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Min-Chi Tsai
(Ph.D. thesis)

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HYDROCARBON SURFACE CHEMISTRY OF PLATINUM AND NICKEL

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(Ph.D. Thesis)

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Hydrocarbon Surface Chemistry of Platinum and Nickel

Min-Chi Tsai

ABSTRACT

The hydrocarbon surface chemistry of Pt and Ni as related to heterogeneous catalysis was pursued in this thesis research. The key issue was to delineate the electronic, compositional and stereochemical features and reaction mechanisms of hydrocarbon adsorbates that facilitate the scission and formation of C-H and C-C bonds. These studies were performed under ultra high vacuum conditions, over a series of crystallographic planes of Pt and Ni.

Reactions of acetylene and hydrogen on Pt(111) and Pt(100) were investigated using primarily thermal desorption spectroscopy and isotopic labeling techniques. Distinguishing features of C-H bond breaking and forming between acetylene and hydrogen as a function of surface crystallography, temperature and pressure were established.

The coordination chemistry of benzene, toluene and pyridine on flat and stepped Pt and Ni surfaces has been defined by chemical displacement reactions, thermal desorption spectroscopy and isotopic labeling studies. Important electronic and stereochemical features of C-H bond breaking and making processes for aromatic hydrocarbons were identified, and distinctive differences between Pt and Ni surfaces were established from this study.

Reactions of cyclic hydrocarbons on flat and stepped Ni and Pt surfaces were investigated using the same approach as for the aromatic hydrocarbons. Dehydrogenation of cyclohexane, cyclohexene and 1,3- and 1,4-cyclohexadiene to form benzene was studied as a function of metal surface, surface crystallography and composition. H-D exchange reactions during dehydrogenation, resulting in all possible mixed benzene species, were evident on all the Pt surfaces studied. Dehydrogenation of C_8 cyclic olefins also led to the formation of delocalized ring species--cyclooctatetraene on a Pt surface. Using selectively labeled molecules, the reaction mechanism for cycloheptatriene conversion to benzene on Ni(100), and for norbornadiene conversion to benzene on Pt(111) and Pt(100) have been incisively studied.

Earl L Muetterties

TO MY PARENTS

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I. INTRODUCTION

The understanding of heterogeneous catalysis at the molecular level is of fundamental importance in surface science.[1,2] Despite the efforts made in the past years, the nature of heterogeneous catalysis is still not clearly defined yet. Much of this is due to the complexity of catalytic transformation under different conditions: temperature, pressure and gas phase composition. Furthermore, the metal catalysts are usually poorly characterized both compositionally and structurally. Therefore, it is both important and necessary to be able to deconvolute the complicated catalytic processes into separate components in order to define the elementary processes of catalytic reactions.

To achieve this goal, a relatively "clean" environment and well-defined metal surface are minimum requirements to begin with. During the past decade, vacuum technology has been rapidly advanced such that an ultra high vacuum system with a typical base pressure of $< 1 \times 10^{-10}$ torr and main residual gases of H_2 and CO can be obtained relatively easily. Along with the advancement of vacuum technology, numerous surface physical techniques that are both ultra-high-vacuum-compatible and surface-sensitive became available for chemisorption studies on single crystal metal surfaces, so that chemisorption processes can be examined on crystallographically and compositionally well-characterized metal surfaces. Important surface physical techniques that are applied routinely are Auger electron spectroscopy, low energy electron diffraction and mass spectrometry which are used for analyzing surface composition, symmetry of ordered surface structures and gas phase composition, respectively. Others which usually require more sophisticated experimentation are: angle-resolved photoemission spectroscopy which yields information about electronic structure and orientation of chemisorbed species, and high resolution electron energy loss spectroscopy which probes vibrational properties of surface species. Although these techniques are widely utilized for surface characterization, none alone can unambiguously provide a complete structural description of chemisorption processes. Consequently, there is a need to apply chemical and physical techniques to surface studies.

Metal surface chemistry, to a first approximation, should have its formal analog to the well-established coordination chemistry of molecular metal complexes, particularly molecular metal clusters.[3] Discrete metal cluster compounds typically consist of three or more metal atoms to form triangular, or polyhedral arrays, which are surrounded by several ligands--atoms (group of atoms), and molecules. The common triangular facial structure of clusters is analogous to the close-packed metal surface structure, and chemisorption of atoms, or molecules on the metal surface resembles the bonding of ligands to the metal clusters. Therefore, the well-established stereochemistry of metal clusters can be a potential guideline to the understanding of the stereochemistry of chemisorbed species, and experimentally well-defined ligand migration on metal clusters can be a potential model for surface mobility of chemisorbed species. Furthermore, the cluster chemical reactions such as the scission of C-H and C-C bonds are commonly found in the interaction of hydrocarbon molecules with metal surfaces, and the cluster-catalyzed reactions such as hydrogenation, isomerization and cyclization, to name a few, are all important catalytic reactions on metal catalysts. Hence molecular metal clusters should provide reasonable approximations of chemisorption processes on the metal surface.

Chemical displacement reactions are structural and stereochemical probes that have been effectively utilized in the delineation of molecular metal complexes. Similar utilization of chemical displacement reactions on single crystal metal surfaces under ultra high vacuum conditions, guided by analogy to the established coordination chemistry, should provide a supplementary set of data.[4] Such a combination of surface chemical and physical techniques will assist a better molecular understanding of chemisorption processes.

A surface study ideally begins with a metal surface with known surface composition and structure. Surface elemental analysis is established by Auger electron spectroscopy[1] in which high energy electrons (1-3 keV) are directed at the metal surface at an angle of 15°, and the ejected, secondary "Auger" electrons, which have their characteristic energy distribution of each element, are analyzed subsequently. Auger electrons with energies of 50 to 100 eV have escape depths of approximately 5 Å . Therefore, Auger electrons emit primarily from the top two layers, although the contribution from deeper layers cannot be totally ignored. The Auger analysis is sensitive to most elements, but is sometimes complicated by the overlapping Auger peaks from different elements. Also, some typical surface impurities, e.g. O and N, have relatively low Auger transition probabilities so that care must be taken in analyzing these elements. If other evidences indicate that the adsorbate does not penetrate into the metal substrate, the relative Auger peak height of the adsorbate to that of the metal itself can serve as a relative measurement of adsorbate concentration.

Low energy electron diffraction is a diagnostic tool for ordered surface structures.[1] A collimated electron beam of 10 to 500 eV is directed at the surface and the diffracted electron beam is accelerated onto a phosphorescent screen for visual display. The diffraction pattern can readily yield information about the symmetry and unit cell of the surface structure. However, the precise atomic positions can only be located by elaborate theoretical calculations using a complex electron scattering theory. Only the simplest chemisorption systems, e.g. sulfur on Ni(100),[5] acetylene on Pt(111)[6] and CO on Ni(100),[7] have been carefully examined up to now. There also is the potential problem in electron diffraction (and Auger) studies of electron initiated decomposition of adsorbates.

A chemisorption experiment begins with a clean, oriented crystal surface as established by Auger electron spectroscopy and low energy electron diffraction. The adsorbate molecules are introduced by a leak valve which is equipped with a metal tubing directed at the crystal so that a directional flow of molecules from the manifold to the crystal face within the vacuum chamber can be produced. The chemisorption state(s) is examined by Auger analysis and ordered adsorbate structures can be detected by a low energy electron diffraction study. At this point, the thermal reversibility of the chemisorption processes can be explored by thermal desorption spectroscopy. Adsorption of gaseous molecules takes place at a pre-selected temperature that is well below the thermal desorption temperature. In thermal decomposition experiments, a linear heating of the crystal (typical heating rate is 25°/sec) is effected after the dosing gas is well evacuated. A mass spectrometer is used for monitoring gas phase products from thermal desorption experiments. In a fully reversible desorption process, a clean metal surface is regenerated and the desorbed molecules can be identified by mass spectrometric analysis. If the thermal reactivity of the adsorbate species is high, competing processes such as thermal decomposition and surface reactions will lead to evolution of other gaseous products that can be monitored by mass spectrometric analysis. Residual elements on the crystal after this experiment can be measured by Auger electron spectroscopy. The identification of the volatile desorption products is based on the mass spectral fragmentation pattern. Uncertainty can arise when the product molecules can exist as more than one isomer and when several product molecules have similar fragmentation patterns.

Complementary to thermal desorption spectroscopy is the chemical displacement reaction which can be effected with minimal surface temperature variation thereby minimizing the thermal reactivity problems. The molecule to be displaced is adsorbed onto the surface initially at a temperature well below any significant desorption or decomposition stage, and the displacing molecule is introduced through the doser while monitoring the gas phase by mass spectrometry. Ideally, the molecule to be displaced should contain at least one element not common to the other so that Auger analysis before and after displacement can give a qualitative measurement of the extent of the displacement reaction. In principle, a molecule that is associatively chemisorbed on the metal surface should be displaceable by a stronger field ligand molecule. A classic example is the facile displacement of acetonitrile on the Ni(111) surface by CO.[8] Normally, the effectiveness of the displacement reaction is dependent upon the activation energy of the displacement reaction. For example, in the case of dissociative chemisorption: oxygen on Ni(111), displacement of oxygen molecules by another molecule requires recombination of chemisorbed oxygen atoms which is a thermodynamically unfavorable process at least at 25°C, and none has been observed yet. Negative displacement reactions essentially provide no definitive structural information about chemisorption states. The detection of isomeric transformation upon chemisorption can be accomplished provided that these isomers exhibit very different bond strength. The failure of displacement of methyl isocyanide[8] was taken as an evidence that the molecule was not isomerized to acetonitrile because the latter is subject to facile displacement by CO at 25°C. The displacement reaction can be performed at any temperature to probe the course of surface reactions, but the maximum temperature range is limited by the temperature of molecular desorption or of irreversible molecular decomposition of the adsorbate.

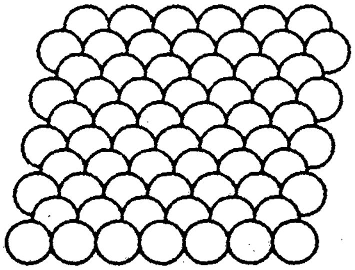
The isotopic labeling technique is combined with thermal desorption experiments and chemical displacement reactions in order to gain mechanistic insight into the chemisorption processes. For reversible desorption or a chemical displacement of chemisorbed molecules, it is possible that these molecules undergo reversible dissociative chemisorption state prior to the desorption process or displacement reaction. Using a mixture of isotopically-labeled adsorbate molecules, it is possible to discern whether there are any measurably fast, reversible bond breaking processes. Isotopic labeling is also used for probing the completeness of displacement reactions. For example, one can use a perdeuterated molecule for initial chemisorption, and a non-deuterium containing molecule for displacement, a thermal desorption study following the displacement reaction probing for the presence of HD, D_2 or other deuterium-containing species will provide a characterization of degree of completeness of displacement. A selectively labeled hydrocarbon molecule with ^{13}C or ^{2}H isotopes can be used for characterization of a regioselective C-H bond breaking process of hydrocarbon adsorbate. For example, the low-temperature C-H bond breaking process for toluene chemisorbed on a Ni(111) surface was established[9] to be selectively centered on the methyl group by monitoring thermal desorption profiles of H_2 and D_2 from a Ni(111)-$C_6H_5CD_3$ (or $C_6D_5CH_3$) chemisorption state. In reversible desorption studies, when multiple thermal desorption maxima are observed and the population of each peak appears to be a function of surface coverage, sequential chemisorption of unlabeled and isotopically labeled molecules can infer whether a rapid migration between differentiable states occurs within the time scale of experiments (minutes). This is effected by sequential chemisorption of the two molecules with pre-selected exposures, according to the coverage dependence of thermal desorption, and then monitoring the desorption maxima of both molecules. The absence of mixing is the positive evidence for the presence of differentiable states in which there is no rapid interchange between states on the surface.

The focus of this thesis work lies in the delineation of electronic, compositional and topographical features of hydrocarbon surface chemistry that facilitate the breaking and making of carbon-hydrogen and carbon-carbon bonds. A range of hydrocarbon molecules from C_2 to C_8 were studied over various crystallographic planes of single crystal platinum and nickel and under ultra high vacuum conditions. The surface physical and chemical techniques of low energy electron diffraction, Auger electron spectroscopy, mass spectrometry, thermal desorption spectroscopy, chemical displacement reactions and isotopic labeling were used as structural and stereochemical probes. The surfaces studied were the low Miller index planes: (111), (100) and (110) (Figure 1), which have metal surface atoms of coordination number 9, 8 and 7, respectively, as well as "stepped" surfaces of (111)-oriented terrace and step (Figure 2) (coordination number 9 and 7, respectively). The Pt(111), Ni(111), Ni(110), Ni(100), Pt 6(111)x(111) and Ni 9(111)x(111) surfaces all have (1x1) symmetry. The clean Pt(100) surface, however, underwent reconstruction to form probably a hexagonal-like overlayer which exhibited a (5x20) low energy electron diffraction pattern. Experiments were performed on surfaces free of impurities unless surface compositional effects were the focus of study.

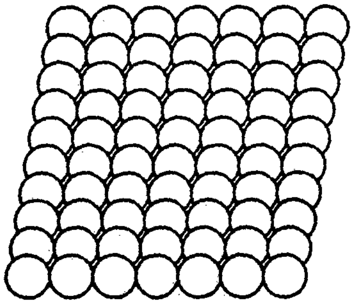
In coordinately unsaturated molecular metal complexes, a possible reaction pathway between a hydrocarbon ligand and the metal center is the generation of a three-center two-electron carbon-hydrogen-metal (C-H-M) bond[10] if stereochemistry allows. Such an interaction can lead to the scission of the C-H bond to form discrete M-H and M-C bonds (internal oxidative addition). This established coordination chemistry should have its formal analog in the metal surface chemistry.

Figure 1

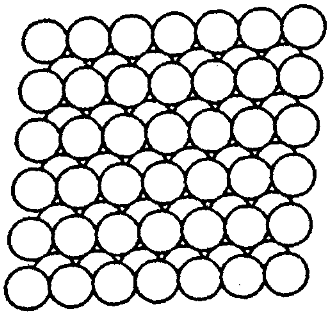
Shown in the figure are the three low Miller index planes of face-centered cubic metals such as platinum and nickel. The (111) surface, on the upper left hand side, is the close-packed, thermodynamically most stable with threefold symmetry and a surface metal atom coordination number of 9. The (100) surface on the upper right has fourfold symmetry and a surface metal atom coordination number of 8. The (110) or the so-called "super-stepped" surface on the bottom has a trough-like structure. The topmost atoms have a coordination number of 7 and the trough atoms, lying half a lattice constant below the plane, have a coordination number of 11.



fcc (111)



fcc (100)

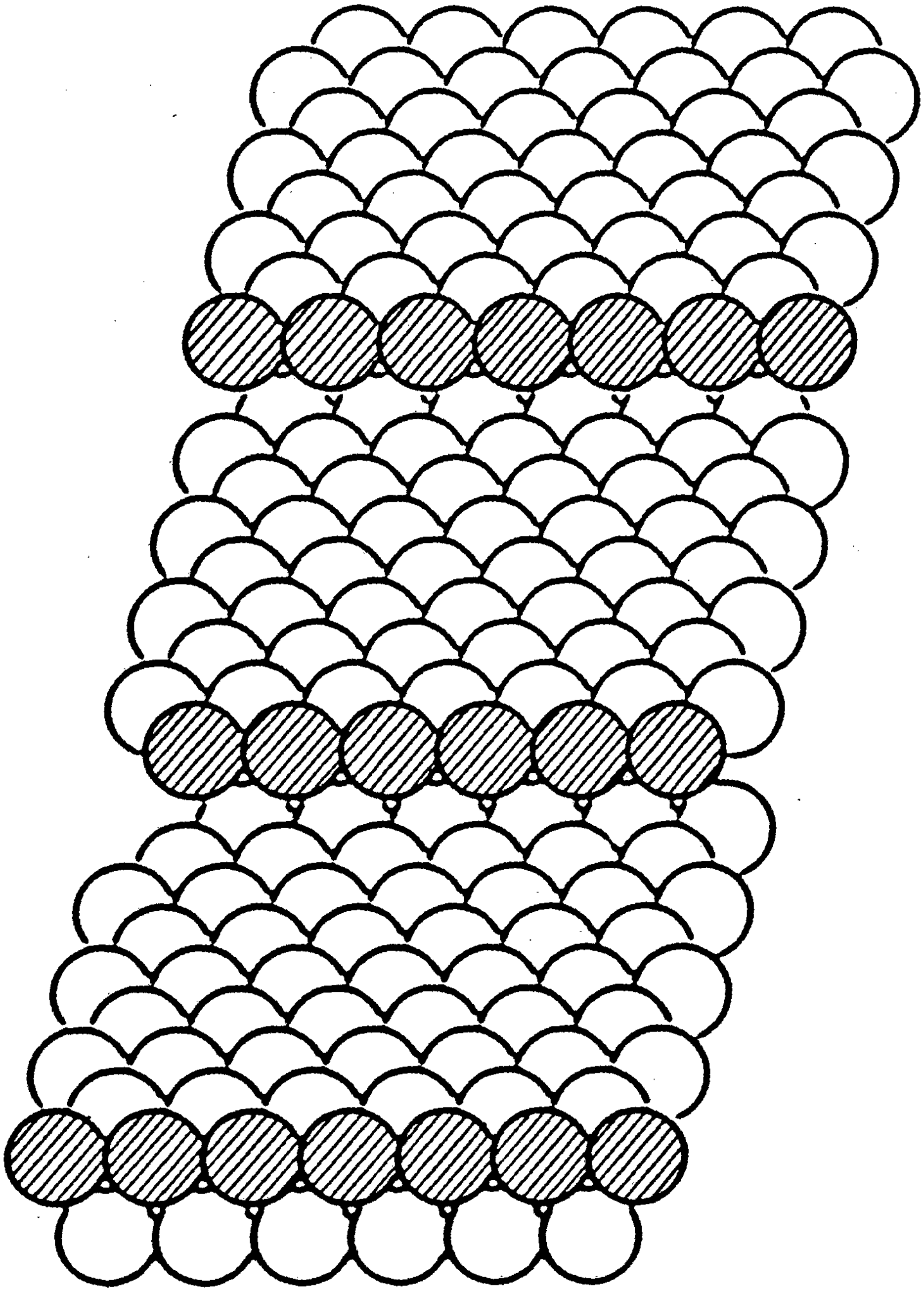


fcc (110)

XBL 802-8036

Figure 2

Illustrated is a stepped surface of an fcc metal designated as M 9(111)x(111). The terrace atoms (open circles) are of (111) orientation, with a coordination number of 9, and the stepped atoms (shaded circles) are also of (111) orientation but have a coordination number of 7. The terrace of this surface is nine-atom wide and the step is of one-atom height.



fcc 9(111)x(111)

XBL 802-8091A

It is postulated that if the stereochemistry of hydrocarbon chemisorption is such that some of the C-H hydrogen atoms are forced to closely approach the surface metal atoms, the C-H-M multicenter interaction will occur. It is noted that under ultra high vacuum conditions, the surface hydrogen atom activity and the concentration of surface hydrocarbon species are relatively low at least with respect to such states at atmospheric pressures. Therefore, C-H bond breaking will be favored relative to C-H bond making. In the chemisorption of unsaturated hydrocarbon molecules, initial interaction should be largely through the energetically more favorable π and π^* orbitals and metal surface orbitals. If some C-H hydrogen atoms on the saturated carbon centers come close to the metal surface because of the stereochemistry of chemisorption, C-H-M multicenter interaction will develop and C-H bond breaking may occur. For cyclic olefins and polyenes (c-C_nH_m) particularly, dehydrogenation to form a delocalized c-C_nH_n species should be an energetically favored process. For hydrocarbons with n an even number, c-C_nH_n species formed by dehydrogenation of parent molecules should be potentially displaceable by another molecule under ultra high vacuum conditions, whereas for hydrocarbons with n an odd number, the c-C_nH_n species cannot be displaced or desorbed, and can only be characterized by photoemission or high resolution electron energy loss spectroscopy. Conversion of olefinic c-C_nH_m (n equals an odd number) to an even-membered cyclic hydrocarbon species requires scission of carbon-carbon bonds which in principle requires relatively high temperatures.

Cyclohexane is thought to coordinate to the flat Ru(0001) surface through several C-H-Ru interactions initially:[11] at 90 K, it exhibits a strong vibrational loss (the so-called C-H "soft" mode) at 2590-2720 cm^{-1} in addition to the normal C-H stretching at 2900-3000 cm^{-1}. Moreover, subsequent dehydrogenation of cyclohexane to benzene is observed at ~ 200 K. A systematic study of ethane, cyclopropane, cyclohexane and cyclooctane adsorption on a Ru(0001) surface[12] has shown that the activation energy of thermal desorption increases monotonically with the number of carbon atoms. It suggests that the molecules are bound in such a way as to maximize the C-H-Ru multicenter interaction, and the bond strength of each multicenter is of the same order of magnitude. On Ir(110), cyclopropane initially dissociatively adsorbs on the surface[13] to give free hydrogen on the surface.

The reactions of C-H bonds with metal surfaces seem to involve the initial development of C-H-M multicenter interaction. It is the purpose of this study to investigate this important postulate of hydrocarbon surface chemistry, and to explore the regions where this postulate breaks down.

II. EXPERIMENTAL

Experiments were conducted in an all-metal bakeable, ultra high vacuum chamber (Varian Assoc.) with a base pressure of $< 2 \times 10^{-10}$ torr. High pumping speeds were achieved by a ring of five 60 liter/sec Triode Ion Pumps (Varian Assoc.) and a titanium sublimation pump, and higher pressure evacuation of the chamber was accomplished by oil-free liquid nitrogen cooled sorption pumps.

The work chamber was equipped with a four-grid, low energy electron diffraction (LEED) optics (Varian Assoc.), which also served as a retarding field analyzer for Auger electron spectroscopy (AES), and a multiplexed quardrupole mass spectrometer (Uthe Technology International, Model 100C). Glancing incidence electron guns for Auger analysis and ion bombardment were used to increase surface sensitivity.

The platinum crystals were spark cut from a single crystal rod (99.999% purity, Materials for Research Corp.) and oriented by Laue X-ray back reflection to within ± 0.5° of the desired crystallographic planes. A wafer of ~ 0.25 inch in diameter and ~ 0.10 inch in thickness was cut into a circular ridge to leave the exposed surface to become ~ 0.19 inch in diameter so that it could be held in the tantalum sample holder (Varian Assoc.) by insertion of a tantalum ring in between them. The sample was then mechanically polished with four grades of alumina papers (the finest particle size of the alumina papers was ~ 10 microns), followed by 1 micron diamond paste and 0.05 micron alumina in water. The crystal surface was checked under the microscope to ensure the absence of pitting or scratches, and a Laue X-ray reflection photograph was taken to be sure that correct orientation was achieved. Before being placed into the chamber, the crystal was chemically etched with warm (~ 60°C) aqua regia for 10 seconds, and rinsed with distilled water and ethanol. This last step helped remove impurities such as Si and Ca.

The crystal was mounted on a manipulator with 2.5 inch offset and 110° flip mechanism (Varian Assoc.) which could carry x-y-z motion and 360° rotation. A button heater (Spectra-Mat, Inc.), consisting of a tungsten filament imbedded in ceramic, was used to indirectly heat the crystal by mechanical contact. A linear heating rate of 25°/sec from 50 to 600°C was typically achieved. Crystal temperature could be varied from 25°C to 1200°C and was monitored by chromel-alumel thermocouple wires (0.005 inch in diameter) spot-welded onto the tantalum ring. A liquid nitrogen cooled, oxygen-free copper block was used to cool the sample from 400°C to 25°C (cooling rate is ~ 40°/min) by mechanically contacting the crystal mount.

The Pt(111) and Pt 6(111)x(111) surfaces were cleaned mainly by O_2 treatment (~ 1×10^{-7} torr O_2 at 900-950°C) and subsequent flashing to ~ 1100°C. The major impurities: P, S and C were usually removed by repeating this cycle. Si and Ca, although present in smaller quantities, were more difficult to remove because of the formation of stable, subsurface oxides. High temperature (1100°C to 1200°C) annealing for prolonged period of time assisted removal of these impurities. If Ca was still present, the crystal was removed from the chamber and retreated with aqua regia. The cleaning procedure for the Pt(100) surface was different from the above two crystals: P, Ca, Si, and S were removed by argon ion bombardment (700 eV electron beam and ~ 3×10^{-5} torr of Ar) at room temperature followed by annealing at ~ 800°C. Carbon removal was effected in ~ 1×10^{-7} torr O_2 atmosphere at ~ 830°C, and the small amount of oxide was decomposed at ~ 1100°C.

Auger electron spectroscopy was used to monitor course of cleaning until none of the impurity peaks were visible. At this point, low energy electron diffraction observation of the surface revealed the diffraction pattern characteristic of the particular crystallographic plane of interest. During the course of surface studies, LEED patterns of the surface were constantly taken, and no evidence of surface faceting was ever found.

The cutting, polishing, cleaning and surface characterization procedures for the Ni single crystals were fully described in the thesis work of Dr. C. M. Friend.[14]

Exposure of the crystal to potential adsorbates was done with dosing "needles" that were attached to the variable leak valves. The purpose was to produce a directional flow of adsorbate molecules onto the front face of the crystal which was brought to within 0.5 inch distance to the doser. During the course of exposure, the background pressure was kept below ~ 1×10^{-9} torr while the effective pressure of the adsorbate molecules on the crystal surface was approximately 10 to 100 times larger than the background. Therefore, the signal of molecules of interest to background was greatly enhanced in the thermal desorption and chemical displacement experiments.

The exposures were estimated using an uncalibrated nude ion gauge (Varian Assoc.). By backfilling the vacuum chamber with a given gas to a pressure of ~ 1×10^{-8} torr for a period of time, the exposure was recorded in terms of "Langmuirs" (1 Langmuir = 1L = 1×10^{-6} torr sec).

The integrated area in the thermal desorption of this exposure was then compared with a separate thermal desorption yield that was made by the usual exposure procedure: the front face of the crystal was directed to the doser while monitoring mass spectrometer parent (or the most intense fragment) ion current and integrating over the exposure time. Thus, a correlation between "Langmuir" exposure and the actual "doser" exposure could be established.

The carbon coverage of the Pt(111) surface throughout this thesis work was based on a plot of Pt(237eV)/C(273eV) Auger peak-to-peak intensity ratio versus absolute surface carbon coverage that was obtained by the radiotracer method.[15] The surface carbon coverage of all the other surfaces were based on Auger peak-to-peak ratio calibrated by LEED structures.

Gas composition of the vacuum chamber was monitored by a quardrupole mass spectrometer ranged from 10^{-5} to 10^{-12} Amp. A programmable peak selector (UTI, PPSD) was interfaced with the mass analyzer which allowed as many as nine mass units, with pre-selected amplifier gain and range, to be monitored in sequence. The data could later be retrieved and plotted as a function of intensity versus time. Thermal desorption experiments were conducted in such a way that the front face of the crystal was brought to within 0.5 inch distance and line-of-sight of the mass filament (ionizer). Therefore, only desorbed molecules with a vector of momentum normal to the front crystal face would most likely be detected, and consequently, desorption from the sides or supporting assembly of the crystal was greatly surpressed.

A dosing needle was equipped on each side of the mass ionizer with 45° geometry. The purpose of using two dosers was to avoid cross contamination of reactant molecules in chemical displacement reactions. Displacement reactions were performed by dosing A molecules onto the surface, followed by introducing B molecules, from the other doser, as a displacing agent while monitoring mass ion current of interest as a function of time. The detection sensitivity of the displaced molecules was unfortunately depressed with this dosing arrangement. However, with the absence of cross contamination, chemical displacement reactions could clearly be observed if they did occur.

Blank experiments were performed in both thermal desorption and chemical displacement reactions to determine whether the chemistry observed was truly associated with the front face of the crystal. A wafer of Pt single crystal was cut from the rod as described earlier. Rubber mask was applied to the side and edge of the crystal so that only the front surface of ~ 0.20 inch in diameter was exposed. The surface was then vapor deposited (in vacuum) first with copper, then with gold (each layer of ~ 200 Å thickness). The gold surface stayed homogeneous up to 400°C. The rubber mask was then removed by acetone to leave the Pt wafer with only the front surface covered by gold. Thermal desorption and displacement experiments were performed in the normal way on this "blank" crystal. It was established that contribution of the chemistry from the places other than the front crystal face was essentially non-detectable. Only three cases were chemisorption occurred on the otherwise "inert" gold surface: pyridine, acetonitrile, and methyl isocyanide were found to desorb at 90-100°C, which were distinguished from that of the respective molecules on the Pt(111) surface and could only be associated with the gold surface.

Acetylene, purchased from Matheson, was passed through a -78°C cold trap before admission to the manifold. Perdeuteroacetylene, 99 atom% C_2D_2, was purchased from Merck; mass spectrometric analysis indicated the C_2D_2 concentration was ~ 95%, Hydrogen (99.95%) and deuterium (99.7%) were purchased from Matheson and Liquid Carbonic, respectively.

Reagent grade benzene and toluene were stored over CaH_2 and used without further purification. The d_6-benzene and d_8-toluene (both from Aldrich Chemical Co., 99.+%) were handled similarly. $C_6H_5CD_3$ and $C_6D_5CH_3$, obtained from Merck & Co., were used without treatment (traces of moisture did not affect the surface chemistry). Trimethylphosphine and perdeuterotrimethylphosphine were synthesized by a modification of a literature preparation.[16,17a]

Cyclohexane (Matheson Coleman & Bell) and d_{12}-cyclohexane (prepared from C_6D_6 + D_2) were dried over Na_2SO_4 and used without further purification. The cyclohexane contained no detectable (permanganate test) amount of unsaturated hydrocarbons. Cyclohexene (Chem. Samples Co., 99.9% purity) and d_{10}-cyclohexene (Merck Isotopes, 99%-d_{10}) were dried over CaH_2. 1,3-cyclohexadiene and 1,4-cyclohexadiene (Chem. Samples Co.) were stored in the vapor phase in high vacuum flasks at 0°C.

Cyclobutene was synthesized[17a] via Diels-Alder reactions of 1,3,5-cyclooctatriene and dimethylacetylenedicarboxylate.[17b] The purity of cyclobutene was checked by mass spectrometry and no trace of other olefins was detected. Cyclopentene, purchased from Matheson Coleman & Bell (~ 98% purity) was stored in high vacuum flasks at 0°C and used without further purification. Cyclobutane was obtained from Columbia Organic Chemicals, Co., Inc. and used without further treatment.

1,3,5-cycloheptatriene (Matheson Coleman & Bell, 95.+% purity), norbornadiene (Aldrich, 99% purity), 1,3,5,7-cyclooctatetraene, 1,3- and 1,5-cyclooctadiene (Aldrich, all of 98% purity), and cis-cyclooctene (Chem. Samples Co.) were used without further treatment.

Preparation of 7-d_1-cycloheptatriene[17a] was via the intermediacy of tropylium tetrafluoroborate and was analogous to the cycloheptatriene synthesis reported by Muller and Fricke[18] except that $NaBD_4$ was substituted for $NaBH_4$. This compound was checked by mass spectral analysis and ^1H-NMR spectrum; there was no detectable benzene present, and the triene was judged to be >95% 7-d_1-cycloheptatriene. 7-d_1-norbornadiene was synthesized[17a] by Na/t-BuOD reduction of 7-chloronorbornadiene in THF.[19] This compound was purified by preparative gas chromatography using a 10' carbowax 20M on Chromosorb W-AW-DMCS column at 60°C. Mass spectral analysis indicated a purity of >95% 7-d_1-norbornadiene and no detectable amount of benzene was seen.

Reagent grade pyridine and d_5-pyridine (Merck Isotopes, 99%-d) were dried over CaH_2 before being used. 2,6-d_2-pyridine, 3,5-d_2-pyridine and 4-d_1-pyridine were prepared by a slight modification of the method of Bak et al.[20]

III. CHEMISTRY OF ACETYLENE ON PLATINUM (111) AND (100) SURFACES

Acetylene is the simplest unsaturated hydrocarbon. Its geometric structure,[21] electronic structure[22] and interactions with organometallic complexes[3] are relatively well defined. Chemisorption of acetylene on metal surfaces has also been a subject of wide interest, especially the chemisorption of acetylene on the crystallographically well-defined transition metal surfaces under ultra high vacuum conditions.[23]

Acetylene chemisorption has been studied by low energy electron diffraction,[6,24-28] ultraviolet photoemission spectroscopy,[29-33] thermal desorption spectroscopy,[32] and high resolution electron energy loss spectroscopy,[34-36] particularly on Pt(111). Low temperature (100-300 K) adsorption of acetylene on the Pt(111) yields a π -bonded chemisorption state with certain degree of rehybridization as suggested by both photoemission and vibrational spectroscopy. At $T > 300$ K, the associatively chemisorbed acetylene undergoes an irreversible transformation to form a new, stable "state" based on an ordered (2x2) low energy electron diffraction pattern being generated after annealing the surface at 350-400 K for one hour, and on the detection of a new surface species in high resolution electron energy loss spectroscopy by either reacting the chemisorbed acetylene with 10^{-7} torr of atomic hydrogen at 350 K for 3 minutes, or annealing a Pt(111)-C_2H_2-H surface at 400 K for one minute. The new acetylene surface species formed at temperatures greater than 300 K on Pt(111) have been proposed as CH_3C,[6,28] CH_3CH,[35,36] and CH_2CH.[33] Careful examination of acetylene chemisorbed on the Pt(111) surface at ~ 300 K by ultraviolet photoemission spectroscopy[30-32] is reported to be in agreement with a σ -bonded HCCH or CCH_2 species. Similar photoemission studies for acetylene chemisorbed on the Pt(100) surface[37] at 150-330 K suggest that the major adsorbate is a complexed HCCH species.

In this study, the reaction of acetylene and hydrogen on the Pt(111) and Pt(100) surfaces was investigated as a function of surface temperature. The purpose was to establish the temperatures where carbon-hydrogen bond breaking and bond making processes were measurably fast under low hydrogen pressures of 10^{-6} to 10^{-11} torr. Isotopic labeling was the diagnostic tool for detecting surface exchange of hydrogen and deuterium from C-H bond breaking and making reactions. Therefore, this probe sensed only those surface C-H bond breaking processes where a C-H bond was converted to a surface-H bond and where the surface-H species had a finite lifetime, but not those processes that might proceed by a 1,2 shift of a hydrogen atom in the adsorbed HCCH species. The temperature range examined was -10°C to 135°C for the Pt(111) and 20°C to 160°C for the Pt(100) surface in which the high temperature limit was set by the free hydrogen desorption maximum which will be described in details later.

Results and Discussion

The thermal desorption behavior of acetylene chemisorbed on Pt(111) at 20°C was first studied as a function of surface coverage. Thermal decomposition of chemisorbed acetylene was the only process detected at relatively low acetylene coverage (< 0.5 C/Pt): hydrogen (H_2) was the only gaseous product with maximal desorption rates occurring at ~ 240°C and ~ 380°C and relative intensities of 1:1, consistent with earlier reports.[32] If perdeuteroacetylene was used,

D_2 desorption maxima would be slightly higher: ~ 245°C and ~ 380°C. At high initial acetylene coverage (> 0.5 to 0.6 C/Pt), the thermal desorption study also showed a small (< 25%) reversible acetylene desorption peak at 160°C. At comparable high coverages, heating of a Pt(111)-C_2H_2-C_2D_2 surface gave all three possible acetylene molecules with desorption maximum of ~ 160°C. Attempts to displace acetylene from Pt(111)-C_2H_2 at 20°C with strong field ligands such as trimethylphosphine and methyl isocyanide were not successful. However, thermal desorption from Pt(111)-C_2H_2-$P(CH_3)_3$ did yield far more acetylene than did acetylene on Pt(111) alone at similar coverage. Trimerization of chemisorbed acetylene to benzene on the Pt(111) surface was never observed for the entire range of surface coverage studied (up to ~ 0.7 C/Pt).

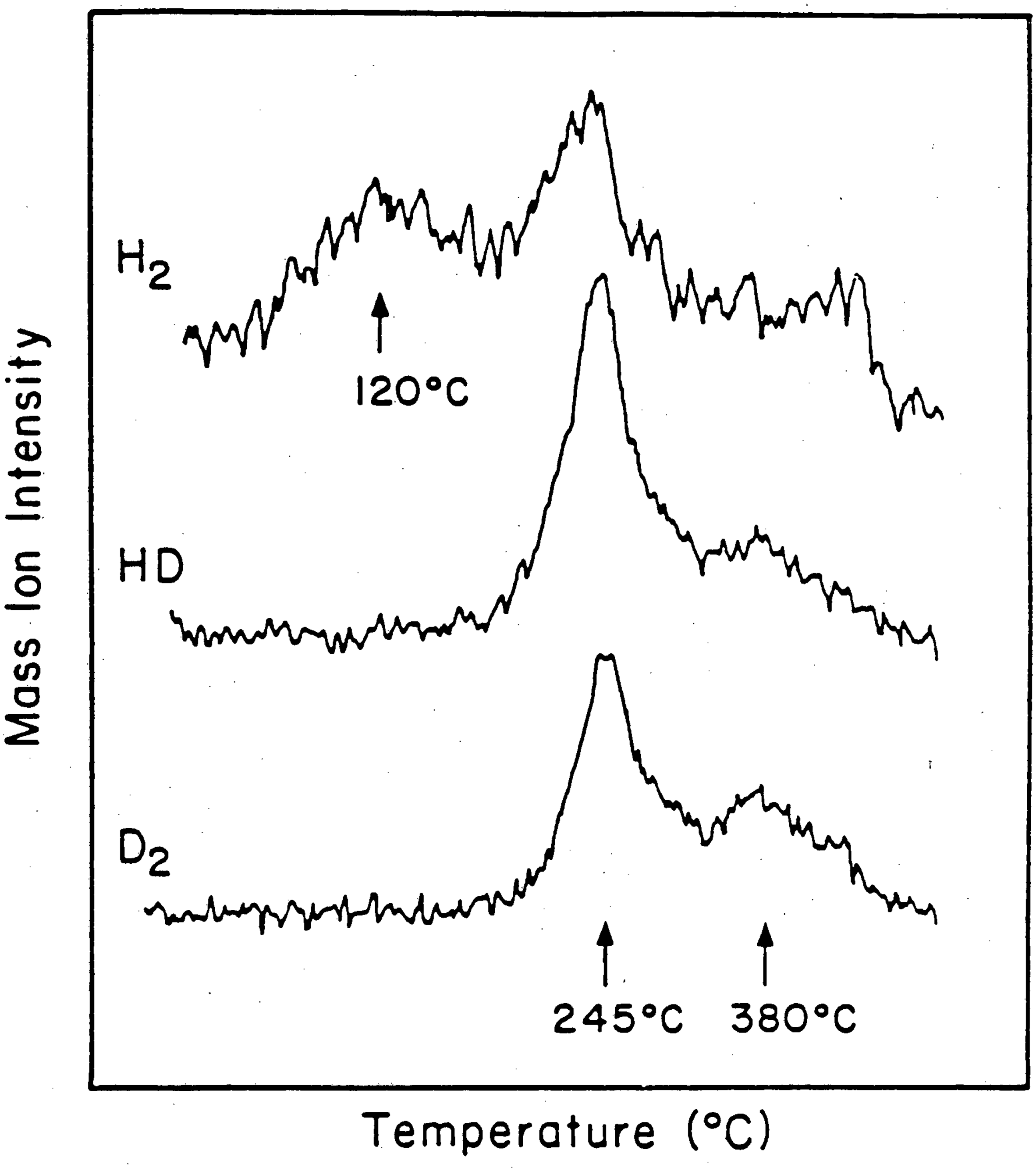
Room temperature adsorption of hydrogen on the Pt(111) surface is dissociative in nature, and desorption of molecular hydrogen is a sensitive function of heating rate and surface coverage. A typical range for hydrogen desorption maximum is ~ 50-150°C at a heating rate of 25°/sec; the temperature maxima for deuterium are slightly higher than those of hydrogen at comparable coverage.

The behavior of a Pt(111) surface co-adsorbed with H_2 and C_2D_2 was studied by thermal desorption. Pt(111)-H-C_2D_2 surfaces were generated at temperatures ranging from -10°C to 50°C and immediately studied by thermal desorption spectroscopy. The resultant spectra consisted of an H_2 desorption maximum at ~ 120°C, characteristic of desorption from a Pt(111)-H surface, two D_2 desorption maxima at ~ 245°C and ~ 380°C, and very small HD desorption at ~ 245°C and ~ 380°C; no D_2 or HD was detected at temperatures characteristic of free hydrogen desorption. The appearance of HD is largely ascribed to the overlap of the broad desorption peaks at ~ 120°C and ~ 245°C for Pt(111)-H and the low-temperature C_2D_2 decomposition process, respectively, and to a small amount (~ 5%) C_2HD contamination in the C_2D_2 sample. Thus under these conditions, there was no significant reaction between chemisorbed acetylene and surface hydrogen atoms.

In contrast to the above experiments, Pt(111)-H-C_2D_2 surfaces annealed at 50°C, 75°C, 100°C and 135°C, respectively, for periods of 1-5 minutes resulted in a significantly different thermal desorption pattern. A representative result was shown in Figure 3 for a 135°C reaction. As in the lower temperature experiments (without annealing processes), the hydrogen molecules that desorbed in the characteristic Pt(111)-H(D) desorption region, 50-150°C, comprised only of H_2, indicating that no C-D bonds were broken to give Pt-D species, up to 135°C. All changes were found in the two higher temperature maxima characteristic of decomposition from chemisorbed acetylene. The desorption maxima at ~ 240°C and ~ 380°C contained not only D_2, but substantial H_2 and HD showing that C-H bonds were formed in the surface reaction of H and C_2D_2 under annealing conditions. The integrated H_2, HD and D_2 intensities for the 240°C and the 380°C maximum were in the relative ratio of $I_{240°C} > I_{380°C}$ with an apparent maximum ratio of 2:1. The observation of an ordered (2x2) low energy electron diffraction pattern, a diagnostic feature of the stable acetylene adsorbate species identified as CH_3C by the previous report,[6,28] was directly correlated with an annealed Pt(111)-H-C_2D_2 surface that gave a thermal desorption spectrum with an intensity ratio of $I_{240°C}$: $I_{380°C} \cong 2 : 1$.

Figure 3

Shown in the figure are the thermal desorption (decomposition) spectra of Pt(111)-H-C_2D_2, formed at ~ 20°C, heated to ~ 135°C for 1 minute, and then cooled down to ~ 35°C prior to the experiment. Plotted are the mass ion current intensity of H_2 (upper curve), HD (middle curve) and D_2 (lower curve) as a function of temperature.



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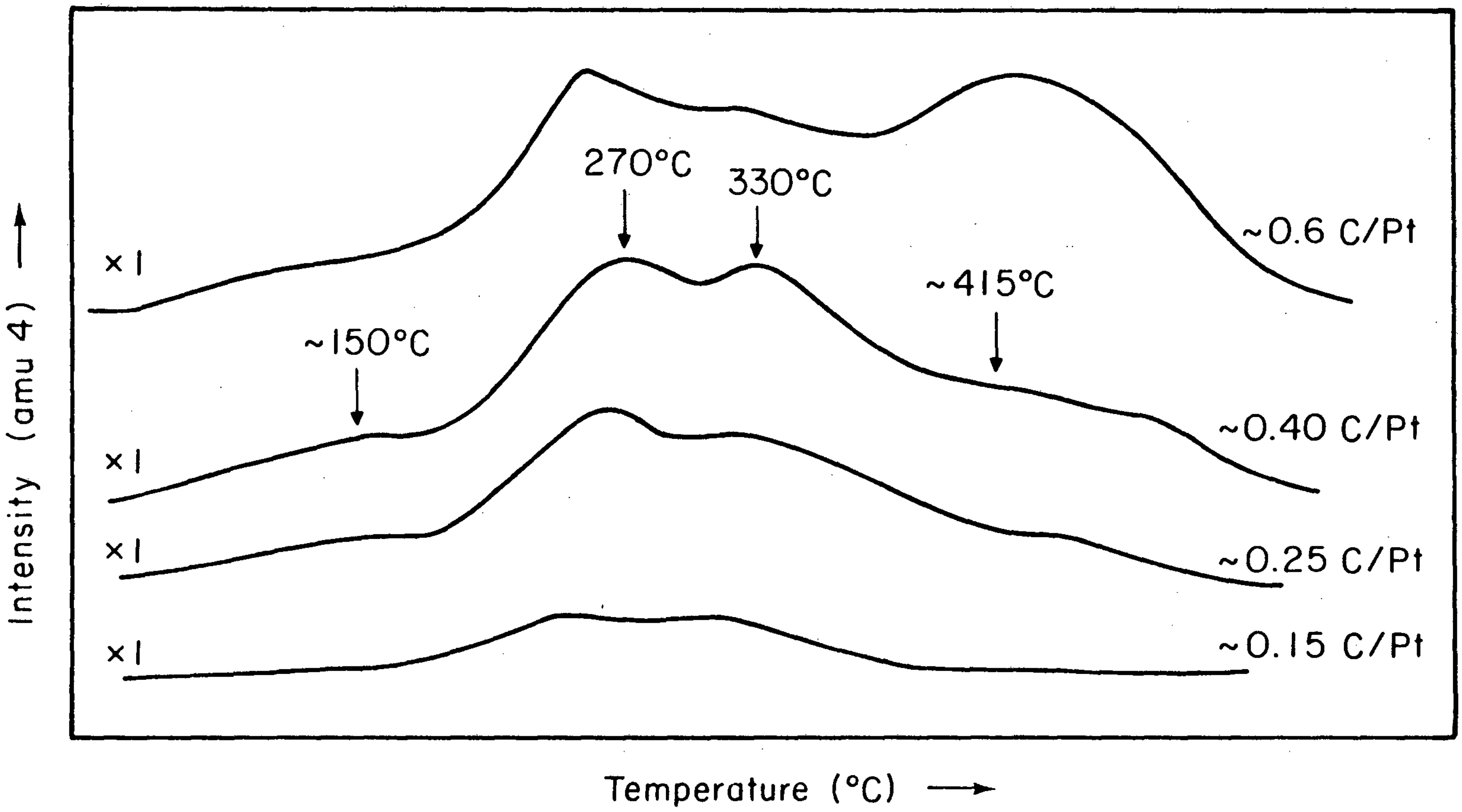
The higher temperature (50-135°C) experiments between acetylene and hydrogen also showed that the rate of formation of C-H bonds increased with increasing temperature. Hence the reaction of acetylene and hydrogen at 20°C could probably be expected, but with lower rates. A Pt(111)-C_2D_2 surface, formed and kept at 20°C, was thereby treated with an H_2 atmosphere of 1×10^{-7} torr for a period of 20 minutes. A subsequent thermal desorption experiment established that C-H bonds had been formed under these conditions and that no C-D bonds were broken: The low-temperature region characteristic of Pt(111)-H(D) consisted only of H_2, the 240°C maximum contained a small H_2, and larger HD and D_2 peaks, and the 380°C maximum contained essentially only HD (small) and D_2 peaks. These results establish that the only reaction between C_2D_2 and H on the Pt(111) surface is hydrogenation.

On the clean Pt(100) surface, chemisorption of acetylene at 25°C readily converted the reconstructed (5x20)-Pt(100) surface to a (1x1)-Pt(100)-C_2H_2 surface. Thermal desorption studies of a Pt(100)-C_2H_2 surface invariably yielded H_2 as the only gaseous product from low (~ 0.15 C/Pt) to high (~ 0.8 C/Pt) acetylene coverages; there was no evidence of acetylene or benzene (or any other hydrocarbon) desorption at these surface coverages. The decomposition process of chemisorbed acetylene yielded a complex hydrogen desorption spectrum, which was a sensitive function of coverage as illustrated in Figure 4. At a surface coverage of ~ 0.4 C/Pt, two major hydrogen desorption peaks were observed at ~ 260°C and ~ 320°C with an approximate intensity ratio of 1:1. Corresponding temperatures for thermal decomposition of C_2D_2 on the Pt(100) surface were at slightly higher temperatures: ~ 270°C and ~ 330°C. There was an additional small peak

Figure 4

The thermal desorption spectra of D_2 from decomposition of Pt(100)-C_2D_2 as a function of surface coverage are shown in this figure. The relative intensities of these D_2 peaks appear to be a sensitive function of coverage; below ~ 0.4 C/Pt coverage, the 270°C and the 330°C maximum are the major desorption peaks with an approximate 1:1 ratio. At high coverages (> 0.6 C/Pt), the D_2 spectra resemble that from decomposition of Pt(100)-C_6D_6 at comparable coverage level.



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observed at 150-170°C at the low coverage, and the hydrogen peak at ~ 400°C only occurred at higher (> 0.5 C/Pt) coverages. The complex, coverage-dependent hydrogen desorption spectrum could not be interpreted unequivocally because of the potential of more than one structurally, or stereochemically differentiable adsorbates derived from Pt(100) and acetylene, as suggested by the photoemission study of Fischer and coworkers.[37]

The reaction of acetylene (at a surface coverage of ~ 0.4 C/Pt) and hydrogen on the Pt(100) surface was investigated from 20°C to 160°C. A Pt(100)-H-C_2D_2 surface, formed from co-adsorption of H_2 and C_2D_2 on Pt(100) at 20°C, was rapidly heated to high temperatures. The resultant thermal desorption spectrum consisted of D_2 desorption mainly at ~ 270°C and ~ 330°C characteristic of decomposition of adsorbed C_2D_2 species, and H_2 desorption at temperature maximum of ~ 150-170°C characteristic of Pt(100)-H. Only a small amount of HD was observed at those D_2 desorption maxima which could largely be attributed to ~ 5% C_2HD contamination in the C_2D_2 sample. Hence there was no detectable reaction between acetylene and hydrogen under these conditions.

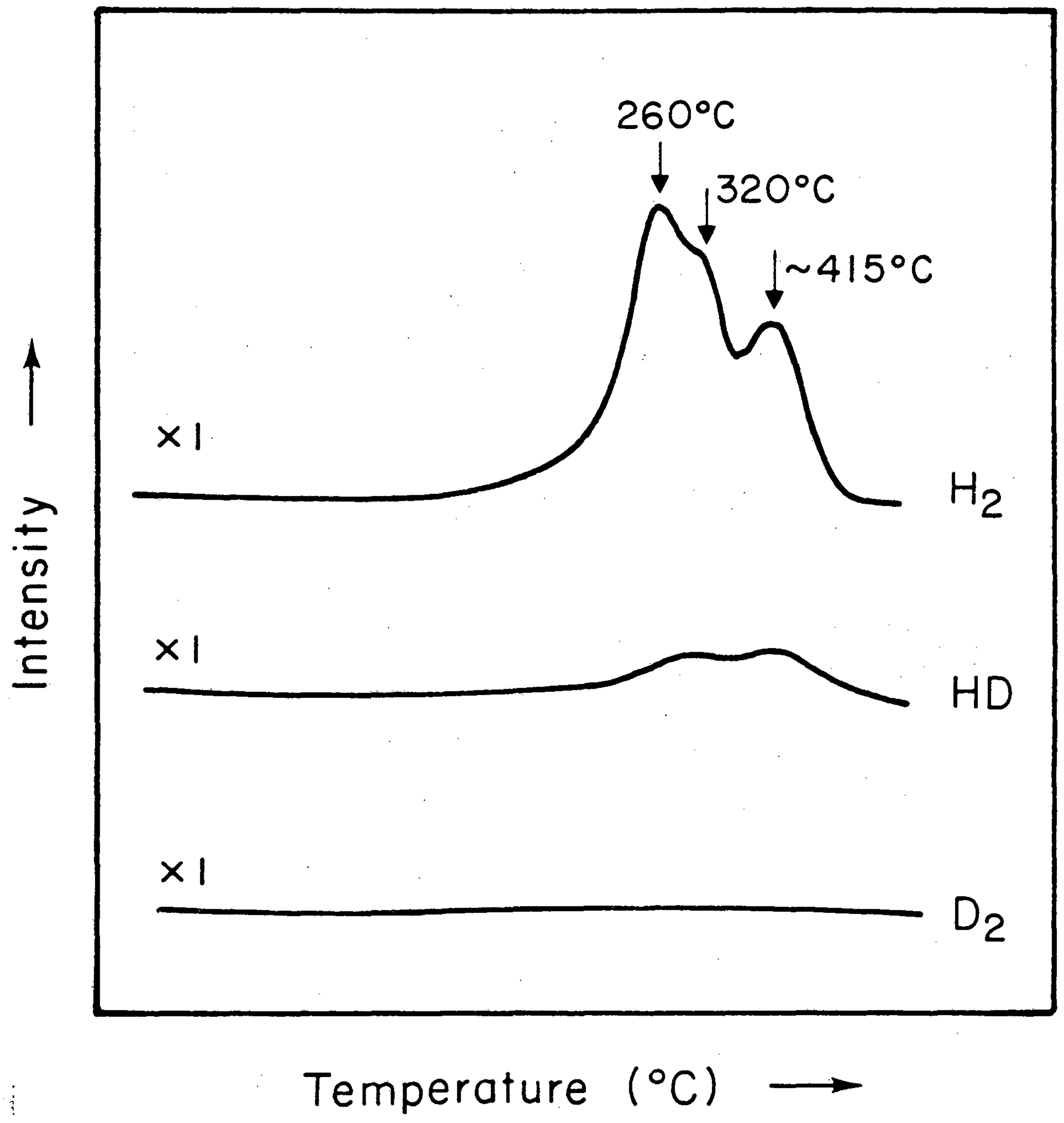
At ~ 20°C, exposure of a Pt(100)-C_2D_2 surface to an H_2 pressure of 10^{-7} torr for a period of 5-15 minutes yielded acetylene adsorbate species that contained a substantial amount of C-H bonds as evidenced by much larger H_2 and HD desorption peaks at ~ 260°C and ~ 320°C in the subsequent thermal decomposition study. A slight modification of this experiment clearly showed that significant C-D bond cleavage occurred at 35°C. A Pt(100)-C_2D_2 state was treated with 10^{-6} torr of H_2 pressure at 30-35°C for 10 minutes, and its thermal decomposition behavior was subsequently followed. The major desorption maxima at ~ 260°C and ~ 320°C were largely H_2 and HD; only a small amount of D_2 was detected at those temperature maxima. Therefore, carbon-hydrogen bond breaking and making reactions of acetylene adsorbate species on the Pt(100) surface were evident at temperatures as low as 20°C, and hydrogen-deuterium exchange at the adsorbate carbon sites was measurably fast at 35°C and 10^{-6} torr of H_2 pressure. All integration data indicated that the net reaction between acetylene and hydrogen on Pt(100) is H-D exchange.

At higher temperatures of 70-160°C, reaction of a Pt(100)-C_2D_2 surface with H_2 pressures of 10^{-7} torr led to nearly complete H-D exchange. Exposure of Pt(100)-C_2D_2 to 1 x 10^{-7} torr of H_2 at 130-160°C for a period of 4 minutes resulted in a thermal desorption spectrum of H_2 (Figure 5) at temperature maxima of ~ 260°C and ~ 320°C, as if it were derived from Pt(100)-C_2H_2 thermal decomposition; no D_2 and only trace amount of HD was observed at those H_2 maxim, as shown in Figure 5, indicating complete exchange of deuterium (C-D bonds) with hydrogen.

Study of acetylene-hydrogen reaction on the two crystallographic planes of platinum, (111) and (100), has established the temperatures at which carbon-hydrogen bond breaking and making processes proceed at moderate rates under low hydrogen pressures of 10^{-6} to 10^{-11} torr. The acetylene-hydrogen reaction on the Pt(111) and Pt(100) surfaces exhibit qualitative and quantitative differences. On the Pt(111) surface, no C-H bond breaking (to form surface-H species) up to temperatures of at least 135°C is detectable, and the only acetylene-hydrogen reaction at 20-135°C is hydrogenation, whereas on the Pt(100)

Figure 5

A $Pt(100)-C_2D_2$ surface, formed at ~ 20°C, was exposed to an H_2 atmosphere of ~ 1×10^{-7} torr for 4 minutes at 130-160°C. The subsequent thermal decomposition spectra of H_2, HD and D_2 are shown in this figure. This pretreatment has led to an almost complete H-D exchange as no D_2 and only trace HD was observed, and the H_2 spectrum is characteristic of decomposition of $Pt(100)-C_2H_2$.



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surface, C-H bond breaking proceeds at temperatures as low as 20°C, and the net acetylene-hydrogen reaction is H-D exchange.

In the initial chemisorption of acetylene on the Pt(111) surface, an energetically favored interaction is probably through π and π^* orbitals of acetylene and appropriate metal surface orbitals. Maximal overlap of these orbitals will result in a stereochemistry such that the C-C bond vector lies almost parallel to the atomically flat (111) surface plane. At some higher temperatures, possible reorganization of HCCH framework may lead to the tipping of the two C-H vectors within a plane normal to the surface and away from the surface. Such a stereochemistry has been found in the molecular metal chemistry,[3] and photoemission studies of Pt(111)-C_2H_2 at ~ 300 K[30-32] also concluded the rehybridization of acetylene to form a "distorted" molecular geometry.

The thermal decomposition of Pt(111)-C_2H_2 does not occur until temperatures exceed 200°C (it was only measurably fast at ~ 240°C or higher) suggesting that the C-H hydrogen atoms are well-removed from the metal surface initially, a stereochemistry that will require relatively high temperatures for the scission of C-H bonds. In the annealing experiments, facile C-H bond breaking (to form surface-H species) for the Pt(111)-C_2H_2, or the Pt(111)-H-C_2H_2 was not observed up to 135°C within time intervals of minutes strongly indicates that the stable species formed from the hydrogenation of Pt(111)-C_2H_2 also does not have any hydrogen atoms close to the metal surface. Of the three models proposed for this species--CH_3C, CH_2CH, and CH_3CH—the first, an ethylidyne species proposed by Kesmodel et al.[6,28] to have the C-C bond vector normal to the surfce plane and all three hydrogen atoms far removed from the surface plane, is fully consistent with the chemical data obtained in this study. Nevertheless, this consideration does not exclude the other two proposed models because either of these could have a stereochemistry such that all hydrogen atoms would be relatively far removed from the metal surface.

In the hydrogenation of Pt(111)-C_2H_2, initially formed at 20°C, the relative intensities of the ~ 240°C peak and ~ 380°C peak from thermal decomposition of the stable, higher-temperature species are approximately 2:1, indicative of a C_2H_3 stoichiometry; however, the broad characters of these hydrogen desorption peaks and the possibility of more than one differentiable species present at these higher temperatures cannot allow an unequivocal conclusion about the decomposition process.

Initial interaction of acetylene on the Pt(100) surface should be analogous to that of the Pt(111); maximal overlap of π and π^* acetylene orbitals and metal surface orbitals should result in a stereochemistry in which the C-C axis lies flat on the (100) surface. However, in sharp contrast to the acetylene chemistry on the Pt(111) surface, C-H bond breaking processes of the acetylene adsorbate species are evident at temperatures as low as 20°C. Hence, it appears that one, or both of the C-H hydrogen atoms can come close to the surface metal atoms at the room temperature chemisorption state (states).

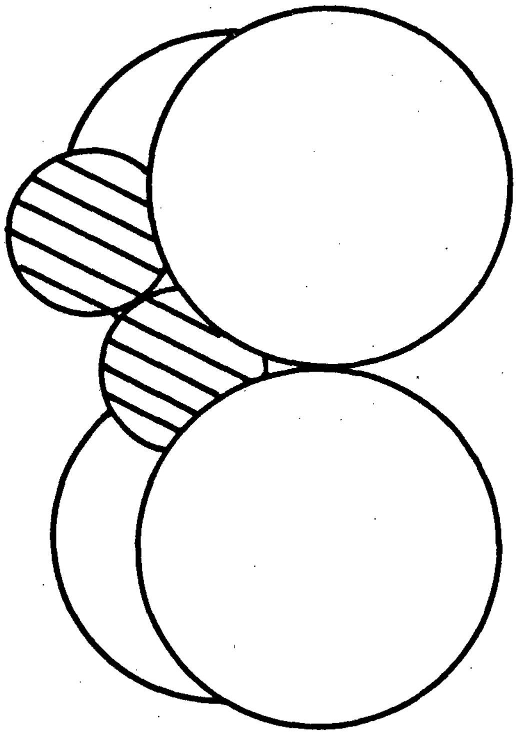
Casalone et al.[38] have studied Ni(100)-C_2H_2 by low energy electron diffraction and concluded that the most favored geometry of the chemisorption is a distorted acetylene molecule with the C-C axis tilted by ~ 40° with respect to the surface plane. Based on a hard sphere model, the maximal tipping of the C-C bond vector of an acetylene adsorbate on the two platinum surfaces, (111) and (100), is ~ 10° and ~ 45°, respectively, with respect to the surface plane (Figure 6). Perhaps, on the Pt(100) surface, it is more likely to generate a C-H-Pt multicenter bond because of the significant tipping of the C-C bond, or of some torsional deformation of the HCCH framework, as discussed by Felter and Weinberg,[39] and thereby enhance the probability of facile C-H bond breaking and ultimately an exchange process.

The substantial differences in the acetylene-hydrogen reaction on the two platinum surfaces may largely be associated with the topographical differences between (111) and (100) surface planes. In fact, ultraviolet photoemission studies of acetylene on the four-fold symmetry (100) surface planes of Pd, Pt and Ir, and hexagonal close packed surface planes of Pd, Pt and Ru at 120-330 K[40] have shown the systematic differences of the bonding and rehybridization of acetylene adsorbates according to the metal substrate structure; transformation of the initial adsorption state to a further rehybridized or deformed surface species is always found on the (111) planes of fcc metals, or the basal plane of hcp metals.

It should be noted that in C-H bond making processes, the rates are a very sensitive function of hydrogen pressure. The low pressure conditions used in this study reflect the low thermodynamic activity of surface hydrogen atoms. In conventional catalysis experiments on platinum surfaces, hydrogenation of acetylene to form ethylene, and ethane occurs at ambient pressures and temperatures, although the rates are not exceptionally high under these conditions. On the Pt(100) surface at 20°C, reaction of C_2H_2 with a hydrogen pressure

Figure 6

Scale model of a three-atom and four-atom section of Pt(111) and Pt(100), respectively, with the two C atoms (shaded spheres) as an HCCH adsorbate are shown in this figure. With the constraint that both C atoms maintain a bonding interaction with surface Pt atoms, the maximal tipping of the C–C axis with respect to the surface plane is ~ 13° and ~ 45° for Pt(111) and Pt(100), respectively. The C–C bond distances are in the range of 1.30 - 1.40 Å .



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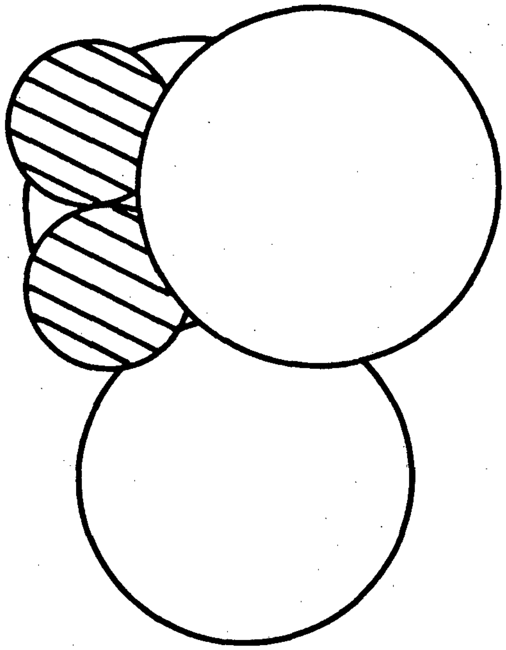


of 10^{-6} torr for a period of 25 minutes resulted in no such hydrogenated products, presumably ethane, as judged by Auger analyses and a final thermal desorption study.

Conclusions

The ultra high vacuum study of acetylene chemisorption on Pt(111) and Pt(100) and of the reaction of hydrogen with the acetylene adsorbate has established distinguishing features of carbon-hydrogen bond breaking and making processes as a function of temperature, pressure, and surface crystallography. The rates for both processes are substantially higher on the Pt(100) surface. Net acetylene-hydrogen reactions, in the temperature range of 20°C to ~ 135°C, are distinctly different on the two surfaces: on Pt(100) the net reaction is hydrogen exchange (H-D exchange) and on Pt(111) the only detectable reaction is hydrogenation. Stereochemical differences in the acetylene adsorbate structure are considered to be the contributing factor to the differences in acetylene chemistry on these two surfaces.

IV. THE COORDINATION CHEMISTRY OF BENZENE AND TOLUENE ON PLATINUM SURFACES

Platinum is an important catalyst for hydrogenation of aromatic hydrocarbon. In order to achieve the fundamental understanding of catalytic hydrogenation on this metal, it is necessary to characterize the chemisorption state of arene molecules on platinum surfaces. Chemisorption studies of benzene and toluene should provide fundamental knowledge about the structure, stereochemistry and surface reactivity of chemisorbed arene molecules.

The coordination chemistry of benzene and toluene on platinum surfaces were investigated under ultra high vacuum conditions. Three different crystallographic planes of platinum, (111), (100) and 6(111)x(111), were employed in order to examine the effects of metal coordination number and substrate geometry upon chemisorption of benzene and toluene. Surface chemical techniques: thermal desorption spectroscopy, chemical displacement reactions and isotopic labeling were extensively used to delineate the stereochemistry as well as C-H bond breaking and making processes of arene chemisorption as a function of surface coverage and temperature. Chemical displacement reactions with trimethylphosphine were the diagnostic reactions for evidence of C-H bond breaking. Accordingly, a description of adsorption and thermal desorption behavior of trimethylphosphine chemisorbed on Pt(111), Pt(100) and Pt 6(111)x(111) is presented first. The qualitative and quantitative differences between platinum and nickel surfaces in arene surface chemistry are also discussed. The nickel surface chemistry was established by Dr. C. M. Friend.[14]

Results and Discussion

1. Trimethylphosphine Chemistry

Trimethylphosphine is a strong field ligand that has been effectively used as a displacement ligand in organometallic compounds. In the displacement reaction of hydrocarbon adsorbates over single crystal metal surfaces, trimethylphosphine is also an effective displacing agent: notable has been the chemical displacement of benzene from a series of nickel surfaces.[9] In this study, trimethylphosphine was also utilized in the chemical displacement of hydrocarbon adsorbates. Although a molecular characterization of the trimethylphosphine chemisorption states on single crystal platinum surfaces was not attempted, the thermal reactivity was carefully examined by isotopic labeling and thermal desorption spectroscopy.

Trimethylphosphine is strongly chemisorbed on Pt(111), Pt 6(111)x(111) and Pt(100) surfaces at 25°C. The thermal desorption behavior of trimethylphosphine on these three surfaces is qualitatively similar. A thermal desorption study of trimethylphosphine chemisorbed on any of the three platinum surfaces, (111), 6(111)x(111) and (100), gave reversible trimethylphosphine desorption as well as thermal decomposition products: methane and hydrogen. Table I summarizes the thermal desorption maxima for $P(CH_3)_3$, CH_4 and H_2 from Pt(111), Pt 6(111)x(111) and Pt(100) surfaces. When $Pt-D-P(CH_3)_3$ states, formed from co-adsorption of D_2 and $P(CH_3)_3$ on the platinum surfaces at 25°C, were heated, the thermal desorption products contained CH_3D, HD and a trace amount of CH_2D_2, in addition to CH_4 and H_2, in the characteristic trimethylphosphine decomposition temperature region. The reversibly desorbed trimethylphosphine contained no deuterium,

Table I

Thermal Desorption of $P(CH_3)_3$ from Platinum Surfaces

Surface	$T_{max}(P(CH_3)_3)$	$T_{max}(CH_4)$	$T_{max}(H_2)$
Pt(111)	~ 160°C*	210°C	220, 260°C
Pt 6(111)x(111)	~ 235°C*	190-205°C	240, 330°C
Pt(100)	~ 200°C*	170°C	170, 235, ~ 410°C*

*very broad desorption.

indicating a desorption derived from an associative chemisorption state.

In general, trimethylphosphine chemisorbed on the Pt(111), Pt 6(111)x(111) and Pt(100) surfaces undergoes at least two competing processes in the thermal desorption experiment: a molecular (associative) desorption process that gives intact trimethylphosphine molecules, and an irreversible thermal decomposition process that yields methane and hydrogen, and a surface contaminated with P and C. The methane probably forms from a rapid surface reaction of the methyl group with chemisorbed hydrogen atoms since methane neither adsorbs nor reacts with the platinum surfaces in the temperature range where experiments were carried out (25-500°C). When surface D atoms are present, the methane product is largely CH_3D and CH_4.

The initial chemisorption state of trimethylphosphine on the Pt(111), Pt 6(111)x(111), or Pt(100) is probably through the donar-acceptor interaction centered on the phosphorus atom. The methyl hydrogen atoms are probably relatively far removed from the metal surface at relatively low temperatures as suggested by the following observation: The first hydrogen or methane desorption maximum from the C-H bond breaking of chemisorbed trimethylphosphine usually was not detected until temperatures exceeded the free hydrogen desorption maximum at the comparable coverage (about 70-100° higher). At some moderate temperatures, interaction of the methyl hydrogen atoms with Pt surface atoms to form multicenter C-H-Pt bonds is probably the intermediate stage for the formation of Pt-H bonds. This surface chemistry is qualitatively similar to that of trimethylphosphine in the coordinately unsaturated complex, $Fe[P(CH_3)_3]_4$, which is mostly $HFe[\eta^2-CH_2P(CH_3)_2][P(CH_3)_3]_3$ in the solution state.[41] The mechanisms of the methane formation cannot be defined from this surface study. A molecular characterization of trimethylphosphine chemisorption processes on the Pt surfaces will require further investigation using high resolution electron energy loss and photoemission spectroscopies.

Throughout this work, trimethylphosphine was used as an effective tool in the chemical displacement reactions. Although there was no attempt to investigate the mechanistic details of the chemical displacement reaction, the combined usage of displacement reactions with thermal desorption, and isotopic labeling studies has yielded valuable information about the structure and stereochemistry of hydrocarbon adsorbates.

2. Benzene Chemistry

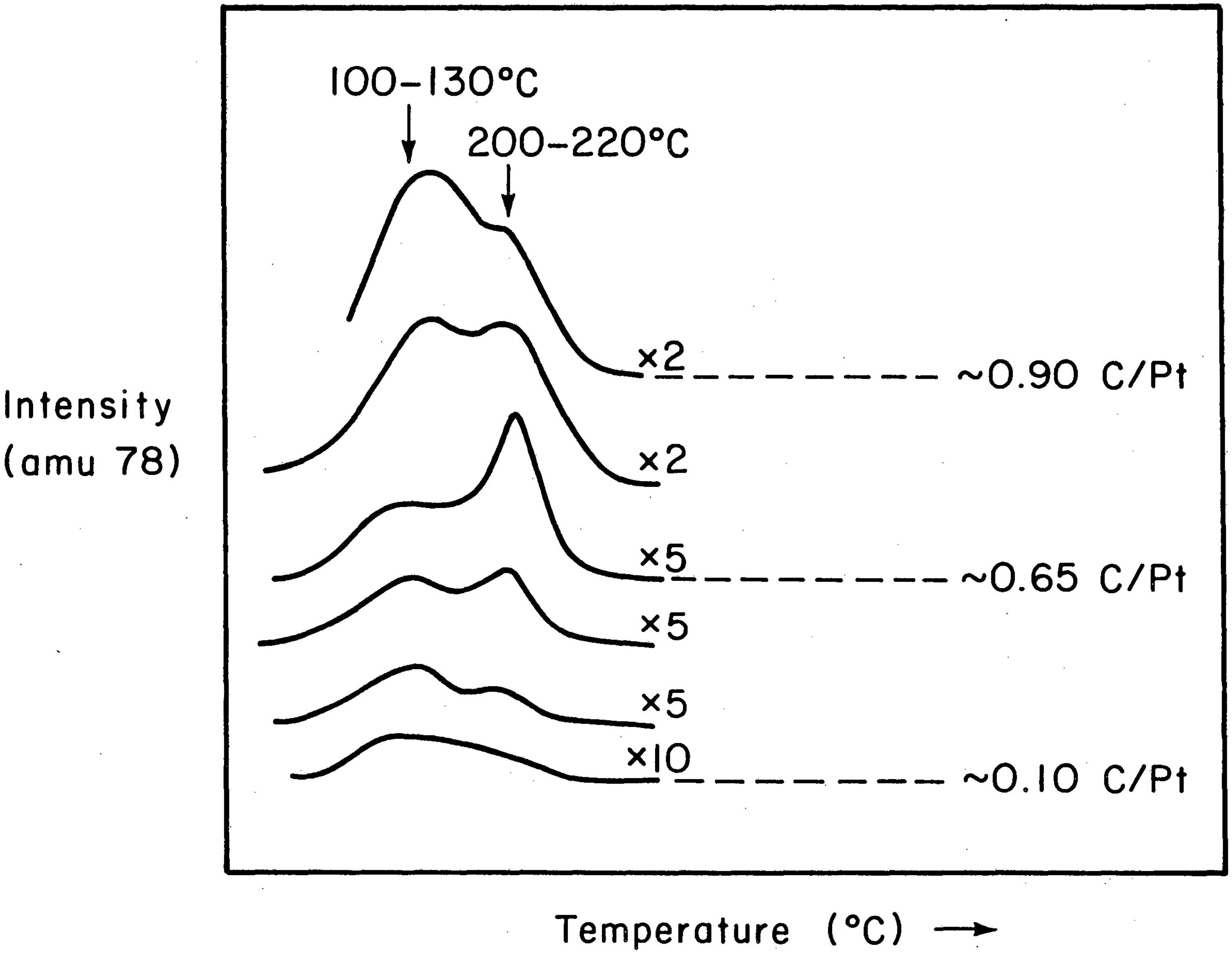
Benzene Chemisorption on Pt(111). Benzene chemisorption on the Pt(111) surface is qualitatively similar to that on the Ni(111) surface although there are significant differences. Thermal desorption studies of a Pt(111)-C_6H_6 surface, formed at 25°C, showed both reversible desorption of benzene molecules and irreversible decomposition to form H_2 in the gas phase, and a carbon-contaminated surface. The Pt(111) benzene chemistry, like the nickel benzene chemistry, showed no evidence of reversible C-H bond breaking. A Pt(111)-C_6H_6-C_6D_6 state, formed (i) at 25°C and (ii) at 25°C followed by annealing at 80°C for two minutes, or 130°C for one minute, showed only C_6H_6 and C_6D_6 in the subsequent thermal desorption study. Additionally, thermal desorption studies of a Pt(111)-C_6D_6-H state, formed from co-adsorption of C_6D_6 and H_2 at 25°C, showed no HD, only H_2, in the region characteristic of hydrogen desorption from Pt(111)-H(D) (T_{max} = 50-150°C). The H_2 desorption from C-H bond breaking of chemisorbed benzene did not occur at measureable rates until temperatures in excess of 200°C.

The thermal desorption characteristics of benzene molecules from a Pt(111)-C_6D_6 were studied as a function of surface benzene coverage as shown in Figure 7. The benzene desorption was complex in nature in that there were at least two benzene desorption maxima resolved, and their relative intensities were coverage-dependent. At very low benzene coverages of less than 0.05 of a monolayer (one monolayer ≡ one carbon atom per platinum atom), no benzene could be thermally desorbed. At ~ 0.1 of a monolayer, there was only one weak, broad desorption at ~ 100-200°C. Above this coverage, two broad desorption maxima at ~ 100-130°C and 200-220°C were resolved with the intensity of the higher temperature peak increased linearly with increasing surface benzene coverages while that of the lower temperature one stayed almost constant. The benzene desorption maximum at 200-220°C saturated at surface coverage of ~ 0.65. Above 0.65 of a monolayer, the low temperature maximum at 100-130°C grew rapidly in intensity as coverage was increased to ~ 0.9 of a monolayer, the effective benzene saturation coverage at 25°C and 10^{-10} torr (assuming that benzene is bound in a plane parallel to the surface, and a 7.2 Å benzene van der Waals radius and 2.76 Å Pt-to-Pt distance, the saturation coverage would be about 0.9 carbon atoms per platinum atom).

The irreversible decomposition of chemisorbed benzene on Pt(111), competitive with reversible benzene desorption, was also examined

Figure 7

Shown in the figure are the thermal desorption spectra of benzene-d_6 from the Pt(111) surface as a function of surface coverage.



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as a function of surface benzene coverage, as shown in Figure 8. Desorption maxima for H_2 were at ~ 260 and ~ 380°C with relative intensities of approximately one-to-one. Desorption maxima for D_2 from thermal decomposition of a Pt(111)-C_6D_6 state were at ~ 270°C and ~ 380°C.

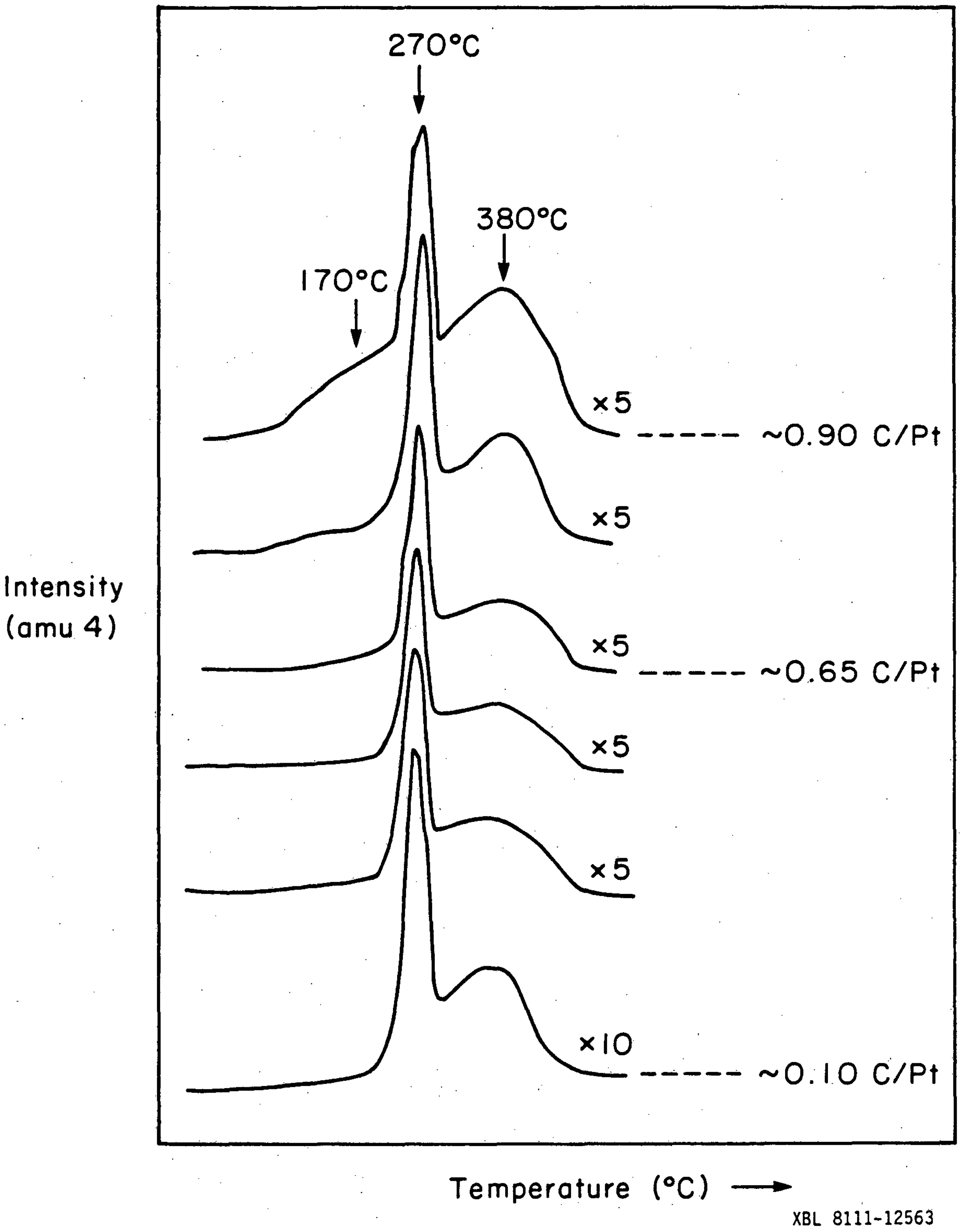
The coverage dependence results for reversible benzene desorption are not in themselves evidence for differentiable benzene chemisorption states for the Pt(111) surface because cooperative effects (from interaction between benzene adsorbates) alone could be the cause for multiple desorption maxima. To pursue this issue of differentiable benzene chemisorption states, sequential chemisorption of C_6H_6 and C_6D_6 was performed at various surface coverages, and the desorption behavior of both molecules was followed subsequently:

(i) C_6D_6 was adsorbed first to less than 0.1 of a monolayer coverage and then C_6H_6 was co-adsorbed to a total coverage of about 0.5-0.65 at 25°C. In the thermal desorption experiment, no C_6D_6 desorption was detected—only C_6H_6 was desorbed at temperature maxima of 100-130°C and 200-220°C. All the chemisorbed C_6D_6 decomposed to form D_2 and HD molecules at ~ 270 and ~ 380°C. Thus there was a strongly and irreversibly chemisorbed benzene (C_6D_6) state and a reversibly chemisorbed benzene (C_6H_6) state(s) on the Pt(111) surface, and there was no detectable interchange between these states.

(ii) C_6D_6 was adsorbed first with less than 0.5 of a monolayer at 25°C and then C_6H_6 was co-adsorbed to a final coverage of ~ 0.75. In the thermal desorption experiment, the higher

Figure 8

Thermal desorption spectra of D_2 from decomposition of chemisorbed benzene-d_6 on the Pt(111) surface as a function of initial surface coverage. These spectra are complementary to the spectra presented in Figure 7 and for each coverage in the two figures, the spectra are derived from a single experiment.



XBL 8111-12563

temperature desorption maximum was dominated by C_6D_6 and the lower temperature maximum by C_6H_6. Thus the benzene (C_6D_6) that adsorbed first resided in the more tightly bound reversible state without significant exchange with the less tightly bound reversible state.

(iii) C_6D_6 was adsorbed on the Pt(111) surface to the saturation coverage, 0.9 of a monolayer, at 25°C. Then the surface was exposed to a C_6H_6 atmosphere of $\sim 10^{-8}$ torr for a period of three minutes at 25°C. Under these conditions, most of the chemisorbed C_6D_6 was displaced by C_6H_6 except the irreversibly bound benzene state: The subsequent thermal desorption experiment yielded C_6H_6 at 100-130°C and 200-220°C with their intensities comparable to those of reversible benzene desorption from a saturation coverage. Only a trace of C_6D_6 was detected at ~ 100-130°C as well as some HD and D_2 at ~ 270 and ~ 380°C.

These experiments establish that there is an initial, irreversibly chemisorbed benzene state on the Pt(111) surface and that benzene exchange through surface migration does not occur between this state and state(s) formed at higher coverages. The reversibly chemisorbed benzene state(s) undergoes nearly complete exchange with benzene (labeled benzene) by a relatively facile displacement at 25°C, a feature consistent with phosphine displacement discussed below. The observation of two reversible benzene desorption maxima does not necessarily indicate two differentiable benzene chemisorption states, but the experiment (ii) cited above is suggestive of two differentiable reversible benzene state with a possibly slow surface migration of benzene between them.

Displacement of benzene by trimethylphosphine at 25°C was also performed as a function of surface coverage. At less than 0.1 of a monolayer of benzene (C_6D_6) coverage, only a small amount of benzene was displaced. The subsequent thermal desorption study showed a C_6D_6 desorption maximum at ~ 150°C and substantial amounts of CH_3D and HD; the chemisorbed C_6D_6 molecules, presumably in the "irreversibly" bound state, could only be displaced to a small extent. At coverages of ~ 0.1-0.9 of a monolayer, substantial amounts of the adsorbed benzene were displaced (> 90% at the saturation coverage). Chemisorption of C_6H_6 to ~ 0.1 and ~ 0.65 of a monolayer were followed by C_6D_6 chemisorption to a final coverage of ~ 0.65 and ~ 0.9, respectively. In both cases, the displacement reaction by trimethylphosphine yielded both C_6H_6 and C_6D_6 molecules. Then, in the following thermal desorption study, only C_6H_6 (at peak maximum of ~ 150°C) and trace amounts of HD and CH_3D were detected. Therefore, the reversible chemisorption state(s) of benzene (C_6D_6) undergoes facile displacement by trimethylphosphine at 25°C.

Sequential adsorption of C_6H_6 and C_6D_6 established that there appear to be two differentiable, reversible benzene chemisorption states on Pt(111) and that chemical displacement by either $P(CH_3)_3$ or a benzene flux is nearly quantitative (~ 90%) at 25°C. The labeling experiment in which C_6D_6 was adsorbed first to < 0.1 of a monolayer and then C_6H_6 was adsorbed to ~ 0.5 of a monolayer established that no C_6D_6 could be thermally desorbed or chemically displaced by trimethylphosphine--all the C_6D_6 species thermally decomposed to form D_2 and HD. This initially and irreversibly chemisorbed benzene state is clearly differentiated from the (reversible) benzene states formed at higher coverages. Interchange between these differentiable states through surface migration or any other process was not evident within the time scale of the experiments (minutes).

Benzene chemisorption on the Pt(111) is largely molecular (nondissociative) in character, like the Ni(111)-benzene chemistry. At least for the reversibly chemisorbed benzene states of Pt(111), the initial benzene-metal surface interaction should be largely through the π and π^* benzene orbitals with appropriate metal surface orbitals for maximal overlap. Such an interaction would have the C_6 ring plane parallel to the metal surface plane. This proposed structure was also supported by Lehwald, Ibach and Demuth[42] from a high resolution electron energy loss study in which two "phases" of benzene chemisorption states on Pt(111) were proposed (based on a different frequency shift): one with the benzene C_6 centroid atop a single Pt atom, and the other with the C_6 centroid atop a three-fold hollow site. The data presented in the above cannot define the translational orientation of the benzene chemisorption states. An electron energy loss study of Pt(111)-C_6H_6 by Netzer and Matthew[43] was also reported to be consistent with a π -bonded benzene. At higher coverage, Stair and Somorjai concluded,[44] from a low energy electron diffraction study, that the C_6 rings were tilted with respect to the surface plane.

Trimethylphosphine displaced $>$ 90% of the chemisorbed benzene on Pt(111) at 25°C, a similar feature was also observed for Ni(111)-C_6H_6 except the displacement was quantitative. However, C-H bond breaking for Ni(111)-C_6H_6 occurs at the temperature range of 100-115°C whereas on the Pt(111) surface, significant dehydrogenation only occurs at temperatures in excess of 200°C.

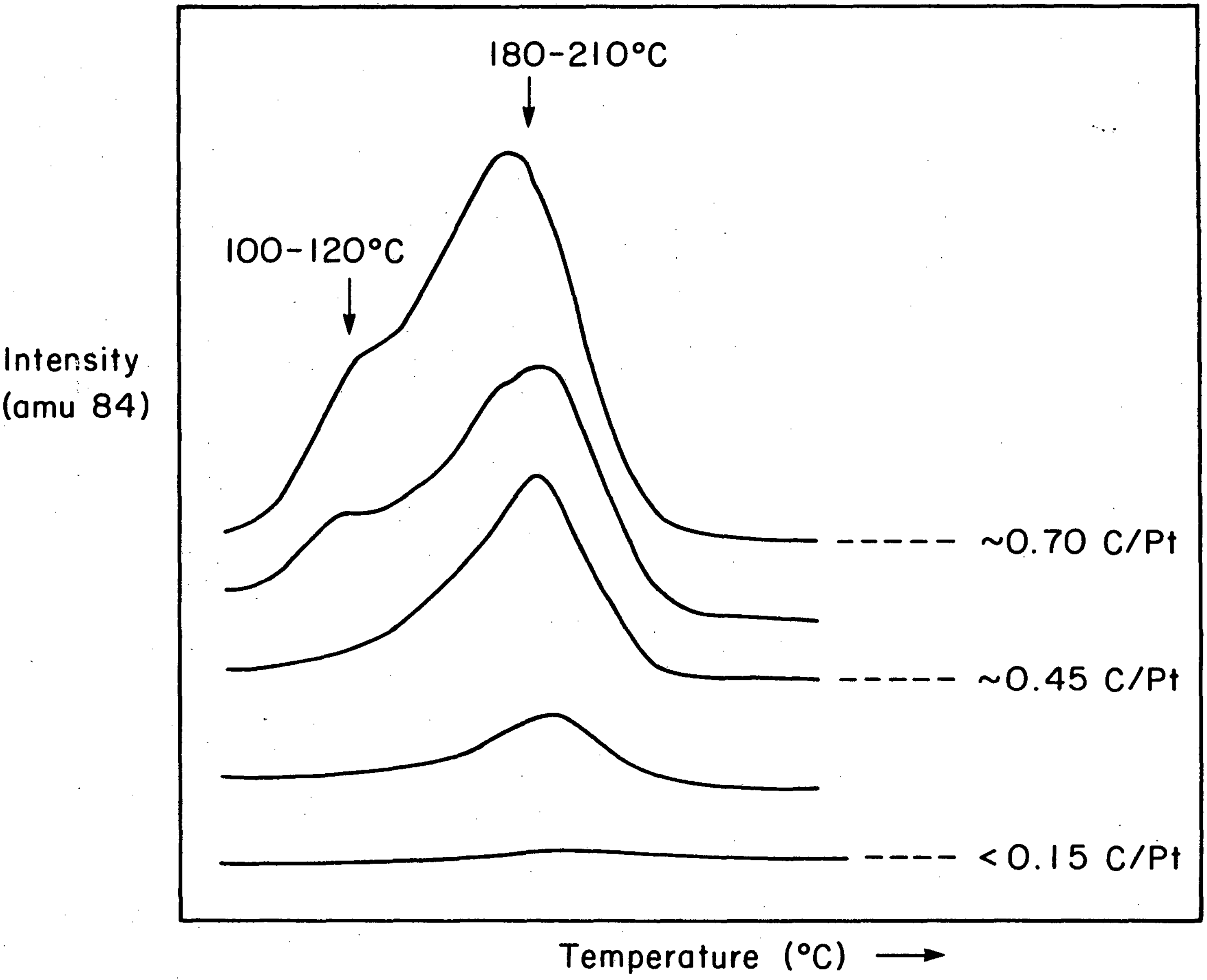
The benzene state on Pt(111) characterized by thermal and chemical displacement irreversibility cannot be structurally defined from this study. It could be either a molecular or a dissociative state. No D_2 desorption peak in the region characteristic of Pt(111)-D in the thermal desorption of Pt(111)-C_6D_6 at < 0.1 coverage was observed, which excludes the dissociative state. This strongly and irreversibly chemisorbed state may be associated with surface imperfection sites which are commonly found for the Pt metal (~ 5-10%). Since the typical imperfections are "steps" and "kinks", the benzene chemistry on the stepped platinum surface should yield valuable information about this point (*vide infra*).

Benzene Chemisorption on Pt 6(111)x(111). Chemisorption of benzene on the Pt 6(111)x(111) surface was also complex in character. The thermal desorption behavior of benzene, initially chemisorbed on Pt 6(111)x(111) at 25°C, was studied as a function of surface coverage as shown in Figures 9 and 10. Like the Pt(111) benzene chemistry, both irreversible benzene decomposition to form H_2 and reversible benzene desorption were observed, and relative extent of each process was highly coverage-dependent.

At low benzene coverages, decomposition of benzene was the dominant process when the Pt 6(111)x(111)-C_6H_6 surface was rapidly heated: Hydrogen desorbed at temperature maxima of ~ 195°C and ~ 355°C with approximately equal intensities, and these maxima shifted 10-20° lower at higher coverages. Decomposition was the prevailing thermal process from low to high surface coverages. At saturation coverages

Figure 9

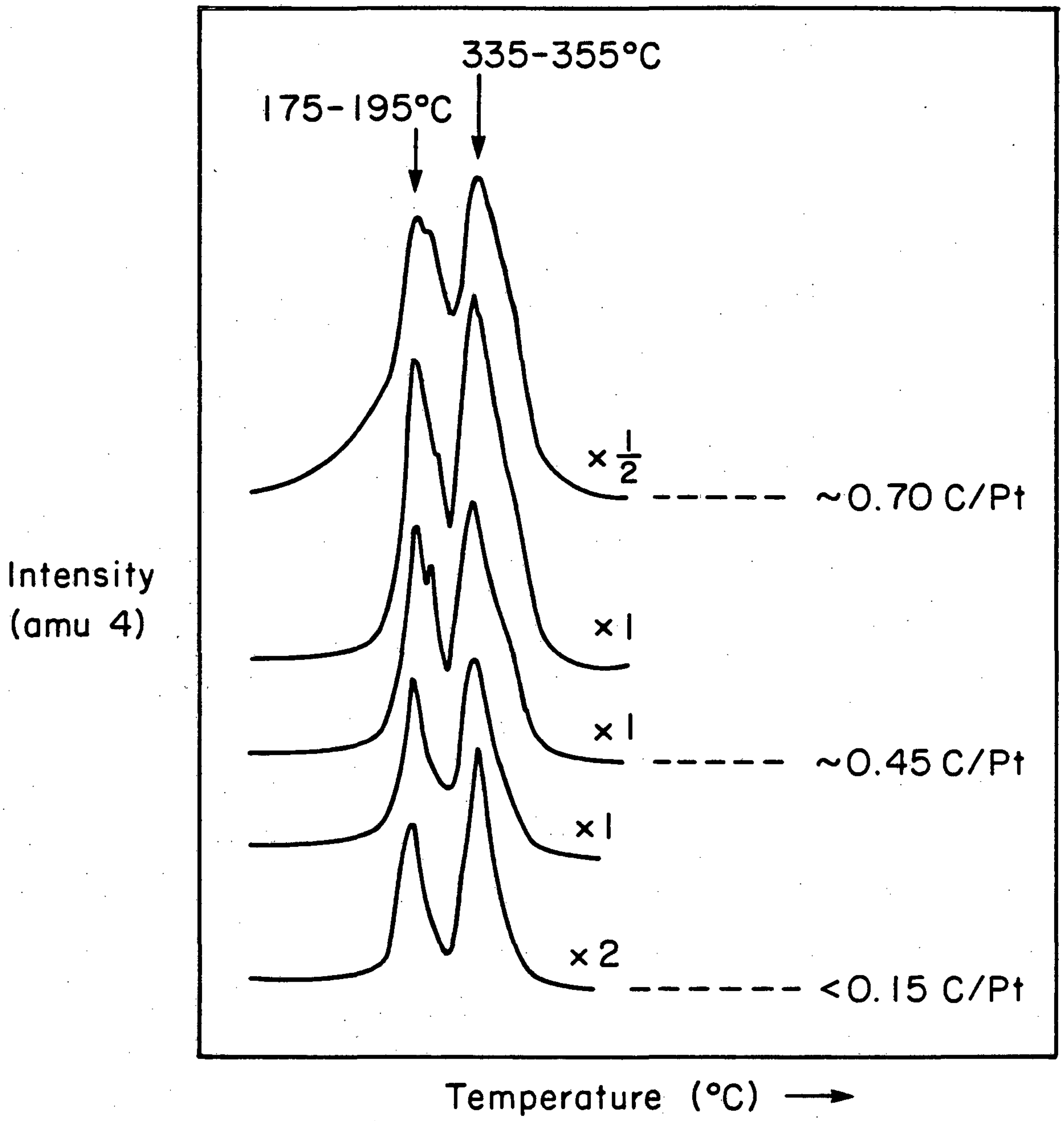
Shown are the thermal desorption spectra for benzene-d_6 from a stepped Pt 6(111)x(111) surface as a function of initial benzene coverage.



XBL 8111-12565

Figure 10

Thermal desorption spectra of D_2 from decomposition of chemisorbed benzene-d_6 on a stepped Pt 6(111)x(111) surface as a function of initial benzene coverage. These spectra are complementary to the spectra presented in Figure 9 and for each coverage in the two figures, the spectra are derived from a single experiment.



XBL 8111-12564

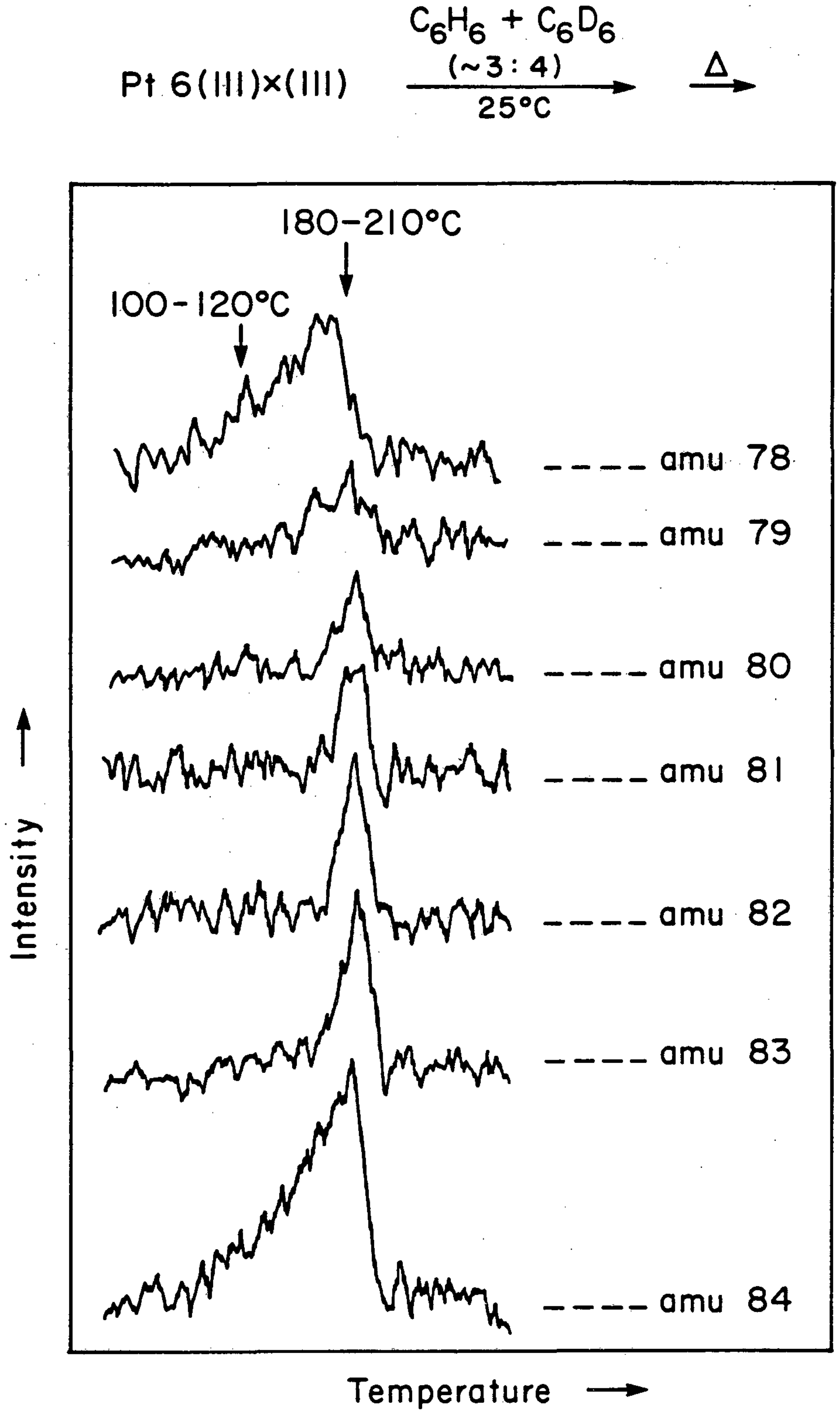
of about 0.7 of a monolayer (at 25°C and 10^{-10} torr), the Pt 6(111)x(111) surface had about 0.25 to 0.30 monolayer of carbon left after thermal desorption experiments. From a thermal desorption study of Pt 6(111)x(111)-C_6D_6-H, it was concluded that there was no significant dehydrogenation of chemisorbed benzene at temperatures lower than ~ 150°C: The thermal desorption result showed H_2 desorption maximum of ~ 130°C while no HD or D_2 could be observed at $T < 150$°C.

Above surface coverages of 0.10-0.15, reversible benzene desorption was observed, competitive with the irreversible benzene decomposition process. From ~ 0.15 to 0.45 of a monolayer coverages, only one benzene desorption maximum at 180-210°C was observed. Above ~ 0.45 benzene coverages, a lower-temperature, broad benzene desorption maximum at 100-120°C grew rapidly in intensity at coverages up to ~ 0.7 of a monolayer.

When thermal desorption studies were carried out for Pt 6(111)x(111)-C_6H_6-C_6D_6 formed at a total coverage of ~ 0.5-0.7, both C_6H_6 and C_6D_6 desorbed at ~ 100-120°C and ~ 180-210°C. In addition, all possible mixed benzene molecules, $C_6H_xD_{6-x}$ (x equals 1 to 5), were detected at the high temperature maximum, 180-210°C. Approximate molar ratios of the various benzene molecules, $C_6H_xD_{6-x}$, were 14, 11, 11, 13, 14, 16, and 20% for x equals 0 through 6, respectively (the initial molar gas phase mixture of C_6H_6 to C_6D_6 was 3 : 4), as shown in Figure 11. Thus reversible C-H(D) bond breaking only resulted in one desorption maximum although both benzene desorption maxima were observed for C_6H_6 and C_6D_6 molecules. This suggests that reversible bond breaking probably does not occur until temperatures above ~ 120°C within the time scale (seconds) of the experiment--This

Figure 11

Adsorption of a mixture of C_6H_6 and C_6D_6 with a gas phase molar ratio of 3:4 onto the Pt 6(111)x(111) surface results in all possible benzene molecules, $C_6H_xD_{6-x}$, in the thermal desorption as shown in this figure. The approximate molar ratios (without correcting the fragmentation of each benzene species in the mass spectral analysis) of $C_6H_xD_{6-x}$ molecules obtained from this experiment are 14, 11, 11, 13, 14, 16, and 20%, respectively, with x equals 0 through 6. It is noted that although both C_6H_6 and C_6D_6 desorb at both temperature maxima: 100-120°C and 180-210°C, the mixed benzene molecules only desorb at the higher temperature maximum.



XBL 8111-12414

was confirmed by the phosphine displacement reactions as a function of surface temperature, as discussed below.

Trimethylphosphine displaced no benzene (C_6D_6) from the stepped platinum surface unless the coverage was greater than ~ 0.15, consistent with the results from thermal desorption experiments. Above such coverages, the displacement of C_6D_6 at 25°C was essentially instantaneous but incomplete (70-80% at the saturation coverage of ~ 0.7 of a monolayer). Thermal desorption studies after chemical displacement reactions showed a C_6D_6 desorption peak at 170-185°C, and CH_3D, CH_4, HD and H_2 in the characteristic trimethylphosphine decomposition regions. This displacement reaction appeared to be temperature-dependent. When displacement with $P(CH_3)_3$ of Pt 6(111)x(111)-C_6D_6 was effected at 120-130°C, C_6D_6 seemed to be quantitatively displaced because in the subsequent thermal desorption, no C_6D_6 could be observed, and much smaller amounts of CH_3D and HD were detected. When trimethylphosphine displacement was effected for Pt 6(111)x(111)-C_6H_6-C_6D_6 (formed at 25°C) at various surface temperatures, the mixed $C_6H_xD_{6-x}$ molecules were only evident at temperatures higher than ~ 140°C. Thus reversible bond breaking, to effect H-D exchange between chemisorbed benzene, required temperatures of at least ~ 140°C, a feature consistent with the thermal desorption results where mixed benzene molecules only desorbed in the higher-temperature maximum of 180-210°C.

The Pt 6(111)x(111)-benzene chemistry was further investigated by generating mixed C_6H_6-C_6D_6 states through sequential chemisorption of C_6H_6 and C_6D_6. C_6D_6 was first adsorbed to the stepped surface to a coverage of ~ 0.45, then C_6H_6 was adsorbed to the saturation coverage, ~ 0.7 of a monolayer. The following thermal desorption study yielded C_6D_6 at 180-210°C and C_6H_6 at 100-120°C. Clearly these two reversible benzene desorption maxima represent two differentiable benzene chemisorption states with negligible surface migration within the time scale of the experiments (minutes). This conclusion is further supported by the following experiment: A Pt 6(111)x(111)-C_6D_6 state was formed at saturation coverage and 25°C, and then exposed to a C_6H_6 atmosphere of 10^{-8} torr for a period of two minutes. The subsequent thermal desorption gave C_6H_6 at 100-120°C and C_6D_6 at 180-210°C (Figure 12), and no evidence was found for $C_6H_xD_{6-x}$ molecules at 180-210°C. Had both C_6H_6 and C_6D_6 been present in the more strongly bound state, $C_6H_xD_{6-x}$ would have been produced in the heating. Thus the strongly bound benzene state (C_6D_6) characterized by a thermal desorption maximum at 180-210°C could not be displaced or exchanged by a high flux of C_6H_6 whereas the weakly bound benzene state could be displaced relatively easily.

Additional evidence of there being more than one benzene chemisorption state on the stepped surface was provided by the displacement reaction after sequential chemisorption of C_6H_6 and C_6D_6: C_6H_6 was first adsorbed to ~ 0.45 coverage, then C_6D_6 was adsorbed to the saturation coverage. Trimethylphosphine displaced both C_6H_6 and C_6D_6 molecules at 25°C, but only C_6H_6, no C_6D_6, was desorbed at 170-185°C, which was accompanied by large amounts of CH_4 and H_2, but only traces of CH_3D and HD. Thus the initial, strongly bound C_6H_6 species did not exchange with the less strongly bound C_6D_6 species.

These experiments established that there are clearly three

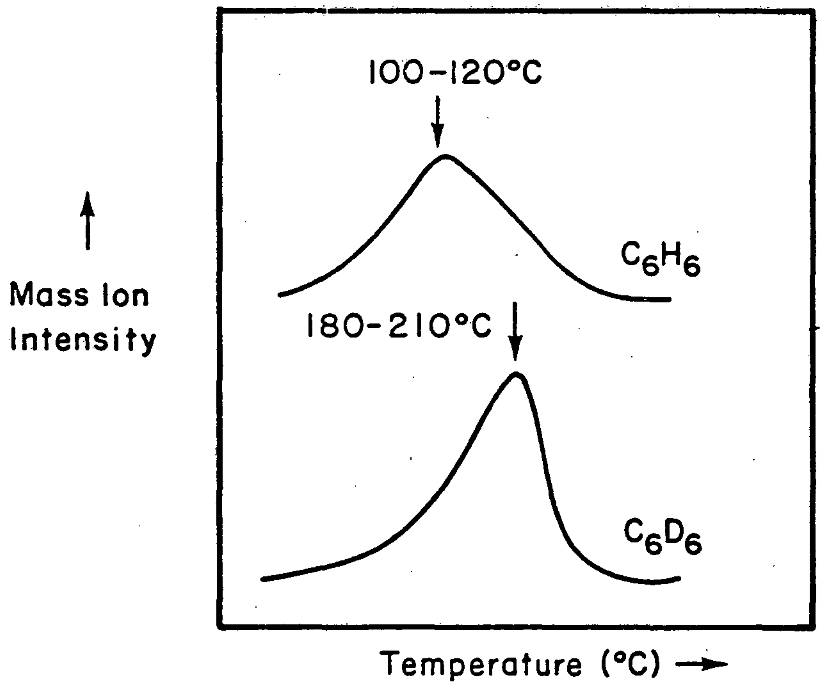
Figure 12

A Pt 6(111)x(111)-C_6D_6 state with a coverage of ~ 0.7 C/Pt atom ratio was formed at ~ 25°C. This surface was then exposed to C_6H_6 at a pressure of ~ 1 x 10^{-8} torr for 2 minutes at 25°C. Shown in this figure are the resultant thermal desorption spectra for C_6D_6 and C_6H_6; C_6D_6 desorbed at 180-210°C while C_6H_6 desorbed at 100-120°C,--facile exchange of C_6D_6 with C_6H_6 only occurred for the benzene state characterized by a desorption maximum of 100-120°C. No significant mixed benzene molecules, $C_6H_xD_{6-x}$, were formed under these conditions.

$$\underset{\theta = 0.6}{\text{Pt } 6(111)\times(111) - C_6D_6} \xrightarrow[25^{\circ}\text{C, 2 min}]{10^{-8}\text{ torr } C_6H_6} \text{Pt } 6(111)\times(111) - C_6D_6 - C_6H_6$$

$$\Delta \Big\downarrow \text{(TDS)}$$

largely C_6H_6 100-120°C
largely C_6D_6 180-210°C



XBL 825-10264

differentiable benzene chemisorption states on the stepped platinum surface: (a) a state characterized by irreversible chemisorption (b) a strongly but reversibly chemisorbed state characterized by a benzene desorption maximum at 180-210°C and (c) a less strongly and reversibly chemisorbed benzene state characterized by a benzene desorption maximum at 100-120°C.

Benzene chemisorption on the stepped Pt 6(111)x(111) surface bears qualitative similarities to that of the Pt(111) surface. Both irreversible and reversible benzene chemisorption states were evident and a large proportion of the chemisorbed benzene was subject to facile displacement by $P(CH_3)_3$. However, this stepped surface is more reactive than the (111) surface in that there is a larger fraction of the chemisorbed benzene (up to ~ 0.15 coverage) that was thermally irreversible and not chemically displaceable. On the Ni 9(111)x(111) surface, less reversible benzene desorption and less than quantitative displacement (by $P(CH_3)_3$) for chemisorbed benzene was also observed, compared with the Ni(111)-C_6H_6 chemistry. Thus, there is a correlation between the fraction of benzene that irreversibly chemisorbs and the density of the surface steps (or step imperfections).

The reversibly chemisorbed benzene species on Pt 6(111)x(111) comprise two differentiable benzene states, as established by the isotopic labeling experiments in both thermal desorption studies and chemical displacement experiments. There is a close correspondence between the (reversible) benzene desorption maxima derived from the Pt(111) and Pt 6(111)x(111) surfaces (such a correspondence was also evident between Ni(111)- and Ni 9(111)x(111)-benzene chemistry). Thus, it is reasonable to assume that the reversibly chemisorbed benzene states on the stepped surface is largely associated with the terrace atoms of (111) crystallography where the benzene ring lies parallel to the terrace plane.

Nevertheless, the presence of steps on the surface should affect the interaction between C-H hydrogen atoms and Pt metal surface atoms. Since some of the C-H hydrogen atoms can closely approach the step atoms of lower coordination number, there should be a generation of C-H-Pt multicenter bonding which can be either the intermediates or transition states in a C-H bond scission process. Extensive benzene dehydrogenation on the Pt 6(111)x(111) surface was occurring at temperatures greater than ~ 150°C while that for the Pt(111) was not evident until temperatures in excess of ~ 220°C, consistent with the above arguments.

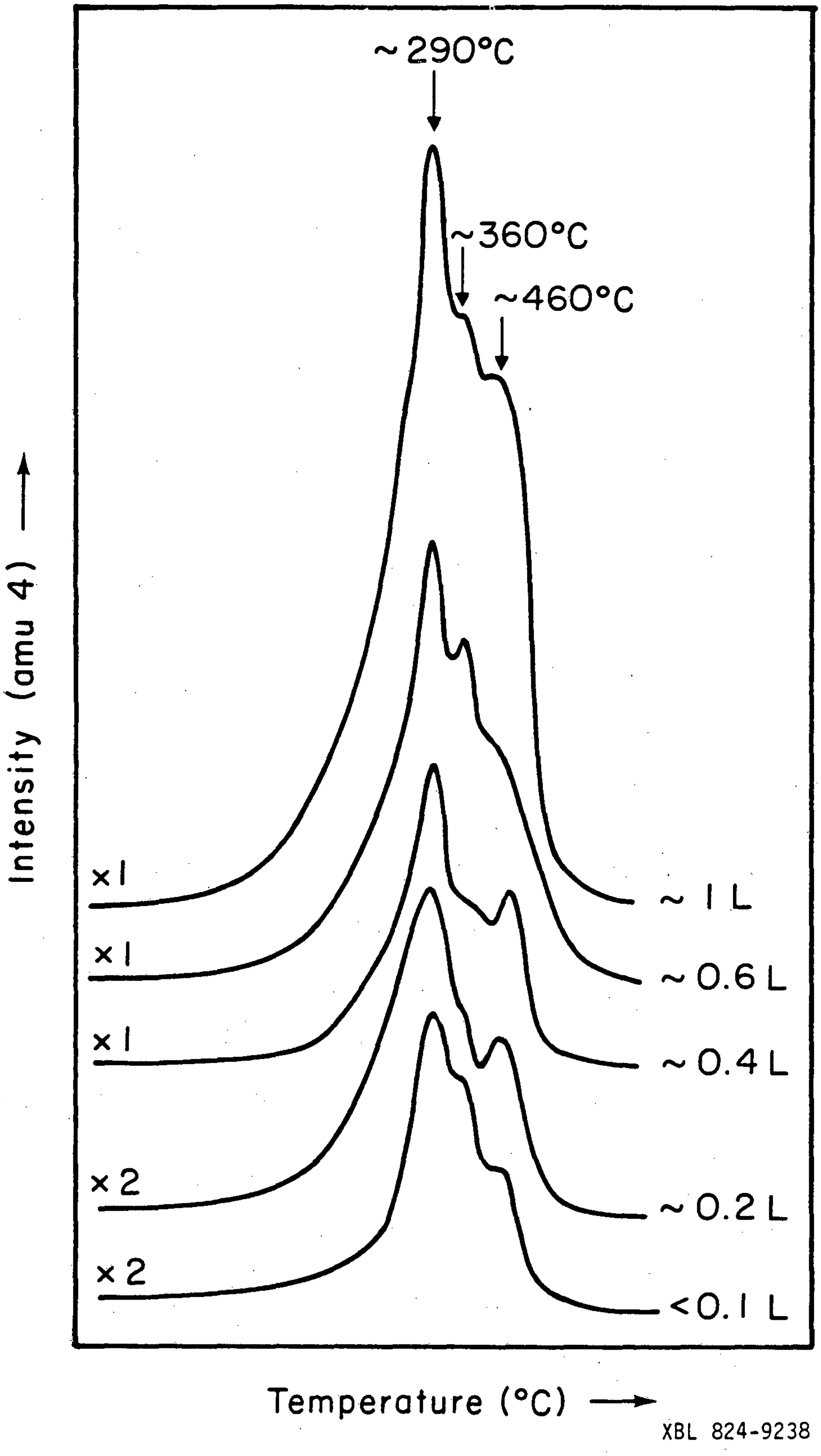
H-D exchange between chemisorbed C_6H_6 and C_6D_6 was not evident on the Pt(111) surface, but was a relatively fast process on the stepped Pt surface at temperatures greater than ~ 140°C. This difference might be ascribed to the topographical differences between the two surfaces, rather than the electronic differences between terrace and step sites, but the above data do not provide the basis for such a distinction. None of the Ni surfaces investigated exhibited reversible C-H bond breaking of chemisorbed benzene. This difference between Pt and Ni is to be ascribed to the electronic differences in the metal d-band structure that result in a greater thermodynamic reactivity of Pt-H than Ni-H.

Benzene Chemisorption on Pt(100). Chemisorption of benzene on the other low Miller index plane of platinum, Pt(100), is also largely molecular in character. At 25°C, adsorption of benzene on the Pt(100)-(5x20) surface readily converted the metal surface structure to Pt(100)-(1x1). The Pt(100) benzene chemistry is qualitatively similar to that of Pt(111) and Pt 6(111)x(111) in that two competing thermal processes, irreversible benzene decomposition to form H_2 and a carbon-contaminated surface, and reversible benzene desorption were observed in the thermal desorption experiments.

Like the Pt(111) and Pt 6(111)x(111) benzene chemistry, thermal decomposition of benzene to give H_2 was the dominant process at very low coverages on Pt(100). Hydrogen desorption maxima observed in the heating of Pt(100)-C_6D_6 were at ~ 295, 360 and 460°C with the relative intensities a function of surface coverage (Figure 13). A smaller HD peak was detected at T_{max} ~ 170°C, the characteristic desorption maximum for Pt(100)-H(D), which indicated some small extent of benzene dehydrogenation at $T < 100$°C. Even at ~ 0.05 L exposure (<< 0.1 C/Pt), reversible benzene desorption could be detected as a broad peak from 100 to 200°C. From ~ 0.1 L to ~ 0.4 L benzene exposures (~ 0.1-0.15 to 0.4-0.5 of a monolayer), the main benzene desorption maximum was at ~ 170-180°C while a smaller benzene maximum at ~ 100-110°C was detected also. Above ~ 0.4 L exposure, there was only one broad benzene desorption observed which maximum shifted from ~ 170°C to ~ 150°C at ~ 1 L exposure (~ 0.9 of a monolayer). From low (~ 0.1 of a monolayer) to high (~ 0.9 of a monolayer) surface coverages, the percentage of the benzene reversibility varied from 20 to 60-65%. Such coverage-dependence of benzene thermal desorption from Pt(100) is shown in Figure 14. Qualitatively, the complex nature of benzene chemisorption on Pt(100) was analogous to that on Pt(111)

Figure 13

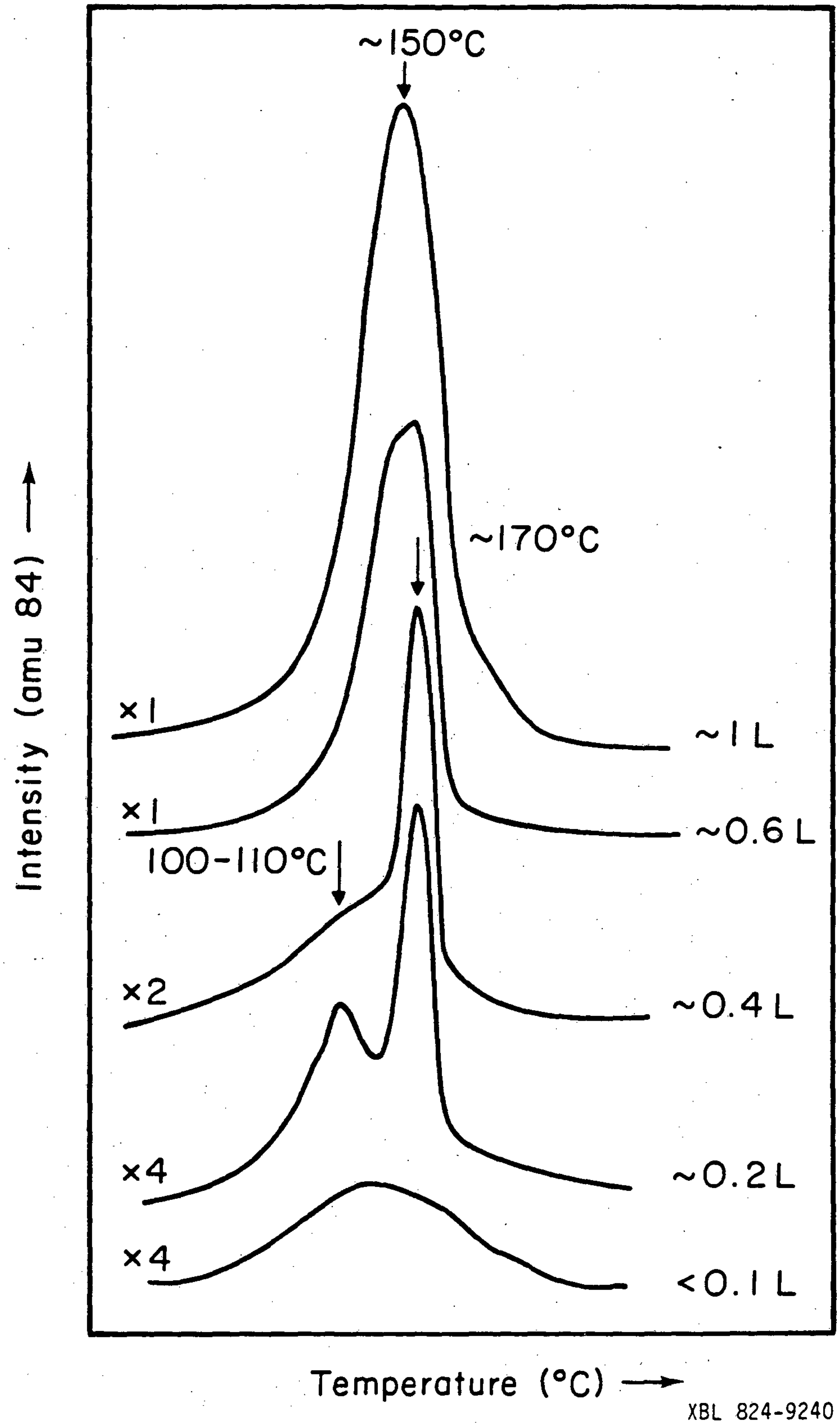
Thermal decomposition of benzene-d_6 chemisorbed on the Pt(100) surface results in multiple D_2 desorption peaks. Shown in this figure are the D_2 desorption spectra as a function of initial benzene coverage.


~290°C
~360°C
~460°C
Intensity (amu 4)
×1
×1
×1
×2
×2
~ 1 L
~ 0.6 L
~ 0.4 L
~ 0.2 L
<0.1 L
Temperature (°C)

XBL 824-9238

Figure 14

Depicted in the figure are the C_6D_6 desorption spectra from a Pt(100) surface as a function of coverage. These benzene spectra are complementary to the D_2 spectra presented in Figure 13 and for each coverage in the two figures, the spectra are derived from a single experiment.


~150°C
~170°C
100-110°C
×1
×1
×2
×4
×4
~1 L
~0.6 L
~0.4 L
~0.2 L
<0.1 L
Intensity (amu 84) →
Temperature (°C) →

XBL 824-9240

and Pt 6(111)x(111) except that the two benzene desorption maxima of the latter two surfaces were still distinguishable at high coverages.

To establish whether the two benzene desorption maxima of Pt(100)-C_6H_6 at $<$ 0.5 of a monolayer represented distinguishable chemisorption states--as established for Pt(111) and Pt 6(111)x(111), sequential population of one state by C_6H_6 and the other by C_6D_6 was attempted. In the subsequent thermal desorption experiment, both C_6H_6 and C_6D_6 desorbed in a relatively fixed molar ratio throughout the entire thermal desorption range for benzene rather than in sequence as was observed in the analogous experiments on Pt(111) and Pt 6(111)x(111) described in previous sections. This experiment suggested that there was no detectable preferential chemisorption. Furthermore, there was no evidence of benzene displacement by benzene, i.e., C_6D_6 was not displaced by C_6H_6 at 25°C and $\sim 10^{-8}$ torr of C_6H_6 flux whereas benzene displacement was readily achieved on Pt(111) and Pt 6(111)x(111) under similar conditions.

Trimethylphosphine displaced benzene (C_6D_6) from Pt(100) at 25°C but was not quantitative. A subsequent thermal desorption experiment still contained significant amounts of C_6D_6 ($T_{max} \sim$ 170°C), CH_3D and HD. The phosphine displacement was probably 60-70% complete at most (compared with $>$ 90% for Pt(111) and 70-80% for Pt 6(111)x(111)). Since the displacement mechanism is unknown, the much less complete displacement of benzene on Pt(100) cannot be unambiguously interpreted.

The most interesting feature of benzene chemisorption on Pt(100) is the observation of reversible C-H bond breaking, a feature that has not been observed for Pt(111) or any other low Miller index planes of nickel. Adsorption of a 1:1 mixture of C_6H_6 and C_6D_6 on Pt(100) at 25°C showed, in thermal desorption, all possible mixed benzene molecules, CH_xD_{6-x} ($x = 1$ to 5), at 170-180°C irrespective of the initial coverages. The molar ratios of the CH_xD_{6-x} molecules were recorded as 33, 7, 7, 7, 7, 7, and 33% for x equals 0 to 6, respectively. The formation of mixed benzene molecules probably did not occur until relatively high temperatures, as demonstrated by the trimethylphosphine displacement experiment. At 25 to 70°C, $P(CH_3)_3$ displacement of Pt(100)-C_6H_6-C_6D_6 yielded only C_6H_6 and C_6D_6 molecules. Mixed benzene molecules were only detected in displacement reactions effected at 100°C or higher. Such thermally activated H-D exchange reactions were also observed for Pt 6(111)x(111)-C_6H_6-C_6D_6. More substantial amounts of mixed benzene molecules were detected on Pt 6(111)x(111) (~ 4 to 5 times higher) than on Pt(100).

Since a large fraction (50-65%) of adsorbed benzene, at moderate coverages, can be thermally desorbed or chemically displaced, benzene chemisorption on Pt(100) is probably largely molecular. Fischer and Keleman have investigated benzene chemisorption on Pt(100) by ultraviolet photoemission spectroscopy,[37] and concluded that chemisorption was through π and π^* orbitals of benzene. Although adsorption of benzene on the clean, reconstructed Pt(100)-(5x20) surface readily converts the surface to the Pt(100)-(1x1) structure, there are still ambiguities about the microscopic structure of Pt(100) at room temperature or higher temperatures. It is possible that the (1x1) LEED pattern does not represent an "atomically flat" Pt(100) surface, but rather, a slightly "buckled" surface layer. If this were the case, some of the adsorbed benzene hydrogen atoms would be relatively close to the Pt metal surface atoms, at least at higher temperatures, to generate the C-H-Pt multicenter bonding. This interaction could be the cause for the high efficiency of reversible C-H bond breaking observed at $T > 100°C$. However, the intrinsic electronic structure of the Pt(100) surface could also be a contributing factor for H-D exchange, and it is not possible to fully characterize the electronic and topographical features that affect C-H bond breaking and making processes for benzene on Pt(100).

3. Toluene Chemistry

Toluene Chemisorption on Pt(111). Chemisorption of toluene on Pt(111) is mostly irreversible. At < 0.5 of a monolayer, no reversible toluene desorption was detected. Even at ~ 0.8 of a monolayer, only ~ 10% of the adsorbed toluene could be reversibly desorbed at 70-110°C with a poorly resolved double maximum. No H-D exchange between the adsorbed C_7H_8 and C_7D_8 molecules was evident in thermal desorption experiments. Chemical displacement of toluene chemisorbed on Pt(111) (at high coverages) by $P(CH_3)_3$ was negative at 25°C. Clearly, the chemisorption behavior of toluene on Pt(111) is distinctly different from that of benzene.

Thermal decomposition of toluene on Pt(111) yielded hydrogen as the only gaseous product. Multiple hydrogen desorption peaks from Pt(111)-C_7D_8 were detected with temperature maxima of ~ 70 (small), 215, 250 and 380°C with the intermediate overlapping desorption peaks having a combined intensity comparable to that of the 380°C peak. To test whether there was any regioselective C-H bond breaking of chemisorbed toluene on Pt(111), thermal desorption experiments using selectively labeled toluene molecules, $C_6H_5CD_3$ and $C_6D_5CH_3$, were performed to monitor the desorption character of H_2, HD and D_2, These hydrogen desorption maxima together with the relative intensities are listed in Table II and compared with the data for $C_6D_5CD_3$. The decomposition characteristics, based on the H_2, HD, and D_2 desorption peaks for Pt(111)-$C_6H_5CD_3$ and Pt(111)-$C_6D_5CH_3$, were complex and there was no clear identification of regioselective C-H bond breaking of toluene on Pt(111). This is in sharp contrast to the toluene decomposition on Ni(111), Ni(100), Ni 9(111)x(111) and Ni 7(111)x(310)[9] where regioselective C-H bond breaking of the methyl group was incisively identified by the labeling experiments. However, for Pt(111)-$C_6H_5CD_3$, all the H_2 desorption appeared at high temperatures and none at 70°C where D_2 and HD were observed. Analogously, only H_2 appeared at 70°C in the decomposition of Pt(111)-$C_6D_5CH_3$. Therefore, there was probably some regioselectivity in the C-H bond breaking process on Pt(111) with aliphatic C-H bond breaking being more facile than that of aromatic.

Toluene Chemisorption on Pt 6(111)x(111). Consistent with benzene chemistry on Pt(111) and Pt 6(111)x(111), toluene chemisorption on the stepped surface was less reversible,--in fact, all the adsorbed toluene decomposed in the thermal desorption experiment, to give hydrogen, from low to near monolayer coverages. Trimethylphosphine also did not displace any of the adsorbed toluene from the stepped Pt surface.

Analogous thermal desorption experiments were performed on Pt 6(111)x(111) with $C_6H_5CD_3$, $C_6D_5CH_3$ as well as $C_6D_5CD_3$, and these

Table II

Decomposition of Toluene on Pt(111) and Pt 6(111)x(111)

Molecule		Temperature Maxima (°C) of Hydrogen Desorption (Intensity*)
Pt(111)		
$C_6D_5CD_3$	D_2:	70(0.2), 215(0.7), 250(0.4), 380(1.0)
$C_6H_5CD_3$	D_2:	70(0.3), 200(1.0), 420(0.8)
	HD:	70(0.25), 210(1.0), 380(1.0)
	H_2:	225(1.0), 360(1.0)
$C_6D_5CH_3$	D_2:	230(0.7), 380(1.0)
	HD:	150(1.5), 380(1.0)
	H_2:	70(0.2), 185(1.0), 380(trace)
Pt 6(111)x(111)		
$C_6D_5CD_3$	D_2:	100(trace), 180(1.0), 240(1.0), 380(2.0)
$C_6H_5CD_3$	D_2:	90(0.3), 170(1.0), 415(0.7)
	HD:	90(trace), 192(3), 400(2)
	H_2:	210(1), 345(1)
$C_6D_5CH_3$	D_2:	235(1.0), 385(1.5)
	HD:	200(1.5), 345(1.0)
	H_2:	100(trace), 165(1.0), 340(trace)

* Relative intensities can be compared only at the given temperature and in the given experiment.

data are summarized in Table II. The thermal decomposition behavior of chemisorbed toluene on Pt 6(111)x(111) appeared to be as complex as the Pt(111) analogs. Four hydrogen (D_2) desorption peaks were detected at temperature maxima of 100 (small), 180, 240 and 380°C. The small hydrogen peak at ~ 100°C consisted of, on heating, D_2 and HD for Pt 6(111)x(111)-$C_6H_5CD_3$ and only H_2 for Pt 6(111)x(111)-$C_6D_5CH_3$. As the analogous arguments presented for both Pt(111)-$C_6H_5CD_3$ and Pt(111)-$C_6D_5CH_3$, these data suggest that there was probably some selective scission of the methyl C-H bonds, although the rates for scission of aliphatic and aromatic C-H bonds were probably very close.

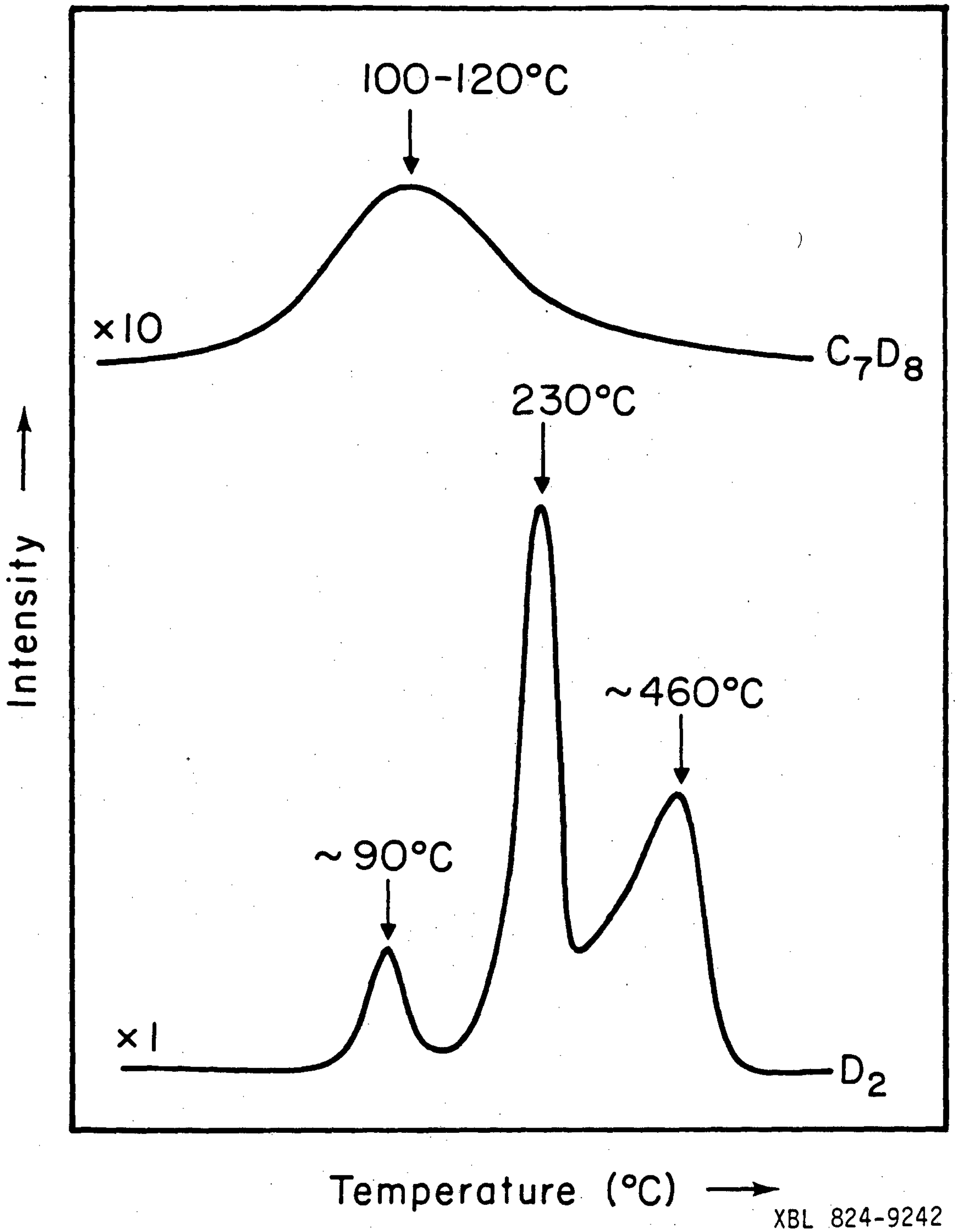
Toluene Chemisorption on Pt(100). The chemisorption of toluene on Pt(100) surface was also complex in character. Qualitative similarities of Pt(100)-toluene chemistry to that of Pt(111) and Pt 6(1111)x(111) were identified in this study, although important differences were also established.

On the Pt(100)-(5x20) surface, chemisorption of toluene at 25°C immediately converted the surface to the Pt(100)-(1x1) structure. Two competing thermal processes were evident at coverages larger than 0.5 of a monolayer (Figure 15). The reversible toluene that desorbed at the temperature maximum of 100-120°C represented ~ 20-30% of the initially adsorbed toluene at ~ 0.8 of a monolayer. These reversibly desorbed toluene molecules contained no detectable amount of mixed toluene molecules when Pt(100)-C_7H_8, formed at ~ 15°C then heated to 60-70°C in a D_2 atmosphere of ~ 10^{-8} torr for 1 min, was subject to the thermal desorption experiment.

Displacement of the chemisorbed toluene, at high coverages, on

Figure 15

Thermal desorption of Pt(100)-$C_6D_5CD_3$ results in molecular C_7D_8 desorption as well as decomposition to give D_2, as shown in this figure. The spectra were obtained from a Pt(100)-$C_6D_5CD_3$ surface formed at ~ 15°C with an initial coverage of ~ 0.8 C/Pt.



XBL 824-9242

Pt(100), by $P(CH_3)_3$ from 20 to 60°C was not successful as was found on Pt(111) and Pt 6(111)x(111). The following thermal desorption showed some toluene (C_7D_8) at $T_{max} \sim 150°C$, and large amounts of CH_3D and HD. The binding of molecular toluene to these Pt surfaces through π and π^* orbitals of the ring should not be very different from that of benzene. The absence of any toluene displacement from Pt(111), Pt(100) and Pt 6(111)x(111) by $P(CH_3)_3$, a sharp contrast to the facile benzene displacement by $P(CH_3)_3$, suggests that the major chemisorption state generated from toluene and Pt(111), Pt(100) or Pt 6(111)x(111) at $T \approx 20°C$ may not be analogous to that derived from benzene.

Decompositon of toluene on Pt(100) is the major thermal process to give H_2 and a C-contaminated surface afterwards. Hydrogen desorbed at three maximal rates: ~ 90, 230 and 460°C with respective relative intensities of 1:3:4 (Figure 15). The low temperature H_2 maximum at 90°C was in the characteristic desorption region of Pt(100)-H, indicating breaking of C-H bond at relatively low temperatures. In order to gain more mechanistic insight into toluene decomposition on Pt(100), thermal decomposition studies of selectively labeled toluene, $C_6H_5CD_3$ and $C_6D_5CH_3$, were performed. As shown in Table III, the 90°C peak consisted of mainly D_2 and a smaller amount of HD for Pt(100)-$C_6H_5CD_3$ (Figure 16), and only H_2 for Pt(100)-$C_6D_5CH_3$. The major fraction of the toluene initially chemisorbed at 15°C on Pt(100) may be selectively converted to Pt(100)-H-$C_6H_5CH_2$ between ~ 15 and 90°C. Beyond this step, the rates of aliphatic and aromatic C-H bond breaking overlap substantially; there is no regioselectivity.

Table III

Decomposition of Toluene on Pt(100)

Molecule	T_{max}(°C) of Hydrogen Desorption (Intensity)*
$C_6D_5CD_3$	D_2: 90(1), 230(3), 460(4)
$C_6H_5CD_3$	D_2: 90(2), 230(2), 460(1)
	HD: 90(trace), 230(14), 460(6)
	H_2: 230(26), 460(18)
$C_6D_5CH_3$	D_2: 230(8), 460(18)
	HD: 230(18), 460(11)
	H_2: 90(3), 230(23), 460(5)
$C_6H_5CD_3$**	D_2: none
	HD: 230(4), 460(2)
	H_2: ~ 100†, 230(20), 460(26)

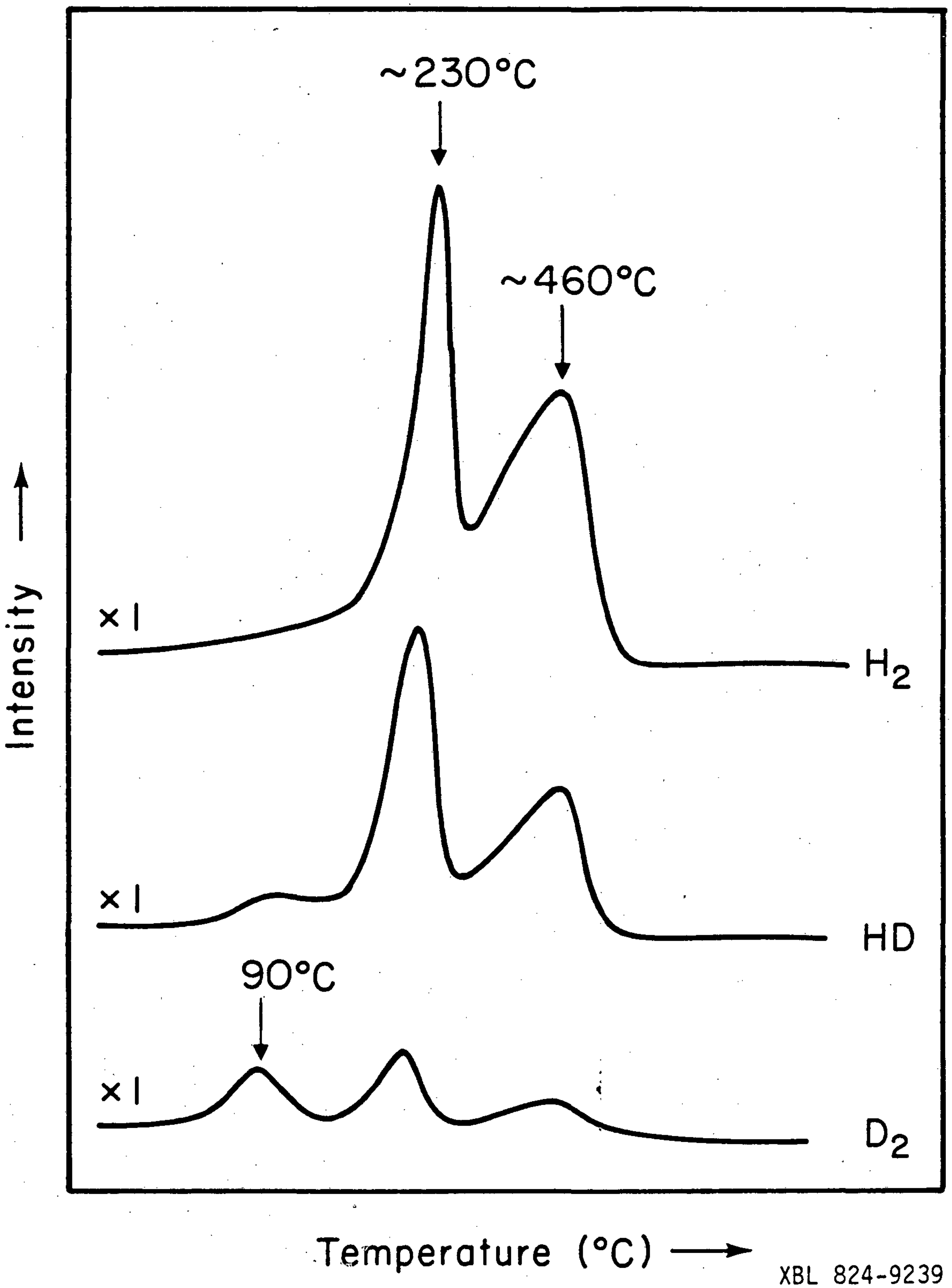
* Relative intensities should be compared in the given toluene decomposition experiment only.

** A Pt(100)-$C_6H_5CD_3$ surface was treated with 1×10^{-7} torr H_2 at 75°C for 5 minutes before thermal desorption.

† very large intensity.

Figure 16

D_2, HD and H_2 desorption spectra derived from thermal decomposition of Pt(100)-$C_6H_5CD_3$ are illustrated in this figure. The lowest hydrogen desorption maximum, ~ 90°C, is characteristic of Pt(100)-H(D) and consisted of D_2 and HD but not H_2 (presumably, the HD arose from the reaction between surface-D species derived from toluene and surface-H species derived from background H_2). Clearly, the initial C-H(D) bond breaking is centered on the methyl group.



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In the acetylene chemistry on the Pt(100) surface, it was established that H-D exchange between H_2 and Pt(100)-D was a facile process. Thus, the postulated surface state generated from chemisorption of $C_6H_5CD_3$ and Pt(100): Pt(100)-$C_6H_5CD_2$ and Pt(100)-D species should undergo facile exchange with H_2 to form Pt(100)-$C_6H_5CD_2$ and Pt(100)-H. In practise, treatment of Pt(100)-$C_6H_5CD_3$, formed and kept at T < 20°C, with 1 x 10^{-7} torr H_2 for 10 minutes yielded, in the following thermal desorption study, H_2 but no HD or D_2 in the characteristic desorption region of Pt(100)-H. The two higher temperature desorption maxima for H_2, HD and D_2 showed some slight indication of H-D exchange between H_2 and Pt(100)-$C_6H_5CD_2$ (the relative intensity of H_2 to HD or D_2 was slightly higher than that derived simply from $C_6H_5CD_3$ chemisorption on Pt(100)).

At higher temperatures, the postulated benzyl species formed from toluene adsorption on Pt(100) underwent extensive H-D exchange. Treatment of Pt(100)-$C_6H_5CD_3$, formed at T < 20°C, at 50°C, 75°C, 100°C and 130°C, respectively, with 1 x 10^{-7} torr H_2 for 5 minutes clearly showed a systematic trend in the extent of H-D exchange from the subsequent thermal desorption study. After the 50°C treatment, some H-D exchange was clearly established by examining the relative intensities of H_2, HD and D_2. After the 75°C treatment, no D_2 and only a small amount of HD was detected at the two higher temperature peaks, 230 and 460°C (Table III). Finally, after the 130°C treatment, H-D exchange between the CD_2 site and H_2 was complete. H-D exchange at the aromatic C-H sites also occurred but more slowly than at the CH_2 site. At 75°C, treatment of

Pt(100)-$C_6D_5CH_3$ with 1 x 10^{-7} torr H_2 for 5 minutes showed a thermal desorption spectrum with slightly more H_2 relative to HD or D_2, whereas at 130°C, a similar H_2 treatment of Pt(100)-$C_6D_5CH_3$ resulted in significantly more H_2 relative to D_2 and HD except that H-D exchange was never complete under these conditions.

The stereochemistry of Pt(100)-benzyl is probably a nearly coplanar C_7 delocalized framework lying parallel to the surface plane whereby the delocalized C_7 π and π^* orbitals could have maximal overlaps with appropriate metal surface orbitals. Such benzyl species was also postulated for toluene chemisorbed on the (111), (100), 9(111)x(111) and 7(111)x(310) planes of nickel[9] in which thermal decomposition of toluene proceeded in a regioselective fashion such that all aliphatic C-H bonds were cleaved prior to scission of any aromatic C-H bonds. The chemisorption of toluene on Pt(100) partially followed this regioselective course: the first C-H bond breaking occurs on an aliphatic C-H bond to give the benzyl species upon chemisorption at T ~ 20°C.

Conclusions

In this study, the coordination chemistry of benzene and toluene on Pt(111), Pt 6(111)x(111) and Pt(100) was investigated by surface chemical techniques. Important electronic and stereochemical features of benzene and toluene chemisorption that facilitate C-H bond breaking and making processes were established. Benzene chemisorption on these Pt surface planes is largely molecular (associative) in character. On the Pt(111) and Pt 6(111)x(111) surfaces, chemisorption of benzene exhibits an initially and irreversibly bound state as well as two differentiable, reversibly bound states. The presence of surface steps (of the Pt 6(111)x(111) surface) led to a higher reactivity toward C-H bond breaking. Benezene chemistry on the two low Miller index planes of Pt, (111) and (100), is distinctly different in that reversible C-H bond breaking occurs on Pt(100). Even more substantial H-D exchange between chemisorbed benzene molecules occurs on the stepped platinum surface. The differences in the benzene chemistry on the three Pt surfaces investigated could be largely attributed to their topographical differences.

In contrast to benzene, toluene chemisorption on the Pt surfaces is mostly irreversible. Thus, although the initial interaction of toluene with the Pt surfaces is probably largely through the aromatic ring, like that of benzene, the final toluene chemisorption state(s) may be very different from that of benzene stereochemically. The initial π -bound state of toluene necessarily brings the methyl hydrogen atoms into close proximity of the metal surface atoms. Consequently, facile C-H bond scission at some higher temperatures can occur to give a benzyl species.

On the Pt(100) surface, experimental data for toluene chemisorption are consistent with formation of a benzyl species at $T < 20°C$. H-D exchange at the CH_2 site of benzyl species was detected at temperatures as low as 50°C and was complete at 130°C. Exchange at the aromatic C-H sites occurs more slowly (was only detected at $T > 75°C$) and was far from complete at 130°C. In general, the toluene chemistry on the Pt surfaces is much more complex than on the Ni analogs. Only partially regioselective

C-H bond scission on the aliphatic group was evident on the Pt surfaces.

V. DEHYDROGENATION REACTIONS OF CYCLOHEXANE, CYCLOHEXENE, AND CYCLOHEXADIENE TO BENZENE ON PLATINUM AND NICKEL SURFACES

The dehydrogenation of cyclohexane and its homologs to aromatics occurs on a large number of Group VIII metal catalysts.[45] In particular, dehydrogenation of cyclohexane to benzene on supported catalysts of Pt and Ni has been a much investigated area[46-49] with Pt being much more active than Ni.[50] Generally, benzene desorption is thought to be the rate-determining step of the catalytic dehydrogenation of cyclohexane, and cyclohexene and cyclohexadiene are postulated to be the reaction intermediates. These catalytic cyclohexane dehydrogenation studies appear to be a "structure-insensitive" reaction,[51]--the rate for dehydrogenation is not dependent upon the form of catalysts. In contrast, studies of cyclohexane dehydrogenation over single crystal Pt surfaces and low pressures ($< 10^{-6}$ torr) by Somorjai and co-workers[52,53] have shown a much higher reactivity for the stepped and stepped-kinked Pt surfaces in conducting C-H bond scission,--a "structure-sensitive" reaction.

In order to gain a better understanding of catalytic cyclohexane dehydrogenation, the Pt and Ni surface chemistry of cyclohexane, cyclohexene and cyclohexadiene was investigated in the context of surface crystallography and surface composition under ultra high vacuum conditions. The Pt and Ni surfaces studied were the low Miller index planes: Pt(111), Pt(100), Ni(111), Ni(100) and Ni(110), and the stepped Pt 6(111)x(111) and Ni 9(111)x(111) surfaces. Surface techniques employed were Auger electron spectroscopy, thermal desorption spectroscopy, isotopic labeling and chemical displacement reactions. Both clean and carbon-contaminated surfaces were investigated in order to pursue the carbon impurity effects on the dehydrogenation reactions of these cyclic hydrocarbons. Since the benzene chemistry on the corresponding surfaces has been characterized by the aforementioned surface techniques (described in the previous chapter for the Pt surfaces and in the thesis work of Dr. C. M. Friend[14] for Ni surfaces), the dehydrogenaton of cyclohexane, cyclohexene or cyclohexadiene to form benzene on the crystallographic planes of Ni and Pt was an ideal extension of this hydrocarbon surface chemistry study with the trimethylphosphine displacement reaction being the diagnostic technique for detecting benzene formation.

Results and Discussion

1. Cyclohexane Chemistry

Adsorption of cyclohexane on the Ni(111), Ni(100), Ni(110) and Ni 9(111)x(111) surfaces was attempted at 0-70°C, 25-200°C, 25-90°C, and 20-70°C, respectively. The upper temperature limit was set by the characteristic benzene desorption temperature from the individual surface because the benzene formation was to be characterized by the subsequent thermal desorption or chemical displacement reactions. Under ultra high vacuum conditions and within the temperature ranges studied, no evidence was found for cyclohexane adsorption on these Ni surfaces as judged by Auger analyses and thermal desorption studies. Probably, the residence time for cyclohexane on these Ni surfaces was too short to effect any significant dehydrogenation process under these conditions.

Cyclohexane showed a relatively higher sticking coefficient on the Pt(111), Pt(100) and Pt 6(111)x(111) surfaces, compared to the Ni surfaces with comparable surface crystallographies. On the Pt(111) surface, adsorption of cyclohexane at -35 to -15°C gave a small cyclohexane desorption peak at ~ 0°C in the thermal desorption experiment. Desorption of cyclohexane was nearly quantitative and was accompanied by a small amount of hydrogen evolution from 200 to 400°C. Adsorption of cyclohexane at ~ 135°C on Pt(111) gave only H_2, no hydrocarbons, at 200-400°C. The saturation coverage of cyclohexane on Pt(111) from -35°C to +135°C was reached at ~ 0.1-0.15 of a monolayer. No benzene was ever detected in the thermal desorption of Pt(111)-C_6H_{12}. However, even if the adsorbed cyclohexane had quantitatively converted to the chemisorbed benzene, no benzene would have been desorbed or displaced at coverages of < 0.1 of a monolayer (see the previous chapter). Displacement of Pt(111)-C_6D_{12} by $P(CH_3)_3$ failed to give any detectable hydrocarbon molecules. However, the subsequent heating of this surface did lead to benzene desorption at the temperature maximum of ~ 150°C. A similar feature was observed in the heating of Pt(111)-C_6D_6-$P(CH_3)_3$ in which the undisplaced C_6D_6, the strongly bound benzene state at < 0.1 of a monolayer, was desorbed at ~ 150°C. Thus, conversion of cyclohexane to benzene probably occurred on the Pt(111) surface, but the surface chemical methods used here could not fully probe such processes.

On the Pt(100) surface, cyclohexane also showed a very small sticking coefficient from 25 to 100°C. Thermal desorption of Pt(100)-C_6D_{12} yielded D_2 as the only gaseous product and a Pt(100) surface with < 0.1 of a monolayer of carbon. Multiple D_2 desorption peaks were observed at temperature maxima of ~ 110, 175, 220 and 345°C. Trimethylphosphine failed to displace benzene (or any other hydrocarbon species) from Pt(100)-C_6D_{12} at 25-100°C. However, as was observed for Pt(111)-cyclohexane chemistry, heating of the surface immediately after the attempted $P(CH_3)_3$ displacement gave benzene desorption at the temperature maximum of ~ 160°C,--a similar feature was also observed in the heating of Pt(100)-C_6D_6-$P(CH_3)_3$. Therefore, there was indirect evidence of benzene formation from cyclohexane dehydrogenation on the Pt(100) surface.

Cyclohexane had the highest sticking coefficient on the stepped Pt 6(111)x(111) surface at 25°C among all the Ni and Pt surfaces studied, and appeared to be saturated at ~ 0.15-0.20 of a monolayer. At such saturation coverage, thermal desorption of Pt 6(111)x(111)-C_6D_{12} showed D_2 as the only gaseous product and a Pt 6(111)x(111)-C surface. As was established in the Pt 6(111)x(111)-benzene chemistry, no molecular benzene desorption could have been observed for surface coverages of $<$ 0.15. Three D_2 desorption peaks were detected at temperature maxima of ~ 110, 195 and 350°C with the two higher temperature maxima being coincident with that of thermal decomposition for Pt 6(111)x(111)-C_6D_6, and the lowest desorption maximum characteristic of Pt 6(111)x(111)-H(D). Although no benzene desorption could be observed from Pt 6(111)x(111)-C_6D_{12}, chemical displacement with $P(CH_3)_3$ at 25°C did yield a small quantity of C_6D_6, and the following heating showed a benzene desorption maximum at 170-190°C, characteristic of thermal desorption of Pt 6(111)x(111)-C_6D_6-$P(CH_3)_3$ at comparable coverages. Thus the chemisorption state of C_6D_{12} on the stepped Pt surface at 25°C could be best characterized as Pt 6(111)x(111)-C_6D_6-D judged from these surface chemical studies. All the benzene that formed from cyclohexane dehydrogenation was probably residing in the most strongly (irreversibly) bound state since all the thermal desorption characteristics of Pt 6(111)x(111)-C_6D_{12} are identical with those of Pt 6(111)x(111)-C_6D_6-D generated from C_6D_6 and D_2 at comparable coverages.

When a mixture of C_6H_{12} and C_6D_{12} was adsorbed initially on Pt(111), Pt(100) or Pt 6(111)x(111), heating of the surface after trimethylphosphine displacement yielded all possible $C_6H_xD_{6-x}$ molecules, indicating that H-D exchange was probably operative in the dehydrogenation process of cyclohexane on these Pt surfaces.

These studies for the Pt surfaces establish a much higher reactivity of cyclohexane on the stepped Pt surface than that of the two low Miller index planes, Pt(111) and Pt(100). If the surface step sites of the Pt 6(111)x(111) surface were associated with the higher reactivity of C-H bond breaking of cyclohexane, the smaller reactivity observed on the Pt(111) and Pt(100) surfaces could be due to the intrinsic surface imperfection sites. Since cyclohexane did not react with the Ni surfaces, Pt appeared to be more reactive than Ni at the temperature ranges studied and under ultra high vacuum conditions. However, it cannot be hereby concluded that the relative rates for C-H bond breaking are higher for Pt than for Ni since the residence time of cyclohexane on the Ni surfaces at 20°C or above is probably much shorter than that of the Pt surfaces.

Low temperature adsorption ($T \approx 140$ K) of cyclohexane[54] has shown that cyclohexane reversibly desorbs from Ni(111) at $T > 170$ K, but dehydrogenates to form benzene on Pt(111) at $T > 200$ K. From this earlier report, Pt(111) shows a larger reactivity than Ni(111) toward cyclohexane dehydrogenation, as was also suggested from this study.

The formation of benzene from cyclohexane dehydrogenation could be a function of adsorption temperature and heating rate with lower temperature and lower heating rates favoring benzene formation. Since cyclohexane dehydrogenation on Ni readily occurs at atmospheric pressures, the failure of these Ni surfaces in effecting cyclohexane dehydrogenation under ultra high vacuum conditions could be simply thermodynamically unfavored.

The initial interaction of cyclohexane with the metal surfaces should be through some saturated C-H bonds, irrespective of its configuration, to form C-H-M multicenter bonding. A possible model is the formation of three C-H-M multicenter bonds with three of the axial hydrogen atoms on one side of the chair form of cyclohexane. Such interaction, although relatively weak in character, could become strong enough for C-H bond breaking, at some elevated temperatures, to form M-H species and more strongly chemisorbed olefinic species (or even benzene). In fact, high resolution electron energy loss studies of cyclohexane on Pt(111) and Ni(111)[54] at $T \approx 140$ K have revealed a strong C-H stretching frequency at 2590 cm^{-1} and 2720 cm^{-1}, respectively, in addition to the normal C-H stretching of saturated hydrocarbon at ~ 2900 cm^{-1}. These previous observations appear to be a strong evidence for C-H bond interaction of cyclohexane with the metal surfaces. From this study, the C-H-M multicenter interaction between cyclohexane and the metal surface is the most prominent on the stepped Pt 6(111)x(111) surface under the ultra high vacuum conditions and temperature ranges investigated.

2. Cyclohexene Chemistry

Cyclohexene had a sticking coefficient comparable to that of benzene on the Ni and Pt surfaces at 25°C. Dehydrogenation of cyclohexene to form benzene occurred on all the Ni and Pt surfaces investigated (Table I).

On the Ni(111) surface, adsorption of cyclohexene at 25°C led to no benzene desorption at ~ 0.3 of a monolayer coverage upon heating. Hydrogen (D_2) was the only gaseous product detected in the thermal desorption of Ni(111)-C_6D_{10}, which desorbed from 140 to 200°C with an unresolved double maximum. The diagnostic experiment of benzene formation from Ni(111)-C_6D_{10} was the trimethylphosphine displacement of a significant amount of C_6D_6 at 25°C. Since surface D atoms were reaction products from C_6D_{10} dehydrogenation on Ni(111), the extent of dehydrogenation could not be precisely established by examining the amounts of the deuterium-containing products, CH_3D and HD, in the subsequent thermal desorption study. However, cyclohexene dehydrogenation on Ni(111) must have been a significant process since the amount of benzene displaced from Ni(111)-cyclohexene was comparable to that from Ni(111)-benzene at similar coverages.

On the Ni(100) surface, the thermal desorption behavior of adsorbed cyclohexene (C_6D_{10}) appeared to be analogous to that of Ni(100)-C_6D_6-D: Heating of Ni(100)-C_6D_{10}, formed at 25°C, resulted in C_6D_6 desorption at 200-220°C, characteristic of benzene desorption from Ni(100)-C_6D_6, as well as D_2 desorption at ~ 130 and ~ 200°C with the former characteristic of Ni(100)-D and the latter characteristic of Ni(100)-C_6D_6 decomposition. In addition, there was a small amount of C_6D_{10} desorbed at ~ 100°C. $P(CH_3)_3$ displacement

Table I

The Thermal Desorption Behavior for Cyclohexene Adsorbed on Ni and Pt

		Thermal Desorption Maxima	
Surface	Coverage (C/M)	C_6D_6	D_2
Ni(111)-C_6D_{10}	~ 0.3	none	140-200°C
Ni(111)-C_6D_6	~ 0.3	115-125°C	180°C
Ni(100)-C_6D_{10}	~ 0.3	200-220°C	130, 200°C
Ni(100)-C_6D_6	~ 0.3	200-220°C	200-220°C
Ni(110)-C_6D_{10}	~ 0.3	200°C (trace)	100, 200°C
Ni(110)-C-C_6D_{10}	~ 0.5	~ 135°C	not detected
Ni(110)-C_6D_6	~ 0.3	100°C	~ 105°C
Ni 9(111)x(111)-C_6D_{10}	~ 0.5	100-110°C	100, 185°C
Ni 9(111)x(111)-C_6D_6	~ 0.5	115-125°C	~ 180°C
Pt(111)-C_6D_{10}	~ 0.5	130-140°C	130, 170, 260, 380°C
Pt(111)-C_6D_6	~ 0,5	100-130, 200-220°C	270, 380°C
Pt(100)-C_6D_{10}	~ 0.6	150-165°C	160, 290, 360, 460°C
Pt(100)-C_6D_6	~ 0.6	150-165°C	290, 360. 460°C
Pt 6(111)x(111)-C_6D_{10}	< 0.15	none	110, 195, 350°C
	~ 0.15-0.45	180-210°C	110, ~ 200, 350°C
	> 0.5	150-155°C(broad)	110, 165, 215, 350°C
Pt 6(111)x(111)-C_6D_6	~ 0.6	100-120, 180-210°C	195, 355°C

of Ni(100)-C_6D_{10} failed to give any detectable amount of hydrocarbon at 25–100°C. The rate of cyclohexene dehydrogenation to form benzene on Ni(100) was probably only fast at temperatures of 100–130°C based on the above key observations: Some intact cyclohexene desorbed at ~ 100°C in the thermal desorption experiment; there was no evidence of benzene formation at temperatures lower than 100°C (judged from $P(CH_3)_3$ displacement); and the maximal rate of the initial dehydrogenation step of cyclohexene to form hydrogen was not reached until ~ 130°C.

Adsorption of cyclohexene on Ni(110) led to the desorption of benzene and hydrogen in the thermal desorption experiment, but there were significant differences in the thermal desorption characteristics between Ni(110)-benzene and Ni(110)-cyclohexene. Thermal desorption of Ni(110)-C_6D_6 resulted in C_6D_6 at ~ 100°C and a broad D_2 peak at ~ 105°C whereas that of Ni(110)-C_6D_{10} gave only a trace amount of C_6D_6 at ~ 200°C and two D_2 peaks at ~ 100 and ~ 200°C with comparable intensities. Although only a trace amount of C_6D_6 was observed from C_6D_{10} dehydrogenation on Ni(110), formation of C_6D_6 was evident at 25°C in the $P(CH_3)_3$ displacement reactions. In the subsequent heating, some benzene desorption was still observed which, with the fact that benzene desorption from Ni(110)-C_6D_{10} being ~ 100° higher than that from Ni(110)-C_6D_6, indicated that some benzene was formed at higher temperatures. Thus, cyclohexene dehydrogenation was probably a very complex process on Ni(110).

Cyclohexene readily converted to benzene on the stepped Ni 9(111)x(111) surface at 25°C. Thermal desorption of Ni 9(111)x(111)-C_6D_{10} gave C_6D_6 at 100–110°C, and D_2 at ~ 100 and ~ 185°C, which were coincident with the desorption behavior of Ni 9(111)x(111)-C_6D_6-D. Formation of benzene at 25°C from cyclohexene dehydrogenation was evident in the chemical displacement reaction with $P(CH_3)_3$.

When a mixture of C_6H_{10} and C_6D_{10} was adsorbed on the Ni(111), Ni(100), Ni(110), or Ni 9(111)x(111) surface, thermal desorption and $P(CH_3)_3$ displacement experiments indicated that there was no evidence of H-D exchange during the dehydrogenation process of the adsorbed cyclohexene molecules.

Conversion of cyclohexene to benzene on Pt(111) appeared to be a thermally activated process. Heating of a Pt(111)-C_6D_{10} surface gave only a single C_6D_6 desorption peak at 130-140°C; a distinctly different behavior was observed for Pt(111)-C_6D_6 in which two broad benzene desorption maxima at 100-130°C and 200-220°C were detected. Thermal decomposition of Pt(111)-C_6D_{10} resulted in four D_2 desorption maxima at ~ 130, 170, 255 and 380°C with approximate relative intensities of 4 : 2 : 2 : 2. The first hydrogen desorption maximum, although in the characteristic desorption region of Pt(111)-H(D), was relatively sharp and appeared to be ~ 30° higher than the desorption temperature for Pt(111)-H at comparable coverages. This indicated a rapid, thermally activated dehydrogenation step of cyclohexene on Pt(111).

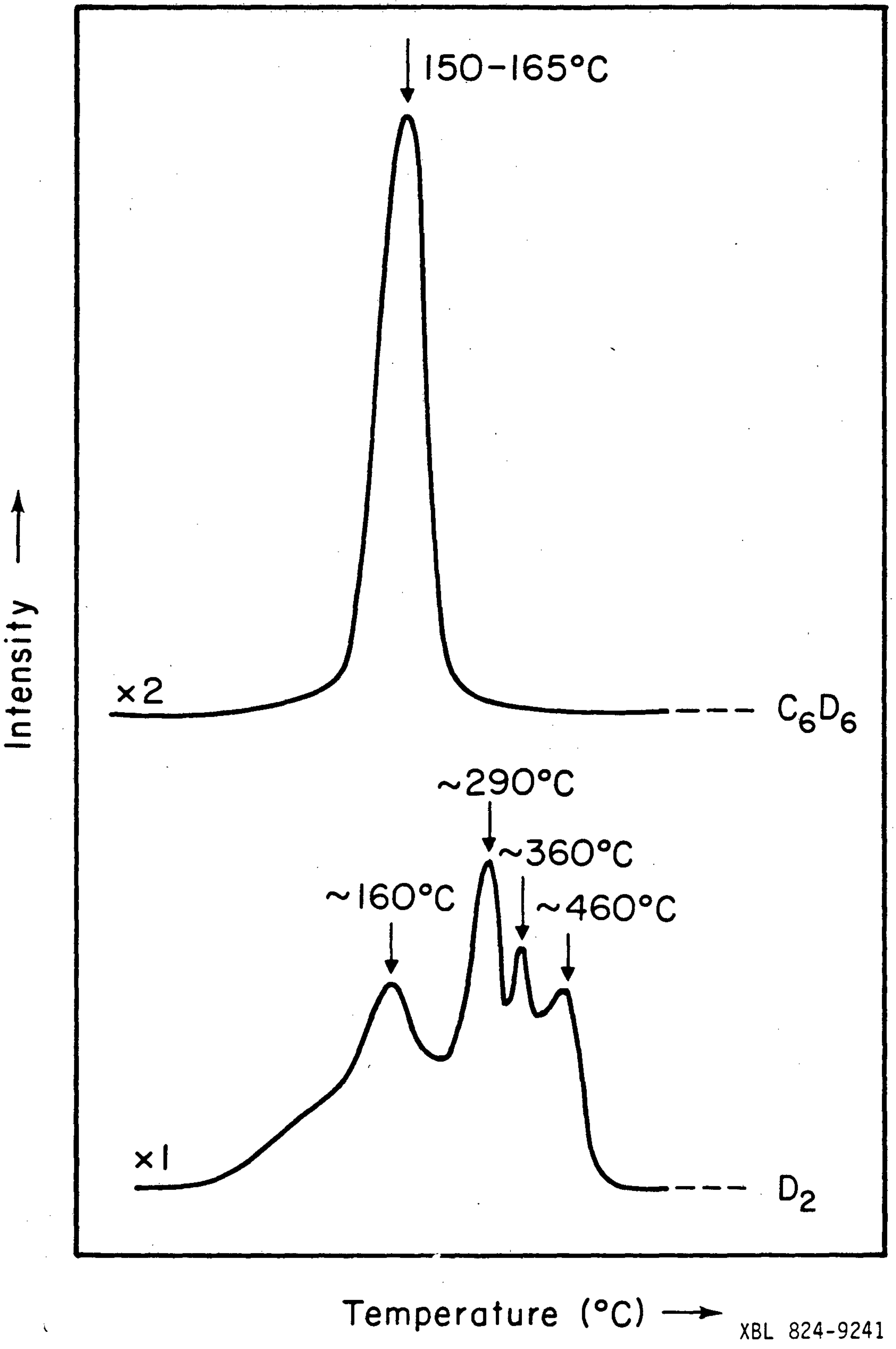
Consistent with the thermal desorption features were the $P(CH_3)_3$ displacement experiments studied as a function of temperature. At 25-70°C, no hydrocarbon species could be detected in the attempted displacement reactions. The subsequent heating still showed benzene desorption at 130-140°C. Only at temperatures of 100°C or higher were there detectable amounts of benzene in the $P(CH_3)_3$ displacement of Pt(111)-C_6D_{10}. Therefore, facile C-H bond breaking of cyclohexene to form benzene on Pt(111) was only a measurably fast process at 70-100°C.

In the Pt(111)-benzene chemistry, it was established that <u>no</u> H-D exchange between chemisorbed C_6H_6 and C_6D_6 molecules was evident even after annealing the Pt(111)-C_6H_6-C_6D_6 surface at 130°C. In contrast to this benzene chemistry, the benzene formed from cyclohexene dehydrogenation underwent extensive H-D exchange: When a mixture of C_6H_{10} and C_6D_{10} was adsorbed on Pt(111), the subsequent thermal desorption experiment, or the $P(CH_3)_3$ displacement reaction effected at $T > 100°C$, yielded all possible $C_6H_xD_{6-x}$ molecules. Thus, the formation of mixed benzene molecules must have occurred at some intermediate stages of cyclohexene dehydrogenation.

In contrast to Pt(111), conversion of cyclohexene to benzene on Pt(100) occurred at 25°C. Thermal desorption of a Pt(100)-C_6D_{10} surface, initially formed at 25°C, was characteristic (Figure 17) of a desorption generated from a Pt(100)-C_6D_6-D surface: The C_6D_6 desorption maximum was at 150-165°C, and D_2 desorption maxima were at ~ 160, 290, 360 and 460°C with the last three peaks characteristic of benzene decomposition on Pt(100), and the first peak characteristic of Pt(100)-H(D). The relative intensities of the four D_2 peaks were ~ 4 : 2 : 2 : 2. Trimethylphosphine displaced C_6D_6 from a Pt(100)-C_6D_{10} at 25°C but was not complete; there were still significant amounts of benzene, CH_3D and HD detected in the subsequent thermal desorption study. The cyclohexene chemistry on Pt(100) was distinctly different from the other low Miller index plane of Pt, Pt(111), where formation of benzene was only fast at 70-100°C.

Figure 17

Thermal desorption of Pt(100)-C_6D_{10} gives two gaseous products: D_2 and C_6D_6, as illustrated in the figure. The C_6D_6 desorption maximum is characteristic of Pt(100)-C_6D_6 desorption; the lowest D_2 maximum is characteristic of Pt(100)-D while the three higher temperature maxima are characteristic of Pt(100)-C_6D_6 decomposition. Clearly, facile dehydrogenation of cyclohexene-d_{10} to form benzene-d_6 occurs on the Pt(100) surface.


150-165°C
Intensity
×2
C_6D_6
~290°C
~360°C
~160°C
~460°C
×1
D_2
Temperature (°C)

XBL 824-9241

H-D exchange process was also observed on the Pt(100) surface when a mixture of C_6H_{10} and C_6D_{10} was adsorbed initially at 25°C. Thermal desorption of Pt(100)-C_6H_{10}-C_6D_{10} gave all possible $C_6H_xD_{6-x}$ molecules at the temperature maximum of 170-180°C, and trimethylphosphine displacement of the mixed benzene molecules was not evident until temperatures of 70°C or higher,--fully consistent with the Pt(100)-benzene chemistry. Thus, on Pt(100), H-D exchange was occurring between the benzene molecules formed from facile dehydrogenation of cyclohexene whereas on Pt(111), it was occurring <u>during</u> cyclohexene dehydrogenation. On both Pt(111) and Pt(100), formation of mixed benzene products was a thermally activated process with temperatures of $\geq$ 70°C required.

Conversion of cyclohexene to benzene was a facile process on the stepped Pt 6(111)x(111) surface at 25°C. The thermal desorption behavior of C_6D_6 from Pt 6(111)x(111)-C_6D_{10} showed a similar coverage dependence to that from Pt 6(111)x(111)-C_6D_6: No benzene was detected at coverages less than ~ 0.15 of a monolayer, only single benzene desorption peak at 180-210°C was observed at coverages of ~ 0.15-0.45 of a monolayer, and a lower temperature maximum at 100-120°C grew in at coverages above ~ 0.45 of a monolayer. Thermal decomposition of Pt 6(111)x(111)-C_6D_{10} resulted in three D_2 maxima at ~ 105, 195 and 350°C, characteristic of D_2 desorption from Pt 6(111)x(111)-C_6D_6-D. At higher surface coverages (> 0.5 of a monolayer), four D_2 maxima were observed: ~ 105, 165, 215 and 350°C with approximate relative intensities of the last three peaks being 1 : 1 : 1.

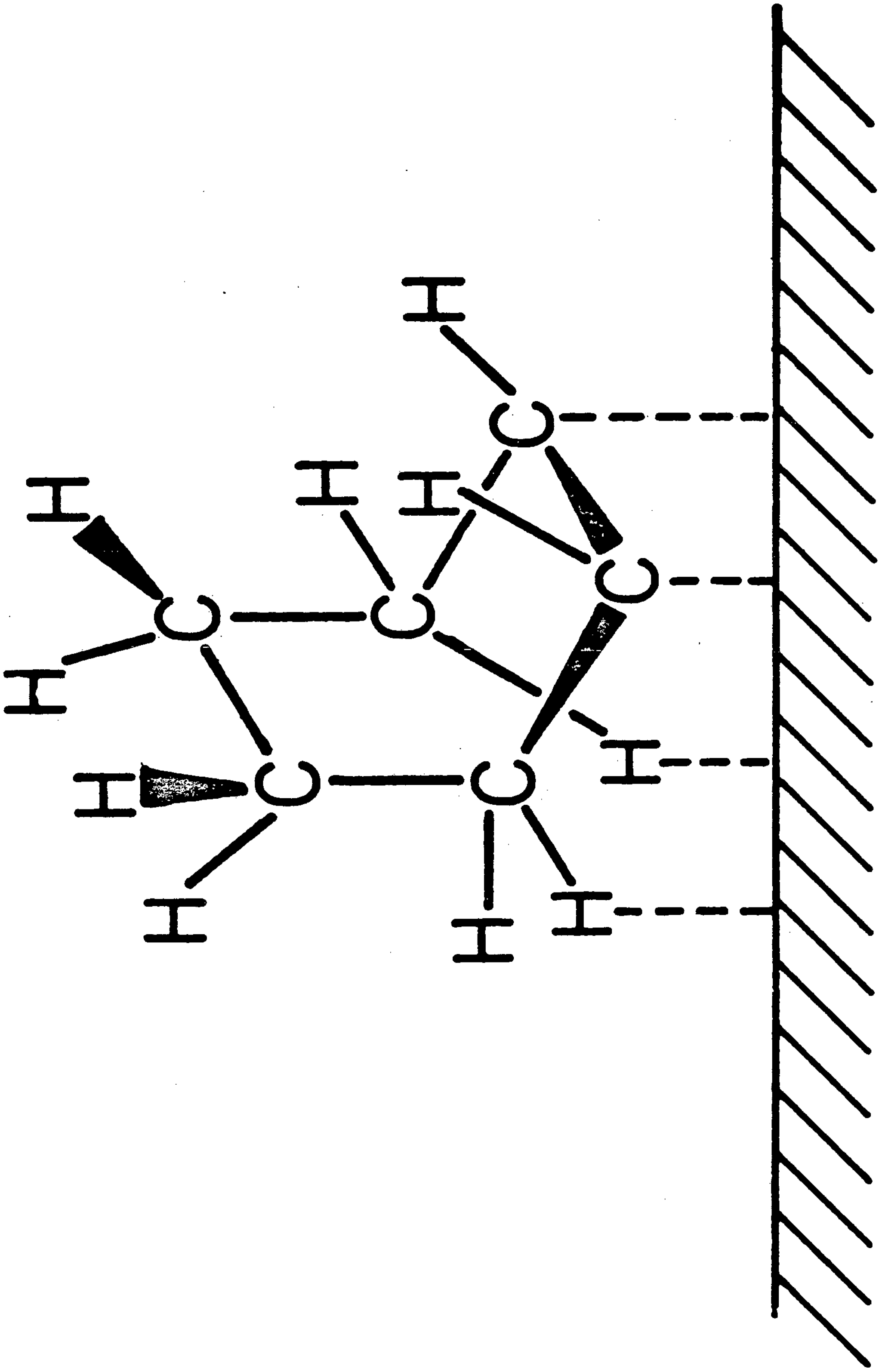
$P(CH_3)_3$ displacement of benzene from cyclohexene adsorption on the stepped Pt surface was evident upon adsorption at 25°C. H-D exchange between C_6H_6 and C_6D_6 molecules, formed from Pt 6(111)x(111)-C_6H_{10}-C_6D_{10}, was evident in both thermal desorption experiments (at desorption maximum of 180-210°C) and $P(CH_3)_3$ displacement reactions effected at $T > 140°C$, consistent with Pt 6(111)x(111)-benzene chemistry.

The initial chemisorption state of cyclohexene on either Ni or Pt surfaces probably involves primarily π and π^* orbitals of the olefin and the appropriate metal surface orbitals. With the olefinic bond of cyclohexene being more or less parallel to the metal surface, irrespective of the C_6 ring conformation, some saturated C-H bonds will naturally come close to the metal surface atoms, as schematically shown in Figure 18, to generate C-H-M multicenter bonding, and consequently, facile C-H bond breaking to form chemisorbed benzene on the metal surfaces will become a favorable process. Generation of the C-H-M multicenter interaction and C-H bond breaking for cyclohexene should occur more readily than for cyclohexane. Also, at least at room temperature or above, the residence time for cyclohexane is probably too short to effect any significant interaction. Consistent with such arguments, benzene formation was observed from cyclohexene adsorption on all the Ni and Pt surfaces, but only a small extent of cyclohexane dehydrogenation was observed on the Pt surfaces.

From this study, the dehydrogenation process of cyclohexene appeared to be a "structure-sensitive" reaction under ultra high vacuum conditions. Most of the Ni and Pt surfaces effected cyclohexene dehydrogenation upon adsorption at 25°C. The Ni(100) and Pt(111) surfaces, however, require much higher temperatures for such conversion process, 100-130°C and 70-100°C, respectively.

Figure 18

A representation of cyclohexene interaction with the metal surface is shown in this figure. The initial chemisorption state for cyclohexene should be largely through the π and π^* orbitals of the olefin such that the olefinic bond lies flat with respect to the surface plane. Such a stereochemistry, irrespective of the ring conformation, will inevitably bring some of the saturated C-H hydrogen atoms into close proximity of the surface atoms so that facile C-H bond breaking will become a favorable process.



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3. Cyclohexadiene Chemistry

Both 1,3- and 1,4-cyclohexadiene adsorbed strongly on the Ni(111), Ni(100), Ni(110) and Ni 9(111)x(111) surfaces at 25°C to form chemisorbed benzene and chemisorbed hydrogen atoms. For all these Ni surfaces, adsorption of either cyclohexadiene isomers followed by thermal desorption experiments showed desorption of benzene with the maximal desorption rates corresponded closely to those observed for benzene adsorbed on the respective surfaces (Table II). However, there was an additional benzene desorption peak derived from the initial cyclohexadiene on both Ni(100) and Ni(110). For Ni(100)-C_6H_8, the additional desorption maximum was at 75-100°C, substantially lower than for Ni(100)-C_6H_6 (200-220°C). For Ni(110)-C_6H_8, the additional desorption maximum was at ~ 200°C, about 100° higher than that for Ni(110)-C_6H_6 (~ 100°C).

Formation of benzene from cyclohexadiene adsorption at 20-40°C on Ni(111), Ni(110) and Ni(100) was established by $P(CH_3)_3$ displacement reactions. Although substantial amounts of benzene (no cyclohexadiene) were displaced by $P(CH_3)_3$ on Ni(100), the dehydrogenation process was not complete at these temperatures as some benzene was still evident in the subsequent thermal desorption.

Like the Ni-cyclohexene chemistry, no H-D exchange was evident for these Ni surfaces when D_2 and 1,3- or 1,4-C_6H_8 were co-adsorbed initially.

Dehydrogenation of either 1,3- or 1,4-cyclohexadiene to benzene also occurred on the Pt(111), Pt(100) and Pt 6(111)x(111) surfaces upon adsorption at 0-30°C. Desorption of benzene from cyclohexadiene adsorption on these Pt surfaces showed analagous features (Table II)

Table II

The Thermal Desorption Behavior of Cyclohexadiene[a] for Ni and Pt

	Thermal Desorption Maxima:	
Surface	Benzene	Hydrogen
Ni(111)-C_6H_8	~ 100°C	140, 210°C
Ni(111)-C_6H_6	115-125°C	180°C
Ni(100)-C_6H_8	75-100, 200°C	120, 210°C
Ni(100)-C_6H_6	200-220°C	200-220°C
Ni(110)-C_6H_8	90, 200°C	100-200°C
Ni(110)-C-C_6H_8	~ 100-200°C[b]	100-200°C
Ni(110)-C_6H_6	~ 100°C	120°C
Ni 9(111)x(111)-C_6H_8	70-85°C	~ 150°C
Ni 9(111)x(111)-C_6H_6	115-125°C	~ 180°C
Pt(111)-C_6H_8[c]	50, 130°C	90, 170, 260, 380°C
Pt(111)-C_6H_6	100-130, 200-220°C	270, 380°C
Pt(100)-C_6H_8	150-165°C	160, 290, 360, 460°C
Pt(100)-C_6H_6	150-170°C	290, 360. 460°C
Pt 6(111)x(111)-C_6H_8	100-120, 175-210°C	110, 165, 200, 350°C
Pt 6(111)x(111)-C_6H_6	100-120, 180-210°C	195, 350°C

[a]. The surface chemistry of both 1,3- and 1,4-C_6H_8 were not detectably different.

[b]. Enhanced benzene desorption relative to the clean Ni(110) surface.

[c]. Adsorption temperature was < 0°C.

as that from benzene adsorption with the exception of Pt(111): the higher temperature (200-220°C) benzene desorption peak of Pt(111)-C_6H_6 was not observed for Pt(111)-C_6H_8, and an additional benzene desorption maximum was observed at ~ 50°C. Since the benzene displacement on any of the Pt surfaces was not quantitative, the extent of cyclohexadiene dehydrogenation could not be concluded from this study. Nevertheless, the benzene displacement from Pt(111)-C_6H_8 at 30°C was much more substantial than that at 0°C (~ twice as much), and only trace C_6H_6 was observed in the following thermal desorption, indicating that the extent of cyclohexadiene dehydrogenation was probably very high at 30°C

H-D exchange in the dehydrogenation process of cyclohexadiene was evident on all the Pt surfaces investigated, in contrast to the Ni surfaces. Reaction of ~ 10^{-7} torr of D_2 with either 1,3- or 1,4-C_6H_8 on Pt(111), Pt(100), and Pt 6(111)x(111) gave C_6H_5D and a small amount of $C_6H_4D_2$ at 130-140°C, 170-180°C, and ~ 200°C, respectively, in addition to C_6H_6.

Conversion of cyclohexadiene to benzene on these Ni and Pt surfaces appeared to require the least activation energy, compared with cyclohexene and cyclohexane. If the initial chemisorption state is largely through the two olefinic bonds of cyclohexadiene, the saturated C-H bonds will be forced to strongly interact with the metal surface. Thus, facile C-H bond breaking of cyclohexadiene to form chemisorbed benzene should be a very favorable process.

4. The Effect of Carbon Impurities on the Dehydrogenation Reaction

Dehydrogenation of cyclohexene and cyclohexadiene to benzene was studied on carbon-contaminated Ni and Pt surfaces as parallel studies to the clean surfaces. The carbon-contaminated surfaces were formed from decomposing benzene or cyclic olefins at elevated temperatures. Of the Ni and Pt surfaces investigated, the partially C-contaminated Ni(110) surface (~ 0.2-0.3 carbon monolayer) was the only surface that showed far more effective dehydrogenation of either cyclohexene or cyclohexadiene to benzene (Figure 19): Much more substantial amounts of benzene desorption were observed and the temperature maximum was shifted from ~ 200°C to ~ 135°C, and almost no H_2 was observed in the thermal desorption. The carbon-induced enhancement of dehydrogenation reactions could be due to either electronic or topographical reasons, but no attempts were made to pursue this point.

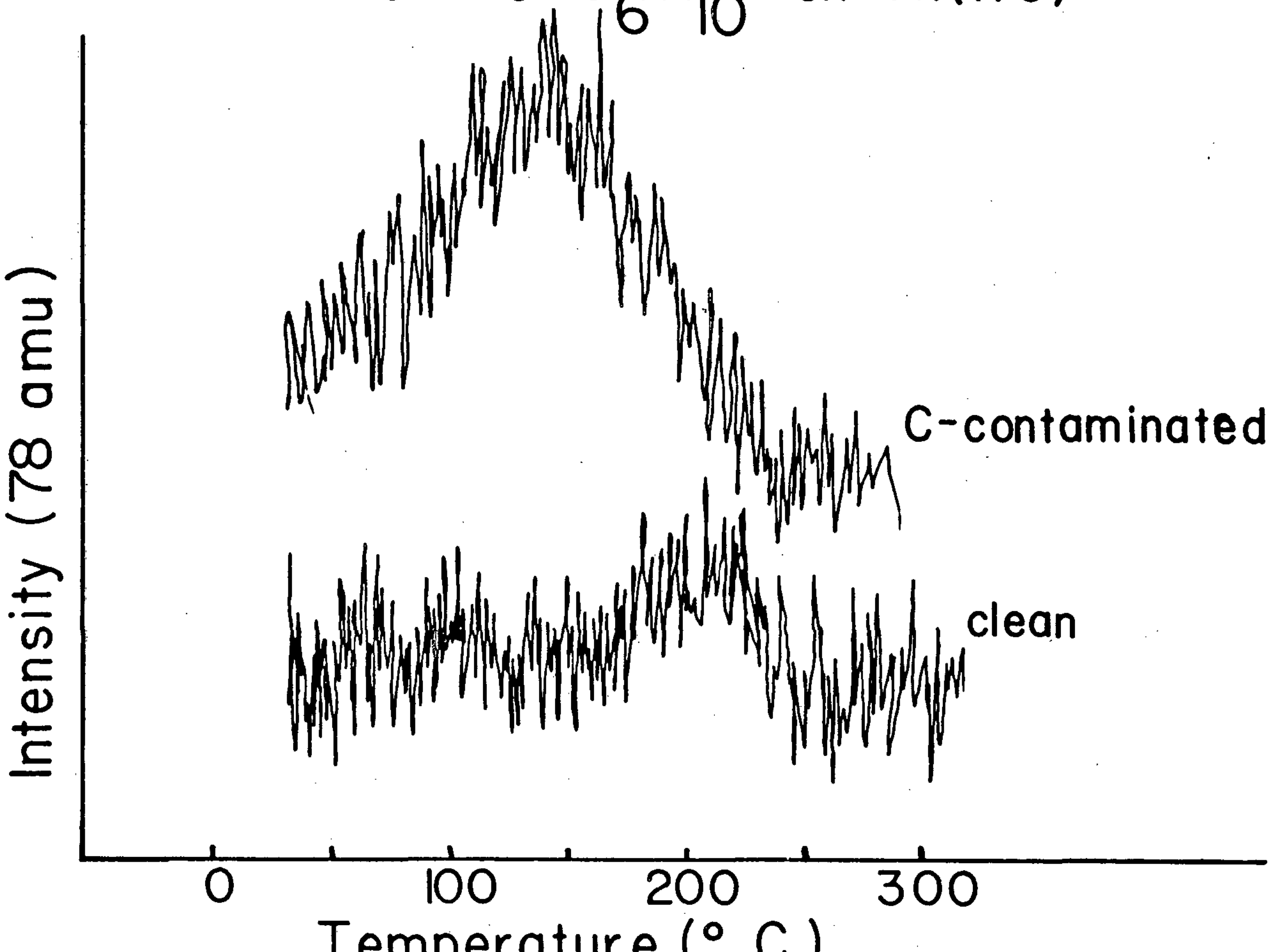
Conclusions

The dehydrogenation of cyclohexane, cyclohexene and cyclohexadiene to form benzene on various Ni and Pt surfaces was studied by surface chemical techniques. Under the ultra high vacuum conditions employed, the conversion of chemisorbed cyclohexane to chemisorbed benzene appears to be a structure-sensitive reaction with the stepped Pt surface being much more active than any of the flat Pt and the Ni surfaces studied. The stepped Ni surface did not exhibit the reactivity of the stepped Pt surface in the cyclohexane dehydrogenation which clearly shows that an electronic effect is responsible for the differential behavior of these two metal surfaces.

Figure 19

Illustrated in this figure is the carbon impurity effect on the cyclohexene dehydrogenation reaction on the Ni(110) surface. On the clean Ni(110) surrface, only a small amount of C_6D_6 was observed in the thermal desorption of Ni(110)-C_6D_{10} with a temperature maximum of ~ 200°C. On a C-covered Ni(110) surface (~ 0.2 - 0.3 C/Ni), much enhanced benzene desorption was observed with the maximum shifted to ~ 135°C and only trace amount of hydrogen was detected. Thus, the C-covered Ni(110) surface is much more effective in the cyclohexene dehydrogenation. Similarly enhanced dehydrogenation of cyclohexadiene on the C-covered Ni(110) surface was also observed.

Thermal Desorption of C_6H_6 following Adsorption of $c\text{-}C_6H_{10}$ on Ni(110)



XBL 811-7817

In contrast to the small reactivity observed for cyclohexane on Ni and Pt surfaces, conversion of cyclohexene and both cyclohexadiene isomers occurred on all the Ni and Pt surfaces investigated. In the thermal decomposition experiments for the cyclohexene and for the cyclohexadiene on the various Ni and Pt surfaces, the benzene and hydrogen desorption maxima were very similar on the respective surfaces (Tables I & II). Therefore, chemisorbed cyclohexadiene is probably an intermediate species in the dehydrogenation of chemisorbed cyclohexene to chemisorbed benzene. For Ni(100) and Pt(111), the activation energy for cyclohexene conversion to benzene was higher than for cyclohexadiene conversion to benzene whereas the rest flat and stepped metal surfaces did not show any significant differences in the dehydrogenation of cyclohexene and cyclohexadiene. In general, the rates of cyclohexene as well as cyclohexadiene dehydrogenation are comparable for both metals with the same crystallography, but the rates did vary as a function of the surface crystallography with the stepped surfaces being the most active ones.

H-D exchange in the dehydrogenation process of cyclohexene and cyclohexadiene was evident on all three Pt surfaces, (111), (100) and 6(111)x(111), but was not detectable on any of the Ni surfaces. The differences in H-D exchange and the cyclohexane chemistry between platinum and nickel are to be ascribed to the electronic differences.

In conclusion, the surface chemistry of cyclohexane, cyclohexene and cyclohexadiene suggests that the generation of C-H-M multicenter bonding is the prerequisite for the subsequent C-H bond breaking to form chemisorbed benzene. The relative ease of dehydrogenation is, in general, cyclohexadiene > cyclohexene > cyclohexane on various Ni and Pt surfaces.

VI. REACTIONS OF CYCLIC OLEFINS AND POLYENES WITH NICKEL AND PLATINUM SURFACES

Dehydrogenation of cyclohexene and the cyclohexadiene isomers to π -bound benzene occurs on various Ni and Pt surfaces under ultra high vacuum conditions. In principle, adsorption of other cyclic hydrocarbon species, especially cyclic olefins and polyenes, on the metal surfaces should also favor dehydrogenation because irrespective of the ring conformation in the initial chemisorption state, some hydrogen atoms of the saturated carbon centers will closely approach the metal surface. The result of the dehydrogenation is probably the generation of a delocalized, C_n ring π -bound to the metal surface:

$$M_{surface} - \underline{c}\text{-}C_nH_m \rightarrow M_{surface} - \underline{c}\text{-}C_nH_n - H_{m-n}.$$

In molecular metal complexes, such ring species are well-characterized from n = 3 through n = 8.

Accordingly, the chemistry of C_4 through C_8 cyclic olefins and polyenes on various low Miller index Ni and Pt surface planes was explored under ultra high vacuum conditions. The surface techniques included were Auger electron spectroscopy, low energy electron diffraction, thermal desorption spectroscopy, isotopic labeling and chemical displacement reactions. Thus, formation of stable, delocalized $\underline{c}\text{-}C_nH_n$ species (n is an even number) could be readily detected if they are thermally reversible or chemically displaceable. However, for the $\underline{c}\text{-}C_nH_n$ species where n is an odd number, the adsorbed radical species cannot be thermally desorbed or chemically displaced, thus the aforementioned surface chemical methods cannot detect these species. Nevertheless, if such C_nH_n species (n equals an odd number) undergo further C-C bond breaking processes to form an even-membered ring, they should be potentially detectable by either thermal desorption or chemical displacement reactions.

The focus of this study lies in the delineation of electronic and stereochemical features of C-H and C-C bond breaking processes for C_8 cyclic olefins and polyenes, cycloheptatriene and norbornadiene on the Pt(111), Pt(100), Ni(100) and Ni(110) surfaces.

Results and Discussion

1. The Chemistry of Cyclooctatetraene, Cyclooctadiene and Cyclooctene on Pt(111)

Adsorption of cyclooctatetraene on Pt(111) at 25°C did not give any ordered structure in LEED study. Thermal desorption of Pt(111)-C_8H_8 at ~ 0.7 of a monolayer yielded some (~ 30% of the adsorbed C_8H_8 species) molecular C_8H_8 desorption at the temperature maximum of ~ 150°C, and large amounts of H_2 at temperature maxima of ~ 120, 325 and 380°C.

Exposure of a Pt(111)-C_8H_8 surface with $P(CH_3)_3$ at 25°C immediately gave C_8H_8 in the gas phase. Following the displacement reaction, the thermal desorption experiment showed a trace of C_8H_8 at ~ 135°C. When $P(CD_3)_3$ was used as a displacing agent, the thermal desorption study after displacement showed significant amounts of H_2, HD and CD_3H which indicated that trimethylphosphine displacement of C_8H_8 on Pt(111) was far from being complete.

For adsorption of 1,3- and 1,5-cyclooctadiene on Pt(111) at ~ 0.6 of a monolayer, no hydrocarbon desorption was evident in the heating process. H_2 was the only gaseous product of thermal decomposition of Pt(111)-C_8H_{12} and the desorption maxima were at ~ 120, 325 and 380°C which were coincident with those observed for Pt(111)-C_8H_8 decomposition. At similar carbon coverage, the intensity of the 120°C H_2 peak for the thermal decomposition of Pt(111)-C_8H_{12} was much more significant (more than two times) than that of Pt(111)-C_8H_8. Possibly, a similar decomposition mechanism was operative for both surfaces.

Conversion of 1,3- or 1,5-C_8H_{12} to C_8H_8 occurred on Pt(111) as shown by the $P(CH_3)_3$ displacement reactions but it appeared to be a complex function of surface coverage and temperature: At ~ 0.6 of a monolayer coverage, C_8H_8 (or any other hydrocarbon species) was not detectable at 25°C but was evident at ~ 100°C; at nearly monolayer coverage, displacement of C_8H_8 from Pt(111)-C_8H_{12} was observed at 25°C.

The chemistry of cis-cyclooctene on Pt(111) was similar to that of cyclooctadiene. No hydrocarbon desorption could be observed from low (~ 0.4-0.6 of a monolayer) to high (~ one monolayer) coverages in the thermal desorption of Pt(111)-C_8H_{14}. The decomposition product of Pt(111)-C_8H_{14}, H_2, desorbed at temperature maxima of ~ 110, 325 and 380°C with the first peak being the most intense.

Displacement reactions of Pt(111)-C_8H_{14} by $P(CH_3)_3$ appeared to be coverage-dependent: At ~ 0.6 of a monolayer, displacement reactions effected at 25°C and at 100°C were not successful; at nearly monolayer coverage, some C_8H_8 was observed at 25°C when the Pt(111)-C_8H_{14} surface was exposed to $P(CH_3)_3$.

In the chemisorption of cyclooctene and of cyclooctadiene on Pt(111), dehydrogenation of c-C_8H_{14} and c-C_8H_{12} to form the delocalized C_8H_8 ring appeared to be a common process. Although the conversion to C_8H_8 was probably not the dominant process in the chemisorption of these C_8 cyclic olefins, the analogy to the C_6 cyclic olefins was clearly established. In the chemisorption of cyclohexene and cyclohexadiene on a series of Ni and Pt surfaces, dehydrogenation to form benzene appeared to be the dominant process.

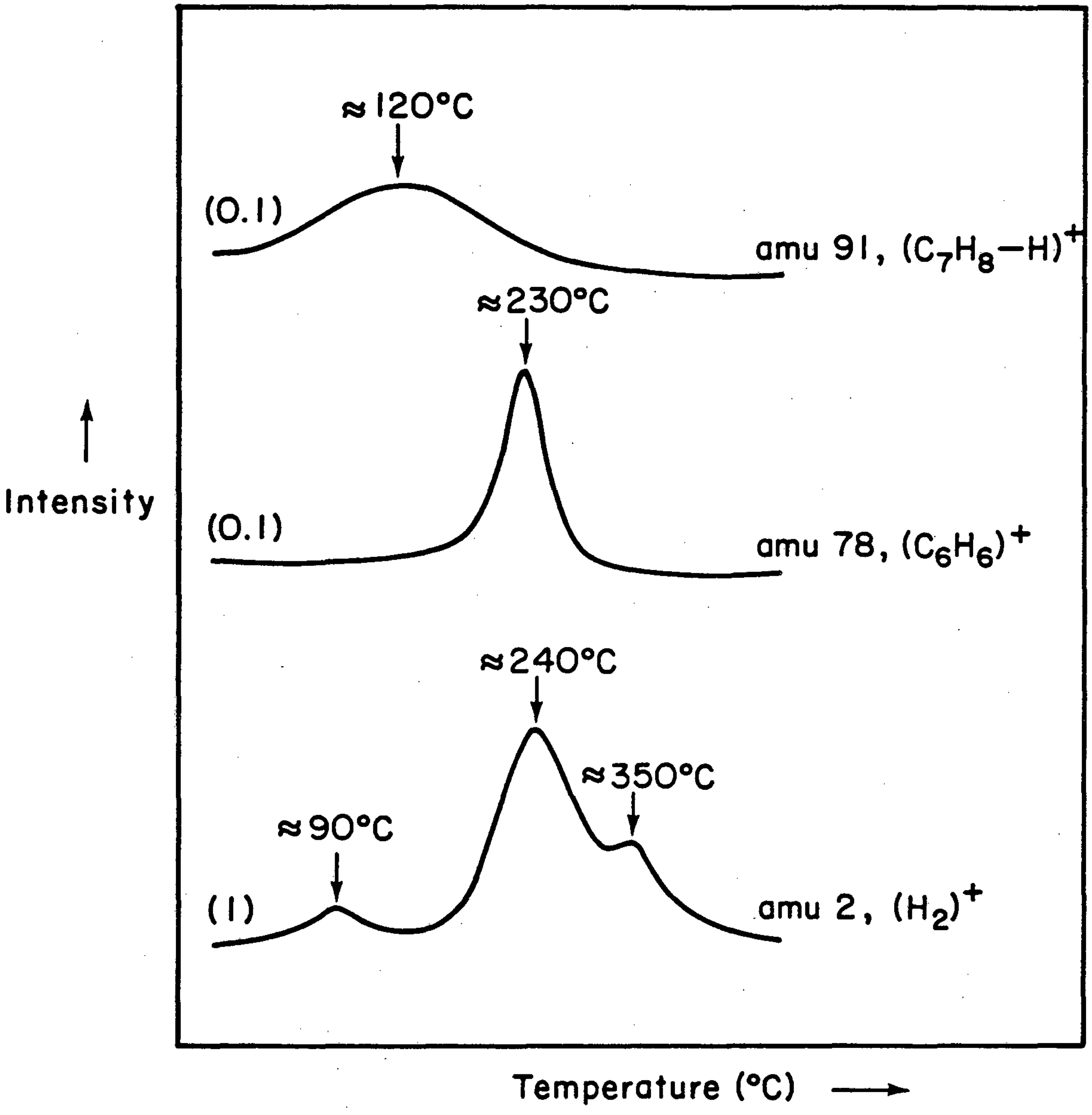
The stereochemistry for cyclooctatetraene adsorption on Pt(111) could not be established from this study. The C_8 ring could be planar with the Pt surface or it could be bound as a diene. Or, both states could be co-existent on the Pt(111) surface. The lowest H_2 desorption maximum for decomposition of Pt(111)-C_8H_8 was at ~ 120°C while that for Pt(111)-C_6H_6 in which C_6H_6 was largely π -bonded with a planar configuration, was at much higher temperature, ~ 260°C, indicating that the chemisorption process for C_8H_8 on Pt(111) was probably very complex in nature.

2. Cycloheptatriene Chemistry of Ni(100), Pt(111), Pt(100) and Ni(110)

1,3,5-cycloheptatriene adsorption on the Ni(100) surface led to three competing processes in the thermal desorption: reversible C_7H_8 desorption at temperature maximum of ~ 120°C, gross decomposition to form H_2 at ~ 90, 240 and 350°C and a C-covered surface, and benzene desorption at ~ 230°C (Figure 20). The first H_2 peak at ~ 90°C was in the characteristic desorption region for Ni(100)-H, and the benzene desorption derived from C-C bond reactions of C_7H_8 was characteristic of Ni(100)-C_6H_6. At cycloheptatriene coverage of ~ 0.7 of a monolayer, the partitioning of these three processes in the thermal desorption was: ~ 15-20% reversible C_7H_8 desorption, ~ 60-70% gross decomposition to give H_2, and ~ 15-20% cycloheptatriene conversion to benzene. Since there was decomposition of C_7H_8 on Ni(100) below ~ 100°C to give

Figure 20

Thermal desorption of Ni(100)-cycloheptatriene comprises three competing processes: molecular C_7H_8 desorption, benzene desorption and decomposition to give H_2. Shown in this figure are the intensities of the major ions: mass 91, 78 and 2 as a function of temperature. For direct comparison of the intensities, the parenthetical numbers should be multiplied. The lowest H_2 maximum at ~ 90°C is characteristic of Ni(100)-H which indicates that facile dehydrogenation of the chemisorbed cycloheptatriene occurs at low temperatures.


≈120°C
(0.1)
amu 91, $(C_7H_8-H)^+$
≈230°C
(0.1)
amu 78, $(C_6H_6)^+$
≈240°C
≈350°C
≈90°C
(1)
amu 2, $(H_2)^+$
Intensity
Temperature (°C)

XBL 822-7944

the first H_2 desorption peak, it was possible that the reversible C_7H_8 desorption was derived from a dissociative state. Accordingly, the thermal desorption experiment of Ni(100)-D-C_7H_8, formed at 25°C, was performed, and all the cycloheptatriene reversibly desorbed contained no deuterium. Thus, there were at least two chemisorption states for C_7H_8 on Ni(100), one was associative in character which gave intact C_7H_8 at ~ 100-120°C in the heating and the other readily decomposed at temperatures below ~ 100°C.

The temperature required for cycloheptatriene conversion to benzene on Ni(100) was established by a series of $P(CH_3)_3$ displacement reactions at various temperatures. From 25°C to 70°C, attempted displacement reactions of Ni(100)-C_7H_8 failed to give any detectable hydrocarbon species whereas at ~ 100°C or above, $P(CH_3)_3$ displacement of C_6H_6 from Ni(100)-C_7H_8 was evident. Thus, conversion of cycloheptatriene to benzene was only a measurable process at ~ 100°C or above.

Formation of C_6H_6 from Ni(100)-C_7H_8 was interesting in the mechanistic context. If the postulate for adsorption of cyclic olefins (or polyenes) on the metal surface was correct, the initial chemisorption state for cycloheptatriene should lead to dehydrogenation to form a delocalized C_7H_7 species. Such species could be the precursor state for benzene formation at some higher temperatures. However, benzene formation from Ni(100)-C_7H_8 could also simply be derived from regioselective scission of the bridging CH_2 group.

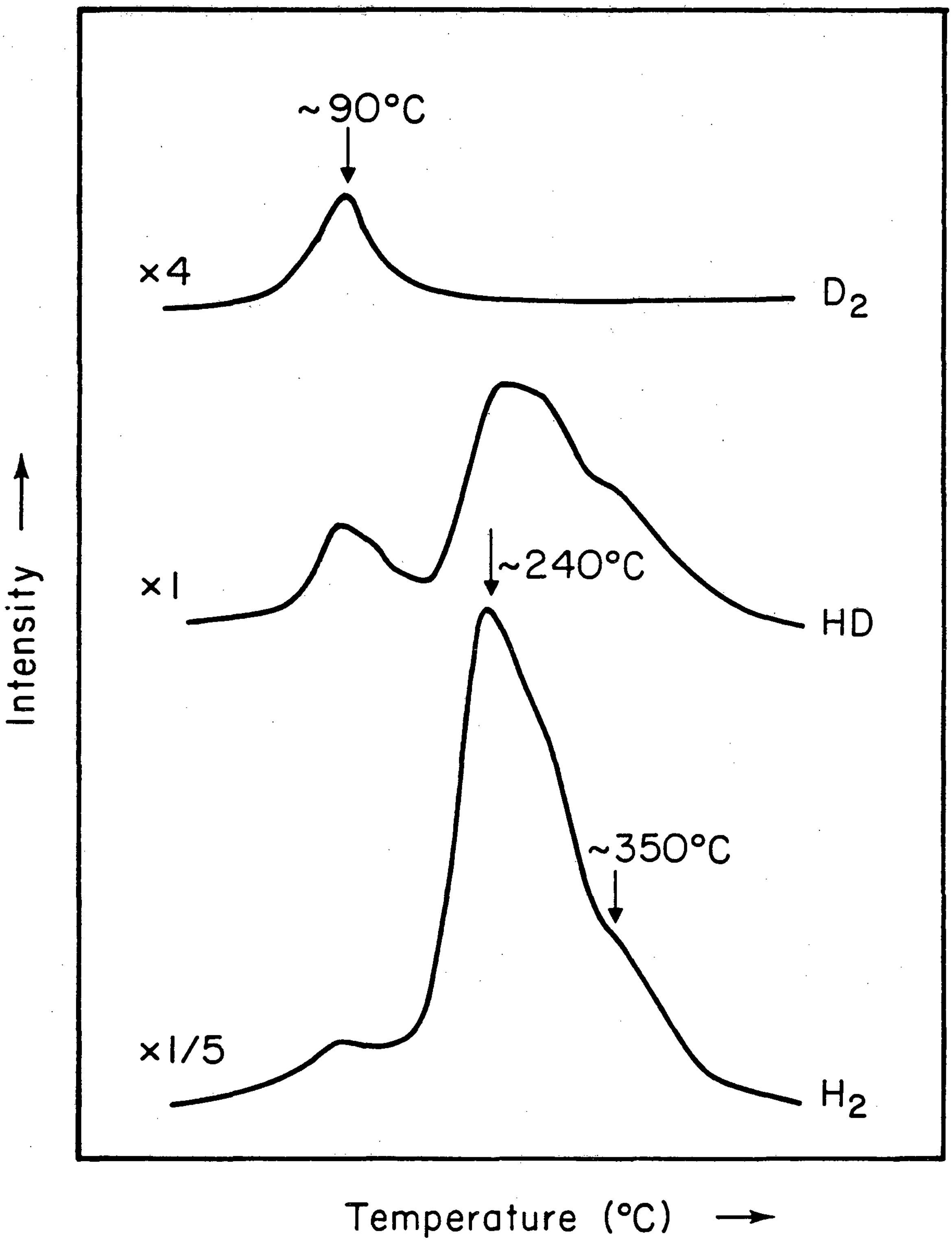
In order to further investigate the mechanistic features of the reaction of cycloheptatriene on Ni(100), thermal desorption experiments of the selectively labeled cycloheptatriene, cycloheptatriene-7-d_1, were performed. The cycloheptatriene desorbed was all C_7H_7D and the benzene molecules consisted of C_6H_5D and C_6H_6 in a 6:8 molar ratio. In addition, the hydrogen desorption spectra (Figure 21) showed that D_2, HD and H_2 were all evident at the ~ 90°C maximum, and the two higher temperature maxima at ~ 240 and 350°C consisted of HD and largely H_2.

Based on these experimental observations, the initial chemisorption state for cycloheptatriene on Ni(100) underwent a facile, selective C-H bond scission below ~ 100°C to form a Ni(100)-C_7H_7-H state which was probably the precursor state to the benzene formation. The key observations for this conclusion being: (i) the D_2, HD and H_2 desorption at ~ 90°C for thermal decomposition of Ni(100)-C_7H_7D (Figure 21) were consistent with the formation of Ni(100)-C_7H_7-D and Ni(100)-C_7H_6D-H below ~ 100°C from the selective breaking of one of the C-H(D) bonds of the saturated CHD bridging group, (ii) displacement of benzene from Ni(100)-C_7H_8 was only evident at $T > 100$°C, and (iii) the ratio of C_6H_5D to C_6H_6 derived from thermal desorption of Ni(100)-C_7H_7D: Conversion of chemisorbed cycloheptatriene-7-d_1 to a delocalized C_7H_7 or C_7H_6D surface species would give a statistical ratio of C_6H_5D to C_6H_6 of 6:8 as observed in this study.

Although no spectroscopic data were available to probe the chemisorption processes of cycloheptatriene on Ni(100), the chemical data obtained in this study were fully consistent with the formation of the delocalized C_7H_7 species generated from facile dehydrogenation of C_7H_8 at temperatures well below 100°C. Thus a significant fraction of the adsorbed cycloheptatriene was probably bound as a triene to the metal surface such that, at relatively low temperatures, one of the CH_2 hydrogen atoms could closely approach the metal surface to cause

Figure 21

D_2, HD and H_2 desorption spectra derived from heating of a Ni(100)-C_7H_7D (cycloheptatriene-7-d_1) are shown in this figure. The lowest hydrogen desorption maximum at ~ 90°C consists of all three hydrogen species, D_2, HD and H_2, indicating an initially facile, selective bond breaking process of the saturated CHD bridging group.



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facile C-H bond scission. Nevertheless, there was some adsorbed cycloheptatriene that intactly desorbed at 100-120°C, suggesting a stereochemistry with all the C-H hydrogen atoms relatively far removed from the metal surface atoms. A possible representation for the molecularly bound cycloheptatriene state, which can also explain the competing C-C bond breaking process at higher temperatures, is shown in Figure 22.

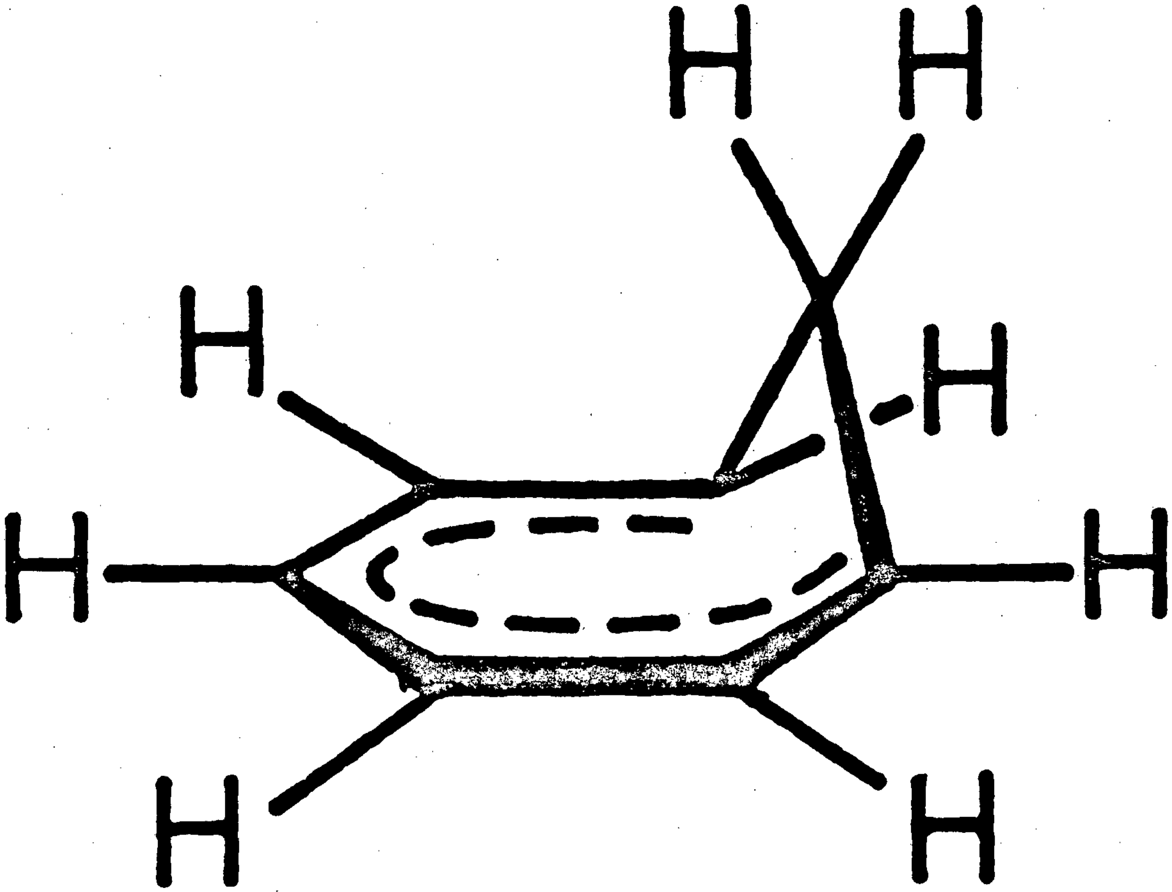
The chemistry of cycloheptatriene on the Pt(111), Pt(100) and Ni(110) surfaces was distinctly different from that of Ni(100) in that no benzene formation from C-C bond breaking of the adsorbed cycloheptatriene was observed. Thermal decomposition to give H_2 and a C-covered surface, and molecular C_7H_8 desorption were the processes detected in the thermal desorption experiment.

Chemisorption of cycloheptatriene on Pt(111) was largely irreversible. Thermal decomposition of Pt(111)-C_7H_8 led to H_2 evolution at ~ 100°C, characteristic of Pt(111)-H desorption, ~ 215 and 250°C (a broad peak with an unresolved double maximum), and ~ 380°C. The relative intensities of the above three H_2 peaks appeared to be ~ 1 : 4 : 3, suggesting facile C-H bond scission of Pt(111)-C_7H_8 at $T < 100°C$ to form a Pt(111)-C_7H_7-H state.

Thermal decomposition of Pt(111)-toluene also showed multiple H_2 peaks at temperature maxima of ~ 70, 215, 250 and 380°C. Although the last three H_2 peaks were coincident with those observed for Pt(111)-cycloheptatriene decomposition, the possible rearrangement of the cycloheptatriene-derived species to a benzyl-like species (or vice versa) can not be resolved without further spectroscopic investigations. The molecular desorption behavior for Pt(111)-toluene and for Pt(111)-cycloheptatriene was distinguishably different: the former occurred

Figure 22

A possible representation for molecularly bound cycloheptatriene state on the Ni(100) surface is shown in this figure. All the C-H hydrogen atoms are relatively far removed from the metal surface so that no facile C-H bond scission could be realized prior to the desorption process.



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at 70-110°C with an unresolved double maximum while the latter was observed at ~ 100-120°C.

For thermal desorption of cycloheptatriene from Pt(100), the maximum rate was observed at ~ 100-120°C. Cycloheptatriene decomposition to give H_2 was observed at ~ 170, 325 and 460°C with approximate relative intensities of 1 : 4 : 3. Since the lowest H_2 peak was in the characteristic desorption region for Pt(100)-H, facile C-H bond breaking of the adsorbed cycloheptatriene to form a C_7H_7 species was a plausible reaction pathway at low temperatures. The small amount of cycloheptatriene desorption from Pt(100) was detected in the same temperature range as that of toluene from Pt(100)-toluene, thus it was not possible to identify the reversibly desorbed C_7H_8 isomer by mass spectrometry. However, the thermal decomposition behavior of cycloheptatriene on Pt(100), a process that represented ~ 80% of the adsorbed molecules, was clearly different from that of toluene; decomposition of Pt(100)-toluene gave H_2 at ~ 90, 230 and 460°C with a ~ 1 : 3 : 4 ratio. Therefore, the major molecular chemisorption state for cycloheptatriene on Pt(100) does not appear to be toluene.

For Ni(110)-cycloheptatriene, the thermal desorption behavior was entirely different from that of Ni(110)-toluene. For cycloheptatriene, reversible desorption at ~ 100°C was accompanied by H_2 evolution at ~ 125 and 250°C in the heating. For toluene, H_2 was the only gaseous product observed with a single maximum at ~ 150°C.

Studies of cycloheptatriene on Pt(111), Pt(100) and Ni(110) did not lead to any direct evidence of formation of the C_7H_7 species, nor did the observed chemistry resemble the toluene chemistry on the respective surface. For Pt(111) and Pt(100), the decomposition behavior of cycloheptatriene was suggestive of the generation of C_7H_7 species from facile dehydrogenation at low temperatures. Conversion of cycloheptatriene to benzene appeared to be a sensitive function of the metal surface and surface crystallography; only the Ni(100) surface mediated the benzene formation at temperatures of ~ 100°C or above.

3. Norbornadiene Chemistry of Pt(111) and Pt(100)

Norbornadiene is another isomer of C_7H_8 besides toluene and cycloheptatriene. The norbornadiene chemistry of Pt(111) and Pt(100) was distinctly different from that of the other two isomers.

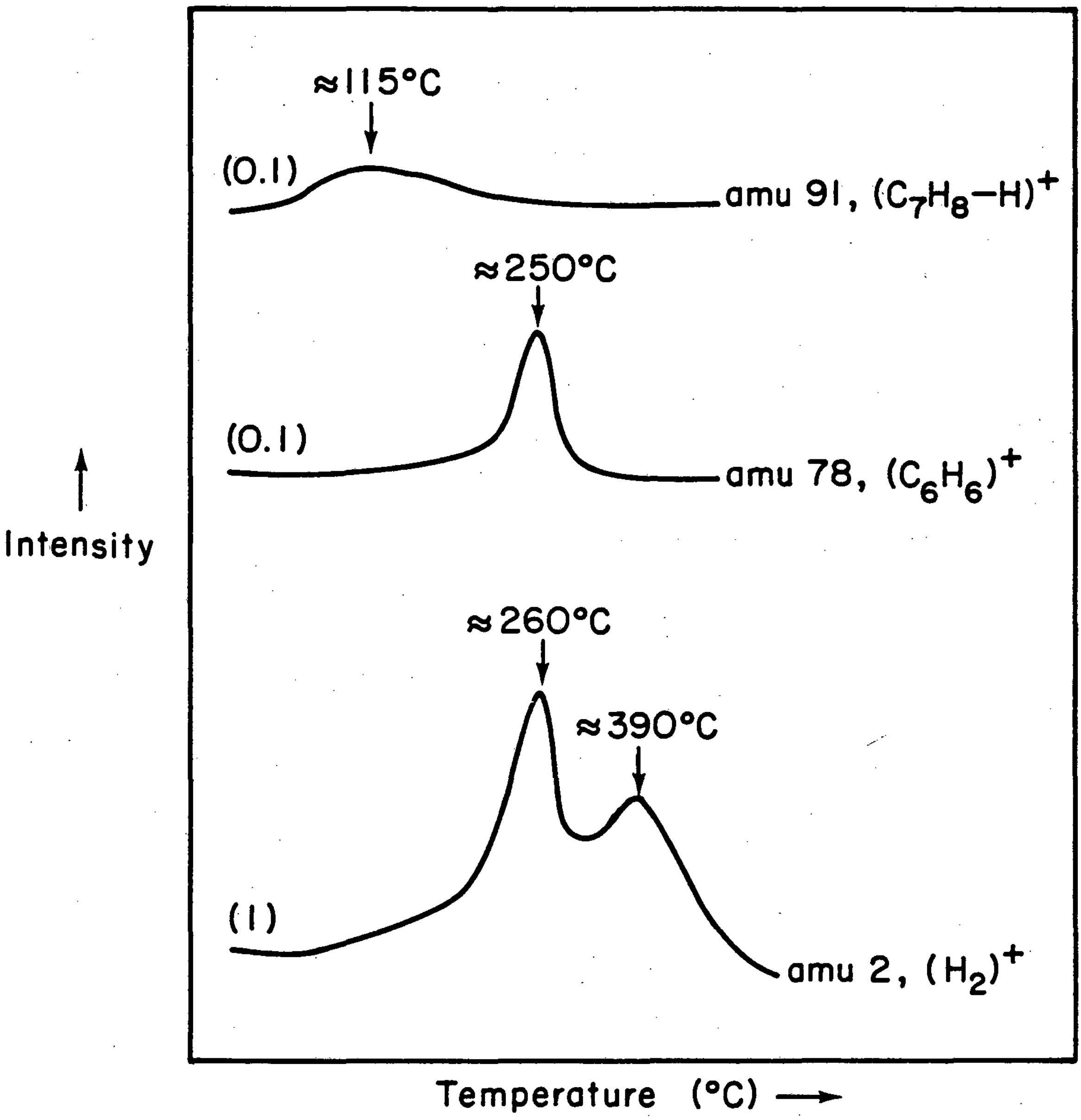
On the Pt(111) surface, norbornadiene showed a very high sticking coefficient at 20°C. Thermal desorption of Pt(111)-C_7H_8 consisted of three competing processes (Figure 23): At a coverage of ~ 0.8 of a monolayer, ~ 20% of the adsorbed C_7H_8 underwent reversible desorption at the temperature maximum of ~ 120°C which was accompanied by large amounts of H_2 desorption at ~ 260 and 390°C, and benzene desorption at ~ 250°C. The yield of benzene was only about 15-20%.

Reversible molecular desorption of adsorbed norbornadiene from Pt(111), and the temperature required for decomposition, $T > 200°C$, strongly suggested an initial stereochemistry of norbornadiene with all C-H hydrogen atoms being relatively far removed from the metal surface atoms. The initial interaction of norbornadiene with Pt(111) was probably through the two olefinic bonds, and the only H atoms that could get close to the metal surface were the olefinic H atoms.

C-C bond breaking of norbornadiene to form benzene also did not occur until high temperatures. The desorption temperature for C_6H_6 derived from Pt(111)-C_7H_8, ~ 250°C, was much higher than that from Pt(111)-C_6H_6, 100-130°C and 200-220°C, indicating that norbornadiene

Figure 23

Heating of a Pt(111)-norbornadiene surface, formed at ~ 20°C, results in three competing processes: molecular C_7H_8 desorption, benzene formation and decomposition to form H_2. Depicted in the figure are the intensities of the major fragments: mass 91, 78 and 2 as a function of temperature. For direct comparison of the intensities, the parenthetical numbers should be multiplied. Note that no C-H bond breaking process to give H_2 is evident at $T < 200°C$. The thermal desorption behavior of Pt(100)-norbornadiene is analogous to that presented in this figure.


≈115°C
(0.1)
amu 91, $(C_7H_8{-}H)^+$
≈250°C
(0.1)
amu 78, $(C_6H_6)^+$
Intensity
≈260°C
≈390°C
(1)
amu 2, $(H_2)^+$
Temperature (°C)

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conversion to benzene was a high temperature process. The incisive identification of the temperature where C-C bond breaking to form benzene occurred was achieved by $P(CH_3)_3$ displacement reactions effected as a function of temperature; C_6H_6 displacement from Pt(111)-C_7H_8 was only evident at $T > 220°C$. Thus benzene formation was only fast at temperatures of 220-250°C, which were also the temperatures where C-H bond scission to give H_2 began.

To investigate the mechanistic feature of norbornadiene conversion to benzene on Pt(111), norbornadiene-7-d_1 was used in thermal desorption experiments. All the benzene molecules derived from the heating of Pt(111)-C_7H_7D was C_6H_6. Thus, regioselective scission of the bridging CH_2 group of norbornadiene at $T > 200°C$ to form C_6H_6 was the only process involved on Pt(111). Possibly, the low temperature chemisorption state of norbornadiene was largely an η^4-diene with the CH_2 group projected away from the surface plane such that regioselective scission of the CH_2 group (or C-H bond scission) could not be achieved. At higher temperatures, some of the chemisorbed norbornadiene could be bonded through a single olefinic bond with the CH_2 bridging group projected toward the surface plane prior to benzene formation.

Norbornadiene chemistry on Pt(100) was remarkably similar to that on Pt(111). Thermal desorption of Pt(100)-C_7H_8 gave reversible C_7H_8 desorption at ~ 120°C, H_2 evolution at ~ 160, 260 and 400°C, and C_6H_6 at ~ 250°C. Since the C_6H_6 desorption from the norbornadiene conversion was at much higher temperatures than that from Pt(100)-C_6H_6 (100-110°C and 170-180°C), formation of benzene was also a high temperature process. Using norbornadiene-7-d_1, it was established that benzene formation on Pt(100) was a more complicated process than that on Pt(111): Both C_6H_6 and C_6H_5D were evident in the thermal desorption of Pt(100)-C_7H_7D with an approximate molar ratio of ~ 5 : 1. Thus, unlike the Pt(111)-norbornadiene chemistry, benzene formation from Pt(100)-norbornadiene appeared not to be a result of the regioselective breaking of the CH_2 bridging group. However, since H-D exchange of Pt(100)-C_6H_6-C_6D_6 was a fast process at T > 70°C, the observation of both C_6H_6 and C_6H_5D molecules in the heating of Pt(100)-C_7H_7D could simply be a result of H-D exchange between the C_6H_6, formed from regioselective breaking of the CHD group, and the D atoms that were in the vicinity of the C_6H_6 molecules.

4. Other C_4 and C_5 Cyclic Olefins

Exploratory studies of cyclobutene adsorption on Pt(111), Pt(100) and Ni(100) were performed using thermal desorption and $P(CH_3)_3$ displacement techniques. No hydrocarbon desorption or displacement from room temperature C_4H_6 adsorption was observed for all the surfaces investigated. H_2 was the only reversible product in the thermal desorption; temperature maxima for decomposition of C_4H_6 were: Pt(111): ~ 100 and 340°C, Pt(100): ~ 135 and 360°C, and Ni(100): ~ 110 and 215°C. The lowest H_2 peak observed on all three surfaces was in the characteristic free hydrogen desorption region on the respective surfaces, suggesting that facile dehydrogenation of C_4H_6 was occurring at low temperatures. However, the nature of the dehydrogenated hydrocarbon species could not be identified from this study.

In the adsorption of cyclopentene on Pt(111) at 25°C, there was still no hydrocarbon desorption in the heating process; H_2 was the only detectable species that desorbed at ~ 75, 270 and 380°C. Presumably, adsorption of cyclopentene on Pt(111) underwent facile dehydrogenation to form a π -C_5H_5 state but such radical species would not be thermally reversible or chemically displaceable.

Formation of surface C_4H_4[55] and C_5H_5 species from dehydrogenation of cyclobutene and cyclopentene, respectively, could, in principle, be a common process on different metal surfaces. Moreover, the dehydrogenation could also be a more favorable process than it appeared from the thermal desorption and chemical displacement studies. The binding of the C_nH_n species to a metal surface may be too strong for facile displacement and its thermal reactivity (C-H and C-C bond breaking) may be too high to allow characterization by thermal desorption. Thus, the identification of the surface species requires either photoemission or surface vibrational spectroscopy.

Conclusions

The reaction of cyclic olefins and polyenes with Ni and Pt surfaces were examined by ultra high vacuum surface techniques. Facile dehydrogenation of the chemisorbed unsaturated $\underline{c}$-C_nH_m species to form the delocalized $\underline{c}$-C_nH_n species appeared to be a common reaction path.

$\underline{c}$-C_8H_8 was generated from chemisorbed $\underline{c}$-C_8H_{12} and $\underline{c}$-C_8H_{14}, respectively, on the Pt(111) surface, as established by $P(CH_3)_3$ dispalcement reactions. Although such reactions for the C_8 cyclic olefins may not be the dominant process on the metal surface, the analogy to the dehydrogenation of C_6 cyclic olefins to C_6H_6 was clearly established.

For the C_7 cyclic olefins, C-H bond and C-C bond breaking processes have been mechanistically defined on Ni and Pt surfaces. Cycloheptatriene was partially reversible on Ni(100). The major chemisorption state of cycloheptatriene on Ni(100) underwent a facile, and selective

C-H bond breaking process at T < 100°C which then underwent further bond breaking processes to form chemisorbed benzene at T > 100°C. Using cycloheptatriene-7-d_1, it was established that benzene formation probably proceeded by nonselective bond breaking processes of the initially (T < 100°C) formed C_7H_7 species.

Norbornadiene chemisorption on Pt(111) was also partially reversible. Measurable C-H bond and C-C bond breaking processes for Pt(111)-norbornadiene were only evident at temperatures higher than 200°C. Conversion of the chemisorbed norbornadiene to benzene was also a high temperature process which only occurred at a fast rate at ~ 220-250°C. Using norbornadiene-7-d_1, the benzene formation on the Pt(111) surface was established to be originated from regioselective breaking of the bridging CH_2 group.

The metal surface chemistry of cyclic olefins and polyenes was relatively complex in that several chemisorption processes could be occurring and the chemistry was dependent upon the metal surface and surface crystallography. Nevertheless, it was still possible to rationalize the surface chemistry of these cyclic hydrocarbons based on the proposed stereochemistry; the key factor being the placement of the C-H hydrogen atoms with respect to the metal surface. If all the C-H hydrogen atoms are placed relatively far removed from the metal surface, then reversible hydrocarbon desorption will occur. If some H atoms can be placed closely to the metal surface, facile C-H bond scission to form a C_nH_n species will be a favored process. If such a C_nH_n species is a radical (n odd), then neither thermal desorption nor displacement will yield a gaseous C_nH_n species. A C_nH_n molecular species (n even) will be potentially thermally reversible or chemically displaceable provided that all the hydrogen atoms are relatively far removed from the surface atoms.

VII. THE COORDINATION CHEMISTRY OF PYRIDINE ON PLATINUM (111) AND NICKEL 9(111)x(111) SURFACES

The coordination chemistry of benzene on the single crystal Pt and Ni surfaces has been established by ultra high vacuum surface techniques (described previously in Chapter IV for platinum surfaces and in the thesis work of Dr. C. M. Friend[14] for nickel surfaces). Chemisorption of pyridine on the metal surfaces is interesting in that the bonding of pyridine could be through either the π and π^* orbitals of the aromatic ring like that of benzene, or it could be largely through the nitrogen atom. The stereochemistry for the former type of interaction, similar to that of benzene, would have the ring lying more or less parallel to the metal surface plane, and the pyridine chemistry would probably be formally analogous to that of benzene. For the latter, the ring would be largely normal to the surface for maximal overlap between the nitrogen donar and acceptor orbitals with the metal surface orbitals, thus substantial differences between pyridine and benzene surface chemistry would be expected. Accordingly, the parallel study of pyridine and benzene on the Pt and Ni surfaces should provide a fundamental understanding of the chemisorption process for delocalized ring systems.

The coordination chemistry of pyridine on Pt(111) and Ni 9(111)x(111) was investigated under ultra high vacuum conditions. Auger electron spectroscopy, thermal desorption spectroscopy and isotopic labeling were the primary techniques used for the delineation of the C-H bond breaking process of pyridine on the two crystallographic planes. Specifically labeled pyridine molecules, NC_5H_5-4-d_1, NC_5H_5-2,6-d_2, and NC_5H_5-3,5-d_2, were effectively utilized in the mechanistic study of pyridine chemisorption processes. The pyridine chemistry on Pt(111) and Ni 9(111)x(111) was compared to the other Ni surface, Ni(100),[56] where formation of α -pyridyl was proposed to be an important intermediate in the reversible pyridine desorption as well as irreversible pyridine decomposition processes.

Results and Discussion

1. Pyridine Chemistry on Pt(111)

Pyridine showed a very high sticking coefficient on the Pt(111) surface at 25°C. Unlike the Pt(111)-benzene chemistry, chemisorption of pyridine was largely irreversible at 25°C; at ~ one monolayer coverage, larger than ~ 60% of the adsorbed pyridine underwent decomposition in the heating process (based on Auger analyses) and the reversibly desorbed pyridine showed a broad peak at the temperature maximum of 110-150°C. The pyridine that reversibly desorbed was derived from a molecular chemisorption state as no mixed pyridine molecules, $NC_5H_xD_{5-x}$, were observed in the thermal desorption study of Pt(111)-NC_5H_5-NC_5D_5. Annealing of a Pt(111)-NC_5H_5-D surface, initially formed at ~ 20°C, at ~ 120°C for one minute also did not yield any detectable amount of deuterium-containing pyridine molecules in the following thermal desorption study.

Thermal decomposition of pyridine on Pt(111) showed multiple H_2 desorption peaks at temperature maxima of ~ 85, 260 and 380°C with an approximate ratio of 0.5 : 2 : 2. In addition, H_2 evolution was detected upon adsorption of pyridine on Pt(111) at 20°C , suggesting that provided the adsorption had been carried out at temperatures lower than 20°C, the lower temperature H_2 peak(s) (below ~ 100°C), the

260°C and the 380°C peak could have had a ~ 1 : 2 : 2 ratio. The lowest H_2 maximum, ~ 85°C, was in the characteristic desorption region for Pt(111)-H which indicated that there was a facile C-H bond breaking process at low temperatures. Thus, although the two higher temperature H_2 desorption maxima at ~ 260 and 380°C for Pt(111)-NC_5H_5 were coincident with those from Pt(111)-C_6H_6, the facile dehydrogenation of pyridine at low temperatures was in sharp contrast to the benzene chemistry where dehydrogenation was only a fast process at $T > 200°C$. Thus, the chemistry of the irreversibly chemisorbed pyridine on Pt(111) indicated an initial stereochemistry with possibly one of the C-H hydrogen atoms closely approached the metal surface. A plausible model for the bonding of such irreversibly chemisorbed pyridine is through the nitrogen atom (σ donar and π acceptor interactions) with the ring plane either normal to the surface or simply tipped to a certain extent. Thus, the two α -CH hydrogen atoms can strongly interact with the metal surface through the wagging mode of this pyridine state and facile C-H bond breaking to form an α -pyridyl species will be a favorable process at low temperatures under ultra high vacuum conditions.

To gain a better understanding of pyridine chemisorption on Pt(111), thermal desorption studies using specifically labeled pyridine molecules, NC_5H_5-4-d_1, NC_5H_5-2,6-d_2 and NC_5H_5-3,5-d_2, were performed, and the desorption behavior for D_2, HD and H_2 was illustrated in Figures 24, 25 and 26. For the lowest hydrogen maximum at ~ 85°C, thermal desorption of both Pt(111)-NC_5H_5-4-d_1 and Pt(111)-NC_5H_5-3,5-d_2 gave exclusively H_2 species whereas that of Pt(111)-NC_5H_5-2,6-d_2 gave both D_2 and HD. Thus, it is clear that the initial pyridine dehydrogenation process proceeded by regioselective C-H bond breaking at α -CH positions.

Figure 24

D_2, HD and H_2 thermal desorption spectra from decomposition of Pt(111)-NC_5H_5-4-d_1 are shown in this figure. The lowest hydrogen maximum at ~ 85°C consists of H_2 species only; HD was not detected until temperatures exceeds ~ 200°C. Thus, the first C-H bond breaking is centered on the α -carbon positions.

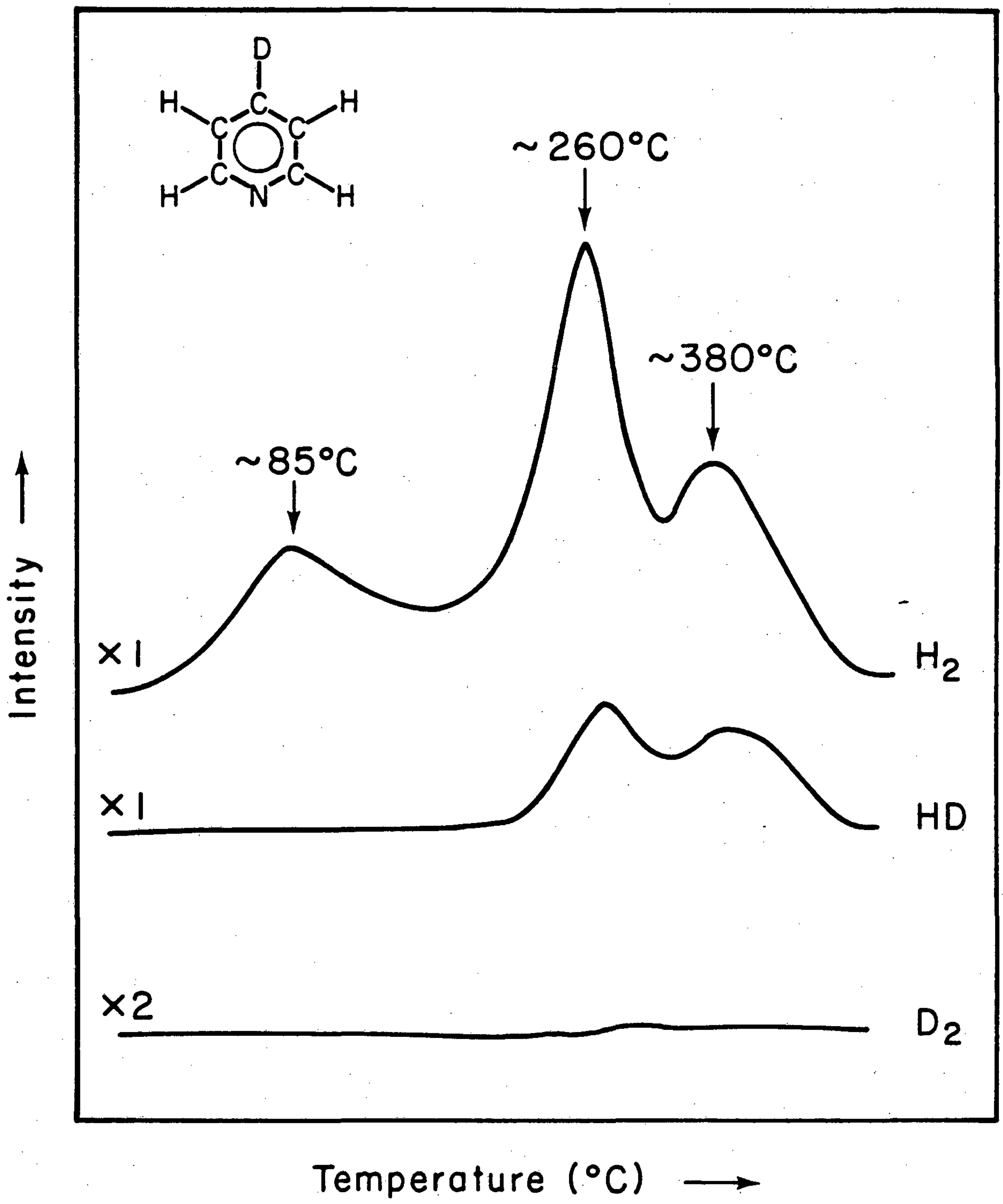

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Figure 25

D_2, HD and H_2 thermal desorption spectra derived from thermal decomposition of Pt(111)-NC_5H_5-2,6-d_2 are shown in this figure. In contrary to the decomposition of NC_5H_5-4-d_1 shown in the previous figure, the lowest hydrogen maximum at ~ 85°C consists of both D_2 and HD where, presumably, HD is originated from the reaction of Pt(111)-D species, from the C-D bond breaking, with the Pt(111)-H species from the background H_2 adsorption. Thus, the first bond breaking process is centered on the α C-D bond, in agreement with the conclusion obtained from decomposition of NC_5H_5-4-d_1.

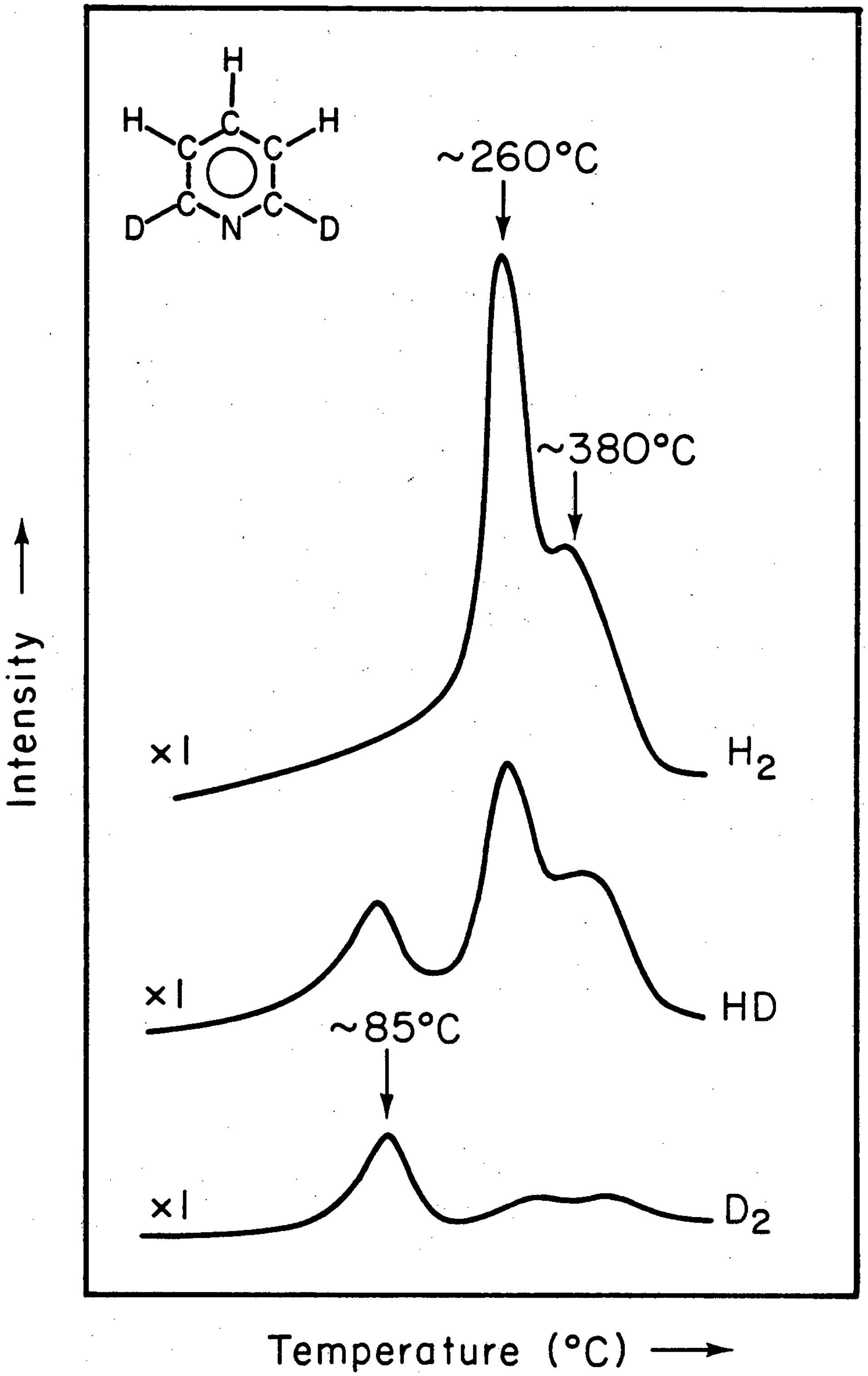

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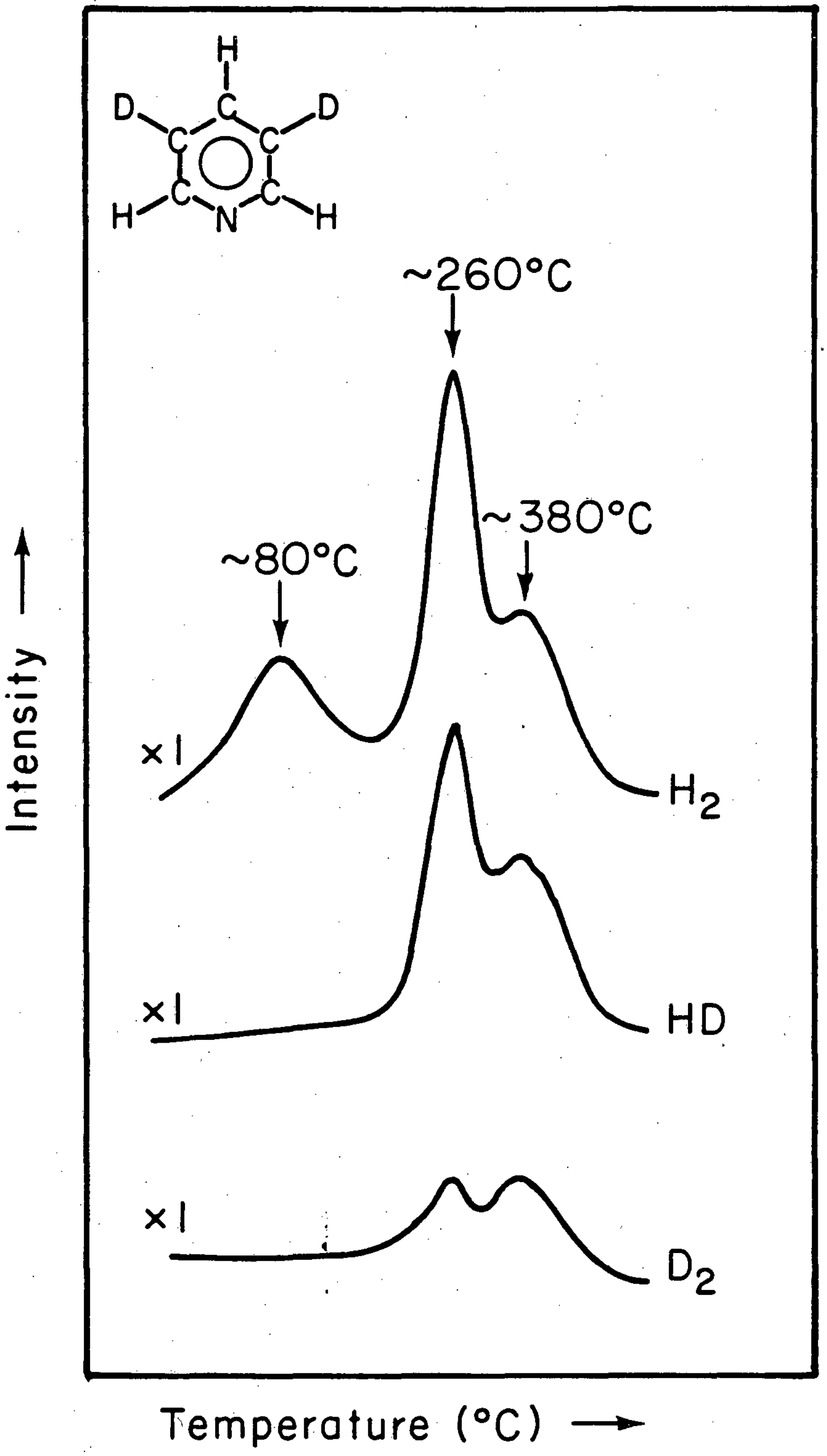
Figure 26

D_2, HD and H_2 thermal desorption spectra derived from thermal decomposition of Pt(111)-NC_5H_5-3,5-d_2 are shown in this figure. Consistent with the decomposition behavior of NC_5H_5-4-d_1 and NC_5H_5-2,6-d_2 on Pt(111), the initial bond breaking process is centered on the α C-H bond as only H_2, but no HD or D_2 was detected in the ~ 85°C maximum. The bond breaking processes at higher temperatures, to give the ~ 260°C and ~ 380°C maximum, appear to be very complex in nature; the desorption behavior of the three hydrogen species is consistent with a mechanism with pair-wise C-H(D) bond breaking of the initially formed α -pyridyl species, although there could be more than one decomposition mechanism operating and the surface pyridine species present could be more complicated than proposed in this study.



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The C-H bond breaking process beyond the first step was complex in nature; the desorption behavior of D_2, HD and H_2 at the 260°C and 380°C maximum was consistent with a pairwise bond breaking mechanism of the initially formed α -pyridyl species, but there could be more than one competing C-H bond breaking mechanism operative and the nature of the pyridine-derived species at high temperatures could be very complicated.

On the Pt(111) surface, pyridine chemisorption consisted of at least two "states": a molecular (nondissociative) chemisorption state that reversibly desorbed at 110-150°C, and an irreversibly chemisorbed state where facile C-H bond breaking at α -CH occurred at low temperatures. The bonding for the molecularly chemisorbed pyridine state was probably largely through the aromatic ring which was more or less parallel to the metal surface plane,--an analogous stereochemistry to that of benzene. Desorption of molecular pyridine from Pt(111) was observed at 110-150°C and no H-D exchange was detected under ultra high vacuum conditions; similarly, the lower temperature benzene desorption maximum was detected at 100-130°C and no H-D exchange between the chemisorbed benzene molecules was detected. The major fraction of the chemisorbed pyridine, however, was probably bonded through the nitrogen atom with significant ring tipping that facile C-H bond breaking at the α -positions could be realized at low temperatures.

The pyridine chemistry on Pt(111) bears an important similarity with that of Ni(100)[56] in that C-H bond breaking processes all proceeded through the initial formation of an α -pyridyl species at low temperatures. However, there were also substansive differences between these two surfaces in that there was clearly a nondissociative pyridine chemisorption state on Pt(111) that did not undergo H-D exchange to form the mixed pyridine molecules whereas extensive H-D exchange was detected on Ni(100) via an α -pyridyl intermediate.

2. Pyridine Chemistry on Ni 9(111)x(111) Surface

Chemisorption of pyridine on the stepped Ni 9(111)x(111) surface also showed two competing processes in the thermal desorption studies. Heating of Ni 9(111)x(111)-NC_5D_5 resulted in reversible NC_5D_5 desorption at ~ 120°C and largely decomposition to give a broad D_2 desorption peak at 110-320°C with an unresolved double maximum at ~ 150 and ~ 280°C. Adsorption of a mixture of NC_5H_5 and NC_5D_5 on Ni 9(111)x(111) gave only NC_5H_5 and NC_5D_5 in the thermal desorption. No mixed pyridine molecules was formed even after a hydrogen treatment at 10^{-6} - 10^{-7} torr and at annealed temperatures: (i) A Ni 9(111)x(111)-NC_5H_5-2,6-d_2 surface, formed at ~ 20°C, was first annealed to 75-80°C in ~ 1 x 10^{-6} torr H_2 for 1 minute, and no NC_5H_4D (mass 80) or $NC_5H_3D_2$ (mass 81) could be detected in the following thermal desorption, indicating that no H-D exchange on α -CH positions occurred. (ii) A Ni 9(111)x(111)-NC_5H_5-2,6-d_2 surface was alternatively exposed to a D_2 atmosphere at ~ 1 x 10^{-7} torr and 75-80°C for 1 minute prior to thermal desorption, and no $NC_5H_2D_3$ (mass 82), NC_5HD_4 (mass 83) or NC_5D_5 (mass 84) was formed under these conditions which indicated that there was no H-D exchange on the 3-, 4-, or 5-CH positions, either. Thus, the pyridine chemistry on this Ni surface was analogous to that of Pt(111) with respect to the absence of reversible C-H bond breaking processes.

The decomposition of pyridine on Ni 9(111)x(111), however, showed a remarkable difference from that of Pt(111) in that no regioselectivity was evident for the C-H bond breaking processes. In the thermal desorption of Ni 9(111)x(111)-NC_5H_5-2,6-d_2, all three hydrogen species, H_2, HD and D_2, were detected at 110-320°C, indicating that no regioselective C-H(D) bond breaking occurred on this surface. Thus, there was no clear indication of formation of α -pyridyl species on this stepped Ni surface.

Conclusions

The coordination chemistry of pyridine on Pt(111) and Ni 9(111)x(111) was investigated under ultra high vacuum conditions. The chemisorption behavior of pyridine appears to be a sensitive function of the metal surface. On the Pt(111) surface, there was a molecular chemisorption state that did not undergo C-H bond breaking prior to thermal desorption. The major fraction of the chemisorbed pyridine on Pt(111) appeared to be bonded largely through the nitrogen atom and underwent a facile, regioselective C-H bond breaking process at low temperatures ($T < 100$°C) to form a chemisorbed α -pyridyl species. On the stepped Ni surface, there was also a molecular pyridine chemisorption state, like the Pt(111)-pyridine chemisorption, but the major, irreversibly chemisorbed pyridine simply underwent non-selective C-H bond breaking at higher temperatures.

Considering the metal substrate for both Pt(111) and Ni 9(111)x(111) having largely (111) orientation, the differences observed for pyridine chemisorption would appear to reflect the differences in the electronic structure of Ni and Pt. However, since regioselective C-H bond breaking has been identified on the other Ni surface, Ni(100),[56] the nature of pyridine chemisorption is probably more complex and a systematic study on various metal surfaces is necessary to obtain a better molecular understanding.

VIII. REFERENCES

1. G. A. Somorjai, "Chemistry in Two Dimentions: Surfaces." Cornell University Press, Ithaca and London, 1981.
2. N. B. Hanney, "Treatise on Solid State Chemistry. Surfaces I and II." (Vol. 6A and 6B) Plenum Press, New York, 1976.
3. E. L. Muetterties, T. N. Rhodin, E. Band, C. F. Bucker and W. R. Pretzer, Chem. Rev., 79, 91 (1979).
4. E. L. Muetterties, Angew. Chem. Int. Ed. Engl., 17, 545 (1978).
5. J. E. Demuth, D. W. Jensen and P. M. Marcus, Phys. Rev. Lett., 32, 1182 (1974).
6. L. L. Kesmodel, L. H. Dubois and G. A. Somorjai, J. Chem. Phys., 70, 2180 (1979).
7. K. Heinz, E. Lang and K. Muller, Surf. Sci., 87, 595 (1979).
8. J. C. Hemminger, E. L. Muetterties and G. A. Somorjai, J. Am. Chem. Soc., 101, 62 (1979).
9. C. M. Friend and E. L. Muetterties, J. Am. Chem. Soc., 103, 773 (1981).
10. E. L. Muetterties, ACS Sym. Ser., 155, 273 (1981).
11. F. M. Hoffmann, T. E. Felter, P. A. Thiel and W. H. Weinberg, J. Vac. Sci. Technol., 18, 651 (1981).
12. T. E. Madey and J. T. Yates, Jr., Surf. Sci., 76, 397 (1978).
13. T. S. Wittrig, P. D. Szuromi and W. H. Weinberg, J. Chem. Phys., 76, 716 (1982).
14. C. M. Friend, Ph.D. Thesis, University of California, Berkeley, California, 1981.
15. S. M. Davis, B. E. Gordon, M. Press and G. A. Somorjai, J. Vac. Sci. Technol., 19, 231 (1981).

16. Inorg. Synth., 9, 59 (1967).

17. (a) Dr. Judith Stein in Prof. E. L. Muetterties' group synthesized trimethylphosphine, perdeuterotrimethylphosphine, cyclobutene, norbornadiene-7-d_1 and cycloheptatriene-7-d_1. (b) J. J. Vanderbilt, Ph.D. Dissertation, University of Michigan, 1978 and the references therein.

18. E. Muller and H. Fricke, Justus Liebigs, Ann der Chemie, 66, 38 (1963).

19. I. T. Harrison and S. Harrison, "Compendium of Organic Synthesis Methods." Wiley-Interscience, New York, 1971.

20. B. Bak, L. Hansen and Rastrup-Andersen, J. Chem. Phys., 22, 2013 (1954).

21. J. H. Callomen and B. P. Stoicheff, Can. J. Phys., 35, 373 (1957).

22. W. E. Palke and W. N. Lipscomb, J. Am. Chem. Soc., 88, 2384 (1966).

23. See for example:

(a) J. E. Demuth and H. Ibach, Surf. Sci., 85, 365 (1979) for acetylene chemisorption on Ni(111); (b) L. H. Dubois, D. G. Castner and G. A. Somorjai, J. Chem. Phys., 72, 5234 (1980) for acetylene chemisorption on Rh(111); and (c) C. Backx, R. F. Willis, B. Feurbacher and B. Fitton, Surf. Sci., 68, 516 (1977) for acetylene chemisorption on W(111), W(100) and W(110).

24. A. E. Morgan and G. A. Somorjai, J. Chem. Phys., 51, 3309 (1969).

25. L. L. Kesmodel, P. C. Stair, R. C. Baetzold and G. A. Somorjai, Phys. Rev. Lett., 36, 1316 (1976).

26. P. C. Stair and G. A. Somorjai, J. Chem. Phys., 66, 2036 (1977).

27. L. L. Kesmodel, R. C. Baetzold and G. A. Somorjai, Surf. Sci., 66, 299 (1977).

28. L. L. Kesmodel, L. H. Dubois and G. A. Somorjai, Chem. Phys. Lett., 56, 267 (1978).

29. W. J. Lo, Y. W. Chung, L. L. Kesmodel, P. C. Stair and G. A. Somorjai, Solid State Commun., 22, 335 (1977).

30. J. E. Demuth, Chem. Phys. Lett., 45, 12 (1977).

31. J. E. Demuth, Surf. Sci., 84, 315 (1979).

32. J. E. Demuth, Surf. Sci., 80, 367 (1979).

33. J. E. Demuth, Surf. Sci., 93, L82 (1980).

34. H. Ibach, H. Hopster and B. Sexton, Appl. Phys., 14, 21 (1977).

35. H. Ibach, H. Hopster and B. Sexton, Appl. Surf. Sci., 1, 1 (1977).

36. H. Ibach and S. Lehwald, J. Vac. Sci. Technol., 15, 407 (1978).

37. T. E. Fischer, S. R. Kelemen and H. P. Bonzel, Surf. Sci., 64, 157 (1977).

38. G. Casalone, M. G. Cattania and M. Simonetta, Surf. Sci., 103, L121 (1981).

39. T. E. Felter and W. H. Weinberg, Surf. Sci., 103, 265 (1981).

40. T. E. Fischer and S. R. Kelemen, Surf. Sci., 74, 47 (1978).

41. T. V. Harris, J. W. Rathke and E. L. Muetterties, J. Am. Chem. Soc., 100, 6966 (1978).

42. S. Lehwald, H. Ibach and J. E. Demuth, Surf. Sci., 78, 577 (1978).

43. F. P. Netzer and J. A. D. Matthew, Solid State Commun., 29, 209 (1979).

44. P. C. Stair and G. A. Somorjai, J. Chem. Phys., 67, 4361 (1977).

45. J. H. Sinfelt, Cata. Rev.-Sci. & Eng., 9, 147 (1974).

46. F. Solymosi, Cata. Rev.-Sci. & Eng., 1, 233 (1968).

47. M. Kraft and H. Spindler, Proc. 4th Int. Cong. Cata. (Moscow, 1968), Akademiai Kiado, Budapest, Vol. II, pp. 286-294, 1971.

48. R. W. Maatman, P. Mahaffy, P. Hoekstra and C. Addink, J. Cata., 23, 105 (1971).

49. J. A. Cusumano, G. W. Dembinski and J. H. Sinfelt, J. Cata., 5, 471 (1966).

50. F. G. Ciapetta, R. M. Dobres and R. W. Baker, "Catalysis." Vol. VI, P. H. Emmet, ed., Van Nostrand Publ. Co., New York, 1958.

51. M. Boudart, Adv. Cata., 20, 153 (1969).

52. J. L. Gland, K. Baron and G. A. Somorjai, J. Cata., 36, 305 (1975).

53. D. W. Blakely and G. A. Somorjai, J. Cata., 42, 181 (1976).

54. J. E. Demuth, H. Ibach and S. Lehwald, Phys. Rev. Lett., 40, 1044 (1978).

55. Adsorption of cyclobutane on Pt(111) at 25-90°C resulted in complete decomposition, upon heating, to give H_2 and ~ 0.15-0.20 monolayer of carbon; three H_2 peaks at temperature maxima of ~ 115, 190 and 285°C (adsorption temperature: $<$ 25°C) were observed with approximate intensities of 4 : 2 : 2. The 115°C peak is in the characteristic free H desorption region which, with the relative intensities of the three H_2 peaks, seemed to indicate facile cyclobutane dehydrogenation on Pt(111) to form a C_4H_4 species. However, attempted displacement reactions of Pt(111)-C_4H_8 with either $P(CH_3)_3$ or CH_3NC at 0-90°C failed to give any detectable amount of hydrocarbon into the gas phase.

56. R. M. Wexler, M.-C. Tsai, C. M. Friend and E. L. Muetterties, J. Am. Chem. Soc., 104, 2034 (1982).

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