

Communications to the Editor

Coordination Chemistry of Metal Surfaces— Carbon Monoxide Chemisorption States on Pt(111)

Sir:

Delineation of the coordination chemistry of metal surfaces with defined crystallography under “clean” conditions is now a viable and extremely active research activity.^{1–3} Here we describe a valuable experimental procedure to ensure that chemistry ascribed to the flat, crystallographically defined surface is, in fact, just that chemistry—particularly for experiments based on thermal desorption⁴ and chemical displacement^{3,5} reactions. Through such experiments, we have shown that surface imperfections,⁶ invariably present even in carefully prepared crystal samples, play an important and detectable role in the spectroscopic and chemical behavior of a real crystal surface. In addition, we call attention to an alternative interpretation of vibrational spectroscopic data for such conceptually simple systems as chemisorbed CO on the close-packed platinum(111) surface.

A common observation in spectroscopic, diffraction, and thermal desorption studies is the apparent presence of two or more chemisorbed states, even at coverages that are substantially lower than one half monolayer. Consider the well-studied example of CO on the Pt(111) surface. All results from thermal desorption studies are identical within experimental error:⁷ there are two well-separated desorption maxima, one of variable intensity at 200 °C which shifts to ~150 °C as initial CO surface coverage increases and one of relatively fixed intensity and position at approximately 280 °C (Figure 1). With substantial CO coverage, the former desorption peak is the larger (~80–90% of the total CO desorption). The higher temperature desorption peak is present in thermal desorption experiments with Pt(111) after 15–30-min exposures of the crystal to the ambient, operating atmosphere in the ultrahigh vacuum chamber (10^{-10} to 10^{-11} Torr; 1 Torr = 133 Pa) which analyzed by mass spectrometry as largely CO and H₂. The major desorption peak has been ascribed uniformly to a CO chemisorption state on a Pt(111) surface and the minor peak has been variously associated with desorptions from other parts of the ultrahigh vacuum system to the edge areas of the crystal or to the ubiquitous imperfections⁶ of a real Pt(111) surface. We have established the last explanation to be the correct one.

In our surface studies,³ thermal desorption⁴ and chemical displacement^{3,5} reactions play a major role in establishing the surface coordination chemistry. Without an experimental blank, there is a major uncertainty as to whether observed thermal desorptions or chemical displacements occur at the crystallographically defined surface of the very small metal crystal.⁸ We have devised a blank experiment based on a crystal of the metal under study that has only the flat exposed face of experimental study covered by a layer of gold (in the platinum system, the blank was prepared from a conventional platinum crystal wafer by vapor deposition of a thin copper layer followed by a thin gold layer—the sides and back of the crystal were masked during the deposition⁹). By using such metal crystal blanks, we have found it possible to establish with certainty the origin of any molecules displaced in thermal desorption or chemical displacement reactions from metal surfaces. Only in three cases have we seen any chemistry associated with the gold surface in the temperature range of 25–400 °C: methyl isocyanide expectedly was chemisorbed

strongly on gold with a thermal desorption maximum at ~130 °C, pyridine behaved similarly, and CH₃CN desorbed at ~90 °C.

Our blank studies demonstrated that the observed thermal desorption of CO from the Pt(111) surface is totally associated with the real exposed crystal surface—not with the sides or back of the crystal or other parts of the vacuum system. The gold-plated crystal blank experiment showed no CO desorption in the 25–400 °C region (see Figure 1). Accordingly, the desorption maximum at 280 °C must be ascribed to thermal desorption from the front surface of the prepared crystal, and, because of the high temperature of this desorption process, desorption from surface imperfection sites is a logical process for this desorption phenomenon. It may be of electronic and structural significance to the issue of imperfection sites that a stepped Pt crystal [e.g., Pt 6(111) × (111)] exhibits a more intense 280 °C thermal desorption maximum and a less intense peak in the 150–200 °C range.^{7,10} Crystals with steps and kinks behave similarly.^{7b} (Thus, there is no evidence of different activation energies for CO desorption from steps and kinks.) We suggest that the most common imperfections on a carefully prepared and annealed Pt(111) surface will be steps and kinks.

Since there is a significant (~10–20%) concentration of chemisorbed CO at imperfections on the Pt(111) surface and since there is a substantial difference, ~5 kcal/mol, in the activation energies for desorption from the (111) surface and for imperfection sites, vibrational studies should detect (resolve) both states. The first detectable state should be the more tightly bound state associated with CO at imperfection sites. In fact, two states are detected by electron loss studies¹⁰—the first to appear in the energy region characteristic of losses due to CO stretching excitation is a loss at 2080 and the second at 1850 cm⁻¹, regions characteristic of terminal M–CO and bridging M_x–CO metal carbonyls, respectively. The current interpretation¹¹ of these data is that CO first chemisorbs on single platinum atoms in the (111) plane (terminal and linear M–C–O) and at higher coverages bridging sites are occupied. However, CO chemisorption apparently occurs first at bridging sites on the (111) surfaces of the closely related metals, nickel and palladium, a stereochemical feature fully consonant with coordination chemistry principles since maximal interaction of the CO carbon atom with surface metal atoms should lower most effectively the surface potential energy at low CO surface coverages on close-packed (111) or (001) surfaces.^{12,13} We, in fact, expect CO also to first go to bridging sites for the (111) surface provided that the temperature of chemisorption is sufficiently high to allow CO migration on the surface and ascribe the first state that appears in the electron loss studies and which apparently involves CO bound to single metal atoms (2080 cm⁻¹) to CO bound at the imperfection sites, *vide infra*. At high coverages, some CO could go to single atom sites in the terrace.¹⁴

In the interpretation of the vibrational data for CO on Pt(111), serious consideration should be given to the possibility that the energy loss at 2080 cm⁻¹ arises from CO chemisorbed at imperfections on a real Pt(111) crystal face¹⁵ and that the CO chemisorbed on the Pt(111) plane has a CO stretching frequency at 1850 cm⁻¹, a region characteristic of a bridging carbonyl—as expected by analogy to the CO chemisorption states on Ni and Pd(111) surfaces and from coordination chemistry principles.^{12,13} Vibrational data for stepped surfaces

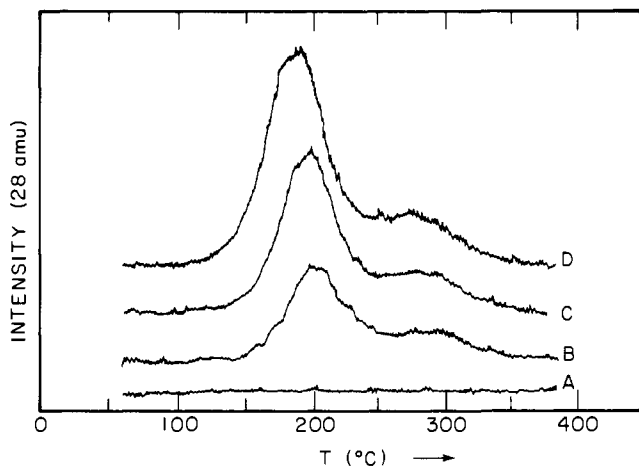


Figure 1. Thermal desorption spectra for CO from a Pt(111) crystal surface. In curve A is shown the spectrum obtained for mass 28 after exposure of the gold-plated platinum blank to 10 L ($L = \text{Langmuirs}$ which is 10^{-6} Torr s) carbon monoxide at 25 °C. Spectra for CO desorptions from CO states from the Pt(111) crystal at CO exposures of 0.1 (curve B), 0.2 (curve C), and 0.3 L (curve D).

support this interpretation. The intensity of the energy loss peak at 2080 cm^{-1} is much greater from the stepped surface $[6(111) \times (111)]$ than from the (111) surface^{7a} for comparable exposures of CO. That is, as steps are added to the imperfections which are always present, the intensity of the loss at 2080 cm^{-1} compared with the 1850-cm^{-1} loss increases.

In addition, we submit that another feature of the vibrational data for CO on Pt(111) supports the thesis that CO is on bridging sites (the state associated with the 1850-cm^{-1} loss) for platinum atoms in a (111) environment. For a given chemisorption state of a molecule or a molecular fragment on a metal surface, the average binding energy for the molecules bound to metal atoms in environments characteristic of the prepared surface should decrease generally to some small but detectable degree as the separation between individual surface molecules decreases (i.e., as the surface coverage increases). In some instances these slight energy changes may be detectable spectroscopically. In sharp contrast, chemisorption states of molecules on imperfection sites of a well-prepared crystal surface should be less perturbed by coverage changes—the imperfection sites generally will not be ordered, contiguous, or subject to correlation effects. For the general case of CO chemisorption states characteristic of the prepared metal surface plane, electron transfer from metal to π^* (π antibonding) CO orbitals should be less extensive as CO coverage increases and the ν_{CO} (stretching frequencies) characteristic of this state should increase—available data from electron loss and infrared reflectance studies of CO on metal surfaces can be so interpreted.^{7a,11} Thus, the chemisorption state which gives rise to the nearly coverage invariant 2080-cm^{-1} energy loss for CO on Pt(111) is best ascribed to CO at surface imperfection sites. The chemisorption state which yields the lower energy ($1850\text{--}1880\text{ cm}^{-1}$) CO stretching loss whose position is coverage dependent with a shift to higher energy with increasing coverage is best ascribed to CO bridge bonded to platinum atoms in a (111) surface environment. Note that the 2080-cm^{-1} loss is ascribed to the most tightly bound CO chemisorption state (imperfection sites). The imperfection or stepped sites have surface metal atoms of lower coordination number (7) than do the terrace sites (9). This rationally accounts for the apparent anomaly of having the bound CO of higher stretching frequency being the more tightly bound CO chemisorption state.

Although imperfections on single-crystal surfaces present substantial difficulties in the interpretation of chemical and spectroscopic data for chemisorption states, we believe that the

above-described blank experiments coupled with a careful assessment of the coordination chemistry as a function of surface crystallography can eventually unravel the intimate features of metal surface coordination chemistry. The implications presented here for platinum surfaces have substantial breadth; e.g., formally analogous phenomena have been established for the chemisorption of benzene and of ethylene on a Pt(111) surface.¹⁷ In contrast, we have not sensed apparent chemisorption states due to crystal imperfections on Ni(111) with a variety of small molecules—a result in keeping with the greater ease of preparing “nearly” perfect surfaces with nickel than with platinum. In the specific case of CO on nickel, both the (111) surface and a stepped surface show a single desorption maximum, at temperatures separated by only 20 °C.¹⁸ Therefore, thermal desorption experiments would not detect steplike imperfections on a Ni(111) surface.

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References and Notes

- Hannay, N. B., Ed. "Treatise on Solid State Chemistry"; Pergamon Press: New York, 1976; Surfaces 1 and 11, Vol. 6A and 6B.
- Rhodin, T. N.; Ertl, G., Eds. "The Nature of the Surface Chemical Bond"; North Holland Press: Amsterdam, 1979.
- Muettterties, E. L. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 545.
- Petermann, L. A. *Prog. Surf. Sci.* **1972**, *3*.
- Muettterties, E. L.; Hemminger, J. C.; Somorjai, G. A. *Inorg. Chem.* **1977**, *16*, 3381.
- As well appreciated by all experimenters in this field, any well-prepared single-crystal surface is still imperfect at the visual, microscopic, and atomic levels. In the well-prepared single crystal the imperfections should not be ordered or regularly distributed—and the imperfection sites or areas should be disjoint and not significantly interactive. There also will be surface imperfections resulting from impurities, but we do not believe that these are significant in our experiments. Our platinum crystal cleaning procedure, particularly for calcium removal, followed that described by D. R. Monroe, University of California Thesis, Berkeley, Calif., 1977, p 18 (we are indebted to Professor R. Merrill for calling this procedure to our attention). Designed experiments with controlled and low carbon contamination of the Pt surface did not yield significantly different thermal desorption results. In brief, the cleaning procedure consisted of treatment of the crystal with hot hydrochloric acid to remove calcium and then a series of distilled water washes. The crystal was treated with O_2 at 10^{-7} Torr at 900 °C for 1 h in the ultrahigh vacuum system and then was quickly heated to 1100 °C for 10 min and cooled. (The crystal was examined by Auger spectroscopy. If either Ca or O 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.) Carbon and sulfur impurities were removed by the oxygen treatment. The Auger spectrum of the crystals used in these studies showed no evidence of O, C, Ca, or S.
- (a) Hopster, H.; Ibach, H. *Surf. Sci.* **1978**, *77*, 109. (b) Blakely, D. W., Ph.D. Thesis, University of California, 1976, p 165.
- The surface area of the flat metal surface is 10^4 to 10^5 smaller than the total metal surface within the exposed ultrahigh vacuum system. The ratio of the area of the exposed crystal face to the area of the sides was $\sim 3:1$.
- The crystal prior to mounting on the crystal holder of the manipulator was masked on the sides and back with aluminum foil. Copper and then gold were vapor deposited on the exposed front face of the crystal. The foil was removed and the crystal was then cleaned with 50% hydrochloric acid and then water. The crystal was mounted and placed in the vacuum chamber.
- McCabe, R. W.; Schmidt, L. D. *Surf. Sci.* **1977**, *66*, 10.
- (a) Krebs, H. J.; Luth, H. *Appl. Phys.* **1972**, *14*, 337. (b) Froitzheim, H.; Hopster, H.; Ibach, H.; Lehwald, S. *Ibid.* **1977**, *13*, 147.
- Muettterties, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91.
- Muettterties, E. L. *J. Isr. Chem.*, in press.
- In the electron loss studies, there is some evidence for increased numbers of CO molecules at single metal atom sites at high CO coverages.^{7a}
- There has been a reluctance to consider this possibility because of the relatively large intensity of the 2080-cm^{-1} loss. However, there need be only a factor of 5 difference in the oscillator strengths for CO bound at imperfection and at (111) sites to account for the apparent intensity discrepancy. There are experimental data in molecular coordination chemistry that clearly show such differences in oscillator strengths are possible and commonly found¹⁶ in CO coordination chemistry.
- Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.
- These studies, to be published, show that benzene chemisorption on Pt(111)

is largely thermally reversible. The thermal desorption studies clearly show there are two distinct chemisorption states. Neither was detected in the blank experiment. The more strongly bound state is ascribed to benzene on Pt(111) and the more weakly to benzene bound at or near imperfection sites.

(18) Erley, E.; Wagner, H. *Surf. Sci.* **1978**, *74*, 333.

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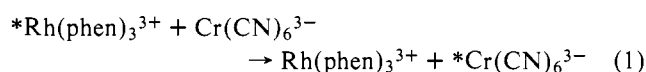
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Energy and Electron-Transfer Processes of the Lowest Excited State of the Tris(phenanthroline)rhodium(III) Complex

Sir:

In the last few years it has been found that the excited states of complexes containing aromatic molecules such as 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen) as ligands are particularly suitable for energy and electron-transfer processes.¹⁻⁵ These complexes are presently the focus of considerable interest because of their potential use in the conversion of light energy into chemical energy.⁶⁻¹⁰ The best studied is certainly the Ru(bpy)₃²⁺ ion, but other Ru(II), Cr(III), Os(II), and Ir(III) complexes have also been the object of photochemical and photophysical investigations.¹⁻⁵ We describe here the characteristics of *Rh(phen)₃³⁺, which is the first excited rhodium complex whose energy and electron-transfer processes have been quantitatively investigated.¹¹ A rather striking aspect of this study is that energy and electron-transfer processes involving *Rh(phen)₃³⁺ have been observed and their rate constants have been measured without relying on directly observable properties (such as absorption or emission spectra) of the excited state.¹³

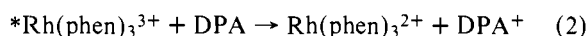
In rigid matrix at 77 K Rh(phen)₃³⁺ exhibits a well structured luminescence emission.¹⁵⁻¹⁸ The emitting state is the lowest π, π^* triplet, with $E^{00} = 22.2$ kK and $\tau = 48$ ms.^{15,16} In contrast to what happens for the analogous Cr(III), Ru(II), Os(II), and Ir(III) complexes,² no emission can be observed¹⁹ in fluid solutions of Rh(phen)₃³⁺ at room temperature. However, the presence of a relatively long-lived excited state upon irradiation (λ 290 nm) of aerated solutions of Rh(phen)₃³⁺ in dimethylformamide (DMF) at room temperature is clearly shown by the occurrence of an energy-transfer process (reaction 1) which causes the sensitization of the well-known²⁰ Cr(CN)₆³⁻ phosphorescence:



A plot¹ of $1/I_{sens}$ vs. $1/[Q]$ (where I_{sens} is the intensity of the sensitized emission and $[Q]$ is the Cr(CN)₆³⁻ concentration) yielded a Stern-Volmer (SV) constant of 3.0×10^3 M⁻¹.²¹ Assuming that the energy transfer occurs at diffusion-controlled rate ($\sim 10^{10}$ M⁻¹ s⁻¹), the (lower limiting) value for the lifetime of *Rh(phen)₃³⁺ is ~ 0.30 μ s. In a few experiments carried out by irradiating deaerated aqueous Rh(phen)₃³⁺ solutions in the presence of biacetyl, the sensitized photophorescence of biacetyl was observed. As the emitting state of biacetyl lies at ~ 20 kK,²² the donor excited state of Rh(phen)₃³⁺ has to be either the $^3\pi, \pi^*$ state which is seen in emission at 77 K ($E^{00} = 22.2$ kK) or some other excited state which lies not much lower than that state. Even in the first case, the lack of appreciable emission from the $^3\pi, \pi^*$ excited state at room temperature is not surprising in view of the five orders

of magnitude decrease of τ , which causes a proportional decrease in the emission intensity.

When a 4×10^{-5} M solution of Rh(phen)₃³⁺ in acetonitrile was flashed at 347 nm with a ruby laser²³ in the presence of variable amounts (1.6×10^{-4} to 2.0×10^{-3} M) of diphenylamine (DPA), a transient spectrum was observed which practically coincided with the well-known spectrum of the DPA⁺ radical cation (λ_{max} 680 nm).²⁴ This indicates that the reaction



takes place and that Rh(phen)₃²⁺ does not appreciably absorb in the 500-700-nm region.²⁵ A plot¹ of $1/A$ vs. $1/[Q]$, where A is the absorbance at 660 nm and $[Q]$ is the DPA concentration, yielded a SV constant of $\sim 2.5 \times 10^3$ M⁻¹. Assuming that reaction 2 takes place at diffusion-controlled rate ($\sim 10^{10}$ M⁻¹ s⁻¹), the (lowest limiting) value for the *Rh(phen)₃³⁺ lifetime in aerated acetonitrile is ~ 0.25 μ s, which is almost the same as that obtained from reaction 1 for aerated DMF solutions. A plot of $1/A$ vs. $1/[Q]$ for the *Cr(bpy)₃³⁺-DPA system yielded a value of 7×10^9 M⁻¹ s⁻¹ for the electron-transfer quenching constant; this value, which is close to the diffusion-controlled one, compares well with that previously obtained for the same system by luminescence quenching experiments.²⁷ This shows that the method of monitoring the absorbance of the electron-transfer products for obtaining the rate constant is reliable. Since *Rh(phen)₃³⁺ is (as we will see later) a better oxidant than *Cr(bpy)₃³⁺, there is no reason to believe that reaction 2 is not diffusion controlled. This means that the actual lifetime of *Rh(phen)₃³⁺ in aerated acetonitrile at room temperature has to be ~ 0.25 μ s.

A few experiments carried out in acetonitrile solutions with 1,3,5-trimethoxybenzene (TMB) as a quencher showed that the TMB⁺ radical cation (λ_{max} 590 nm)²⁸ was generated at a nearly diffusion-controlled rate. Since the reduction potential of the TMB⁺/TMB couple is 1.49 V vs. SCE,²⁹ it follows that *Rh(phen)₃³⁺ has to be a very powerful oxidant. This is not surprising because a value of 2.00 V vs. SCE is expected² for the *Rh(phen)₃³⁺/Rh(phen)₃²⁺ couple on the basis of the reduction potential of the Rh(phen)₃³⁺/Rh(phen)₃²⁺ couple (-0.75 V)³⁰ and the excited-state spectroscopic energy of the $^3\pi, \pi^*$ state (2.75 eV).¹⁵ This means that *Rh(phen)₃³⁺ is expected to be a much stronger oxidant than all the excited Ru(II), Cr(III), and Os(II) complexes and even than most of the excited Ir(III) complexes that have been studied up until now.^{1,31} The availability of excited states which cover a wide range of redox potentials is, of course, important for both systematic studies (e.g., that one described in ref 32) and practical applications.

In view of the spectroscopic¹⁵⁻¹⁸ and electrochemical³⁰ analogies between Rh(phen)₃³⁺ and Rh(bpy)₃³⁺, the results reported above contribute to the elucidation of some interesting results recently obtained by Lehn et al.^{6,12} In the production of hydrogen upon ultraviolet irradiation of aqueous solutions containing Rh(bpy)₃³⁺ and triethanolamine (TEOA),¹² the excited-state reaction has to be of the type of reaction 2. Secondary reactions of Rh(bpy)₃²⁺ will then lead to hydrogen formation. On the other hand, in the production of hydrogen upon visible irradiation of aqueous solutions containing Ru(bpy)₃²⁺, Rh(bpy)₃³⁺, and TEOA,^{6,10,12} the excited ruthenium complex ($E^{00} = 17.1$ kK)² cannot transfer electronic energy to the rhodium complex. Rather, electron transfer from *Ru(bpy)₃²⁺ to Rh(bpy)₃³⁺ has to occur with formation of Rh(bpy)₃²⁺, which again leads to hydrogen generation, and Ru(bpy)₃³⁺, which is then reduced by TEOA.

A systematic investigation on the photochemical and photophysical properties of Rh(phen)₃³⁺ and other Rh(III) complexes is in progress in our laboratories.