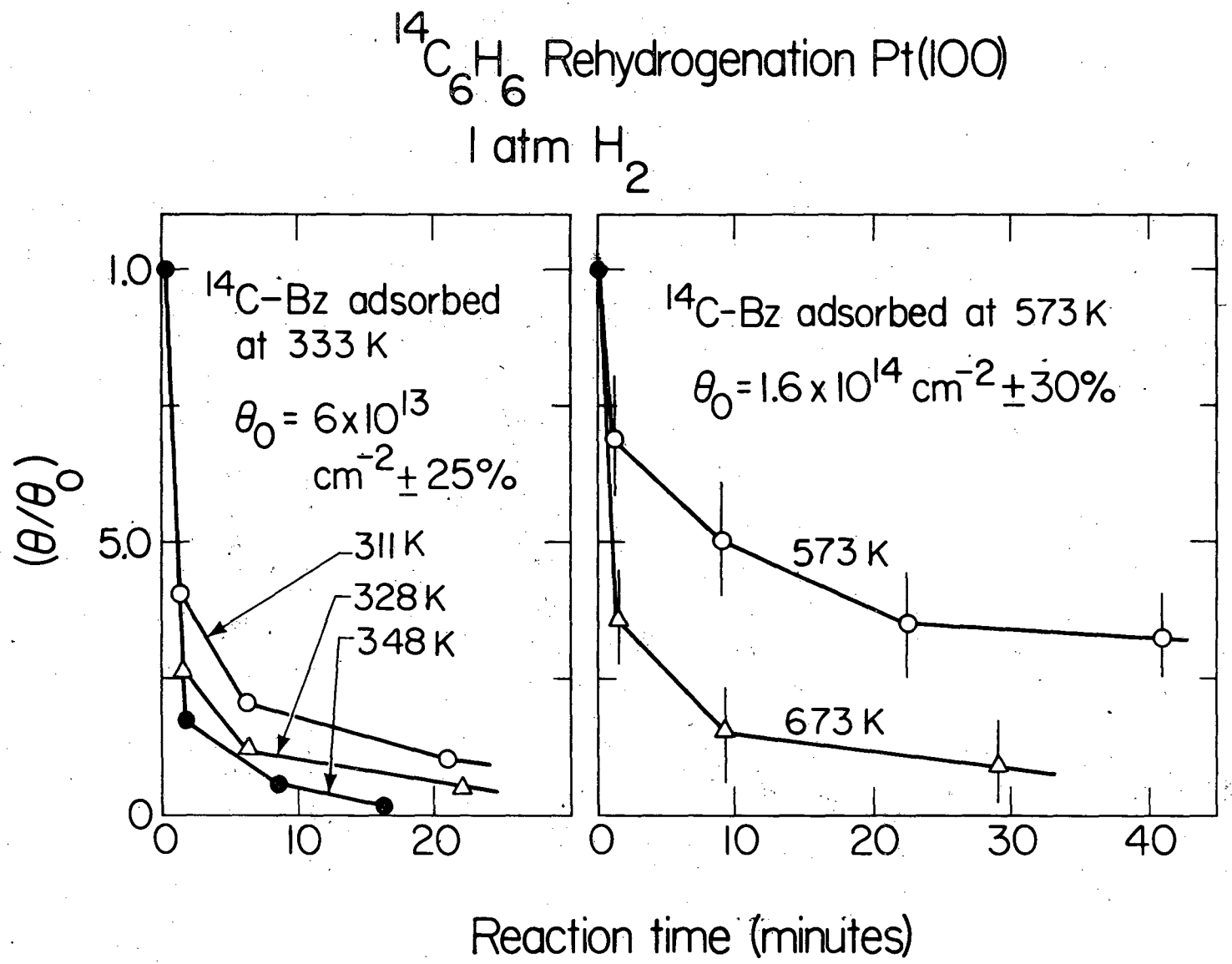
XBL 812-5151A

Fig. 11



XBL 815-5660A

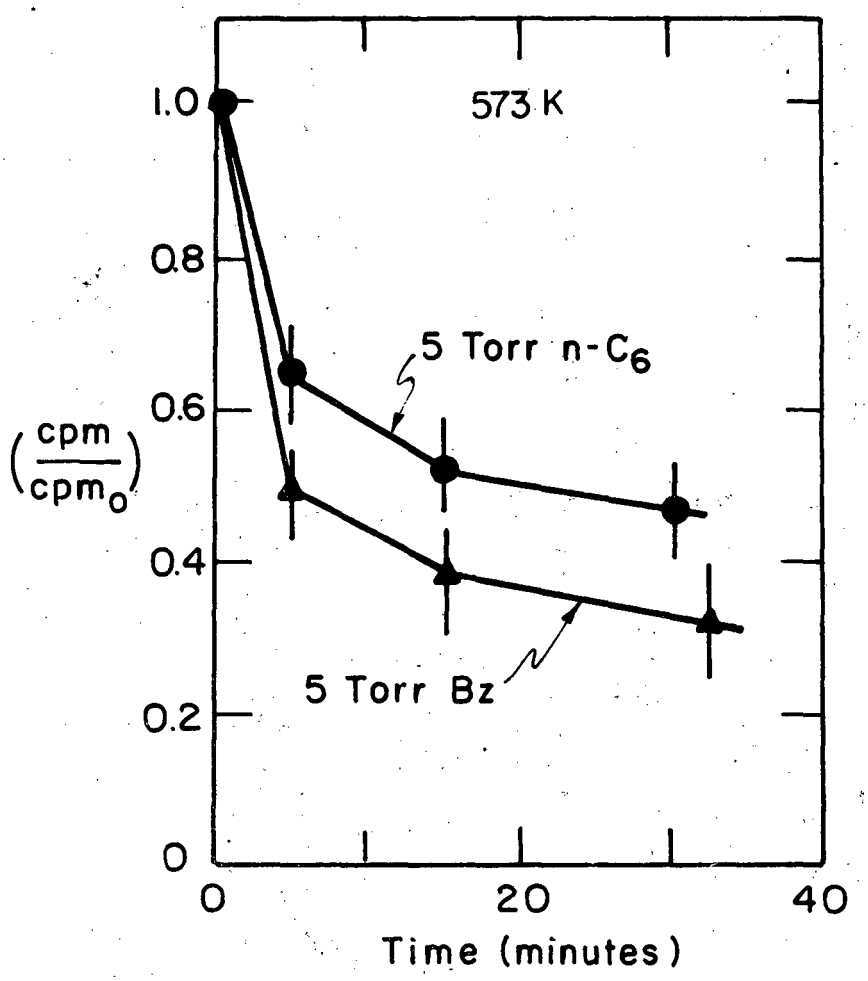
Fig. 12



XBL 818-1102A

Fig. 13

Hydrogen Transfer from Unlabelled Hydrocarbons to $^{14}C-C_6H_6$ Deposited on Pt(111) at 573 K



XBL 808-5690A

Fig. 14

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