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SURFACES. THE CONVERSION OF CYCLOHEXANE, CYCLO-  
HEXENE AND CYCLOHEXADIENE TO BENZENE.

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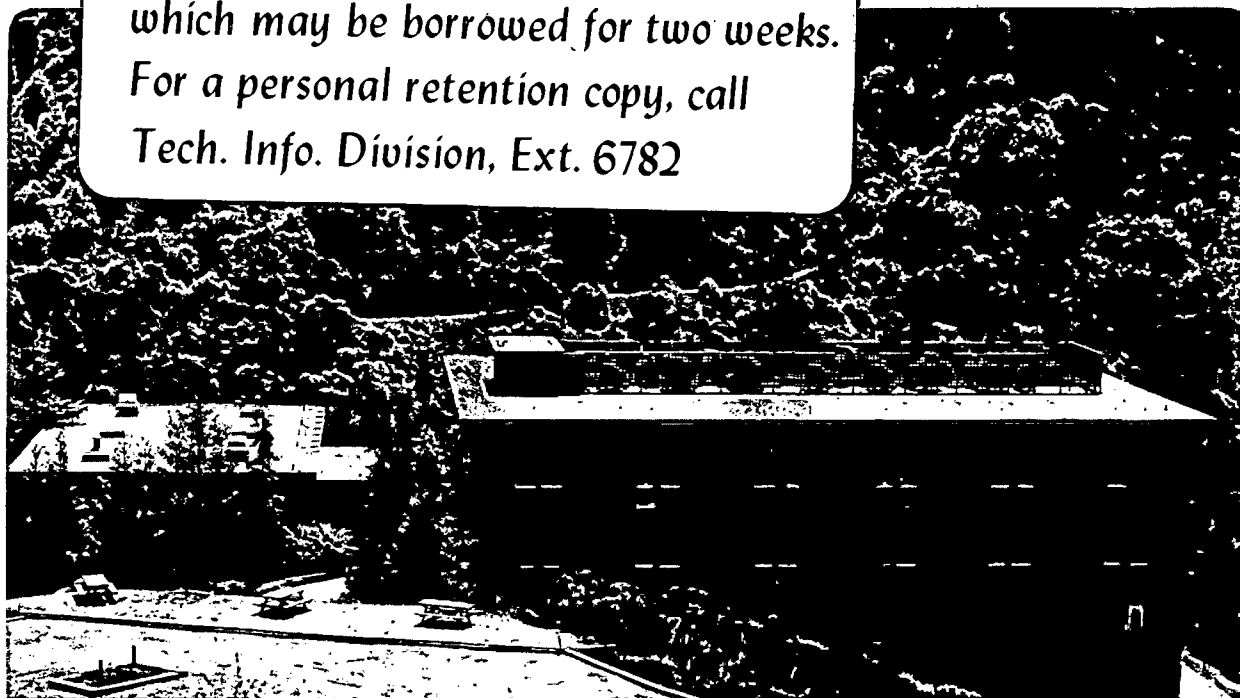
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Dehydrogenation Processes  
on Nickel and Platinum Surfaces  
The Conversion of Cyclohexane, Cyclohexene  
and Cyclohexadiene to Benzene.

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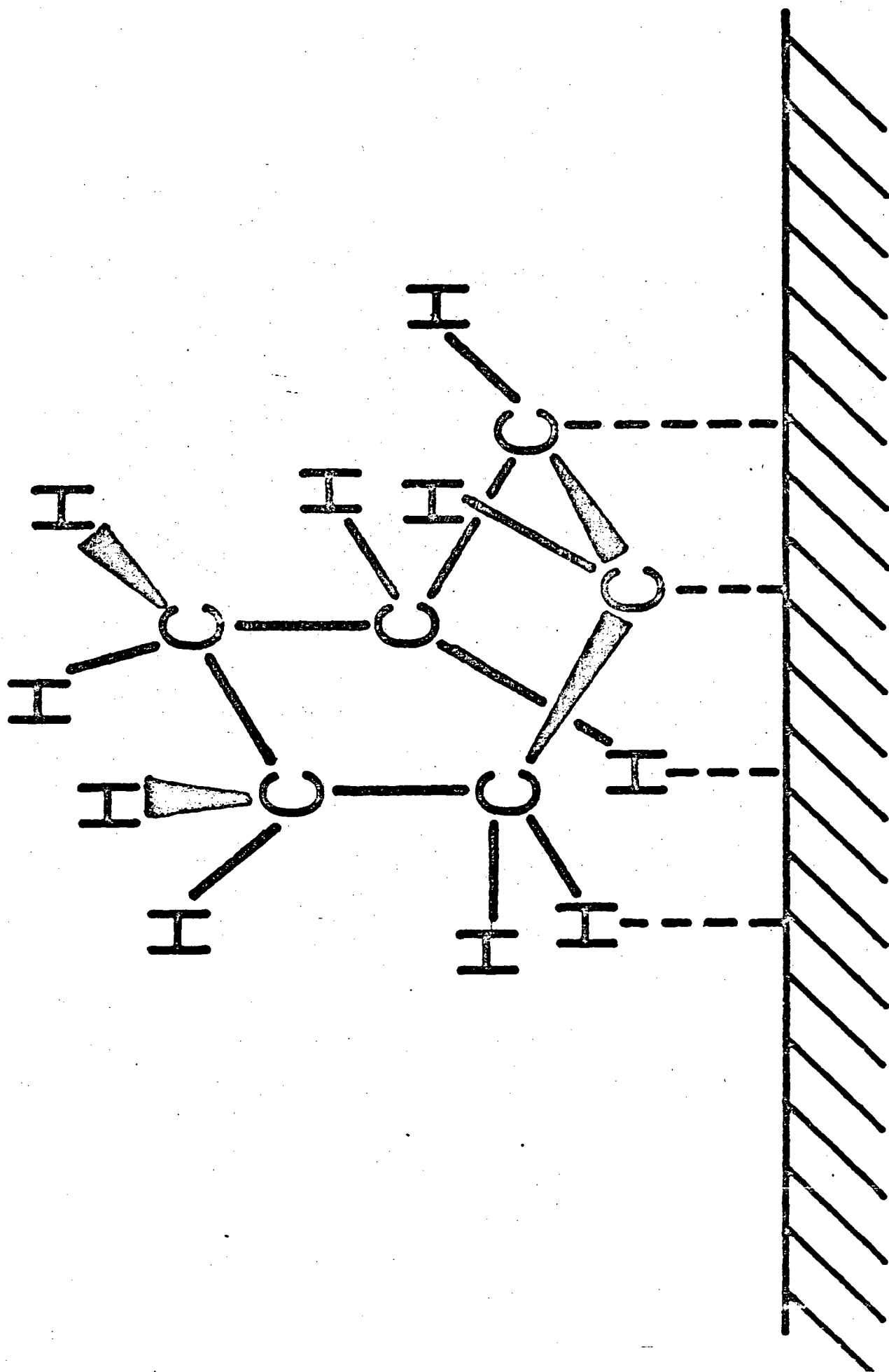
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ABSTRACT

Described is the surface coordination chemistry of cyclohexane, 1,3 and 1,4-cyclohexadiene and cyclohexene on the low Miller index planes and a stepped surface of nickel and on the platinum (111) and stepped 6(111)x(111) surfaces as established by thermal desorption spectroscopy, chemical displacement reactions, and isotopic labeling studies. Cyclohexane did not react with Ni(111) at 0 to 70°C, Ni(110) at 20-90°C, Ni(100) at 25-200°C, and Ni 9(111)x(111) at 20-70°C. A similar behavior was observed for Pt(111) at -35 to +135°C although a small degree of dehydrogenation was evident on this surface. Definite evidence for cyclohexane conversion to benzene was obtained for the stepped platinum surface; the reactivity of this stepped surface toward cyclohexane was substantially higher than the platinum (111) plane. Cyclohexene and 1,3 and 1,4-cyclohexadiene were converted, at least partially, to benzene on all the nickel and platinum surfaces. Hydrogen-deuterium (C-H) exchange during the conversion of a mixture of chemisorbed  $C_6H_{10}$  and  $C_6D_{10}$  and of a mixture of chemisorbed cyclohexadiene and deuterium atoms to benzene was evident only for the platinum surfaces. Carbon significantly altered the cyclohexene chemistry on Ni(110); Ni(110)-C was far more effective than the clean surface for dehydrogenation of cyclohexene to benzene. A substantial carbon effect on the chemistry of the other surfaces was not evident.

In our recent studies of the coordination chemistry of metal surfaces, we have attempted to delineate the electronic and stereochemical features of hydrocarbon surface chemistry that facilitate the breaking or forming of carbon-hydrogen bonds.<sup>1-9</sup> Stereochemical features that enable facile carbon-hydrogen bond breaking were incisively identified in an earlier<sup>1</sup> study of benzene and toluene chemisorption on five, crystallographically different nickel surfaces and on two platinum surfaces.<sup>2</sup> An unsaturated hydrocarbon molecule in the initial adsorption process should interact largely through the most energetically favorable donor  $\pi$  and acceptor  $\pi^*$  orbitals with appropriate metal surface orbitals. Thus, on an atomically flat surface, benzene should form a chemisorption state in which the  $C_6$  ring would lie largely in a plane parallel to the surface plane—a stereochemical feature supported by chemical, spectroscopic and diffraction data for a number of metal surfaces.<sup>1, 10</sup> Toluene should behave analogously but such a stereochemistry necessarily places methyl group hydrogen atoms close to surface metal atoms—a geometric feature that should facilitate C-H bond breaking; in fact, aliphatic C-H bonds of chemisorbed toluene are readily and selectively cleaved on Ni(111) and Ni(100).<sup>1</sup> In an analogous fashion, a cycloalkene such as cyclohexene should initially chemisorb with the olefinic bond more or less parallel to the surface plane which then, irrespective of the  $C_6$  ring conformation, will place some saturated C-H bonds close to the surface metal atoms as schematically shown in 1. Hence, dehydrogenation should be a facile process at least for



metal surfaces that are relatively good electron donors. One reaction course that should be favorable for the cycloalkene dehydrogenation on atomically flat metal surfaces would be the generation of a delocalized  $\pi$ - $C_nH_n$  species bound to the surface—with the carbon atoms largely lying in a plane parallel to the surface plane at least where  $n$  is relatively small. We are in the process of characterizing the surface chemistry of cycloalkanes, cycloalkenes and cycloalkadienes in the range of  $n=3$  to  $n=8$ . Here we present the chemistry of the  $C_6$  ring compounds for nickel and platinum surfaces.

### EXPERIMENTAL

Reagents and Procedures - Cyclohexane (Matheson Coleman & Bell) and  $d_{12}$ -cyclohexane (prepared from  $C_6D_6 + D_2$ ) were dried over sodium sulfate. Cyclohexene (Chem Samples, Co., 99.9% purity), and  $d_{10}$ -cyclohexene (Merck Isotopes, 99%  $d_{10}$ ) were dried over calcium hydride. The cyclohexane contained no detectable (permanganate test) amounts of unsaturated hydrocarbons. 1,3-cyclohexadiene and 1,4-cyclohexadiene (Chem. Samples, Co.) were stored in the vapor phase in glass containers held at  $0^\circ C$ . Trimethylphosphine was prepared and purified as described earlier.<sup>1</sup> The purity of these reagents was checked by mass spectrometry and gas chromatography.

All experiments were performed in an all-metal bakeable ultra high vacuum system with a base pressure of  $10^{-10}$  torr.<sup>1</sup> Procedures for chemisorption, thermal desorption experiments and chemical displacement reactions have been described by Friend and Muetterties.<sup>1</sup> Heating rates of  $25^\circ sec^{-1}$  were used. Procedures for cutting, polishing and cleaning of the nickel and platinum crystals were as described earlier.<sup>1,4,8</sup> Calibration of Auger spectral intensities for carbon coverages on nickel and on platinum and the surface chemistry of trimethylphosphine on nickel and platinum surfaces are reported in references 1 and 2.

Cyclohexane

Demuth, Ibach and Lehwald<sup>11a</sup> have shown that cyclohexane chemisorbed on Ni(111) at low temperatures desorbs at  $\sim -100^\circ\text{C}$  in a quantitative fashion. Consistent with this report, we found no evidence of cyclohexane reaction<sup>11b</sup> with Ni(111) at  $0-70^\circ\text{C}$  nor with Ni(110) at  $25-90^\circ\text{C}$ , Ni(100) at  $25-200^\circ\text{C}$  and Ni 9(111)x(111)<sup>11c</sup> at  $20-70^\circ\text{C}$ . Hence the residence time for cyclohexane on these surfaces within these temperature ranges and under the ultra high vacuum conditions was short relative to the rate of any dehydrogenation process; we presume there can be no retention of any cyclohexane derived species on these surfaces above  $\sim 20^\circ\text{C}$  under these conditions unless there is dehydrogenation.

Cyclohexane chemisorption on Pt(111) is partially reversible with a  $0^\circ\text{C}$  temperature for maximum desorption rate. when Pt(111)- $\text{C}_6\text{H}_{12}$  is formed at  $-15$  to  $-35^\circ\text{C}$ . The desorption was nearly quantitative although a small amount of hydrogen was desorbed from the surface at much higher temperatures. There was a weak, broad  $\text{H}_2$  desorption between  $200$  and  $400^\circ\text{C}$  and no benzene was detected in the thermal desorption experiment. However, even if the cyclohexane that reacted were quantitatively converted to benzene, no benzene would have been desorbed at these coverages of  $<0.1$  of a monolayer.<sup>2,12</sup> In fact, high resolution electron energy loss studies indicate that cyclohexane is converted to benzene on Pt(111) at  $\sim -73^\circ\text{C}$ .<sup>11a</sup> Treatment of Pt(111) with cyclohexane at  $134^\circ\text{C}$  gave a state that yielded only hydrogen, no benzene, in a thermal desorption experiment; the platinum surface had about a tenth of a monolayer of carbon after the thermal desorption experiment. A monolayer throughout this article is defined as one carbon atom per surface metal atom. It is important to note that our thermal desorption studies were not done as a function of heating rate. The conversion of cyclohexane to benzene is competitive with cyclohexane desorption and there may be a significant dependence in the partitioning between these two processes on heating rate.

Cyclohexane had a much higher sticking coefficient on Pt 6(111)x(111) than on Pt(111) and appeared to saturate at a coverage of about  $0.15$  to  $0.20$  of a monolayer. For this surface, the thermal desorption and displacement reactions



clearly established that dehydrogenation to benzene had occurred. (In assessing the experimental results, it is essential to keep in mind that benzene chemisorbed at below  $\sim 0.15$  monolayer coverage on this stepped platinum surface cannot be thermally desorbed or displaced by trimethylphosphine at  $30^\circ\text{C}$  as intact benzene). No benzene was detected in thermal desorption reaction of the stepped surface treated with cyclohexane ( $\sim 0.20$  monolayer) and only traces of benzene were displaced by trimethylphosphine at  $20^\circ\text{C}$ . In the thermal desorption experiment, there were three  $\text{H}_2$  desorption maxima at  $\sim 110$ ,  $195$  and  $350^\circ\text{C}$ , the last two of which correspond precisely to the desorption maxima of  $\sim 195$  and  $350^\circ\text{C}$  for  $\text{H}_2$  derived from benzene decomposition on this surface.<sup>2</sup> The chemisorption state generated in the cyclohexane reaction with the stepped surface<sup>11c</sup> appears to be best characterized as  $\text{Pt } 6(111)\times(111)\text{-C}_6\text{H}_6\text{-H}$  at least at temperatures  $>100^\circ\text{C}$ , with all the benzene molecules residing in the most strongly (irreversibly) bound state, because all the thermal characteristics of this surface are identical<sup>2</sup> with those of  $\text{Pt } 6(111)\times(111)\text{-C}_6\text{H}_6\text{-H}$  generated from  $\text{C}_6\text{H}_6$  and  $\text{H}_2$  at the same coverage level. Remaining open sites on this  $\text{Pt } 6(111)\times(111)\text{-C}_6\text{H}_6\text{-H}$  surface were incapable of effecting cyclohexane dehydrogenation and coverages above  $0.20$  could not be realized at moderate temperatures and the low pressures of the ultra high vacuum system. Treatment of this saturated state with trimethylphosphine, whereupon traces of benzene were displaced, followed by thermal desorption<sup>13</sup> did yield gaseous benzene at a desorption maximum of  $170\text{-}190^\circ\text{C}$ . When the saturated state was generated from a mixture of  $\underline{\text{C}}\text{-C}_6\text{H}_{12}$  and  $\underline{\text{C}}\text{-C}_6\text{D}_{12}$ , the desorbed benzene included all possible  $\text{C}_6\text{H}_x\text{D}_{6-x}$  molecules.

These experiments establish for the platinum system a significant difference between the atomically flat (111) and stepped  $6(111)\times(111)$  surface in the dehydrogenation of cyclohexane. Were the small reactivity of the  $\text{Pt}(111)$  surface toward cyclohexane due solely to surface imperfections (steps), then the difference between the flat and stepped surface might be a qualitative one but there are plausible alternative explanations. Since cyclohexane did not react with nickel surfaces,<sup>11c</sup> one might be tempted to conclude these surfaces are less reactive than their platinum analogs. Such a conclusion

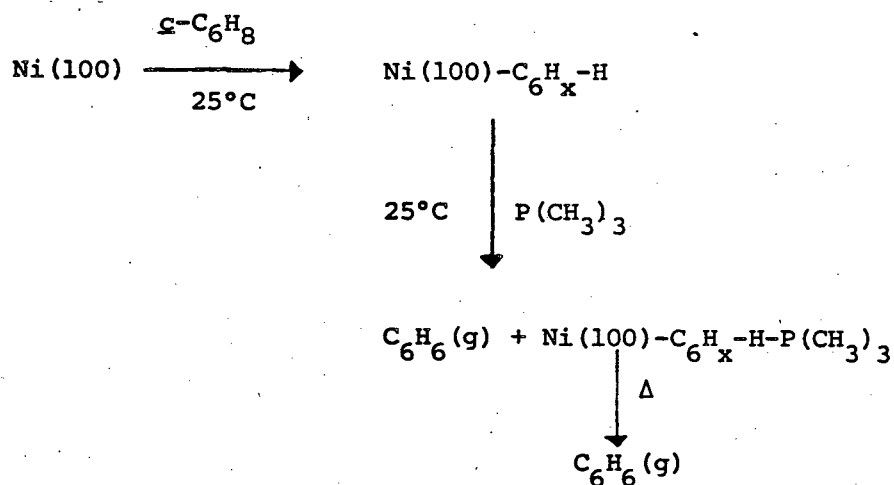
about relative reactivity, i.e., relative rates of cyclohexane carbon-hydrogen bond scission, is not warranted. Residence time for cyclohexane itself, under ultra high vacuum conditions, is very short for the nickel surfaces with respect to platinum at temperatures of 0 to 20°C. Perhaps cyclohexane bonding, ostensibly through C-H-M<sub>surface</sub> multicenter bonds,<sup>6,9</sup> is more robust for platinum than for nickel because for comparable surface topographies, the temperature for thermal desorption is higher for platinum than for nickel.

### Cyclohexadiene

Both 1,3- and 1,4-cyclohexadiene adsorbed strongly on the three low Miller index planes of nickel, (111), (110) and (100) to form chemisorbed benzene and chemisorbed hydrogen atoms. For all three surfaces, adsorption of either cyclohexadiene isomer followed by a thermal desorption experiment showed desorption of benzene. These experiments are summarized in Table I and as reference points, the thermal desorption characteristics of benzene itself on these surfaces also are presented. On all three surfaces, benzene thermal desorption was observed with maximal desorption rates that corresponded closely to those observed for benzene adsorbed on the respective surfaces. However, in the case of the (110) and (100) surfaces, there was an additional benzene desorption peak derived from the initial cyclohexadiene. For Ni(100)- $\underline{\text{C}}\text{-C}_6\text{H}_8$ , the additional desorption maximum was at 75-100°C substantially lower than for Ni(100)- $\text{C}_6\text{H}_6$ —whereas for Ni(110)- $\underline{\text{C}}\text{-C}_6\text{H}_8$ , the additional desorption maximum was at ~200°C, approximately 100° higher than that for Ni(110)- $\text{C}_6\text{H}_6$ . We also note that Ni(110)-C (0.2 carbon coverage) was more effective in dehydrogenating cyclohexadiene than was the clean (110) surface: more effective in that more benzene was desorbed and also the desorption maximum shifted to slightly lower temperatures.

The dehydrogenation of cyclohexadiene to benzene occurred at or near room temperature on these three nickel surfaces as established by trimethylphosphine displacement reactions. Thus, adsorption of either 1,3- or 1,4-cyclohexadiene on Ni(111) and on Ni(100) at 20-40°C followed by exposure of the crystal to trimethyl-

phosphine led to the displacement of substantial amounts of benzene (no cyclohexadiene displacement was detected). Nevertheless, the dehydrogenation reaction was not quantitative at these temperatures as shown by the following specific reaction sequence for Ni(100):



The two platinum surfaces, Pt(111) and Pt 6(111)x(111) also effected dehydrogenation of the 1,3- and 1,4-cyclohexadienes to benzene at 0-30°C, although the dehydrogenation was not complete at 0°C. Specific results obtained with these two surfaces with respect to the thermal desorption and chemical displacement reactions are summarized in Table II. As in the nickel surface chemistry, there was no detectable difference in the surface chemistry of the two cyclohexadiene isomers.

In the thermal desorption experiments with 1,3- or 1,4-cyclohexadiene on these two platinum surfaces, the benzene thermal desorption peaks corresponded closely to those for benzene itself (see Table II) except that the higher temperature (200-220°C) desorption peak characteristic of Pt(111)-C<sub>6</sub>H<sub>6</sub> was not observed for Pt(111)-c-C<sub>6</sub>H<sub>8</sub> and an additional benzene desorption maximum was observed at 50°C. Because neither benzene desorption nor displacement was quantitative<sup>2</sup> for Pt(111)-C<sub>6</sub>H<sub>6</sub> or for Pt 6(111)x(111)-C<sub>6</sub>H<sub>6</sub>, a quantitative assessment of the extent of cyclohexadiene dehydrogenation to benzene cannot be made—however, the extent of dehydrogenation to benzene at 30°C was very high for both surfaces. H-D exchange was observed on the stepped surface during the dehydrogenation process; a Pt 6(111)x(111)-c-C<sub>6</sub>H<sub>8</sub> surface was treated with D<sub>2</sub> at 10<sup>-7</sup> torr and ~130°C for two minutes; C<sub>6</sub>H<sub>6</sub>, C<sub>6</sub>H<sub>5</sub>D and a trace of C<sub>6</sub>H<sub>4</sub>D<sub>2</sub> were desorbed at ~200°C in a subsequent thermal desorption experiment.

## Cyclohexene

Cyclohexene was converted to benzene on all the nickel and platinum planes. Results for thermal desorption and for trimethylphosphine displacement reactions based on cyclohexene adsorbed on these surfaces are presented in Table III along with relevant thermal desorption characteristics of benzene adsorbed on the respective surfaces. Not listed are experiments in which the adsorbate was a 1:1 mixture of cyclohexene and  $d_{10}$ -cyclohexene. For these experiments, the only benzene molecules detected in either thermal desorption or phosphine displacement reactions were benzene and  $d_6$ -benzene with the exception of the experiments on platinum surfaces, discussed below. Thus no H-D exchange was observed under the cyclohexene dehydrogenation process conditions for any of the nickel surfaces including Ni(110)-C and Ni 9(111)x(111). Earlier studies<sup>1</sup> of benzene surface chemistry on nickel surfaces had shown no evidence of H-D exchange between adsorbed  $C_6H_6$  and  $C_6D_6$  even at elevated temperatures, e.g. Ni(100)- $C_6H_6$ - $C_6D_6$  after annealing at 150°C produced only  $C_6H_6$  and  $C_6D_6$  in the phosphine displacement reaction. It is also notable that the small intensity cyclohexene desorption peak for Ni(100)- $\underline{c}$ - $C_6H_{10}$ - $\underline{c}$ - $C_6D_{10}$  consisted only of  $\underline{c}$ - $C_6H_{10}$  and  $\underline{c}$ - $C_6D_{10}$  molecules.

H-D exchange between adsorbed  $C_6H_6$  and  $C_6D_6$  was not observed for Pt(111) even after annealing at  $\sim 130^\circ C$  but was for Pt 6(111)x(111).<sup>2</sup> In the dehydrogenation of cyclohexene to benzene on these two platinum surfaces, the observation for an initial adsorbate mixture of  $\underline{c}$ - $C_6H_{10}$  and  $\underline{c}$ - $C_6D_{10}$  in either the thermal desorption experiment or the phosphine displacement reaction (effected at  $>125^\circ C$  and  $100^\circ C$ , respectively, for the stepped and the (111) surfaces) was that a mixture of all possible  $C_6H_xD_{6-x}$  molecules desorbed. Since H-D exchange was not observed for Pt(111)- $C_6H_6$ - $C_6D_6$  up to  $\sim 130^\circ C$ , the H-D exchange process observed in the cyclohexene dehydrogenation on Pt(111) must occur at some intermediate state before chemisorbed benzene is generated. Probably, a similar intermediate exchange is operative for the stepped surface. There was a rate differential in benzene formation on these two platinum surfaces: benzene formation was extensive at 20°C for the stepped surface whereas benzene formation was fast on Pt(111) only

at  $\sim 100^\circ\text{C}$ .

Differences among the various surfaces in their facility in effecting cyclohexene dehydrogenation is evident from inspection of the data in Table III. Dehydrogenation of adsorbed cyclohexene to adsorbed benzene was not detectable at  $25^\circ\text{C}$  for either Pt(111) or Ni(100); the rate of cyclohexene conversion to benzene was high only at temperatures of  $100\text{--}130^\circ\text{C}$  and  $\sim 70^\circ\text{C}$ , respectively. For Ni(100)- $\underline{\text{C}}\text{-C}_6\text{H}_{10}$ , there was no displacement of benzene (or cyclohexene) at  $25^\circ\text{C}$  or at  $100^\circ\text{C}$ ; the rate of cyclohexene dehydrogenation on this surface was fast only at temperatures of  $\sim 130^\circ\text{C}$ . In contrast, the stepped platinum and nickel surfaces converted cyclohexene to chemisorbed benzene at  $25^\circ\text{C}$  based on the observed displacement of benzene by trimethylphosphine after adsorption of cyclohexene on these surfaces at  $25^\circ\text{C}$ .

As observed for the dehydrogenation of cyclohexadiene to benzene, the partially carbided Ni(110) surface (0.2 carbon monolayer) was far more effective than the clean surface in the dehydrogenation of cyclohexene to benzene although most of the benzene formation occurred above  $200^\circ\text{C}$  (Figure 1). These effects may be electronic or topographical (surface); no objective explanation can be reached on the data reported herein. The presence of carbon did not significantly affect the cyclohexene or cyclohexadiene surface chemistry of Ni(111) or Ni(100).

#### Summary

In the thermal desorption experiments for cyclohexene and for the cyclohexadienes on the various platinum and nickel surfaces, the hydrogen desorption maxima were very similar for the olefin and the diene on a given metal surface (see Tables I-III). Probably, chemisorbed cyclohexadiene is an intermediate in the dehydrogenation of adsorbed cyclohexene to adsorbed benzene. For Ni(100) and Pt(111), the activation energy for cyclohexene conversion to benzene was higher than for cyclohexadiene conversion to benzene. Still higher in activation energy was the cyclohexane dehydrogenation to benzene which was a significant process only on the stepped platinum surface. It is only this cyclohexane chemistry on the stepped platinum surface and the facility of H-D exchange in the intermediate stages of the cyclo-

hexene (or cyclohexane) to benzene dehydrogenation process that literally distinguishes the platinum from the nickel surface chemistry. The stepped nickel surface did not exhibit the reactivity of the stepped platinum surface in H-D exchange and in cyclohexene chemistry which clearly shows that an electronic effect is responsible for the differential behavior of these two metal surfaces. Basically, the rates of cyclohexene dehydrogenation (and also cyclohexadiene dehydrogenation) are comparable for both metals (same crystallography) but the rates did vary as a function of the surface crystallography, with stepped surfaces the most active ones.

Catalytic studies of transition metals for the specific dehydrogenation process of cyclohexane conversion to benzene clearly show platinum to be the most active metal.<sup>15</sup> Our ultra high vacuum studies show platinum, particularly the stepped platinum surface to be more active than all the nickel surfaces for cyclohexane conversion to benzene. Cyclohexane dehydrogenation to gaseous benzene has been characterized<sup>16-18</sup> as a structure-insensitive<sup>19,20</sup> reaction, i.e., a reaction insensitive to the details of the metal surface. Our studies establish that cyclohexane conversion to chemisorbed benzene under ultra high vacuum conditions and low temperatures is structure sensitive<sup>21</sup> — the stepped platinum surface converted cyclohexane to benzene whereas the flat (111) surface was either inactive<sup>22</sup> or possessed a low activity for this reaction at 20-100°C. See Figure 2 for pressure dependence of the cyclohexane-benzene equilibrium.

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11. (a) Demuth, J.E., Ibach, H., and Lehwald, S., Phys. Rev. Lett., 1978, 40, 1044.  
(b) The upper temperature limits in our experiments were set by the  
characteristic temperature for benzene desorption from the individual  
surfaces in that the characterization of the benzene chemisorption state  
was based on subsequent benzene thermal desorption or benzene displacement by  
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(c) Lehwald, S., and Ibach, H., Surf. Sci., 1979, 89, 425, concluded, from  
a high resolution energy loss study, that cyclohexane converted to benzene  
on a Ni 5(111)x(110) surface at  $T < -13^{\circ}\text{C}$ . In contrast, we found no evidence  
of dehydrogenation of cyclohexane on Ni 9(111)x(111) surfaces on adsorption

at 20-70°C. Extent of cyclohexane conversion to benzene may be a sensitive function of the heating rate with low rates favoring dehydrogenation over desorption.

12. With benzene coverages of  $<0.1$  monolayer on Pt(111), no benzene desorption was observed in the thermal desorption experiment<sup>2</sup>—nor was any benzene displaced by trimethylphosphine at these low coverages.<sup>2</sup>
13. We have often observed a greater thermal reversibility in the desorption of hydrocarbons when trimethylphosphine was coadsorbed on the surface.
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21. In the catalytic dehydrogenation of cyclohexane as operated on a commercial basis (Figure 2), the rate determining step appears to be benzene desorption,<sup>15</sup> a process that is structure-insensitive. For our ultra high vacuum studies, the process studied is the conversion of chemisorbed cyclohexane to chemisorbed benzene—a process that is structure-sensitive.
22. The apparent low activity for the (111) surface may have been due to step imperfections on the crystal surface.



Table I.

Thermal Desorption Experiments for  
1,3- and 1,4-Cyclohexadiene and for  
Benzene on Ni(111), Ni(110), and Ni(100).

<u>Nickel Surface</u>	<u>Adsorbate</u> <sup>a,b</sup>	<u>Benzene Desorption Maximum</u>	<u>Hydrogen Desorption Maxima</u>
(111)	cyclohexadiene <sup>c</sup>	~100°C	140, 210°C
(111)	benzene	115-125°C	180°C
(110)	cyclohexadiene	90, 200°C	100-200°C
(110)-C	cyclohexadiene	90, 200°C <sup>d</sup>	100-200°C
(110)	benzene	~100°C	120°C
(100)	cyclohexadiene	75-100, 200°C	120, 210°C
(100)	benzene	200-220°C	200-220°C

a. There was no significant difference in behavior between the 1,3 and 1,4 isomers

b. Adsorption temperature was ~25°C.

c. Adsorption temperatures of 25, 50 and 75°C.

d. Enhanced benzene desorption relative to the clean (110) surface.

Table II.

**Thermal Desorption and Trimethylphosphine  
Displacement Experiments for 1,3 and 1,4-  
Cyclohexadiene<sup>a</sup> on Platinum Surfaces.**

<u>Platinum Surface</u>	<u>Adsorbate<sup>a</sup></u>	<u>Adsorption Temperature</u>	<u>Thermal Desorption: Benzene Desorption Maxima</u>	<u>Thermal Desorption: H<sub>2</sub> Desorption Maxima</u>	<u>Trimethylphosphine Displacement of Benzene</u>
Pt(111)	cyclohexadiene	0°C	50,130°C	90,170,260,380°C	
Pt(111)	benzene	25°C	100-130; 200-220°C	270,380°C	
Pt(111)	cyclohexadiene	0°C			incomplete <sup>b</sup>
Pt(111)	cyclohexadiene	30°C			fairly complete <sup>c</sup>
Pt 6(111)x(111)	cyclohexadiene	25°C	100-120, 175-210°C	110,165,200,350°C	
Pt 6(111)x(111)	benzene	25°C	100-120,180-210°C	195,355°C	
Pt 6(111)x(111)	cyclohexadiene	25°C			fairly complete <sup>c</sup>

- a. The surface chemistry of the two cyclohexadiene isomers were not detectably different.  
 b. The intensity of the benzene desorption peak was ~ 1/2 that for the experiment where the adsorption temperature and temperature of the displacement reaction was 30°C.  
 c. Only traces of benzene were thermally desorbed after the displacement reaction.

Table III.

Thermal Desorption and Trimethylphosphine  
Displacement Reactions for Cyclohexene  
Adsorbed on Nickel and Platinum Surfaces.

Surface	Adsorbate	Adsorption Temperature	Adsorbate Coverage	Thermal Desorption: Benzene Desorption Maximum	Thermal Desorption: Hydrogen Desorption Maximum	Trimethylphosphine Displacement of Benzene
Ni(111)	C <sub>6</sub> H <sub>10</sub>	25°C	~0.3	none	140-200°C (double max. <sup>a</sup> )	
Ni(111)	C <sub>6</sub> H <sub>6</sub>	25°C	~0.3	115-125°C	180°C	
Ni(111)	C <sub>6</sub> H <sub>10</sub>	65°C	~0.3			Extensive <sup>b</sup>
Ni(110)	C <sub>6</sub> H <sub>10</sub>	25°C	~0.3	200°C (trace)	100, 200°C	
Ni(110)-C	C <sub>6</sub> H <sub>10</sub>	25°C	~0.3	135°C (v. broad)	Not detected	
Ni(110)	C <sub>6</sub> H <sub>6</sub>	25°C	~0.3	100°C	105°C(broad)	
Ni(100)	C <sub>6</sub> D <sub>10</sub>	25°C	~0.3	220°C (140°C-C <sub>6</sub> D <sub>8</sub> )	130, 200°C	
Ni(100)	C <sub>6</sub> H <sub>6</sub>	25°C	~0.3	200-220°C	200-220°C	
Ni(100)	C <sub>6</sub> H <sub>10</sub>	25, 100°C	~0.3			None
Ni 9(111)x(111)	C <sub>6</sub> H <sub>10</sub>	25°C	~0.5	100-110°C	100, 185°C	
Pt(111)	C <sub>6</sub> H <sub>10</sub>	25°C	~0.5	130-140°C	130, 170, 260, 380°C	
Pt(111)	C <sub>6</sub> H <sub>6</sub>	25°C	~0.5	100-130, 200-220°C	270, 380°C	
Pt(111)	C <sub>6</sub> H <sub>10</sub>	25-70°C	~0.5			None <sup>c</sup>
Pt(111)	C <sub>6</sub> H <sub>10</sub>	100°C	~0.5			Extensive
Pt(111)	C <sub>6</sub> H <sub>10</sub>	130°C	~0.5			Essentially complete <sup>d</sup>
Pt 6(111)x (111)	C <sub>6</sub> H <sub>10</sub>	25°C	<0.5	None	110, 195, 350°C	
Pt 6(111)x (111)	C <sub>6</sub> H <sub>10</sub>	25°C	>0.5	150-155°C (v. broad)	110, 165, 215, 350°C	
Pt 6(111)x (111)	C <sub>6</sub> H <sub>10</sub>	25°C	0.15- 0.50	180-210°C	110, 165, 215, 350°C	
Pt 6(111)x (111)	C <sub>6</sub> H <sub>6</sub>	25°C	~0.5	100-120, 180-210°C	185, 355°C	
Pt 6(111)x (111)	C <sub>6</sub> H <sub>10</sub>	25°C	~0.5			Extensive

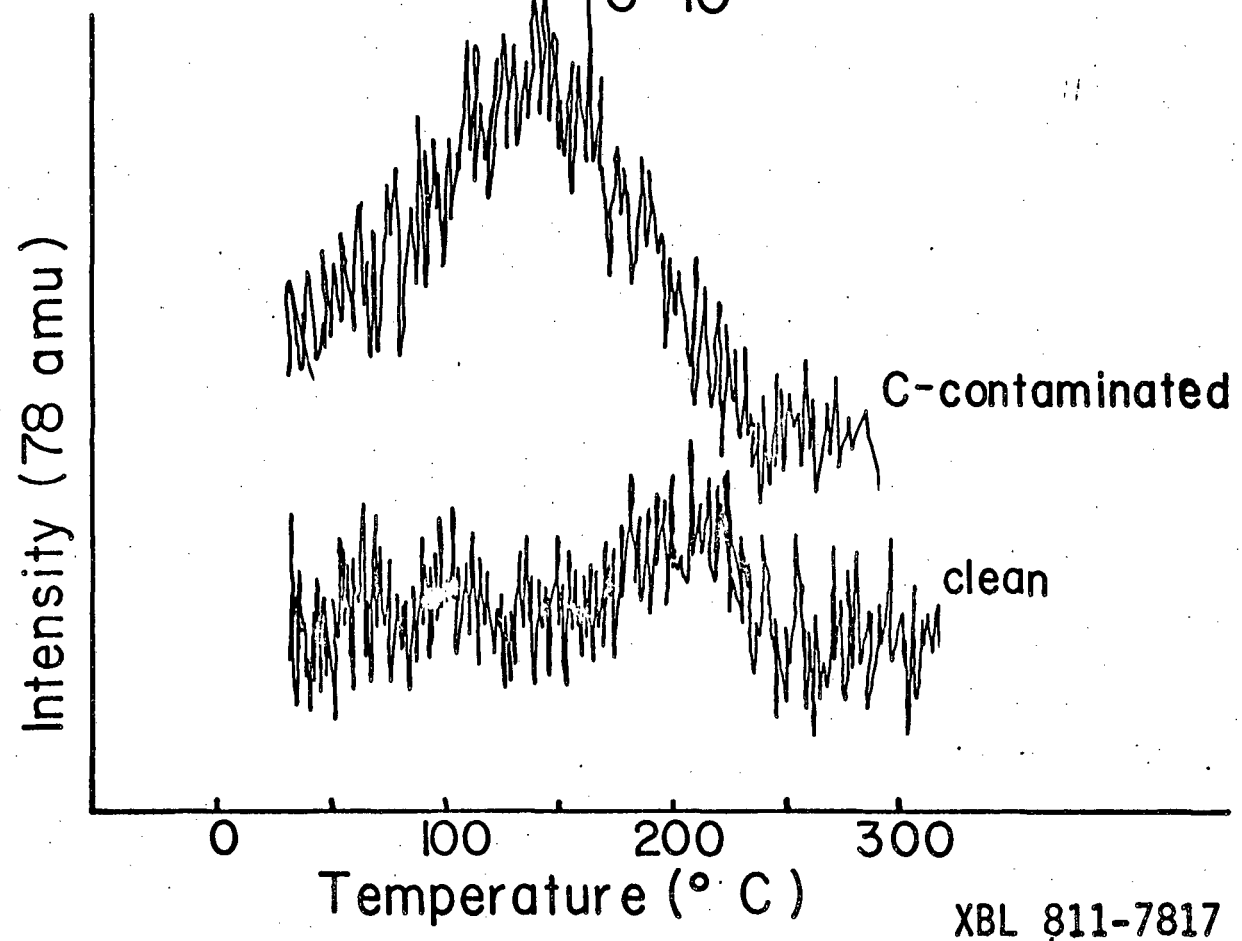
a. Poorly resolved double maximum. b. Comparable desorption peak intensity as for the Ni(111)-C<sub>6</sub>H<sub>6</sub> + P(CH<sub>3</sub>)<sub>3</sub> experiment (same coverage for cyclohexene and benzene, respectively). c. A subsequent thermal desorption experiment yielded some benzene desorption. d. Using C<sub>6</sub>D<sub>10</sub> in place of C<sub>6</sub>H<sub>10</sub> gave C<sub>6</sub>D<sub>6</sub> in the displacement reaction. After displacement, a thermal desorption experiment yielded only small amounts of D<sub>2</sub>, HD and CH<sub>3</sub>D (methane is formed in the decomposition of the phosphine).

Figure 1

Thermal desorption experiments for Ni(110)- $\underline{c}$ -C<sub>6</sub>H<sub>10</sub> and for Ni(110)-C- $\underline{c}$ -C<sub>6</sub>H<sub>10</sub> illustrating the more effective dehydrogenation of cyclohexene to benzene on the carbided surface than on the clean surface (monitored by the intensity of mass 78 as a function of temperature). Note also the substantial shift to lower temperatures for the benzene desorption maximum for the carbided surface relative to the clean surface. The heating rate in these experiments was 25° sec<sup>-1</sup>.

# Thermal Desorption of $C_6H_6$ following Adsorption

of  $c-C_6H_{10}$  on Ni(110)



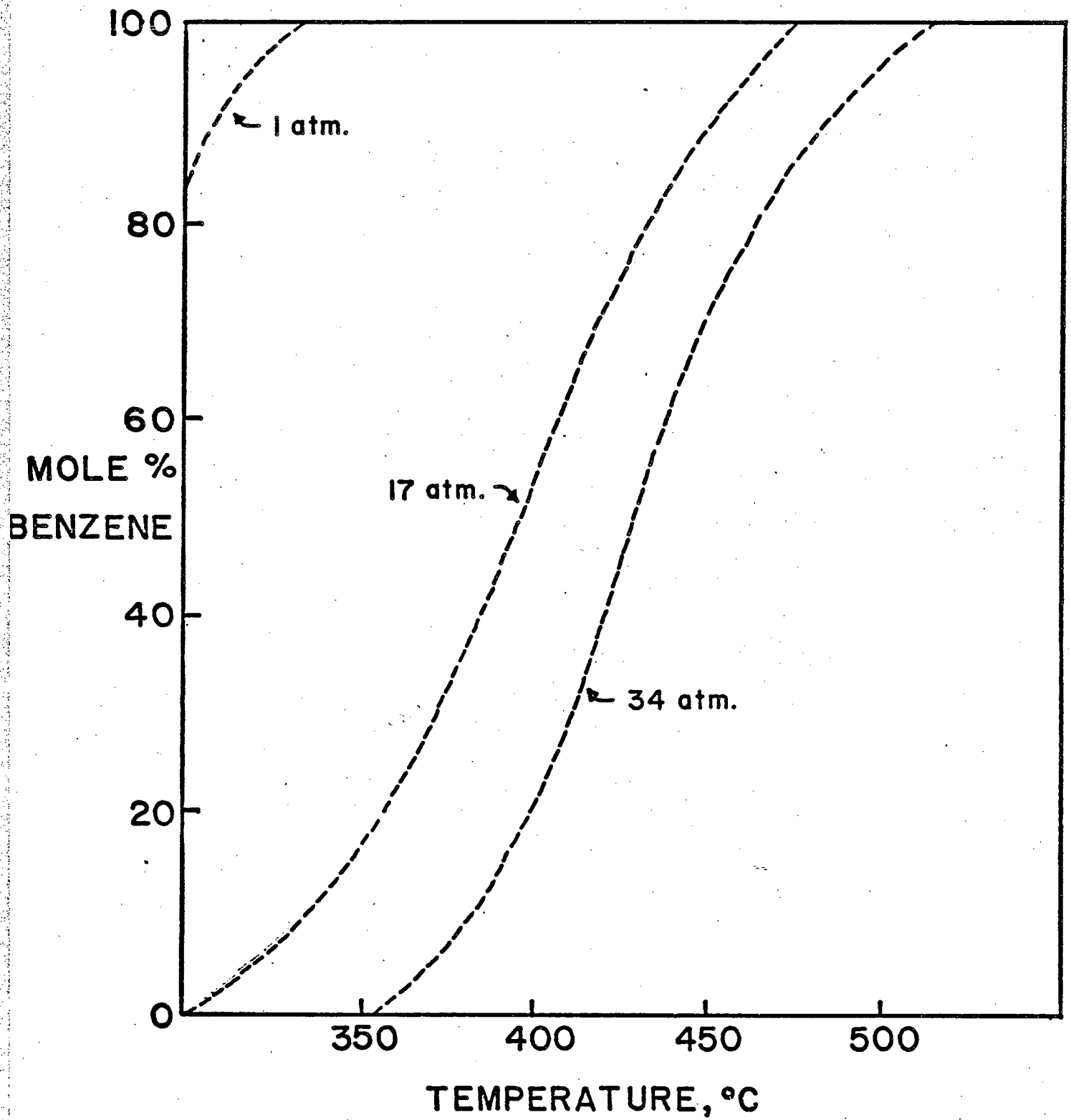
XBL 811-7817

FIGURE 1.

Figure 2.

Presented in the figure is a graphical representation of the equilibrium  $\text{c-C}_6\text{H}_{12} \longrightarrow \text{C}_6\text{H}_6 + 3\text{H}_2$  as a function of temperature and pressure (the ratio of hydrogen to hydrocarbon is ten).<sup>14</sup> Typical operating conditions for conversion of hydrocarbons to aromatic compounds is close to 500°C and pressures of ~10 atmospheres.

Figure 2



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