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Authors

Muetterties, E.L.

Tsai, Min-Chi.

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Organometallic Chemistry of
Metal Surfaces - Ultra
High Vacuum Studies

E. L. Muettertides and Min-Chi Tsai
Department of Chemistry
University of California
and
Division of Materials and Molecular Research
Lawrence Berkeley Laboratory
Berkeley, California 94720

Abstract

The effect of one type of molecule on another for chemisorption states on a platinum (111) surface is described. This effect was assayed from chemical displacement and thermal desorption experiments. Molecules studied in this fashion included CH_3CN , CH_3NC , $\text{C}_5\text{H}_5\text{N}$, $\text{P}(\text{CH}_3)_3$, CO , PF_3 , C_6H_6 , and C_2H_4 . The chemistry of Pt(111) is generally distinct from that of Ni(111) in both a qualitative and quantitative fashion.

Introduction

The interaction between organic and inorganic molecules and a metal surface is dependent upon the character of the surface crystallography and surface composition as well as the extent of surface coverage by the molecule in question.¹ No molecular species, in particular no metal cluster, has the potential heterogeneity that is intrinsic to real metal surfaces.² Hence comparison of aspects of organometallic chemistry for real metal surfaces which are "dirty" with the common contaminant elements of carbon, sulfur and oxygen and are crystallographically diverse--with metal clusters which are compositionally and structurally well defined--is not realistic.² However, the comparison is potentially instructive when the metal surface is crystallographically and compositionally uniform and well-defined.^{1,2} Accordingly, we have initiated a chemical and physical study of chemisorption states on metal surfaces with defined crystal planes and surface composition.^{1,3} We describe here some salient features of these surfaces, specifically the platinum (111) surface. The focus is on displacement reactions at this metal surface. These studies were necessarily effected under ultra high vacuum conditions¹ so that a uniform surface composition could be defined and maintained and that the surface science electron spectroscopies could be utilized.¹

Experimental

All experiments were performed in an ultra-high vacuum chamber (Varian) with a base pressure of 5×10^{-11} torr. The ambient background gases were composed mainly of H_2 and CO. Single crystal platinum (Materials for Research Corp.), 99.9999% in purity, was oriented to within 0.5° of the (111) plane using Laue X-ray back reflections. A wafer, $\frac{1}{4}$ in. in diameter

and .050 inches thick, was spark eroded. The crystal was mechanically and chemically polished. The final mechanical polish was with .05 micron alumina. Subsequently, the crystal was etched in a hot, 1:1 mixture of concentrated hydrochloric acid and water. The final chemical etch facilitated removal of calcium.

The cleaning procedure followed that was described by D. R. Monroe.⁴ The platinum was treated with O_2 at 10^{-7} torr at $900^\circ C$ for 1-24 hr. in the vacuum chamber to remove carbon and sulfur. Then the crystal was quickly heated to $1100^\circ C$ for 10 min. and then cooled. The crystal was examined by Auger spectroscopy. If either calcium or oxygen was detected, the crystal was removed and treated with hydrochloric acid again. This procedure was repeated until there was no detectable oxygen or calcium by Auger spectroscopy. The Auger spectrum of the crystals used in these studies showed no evidence of O, C, Ca or S.

Research grade reagents were used in all experiments. The reagent gas was exposed to the platinum crystal through a variable leak valve equipped with a "needle" such that the gas was directed at the crystal face, thus minimizing background contamination. Thermal desorption experiments were performed by heating the crystal at a rate of $25^\circ C/sec$. The crystal was indirectly heated by a tungsten-rhenium filament imbedded in a ceramic block (Spectra-Mat, Inc.) held in mechanical contact with the sample. Chromel-Alumel thermocouple wires were used for temperature measurement. A quadrupole mass spectrometer (Uthe Technology International) was used to monitor the evolving gaseous products in the thermal desorption and displacement experiments.

The Ligand Exchange Reaction in Surface Organometallic Chemistry

A classic reaction type in organometallic and coordination chemistry is ligand exchange. This reaction was utilized by Werner and by Chernyaev in their pioneering studies of transition metal coordination complexes to elucidate stereochemical features. In a formally analogous fashion, we have attempted to exploit this type of reaction in surface chemistry.^{1,3} The experimental protocol begins with chemisorption of one molecule on the metal crystal under study. Then, a gaseous flux of the second molecule is directed to the surface of the crystal while the gas phase above the surface is monitored by mass spectrometry. Ligand displacement should occur if the displacing molecule is more strongly bound than the initially chemisorbed molecule, if there is sufficient activation energy for the displacement reaction, and if there are no significant synergistic effects between the two bound molecules. These experiments are typically effected under conditions such that the surface coverage by the first molecule is substantially less than saturation -- typically less than one-quarter of a monolayer coverage. Thus there is extensive open space for chemisorption of the displacing molecule. Under these conditions, the displacement reaction for the surface case must be associative in character -- it is formally analogous to displacement reactions centered at coordinately unsaturated metal complexes; e.g., square planar d^8 complexes.

It is instructive to consider a specific example of a displacement reaction at a metal surface. Acetonitrile is a relatively weak field ligand in transition metal complexes. Consistently, acetonitrile is weakly bound on nickel and platinum surfaces: Reversible thermal desorption of acetonitrile proceeded at temperatures of $\sim 90^\circ$ and 110°C from $\text{Ni}(111)$ ⁵ and $\text{Pt}(111)$ surfaces, respectively. Acetonitrile, in fact, was displaced from nickel surfaces by stronger ligands such as carbon monoxide.⁵ Displacement was rapid and complete at 20°C . Gaseous acetonitrile, detected by mass

spectrometry, appeared virtually instantaneously with the introduction of carbon monoxide and displacement was complete within seconds at 20°C.⁵ Acetonitrile in molecular zerovalent transition metal chemistry is also a readily displaceable ligand as practically illustrated in the synthetic utility of molecular species like $\text{Mo}(\text{CO})_3(\text{NCCH}_3)_3$. Since acetonitrile is bound only through the nitrogen atom at the nickel surface⁵ as it is generally bound in molecular coordination chemistry and since it is readily displaced from nickel surfaces, the crude analogy between metal surfaces and metal coordination complexes (or clusters) is viable in this specific case of nickel. However, the platinum metal surface chemistry diverges from that of nickel. Acetonitrile was not displaced from a Pt(111) surface by carbon monoxide at 20°C. Thermal desorption studies for the Pt(111)-NCCH₃-CO surface showed a thermal desorption temperature maximum for CH₃CN that was indistinguishable from that for CH₃CN from a Pt(111)-NCCH₃ surface. It were as if the acetonitrile molecules did not sense the presence of carbon monoxide on the Pt(111) surface, a sharp and seemingly inexplicable contrast to the nickel system. There is here the implication that a much more localized bonding representation is appropriate for Pt(111)-NCCH₃-CO than for Ni(111)-NCCH₃-CO at least with respect to the acetonitrile molecules. It should be noted that both CH₃CN and CO chemisorption were fully molecular (associative) in character. There was no evidence of reversible bond breaking up to the thermal desorption temperature. This feature was established by labelling studies: Thermal desorption of acetonitrile from a Pt(111)-NCCD₃-¹⁵NCCH₃ surface produced only gaseous CD₃CN and CH₃C¹⁵N molecules; no cross labeled molecules were detected. Similarly, thermal desorption of carbon monoxide from a Pt(111)-¹³CO-C¹⁸O surface yielded no ¹³C¹⁸O molecules (in fact no exchange was observed at temperatures up to 300°C for this specific platinum surface plane).

The chemical behavior of nickel and platinum surfaces was, however, fully analogous for benzene chemisorption. Benzene was found to be weakly bound on

both Ni(111) and Pt(111) surfaces; thermal desorption⁷ maxima were similar although neither metal exhibited complete thermal desorption of the chemisorbed benzene molecules. Both Ni(111)-C₆H₆⁸ and Pt(111)-C₆H₆ surfaces reacted with trimethylphosphine at 20°C to yield gaseous (displaced) benzene. This reaction has its formal parallel in molecular coordination chemistry where phosphine displacement of benzene in $(\eta^6\text{-C}_6\text{H}_6)_2\text{M}$ complexes has been demonstrated.⁹

The distinction for M-(NCCH₃)-(CO) chemisorption states, however, remains for the nickel and platinum systems. A further indication of apparent anomalous behavior in the platinum system was evident in a series of attempted displacement reactions of acetonitrile from Pt(111). Neither strong donor molecules nor strong acceptor molecules displaced acetonitrile from Pt(111) but both classes of "displacing" molecules substantially affected the thermal desorption temperature for the acetonitrile (Table 1). Curiously, the presence of strong donor molecules, like trimethylphosphine and pyridine on the Pt(111) surface significantly raised the temperature maximum by 20-40° for CH₃CN thermal desorption whereas the presence of a strong acceptor molecule like PF₃ lowered the temperature maximum by about 20°C. These results seem unusual if acetonitrile is considered to be simply a weak donor ligand because intuitively we could expect a strong donor molecule to displace the weak acetonitrile donor ligand or at least lower the thermal desorption temperature of the acetonitrile from that for Pt(111)-NCCH₃. For nickel (111)⁸, acetonitrile was quantitatively displaced at 20°C from the surface by trimethylphosphine whereas in the platinum case, the acetonitrile was not displaced and the thermal desorption temperature for acetonitrile was raised by 40°, relative to Pt(111)-(NCCH₃), by the presence of the strong donor, trimethylphosphine. Possibly the binding of acetonitrile to platinum is qualitatively different than to nickel. The relevant donor and acceptor molecular orbitals in acetonitrile are the 6a₁ donor orbital which lies at very low energy, -0.6424 a.u., and the 3σ* acceptor orbital which is at high energy, 0.358 a.u.¹⁰; both are centered more at carbon (CN carbon) than at

nitrogen thus reducing any donor or acceptor interaction. Perhaps, acetonitrile interaction is largely through a σ donor interaction of the $6a_1$ orbital for the nickel surface and more through a π acceptor interaction of the $3e^*$ orbital for the platinum surface. Then, with synergistic bonding between acceptor acetonitrile and a donor phosphine ligand, the enhanced binding of acetonitrile on the $\text{Pt}(111)\text{-(NCCH}_3\text{)-(P(CH}_3\text{)}_3\text{)}$ surface becomes explicable. Also explicable then would be the observed lowering of the acetonitrile desorption temperature by the presence of the strong acceptor, PF_3 . Evaluation of the relative extent of donor and acceptor interaction of the acetonitrile with nickel and platinum surface orbitals obviously requires a knowledge of the precise stereochemistry of the CH_3CN bonding at the surface and a measure of overlaps. The detailed stereochemistry is not established although both surfaces seem to have the CH_3CN molecule oriented with the CN vector normal to the surface. Hence, the suggestion of greater acceptor bonding of acetonitrile on the platinum surface must remain simply a suggestion unless our vibrational studies of the $\text{Pt}(111)\text{-(NCCH}_3\text{)}$ and $\text{Ni}(111)\text{-(NCCH}_3\text{)}$ states resolve the stereochemical issues. As a complementary study, we will attempt to explore analogous issues in molecular chemistry by the synthesis and the structural, physical, and chemical characterization of complexes of the type $\text{M[PR}_3\text{]}_2$ or $3(\text{NCCH}_3)$ with $\text{M} = \text{Ni}$ and Pt .

Benzene and ethylene were like carbon monoxide insofar as their effect on acetonitrile binding to $\text{Pt}(111)$: Neither displaced CH_3CN from $\text{Pt}(111)$ and their presence did not significantly alter the thermal desorption temperature of CH_3CN from $\text{Pt}(111)$.

A caveat must be presented in this general discussion of the significance of thermodynamic and electronic factors in the displacement or desorption reactions from

mixed chemisorption states on metal surfaces. No molecular or geometric features of the mechanism of a chemical displacement or a thermal desorption experiment has been established. Desorption could be a simple one step process of increased amplitudes of ligand-surface vibration until dissociation is achieved. Desorption or displacement could also be a multi step process. For example, a molecule A could be chemisorbed on a close packed surface and oriented such that the donor atom of A is located on a three-fold surface site. Desorption directly from this site could be high in energy relative to migration of A first to a two-fold site then to a sitting atop a single metal surface atom site and from there desorption. If a second molecule B is chemisorbed on this hypothetical M(111)-(A) surface and if the donor atom of B is energetically best placed at a sitting atop site, then the energetically favored site for A desorption will be less accessible and the activation energy for A desorption from M(111)-(A)-(B) could rise even though (B) did not directly affect the ground state energetics of the binding of A.

Clearly, there are many thermodynamic, kinetic, and stereochemical features of metal surface-organometallic reactions (specifically displacement and desorption reactions) that remain to be established. We are actively seeking a structural, thermodynamic, and kinetic characterization of mixed chemisorption states and their displacement and thermal desorption features at well-defined metal surface planes because these mixed chemisorption states are directly relevant to catalytic reactions.

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E. L. Muettertides and Min-Chi Tsai
Department of Chemistry, University of
California, Berkeley, California 94720
and Division of Materials and Molecular
Research, Lawrence Berkeley Laboratory,
Berkeley, California 94720

Thermal Desorption
for CH_3CN from
Pt(111)

<u>Chemisorption State</u>	<u>Thermal Desorption Temperature Maximum for Acetonitrile</u>
$\text{Pt(111)}-\text{NCCD}_3$	$\sim 110^\circ\text{C}$
$\text{Pt(111)}-\text{NCCD}_3-\text{CO}$	$\sim 110^\circ\text{C}$
$\text{Pt(111)}-\text{NCCH}_3-\text{D}_2(\text{D})$	$\sim 110^\circ\text{C}^*$
$\text{Pt(111)}-\text{NCCD}_3-\text{C}_6\text{H}_6$	$\sim 110^\circ\text{C}^*$
$\text{Pt(111)}-\text{NCCD}_3-\text{C}_2\text{H}_4$	$\sim 110^\circ\text{C}^*$
$\text{Pt(111)}-\text{N}^{15}\text{CCH}_3-\text{P}(\text{CH}_3)_3$	$\sim 150^\circ\text{C}^*$
$\text{Pt(111)}-\text{NCCD}_3-\text{P}(\text{CH}_3)_3$	$\sim 150^\circ\text{C}^*$
$\text{Pt(111)}-\text{NCCD}_3-\text{NC}_5\text{H}_5$	$\sim 135^\circ\text{C}^*$
$\text{Pt(111)}-\text{NCCD}_3-\text{CNCH}_3$	$\sim 140^\circ\text{C}^*$
$\text{Pt(111)}-\text{NCCD}_3-\text{CH}_3\text{C}\equiv\text{CCH}_3$	125°C^*
$\text{Pt(111)}-\text{NCCD}_3-\text{PF}_3$	$\sim 95^\circ\text{C}$

* No H-D exchange observed under the experimental conditions of thermal desorption.

References

1. E. L. Muetterties, *Angew. Chem., Intern. Ed., Engl.*, 17 545 (1978).
2. E. L. Muetterties, T. N. Rhodin, E. Band, C. F. Brucker, W. R. Pretzer, *Chem. Rev.* 79 91 (1979).
3. E. L. Muetterties, J. C. Hemminger, G. A. Somorjai, *Inorg. Chem.*, 16 3381 (1978).
4. D. R. Monroe, University of California Thesis, Berkeley, California (1977), p. 18.
5. J. C. Hemminger, E. L. Muetterties, and G. A. Somorjai, *J. Am. Chem. Soc.*, 101 62 (1979).
6. Interestingly, we find the apparent higher binding strength of acetonitrile to platinum relative to nickel is a general phenomenon for donor or donor-acceptor molecules. Thermochemical measurements of molecular binding strengths in nickel(0) and platinum(0) complexes should be made as a further check of thermochemical relationships between surfaces and discrete coordination metal complexes.
7. The thermal desorption experiment monitors a kinetic process and provides a measure of the activation energy for desorption. The activation energy sets an upper limit to the heat of chemisorption, cf. Petermann.
8. C. M. Friend and E. L. Muetterties, in press.
9. W. E. Silverthorn, *Adv. Organomet. Chem.*, 13 47 (1975).
10. W. L. Jorgensen and L. Salem, The Organic Chemist's Book of Orbitals, Academic Press, New York, 1973.

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