Coordination Chemistry of Metal Surfaces. 2.[1] Chemistry of CH_3CN and CH_3NC on Nickel Surfaces

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Abstract: The coordination chemistry of the isomeric molecules CH_3CN and CH_3NC on a nickel surface has been studied as a function of surface crystallography and surface composition by electron spectroscopic and diffraction techniques, by chemical displacement reactions, by thermal desorption spectrometry, and by isotopic labeling experiments. The surfaces studied were the low Miller index planes (111), (110), and (100) and also the stepped and stepped-kinked planes 9(111) × (111) and 7(111) × (310), respectively. Effects of surface carbon, sulfur, and oxygen contaminant atoms on the chemistry were examined for these surfaces. Acetonitrile was weakly and reversibly bound on the (111), stepped, and stepped-kinked surface and was probably oriented with the CN vector normal to the flat surface sections. The thermal desorption temperature was about 90 °C. Some irreversible decomposition, probably focused at step or kink sites, was observed in the thermal desorption experiments. Consistently then, acetonitrile on the super-stepped (110) surface largely underwent decomposition on heating; very little reversible chemisorption was observed. Binding of the nitrile on the (100) surface was significantly different than for the more closely packed (111) surface; the thermal desorption temperature maximum was about 20 °C higher than for Ni(111)–$NCCH_3$. The Ni(100)–$NCCH_3$ state was ordered, $c(2 \times 2)$; here the nitrile nitrogen atom may lie in the fourfold sites. Labeling studies of the acetonitrile chemisorption showed there was no reversible bond breaking process from 20 to ~100 °C. Neither carbon nor sulfur contaminant atoms qualitatively altered this nickel surface–acetonitrile chemistry. In sharp contrast to acetonitrile, methyl isocyanide was strongly bound to all the nickel surfaces and essentially could not be thermally desorbed from the clean surfaces; decomposition to $H_2(g)$ and $N_2(g)$ prevailed. Sulfur contaminant atoms on the nickel surfaces did not alter this chemistry but carbon did. Methyl isocyanide chemisorbed on carbon containing Ni(111), Ni[9(111) × (111)], and Ni[7(111) × (310)] surfaces rearranged on heating and desorbed as acetonitrile at ~90 °C. The chemistry was similar on the carbon-containing (110) and (100) surfaces to that for acetonitrile on the respective Ni(110)–C and Ni(100)–C surfaces. Thus, isomerization of the isocyanide also appeared to prevail on these surfaces. Structural aspects of this surface chemistry are discussed. Experiments with "real" nickel surfaces on which isomerization of CH_3NC to CH_3CN was demonstrated are also described. Oxygen (oxide) contamination of all the nickel surfaces drastically reduced the sticking coefficient of the two isomeric molecules; essentially no chemisorption was observed at 10^{-8}–10^{-10} torr and 20 °C.

Introduction

We describe here the chemistry of the isomeric molecules, acetonitrile and methyl isocyanide, on nickel surfaces as a function of surface crystallography and surface composition.[2] Both molecules exhibited a behavior that was dependent upon the crystallography of the metal atoms at the surface and to the presence of such common surface contaminant atoms as carbon and oxygen. This comprehensive analysis has allowed a rational extension to a study of real surfaces, nickel catalysts, and to the first demonstration of a metal surface catalysis of the isomerization of CH_3NC to CH_3CN. Preliminary studies of CH_3CN and CH_3NC chemisorption on a clean Ni(111) surface had been described earlier by us.[3]

Experimental Section

Preparation of Methyl Isocyanide. Methyl isocyanide was prepared essentially by the method of Casanova and co-workers.[4] A 1-L three-neck flask equipped with 100-mL pressure equalizing dropping funnel, magnetic stir bar, and a receiver trap cooled in a dry ice–acetone bath was charged with 259 g (2.0 mol) of quinoline (Aldrich Chemical Co.) freshly distilled from zinc dust and 143 g (0.75 mol) of *p*-toluenesulfonyl chloride (MC&B Chemical Co.). The solution was heated to 75 °C by an oil bath and the system evacuated to a pressure of 15 mm. While the solution was vigorously stirred, 30 g (0.5 mol) of *N*-methylformamide (Aldrich Chemical Co.) was added dropwise. The addition was complete in 45 min. The material which collected in the receiver was vapor transferred into a storage flask equipped with a Kontes high vacuum stopcock and stored under vacuum at −78 °C.

Preparation of Methyl-d_3 Isocyanide. CD_3I in a sealed ampule was purchased from Aldrich Chemical Co. and used without further purification. KCN and $AgNO_3$ were obtained from Mallinckrodt Chemicals. AgCN was prepared by reaction of equimolar amounts of KCN and $AgNO_3$ in aqueous solution. D_2O was purchased from Bio-rad.

Methyl-d_3 isocyanide was prepared by a modification of the method of Gautier.[5] A 100-mL side-arm single-necked flask equipped with a stir bar and a water-cooled reflux condensor was charged with 8.0 g (0.6 mol) of AgCN and 8.7 g (0.6 mol, 3.9 mL) of CD_3I. The flask was purged with argon and heated by a steam bath for 4 h during which time either a brown liquid or gummy solid formed. Stirring was interrupted and the flask allowed to cool to room temperature. A saturated solution of KCN in D_2O was then added with stirring. Stirring was continued for $^1/_2$ h, and a brown liquid layer above the water became apparent. Impure methyl isocyanide (largely contaminated with methyl iodide) was collected by vapor transfer of the volatile material into a storage flask equipped with a Kontes high vacuum stopcock. The methyl isocyanide was purified by preparative scale gas chromatography by using a 5-ft 20% Carbowax 20 M on Chromosorb W column at 60 °C. The purity of the sample was established by mass spectral analysis and by gas chromatography (99.7%).

Preparation of Methyl Isocyanide-^{13}C. Methyl iodide, purchased from Mallinckrodt Chemical, was purified by distillation and stored in a dark bottle over a bead of mercury. $K^{13}CN$ (56% isotopically labeled) was purchased from Isomet Co. $Ag^{13}CN$ (56% labeled) was prepared by reaction of equimolar amounts of $K^{13}CN$ and $AgNO_3$ in aqueous solution.

Methyl isocyanide-^{13}C was prepared and purified in a manner analogous to that of methyl-d_3 isocyanide. Mass spectral results indicated the purity of the sample to be greater than 99.8% methyl isocyanide of which 56% was $CH_3N^{13}C$.

Acetonitrile-d_3, Acetonitrile-^{15}N and Trimethylphosphine. CD_3CN (99+% d) and $CH_3C^{15}N$ (99% ^{15}N) were purchased from Aldrich Chemical Co. and Stohler Isotope Chemicals, respectively. Trimethylphosphine was prepared by a modification[6] (di-*n*-butyl ether as solvent) of a procedure described in ref 7.

Ultrahigh Vacuum Studies. Experiments were performed in a bakeable, ultrahigh vacuum chamber (Varian) with a minimum 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.

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[1] C. M. Friend, R. M. Gavin, E. L. Muetterties, and M.-C. Tsai, *J. Am. Chem. Soc.*, **102**, 1717 (1980).

[2] E. L. Muetterties, *Angew Chem., Int. Ed. Engl.* **17**, 545 (1978).

[3] J. C. Hemminger, E. L. Muetterties, and G. A. Somorjai, *J. Am. Chem. Soc.*, **101**, 62 (1979).

[4] J. Casanova, R. Schuster, and N. Werner, *J. Chem. Soc.*, 4280 (1963).

[5] M. Gautier, *Ann. Chim. Phys.*, **27**, 103 (1869).

[6] R. R. Schrock, personal communication.

[7] *Inorg. Synth.* **9**, 59 (1967).

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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[8] (etched) with a 3:1:1:5 mixture of the concentrated acids HNO_3, H_2SO_4, H_3PO_4, and CH_3COOH 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 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 $0.5–1.0 \times 10^{-7}$ torr of O_2 for 1–2 min at a crystal temperature of $\sim$350 °C. This was followed by treatment with 1×10^{-7} torr of H_2 for 5–10 min at $\sim$400 °C. This cleaning procedure 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.

Approximate gas exposures were calibrated by back-filling the chamber with a given gas to a total pressure of $\sim 10^{-8}$ torr while monitoring the mass spectrometer parent ion current to yield a pressure vs. parent ion current relationship.

During all gas exposures the parent ion current was monitored as a function of time and then integrated over time to yield an exposure in terms of langmuirs (1 langmuir = 10^{-6} torr s).

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 desorption from the cooling block surface did not contribute detectably to the background). The distance from the front face of the crystal to the ionizer was approximately 1 in. This orientation yielded the maximum signal. All thermal desorption (and chemical displacement) experiments were performed without prior exposure to an electron beam.

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. This orientation decreased the mass spectrometer ion current for gases derived from the crystal during a displacement reaction as compared to a thermal desorption with the alternative orientation. Exposures of the methyl isocyanide species were all in the range of $0.1–0.5 \times 10^{-6}$ torr s, and acetonitrile exposures were in the range of $0.1–1.0 \times 10^{-6}$ torr s. The mixtures in the double-label experiments were 33% $CH_3N^{13}C$, 16% CH_3NC, and 51% CD_3NC for the isocyanide and 40% $CH_3C^{15}N$ and 60% CD_3CN for the acetonitrile. Trimethylphosphine exposures were 0.3×10^{-6} torr s. 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 oxide was ordered with a $c(2 \times 2)$ low energy electron diffraction pattern. Carbon- and carbon/nitrogen-contaminated surfaces were prepared by thermally decomposing C_6H_6 and CH_3NC, respectively. Approximate carbon coverages were estimated by using Auger calibration curves[9] based on decomposed benzene. Sulfur-contaminated surfaces were prepared by annealing the nickel crystal at approximately 1000 °C, inducing surface segregation of sulfur. Both the carbon and the carbon/nitrogen overlayers yielded different ordered, complex low-energy electron diffraction patterns. The sulfur overlayer was not checked for ordering. Relative sticking coefficients were estimated by comparison of the amount of volatile products obtained in the thermal desorption experiments from the C-, S-, and O-contaminated surfaces with that from the clean surface.

Blank experiments were performed in order to verify that the chemistry observed was associated with the 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 metal), followed by a copper strike. The exposed face was then gold plated by using a low concentration cyanide commercial 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[8] (etched) as for all nickel crystals (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-plated 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 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.

Preparation of Raney Nickel. Aluminum–nickel alloy (50/50) was purchased from Alfa Chemical Products. The alloy (250 g) was slowly added to 1 L of 25% NaOH such that the temperature of the solution was maintained between 50 and 70 °C. Vigorous generation of hydrogen gas occurred throughout the addition. After the addition was complete, the temperature was raised to 90 °C and the reaction system was kept at this temperature for 1.5 h at which time hydrogen evolution had ceased. The solution was decanted from the black solid, and to this solid was added 1 L of 25% NaOH. The mixture was heated to 95 °C for 1 h. The solution was then cooled to room temperature. The active Raney nickel was washed with water until the washings were neutral. The Raney nickel was then collected and dried under vacuum.

Catalytic Isomerization of Methyl Isocyanide by Raney Nickel. The reaction vessel consisted of a quartz-fritted U-tube with a storage flask on each side isolated by stopcocks. Approximately 1 g of Raney nickel was placed on the frit and the system evacuated. Methyl isocyanide was introduced from one storage flask, allowed to pass over the Raney nickel, and collected in the receiving flasks which had been cooled to −197 °C. The contact time was approximately 5 s. The collected products were analyzed by gas chromatography by using an 8% Carbowax on Chromosorb W column at 60 °C. The temperature of the reaction vessel was increased by 25 °C intervals until analysis of the product indicated acetonitrile formation. Acetonitrile was first detected at 150 °C; at 200 °C, nearly one-fourth of the isocyanide had isomerized. A blank experiment in which the Raney nickel was replaced by quartz beads indicated that no acetonitrile was formed below 250 °C under the conditions that the Raney nickel isomerized the isocyanide.

Results and Discussion

Acetonitrile. The chemisorption of acetonitrile on all the nickel surfaces, depicted in Figures 1–4, was weak and with the exception of the (110) surface was largely reversible in a thermal context. Surface contamination by sulfur as well by carbon atoms (up to 0.6 monolayer coverage) did not qualitatively alter the surface chemistry although the sticking coefficient was reduced and the saturation coverage was lower when these contaminant atoms were present. The thermal desorption temperature maximum for acetonitrile did not significantly change in going from a clean surface plane to one with sulfur or carbon contamination. However, contaminant oxygen (oxide) atoms so greatly reduced the sticking coefficient of acetonitrile that the chemistry could not be explored at the typical ultrahigh vacuum pressure range

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[8] C. J. Smithells, "Metals Reference Book", Butterworths, Washington, D.C., 1962.

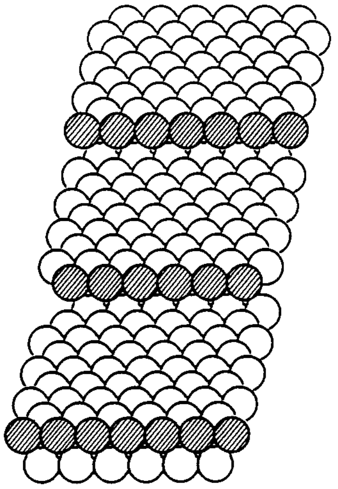

Figure 1. In this representation of the Ni[9(111) × (111)] surface, which may be alternatively indexed as Ni(997), the cross-hatched circles represent nickel atoms at step sites and the unshaded circles, nickel atoms in (111) terrace sites. The coordination numbers for step and terrace metal atoms are 7 and 9, respectively.

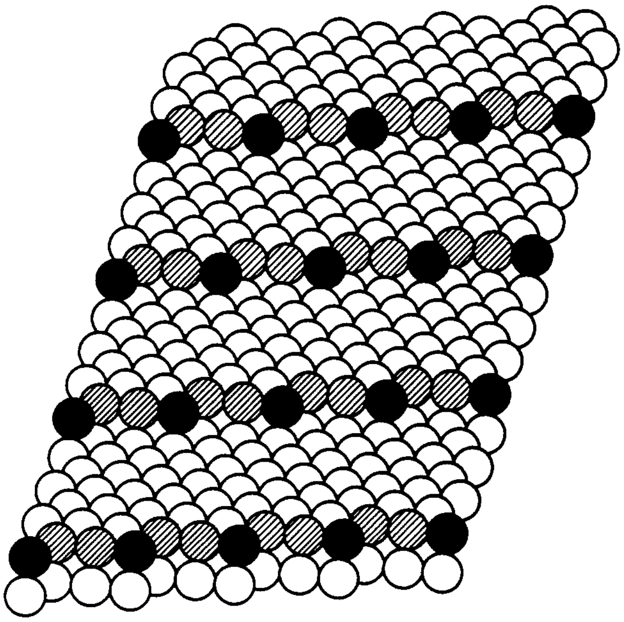

Figure 2. Illustrated here is the Ni[7(111) × (310)] surface. Alternatively, this surface may be indexed as Ni(10,8,7). In this representation, the cross-hatched and shaded circles represent nickel atoms at step and kink sites, respectively. The coordination numbers of metal atoms in the step, kink, and terrace sites are 7, 6 and 9, respectively.

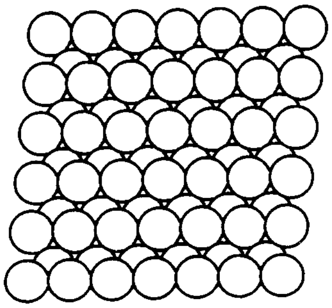

Figure 3. This is a representation of the low Miller index Ni(110) surface, which may be alternatively indexed as a Ni[2(111) × (111)]. The coordination numbers of the exposed metal atoms and those in the steps and in the troughs or valleys are 7 and 11, respectively.

of 10^{-10}–10^{-11} torr; essentially no chemisorption was detected under these conditions.

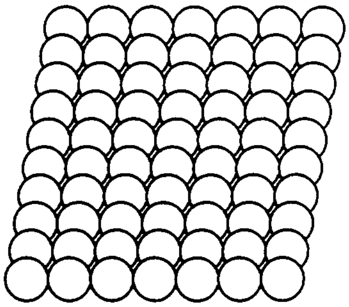

Figure 4. The low Miller index Ni(100) surface, shown above, has surface metal atoms of coordination number 8.

On the close packed (111) surface, acetonitrile formed an ordered $p(2 \times 2)$ structure.[3] Thermal desorption of the nitrile was nearly quantitative; only 1 or 2% of the molecules underwent decomposition as evidenced by hydrogen (H_2) desorption from the crystal[10] and carbon and nitrogen presence[11] on the crystal after the desorption experiment. This small amount of decomposition occurred during the thermal desorption process and not during the initial chemisorption process at 25 °C because both CO and $P(CH_3)_3$ quantitatively[12] displaced the nitrile from the surface at 25 °C. There was no evidence of reversible bond breaking in the chemisorption or thermal desorption processes: thermal desorption of CD_3CN and $CH_3C^{15}N$ from the surface gave only these two gaseous molecules; no cross-labeled molecules were detected by mass spectrometry. Hence, acetonitrile chemisorption on Ni(111) is weak, molecular (associative), and ordered with no reversible bond breaking process operative up to the thermal desorption temperature of 90 °C. On the basis of analogous experiments, the stepped 9(111) × (111) and stepped-kinked 7(111) × (310) surfaces displayed an acetonitrile coordination chemistry identical with that of the (111) surface except that the extent of irreversible decomposition that occurred during the thermal desorption process was slightly greater, ~5 and 15%, respectively.

Acetonitrile was essentially irreversibly chemisorbed on the super-stepped[13] (110) surface. Only about 10% of the nitrile desorbed at ~110 °C; the nitrile desorption was accompanied by H_2 desorption. The fraction of molecules that were thermally desorbed underwent no reversible bond breaking; desorption from Ni(110)-($NCCD_3$)-($^{15}NCCH_3$) produced only CD_3CN and $CH_3C^{15}N$ molecules. Carbon contamination of this surface did not substantially alter the acetonitrile desorption characteristics as found for the close-packed surfaces. Neither trimethylphosphine nor carbon monoxide displaced acetonitrile from the (110) surface in sharp contrast to the (111) surface.

On the flat but less densely packed (100) surface, acetonitrile chemisorption was thermally reversible to about the same degree as on the 7(111) × (310) surface. The thermal desorption maximum was ~110 °C, slightly higher than on the close-packed surfaces, and was relatively broad. Isotopic labeling studies showed no evidence of reversible bond breaking in the thermal desorption process. On this (100) surface, acetonitrile formed an ordered $c(2 \times 2)$ state. Thus, the acetonitrile molecule must be normal to the surface. As for the Ni(110)-($NCCH_3$) state, carbon

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(9) (a) J. P. Biberian and G. A. Somorjai, *Appl. Surf. Sci.*, **2**, 352 (1979). (b) In our experiments, the presence of nitrogen may have made the carbon coverage estimates slightly on the high side for the carbon-contaminated surfaces obtained from CH_3NC.

(10) Hydrogen from CH_3CN or deuterium from CD_3CN decomposition began to appear ~90 °C, about the same temperature as for the thermal desorption temperature maximum for acetonitrile, and peaked at ~140 °C.

(11) The Auger analysis was used to determine the presence of carbon and nitrogen.

(12) In the CO displacement, the Auger analysis of the surface after the displacement showed only C and O to be present; nitrogen was not detected. In the $P(CH_3)_3$ displacement, Auger analysis showed no nitrogen to be present after the displacement reaction. Subsequent thermal desorption yielded no CD_3CN, D_2, or HD.

(13) This low Miller index plane is a stepped surface, or fully ruffled surface, in that it may be described alternatively as a 2(111) × (111) surface.

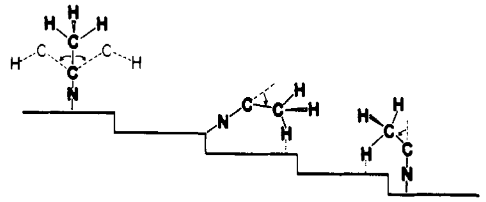

Figure 5. Illustrated in the schematic drawing are possible bonding modes of acetonitrile on flat, stepped, and stepped-kinked nickel surfaces. The proposed bonding configuration for CH_3CN on the flat (111) and (100) surfaces is depicted on the left. The C–N vector is essentially perpendicular to the flat plane. For this model, significant bending of the methyl group with respect to the C–N vector does not bring the hydrogen atoms in close proximity to the metal surface as shown with dashed lines. This geometric feature decreases the probability of thermal decomposition via C–H bond scission. The structures to the right show two possible modes for CH_3CN chemisorption at or near step and/or kink sites. Both models allow for a close approach of one or more of the hydrogen atoms to the metal surface, thus facilitating C–H bond cleavage leading then to irreversible decomposition. These postulated models can account for the difference in degree of thermal reversibility observed for CH_3CN chemisorbed on the flat (111) and (100), stepped 9(111) × (111) and (110), and stepped-kinked 7(111) × (310) surfaces.

monoxide did not displace acetonitrile from the (100) surface but trimethylphosphine did.

A Structural and Mechanistic Characterization of CH_3CN Chemisorption on Nickel Surfaces. All the physical and chemical data indicate that on Ni(111) the acetonitrile CN vector is normal to the surface. The ordered $p(2 \times 2)$ structure with a coverage of ~0.25 at 0 °C is most readily explained with the CN vector normal to the surface, and the latter situation on symmetry grounds is required for the ordered $c(2 \times 2)$ CH_3CN chemisorption state on Ni(100).[14] Most significant was the supporting chemical data. The thermal desorption process was nearly quantitative; only a small fraction of the chemisorbed molecules underwent irreversible C–H bond breaking.[15] Typically, we find that irreversible C–H bond cleavage occurs if C–H hydrogen atoms, especially activated C–H hydrogen atoms, can easily and closely approach the surface metal atoms.[16] Thus, the observations for Ni(111)–$NCCH_3$ strongly suggest that the C–N vector in chemisorbed acetonitrile is normal or nearly normal to the surface plane with the C–H hydrogen atoms distal to the surface nickel atoms (see Figure 5). This bonding feature for acetonitrile is analogous to that in molecular mononuclear, and in most[17] polynuclear, metal acetonitrile complexes where the nitrogen atom only is bonded (and weakly bonded) to a metal atom.[18] The low-energy election diffraction data for the $p(2 \times 2)$ ordered chemisorption state of acetonitrile on Ni(111) do not determine registry.[19]

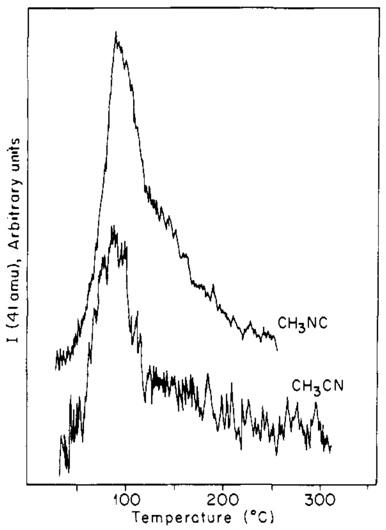

Figure 6. An illustration of the similar desorption characteristics for CH_3CN and CH_3NC on a carbon-contaminated Ni(111) surface is shown in this figure. Presented above are thermal desorption spectra obtained after exposing a carbon and nitrogen-contaminated Ni(111) surface to 0.5×10^{-6} torr s of CH_3NC and 2.0×10^{-6} torr s of CH_3CN at approximately 25 °C. The approximate carbon coverages[9] prior to exposure were 0.4 and 0.5 of a monolayer for CH_3NC and CH_3CN, respectively. Thermal desorption profiles obtained for a Ni{9(111) × (111)} surface under comparable conditions were essentially the same as those shown for Ni(111).

Expectedly, the coordination features of acetonitrile bound to the largely close-packed but stepped or stepped-kinked surfaces, the 9(111) × (111) and 7(111) × (310) surfaces, were analogous to those for the (111) surface to a first approximation. The only differentiation arose in the quantitative features of the thermal desorption process where the degree of irreversible decomposition increased in the order (111) < 9(111) × (111) < 7(111) × (310). Closer approach of C–H hydrogen atoms of the bound acetonitrile to surface metal atoms, near stepped or kinked sites, is possible for these surfaces than for the (111) surface—and the potential for C–H bond cleavage is accordingly higher as illustrated in Figure 5. Thus, the relative thermal reactivity of the three related surfaces is explicable on a crystallographic and stereochemical rationale (Figure 5).

Since much more C–H bond cleavage (~90%) occurred in the process of CH_3CN thermal desorption from Ni(110)–($NCCH_3$) than from close-packed surfaces, the bound acetonitrile molecules must be positioned such that the C–H hydrogen atoms are much closer or can approach much closer to the surface metal atoms than for the more closely packed Ni(111)–$NCCH_3$ surface.[20] The fact that CO and $P(CH_3)_3$ did not displace CH_3CN from this surface further differentiates the Ni(110)–($NCCH_3$) surface chemistry from that of Ni(111)–($NCCH_3$).[22]

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(14) For the ordered $p(2 \times 2)$ state, the saturation surface coverage by acetonitrile was about 25%. The coverage, unit cell data, and the symmetry considerations are nicely accommodated by an ordered state with the acetonitrile molecule normal to the surface (on average one CH_3CN per four nickel atoms). If the C–N vector of the chemisorbed acetonitrile molecule were more or less parallel to the surface, the molecule would not fit in the unit cell unless the C–C bond vector made a near 90° angle to the C–N bond vector and even, in this case, the fit would be tight. Also, an ordered state with a $p(2 \times 2)$ unit cell based on a bound acetonitrile molecule in which the CN vector was more or less parallel to the surface plane is, because all C–N dipoles would have to be ordered, a less probable statistical event than the case for the proposed orientation with acetonitrile molecules bound more or less normal to the surface plane. For the $c(2 \times 2)$ CH_3CN chemisorption state on Ni(100), the acetonitrile molecule must be normal to the surface.

(15) In addition, no reversible C–H bond breaking occurred up to the thermal desorption temperature as established by the labeling studies.

(16) For example, we find irreversible C–H bond breaking to prevail for C_2H_4 and C_2H_2 on Ni(111). Also, see the later discussion of CH_3NC stereochemistry and of C–H bonds breaking in Ni(111)–$CNCH_3$. In addition, we have defined the disjoint behavior of benzene and toluene chemisorption on Ni(111) and Ni(100) where irreversible C–H (aliphatic) bond breaking occurs for toluene because of close approach of the aliphatic C–H hydrogen atoms in the initially π-bond toluene molecule (C. M. Friend and E. L. Muetterties[17]).

(17) See later discussion[20,21] of the one established, exceptional case where an acetonitrile ligand in a molecular metal cluster has the carbon and nitrogen nitrile atoms bonded to cluster metal atoms.

(18) See discussion in ref 3. Structural data for η^1-$NCCH_3$ ligands in cluster molecules will be presented: J. Kouba and E. L. Muetterties, unpublished data.

(19) The acetonitrile nitrogen atom may be over a single nickel atom or over two or at the center of three metal atoms or at any other point in the Ni(111) unit cell. All known metal clusters[17] with simple donor acetonitrile ligands have this ligand bound through the nitrogen atom to a single cluster metal atom. However, all these clusters are coordinately saturated whereas the ordered Ni(111)–($NCCH_3$) surface is really coordinately unsaturated and here the nitrogen atom may be over two- or three-fold sites rather than atop a single metal atom.

(20) The acetonitrile molecules may be bound largely through the nitrogen atom to the recessed surface nickel atoms (Figure 3) in the (110) surface, or alternatively both the carbon and nitrogen atoms of the nitrile function may be bound to surface metal atoms. Either array could bring the C–H hydrogen atoms close to the surface. Note that there is one precedent[21] in molecular metal cluster chemistry where both the carbon and nitrogen nitrile atoms of a CH_3CN ligand are bound.

(21) M. A. Andrews, C. B. Knobler, and H. D. Kaesz, *J. Am. Chem. Soc.*, **101**, 7260 (1979), describe the structural details for $Fe_3(\eta^2\text{-}NCCH_3)(CO)_9$.

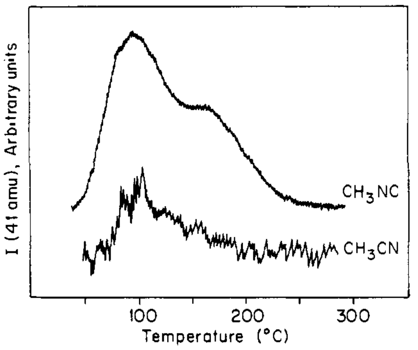

Figure 7. Presented as a parallel to the desorption characteristics for Ni(111)-C-NCCH$_3$ are thermal desorption spectra obtained after exposing a carbon and nitrogen-contaminated Ni[7(111) × (310)] to 0.2 × 10^{-6} torr s of CH$_3$NC and 0.2 × 10^{-6} torr s of CH$_3$NC at approximately 25 °C. Approximate carbon coverages[9] prior to exposure were 0.2 and 0.4 of a monolayer for CH$_3$NC and CH$_3$CN, respectively. Crystallographic effects on CH$_3$CN and CH$_3$NC thermal desorption from carbon contaminated surfaces are further illustrated in Figures 8 and 9.

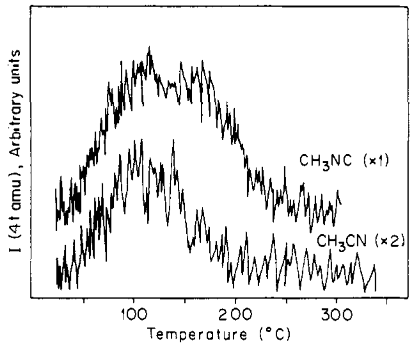

Figure 8. Shown in the figure are thermal desorption spectra obtained after exposing a carbon and nitrogen-contaminated Ni(110) surface to 0.6 × 10^{-6} torr s of CH$_3$NC and 0.3 × 10^{-6} torr s of CH$_3$NC at approximately 25 °C. Approximate carbon coverages[9] prior to exposure were 0.8 and 0.6 of a monolayer for CH$_3$NC and CH$_3$CN, respectively.

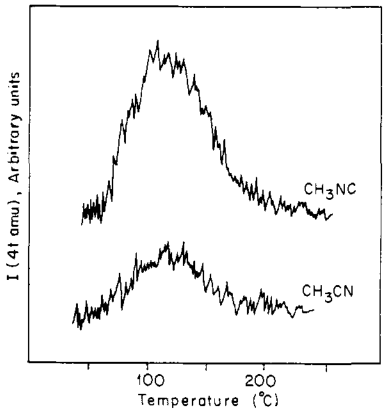

Figure 9. Final comparison of CH$_3$CN and CH$_3$NC thermal desorption behavior is shown in the thermal desorption spectra obtained after exposure of a carbon and nitrogen-contaminated Ni(100) surface to 0.2 and 0.8 × 10^{-6} torr s of CH$_3$NC and CH$_3$CN, respectively, at approximately 25 °C. Approximate carbon coverages prior to exposure were 0.6 and 0.3 of a monolayer for CH$_3$NC and CH$_3$CN, respectively.

Acetonitrile chemisorption on the flat but less closely packed (100) surface was distinguished by two features. The thermal desorption temperature maximum was slightly higher than for the (111) and related surfaces,[23] and the extent of decomposition during thermal desorption was slightly higher than that for Ni(111) and roughly comparable to that for Ni[7(111) × (310)]. This higher thermal reactivity for the (100) relative to the (111) surface might be due to geometric factors.[24]

Methyl Isocyanide. As expected by analogy to molecular coordination chemistry, methyl isocyanide interacted much more strongly with the nickel surfaces than did the isomer, acetonitrile. The sticking coefficient was 1 or close to 1, and the isocyanide was irreversibly bound to all surfaces. Attempted thermal desorption of CH$_3$NC from the nickel surfaces yielded only a trace to a few percent of the 41 mass ion expected in the mass spectrum for a C$_2$NH$_3$ molecule, hydrogen gas above 120 °C and nitrogen about 500 °C. The presence of sulfur atoms, at a 0.1–0.3 monolayer coverage level, did not alter detectably the chemistry of these surface planes with the one exception that the sticking coefficient was slightly lowered by the presence of sulfur.

Carbon atom contamination of the nickel surfaces qualitatively altered the surface chemistry of methyl isocyanide. To a first approximation, the chemistry of methyl isocyanide on the carbon-contaminated nickel planes resembled that of acetonitrile on the clean, and on the carbon-contaminated, nickel surfaces (Figures 6–9). Thus chemisorption of the isocyanide on Ni(111)–C, 0.2–0.8 of a monolayer of carbon, followed by heating of the crystal led to desorption of a molecule with a mass of 41 amu. The maximum for this thermal desorption was ~90 °C, the same as that for thermal desorption of acetonitrile from either Ni(111)–NCCH$_3$ or from Ni(111)–C–NCCH$_3$ (Figure 6). Although the mass spectrometric experiment cannot in this case distinguish between CH$_3$CN and CH$_3$NC because of their similar ionization characteristics, we are reasonably certain (see later discussions) that the molecule desorbing from the Ni(111)–C–CNCH$_3$ surface is acetonitrile, the more thermodynamically stable isomer—but this is not a definitive characterization.

The isomerization of CH$_3$NC that occurred on the Ni(111)–C surface appeared to be an intramolecular process. Thermal desorption from the Ni(111)–C–^{13}CNCH$_3$–CNCD$_3$ surface yielded only the CH$_3$^{13}CN and CD$_3$CN molecules—no cross-labeled molecules were formed.[25] Furthermore, desorption from a Ni(111)–^{13}C–CNCD$_3$ surface gave no CD$_3$CN molecules of enhanced ^{13}C content. Essentially, the same chemistry was observed for methyl isocyanide on the carbon-contaminated stepped Ni[9(111) × (111)]–C surface; the thermal desorption curve for this system matched that for desorption from Ni[9(111) × (111)]–NCCH$_3$ (Figure 6). The temperature at which the apparent isomerization was occurring has not been established rigorously. Attempted displacement reactions indicated that the isomerization was occurring very near to 90 °C. Since neither CO nor P(CH$_3$)$_3$ effected acetonitrile displacement from Ni(111)–C–CNCH$_3$ at 20–70 °C, no significant degree of isomerization could have occurred up to ~70 °C because both molecules rapidly and quantitatively displaced acetonitrile from this surface.

The behavior of methyl isocyanide on the carbon-contaminated stepped-kinked 7(111) × (310) surface was analogous to that on the (111) and the stepped surfaces except that in addition to the

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(22) This differential displacement behavior presently cannot be interpreted in a mechanistic context, but these negative displacement experiments raise the possibility that acetonitrile chemisorbs on this surface in a dissociative fashion.

(23) The (100) surface with exposed metal atoms of coordination number of 8 (compared to 9 for the close packed planes) should be a better donor plane than the (111). Consistent with this suggestion, we have found that benzene, bound as a molecule, was more strongly bonded on the (100) than on the (111) surface (C. M. Friend and E. L. Muetterties, following paper in this issue). However, the binding energies for carbon monoxide on these two surfaces appear to be comparable.

(24) For example, if the nitrogen atoms of the acetonitrile molecules chemisorbed on Ni(100) were centered at the fourfold sites, the C–H hydrogen atoms could more easily approach surface metal atoms on the (100) surface than on the (111) surface because of the larger interstices at fourfold sites in the former than of those at threefold sites on the latter. With a tilt of the CN vector to 15° from the metal surface normal, a bending of the N–C–C angle in acetonitrile of only about 40° would be required to bring the C–H hydrogen atoms within bonding distance of (100) surface metal atoms.

(25) The actual mixture used in the experiments (see Experimental Section) contained CH$_3$NC, CH$_3$N^{13}C, and CD$_3$NC. In the thermal desorption experiments, the relative intensities for the parent ions of these molecules were unchanged from that of the initial mixture.

desorption maximum for the isomerization product, acetonitrile, at 90 °C there was an additional small desorption maximum at 150 °C for a molecule of mass 41. We cannot state whether this desorption was due to acetonitrile or methyl isocyanide because CH_3CN thermal desorption from this stepped-kinked surface showed only a peak centered at 90 °C (Figure 7).

Thermal desorption studies for methyl isocyanide on the other nickel low Miller index planes were also altered by the presence of carbon on the surface. From the Ni(110)–C–$CNCH_3$ surface, there was a weak and very broad desorption of a molecule of atomic mass 41. Labeling studies with CD_3NC and $CH_3N^{13}C$ produced no new cross-labeled species in this desorption experiment. Since the shape and position of the desorption peak was very similar to that for CH_3CN desorption from Ni(110)–C–$NCCH_3$ and Ni(110)–$NCCH_3$ (Figure 8), a small fraction of the isocyanide on the Ni(110)–C surface appears to isomerize and desorb as acetonitrile. Also observed in the thermolysis of Ni(110)–C–$CNCH_3$ was hydrogen cyanide (thermal desorption maximum at ~200 °C—mass 27 from $CNCH_3$ and mass 28 from $CNCD_3$). The carbon source for the carbon in the hydrogen cyanide was shown to be the methyl carbon by the decomposition of $^{13}CNCH_3$ on this surface whereby no ^{13}C incorporation in the product HCN was detected by mass spectrometry.

Heating of the Ni(100)–C–$CNCH_3$ surface produced molecules of mass 41 over a broad temperature range of ~100–160 °C; labeling studies showed no isotope label interchange in the molecules generated in this range. Since the range substantially overlapped the broad desorption peak for CH_3CN from Ni(100)–C–$NCCH_3$ (Figure 9), it appears that CH_3NC isomerization to CH_3CN also occurred on this surface.

Hydrogen cyanide was a pervasive decomposition product of methyl isocyanide on all the clean surfaces and on the carbon-contaminated surfaces. The decomposition sequence was not the major one because Auger analysis of the crystals after heating to 300–400 °C showed that nitrogen was still present on the surface. Temperatures for the HCN desorption maxima were in the range of 150–200 °C, specifically 150 °C for the stepped-kinked surface, 185 °C for Ni(100), and 200 °C for Ni(110). The carbon atom source for the carbon in the HCN was the methyl carbon atom as established in the decomposition of $CH_3N^{13}C$ on Ni(110)–C, Ni(100)–C, and Ni[7(111) × (310)] where no ^{13}C incorporation in the product HCN was detected by mass spectrometry. Note that no HCN was formed in the thermal heating of nickel surfaces with chemisorbed acetonitrile.

Catalyst Studies. Since thermal isomerization of gaseous CH_3NC to CH_3CN is a well-characterized reaction and since a variety of compounds are reported to catalyze the isomerization of isocyanides,[26] we expected to find literature reports of the isomerization of CH_3NC at a metal surface but found none. We then sought an experimental demonstration of the catalytic reaction.

Exposure of liquid CH_3NC to nickel surfaces at temperatures of 50–150 °C led to no detectable isomerization of the isocyanide over multihour reaction periods. Nickel surfaces studied were Raney nickel, bulk granular nickel obtained by reduction of nickel oxide formed from pyrolysis of hydrated nickel nitrate, and finely divided nickel from the hydrogenation of bis(1,5-cyclooctadiene)nickel. Identical results were obtained with these surfaces without and with benzene or isocyanide surface pretreatment analogous to the ultrahigh vacuum procedures. In some cases, the metal surface appeared to have discolored suggesting that polymerization of the isocyanide on the nickel surface might be deactivating the nickel catalysts. Thus if the concentration of chemisorbed isocyanide molecules on the irregular surfaces could be minimized, the polymerization reaction rate might be sufficiently depressed to allow isomerization of the isocyanide molecules. In fact, we demonstrated that the isomerization process could be effected smoothly with Raney nickel at 150–200 °C with a flow reaction in which the contact time was short (~5 s). Catalytic isomerization of CH_3NC to CH_3CN was a fast reaction and was the dominant reaction under these conditions. This catalytic isomerization appears to be the first reported, high-yield surface-catalyzed isomerization of an isocyanide.

Stereochemical and Mechanistic Features of CH_3NC Surface Chemistry. None of our experimental data directly address the issue of how methyl isocyanide is bound to the clean nickel surface. However, since the chemisorption on all clean nickel planes was thermally irreversible, we suspect that the N–C vector of the bound isocyanide is not normal but more or less parallel to the surface plane with both the isocyanide carbon and nitrogen atoms within bonding distance of surface metal atoms, thereby bringing the methyl hydrogen atoms close to surface metal atoms. With such a configuration, irreversible C–H bond breaking should be a facile process as observed for all the clean nickel surfaces. There is a precedent for an isocyanide ligand bound to several metal atoms through both the isocyanide carbon and nitrogen atoms.[27]

The role of carbon in changing the Ni–$CNCH_3$ surface chemistry was not defined,[28] but isomerization of the isocyanide at these Ni–C surfaces appears to be intramolecular as is the case for the high-temperature gas-phase isomerization of CH_3NC.

Conclusions

Studies of metal crystals under ultrahigh vacuum conditions can reveal basic coordination chemistry principles that can be extended to the chemistry of the "heterogeneous" metal surfaces. Probably, we would not have discovered the catalytic isomerization reaction of CH_3NC to CH_3CN on nickel surfaces had the chemistry of nickel crystals not been studied under ultrahigh vacuum conditions, as a function of surface crystallography and surface impurity centers. The role of carbon surface impurity centers in inhibiting gross thermal decomposition or in promoting isomerization of methyl isocyanide cannot be characterized from our studies although we suspect that a key factor is inhibition of the C–H bond-breaking reaction; carbon impurity atoms serving as donor atoms should reduce the efficiency of a nickel surface in C–H bond-breaking processes.

Vibrational studies (high-resolution electron-energy-loss spectroscopy) are planned for the Ni(111)–acetonitrile and –methyl isocyanide and Ni(100)–acetonitrile and –methyl isocyanide systems as a function of temperature, and these may resolve, at least partially, the remaining stereochemical and mechanistic issues.

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(26) Cf. F. Milich, *Chem. Rev.*, **72**, 101 (1972).

(27) V. W. Day, R. O. Day, J. S. Kristoff, F. J. Hirsekorn, and E. J. Muetterties, *J. Am. Chem. Soc.*, **97**, 2571 (1975).

(28) The carbon may principally function as a donor and thereby decrease the surface metal atom capability (more electron rich surface) to effect the irreversible C–H bond-breaking process.