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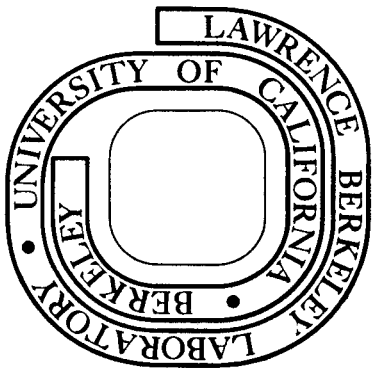

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The Effect of Strongly Bound Oxygen on the Dehydrogenation and Hydrogenation Activity and Selectivity of Platinum Single Crystal Surfaces

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Abstract

The dehydrogenation of cyclohexene and cyclohexane, and the hydrogenation of cyclohexene were studied on the clean and preoxidized surfaces of three platinum single crystals - a Pt(111), a stepped Pt(S)-[6(111)x(100)] and a kinked Pt(S)-[7(111)x(310)] - at low pressure (10^{-6} to 10^{-5} torr total pressure), at 150°C. Oxygen coverages were monitored by Auger electron spectroscopy (AES), an Auger peak ratio of O_{510}/Pt_{237} = .5 having been determined to correspond to approximately 5 x 10^{14} oxygen atoms/cm^2. The surface structures of the clean and oxidized platinum crystals were determined by low energy electron diffraction (LEED): after high temperature (800°C) oxygen treatment, the predominant oxygen structure observed on the Pt(111) was a (2x2); the predominant oxygen structure observed on both the Pt(S)-[6(111)x(100)] and the Pt(S)-[7(111)x(310)] was a $(\sqrt{3} \times \sqrt{3})$-R30°. Low coverages of strongly bound oxygen enhanced the rates of the dehydrogenation and hydrogenation reactions, and changed the selectivity of cyclohexene dehydrogenation to benzene over hydrogenation to cyclohexane. These effects of preoxidation on catalytic rates and selectivity were found to be sensitive to the structure of the platinum surface, kink sites playing a particularly active role in the enhancement of dehydrogenation and hydrogenation activity by strongly bound oxygen. Three models are discussed which relate the oxidation of platinum surfaces to the observed effects on catalytic reactivity and the structure sensitivity. A change in the electronic structure of the platinum surface through oxidation provides the best general model for explaining the oxygen effects, though complex formation

involving the adsorbed oxygen or surface reconstruction during oxidation may also be important.

Introduction

In recent years there have been a number of studies of the adsorption of oxygen on both polycrystalline and single crystal platinum surfaces[1-18]. The oxygen adsorption is thought to be dissociative except at very low temperature[1-5] and two states of oxygen atoms on platinum can be distinguished[6-8]. After low temperature exposures (<500°C), the oxygen which has chemisorbed ("reactive" oxygen) reacts readily with either hydrogen or carbon monoxide, even at room temperature, and can be desorbed at about 500°C. The second observed state of oxygen, which starts to form extensively with exposures at platinum temperatures above 500°C, is relatively nonreactive: this state is stable in vacuum to about 800°C[8,9], in hydrogen to about 500°C[8], and in carbon monoxide to about 700°C[6,7]. Because of the strong interaction between the oxygen and platinum atoms, this state has been extensively referred to as platinum oxide in the literature, even though there are relatively few cases where workers have positively identified the epitaxial growth of a layer of stoichiometric PtO_2[10,11] or PtO[6] on the surface. Although bulk platinum oxide is not stable at temperatures above 500°C[19,20], it has been noted[21-23] that a thin film of stable surface oxide might form under these conditions, due to the difference of energy states, and hence in the chemical bonding, at a surface as compared to the bulk material. Thus, we will henceforth refer interchangeably to the state of strongly bound, relatively nonreactive oxygen at the surface as platinum oxide. The oxide surface coverage obtained depends on the oxygen pressure, the exposure time and the exposure temperature [7,8], and

there is evidence that the oxide can be many layers thick, with significant diffusion of oxygen atoms into the bulk[8,9,24].

Our interest in the oxidation of platinum was to determine how the preadsorption of low coverages of strongly bound, non-reactive oxygen would affect the catalysis of hydrocarbon reactions by platinum. This question could be of considerable importance with respect to supported platinum catalysts, where strongly bound oxygen could be introduced by oxygen pretreatments or might arise naturally through interactions of platinum with the oxide support. The study of oxidized platinum as a catalyst is not new - it was reported by Adams and coworkers in 1922[25,26] that platinum oxide is a better catalyst than ordinary platinum black for the hydrogenation of organic compounds - but has not been extensive. Poltorak and coworkers[27,28] studied the dehydrogenation of cyclohexane and hydrogenation of cyclohexene as a function of dispersion on supported platinum catalysts, and reported that preoxidation of the catalysts at 400°C resulted in a significant enhancement of activity on the highly dispersed catalysts, but that the catalysts with large platinum crystallites showed no effect.

In this paper we report on the catalytic effect of preoxidation of three well-characterized platinum single crystal surfaces - a Pt(111), a stepped Pt(S)-[6(111)x(100)] and a kinked Pt(S)-[7(111)x(310)]. We have observed that low coverages of strongly bound oxygen enhance the rates of cyclohexene and cyclohexane dehydrogenation to benzene at low pressure (10^{-6} to 10^{-5} torr total pressure) and change the selectivity of cyclohexene dehydrogenation over hydrogenation to cyclohexane. Furthermore, the effect of pre-

oxidation on catalytic rates and selectivity was found to be sensitive to the presence of surface irregularity sites: kink sites were found to play a particularly active role in the dehydrogenation activity enhancement by strongly bound oxygen. Three models are discussed which relate the oxidation of the platinum surfaces to the observed effects on catalytic reactivity and the structure sensitivity.

EXPERIMENTAL

Apparatus and experimental procedure.

The experiments were performed in two separate ultrahigh vacuum chambers, for which a schematic is shown in Figure 1. A catalyst sample was mounted in the vacuum chamber by spotwelding short pieces of .38 mm wire (either tantalum or platinum) to the edge of the sample at one end and to stainless steel supports at the other. These stainless steel supports were suspended from the sample manipulator, the rotation of which allowed both sides of the catalyst to be cleaned and characterized. The sample was heated resistively and its temperature was monitored by a platinum/platinum - 10% rhodium thermocouple spotwelded to the sample edge.

Each chamber was equipped with an ion bombardment gun for sputter cleaning of the catalyst surface, a retarding grid Auger electron spectrometer to determine the catalyst surface composition, and low energy electron diffraction optics for observing the catalyst surface structure. The pumping system for each chamber consisted of an ion pump and a 2-inch, liquid nitrogen trapped diffusion pump, each of which could be independently isolated from the reaction chamber. Background pressures with the ion pump alone and diffusion pump alone were roughly $1x10^{-9}$ torr and $1x10^{-8}$ torr respectively for the first UHV chamber, and $3x10^{-9}$ torr and $5x10^{-8}$ torr respectively for the second.

After surface characterization, hydrogen, then the hydrocarbon reactant were introduced into the reaction chamber independently by the use of two variable leak valves. The catalyst sample was brought to the reaction temperature, 150°C, before introduction of

the hydrocarbon. The cyclohexene dehydrogenation experiments were carried out with $1x10^{-6}$ torr of hydrogen and $6x10^{-8}$ torr of cyclohexene; the cyclohexane dehydrogenation experiments were carried out using $1x10^{-5}$ torr of hydrogen and $2x10^{-6}$ torr of cyclohexane.

The hydrocarbon reactants were Matheson "Spectroquality" chemicals. They were degassed by several cycles of cooling the reagent to liquid nitrogen temperature followed by pumping on the reagent container with a sorption pump. A UTI 100C quadrupole mass spectrometer was used to monitor the partial pressures of reactant and product gases as a function of time, having been first calibrated with a nude ionization gauge (the corrections were not made for the different ionization cross sections in the ion gauge of the reactants and products).

The reactions were carried out under constant flow conditions by valving off the ion pump and pumping continuously on the chamber with the diffusion pump. The conductance-limited value of the pumping speed (measured with the valve to the chamber open fully) under these conditions was 10 l/sec for hydrogen, .8 l/sec for cyclohexane and .5 l/sec for cyclohexene and benzene for the first UHV chamber, and 3.3 l/sec for hydrogen, 1.1 l/sec for cyclohexane and .7 l/sec for cyclohexene and benzene for the second. Under these conditions, it is assumed that the gases in the reaction chamber (about 15 liters in volume) are well-mixed, since even at $1x10^{-5}$ torr the mean free path (approximately 5 meters) is much larger than the dimensions of the chamber.

Reactions were typically run for 100 to 200 minutes, by which time the measured reactivity closely approached that of a blank,

control reaction due to the poisoning of the platinum surface. Upon termination of an experiment, the reaction chamber was pumped down with the ion pump, and the catalyst surface once again characterized by AES and LEED.

Catalysts.

The catalysts used in this study were platinum wafers, approximately 1 mm thick, cut from 99.999% pure single crystal rods. Each of the three samples reported on was cut from a different rod, two of which were obtained from Materials Research Corporation and the third from Research Organic/Inorganic Chemical Corporation. The slices were prepared as follows: the single crystal rod was oriented, using Laue back-reflection x-ray techniques; a 1-2 mm thick wafer was cut by an electrical discharge, or "spark cutting" process; both sides of the single crystal slice were mechanically polished to the desired crystallographic orientation, the final polishing step being .05 alumina powder/water slurry.

The impurities observed in all three platinum crystals studied were calcium, carbon, phosphorus and sulfur. The calcium was removed from the surface by sputtering with 500 eV argon ions, with the sample at 900°C; carbon, phosphorous and sulfur were removed by oxidation at 700-800°C in 1×10^{-7} torr of oxygen. Residual adsorbed oxygen from brief oxidation treatments could be removed by heating the sample to 1000°C in vacuum.

The clean surface structure of each platinum catalyst was determined by low energy electron diffraction. Shown in Figure 2 are clean surface LEED patterns and surface schematics for the

three samples studied. The first was a hexagonally close-packed Pt(111) surface. The second was a stepped surface, Pt(S)-[6(111)x (100)]↔Pt(755), which was cut 9.5°± .5°from the (111) plane in the direction of the (100) plane on the [01$\bar{1}$] zone. It has (111) terraces averaging 6 atoms wide and a step density of approximately 2.6×10^{14} step atoms/cm^2 or 17% of the surface atoms. The third sample was a kinked surface, Pt(S)-[7(111)x(310)]↔Pt(10,8,7); it was cut 8.5° ± .5° from the (111) plane towards the (310) plane on the [$\bar{1}3\bar{2}$] zone, and is therefore rotated 19° ± 1° from the [01$\bar{1}$] zone. For this surface, the (111) terraces average 7 atoms wide. The orientation of the steps is now a high Miller Index plane, (310), and approximately every third atom along each step is in a kink position; this gives a kink density representing about 6% of the surface atoms.

The clean surface structures, as determined by LEED, agreed well with those predicted by the Laue back reflection x-ray diffraction patterns. The surface area of the Pt(111) and the Pt(S)-[7(111) x (310)] was .6 cm^2; the surface area of the Pt(S)-[6(111)x(100)] was 1.1 cm^2.

The surface composition of the catalyst samples was determined before and after reactions by Auger electron spectroscopy. It was particularly important to ascertain that all carbon, calcium, phosphorus and sulfur impurities had been removed by cleaning procedures before a reaction was started. AES was also used to monitor the oxygen coverage of the catalysts. The oxygen coverage is reported as a ratio of the oxygen 510 eV (O_{510}) Auger peak intensity to the platinum 237 eV (Pt_{237}) Auger peak intensity.

It was determined that a ratio of O_{510}/Pt_{237} = .5 represents approximately one monolayer coverage (see Appendix). In Figure 3, an AES spectrum of a clean platinum catalyst surface is shown in (a), and the spectrum of a catalyst sample with an oxygen coverage greater than one monolayer is shown in (b).

Oxygen treatment of platinum single crystals.

To adsorb oxygen onto the platinum, the single crystal samples in this study were treated at about 800°C, at pressures of oxygen ranging from $1x10^{-7}$ torr to $1x10^{-4}$ torr, with exposure times from several minutes to many hours. Under these conditions, the oxygen should adsorb in the oxide state, as discussed in the introduction, and this was experimentally observed. Auger spectra of the oxygen-treated platinum (taken either at 800°C or after cooling the sample to room temperature) showed minima at 489 and 510 eV (see Figure 3-B), a chemical shift of about 7 eV from the minima seen at 496 and 517 eV for reactive oxygen on platinum[7,11,29].

The adsorbed oxygen was observed to be very stable. The platinum samples could be left overnight at room temperature in a relatively high ambient background of both hydrogen and carbon monoxide with no significant decrease in the O_{510}/Pt_{237} Auger peak ratio. The oxygen could not be removed by heating the platinum in vacuum at temperatures below 800°C; to remove final traces of nonreactive oxygen, it was necessary to alternate argon ion sputtering with extended heating of the samples above 900°C. The adsorbed oxygen was also stable under reaction conditions of up to $1x10^{-5}$ torr of hydrogen at 150°C. The intensity of the O_{510}

Auger peak did not change significantly during the course of the reactions. (Small changes, however, were not readily detectable because of the buildup of approximately 3/4 of a monolayer of carbon on the catalyst surface during a reaction - the attenuation by the carbon layer leads to an increase in the O_{510}/Pt_{237} Auger peak ratio during the reaction and thus makes comparison of this ratio before and after the reaction unreliable.)

It has already been noted that the oxygen coverage of the platinum surfaces depended on the oxygen pressure, the exposure time and the exposure temperature. At a given oxygen pressure and exposure temperature, the increase in coverage was not always a reproducible function of time. It was particularly difficult to reproduce high coverages of oxygen (greater than one monolayer), most notably on the Pt(111) and the Pt(S)-[7(111)x(310)] after several months of experimentation. Additional variables that seemed to be important were: (1) The pressure of residual background gases - relatively high pressures of hydrogen and carbon monoxide slowed down the uptake of oxygen by the platinum catalysts. (2) The concentration of bulk and/or surface impurities - for each of the three platinum samples studied, it was possible to adsorb higher concentrations of oxygen in shorter exposure times when the sample was initially introduced into ultra-high vacuum with all observed impurities (i.e. calcium, carbon, sulfur and phosphorus) present in the bulk than at any later time after numerous cleaning cycles. This initial "advantage" did not require impurities present on the surface (within the detection limits of AES), nor was it regained by exposing the sample to atmospheric conditions,

even for several days. Our observations rule out any enhancement of oxygen adsorption by carbon (which has been shown by other experiments to be an inhibitor to oxygen adsorption[30-32]) or calcium (there was no correlation between the periodic fluctuations of this impurity at the surface and the concentration of adsorbed oxygen); however, there was no conclusive evidence that sulfur and/or phosphorus were responsible for the initial ease of oxygen adsorption on platinum. There was no indication that surface roughness was an important factor in this change of the platinum samples with time, as good, sharp LEED patterns could be obtained from the surfaces during the initial stage when oxygen was more readily adsorbed, and later roughening of the surface by argon ion sputtering could not reproduce this initial stage. (3) Previous oxygen and heat treatment of the sample - the increase of oxygen coverage with time was more rapid if the sample had previously undergone long oxygen exposures and only short periods of heating above 900°C than if the sample had been rigorously cleaned by ion sputtering and extended high temperature heating. The controlling factor here seems to be the concentration of oxygen remaining in the bulk from previous oxygen exposures.

There are two ways to achieve a given oxygen coverage on a platinum sample: the sample can be exposed to oxygen until the desired coverage is attained, or the sample can be exposed until a coverage greater than that desired is reached, at which time the sample is heated above 900°C or argon ion sputtered to remove nonreactive oxygen until the desired coverage is reached. It was observed that the reactivity of a platinum sample was significantly

different at a given oxygen coverage depending on which of these two approaches was used, the reactivity being higher when the first approach was taken (i.e. oxygen exposure to desired coverage). The reactions reported on below were all carried out after the platinum samples had been oxidized by this first, direct approach. The results of experiments run after the platinum catalysts had been heated to high temperature or ion sputtered to reach the desired oxygen coverage will be reported at a later time[33].

RESULTS

LEED studies of nonreactive oxygen adsorbed on platinum.

The low energy electron diffraction (LEED) of each platinum single crystal catalyst was studied before and after oxygen treatments and reactive studies. The clean surface LEED patterns are shown in Figure 2. The onset of an ordered oxygen structure on the platinum surfaces was observed in each case at an oxygen coverage of about O_{510}/Pt_{237} = .2 (somewhat less than one half monolayer). The ordered structures were initially observed on isolated parts of both faces of the crystals; at an oxygen coverage of about one monolayer (O_{510}/Pt_{237} = .5), the ordered structures were observed to be uniform over both sides of the crystals.

The oxygen structure observed on the Pt(111) was a (2x2), illustrated in Figure 4-A for an oxygen coverage of O_{510}/Pt_{237} = 1.9. Sometimes a faint $(\sqrt{3} \times \sqrt{3})$-R30° oxygen structure was observed simultaneously with the (2x2) oxygen structure on the Pt(111), but it was not uniform over the surface. A $(\sqrt{3} \times \sqrt{3})$-R30° oxygen structure was observed on both the Pt(S)-[6(111)x(100)] and the Pt(S)-[7(111)x(310)], as illustrated in Figure 4-B for the stepped surface at an oxygen coverage of O_{510}/Pt_{237} = .65, and in Figure 4-C for the kinked surface at an oxygen coverage of O_{510}/Pt_{237} = .85. A faint (2x2) oxygen structure was sometimes observed simultaneously with the $(\sqrt{3} \times \sqrt{3})$-R30° oxygen structure on both the stepped and kinked surface (such a (2x2) oxygen structure appears very faintly in Figure 4-C of the kinked surface). In no case were the diffraction spots arising from the adsorbed oxygen observed as doublets, indicating that the diffraction from oxygen adsorbed on

two adjacent terraces of the stepped or kinked surface was not coherent.

There are two additional observations to be made from the LEED patterns of oxygen adsorbed on the Pt(S)-[6(111)x(100)] and the Pt(S)-[7(111)x(310)]. On both of these surfaces, a single broad, diffuse spot was sometimes observed between the specular and first order spots of the platinum substrate, as seen in Figure 4-B on the stepped surface. This spot appeared over a wide range of coverages (from less than half a monolayer to more than one monolayer), either in the absence of or presence of another oxygen ordered structure. It appears on the stepped surface at an angle of about 20° from the (0,0) doublet (this angle can be derived from measurements taken from the LEED photograph, as described elsewhere[34]) in a direction which is perpendicular to the step edges (as indicated by the doublet splitting). This would seem to indicate that this spot is centered at the specular reflection from the macroscopic plane of the surface, i.e. the Pt(755), which lies at an angle of about 9.5° from the terrace (111) planes in the appropriate direction (remembering that the angle measured from the photograph should be twice the angle between the reflecting planes). The position of the diffuse spot on the kinked surface LEED pattern leads to the same interpretation, that it is centered at the specular reflection of the Pt(10,8,7) plane. Perhaps the ordering of the oxygen atoms along the step and kink edges leads to the beginnings of a registry between oxygen atoms on adjacent terraces, which would lead to coherent diffraction by the oxygen atoms in the specular direction of the macroscopic plane (which

is determined by the step and kink platinum atoms).

We have also observed a third spot between the two spots of the platinum substrate doublets in the presence of a well-ordered oxygen structure on both the stepped and kinked crystals. These spots, as seen in Figure 4-C, are the (0,0) and second order spots due to the ordered oxygen adsorbate layer.

The surface structures of the platinum catalysts were also checked after a hydrocarbon reaction had been run. The ordered oxygen structures were stable under reaction conditions, as were the clean platinum surface structures. The buildup of disordered carbon during a reaction (approximately 3/4 of a monolayer) resulted in a very high background intensity, but did not otherwise alter the LEED pattern observed before starting a run.

The dehydrogenation and hydrogenation of cyclohexene.

The reaction of cyclohexene in the presence of excess hydrogen was studied on the three platinum single crystal catalysts with clean surfaces and for a series of oxygen coverages. The standard conditions used for these experiments were 6×10^{-8} torr of cyclohexene and 1×10^{-6} torr of hydrogen, and a catalyst temperature of 150°C. Turnover numbers, the number of product molecules per second per platinum surface atom, were calculated as a function of time from the mass spectrometer data using the following equation: $T_i = 21\ P_i S_i / A$, where T_i is the turnover number, P_i the partial pressure in torr and S_i the pumping speed in cm^3/sec for the i-th product and A is the surface area in cm^2 of the platinum sample.

On the clean platinum surfaces, the only detectable product

from cyclohexene was the dehydrogenation product, benzene. A plot of turnover number for benzene production as a function of time for two clean surface experiments is shown in Figure 5. One experiment shown was on the Pt(111) and the other on the Pt(S)-[7(111)x(310)]; the clean surface reactivity of cyclohexene on the Pt(S)-[6(111)x(100)] was very similar to that shown for the kinked surface. These curves have been corrected for any background partial pressure of benzene in the reaction chamber (measured after introducing the hydrogen and heating the platinum sample to 150°C) and for the reactivity of the reaction chamber (this was measured by periodic "blank" control runs, with the platinum sample poisoned and at room temperature, or with no platinum sample in the chamber). The production of benzene from cyclohexene over the platinum catalysts typically passed through a maximum after 2 to 3 minutes, fell off rapidly during the next 5 to 10 minutes, then slowly approached the background reactivity level over the next 100 to 200 minutes. The maximum in the turnover number as a function of time varied by about ±15% during a series of experiments on a given platinum sample under standard reaction conditions in a given reaction chamber, and it is this maximum turnover number which will be reported as a function of oxygen coverage. For calibration purposes, clean surface reactivities were checked for all three platinum samples in both reaction chambers. For the cyclohexene reaction, the relative clean surface values agreed very well between the two systems, but the absolute values differed consistently by a factor of two. Rather than redo all calibrations for both systems, average absolute values have been reported.

The dehydrogenation reactivity of cyclohexene on the Pt(111) sample peaked at approximately one half the maximum values observed for both the stepped and kinked samples. The maximum reactivity was achieved earlier on the Pt(111), and fell off more rapidly as well. By integrating the curves of turnover number as a function of time, it was determined that the total reactivity observed was 0.15 molecule/Pt surface atom on the clean Pt(111), 0.30 molecule/Pt surface atom on the clean Pt(S)-[6(111)x(100)] and 0.35 molecule/Pt surface atom on the clean Pt(S)-[7(111)x(310)]. The buildup of approximately 0.8 monolayer of a carbonaceous deposit was observed on all three platinum samples during a cyclohexene reaction, whether or not there was oxygen on the surface. The carbon coverage was determined by measuring the C_{272}/Pt_{237} Auger peak intensity ratio; calibration showed that $C_{272}/Pt_{237} = 3.2$ represents one monolayer coverage[35].

On the oxygen covered surfaces, the hydrogenation product, cyclohexane, was observed as a product of the cyclohexene reaction, as well as the dehydrogenation product, benzene. The shape of the curves of turnover number as a function of time for benzene production did not change significantly with oxygen coverage for any of the three platinum samples studied. For cyclohexane production, the turnover numbers were an order of magnitude lower than for benzene production; the reactivity with time followed the same trends illustrated in Figure 5 for the dehydrogenation product, but the maximum cyclohexane production was reached one to two minutes earlier than the maximum benzene production.

The maximum turnover numbers for benzene production from

cyclohexene are plotted as a function of oxygen coverage in Figure 6 for the three platinum samples. The largest effect on reactivity of the adsorbed oxygen was observed on the kinked Pt(S)-[7(111)x(310)] surface. On this surface, the benzene production exhibits a maximum at an oxygen coverage of about 1/2 monolayer (O_{510}/Pt_{237} = .25) that represented an increase in reactivity of about six times over the clean surface (the total reactivity increased to about 2 molecules/Pt surface atom at this maximum). At oxygen coverages greater than one monolayer, the benzene production fell off to a relatively constant value that was less than that observed for the clean kinked surface.

An enhancement of the benzene production with oxygen adsorption was also observed on the stepped Pt(S)-[6(111)x(100)] and the Pt(111) surfaces. In these two cases, the benzene production shows a maximum at a lower oxygen coverage, about 1/3 monolayer (O_{510}/Pt_{237} = .15), and the increase in reactivity was about a factor of two over the clean surfaces. At higher oxygen coverages, the benzene production decreased to values lower than those observed for the clean surfaces.

The maximum turnover numbers for cyclohexane production from cyclohexene are plotted as a function of oxygen coverage in Figure 7 for the three platinum samples. At the low pressure conditions under which these reactions were carried out the dehydrogenation product is thermodynamically favored over cyclohexane production. Cyclohexane formation was below the level of detectability in all of the experiments over the clean platinum surfaces. With the addition of adsorbed oxygen, the product cyclohexane was observed

with the kinked Pt(S)-[7(111)x(310)] and the stepped Pt(S)-[6(111)x(100)], but remained undetectable with the Pt(111). On both the kinked and stepped surfaces, the maximum hydrogenation activity occurred at about 1/3 monolayer oxygen coverage (O_{510}/Pt_{237} = .15) and was greater for the kinked surface. Hydrogenation activity on the kinked surface decreased to undetectable levels at oxygen coverages greater than one monolayer, but low levels of activity were observed on the stepped surface at high oxygen coverages. As the rate of cyclohexane production from cyclohexene was close to the detection limit of the systems, the turnover numbers reported for this reaction have greater uncertainty than those for benzene production under the same conditions.

The detection of two products (benzene and cyclohexane) from cyclohexene on oxygen covered platinum made it possible to consider the selectivity of dehydrogenation over hydrogenation as a function of oxygen coverage. The turnover numbers for benzene and cyclohexane production on the kinked Pt(S)-[7(111)x(310)] surface have been replotted together as a function of oxygen coverage in Figure 8. It can be seen that the ratio of benzene to cyclohexane varies from greater than 40:1 on the clean surface (assuming that a turnover number of $1x10^{-5}$ molecules/sec/Pt atom could be detected) to about 10:1 at O_{510}/Pt_{237} = .13 to about 100:1 at O_{510}/Pt_{237} = .22. Thus, it can be seen that the selectivity of the kinked catalyst changes markedly with small changes in oxygen coverage during the buildup of half a monolayer of oxygen on the platinum. The selectivity of dehydrogenation over hydrogenation also decreases from greater than 40:1 on the clean surface to about 10:1 at

O_{510}/Pt_{237} = .27 on the stepped Pt(S)-[6(111)x(100)], but does not seem to increase again at higher oxygen coverages. The selectivity cannot be discussed for the Pt(111), as the hydrogenation product was not detected with this surface.

The dehydrogenation of cyclohexane.

The reaction of cyclohexane in the presence of excess hydrogen was also studied on the three platinum samples with clean surfaces and for a series of oxygen coverages. The standard conditions used for these experiments were $2x10^{-6}$ torr of cyclohexane and $1x10^{-5}$ torr of hydrogen and a catalyst temperature of 150°C. The only detectable product from cyclohexane was the dehydrogenation product, benzene; though higher reagent pressures were used in the cyclohexane experiments than in the cyclohexene experiments, the rate of benzene production from cyclohexane was still an order of magnitude lower than from cyclohexene. Again, since this lower level of reactivity is close to the detection limit of the systems, the turnover numbers for benzene production from cyclohexane have a greater uncertainty than those for benzene production from cyclohexene.

A plot of benzene production from cyclohexane as a function of time for two clean surface experiments is shown in Figure 9. One experiment shown was on the Pt(111) and the other on the Pt(S)-[6(111)x(100)]; the clean surface reactivity of cyclohexane on the Pt(S)-[7(111)x(310)] was very similar to that shown for the stepped surface. Again, these curves have been corrected for any background partial pressure of benzene and for the reactivity of

the reaction chamber. The production of benzene from cyclohexane over the platinum catalysts typically passed through a maximum after 5 to 7 minutes, then approached the background reactivity level over 100 to 200 minutes. The maximum turnover number as a function of time was the same for all three clean platinum surfaces within the experimental error (absolute values from the two reactor systems have been averaged). The maximum benzene reactivity, however, was achieved earlier on the Pt(111), and decreased more rapidly than on either the stepped or kinked surfaces. Buildup of approximately 0.7 monolayer of a carbonaceous deposit was observed on all three platinum samples during a cyclohexane experiment, whether or not there was oxygen on the surface. This was slightly less than the carbon buildup observed for the cyclohexene reactions, in spite of the greater hydrocarbon reagent pressure and lower hydrogen to hydrocarbon ratio.

It is appropriate to note at this point that the cyclohexane reaction was studied on the clean Pt(111) sample when it was mounted on the sample manipulator with short pieces of platinum wire and when mounted with short pieces of tantalum wire. No significant difference in reactivity was observed, leading to the conclusion that the platinum support wires, when used, did not add significant undesired reactivity to that of the platinum single crystal catalysts.

The maximum turnover numbers for benzene production from cyclohexane are plotted as a function of oxygen coverage in Figure 10 for the three platinum samples. The effect of adsorbed oxygen on the cyclohexane dehydrogenation reactivity of the kinked

Pt(S)-[7(111)x(310)] is similar to the effects previously observed for cyclohexene dehydrogenation and hydrogenation. The reactivity goes through a maximum at an oxygen coverage of about O_{510}/Pt_{237} = .12 (approximately ¼ monolayer), then decreases again, starting to level off at a value which is, in this case, greater than that of the clean surface reactivity.

The effect of adsorbed oxygen on the benzene production from cyclohexane on the Pt(111) surface follows a different trend than those previously described. The reactivity increases from the clean surface value to a maximum at a coverage of about O_{510}/Pt_{237} = .15; rather than decrease again, this maximum reactivity is maintained in the presence of higher oxygen coverages up to and greater than one monolayer. It is interesting to note that the reactivity of the kinked surface at higher oxygen coverages starts to level off at a value close to this maximum reactivity maintained on the Pt(111) surface.

No oxygen coverage effects were observed on the stepped Pt(S)-[6(111)x(100)] sample for cyclohexane dehydrogenation, up to monolayer coverages. The benzene production from cyclohexane was checked for the clean surface and at various oxygen coverages in each of the reaction chambers with the same result.

DISCUSSION

AES and LEED Studies

The formation of a surface layer of stable platinum oxide on the three platinum samples studied was evidenced by the observed chemical shift of the oxygen Auger peaks to lower energy (510 eV versus 517 eV) and by the stability of the adsorbed oxygen under vacuum and reducing conditions. Ordered oxygen structures were observed by LEED, but no attempt was made to determine the stoichiometry, PtO_x, of the oxide layer from the data. The O_{510}/Pt_{237} Auger peak intensity ratio was calibrated (see Appendix) in conjunction with the LEED data on the Pt(S)-[6(111)x(100)], obtaining $O_{510}/Pt_{237} = .5$ at a coverage of approximately one monolayer, that was one oxygen atom for every three platinum surface atoms, or approximately 5×10^{14} oxygen atoms/cm^2. This is in reasonable agreement with previous calibrations of the Auger signal with coverage[36-39].

In oxygen treating these three platinum samples with a varied concentration of surface defects (step and kink sites), no structure dependence was noted; approximately the same oxygen surface coverages were obtained on each sample at a given oxygen pressure, exposure time and exposure temperature. This question was not addressed in detail, however, and a small structure dependency could easily have been masked by other variables that were difficult to control (e.g., variation of residual H_2 or CO in the ambient background, or the concentration of bulk impurities) from one oxygen exposure to the next, or from crystal to crystal. The decrease in saturation coverages obtained on a platinum sample

after many oxygen treatments and hydrocarbon reactions was especially difficult to control, and is a problem which has been reported by other groups[40,41].

There is no general agreement in the literature as to the ordered structures observed by LEED in the presence of an oxide layer on platinum single crystals. We observed a strong (2x2) oxygen structure on the Pt(111) (Figure 4-A), sometimes accompanied by a faint $(\sqrt{3} \times \sqrt{3})$-R30° oxygen structure. Merrill and coworkers[8,42] observed a strong $(\sqrt{3} \times \sqrt{3})$-R30° oxygen structure, accompanied by a weak (3x15) oxygen structure on the oxidized Pt(111). There is, however, good agreement that chemisorption of oxygen at <u>low</u> temperature (i.e., "reactive" oxygen) gives rise to an ordered (2x2) oxygen structure on the Pt(111)[8,31,36,43-45] and on stepped surfaces close to the Pt(111)[39,44,46]. Légaré and coworkers[10,11] observed complex LEED patterns on the Pt(111) at high oxide coverages that they relate to the growth of an epitaxial layer of PtO_2 with a slightly larger real unit cell than the substrate Pt(111); the interpretation of their results, however, is difficult because of their failure to remove a substantial concentration of surface calcium.

On both the Pt(S)-[6(111)x(100)] and Pt(S)-[7(111)x(310)] we observed a $(\sqrt{3} \times \sqrt{3})$-R30° oxygen structure (Figure 4-B&C), sometimes accompanied by a faint (2x2) oxygen structure. Légaré et al.[11] have also investigated the oxidation of a Pt(S)-[6(111)x(100)] by LEED and AES; after high pressure oxygen adsorption at 500°C, they observe simultaneously (2x2) and $(\sqrt{3} \times \sqrt{3})$-R30° oxygen structures, as well as spots they associate with the growth of an epitaxial

layer of PtO_2. In our work, and in the work of Légaré et al.[11], the diffraction spots arising from the adsorbed oxygen were not observed as doublets; Gland and Korchak[39], however, observed splitting of the oxygen (2x2) structure on a Pt(S)-[12(111)x(111)] after adsorption of oxygen at low temperature.

Our results on the stepped and kinked platinum surfaces seem to indicate that the presence of a high density of defect sites favors the formation of the $(\sqrt{3} \times \sqrt{3})$-R30° oxygen structure over the (2x2) oxygen structure; perhaps the density of defect sites on a given Pt(111) surface determines which structure is observed. For each platinum surface studied, the oxygen structures observed after oxidation were very stable in vacuum and under the highly reducing conditions of the hydrocarbon reactions.

Reactivity Studies

The experimental results reported here lead to two important conclusions: (1) low coverages of strongly bound, nonreactive oxygen on platinum catalysts enhance the dehydrogenation rates of both cyclohexene and cyclohexane to benzene, and change the selectivity of dehydrogenation over hydrogenation for the cyclohexene reaction; (2) the effect of preoxidation on the reactivity of the platinum surfaces is structure sensitive, the reactivity being most enhanced on the kinked surface. The role that oxygen plays in changing the reactivity and selectivity of platinum catalysts is as yet poorly understood, but there are three models that might explain the observed effects. These models have been previously discussed by McCabe and Schmidt[40-47] with respect to

the enhanced bonding of H_2 and CO that they observed on oxidized platinum surfaces.

The first model postulates that the formation of a surface layer of oxide will result in a change in the electronic structure of the surface platinum atoms: in the oxide, the adsorbed oxygen atoms would tend to remove platinum valence electrons, and the surface platinum atoms would become positively charged. This change in electronic structure could affect the binding of hydrogen and hydrocarbon reactants, intermediates, and products to the catalyst surface, which in turn could change the rates and selectivity of the observed reactions. Since the presence of high concentrations of step and kink defect sites has a large effect already on the electronic structure of the clean platinum surfaces[48] the formation of a surface oxide might change the electronic structure of each surface site differently, giving rise to the observed structure sensitivity of the preoxidation on the reactions. McCabe and Schmidt[40,47] have determined that oxide covered platinum surfaces have new binding sites for both hydrogen and carbon monoxide with significantly higher binding energies than on the clean surfaces; in addition, they observed that the initial sticking coefficient for hydrogen was higher by almost a factor of two on the oxidized surface, falling to a low value as soon as the higher binding energy state was populated. This enhanced bonding of hydrogen could explain the large increase in hydrogenation activity of cyclohexene to cyclohexane observed on two of the platinum catalysts that we studied. Upon low temperature adsorption of oxygen on platinum, the work function increases by about 1 ev[40,42,49,50];

with high temperature oxidation, on the other hand, the work function has been shown to decrease by about 1 ev[8, 10,42]. This decrease would seem to indicate that oxidation leads to adsorbed oxygen atoms beneath the surface platinum atoms; the positively charged surface metal atoms would thus be readily available for bonding with hydrogen and hydrocarbons.

The second model proposes that the strongly adsorbed oxygen atoms are active in compound formation with other adsorbates such as hydrogen and hydrocarbons; such oxygen containing compounds could provide alternate pathways for dehydrogenation or hydrogenation, thus changing observed reaction rates and selectivity. For example, the formation of hydroxyl groups on the surface might enhance the hydrogenation activity of cyclohexene to cyclohexane. An oxygen atom strongly adsorbed at a step or kink platinum site might show different activity for compound formation than an oxygen atom at a (111) terrace site; this could provide an explanation for the observed structure sensitivity of the reactivity and selectivity on oxidized platinum catalysts.

The third model is that the oxidation of the platinum surface results in a reconstruction or rearrangement of the surface atoms. The enhancement of dehydrogenation activity and the change in selectivity could then be postulated to arise from the creation of new active sites during this rearrangement; the structure sensitivity could arise from a variation in the ease of reconstruction from surface to surface. Platinum dispersed as small particles on oxide supports has been observed to exhibit increased mobility under oxidizing atmospheres[51,52] and LEED observations indicate that the Pt(110) surface reconstructs after extensive heating in

oxygen[6,43,49]. A similar surface rearrangement has been observed by Amariglio and coworkers[53] to occur on platinum and nickel during the synthesis of water from oxygen and hydrogen, and they postulate that sites formed by this reaction are active for ethylene hydrogenation[54-56]. The mechanism they propose cannot be used to explain our results, however, due to the nonreactivity of the strongly bound oxygen with hydrogen under our experimental conditions.

Consideration of the structure sensitivity of the observed oxidation effects on reactivity and selectivity will provide additional information for the critical appraisal of the three proposed models. Before discussing the effect of oxygen on the platinum structure sensitivity, a brief look at the clean surface structure sensitivity is in order. For the dehydrogenation of cyclohexene to benzene, the observed order of reactivity was Pt(S)-[7(111)x(310)] ≈ Pt(S)-[6(111)x(100)] > Pt(111), where the Pt(111) was a factor of two less reactive than the stepped and kinked surfaces. Blakely and Somorjai[57] reported that the dehydrogenation of cyclohexene to benzene requires the presence of step sites and does not occur on the Pt(111) surface. The Pt(111) surface was observed to poison more rapidly than the other two surfaces. The catalyst poisoning is believed to arise from the buildup of a carbonaceous deposit on the surface during the course of the reaction-carbon coverages of approximately .8 monolayer were observed on all three surfaces after a cyclohexene experiment. The poisoning mechanism was not studied in detail, however. Since the poisoning characteristics and carbon buildup did not change significantly with preoxidation of the platinum catalysts, and

since the strongly bound oxygen was nonreactive under the reaction conditions, the oxygen enhancement of dehydrogenation rates cannot be explained by a simple "clean-off" reaction with the adsorbed oxygen that would delay carbon buildup on the catalyst surface.

For the dehydrogenation of cyclohexane to benzene, all three platinum surfaces studied showed about the same level of reactivity. This result agrees well with studies on dispersed platinum catalysts at high pressure which indicated that the dehydrogenation of cyclohexane to benzene is structure insensitive[28,58,59]. Our result on the Pt(111) is not in agreement with the relatively low turnover number reported by Blakely and Somorjai[57] on a Pt(111) in comparison to several stepped and kinked surfaces under low pressure conditions. The Pt(111) surface was observed to poison more rapidly for cyclohexane dehydrogenation than the other two surfaces; Mitrofanova et al.[27] observed that supported platinum catalysts with low dispersion (large metal crystallites) poisoned more rapidly than catalysts with very high dispersion for this same reaction under high pressure conditions.

Preoxidation of the platinum catalyst surfaces resulted in an enhancement of benzene production from cyclohexene on all three surfaces studied; however, the relative enhancement of reactivity on the kinked Pt(S)-[7(111)x(310)] surface was more than three times that on either the Pt(111) or stepped Pt(S)-[6(111)x(100)], and the maximum enhancement on the kinked surface occurred at an oxygen coverage (O_{510}/Pt_{237} = .25) significantly higher than on the other two surfaces (O_{510}/Pt_{237} = .15). Thus, although the presence of kink sites did not significantly increase the clean surface

reactivity of the kinked surface over that of the stepped surface, the presence of kink sites markedly affected the change in reactivity in the presence of low coverages of strongly bound oxygen. The relative enhancement of cyclohexene dehydrogenation to benzene on the stepped surface was very similar to that on the Pt(111), the rates over the stepped surface being about twice the rates over the Pt(111) surface at any oxygen coverage.

The enhancement of cyclohexene hydrogenation to cyclohexane was also greater (by about a factor of two) for the kinked surface than for the stepped surface, and the selectivity of dehydrogenation over hydrogenation as a function of oxygen coverage differed considerably for these two surfaces; the dehydrogenation reaction was not detected on the Pt(111), even at low oxygen coverages. Poltorak and Boronin[28] observed that highly dispersed platinum catalysts showed an enhancement of cyclohexene hydrogenation after oxidation at 400°C, while the reactivity of supported catalysts with low dispersion was not significantly altered; our results are in good qualitative agreement with these high pressure experiments on supported catalysts if we assume that highly dispersed metal particles have a high concentration of low-coordination step and kink sites, while the larger particles on low dispersion catalysts are fairly representative of low index planes such as the Pt(111).

The enhancement of cyclohexene dehydrogenation by low oxygen coverages seems too large, particularly on the kinked surface, to be explained by surface reconstruction with the creation of new active sites, especially in view of the observation that the

LEED pattern from the platinum substrate did not change significantly with oxygen coverage for any of the three surfaces studied. It seems that a change in the electronic structure of the platinum surface atoms due to the preoxidation and/or the formation of surface compounds involving oxygen must be largely responsible for the observed enhancement and change in selectivity. Apparently, the presence of platinum kink sites promotes particularly favorable surface electronic changes and/or enhances compound formation. Although the formation of hydroxyl groups might be important in the observed hydrogenation activity, the decrease in the work function observed with the strongly bound oxygen[8,10,42] leads to an interpretation that a significant proportion of the adsorbed oxygen is below the platinum surface atoms and prompts us to believe that compound formation is not the primary mechanism for enhancement of dehydrogenation activity.

For cyclohexane dehydrogenation to benzene, preoxidation of the platinum catalyst surfaces resulted in reactivity enhancement on only two of the surfaces, the kinked Pt(S)-[7(111)x(310)] and the Pt(111). The maximum enhancement on the kinked surface was about twice that for the Pt(111) and the observed variation of turnover number with oxygen coverage was markedly different for the two surfaces. On the kinked surface, the reactivity passes through a maximum, then decreases again, the same trend as observed for cyclohexene dehydrogenation and hydrogenation on all three surfaces; on the Pt(111), the reactivity increases to a maximum which is maintained in the presence of higher oxygen coverage. The reactivity of the kinked surface at high oxygen coverages starts

to level off at a value close to this maximum reactivity maintained on the Pt(111) surface. It is interesting to note that cyclohexane dehydrogenation to benzene is maintained at a reactivity level above that of the clean surfaces at high oxygen coverages for both the kinked and Pt(111) surfaces whereas the rate of cyclohexene dehydrogenation to benzene fell off to values lower than on the clean surfaces for each platinum catalyst at high oxygen coverage. Again, it seems to be the kink sites that play an important role in dehydrogenation activity enhancement at low oxygen coverages, even though they do not significantly increase this reactivity on the clean kinked surface. Our results are in qualitative agreement with those of Mitrofanova et al.[27] at higher pressures; they observed that cyclohexane dehydrogenation to benzene was enhanced on highly dispersed platinum catalysts after oxidation at 400°C while the reactivity of low dispersion catalysts was not significantly altered.

The lack of any enhancement by strongly bound oxygen of cyclohexane dehydrogenation activity on the stepped Pt(S)-[6(111)x(100)] was unexpected and is still not understood. It cannot easily be explained by any of the three models that have been proposed to explain the effects of oxidation on the reactivity and selectivity of platinum catalysts. Possibly the Pt(S)-[6(111)x(100)] was contaminated by a low concentration of an impurity that we did not detect (though none of our AES data leads us to suspect impurity problems). The experiments should certainly be repeated on a second Pt(S)-[6(111)x(100)] to clarify this finding.

It is clear from the work of Poltorak and coworkers[27,28]

that preoxidation of supported platinum catalysts can also significantly enhance dehydrogenation and hydrogenation rates over the platinum at higher pressures. The enhancement that they observed was a function of the platinum dispersion, the highly dispersed catalysts being most strongly affected by preoxidation. Strongly bound oxygen on supported platinum catalysts might arise through an interaction of the metal with the oxide support, or can be introduced by oxygen pretreatment. Although we produced the platinum surface oxide by high temperature treatment (800°C), low temperature studies of oxygen adsorption on platinum have shown that 1 to 5% strongly bound nonreactive oxygen can be detected even after mild oxygen pretreatments [6,40,45,60,61].

CONCLUSIONS

Low coverages of strongly bound oxygen enhance the rates and change the selectivity for dehydrogenation and hydrogenation reactions on platinum catalysts. These oxygen effects are sensitive to the structure of the platinum surface, kink sites playing a particularly important role in the enhancement of dehydrogenation and hydrogenation activity by low coverages of oxygen. Analysis of our results indicate that a change of the electronic structure of the platinum surface through oxidation provides the best general model for explaining the oxygen effects, though surface reconstruction during oxidation or complex formation involving the adsorbed oxygen may also be important.

Our results demonstrate that additives such as oxygen, in addition to surface irregularities, can play important roles in optimizing the rates and selectivity of hydrocarbon reactions over platinum catalysts. For supported catalysts, strongly bound oxygen could be introduced by oxygen pretreatments, or might arise naturally through interactions of platinum with the oxide support.

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APPENDIX

Determination of oxygen coverages

We have determined the oxygen coverage using a method reported recently by Biberian and Somorjai.[35] It consists of plotting the Auger peak-to-peak signal intensity from the substrate against the similar signal from the adsorbate. The curve is composed of segments of straight lines, the first break indicating the completion of one monolayer of adsorbate. This method is more sensitive when utilizing an Auger transition of high energy for the adsorbate, and of low energy for the substrate.

We have applied this method to the calibration of oxygen on a Pt(S)-[6(111)X(100)] surface. The 64eV and 237eV Auger peak-to-peak signal intensities of platinum were monitored as a function of the 510eV Auger peak-to-peak signal intensity from the oxygen while heating the crystal at 800°C in $5X10^{-7}$ torr of oxygen. This is plotted for the 64eV platinum peak in Figure 11; the position of the break as shown in the figure indicates that the formation of a monolayer of oxygen occurs at $O_{510}/Pt_{64}=0.11$ and $O_{510}/Pt_{237}=0.5$.

The LEED structure observed at the formation of an oxygen monolayer was $(\sqrt{3}X\sqrt{3})$-R30°. A simple model giving rise to this structure will place one adsorbed oxygen atom on the surface for every three platinum surface atoms. Based on this model the ratio $O_{510}/Pt_{237}=0.5$ corresponds to about $5X10^{14}$ atoms of oxygen/cm^2.

The Auger peak-to-peak signal intensity from the oxygen is proportional to the amount of adsorbed oxygen during the formation of the first monolayer, however, the ratio O_{510}/Pt_{237} is not proportional to the coverage because of the attenuation of the platinum

Auger peak-to-peak signal intensity by the adsorbed oxygen. The 237eV platinum Auger transition is attenuated by 26% during the formation of a monolayer of oxygen. Taking this factor into consideration, we obtain the following relation [35]:

$$\theta = [0.26 + 0.37\ Pt_{237}/O_{510}]^{-1}$$

where θ=1 corresponds to one oxygen atom for every three platinum surface atoms or $5X10^{14}$ oxygen atoms/cm^2. In Table 1, the oxygen coverages and surface concentrations are listed for different values of the O_{510}/Pt_{237} Auger peak ratio.

Our calibration is in fairly good agreement with others[36-39] considering that the orientation of the surfaces, the temperature of adsorption and the type of AES analyzer used were different. Bonzel and Ku[36] find a ratio O_{510}/Pt_{237}=0.65 for one monolayer of oxygen adsorbed at about 300°C ($7.5X10^{14}$ oxygen atoms/cm^2) on Pt(111) using a Cylindrical Mirror Analyzer (CMA). Weber et al.[37] obtain a ratio 0.5 for one monolayer of oxygen ($8X10^{14}$ oxygen atoms/cm^2) with polycristalline platinum at room temperature. Wilf and Dawson[38] measure a ratio 0.55 for one monolayer of oxygen ($3.5X10^{14}$ oxygen atoms/cm^2) on Pt(110) with a retarding grid analyzer (RGA) after adsorption at room temperature. Gland and Korchak[39] report a ratio of 0.5 for one monolayer of oxygen ($4X10^{14}$ oxygen atoms/cm^2) with Pt(S)-[12(111)X(111)] using a CMA.

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Table Caption

Table I. Oxygen coverages (θ) and surface concentrations for various values of the O_{510}/Pt_{237} Auger peak ratio, where θ=1 corresponds to one oxygen atom for every three platinum surface atoms, or $5X10^{14}$ oxygen atoms/cm^2.

Table 1

O_{510}/Pt_{237}	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.45	0.50
θ	0.13	0.25	0.37	0.47	0.57	0.67	0.76	0.84	0.92	1.0
oxygen atoms/cm^2 X 10^{-14}	0.65	1.3	1.9	2.4	2.9	3.4	3.8	4.2	4.6	5.0

Figure Captions

Figure 1. Schematic diagram of reaction chambers used for low pressure catalytic reaction studies.

Figure 2. Low-energy electron diffraction patterns and schematic representations of the three platinum surfaces studied:
(a) Pt(111)
(b) Pt(S)-[6(111)X(100)] ↔ Pt(755)
(c) Pt(S)-[7(111)X(310)] ↔ Pt(10,8,7)

Figure 3. Auger electron spectra of (a) a clean platinum catalyst surface, and (b) a platinum catalyst surface with an oxygen coverage greater than $5X10^{14}$ oxygen atoms/cm^2 after treatment at 800°C in $1X10^{-6}$ torr oxygen.

Figure 4. Ordered oxygen structures observed by low energy electron diffraction on the three platinum surfaces studied:
(a) (2X2)-O on Pt(111)
(b) $(\sqrt{3}X\sqrt{3})$-R30°-O on Pt(S)-[6(111)X(100)]
(c) $(\sqrt{3}X\sqrt{3})$-R30°-O on Pt(S)-[7(111)X(310)]; a faint (2X2)-O is also present.

Figure 5. Benzene production from cyclohexene as a function of time on the clean kinked Pt(S)-[7(111)X(310)] surface (-●-) and the clean Pt(111) surface (···▲···). Reaction conditions: catalyst temperature, 150°C; cyclohexene pressure, $6X10^{-8}$ torr; hydrogen pressure, $1X10^{-6}$ torr.

Figure 6. Maximum turnover numbers for benzene production from cyclohexene as a function of oxygen coverage (O_{510}/Pt_{237} =.5 corresponds to about $5X10^{14}$ oxygen atoms/cm^2) on Pt(S)-[7(111)X(310)](-●-), Pt(S)-[6(111)X(100)](--□--), and Pt(111)(···▲···). Reaction conditions: catalyst

temperature, 150°C; cyclohexene pressure, $6X10^{-8}$ torr; hydrogen pressure, $1X10^{-6}$ torr.

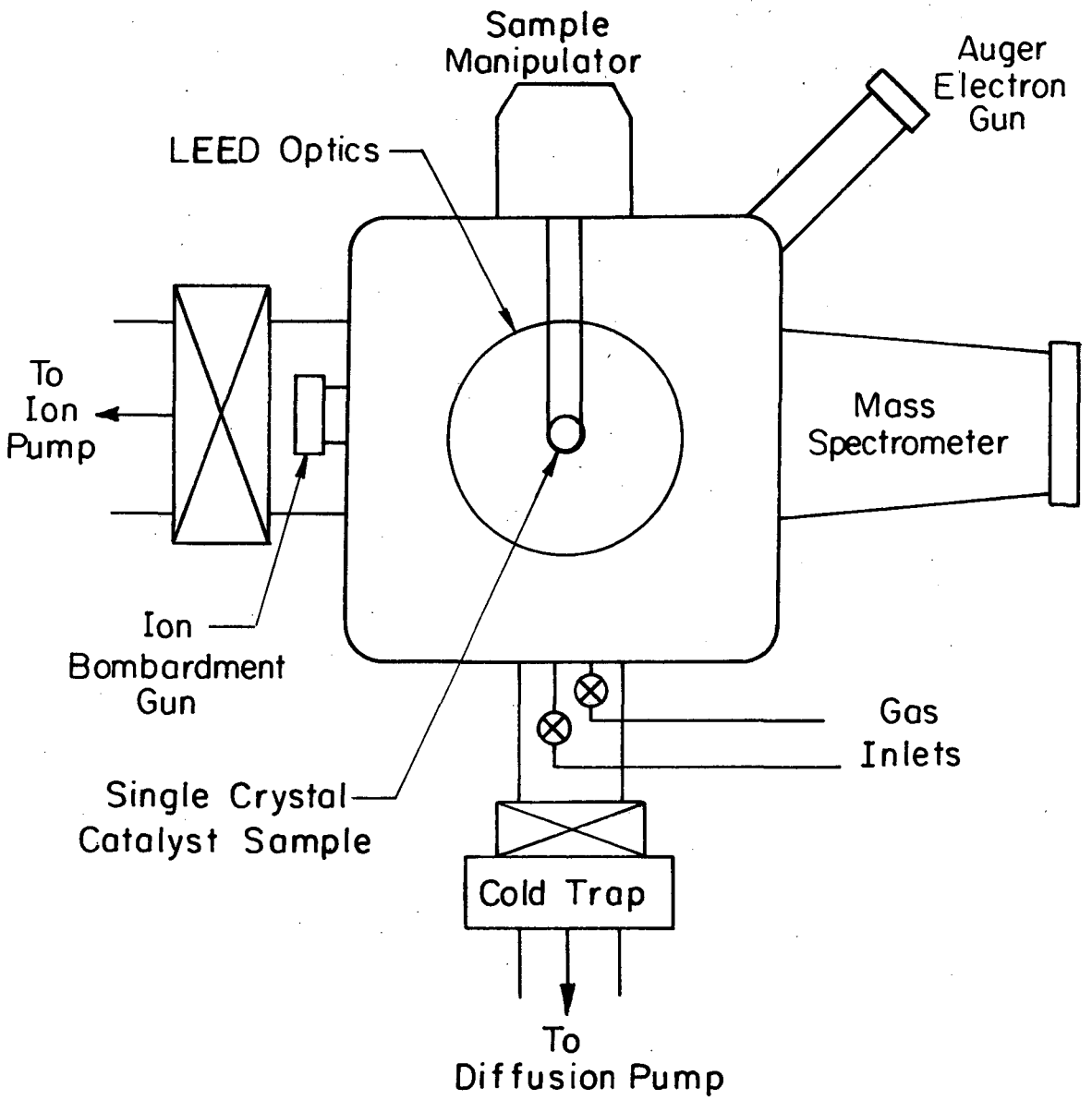
Figure 7. Maximum turnover numbers for cyclohexane production from cyclohexene as a function of oxygen coverage on Pt(S)-[7(111)X(310)](-●-), Pt(S)-[6(111)X(100)](--□--), and Pt(111)(•••▲•••). Reaction conditions: catalyst temperature, 150°C; cyclohexene pressure, $6X10^{-8}$ torr; hydrogen pressure, $1X10^{-6}$ torr.

Figure 8. Maximum turnover numbers for benzene production from cyclohexene (-●-) and for cyclohexane production from cyclohexene (--□--) as a function of oxygen coverage on Pt(S)-[7(111)X(310)] showing the change in selectivity of cyclohexene dehydrogenation over hydrogenation. Reaction conditions: catalyst temperature, 150°C; cyclohexene pressure, $6X10^{-8}$ torr; hydrogen pressure, $1X10^{-6}$ torr.

Figure 9. Benzene production from cyclohexane as a function of time on the clean stepped Pt(S)-[6(111)X(100)] surface (--□--) and the clean Pt(111) surface (•••▲•••). Reaction conditions: catalyst temperature, 150°C; cyclohexane pressure, $2X10^{-6}$ torr; hydrogen pressure, $1X10^{-5}$ torr.

Figure 10. Maximum turnover numbers for benzene production from cyclohexane as a function of oxygen coverage on Pt(S)-[7(111)X(310)](-●-), Pt(S)-[6(111)X(100)](--□--), and Pt(111)(•••▲•••). Reaction conditions: catalyst temperature, 150°C; cyclohexane pressure, $2X10^{-6}$ torr; hydrogen pressure, $1X10^{-5}$ torr.

Figure 11. The 64eV Auger peak-to-peak signal intensity of platinum plotted as a function of the 510eV Auger peak-to-peak signal intensity of adsorbed oxygen while heating the crystal at 800°C in $5X10^{-7}$ torr of oxygen. The position of the break indicates that the formation of a monolayer of oxygen ($5X10^{14}$ oxygen atoms/cm^2) occurs at O_{510}/Pt_{237} =0.11 and O_{510}/Pt_{237}=0.5 (not shown).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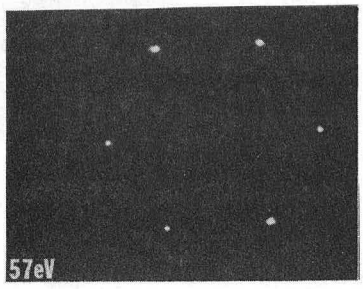
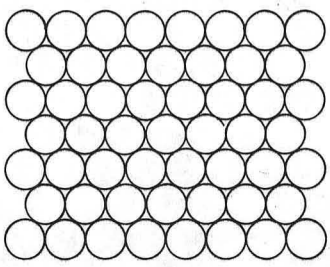
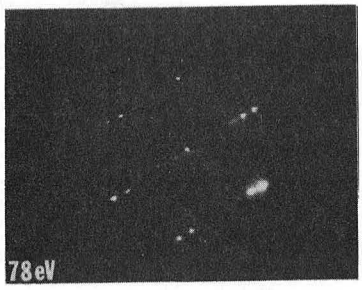
Gun
Gas
Inlets
Single Crystal
Catalyst Sample
Cold Trap
To
Diffusion Pump
XBL 785-4952

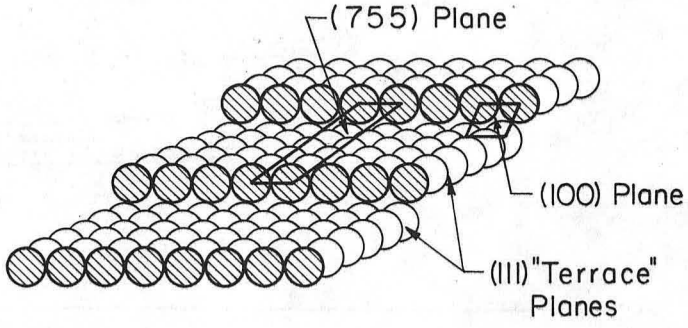
Figure 1.



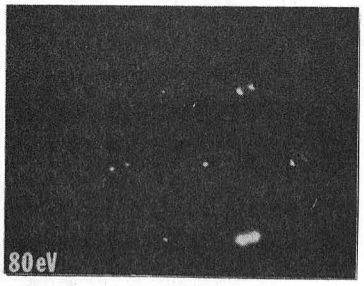


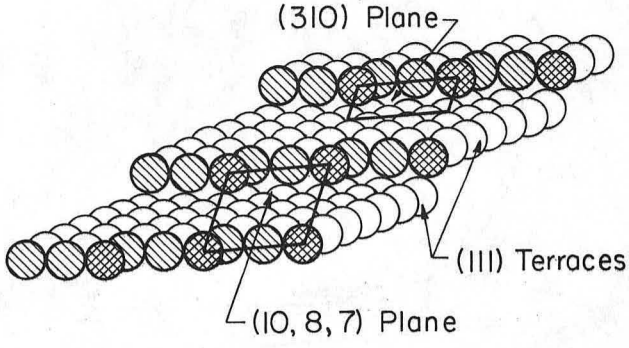
A. Pt (111)





B. Pt (S)-[6 (111)x(100)]↔Pt (755)





C. Pt (S)-[7 (111)x(310)]↔Pt (10,8,7)

Figure 2

XBB 785-5471

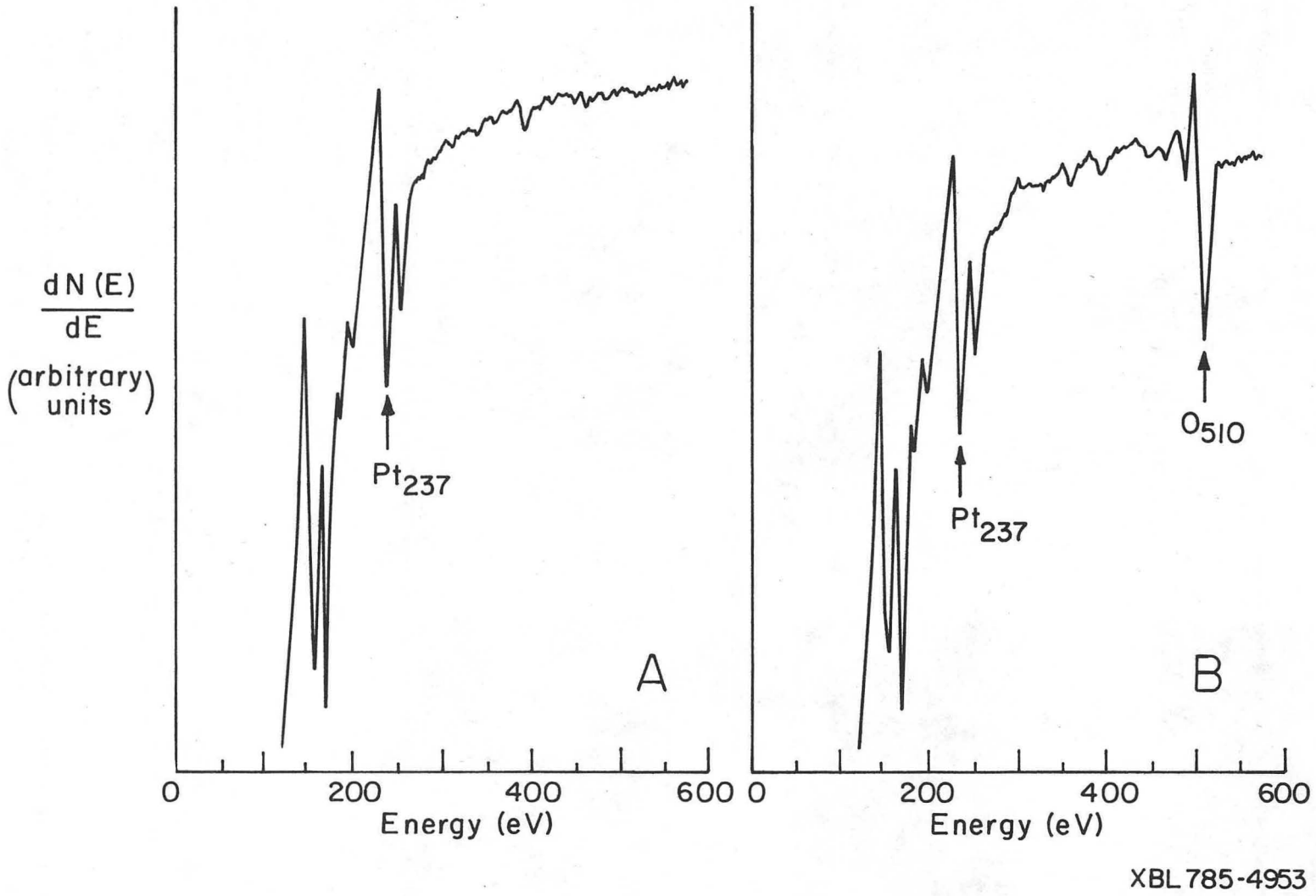

dN(E)/dE (arbitrary units)
Pt237
A
0
200
400
600
Energy (eV)
Pt237
O510
B
0
200
400
600
Energy (eV)
XBL785-4953

Figure 3

Figure 4

XBB 784-4752

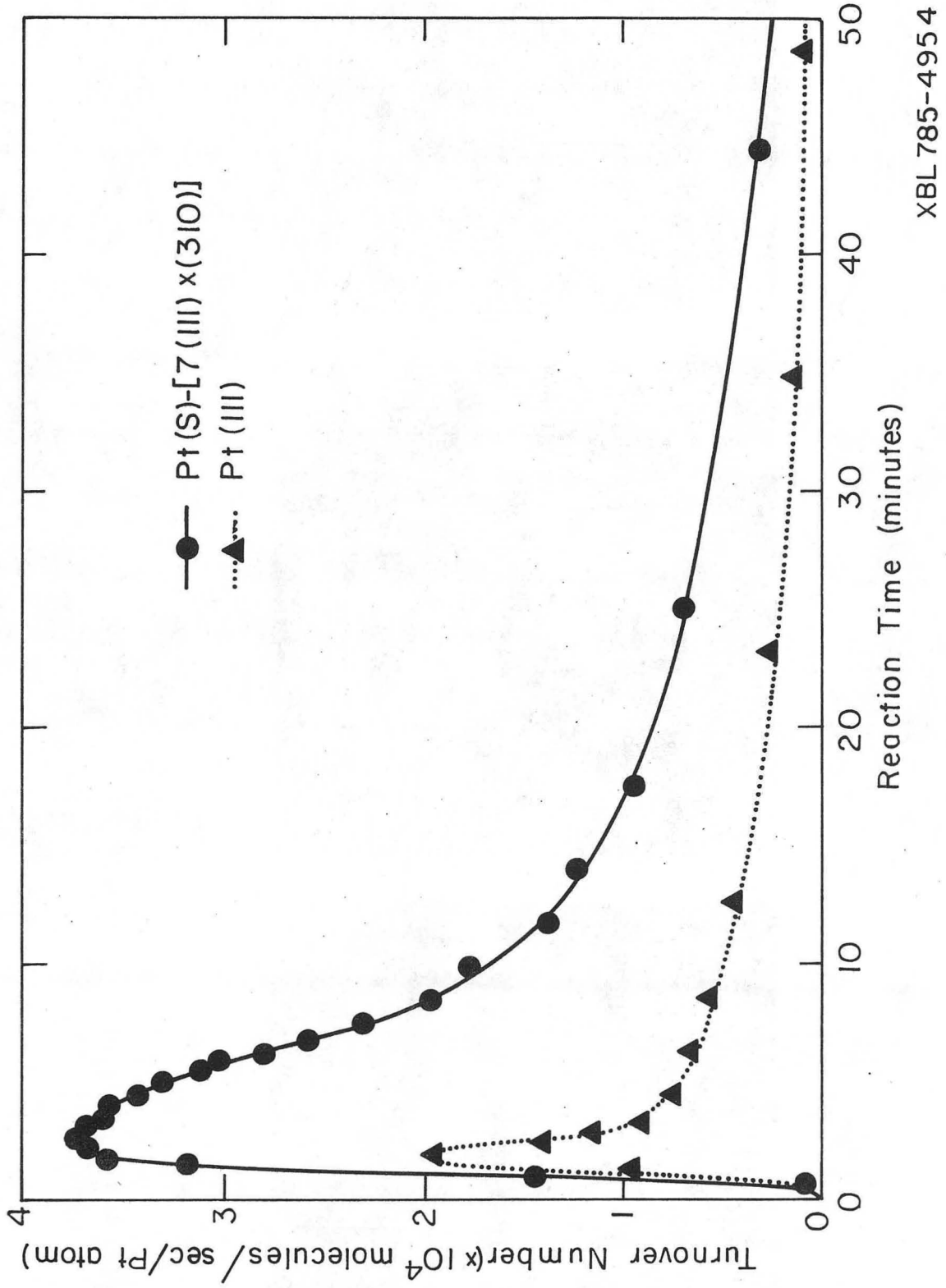

Turnover Number(x 10^4 molecules/ sec/Pt atom)
Reaction Time (minutes)
Pt(S)-[7(111) x(310)]
Pt (111)
0
1
2
3
4
10
20
30
40
50
XBL 785-4954

Figure 5

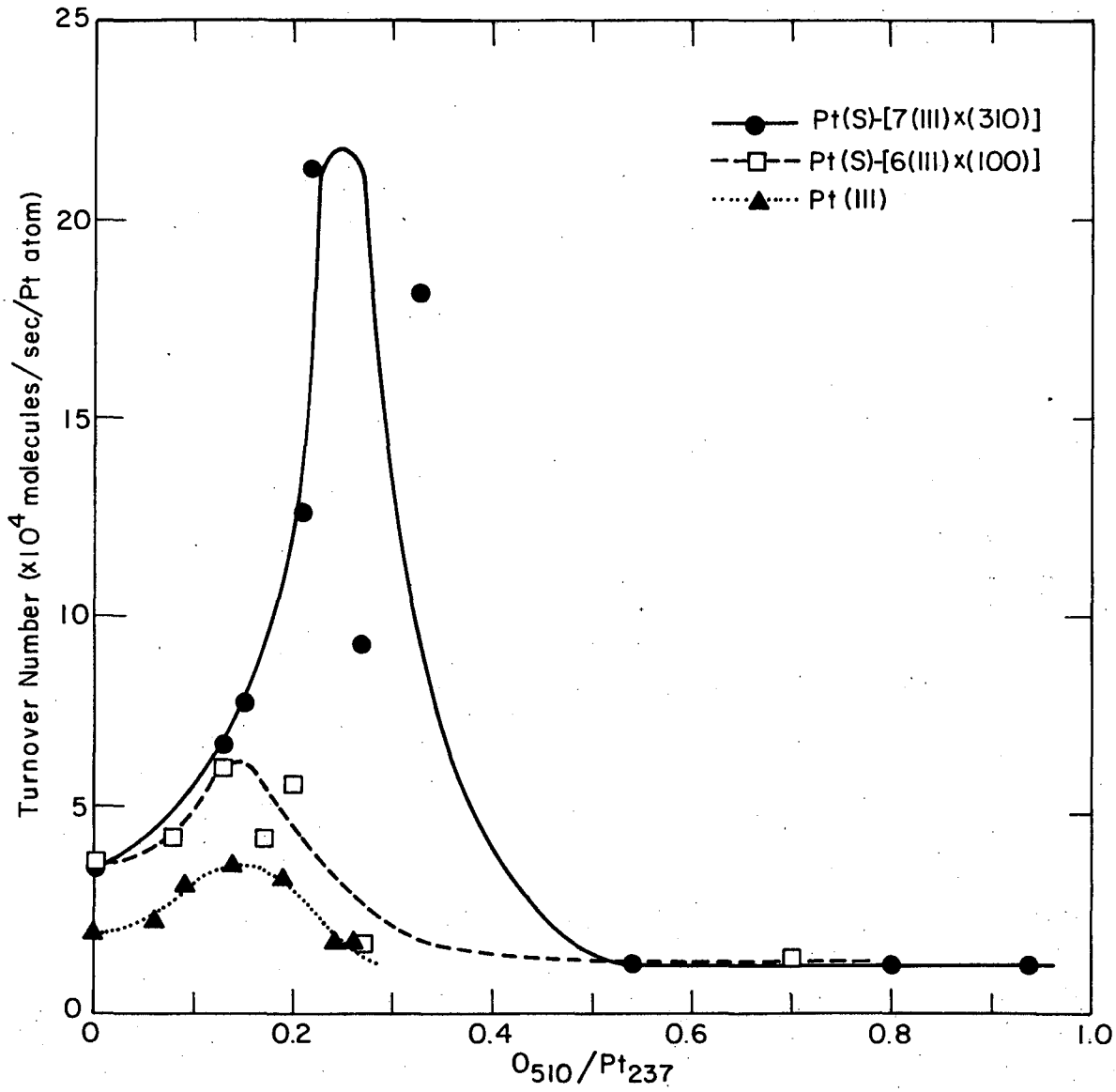

Pt(S)-[7(111)x(310)]
Pt(S)-[6(111)x(100)]
Pt (111)
Turnover Number (x10^4 molecules/sec/Pt atom)
O510/Pt237
0
5
10
15
20
25
0.2
0.4
0.6
0.8
1.0
XBL 785-4959

Figure 6

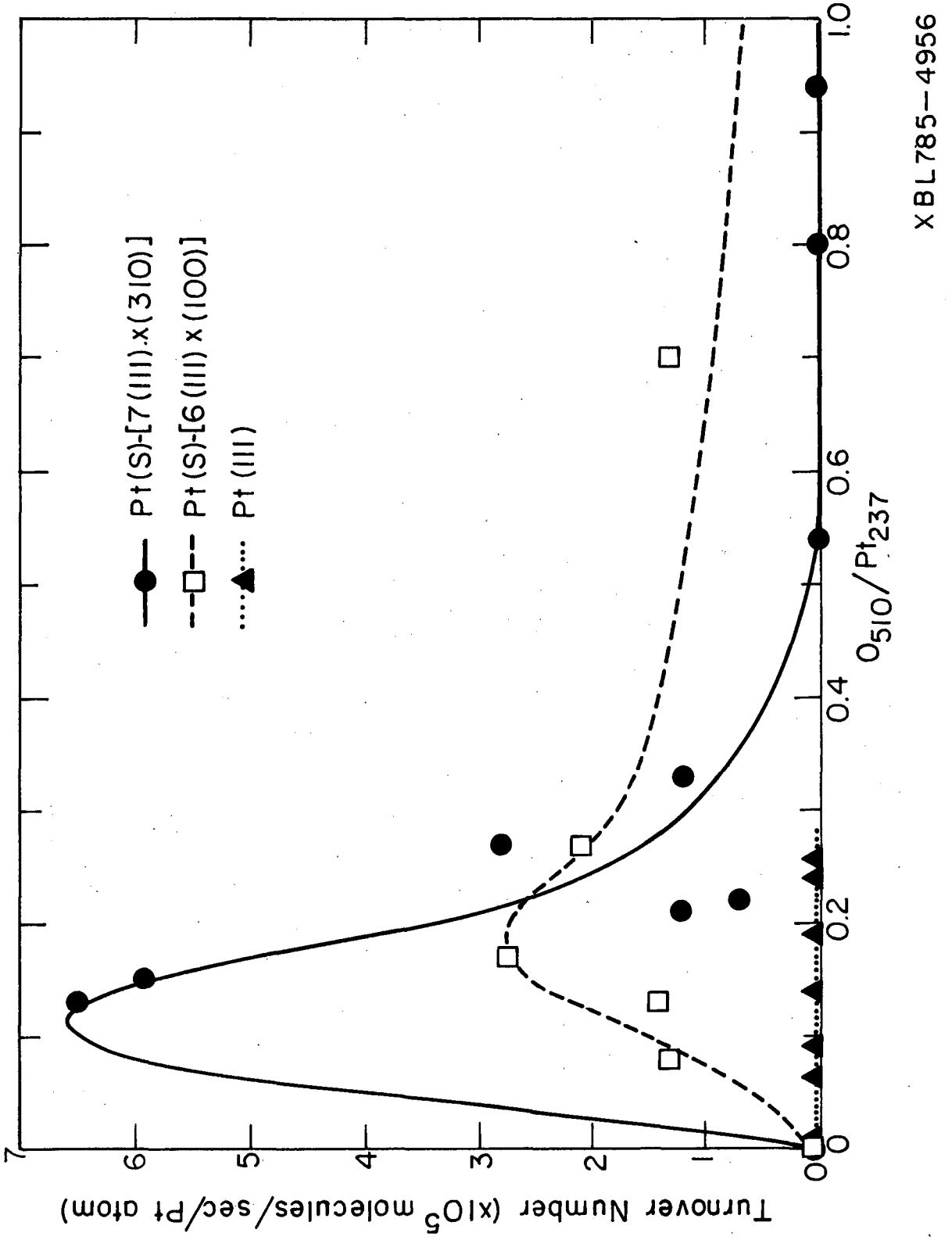

Turnover Number (x10^5 molecules/sec/Pt atom)
O_{510}/Pt_{237}
Pt(S)-[7(111).x(310)]
Pt(S)-[6(111) x (100)]
Pt (111)
0
1
2
3
4
5
6
7
0.2
0.4
0.6
0.8
1.0
XBL785-4956

Figure 7

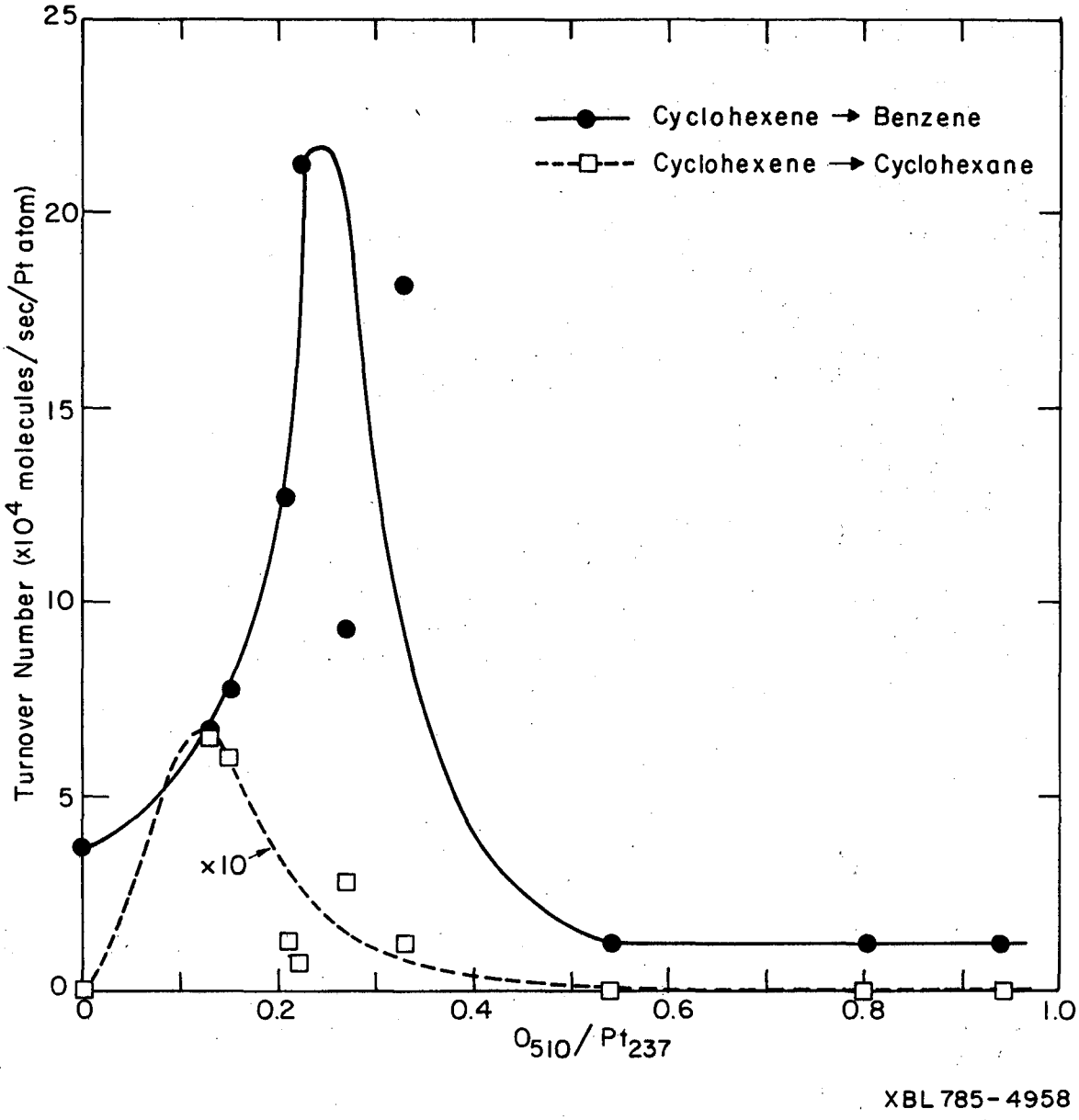
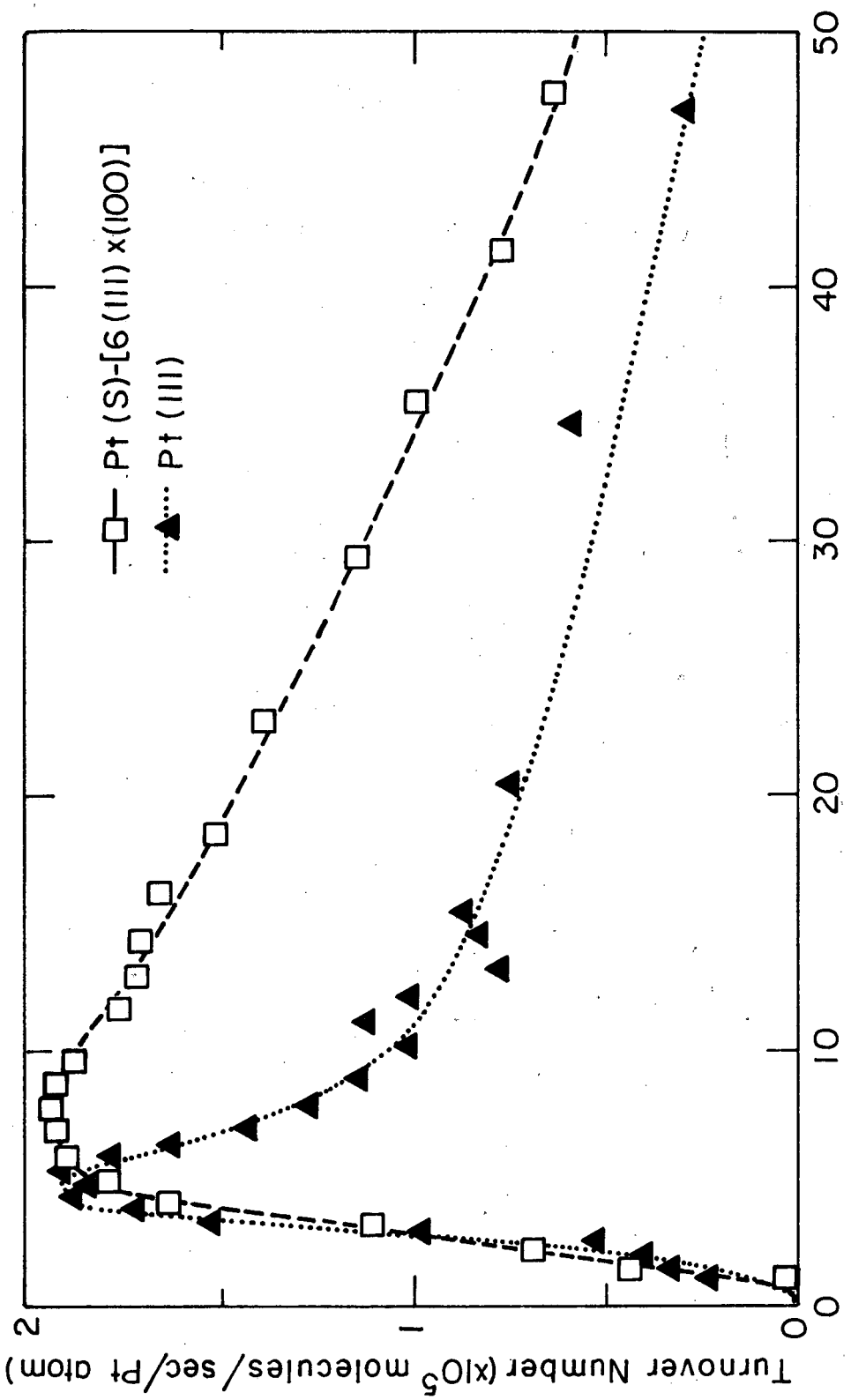
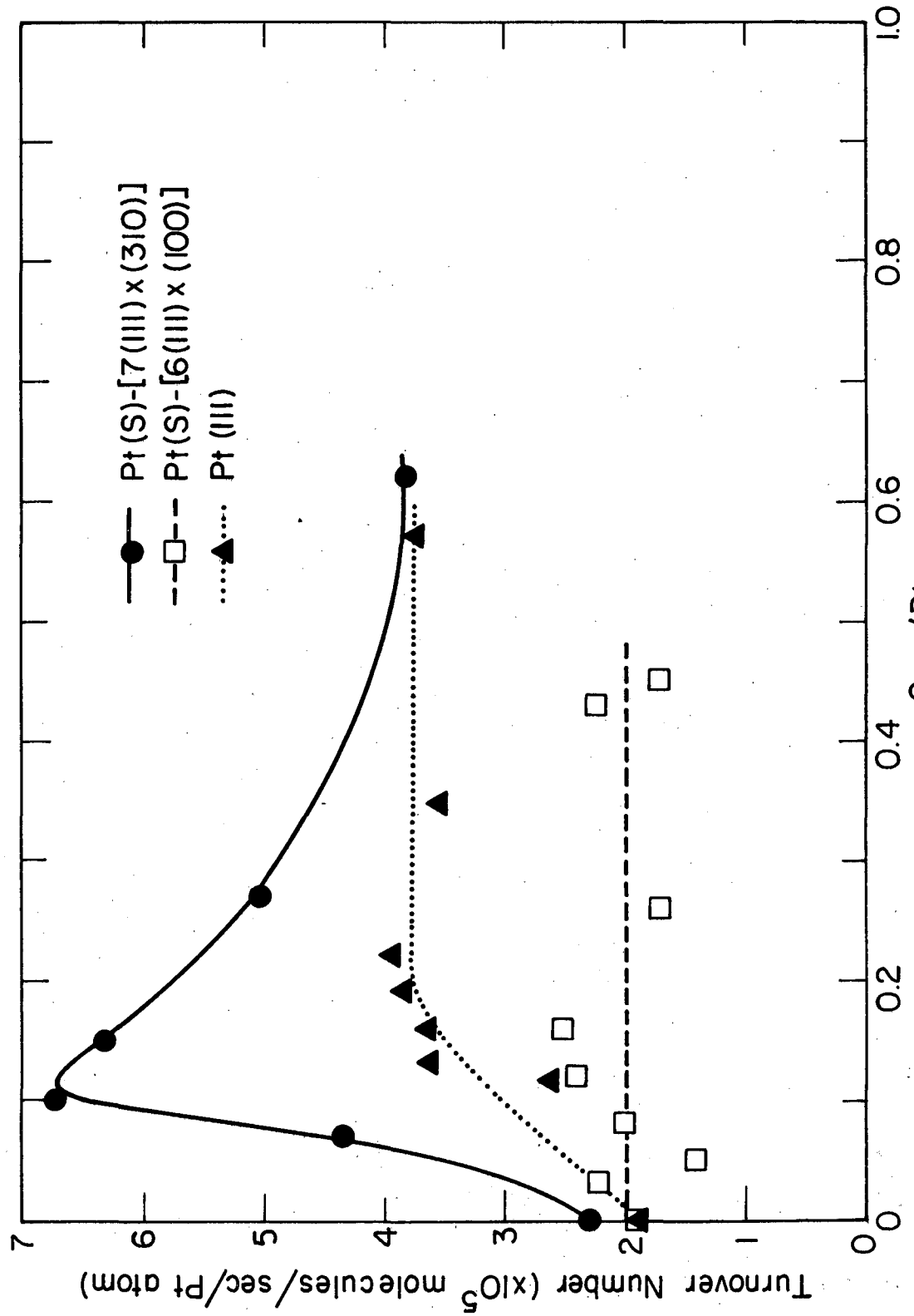

Cyclohexene → Benzene
Cyclohexene → Cyclohexane
Turnover Number (x10⁴ molecules/sec/Pt atom)
O510/Pt237
x10
0
5
10
15
20
25
0.2
0.4
0.6
0.8
1.0
XBL 785-4958

Figure 8



XBL 785-4955

Figure 9



XBL785-4957

Figure 10

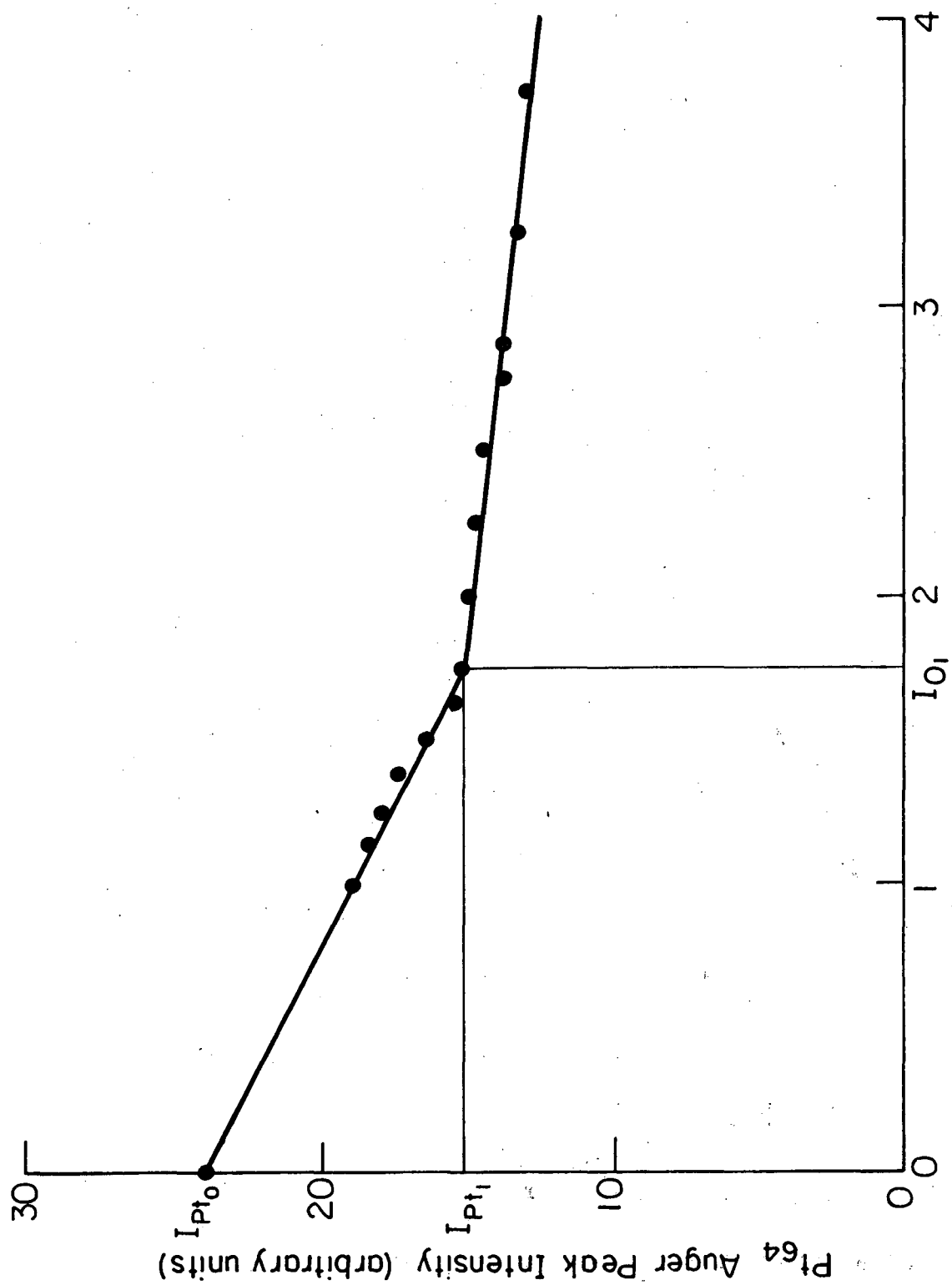


Figure 11

U.S.GPO:1978-789-158/(F)12

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