LBL-14861
Preprint c.2

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

RECEIVED
LAWRENCE
BERKELEY LABORATORY
SEP 30 1982
LIBRARY AND
DOCUMENTS SECTION

Materials & Molecular Research Division

Submitted to the Journal of Physical Chemistry

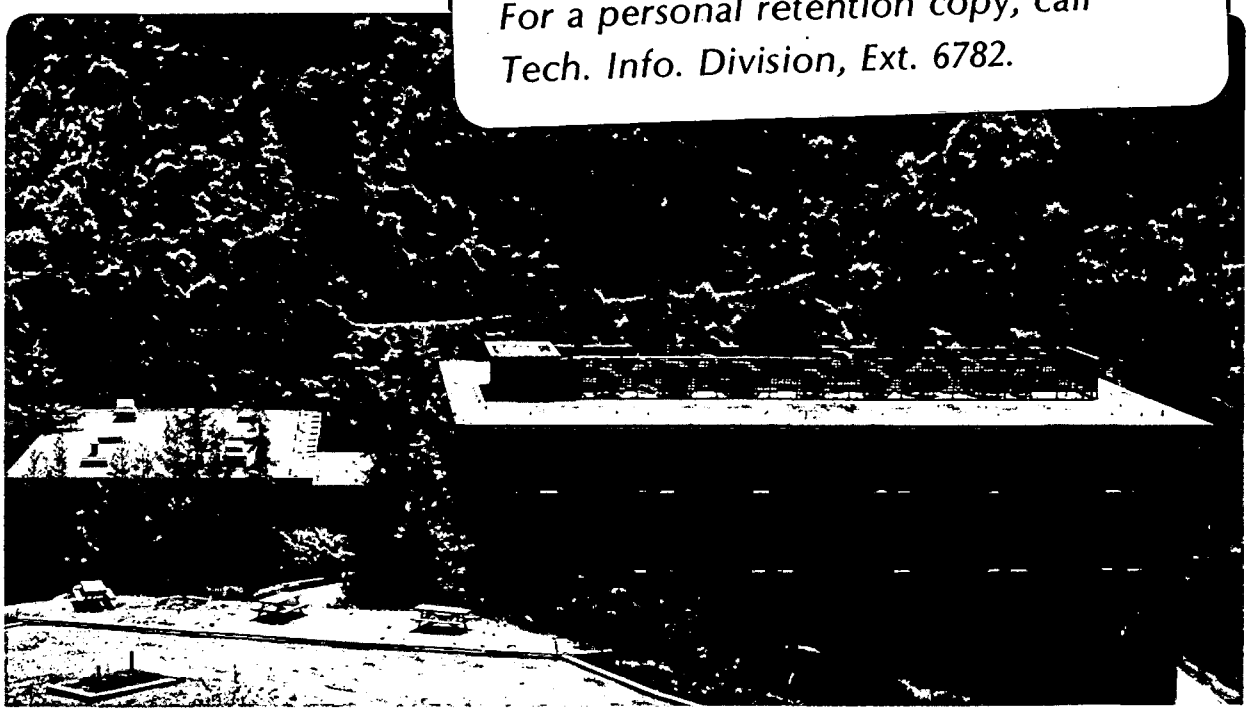
THE COORDINATION CHEMISTRY OF BENZENE, TOLUENE, CYCLOHEXADIENES, CYCLOHEXENE AND CYCLOHEXANE ON Pt(100)

Min-Chi Tsai and E.L. Muetterties

August 1982

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 6782.



Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

LBL-14861 c.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL-14861

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

Min-Chi Tsai and E. L. Muetterties*

Materials and Molecular
Research Division
Lawrence Berkeley Laboratory

and

Department of Chemistry
University of California
Berkeley, California 94720

This work was supported by the Director, Office of Energy Research, Office of Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098; and by the National Science Foundation.
This manuscript was printed from originals provided by the authors.

ABSTRACT

The surface chemistry of benzene, toluene, cyclohexane, cyclohexene, and cyclohexadienes on Pt(100) are 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 CH_2 site than at aromatic C-H sites. Cyclohexane, cyclohexene and cyclohexadienes chemisorbed on Pt(100) to form benzene with the expected relative ease of dehydrogenation of cyclohexadienes $\geqq$ cyclohexene > cyclohexane.

INTRODUCTION

Earlier studies have established the coordination chemistry of benzene, toluene, cyclohexane, cyclohexene, 1,3- and 1,4-cyclohexadiene on the atomically flat Pt(111), stepped Pt 6(111)x(111) as well as the low and high Miller index planes of nickel surfaces.[1-3] These studies were conducted under ultra high vacuum conditions using 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 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

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 & Bell) and cyclohexane-d_{12} (prepared from $C_6D_6 + D_2$) were dried over Na_2SO_4 and used without further purification. Cyclohexene (Chem. Samples Co., 99.9%) and cyclohexene-d_{10} (Merck Isotopes, 99%-d_{10}) were

dried over CaH_2. 1,3- and 1,4-cyclohexadiene (Chem. 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 ultra high 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, (5x20) LEED pattern which transformed to the (1x1) 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 = 1L = 1×10^{-6} torr sec).

Trimethylphosphine Chemistry on the Pt(100) Surface

Trimethylphosphine was strongly chemisorbed on the Pt(100) surface. Thermal desorption yielded trimethylphosphine ($T_{max} \cong 200°C$), methane ($T_{max} \cong 170°C$) and hydrogen ($T_{max} \cong 170$, 235 and 410°C). Thus, molecular desorption and decomposition of chemisorbed trimethylphosphine are competing thermal processes. When deuterium was co-adsorbed with trimethylphosphine, CH_3D 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 reference 6b,c) 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 benzene[2] was observed for the Pt(111) and Pt 6(111)x(111) surfaces. Thermal desorption 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 Figs.1 and 2. At low coverages, the thermal decomposition process was the dominant process. As coverage was increased, the degree of reversible benzene desorption increased from ∿20% to ∿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 Fig.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 ∿170 to 150°C. Only one broad maximum at ∿150°C was resolvable at coverages above ∿0.6. Qualitatively, this benzene chemisorption behavior was analogous to that on Pt(111) and Pt 6(111)x(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 established[2] for Pt(111) and Pt 6(111)x(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 co-desorbed in a relatively fixed molar ratio throughout the thermal desorption range rather than desorbing sequentially as was observed in the analogous experiments[2] on Pt(111) and Pt 6(111)x(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)-C_6D_6 by benzene, i.e., C_6D_6 was not displaced by C_6H_6

at 25°C and $\sim 10^{-8}$ torr C_6H_6 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 close packed planes of platinum.

Presumably, a major fraction of the chemisorbed benzene is π-bound and has the C_6 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 CH_3D 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)-C_6H_6-C_6D_6 yielded only C_6H_6 and C_6D_6 molecules below ~150°C and all possible $C_6H_{6-x}D_x$ molecules began to appear above this temperature.[8] The reversible C-H bond formation is not a significant process until relatively high temperatures are 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)-C_6H_6-C_6D_6 yielded only C_6H_6 and C_6D_6 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)x(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)-(1x1) platinum surface at 20°C at coverages as low as 0.1 of a monolayer (see also reference 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)-(1x1) surface itself are not defined unambiguously. In any case, the greater effectiveness of the Pt(100) surface for H-D exchange in 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]

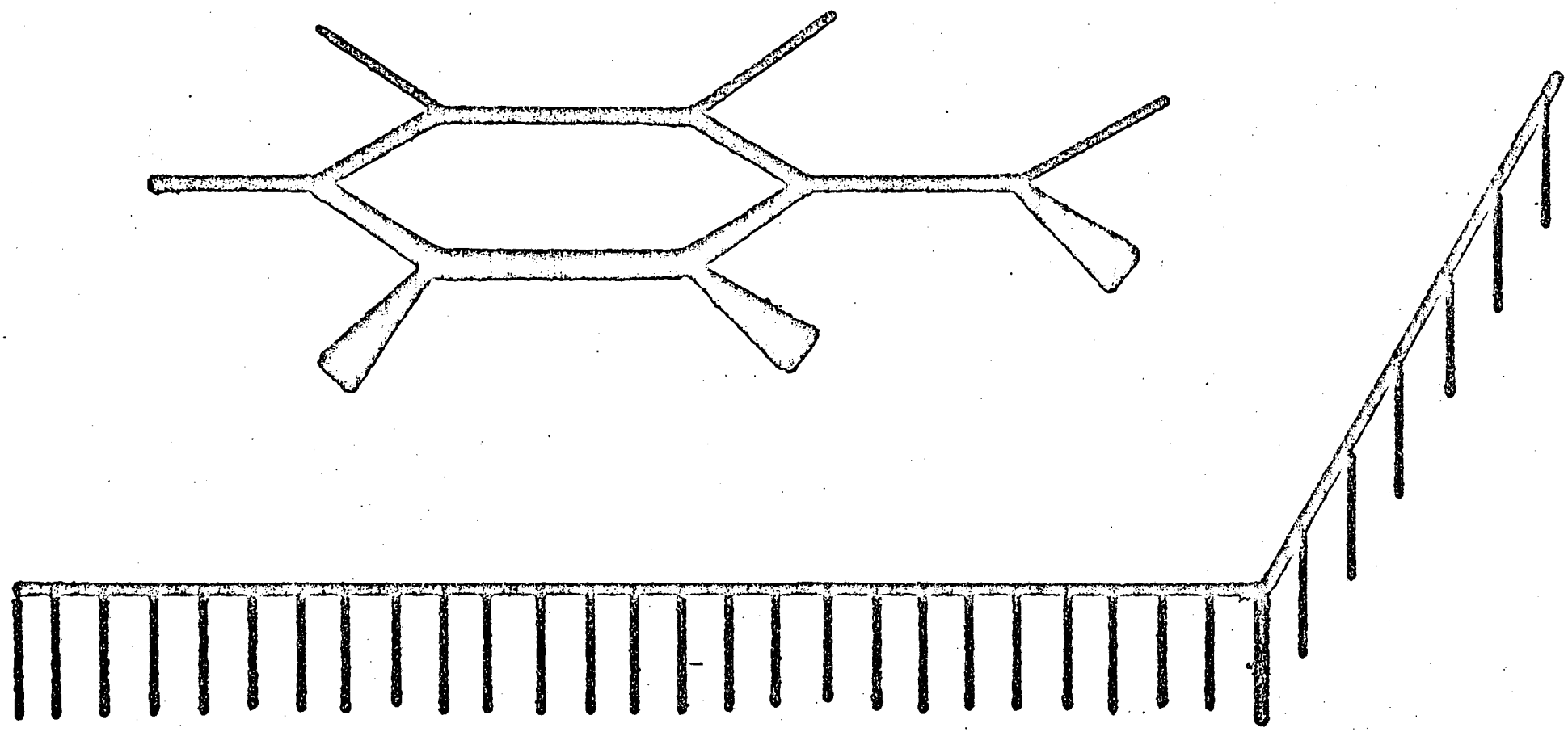
Toluene Chemistry

Toluene chemisorption behavior on the Pt(100) surface was relatively complex and similar, but not identical, to that on Pt(111) and Pt 6(111)x(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 ∿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 desorbed 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 one minute 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 ultra high 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 ∿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. To enable an unambiguous identification of the site of initial C-H bond breaking, 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)-$C_6H_5CD_3$ (Fig.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)-$CD_2C_6H_5$ 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 ten minutes generated a surface that in the thermal desorption experiment yielded H_2 but no HD or D_2 in the low temperature region of ∿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 generated 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)-$CH_2C_6H_5$ and Pt(100)-H at some temperature below ∿20°C. Such a state was postulated for toluene chemisorbed on Ni(111), Ni(100), Ni 9(111)x(111) and Ni 7(111)x(310).[1] A chemically appealing stereochemistry for Pt(100)-benzyl would be a nearly co-planar C_7 delocalized framework[10] in a plane parallel to the Pt(100) surface plane whereby the delocalized C_7 π donor and π^* acceptor orbitals could maximally interact with surface metal orbitals of appropriate symmetry as shown in 1.



1
~

On the aforementioned nickel surfaces, but not on Ni(110), Pt(111) and Pt 6(111)x(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 benzyl) 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 five minutes 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 (Table I). After H_2 treatment at 130°C for three minutes, exchange was essentially complete. HD exchange at aromatic C-H sites also occurred but more slowly than at the CH_2 site. Exchange was only partial after treatment of a surface, formed from $C_6D_5CH_3$ on Pt(100), with H_2 at 10^{-7} torr for five minutes 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°C to 100°C. Heating of a Pt(100)-(5x20)-c-C_6D_{12} surface, formed at 25°C, gave D_2 as the only gaseous

product with desorption maxima at ∿110,175, 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)-(5x20)-c-C_6D_{12} 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)x(111).[3] The latter exhibited the highest potential for cyclohexane conversion to benzene. The two Pt planes of (111) and (100)-(5x20) are of comparable efficacy in the dehydrogenation of cyclohexane to benzene under the ultra high 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)-(5x20) to Pt(100)-(1x1) 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 ∿160, 290, 360 and 460°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, CH_3D 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 ∿+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)x(111). Thus, the surface states formed at 25°C from $\underline{c}$-C_6H_{10} and $\underline{c}$-C_6D_{10} or from $\underline{c}$-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.

Acknowledgements

This research was supported by the National Science Foundation and by the Director, Office of Energy Research, Office of Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

REFERENCES

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 0000.
3. Tsai, M.-C.; Friend, C.M.; Muetterties, E.L. J. Am. Chem. Soc. 1982, 104, 0000.
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. in 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.
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. Surf. Sci. 1979, 85, 335. (f) Hofmann, P.; Horn, K.; Bradshaw, A.M.; Surf. Sci. 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.
9. Muetterties, E.L.; Tsai, M.-C.; Kelemen, S.R. Proc. Natl. Acad. Sci., USA, 1981, 18, 6571.
10. We are obtaining spectroscopic data, high resolution energy loss and photoemission data, to test this hypothesis.
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 sec^{-1}. Formation of chemisorption states at lower temperatures or use of lower heating rates favorshigher yields of benzene (gas phase).

TABLE I: DECOMPOSITION OF TOLUENE ON Pt(100)

MOLECULE	T_{max} (°C) of Hydrogen Desorption (Intensity)*	
$C_6D_5CD_3$	D_2:	90(1), 230(3), 460(4)
$C_6H_5CD_3$	D_2:	90(2), 230(2), 460(1)
	HD:	90 (trace), 230(14), 460(6)
	H_2:	230(26), 460(18)
$C_6D_5CH_3$	D_2:	230(8), 460(18)
	HD:	230(18), 460(11)
	H_2:	90(3), 230(23), 460(5)
$C_6H_5CD_3$**	D_2:	none
	HD:	230(4), 460(2)
	H_2:	100‡, 230(20), 460(26)

* Relative intensities should be compared in the given toluene decomposition experiment only.

** A Pt(100)-$C_6H_5CD_3$ surface was treated with 1×10^{-7} torr H_2 at 75°C for 5 min before thermal desorption.

‡ Very large intensity

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 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 $\sim 25°\ sec^{-1}$. For comparative purposes, the curve intensities should be divided by the scale factor.

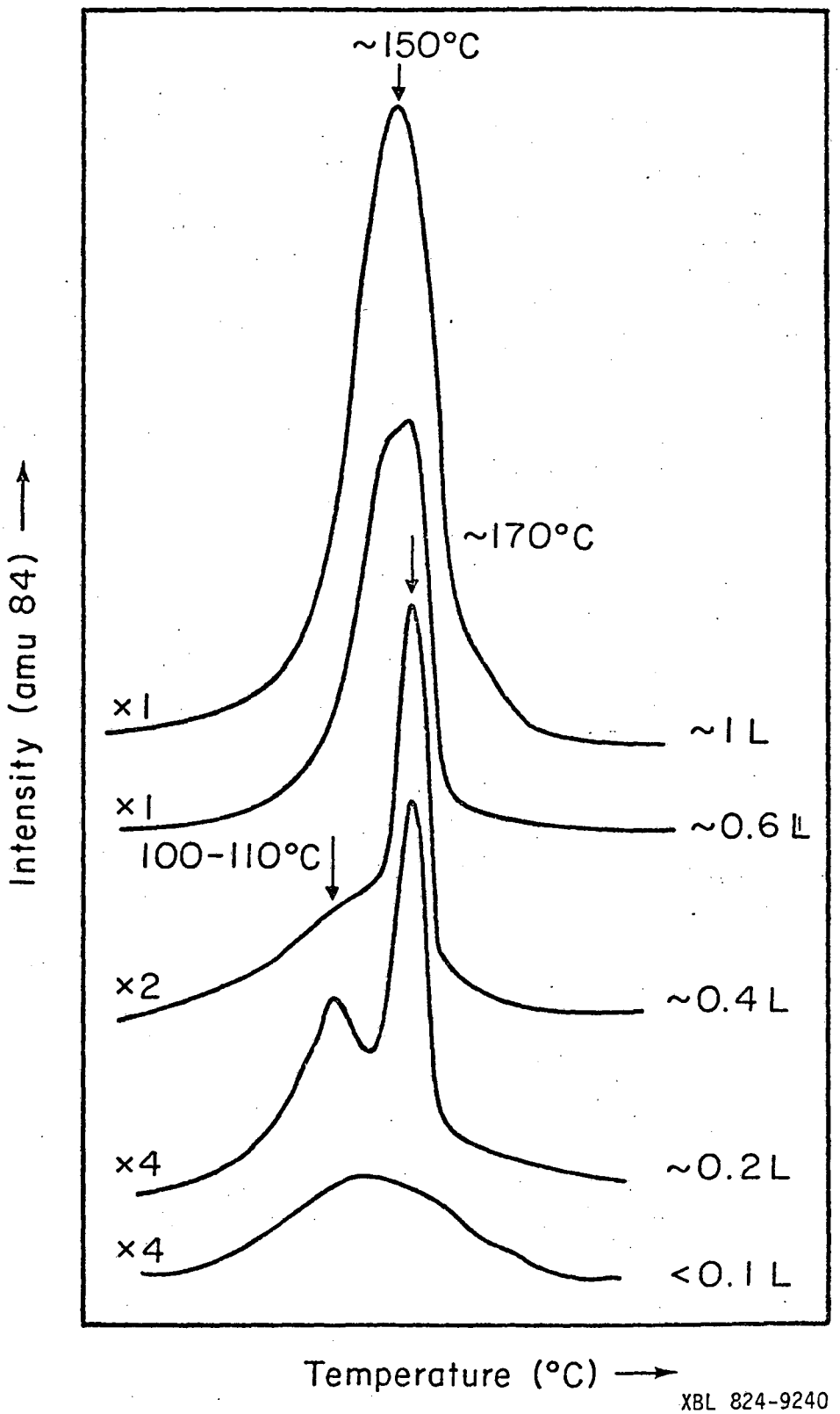
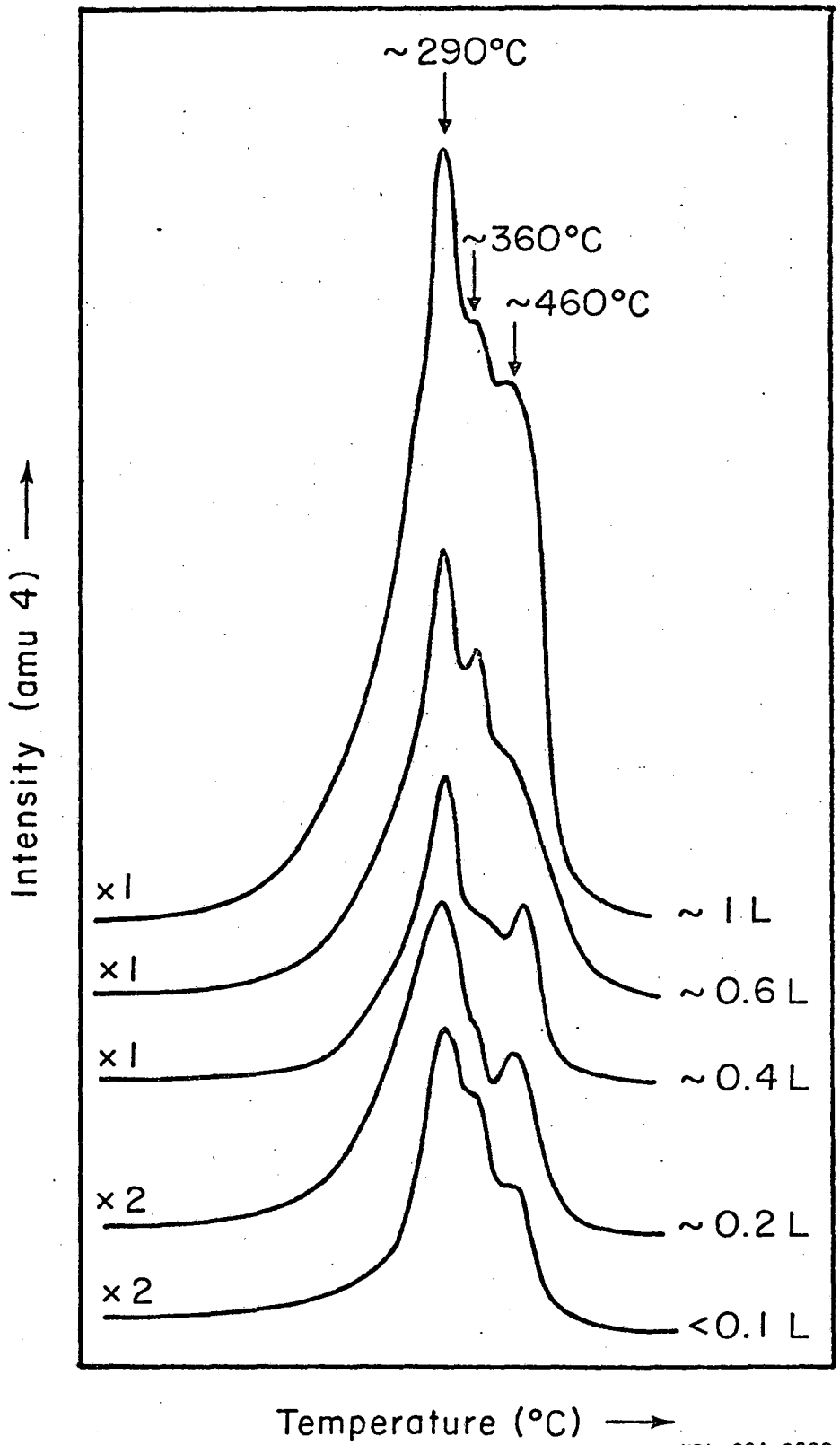

~150°C
~170°C
100-110°C
×1
×1
×2
×4
×4
~1 L
~0.6 L
~0.4 L
~0.2 L
<0.1 L
Intensity (amu 84)
Temperature (°C)
XBL 824-9240

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.


~290°C
~360°C
~460°C
Intensity (amu 4)
×1
×1
×1
×2
×2
~1 L
~0.6 L
~0.4 L
~0.2 L
<0.1 L
Temperature (°C)

XBL 824-9238

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-d_8 surface formed at 20°C with an initial coverage of $\sim$0.8 of a monolayer (0.8 C/Pt) and with a heating rate of $\sim$25° sec^{-1}.

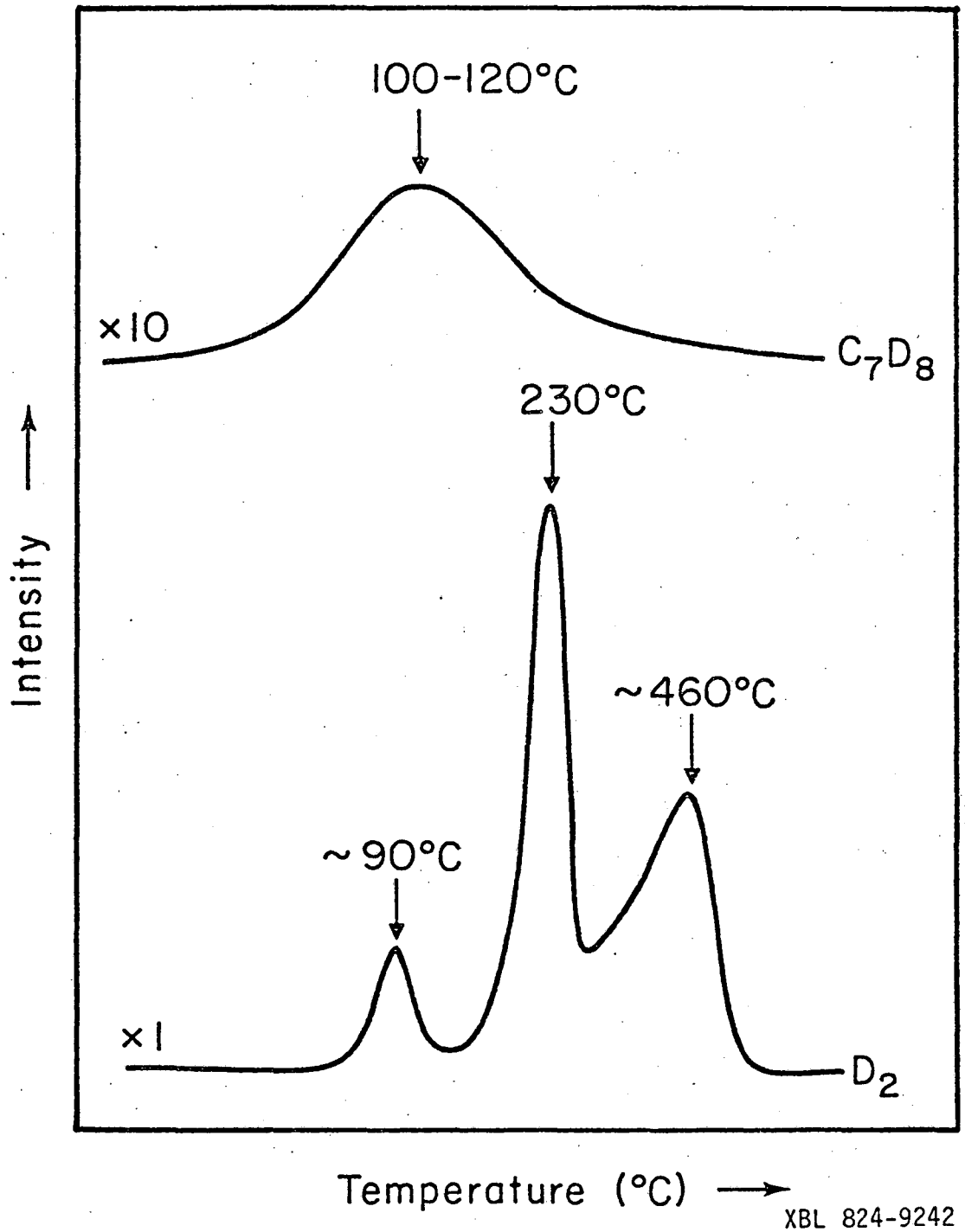

100-120°C
×10
C_7D_8
230°C
~460°C
~90°C
×1
D_2
Intensity
Temperature (°C)
XBL 824-9242

Figure 4.

Thermal decomposition of $C_6H_5CD_3$ chemisorbed on Pt(100) produces H_2, HD and D_2, as shown in this figure. The lowest temperature hydrogen desorption maximum at ∿90°C is characteristic of Pt(100)-H(D) and consisted of D_2 and HD (presumably the HD arose from background H_2 in the chamber). H_2 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° sec^{-1} in this decomposition experiment.

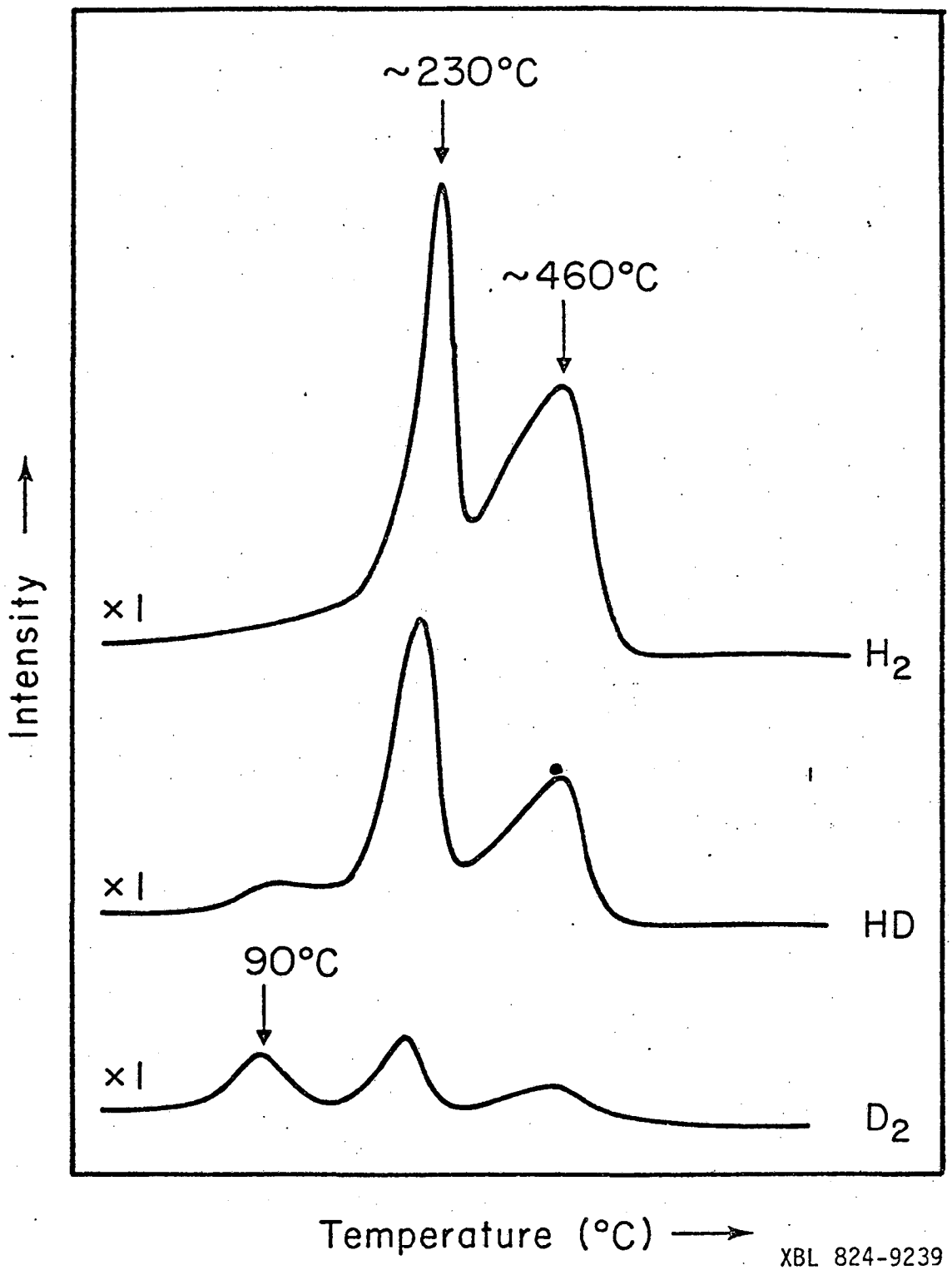
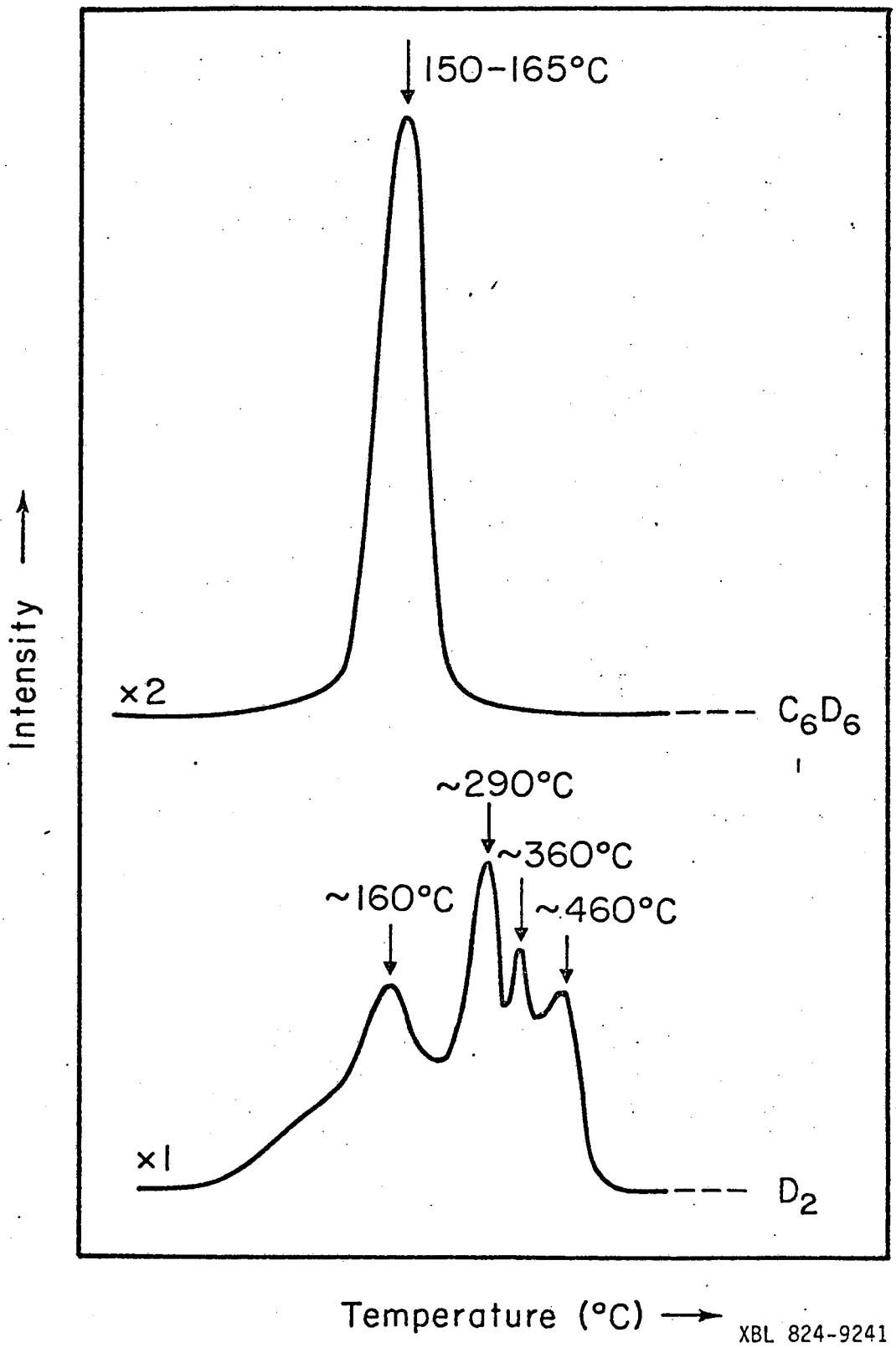

~230°C
~460°C
Intensity
×1
H2
×1
HD
90°C
×1
D2
Temperature (°C)
XBL 824-9239

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°sec^{-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)-C_6D_6.


150-165°C
Intensity
×2
C_6D_6
~290°C
~360°C
~160°C
~460°C
×1
D_2
Temperature (°C)
XBL 824-9241

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720