There is a close correspondence between the temperatures for maximal rates of benzene desorption from the (111) and the 6(111)×(111) platinum surfaces (a close correspondence was also evident between the nickel (111) and 9(111)×(111) surface chemistry of benzene[1]). Thus it is reasonable to assume that the chemisorption states of benzene reversibly bound on the platinum stepped surface are *largely* associated with the terrace planes of (111) crystallography.

We note that steps (or step imperfections) should affect the distance relationship between benzene C–H hydrogen atoms and surface metal atoms. Either by ring tipping or simply close approach of the molecule to (raised) step metal atoms, there should be a generation of C–H–metal atom multicenter bonding which forms can be either intermediates or transition states to C–H bond breaking (largely irreversible) processes.[1,17-19]

Hydrogen–deuterium exchange between initially chemisorbed C_6H_6 and C_6D_6 molecules was not detected on Pt(111), but was established to be a relatively fast reaction at $\sim$140 °C on Pt[6(111)×(111)]. This difference in chemical reactivity between these two surfaces is ascribed to the obvious topographical differences between the surfaces (see above) rather than to electronic differences between step and terrace sites. None of the nickel surfaces investigated earlier[1] effected H–D exchange between chemisorbed C_6H_6 and C_6D_6.

Moyes, Baron, and Squire[20] have shown that H–D exchange between C_6H_6 and C_6D_6 proceeds at rates of $\sim$9% μmol min^{-1} (mg-cat.)$^{-1}$ at 0 °C and ambient pressures on a platinum wire. Two factors literally distinguish these observations from ours for the two clean platinum surface planes: (1) the hydrogen (deuterium) atom surface activity at ambient pressures was many orders of magnitude higher than in the ultra-high-vacuum studies, and (2) the surface of the wire would have been very irregular on the atomic scale. There are no obvious inconsistencies between the two sets of studies.

Acknowledgment. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. We thank Mr. S. Mark Davis for the carbon-on-platinum Auger calibration data and Mr. K. Shanahan for the suggestions regarding the sequential labeled-benzene experiments.

Registry No. Pt, 7440-06-4; $CD_3C_6D_5$, 2037-26-5; $CD_3C_6H_5$, 1124-18-1; $CH_3C_6D_5$, 1603-99-2; C_6D_6, 1076-43-3; C_6H_6, 71-43-2; $P(CH_3)_3$, 594-09-2.

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

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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)×(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)×(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 that of the platinum (111) plane. Cyclohexene and 1,3- and 1,4-cyclohexadiene were converted, at least partially, to benzene on all of 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.

Introduction

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.[1-9] Stereochemical features that enable facile carbon–hydrogen bond breaking were incisively identified in an earlier[1] study of benzene and toluene chemisorption on five, crystallographically different

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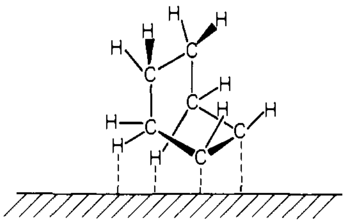
nickel surfaces and on two platinum surfaces.[2] An unsaturated hydrocarbon molecule in the initial adsorption process should interact largely through the most energetically favorable donor π and acceptor π^* orbitals with appropriate metal surface orbitals. Thus, on an atomically flat surface, benzene 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.[1,10] 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).[1] 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 $c\text{-}C_nH_n$ 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 Section

Reagents and Procedures. Cyclohexane (Matheson Coleman & Bell) and cyclohexane-d_{12} (prepared from $C_6D_6 + D_2$) were dried over sodium sulfate. Cyclohexene (Chem Samples Co., 99.9% purity), and cyclohexene-d_{10} (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 °C. Trimethylphosphine was prepared and purified as described earlier.[1] 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.[1] Procedures for chemisorption, thermal desorption experiments, and chemical displacement reactions have been described by Friend and Muetterties.[1] Heating rates of 25° s^{-1} were used. Procedures for cutting, polishing, and cleaning of the nickel and platinum crystals were as described earlier.[1,4,8] 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 ref 1 and 2.

Results and Discussion

Cyclohexane. Demuth, Ibach, and Lehwald[11a] have shown that cyclohexane chemisorbed on Ni(111) at low temperatures desorbs at ~−100 °C in a quantitative fashion. Consistent with this report, we found no evidence of cyclohexane reaction[11b] with Ni(111) at 0–70 °C nor with Ni(110) at 25–90 °C, Ni(100) at 25–200 °C and Ni[9(111)×(111)][11c] at 20–70 °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 ~20 °C under these conditions unless there is dehydrogenation.

Cyclohexane chemisorption on Pt(111) is partially reversible with a 0 °C temperature for maximum desorption rate when Pt(111)-$c\text{-}C_6H_{12}$ is formed at −15 to −35 °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 H_2 desorption between 200 and 400 °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.[2,12] In fact, high-resolution electron energy loss studies indicate that cyclohexane is converted to benzene on Pt(111) at ~−73 °C.[11a] Treatment of Pt(111) with cyclohexane at 134 °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)×(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 ~0.15 monolayer coverage on this stepped platinum surface cannot be thermally desorbed or displaced by trimethylphosphine at 30 °C as intact benzene). No benzene was detected in thermal desorption reaction of the stepped surface treated with cyclohexane (~0.20 monolayer) and only traces of benzene were displaced by trimethylphosphine at 20 °C. In the thermal desorption experiment, there were three H_2 desorption maxima at ~110, 195, and 350 °C, the last two of which correspond precisely to the desorption maxima of ~195 and 350 °C for H_2 derived from benzene decomposition on this surface.[2] The chemisorption state generated in the cyclohexane reaction with the stepped surface[11c] appears to be best characterized as Pt[6(111)×(111)]–C_6H_6–H, at least at temperatures >100 °C, with all the benzene molecules residing in the most strongly (irreversibly) bound state, because all the thermal characteristics of this surface are identical[2] with those of Pt[6(111)×(111)]–C_6H_6–H generated from C_6H_6 and H_2 at the same

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(10) References that present data supporting this stereochemical representation are: (Ni(111) and Pt(111)) Lehwald, S.; Ibach, H.; Demuth, J. E. *Surf. Sci.* **1978**, *78*, 577. (Ni(111) and Ni(100)) Bertolini, J. C.; Rousseau, J. *Ibid.* **1979**, *89*, 467.

(11) (a) Demuth, J. E.; Ibach, H.; 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 trimethylphosphine. (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)×($\bar{1}$10)] surface at T <−13 °C. In contrast, we found no evidence of dehydrogenation of cyclohexane on Ni[9(111)×(111)] surfaces on adsorption at 20–70 °C. The 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,[2] nor was any benzene displaced by trimethylphosphine at these low coverages.[2]

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

nickel surface	adsorbate[a,b]	benzene desorption max, °C	hydrogen desorption max, °C
(111)	cyclohexadiene[c]	~100	140, 210
(111)	benzene	115–125	180
(110)	cyclohexadiene	90, 200	100–200
(110)-C	cyclohexadiene	90, 200[d]	100–200
(110)	benzene	~100	120
(100)	cyclohexadiene	75–100, 200	120, 210
(100)	benzene	200–220	200–220

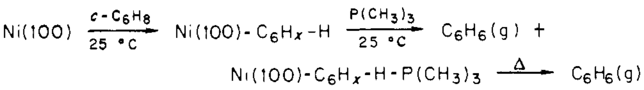
[a] There was no significant difference in behavior between the 1,3 and 1,4 isomers. [b] Adsorption temperature was ~25 °C. [c] Adsorption temperatures of 25, 50, and 75 °C. [d] Enhanced benzene desorption relative to the clean (110) surface.

coverage level. The remaining open sites on this Pt[6(111)×(111)]–C_6H_6–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[13] did yield gaseous benzene at a desorption maximum of 170–190 °C. When the saturated state was generated from a mixture of $c\text{-}C_6H_{12}$ and $c\text{-}C_6D_{12}$, the desorbed benzene included all possible $C_6H_xD_{6-x}$ molecules.

These experiments establish for the platinum system a significant difference between the atomically flat (111) and stepped 6(111)×(111) surface in the dehydrogenation of cyclohexane. Were the small reactivity of the 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,[11c] one might be tempted to conclude that these surfaces are less *reactive* than their platinum analogues. Such a conclusion about relative reactivity, i.e., relative rates of cyclohexane carbon–hydrogen bond scission, is not warranted. Possibly, the residence time for cyclohexane, under ultra-high-vacuum conditions, is too short for the dehydrogenation on the nickel surfaces with respect to platinum at temperatures of 0 to 20 °C. Cyclohexane bonding, ostensibly through C–H–$M_{surface}$ multicenter bonds,[6,9] appears to be 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)–$c\text{-}C_6H_8$, the *additional* desorption maximum was at 75–100 °C, substantially lower than for Ni(100)–C_6H_6, whereas for Ni(110)–$c\text{-}C_6H_8$, the *additional* desorption maximum was at ~200 °C, approximately 100° higher than that for Ni(110)–C_6H_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.

Scheme I



$$\mathrm{Ni(100)} \xrightarrow[25\ ^\circ\mathrm{C}]{c\text{-}C_6H_8} \mathrm{Ni(100)}\text{-}C_6H_x\text{-}H \xrightarrow[25\ ^\circ\mathrm{C}]{P(CH_3)_3} C_6H_6(g) + \mathrm{Ni(100)}\text{-}C_6H_x\text{-}H\text{-}P(CH_3)_3 \xrightarrow{\Delta} C_6H_6(g)$$

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 trimethylphosphine 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 specific reaction sequence for Ni(100) in Scheme I.

The two platinum surfaces, Pt(111) and Pt[6(111)×(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_6H_6 was not observed for Pt(111)–$c\text{-}C_6H_8$ and an additional benzene desorption maximum was observed at 50 °C. Because neither benzene desorption nor displacement was quantitative[2] for Pt(111)–C_6H_6 or for Pt[6(111)×(111)]–C_6H_6, 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)×(111)]–$c\text{-}C_6H_8$ surface was treated with D_2 at 10^{-7} torr and ~130 °C for 2 min; C_6H_6, C_6H_5D, and a trace of $C_6H_4D_?$ 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 cyclo-

Table II. Thermal Desorption and Trimethylphosphine Displacement Experiments for 1,3- and 1,4-Cyclohexadiene[a] on Platinum Surfaces

platinum surface	adsorbate[a]	adsorption temp, °C	maxima, °C: thermal desorption: benzene desorption	maxima, °C: thermal desorption: H_2 desorption	trimethylphosphine displacement of benzene
Pt(111)	cyclohexadiene	0	50, 130	90, 170, 260, 380	
Pt(111)	benzene	25	100–130, 200–220	270, 380	
Pt(111)	cyclohexadiene	0			incomplete[b]
Pt(111)	cyclohexadiene	30			fairly complete[c]
Pt[6(111)×(111)]	cyclohexadiene	25	100–120, 175–210	110, 165, 200, 350	
Pt[6(111)×(111)]	benzene	25	100–120, 180–210	195, 355	
Pt[6(111)×(111)]	cyclohexadiene	25			fairly complete[c]

[a] The surface chemistry of the two cyclohexadiene isomers were not detectably different. [b] The intensity of the benzene desorption peak was ~one-half 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

				maxima, °C		trimethyl-phosphine displacement of benzene
surface	adsorbate	adsorption temp, °C	adsorbate coverage	thermal desorption: benzene desorption	thermal desorption: hydrogen desorption	
Ni(111)	C_6H_{10}	25	~0.3	none	140-200 (double max[a])	
Ni(111)	C_6H_6	25	~0.3	115-125	180	
Ni(111)	C_6H_{10}	65	~0.3			extensive[b]
Ni(110)	C_6H_{10}	25	~0.3	200 (trace)	100, 200	
Ni(110)-C	C_6H_{10}	25	~0.3	135 (v br)	not detected	
Ni(110)	C_6H_6	25	~0.3	100	105 (br)	
Ni(100)	C_6D_{10}	25	~0.3	220 (140, C_6D_8)	130, 200	
Ni(100)	C_6H_6	25	~0.3	200-220	200-220	
Ni(100)	C_6H_{10}	25, 100	~0.3			none
Ni[9(111)×(111)]	C_6H_{10}	25	~0.5	100-110	100, 185	
Pt(111)	C_6H_{10}	25	~0.5	130-140	130, 170, 260, 380	
Pt(111)	C_6H_6	25	~0.5	100-130, 200-220	270, 380	
Pt(111)	C_6H_{10}	25-70	~0.5			none[c]
Pt(111)	C_6H_{10}	100	~0.5			extensive
Pt(111)	C_6H_{10}	130	~0.5			essentially complete[d]
Pt[6(111)×(111)]	C_6H_{10}	25	<0.15	none	110, 195, 350	
Pt[6(111)×(111)]	C_6H_{10}	25	>0.5	150-155 (v br)	110, 165, 215, 350	
Pt[6(111)×(111)]	C_6H_{10}	25	0.15-0.50	180-210	110, 165, 215, 350	
Pt[6(111)×(111)]	C_6H_6	25	~0.5	100-120, 180-210	195, 355	
Pt[6(111)×(111)]	C_6H_{10}	25	~0.5			extensive

[a] Poorly resolved double maxima. [b] Comparable desorption peak intensity as for the Ni(111)-C_6H_6 + $P(CH_3)_3$ experiment (same coverage for cyclohexene and benzene, respectively). [c] A subsequent thermal desorption experiment yielded some benzene desorption. [d] Using C_6D_{10} in place of C_6H_{10} gave C_6D_6 in the displacement reaction. After displacement, a thermal desorption experiment yielded only small amounts of D_2, and HD, and CH_3D (methane is formed in the decomposition of the phosphine).

hexene 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 cyclohexene-d_{10}. For these experiments, the only benzene molecules detected in either thermal desorption or phosphine displacement reactions were benzene and benzene-d_6 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)×(111)]. Earlier studies[1] 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)-*c*-C_6H_{10}-*c*-C_6D_{10} consisted only of *c*-C_6H_{10} and *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 ~130 °C but was for Pt[6(111)×(111)].[2] In the dehydrogenation of cyclohexene to benzene on these two platinum surfaces, the observation for an initial adsorbate mixture of *c*-C_6H_{10} and *c*-C_6D_{10} in either the thermal desorption experiment or the phosphine displacement reaction (effected at >125 and 100 °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 ~130 °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.[14a] 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 ~100 °C.

Differences among the various surfaces in their ability to effect cyclohexene dehydrogenation is evident from inspection of the data in Table III. Dehydrogenation of adsorbed cyclohexene to adsorbed benzene was not detectable at 25 °C for either Pt(111) or Ni(100); the rate of cyclohexene conversion to benzene was high only at temperatures of 100-130 and ~70 °C, respectively. For Ni(100)-*c*-C_6H_{10}, there was no displacement of benzene (or cyclohexene) by trimethylphosphine at 25 or 100 °C; the rate of cyclohexene dehydrogenation on this surface was fast only at temperatures of ~130 °C. In contrast, the stepped platinum and nickel surfaces converted cyclohexene to chemisorbed benzene at 25 °C based on the observed displacement of benzene by trimethylphosphine after adsorption of cyclohexene on these surfaces at 25 °C.

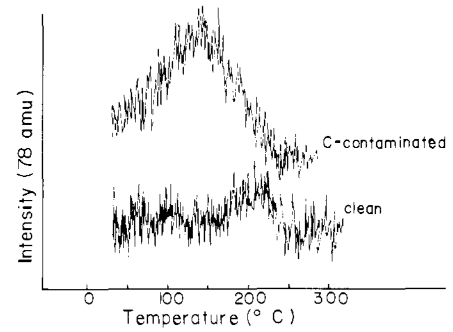


Figure 1. Thermal desorption experiments for Ni(110)-*c*-C_6H_{10} and for Ni(110)-C-*c*-C_6H_{10} illustrating the more effective dehydrogenation of cyclohexene to benzene on the carbided surface than on the clean surface (monitored by the intensity of mass 78 as a function of temperature). Note also 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° s^{-1}.

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 °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,

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(13) We have often observed a greater thermal reversibility in the desorption of hydrocarbons when trimethylphosphine was coadsorbed on the surface.

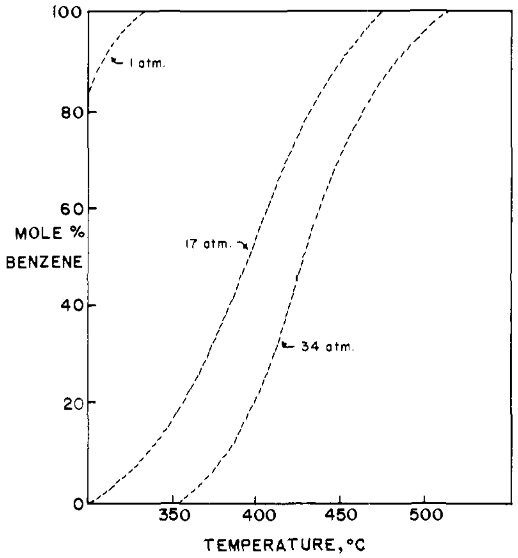

Figure 2. Presented in the figure is a graphical representation of the equilibrium $c\text{-}C_6H_{12} \rightarrow C_6H_6 + 3H_2$ as a function of temperature and pressure (the ratio of hydrogen to hydrocarbon is 10).[14] Typical operating conditions for conversion of hydrocarbons to aromatic compounds is close to 500 °C and pressures of ~10 atm.

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[14b] 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 cyclohexene, cyclohexadiene, and cyclohexane to benzene dehydrogenation process that literally distinguish 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 cyclohexane chemistry. 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.[15] 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[16-18] as a *structure-insensitive*[19,20] 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;[21] the stepped platinum surface converted cyclohexane to benzene whereas the flat (111) surface was either inactive[22] 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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Registry No. Ni, 7440-02-0; Pt, 7440-06-4; C_6H_{10}, 110-83-8; C_6H_6, 71-43-2; $P(CH_3)_3$, 594-09-2; 1,3-cyclohexadiene, 592-57-4; 1,4-cyclohexadiene, 628-41-1; cyclohexane, 110-82-7.

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[14] (a) H–D exchange also occurred at intermediate stages of cyclohexadiene dehydrogenation on Pt(111): a chemisorption state derived from D_2 and cyclohexadiene on Pt(111), on heating, yielded C_6H_6, C_6H_5D, and $C_6H_4D_2$. (b) The conversion of cyclohexadiene to benzene on Pt(111) has been proposed based on ultra-high-vacuum studies using work function and low-energy electron diffraction data; c.f., Gland, J. L.; Baron, K.; Somorjai, G. A. *J. Catal.* **1975**, *36*, 305.

(15) Ciapetta, F. G.; Dobres, R. M.; Baker, R. W. "Catalysis", Emmet, P. H., Ed.; Van Nostrand: New York, 1958; Vol VI.

(16) Cusamino, J. A.; Dembinski, G. W.; Sinfelt, J. H. *J. Catal.* **1966**, *63*, 2309.

(17) Kraft, M.; Spindler, H. "Proceeding of the 4th International Congress on Catalysis", Akamediai, Kiado: Budapest, 1971; Vol. II.

(18) The rate-determining step in this process generally appears to be desorption of benzene.

(19) Taylor, H. S. *Proc. R. Soc. London, Ser. A* **1925**, *108*, 105.

(20) Boudart, M. *Adv. Catal.* **1969**, *20*, 153.

(21) In the catalytic dehydrogenation of cyclohexane as operated on a commercial basis (Figure 2), the rate-determining step appears to be benzene desorption,[15] 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.