Kramer's theory of Beece et al., which provides explicitly for nonstatic barriers and for coupling to the solvent motion, leads to a similar conclusion for the BR/HSA system. The observed value of κ, 0.14, according to Beece et al., is consistent with the bilirubin being bound in a relatively rigid protein pocket with at least that portion of the molecule that twists probably not exposed to the aqueous medium. Within the protein pocket, bilirubin must be relatively free to isomerize.

Experimental Section

Materials. (Z,Z)-Bilirubin IXα, obtained from Sigma Chem. Co., was purified by washing a chloroform solution of it with aqueous NaHCO$_3$ according to Lightner, et al.[24] Defatted human serum albumin was prepared from fresh blood according to methods described previously.[25] Sucrose, density gradient grade, was also purchased from Sigma Chem. Co.

Bilirubin in solid poly(methyl methacrylate) was prepared as follows. Bilirubin (4.5 μM) was dissolved in freshly distilled methyl methacrylate and the solution placed in a 12-mm diameter Pyrex tube equipped for sealing. After degassing by the freeze-pump-thaw method, the tube was sealed and placed in an oven at 60 °C. The clear solid polymer obtained after 4 days was removed from the tube was machined to a 1 × 0.3 × 0.3 cm block, and the faces of the block were polished. The absorption spectrum of bilirubin in the polymer was virtually identical with that in the monomer solution. The concentration of bilirubin in the polymer block was close to 5 μM due to the contraction upon polymerization.

Quantum Yield Measurements. Quantitative spectrofluorometry was performed using a computer-controlled photon-counting spectrofluorometer. This instrument is equipped to correct for excitation light intensity variation and for the wavelength dependence of detection sensitivity. The optical configuration was such that intensity measurements were independent of the index of refraction of the sample (for constant sample absorbance and fluorescence yield). The variation in repeated intensity measurements was less than 5%.

Quantum yield values were determined by comparing integrated fluorescence intensities against those obtained from solutions of acridine yellow in ethanol (matched for absorbance at the excitation wavelength) for which a fluorescence yield value of 0.86 was previously determined.[26]

Values of Viscosity and Refractive Index. Viscosity and refractive index values for water and aqueous sucrose solutions were obtained from various published tables.[27,28] Plots of values from these tables were made when it was necessary to interpolate between table entries.

Acknowledgment. We thank William E. Blumberg for helpful discussions and F. H. Doleiden for technical assistance.

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(24) D. A. Lightner, T. A. Wooldridge, and A. F. McDonagh, *Proc. Natl. Acad. Sci. U.S.A.*, **76**, 29 (1979).

(25) A. A. Lamola, J. Eisinger, W. E. Blumberg, et al., *Anal. Biochem.*, **100**, 25 (1979).

(26) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules", Academic Press, New York, 1971, p 407.

(27) "National Research Council International Critical Tables of Numerical Data, Physics, Chemistry, and Technology", Vol. II, McGraw-Hill, New York, 1927, pp 337-344.

(28) "Handbook of Chemistry and Physics", 53rd ed., CRC Press, Cleveland, OH, 1972, p E211, D218.

Platinum Metal Surface Chemistry of Benzene and Toluene

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Received September 3, 1981

Abstract: The coordination chemistry of benzene and toluene on Pt(111) and Pt[6(111)×(111)] has been defined by thermal desorption spectrometry, isotopic labeling studies, and chemical displacement reactions. Benzene chemisorption was largely molecular (nondissociative) on Pt(111) but less so on the stepped surface. At temperatures above 100 °C, reversible benzene desorption and benzene decomposition were competing reactions. More than one *differentiable* benzene chemisorption state was present on both surfaces. Exchange experiments established that the rate of surface migration of chemisorbed benzene *between* states on these surfaces was very low. One sharp distinction in the benzene chemistry of the two platinum surfaces was that *reversible* C–H bond breaking occurred on the stepped surface but not on Pt(111). Whereas toluene chemisorption on nickel surfaces is fully irreversible, toluene chemisorbed on Pt(111) was partially desorbed as the toluene molecule at 70–110 °C. Studies with C$_6$H$_5$CD$_3$ and C$_6$D$_5$CH$_3$ suggested that the faster low-temperature C–H bond breaking process is centered on the methyl-group C–H bonds. Chemisorption of mesitylene and *m*-xylene on Pt(111) was partially reversible.

Introduction

Earlier studies established the coordination chemistry of benzene and toluene on the low Miller index planes of nickel and on a stepped and a stepped-kinked nickel surface.[1] This coordination chemistry study was effected under ultra-high-vacuum conditions; the primary diagnostic or characterization techniques were Auger electron spectroscopy, low-energy electron diffraction, thermal desorption spectrometry, isotopic labeling studies, and chemical displacement reactions.[2,3] We describe here an analogous study of benzene and toluene chemisorption on an atomically flat and a stepped platinum surface, Pt(111) and Pt[6(111)×(111)]. Distinctive and important differences in this arene chemistry between platinum and nickel surfaces were established.

Experimental Section

Reagents and Procedures. Toluene (reagent grade), toluene-d_8 (Aldrich Chemical Co., 99+%), benzene (reagent grade), and benzene-d_6 (Aldrich Chemical Co., 99+%) were dried over calcium hydride prior to use. C$_6$D$_5$CH$_3$ and C$_6$H$_5$CD$_3$ obtained from Merck and Co. were used without treatment (traces of moisture did not detectably affect the surface chemistry). Hydrogen (Matheson, 99.95%) and deuterium (Liquid Carbonic, 99.7%) were used without further purification. Trimethylphosphine was prepared and purified as described earlier.[1]

Address correspondence to this author at the Department of Chemistry, University of California.

(1) (a) Friend, C. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1981**, *103*, 773. (b) These were the nickel (111), (110), (100), 9(111)×(111), and 7(111)×(310) surfaces.

(2) Friend, C. M.; Gavin, R. M.; Muetterties, E. L.; Tsai, M.-C. *J. Am. Chem. Soc.* **1980**, *102*, 1717.

(3) Muetterties, E. L.; Tsai, M.-C. *Bull. Soc. Chim. Belg.* **1980**, *89*, 813.

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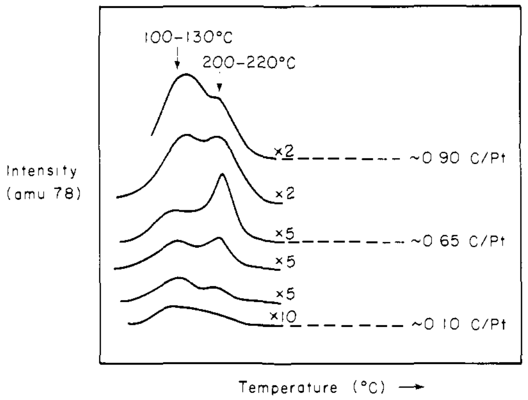

Figure 1. Thermal desorption spectrum of benzene chemisorbed on Pt(111) as a function of surface coverage. The heating rate was 25 °C s^{-1}.

All experiments were performed in an all-metal bakeable ultra-high-vacuum chamber with a base pressure of 10^{-10} torr.[1] Procedures for chemisorption, standardization, and calculation of Auger spectral intensities for carbon coverages on nickel, thermal desorption experiments (heating rates of 25° s^{-1}) and chemical displacement reactions have been described by Friend and Muetterties.[1] Auger spectral intensities for carbon coverages on platinum were calibrated with the data obtained with the ^{14}C (derived from ^{14}C-enriched benzene by thermal decomposition of the benzene on the surface) and radiation analysis by Mr. S. Mark Davis[4] of the U.C.B. Chemistry Department. Procedures for cutting, polishing, and cleaning of the platinum crystals were as described earlier.[2,3]

Trimethylphosphine Chemisorption and Thermal Desorption Behavior on Platinum Surfaces. Trimethylphosphine was strongly chemisorbed on Pt(111) and Pt[6(111)×(111)]. Thermal desorption yielded trimethylphosphine, hydrogen, and methane. Desorption maximal rates were observed at the indicated temperatures. Pt(111): $P(CH_3)_3$, 160 °C; CH_4, 210 °C; H_2, 220 and 260 °C. Pt[6(111)×(111)]: $P(CH_3)_3$, 234 °C; CH_4, 190–204 °C; H_2, 240 and 330 °C. When trimethylphosphine and deuterium were adsorbed before the thermal desorption experiment, then CH_4 and CH_3D, and H_2 and HD, were observed in the characteristic trimethylphosphine decomposition regions; the trimethylphosphine that desorbed intact contained no deuterium.

Results

Benzene on Platinum(111). Benzene chemisorption on Pt(111) bears qualitative similarities to that on Ni(111)[1] although there are significant differences. Thermal desorption experiments showed both molecular or reversible chemisorption of the benzene molecule and irreversible decomposition to form $H_2(g)$ and a carbon-contaminated platinum surface; the specific features of the desorption phenomenon are discussed below. Like the nickel–benzene surface chemistry[1], this Pt(111) benzene chemistry showed no evidence of reversible C–H bond breaking. The only benzene molecules thermally desorbed from a Pt(111)–C_6D_6–C_6H_6 state, formed (i) at 25 °C and (ii) at 25 °C and then annealed at 80 °C for 2 min or at 130 °C for 1 min, were C_6H_6 and C_6D_6. Additionally, thermal desorption experiments with at Pt(111)–C_6D_6–H state, formed at 20 °C, yielded no HD desorption peak, only H_2, in the region characteristic of Pt(111)-H(D). Significant carbon–hydrogen bond breaking does not occur at measurable rates for Pt(111)–C_6H_6(C_6D_6) until temperatures in excess of 200 °C are attained.

The thermal desorption characteristics for Pt(111)–C_6H_6 were more complicated than for Ni(111)–C_6H_6[1] as shown in Figure 1. At very low benzene coverages of less than 0.05 monolayer, no benzene was detectably desorbed (a monolayer in this study is defined as a ratio of one carbon atom per surface platinum atom). At 0.1 to 0.5 of a monolayer, there were two very broad benzene maxima at ~100–130 and 200–220 °C. The higher temperature peak saturated at 0.65 of a monolayer. Above 0.65 of a monolayer, the low-temperature maximum at ~100–130 °C grew rapidly in intensity as coverage was increased to ~0.9 of a monolayer, the effective saturation coverage at 25 °C and 10^{-10} torr (assuming that benzene is bound in a plane parallel to the surface and a 7.2-Å benzene van der Waals radius, the saturation coverage would be about 0.9 carbon atoms per platinum atom). These coverage dependence results do not in themselves establish differentiable benzene chemisorption states for this platinum surface because cooperative effects alone could be responsible for the phenomenon. Nevertheless, the results cited below do clearly establish the presence of more than one benzene chemisorption state.

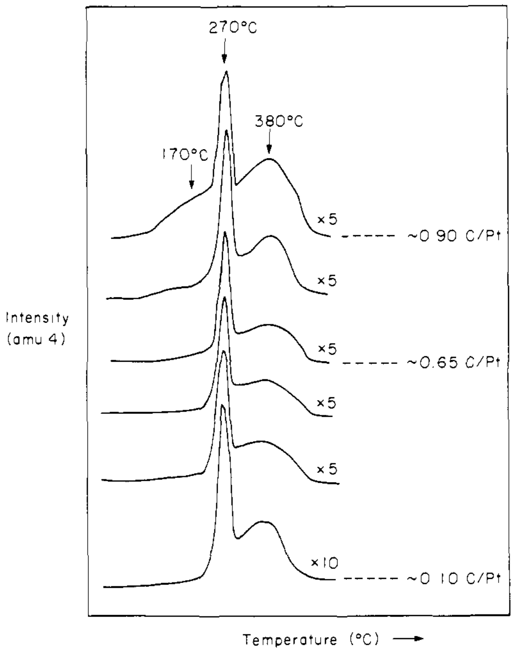

Figure 2. Presented in this figure are the thermal decomposition spectra for benzene-d_6 chemisorbed on Pt(111) as a function of initial benzene surface coverage. The heating rates in all experiments were 25 °C s^{-1}. These spectra are complementary to the spectra presented in Figure 1, and, for each coverage in the two figures, the spectra are derived from a single desorption experiment.

The thermal desorption spectra showed the irreversible benzene decomposition process, competitive with benzene thermal desorption, by hydrogen desorption maxima at ~260 and at ~380 °C with relative intensities of about 1:1 (Figure 2). For Pt(111)–C_6H_6–C_6D_6 surfaces, all three hydrogen species (H_2, HD, and D_2) exhibited desorption maxima near 260 and 380 °C (D_2 appeared ~10° higher than H_2 in the lower temperature peak).

The presence of more than one benzene chemisorption state on Pt(111) and the absence of significant surface migration of the adsorbed benzene species were established by the following isotopic labeling experiments.

(i) A Pt(111)–C_6D_6 state was formed with less than 0.1 monolayer coverage at 20 °C, and then C_6H_6 was coadsorbed to a total coverage of about 0.5 to 0.6. In the thermal desorption experiment, no C_6D_6 desorption was detected; only C_6H_6 desorbed in the 100–130 and 200–220 °C regions. The decomposition of the strongly and irreversibly adsorbed C_6D_6 molecules was shown by the desorption of D_2 and HD in the thermal desorption experiment. Thus, there was no significant interchange between benzene (C_6D_6) in the irreversibly chemisorbed state and benzene (C_6H_6) in the reversibly chemisorbed state(s).

(ii) A Pt(111)–C_6D_6 state was formed with less than a coverage of 0.5 at 20 °C, and then C_6H_6 was coadsorbed to a final coverage close to 0.65. In the subsequent thermal desorption experiment, the higher temperature desorption peak was dominated by C_6D_6 and the low-temperature peak was largely C_6H_6. Under these conditions, benzene exchange between the more tightly bound and less tightly bound reversible states was small.

(iii) A Pt(111)–C_6D_6 state with saturation coverage of ~0.9 was formed at 20 °C. Then this surface was exposed to a C_6H_6 atmosphere of ~10^{-8} torr for a period of 3 min. Under these

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(4) Davis, S. M.; Gordon, B. E.; Press, M.; Somorjai, G. A. *J. Vac. Sci. Technol.* **1981**, *19*, 231.

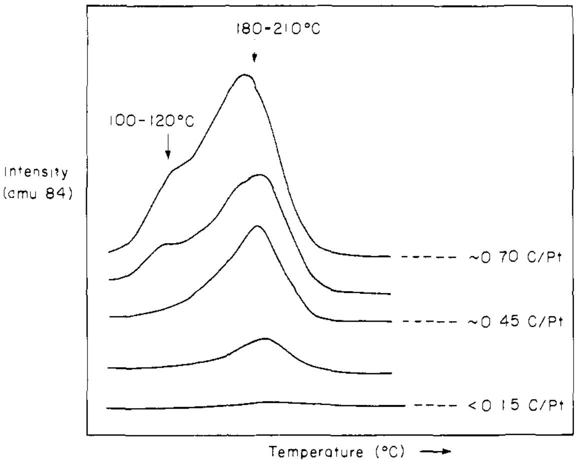

Figure 3. The thermal desorption spectra for benzene-d_6 chemisorbed on Pt[6(111)×(111)] are shown as a function of initial coverage. The heating rate in each experiment was 25 °C s^{-1}.

conditions, most of the C_6D_6 was displaced by C_6H_6 although small amounts of HD and D_2 were detected in the characteristic regions of benzene thermal decomposition.

These experiments establish that there is an initial, irreversibly chemisorbed state and that benzene exchange through surface migration does not occur between this state and states formed at higher coverages. Benzene exchange by displacement for molecules adsorbed above the initial, irreversibly chemisorbed benzene state is relatively facile, a feature consistent with the phosphine displacement reactions described below. Because all the benzene molecules adsorbed beyond the point of the irreversible chemisorption state can be displaced, although slowly, by benzene (labeled benzene), the two benzene thermal desorption maxima are not necessarily indicative of two differentiable benzene chemisorption (reversible) states. Nevertheless, experiment ii cited above is suggestive of two differentiable reversible chemisorption states; surface migration of benzene molecules must be very slow between these states.

At benzene coverages below 0.1 monolayer coverage, trimethylphosphine displaced only traces of benzene. Subsequent heating yielded a C_6D_6 desorption maximum at ~150 °C[5a] and then substantial desorption of HD and CH_3D. Above this coverage level, substantial (>90%) quantities of the adsorbed benzene were displaced. Chemisorption of C_6H_6 to ~0.5 monolayer coverage was followed by C_6D_6 chemisorption to ~0.65 (total) monolayer coverage. In a subsequent trimethylphosphine displacement reaction, both C_6H_6 and C_6D_6 were detected. Then, in an ensuing thermal desorption experiment, only C_6H_6 (peak maximum at ~150 °C) and trace amounts of HD and CH_3D were detected. Clearly, these experiments affirm that there is an initially and "strongly chemisorbed state" that is not significantly reversibly desorbed thermally or displaced by trimethylphosphine at 25 °C—and that adsorbed benzene does not undergo exchange between the irreversibly bound state and reversibly bound states by surface migration or by any other process. This strongly chemisorbed (irreversible) benzene state could be either molecular or dissociative in character although no evidence supportive of a dissociative state was derived in our studies.

Benzene on Pt[6(111)×(111)]. Benzene chemisorption on the stepped 6(111)×(111) surface of platinum was complex in character. This surface was more reactive than the (111) surface; irreversible benzene chemisorption was more extensive, and, most significantly, *reversible* C–H bond breaking was evident for the benzene chemisorption state(s) on the stepped platinum surface.

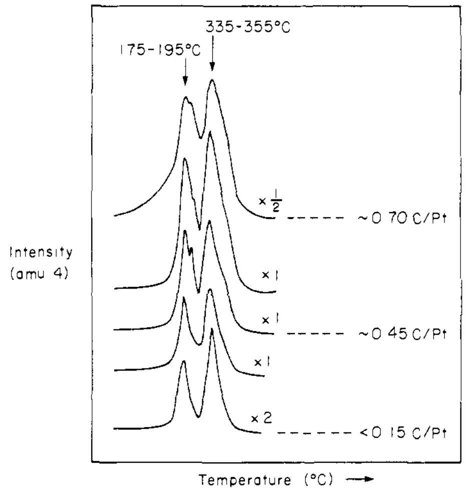

Figure 4. Presented in this figure are the thermal decomposition spectra for benzene-d_6 chemisorbed on Pt[6(111)×(111)] as a function of initial benzene surface coverage. The heating rates in all experiments were 25 °C s^{-1}. These spectra are complementary to the spectra presented in Figure 3, and, for each coverage in the two figures, the spectra are derived from a single desorption experiment.

The thermal desorption and reactivity behavior of chemisorbed benzene on Pt[6(111)×(111)] was highly coverage dependent (Figure 3). At low benzene coverages, decomposition of benzene was the only detectable thermal process: hydrogen desorbed with maxima of ~195 and 355 °C with approximate equal intensities and these maxima shifted 10–20° lower at higher coverages. Reversible benzene desorption was observed only at coverages greater than about 0.15 monolayer (vide infra). At saturation coverages of about 0.7, the thermal desorption experiment left a Pt[6(111)×(111)]–C surface that contained about 0.25 to 0.30 of a monolayer of carbon.

Decomposition was the prevailing thermal process for Pt[6(111)×(111)]–C_6D_6 (Figure 4). Absence of significant dehydrogenation of benzene below 200 °C, within the time scale of the thermal desorption experiments, was indicated by the absence of D_2 or HD desorption in the 50 to 200 °C region observed for Pt[6(111)×(111)]–D. At benzene coverages above 0.15 and up to ~0.45, reversible benzene desorption was observed at 180–210 °C. At benzene coverages above ~0.45, a "new" benzene thermal desorption peak appeared at ~100–120 °C. Benzene saturation coverage at 20 °C and 10^{-9} to 10^{-10} torr was reached at ~0.7.

Thermal desorption experiments for Pt[6(111)×(111)]–C_6H_6–C_6D_6 formed at a total carbon coverage of ~0.5 yielded only C_6H_6 and C_6D_6 molecules at the low-temperature maximum of 100–120 °C and all possible $C_6H_xD_{6-x}$ molecules at the high-temperature maximum of 180–210 °C. Approximately, the molar ratios of the various benzene molecules, $C_6H_xD_{6-x}$, were 14, 11, 11, 13, 14, 16, and 20% for x equal 0 through 6, respectively, derived from an initial 3:4 molar gas-phase mixture of C_6H_6 to C_6D_6. Reversible bond breaking occurred on this surface only at temperatures above 120 °C within the time scale (seconds in the 120–200 °C range) of the thermal desorption experiment. Consistent with these experiments was the observation that $C_6H_xD_{6-x}$ molecules were displaced by trimethylphosphine from Pt[6(111)×(111)]–C_6H_6–C_6D_6 only at temperatures of ~ 140 °C and above.

Trimethylphosphine displaced no benzene from the stepped platinum surface unless the coverage was greater than ~0.15, consistent with the thermal desorption experiments. Above such coverages, the displacement was virtually instantaneous but incomplete. With initial coverages of about 0.5, the displacement of benzene was about 70–80% complete. After trimethylphosphine displacement was effected, thermal desorption yielded a benzene desorption peak at 170–190 °C showing that the more strongly bound benzene had been incompletely displaced (no low-temperature, 100–120 °C benzene desorption maximum was observed in this experiment). For a Pt[6(111)×(111)]–C_6H_6–C_6D_6 surface

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[5] (a) We have observed a greater thermal reversibility in the desorption of hydrocarbons when trimethylphosphine was coadsorbed on the surface. (b) A large kinetic isotope effect may be operative for the C–H bond-breaking processes for toluene chemisorbed on the platinum surfaces, and such an effect would obfuscate the detection of regioselectivity in C–H bond breaking by the thermal desorption studies employed for the two labeled toluene molecules.

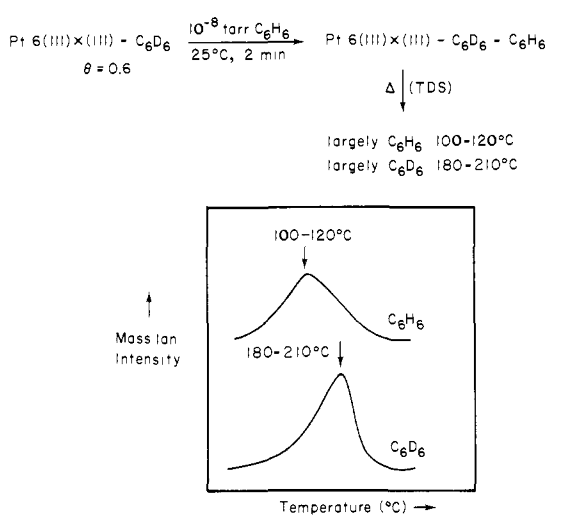
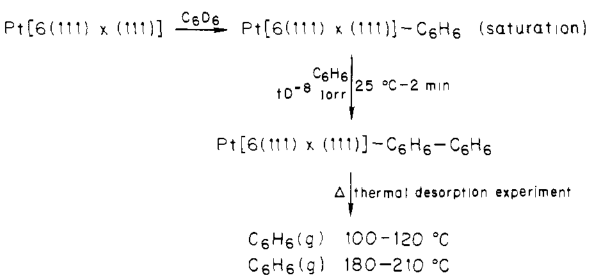


Figure 5. A Pt[6(111)×(111)]–C_6D_6 state with a coverage of 0.6 C/Pt atom ratio was formed at 25 °C. Then this surface was exposed to C_6H_6 at a pressure of 1×10^{-8} torr for 2 min at 25 °C. After evacuation a thermal desorption experiment was performed (heating rate of 25 °C s^{-1}). Shown are the thermal desorption spectra for C_6D_6 and C_6H_6. No mixed benzenes, $C_6H_xD_{6-x}$, were formed under these conditions.

Scheme I



formed at 20 °C, only C_6D_6 and C_6H_6 molecules were displaced by trimethylphosphine. Displacement of mixed $C_6H_xD_{6-x}$ molecules only occurred when the crystal was heated to ~140 °C *before* displacement was effected. Thus H–D exchange required temperatures of 140 °C with *a background pressure of* $\sim 10^{-10}$ *torr*. Consistent with these results, no HD molecules were formed below ~130 °C from Pt[6(111)×(111)]–D–C_6H_6.

Incisive evidence for differentiable chemisorption states on this stepped surface was obtained from sequential chemisorption of C_6D_6 and then C_6H_6 followed by thermal desorption. The key experiment was as follows: C_6D_6 was first adsorbed on the stepped surface to a carbon coverage of ~0.45 to 0.50 (C/Pt), and then C_6H_6 was adsorbed to a final total carbon coverage of 0.6 to 0.7. In the thermal desorption experiment, C_6D_6 desorbed largely in the high-temperature region (T_{max} = 180–210 °C) and C_6H_6 in the low region (T_{max} = 100–120 °C). Clearly, the chemisorbed benzene molecules do not migrate significantly between states on this surface under these conditions; otherwise, exchange between the differentiable chemisorption states would have been observed. This conclusion concerning lack of benzene exchange between states is also supported incisively by a sequential double label experiment in which the strongly chemisorbed state (C_6D_6) characterized by a thermal desorption maximum at 180–210 °C could not be displaced or exchanged by a high flux of C_6H_6 whereas the weakly chemisorbed state was displaced. This experiment is schematically outlined in Scheme I (see Figure 5).

Consistently, the benzene desorbed at 180–210 °C did not contain any significant amounts of $C_6H_xD_{6-x}$ molecules; if both C_6H_6 and C_6D_6 had been present in the more strongly chemisorbed state, then $C_6H_xD_{6-x}$ molecules would have been produced in the thermal desorption experiment as discussed above. Thus, on the stepped platinum surface, there are three differentiable chemisorption states: (a) a state characterized by irreversible chemisorption, (b) a strongly but reversibly chemisorbed state characterized by a benzene desorption maximum at 180–210 °C, and (c) a moderately and reversibly chemisorbed state characterized by a benzene desorption maximum at 100–120 °C.

Table I. Decomposition of Toluene on Pt(111) and Pt[6(111)×(111)]: Hydrogen Desorption Spectra

surface	molecule	temp (°C) of hydrogen desorption maxima (intensity[a])
Pt(111)	$CD_3C_6D_5$	D_2: 70 (0.2), 215 (0.7), 250 (0.4), 380 (1.0)
	$CD_3C_6H_5$	D_2: 70 (0.3), 200 (1.0), 420 (0.8) HD: 70 (0.25), 210 (1.0), 380 (1.0) H_2: 225 (1.0), 360 (1.0)
	$CH_3C_6D_5$	D_2: 230 (0.7), 380 (1.0) HD: 150 (1.5), 380 (1.0) H_2: 70 (0.2), 185 (1.0), 380 (trace)
Pt[6(111)×(111)]	$CD_3C_6D_5$	D_2: 100 (trace), 180 (1.0), 240 (1.0), 380 (2.0)
	$CD_3C_6H_5$	D_2: 170 (1.0), 415 (0.7), 90 (0.3) HD: 192 (3), 400 (2), 90 (trace) H_2: 210 (1), 345 (1)
	$CH_3C_6D_5$	D_2: 235 (1.0), 385 (1.5) HD: 200 (1.5), 340 (1.0) H_2: 165 (1.0), 340 (trace), 100 (trace)

[a] Relative intensities can be compared only at the given temperature.

Another experiment using the displacement reaction also established that there is more than one benzene chemisorption state on the stepped surface. At 20 °C, C_6H_6 was adsorbed to a coverage of ~0.5, and then C_6D_6 was adsorbed to near saturation coverage. Trimethylphosphine displaced both C_6H_6 and C_6D_6 at 20 °C. The surface was then heated: C_6H_6 desorbed at 170–184 °C but no C_6D_6 desorption was detected; large amounts of CH_4 and H_2, with only traces of CH_3D and HD, were also formed from trimethylphosphine and benzene thermal decomposition. Clearly, the initial strongly bound C_6H_6 species did not exchange with the less strongly bound C_6D_6 species.

Toluene Chemisorption on Pt(111). Toluene chemisorption behavior on the platinum surfaces was much more complex than on nickel. Chemisorption was largely irreversible and no toluene could be displaced by trimethylphosphine.

Pt(111)–C_7H_8, formed at 20 °C and high coverages of ~0.8, yielded in the thermal desorption experiment a small intensity toluene desorption peak spread over 70 to 110 °C with an apparent but poorly resolved double maximum. The fraction of toluene desorbed was less than 10%. At lower coverage, e.g., 0.2–0.3, no toluene was detected in the thermal desorption experiment. Decomposition of initially chemisorbed toluene-d_8 was evident in the thermal desorption experiment by the D_2 desorption maxima at 70 (very small), 215, 230, and 380 °C with the intermediate overlapping desorption peaks having a combined intensity comparable to that of the 380 °C peak. For comparison, the H_2, D_2, and HD desorption maxima for the specifically labeled toluene molecules, $CD_3C_6H_5$ and $CH_3C_6D_5$, are listed in Table I with a comparison of the analogous data for $CD_3C_6D_5$. There was no unequivocal evidence that aliphatic C–H bond breaking occurred more readily than aromatic C–H bond breaking in the toluene species chemisorbed on this platinum surface whereas these two processes were clearly differentiated for the Ni(111), Ni(100), Ni[9(111)×(111)], and Ni[7(111)×(310)] surfaces. Nevertheless, there probably was some regioselectivity[5b] in the C–H bond breaking on this surface with aliphatic C–H bond breaking being more facile than that of aromatic C–H. For $CD_3C_6H_5$, all the H_2 produced appeared at high temperatures and none at low temperature, 70 °C, where D_2 and HD were observed. Analogously, only H_2 appeared at low temperature, 70 °C, in the decomposition of $CH_3C_6D_5$.

For the Pt(111)–$C_6H_5CH_3$–$C_6D_5CD_3$ chemisorption state, thermal desorption yielded only $C_6H_5CH_3$ and $C_6D_5CD_3$ molecules; there was no evidence of H–D exchange between the toluene molecules that reversibly desorbed. These results are analogous to those for benzene chemisorption on this close-packed surface of platinum.

Mesitylene and *m*-xylene also reversibly chemisorbed on Pt(111), but as in the case of toluene, the thermal reversibility was substantially less than 50%. Mesitylene thermal desorption was characterized by a broad peak that began at ~60 °C and tailed off at ~220 °C. The xylene desorption peak was also broad and exhibited maxima at ~70 and 125 °C.

Toluene Chemisorption on Pt[6(111)×(111)]. On this stepped surface, toluene chemisorption was thermally irreversible at initial low to near saturation coverages at 10^{-9} to 10^{-10} torr. Trimethylphosphine did not displace toluene from this surface.

In the thermal desorption (decomposition) experiments for Pt[6(111)×(111)]–$CD_3C_6D_5$, the only gaseous species desorbed was deuterium with maxima at 100 (small), 180, 240, and 380 °C. The complexity of this thermal decomposition precludes any simple interpretation (as for the Pt(111)–toluene decomposition). The only permissible conclusion is the obvious one: there are at least four differentiable (rates) C–H bond-breaking processes. In Table I are listed the thermal decomposition data for $CD_3C_6D_5$, $CD_3C_6H_5$, and $CH_3C_6D_5$ on the stepped platinum surface. The data for the specifically labeled deuterium substituted toluene molecules *suggest* that the rate of aliphatic C–H bond breaking was higher than for aromatic C–H bond breaking, but these two bond-breaking steps were not grossly different in a rate context.[5b]

Discussion

Although there are formal similarities between nickel and platinum in their benzene and toluene surface chemistry, there are substantial and important differences. The most significant difference was in the *reversible* C–H bond-breaking process whereby mixed $C_6H_xD_{6-x}$ molecules formed from coadsorbed C_6H_6 and C_6D_6 molecules. No such process was observed[1] for any of the nickel surfaces[4] investigated whereas this process was relatively fast on Pt[6(111)×(111)] at temperatures of ~140 °C. Such a difference is to be expected between these two metals. A C–H bond-breaking process such as:

$$M_{surface}–C_6H_6 \rightarrow M_{surface}–H–C_6H_x$$

should be more favorable thermodynamically for nickel than for platinum (for example, on metallic films, the Ni–H chemisorption bond energy is larger than that for platinum, 63 ± 2 kcal/mol[6] vs. 57 ± 2 kcal/mol[7]). Consequently, the reverse reaction of the C–H bond formation

$$M_{surface}–H–C_6H_x \rightarrow M_{surface}–C_6H_6$$

which is an intrinsically unfavorable process *under the ultra-high-vacuum conditions* wherein the surface hydrogen atom activity is very low, should be more favorable for platinum than for nickel.

Basically, benzene chemisorption on Pt(111) is molecular (nondissociative) like that for Ni(111) where benzene can be quantitatively displaced by trimethylphosphine and where C–H bond breaking is measurably fast (minutes) only at temperatures of 100–115 °C. Nevertheless, there is a very small fraction of the benzene molecules chemisorbed on Pt(111) that can neither be thermally desorbed nor displaced by trimethylphosphine. The labeling experiment in which C_6D_6 was first adsorbed to <0.1 of a monolayer, and then C_6H_6 was adsorbed to ~0.5 of a monolayer, established that no C_6D_6 could be thermally desorbed or chemically displaced—all the C_6D_6 species thermally decomposed to give D_2 (and HD). Hence there are at least two[8] different chemisorption states for benzene on Pt(111), as on the stepped surface, up to a saturation coverage at 10^{-10} to 10^{-11} torr. Also, there is no exchange between states via surface migration of adsorbate species, at least within the time scale of minutes. Based on sequential adsorption of C_6D_6 and C_6H_6 experiments, there appears to be two differentiable, reversibly bound benzene states on Pt(111); interchange (by either surface migration or displacement or both) of labeled benzene between states was relatively slow.

We particularly note that this technique of separately adsorbing different isotopically labeled molecules and then monitoring the individual molecules for reversible desorption and/or decomposition in either a thermal desorption or chemical displacement experiment should be generally applicable to surface studies for potential identification of differentiable adsorption states of molecules and for monitoring surface migration of adsorbates between differentiable states.[9]

The major reversibly chemisorbed benzene state on Pt(111) should be bound to the surface metal atoms through interactions of the initial π and π^* benzene orbitals with appropriate orbitals of surface metal atoms with the C_6 ring plane parallel to the surface plane as proposed for Ni(111)–C_6H_6 and Ni(100)–C_6H_6.[1] In fact, Lehwald, Ibach, and Demuth[10] have proposed this representation for Pt(111)–C_6H_6 based on high-resolution electron energy loss data.[11,12] They proposed that there are two "phases" of benzene chemisorbed (less than monolayer coverage) on this surface and that one is represented by the benzene C_6 centroid centered over a single platinum atom and the second one by the benzene C_6 centroid centered over a threefold hollow site. Our data provide no information about the translational orientation of the chemisorbed benzene. Low-energy electron diffraction data[10,13,14] are not inconsistent with the Lehwald, Ibach, and Demuth conclusions for Pt(111)–C_6H_6 at submonolayer coverages (at high benzene coverages, Somorjai and co-workers[15] concluded from low-energy electron diffraction data that the C_6 rings were tilted with respect to the surface plane).

The benzene state on Pt(111) characterized by thermal and chemical displacement irreversibility cannot be structurally defined from our data. It could be a dissociative state (nonmolecular), but there was no evidence of a D_2 desorption peak in the region characteristic of Pt(111)–D in the thermal desorption experiment for Pt(111)–C_6D_6 (<0.1 monolayer coverage). This benzene state may be representative of benzene chemisorbed at imperfection sites.[16] The common imperfections are steps, and, in fact, a more significant fraction of benzene chemisorbed on the stepped Pt[6(111)×(111)] surface was irreversibly chemisorbed as judged by thermal desorption and trimethylphosphine displacement experiments. As established by the sequential C_6D_6 and C_6H_6 chemisorption experiments, there are at least two states for benzene on this stepped surface: one is largely irreversibly bound, and there is not facile interchange (adsorbate) between these states by surface migration.

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(7) Christmann, K.; Ertl, G.; Pignet, T. *Surf. Sci.* **1976**, *54*, 365.

(8) The appearance of another (third) low-temperature benzene desorption maximum at high benzene coverages does not necessarily implicate another differentiable chemisorption state because cooperative effects due to intermolecular interactions of benzene chemisorbed molecules (which could be structurally and stereochemically nondifferentiable) could be the genesis of this third detectable desorption peak. We consider distinguishable chemisorption states to differ substantially in a short range order context and to possess different structural or stereochemical features.

(9) For example, preadsorption of $^{12}C^{16}O$ to a particular coverage followed by adsorption of $^{13}C^{18}O$ on a metal surface, established by vibrational spectroscopy to exhibit two substantially different CO stretching frequencies, could be monitored by thermal desorption spectrometry, chemical displacement reactions, or vibrational spectroscopy for exchange of the labeled CO molecules between sites. This study could be carried out in a series of experiments to follow exchange as a function of time and temperature.

(10) Lehwald, S.; Ibach, H.; Demuth, J. E. *Surf. Sci.* **1978**, *78*, 577.

(11) Similar conclusions were presented by Netzer and Matthew from an electron energy loss study of Pt(111)–C_6H_6: Netzer, F. P.; Matthew, J. A. D. *Solid State Commun.* **1979**, *29*, 209.

(12) Palazov (*J. Catal.* **1975**, *30*, 13) proposed π-bonding of benzene to platinum on alumina-supported platinum based on an infrared study.

(13) Bertolini, J. C.; Rousseau, J. *Surf. Sci.* **1979**, *89*, 467.

(14) A low-energy electron diffraction study of Ni(111)–C_6H_6 has been interpreted in terms of a C_6 ring parallel to the surface plane with the C_6 centroid centered over a single metal atom, as have high-resolution electron energy loss data by Lehwald, Ibach, and Demuth[10], although a two-"phase" situation for nickel was also proposed, as for platinum, based on the vibrational[10] data.

(15) Firment, L. E.; Somorjai, G. A. *Surf. Sci.* **1979**, *84*, 275, and references therein.

(16) As we had noted earlier, platinum is a relatively soft metal, and it is difficult to generate a specific surface plane without a detectable (chemically or spectroscopically) fraction of imperfections; see discussion by Friend et al.[2]

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 ~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 ~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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