

Mechanism of Dehydrocyclization of 1-Hexene to Benzene on Cu₃Pt(111)

Andrew V. Teplyakov^{*,†} and Brian E. Bent[‡]

Chemistry Department, Columbia University, New York, New York 10027

Received: May 24, 1997; In Final Form: August 18, 1997[©]

Even though dehydrocyclization is widely practiced in heterogeneous catalysis for the conversion of straight chain hydrocarbons into aromatic compounds, knowledge of the mechanism of this process remains limited, largely because it has not previously been possible to carry out the reaction under conditions amenable to detailed mechanistic studies. We report here ultrahigh vacuum studies of the dehydrocyclization of submonolayer coverages of 1-hexene to benzene on a Cu₃Pt(111) single-crystal surface. On the basis of temperature-programmed reaction/desorption (TPR/D) studies of dehydrocyclization of 1-hexene as compared to the reactions of cyclohexene, 1,3-cyclohexadiene, 1,4-cyclohexadiene, benzene, 1,3-hexadiene, and 1,3,5-hexatriene with a Cu₃Pt(111) surface, it is found that a rate-determining step in the overall reaction is cyclization. The obtained results show that at low coverages of mono- and bi-unsaturated cyclic compounds, benzene is the only gas-phase hydrocarbon product of reaction of these compounds with a Cu₃Pt(111) surface, while after a certain threshold in coverage, molecular desorption of these compounds commences. The temperature of benzene evolution for all the cyclic compounds studied is between 200 and 300 K, whereas for linear chain hydrocarbons this temperature is ~400 K. TPR/D studies of product hydrogen evolution show that all cyclic compounds evolve hydrogen upon reaction with the surface at the temperatures close to that of hydrogen recombination–desorption reaction, 220–290 K. On the other hand, 1-hexene evolves hydrogen upon reaction with this surface at two different temperatures: ~270 and ~405 K. Combining these results with the studies of hydrogen evolution from 1,3,5-hexatriene, which occurs at 400 K, we suggest that cyclization is a rate-determining step and that mono- and bi-unsaturated C₆ cyclic compounds are not the reaction intermediates for the dehydrocyclization of 1-hexene to benzene.

Introduction

Catalytic transformation of aliphatic hydrocarbons into aromatic compounds has a variety of applications in different industrial processes. Although the production of benzene itself nowadays is being avoided because of its carcinogenic properties, aromatization reactions are of major importance in the petroleum refinement industry for increasing the octane number of gasoline range hydrocarbons. Success in the development of effective catalysts for aromatization is based largely on Bernard's discovery¹ that platinum supported on the K⁺-exchanged form of zeolite L had much higher reactivity and selectivity for this reaction than previously known catalysts. For the last 15 years this catalyst has been thoroughly studied and different modifications have been made. With few exceptions, where Ga-alumosilicates,² TiO₂–ZrO₂,³ selenium dioxide–trimethylsilyl polyphosphate⁴ and some other catalysts^{5,6} were used in the aromatization reaction, almost all the most successful catalysts for this process were based on noble metals, mostly platinum.

Since the platinum-containing industrial catalysts are usually used as supported platinum,^{7–11} studies of the real catalysts were limited by the number of techniques available for characterization of the reaction occurring on such surfaces. Chromatography was the most valuable technique to quantify the reaction products. Vibrational spectroscopy^{12a} and temperature-pro-

grammed reaction^{12b} were rarely used. Nevertheless, some valuable findings have been made about the mechanism of the aromatization reaction. Unfortunately, all these reaction mechanisms have been obtained indirectly, by the methods associated with the analysis of the distribution of the products of the reaction in a steady-state regime. It should be mentioned that for all high-pressure studies the interpretation of the results, especially from the point of view of thermodynamics, was extremely difficult because of complications related to the presence of reactions different from dehydrocyclization (isomerization, hydrogenolysis, etc.) during the course of experiment. The approach applied in the studies presented here is based on temperature-programmed desorption studies of submonolayer coverages of hydrocarbons adsorbed on a catalytic single-crystal surface at cryogenic temperatures (110 K), followed by heating with a linear temperature ramp. Under these conditions, the adsorption step is essentially irreversible, and activation energies for the multistep chemical processes can be determined on the basis of the temperature of each step.

Platinum itself became a focus of detailed research in a form of single crystals, as soon as ultrahigh vacuum systems and techniques had become available. The interest was based on the unusual reactivity of this noble metal toward reactions with hydrocarbons and their fragments. Pure platinum proved to be a poor catalyst for aromatization reactions if the cyclization was one of the steps of this process, because of complications related to isomerization and hydrogenolysis^{13–18} competing with dehydrocyclization reaction. However, when aromatization was achieved by dehydrogenation of C₆ cyclic hydrocarbons, platinum showed excellent activity in this reaction.^{19–29} The only complication to this reaction was the complete decomposition pathway leaving carbonaceous deposits on platinum surfaces even after benzene was formed. The decomposition led to a

* Corresponding author.

† Present address: New York University, Chemistry Department, 100 Washington Square East, Room 1018, New York, NY 10003. Tel, (212) 998-8441; fax, (212) 260-7905; e-mail, avt2@is6.nyu.edu.

‡ Deceased. Please send correspondence to: George W. Flynn, Chemistry Department, Columbia University, New York, NY 10027. Tel, (212) 854-4162; fax, (212) 932-1289; e-mail, flynn@chem.columbia.edu.

© Abstract published in *Advance ACS Abstracts*, October 1, 1997.

decrease in the reactivity and in the end to a complete coking of the platinum surface.

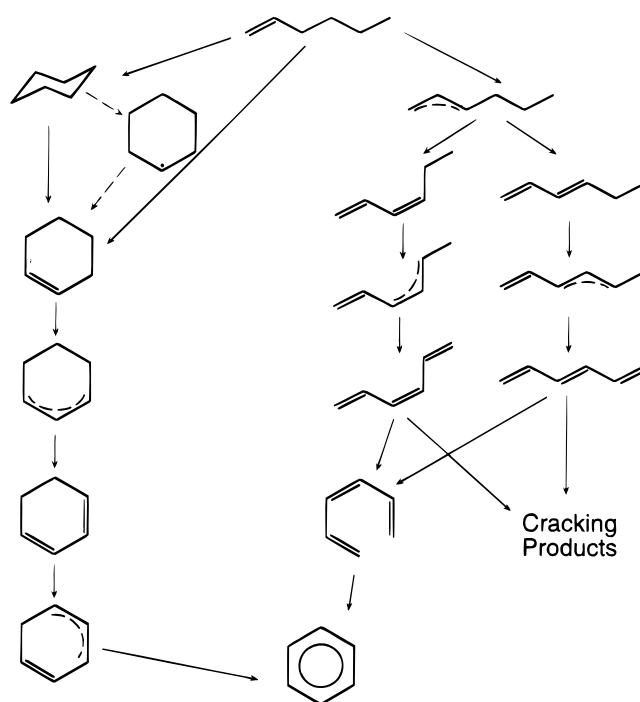
Another way toward obtaining a better catalyst for aromatization reaction is based on altering the properties of platinum by alloying it with other metals.^{30,31} In the late 70s it has been shown by de Jongste et al. that by alloying copper with platinum³² one can obtain a material whose reactivity and selectivity toward aromatization can be altered by varying the amount of the components in the alloy.^{33–35} At certain copper–platinum ratios this alloy proved to be an effective catalyst for dehydrocyclization of *n*-hexane leading to the formation of benzene. de Jongste's knowledge of the structure of the Cu–Pt material was mainly based on the amount of either component in the original mixture, but now, 15 years later, a single crystal of some Pt–Cu alloys can be obtained and characterized. The surface alloys of Sn/Pt(111),^{36,37} Au/Pt(100),^{38,39} and Pt/Au(100)^{38,39} single-crystal surfaces were studied in ultrahigh vacuum (UHV) as catalysts for dehydrogenation of C₆ cyclic hydrocarbons to benzene. It was found that surface alloys of platinum with gold and tin may drastically increase the rate of dehydrogenation reaction. To the best of our knowledge, the only UHV studies of cyclization of C₆ linear hydrocarbons on alloy single-crystal surfaces are reported in refs 40 and 41, but the results presented in these references describe the dehydrocyclization reaction at pressures of ~20 Torr with subsequent characterization at UHV conditions. While the possibility of studying a dehydrocyclization reaction in a monolayer regime has been suggested for dehydrocyclization of *n*-heptane to toluene on platinum surfaces in ref 14, this reaction was only a small percent of the overall conversion of *n*-heptane, so that the detailed mechanistic study was practically impossible for this chemical system.

For the studies presented here, we chose the Cu₃Pt(111) single crystal as a model surface because it has been shown by de Jongste that at this Cu-to-Pt ratio the selectivity of the material toward aromatization reaction is quite high. Another reason for choosing this alloy was the fact that the Cu₃Pt(111) surface does not contain Pt–Pt bonds, meaning that only the single Pt metal centers or the Cu–Pt alloy sites can participate in the reaction.

Studies presented in this paper have been performed in UHV conditions and made use of temperature-programmed reaction/desorption spectroscopy (TPR/D) to probe surface reaction mechanisms and products of the reaction of 1-hexene with a Cu₃Pt(111) single-crystal surface. The pathways available for the dehydrocyclization reaction to occur are shown in Scheme 1. The first mechanism involves cyclization as the first step of the overall transformation followed by dehydrogenation to form benzene. The other mechanism suggests dehydrogenation, leading to formation of a multiunsaturated linear intermediate as a first step followed by cyclization to form benzene. Similar mechanisms have been suggested for the dehydrocyclization reaction pathway on supported platinum (see, for example, ref 42 and references therein).

Furthermore, results of temperature-programmed reaction/desorption (TPR/D) studies of reaction of 1-hexene with a Cu₃Pt(111) surface were compared with those of reaction of other model compounds. This comparison suggests that after adsorption of 1-hexene on a Cu₃Pt(111) single-crystal surface, two steps are responsible for the benzene formation: dehydrogenation and cyclization. Dehydrogenation occurs at temperatures below 350 K for all the compounds studied except for hexane and cyclohexane, which do not interact chemically with the surface and desorb molecularly below 250 K. Since benzene evolution from 1-hexene occurs at 405 K, the dehydrogenation step cannot be considered rate determining, whereas the most

SCHEME 1: Benzene Formation from 1-Hexene on Cu₃Pt(111)



reasonable explanation for such a high temperature of benzene formation is that the rate-determining step is the formation of a cyclic intermediate. These results have been confirmed by comparison with hydrogen evolution after the dehydrogenation/cyclization reaction of the compounds studied.

Experimental Section

The experimental results presented here were obtained in an ultrahigh-vacuum chamber with background pressure of $\sim 5 \times 10^{-10}$ Torr equipped with an Auger electron spectrometer (AES), a high-resolution electron energy loss spectrometer, a differentially pumped quadrupole mass spectrometer, an ion gun for surface cleaning, a low-energy electron diffraction apparatus (LEED), and a setup for reflection–absorption infrared spectroscopy. A detailed description of this vacuum system is published elsewhere.⁴³

The Cu₃Pt(111) single crystal was obtained from Material-Technologie & Kristalle GmbH (Jülich, Germany) as a circular disk (1 cm diameter and 2 mm thickness) polished to a mirror finish on one of the (111) surfaces. The crystal was mounted on a resistive heating element attached to a manipulator. The temperature of the crystal was measured by a chromel–alumel thermocouple whose junction was wedged into the hole on the side of the crystal. Crystal temperatures as low as 110 K could be achieved by cooling with liquid nitrogen. Heating was provided by a dc power supply (Hewlett-Packard, 6291A), controlled by a temperature programmer (Eurotherm 818 P). A temperature ramp of 3 K/s was used in the temperature-programmed desorption studies. The crystal was cleaned as described in ref 44 by Ar⁺ sputtering at 550 K for 15 min followed by annealing in UHV at 840 K for 20 min to free the surface of carbon, sulfur, and oxygen as confirmed by AES. A (1 × 1) diffraction pattern was observed by LEED.⁴⁵

All hydrocarbons used in the studies presented here were purchased from Aldrich and had a purity not less than 99%. They were purified by several freeze–pump–thaw cycles before introduction into the chamber, and the purity of the dosing gas was confirmed *in situ* by mass spectrometry. All the exposures are reported in langmuirs, where 1 langmuir is 10^{-6} Torr·s.

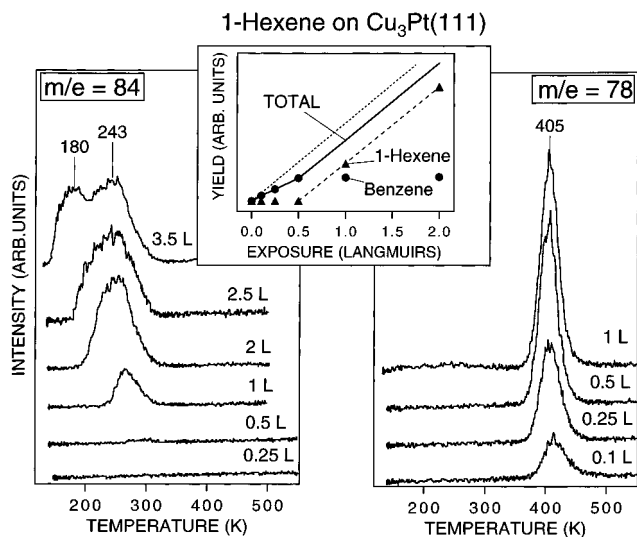


Figure 1. TPR/D studies of 1-hexene dehydrocyclization on a $\text{Cu}_3\text{Pt}(111)$ surface tracing $m/e^+ = 84$ (1-hexene molecular desorption) and $m/e^+ = 78$ (benzene formation). The inset shows the balance of peak areas evidenced in the TPR/D plots of $m/e^+ = 84$ and $m/e^+ = 78$ corrected for the mass spectrometer sensitivity plotted versus 1-hexene exposure. (L = langmuir.)

For the TPD experiments, the adsorbate-covered surface was positioned line-of-sight to the mass spectrometer, about 2 mm from a 2 mm diameter sampling aperture that was used to detect selectively the molecules desorbing from the center of the single-crystal surface.

Results

Figure 1 presents the results of TPR/D studies of 1-hexene adsorption and reaction on a $\text{Cu}_3\text{Pt}(111)$ surface as a function of 1-hexene exposure. The evolution of masses 84 and 78 for exposures of the $\text{Cu}_3\text{Pt}(111)$ surface to different amounts of 1-hexene corresponds to 1-hexene molecular desorption and benzene formation and desorption, respectively. The TPD peaks for mass 84 represent molecular desorption of 1-hexene as was confirmed by following masses 84 and 27 at electron impact ionization energy 70 eV and mass 84 at an electron impact energy 9 eV (to eliminate cracking and isolate the molecular ion⁴⁶). It should be noted that these values of the electron impact ionization energy are the values from the mass spectrometer control panel. There is evidence that the actual values are slightly higher.⁴⁷ Molecular desorption of 1-hexene is not observed for exposures less than 0.5 langmuir. Above 0.5 langmuir there is a linear increase in the peak area as a function of exposure, as shown in the inset of Figure 1. This molecular desorption occurs at 270 K for low exposures (1 langmuir) and shifts down in temperature upon increasing the exposure. At 3 langmuirs, a second feature appears on the spectra at 180 K. Given that the onset for second layer desorption at 150 K (not shown) occurs for an exposure of 5 langmuirs the 180 K peak presumably corresponds to a second adsorption site in the monolayer.

For exposures less than 0.5 langmuir, where 1-hexene is not evolved molecularly from the surface, benzene ($m/e^+ = 78$) evolution is detected as a single peak at 405 K, as shown in Figure 1. The temperature of this peak is independent of the 1-hexene exposure and the peak area grows linearly with exposure up to a saturation value of 0.5 L. By tracing masses 78 and 77 at 70 eV electron impact ionization energy and mass 78 at 9 eV electron impact energy, this peak was assigned to benzene formation and desorption.

1-Hexene and benzene were the only gas-phase hydrocarbon species detected for the interaction of 1-hexene with Cu_3Pt -

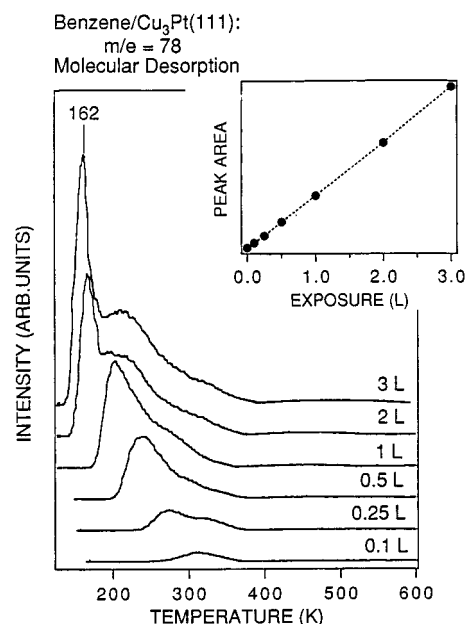


Figure 2. TPR/D studies of benzene molecular desorption from a $\text{Cu}_3\text{Pt}(111)$ surface tracing $m/e^+ = 78$. The inset shows the benzene desorption peak areas plotted vs exposure. (L = langmuir.)

(111). The total peak areas of these compounds (corrected for the mass spectrometer sensitivities) are plotted in the inset of Figure 1. Note that the total area of these two features is not a straight line, a result that indicates (in the absence of a nonlinearity in the adsorption rate) that there are other products of the reaction. Consistent with this inference, Auger electron spectroscopy studies show that carbon remains on the surface after annealing to 840 K. The amount of carbon for exposures > 0.5 langmuir corresponds to $4 \pm 1\%$ of a monolayer of 1-hexene. Since the amount of 1-hexene reacted corresponds to $13 \pm 2\%$ of a saturation monolayer of 1-hexene and the amount of benzene evolved corresponds to $9 \pm 2\%$ of a saturation monolayer of 1-hexene, we conclude that for exposures less than 0.5 langmuir, $70 \pm 10\%$ of the adsorbed 1-hexene is converted to benzene and $30 \pm 10\%$ decomposes to deposit carbon and evolve hydrogen. Consistent with this conclusion, we find that if saturation exposures of 1-hexene are repeated without surface cleaning to remove carbon between the measurements, the area of the benzene peak decreases by $30 \pm 5\%$.

Figure 2 presents TPD studies following the adsorption of benzene on a $\text{Cu}_3\text{Pt}(111)$ surface. Benzene molecules desorb molecularly from the surface without undergoing decomposition. At low exposures the desorption of benzene occurs at ~ 310 K. This temperature shifts down to 200 K upon increasing benzene exposure to 1 langmuir. Further increase of exposure results in a second desorption feature at 162 K which is saturated at 3 langmuirs. Given that the desorption temperature of benzene from the second layer is ~ 15 K lower (the results are not presented here), this feature can be assigned to the desorption from a different site on the alloy surface. Areas of the TPD peaks are plotted vs benzene exposure up to a monolayer saturation in the inset of Figure 2 and show a linear increase with exposure, supporting the conclusion of the molecular desorption of benzene as opposed to decomposition. On the basis of these TPD spectra for the molecular desorption of benzene from $\text{Cu}_3\text{Pt}(111)$, which show benzene evolution at temperatures between 160 and 310 K with no decomposition, we conclude that evolution of benzene from 1-hexene at 405 K is a reaction-limited desorption process.

Having found that benzene formation by 1-hexene on a $\text{Cu}_3\text{Pt}(111)$ surface is reaction limited, one can determine further whether the rate of benzene evolution is limited by dehydro-

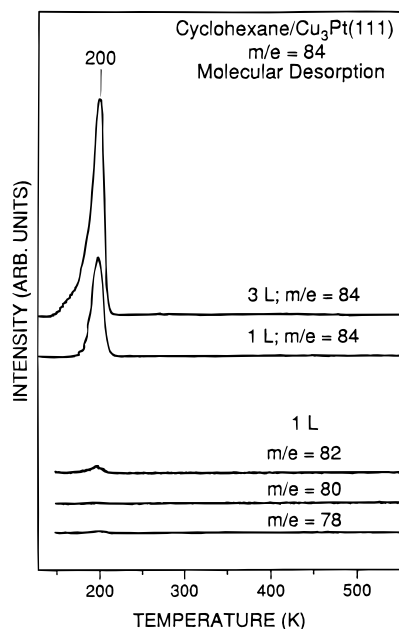


Figure 3. TPR/D studies of cyclohexane molecular desorption from a $\text{Cu}_3\text{Pt}(111)$. TPR/D traces of masses 82, 80, and 78 are presented as a proof of the absence of chemical transformation of cyclohexane on this surface. (L = langmuir.)

genation or cyclization. The studies of cyclohexane, cyclohexene, 1,3-cyclohexadiene, and 1,4-cyclohexadiene have been performed to analyze the dehydrogenation step. Because all these compounds are cyclic, the only reaction needed for any of them to produce benzene is the dehydrogenation reaction.

The TPD studies of cyclohexane desorption from $\text{Cu}_3\text{Pt}(111)$ are presented in Figure 3. The results of these studies suggest that cyclohexane does not undergo any chemical transformation on the $\text{Cu}_3\text{Pt}(111)$ surface and simply desorbs molecularly without decomposition, which is also confirmed by AES. No dehydrogenation products are observed as shown in Figure 3 by tracing masses 78 (benzene), 80 (cyclohexadienes), and 82 (cyclohexene). A small peak observed in the TPD spectra of

masses 78 and 82 matches in temperature and shape the molecular desorption peak observed for mass 84 and corresponds to the cracking fragment of desorbing cyclohexane. The fact that cyclohexane was not found to undergo any chemical changes on Cu_3Pt reflects the low activation energy of desorption for this hydrocarbon compared to the activation energy of dehydrogenation on a $\text{Cu}_3\text{Pt}(111)$ surface. This disadvantage can probably be overcome at high pressure, conditions beyond the scope of this investigation.

TPR/D studies of cyclohexene on a $\text{Cu}_3\text{Pt}(111)$ surface are presented in Figure 4. Similar to the case of 1-hexene, no molecular desorption is observed for cyclohexene exposures less than 0.5 langmuir. However, benzene evolution is evidenced at 290 K, which is much lower than that from the reaction of 1-hexene. This 290 K feature saturates when the cyclohexene exposure reaches 0.5 langmuir and does not change upon further increase in exposure, but at the same time molecular desorption of cyclohexene commences. Peaks below 250 K present in TPR/D spectra of mass 78 correspond in temperature and shape to the peaks recorded for mass 82 describing molecular desorption of cyclohexene and represent the cracking pattern of this compound. On the other hand, the feature above 250 K in the benzene evolution spectrum represents the combination of benzene formation and desorption. The peak at 290 K shows the reaction-limited evolution of benzene whereas the broad peak superimposed with the peak at 290 K and tailing to ~ 370 K represent the desorption of benzene formed during cyclohexene dehydrogenation at lower temperatures. This can be proven by comparing the TPR/D spectra of Figure 4 with those of molecular desorption of benzene shown in Figure 2. Benzene is the only hydrocarbon product of cyclohexene transformation by the $\text{Cu}_3\text{Pt}(111)$ surface, as confirmed by the linear increase of total area of TPR/D peaks at masses 78 and 82 in the inset of Figure 4 (corrected for the mass spectrometer sensitivity) and by the absence of decomposition as confirmed by AES.

The TPR/D studies of the interaction of 1,3- and 1,4-cyclohexadienes with a $\text{Cu}_3\text{Pt}(111)$ surface are presented in Figures 5 and 6, respectively. The behavior of these hydro-

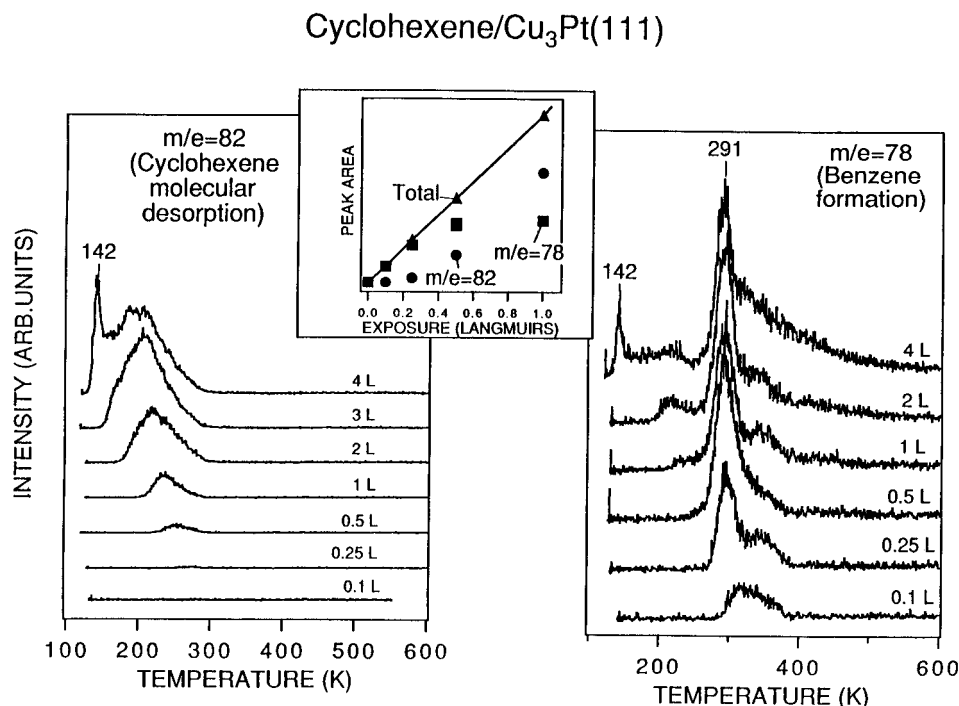


Figure 4. TPR/D studies of cyclohexene dehydrogenation on a $\text{Cu}_3\text{Pt}(111)$ surface tracing $m/e^+ = 82$ (cyclohexene molecular desorption) and $m/e^+ = 78$ (benzene formation). The inset shows the balance of peak areas evidenced in the TPR/D plots of $m/e^+ = 82$ and $m/e^+ = 78$ corrected for the mass spectrometer sensitivity plotted versus cyclohexene exposure. (L = langmuir.)

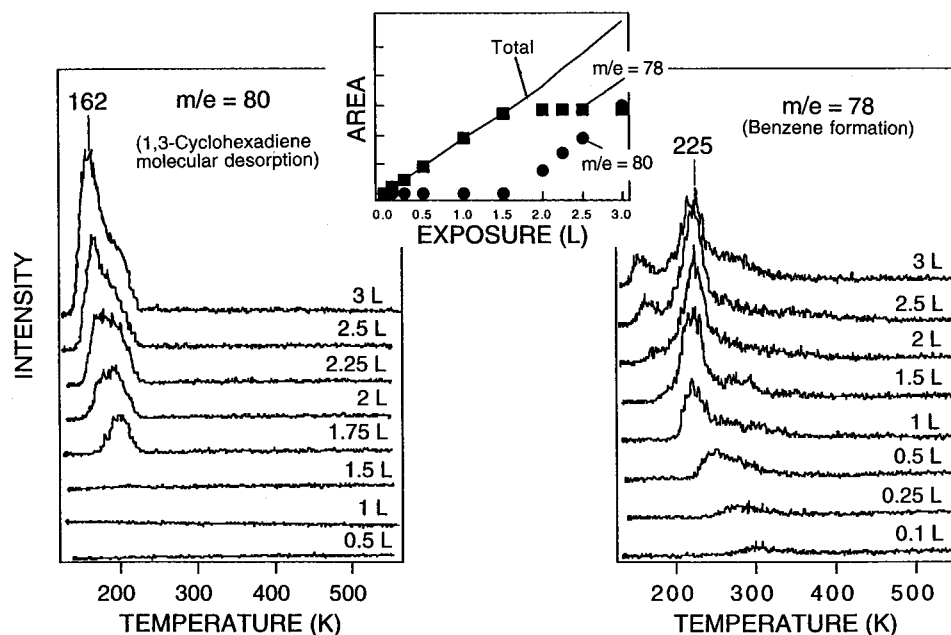
1,3-Cyclohexadiene/ $\text{Cu}_3\text{Pt}(111)$ 

Figure 5. TPR/D studies of 1,3-cyclohexadiene dehydrogenation on a $\text{Cu}_3\text{Pt}(111)$ surface tracing $m/e^+ = 80$ (cyclohexadiene molecular desorption) and $m/e^+ = 78$ (benzene formation). The inset shows the balance of peak areas evidenced in the TPR/D plots of $m/e^+ = 80$ and $m/e^+ = 78$ corrected for the mass spectrometer sensitivity plotted versus 1,3-cyclohexadiene exposure. (L = langmuir.)

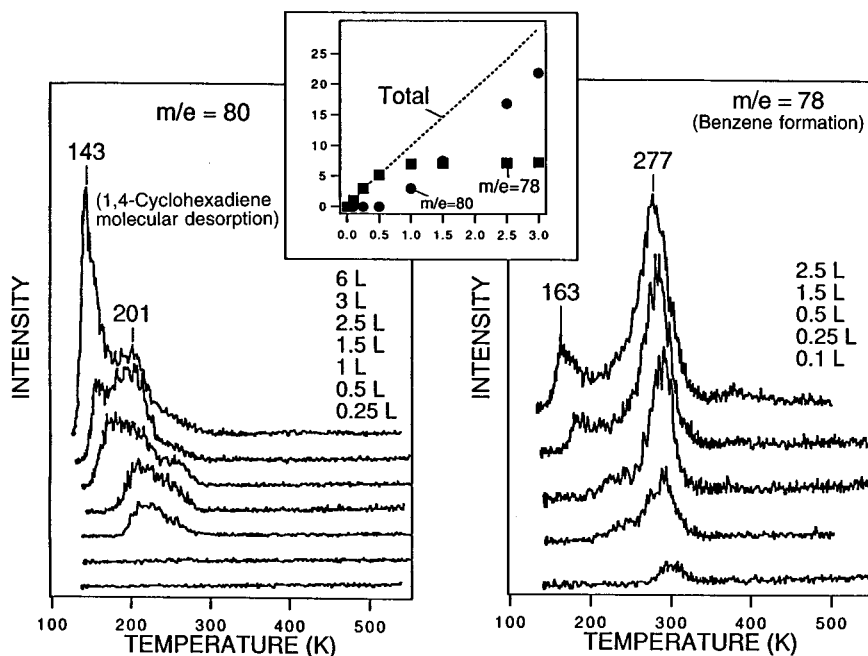
1,4-Cyclohexadiene/ $\text{Cu}_3\text{Pt}(111)$ 

Figure 6. TPR/D studies of 1,4-cyclohexadiene dehydrogenation on a $\text{Cu}_3\text{Pt}(111)$ surface tracing $m/e^+ = 80$ (cyclohexadiene molecular desorption) and $m/e^+ = 78$ (benzene formation). The inset shows the balance of peak areas evidenced in the TPR/D plots of $m/e^+ = 80$ and $m/e^+ = 78$ corrected for the mass spectrometer sensitivity plotted versus 1,4-cyclohexadiene exposure. (L = langmuir.)

carbons on the alloy surface is essentially the same as that of cyclohexene. No residual surface carbon was detected by AES after the surface was heated to 700 K and no other reaction products, except for benzene and hydrogen, have been observed. 1,3-Cyclohexadiene does not exhibit any molecular desorption until the exposure reaches 1.5 langmuirs, 50% of a monolayer. Upon increasing the diene exposure, molecular desorption commences. 1,4-Cyclohexadiene quantitatively evolves benzene up to 0.7 langmuir (20% of a monolayer), and upon further increase in diene exposure, molecular desorption commences. Interestingly, in the case of 1,4-cyclohexadiene, benzene is

evolved at 277 K, which is very close to the temperature of benzene evolution from cyclohexene. On the other hand, the formation of benzene by 1,3-cyclohexadiene is evident in Figure 5 as an overlap of two features: a sharp 225 K TPD peak indicates the reaction-limited evolution of benzene, whereas a broad feature tailing to higher temperatures suggests that some of the benzene formed during this reaction stays on the surface after the formation rather than immediately desorbing to the gas phase. These differences in the behavior of 1,3- and 1,4-cyclohexadienes on a $\text{Cu}_3\text{Pt}(111)$ surface are addressed in the Discussion section.

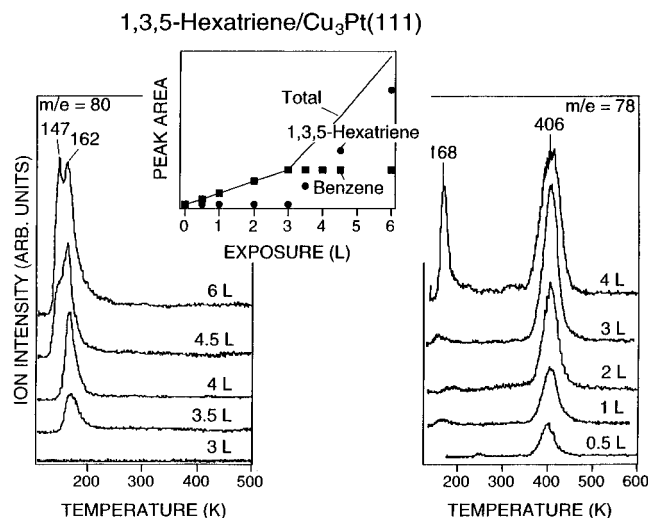


Figure 7. TPR/D studies of 1,3,5-hexatriene aromatization on a $\text{Cu}_3\text{Pt}(111)$ surface tracing $m/e^+ = 80$ (1,3,5-hexatriene molecular desorption) and $m/e^+ = 78$ (benzene formation). The inset shows the balance of peak areas evidenced in the TPR/D plots of $m/e^+ = 80$ and $m/e^+ = 78$ corrected for the mass spectrometer sensitivity plotted versus 1,3,5-hexatriene exposure. (L = langmuir.)

The interaction of 1,3,5-hexatriene with a $\text{Cu}_3\text{Pt}(111)$ surface has been analyzed on the basis of the TPR/D results in Figure 7. Unlike the C_6 cyclic compounds discussed above, hexatriene needs to undergo only a cyclization step to evolve benzene, and no additional dehydrogenation is necessary. Tracing of $m/e^+ = 80$ shows no 1,3,5-hexatriene molecular desorption for the exposures up to 3.0 L, which corresponds to 75% of a monolayer. However, such a high reactivity is coupled with an extremely low selectivity to benzene formation, since the AES studies and TPR/D peak area analysis show that only 30% of the hexatriene molecules lead to the formation of benzene, with the other 70% decomposing to leave carbon on the surface.

Because the only step needed for 1,3,5-hexatriene to form benzene is cyclization, the temperature of benzene evolution from the reaction of hexatriene with a $\text{Cu}_3\text{Pt}(111)$ surface should provide a definitive answer to the question of which step is rate determining in the benzene formation on this surface. The temperature of benzene evolution from 1,3,5-hexatriene is 406 K, which is nearly identical with the temperature of benzene evolution from 1-hexene, indicating that cyclization is indeed the rate-determining step.

To compare all the compounds studied with respect to the same reference point, the evolution of hydrogen, $m/e^+ = 2$, is presented in Figure 8. 1,3- and 1,4-Cyclohexadienes and cyclohexene show hydrogen evolution between 220 and 320 K. The same temperature range is observed for the evolution of hydrogen adsorbed on a $\text{Cu}_3\text{Pt}(111)$ surface from background, as shown in the bottom spectrum of Figure 8. Comparison of the peak temperatures and shapes for hydrogen recombination/desorption with those of benzene evolution suggests that in the case of cyclohexene and 1,3-cyclohexadiene, hydrogen evolution is limited by the hydrogen recombination and desorption. However, for 1,4-cyclohexadiene, hydrogen evolution is limited by the dehydrogenation of the hydrocarbon. Results of the $m/e^+ = 2$ TPR/D studies of 1-hexene presented in Figure 8 show two features: one at 280 K and another at 395 K. The area of the low-temperature feature is approximately twice as large as that at 395 K. This ratio is qualitatively consistent with the initial dehydrogenation of 1-hexene to lose four hydrogen atoms by 350 K and an additional two hydrogen atoms to form benzene at 400 K. However, this statement is strictly correct only for a 100% conversion of 1-hexene to benzene. Since 30% of the 1-hexene is converted to elemental carbon and hydrogen for

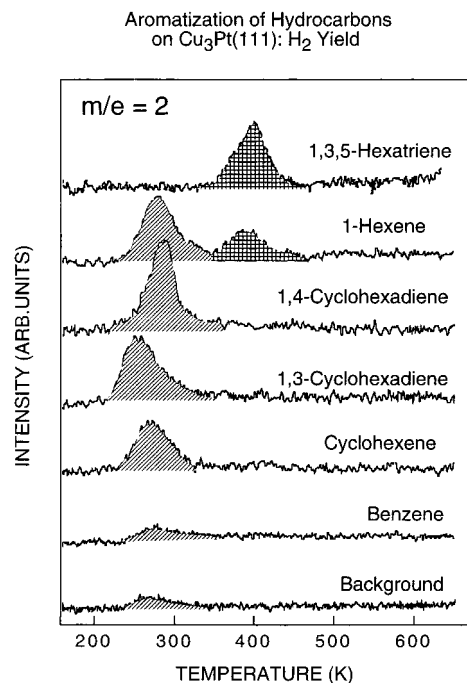


Figure 8. TPR/D studies of hydrogen ($m/e^+ = 2$) evolution after exposure of a $\text{Cu}_3\text{Pt}(111)$ surface to a monolayer of a hydrocarbon studied.

this 0.5 langmuir exposure of 1-hexene, additional hydrogen evolution that is *not* associated with the conversion of 1-hexene to benzene is expected. No additional hydrogen evolution for the temperatures up to 650 K has been observed in these studies, implying either that this evolution occurs above 650 K or that this hydrogen evolution resulting from complete hydrocarbon decomposition indeed overlaps with the peaks below 500 K. Interestingly, some hydrogen evolution starts being noticeable for 1,3,5-hexatriene reaction with a $\text{Cu}_3\text{Pt}(111)$ surface between 600 and 650 K, but the conclusion about the exact amount of hydrogen evolved at this temperature range cannot be made since the current TPD result only captures the beginning of this hydrogen desorption feature. Furthermore, the estimation of peak areas for hydrogen evolution is also complicated by the high hydrogen background. As a result, the peak areas can be calculated only with an accuracy of about 20%. This means that the amount of hydrogen evolved from the complete hydrocarbon decomposition on a $\text{Cu}_3\text{Pt}(111)$ surface may be comparable to the error of measurements. Although it is rather difficult to predict the amount of hydrogen produced by such a reaction without knowing the exact pathway of decomposition, it seems plausible that two TPD features of hydrogen from 1-hexene correspond to the two steps of the dehydrocyclization reaction. The strongest evidence is provided by the comparison of hydrogen evolution from 1-hexene and 1,3,5-hexatriene. The important point to note is that the high-temperature peaks of these two molecules match perfectly in temperature, supporting the hypothesis that cyclization is the rate-limiting step in the overall dehydrocyclization reaction.

The last compound studied was 1,3-hexadiene (spectra not shown). Although no detailed analysis of the reaction of this compound with a $\text{Cu}_3\text{Pt}(111)$ surface has been made, the temperature of benzene formation from 1,3-hexadiene is practically the same as for other linear compounds studied.

Discussion

As stated in the Introduction section, the dehydrocyclization reaction is an important step in many industrial processes. This reaction has been studied extensively under high-pressure

TABLE 1

hydrocarbon	<i>T</i> , K (H ₂ evolution)	<i>T</i> , K (benzene evolution)	<i>E_a</i> , ^a kcal/mol (benzene formation)	% of a monolayer reacted	% of reaction leading to benzene formation
1-hexene	281, 393	405	25.1	13	70
hexane	NO	NO	NO	NO	NO
1,3-hexadiene		390	24.2		
1,3,5-hexatriene	399	406	25.1	75	30
cyclohexane	NO	NO	NO	NO	NO
cyclohexene	271	291	17.8	17	100
1,3-cyclohexadiene	257	225	13.7	50	100
1,4-cyclohexadiene	285	277	17.0	20	100
benzene	NO	210			

^a *E_a* is calculated based on the peak temperature using the Redhead method for first-order reaction and assuming a 10^{13} s^{-1} preexponential factor.

conditions, but little is known about the mechanism of this reaction. Even less information is available about the nature of the intermediates in this reaction, since UHV studies, which might be able to uncover the mechanistic uncertainties, have been complicated by the competing isomerization and decomposition pathways.

Two major pathways available for the dehydrocyclization reaction to occur have been suggested. Both are shown in Scheme 1. The first mechanism involves cyclization as the first step of the overall transformation. This cyclization step, leading to the formation of either saturated or partially dehydrogenated cyclic species, is followed by the dehydrogenation to form benzene. The other possibility is that the dehydrogenation reaction to form mono-, then bi-, and, finally, tri-unsaturated intermediates precedes the cyclization step.

Thus, there are two major questions that we attempted to answer: (1) if we assume that the formation of cyclic intermediate is the first step of the dehydrocyclization reaction, can we produce benzene starting with partially dehydrogenated cyclic compounds, and if so, then (2) are the rate and activation energy for benzene formation by proposed cyclic intermediates higher or lower than the activation parameters for benzene formation by 1-hexene? The answer to the first question was shown to be positive. All the cyclic compounds studied here, except for cyclohexane, showed reactivity toward benzene formation on Cu₃Pt(111). (The major cause for cyclohexane not to show any reactivity can be related to ultrahigh vacuum conditions.) We can then compare the activation energy and the rate of benzene formation by all cyclic compounds to those by 1-hexene. The activation parameters for the aromatization reaction in all the compounds studied are presented in Table 1. It is easily seen that for cyclic hydrocarbons the activation energy for benzene formation is approximately 9.4 ± 2.0 kcal/mol lower than that for 1-hexene. This translates into 7 ± 2 orders of magnitude difference in the reaction rate at a common temperature of 350 K as calculated by the Redhead method for the first-order reaction assuming a preexponential factor of 10^{13} s^{-1} .⁴⁸ The much higher activation energy for the dehydrocyclization of 1-hexene and 1,3,5-hexatriene to benzene than for the aromatization of cyclic compounds on a Cu₃Pt(111) surface suggests that the dehydrogenation step is not rate determining in the overall dehydrocyclization reaction. On the contrary, all the TPR/D results presented above propose that the formation of a cyclic intermediate is the rate-determining step in the dehydrocyclization reaction. The question remaining unanswered is if the rate of formation of such a cyclic intermediate is limited by C-H bond breaking or the formation of a C-C bond. The results presented in this paper cannot answer this question. Analysis of analogous systems on copper or platinum single-crystal surfaces cannot be made until the nature of the surface intermediate in the dehydrocyclization reaction is uncovered. Some remarks on comparison of copper, platinum, and copper-platinum alloy are made in a separate paper.⁴⁹

The conclusion about cyclization being the rate-determining step in the dehydrocyclization reaction is substantiated by TPR/D studies of hydrogen evolution from reactions of the hydrocarbons studied with a Cu₃Pt(111) surface. Cyclohexene and cyclohexadienes evolve hydrogen between 220 and 320 K, which is the same temperature range as for benzene formation by these hydrocarbons. On the other hand, 1-hexene produces hydrogen at two different temperatures at 280 K and at 395 K, with the latter corresponding to the temperature of benzene evolution resulting from the reaction of 1-hexene with a Cu₃Pt(111) surface. The ratio of the areas of these two features suggests that 1-hexene loses four hydrogen atoms at 280 K and the other two at 395 K, leading to benzene formation. This suggests that the formation of benzene by 1-hexene on a Cu₃Pt(111) surface is not limited by the dehydrogenation reaction observed in cyclic compounds at low temperatures but rather by the cyclization reaction with the loss of two additional hydrogen atoms at 400 K.

Another interesting issue that can be addressed on the basis of the results presented in this paper is the site requirements for the dehydrocyclization reaction on a Cu₃Pt(111) surface. First, each platinum atom on this (111) surface is surrounded by six copper atoms, which means that no platinum clusters or even pairs are necessary for the dehydrocyclization to proceed. On the other hand, this reaction is not observed on pure copper. The effect of platinum on this reaction can be 2-fold. First, platinum atoms may participate in dehydrogenation and cyclization steps by themselves, making it necessary for the hydrocarbon molecules to be in a certain geometric arrangement prior to the reaction. Alternatively, platinum may modify the properties of the alloy in such a way that copper sites become more reactive and can actually participate in either one or both steps of the dehydrocyclization reaction.

As shown in Table 1, only a small fraction of adsorbed monolayer of hydrocarbons participates in the chemical reaction with the surface. Interestingly, the highest reactivity is exhibited by 1,3-cyclohexadiene, which only needs to lose a pair of adjacent hydrogen atoms to form benzene. Supposedly, participation of only one surface reactive site is required in order for this transformation to occur. The activation energy for this dehydrogenation process is the lowest among the hydrocarbons studied here. On the other hand, 1,4-cyclohexadiene shows the same reactivity as cyclohexene, and activation energies calculated on the basis of the Redhead method⁴⁸ are similar for these two compounds. Such similarities probably mean that the loss of two pairs of adjacent hydrogen atoms in a C₆ cyclic compound requires the same number of reactive surface sites as the elimination of two nonadjacent hydrogen atoms in 1,4-cyclohexadiene. Whether this reaction proceeds via an allylic-type intermediate or the simultaneous loss of both hydrogen atoms cannot be answered on the basis of the results presented in this paper, but the requirement of multiple surface sites to participate in this reaction seems reasonable.

The term "reactive site" used in the previous paragraph is not and probably cannot be defined for the studies presented here. For the studies of the reactivity of platinum itself, tin⁵⁰ and bismuth⁵¹ were used as inert components of the alloys. Studies presented in ref 51 suggest that the number of platinum atoms required for the dehydrogenation of cyclic hydrocarbons on a Pt(111) surface can be as large as six in addition to those required for adsorption.

Recent theoretical studies by Hammer and Nørskov⁵² show that the electronic structures of platinum and copper in the Cu₃-Pt alloy are quite different from the electronic structures of either pure platinum or copper. This is in agreement with the difference in chemical properties between Cu, Pt, and Cu₃Pt. However, even though the electronic structures of Cu and Pt within the (111) surface of Cu₃Pt alloy are quite similar,⁵² this cannot answer the question of whether the dehydrogenation and cyclization steps, or maybe only one of them, require the presence of a Pt-center.

Finally, although general trends in chemical and physical properties of bimetallic surfaces are reviewed extensively in ref 53, the number of studies on the reactivities of Cu-Pt alloys is very limited. Further theoretical and experimental studies are required to determine the nature of the reactive site on a Cu₃-Pt(111) surface.

Conclusions

TPR/D studies show that 1-hexene chemically reacts with a Cu₃Pt(111) surface at low coverages, while upon increasing coverage molecular desorption of 1-hexene commences. In the course of this reaction 70 ± 10% of reacted 1-hexene produces benzene and hydrogen, with the other 30 ± 10% decomposing to leave carbon on the surface as confirmed by AES. Comparison of the rates of benzene and hydrogen evolution from the aromatization of 1-hexene with other linear and cyclic unsaturated hydrocarbons suggests that the rate-determining step in the dehydrocyclization of 1-hexene is not the dehydrogenation step but rather the cyclization step, which is accompanied by the loss of two additional hydrogen atoms.

Acknowledgment. Financial support from the National Science Foundation (Grant No. CHE-93-18625), The Dow Chemical Company, and Union Carbide as part of their Innovation Recognition Program is gratefully acknowledged.

References and Notes

- Bernard, J. R. *Proc. 5th Int. Conf. Zeolites* **1980**, 66.
- Kanai, J.; Kawata, N. *Appl. Catal.* **1989**, 55, 115.
- Fung, J.; Wang, I. *J. Catal.* **1991**, 130, 577.
- Lee, J. G.; Kim, K. C. *Tetrahedron Lett.* **1992**, 33, 6363.
- Popova, Z.; Aristirova, K.; Dimitrov, C. *Collect. Czech. Chem. Commun.* **1992**, 57, 2553.
- Lanh, H. D.; Tuan, V. A.; Kosslick, H. *Appl. Catal. A* **1993**, 103, 205.
- Joshi, P. N.; Bandyopadhyay, R.; Awate, S. V.; Shiralkar, V. P.; Rao, B. S. *React. Kinet. Catal. Lett.* **1994**, 53, 231.
- Dai, L.-X.; Sakashita, H.; Tatsumi, T. *J. Catal.* **1994**, 147, 311.
- Kharson, M. S.; Dzigvashvili, T. R.; Dolidze, A. V.; Kiperman, S. L. *Kinet. Catal.* **1991**, 32, 344.
- Zheng, J.; Dong, J.-L.; Yan, A.-Z. *Appl. Catal. A* **1995**, 126, 141.
- Paál, Z.; Tétényi, P. *J. Catal.* **1973**, 30, 350.
- (a) Dimitrov, C.; Bezouhanova, T. P.; Kovacheva, P. H.; Dineva, R. K. *Dokl. Bolg. Akad. Nauk* **1979**, 32, 1231. (b) Zimmer, H.; Rozanov, V. V.; Sklyarov, A. V.; Paál, Z. *Appl. Catal.* **1982**, 2, 51.
- Davis, S. M.; Zaera, F.; Somorjai, G. A. *J. Catal.* **1984**, 85, 206.
- Joyner, R. W.; Lang, B.; Somorjai, G. A. *J. Catal.* **1972**, 27, 405.
- Gillespie, W. D.; Herz, R. K.; Petersen, E. E.; Somorjai, G. A. *J. Catal.* **1981**, 70, 147.
- Dauscher, A.; Garin, F.; Maire, G. *J. Catal.* **1987**, 105, 233.
- Garin, F.; Aeyach, S.; Legaire, P.; Maire, G. *J. Catal.* **1982**, 77, 323.
- Garin, F.; Maire, G. *Acc. Chem. Res.* **1989**, 22, 100.
- Tsai, M.-C.; Friend, C. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1982**, 104, 2539.
- Davis, S. M.; Somorjai, G. A. *J. Catal.* **1980**, 65, 78.
- Land, D. P.; Pettiette-Hall, C. L.; McIver, R. T.; Hemminger, J. C. *J. Am. Chem. Soc.* **1989**, 111, 5970.
- Martin, R.; Gardner, P.; Tüshaus, M.; Bonev, C.; Bradshaw, A. M. *J. Electron. Spectrosc. Relat. Phenom.* **1990**, 54/55, 773.
- Pettiette-Hall, C. L.; Land, D. P.; McIver, R. T.; Hemminger, J. C. *J. Am. Chem. Soc.* **1991**, 113, 2755.
- Bussel, M. E.; Henn, F. C.; Campbell, C. T. *J. Phys. Chem.* **1992**, 96, 5978.
- Henn, F. C.; Diaz, A. L.; Bussel, M. E.; Hugenschmidt, M. B.; Domagala, M. E.; Campbell, C. T. *J. Phys. Chem.* **1992**, 96, 5965.
- Hugenschmidt, M. B.; Diaz, A. L.; Campbell, C. T. *J. Phys. Chem.* **1992**, 96, 5974.
- Parker, D. H.; Pettiette-Hall, C. L.; Li, Y.; McIver, R. T.; Hemminger, J. C. *J. Phys. Chem.* **1992**, 96, 1888.
- Land, D. P.; Erley, W.; Ibach, H. *Surf. Sci.* **1993**, 289, 237.
- Lamont, C. L. A.; Borbach, M.; Stenzel, W.; Conrad, H.; Bradshaw, A. M. *Chem. Phys. Lett.* **1994**, 230, 265.
- Cheng, A. H.; Dooley, K. M.; Price, G. L. *J. Catal.* **1989**, 116, 325.
- Saymeh, R. A.; Asfour, H. M.; Mahmoud, S. S. *Indian J. Chem.* **1995**, 34B, 546.
- de Jongste, H. C.; Kuijers, F. J.; Ponec, V. *Prep. Catal., Proc. Int. Symp. 1975* **1976**, 207.
- de Jongste, H. C.; Kuijers, F. J.; Ponec, V. *Proc. Int. Congr. Catal., 6th, 1976* **1977**, 2, 915.
- de Jongste, H. C.; Ponec, V. *J. Catal.* **1980**, 63, 389.
- de Jongste, H. C.; Ponec, V.; Gault, F. G. *J. Catal.* **1980**, 63, 395.
- Xu, C.; Tsai, Y.-L.; Koel, B. E. *J. Phys. Chem.* **1994**, 98, 585.
- Xu, C.; Koel, B. *Surf. Sci.* **1994**, 304, 249.
- Sachtler, J. W. A.; Van Hove, M. A.; Bibérian, J. P.; Somorjai, G. A. *Phys. Rev. Lett.* **1980**, 45, 1601.
- Sachtler, J. W. A.; Bibérian, J. P.; Somorjai, G. A. *Surf. Sci.* **1981**, 110, 43.
- Yeates, R. C.; Somorjai, G. A. *J. Catal.* **1987**, 103, 208.
- Sachtler, J. W. A.; Somorjai, G. A. *J. Catal.* **1983**, 81, 77.
- Paál, Z. In *Catalytic Naphta Reforming: Science and Technology*; Marcel Dekker, Inc.: New York, 1995.
- Jenks, C. J.; Bent, B. E.; Bernstein, N.; Zaera, F. *J. Am. Chem. Soc.* **1993**, 115, 308.
- Castro, G. R.; Schneider, U.; Busse, H.; Janssens, T.; Wandelt, K. *Surf. Sci.* **1992**, 269/270, 321.
- The surface structure and composition of Cu₃Pt(111) has recently been studied by Wandelt and co-workers, and their early papers reported a (2 × 2) LEED pattern for this surface.^{45a-c} This is the diffraction pattern that one would expect for ideal termination of the bulk lattice, and it corresponds to a lattice of isolated Pt atoms, each surrounded by six nearest neighboring Cu atoms in the plane. More recent papers from Wandelt et al. report a (1 × 1) pattern for Cu₃Pt(111),^{45d,e} which is the same as is observed here. The similarities between the bonding and reactions of CO and H₂ on the surfaces with these two different LEED patterns suggest that in both cases the surface Pt atoms are surrounded by Cu even though long range order of the Pt atoms is absent on the (1 × 1) surface. Low-energy ion-scattering studies indicate that the surface is enriched in copper by only 5%.^{45d,e} (a) Schneider, U.; Busse, H.; Linke, R.; Castro, G. R.; Wandelt, K. *J. Vac. Sci. Technol. A* **1994**, 12, 2069. (b) Linke, R.; Schneider, U.; Busse, H.; Becker, C.; Schröder, U.; Castro, G. R.; Wandelt, K. *Surf. Sci.* **1994**, 307, 407. (c) Becker, C.; Schröder, U.; Castro, G. R.; Schneider, U.; Busse, H.; Linke, R.; Wandelt, K. *Surf. Sci.* **1994**, 307, 412. (d) Shen, Y. G.; O'Connor, D. J.; Wandelt, K.; MacDonald, R. J. *Surf. Sci.* **1995**, 328, 21. (e) Shen, Y. G.; O'Connor, D. J.; Wandelt, K.; MacDonald, R. J. *Surf. Sci.* **1995**, 331-333, 746.
- Xi, M.; Bent, B. *J. Vac. Sci. Technol. B* **1992**, 10, 2440.
- Lin, J.-L.; Bent, B. *J. Am. Chem. Soc.* **1993**, 115, 2849.
- Redhead, P. A. *Vacuum* **1962**, 12, 203.
- Teplakov, A. V.; Gurevich, A. B.; Garland, E. R.; Bent, B. E.; Chen, J. G. Accepted for publication in *Langmuir*.
- Xu, C.; Peck, J. W.; Koel, B. E. *J. Am. Chem. Soc.* **1993**, 115, 751.
- Campbell, C. T.; Campbell, J. M.; Dalton, P. J.; Henn, F. C.; Rodriguez, J. A.; Seimanidis, S. G. *J. Am. Chem. Soc.* **1989**, 93, 806.
- Hammer, B.; Nørskov, J. K. *Surf. Sci.*, in press.
- Rodriguez, J. A. *Surf. Sci. Rep.* **1996**, 24, 223.