

## The Effect of Gold on Hydrogenolysis, Isomerization, and Dehydrocyclization Reactions on Polycrystalline Platinum and Iridium Foils

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Received August 21, 1975

The effect of the addition of gold to polycrystalline platinum and iridium foil samples on the initial reaction rates for the hydrogenolysis of propane, isobutane and *n*-heptane, the isomerization of isobutane, and the dehydrocyclization of *n*-heptane to toluene has been studied. These studies were carried out on samples of area  $\sim 1$  cm<sup>2</sup> cleaned and maintained under UHV (ultrahigh vacuum) conditions and in a 5:1 hydrogen to hydrocarbon ambient at a total pressure in the 10<sup>-4</sup>-Torr range. Mass spectroscopy was used to monitor the reactions in a temperature range of 100-500°C. The platinum-gold and iridium-gold samples were prepared by evaporating several monolayers of gold on the cleaned surfaces and annealing under vacuum until the desired surface concentration of gold was obtained as determined by Auger electron spectroscopy. The nature of the resulting surfaces was further studied by chemisorption of carbon monoxide.

The rates of hydrogenolysis and isomerization on the pure platinum and iridium surfaces were found to be within a factor of 5 of the corresponding rates measured by others at higher pressures (48 Torr-1 atm), suggesting that the hydrogen to hydrocarbon ratio is more important to the rates than absolute pressure. Absolute pressure was found to play a more important role in dehydrocyclization where a two-order-of-magnitude difference in the rate on platinum was observed between the low pressure studies described in this paper and the high pressure studies carried out by others. Platinum was found in general to be more active for hydrogenolysis and isomerization while iridium was the more active for dehydrocyclization. Time-dependent poisoning of the rates, the existence of a rate maximum as a function of temperature, and the predominance of low molecular weight hydrogenolysis products are attributed to the lower hydrogen pressures used in this work.

The addition of gold to the platinum and iridium surface decreases the rates for all reactions studied. An approximately linear decrease in isomerization rate as a function of gold coverage was observed while hydrogenolysis and dehydrocyclization decreased in a similar fashion with each other and much more rapidly than isomerization. Thus the selectivity for isomerization as compared to hydrogenolysis is increased with increasing gold coverage while little change is expected for dehydrocyclization. These results coupled with differences in the time-dependent poisoning of the various reactions suggest that different surface sites are responsible for isomerization than for hydrogenolysis and dehydrocyclization.

### INTRODUCTION

Alloys and other multicomponent metal systems are being used with increasing frequency as catalysts for a variety of hydro-

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carbon reactions (1). Their outstanding features are (1) improved selectivity for multiple path reactions, (2) improved activity, and (3) better resistance to deactivation (2). It is hoped that by understanding the surface science of catalysis on these

systems one may develop new catalysts that are either less costly or more active and selective than the single metal component systems. Finding substitutes for or improving the catalytic behavior of metals such as platinum and iridium is particularly important due to their cost and scarcity. The effect of multicomponent metal systems on catalytic reactions has been extensively studied and several review articles (2-4) have been written that deal with this subject.

The addition of a catalytically inactive metal such as copper, silver, or gold of the Ib group of the periodic table to an active metal, e.g., a member of the 8 group, dramatically alters the selectivity of the active component towards such reactions as hydrogenolysis, isomerization, dehydrocyclization, and hydrogenation/dehydrogenation, some or all of which can take place simultaneously (2). In general, it has been found that on surfaces such as supported nickel-copper (5) and nickel-copper powders (6), supported palladium-gold (7), and platinum-gold (7,8), evaporated films of iridium-gold (9), and others (2), hydrogenolysis activity is quenched much more rapidly than isomerization, hydrogenation/dehydrogenation, or deuterium exchange, leading to the conclusion that reactions involving C-C bond scission are more inhibited than those involving C-H bond scission on the addition of a second, inactive metal to the pure catalyst (2,6). Both geometrical and electronic factors have been proposed to explain the observed behavior (10). However, quantitative conclusions are difficult to make because of uncertainties (both geometrical and compositional) of the nature of the surfaces studied. The geometrical structure of the surface and the presence of defects of various kinds also play an important role in catalytic selectivity, as has been verified in this laboratory (11-13) and in others (14). Thus it is desirable to employ surfaces that

are as well defined as possible in studies of this nature.

These considerations have motivated the present work involving studies of the hydrogenolysis of propane, isobutane, and *n*-heptane; the isomerization of isobutane to *n*-butane; and the dehydrocyclization of *n*-heptane to toluene on pure polycrystalline foils of platinum and iridium and as a function of gold concentration on these samples. The bimetallic surfaces were formed by depositing gold on the platinum or iridium substrates from an *in situ* source and annealing in ultrahigh vacuum to obtain the desired gold concentration as determined by Auger electron spectroscopy. Chemical titration of carbon monoxide on the platinum-gold surface was carried out to determine its nature further. Following the determination of reaction rates at a certain gold concentration, the surfaces could be rendered gold-free by heating to high temperatures in preparation for similar studies at a different concentration. This technique has the advantage of being able to explore the catalytic behavior rapidly as a function of gold concentration because of the ease of preparation. Several different platinum and iridium samples were used in this investigation. Mass spectrometry was used to monitor the reactivity of these surfaces as a function of gold concentration at low reactant pressures ( $3 \times 10^{-4}$  Torr). Surface cleanliness was insured by employing ultrahigh vacuum (UHV) techniques.

It has been shown previously (11-13) that one may study catalytic reactions of low reaction probability on surfaces of area not larger than 1 cm<sup>2</sup> at low pressures or at high pressures using mass spectrometry or gas chromatography, respectively, to detect the reaction products. We have also used samples of small area in the present study and were successful in determining product distributions, turnover numbers, and their changes with surface gold concentration.

## EXPERIMENTAL

*Apparatus and Materials*

The experiments were carried out in a modified ion-pumped, Varian, LEED-Auger, UHV system. Base pressures in the low  $10^{-9}$ -Torr range were obtained following bakeout of the system at 250°C. Background gases consisted mainly of hydrogen, carbon monoxide, and small amounts of argon, carbon dioxide, and water. Total pressures were measured by a Varian nude ionization gauge and partial pressure by an EAI quadrupole mass spectrometer. The mass spectrometer was also used to monitor the partial pressure of the reactant and product gases during the experiments and was calibrated by the ionization gauge. Both the mass spectrometer ion source and ionization gauge were equipped with thoriated-iridium filaments to minimize interaction with the ambient gases. Auger electron spectroscopy was employed to monitor surface composition. Auger electrons were excited by a glancing incidence electron gun and energy analyzed and collected by the four-grid LEED optics according to established techniques (15).

The platinum and iridium samples, each having total area of about 1 cm<sup>2</sup>, were cut from 0.025-cm-thick polycrystal stock sheet of purity 99.95 and 99.8%, respectively. The samples were etched in hot aqua regia and spotwelded to heavy tantalum supports which were provided for ohmic heating. No evidence was found for appreciable catalytic activity of the tantalum supports during the experiments discussed in this paper.

The sample and its supports were mounted on a Varian rotatable manipulator so that the samples could be positioned approximately in the center of the vacuum chamber and rotated to the proper positions for gold evaporation, Auger spectroscopy, etc. Sample temperature was monitored by a thermocouple spotwelded to the sample.

Platinum vs platinum-10% rhodium and tungsten vs tungsten-26% rhenium thermocouples were used for the platinum and iridium samples, respectively.

All gases used in this work were "instrument" or "research" grade obtained in metal cylinders and connected to the common gas manifold through pressure regulators. The gas manifold was connected to the system through a Varian leak valve. Normal heptane was admitted to the manifold, and to the system through the leak valve, from a glass reservoir containing a small amount of the "reagent" grade liquid which had been further purified by pumping on it.

*Surface Cleaning*

Dominant bulk impurities were found to be calcium in platinum and oxygen in iridium and, as they segregated to the surface, could be removed by ion bombardment and sputtering by argon ions. Surface carbon could be removed from both surfaces by heating the sample at 1000°C for several minutes in a  $5 \times 10^{-7}$ -Torr oxygen environment. Surface oxygen from this treatment was removed by heating to 1300°C (platinum) or 1600°C (iridium). Following this procedure, an estimated maximum of several percent of the surface was found to be covered by impurities, as estimated by Auger electron spectroscopy, and were primarily calcium on platinum and oxygen on iridium.

*Formation of the Bimetallic Surfaces*

The bimetallic surfaces used in this investigation were formed by a procedure somewhat similar to that of Bonzel and Wynblatt (16). Gold was evaporated onto both sides of the clean sample from an *in situ* evaporation source consisting of a tungsten basket loaded with gold and shielded to reduce unnecessary deposition of gold on other parts of the system. Sufficient gold was deposited on the surface

to eliminate the substrate Auger peaks. The gold-covered sample was then annealed at about 1000°C allowing gold to vaporize from the surface or diffuse into the bulk. The annealing process was continued for a period of several minutes until the desired surface concentration of gold had been obtained as determined by Auger electron spectroscopy. The gold-contaminated surface could be rendered gold-free by heating the sample to 1000–1600°C for periods of several minutes. Following this treatment no evidence was seen for the presence of residual gold on the surface within the limits of detection of the Auger spectrometer (fractional coverage  $\theta_{Au} \sim 0.05$ ). The presence of a small amount of residual gold on the surface was evidenced, however, by an inability to reproduce hydrogenolysis results that had been obtained on surfaces uncontaminated by gold.

Auger spectra taken on a clean iridium surface, the same surface following gold evaporation, and the resulting surface following annealing are shown in Fig. 1. The 141-eV gold Auger peak, corresponding to the  $N_5N_6N_6$  transition, was used to determine the fraction of the surface covered by gold. The interpretation of the gold peak heights is complicated by a lack of knowledge concerning the distribution of gold on the surface resulting from the above treatment. The Auger peak height ( $h$ ) is proportional to (17)  $\sum_i N_i a_i$ , where  $N_i$  is the number of emitting gold atoms in the  $i$ th layer and  $a_i$  is an attenuation factor dependent on the layer depth and on back-scattering and screening effects (17). If the gold exists on the surface in amounts of a monolayer or less with no substantial penetration into the bulk, then only one term in the above series is needed and the surface coverage is directly proportional to Auger peak height. The surface coverage would also be directly proportional to peak height if penetration into the lattice (alloying) occurs with the same number of gold atoms in each layer where  $a_i$  is large. However, if

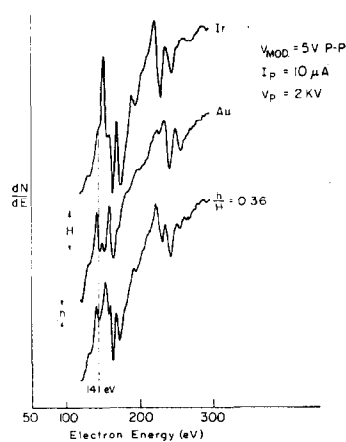


FIG. 1. Auger spectra (second derivative of Auger current vs electron energy) for an iridium polycrystalline surface, the same surface following evaporation of gold, and following annealing at 1000°C yielding a surface having a value of  $h/H = 0.36$ . A small peak is present at 270 eV in the iridium and iridium-gold spectra corresponding to the presence of surface carbon.

alloying occurs with a concentration gradient into the bulk, the surface coverage need no longer be simply proportional to peak height. Furthermore, it is not possible to determine directly from the Auger peak heights the point at which exactly one monolayer of gold exists on the surface in the event alloying does not occur.

In order to resolve these questions it is necessary to calibrate the Auger peak heights in some way, e.g., by some technique that counts only surface atoms of one kind. This was carried out for platinum by exposing the surface to the same exposure (near saturation) of carbon monoxide, which adsorbs only on the platinum metal atoms, and flashing the surface to determine the amount originally adsorbed. The result of this titration is shown in Fig. 2 where the ordinate is proportional to the amount of carbon monoxide adsorbed and the abscissa is the Auger peak height ( $h$ ) of the annealed bimetallic surface normalized to the Auger peak height ( $H$ ) of the surface covered with sufficient gold so that substrate features are

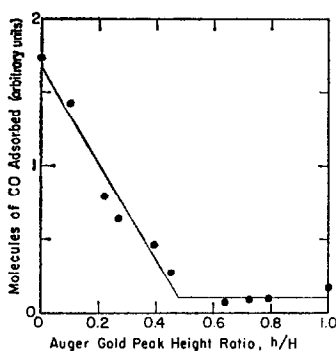


Fig. 2. Amount of carbon monoxide adsorbed (determined by flash desorption) following an exposure of 60 Langmuirs (1 Langmuir =  $10^{-6}$  Torr sec) as a function of the ratio of gold Auger peak heights ( $h/H$ ) for surfaces prepared according to the method described in the text. The straight line for  $h/H < 0.5$  is a least-squares fit to the data points.

not seen. This ratio is

$$h/H = \frac{\sum_i N_i a_i}{N^{(m)} \sum_i a_i},$$

where  $N^{(m)}$  is the number of gold atoms in a monolayer and it is assumed that the  $a_i$ 's are the same regardless of whether the emitting gold atom is in a pure gold matrix or in a gold-platinum matrix, i.e., back-scattering and screening effects are matrix independent. It is seen in Fig. 2 that the amount of carbon monoxide adsorbed decreases approximately linearly with increasing  $h/H$  until a value of  $h/H \sim 0.5$  is reached. For larger values of  $h/H$  the amount adsorbed does not change to a maximum value of  $h/H = 1.0$ . The small amount of carbon monoxide adsorbed for  $h/H > 0.5$  is probably due to adsorption on edges and supports not covered by gold. These results indicate that the surface becomes covered by a monolayer of gold at  $h/H \sim 0.5$  and that for values of  $h/H < 0.5$ ,  $h/H$  is directly proportional to  $\theta_{Au}$ . It is possible to calculate approximately the value of  $h/H$  corresponding to one monolayer of gold lying on top of a pure platinum substrate. Converting the sums in the previous equation to integrals and assuming  $a_i$  is due only to the attenuation of Auger

electrons, because of the finite mean free path,  $\lambda$ , of the hot electrons, we obtain

$$h/H = \frac{\int_0^d e^{-z/\lambda} dz}{\int_0^\infty e^{-z/\lambda} dz} = 0.44,$$

using a value of  $\lambda = 5 \text{ \AA}$ , estimated from the behavior (18) of electron mean free path vs energy at the Auger peak position of 141 eV, and a value of  $d = 2.92 \text{ \AA}$ , corresponding to the diameter of a gold atom. The calculated value of  $h/H$  is in good agreement with the experimental value of 0.47 obtained by carbon monoxide titration. It will be assumed that the iridium-gold surface behaves in a manner similar to platinum-gold.

The surface gold concentration did not appear to change substantially during the course of a reaction run. Heating a partially gold-covered surface under vacuum at 400°C for periods up to 30 min resulted in no observable changes in  $h/H$ .

#### Procedure

The procedure employed during the reaction experiments was as follows. The freshly cleaned or alloyed samples were allowed to cool to within a few degrees of room temperature. The vacuum chamber was then isolated from the ion pump by closing the gate valve. The hydrocarbon reactant gas was admitted to the vacuum chamber to a pressure of  $5 \times 10^{-5}$  Torr followed by hydrogen to a total pressure of  $3 \times 10^{-4}$  Torr. The hydrogen to hydrocarbon ratio of 5:1 was chosen for experimental convenience but other ratios were occasionally used to determine the effect of its variation on reaction rate. Repetitive mass scans every 30 sec were then begun and recorded, covering both the reactant and expected product mass peaks, and were continued throughout the experiment. After several minutes had elapsed the sample was heated within a few seconds to the desired reaction temperature and held at this value

for 5–10 min at which time the experiment was ended. After the gases were pumped out, an Auger spectrum was taken to check for changes in alloy composition and the presence of surface carbon.

### Data Analysis

The mass spectra were analyzed by attributing any change in mass peaks on heating the sample to the reaction temperature to reactions taking place on the sample.

For hydrogenolysis reactions, the difference in the slopes (rate of increase) of the  $m/e = 16$  and 30 peaks before and initially after heating was taken as proportional to the rate of hydrogenolysis to methane and ethane, respectively. The slopes were obtained from the data by least-squares fits.

Maximum sensitivity for the detection of *n*-butane as an isomerization product of isobutane is obtained by looking for changes in the ratio of two suitably chosen mass peaks in the isobutane cracking pattern such as  $m/e = 58$  and 42. These masses were chosen because the  $m/e = 58$  peak increases and the  $m/e = 42$  peak decreases as isomerization proceeds. Due to the difficulty of observing small changes in the ratio of two relatively large numbers, the sensitivity for observing isomerization was found to be low. The changes were of the order of or slightly greater than the noise and short-term drift of the mass spectrometer (several tenths of a percent). Because of this, a consistent statistical analysis was applied to each isomerization run at a different gold coverage. A least-squares fit to the ratios for periods of 5 min before and 5 min after heating the sample to the reaction temperature gave two slopes of which the difference was taken as proportional to the average initial reaction rate for isomerization.

The detection of toluene as a dehydrocyclization product was made possible by observing changes in its parent  $m/e = 91$

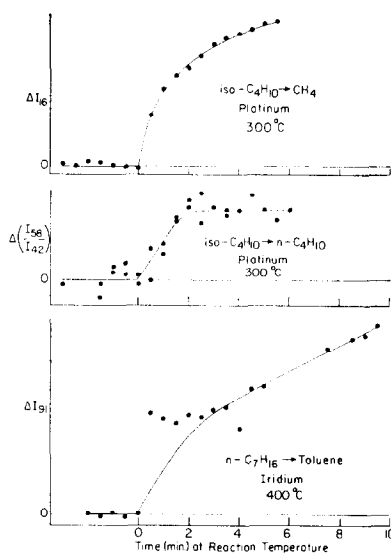


FIG. 3. Observed changes in the mass spectrometer ion current ( $I$ ) for hydrogenolysis, isomerization (composite of two runs), and dehydrocyclization products as a function of time at the reaction temperature (sample heated to the reaction temperature at  $t = 0$ ). The dehydrocyclization data have been corrected for toluene pumping and an  $m/e = 91$  component present in the *n*-heptane cracking pattern.

peak, corrected for a component present in the *n*-heptane cracking pattern. The rate at which the  $m/e = 91$  peak increased, following heating, was found to assume a steady-state value after a period of several minutes had elapsed. The rate of toluene formation was taken as proportional to this steady-state slope. In some cases the slope was found to decrease slowly with time and an average slope, obtained over a period of several minutes, was taken as proportional to the reaction rate.

Typical behavior of the  $m/e = 16$  peak (hydrogenolysis of isobutane on platinum at 300°C), the ratio of the  $m/e = 58$  and 42 peaks (isomerization of isobutane on platinum at 300°C), and the  $m/e = 91$  peak (dehydrocyclization of *n*-heptane to toluene on iridium at 400°C) before and after heating the sample to the reaction temperature are shown in Fig. 3.

The reaction rates are expressed either as a reaction probability,  $R$ , defined as the probability that an incident hydrocarbon molecule will yield the specified product molecule or as a turnover number,  $N$ , defined as the number of the product molecule desorbed per second per surface metal atom.

#### Effect of Background Gases

Although the ease of observing the reaction products is greater under no-pumping conditions than for flow conditions, a potential problem exists due to the buildup of possible catalytic poisons such as carbon monoxide by, for example, displacement from the chamber walls by hydrocarbon gas adsorption. Although in some cases, as with the *n*-heptane studies, carbon monoxide pressures could build up to as high as  $10^{-5}$  Torr, no evidence was found that this high carbon monoxide partial pressure caused adsorption and consequent poisoning of the surface during the course of the experiment. Heating the sample to temperatures as high as  $1000^{\circ}\text{C}$  caused little or no change in the  $m/e = 28$  peak. Although

carbon monoxide normally adsorbs on both platinum and iridium, the presence of the reactant gases evidently prevented adsorption of carbon monoxide from taking place at the elevated temperatures used in these studies ( $100\text{--}500^{\circ}\text{C}$ ).

#### RESULTS

The rates of the various reactions (hydrogenolysis, isomerization, and dehydrocyclization) were studied as a function of temperature. It was found that there is an optimum temperature that yields a maximum rate for these reactions. These temperatures are listed in Table 1 along with the corresponding reaction rates observed for the various reactions on the platinum and iridium surfaces in the absence of gold. Figure 4 shows the temperature dependence of the reaction probabilities for the hydrogenolysis of propane to methane on platinum foils, the isomerization of isobutane to *n*-butane on platinum, and the dehydrocyclization of *n*-heptane to toluene on iridium. The hydrogenolysis of propane, isobutane, and the isomerization of isobu-

TABLE 1  
Reactions on Pure Platinum and Iridium Surfaces<sup>a</sup>

Surface		$\text{C}_3\text{H}_8$	iso- $\text{C}_4\text{H}_{10}$	<i>n</i> - $\text{C}_7\text{H}_{16}$
Hydrogenolysis to $\text{CH}_4$ ( $R_{\text{min det}} \sim 1 \times 10^{-7}$ )				
Platinum	$N$	$2.3 \times 10^{-3}$ ( $300^{\circ}\text{C}$ )	$1.1 \times 10^{-3}$ ( $300^{\circ}\text{C}$ )	$7.4 \times 10^{-4}$ ( $270^{\circ}\text{C}$ )
	$R$	$1.5 \times 10^{-4}$	$8.2 \times 10^{-5}$	$7.2 \times 10^{-5}$
Iridium	$N$	$8 \times 10^{-5}$ ( $320^{\circ}\text{C}$ )	$2.1 \times 10^{-4}$ ( $320^{\circ}\text{C}$ )	$1.8 \times 10^{-4}$ ( $\sim 100^{\circ}\text{C}$ )
	$R$	$5.2 \times 10^{-6}$	$1.6 \times 10^{-5}$	$1.7 \times 10^{-5}$
Isomerization of iso- $\text{C}_4\text{H}_{10}$ to <i>n</i> - $\text{C}_4\text{H}_{10}$ ( $R_{\text{min det}} \sim 2 \times 10^{-5}$ )				
Platinum	$N$	$3 \times 10^{-3}$ ( $300^{\circ}\text{C}$ )		
	$R$	$2.0 \times 10^{-4}$		
Iridium	$N$	$8.8 \times 10^{-4}$ ( $320^{\circ}\text{C}$ )		
	$R$	$6.5 \times 10^{-5}$		
Dehydrocyclization of <i>n</i> - $\text{C}_7\text{H}_{16}$ to toluene ( $R_{\text{min det}} \sim 2 \times 10^{-8}$ )				
Platinum	$N$	$1.7 \times 10^{-6}$ ( $400^{\circ}\text{C}$ )		
	$R$	$1.7 \times 10^{-7}$		
Iridium	$N$	$1.1 \times 10^{-5}$ ( $400^{\circ}\text{C}$ )		
	$R$	$1.1 \times 10^{-6}$		

<sup>a</sup>  $P_{\text{HC}} = 5 \times 10^{-6}$  Torr;  $P_{\text{H}_2} = 2.5 \times 10^{-4}$  Torr.  $R$ , Reaction probability  $N$ , turnover number.

tane to *n*-butane had maximum rates at about 300 and 320°C on the platinum and iridium foils, respectively. For hydrogenolysis of *n*-heptane the optimum temperature is 270°C for platinum and as low as 100°C for iridium. For dehydrocyclization of *n*-heptane, the optimum temperature is 400°C for both platinum and iridium. The reaction rates that are listed in Table 1 and are compared in the discussion that follows are the maximum rates obtained at these optimum temperatures. The uncertainties or probable errors in the turnover numbers are also given in Table 1 as minimum detectable rates.

Our studies may be divided into four parts. Low pressure studies of hydrogenolysis, isomerization, and dehydrocyclization on pure platinum and iridium polycrystalline foils and the effect of gold on the reaction rates.

#### *Hydrogenolysis on Pure Platinum and Iridium Foils*

The rate of hydrogenolysis was found to increase nearly linearly with hydrogen pressure over a range of hydrogen:hydrocarbon ratios of 0:1–20:1 at a reactant hydrocarbon pressure of  $5 \times 10^{-5}$  Torr. As expected, no hydrogenolysis occurred in the complete absence of hydrogen. Changing the hydrogen pressure also affected the temperature dependence of the reaction rates. When the hydrogen pressure was increased, the peak in the hydrogenolysis rate was observed to shift to higher temperatures. In the following, unless otherwise specified, the hydrogen:hydrocarbon ratio was 5:1 with the hydrocarbon pressure at  $5 \times 10^{-5}$  Torr.

In general, methane was the only hydrogenolysis product observed in this study. The only exception was the observation of a small amount of ethane production from propane hydrogenolysis at 350°C on pure platinum. Ethane was also observed from this reaction on a 20% gold–80% platinum surface. Ethane was not observed from pure

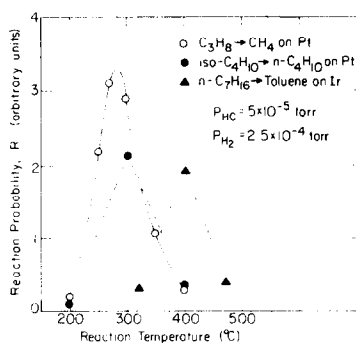


FIG. 4. Reaction probability ( $R$ ) as a function of reaction temperature for hydrogenolysis, isomerization, and dehydrocyclization.

platinum for temperatures higher or lower than 350°C. At 350°C the turnover number was  $2.2 \times 10^{-5}$  on the pure surface. In the following discussion the hydrogenolysis rates are those for methane as the product.

As shown in Table 1, the maximum hydrogenolysis rates for propane and isobutane on platinum are  $N = 2.3 \times 10^{-3}$  and  $1.1 \times 10^{-3}$ , respectively, and they occur at the same temperature (300°C). These rates are larger than the corresponding ones on iridium which are  $N = 8 \times 10^{-5}$  and  $2.1 \times 10^{-4}$  for propane and isobutane, respectively. Maximum hydrogenolysis occurs at the slightly higher temperature of 320°C on iridium. The maximum rate of *n*-heptane hydrogenolysis on platinum was found to occur at 270°C with a turnover number of  $7.4 \times 10^{-4}$ , while on iridium the maximum was found to occur at the lower temperature of  $\sim 100^\circ\text{C}$  with a turnover number of  $1.8 \times 10^{-4}$ . At 100°C, the turnover number for *n*-heptane on platinum was  $8.2 \times 10^{-5}$ . Thus, at the same temperature hydrogenolysis of *n*-heptane occurs more readily on iridium while hydrogenolysis of propane and isobutane occur more readily on platinum.

As shown in Fig. 3, the rate of hydrogenolysis of isobutane on platinum decreases in a continuous fashion with time with no evidence of the onset of steady-state behavior during the time the reaction



was observed ( $\sim 10$  min). This behavior also characterized propane and *n*-heptane hydrogenolysis on platinum. For iridium, on the other hand, the rate of hydrogenolysis for all the hydrocarbons studied had a constant or steady-state value for a similar time period. This behavior was independent of whether gold was present on the surfaces or not. Carbon Auger peaks corresponding to several tenths of a monolayer of carbon were always observed at the conclusion of these reactions.

It is interesting to compare the present results with similar studies carried out by other investigators. Anderson and Avery (19) have studied the rate of hydrogenolysis and isomerization of isobutane on deposited oriented and random orientation platinum films in a 12:1  $H_2$ :HC mixture at a total pressure of 48.2 Torr. A calculation based on their data yields a turnover number of  $5.5 \times 10^{-3}$  for isobutane hydrogenolysis to methane at 300°C on a polycrystalline deposited platinum film, as compared to  $1.1 \times 10^{-3}$  obtained in the present work at 300°C. No evidence for a temperature maximum in hydrogenolysis rate was observed in their work. Methane, ethane, and propane hydrogenolysis products were found to occur in the ratios 24:6:20, respectively. Carter *et al.* (20) have studied hydrogenolysis and dehydrocyclization of *n*-heptane on platinum, iridium, and other noble metal powders in a 5:1  $H_2$ :HC environment at a total pressure of 1 atm. A calculation based on their data yields a turnover number of  $1.4 \times 10^{-3}$  for *n*-heptane hydrogenolysis to methane on platinum at a temperature of 270°C and a value of  $3.6 \times 10^{-5}$  at 100°C on iridium as compared to  $7.4 \times 10^{-4}$  at 270°C and  $1.8 \times 10^{-4}$  at 100°C obtained in the present work, respectively. Here, as with Anderson and Avery, no evidence was seen for a temperature maximum in the hydrogenolysis rate. The hydrogenolysis product distribution from methane to hexane ( $C_1:C_2:C_3\dots$ ) was 31:13:17:16:9:14 on

platinum and 21:21:15:14:14:15 on iridium. Furthermore, at the same temperature, Carter *et al.* (20) found that hydrogenolysis of *n*-heptane occurred more readily on iridium than on platinum as was observed in the present study at 100°C. This has also been found to be the case for other gases on these metals (21).

For platinum and iridium the turnover numbers for isobutane and *n*-heptane hydrogenolysis to methane observed by Anderson and Avery (19) and by Carter *et al.* (20) are within a factor of 5 of the corresponding values observed in this work. This agreement is surprising considering the seven-orders-of-magnitude pressure range encompassed by these results.

#### *Isomerization on Platinum and Iridium Foils*

Platinum is generally found to be one of the best catalysts for isomerization reactions (21). This was also found to be true in the present work in comparison with iridium, as seen in Table 1 for the isomerization of isobutane to *n*-butane. The maximum turnover number of platinum occurred at 300°C and had the value  $3 \times 10^{-3}$ , while a maximum value of  $8.8 \times 10^{-4}$  was obtained on iridium at 320°C. The temperatures for which isomerization is at a maximum are the same as those for hydrogenolysis on each surface. However, turnover numbers for isomerization were found to be greater than those for hydrogenolysis by a factor of about 3 on platinum and about 4 on iridium.

Isomerization of isobutane on platinum as a function of hydrogen pressure was found to display a maximum in rate at a hydrogen:hydrocarbon ratio of about 5:1. No isomerization was observed in the absence of hydrogen. However, too much hydrogen was found to quench the reaction.

As seen in Fig. 3, isomerization of isobutane on platinum was found to cease completely within minutes after beginning the reaction, possibly due to poisoning by

carbon buildup on the surface. The extent of poisoning of isomerization on iridium also appeared to be rapid but could not definitely be determined due to the large uncertainty in the data as was also the case for the platinum-gold surfaces.

Anderson and Avery (19), in the study mentioned earlier, investigated the isomerization of isobutane on polycrystalline platinum films at a total pressure of 48.2 Torr. The turnover number calculated from their data at 300°C yields a value of  $5.5 \times 10^{-3}$ , in close agreement with the number obtained in the present work ( $3 \times 10^{-3}$ ). Carter *et al.* (20) found that hydrogenolysis and isomerization occurred to roughly the same degree for *n*-heptane reactions on platinum powders at 1 atm pressure in agreement with Anderson and Avery (19) and the present work for isobutane.

#### *Dehydrocyclization of n-Heptane on Platinum and Iridium Foils*

The maximum turnover numbers for dehydrocyclization of *n*-heptane to toluene on pure platinum and iridium are shown in Table 1 and are  $1.7 \times 10^{-6}$  and  $1.1 \times 10^{-5}$ , respectively, at the same maximum temperature (400°C) for both metals. Dehydrocyclization was found to occur at a higher temperature and with lower turnover numbers on both metals as compared to isomerization and hydrogenolysis. An interesting result is that this reaction takes place about a factor of 10 times more readily on iridium than on platinum under the experimental conditions used in this study.

As shown in Fig. 3, dehydrocyclization of *n*-heptane on iridium proceeds at a constant rate after an initial period of several minutes despite the buildup of carbon on the surface. Similar behavior was observed on platinum. A large graphitic carbon Auger peak corresponding to about a half of a monolayer was observed at the conclusion of the dehydrocyclization run depicted in

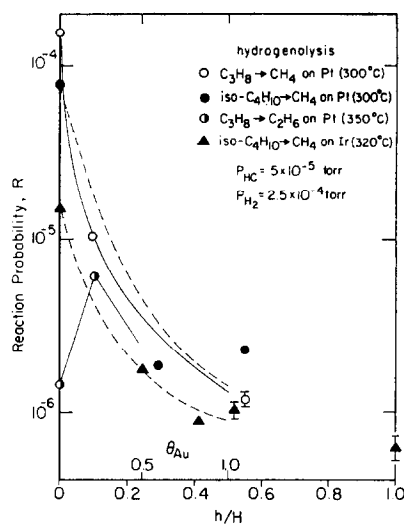


FIG. 5. Reaction probability ( $R$ ) of hydrogenolysis reactions as a function of the Auger peak height ratio,  $h/H$ , and the fraction of the surface covered by gold,  $\theta_{Au}$ . Probable errors in the data points are shown.

Fig. 3. On the other hand, on platinum-gold and iridium-gold surfaces, the reaction appeared to poison in that the rate would slowly decrease throughout the remainder of the experiment. At a pressure of 1 atm, Carter *et al.* (20) observed no dehydrocyclization of *n*-heptane to toluene on iridium powders. A turnover number of  $1.3 \times 10^{-4}$  at 275°C, the only temperature employed, calculated from their data on platinum powders, is two orders of magnitude larger than found in the present work on platinum at 400°C ( $1.7 \times 10^{-6}$ ).

#### *The Effect of Gold on the Reaction Rates*

The effect of gold on the platinum and iridium surfaces for hydrogenolysis, isomerization, and dehydrocyclization is shown in Figs. 5-7. The value of  $\theta_{Au} = 1$  corresponds to a monolayer of gold determined earlier, i.e., to a value of  $h/H = 0.5$ .

Hydrogenolysis of propane and isobutane on the bimetallic surfaces is shown in Fig. 5. The rate of hydrogenolysis of both propane and isobutane on platinum and iridium de-

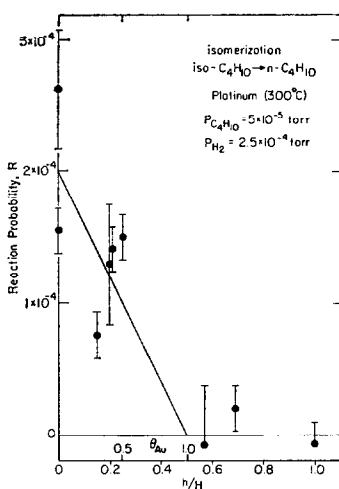


Fig. 6. Isomerization reaction probability ( $R$ ) on a linear scale on platinum as a function of the Auger peak height ratio,  $h/H$ , and the fraction of the surface covered by gold,  $\theta_{Au}$ . Probable errors in the data points are shown.

creases uniformly and rapidly with increasing surface gold coverage. The residual hydrogenolysis activity for a completely gold-covered surface is likely due to the presence of active surface areas (edges, corners, etc.) not covered by gold or by small contributions from the supports.

The formation of ethane as a hydrogenolysis product of propane was observed on a 20% gold–80% platinum surface. On this surface, both ethane and methane have maximum rates of formation at 320°C, and the turnover number for ethane was 20% of that for methane. The dependence of gold coverage on hydrogenolysis rate of propane to ethane at 350°C is shown in Fig. 5.

Isomerization of isobutane to *n*-butane on platinum decreases approximately linearly with gold coverage as shown in Fig. 6. A similar curve for iridium could not be obtained because the turnover numbers were too small. Since hydrogenolysis decreases much more rapidly with increasing gold coverage than isomerization, the selectivity for isomerization over hydrogenolysis is greatly enhanced by alloying.

The effect of gold on the dehydrocyclization of *n*-heptane to toluene on iridium is shown in Fig. 7. As with hydrogenolysis, the rate decreased very rapidly with increasing gold coverage. In this case a significant enhancement in selectivity for dehydrocyclization over hydrogenolysis would not be expected, because of their similar behavior as a function of gold coverage.

However, Plunkett and Clark (9), in a study of *n*-hexane reactions on evaporated iridium and iridium–gold films in a 10:1 hydrogen:hydrocarbon ambient at a hydrocarbon gas pressure  $\sim 1$  Torr, found an enhancement in dehydrocyclization to benzene over hydrogenolysis on the alloy surface compared to pure iridium surfaces for temperatures greater than 290°C. Auger electron spectroscopy was not used in this investigation so dependence on gold coverage could not be determined.

## DISCUSSION

We have been able to study the rates of various hydrocarbon reactions, some of low reaction probability, on polycrystalline foils of platinum and iridium of area of the order of 1 cm<sup>2</sup>. In addition, using a simple

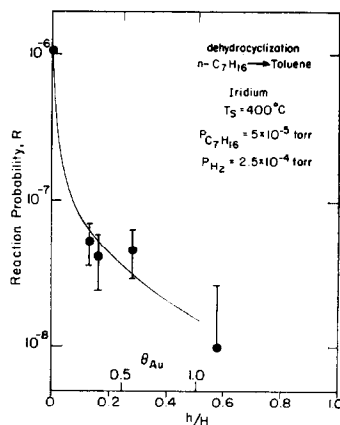


Fig. 7. Dehydrocyclization reaction probability ( $R$ ) on iridium as a function of the Auger peak height ratio,  $h/H$ , and the fraction of the surface covered by gold,  $\theta_{Au}$ . Probable errors in the data points are shown.

evaporation technique, we could monitor changes in rates and product distributions at low pressures ( $3 \times 10^{-4}$  Torr total pressure) as a function of surface gold concentration. This technique holds great promise to test the catalytic behavior of a large number of alloy systems rapidly and reliably. It will be convenient to discuss separately the results obtained on the pure foils, the nature of the bimetallic surfaces, and the effect of gold on the reactions.

#### *Reactions on the Pure Polycrystalline Platinum and Iridium Surfaces*

The reaction rates observed in the present work exhibit a maximum as a function of temperature which is not found in the work of Anderson and Avery (19) and Carter *et al.* (20) carried out at much higher pressures (48.2 Torr and 1 atm, respectively). The appearance of an optimum temperature is most likely the result of our low pressure experimental conditions. This is supported by the observation that the maximum hydrogenolysis rate would shift to higher temperatures when hydrogen pressure was increased.

Despite the seven-orders-of-magnitude pressure range covered by our studies and those of Anderson and Avery (19) and Carter *et al.* (20), there is less than an order of magnitude difference in the reaction rates observed for comparable hydrogenolysis and isomerization reactions at the same temperatures. The hydrogenolysis rate of propane appears to increase linearly with hydrogen pressure within the limits of pressure range of our investigations ( $P_{H_2} \leq 1 \times 10^{-3}$  Torr). For propane hydrogenolysis on platinum, a fourfold increase in hydrogen pressure would double the turnover number. At higher pressures the rate of hydrogenolysis either must become hydrogen-pressure independent or follow a very different hydrogen-pressure dependence than at low pressures in order to explain the comparatively small differ-

ence in reaction rates. These considerations indicate that adsorption of the reactants is not the rate-limiting step over this pressure range ( $10^{-4}$  Torr–1 atm) and that the ratio of hydrogen to hydrocarbon partial pressure may be the more important parameter. The importance of hydrogen to hydrocarbon ratio is also indicated by our results on the hydrogen-pressure dependence of isomerization in that this reaction was quenched in a 20:1 as well as a 0:1 hydrogen to hydrocarbon ratio. Both Anderson and Avery, and Carter *et al.* employed hydrogen to hydrocarbon ratios (12:1 and 5:1, respectively) corresponding closely to our 5:1 ratio.

Dehydrocyclization on iridium was found to occur at a rate higher than on platinum by a factor of 10. This surprising result is in contrast to the results of Carter *et al.* (20) who observed no dehydrocyclization of *n*-heptane on iridium powders at 1 atm total pressure. Also, the rate of dehydrocyclization on platinum powders observed at this pressure and at 275°C by Carter *et al.* is some two orders of magnitude larger than our rate measured at 400°C at low pressure on platinum foils. Thus, in contrast to hydrogenolysis and isomerization reactions, reactant gas pressures appear to play an important role in dehydrocyclization.

A major difference in our low pressure studies and the high pressure studies of others (19–21) of hydrogenolysis is in the distribution of hydrogenolysis products rather than in reaction rates. We find low molecular rate products exclusively ( $CH_4$ , and some  $C_2H_6$ ), within the limits of detection, while at high pressures higher molecular rate products have been found to be in abundance by others. It seems likely that the lower hydrogen pressures that result in lower hydrogen atom coverages are responsible for the large shift in product distributions. The conclusion, then, is that a higher hydrogen surface concentration increases the production of higher molecular

weight hydrogenolysis products while the rate of hydrogenolysis and isomerization reactions is little affected by variation of the total pressure and is controlled mainly by the hydrogen to hydrocarbon ratio. Also, the presence of a temperature-dependent poisoning is determined by the hydrogen presence.

The low hydrogen pressures employed in the present study were also likely responsible for the time-dependent poisoning observed to various degrees for all reactions. The buildup of dehydrogenated carbonaceous species on the surface, as evidenced by the observation of carbon Auger peaks, occurs more rapidly than their hydrogenation and removal from the surface by the hydrogen ambient and leads to the diminishing reaction rates observed.

#### *Nature of the Platinum-Gold and Iridium-Gold Surface*

The equilibrium platinum-gold system displays a miscibility gap below a critical temperature of about 1250°C (22). Below this temperature for a certain composition range (dependent on temperature) there exist two homogeneous phases in equilibrium whose individual compositions are constant. The relative amounts of the two phases vary according to the overall composition of the sample. The final equilibrium configuration taken by the alloy depends on the kinetics, i.e., on the relative diffusion coefficients (23-25). Although far from equilibrium, it is expected that the kinetics will determine the configuration taken by the samples employed in the present work as well. It was shown, using carbon monoxide chemisorption, that for values of  $h/H$  less than 0.5 the coverage of platinum decreases linearly with  $h/H$  and that at  $h/H \sim 0.5$  a monolayer of gold exists on the surface. Although carbon monoxide-induced surface enrichment of platinum on platinum-gold surfaces has been observed (23), it is a very slow process

and consequently cannot explain these results. The maximum solubility of gold in platinum at 1000°C (the annealing temperature) is about 10% (22), and alloying to this extent may take place at the platinum-gold interface on beginning the annealing. A transition region containing this composition is thus formed and its thickness increases as annealing is continued. Since the diffusion coefficient of gold in platinum is much greater than that for platinum in gold, the tendency for platinum to diffuse into the alloy region during annealing would be countered by diffusion of gold into this region to maintain the maximum gold concentration at about 10%. For surface gold concentration greater than this the gold atoms would be adsorbed on top of the alloy transition layer. Thus, it is envisioned that part of the surface is alloyed and part consists of gold atoms chemisorbed on top of the alloy layer. Since the solubility of gold in iridium is even smaller, of the order of several percent (9), the extent of alloying is less important than for platinum.

How the nonalloyed gold atoms are distributed on the surface is important in interpreting the dependence of reaction rates on surface gold coverage. It would be expected that for metal atoms adsorbed on a metal substrate where the heats of sublimation are similar, as is the case for platinum, gold, and iridium, clustering and island formation would be important.

Polycrystalline surfaces likely display a variety of defects such as steps, kinks, and grain boundaries as well as a variety of low index single crystal planes. Consequently, it would be expected that the gold atoms would be preferentially adsorbed at these sites because of the larger adsorption energies available to them. Such defect sites would likely be where the clusters and islands of gold are nucleated. The behavior of reaction rates as a function of gold coverage will be discussed with the aid of these ideas.

*Effect of Gold on the Hydrocarbon Reaction on the Polycrystalline Platinum and Iridium Surfaces*

The effect of gold on the reaction rates for hydrogenolysis, isomerization and dehydrocyclization are shown in Figs. 5-7, respectively, and are compared in Fig. 8 where the rates have been normalized to their values on the pure surfaces and have been corrected for their residual activity for  $\theta_{Au} \geq 1$ . These results show, as is most clearly seen in Fig. 8, that isomerization behaves in a manner essentially different than either hydrogenolysis or dehydrocyclization as a function of gold coverage. Isomerization activity per surface platinum atom is approximately constant while rapidly decreasing for hydrogenolysis and dehydrocyclization as gold coverage increases. Thus, the selectivity for isomerization increases with gold coverage while the selectivity for dehydrocyclization does not appear to change significantly. This implies that hydrogenolysis and dehydrocyclization occur at different sites than isomerization for the surfaces employed in this investigation and that reactions involving the breaking of C-C bonds (hydrogenolysis or dehydrocyclization) are more inhibited by the presence of gold than those reactions which involve no change (isomerization). The different time-dependent poisoning behavior of the various reactions is further evidence for the existence of different sites. Isomerization was found to poison completely within a couple of minutes following heating the sample to the reaction temperature (Fig. 3) whereas hydrogenolysis and dehydrocyclization were only partially poisoned.

It is interesting to attempt an interpretation of these results in terms of existing theories of mechanisms and intermediates for these reactions. Isomerization of isobutane is thought to take place (19) on platinum through bond-shift involving a 1-3 diadsorbed or triadsorbed intermediate

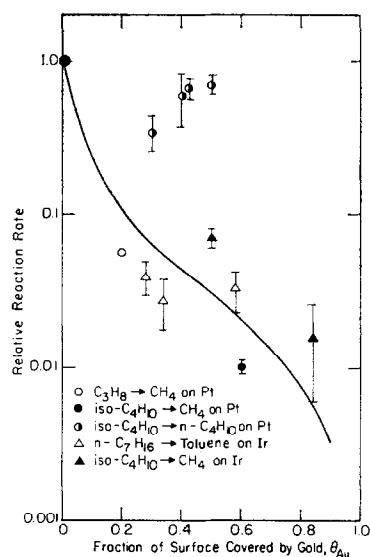


FIG. 8. Hydrogenolysis, isomerization, and dehydrocyclization data from Figs. 5-7 normalized to their reaction rates on the pure surfaces as a function of the fraction of the surface covered by gold,  $\theta_{Au}$ . The rates have been corrected for their residual activity for  $\theta_{Au} \geq 1$ . The curve is a best fit to the data and is based on a model discussed in the text.

requiring doublets or triplets of nearest neighbor atoms on the surface as on low index planes. As discussed above, the surfaces employed in this investigation are likely to be made up of large areas of essentially pure platinum or iridium atoms (with  $\leq 10\%$  gold) and islands or clusters of pure gold atoms centered on defects. Consequently, it would be expected that isomerization activity by the above bond-shift mechanism would decrease approximately linearly with increasing gold coverage on our surfaces, as is observed. However, it has also been proposed (19) that the same intermediate for isomerization is responsible for hydrogenolysis of isobutane, and this is not in accord with our results. Thus, other sites, e.g., defect sites that can be blocked by adsorbed gold, must be postulated as responsible for hydrogenolysis activity. Carbocyclic or  $\pi$ -allyl/olefin adsorbed species as reaction intermediates are favored by single atom sites of low coordination as

would be found at defect sites such as steps and kinks (26). It is thought (26) that such intermediates can lead to hydrogenolysis and thus may be responsible for the hydrogenolysis of isobutane on our surfaces as well as the hydrogenolysis of propane which behaves very similarly to isobutane as a function of gold coverage as shown in Fig. 5. Further evidence for the existence of such sites is the observation that cyclohexane hydrogenolysis requires the presence of kinks on a stepped platinum surface in order to take place (13). Since cyclization reactions can take place by way of carbocyclic intermediates (27), the existence of such sites is also suggested by the behavior of dehydrocyclization activity as a function of gold coverage. As shown in Fig. 8, dehydrocyclization activity decreases with gold coverage in a manner similar to that of hydrogenolysis.

Figure 8 also shows that the reaction rates for dehydrocyclization and hydrogenolysis decrease with gold coverage in a corresponding manner to the expected decrease in the number of defect sites as given by the curve in the figure. The curve in Fig. 8 is a plot of the fraction of defect sites not covered by gold as a function of gold coverage and was calculated from a simple model based on the following considerations. It is assumed that there are two types of sites on the surface. Defect sites are characterized by an energy  $E_d$ , number density of sites  $X_d$ , and number of sites occupied by gold atoms,  $N_d$ . Normal sites are characterized by an energy  $E_n$ , number density  $X_n$ , and occupation  $N_n$ . Elementary statistical considerations (28) yield the following relationship between these parameters and the absolute temperature  $T$ ;

$$\frac{N_d}{N_n} = \frac{X_d - N_d}{X_n - N_n} e^{(E_d - E_n)/kT},$$

where  $N_d + N_n = N$ ,

$$\theta_{Au} = (N_d/X_d + X_n),$$

and the parameter

$$\delta = X_n/X_d,$$

the ratio of normal sites to defect sites. The solid curve in Fig. 8 is a plot of  $(X_d - N_d)/X_d$  and is a best fit to the data in the figure and was obtained using values of  $\delta = 100$  and  $(E_d - E_n)/kT = 3.5$ , although the dependence on  $\delta$  is very weak.

Thus, it is possible to rationalize our results by postulating different reaction sites for isomerization and hydrogenolysis and similar sites for hydrogenolysis and dehydrocyclization. This results in the observed increase in selectivity for isomerization and essentially no change in selectivity for dehydrocyclization as compared to hydrogenolysis as the surface gold concentration is increased.

In using polycrystalline platinum and iridium foils in these studies we have not been able to investigate the surface structure sensitivity of the various catalytic reactions in a controlled way. Single crystal surfaces with well-defined orientation and with controlled density of surface steps and kinks should be utilized for this purpose. These studies are in progress. Correlation of reaction rates and product distributions that are obtained at low and high pressures ( $10^{-4}$  vs  $10^3$  Torr) are necessary to elucidate why the reaction rates at high and low pressures for hydrogenolysis and isomerization are so similar while the product distributions are so different. These pressure-dependence studies are also in progress.

#### ACKNOWLEDGMENTS

This work was done under the auspices of the Office of Naval Research and the U. S. Energy Research and Development Administration.

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