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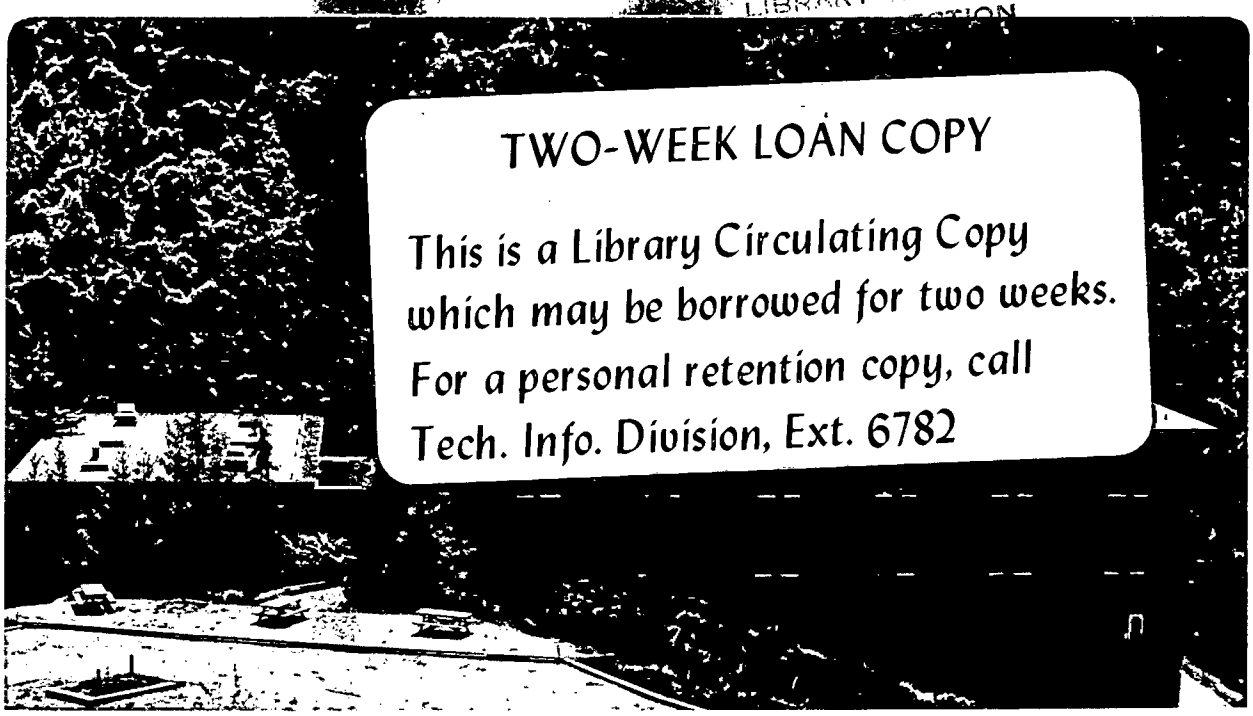

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The Chemistry of Acetylene on Platinum (111) and (100) Surfaces.

(Chemisorption/Ultra High Vacuum/Metal Surface Chemistry/Hydrocarbon Reactions)

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ABSTRACT An ultra high vacuum experimental 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 pressure, temperature, and surface crystallography. The rates for both processes are substantially higher on the Pt(100) surface. Net acetylene-hydrogen processes, in the temperature range of 20 to ∿130°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 a contributing factor to the differences in acetylene chemistry on these two surfaces.

Essential to an in-depth understanding of hydrocarbon chemistry mediated at metal surfaces is the delineation of the surface electronic, topological and compositional features that significantly affect carbon-hydrogen bond making and breaking processes. Because the activation energy for carbon-hydrogen bond breaking is typically much lower than for carbon-carbon bond breaking, it is in principle, experimentally easier to study this type of reaction. Using primarily the techniques of thermal desorption spectroscopy, displacement reactions, and isotopic labelling under ultra high vacuum conditions, we had successfully defined molecular features of benzene and toluene chemistry on a range of nickel surface planes.[1] We describe here an analogous study of acetylene chemisorption and acetylene reactions on the flat platinum (111) and (100) planes. This study establishes the temperatures required for carbon-hydrogen bond making and for carbon-hydrogen bond breaking for the acetylene molecule on these platinum surfaces and also sets certain limits for the compositional and stereochemical features of the chemisorbed species derived from acetylene.

EXPERIMENTAL

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

Procedure. The basic ultra high vacuum system, the experimental protocols, and the source and the cleaning procedure for the platinum (111) crystals have been described in full in earlier papers.[2-4] The cleaning procedure for Pt(100) is that described by Fischer, Kelemen and Bonzel,[5] and the clean platinum surface generated showed the 5x20 low energy electron diffraction pattern. The 5x20 surface converted to the 1x1 structure with exposure to acetylene.[5] The 1x1 surface is stabilized by the presence of acetylene and is present during the hydrogenation and dehydrogenation processes discussed in this article.

RESULTS

Acetylene is the simplest unsaturated hydrocarbon. Its geometric structure, electronic structure, and organic chemistry are quite precisely defined.[6-8] The molecular details of acetylene interactions with inorganic and organometallic complexes also are relatively well-defined.[9,10] Catalytic acetylene chemistry based on solid state or solution state catalysts is well-explored in terms of reaction products although the molecular features of the catalytic reaction mechanism are not fully defined.[8,9,11] The basic features of acetylene chemisorption on metal surfaces is a much investigated area, especially the chemisorption of acetylene on crystallographically defined metal surfaces under ultra high vacuum conditions. However, full understanding at the molecular level has not been reached for the acetylene surface case. A careful analysis of the acetylene surface science literature[12-28] (an excellent general discussion is that of Demuth[12]) reveals certain complications common to surface chemistry, especially hydrocarbon surface chemistry. The complications are fully recognized

by the surface scientists but are often ignored in the discussion of specific scientific investigations. Critical limitations or complications are:

(1) As the complexity of the adsorbate species increases from an atom to a diatomic to a polyatomic molecule, the probability that compositionally or stereochemically differentiable adsorbate states will be formed under a specific set of experimental conditions, generally increases.

(2) The sensitivities of the various common electron spectroscopic or diffraction techniques to a given adsorbate species obviously are not necessarily directly related. Thus, in the case of chemisorption of a molecule that gives rise to two or more differentiable adsorbate species, the possibility arises that different techniques will primarily sense different adsorbate species. Low energy electron diffraction for example senses only adsorbates that have long range order.

(3) The lifetime of a chemisorption state or set of states is finite. This state may alter during the time period of a spectroscopic or diffraction study and, of course, the electron or photon beam may effect surface state transformations.

(4) The character of the chemisorption state can be a very sensitive function of temperature, pressure (background pressure), surface contaminants, and surface coverages. Molecules present in the ultra high vacuum system can and

do react with the metal surface or with the chemisorbed species. In fact, as it is now recognized,[23] hydrogen reacts with acetylene chemisorbed on Pt(111).

(5) In specific spectroscopic or diffraction studies, there naturally are attempts to enhance spectral or diffraction features. In these attempts, time scale or seemingly minor temperature, pressure or coverage variations may not be explicitly reported--yet minor excursions in such experimental variables may wreak substantial changes in surface adsorbate species.

All of these are real problems for the seemingly simple system of acetylene chemisorption on metal surfaces and are particularly evident for the chemisorption of acetylene on Pt(111).

The <u>states</u> of acetylene chemisorption on Pt(111) have been examined by thermal desorption spectroscopy,[13] ultraviolet photoemission spectroscopy,[12-14,16] low energy electron diffraction[17-22] and high resolution electron energy loss spectroscopy.[23-26] Most scientific attention has been given recently to the data and conclusions derived from the last two techniques. Although originally the data from these two techniques were referenced to a "stable" Pt(111)-C_2H_2 state, the data are relevant only to a species or set of species generated by a higher temperature reaction between hydrogen and the original chemisorbed acetylene species (<u>vide infra</u>). This adsorbate has been described as CH_3C[21,22], CH_2CH[13] and as CH_3CH.[23-26] Careful photoemission studies done as a function of temperature for C_2H_2 chemisorbed on Pt(111) at or near 20°C are reported to be consistent with sigma bonded HCCH or CCH_2 species.[12-14] Analogous photoemission studies for Pt(100)-C_2H_2 at 20°C suggest that the major adsorbate is a complexed HCCH species.[5,15]

Our studies of acetylene chemisorption on Pt(111) and on Pt(100), definitively establish the temperatures at which C-H bond breaking and bond making processes occur at moderate rates. Our detection of carbon-hydrogen bond breaking at low temperatures, 20-135°C, was based on isotopic labelling or exchange of hydrogen and deuterium and the established fast site exchange of H and D atoms on a metal surface. This probe sensed only those surface carbon-hydrogen bond breaking processes in which a C-H bond was converted to a $Pt_{surface}$-H bond and in which the $Pt_{surface}$-H species had a finite lifetime. A carbon-hydrogen bond breaking process for an adsorbed HCCH species that proceeded simply by a 1,2 shift of a hydrogen atom to give CCH_2 would not be detected by our experimental procedure.

Consistent with earlier reports, we found that the thermal desorption spectrum for Pt(111)-C_2H_2, formed at 0-20°C, consisted of two broad hydrogen (H_2) desorption peaks with maximum desorption rates occurring at ∿240 and 380°C with relative intensities of 1:1. For Pt(111)-C_2D_2, the two D_2 thermal desorption maxima were at 245 and 380°C. At high initial acetylene coverages (>0.5 to 0.6 of a monolayer), the thermal desorption spectrum for Pt(111)-C_2H_2 also showed a small (<25%) reversible desorption peak for acetylene at 160°C. At comparable high coverages, Pt(111)-C_2H_2-C_2D_2 showed all three possible acetylene molecules desorbed at ∿160°C. Attempts to displace acetylene from Pt(111)-C_2H_2 at 20°C with strong field ligands like trimethylphosphine and methyl isocyanide were unsuccessful—in sharp contrast to the facile displacement of benzene from Pt(111)-C_6H_6 by trimethylphosphine. However, thermal desorption of acetylene from Pt(111)-C_2H_2-$P(CH_3)_3$ did yield far more acetylene than did an analogous

acetylene coverage on Pt(111) alone. No benzene was detected in thermal desorption experiments involving Pt(111)-C_2H_2.

Thermal desorption of hydrogen from Pt(111) is a sensitive function of coverage and heating rate but the typical range for the maximum following adsorption near 20°C is ∿50-150°C; the temperature maximum for deuterium is slightly higher than for hydrogen at comparable coverages.

A Pt(111)-H-C_2D_2 surface was formed at temperatures in the range of -10 to +50°C by first chemisorbing hydrogen and then perdeuteroacetylene. Thermal desorption immediately following the adsorption processes yielded an H_2 maximum at 120°C, characteristic of a Pt(111)-H surface; no D_2 or HD was detected in this low temperature region. Characteristic of Pt(111)-C_2D_2, there were two D_2 desorption maxima at ∿245 and 380°C. A small HD desorption maximum at 245°C and a very small HD maximum at 380°C were also observed. The appearance of HD is largely ascribed to the overlap of the broad 120 and 240°C desorption peaks for Pt(111)-H and the low temperature acetylene decomposition process, respectively, and to a small amount (∿5%) of C_2HD impurity in the C_2D_2 sample. Hence, under these conditions, there was no detectable reaction between C_2D_2 and the hydrogen atoms on the surface.

In contrast to the above experiment at 20°C and low hydrogen surface activities, Pt(111)-H-C_2D_2 surfaces when heated to temperatures above 50°C for periods of about 1-5 minutes yielded a significantly different desorption pattern as shown in Figure 1 for a 135°C reaction. As in the lower temperature experiments, only H_2 showed a desorption maximum in the temperature region characteristic of Pt(111)-H(D). All changes were in the ∿240 and 380°C peaks. Substantial H_2 and HD maxima

were observed near 240°C with small maxima for these two molecules at ∿380°C. The integrated H_2, HD and D_2 intensities for the 260°C and 400°C maxima were in the relative ratio of $I_{240°C} > I_{380°C}$ with an apparent maximum ratio of about 2:1. The results establish that no $Pt_{surface}$-D bonds are broken up to 135°C and that the net reaction between C_2H_2 (C_2D_2) and H adsorbed on this Pt(111) surface is hydrogenation.

The higher temperature (50-135°C) reactions between adsorbed C_2D_2 and H on Pt(111) indicated that reactions should occur at a measurable rate at 25°C. To test this implication, a Pt(111)-C_2D_2 surface, generated and maintained at 20°C, was treated to an H_2 atmosphere of 10^{-7} torr for twenty minutes. A subsequent thermal desorption experiment established that carbon-hydrogen bonds had been formed under these conditions and that no carbon-deuterium bonds had been cleaved: there was only an H_2 desorption peak in the low temperature region characteristic of Pt(111)-H, a very small H_2 and larger HD and D_2 peaks at 240°C, and essentially only HD (small) and D_2 peaks at 380°C.

In the thermal pretreatment of Pt(111)-H-C_2D_2, there was a direct correlation between the increase in the H_2 and HD desorption peaks at ∿240 and 380°C, and the development of a 2x2 low energy electron diffraction pattern for Pt(111)-H-C_2D_2, which pattern is the diagnostic feature for the acetylene adsorbate species identified[21,22] as CH_3C in the low energy electron diffraction studies of Somorjai and coworkers.[21,22]

Acetylene chemisorbed on Pt(100) in an irreversible fashion. Rapid heating of Pt(100)-C_2H_2 (or C_2D_2) yielded no detectable

acetylene or any other hydrocarbon such as benzene. Hydrogen, formed by carbon-hydrogen bond scission of acetylene adsorbed at coverages of ∿0.5, evolved with two major desorption peaks at ∿260 and 320°C. There were, however, additional small maxima, and the spectral profile was dependent upon coverage as shown in Figure 2. No attempt is made here to mechanistically interpret the fine structure of the desorption spectra: because the platinum 5x20 $\rightleftharpoons$ 1x1 surface reconstruction is a function of adsorbate coverage and potentially a function of temperature, there is a reasonable probability that there are more than one structurally or stereochemically differentiable adsorbates derived from Pt(100) and acetylene.

The chemistry of acetylene on Pt(100) was substantially different from that on Pt(111) in that carbon-hydrogen bond making and also bond breaking was far more facile on Pt(100). Exposure of Pt(100)-C_2D_2, formed at 20°C, to a hydrogen pressure of 10^{-7} to 10^{-11} torr for a period of 5-15 minutes yielded adsorbate species that contained a substantial amount of carbon-hydrogen bonds as evidenced by large H_2 and HD desorption maxima at 260 and 320°C in the subsequent thermal desorption (decomposition) experiment. A slight modification of this experiment established that carbon-deuterium bond breaking occurred at 35°C. A Pt(100)-C_2D_2 state formed at ∿35°C was treated with H_2 at 10^{-6} torr for 10 minutes. Then the thermal desorption (decomposition) experiment was performed. The major desorption peaks in the region characteristic of carbon-hydrogen bond breaking were largely those of H_2 and HD with only a small amount of D_2. Hydrogen-deuterium exchange at the adsorbate carbon sites was nearly complete under these conditions. All integration data indicated that the net reaction on this surface was H-D exchange.

At higher temperatures of 70-130°C, exposure of Pt(100)-C_2D_2 to a hydrogen pressure of 10^{-7} torr led to a rapid hydrogen-deuterium exchange. After exposure of several minutes, the thermal desorption spectra consisted largely of H_2 with only trace amounts of HD and no D_2 detected at the two major desorption temperatures characteristic of the carbon-hydrogen (deuterium) bond breaking processes.

DISCUSSION

Isotopic labelling of the acetylene-hydrogen reaction on the two atomically flat platinum(111) and (100) planes has allowed identification of the temperatures at which carbon-hydrogen bond making and bond breaking processes proceed at moderate rates under low hydrogen presures of 10^{-7} to 10^{-11} torr. Quantitatively and qualitatively, the acetylene-hydrogen reaction is different on the Pt(111) and Pt(100) surfaces. The most distinguishing feature for Pt(111) is the absence of measurable carbon-hydrogen bond breaking (to form $Pt_{surface}$-H species) up to temperatures of at least 120°C whereas the process is detectable at 20°C for Pt(100). For Pt(100), the net reaction between adsorbed acetylene and hydrogen atoms at 20 to 135°C is hydrogen exchange (H-D exchange) whereas on Pt(111), the only reaction is hydrogenation.

In the initial interaction of acetylene with the flat Pt(111) surface plane, the carbon-carbon bond probably is in a plane nearly parallel to the metal surface plane in order to allow maximal overlap of the π and π^* acetylene orbitals with appropriate metal surface orbitals. The situation for the Pt(100) flat plane may be analogous but the possibility of significant tipping of the C-C bond vector with respect to the surface plane is higher (see Figure 3). At moderate temperatures, there should be some reorganization (often referred to as rehybrization of the HCCH framework[5,12,13,15]), and if molecular metal coordination chemistry is an appropriate guide for this acetylene chemistry, the two carbon-hydrogen vectors should be tipped, within a plane normal to the surface and away from the surface plane. This type of interaction is consistent with ultraviolet photoemission data[12,13]

for Pt(111)-C_2H_2. Furthermore, the relatively high activation energy required for carbon-hydrogen bond scission (to form $Pt_{surface}$-H species) on Pt(111)-C_2H_2 strongly implicates a stereochemistry in which the C-H hydrogen atoms are well-removed from the surface metal atoms.[29-31] Carbon-hydrogen bond scission for what was initially Pt(111)-C_2H_2 was measurably fast only at temperatures near 240°C (this statement relates to the time scale of seconds and pressures of $\sim 10^{-10}$ torr of the thermal desorption experiment). Rapid carbon-hydrogen bond breaking (to form $Pt_{surface}$-H species) was not observed even at 135°C within a time interval of minutes for the Pt(111)-C_2D_2 state, formed initially at 20°C. Thus, following the above reasoning, we suggest that the adsorbate species formed from the hydrogenation of Pt(111)-C_2H_2 does not have any of the hydrogen atoms near the surface metal atoms. Of the three models proposed for this species, CH_3C,[21,22,28] CH_2CH[13,32] and CH_3CH[23-26] the first, an ethylidyne species proposed by Kesmodel, Dubois and Somorjai[21,22] to have the C-C bond vector normal to the surface plane, is fully consistent with our chemical and isotopic labelling experiments simply because this model would have all hydrogen atoms far removed from the surface plane. This consideration does <u>not</u> exclude the other two proposed models because either of these could have a stereochemistry[29] such that all hydrogen atoms would be relatively distant from surface metal atoms.

In contrast to Pt(111), we found carbon-hydrogen bond breaking in the acetylene adsorbate on Pt(100) to be measurable at temperatures of 20°C. In light of this facile bond breaking process and of the ultraviolet photoemission data[5,15] which are consistent with a slightly

reorganized or "rehybridized"[5,15] acetylene framework for Pt(100)-C_2H_2, we suggest that either the C-C bond vector is tipped with respect to the metal surface plane or that the HCCH adsorbate species is not coplanar through some torsional deformation, a deformation discussed by Felter and Weinberg.[27] Either possibility could bring one or both hydrogen atoms sufficiently close to the surface as to generate a C-H-Pt multicenter bond,[29-31] and thereby enhance the probability of facile carbon-hydrogen bond breaking and ultimately an exchange process. Recently, Casalone, Cattania and Simonetta[33] have proposed on the basis of a low energy electron diffraction study of Ni(100)-C_2H_2 that the C-C bond vector is tipped by some 50° from the surface plane—a value close to the geometric estimate noted in Figure 3.

It is important to note that in all results and discussions relating to the particular process of carbon-hydrogen bond making that the rates are a very sensitive function of hydrogen pressure which establishes the thermodynamic activity of the surface hydrogen atoms. The low rates reported herein are simply a reflection of the very low pressure conditions. Hydrogen and acetylene are converted to ethylene and then to ethane on a platinum surface at ambient pressures and temperatures although even under these conditions the rates are not exceptionally high. We saw no evidence that the adsorbate was removed from the Pt(100) surface, presumably as ethane, by flowing hydrogen over the Pt(100)-C_2H_2 surface at 20°C and 10^{-6} torr pressure within a 25 minute period as judged by Auger analysis and by a final thermal desorption experiment.

In the thermal decomposition of acetylene in Pt(111)-C_2H_2 formed at 20°C, the relative intensities of the two H_2 desorption peaks are approximately 1:1 suggestive of an intermediate C_2H state in the thermal decomposition of Pt(111)-C_2H_2. This may be the case, but we do not believe that these data alone allow such a conclusion because of the very broad character of the two desorption peaks (there may in fact be more than two desorption peaks) and because of the possibility that more than one differentiable adsorbate species is present at these higher temperatures. The relative intensities of the two hydrogen desorption peaks for the higher temperature species generated from Pt(111)-C_2H_2 and hydrogen are approximately 2:1, suggestive of a C_2H_3 adsorbate species; however, for the reasons stated above, we do not believe that the data from the desorption (decomposition) experiments alone allow such a conclusion to be made.

We note a curious coincidence in the temperature for the maximum rate of hydrogen evolution in the highest temperature decomposition process for Pt(111)-C_2H_2. The temperature is ∿380°C. It is coincident with the highest temperature decomposition peak for Pt(111)-C_2H_4, Pt(111)-C_6H_6, and Pt(111)-cyclohexene. This may be no more than a coincidence or it <u>may</u> reflect a common feature in the ultimate decomposition mechanism on this platinum surface of hydrocarbon adsorbates or at least certain interrelated hydrocarbons (ethylene can be dehydrogenated to acetylene, acetylene can be catalytically trimerized to benzene, and cyclohexene can be dehydrogenated

to benzene on platinum). For Pt(100), the acetylene desorption spectrum is a function of adsorbate coverage in that there is no high temperature hydrogen peak at low coverages (Figure 2). Benzene shows a different coverage dependence; nevertheless, benzene and acetylene have similar high temperature H_2 peaks at high adsorbate coverages on Pt(100).

In summary, we note that the substantive differences in the acetylene surface chemistry between Pt(111) and Pt(100) appear to be intimately associated with the topographical differences between these two surfaces. Similar differences may be observed for acetylene chemistry on other second and third row Group VIII metal surfaces which can be directly related to the topographical features of the metal substrate.

Salmerón and Somorjai have studied H-D exchange reactions, mediated on a Pt(111) surface, between D_2 and a variety of hydrocarbons including acetylene.[34] Their experimental results for acetylene on Pt(111) are similar to those described in this article.

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Figure 1. A Pt(111)-H-C_2D_2 surface was formed at ∿20°C and then was heated to 135°C for one minute. After cooling to ∿35°C, the thermal desorption (decomposition) experiment was performed. Presented above are the thermal desorption spectra in which the desorption of H_2, HD and D_2 were monitored by mass spectrometry. Plotted are the mass 2,3 and 4 ion intensities as a function of temperature (the heating rate was 25°sec^{-1} and the rate was linear above ∿60°C). The low temperature maximum for H_2 is in the region characteristic of Pt(111)-H. The absence of HD or D_2 desorption in this low temperature range established unequivocably that C-D bonds were not broken at measurable rates to form $Pt_{surface}$-H bonds up to and at 135°C within the time scale of this experiment. The high temperature desorption maxima at ∿240° and 380°C characteristic of C-H bond breaking for the adsorbate species are detectable for all three species H_2, HD and D_2, showing that C-H bonds were formed in the surface reaction of H and C_2D_2 at temperatures of 135°C (or below). The much larger intensity of the 240°C desorption peaks relative to the 380°C peak for H_2 and HD does not necessarily imply that specific (in a structural or stereochemical context) C-H(D) bond types are broken at 240°C; the intensity differences may reflect largely a kinetic isotopic effect.

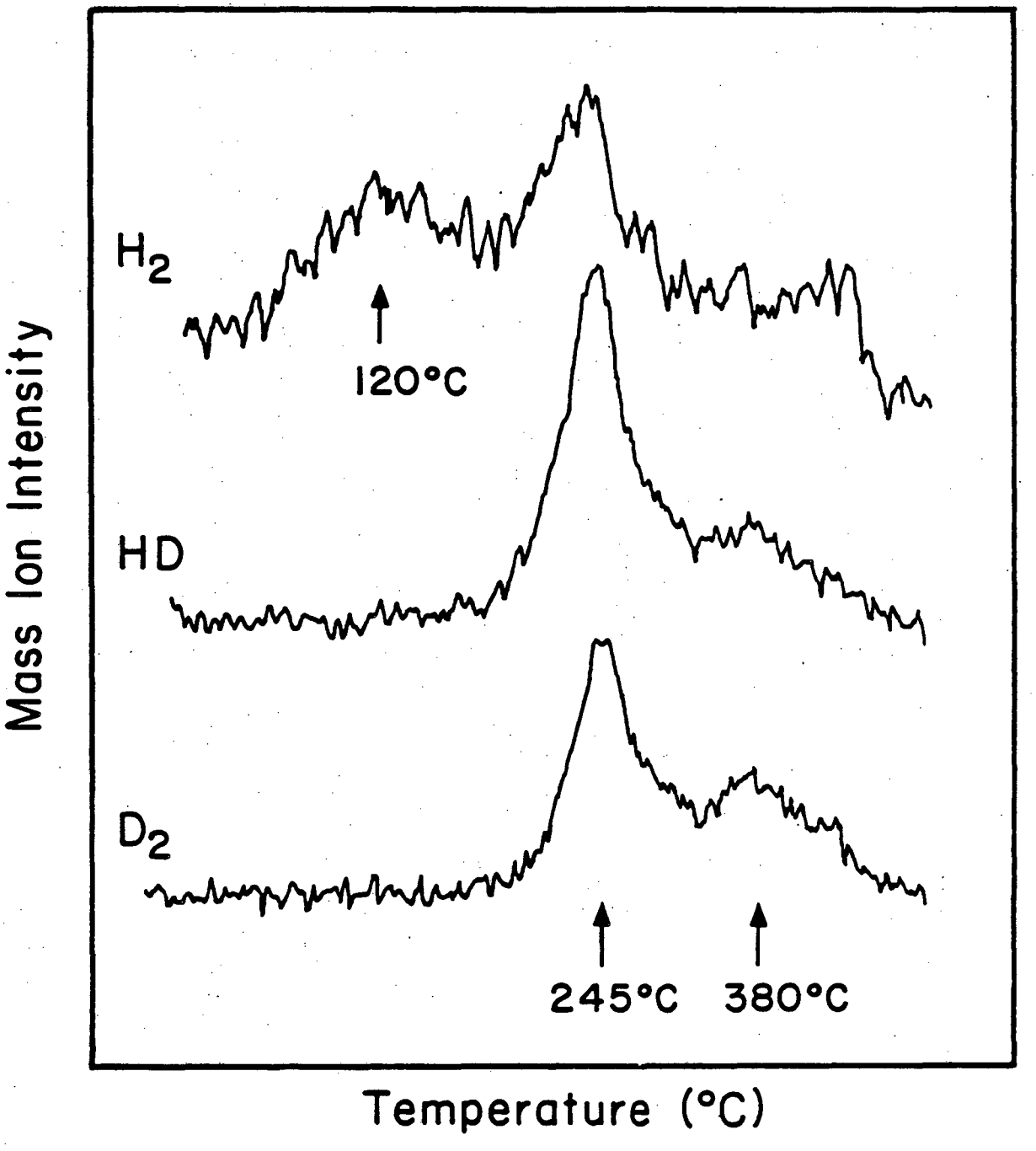


Figure 1

Figure 2. Illustrated above are the hydrogen desorption spectra obtained by Fischer, Kelemen and Bonzel[5], for the thermal desorption (decomposition) of Pt(100)-C_2H_2 as a function of fractional coverage, θ, of the platinum surface. The essential desorption line shapes and the temperatures for the desorption maxima were fully reproduced in this present study; the temperature maximum for D_2 desorption from Pt(100)-C_2D_2 were shifted to slightly higher temperatures, ∿5°. The weak, lowest temperature maximum observed for this Pt(100)-C_2H_2 system is close to a maximum observed for Pt(100)-H and, therefore, may represent desorption of H_2 from $Pt_{surface}$-H species formed by partial dehydrogenation of the acetylene adsorbate at temperatures between ∿50 and 160°C.

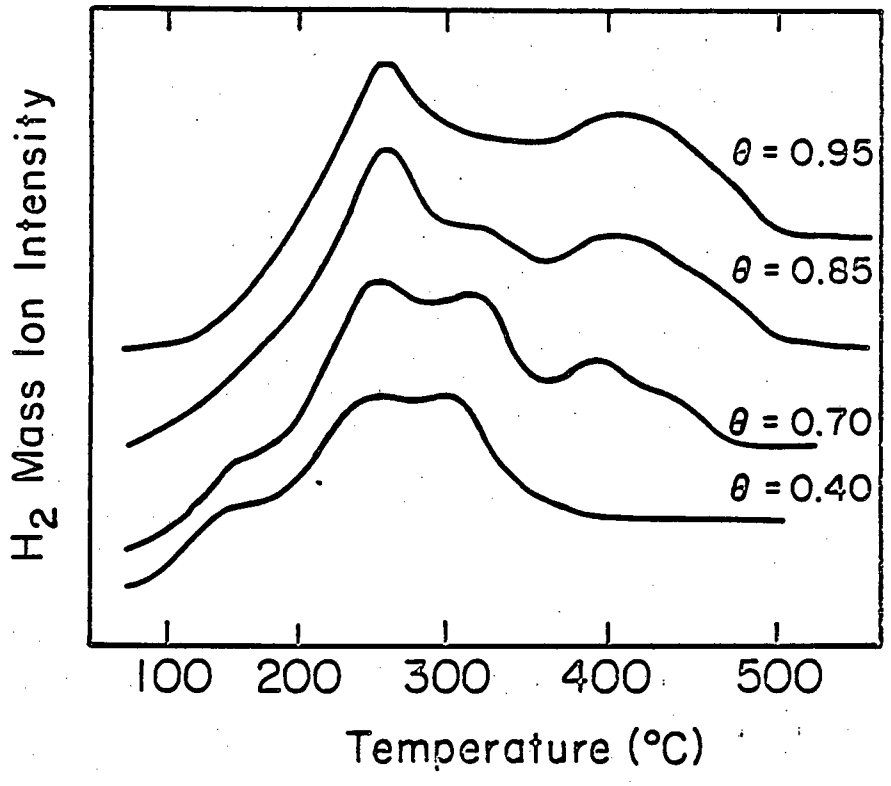
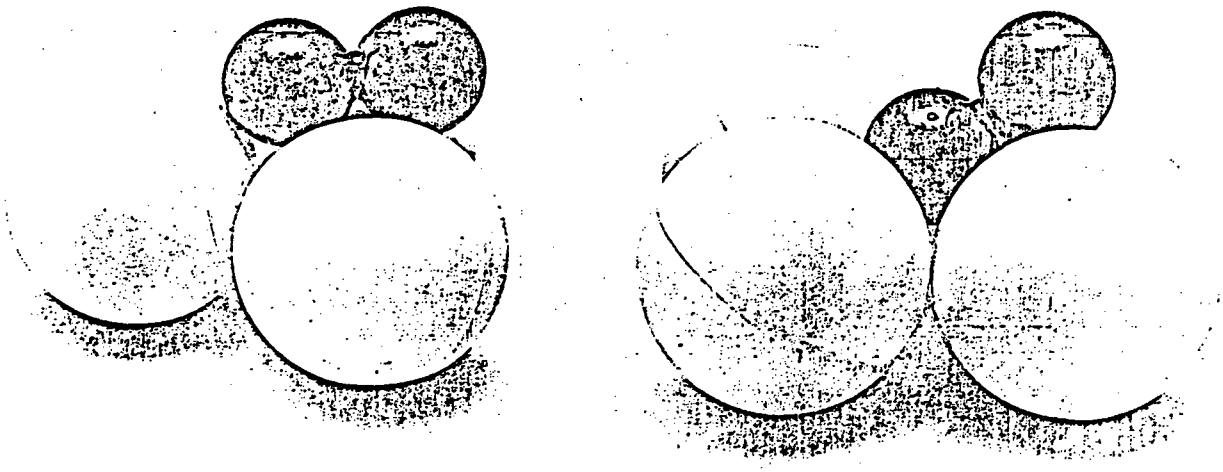


Figure 3. This is a scale photograph of a three-atom and four-atom section of Pt(111) and Pt(100) with the two carbon atoms (smaller dark spheres) of a HCCH adsorbate that illustrates the topographically-defined potential for tipping of the C-C bond vector of the acetylene adsorbate, with the constraint that both carbon atoms maintain a bonding interaction with surface platinum atoms, with respect to the surface plane for the two platinum surfaces. This potential for tipping could be realized in the adsorbate ground state structure or in thermally excited states. Clearly, the potential is greater for the (100) surface. With C-C bond distances in the range of 1.30 to 1.40Å, the angles generated by the C-C vector and the surface plane is ∿13 and 45° for the (111) and (100) surfaces, respectively.



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