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SURFACE SCIENCE AND CATALYSIS

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ABSTRACT

Modern surface science studies have explored a large number of metal catalyst systems. Three classes of catalytic reactions can be identified: 1) those that occur over the metal surface; 2) reactions that take place on top of a strongly adsorbed overlayer and 3) reactions that occur on co-adsorbate modified surfaces. Case histories for each class are presented.

The first class of reactions is structure sensitive, and rough surfaces are needed for high reactivity. Ammonia synthesis, H_2/D_2 exchange and complex hydrocarbon reaction studies all indicate the importance of high coordination sites that are present on atomically rough, open crystal surfaces, mostly in the second layer. A model is presented that correlates increased charge fluctuations at these sites with enhanced catalytic activity.

The second class of reactions includes ethylene hydrogenation. It occurs via hydrogen transfer through a tenaciously held ethylidyne overlayer to weakly adsorbed ethylene molecules on top of this layer.

Most catalytic reactions occur on coadsorbate modified metal surfaces. Sulfur, potassium, carbonaceous fragments and another metal constituents are employed most frequently as surface modifiers. These additives block sites and alter the bonding of the reactants thereby changing the reaction paths. Their effects will be demonstrated through discussions of the CO/benzene, S/thiophene and CO/K interactions.

SURFACE SCIENCE AND CATALYSIS

INTRODUCTION

The mating of surface science and heterogeneous catalysis has induced a rapid growth of catalysis science over the past 10 years. In this lecture I shall present a new view of catalytic reactions that emerges from these studies. This perspective builds on decades of catalytic investigations that determined turnover rates for a wide variety of reactions in the temperature range that has been found technologically useful (Davis 1982^a). These are shown for hydrocarbon reactions over platinum in Figure 1. Turnover rates between 10^{-4} and 10^2 are used in the various technologies, and thus the temperature employed is adjusted to obtain the desired rates. The turnover rates are usually calculated by dividing the rate by the total number of surface atoms. Thus it presents a conservative estimate of the rate, which may be an order of magnitude higher if the concentration of active sites is 10% of the total number of surface sites. The more complex isomerization, cyclization, dehydrocyclization, and hydrogenolysis reactions have activation energies in the range of 35 - 45 kcal/mole and thus high temperatures are required to carry them out at the desired rates. Hydrogenation has activation energies of 6 - 12 kcal/mole and therefore may be performed at high rates at 300K or below (Somorjai 1981). Thus, there are at least two classes of catalytic reactions that are performed at high and at low temperatures under very different reaction conditions.

Surface science studies of catalysts are usually carried out either using the real, high surface area ($\sim 10^2 \text{ m}^2/\text{gm}$) system or a low surface area ($\sim 1 \text{ cm}^2$) model system. The most frequently used techniques for surface studies of catalysts are listed in Table I. Among them, infrared spectroscopy, solid state NMR and X-ray photoelectron spectroscopies appear to be the most frequently employed for studies of real, high surface area catalysts. Extended X-ray absorption fine structure and near edge X-ray extended absorption fine structure measurements that require high intensity synchrotron radiation provide very valuable information on the interatomic distances and number of nearest neighbors of small catalyst particles dispersed on high surface area supports. Electron and ion scattering techniques are especially useful for studies of model, small area catalyst systems because of their high surface sensitivity (Somorjai 1981). Small area catalysts can be well-characterized in ultra-high vacuum ($\sim 10^{-9}$ torr), and then placed in a high pressure environment ($1\text{--}10^2$ atm) by a low pressure/ high pressure instrumentation that is displayed in Figure 2. At high pressures the reaction kinetics are monitored by gas chromatography, and easy cycling between low pressure and high pressures permits intermittent surface analysis of the catalyst (Cabrera et al. 1982). The use of high surface area catalysts in combined catalysis and surface science studies allows us to study directly the real, working catalysts. Its drawback is the difficulty to well-characterize such a complex high surface area heterogeneous system. Model single crystal or similar surfaces are much easier to characterize by the techniques of modern surface science. However, it is more difficult to correlate their catalytic behavior or surface properties to the behavior of the real, high area catalyst systems.

There are several technologically important catalyst systems that have been subjected to combine surface science and kinetic studies. These are listed in Table 2. The systems studied have been mostly metals. The results of these investigations suggest that there are three classes of catalytic reactions: 1) those that occur directly on the metal surface; 2) reactions that occur on top of a strongly bound layer of adsorbates in the second layer and 3) reactions that occur on co-adsorbate modified surfaces. I shall present examples of each of these reaction classes below.

There are major differences between the surface species that are usually studied by surface science at low pressures and those that are likely to be important surface species at high pressures during the catalytic reactions. This may be demonstrated in Figure 3 which shows data obtained in Professor Ertl's laboratory for the heat of adsorption of CO as a function of coverage over a Pd crystal surface (Conrad et al. 1974). At low coverages, the heat of adsorption per mole is high and these strongly adsorbed molecules are the subject of low pressure surface science studies because of their stability that makes such studies easy. Their structures (Andersson et al. 1978 and Behm et al. 1979) are shown in Figure 3a and 3b. At higher coverages the average heat of adsorption drops significantly due mostly to repulsion among the adsorbed molecules. The overall heat of adsorption drops to around 10 kcal/mole. Catalytic reactions are carried out at high coverages and these weakly adsorbed molecules are those that participate in the reaction that occurs at high turnover frequency. One surface structure that was obtained (Van Hove et al. 1983) at the higher coverage is shown in Figure 3c. Because of the repulsive interaction the CO molecules no longer occupy only top or bridge sites, but they are relocated in sites of lower symmetry to maximize the distance among them.

Let us consider a catalytic reaction where the desorption of the product molecules is the rate limiting step. In Figure 4 a plot of the turnover rate is presented as a function of the activation energy for the reaction at different temperatures. In obtaining these values, we assume a preexponential factor of 10^{12}sec^{-1} . Molecules that have desorption activation energies of less or equal to that represented by the solid line at the given temperature can participate in the catalytic reactions while those that have higher activation energies are too strongly bound to be able to turn over at the observed rates. Of course, those molecules that are bound so weakly as to have very small activation energies of desorption may not be able to react either, because their surface residence times are very short. Nevertheless, the surface coverages of weakly adsorbed species may be controlled by the reactant pressure. High pressures favor catalytic reactions that involve weakly bound adsorbates. In Figure 4 the turnover rates and reaction activation energies of the hydrogenation of C_2H_4 and the ammonia synthesis are indicated to show two reactions that occur under widely different conditions.

1. Catalytic Reactions on Metal Surfaces

These reactions usually involve strongly adsorbed intermediates and are surface structure sensitive. Atomically rough surfaces usually exhibit the highest turnover rates. Perhaps the best example of this type of process is the synthesis of ammonia. Figure 5a shows the rates over three iron single crystal surfaces. The (111) orientation crystal face is about 500 times as

active as the (110) close packed surface (Spencer et al. 1982). Chemisorption studies by Ertl show equally large differences in the sticking probability of N_2 on these surfaces (Ertl 1981) confirming that the dissociation of N_2 is the rate limiting step in this reaction. The ammonia synthesis over Re crystal surfaces shows even larger structure sensitivity (Asscher et al. 1984) (Figure 5b); the $(11\bar{2}1)$ and $(11\bar{2}0)$ crystal faces of this hcp metal are over a thousand times as active as the close packed (0001) crystal face. Figure 5c shows the 3 metal surfaces that are the most active for ammonia synthesis. These surfaces are rough on the atomic scale and have open structures that expose high coordination sites especially in the second layer. These atoms with large numbers of nearest neighbors are accessible to the incoming N_2 molecules and appear to be most active for dissociation.

Recently a theory of metal catalysis has been proposed (Falicov et al. 1985) that considers those sites most active in breaking and forming chemical bonds to have a high concentration of degenerate electronic states of low energy permitting charge fluctuations. There are electronic configurational fluctuations or spin fluctuations that may occur. Electronic configurational fluctuations are the largest at metal sites of high coordination. These are shown for a nickel surface on which six atoms are placed in Figure 6. The higher the atomic coordination of the site, the higher the density of electron hole states, n . High coordination sites may be made available in catalytic reactions by using surfaces with open atomic structures so that atoms in the second layer become available to the incoming reactants, or by using stepped and kinked surfaces (Somorjai 1981). The latter surfaces contain in-step

atoms of high coordination that are very active in catalytic reactions. Studies of $\text{H}_2\text{-D}_2$ exchange (Salmeron et al. 1977) (Salmeron et al. 1979), hydrogenolysis (Gillespie 1981) and dehydrocyclization reactions over stepped Pt surfaces clearly indicate the higher reactivity of these sites for H-H, C-H or C-C bond breaking.

While the structure sensitivity of many reactions other than ammonia synthesis is well documented by careful catalytic studies, the magnitude of structure sensitive variations are smaller, about a factor of 5 or 10, than that for the N_2/H_2 synthesis. More complex reactions require several consecutive reaction steps, some of which are structure sensitive. The need for a more complex catalyst surface in many other reactions will be demonstrated later in this paper.

The ammonia synthesis may be viewed as an example of a reaction that obeys Langmuir-Hinshelwood kinetics, being dominated by the reactions between adsorbed species on the metal surface.

Catalytic reactions that require high coordination metal sites are unique to solid surfaces. Metallo-organic species or clusters frequently used in homogeneous catalysis do not have sufficiently large numbers of metal atoms to produce these high coordination sites. Homogeneous and heterogeneous catalytic reactions may be compared when we consider another class of catalytic reactions next that occur in the second layer and not directly on the metal surface.

2. Catalysis on Top of an Overlayer. The Hydrogenation of Ethylene.

This facile reaction that occurs at 300K or below at atmospheric pressures on many transition metal surfaces has been the subject of investigations of many researchers including Farkas & Farkas (1934), Eley (1936), Beeck (1950), Twigg and Rideal (1939), Schuit (1950), Horiuti and Polanyi (1934), Roberts (1963) and many others (Horiuti et. al. 1968). I shall restrict my comments to platinum and rhodium which are among the most active catalysts for this process. Table 3 indicates that the hydrogenation occurs equally well on Pt crystals, films, foils and supported particles indicating that the reaction is structure insensitive (Zaera et al. 1984). When the clean metal surfaces are exposed to ethylene, a strongly adsorbed ordered layer of ethylidyne, C_2H_3 , forms. This molecule is shown in Figure 7 along with its vibrational spectrum obtained by HREELS. The kinetics of ethylene hydrogenation and those of ethylidyne have been studied extensively over the (111) faces of Rh and Pt and the rates of these processes are displayed in Figure 8. Ethylene hydrogenation occurs at a rate six orders of magnitude higher than the rehydrogenation of the strongly adsorbed ethylidyne. Even the deuteration of the methyl group of ethylidyne occurs very slowly. ^{14}C labeling of the ethylidyne and the vibrational spectroscopy studies confirm these findings (Zaera et al. 1984 and Koel et al. 1984).

Yet the (111) faces of Pt and Rh are covered with a monolayer of ethylidyne during ethylene hydrogenation, since reaction rates are nearly identical over initially clean surfaces and surfaces precovered with ethylene (Zaera et al. 1984 and Beeck 1950). Vibrational spectroscopy studies confirm

that the adsorbed monolayer structure on these surfaces after hydrogenation is ethylidyne (Wieckowski et al. 1984). Thus, ethylene hydrogenation occurs rapidly on the C_2H_3 -covered surface. The packing of the ethylidyne ordered overlayer does not permit C_2H_4 adsorption directly on the metal surface, as proven by detailed surface science studies with C_2H_4 and C_2D_4 . On the other hand thermal desorption studies show that $H_2(D_2)$ can be dissociatively adsorbed on the ethylidyne-covered metal surface up to about 1/4 monolayer coverage (Wieckowski et al. 1984).

A reaction model that explains these results is shown in Figure 9. A hydrogen atom is transferred to the ethylene molecule that is weakly adsorbed on top of the ethylidyne in the second layer perhaps by forming an ethylidene intermediate. Such a model of hydrogen transfer from a hydrocarbon to ethylene was first proposed by Thomson and Webb (Thomson et al. 1976) and our studies (Thomson et al. 1976) corroborate their findings. Our mechanism is of the Eley-Rideal type and is characterized by a low activation energy and structure insensitivity.

However there are other mechanisms of C_2H_4 hydrogenation that our studies and those of others have uncovered (Figure 9). At higher temperatures, the rate of rehydrogenation of C_2H_3 is significant and the bare metal becomes available in part for C_2H_4 hydrogenation. During the electrochemical hydrogenation of C_2H_4 the Pt surface is covered with a layer of hydrogen atoms (hydride) that react rapidly with the approaching C_2H_4 and do not permit the formation of ethylidyne (Wieckowski et al. 1984). Thus the complexity of such reaction cannot be underestimated.

Nevertheless, it provides an example of reactions of weakly adsorbed molecules in the second layer, an important class of catalytic reactions that could occur at low temperatures or at high pressures. The hydrogenation of CO over certain transition metals that exhibit positive order dependence on both H_2 and CO pressures is thought to occur this way (Logan et al. 1984).

These types of reactions may be compared with homogeneous catalytic reactions which are facile, occurring at lower temperatures, and include hydrogenation or hydroformylation. Since the metal plays secondary roles in this process high coordination sites are not needed to carry out the reactions. It is hoped that future studies will reveal the possible correlation between homogeneous catalytic reactions and heterogeneous reactions of this type.

3. Reactions Over Co-adsorbate Modified Metal Surfaces

It appears that most of the catalytic reactions that have been studied so far belong to this class. When two species, atoms or molecules, co-adsorb their chemisorption characteristics are altered. Let us consider the relatively weak interaction of benzene and CO when co-adsorbed on Pt and Rh(111) crystal surfaces. Benzene forms a disordered monolayer over Pt in the absence of CO. When CO is introduced several ordered structures form that are detectable by LEED. These structures change depending on the CO/benzene ratio on the surface which can be monitored by HREELS and TDS. Figure 10 shows the various ordered structures that consist of mixed CO-benzene layers with 1, 2 or 3 CO molecules in the unit cell. The ordering of benzene may be facilitated by the weak attractive interaction with CO that blocks certain alternative adsorption sites. It should be noted that CO is located in a

3-fold site (as determined by LEED surface crystallography (Van Hove et al. 1985) and HREELS) that it would never occupy in the absence of benzene. Benzene exhibits a distorted Kekule structure with alternate 1.33Å and 1.8Å bond lengths.

Let us now consider the interaction of coadsorbed sulfur with thiophene that occurs during the hydrodesulfurization of thiophene on the Mo(100) crystal surface (Gellman et al. 1984^a). This gentle reaction removes the sulfur from the molecule as H₂S in the presence of hydrogen, leaving behind a C₄ species that readily hydrogenates to butadiene, butene and butane without fragmentation. Molybdenum metal strongly adsorbs and decomposes thiophene and butenes as shown by surface studies and thus the clean surface cannot be an active catalyst (Gellman et al. 1984^b). MoS₂ is a layer compound and its basal plane holds thiophene so weakly (Salmeron et al. 1982^a) that its thermal desorption occurs at 165K. Thus this surface is not chemically active. The active Mo surface contains about 1/2 monolayer of strongly adsorbed sulfur. These atoms block the metal sites where thiophene decomposition would occur. ³⁵S labeling studies indicate that these sulfur atoms remain permanently on the metal surface during the catalytic reactions. The sulfur atom that is removed from the thiophene occupies sites of weaker bonding where hydrogenation to H₂S and subsequent desorption occurs while the C₄ species partly hydrogenate also and desorb (Gellman et al. 1985).

Thus the blockage of certain adsorption sites on the surface of early transition metals attenuates their strong bonding and permits the catalytic reaction to occur.

Potassium is frequently used as a promoter in many catalytic reactions. The hydrogenation of CO and the synthesis of NH_3 are perhaps the best known examples of potassium promotion. Potassium has a very high heat of adsorption at low coverages (~ 60 kcal/mole) on most transition metal surfaces indicating complete ionization of the atom (Garfunkel 1982). At higher coverages, however, mutual depolarization of the charged potassium species leads to neutralization. When $\sim 50\%$ coverage is reached the heat of adsorption equals the heat of sublimation of metallic potassium (~ 23 kcal/mole) indicating that the adsorbed atoms are no longer ionized.

The co-adsorption of potassium with CO leads to the strengthening of the M-C bond by over 11 kcal/mole and the simultaneous weakening of the C=O bond as shown by temperature programmed desorption and HREELS studies, respectively (Garfunkel et al. 1983 and Crowell et al. 1982). This is because the charge that is transferred from the potassium to the transition metal finds its way into the molecular orbitals, both bonding and antibonding of CO. On the clean Rh(111) surface, CO stays molecularly adsorbed at low pressures while it dissociates near its desorption temperature in the presence of potassium (Crowell et al. 1985). This can be studied by the adsorption of a mixture of $^{12}\text{C}^{18}\text{O}$ and $^{13}\text{C}^{16}\text{O}$ and detecting $^{13}\text{C}^{18}\text{O}$, the product of scrambling which clearly identifies that dissociation of molecular CO occurred. In Figure 11 we show that 3 CO molecules may dissociate per potassium atom at a potassium coverage where maximum charge transfer to the transition metal occurs. Thus potassium exerts a strong electronic influence that alters the bonding of CO and of hydrocarbons or N_2 as has been studied extensively and demonstrated.

The catalytic properties of transition metals may also be altered by alloying using another metal that may be considered a coadsorbate as well. For example, the addition of gold to Pt markedly changes the catalytic selectivity during the reaction of n-hexane. This is shown in Fig. 12a. When gold is deposited on the Pt(111) crystal face and then alloyed by heat treatment. Its presence greatly enhances the rate of isomerization while it simultaneously reduces the hydrogenolysis and dehydrocyclization rates. This effect on the reaction selectivity was attributed to preferential removal of high coordination 3-fold sites by gold substitution. These Pt sites are responsible for the hydrogenolysis and dehydrocyclization reactions while isomerization occurs at bridge sites that are not much effected by the presence of gold. However, the effect of alloying is also surface structure sensitive (Yeates et al. 1985) as shown in Figure 12b. When a Pt(100) crystal face is used, the change of catalytic selectivity is not observed. All reaction rates decline in proportion to the presence of the inactive gold on the Pt surface.

Finally, we should consider the ever present strongly adsorbed carbonaceous deposit as a co-adsorbate that alters the catalytic behavior of the transition metal. The alkylidyne species that are often present at 300K or below on transition metal surfaces dehydrogenate sequentially (Salmeron et al. 1982^b) as the temperature is increased. Depending on the transition metal either C-H or simultaneous C-H and C-C bond breaking may occur leaving behind carbonaceous fragments that are readily detectable by HREELS (Koestner et al. 1983). Some of these are shown in Figure 13. CH, C₂, C₂H, CH₂, and C₂H₃ fragments have been identified (Davis et al. 1982^b and Minot

et al. 1982) although they undergo polymerization at higher temperatures and finally a graphite or carbide layer that contains no hydrogen will form. The presence of the carbonaceous fragments is essential on many metal catalyst surfaces since these fragments readily transfer hydrogen as long as they contain a large concentration of C-H bonds. The catalyst surface deactivates upon graphitization of this carbonaceous overlayer. The working Pt catalyst for hydrocarbon conversion reactions requires both bare metal sites of appropriate structure and the presence of a hydrogen-transferring carbonaceous overlayer, that adsorbs reaction intermediates only weakly, to attain optimum catalytic activity and selectivity. In addition, active kink sites, that would carry out the undesirable hydrogenolysis reaction, could be blocked by strongly adsorbed sulfur. Reaction selectivity is further enhanced by the presence of a second component metal for selective metal catalysis. Thus the active and selective catalyst is a complex system indeed. But it is also within our ability to understand and control.

It might be worthwhile to summarize the essential contributions of modern surface science to heterogeneous catalysis. It has contributed new methods for catalyst characterization on the atomic scale, it and it has elucidated the roles of surface structure and of co-adsorbates of many types. As a result a molecular view of heterogeneous catalysis has emerged.

There are many opportunities for research in catalysis science that could open up new directions for technology as well. Among them are the need to develop time resolved techniques for the detection of short lived species on

the surface. It appears that catalysis at low temperatures around 300K and in aqueous phase is being used by nature successfully, but has not received the attention of catalytic researchers that it deserves. The catalysis of molecules in their excited states is another area of research opportunities in catalysis science.

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FIGURE CAPTIONS

- Fig. 1 Block diagram for hydrocarbon conversion over platinum catalysts showing the approximate range of reaction rates and temperature regimes that are most commonly studied.
- Fig. 2 Schematic representation of the experimental apparatus utilized to carry out the catalytic reaction rate studies on small area single crystal or polycrystalline surfaces at low and high pressures in the 10^{-7} to 10^{+4} torr range.
- Fig. 3 Isoteric heat of adsorption for CO on the Pd(111) crystal face as a function of coverage.
- Fig. 3a Top site bonding structure of carbon monoxide on Ni(100) from low energy electron diffraction and electron spectroscopy studies.
- Fig. 3b Bridge site adsorption structure of carbon monoxide on Pd(100) at a half monolayer coverage.
- Fig. 3c Structure determined by low energy electron diffraction for a saturation coverage of carbon monoxide on Rh(111). Top and side views are shown. Large circles represent rhodium atoms while smaller

circles correspond to carbon and oxygen atoms. Solid lines show the structure expected for hexagonal close packing of the carbon monoxide while dotted circles depict the actual structure.

- Fig. 4 The turnover rates as a function of the activation energy for reactions at different temperatures. Preexponential factor of 10^{12} sec^{-1} is assumed.
- Fig. 5 The structure sensitivity of catalyzed ammonia synthesis on (a) iron and (b) rhenium single crystal surfaces.
- Fig. 5c The metal surfaces that are most active for ammonia synthesis.
- Fig. 6 A model of the nickel (111) surface with six atom cluster placed on top of it.
- Fig. 7 Ethylidyne on rhodium (111). The stable room temperature structure of chemisorbed ethylene,--its atomic structure and HREEL spectra.
- Fig. 8 The turnover rates for ethylene hydrogenation, the rehydrogenation of ethylidyne, and the deuteration of the methyl group on ethylidyne on platinum and rhodium crystal surfaces.
- Fig. 9 Models of ethylene hydrogenation.
- Fig. 10 An ordered surface structure composed of carbon monoxide and benzene in the same unit cell.

Fig. 11 The amount of dissociated carbon monoxide per potassium atom as a function of potassium coverage on the rhodium (111) single crystal surface.

Fig. 12 The rates of formation of various products from n-hexane conversion as a function of fraction gold-coverage for gold platinum alloys that were prepared by vaporizing gold onto (a) platinum (111) and (b) platinum (100) crystal surfaces respectively.

Fig. 13 Schematic representation of the various organic fragments that are present on metal surfaces at high temperature. The presence of CH, C₂, C₂H, CH₂ and CCH₃ species have been detected.

FREQUENTLY USED TECHNIQUES OF SURFACE SCIENCE FOR STUDIES OF CATALYSTS

- ELECTRON SCATTERING
ELECTRON SPECTROSCOPIES (XPS, HREELS, AES)
LOW ENERGY ELECTRON DIFFRACTION (LEED)
ELECTRON MICROSCOPY
- PHOTON SCATTERING (HIGH AND LOW INTENSITIES)
SPECTROSCOPIES (IR, FTIR, RAMAN, SOLID STATE NMR,
ESR, EXAFS, MEXAFS, LASER TECHNIQUES)
GRAZING ANGLE X-RAY DIFFRACTION
- MOLECULE AND ION SCATTERING
MOLECULAR BEAM-SURFACE INTERACTION
SIMS, ISS
- OTHER TECHNIQUES
RADIOTRACER LABELING
MOSSBAUER SPECTROSCOPY
THERMAL DESORPTION

Table 1

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Surface Science Studies of Catalyst Systems

- **1) Hydrogen-Deuterium Exchange by Platinum**
- **2) Oxidation of Carbon Monoxide by Platinum**
- **3) Hydrogenation of Ethylene by Pt, Rh.**
- **4) Ammonia Synthesis by Iron, Rhenium**
- **5) Hydrocarbon Conversion by Platinum
(dehydrocyclization, isomerization,
hydrogenolysis, hydrogenation,
dehydrogenation)**
- **6) Hydrogenation of Carbon Monoxide by Transition
Metals (Fe, Ni, Rh, Ru , Rd, Co, Mo)**
- **7) Partial Oxidation of Ethylene by Silver and
Methanol by Molybdenum Oxide**
- **8) Hydrodesulfurization of Tiophene by
Molybdenum**

XBL 852-1333

Comparison of ethylene hydrogenation kinetic parameters
for different platinum catalysts.

Catalyst	Log Rate ^a	a ^b	b ^b	E _a (Kcal/mole)	Ref.
Platinized foil	1.9	-0.8	1.3	10	11
Platinum evaporated film	2.7	0	1.0	10.7	12
1% Pt/Al ₂ O ₃	—	-0.5	1.2	9.9	5
Platinum wire	0.6	-0.5	1.2	10	13
3% Pt/SiO ₂	1.0	—	—	10.5	14
0.05% Pt/SiO ₂	1.0	0	—	9.1	15
Pt (111)	1.4	-0.6	1.3	10.8	Our work

a) Rate in molec/Pt atom.sec, corrected for the following conditions:

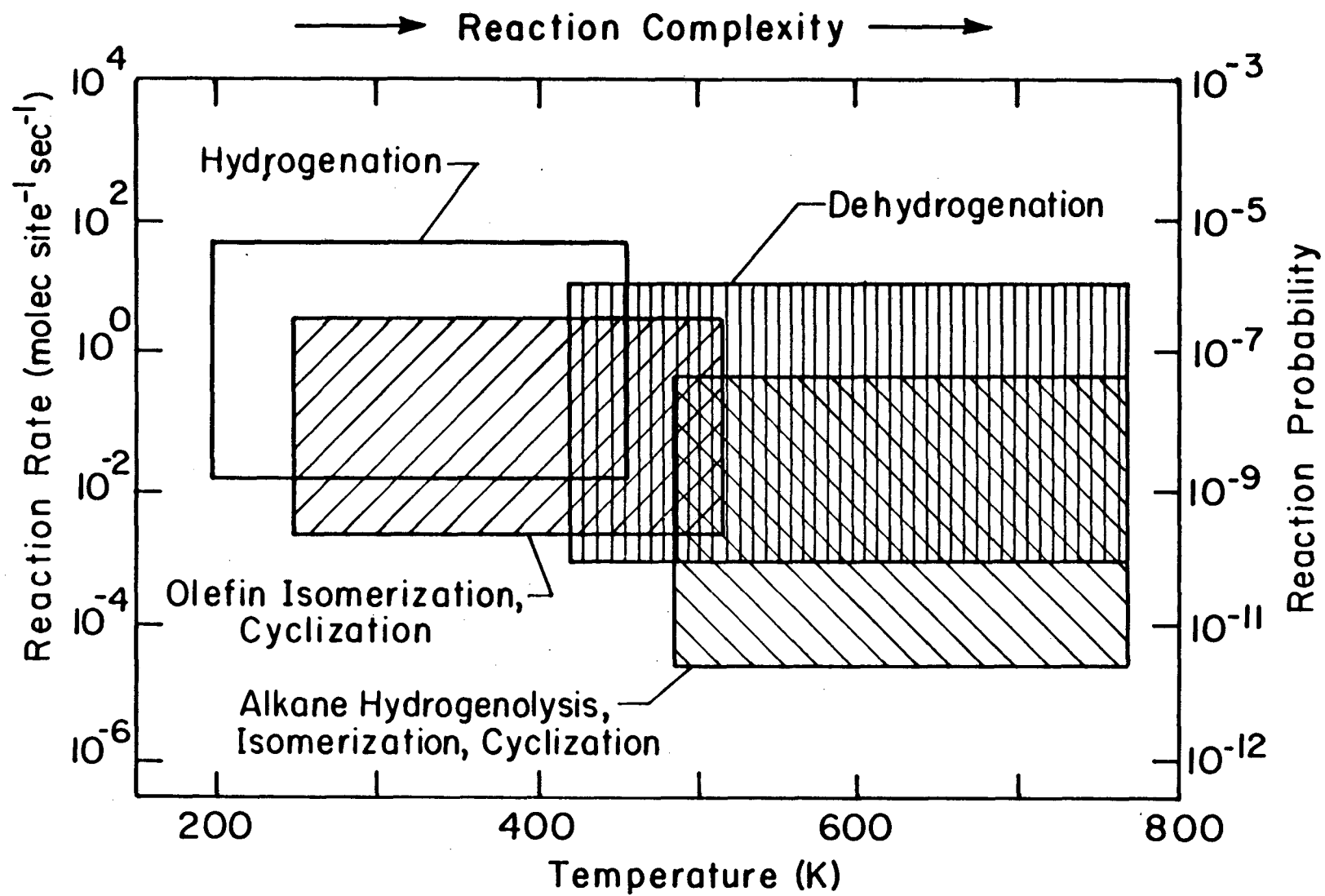
T = 323K, $P_{C_2H_4} = 20$ torr, $P_{H_2} = 100$ torr.

b) Orders in ethylene (a) and hydrogen (b) partial pressures.

XBL 852-1331

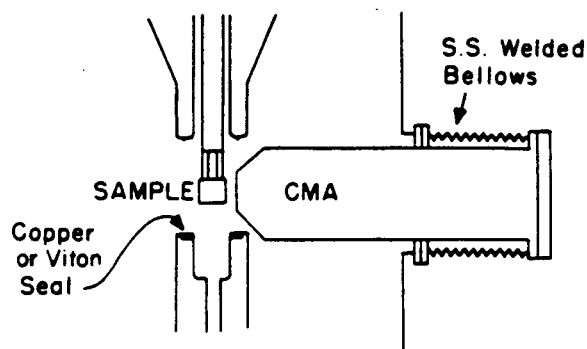
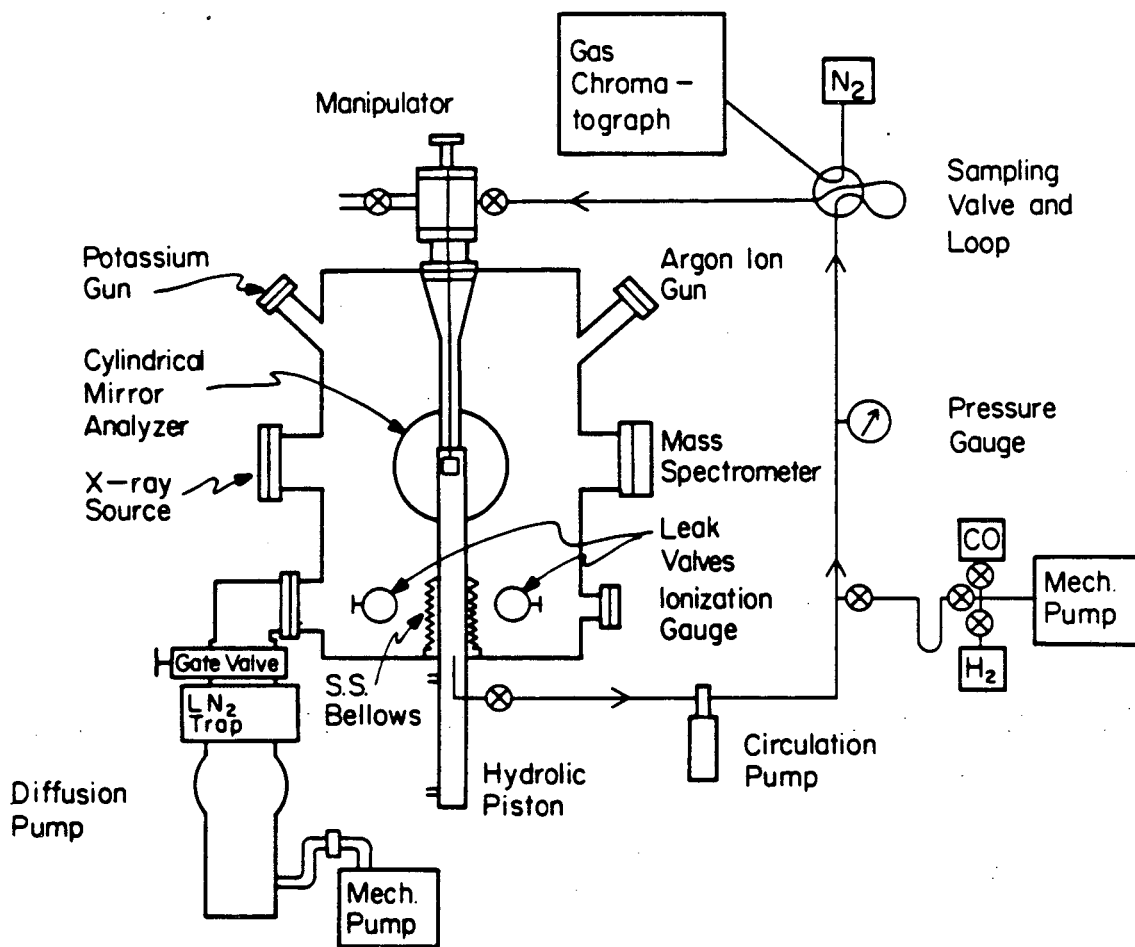
Table 3

Fig. 1



XBL806-5278

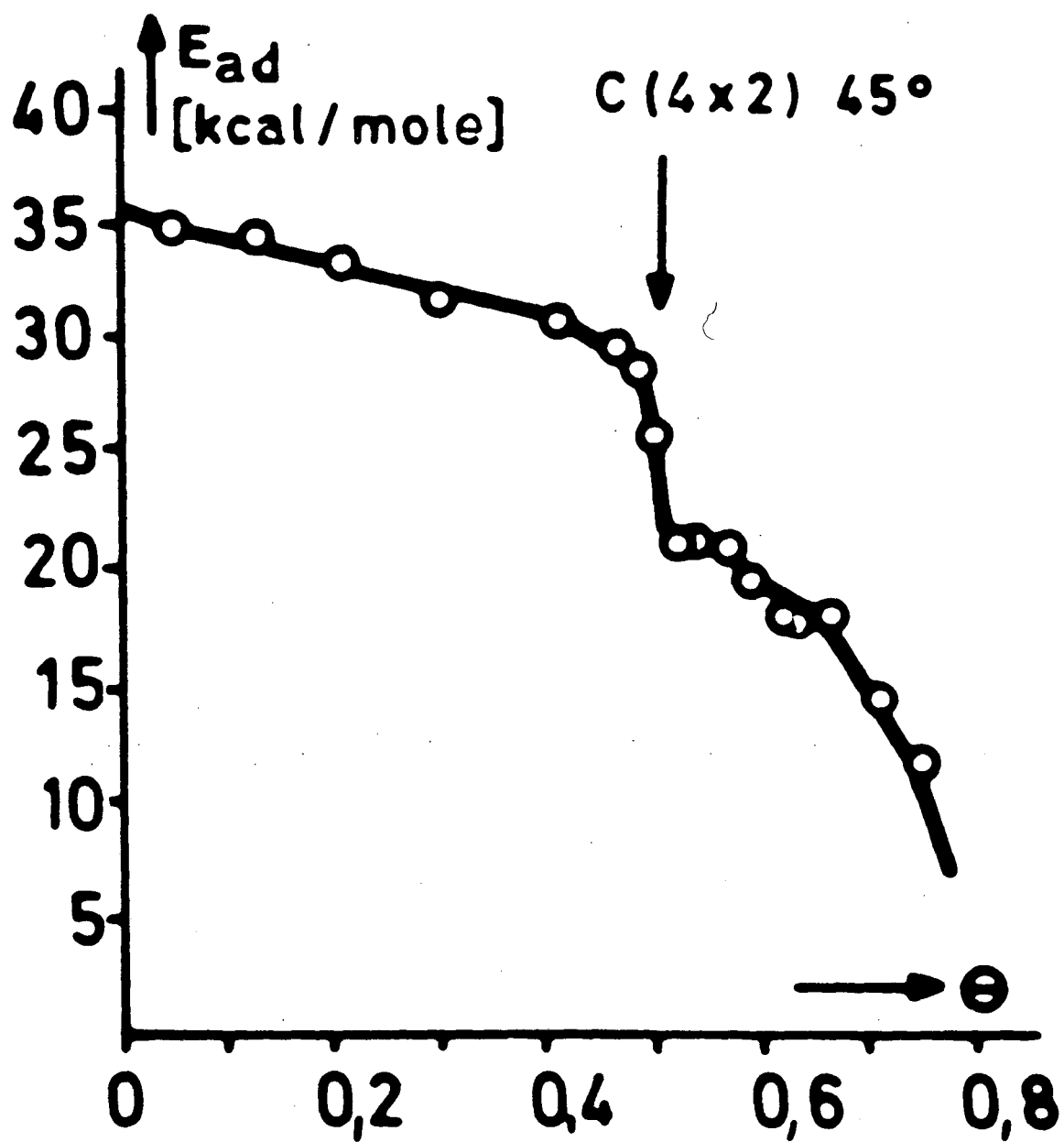
HIGH PRESSURE / LOW PRESSURE CHAMBER FOR CATALYST SURFACE STUDIES



SIDE VIEW WITH HIGH PRESSURE CELL OPEN

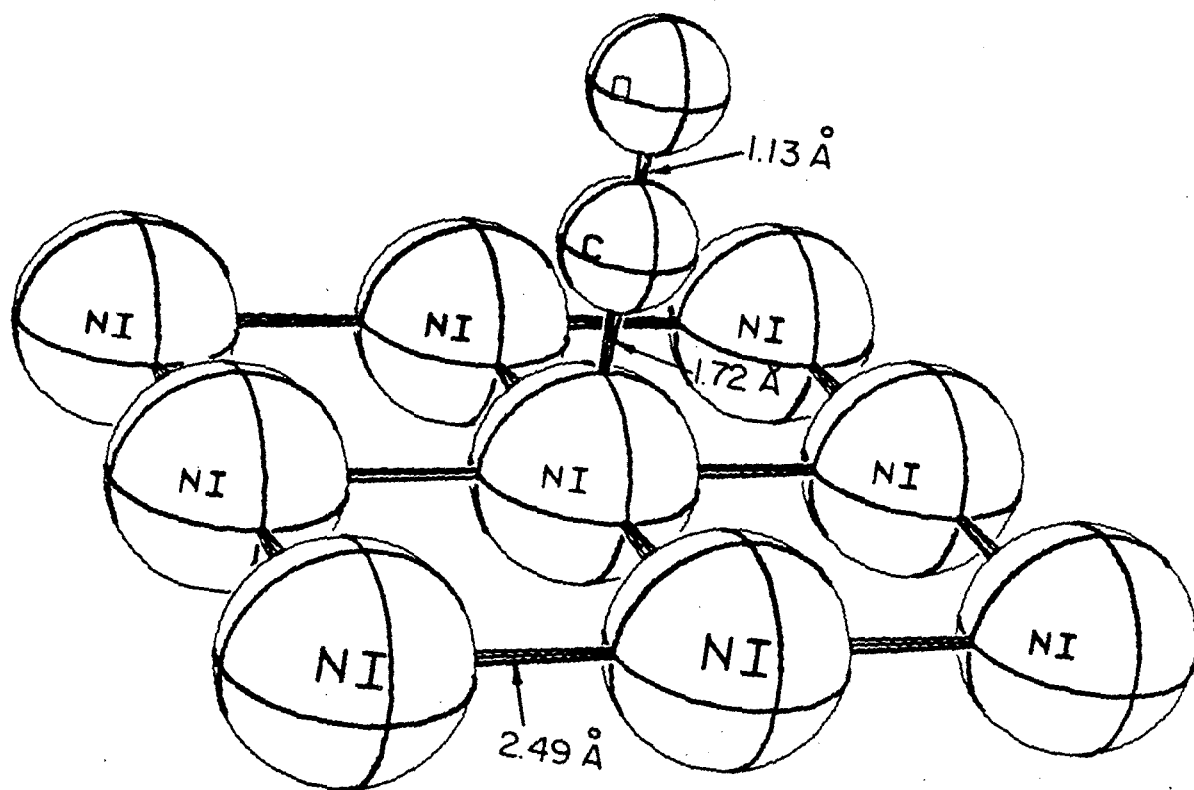
XBL 832-8401

Fig. 2



XBL 7911-12823

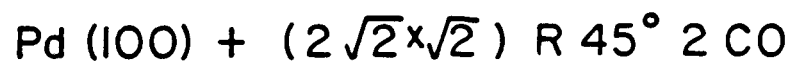
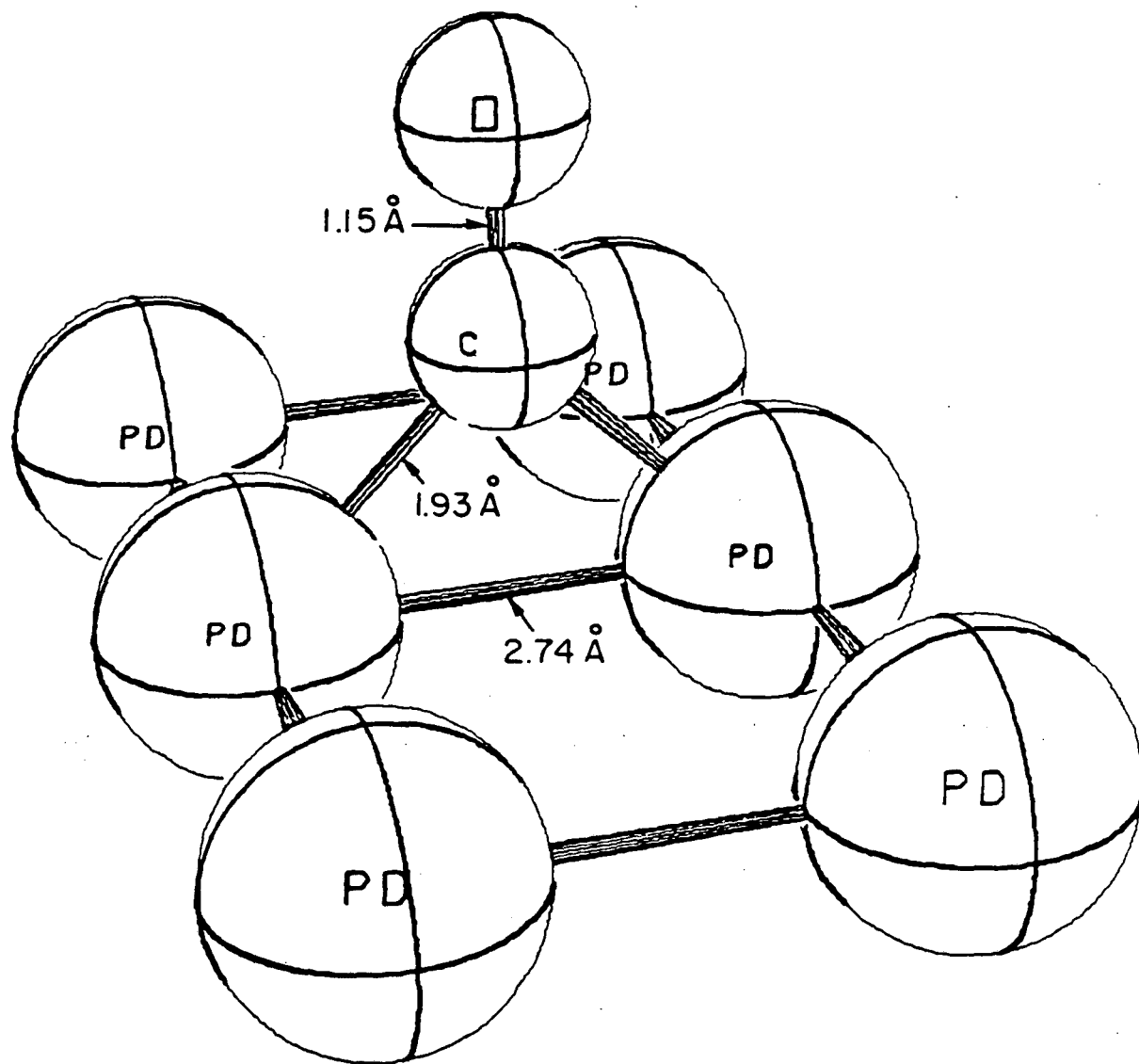
Fig. 3



Ni (100) + c(2x2) CO

XBL 794-6169

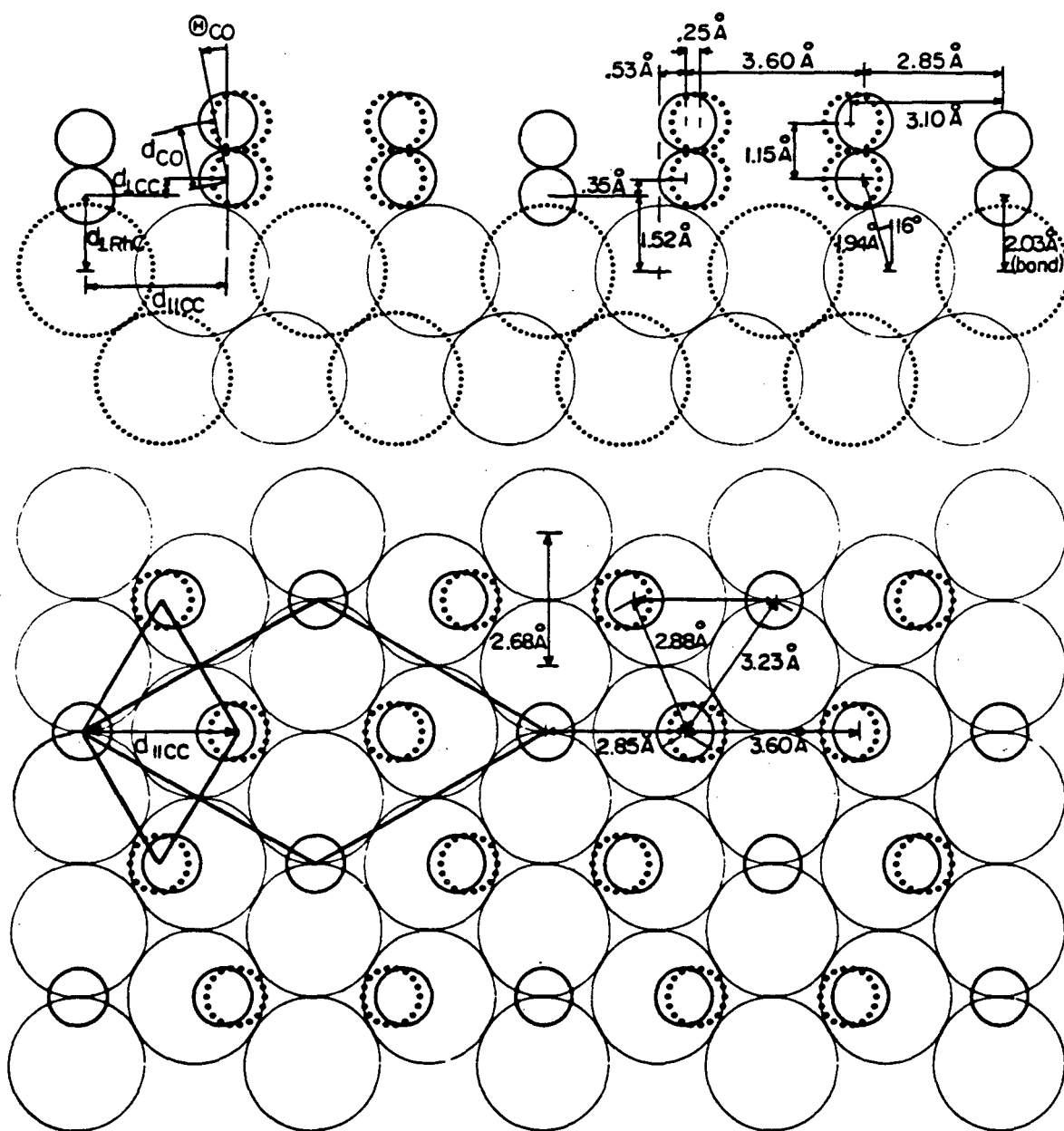
Fig. 3a



XBL794-6170

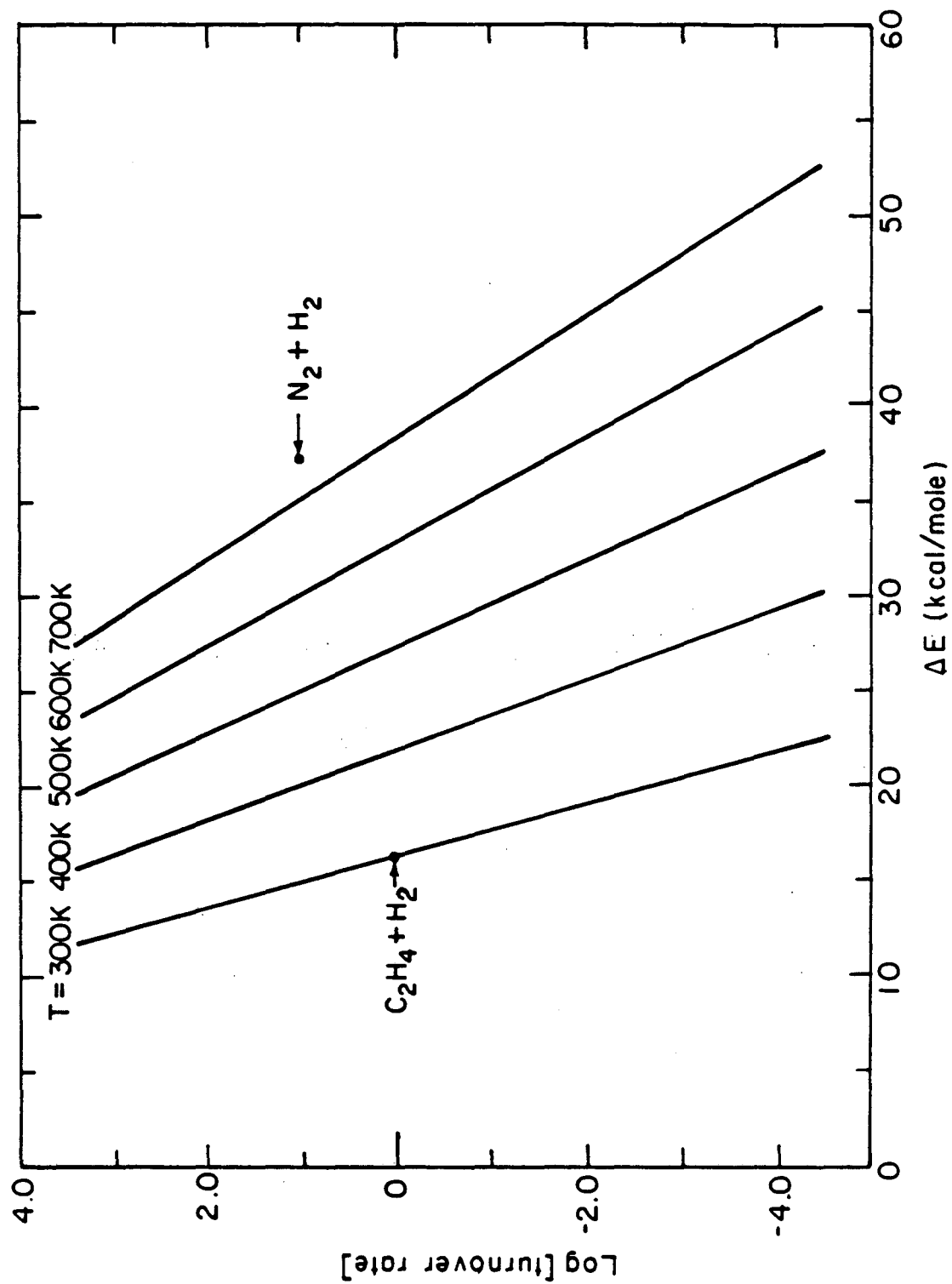
Fig. 3b

Rh(III) (2x2) - 3 CO



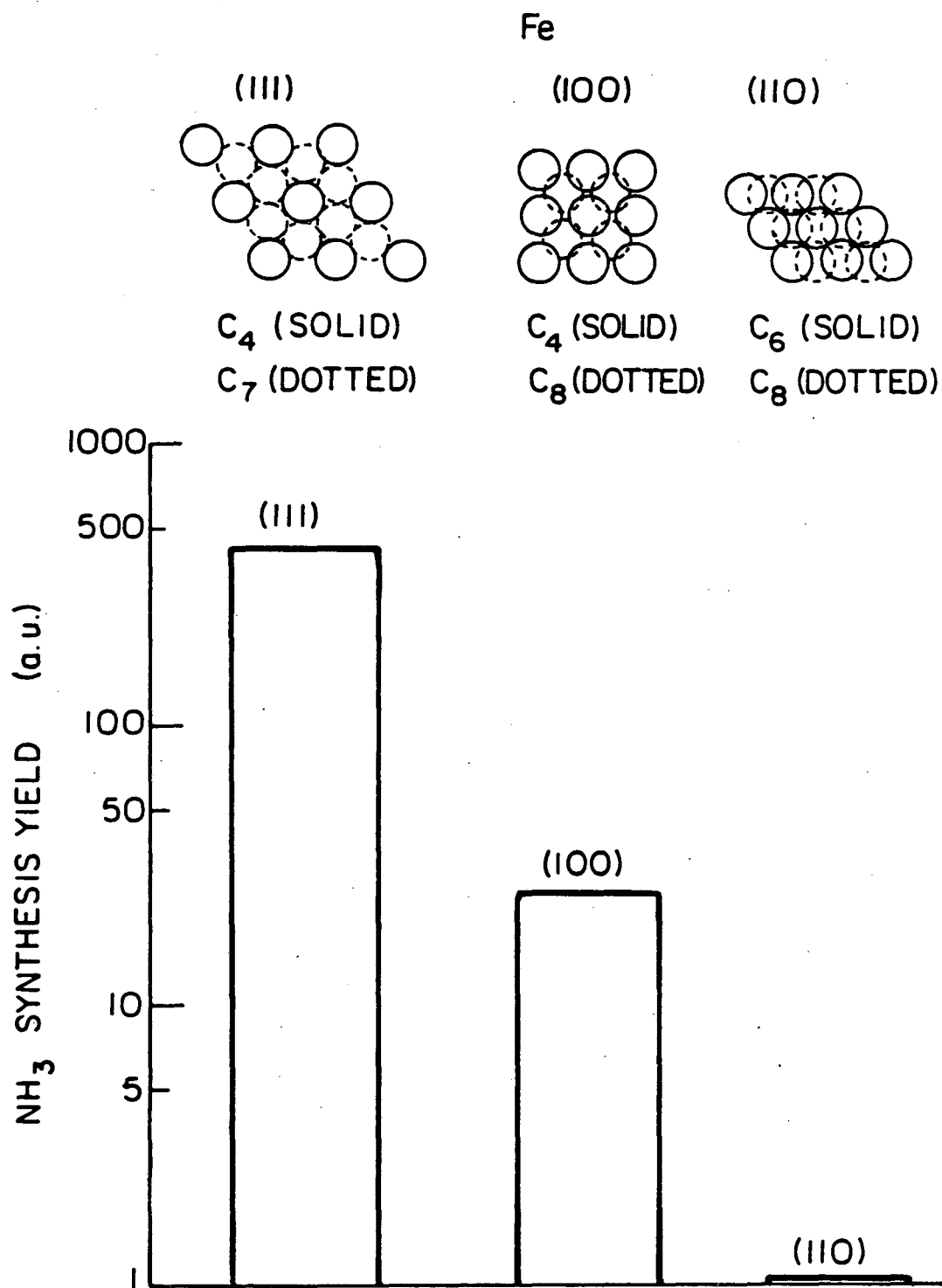
XBL 828-6270

Fig. 3c



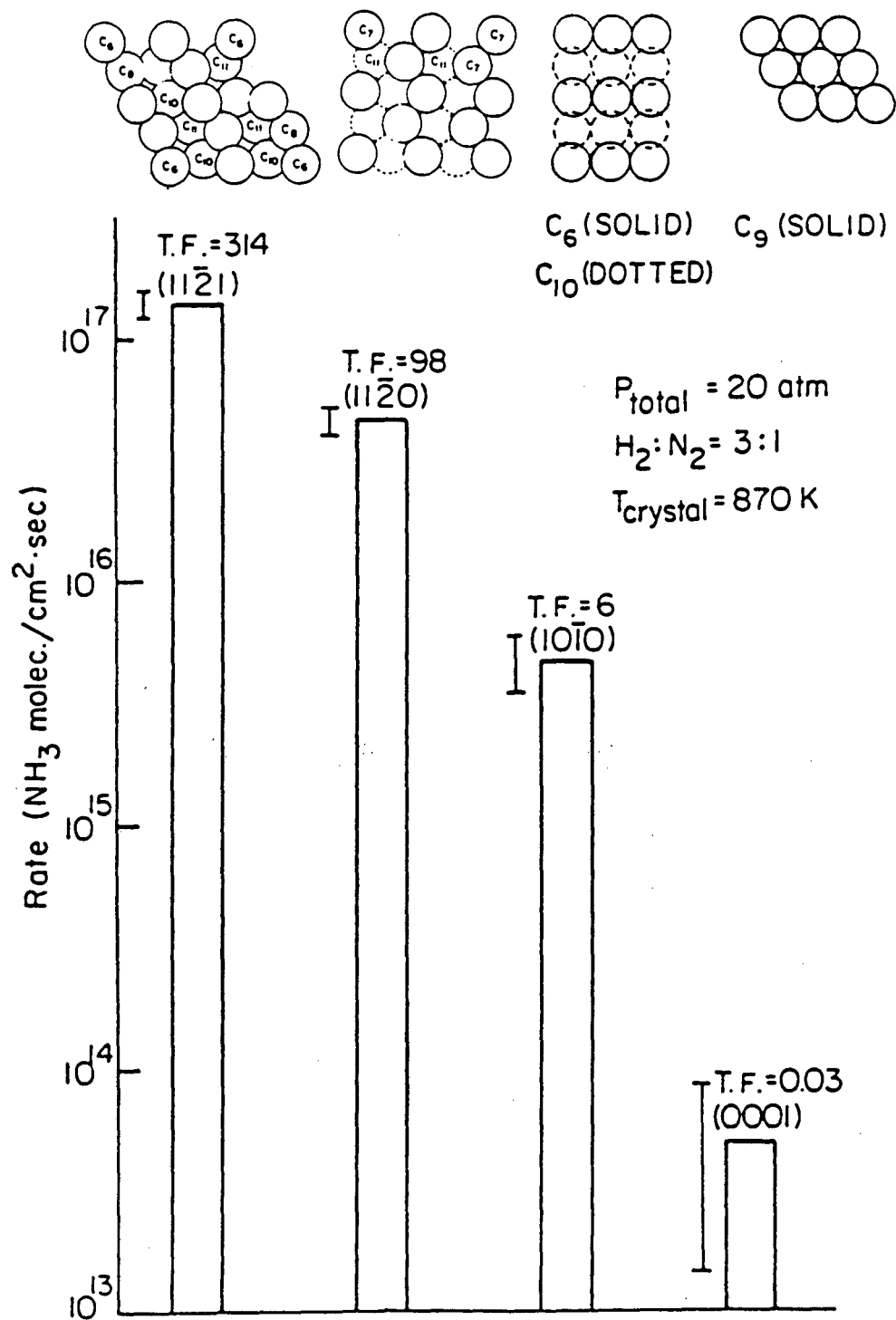
XBL 852-5826

Fig. 4



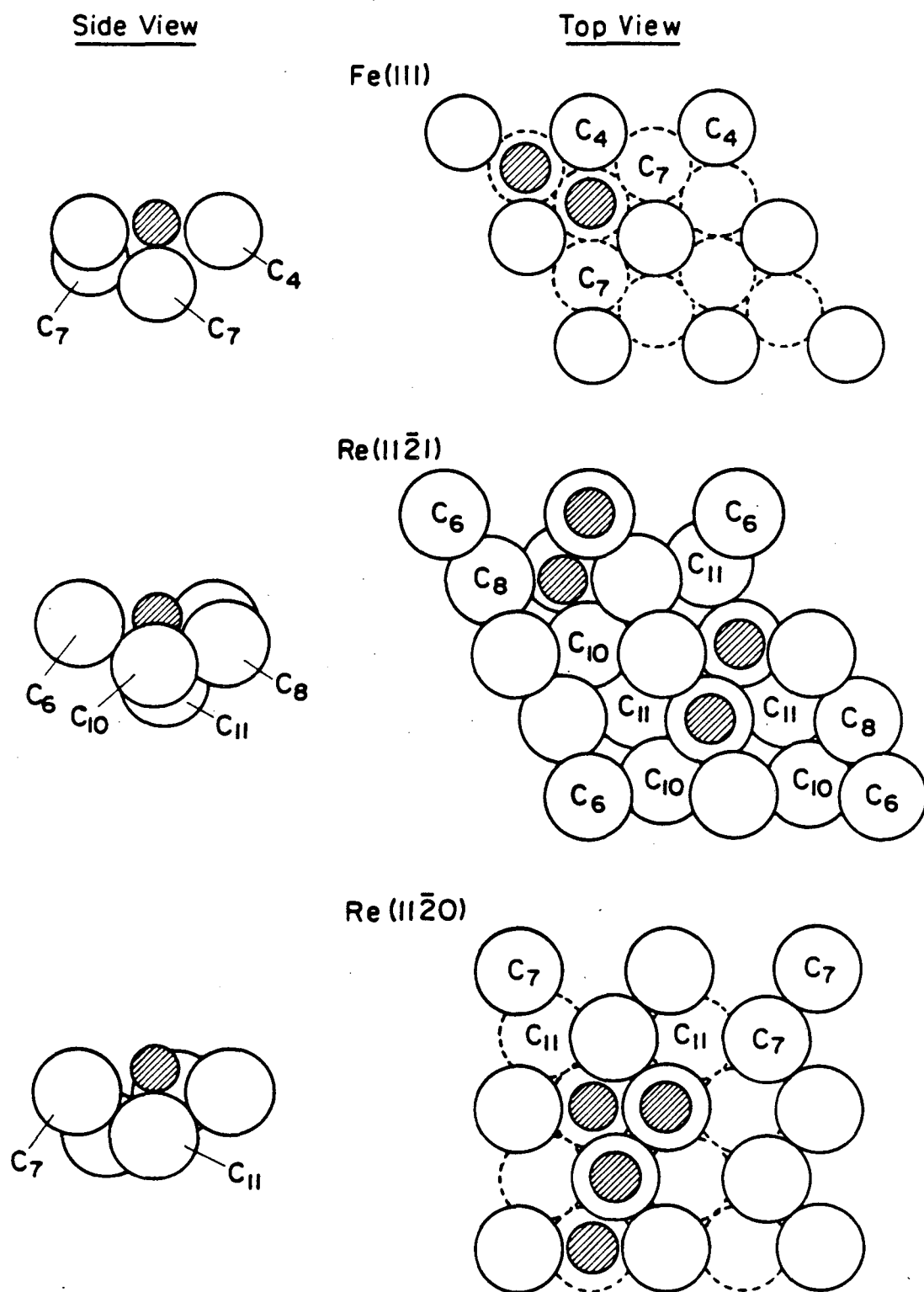
XBL 839-6407

Fig. 5a



XBL 845-1900

Fig. 5b

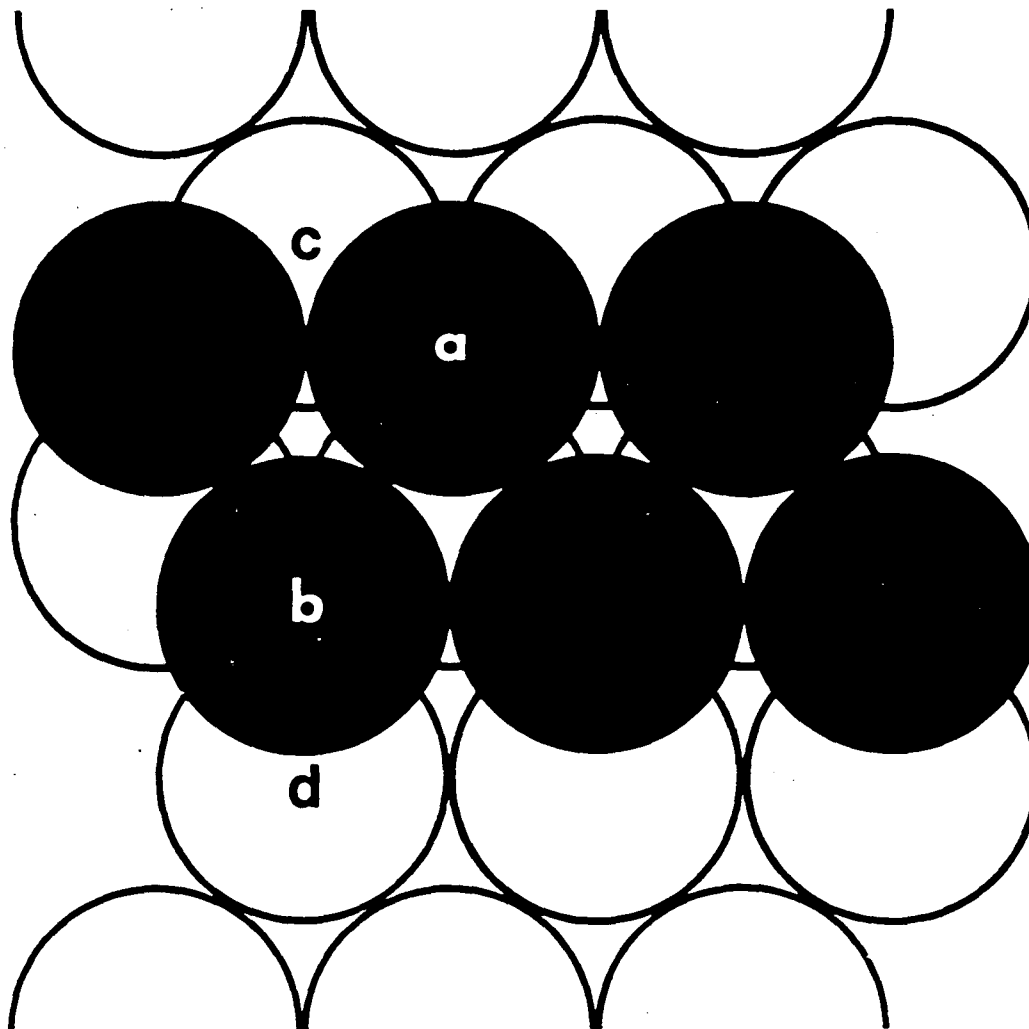


XBL842-6648

Fig. 5c

NICKEL d-SHELL OCCUPIED BY 9.44 ELECTRONS

BULK NICKEL	$Z(\text{Ni})=12$	$n = 0.56$
(111) SURFACE NICKEL ATOM	$Z(\text{Ni})= 9$	$n = 0.38$
OUTSTEP NICKEL ATOM a (FIG. 1)	$Z(\text{Ni})= 7$	$n = 0.25$
OUTSTEP NICKEL ATOM b (FIG. 1)	$Z(\text{Ni})= 7$	$n = 0.24$
INSTEP NICKEL ATOM c (FIG. 1)	$Z(\text{Ni})=11$	$n = 0.52$
INSTEP NICKEL ATOM d (FIG. 1)	$Z(\text{Ni})=10$	$n = 0.45$
Ni UNDER A (111) Cu MONOLAYER	$Z(\text{Ni})= 9$ $Z(\text{Cu})= 3$	$n = 0.52$
Ni MONOLAYER ON Cu(111)	$Z(\text{Ni})= 3$ $Z(\text{Cu})= 6$	$n = 0.46$



XBL 852-1103

Fig. 6

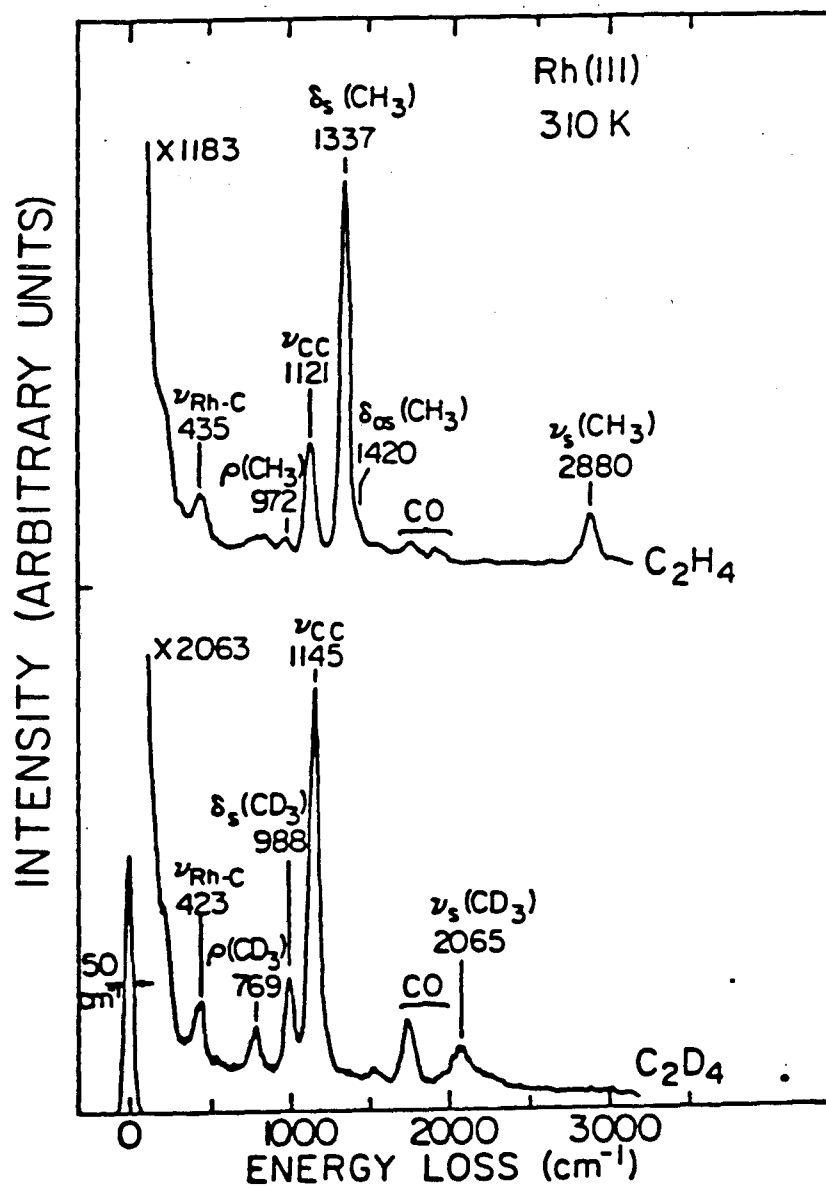
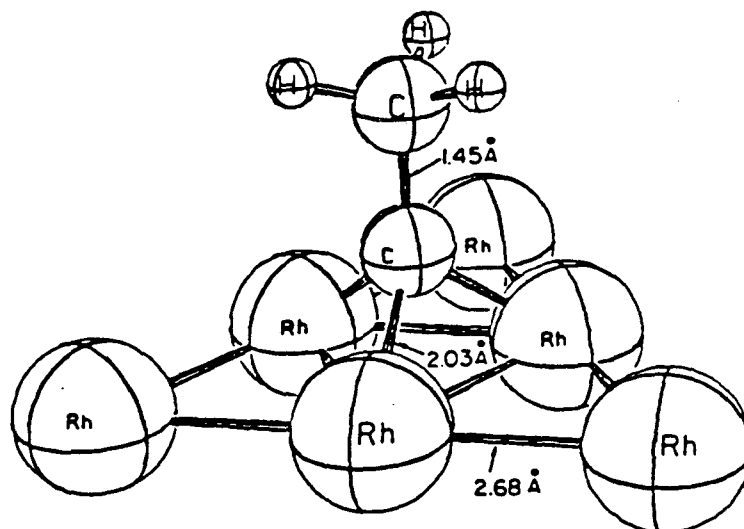
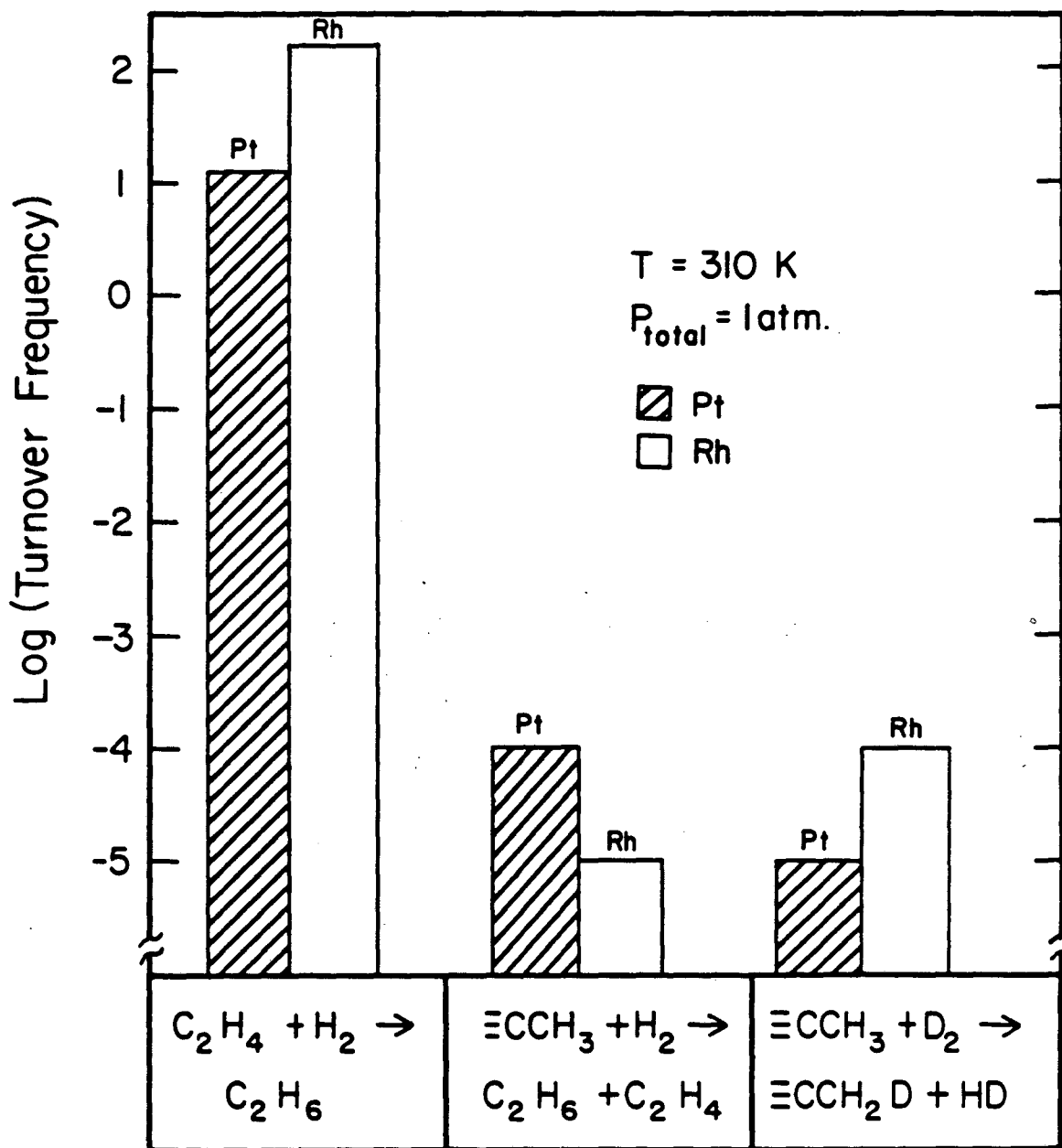


Fig. 7

Comparison of Hydrogenation Rates over Pt(III) and Rh(III) Single-Crystal Surfaces

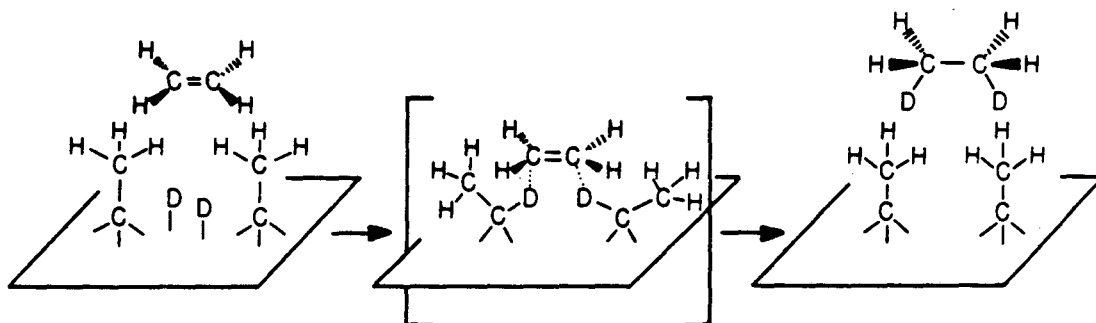


XBL 846-2487

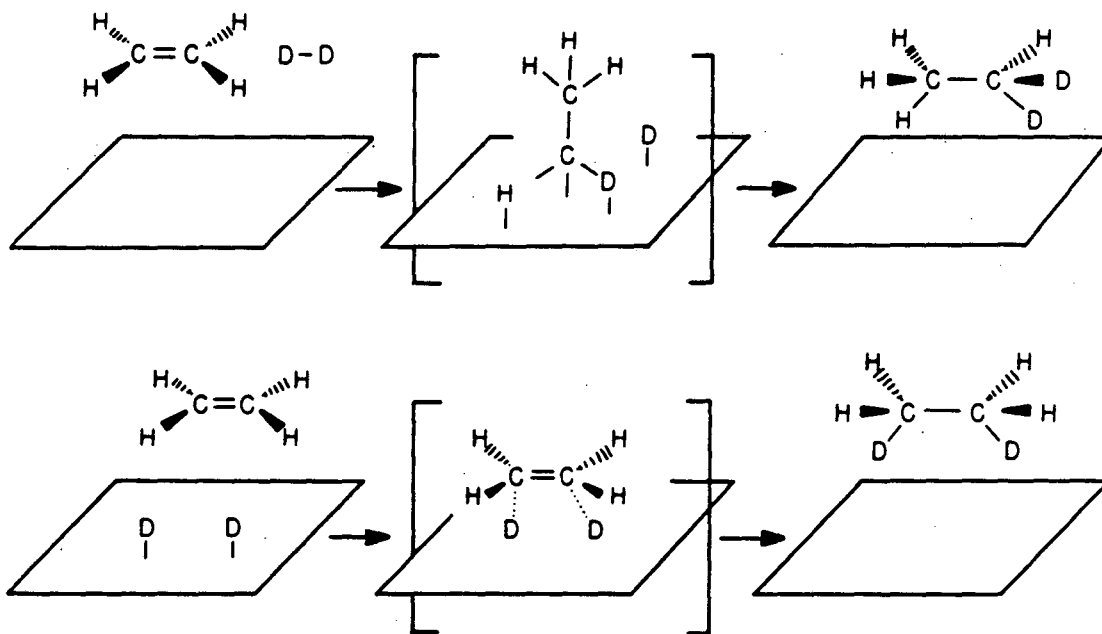
Fig. 8

Proposed Mechanisms for Ethylene Hydrogenation Over Platinum Metals

< 350 K

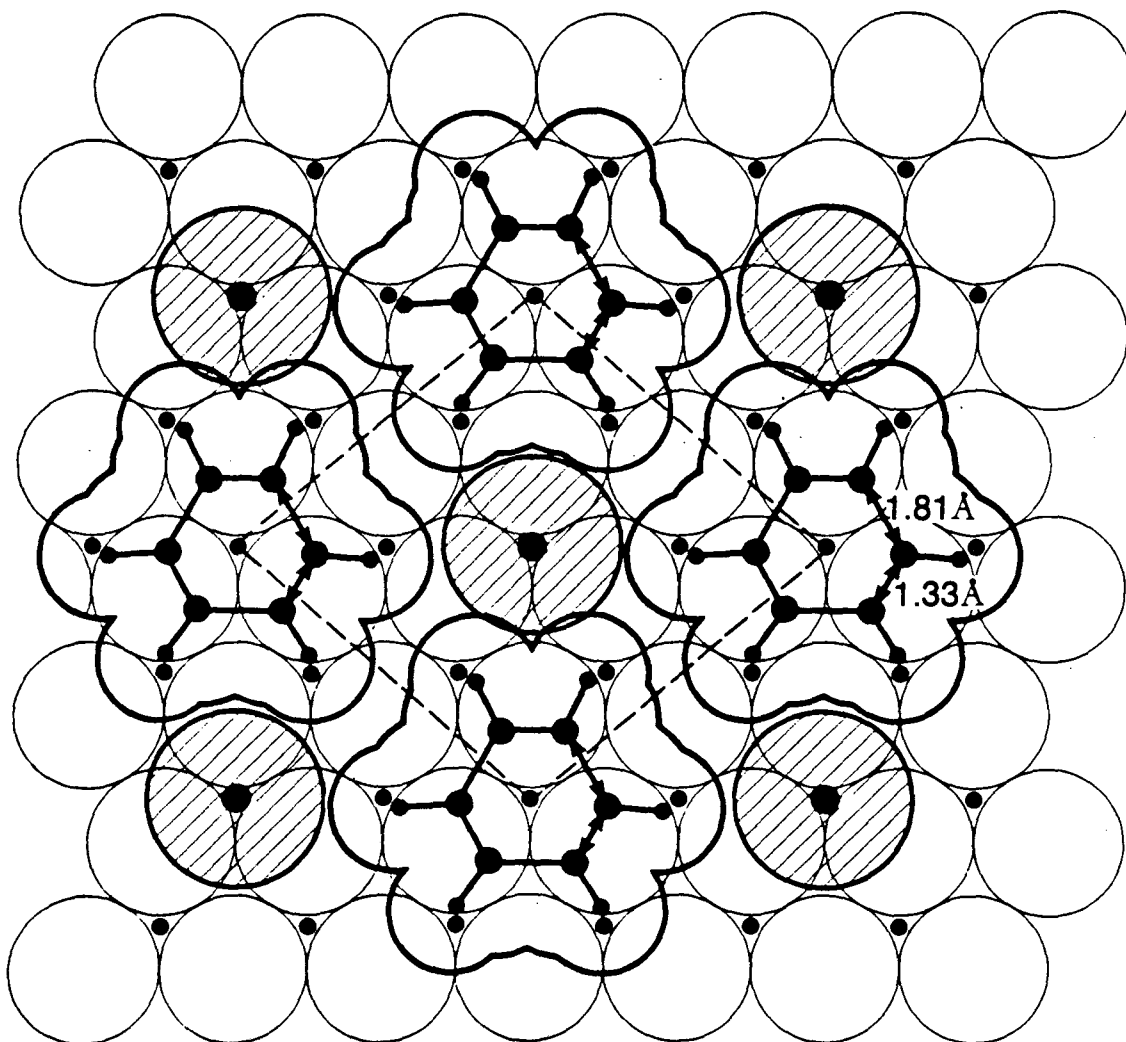
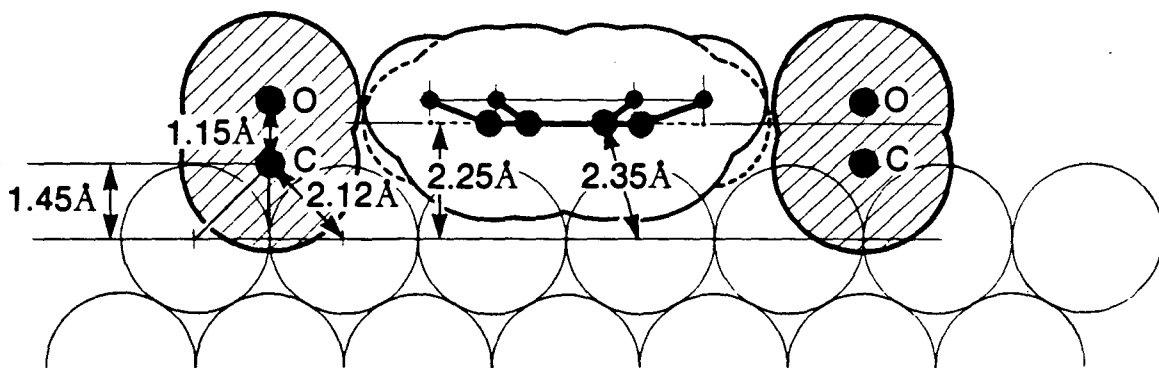


> 350 K



XBL 8412-5412

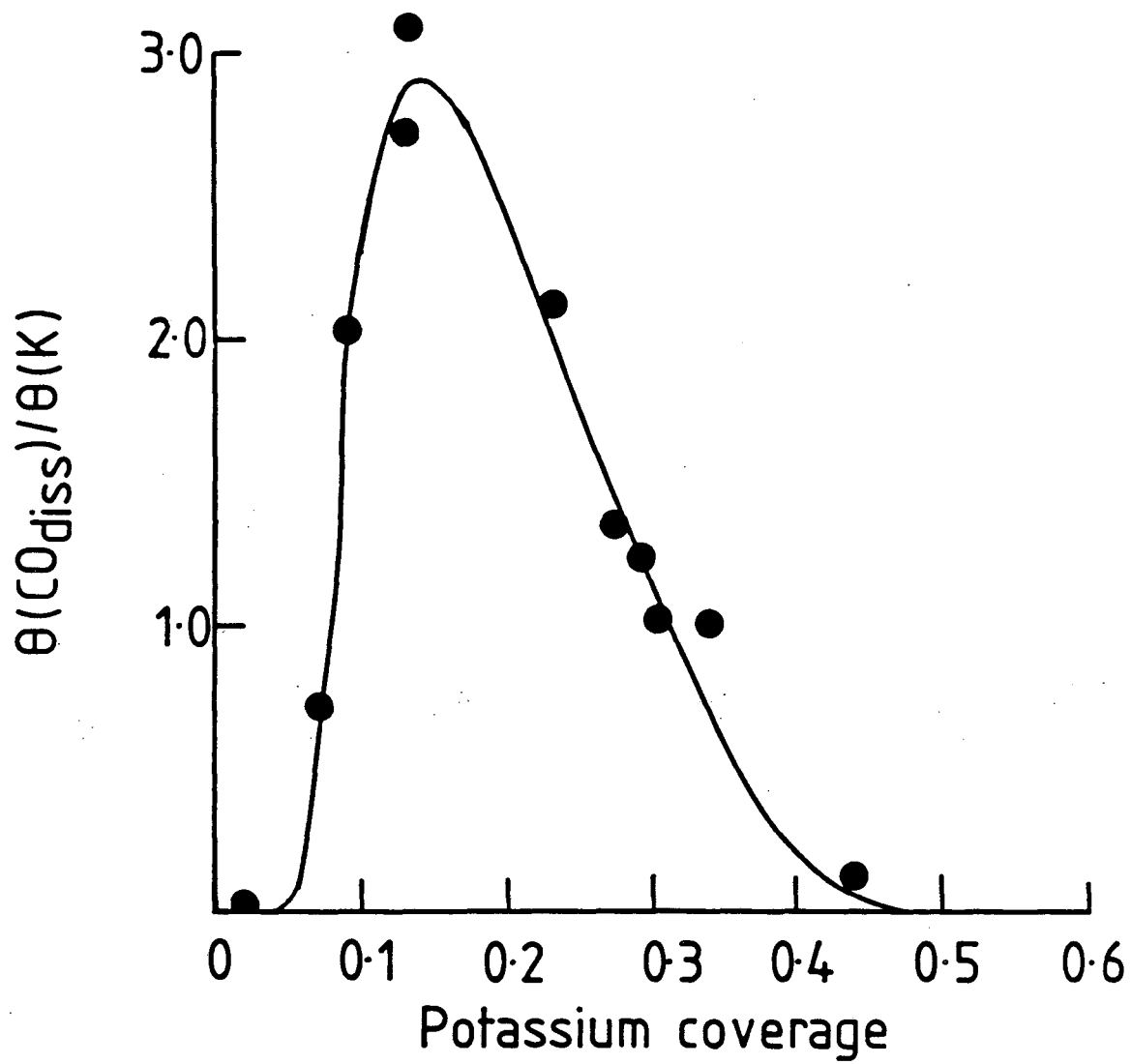
Fig. 9



$\text{Rh}(111)-\left(\begin{smallmatrix} 31 \\ 13 \end{smallmatrix}\right)-\text{C}_6\text{H}_6 + \text{CO}$

XBL 851-9917

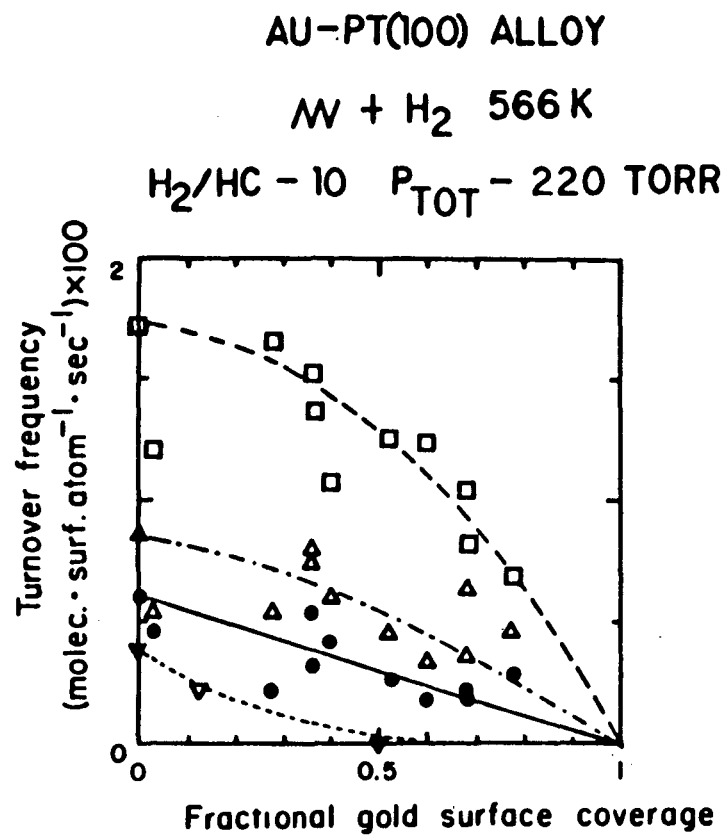
Fig. 10



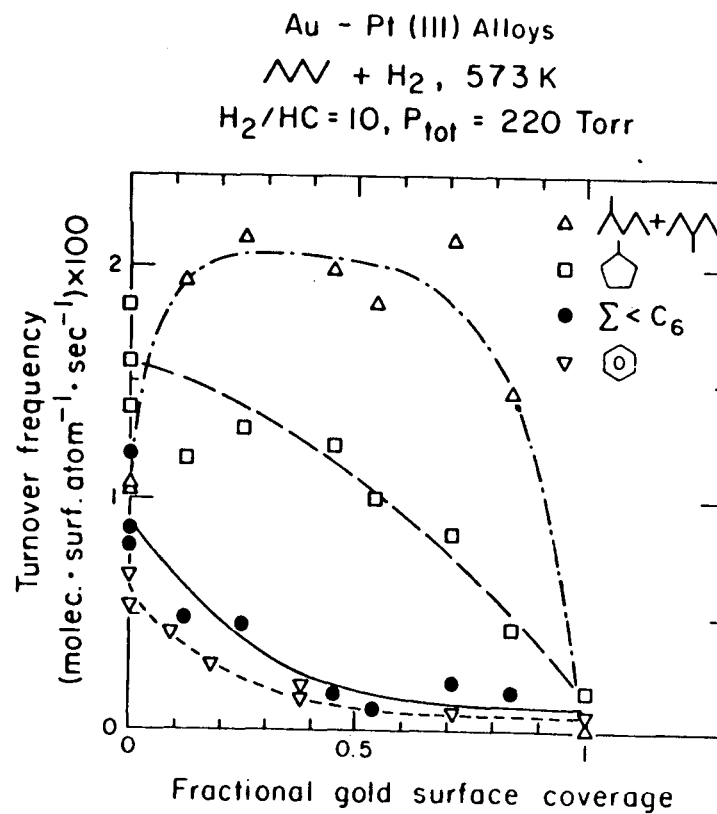
XBL 847-3016

Fig. 11

Fig. 12

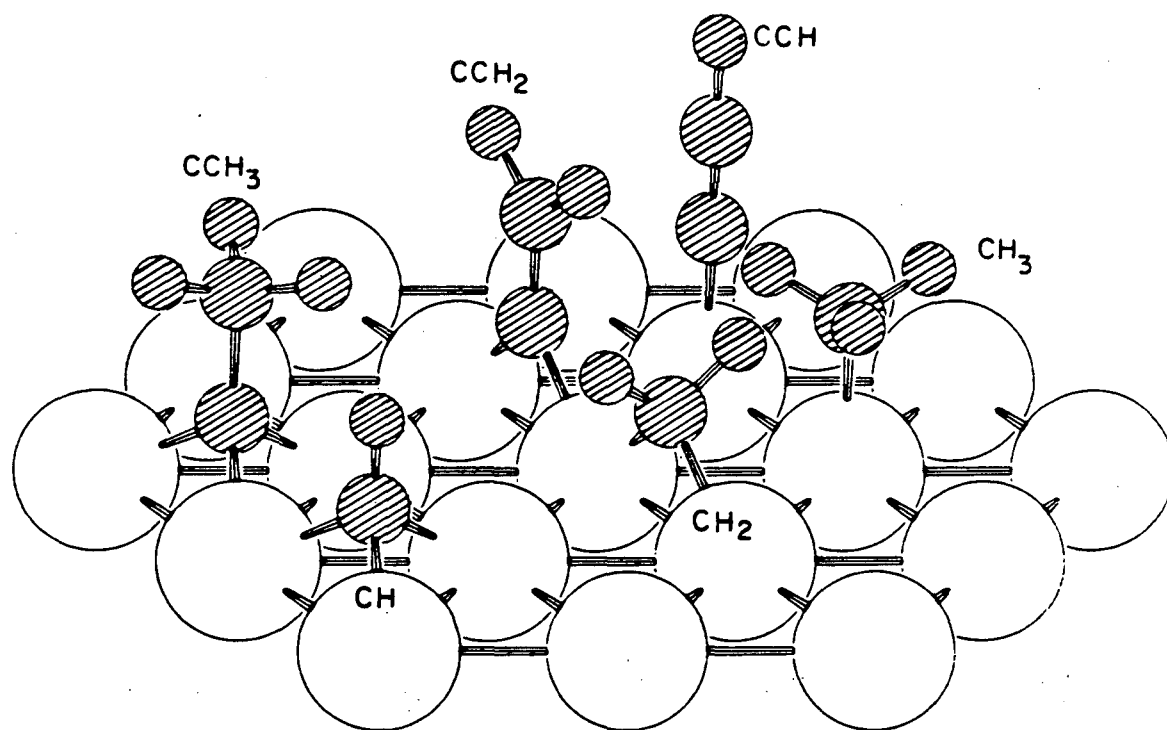


b



a

XBL 819-2495A



XBL 826-5941

Fig. 13

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