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Coordination Chemistry of Metal Surfaces. 3.[1] Benzene and Toluene Interactions with Nickel Surfaces

C. M. Friend and E. L. Muetterties*

Contribution from the Department of Chemistry and Division of Materials and Molecular Research, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720.

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Abstract: The coordination chemistry of benzene and toluene on a nickel surface is defined in terms of surface crystallography and surface composition. Nickel surfaces studied included the low Miller index planes (111), (110), and (100) and the stepped and stepped-kinked surfaces 9(111) × (111) and 7(111) × (310), respectively. The individual effects of the surface contaminants, carbon and oxygen, were established for low surface coverages (0.1–0.5 of a monolayer). Benzene chemisorption was fully associative (molecular) on Ni(111) up to ~100 °C; no H–D exchange occurred between C_6H_6 and C_6D_6 up to these temperatures. Up to ~100 °C, benzene was quantitatively displaced as $C_6H_6(g)$ by $P(CH_3)_3$. Benzene thermal desorption occurred at ~115–125 °C; this reversible desorption was accompanied by extensive irreversible decomposition to $H_2(g)$ + Ni(111)–C. An analogous behavior was observed for benzene chemisorbed on the stepped and stepped-kinked surface; the only variance was in the degree of molecular chemisorption wherein the degree was reduced from ~100% on the (111) by several percent for the stepped or stepped-kinked surfaces. On the (110) surface, the degree of benzene thermal desorption and the degree of benzene chemical displacement by $P(CH_3)_3$ was comparable to the stepped-kinked surface. The chemisorption of benzene on Ni(100) was differentiated qualitatively and quantitatively from the other surfaces: the degree of thermal reversibility was higher than and the temperature for the thermal desorption maximum was ~100 °C higher than that for Ni(111). Like all other surfaces, labeling studies with $D_2 + C_6H_6$ and with $C_6H_6 + C_6D_6$ on Ni(100) showed that H–D exchange did not occur. The nickel surface chemistry for toluene was sharply different from that for benzene. Toluene chemisorption on all the nickel surfaces was thermally irreversible, and toluene was not displaced from these surfaces by strong field ligands like $P(CH_3)_3$ and CH_3NC. Heating the Ni–toluene surfaces led to hydrogen evolution at temperatures characteristic of the surfaces. For the decomposition of $C_6D_5CD_3$ on Ni(111) there were two D_2 thermal desorption maxima, ~130 and 190 °C. For the analogous decomposition of $C_6H_5CD_3$ and $C_6D_5CH_3$ respectively, there were *single* D_2 desorption curves with maxima at ~130 and ~185 °C, respectively. Thus, aliphatic C–H bonds are broken first and no aromatic C–H bond is broken until temperatures near 160 °C are attained. An essentially identical behavior was observed for the stepped and stepped-kinked surfaces, and an analogous behavior was observed for the (100) surface with the aliphatic and aromatic C–H hydrogen (or deuterium) atoms appearing as H_2 (or D_2) at ~110 and 230 °C, respectively. In contrast, there was no detectable difference in rates of aliphatic and aromatic C–H bond breaking for Ni(110)–C_7H_8; only one H_2 desorption maximum was evident at 150 °C. Structural and stereochemical features of benzene and toluene chemisorption of these nickel surfaces are discussed. The presence of carbon did not qualitatively alter the benzene or toluene chemistry on these surfaces but oxide oxygen so greatly reduced the sticking coefficient of these two molecules that a study at the 10^{-10}–10^{-11} torr pressures of conventional ultrahigh vacuum experiments was not feasible.

Introduction

Scientifically and technologically important are the reactions of unsaturated hydrocarbons at a metal surface. We seek a better molecular understanding of basic chemisorption processes and mechanistic insight into the catalytic reactions of these molecules. To this end, we have initiated an ultrahigh vacuum investigation of the interactions of these molecules at metal surfaces as a function of surface crystallography and surface composition. Described here is a study of the nickel surface chemistry of benzene and toluene, two obviously closely related species whose surface chemisry we show to be qualitatively different.

Experimental Section

Experiments were performed in a bakeable, ultrahigh vacuum chamber (Varian) with a base pressure of 10^{-10}–10^{-11} torr. A 99.999% purity single-crystal nickel rod (Materials for Research Corp.), 0.375 in. in diameter, was oriented to within 0.5° of the desired crystallographic plane by using Laue X-ray back-reflection. With use of spark erosion, a wafer was cut such that the exposed surface was circular with approximately a 0.25-in. diameter and a circular ridge $^5/_{16}$ in. in outside diameter. The crystal was mechanically polished; the final step being with 0.05-μm alumina. Prior to being placed in the chamber, the crystal was chemically polished (etched) with a 3:1:1:5 mixture of the concentrated acids HNO_3, H_2SO_4, H_3PO_4, and CH_3COOH[2] and subsequently rinsed with distilled water and then ethanol.

The crystal was mechanically mounted by means of a tantalum cup that fit over the $^5/_{16}$-in. ridge. A "button" heater (Spectra Mat Inc.), consisting of a tungsten filament imbedded in ceramic, was mechanically held in place by the tantalum cup and used to indirectly heat the sample. Typical heating rates were 25 °C s^{-1} and were linear between 50 and 400 °C. A liquid-nitrogen cooled, oxygen-free copper block was used to cool the crystal from 400 to 25 °C in approximately 5–10 min via mechanical contact with the mount. Chromel–alumel thermocouple wires, spot welded to the $^5/_{16}$-in. ridge of the crystal, were used for temperature measurement.

The nickel crystal was cleaned under vacuum by a combination of ion-sputtering and chemical techniques. Sulfur and phosphorus were removed by bombardment with 500-eV Ar^+ ions. Carbon and nitrogen were removed by treatment with 0.5–1.0 × 10^{-7} torr of O_2 for 1–2 min at a crystal temperature of 350 °C. This was followed by treatment with 1 × 10^{-7} torr of H_2 for 5–10 min at 400 °C. This sequence of surface treatment was repeated until the surface was clean. Surface cleanliness and composition were monitored by using four-grid, retarding-field Auger electron spectroscopy. Low-energy electron diffraction was used to verify the crystallographic orientation of the surface and to identify ordered overlayer structures.

Gas composition in the vacuum system was monitored with a quadrupole mass spectrometer (Uthe Technology International, Model 100C) in conjunction with a programmer which externally drove the mass spectrometer and stored the output. This allowed for scanning and storage of the ion current for several different mass units in rapid succession (15 ms). With use of this configuration, the relative amounts of different isotopic species were compared upon exposure of the crystal and in thermal desorption or chemical displacement reactions. Thermal desorption was performed with the front face of the crystal normal to the line of sight of the mass spectrometer ionizer and isolated from the cooling block (experiments with and without the cooling block established that the block did not detectably contribute to the background desorption). The distance from the front face of the crystal to the ionizer was approximately 1 in. This configuration yielded the maximum signal. All thermal desorption (and chemical displacement) experiments were performed without prior exposure to an electron beam.

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(1) C. Friend, J. Stein, and E. L. Muetterties, *J. Am. Chem. Soc.*, preceding paper in this issue.

(2) C. J. Smithells, "Metals Reference Book", Vol. I, 3rd ed., Butterworths, Washington, D.C., 1962, p 226.

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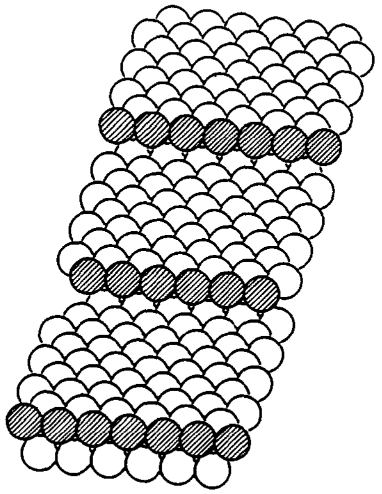

Figure 1. Shown above is the Ni[9(111) × (111)] surface, which may be alternatively indexed as Ni(997). In this illustration, the cross-hatched circles represent nickel atoms at step sites and the open circles represent nickel atoms in (111) terrace sites. The step and terrace atoms have coordination numbers of 7 and 9, respectively.

The chemicals used in this study were reagent grade benzene and toluene which were stored over calcium hydride; the C_6D_6 and $C_6D_5CD_3$ reagents (99+% d), obtained from Aldrich Chemical Co., were handled similarly; $C_6D_5CH_3$ and $C_6H_5CD_3$ reagents, obtained from Merck and Co., were used without treatment (the presence of traces of moisture did not detectably affect the surface chemistry). Trimethylphosphine was prepared by a modification[3] (di-*n*-butyl ether as the solvent) of a procedure cited in ref 4.

Gas exposures were performed with a variable leak valve equipped with a dosing "needle" such that the gases could be introduced in close proximity to the surface, thus minimizing background contamination. Two separate valve-needle assemblies mounted symmetrically with respect to the mass spectrometer were used to introduce the different gases in displacement reactions. This avoided contamination of the displacing gas in the leak valve. During displacement reactions, the crystal face was directed 45° away from the line of sight of the mass spectrometer ionizer (so as to face the second valve assembly). This configuration decreased the mass spectrometer signal of gases evolved from the crystal during a displacement reaction as compared to a thermal desorption. The time interval between the two gas exposures in a displacement reaction was between 1 and 5 min. Exposures of the benzene species were all in the range of $0.3-6.0 \times 10^{-6}$ torr s. Toluene exposures were in the range of $0.2-6.0 \times 10^{-6}$ torr s. Trimethylphosphine and methyl isocyanide exposures were approximately 0.3 and 0.5 torr s, respectively. Oxide formation was effected by a prolonged exposure (5–10 min) of the crystal to 5×10^{-8} torr of O_2 with a crystal temperature of 350 °C. The Ni(111) oxide was ordered with a $c(2 \times 2)$ low-energy electron diffraction pattern. Carbon-contaminated surfaces were prepared by thermally decomposing benzene on the nickel surface. The carbon overlayer was ordered, but the diffraction pattern was complex. It did not correspond to a graphite ring structure. Approximate carbon coverages were estimated by using Auger calibration curves based on thermally decomposed benzene.[5,6]

Blank experiments were performed in order to verify that the chemistry observed was associated with the front exposed nickel surface. A wafer of single-crystal nickel was cut as described above. The wafer was soft-soldered onto a copper disk (0.06 in. thick, 0.75 in. diameter), with a copper wire attached for handling. A rubber mask was applied to the front edges of the nickel crystal such that only the 0.25-in. diameter surface was exposed. The masking procedure was repeated three times at 8-h intervals. The sample was prepared for plating in a series of steps, with rinsing between each step. Trichloroethylene was used as a degreaser, followed by cleaning with a caustic cleaner and then hydrochloric acid. Next, the surface was activated by a nickel chloride–hydrochloric acid strike (electrodeposition of a very thin layer of nickel), followed by a copper strike. The exposed nickel face was then gold plated by using a commercial (low cyanide concentration) process (Technic Hg Gold Process). The final thickness of the gold layer was 2×10^{-4} in. Following the plating, the rubber mask was peeled away and the crystal removed from the copper disk. Excess solder on the back of the nickel crystal was mechanically removed with silicon carbide paper. The sample was then chemically polished (etched) as for all nickel samples[2] (see above). This was followed by rinsing with water and ethanol. The gold surface appeared homogeneous with no visible sign of nickel. No nickel was detected when the crystal was examined in the vacuum chamber by Auger electron spectroscopy. The gold-plate blank crystal was cleaned in the vacuum chamber by the O_2 and H_2 treatment described above for the cleaning of the nickel surface. For the experiments described in this paper, the gold-plated crystal blank experiments definitively established that the edges and the back of the nickel crystal, the crystal holder, and

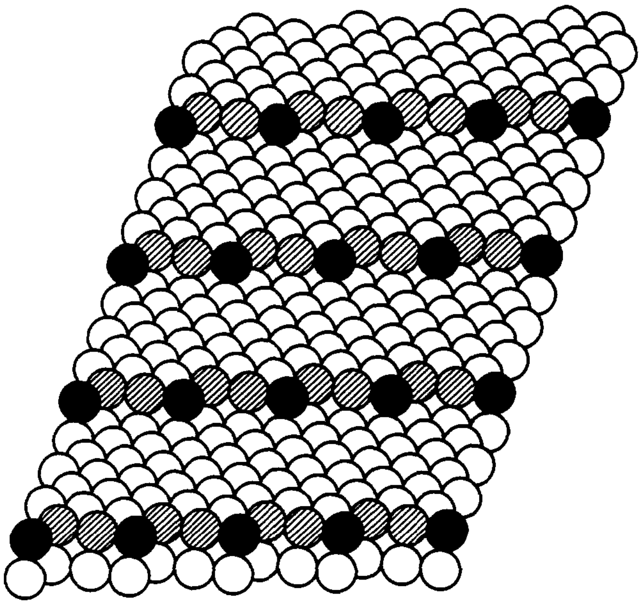

Figure 2. Illustrated in the figure is the stepped-kinked Ni[7(111) × (310)] surface which may be alternatively indexed as Ni(10,8,7). In this representation, the shaded circles are nickel atoms in kink sites, which have a coordination number of 6, and the cross-hatched circles are nickel atoms in step sites, which have a coordination number of 7.

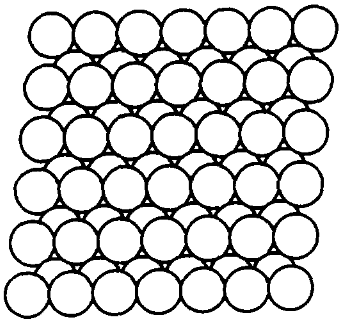

Figure 3. Shown in the figure is the Ni(110) surface, which may be alternatively indexed as the super-stepped Ni[2(111) × (111)]. The nickel atoms in the top layer and troughs have coordination numbers of 7 and 11, respectively.

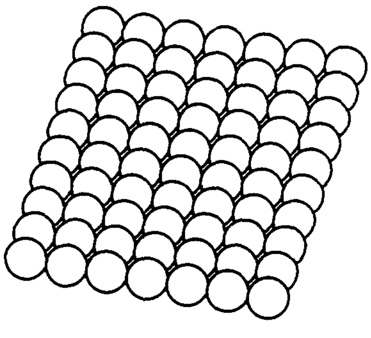

Figure 4. The low Miller index Ni(100), depicted in the figure, has a surface atom coordination number of 8.

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(3) R. R. Schrock, personal communication.

(4) *Inorg. Synth.*, **9**, 59 (1967).

(5) J. P. Biberian and G. A. Somorjai, *Appl. Surf. Sci.* **2**, 352 (1979).

(6) (a) These estimates are based on Auger data and comparison with standardized Ni–C Auger data. (b) The monolayer values are based on the number of carbon atoms per surface nickel atom.

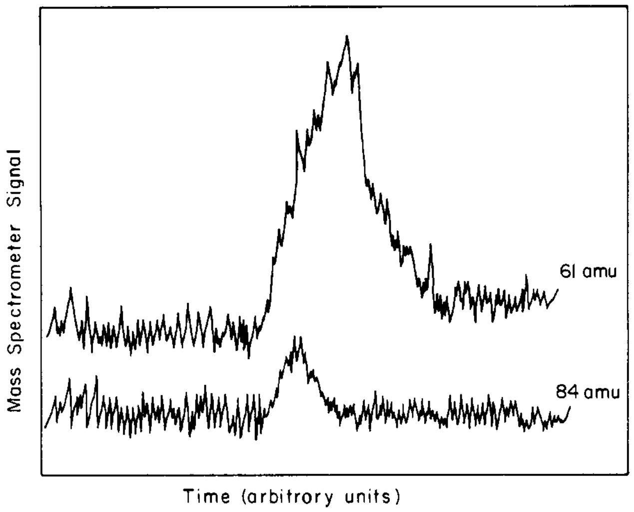


Figure 5. The mass spectrometer profile during a chemical displacement reaction of C_6D_6 by $P(CH_3)_3$ on Ni(111) at 25 °C is shown in the figure. A sharp desorption of C_6D_6 (84 amu) shown in the lower trace is detected upon exposure of the nickel crystal to the displacing gas, $P(CH_3)_3$ (61 amu), shown in the upper trace. The total time elapsed in the figure is approximately 20 s and the initial exposures of C_6D_6 and $P(CH_3)_3$ were 0.6 and 0.04×10^{-6} torr s, respectively.

all other exposed surfaces in the UHV chamber did *not* contribute detectably to any thermal desorption or chemical displacement reaction *as monitored by mass spectrometry*. Thus, the results cited below pertain, in fact, only to the front, crystallographically defined crystal face.

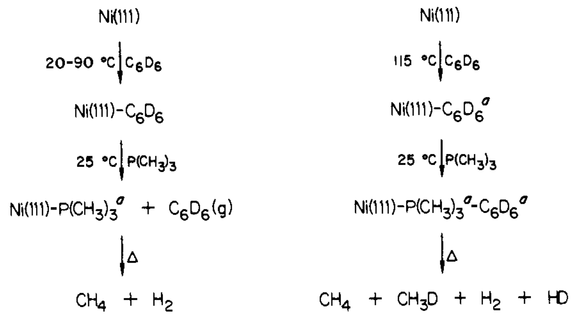
Results and Discussion

We discuss in detail first the coordination chemistry for benzene on the flat close-packed Ni(111) surface and then compare this chemistry with the other surfaces (Figures 1–4). A structural and stereochemical discussion of the benzene chemisorption states on all surfaces is deferred to a later section.

Benzene chemisorption on Ni(111) at ~0.1–0.3 monolayer coverages was only partially reversible in a thermal context. Heating of the Ni(111)-C_6H_6 crystal gave a benzene thermal desorption maximum at 115–125 °C which was followed by a single hydrogen desorption curve that peaked at ~180 °C. Experiments with C_6D_6 revealed no significant isotope effects on the desorption and the decomposition processes. Similar experiments with Ni(111)-C_6D_6-C_6H_6 yielded only C_6H_6 and C_6D_6 molecules in the desorption process and all three possible decomposition products H_2, HD, and D_2. Thus, there was no reversible H–D exchange between the chemisorbed benzene molecules within the temperature range of 20–120 °C.[7]

The thermal desorption experiments alone do not define the temperature at which C–H bond breaking occurs for the fraction of benzene molecules that decompose on the surface under the conditions of attempted thermal desorption. However, this temperature has been defined from our chemical displacement reactions with CH_3NC and $(CH_3)_3P$. Since the latter displacing agent provided the most complete characterization, the critical thermal behavior of Ni(111)-$P(CH_3)_3$ is described here and the displacement reactions in the following paragraph. The phosphine interacted strongly with the nickel surface; the sticking coefficient was probably 1 or close to 1. On heating, Ni(111)-$P(CH_3)_3$ decomposed to form gaseous methane and hydrogen with thermal desorption maxima at 90 and 98 °C, respectively. Preexposure of the crystal to deuterium followed by trimethylphosphine chemisorption and then thermal decomposition led to the deuterium-containing products CH_3D and HD (also CH_4 and H_2) at 90 and 98 °C, respectively. We have no data that reveal the molecular features of the phosphine chemisorption state.[8]

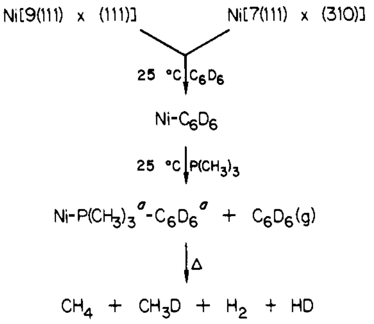
Scheme I



(no deuterium-containing products)

[a] Character of chemisorption state is not defined.

Scheme II



[a] Character of chemisorption state is not defined.

Exposure of a Ni(111)-C_6D_6 surface at 20 °C to gaseous $P(CH_3)_3$ led to immediate displacement of C_6D_6 (Figure 5). Displacement was quantitative as judged through a subsequent thermolysis experiment in which only CH_4 and H_2, the characteristic gaseous decomposition products from Ni(111)-$P(CH_3)_3$, were observed. No deuterium-containing species were detected. Here, the displacement reaction unequivocably established benzene chemisorption on Ni(111) to be fully molecular (associative[9]). Chemisorption and displacement processes occurred without reversible C–H bond breaking as was shown by the reaction sequence (1), where no cross-labeled benzene molecules were formed. By

$$\mathrm{Ni(111)} \xrightarrow[C_6D_6]{C_6H_6} \mathrm{Ni(111)}\text{-}C_6H_6\text{-}C_6D_6 \xrightarrow{P(CH_3)_3} C_6H_6(g) + C_6D_6(g) \quad (1)$$

a fully analogous set of reactions, the chemisorption of benzene on Ni(111) at temperatures up to ~90 °C was shown to be identical with that at 20 °C.[10] However, chemisorption of benzene on Ni(111) at 115 °C produced a state that on subsequent exposure to trimethylphosphine at 25 °C yielded no gaseous benzene (see Scheme I that illustrates the 20 and 115 °C surface experiments). Thus, irreversible C–H bond breaking is measurably fast on the Ni(111) surface for benzene only at temperatures above 100 °C. Clearly then, the partial thermal irreversibility of benzene chemisorption was due to an irreversible C–H bond-breaking process that was competitive with the thermal desorption process.

Methyl isocyanide[1] also was active as a displacement agent for benzene on these surfaces, but for some reason this isocyanide did not quantitatively displace the benzene from these surfaces.[11]

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(7) The time scale for the ~20 °C characterization of no exchange was ca. 3 min. Within the context of the desorption experiment in which the heating rates were about 25 °C/s, the time scale for the 120 °C characterization is ~40 ms.

(8) We write this state as Ni(111)-$P(CH_3)_3$ but do not know whether the phosphine partially or wholly fragments on chemisorption or chemisorbs without C–H or P–C bond cleavage reactions although present data indicate that fragmentation occurs at 20 °C.

(9) The terms associative and dissociative, respectively, are used in surface science to denote chemisorption processes that occur without and with bond breaking in the adsorbate molecule.

(10) The protocol consisted of benzene (or C_6H_6 + C_6D_6) chemisorption on the surface at some specific temperature, cooling the crystal to 25 °C, exposing the crystal to a flux of trimethylphosphine at 25 °C, and then heating the crystal.

Displacement behavior with this molecule was otherwise identical with that of trimethylphosphine—including the displacement behavior as a function of the temperature of the benzene chemisorption.

Understandably, the stepped Ni[9(111) × (111)] and stepped-kinked Ni[7(111) × (310)] surfaces displayed a benzene coordination chemistry that was quantitatively and qualitatively identical with that of the Ni(111) surface—with but one key exception that ostensibly reflected the geometric perturbations of the step and kink zones of these planes (see stereochemical discussion in a later section). The behavioral difference centered on the quantitative features of benzene displacement by trimethylphosphine. Not all the benzene was displaced by the phosphine indicating that a small percentage (~10%) of the benzene on these surfaces either was present in different environments or was dissociatively[9] chemisorbed (vide infra). The crucial features of these displacements on stepped and stepped-kinked surfaces are shown in Scheme II and should be contrasted to Ni(111) shown in Scheme I.

Benzene chemisorption behavior on Ni(110) was similar to that on Ni(111) except that the thermal desorption maximum was lower, ~100 °C, and the desorption curve was much broader. Those benzene molecules that desorbed did not undergo H–D exchange.[12] Trimethylphosphine did not quantitatively displace benzene from the Ni(110)–C_6D_6, and thermolysis then led to methane formation at 100 °C wherein both CH_4 and CH_3D were present.[13a]

On the more open Ni(100) surface, benzene surface chemistry was quantitatively different than on the flat but close-packed (111) surface. Thermal desorption of C_6D_6 from Ni(100) was partial but more complete (factor of ~2) than for the (111) surface, and the desorption temperature maximum was about 100 °C higher than for Ni(111). The desorption temperature maximum was 200–220 °C, and this maximum was coincident with that for D_2 that was formed from the competing process of benzene thermal decomposition. No H–D exchange occurred between C_6D_6 and C_6H_6 molecules up to the thermal desorption temperatures of ~220 °C; only C_6D_6 and C_6H_6 were thermally desorbed from Ni(100)–C_6D_6–C_6H_6. Trimethylphosphine displaced C_6D_6 from the (100) surface and there was no evidence of deuterium incorporation in the trimethylphosphine decomposition products[13b] of CH_4 and H_2. Control experiments of the temperature of C_6H_6 chemisorption, as done for the (111) surface, established that C–H bond breaking on this (100) surface occurs at a measurable rate only at temperatures above 150 °C. Up to 150 °C, benzene chemisorption on Ni(100) is fully associative (molecular) as shown by subsequent quantitative displacement of benzene by phosphine.

Carbon impurities on these nickel surfaces did not qualitatively alter the surface chemistry. The only discernible effect was a reduction in sticking coefficient with the consequence that surface coverage at a given pressure was reduced. Oxygen as oxide so sharply reduced the benzene- and toluene-sticking coefficient that a study of these partially oxidized surfaces at the pressures of the ultrahigh vacuum studies was not practicable; there was no detectable chemisorption of either benzene or toluene at 25 °C and 10^{-8}–10^{-10} torr.

Toluene Chemisorption. Toluene irreversibly chemisorbed on all the nickel surfaces. Thermolysis yielded only hydrogen as a gaseous species. The presence of carbon impurities (0.1–0.3 of a monolayer) did not qualitatively alter this chemistry. Neither trimethylphosphine nor methyl isocyanide displaced toluene from these surfaces at 25 °C.

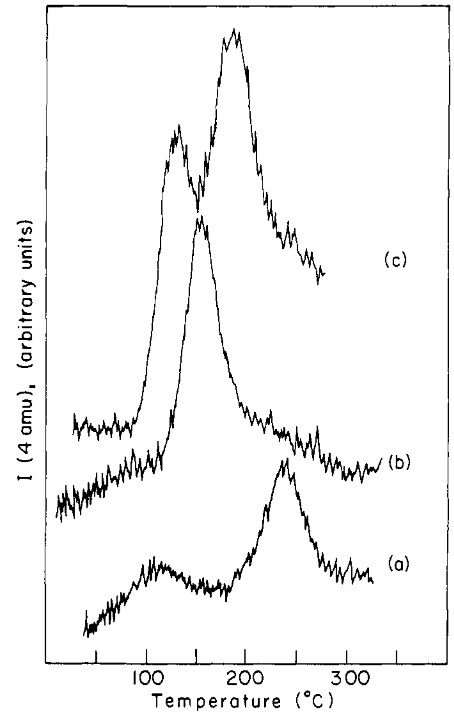

Figure 6. The thermal decompositions of perdeuteriotoluene to yield gaseous D_2 from the three low Miller index planes (a) Ni(100) (b) Ni(110), and (c) Ni(111) are shown in the figure. The C_7D_8 exposures in the three cases were (a) 0.2 × 10^{-6} torr s, (b) 0.5 × 10^{-6} torr s, (c) 0.5 × 10^{-6} torr s at a crystal temperature of 25 °C. The D_2 profiles obtained from the thermal decomposition of C_7D_8 on the stepped Ni[9(111) × (111)] and the stepped-kinked Ni[7(111) × (310)] under comparable conditions were essentially identical with that observed for Ni(111) shown in (c).

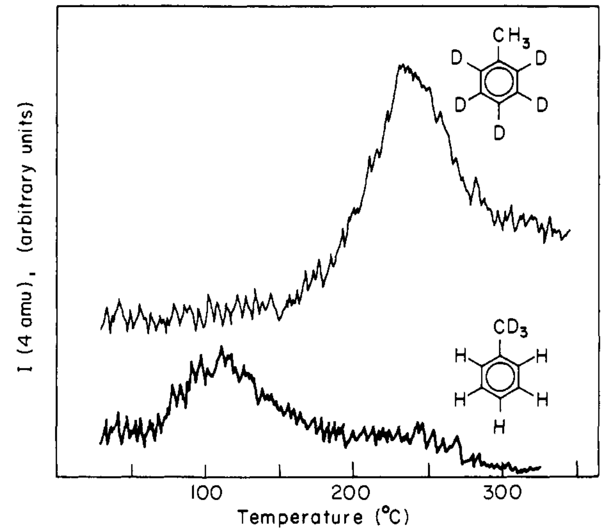

Figure 7. The D_2 profiles obtained from thermal decomposition of the deuterium-labeled toluenes, $CD_3C_6H_5$ and $CH_3C_6D_5$, adsorbed at 25 °C on the Ni(100) surfaces are shown above. The apaproximate exposure in the two cases was 0.2 × 10^{-6} torr s for $CD_3C_6H_5$ and $CH_3C_6D_5$.

Toluene thermal decomposition on these nickel surfaces was monitored by hydrogen desorption from the surfaces. The character of the hydrogen desorption curves is illustrated in Figure 6. This figure clearly shows characteristic hydrogen desorption curves for the close-packed (111) surface, for the flat but more open (100) surface, and for the super stepped (110) surface. For the first two types of surfaces, the bimodal character of the hydrogen desorption curves implied that different types of toluene

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[11] Specifically, this was illustrated by the reaction sequence

$$\text{Ni(111)–}C_6D_6 \xrightarrow{CH_3NC} C_6D_6 + \text{Ni(111)–}C_6D_6\text{–CNCH}_3 \xrightarrow{\Delta} \text{HD (among other products)}$$

[12] Established by desorption experiments with a C_6H_6–C_6D_6 mixture.

[13] (a) The thermal behavior for trimethylphosphine on Ni(110) was quite different from that for Ni(111). Methane peaked at ~100 °C and hydrogen at much higher temperatures of ~170 °C and the latter curve was extremely broad with a half-height width of ~140 °C (25 °C/s heating rate). (b) A characteristic behavior was also evident for the Ni(100)–$P(CH_3)_3$ state where two H_2 desorption peaks (broad) with maxima at 115 (weak) and 180 °C and two CH_4 peaks (broad) with maxima at 117 (weak) and 134 °C were observed.

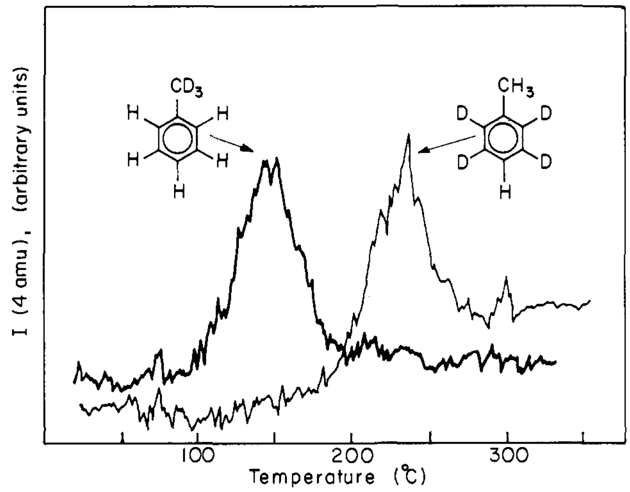

Figure 8. In this figure, the thermal desorption spectra of deuterium obtained by thermally decomposing $CD_3C_6H_5$ and $CH_3C_6D_5$ on Ni(111) are presented. Initial adsorption was carried out a approximately 25 °C with exposures of 0.3 × 10^{-6} torr s of $CD_3C_6H_5$ and 0.2 × 10^{-6} torr s of $CH_3C_6D_5$.

C-H bonds were cleaved at different temperatures. Accordingly, the thermal decomposition of the isomeric molecules $C_6H_5CD_3$ and $C_6D_5CH_3$ was examined on these surfaces. For the Ni(100)-toluene surface, a single D_2 desorption curve was observed for $C_6H_5CD_3$ and for $C_6D_5CH_3$ with desorption maxima at ~110 and 230 °C, respectively (Figure 7).[14] A fully analogous behavior was extant for the Ni(111), Ni[9(111) × (111)], and Ni[7(111) × (310)] surfaces. For each surface there was a single D_2 desorption peak for $C_6H_5CD_3$ and for $C_6D_5CH_3$ with desorption maxima at ~130 and 185 °C, respectively (Figure 8).[15] Since toluene thermal decomposition on Ni(110) yielded a single hydrogen desorption maximum at 150 °C, no differentiation in D_2 desorption curves between $C_6H_5CD_3$ and $C_6D_5CH_3$ was expected—and none was observed.

These labeled toluene studies established that for the flat surfaces, aliphatic C-H bond breaking proceeds before aromatic C-H bond breaking. No aromatic C-H bonds were broken before temperatures of ~160 and ~200 °C, respectively, for the Ni(111) and Ni(100) surfaces. Conversely, all aliphatic C-H bonds in chemisorbed toluene were broken *below* or at temperatures of ~130 and 100 °C for the Ni(111) and Ni(100) surfaces, respectively. Because hydrogen desorption from these surfaces is an activated process, temperatures of 70 and 120 °C are required before hydrogen atoms on the surface recombine and desorb as H_2 (or D_2) from the Ni(100) and Ni(111) surfaces, respectively, at saturation coverages. Thus, some C-H bonds in toluene *could* be cleaved at temperatures as low as 25 °C. Our experiments do not define the temperature at which C-H bond cleavage *first* occurs for toluene (whereas this temperature was defined for the benzene case).

Structural, Stereochemical, and Mechanistic Features of Benzene and Toluene Surface (Nickel) Chemistry. Our data rigorously establish that benzene chemisorption on nickel is wholly or partially associative (no bond cleavage), that the degree of irreversible dissociative chemisorption appears to be a function of surface roughness, e.g., steps, and that no H-D exchange occurs between chemisorbed C_6H_6 and C_6D_6 molecules up to the benzene thermal desorption temperatures. Benzene chemisorption at 20-100 °C is wholly associative on the (111) and (100) surfaces but as indicated by the phosphine displacement reactions a fraction of the benzene molecules appear to chemisorb at 25 °C with irreversible C-H bond cleavage on the stepped, stepped-kinked, and (110) surfaces. We generally observe facile C-H bond cleavage for organic molecules if the initial donor or donor acceptor interaction of the organic molecule with the surface has a stereochemistry wherein a hydrogen atom of a C-H bond, particularly an activated C-H bond, closely approaches the metal surface.[16] Assuming for the moment that the preferred orientation for a chemisorbed benzene molecule is with the C_6 plane parallel to the surface plane, possible close approach of CH hydrogen atoms to step or kink metal atoms on a stepped or stepped-kinked surface is inevitable, for some of the chemisorbed benzene molecules, as illustrated in Figure 9. For the super stepped (110) surface (Figure 3), it seems probable that an even larger fraction of

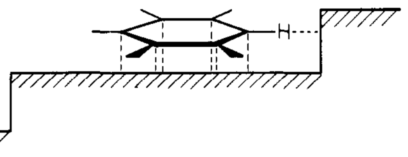

Figure 9. One possible model for benzene adsorbed near step or kink sites is depicted above. In this model the benzene molecule coordinates to the surface via a π interaction with the ring essentially parallel to the (111) terrace. One or more hydrogen atoms may then be in close proximity to the lower coordination number step or kink atoms, thus factilitating C-H bond cleavage. This may account for the partial C-H bond scission observed at 25 °C on the stepped Ni[9(111) × (111)] and stepped-kinked Ni[7(111) × (310)] surfaces in contrast to the Ni(111) surface.

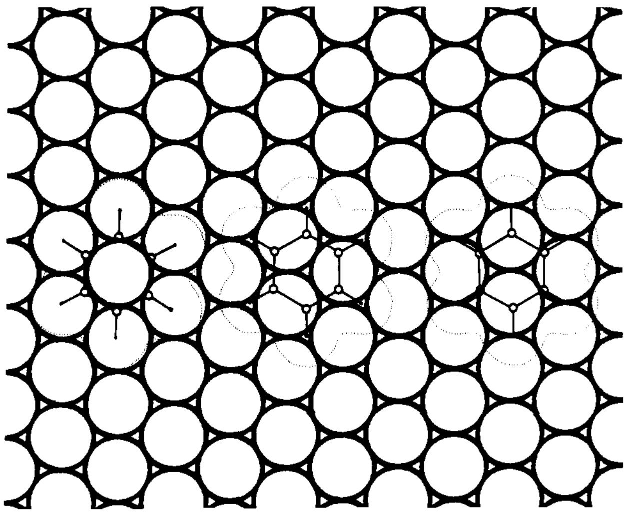

Figure 10. Possible stereochemical features of benzene chemisorbed on a Ni(111) surface are illustrated in the figure. Each of the possible registries are consistent with the $(2\sqrt{3} \times 2\sqrt{3})R30°$, unit cell established by low-energy electron diffraction studies[19] and vibrational (high-resolution electron energy loss) data.[18,19] The benzene bond distances were derived from an X-ray and neutron diffraction study[27] of $C_6H_6Cr(CO)_3$; the dotted line defines the van der Waals outline of the benzene molecule. On the left, the C_6 centroid and all of the hydrogen atoms are centered atop a single nickel atom. (Note that a rotation of 30° about the C_6 symmetry axis of the benzene molecule places the hydrogen atoms over twofold bridge sites.) The models depicted in the center place the C_6 centroid and the six hydrogen atoms over threefold sites. On the right, the C_6 centroid and all of the hydrogen atoms are above twofold bridge sites. In addition to these three there is an infinite number of possible stereochemistries (registries) that would be consistent with the diffraction and spectroscopic data. To enhance the bonding of the benzene molecule to the surface, the hydrogen atoms are probably not in the C_6 ring plane but displaced toward the metal surface plane.

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[14] Because of the ubiquitous hydrogen (H_2) contamination of the ultrahigh vacuum system and of the extremely fast H-D exchange between D_2 and H_2 at metal surfaces, there also was a trace HD desorption peak for $C_6H_5CD_3$ and for $C_6D_5CH_3$ at ~170 °C.

[15] Again, because of system contamination by H_2, HD desorption maxima were also observed—a single maximum for $C_6D_5CH_3$ at ~185 °C and two maxima for $C_6H_5CD_3$ at ~130 and ~160 °C. The appearance of the HD peak in the higher temperature region for $C_6H_5CD_3$ decomposition was probably due to the slight overlap of the two characteristic hydrogen desorption peaks-not all the D on the surface from the initial process(es) was necessarily desorbed before the second process began. For Ni(100), the two desorption processes were much better separated in time (temperature) and only the low temperature HD desorption was observed for $C_6H_5CD_3$.

[16] This type of behavior is also observed in coordinately unsaturated molecular metal or metal cluster complexes.

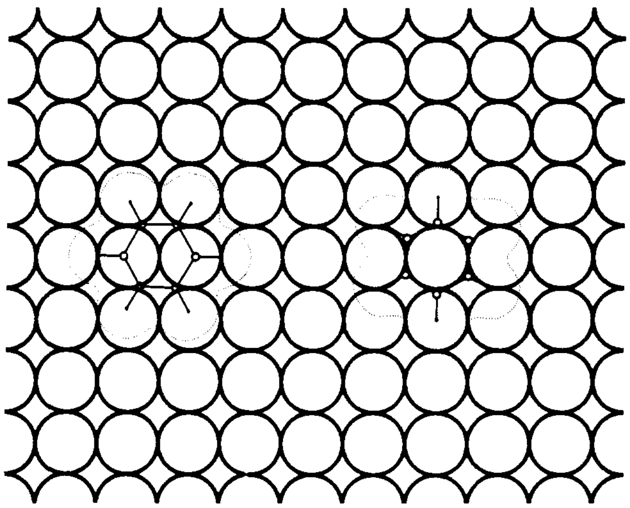

Figure 11. The possible stereochemistries for benzene chemisorbed on Ni(100) are considered here for comparison with Ni(111)-C_6H_6. Both representations are consistent with the *c*(4 × 4) unit cell established by low-energy electron diffraction studies.[19] On the left, the aromatic C_6 centroid is placed atop a single metal center with two of the hydrogen atoms in atop sites and the remaining set of four hydrogen atoms near twofold sites. On the right, the C_6 centroid and two of the hydrogen atoms are centered over twofold bridge sites with the other four hydrogen atoms atop a single nickel atom. An infinite array of stereochemistries can be described and can be consistent with the diffraction data.

chemisorbed benzene molecules will have C-H hydrogen atom close to metal atoms; in fact, the degree of apparent dissociative[9] benzene chemisorption was higher on this surface than the other low Miller index surfaces examined in our study.

What is the stereochemistry of the benzene chemisorption state? Chemical intuition and precedent in molecular coordination chemistry[17a] would place the benzene molecule flat and in a plane parallel to the surface plane, for flat surfaces like the (111) and (100) planes, to allow maximal bonding interactions between surface orbitals and the π and π^* benzene ring orbitals and also the hydrogen atom 1s orbitals.[17b] There are supportive earlier analyses, from vibrational[18,19] and photoelectron[20] spectroscopy, for characterization of a planar benzene bonded in a plane parallel to the Ni(111) and Ni(100) surfaces in the 25 °C chemisorption state. An analysis[19] of low-energy election diffraction data had established ordered chemisorption states for benzene on both the (111) and (100) nickel surfaces, but the data do not define the registry of the C_6 centroid with respect to a point on either the (111) or (100) surface (see Figure 10 and the following discussion).

The benzene thermal desorption data provide information about the upper limit for the heats of chemisorption on these surfaces. Estimates for the activation energies for thermal desorption are on the order of 25, 20, and 30 kcal/mol for the (111), (110), and (100) surfaces respectively. Using these data as upper estimate for the chemisorption heats, we can compare these with estimates of arene-metal bond energies in molecular coordination compounds. No thermochemical data are available for arene-nickel complexes, but good estimates are available for benzene and for toluene binding strengths (enthalpy contributions) in (η^6-arene)Cr(CO)$_3$ complexes, namely, 42.5 and 41.5 kcal/mol, respectively.[21] Thus, the activation energy for benzene desorption from the flat surfaces is slightly less than the energy of the arene bond to a first-row transition metal.[22] The activation energy for benzene desorption from the super stepped (110) is about half the energy of an arene-metal bond. This much lower value is not unreasonable since there can be no especially congruent array of potentially bonding benzene orbitals with surface orbitals on this super-stepped surface. The relatively low benzene desorption temperature for the (111) surface vis-a-vis the (100) surface requires comment. As partially illustrated in Figures 10 and 11, there should be no *large* differentiation between the (111) and (100) surfaces for benzene chemisorption strengths based on stereochemical factors; in fact, these factors favor the (111) surface. Symmetry arguments are not applicable because of the density of states for the surface metal orbitals. There remains the possibility that the observed benzene desorption temperature on Ni(111) is not representative of the average chemisorbed benzene molecule because either the desorbed benzene molecules represent not the ordered state but a second state, superimposed on the former, wherein only a partial segment of the benzene orbitals have access to the surface metal orbitals, or the desorbed benzene molecules are associated with states that are perturbed by the ubiquitous surface imperfections of a real single crystal.[23] Since the distinctions between the thermal desorption behavior for benzene on Ni[9(111) × (111)] and Ni[7(111) × (310)] surfaces were experimentally nondifferentiable from Ni(111), the latter explanation seems untenable. The apparent higher bond energy for benzene bound to the Ni(100) surface with respect to the Ni(111) surface can be explained by the lower work function and the higher d orbital occupancy of the (100) surface *if* benzene is largely functioning as an acceptor molecule.

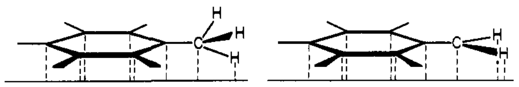

Figure 12. Illustrated in the figure are two possible models for room-temperature toluene chemisorption on nickel surfaces. The aromatic ring may π coordinate to the surface bringing the methyl hydrogen atoms in close proximity to the nickel surface. An intact methyl group hydrogen atom may bond with metal atoms at the surface, as shown on the left, or an aliphatic C-H bond may be cleaved, yielding the benzyl species shown on the right. Either model would be consistent with the facile aliphatic C-H bond scission observed in the thermal decomposition experiments of toluene on nickel.

Toluene chemisorption on all the nickel surfaces were they clean or contaminated by carbon atoms was thermally irreversible and not subject to displacement by trimethylphospine. Since thermochemical studies[21] show no significant binding strength differentiation between benzene and toluene in molecular and mononuclear metal-arene complexes, the qualitatively different behavior between benzene and toluene on these nickel surfaces must be sought. In fact, we tentatively suggest that toluene is bound at room temperature on the flat (111) and (100) surfaces not as the toluene molecule but as a planar benzyl radical. Toluene should initially chemisorb in a fashion analogous to that proposed for benzene, but this necessarily places methyl group hydrogen atoms in close proximity to the surface metal atoms whereby aliphatic C-H bond cleavage of these activated C-H bonds should be facilitated and a planar C_7 benzyl species may be generated (Figure 12). The latter species can optimally bond with metal surface orbitals through all seven carbon atom donor and acceptor orbitals and all seven hydrogen atom 1s orbitals.[17b] All the labeling studies support this representation. None of the data allow such mechanistic interpretations for the (110) surface but here too the toluene chemisorption state probably does not comprise an intact toluene molecule. All the data indicate that the toluene behavior on the stepped and stepped-kinked surfaces is analogous to that on the (111) surface.

Relevance of the Ultrahigh Vacuum Studies to Real Chemical Surfaces. The questioning of relevance for ultrahigh vacuum (UHV) studies of single-crystal surfaces to real surfaces under ambient conditions is persistent and realistic. Do our studies

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(17) (a) See W. E. Silverthorn, *Adv. Organomet. Chem.*, **13**, 47 (1975), for a review of arene-metal complexes. (b) The hydrogen atoms are probably displaced out of the C_6 ring plane toward the metal surface atoms to increase the C-H-Ni interaction.

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

(19) J. C. Bertolini and J. Rousseau, *Surf. Sci.*, 89, 467 (1979).

(20) J. E. Demuth and D. E. Eastman, *Phys. Rev.*, 13, 1523 (1976).

(21) F. A. Adedeji, D. L. S. Brown, J. A. Connor, M. L. Leung, I. M. Paz-Andrade, and H. A. Skinner, *J. Organomet. Chem.*, 97, 221 (1975).

(22) It is reasonable to presume that the bond energy for a C_6H_6-Cr^0 complex would be higher than for a d^{10} C_6H_6-Ni^0 complex.

(23) See discussion of imperfection site surface chemistry by C. M. Friend, M. C. Tsai, R. Gavin, and E. L. Muetterties, *J. Am. Chem. Soc.*, **102**, 1717 (1980).

provide any real measure, for example, of catalytic surfaces in benzene or toluene reactions? Extant data[24] that demonstrate rapid H-D exchanges between C_6H_6–C_6D_6 or D_2–C_6H_6 mixtures or nickel films at 0–20 °C are in sharp contrast to our observations that no exchange was measurable under UHV conditions at 20–100 °C on clean or on carbon-contaminated surfaces, suggesting that extrapolation from UHV studies to "real" surfaces is not valid, at least in this case. However, we submit that our results are not only relevant but suggestive of opportunities for stereoselective catalytic reactions. The absence of reversible or irreversible benzene C–H bond breaking on the flat (111) or (100) surfaces at 20–100 °C but not for toluene suggests that small nickel crystals, e.g., cube octahedra, with largely (111) or (100) faces could be used for the fully selective introduction of deuterium into the alkyl hydrogen atom sites of alkyl-substituted benzenes. Partial selectivity to H–D exchange in the aliphatic C–H sites of toluene has been achieved with ordinary nickel surfaces.[25] Presently, we are seeking evaporative techniques for the selective formation of small nickel cube octahedral crystals and then a test of our hypothesis.[26]

We suggest that measurable rates of aromatic C–H bond breaking in arenes occur at 20 °C only at or near nonplanar sites of a nickel surface. Our failure to observe reversible H–D exchange between C_6H_6 and C_6D_6 on the stepped, stepped-kinked, and (110) surfaces probably reflected the low activity of surface hydrogen atoms under the conditions of our ultrahigh vacuum experiments. Extension of the studies to high pressures will be made when an appropriately modified UHV system has been completed in our laboratory. Under the UHV conditions, there was no evidence for C–H bond *formation* on these nickel surfaces.

Acknowledgment. The advice and suggestions of Dr. Judith Stein were especially valuable to our studies. We also are indebted, for support of the research, to the Division of Chemical Sciences, Office of Basic Energy Services, U.S. Department of Energy under contract No. W-4705-Eng.-48. We gratefully acknowledge Mr. A. Harcourt for the gold plating of the nickel crystal blank. Discussions with Dr. Evgeny Shustorovich were extremely helpful in the consideration of factors responsible for the higher activation energy for benzene desorption from Ni(100) than from Ni(111). We also thank the reviewers for constructive comments.

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(24) An especially valuable review of benzene chemisorption is that of R. B. Moyes and P. B. Wells, *Adv. Catal.*, **23**, 121 (1978).

(25) E. Crawford and C. Kemball, *Trans. Faraday Soc.*, **58**, 2452 (1962), showed H–D exchange between D_2 and alkylbenzenes on nickel films to be faster with α-C–H hydrogen atoms than with ring hydrogen atoms. For toluene, the ratio of $k_{CH_3}/k_{C_6H_5}$ was ~13 at 0 °C for unsintered nickel films. In the case of sintered films, the ratio of initial exchange rates $k_{CH_3}/k_{C_6H_5}$ was 230 at 120 °C.

(26) These studies are being made by Dr. Judith Stein in our laboratory. Preliminary studies with the irregular, Raney nickel surface indicated that there was little or no selectivity to the aliphatic C–H bonds in H–D exchange experiments with $C_6H_5CH_3$ and $C_6D_5CD_3$ mixtures.

(27) B. Rees and P. Coppens, *Acta Crystallogr., Sect. B*, **B29**, 2515 (1973).

The Tetradecaisopropoxydihydridotetratungsten Story

M. Akiyama,[1a] M. H. Chisholm,*[1b] F. A. Cotton,*[1c] M. W. Extine,[1c] D. A. Haitko,[1b] J. Leonelli,[1b] and D. Little[1a]

Contribution from the Departments of Chemistry, Princeton University, Princeton, New Jersey 08540, Indiana University, Bloomington, Indiana 47405, and Texas A&M University, College Station, Texas 77843. *Received September 12, 1980*

Abstract: Tetradecaisopropoxydihydridotetratungsten, $W_4(\mu\text{-}H)_2(O\text{-}i\text{-}Pr)_{14}$, has been isolated from the reaction between $W_2(NMe_2)_6(M{\equiv}M)$ and excess 2-propanol and has been characterized by IR, NMR, mass spectroscopy, and a single-crystal X-ray study. The latter reveals a centrosymmetric molecule, $[W_2(\mu\text{-}H)(O\text{-}i\text{-}Pr)_7]_2$, having a chain of four tungsten atoms with two short, 2.446 (1) Å, and one long, 3.407 (1) Å, tungsten-to-tungsten distances. Each tungsten atom is coordinated to five oxygen atoms and a bridging hydride in a distorted octahedral geometry. The terminal tungsten atoms each have three terminal O-*i*-Pr ligands, but the internal tungsten atoms have only one which creates inequality in the formal oxidation states of the two types of tungsten atoms. Cryoscopic molecular weight determinations showed that the tetranuclear moiety is preserved in benzene, while in *p*-dioxane the molecule dissociates into two dinuclear fragments. NMR studies show that the molecule is fluxional on the NMR time scale: the seven crystallographically different O-*i*-Pr ligands are rapidly scrambled and the hydride ligand sees two equivalent (time averaged) tungsten atoms. The hydride resonance appears as a singlet at δ 7.87, flanked by satellites of roughly one-fifth intensity due to coupling two tungsten-183 nuclei (^{183}W, $I = {}^1/_2$, 14.4% natural abundance), $J_{^{183}W-^1H} = 96$ Hz. $W_4(\mu\text{-}H)_2(O\text{-}i\text{-}Pr)_{14}$ reacts with pyridine to form a Lewis base adduct or solvent compound $W_2(\mu\text{-}H)(O\text{-}i\text{-}Pr)_7(py)_x$ but does not eliminate *i*-PrOH to give the known compound $W_2(O\text{-}i\text{-}Pr)_6(py)_2$. The bridging hydride ligand is not labile to exchange with the hydroxyl proton of *i*-PrOH but rapidly reacts with a number of unsaturated hydrocarbons (C_2H_4, $CH_2{=}C{=}CH_2$, 1-butene, $PhC{\equiv}CPh$) to give either products of M–H insertion or isomerization. Crystal data for $W_4(\mu\text{-}H)_2(O\text{-}i\text{-}Pr)_{14}$ are as follows: $a = 12.645$ (4) Å, $b = 13.157$ (4) Å, $c = 9.788$ (3) Å, $\alpha = 102.43$ (2)°, $\beta = 67.80$ (2)°, $\gamma = 101.05$ (2)°, $V = 1461.5$ (7) Å^3, space group $P\bar{1}$.

Introduction

Previously we have shown[2] that tungsten, unlike molybdenum, does not form an extensive series of dinuclear hexaalkoxides ($M{\equiv}M$). Indeed, only the extremely bulky *tert*-butoxy ligand gave a simple dinuclear compound, $W_2(O\text{-}t\text{-}Bu)_6$, in the alcoholysis reaction (1), and this was not thermally stable. The reaction

$$M_2(NMe_2)_6 + ROH\ (\text{excess}) \rightarrow M_2(OR)_6 + 6\ HNMe_2 \quad (1)$$

$$M = Mo,^3\ R = t\text{-Bu},\ i\text{-Pr},\ Me_3Si,\ Me_3CCH_2;\ M = W,^2\ R = t\text{-Bu only}$$

involving 2-propanol and pyridine as solvent gave $W_2(O\text{-}i\text{-}Pr)_6(py)_2$ which contained four-coordinate tungsten atoms united by a triple bond. Tungsten showed a marked preference, relative to mo-

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(1) (a) Princeton University. (b) Indiana University. (c) Texas A&M University.

(2) M. Akiyama, M. H. Chisholm, F. A. Cotton, M. W. Extine, D. A. Haitko, D. Little, and P. E. Fanwick, *Inorg. Chem.*, **18**, 2266 (1979).

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