End-On and Side-On Bonding of Ketones to Surfaces: Acetone on the Ru(001) and Pt(111) Surfaces

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High-resolution electron-energy-loss spectroscopy has verified the existence of two fundamentally different types of adsorbed acetone, η^1-bonded acetone on Pt(111) and η^2-bonded acetone on Ru(001). On a Ru(001) surface, the Lewis acidity of which has been increased by the presence of oxygen adatoms, the η^1 and η^2 forms of acetone coexist. The η^1-bonded acetone desorbs molecularly, whereas η^2-bonded acetone is a precursor to dissociation on the surface.

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Previous investigations[1-15] concerning the bonding of prototypical ketones to metal centers in organometallic complexes have provided a qualitatively consistent picture of the effect of the Lewis acidity of a metal on its selectivity toward various possible configurations for the bonding of the ketonic ligands. The advent of high-resolution electron-energy-loss spectroscopy (EELS) for the vibrational analysis of adsorbed overlayers on solid surfaces has rendered feasible incisive studies of the organometallic chemistry of macroscopic, well-defined single-crystalline surfaces[16] and a rigorous comparison to the chemistry of analogous homogeneous complexes. In this Letter, new and unprecedented results are reported concerning the interaction of acetone (a weak donor ligand) with the close-packed Pt(111) and Ru(001) surfaces, as well as the Ru(001) surface on which an ordered $p(2\times 2)$ overlayer[17] of atomic oxygen is present.[18-20] The contrasting bonding configurations and the possible decomposition of acetone observed on these surfaces systematize the chemical effects of relative Lewis acidities of metals,[21] while clarifying the comparative chemistry of these surfaces and their relationship to analogous coordination complexes.

Descriptions of the EEL spectrometers (and the UHV chambers in which they are contained) used for the Ru (Ref. 22) and Pt (Ref. 23) studies have been published previously. A typical resolution in both spectrometers (for a disordered overlayer of low electron reflectivity) is 80 cm^{-1} (full width at half maximum of the elastically scattered electron beam), and optimum resolutions are below 40 cm^{-1}. Atomically clean single-crystalline surfaces were prepared by Ar^+ sputtering and chemical cleaning with oxygen followed by high-temperature reductive annealing.[24] The ordered $p(2\times 2)$ overlayer of atomic oxygen on Ru(001) was prepared by exposing the clean surface to 0.8 L of oxygen (1 L = 1 langmuir ≡ 10^{-6} Torr s) at 95 K, followed by thermal ordering at a temperature of approximately 350 K.[18-20] The Pt crystal was exposed to acetone with a directional beam doser consisting of a multichannel array of microcapillaries, whereas the Ru crystal was exposed to acetone by backfilling the UHV chamber. The acetone was degassed with multiple freeze-pump-thaw cycles before use, and its purity was verified *in situ* mass spectrometrically.

EEL spectra for acetone adsorbed on the three surfaces are shown in Fig. 1, and a summary of the surface structures, the measured vibrational frequencies, and the mode assignments is presented in Table I. Spectra obtained for adsorption of $(CD_3)_2CO$ rather than $(CH_3)_2CO$ are shown in Figs. 1(b) and 1(c), since they afford better clarity and resolution of the signature modes critical to the identification of the adsorbed species.

On the Pt(111) surface, the EEL spectrum of adsorbed acetone, shown in Fig. 1(a), exhibits (dipolar enhanced) modes of both A_1 and B_1 symmetry and a down-shifted carbonyl stretching frequency (relative to liquid acetone or acetone multilayers condensed on the Pt and Ru surfaces). Consequently, on Pt(111) acetone is bonded in an η^1 (end on) fashion through the oxygen atom with C_s symmetry (a mirror plane through the plane of the molecule, perpendicular to the surface), and a Pt–O=C bond angle that is less than 180°, as shown in Fig. 2(a). The bonding of the acetone to the Pt(111) surface is typical of a weak donor ligand since the temperature corresponding to the maximum rate of desorption of molecular ace-

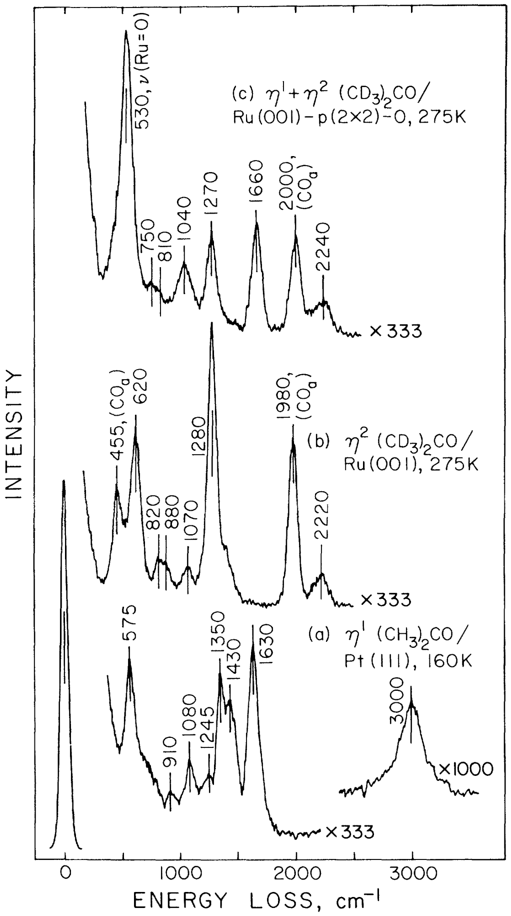

FIG. 1. EEL spectra for (a) a monolayer of $(CH_3)_2CO$ on the Pt(111) surface; (b) a monolayer of $(CD_3)_2CO$ on the Ru(001) surface; and (c) a monolayer of $(CD_3)_2CO$ on the Ru(001) surface with an ordered $p(2\times 2)$ overlayer of oxygen adatoms present. Features at 455 and 1980–2000 cm^{-1} in spectra (b) and (c) are due to adsorbed CO from the onset of decompsotion of the η^2 acetone. All spectra were recorded in the specular direction where dipolar scattering dominates the inelastic electron scattering cross section (Ref. 16).

tone is 185 K, suggesting a binding energy of approximately 11.5 kcal/mol.

It has been recognized for a number of years that acetone can bond coordinately in an η^1 configuration in various organometallic complexes.[1-8] The frequencies observed for η^1 acetone on the Pt surface are in good agreement with those reported previously for homogeneous (monometallic) complexes of η^1-bonded acetone.[1,7,8]. In x-ray diffraction crystallographic structural determinations of Ru complexes of η^1-bonded acetone, the Ru–O=C bond angle ranges from 135° to 153°, and the $Ru–O=C–C_2$ torsional angles are within

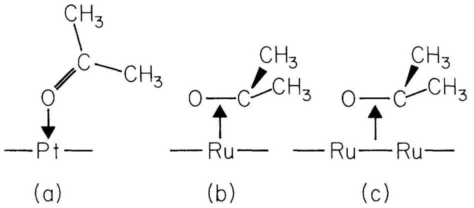

FIG. 2. Schematic bonding configurations for (a) η^1 acetone on Pt(111) and Ru(001) on which a $p(2\times 2)$ oxygen adatom superstructure exists; (b), (c) η^2 acetone on Ru(001).

7° of planarity.[7,8] The frequency of the carbonyl stretching mode shifts from 1710 cm^{-1} in liquid acetone to approximately 1630 cm^{-1} on the Pt surface and is down shifted similarly in the organometallic complexes of Ru.[7,8] Consequently, especially since the acetone is adsorbed with C_s symmetry, quite similar bonding occurs in η^1-bonded acetone complexes and on the extended, close-packed surface of Pt.

At 275 K on the Ru(001) surface, a temperature at which all the acetone has desorbed reversibly from Pt, the acetone is bonded in an η^2 (side on) configuration as indicated schematically in Figs. 2(b) and 2(c).[27] This form of adsorbed acetone is identified by a substantially down-shifted carbonyl stretching mode at 1280 cm^{-1}, isopropyl-like rocking modes at 990 and 1170 cm^{-1}, and a skeletal mode at 670 cm^{-1} [at 1280, 820, and 880, and 620 cm^{-1} for $(CD_3)_2CO$, respectively; see Table I and Fig. 1(b)]. The feature at 670 cm^{-1} is due to the $\pi(CO)$ mode of acetone which is transformed from B_2 to A' symmetry as the symmetry of the acetone skeleton is lowered from C_{2v} to C_s (a mirror plane through the C=O bond, perpendicular to the surface) with the rehybridization of the ketonic carbon atom from sp^2 to nearly sp^3 upon adsorption. This η^2 form of acetone on Ru is a stable intermediate in the decomposition of the acetone. The rapid decomposition of η^2 acetone to adsorbed CO, CH_x fragments ($x \leq 3$), and hydrogen adatoms occurs at temperatures slightly above 275 K.

A number of side-on bonded ketonic and related homogeneous complexes which resemble the η^2-bonded acetone on the Ru(001) surface have been reported.[9-15] In particular, the analogy with two zero-valent complexes of nickel are noteworthy, namely, (hexafluoroacetone)*bis*(triphenylphosphine) nickel(0),[9] and (benzophenone)*bis*(triethylphosphine) nickel(0).[13] An extension of the carbonyl bond length by approximately 0.1 Å in both

TABLE I. Vibrational frequencies (in inverse centimeters) observed with high-resolution electron-energy-loss spectroscopy of η^1 acetone on Pt(111), η^2 acetone on Ru(001), and a mixture of η^1 and η^2 acetone on Ru(001)$p(2\times 2)$-O. [Corresponding frequencies for deuterated acetone, $(CD_3)_2CO$, are given in brackets. The mode assignments, their symmetry types, and the ir and Raman frequencies of liquid acetone are listed as well.]

Mode	Symmetry C_{2v}	C_s	ir and Raman of liquid[a]	EELS on Pt(111) η^1	EELS on Ru(001) η^2	EELS on Ru(001)$p(2\times 2)$-O η^1	η^2
			3004[2255] (*s*)				
$\nu(CH_3)$			2964[2222] (*s*)	3000[2250]	2970[2220]	2970[2240]	2970[2240]
			2924[2111] (*s*)				
ν_s (CO)	A_1	A'	1710[1701] (*vs*)	1630[1630]	1280[1280]	1660[1660]	1280[1270]
			1430[1085] (*s*)	1430		1420[1040]	
$\delta(CH_3)$			1361[1037] (*vs*)	1350[1030]	1370[1070]		1370[1040]
			1356[1036] (*w*)				
ν_a (Me-C-Me)	B_1	A''	1220[1245] (*vs*)	1245[1290]			
			1092 (*m*)		1170[880]	1090	
$\omega(CH_3)$			1066[890] (*m*)	1080	990[820]		960[810]
			902 (*m*)	910		890[750]	
ν_s (Me-C-Me)	A_1	A'	786[695] (*w*)				
δ(CO)	B_1	A''	530[478] (*s*)	575[530]		b	
π(CO)	B_2	A'	393[331] (*w*)[c]		670[620]		b
δ(Me-C-Me)	A_1	A'	493[410] (*w*)[c]				

[a] Ref. 25.

[b] Obscured by the very strong ν_s (Ru = O) mode at 530 cm^{-1}.

[c] The original assignments of these modes (Ref. 25) have been reversed by Raman polarization measurements (Ref. 26).

complexes is strong evidence of π bonding to the nickel (i.e., π donation and π^* back-donation). If the bonding is thought of in terms of the Dewar-Chatt-Duncanson model,[28,29] then in view of the importance of back-bonding, side-on (π-bonded) ligands are stabilized by electronegative substituents on the ligand which serve to lower the energy of the π^* orbital. There is a concomitant need for "electron rich" metals, i.e., those in low formal oxidation states, to facilitate this type of bonding. This is the reason why only rather recently has η^2-bonded acetone been observed in a low-valent homogeneous Ta complex[15] compared to the earlier observation of an η^2-bonded hexafluoroacetone complex with Ni.[9] This is also the reason why the more "electron rich" Ru surface binds acetone in an η^2 configuration, whereas a geometrically identical surface of Pt does not. The degree of rehybridization of the ketonic carbon atom is similar in the Ta(η^5-C_5Me_5)(η^2-acetone)Me_2 complex (Me = CH_3)[15] compared to η^2 acetone on the Ru surface as judged by the carbonyl stretching frequencies, 1200 cm^{-1} in the former and 1280 cm^{-1} in the latter.

If the Lewis acidity of the Ru surface is increased by the adsorption of an ordered $p(2\times 2)$ overlayer of oxygen adatoms (corresponding to a quarter-monolayer surface coverage), the behavior of the (subsequently) chemisorbed acetone is *qualitatively different* from that of acetone on reduced Ru, as is evident from the EEL spectrum in Fig. 1(c). In the presence of the oxygen overlayer, a significant fraction of the adsorbed acetone exists as an η^1 ligand which desorbs *molecularly* near 300 K. This is a consequence of a through-metal depletion of the electron density on the surface Ru atoms due to the presence of the electronegative oxygen adatoms. On this modified Ru surface of greater Lewis acidity, the acetone adsorbs as a donor ligand with a binding energy considerably greater than on the reduced Pt surface. Consequently, the modified surface of Ru behaves similarly, but not identically, to the Pt surface. This fact is also apparent from the coexistence of η^1 and η^2 acetone on the Ru(001)$p(2\times 2)$-O surface [cf. Table I and Fig. 1(c)], whereas the η^2 form of acetone does not exist on reduced Pt.

To summarize, high-resolution EELS measurements have verified the existence of two fundamentally different types of adsorbed acetone, η^1-bonded acetone on Pt(111) and η^2-bonded acetone on Ru(001). On a Ru(001) surface, the Lewis acidity of which has been increased by the presence of oxygen adatoms, the η^1 and η^2 forms of acetone coexist. The η^1-bonded acetone desorbs molecularly, whereas η^2-bonded acetone is a precursor to dissociation to chemisorbed CO, CH_x fragments, and hydrogen. These results systematize the nature of the bonding of (ketonic) organometallic ligands to metal clusters and to metal surfaces, i.e., they provide a quantification of the so-called "metal-cluster, metal-surface analogy." More detailed descriptions and discussions of the results reported here are in preparation.[30, 31]

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[17] In a $p(2\times 2)$ overlayer, both edges of the primitive unit cell of the adsorbate lattice are twice the magnitude of those of the primitive unit cell of the substrate, i.e., the area of the former is four times that of the latter, and the fractional surface coverage is 0.25. For a detailed discussion of surface crystallography, see M. A. Van Hove, W. H. Weinberg, and C.-M. Chan, *Low-Energy Electron Diffraction* (Elsevier, Amsterdam, 1983).

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