integrating the t_2 integral by parts gives

$$I_{\mu} = \frac{\Gamma\left(\frac{\mu+2}{2}\right)}{2} \int_0^{\infty} dt_1 \exp(1[\beta - \lambda_2]t_1)h(t_1)$$
 (A-7)

with

$$h(t_{1}) = \int_{t_{1}}^{\infty} \exp(-\lambda_{2}\tau) {}_{1}F_{1}\left(\frac{\mu+2}{2};1;-r^{2}/4\tau\right) \times \\ (\lambda_{1} - \lambda_{2})^{-1}\tau^{-(\mu+2)/2} dt - \\ \exp(-[\lambda_{1} - \lambda_{2}]t_{1}) \int_{0}^{\infty} \exp(-\lambda_{1}[\tau + t_{1}]) \times \\ {}_{1}F_{1}\left(\frac{\mu+2}{2};1;-r^{2}/4(\tau+t_{1})\right) (\lambda_{1} - \lambda_{2})^{-1}(\tau + t_{1})^{-(\mu+2)/2} d\tau$$
(A-8)

Substituting $\tau' = \tau + t_1$ in the second integral in eq A-8 and then integrating eq A-7 by parts gives

$$I_{\mu} = \frac{\Gamma\left(\frac{\mu+2}{2}\right)}{2} \left[\frac{I_{\mu}(\lambda_{1})}{(\lambda_{1}-\beta)(\lambda_{1}-\lambda_{2})} + \frac{I_{\mu}(\lambda_{2})}{(\lambda_{2}-\beta)(\lambda_{2}-\lambda_{1})} + \frac{I_{\mu}(\beta)}{(\beta-\lambda_{1})(\beta-\lambda_{2})} \right]$$
(A-9)

where

$$I_{\mu}(\alpha) \equiv \int_{0}^{\infty} \exp(-\alpha\tau) {}_{1}F_{1}\left(\frac{\mu+2}{2};1;-r^{2}/4\tau\right)\tau^{-(2+\mu)/2} d\tau$$
(A-10)

The integrals required here involve $\mu = 0$ and $\mu = 2$, for which

$${}_{1}F_{1}\left(\frac{\mu+2}{2};1;-r^{2}/4\tau\right) = \exp(-r^{2}/4\tau) \qquad \mu = 0$$
$$= \exp(-r^{2}/4\tau)[1 - r^{2}/4\tau] \qquad \mu = 2$$

(see ref 51, p 100). Using known integrals (ref 49, p 119), one can write eq A-10 as

$$I_0(\alpha) = 2K_0(r\alpha^{1/2})$$

$$I_3(\alpha) = (4\alpha^{1/2}/r)K_1(r\alpha^{1/2}) - 2\alpha K_2(r\alpha^{1/2})$$

$$= -2\alpha K_0(r\alpha^{1/2})$$
(A-11)

where K_i is the *i*th order McDonald function, and the last equality follows from the recursion relationship⁴⁹ among K_0 , K_1 , and K_2 . Thus, substituting eq A-11 into eq A-9 gives

$$\begin{split} I_{0} &= \\ & \frac{K_{0}(r\lambda_{1}^{1/2})}{(\lambda_{1} - \beta)(\lambda_{1} - \lambda_{2})} + \frac{K_{0}(r\lambda_{2}^{1/2})}{(\lambda_{2} - \beta)(\lambda_{2} - \lambda_{1})} + \frac{K_{0}(r\beta^{1/2})}{(\beta - \lambda_{1})(\beta - \lambda_{2})} \\ I_{3} &= - \Bigg[\frac{\lambda_{1}K_{0}(r\lambda_{1}^{1/2})}{(\lambda_{1} - \beta)(\lambda_{1} - \lambda_{2})} + \frac{\lambda_{2}K_{0}(r\lambda_{2}^{1/2})}{(\lambda_{2} - \beta)(\lambda_{2} - \lambda_{1})} + \frac{\beta K_{0}(r\beta^{1/2})}{(\beta - \lambda_{1})(\beta - \lambda_{2})} \Bigg] \end{split}$$

The three integrals I', I_0 , and I_3 suffice to obtain the expression for the radial distribution function in eq 100.

Coordination Chemistry of Benzene, Toluene, Cyclohexadienes, Cyclohexene, and Cyclohexane on Pt(100)

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The surface chemistry of benzene, toluene, cyclohexane, cyclohexene, and cyclohexadienes on Pt(100) is described. Benzene chemisorption was largely molecular although H–D exchange between chemisorbed C_6H_6 and C_6D_6 was observed at temperatures of 100 °C and above. Toluene chemisorbed with bond breaking to give Pt-(100)-benzyl. This benzyl species ($C_6D_5CD_2$) underwent H-D exchange with chemisorbed hydrogen. Exchange was more facile at the CH₂ site than at aromatic C-H sites. Cyclohexane, cyclohexane, and cyclohexadienes chemisorbed on Pt(100) to form benzene with the expected relative ease of dehydrogenation of cyclohexadienes \geq cyclohexene > cyclohexane.

Introduction

Earlier studies have established the coordination chemistry of benzene, toluene, cyclohexane, cyclohexene, and 1,3- and 1,4-cyclohexadiene on the atomically flat Pt(111), stepped Pt 6(111)×(111), as well as the low and high Miller index planes of nickel surfaces.^{1–3} These studies were

conducted under ultrahigh vacuum conditions with thermal desorption spectroscopy, isotopic labeling, chemical displacement reactions, low-energy electron diffraction, and Auger electron spectroscopy as primary diagnostic techniques. Electronic and stereochemical features that facilitate carbon-hydrogen bond breaking and making were

⁽¹⁾ Friend, C. M.; Muetterties, E. L. J. Am. Chem. Soc. 1981, 103, 773. (2) Tsai, M.-C.; Muetterties, E. L. J. Am. Chem. Soc. 1982, 104 2534.

delineated in this earlier work. Described here is an analogous study on the Pt(100) surface. A distinctive difference in this chemistry is the *reversible* carbon-hydrogen bond breaking observed for Pt(100) as contrasted to the largely irreversible carbon-hydrogen bond breaking on the related, atomically flat (111) surface.

Experimental Section

Reagents and Procedures. Reagent grade benzene and toluene were stored over CaH_2 and used without further purification. The benzene- d_6 and toluene- d_8 (both from Aldrich Chemical Co., 99+%) were treated similarly. $C_6H_5CD_3$ and $C_6D_5CH_3$, obtained from Merck & Co., were used without treatment. Cyclohexane (Matheson Coleman and Bell) and cyclohexane- d_{12} (prepared from $C_6D_6 + D_2$) were dried over Na₂SO₄ and used without further purification. Cyclohexene (Chemical Samples Co., 99.9%) and cyclohexene- d_{10} (Merck Isotopes, 99% d_{10}) were dried over CaH₂. 1,3- and 1,4-cyclohexadiene (Chemical Samples Co.) were stored in the vapor phase in vacuum flasks at 0 °C. Trimethylphosphine was synthesized by a modification of a literature method.¹ Hydrogen (99.95%) and deuterium (99.7%) were purchased from Matheson and Liquid Carbonic, respectively.

All experiments were performed in an all-metal bakeable ultrahigh vacuum chamber with a base pressure of $<2 \times 10^{-10}$ torr.¹ Procedures for cutting, polishing, and cleaning the platinum crystal,^{4,5} and chemisorption, thermal desorption experiments, and chemical displacement reactions have been described earlier.¹ The clean Pt(100) surface exhibited a reconstructed, (5×20) LEED pattern which transformed to the (1×1) surface structure upon chemisorption of benzene, toluene, and cyclic olefins.⁶a Exposures were estimated with an uncalibrated nude ion gauge and expressed as langmuirs (1 langmuir = 1 × 10⁻⁶ torr s).

Trimethylphosphine Chemistry on the Pt(100) Surface. Trimethylphosphine was strongly chemisorbed on the Pt(100) surface. Thermal desorption yielded trimethylphosphine ($T_{\rm max} \simeq 200$ °C), methane ($T_{\rm max} \simeq 170$ °C), and hydrogen ($T_{\rm max} \simeq 170$, 235, and 410 °C). Thus, molecular desorption and decomposition of chemisorbed trimethylphosphine are competing thermal processes. When deuterium was coadsorbed with trimethylphosphine, CH₃D and HD were also observed along with CH_4 (no CH_4 is seen in the fragmentation of $P(CH_3)_3$ itself) and H_2 in the characteristic trimethylphosphine decomposition regions but the reversibly desorbed trimethylphosphine contained no deuterium. The surface after the thermal desorption experiment contained P and C atoms due to the fraction of trimethylphosphine molecules that decomposed. Ethane was not detected in the surface effected decomposition of trimethylphosphine. No attempt is made here to interpret the molecular details of trimethylphosphine surface chemistry. Trimethylphosphine was simply employed as a displacement reagent for molecules chemisorbed (see ref 6b and 6c) on Pt(100) as in earlier studies.¹⁻³

Results and Discussion

Benzene Chemistry. Benzene chemisorption on the Pt(100) surface is partially molecular (associative) in character; a similar behavior for benzene² was observed for the Pt(111) and $Pt 6(111) \times (111)$ surfaces. Thermal de-



Figure 1. Thermal desorption spectra of benzene- d_6 chemisorbed on Pt(100) are shown as a function of benzene exposure. The correlations between Langmuir (L) exposure and surface coverage are approximately: 0.1L: 0.1–0.15 C/Pt, 0.4L: 0.4–0.5 C/Pt, 0.6L: 0.6 C/Pt, and 1L: 0.9 C/Pt where surface coverage is expressed as the ratio of carbon atoms to platinum atoms. The heating rate in the thermal

desorption experiments was ~25 °C s⁻¹. For comparative purposes,

the curve intensities should be divided by the scale factor.



Figure 2. Presented above are thermal decomposition spectra for benzene- d_6 chemisorbed on Pt(100) as a function of benzene exposure. These spectra are complementary to the spectra presented in Figure 1 and, for each specific coverage in the two figures, the spectra are derived from a single desorption experiment.

sorption experiments established that there were competing thermal processes of reversible benzene desorption and irreversible benzene decomposition (to yield H_2 and a carbon-contaminated surface) as shown in Figures 1 and

⁽⁴⁾ Friend, C. M.; Gavin, R. M.; Muetterties, E. L.; Tsai, M.-C. J. Am. Chem. Soc. 1980, 102, 1717.
(5) Muetterties, E. L.; Tsai, M.-C. Bull. Soc. Chim. Belg. 1980, 89, 813.

 ^{(6) (}a) Gland, J. L.; Somorjai, G. A. Adv. Colloid Interface Sci. 1976,
 (5) 205. (b) Muetterties, E. L. Angew. Chem. 1978, 90, 577. (c) Hemminger, J. C.; Muetterties, E. L.; Somorjai, G. A. J. Am. Chem. Soc. 1979,
 101, 62.

2. At low coverages, the thermal decomposition process was the dominant process. As coverage was increased, the degree of reversible benzene desorption increased from $\sim 20\%$ to $\sim 60\%$, based on Auger analysis, in the limits of 0.1 to 0.6-0.9 of a carbon monolayer. The latter is expressed throughout this article as the number of carbon atoms per platinum atom. The character of the benzene desorption spectrum was also a function of coverage as illustrated in Figure 1. There were two distinct desorption maxima at low coverages, one of low intensity, at ~ 110 °C and the major peak at ~ 170 °C. With increasing coverage, the major peak increased in intensity and the temperature of the maximum decreased slightly from \sim 170 to 150 °C. Only one broad maximum at \sim 150 °C was resolvable at coverages above ~ 0.6 . Qualitatively, this benzene chemisorption behavior was analogous to that on Pt(111) and $Pt6(111) \times (111)^2$ except that the two desorption maxima were distinguishable even at high coverages on these two surfaces.

To test whether the two benzene desorption maxima on Pt(100) represented distinguishable chemisorption states, as was established² for Pt(111) and $Pt 6(111) \times (111)$, selective population of one state by C_6D_6 and the other by C_6H_6 was attempted by sequential exposure of the (100) crystal to C_6D_6 and then to C_6H_6 . In the subsequent thermal desorption experiment, C_6H_6 and C_6D_6 codesorbed in a relatively fixed molar ratio throughout the thermal desorption range rather than desorbing sequentially as was observed in the analogous experiments² on Pt(111) and Pt $6(111) \times (111)$. This experiment suggested that there was no detectable preferential chemisorption. Furthermore, there was no evidence of benzene (C_6D_6) displacement from Pt(100)–C₆D₆ by benzene, i.e., C₆D₆ was not displaced by C₆H₆ at 25 °C and $\sim 10^{-8}$ torr C₆H₆ pressure. Displacement of chemisorbed benzene (C_6D_6) by benzene (C_6H_6) was demonstrated for the other platinum surfaces. We have no explanation for these differences in benzene surface chemistry on Pt(100) and the closed packed planes of platinum. Presumably, a major fraction of the chemisorbed benzene is π bound and has the C₆ plane parallel to the surface plane.⁷

Trimethylphosphine displaced benzene (C_6D_6) chemisorbed on Pt(100). This displacement effected at 25 °C was not quantitative because, in a thermal desorption (decomposition) experiment performed after the displacement reaction, the characteristic trimethylphosphine decomposition products of methane and hydrogen contained CH₃D and HD.

Carbon-hydrogen bond breaking was a partially reversible process in the Pt(100)-benzene surface chemistry in sharp contrast to that of the other atomically flat plane, Pt(111), and of all nickel surfaces where no such process was detected. Desorption from Pt(100)-C₆H₆-C₆D₆ yielded only C₆H₆ and C₆D₆ molecules below ~150 °C and all possible C₆H_{6-x}D_x molecules began to appear above this temperature.⁸ The reversible C-H bond formation is not a significant process until relatively high temperatures are



Figure 3. Rapid heating of toluene chemisorbed on Pt(100) results in molecular toluene desorption and in decomposition to give hydrogen as shown in this figure. The spectra were obtained with a Pt(100)-toluene-d₈ surface formed at 20 °C with an initial coverage of ~0.8 of a monolayer (0.8 C/Pt) and with a heating rate of ~25 °C s⁻¹.

 TABLE I: Decomposition of Toluene on Pt(100)

molecule	$T_{\max}(^{\circ}C)$ of hydrogen desorption (intensity) ^a
$C_6D_5CD_3$ $C_6H_5CD_3$	$\begin{array}{l} D_2: \ 90 \ (1), \ 230 \ (3), \ 460 \ (4) \\ D_2: \ 90 \ (2), \ 230 \ (2), \ 460 \ (1) \\ HD: \ 90 \ (trace), \ 230 \ (14), \ 460 \ (6) \\ \end{array}$
$C_6D_5CH_3$	H ₂ : 230 (26), 460 (18) D ₂ : 230 (8), 460 (18) HD: 230 (18), 460 (11) H: $230 (18), 230 (23), 460 (5)$
C ₆ H ₅ CD ₃ ^b	$\begin{array}{l} \text{H}_{2}^{1} & \text{so}(3), 230(23), 400(3)\\ \text{D}_{2}^{2} & \text{none}\\ \text{HD}: & 230(4), 460(2)\\ \text{H}_{2}^{2}: & 100,^{c} & 230(20), 460(26) \end{array}$

^a Relative intensities should be compared in the given toluene decomposition experiment only. ^b A Pt(100)- $C_eH_sCD_3$ surface was treated with 1×10^{-7} torr of H_2 at 75 °C for 5 min before thermal desorption. ^c Very large intensity.

attained. Incisive identification of the temperature range in which H–D exchange was detectably fast for the chemisorbed benzene molecules was achieved through a series of experiments in which benzene was displaced by trimethylphosphine as a function of temperature. Displacement of benzene from Pt(100)–C₆H₆–C₆D₆ yielded only C₆H₆ and C₆D₆ at 25 to 70 °C. Doubly labeled benzene molecules were detected only when the displacement temperature was 100 °C or higher. The stepped Pt 6(111)×(111) benzene surface behaved analogously; the H–D benzene exchange process on this surface required temperatures of 140 °C or greater.

Although the low-energy electron diffraction data for $Pt(100)-C_6H_6$ clearly establish a $Pt(100)-(1\times1)$ platinum surface at 20 °C at coverages as low as 0.1 of a monolayer (see also ref 6a), there could be some degree of reconstruction of this surface at higher temperatures. Thus, the relatively high efficacy of this surface in promoting H–D exchange (at ~100 °C and above) between chemisorbed C_6H_6 and C_6D_6 molecules may not relate necessarily to the intrinsic topographical and electronic features of an atomically flat Pt(100) surface; in fact, the precise topographical features of the Pt(100)-(1×1) surface itself are not defined unambiguously. In any case, the greater effectiveness of the Pt(100) surface for H–D exchange in

^{(7) (}a) Analysis of spectroscopic and diffraction data for benzene on Ni(100), Pd(100), Ni(111), and Pt(111) have been interpreted in terms of π -bound benzene in a plane parallel to the surface plane. (b) Lehwald, S; Ibach, H; Demuth, J. E. Surf. Sci. 1978, 78, 577. (c) Netzer, F. P.; Matthew, J. A. D. Solid State Commun. 1979, 29, 209. (d) Bertolini, J. C.; Rousseau, J. Surf. Sci. 1979, 89, 467. (e) Nyberg, G. L.; Richardson, N. V. Ibid. 1979, 85, 335. (f) Hofmann, P.; Horn, K.; Bradshaw, A. M. Ibid. 1981, 105. L260.

⁽⁸⁾ The molar percentages approximately were C_6H_6 , 35; C_6H_5D , 7; $C_6H_4D_2$, 5.5; $C_6H_3D_3$, 5; $C_6H_2D_4$, 5.5; C_6HD_5 , 7; and C_6D_6 , 35%. Clearly most of the chemisorbed benzene molecules did not undergo H-D exchange. Beyond this obvious fact, we forego any mechanistic interpretation of the exchange results.

chemisorbed hydrocarbons than that of the Pt(111) surface may be general; earlier we noted that H–D exchange was more facile between C_2D_2 and H_2 on Pt(100) than on Pt-(111).⁹

Toluene Chemistry. Toluene chemisorption behavior on the Pt(100) surface was relatively complex and similar to, but not identical with that on Pt(111) and Pt 6(111)- \times (111) surfaces. There were two major competing thermal reactions of reversible toluene desorption and of decomposition (Figure 3) to hydrogen and Pt(100)-C (Table I). A maximum rate of toluene desorption was observed at \sim 100–120 °C but the desorption of toluene was observed only at high coverages (above 0.6 of a monolayer) and even then represented only about 20% of the toluene originally chemisorbed (at 0.8 monolayer coverage). This reversibly adsorbed toluene underwent no reversible C-H bond breaking: $Pt(100)-C_7H_8$ treated first at 70 °C with D_2 at 10^{-7} torr for 1 min and then subjected to the thermal desorption experiment yielded no detectable toluene molecules containing deuterium.

Toluene chemisorbed on Pt(100) was not displaceable by trimethylphosphine at 20 and at 60 °C. These experiments were effected with initial high coverages of the surface by toluene—conditions under which a thermal desorption experiment would produce partial desorption of toluene. Since the binding of toluene to the surface through the ring π and π^* orbitals should not be significantly different from the corresponding binding of benzene and since benzene is partially displaceable by trimethylphosphine, these results *suggest* that the major chemisorption state generated from toluene and Pt(100) at 20 °C may not be analogous to that derived from benzene.

Toluene decomposition is the major thermal process on Pt(100) under ultrahigh vacuum conditions. The end products of decomposition are $H_2(g)$ and Pt(100)-C. Hydrogen desorption from the surface was characterized by three desorption maxima at \sim 90, 230, and 460 °C, with respective relative intensities of 1, 3, and 4. The low temperature maximum was coincident with that observed for Pt(100)-H indicating C-H bond breaking in chemisorbed toluene at temperatures below ~ 90 °C. As discussed below, the formation of a Pt(100)-benzyl species is postulated. So that an unambiguous identification of the site of initial C-H bond breaking could be performed, the thermal decomposition behavior of $C_6H_5CD_3$ and $C_6D_5CH_3$ chemisorbed on Pt(100) was investigated. As shown in Table I, the composition of the 90 °C peak was D_2 and a smaller amount of HD for $Pt(100)-C_6H_5CD_3$ (Figure 4) and was only H_2 for $Pt(100)-C_6D_5CH_3$. Since H-D exchange between H_2 and Pt(100)-D is a facile process, hydrogen treatment of the surface state generated from $C_6H_5CD_3$ should convert the postulated Pt(100)-C- $D_2C_6H_5$ and Pt(100)-D species to $Pt(100)-CD_2C_6H_5$ and Pt(100)-H. Consistent with the hypothesis, such a treatment with H_2 at 10^{-7} torr and 20 °C for 10 min generated a surface that in the thermal desorption experiment yielded H_2 but no HD or D_2 in the low temperature region of $\sim 90-100$ °C; the two higher temperature desorption maxima for H_2 , HD, and D_2 were, for each species, in a relative intensity relationship characteristic of the state(s) simply generarted from $C_6H_5CD_3$ chemisorption on Pt-(100).

Clearly, the major fraction of toluene initially chemisorbed at 20 °C on Pt(100) is selectively converted to Pt(100)-CH₂C₆H₅ and Pt(100)-H at some temperature below ~20 °C. Such a state was postulated for toluene



Figure 4. Thermal decomposition of C₆H₅CD₃ chemisorbed on Pt(100) produces H₂, HD, and D₂, as shown in this figure. The lowest temperature hydrogen desorption maximum at ~90 °C is characteristic of Pt(100)-H(D) and consisted of D₂ and HD (presumably the HD arose from background H₂ in the chamber). H₂ was not detected at ~90 °C. Clearly, the initial carbon-hydrogen bond-breaking process is centered primarily on the aliphatic C-H(D) bond. The heating rate was ~25 °C s⁻¹ in this decomposition experiment.

chemisorbed on Ni(111), Ni(100), Ni 9(111)×(111), and Ni 7(111)×(310).¹ A chemically appealing stereochemistry for Pt(100)-benzyl would be a nearly coplanar C₇ delocalized framework¹⁰ in a plane parallel to the Pt(100) surface plane whereby the delocalized C₇ π donor and π^* acceptor orbitals could maximally interact with surface metal orbitals of appropriate symmetry as shown in 1.



On the aforementioned nickel surfaces, but not on Ni-(110), Pt(111), and Pt 6(111)×(111), the thermal decomposition of toluene proceeded in a regioselective fashion such that all aliphatic C-H bonds were cleaved prior to scission of any aromatic C-H bonds. Decomposition of toluene on Pt(100) only partially followed this regioselective course; the first C-H bond broken is an aliphatic C-H bond to give the benzyl species. Beyond the first step, the rates of aliphatic and aromatic C-H bond breaking on Pt(100) overlap as shown by the data presented in Table I.

At elevated temperatures, the hydrocarbon species (postulated to be benyzyl) formed from toluene on Pt(100) underwent extensive H–D exchange. For example, the species generated from $C_6H_5CD_3$ after treatment with H_2 at 10^{-7} torr and 75 °C for 5 min contained very little deuterium as shown by a subsequent thermal desorption experiment wherein no D_2 and only small amounts of HD formed in the high temperature regions of 230 and 460 °C

⁽¹⁰⁾ We are obtaining spectroscopic data, high-resolution energy loss and photoemission data, to test this hypothesis.



Figure 5. When cyclohexene chemisorbed on Pt(100) is rapidly heated, the cyclohexene first is dehydrogenated to chemisorbed benzene. At higher temperatures, there arise two competing processes for chemisorbed benzene: thermal desorption of benzene and thermal decomposition of benzene to give hydrogen and Pt(100)–C. These features are illustrated above with the thermal desorption (and decomposition) spectra (25 °C s⁻¹ heating rate) for a Pt(100)–cyclohexene-*d*₁₀ chemisorption state formed initially at 20 °C. The lowest temperature hydrogen desorption maximum is in the characteristic region of Pt(100)–H(D). The last three hydrogen desorption maxima and the benzene desorption maximum are characteristic of Pt(100)–C₆D₈.

(Table I). After H₂ treatment at 130 °C for 3 min, exchange was essentially complete. HD exchange at aromatic C-H sites also occurred but more slowly than at the CH₂ site. Exchange was only partial after treatment of a surface, formed from C₆D₅CH₃ on Pt(100), with H₂ at 10⁻⁷ torr for 5 min at 130 °C.

Dehydrogenation of Cyclohexane, Cyclohexene, and Cyclohexadiene to Benzene. Dehydrogenation reactions of cyclohexane, cyclohexene, and cyclohexadiene on a range of low Miller index planes as well as stepped surfaces of Ni and Pt have been previously investigated.³ Analogous studies were effected on the Pt(100) surface to delineate the electronic and topographical features that affect the chemistry of these cyclic hydrocarbons on this surface. Cyclohexane showed a very small sticking coefficient from 25 to 100 °C. Heating of a $Pt(100)-(5\times 20)-c-C_6D_{12}$ surface, formed at 25 °C, gave D₂ as the only gaseous product with desorption maxima at \sim 100, 175, 220, and 345 °C and a platinum surface with a small amount of residual carbon (<0.1 C/Pt). Trimethylphosphine failed to displace benzene (or any other hydrocarbon species) on exposure Pt(100)-(5×20)-c-C₆D₁₂ to the phosphine at temperatures of 25 to 100 °C.^{11,12} However, exposure of a Pt(100)- cyclohexane surface to trimethylphosphine followed by a thermal desorption experiment did lead to benzene desorption from the surface at 160 °C. A similar behavior was observed for cyclohexane chemisorbed on Pt(111) and Pt $6(111)\times(111)$.³ The latter exhibited the highest potential for cyclohexane conversion to benzene. The two Pt planes of (111) and (100)-(5×20) are of comparable efficacy in the dehydrogenation of cyclohexane to benzene under the ultrahigh vacuum conditions described above.

Cyclohexene dehydrogenation to form benzene was a facile process on Pt(100) at 25 °C. Like benzene, both cyclohexene and cyclohexadiene chemisorption effected the reconstruction of the clean Pt(100)-(5×20) to Pt-(100)-(1×1) even at low coverages of ~ 0.1 monolayer. Thermal desorption from a $Pt(100)-c-C_6D_{10}$ surface, initially formed at 25 °C, was fully analogous (Figure 5) to that of a desorption from a $Pt(100)-C_6D_6-D$ surface: the C_6D_6 desorption maximum was at 150-165 °C and D_2 desorption maxima were at $\sim 160, 290, 360, \text{ and } 460 \ ^\circ\text{C}$ with the last three peaks characteristic of benzene decomposition on Pt(100), and the first characteristic of Pt(100)-H(D). Trimethylphosphine displaced C_6D_6 from a $Pt(100)-c-C_6D_{10}$ surface at 25 °C but was not complete; significant amounts of benzene, CH₃D, and HD were detected in the subsequent thermal desorption (decomposition) experiment. Cyclohexene chemistry on the Pt(100)surface is distinctly different from that of the other flat platinum surface, Pt(111), where formation of benzene is a thermally more activated process occurring at a rapid rate only at temperatures above $\sim +70$ °C.^{3,11,12}

Both 1,3- and 1,4-cyclohexadiene readily converted to benzene on the Pt(100) surface: thermal desorption of benzene was observed at 150–165 °C accompanied by hydrogen desorption at 160, 290, 365, and 460 °C. Trimethylphosphine displaced benzene at 25 °C from a surface formed from the dienes and Pt(100) at 25 °C. Dehydrogenation of cyclohexadienes to benzene on the flat and stepped Ni and Pt surfaces previously studied was also a rapid reaction at 25 °C.

In the dehydrogenation of cyclohexadienes or cyclohexene to benzene on Pt(100), there was reversible C-H bond breaking as was observed earlier on Pt(111) and Pt $6(111) \times (111)$. Thus, the surface states formed at 25 °C from $c-C_6H_{10}$ and $c-C_6D_{10}$ or from $c-C_6H_8$ and D_2 on Pt-(100) produced multiply labeled benzene molecules, $C_6H_{6-x}D_x$, in a thermal desorption experiment (maximum rate at +170–180 °C) and in a trimethylphosphine displacement reaction effected at temperatures above +70 °C.

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⁽¹¹⁾ Note that at low benzene coverages on all these platinum surfaces, benzene can neither be thermally desorbed nor chemically displaced.

⁽¹²⁾ All these observations about dehydrogenation of cyclohexane or cyclohexene to benzene on the metal surfaces relate to initial chemisorption states formed at 20 °C and to thermal desorption experiments with heating rates of 20-30 °C s⁻¹. Formation of chemisorption states at lower temperatures or use of lower heating rates favors higher yields of benzene (gas phase).