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METHYLCYCLOPENTANE CONVERSION OVER PLATINUM SINGLE CRYSTAL  
SURFACES: EVIDENCE FOR THE CYCLIC MECHANISM OF n-HEXANE ISOMERIZATION

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Abstract

The surface structure and temperature dependence of methylcyclopentane conversion was investigated near atmospheric pressure at 540-650K over four platinum single crystal surfaces with flat (100) and (111), and stepped (332) and (557) orientations. The atomic structure and surface composition of the active catalysts were determined before and after reactions using low energy electron diffraction and Auger electron spectroscopy.

Selective ring opening to produce 2- and 3-methylpentanes readily occurred on both flat surfaces studied, the (111) and the (100). The rate of formation of methylpentanes was found to be nearly 3.5 times faster on the (100) surface than on the (111) surface. The presence of steps on the platinum surface had no significant effect on the rates of ring opening or aromatization since these line defects were quickly covered with carbonaceous deposits as shown by carbon monoxide titration of the active sites.

Methylcyclopentane and n-hexane yield the same distribution of isomers (2- and 3-methylpentanes), and the activation energy for the formation of these products from both n-hexane and methylcyclopentane are identical within experimental error. These results indicate that the formation of methylcyclopentane on the platinum surface is an intermediate step for the isomerization of n-hexane.

The formation of benzene from methylcyclopentane was found to be much slower than it is from n-hexane on these platinum single crystals. This suggests that platinum alone cannot catalyze the ring opening of methylcyclopentane. Additional sites, like those found on alumina supported platinum, are required for this reaction to occur.

### Introduction

The reaction of methylcyclopentane with hydrogen has been extensively studied over different types of platinum catalysts [1-18]. Methylcyclopentane is a particularly interesting reactant because its ring opening is highly sensitive to changes in the surface structure [4]. Furthermore, an investigation of the mechanistic details for this reaction can give a better understanding of the isomerization of longer chain alkanes (6 carbon atoms or longer) as it is believed that methylcyclopentane is the intermediate from which the C<sub>6</sub> isomers are produced [19,20]. Gault and coworkers have studied the effect of particle size on the product selectivity [2-10]. They concluded that there are at least two types of carbon-carbon bond breaking processes operating simultaneously: a non-selective mechanism occurring predominantly on highly dispersed catalysts, and a second one, involving only secondary carbon atoms, occurring mainly on particles 20Å in diameter or larger. Kramer et.al. [14-16] have performed experiments which indicate that the differences in selectivity with particle size may be due to changes in the interface between metal and support. Other factors alter these reactions as

well: the acidity of the support, for example, seems to have no effect on hydrogenolysis selectivity, but it is a crucial factor for benzene formation [17,18]. Paal et al. [11-13] have also shown that hydrogen partial pressure (or surface coverage) considerably affects the selectivity of these processes.

In the present work the structure sensitivity of methylcyclopentane conversion was investigated over several platinum single crystals. The kinetic parameters for the reactions were measured over the flat Pt(111) and Pt(100), and the stepped Pt(332) and Pt(557) surfaces. An investigation of the ring opening, hydrogenolysis, and aromatization of methylcyclopentane show no significant differences in either activity or selectivity among the (111), (332), and (557) surfaces, all of which have terraces of the (111) orientation. A selective ring opening mechanism was predominant, giving 2- and 3-methylpentanes as the major products. Although the Pt(100) surface displayed higher activity for methylcyclopentane conversion at 300 K, the activation energies were similar to those for Pt(111). The similarities found between methylcyclopentane ring opening and n-hexane isomerization suggests that n-hexane isomerizes mainly through a five membered cyclic intermediate. Very little aromatization to benzene was observed on all surfaces studied. The benzene yield was found to be significantly greater from n-hexane than it was from methylcyclopentane, which proves that n-hexane aromatization does not proceed through the formation and enlargement of a five membered ring over the metallic surface.

## Experimental

All of the experiments were carried out in an ultra-high vacuum (UHV) high pressure apparatus designed for combined UHV surface analysis and high pressure studies using small area catalyst samples, as described in detail in a previous publication [21]. This system is equipped with four grid electron optics for low energy electron diffraction (LEED) and Auger electron spectroscopy (AES) experiments, an ion gun for crystal cleaning, a quadrupole mass spectrometer, and a retractable internal isolation cell that constitutes part of a microbatch reactor in the  $10^{-2}$ -10 atm pressure range. The reaction cell and external recirculation loop were connected to an isolatable pressure gauge, a stainless steel bellows pump for circulation of the gases, and a gas chromatograph sampling valve. Hydrocarbon conversion was monitored with an HP3880 gas chromatograph equipped with two columns switched by a pneumatic valve for alternative sample analysis: a 5% TCEP on Chromosorb C column for benzene detection, and a 0.19% picric acid on Carbopack for the rest of the analysis.

Platinum single crystals (99.998% purity) were cut to within 1° degree of the (100), (111), (332), and (557) orientations using standard procedures. Idealized atomic surface structures for these crystals are shown in Fig. 1. The resulting thin discs (~0.5 mm thick) had about 1.5 cm<sup>2</sup> total area, of which less than 30% was polycrystalline (the edges of the crystal and the supporting platinum wires). The crystal was spot-welded to a rotatable manipulator by



using a series of platinum, gold and copper supports which enabled the crystal to be heated to 1400 K without significant heating of any other part of the system [22]. One of the gold wires was also in contact with an electrically isolated liquid nitrogen reservoir so the sample could be cooled below 150K in less than five minutes. Both faces of the single crystal disks were cleaned by repeated argon ion sputtering, oxygen treatment, and annealing, until a well-defined LEED pattern was observed, and no impurities were detected by AES. Research purity methylcyclopentane (Phillips, 99.96%) was outgassed by repeated freeze-pumping cycles at 77 K before use. Hydrogen (Matheson, 99.99% purity) was used as supplied.

In order to perform high pressure experiments, the reaction cell was closed, enclosing the clean crystal within the high pressure loop. Methylcyclopentane and hydrogen were sequentially introduced to the desired pressures. Circulation was then started and the crystal was heated to the reaction temperature. The whole process took about 2-3 minutes. The reaction temperature was continuously regulated to within  $\pm 2$  K with a precision temperature controller and a chromel-alumel thermocouple spot-welded to either the edge or to one face of the crystal. The temperature calibration was carefully checked by using an isobutane-isobutene equilibrium mixture [23].

The product formation was followed by periodic analysis using gas chromatography. After completion of the reaction, the crystal was cooled to room temperature, the loop evacuated to below  $10^{-3}$  torr with a sorption pump, and the cell opened to expose the sample to

ultra-high vacuum. The state of the surface was examined with LEED, AES, and thermal desorption spectroscopy (TDS), either monitoring  $H_2$  (2 amu) evolution or performing CO titrations [24].

### Results

Methylcyclopentane (MCP) conversion was studied over the flat Pt(111) and Pt(100), and the stepped Pt(557) and Pt(332) single crystals. The reactions were usually performed at 573 K and 20 torr of MCP and either 200 or 600 torr of  $H_2$  unless otherwise indicated. Typical product accumulation curves obtained as a function of time are shown in Fig. 2. The main products were 2- and 3-methylpentane (2MP and 3MP), with some n-hexane (n-H), methane ( $CH_4$ ) and cyclopentane (CP). Very little benzene and other light alkanes were also detected. Accumulation curves for 3MP and n-H over the Pt(111), Pt(557) and Pt(332) surfaces studied are shown in Fig. 3. They displayed similar activities. Initial reaction rates at 573K were determined by the slope of such curves at the start of the runs and are summarized in Table 1 for the four surfaces. They were accurate to about  $\pm 30\%$ .

The temperature dependence was determined for hydrogenolysis and aromatization reactions over Pt(111) and Pt(100) at a total pressure of 220 torr [25]. Examples are shown in Fig. 4. Benzene and 2- and 3-methylpentane formation rates were lower than those expected from Arrhenius behavior at high temperatures. Activation energies were calculated for the Pt(111) and Pt(100) surfaces from the low

temperature region, and the following values were obtained in Kcal/mole: 15-16 for 2- and 3-methylpentane, 14-18 for methane, 25-26 for hydrogenolysis products  $C_2-C_5$ , and around 30 for benzene. (See Table 2). A negative order on hydrogen partial pressure was observed for 2- and 3-methylpentane formation [25].

A continuous decrease in activity was observed with time for most products (Fig. 2), the deactivation resulting from the formation of strongly chemisorbed carbonaceous deposits which covered a significant fraction of the surface. The fraction of bare platinum remaining after methylcyclopentane experiments was determined by CO titration [24], and the amount of CO binding to the surface was found to decrease with increasing reaction temperature (Fig. 5). The steps of the Pt(332) and (557) surfaces were always found to be covered by carbon deposits as CO titrations performed after reactions never displayed the high temperature shoulder characteristic of CO thermal desorption from clean stepped surfaces [25,28]. In addition, the surface carbon remaining after reaction was found to increase with increasing reaction temperature as determined by Auger electron spectroscopy [26] (Fig. 5). These results show that at higher temperatures more carbon was irreversibly bound to the surface, and that there was a corresponding reduction in the area of uncovered metal. All surfaces studied showed a similar carbon concentration following reactions for a given temperature. Similar observations were reported for n-hexane conversion [27]. Further characterization of the hydrocarbon overlayer was carried out after reactions by applying a linear heating ramp to

the platinum crystal and recording the 2 amu thermal desorption spectrum which was generated by the thermal decomposition of the carbonaceous overlayer [25]. The hydrogen desorption spectra obtained were characterized by two broad peaks centered around 460 and 700 K on the (111) terraces. The contribution from the first peak diminished relative to that from the 700 K peak at higher reaction temperatures. The total H<sub>2</sub> yield from TDS increased when higher H<sub>2</sub> pressures were used for the reaction. On Pt(100), three peaks were observed at 430, 560 and 640 K, and the relative area of the two low temperature peaks decreased at the expense of the 640 K peak as the reaction temperature was increased.

### Discussion

The present paper is mainly directed towards the study of the dependence of methylcyclopentane conversion rates on the atomic structure of the metal catalyst. Although extensive work has been performed on supported catalysts, no definite conclusions have been obtained, mainly due to the lack of knowledge of the metal structure in the practical catalysts. By using single crystal surfaces, two major components of the structure sensitivity of the reaction rate can be observed: 1) the activity between low (step and kink) and high (terrace) coordination atoms can be differentiated; 2) differences among the different close-packed terrace surfaces can be measured. In the present report we have used the stepped Pt(332) and Pt(557) surfaces, both having terraces in the (111) orientation, for the study

of activity on steps, and Pt(111) and Pt(100) surfaces for the analysis of changes due to the geometry of Pt atoms on the terraces.

New information about the structure sensitivity of methylcyclopentane conversion has been obtained. The MCP reactions over flat Pt(111), and stepped Pt(557) and Pt(332) surfaces did not exhibit significant differences in activity under our experimental conditions. These three surfaces have (111) terraces, and our results show that flat bare surface, and not the steps, are important for the MCP conversion. Furthermore, CO titration experiments indicate that steps on the catalyst surfaces become covered and deactivated by the carbonaceous deposits soon after the reaction is started, thereby inhibiting the reactivity of the steps under our reaction conditions. The deactivation of the steps was also observed during n-hexane conversion on the same surfaces [23-25, 28].

MCP conversion was faster on Pt(100) than on Pt(111). This result is in agreement with those obtained for several other light alkanes [23] where isomerization was always 3-5 times faster on Pt(100) as compared to Pt(111). However, activation energies were similar for the different reactions over both surfaces. This suggests that the differences in activity are in the pre-exponential factor and are possibly due to geometric effects.

The product distribution for MCP conversion over all three surfaces indicated that carbon-carbon bond breaking occurs selectively between secondary carbons, that is between carbon atoms with two hydrogen atoms bonded to them. The main reaction products were 2- and 3-methylpentane; very little n-hexane, cyclopentane, or methane was formed. Similar results have been obtained over low dispersion supported catalysts [2,5,9,10,13,14,15,20]. Such a product distribution has been attributed to a selective ring opening mechanism for methylcyclopentane. Because this mechanism requires two secondary carbons and since a negative order in hydrogen pressure is observed for methylpentane formation, it has been suggested that the reaction intermediate is a highly dehydrogenated species, probably an  $\alpha\alpha\beta\beta$  tetraadsorbed moiety. Furthermore, while the 3-methylpentane production rate decreases with reaction time, 2-methylpentane is formed at a nearly constant rate for at least two hours (Fig. 2) over the Pt(111) surface. The 3MP/2MP ratio shown in Fig. 6 changes with reaction time from an initial value of 10 reaching a steady state value of 0.5 after about two hours. This indicates that there may be an additional mechanism for selective ring opening requiring specific

sites that are quickly covered by the carbon deposits during the first minutes of reaction. The combination of the two selective mechanisms are required to explain both the selectivity towards 2MP and 3MP over n-hexane and the change of the 3MP/2MP ratio with time. Additionally, the differences in activation energies indicate that pathways for 2MP and 3MP ( $E_a = 15$  Kcal/mole) are different than those for n-hexane, cyclopentane, and methane formation ( $E_a = 18-19$  Kcal/mole for CP and methane formation).

Multiple carbon-carbon bond scission resulted in the production of small alkanes having less than six carbon atoms, and this process produced less than 10% of the total hydrocarbon products formed on all the surfaces studied although the Pt(100) displayed rates ~30 times higher than the Pt(111). The rates of formation of methane and CP were very close on the Pt(111) surface, but the rate of formation of methane over the Pt(100) surface more closely correlated with the formation of n-pentane. The breaking of one bond is predominant for MCP over the four surfaces studied. This effect has also been observed for other hydrocarbons on the same platinum surfaces [23].

Only small amounts of benzene were produced, indicating that platinum alone is not a good catalyst for ring enlargement or aromatization. A higher benzene yield has been obtained from n-hexane [27]. It has been shown that both the dehydrogenation properties of platinum and the acidic sites found on some supported platinum catalysts are needed for this reaction to occur [17,18].

One possible mechanism that has been suggested is that MCP molecules dehydrogenate over platinum followed by ring enlargement over acidic sites on the support through a carbonium ion intermediate. This implies that benzene formation from n-hexane over platinum, which is readily observed in single crystal studies, does not proceed via a five member cyclic intermediate as does isomerization, but rather proceeds through a direct 1-6 ring closure. Dautzenberg and Platteeuw [34,35] reached a similar conclusion based on the fact that while n-hexane produces both MCP and benzene, 2-methylpentane only produces MCP over the same catalyst. Sinfelt and collaborators [36] using n-heptane, and Davis et al. [37], using larger hydrocarbons, observed the same behavior. On the other hand, Gault and co-workers [38] and Davis [39,40] used labelled compounds to conclude that some 1,5 ring closure was important for the production of aromatic compounds.

All the preceding arguments lend further insight into the mechanism of hydrocarbon isomerization. Light alkanes isomerize by a bond-shift mechanism, but hydrocarbons with chains longer than five carbon atoms can alternatively isomerize through a five or six member ring intermediate [19,20,29-31]. Gault et al. have used  $^{13}\text{C}$  labelled compounds to prove that for most platinum catalysts, this cyclic mechanism is predominant for heavy hydrocarbons isomerization [19,32]. Several pieces of evidence suggest that this is also true in our case. For example, the change in the 2- and 3-methylpentane ratio as a function of reaction time for methylcyclopentane ring opening parallels the same trend obtained for n-hexane isomerization (Fig. 6). Also,



n-hexane and MCP were found to block the steps of stepped platinum surfaces, and at the reaction conditions employed, it was found that n-hexane isomerization [25,28] and MCP ring opening take place on surface terraces, and not on kink or step sites. Finally, the temperature and hydrogen pressure dependence for isomerization and MCP formation from n-hexane are very similar [25,27,33]. In conclusion, n-hexane isomerization over platinum single crystal surfaces seems to proceed preferably via a five membered ring intermediate, i.e., a cyclic mechanism that takes place on the close packed terraces of the metal with no appreciable dependence on surface defect concentration. Similar conclusions have been reported for low dispersion platinum catalysts where selective carbon-carbon bond breaking is the predominant mechanism [2,3,4,10]. The same studies concluded that there is bond-shift contribution to the total isomerization activity over catalysts with large metallic particles. The structure sensitivity reported by the French group suggests two parallel trends as the particle size increases; a transition from non-selective to selective ring opening, and an increased importance of bond-shift for isomerization [3]. However, recent experiments by Kramer et al. indicate that the structure sensitivity observed could be attributed to the metal-support boundary [15,16]. By independently varying the interface area for the same catalyst dispersion, they concluded that selective ring opening of MCP could be assigned to the platinum metal, while the non-selective bond scissions are catalyzed by the sites at the platinum-support interface. Their conclusion is consistent with our findings of only selective ring opening over the platinum single crystal surfaces.

Garin and co-workers have recently studied hydrocarbon reforming over platinum (111), (119), and (557) single crystal surfaces [3]. They conclude that the cyclic mechanism for isomerization accounted for 80% or more of all isomerization products in most cases. They also reported some structure sensitivity in which the bond-shift mechanism became most important over the Pt(557) crystal. Their explanation was based on a surface reconstruction that takes place under high pressures of hydrogen. We have not observed such reconstructions in our laboratory, but CO titrations indicate that even if the reconstruction does occur, it should not alter the reactivity of the surface since carbonaceous deposits block all low coordination platinum atoms at steps and kinks. Most of their methylcyclopentane ring opening results qualitatively agree with ours: the product distribution indicates the predominance of 2- and 3-methylpentane as major products, some n-hexane and cyclopentane production, and very small amounts of benzene. Perhaps the reconstruction observed by the French group was due to the presence of small amounts of sulfur on the surface, as has been observed by Bernasek [41].

In summary, we conclude that methylcyclopentane ring opening on Pt single crystals proceeds through a selective bond breaking mechanism and that it occurs preferentially over the flat (111) and (100) terraces because the steps and other defects are blocked by carbonaceous deposits. N-hexane isomerization proceeds through a five membered cyclic intermediate (MCP), but it appears that such a pathway is not important for aromatization reactions over the unsupported metal.

### Acknowledgements

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Table 1

Initial reaction rates for methylcyclopentane conversion over  
platinum single crystal surfaces.

T=573 K,  $P_{\text{MCP}}=20$  Torr,  $P_{\text{H}_2}=600$  Torr

TF ( $\times 10^{-4}$  molec/Pt atom  $\cdot$  S)<sup>a</sup>

Surface	2MP + 3MP	n-H	CP	CH <sub>4</sub>	$\Sigma\text{C}_6$	Bz
Pt(100)	7100	280	5	8	35	-
Pt(111)	2100	200	2	7	1	10
Pt(557)	3200	150	5	6	-	30
Pt(332)	2500	130	2	3	-	-

- a) Turnover frequency. 2MP  $\equiv$  2-methylpentane, 3MP  $\equiv$  3-methylpentane, n-H  $\equiv$  n-hexane, CP  $\equiv$  cyclopentane,  $\Sigma\text{C}_6$   $\equiv$  multiple hydrogenolysis, Bz  $\equiv$  benzene.

Table 2

Activation energies for methylcyclopentane conversion over  
Pt single crystal surfaces.

$P_{\text{MCP}} = 20 \text{ Torr}$ ,  $P_{\text{H}_2} = 200 \text{ Torr}$

Reaction	$E_a$ (Kcal/mole)				
	2MP + 3MP	CP	CH <sub>4</sub>	$\Sigma\text{C}_6$	Bz
Pt(111)	15	19	18	25	$\geq 30$
Pt(100)	16	-	14	26	-

Figure Captions

Fig. 1: Idealized atomic structures for platinum single crystal surfaces.

Fig. 2: Product accumulation curves measured as a function of reaction time at 573 K for methylcyclopentane conversion over Pt(557).

$$P_{\text{MCP}} = 20 \text{ Torr and } P_{\text{H}_2} = 600 \text{ Torr.}$$

Fig. 3: Product accumulation curves measured as a function of reaction time at 573 K for 3-methylpentane and n-hexane formation from methylcyclopentane over platinum single crystal surfaces. Same conditions as Fig. 2.

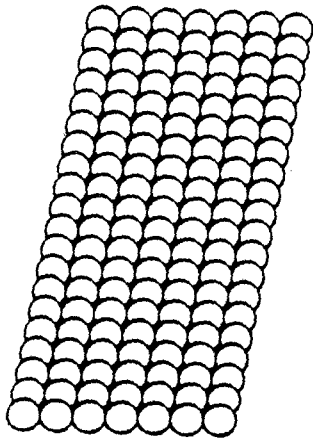
Fig. 4: Arrhenius plots for methylcyclopentane conversion over Pt(111).  $P_{\text{MCP}} = 20 \text{ Torr, } P_{\text{H}_2} = 200 \text{ Torr.}$

Fig. 5: Temperature dependence of the C/Pt atomic ratio and fraction of uncovered platinum surface measured following methylcyclopentane reaction studies over Pt(111) and Pt(100) single crystals.

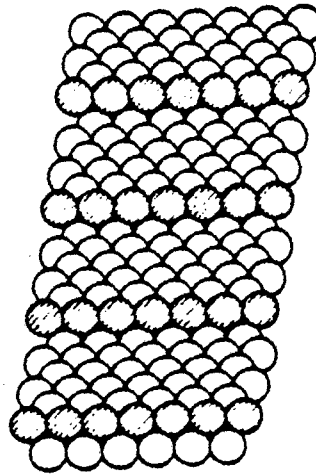
Fig. 6: 2- to 3-methylpentane ratio as a function of reaction time from n-hexane isomerization (left frame) and methylcyclopentane hydrogenolysis (right frame) reaction studies over Pt(332) single crystal surfaces. The ratio of reaction rates is also shown for the methylcyclopentane case.

$$P_{\text{MCP}} = 20 \text{ Torr, } P_{\text{H}_2} = 600 \text{ Torr, and } T = 573 \text{ K.}$$

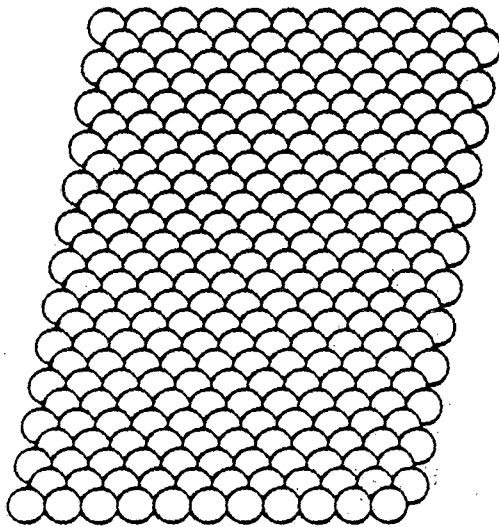




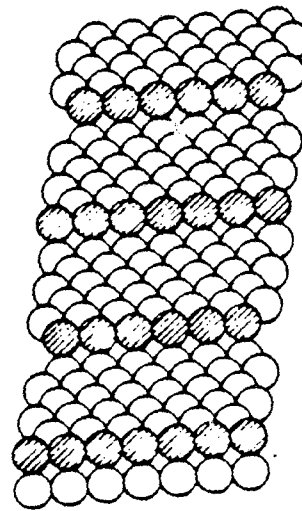
fcc (100)



fcc (111)



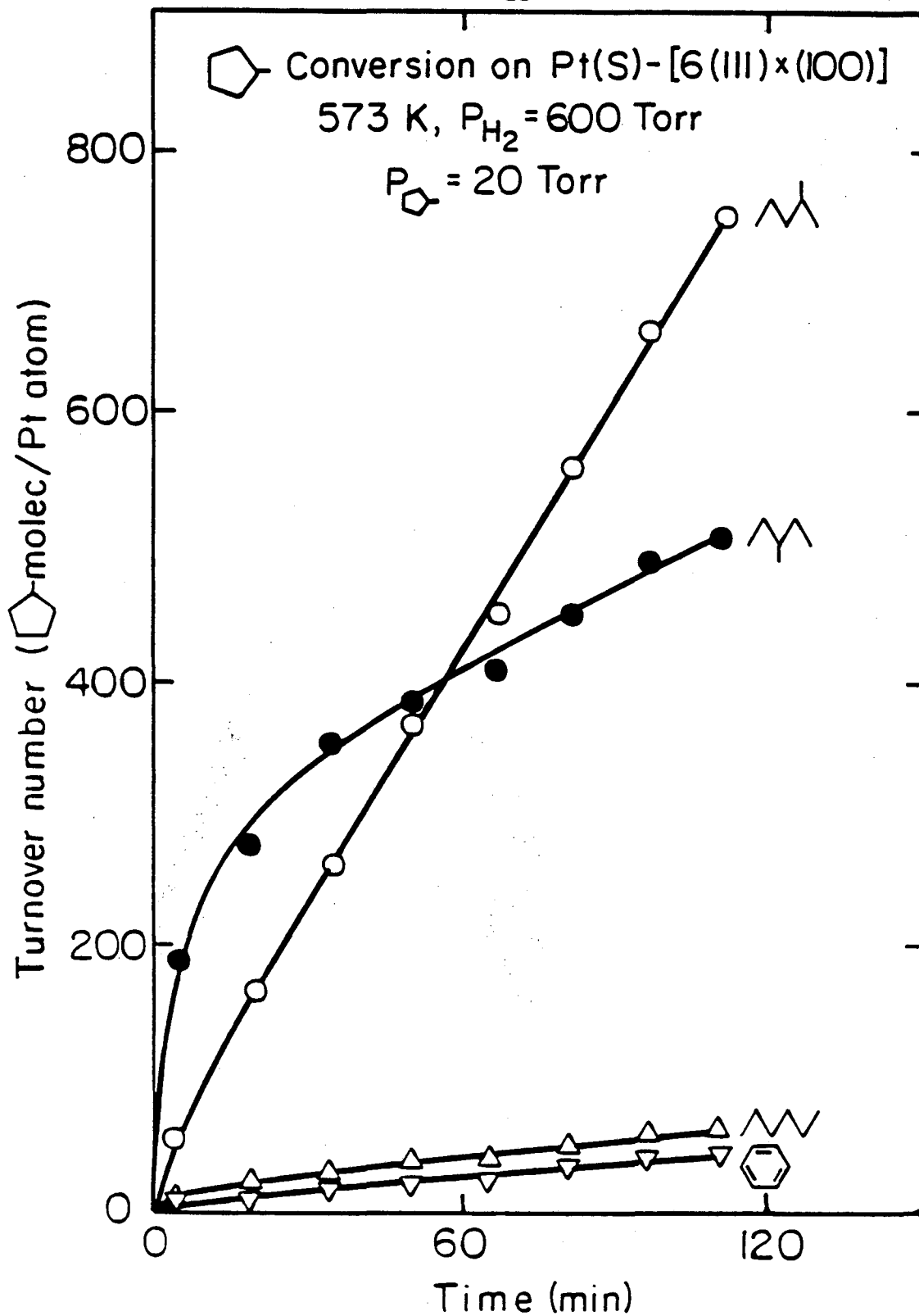
fcc (111)



fcc (111)

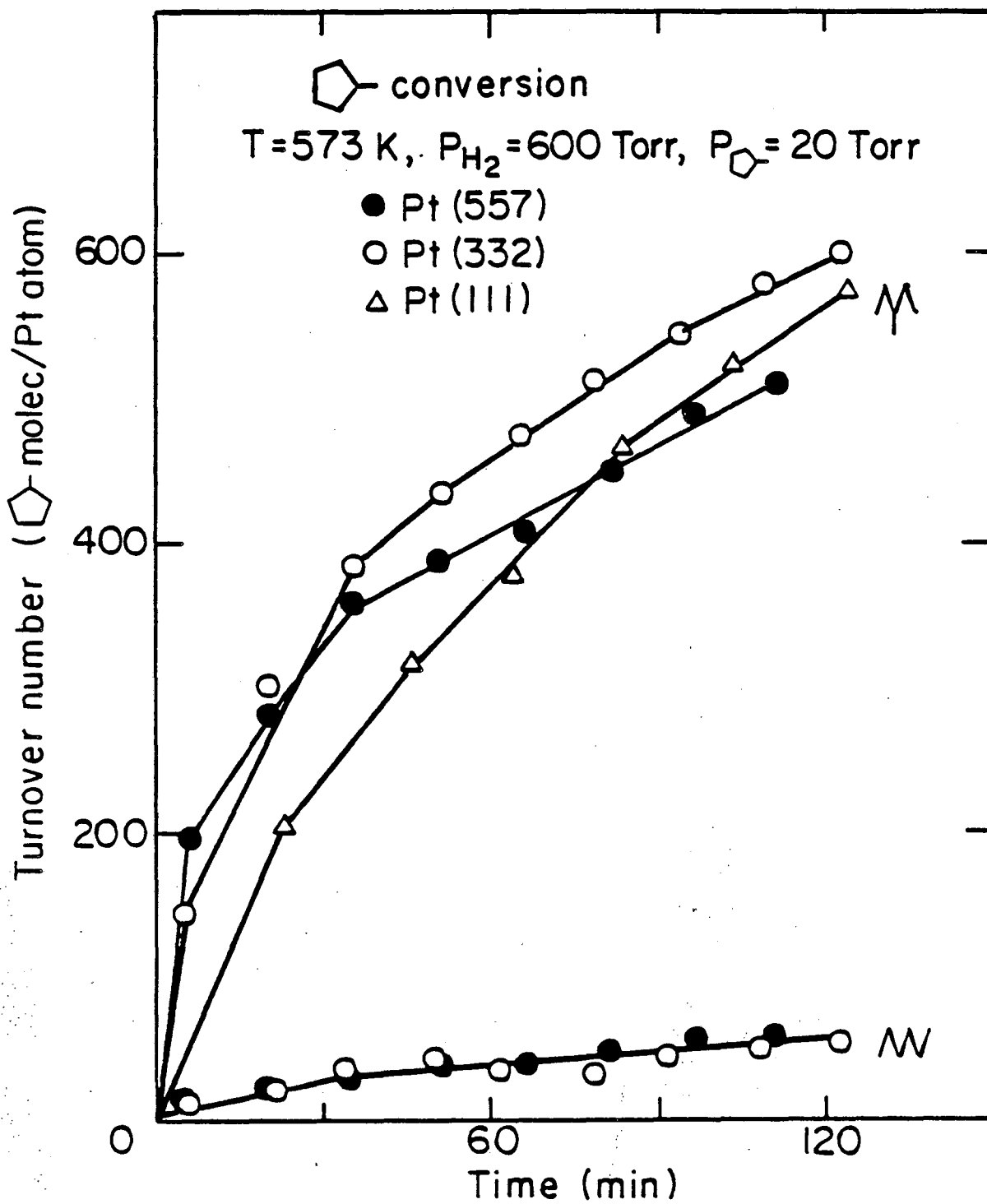
XBL 819-2032C

Fig. 1



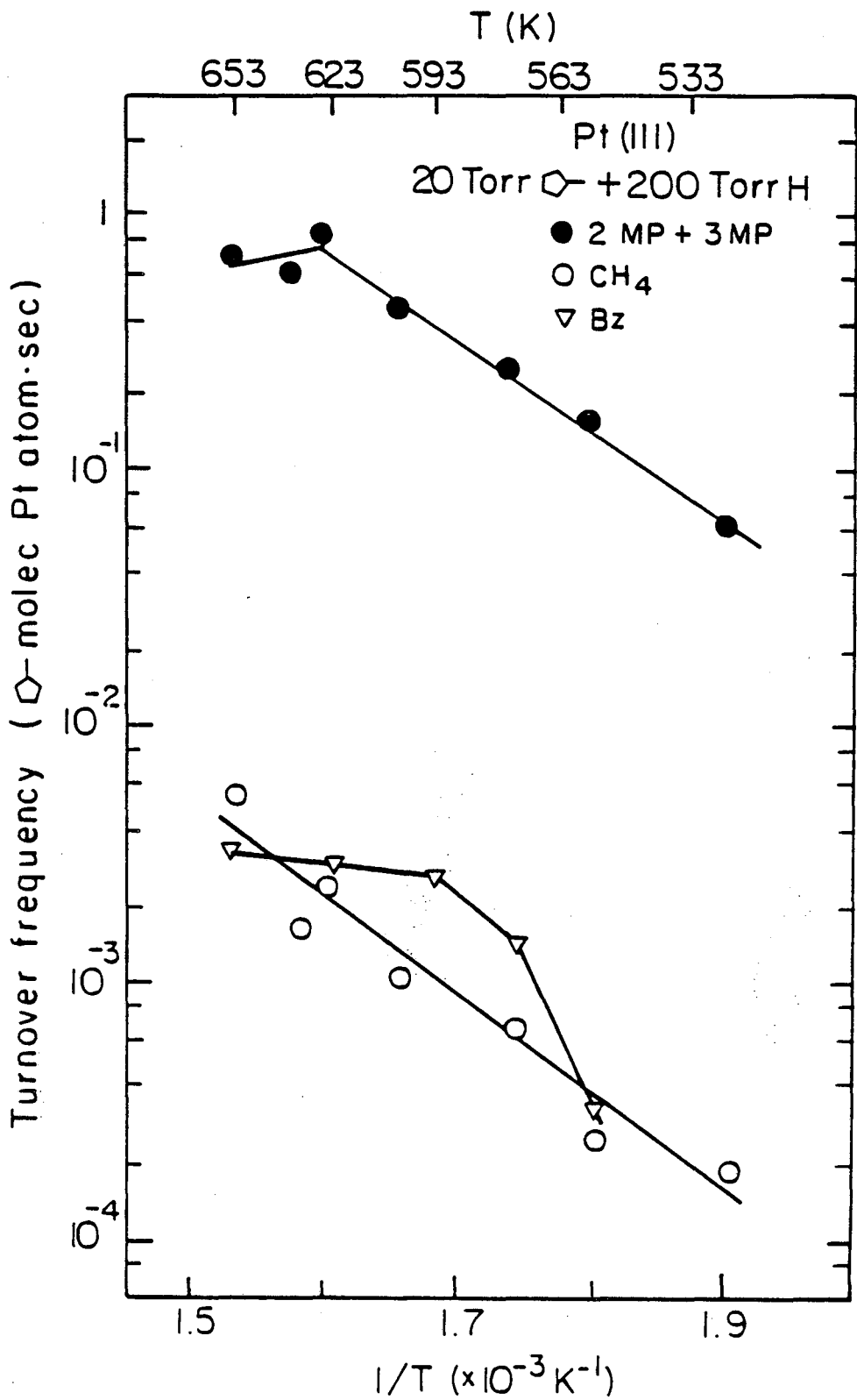
XBL 845 - 6955 A

Fig. 2



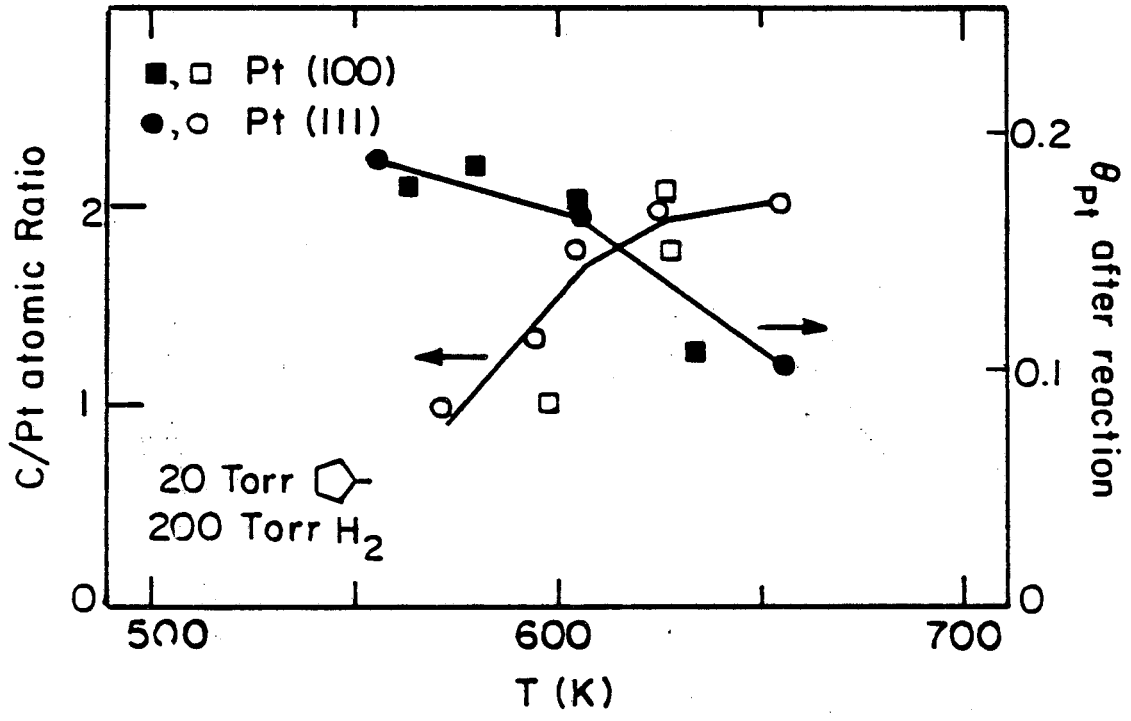
XBL 846-7055

Fig. 3



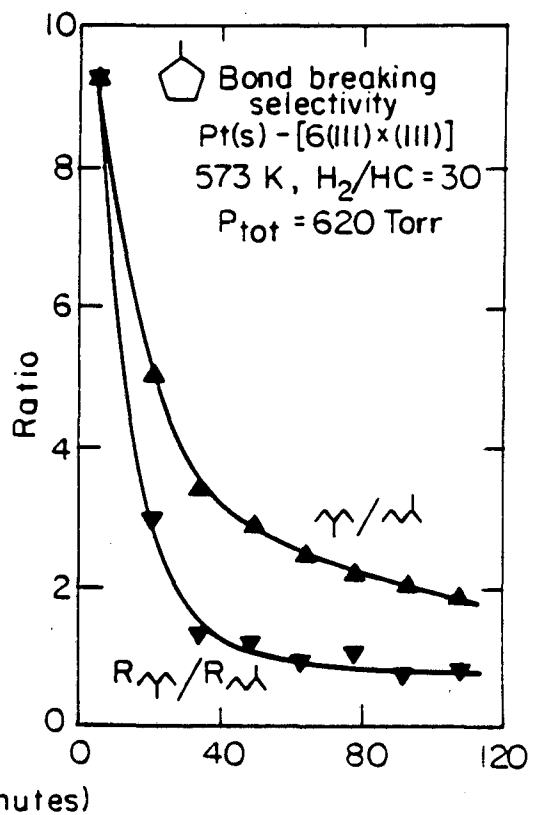
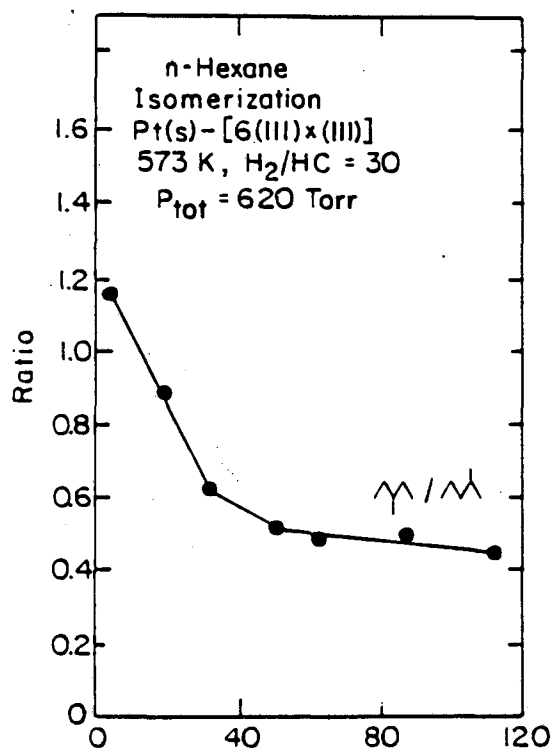
XBL 8412-5857

Fig. 4



XBL 846-7053

Fig. 5



XBL819-65408

Fig. 6

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