All the above clearly confirms previous findings concerning the usefulness of the 7/3(SZ) basis sets in creating a library of analytical pair potentials for associations involving molecules of biological interest.

Before finishing this section, let us make some comments on the CP method used in this work to correct for the error arising from the superposition of the basis sets.

Doubts have been reported in the literature concerning the use of the CP method to correct for the BSSE.[37,38] However, other recent literature also gives some examples in which the use of the CP method results in much improved interaction energies when calculated with small basis sets.[39-41] Therefore, at this moment, a definitive conclusion about the validity of the use of the CP method cannot be determined.[42] Furthermore, most of the above studies[37-41] have been carried out on small systems, and we feel that extrapolation to larger systems is not straightforward. In fact, on the basis of the origin of the BSSE it seems reasonable to infer that as long as the number of atoms *directly involved* in the molecular association grows, an increase in the BSSE should be expected.

The above discussion combined with previous experience in using 7/3(SZ) basis sets (see, for example, ref 17 and 43 for a discussion concerning this point) have been the reasons to include the CP correction in the present work.

Conclusions

By performing an extensive number of SCF calculations at the Hartree–Fock level, an ab initio analytical pair potential for the computation of the interaction energies between aliphatic amino acids (without sulfur) has been derived. Because of the complexity of the potential hypersurfaces for the interaction between pairs of amino acids, special attention has been focused on the generation of the conformations from which the parameters of the analytical pair potential have been obtained.

Since parameters for the interactions between amino acids and water, as well as for the interaction between water molecules, are already available in the literature, the present-day potential library provides a powerful tool for dealing with a wide variety of problems involving molecules of biological interest.[44] In particular, amino acids are the units from which proteins are built-up. In this regard, the determination of the 3-D structure of proteins is a most important topic that could be tackled by using the analytical pair potential developed in this paper. Some preliminary research is being conducted in order to test the appropriateness of our intermolecular pair potential for dealing with structural problems in proteins involving intramolecular interactions.

Acknowledgment. One of us (J.A.S.) thanks the Ministerio de Educacion y Ciencia (Spain) for a fellowship as well as IBM-Kingston for its very generous hospitality and support.

Registry No. Alanine, 56-41-7; serine, 56-45-1.

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(37) Frisch, M. J.; Del Bene, J. E.; Binkley, J. S.; Shaefer, H. F., III *J. Chem. Phys.* **1986**, *84*, 2279.

(38) Schwenke, D. W.; Truhlar, D. G. *J. Chem. Phys.* **1985**, *82*, 2418.

(39) Greenwood, H. H.; Plant, J. S. *Int. J. Quantum Chem.* **1986**, *30*, 127.

(40) Szczesniak, M. M.; Scheiner, S. *J. Chem. Phys.* **1986**, *84*, 6328.

(41) Bonaccorsi, R.; Cammi, R.; Tomasi, J. *Int. J. Quantum Chem.* **1986**, *29*, 373.

(42) For an extended review on the basis sets we refer to the very recent work by Davidson and Feller: Davidson, E. R.; Feller, D. *Chem. Rev.* **1986**, *86*, 681.

(43) Kolos, W. *Theor. Chim. Acta (Berlin)* **1979**, *51*, 219.

(44) Clementi, E. *J. Phys. Chem.* **1985**, *89*, 4426.

Brønsted Basicity of Atomic Oxygen on the Au(110) Surface: Reactions with Methanol, Acetylene, Water, and Ethylene

Duane A. Outka and R. J. Madix*

Contribution from the Departments of Chemical Engineering and Chemistry, Stanford University, Stanford, California 94305. *Received May 1, 1986*

Abstract: The adsorption and reactions of methanol, acetylene, water, and ethylene were investigated on clean and oxidized Au(110) surfaces by temperature-programmed reaction spectroscopy. All of these molecules are only weakly and molecularly adsorbed on the clean Au(110) surface. Methanol, acetylene, and water, however, react with the oxidized surface. Methanol, activated by 0.25 monolayer of oxygen adatoms, reacts to form water, methyl formate, hydrogen, and carbon dioxide. A stable methoxy intermediate is identified in these reactions. Acetylene reacts to form water and carbon dioxide, and water is more strongly bonded to the Au(110) surface in the presence of oxygen adatoms. Ethylene is the only one of these molecules which does not react with oxygen adatoms on Au(110). This pattern of reactivity parallels that associated with the acidity of these molecules as measured in the gas phase which has been observed on Cu(110) and Ag(110) surfaces. These results complete the studies necessary to demonstrate the Brønsted base character of oxygen adatoms on all of the group 1B metals.

1. Introduction

Atomic oxygen activates copper and silver surfaces toward reaction with a variety of molecules. One of the principal mechanisms for this activation is a Brønsted base reactivity where atomic oxygen abstracts an acidic hydrogen atom from an adsorbed molecule. Among the molecules for which this reaction occurs are formic acid,[1-5] methanol,[6-9] acetylene,[10,11] ethanol,[12] water,[13,14] acetic acid,[15] hydrogen sulfide,[16] hydrogen chloride,[16] and propylene.[17] In the absence of oxygen adatoms, some of these molecules are completely unreactive, particularly on silver surfaces. Despite the diverse functional groups of the molecules involved, the reactivity of oxygen toward these molecules on copper or silver

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(1) Sexton, B. A. *Surf. Sci.* **1979**, *88*, 319.

(2) Ying, D. H. S.; Madix, R. J. *J. Catal.* **1980**, *61*, 48.

(3) Barteau, M. A.; Bowker, M.; Madix, R. J. *Surf. Sci.* **1980**, *94*, 303.

(4) Bowker, M.; Madix, R. J. *Surf. Sci.* **1981**, *102*, 542.

(5) Sexton, B. A.; Madix, R. J. *Surf. Sci.* **1981**, *105*, 177.

(6) Wachs, I. E.; Madix, R. J. *J. Catal.* **1978**, *53*, 208.

(7) Wachs, I. E.; Madix, R. J. *Surf. Sci.* **1978**, *76*, 531.

(8) Felter, T. E.; Weinberg, W. H.; Lastushkina, G. Y.; Zhdau, P. A.; Boneskov, G. K.; Hrbek, J. *Appl. Surf. Sci.* **1983**, *16*, 351.

(9) Bowker, M.; Madix, R. J. *Surf. Sci.* **1980**, *95*, 190.

(10) Barteau, M. A.; Madix, R. J. *Surf. Sci.* **1982**, *115*, 355.

(11) Outka, D. A.; Friend, C. M.; Jorgensen, S.; Madix, R. J. *J. Am. Chem. Soc.* **1983**, *105*, 3468.

(12) Wachs, I. E.; Madix, R. J. *Appl. Surf. Sci.* **1978**, *1*, 303.

(13) Bowker, M.; Barteau, M. A.; Madix, R. J. *Surf. Sci.* **1980**, *92*, 528.

(14) Spitzer, A.; Lüth, H. *Surf. Sci.* **1982**, *120*, 376.

(15) Bowker, M.; Madix, R. J. *Appl. Surf. Sci.* **1981**, *8*, 299.

(16) Moroney, L.; Rassias, S.; Roberts, M. W. *Surf. Sci.* **1981**, *105*, L249.

(17) Barteau, M. A.; Madix, R. J. *J. Am. Chem. Soc.* **1983**, *105*, 344.

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surfaces has been shown to be related to their acidity as measured in the gas phase.[18,19] Recently, atomic oxygen has been shown to bind *reversibly* to the surface of the other group 1B metal, gold.[20,21] In this study we have examined atomic oxygen on the Au(110) surface for this Brønsted base reactivity toward a variety of molecules using temperature-programmed reaction spectroscopy (TPRS).

Few previous reaction studies have been performed on gold surfaces under ultrahigh vacuum (UHV) conditions because of the low reactivity of this metal. Of the molecules under consideration in this study, only multilayers of water have been studied on gold under UHV conditions.[22] Other molecules of interest to the theme of this paper have been studied, however. In particular, the adsorption of formic acid, HCOOH, has been examined on several crystallographic faces of gold with a diverse variety of reactions reported.[23-26] On the Au(110) surface, however, the behavior is quite similar to that observed on Ag(110) surfaces, as formic acid is unreactive toward the clean surface but reacts in a Brønsted acid–base manner with oxygen adatoms.[25] Formic acid adsorption on clean Au(111) surfaces is also molecular.[26] Oxygen adatoms have also been observed to activate the Au(110) surface toward the adsorption of formaldehyde by nucleophilic attack.[25]

Several studies of gold reactivity have also been performed near ambient pressure conditions in order to evaluate catalytic reactivity.[28,29] Methanol oxidation on gold has been of particular interest for comparison to copper and silver, which is used as an industrial catalyst for conversion of methanol to formaldehyde. In these studies gold is reported to catalyze the oxidation of methanol to formaldehyde and water with little CO or CO_2 production. The oxidation of ethylene on gold has also been reported to proceed to CO_2 and H_2O.[30]

In this study, the reactivity of oxygen adatoms toward a variety of molecules is found to correlate with the acidity of the molecules involved. This pattern of reactivity is the same as that found for atomic oxygen on copper and silver surfaces. In addition, a methoxy group, CH_3O is identified as an intermediate in the oxidation of methanol.

2. Experimental Section

The experiments were performed in a stainless steel vacuum chamber with a base pressure of 8×10^{-10} torr. The chamber was equipped with a double-pass cylindrical mirror analyzer for Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED) to check surface order. The TPRS was performed with simultaneous monitoring of up to eight different *m/e* signals by computer control of the mass spectrometer.

The Au(110) crystal was cleaned using the procedure of ref 20. In particular, no silicon or calcium impurities were detected by examining the surface for their AES signals at 1620 and 280 eV, respectively. The absence of these impurities was also indicated by the reversible adsorption of atomic oxygen.[20,21] Low-energy electron diffraction examination of the surface showed the characteristic p(1×2) reconstruction of the clean Au(110) surface.[33-35]

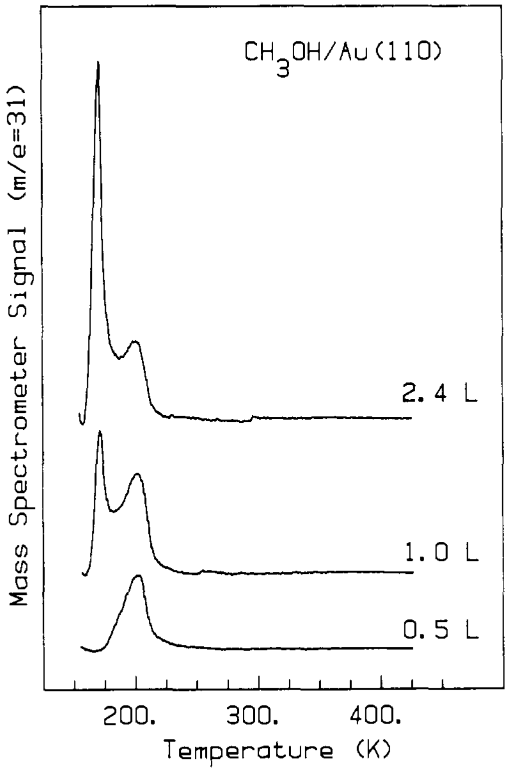

Figure 1. TPD spectra for methanol desorption from the clean Au(110) surface as a function of coverage. The two desorptions at 200 and 175 K are attributed to a monolayer and multilayer, respectively. The heating rate was 3 K s^{-1}.

Atomic oxygen adsorption was induced by a platinum filament located 5 mm in front of the sample and heated to 1400 K during oxygen treatment at 5×10^{-7} torr.[20] This treatment did not deposit platinum on the sample as indicated by the absence of the Pt AES peaks at 1967 or 2044 eV. Oxygen adsorption was performed with the sample cold (120 K), or cooling, followed by a momentary anneal to 475 K in order to ensure the absence of any molecular oxygen state and to provide a uniform thermal treatment for the oxygen adlayers.

The coverages of atomic oxygen on the Au(110) surface were estimated from AES. Like Pt(110)[34] and Ir(110),[35] no ordered atomic oxygen overlayers were formed on Au(110) surface, so coverages could not be correlated with LEED. Therefore, the coverage of oxygen was estimated from the ratio of the $dN(E)/dE$ peak heights of the O (KVV) AES signal at 520 eV to the Au peak at 238 eV. The O/Au AES ratio was converted to coverage by comparison to the O/Pt AES ratio of 0.3 observed for a p(2×2) oxygen adlayer on Pt(111) which correspond to 3.9×10^{14} oxygens atoms cm^{-2}.[36] This calibration was corrected for the relative sensitivity of the AES transition for the different metals: Au(238)/Pt(237) = 0.95.[37] Thus a typical oxygen coverage on Au(110) with an O/Au AES ratio of 0.3 corresponds to 4.1×10^{14} oxygen atoms cm^{-2}. This is equivalent to 0.24 monolayer where 1.0 monolayer is defined as 1.7×10^{15} atoms cm^{-2}, which includes all of the exposed gold atoms in the top three rows of the reconstructed (110) surface.

The methanol was treated with a drying agent, anhydrous $MgSO_4$, to remove traces of water, and dissolved air was removed by freeze–pump–thaw cycles. Labeled methanol, CD_3OH (99% D), was obtained from Stohler Chemicals. The acetylene (99.6%) was passed through a dry ice–acetone bath to remove traces of an acetone stabilizer. Labeled acetylene, C_2D_2 (99+% D), was obtained from Merck and Co. and used without further purification. The water sample was triply distilled and degassed by heating to boiling for several minutes. The ethylene was of 99.5% purity and used without further purification. Exposures of all gases are reported using uncorrected ion gauge readings.

3. Results and Analysis

a. Methanol. Methanol was adsorbed molecularly on the clean Au(110) surface. Figure 1 shows the temperature-programmed

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(18) Barteau, M. A.; Madix, R. J. *Surf. Sci.* **1982**, *120*, 262.
(19) Jorgensen, S. W.; Madix, R. J. *Surf. Sci.* **1983**, *130*, L291.
(20) Canning, N. D. S.; Outka, D.; Madix, R. J. *Surf. Sci.* **1984**, *141*, 240.
(21) Pireaux, J. J.; Chtaib, M.; Delrue, J. P.; Thiry, P. A.; Liehr, M.; Caudano, R. *Surf. Sci.* **1984**, *141*, 211, 221.
(22) Brundle, C. R.; Roberts, M. W. *Surf. Sci.* **1973**, *38*, 234.
(23) Chtaib, M.; Delrue, J. P.; Caudano, R. *Phys. Scr.* **1983**, *T4*, 133.
(24) Chtaib, M.; Thiry, P. A.; Delrue, J. P.; Pireaux, J. J.; Caudano, R. *J. Electron Spectros. Relat. Phenom.* **1983**, *29*, 293.
(25) Outka, D. A.; Madix, R. J. *Surf. Sci.* **1987**, *179*, 361.
(26) Chtaib, M.; Thiry, P. A.; Pireaux, J. J.; Delrue, J. P.; Caudano, R. *Surf. Sci.* **1985**, *162*, 245.
(27) Outka, D. A.; Madix, R. J. *Surf. Sci.* **1987**, *179*, 351.
(28) Kishimoto, S. *J. Phys. Chem.* **1973**, *77*, 1719.
(29) Schwank, J. *Gold Bull.* **1983**, *16*, 4.
(30) Cant, N. W.; Hall, W. K. *J. Phys. Chem.* **1971**, *75*, 2914.
(31) Wolf, D.; Sagodzinski, H.; Moritz, W. *Surf. Sci.* **1978**, *77*, 265, 283.
(32) Kuk, Y.; Feldman, L. C.; Robinson, I. K. *Surf. Sci.* **1984**, *138*, L168.
(33) Robinson, I. K. *Phys. Rev. Lett.* **1983**, *50*, 114.
(34) Wilf, M.; Dawson, P. T. *Surf. Sci.* **1977**, *65*, 399.
(35) Nieuvwnhuys, B. E.; Somorjai, G. A. *Surf. Sci.* **1972**, *72*, 8.
(36) Gland, J. L. *Surf. Sci.* **1980**, *93*, 487.
(37) *Handbook of Auger Electron Spectroscopy*, 2nd ed.; Physical Electronics: Eden Prairie, MN, 1976.

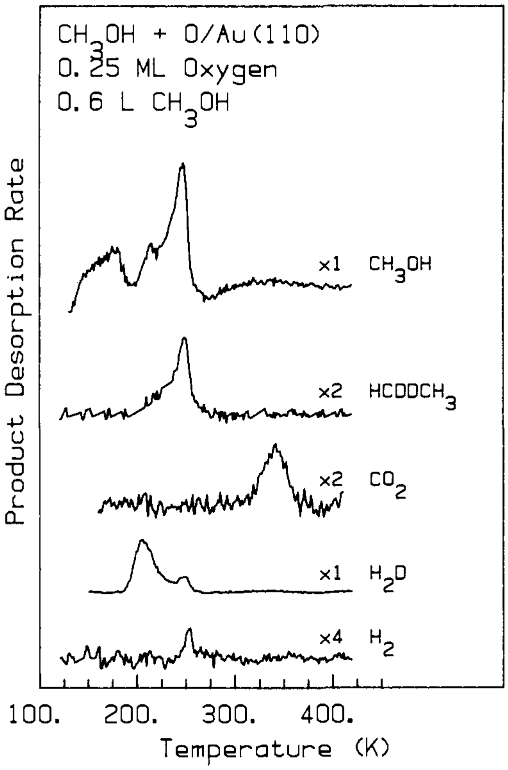

Figure 2. TPRS following exposure of 0.6 L (approximately 0.13 monolayer) of methanol onto an Au(110) surface with 0.25 monolayer of oxygen adatoms. In this experiment the oxygen adatoms were in excess. The spectra of CH_3OH and H_2O have been corrected to remove interference from cracking of the other products, and all of the peaks have been corrected to account for their different sensitivities in the mass spectrometer.[48,49] The heating rate was 11 K s^{-1}.

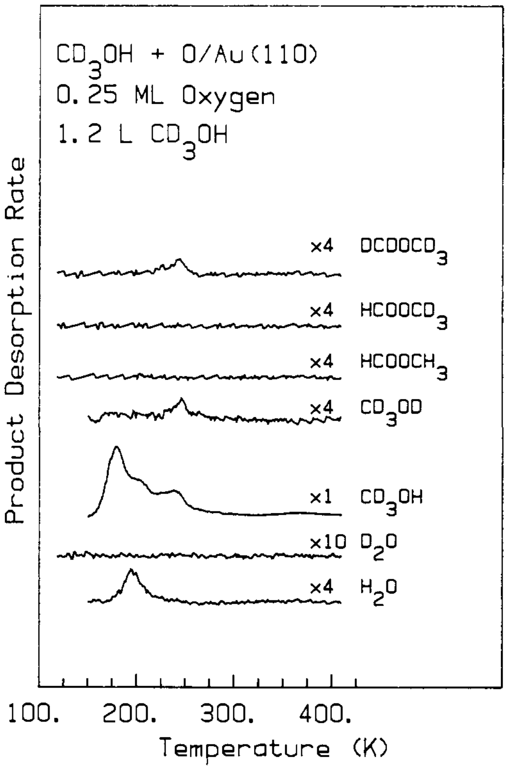

Figure 3. TPRS following exposure of 1.2 L (approximately 0.25 monolayer) of CD_3OH onto an Au(110) surface with 0.25 monolayer of oxygen adatoms. In this experiment the oxygen adatoms were in excess. The spectra of H_2O, CD_3OH, and CD_3OD have been corrected to remove interference from cracking of the other products, and all of the peaks have been corrected to account for their different sensitivities in the mass spectrometer.[50] The heating rate was 11 K s^{-1}.

desorption (TPD) of methanol (*m/e* 31) from the clean Au(110) surface as a function of coverage. Desorption peaks were observed at 200 and 175 K. There were no indications of decomposition products such as H_2O (*m/e* 18), H_2 (*m/e* 2), CO (*m/e* 28), or CO_2 (*m/e* 44) during heating, nor was there residual carbon or oxygen on the surface at temperatures above the desorption peaks. The absence of decomposition products and the low temperatures of desorption indicate that the methanol is molecularly adsorbed in these two states. The desorption peak at 200 K filled first and is ascribed to methanol in direct contact with the surface, a monolayer state. The activation energy for desorption of this state was estimated to be 12 kcal mol^{-1} from the peak desorption temperature, assuming a preexponential factor of 1×10^{13} s^{-1}. The lower temperature peak did not saturate with exposure and showed behavior expected for a zero-order reaction and is ascribed to multilayer adsorption.

Methanol reacted on the Au(110) surface in the presence of oxygen adatoms. Figure 2 shows the TPRS following an exposure of 0.6 L (1.0 L is an exposure equivalent to 1×10^{-6} torr for 1 s—approximately 0.13 monolayer) of methanol onto a surface containing 0.25 monolayer of oxygen adatoms. The oxygen adatoms were consumed by reaction with the methanol upon adsorption and during heating, since no recombination and desorption of oxygen were observed near the expected desorption temperature of 600 K. Oxidation of the methanol was also indicated by the evolution of water and other oxidation products. The various products were desorbed at three distinct temperatures corresponding to distinct surface reactions. The first reaction occurred at 200 K where H_2O was detected. Isotope experiments showed (see below) that this was due to abstraction of the hydroxyl hydrogen of methanol by oxygen adatoms to form surface hydroxyls which subsequently formed water. Molecularly adsorbed methanol was also observed to desorb below 200 K. The second reaction occurred at 250 K where methanol, methyl formate, water, and traces of hydrogen were desorbed. Isotope experiments link these products to the reactions of a methoxy group. The third reaction occurred at 340 K where CO_2 was desorbed. This is the characteristic temperature for formate (HCO_2) decomposition on Au(110),[25] indicating that formate is a side product of methanol oxidation. Formaldehyde was not a product of methanol oxidation on Au(110), which is unusual because it is the principal product of methanol oxidation on Cu(110) and Ag(110). The experiments here were performed at relatively high oxygen coverages, however, so that further study will be required to determine if formaldehyde is produced on gold at lower surface concentrations.

Atomic oxygen reacted with methanol like a Brønsted base to abstract the acidic hydroxyl hydrogen. This behavior is deduced from experiments with labeled methanol, CD_3OH (Figure 3). Figure 3 shows that oxidation of CD_3OH produced water at 200 K which was entirely H_2O with no D_2O. Thus the first reaction in methanol oxidation is attributed to abstraction of the acidic hydroxyl hydrogen by oxygen adatoms to form $OH_{(a)}$ or $H_2O_{(a)}$. These latter species recombine or desorb at 200 K as H_2O with the overall reaction:

$$2CD_3OH_{(a)} + O_{(a)} \rightarrow H_2O_{(g)} + 2CD_3O_{(a)} \qquad (1)$$

The second step in methanol oxidation was the reactions of the methoxy group at 250 K. This was deduced from experiments with CD_3OH and the desorption of completely deuterated products at this temperature. Figure 3 shows that these products were CD_3OD (major fragment, *m/e* 34) and $DCOOCD_3$ (*m/e* 64). Note that the starting material was CD_3OH so that CD_3OD must have come from methoxy decomposition. The first step in this decomposition was cleavage of a C–D bond:

$$2CD_3O_{(a)} \rightarrow CD_2O_{(a)} + CD_3OD_{(g)} \qquad (2)$$

with the deuterium being scavenged by another methoxy to form $CD_3OD_{(g)}$. Gold is unique in that the remaining surface species, formaldehyde (CD_2O), did not desorb as on Cu(110) and Ag(110). A simple explanation for this comes from previous studies of formaldehyde adsorption on an oxidized Au(110) surface[25] where

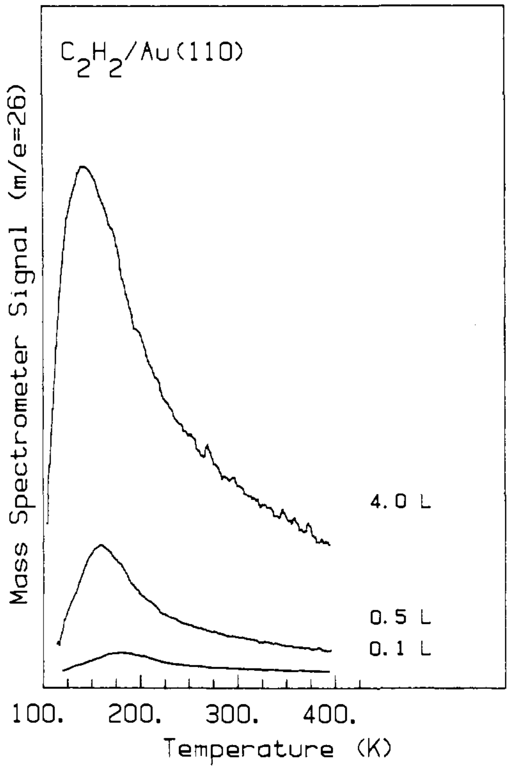

Figure 4. TPD spectra of acetylene from the clean Au(110) surface as a function of coverage. The heating rate was 3 K s^{-1}.

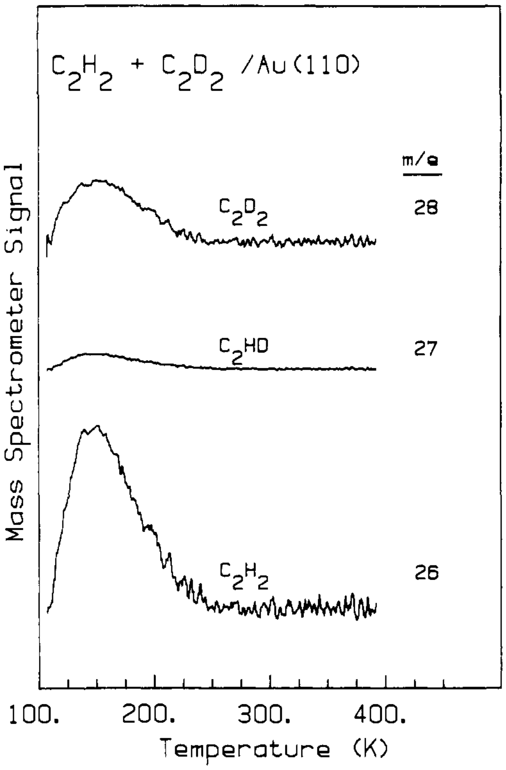

Figure 5. TPD spectrum following the coadsorption of 0.25 L (approximately 0.06 monolayer) each of C_2H_2 and C_2D_2 onto a clean Au(110) surface. The acetylene was deduced to be adsorbed molecularly since no significant C_2HD (*m*/*e* 27) was desorbed. The heating rate was 11 K s^{-1}. All of the curves are on the same scale.

it was found that formaldehyde did not desorb until 285 K. Instead, it is proposed that a reaction between formaldehyde and methoxy occurs which accounts for the methyl formate evolved:

$$CD_3O_{(a)} + CD_2O_{(a)} \rightarrow DCOOCD_{3(g)} + D_{(a)} \qquad (3)$$

The deuterium atom is largely scavenged by methoxy to form more CD_3OD:

$$CD_3O_{(a)} + D_{(a)} \rightarrow CD_3OD_{(g)} \qquad (4)$$

This explains the appearance of completely deuterated methyl formate with no partially hydrogenated products such as $HCOOCD_3$ (*m*/*e* 63) or $HCOOCH_3$ (*m*/*e* 60). This mechanism is proposed rather than one involving a $CDO_{(a)}$ intermediate because formaldehyde itself does not form such a species on an oxidized Au(110) surface.[25] The presence of the methoxy and/or atomic oxygen on the Au(110) surface also appears to stabilize molecular methanol CD_3OH to a temperature higher than normal, 250 K. This is presumably due to hydrogen bonding between these two species. This methanol is not directly involved in the decomposition of methoxy, however, since no hydrogen was incorporated into the products of the further reaction of the methoxy. From the peak temperature of the methoxy decomposition the activation energy was estimated to be 14 kcal mol^{-1}, assuming a preexponential factor of 1×10^{13} s^{-1}. For comparison, log (preexponential factor) on Cu(110) has been measured to be 12.7.[7]

The third step in methanol oxidation is decomposition of a formate intermediate at 340 K. Formic acid and formaldehyde oxidation on Au(110)[25] have been observed to form a formate species which decomposes at this temperature. The formation of formate from methoxy probably occurs by oxidation of the adsorbed formaldehyde resulting from methanol oxidation, which is a reaction which has been identified on Au(110).[25]

b. Acetylene. Acetylene was molecularly adsorbed on the clean Au(110) surface and desorbed without decomposition. Figure 4 shows the TPD of C_2H_2 from the clean Au(110) surface as a function of coverage. A single broad desorption peak was observed between 125 and 200 K. No decomposition products such as H_2, C_2H_4 (*m*/*e* 28), C_2H_6 (*m*/*e* 30), or C_6H_6 (*m*/*e* 78) were detected during heating, nor was there residual carbon on the surface following heating to above the desorption peak. The adsorption of acetylene was completely molecular as shown by the absence of isotope exchange between coadsorbed C_2H_2 and C_2D_2 (Figure 5). In this experiment 0.25 L each of C_2H_2 and C_2D_2 were coadsorbed onto a clean Au(110) surface. The C_2D_2 parent ion is *m*/*e* 28 and the C_2H_2 parent ion is *m*/*e* 26 (approximately 20% of the *m*/*e* 26 peak was due to cracking of C_2D_2). The *m*/*e* 27 signal was due exclusively to C_2HD and was less than 5% of the size of the acetylene desorbed; it was attributed to an impurity in the C_2D_2 and C_2H_2. Thus isotopic exchange did not occur for acetylene on the Au(110) surface, implying that the adsorption was molecular. The acetylene desorption peak was rather broad and had an ill-defined shape. The breadth of this peak was not due to desorption from crystal supports since there was a collimator over the ionizer of the mass spectrometer. Neither was width of this peak due to pumping since quite narrow desorption peaks were observed for water and methanol which have comparable pumping speeds. The width of the acetylene desorption was typical of nonhydrogen-bonded adsorbates on Au(110). The reason for this broad desorption profile is not obvious, but one explanation is that the nonhydrogen-bonded molecules are so weakly attracted to the surface that they have no well-defined binding site. Therefore, they occupy a variety of binding sites with a variety of binding energies and consequently desorb in a broad peak. A rough estimate of the desorption activation energy for acetylene is 10 kcal mol^{-1}.

Acetylene was reactively chemisorbed on the Au(110) surface in the presence of oxygen adatoms, however. Figure 6 shows the TPRS following an exposure of 0.25 L of C_2H_2 onto a surface with 0.6 monolayer of $O_{(a)}$. The oxidation products were H_2O at 205 K and CO_2 at 525 K. Unreacted acetylene desorbed near 150 K while unreacted oxygen desorbed near 600 K. No H_2, CH_4 (*m*/*e* 16), or additional C_2H_2 peaks were observed. A peak for CO (*m*/*e* 28) was observed coincident with the CO_2 desorption, but it is attributed to a cracking fragment of the CO_2.

Oxygen atoms reacted with acetylene like a Brønsted base, deduced from the desorption temperature of the water from acetylene oxidation, 205 K, the same temperature at which water

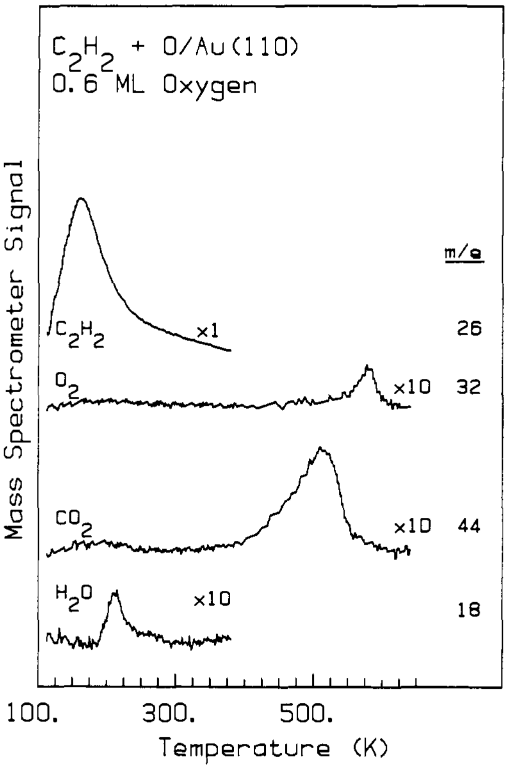

Figure 6. TPRS following exposure of 0.25 L (approximately 0.06 monolayer) of acetylene onto the Au(110) surface with 0.6 monolayer of oxygen adatoms. The oxidation products were H_2O at 215 K and carbon dioxide at 500 K. Excess acetylene and oxygen desorbed at their usual temperature, approximately 150 and 600 K, respectively. The heating rate was 11 K s^{-1}.

evolution due to reaction with formic acid[25] and methanol (see above) occurred on Au(110). This result suggests the following overall reaction:

$$2C_2H_{2(a)} + O_{(a)} \rightarrow 2C_2H_{(a)} + H_2O_{(g)} \tag{5}$$

Since no other hydrogen-containing product was evolved, the hydrogen removal apparently continued at 205 K:

$$2C_2H_{(a)} + O_{(a)} \rightarrow H_2O_{(g)} + C_{2(a)} \tag{6}$$

There was no indication of a stable $C_2H_{(a)}$ intermediate as observed on Ag(110) where a second C_2H_2 desorption was observed due to $C_2H_{(a)}$ disproportionation.[10] Instead the residual carbon merely reacted with oxygen adatoms near 500 K to evolve $CO_{2(g)}$. Because of the high coverages of oxygen used in these studies, however, we cannot rule out entirely the possible existence of a stable C_2H species on Au(110) at low oxygen coverages.

c. Water. Water was molecularly adsorbed on the clean Au(110) surface. Figure 7 shows the TPD of water from the clean Au(110) surface. Two desorption peaks were observed at 190 and 185 K which are attributed to monolayer and multilayers, respectively. The activation energies for desorption of these are estimated to be 11–12 kcal mol^{-1} assuming a preexponential factor of 1×10^{13} s^{-1}. Both peaks had a zero-order shape as suggested by the steep trailing edge and increase in peak temperature with coverage. The desorption of a multilayer is usually zero order, but the zero-order desorption of a monolayer is unusual. For example, the desorption of methanol from the monolayer in Figure 1 is not zero order. Such a shape may also suggest attractive interactions between the adsorbed water molecules in the monolayer which is consistent with the tendency of water to form hydrogen bonds. Following the desorption of water from Au(110) there was no residual oxygen on the surface to indicate decomposition. Thus the adsorption was molecular.

Following the adsorption of water of an oxidized Au(110) surface, a new TPRS peak was observed at 215 K ascribed to either oxygen-stabilized water or disproportionation of surface hydroxyl groups. Figure 8 shows the TPRS following adsorption of H_2O onto a surface with 0.4 monolayer of $^{18}O_{(a)}$. The normal water desorption peak was observed at 190 K. The oxygen label was extensively mixed with the adsorbed water owing to the ease

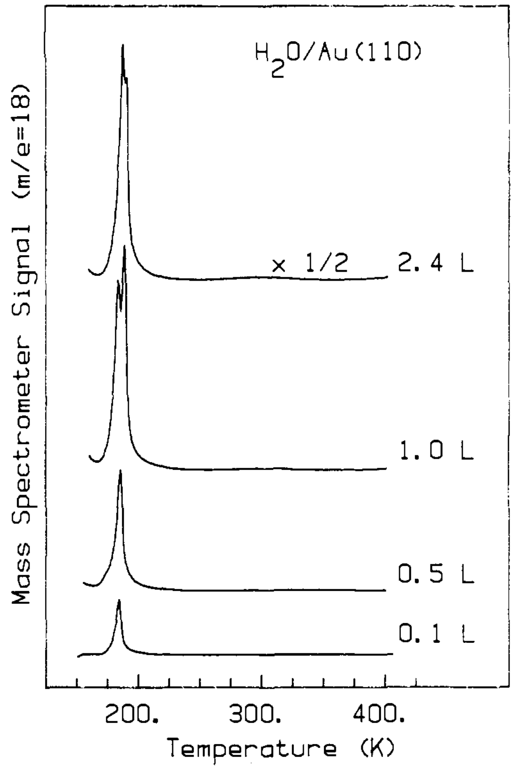

Figure 7. TPD spectra of water from the clean Au(110) surface as a function of coverage. The two desorption peaks at 190 and 185 K are attributed to a monolayer and multilayer state, respectively. The heating rate was 3 K s^{-1}.

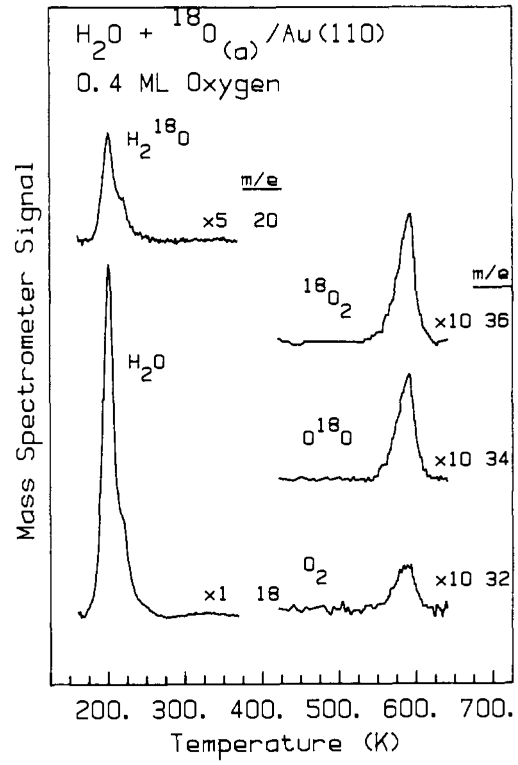

Figure 8. TPRS following exposure of 1.0 L of water onto an Au(110) surface with 0.4 monolayer of oxygen-18 adatoms. An oxygen-stabilized water state was observed as a shoulder at 215 K. Excess water and oxygen desorbed at their usual temperatures, 190 and 600 K, respectively. The heating rate was 11 K s^{-1}.

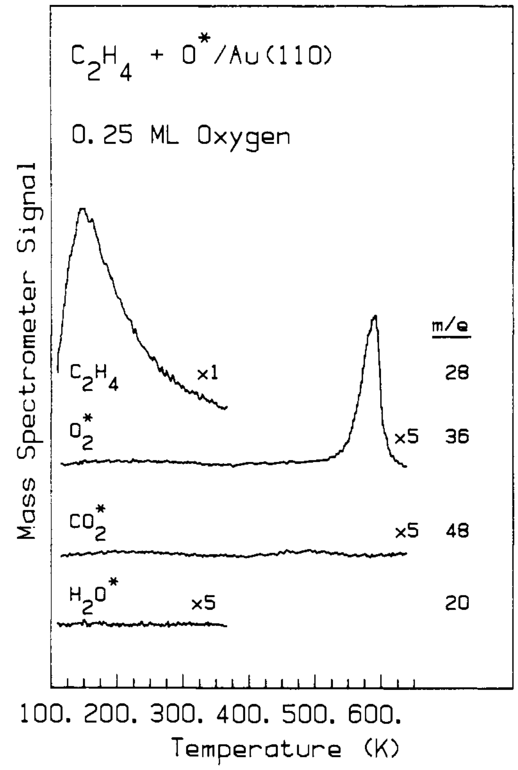

Figure 9. TPD spectrum following exposure of 1.0 L (approximately 0.25 monolayer) of C_2H_4 onto an Au(110) surface with 0.25 monolayer of oxygen-18 adatoms. No reaction occurred. Ethylene and oxygen desorbed at the same temperatures as observed on the clean Au(110) surface, approximately 150 and 600 K, respectively. The heating rate was 11 K s^{-1}.

of the realignment of the hydrogen bonds in water. The mixing was not complete, however, since the adsorbed water contained predominately ^{16}O while the oxygen adatoms which desorbed near 600 K contained predominately ^{18}O. In addition to the isotope mixing, the presence of oxygen adatoms led to a shoulder in the water desorption at 215 K. This was especially apparent in the $H_2{}^{18}O$ (*m/e* 20) spectrum. This shoulder was within 5 K of the water desorption peaks in the oxidation of formic acid,[25] methanol, and acetylene on Au(110), suggesting that they have a common origin. There are two possibilities. The first is hydroxyl recombination:

$$2OH_{(a)} \rightarrow H_2O_{(g)} + O_{(a)} \qquad (7)$$

The second possibility is oxygen-stabilized water either through hydrogen bonding or indirectly via changes in the surface electronic state. Further spectroscopic studies are required to distinguish between these possibilities.

d. Ethylene. Ethylene was molecularly adsorbed on both the clean and oxidized Au(110) surface. Figure 9 shows the TPD following exposure of 1.0 L of C_2H_4 onto a surface with 0.25 monolayer of ^{18}O adatoms. On the clean or oxidized surface a broad C_2H_4 desorption was observed in the range 100–200 K, rather like acetylene. As noted earlier, such broad desorption peaks were common for non-hydrogen-bonded molecules studied here. Also like acetylene, there was no evidence for ethylene decomposition on clean Au(110) such as H_2 or C_2H_6 desorption or residual carbon on the surface after desorption. Ethylene differed from acetylene, however, in that no reaction occurred with oxygen adatoms. For example, Figure 9 shows no $H_2{}^{18}O$ (*m/e* 20) or $C^{18}O_2$ (*m/e* 48) desorption. Only C_2H_4 desorption near 150 K and $^{18}O_2$ desorption near 600 K are observed. The absence of any oxidation products from ethylene clearly indicates that its adsorption on Au(110) was molecular.

4. Discussion

Gold is well-known for its resistance to corrosion, and the weak adsorption observed in this study on the clean Au(110) surface is consistent with this low reactivity. This weak adsorption behavior also establishes a trend of decreasing reactivity on descending elements of the group 1B column of the periodic table. For example, the molecular binding energies of the species studied on clean Au(110) were less than or comparable to those on Ag(110) and usually substantially less than on Cu(110). In the case of methanol, the energies for desorption from the monolayer states from these metals are 12 kcal mol^{-1} for Au(110), 14.7 kcal mol^{-1} for Ag(110),[7] and 16.7 kcal mol^{-1} for Cu(110).[6] Acetylene and ethylene were only weakly adsorbed on both Au(110) and Ag(110)[13,38,39] with broad desorption maxima at 100–200 K corresponding to binding energies of roughly 10 kcal mol^{-1}, whereas acetylene and ethylene on Cu(110) have desorption activation energies of 22 and 13 kcal mol^{-1}, respectively.[11,40] Water is only weakly adsorbed on all three metals with desorption activation energies of 11–12 kcal mol^{-1} for Au(110), 11.6 kcal mol^{-1} for Ag(110),[41] and 10.5–12.5 kcal mol^{-1} for Cu(110).[42-44] The adsorption of water on clean silver is somewhat anomalous in that no distinct monolayer desorption peak has been observed on a variety of crystal planes.[38,41] The reactivity of the group 1B metals also decreased upon descending the periodic table. Copper is clearly the most reactive since it will dissociatively adsorb acetylene[11,40] and methanol.[6,9] Silver and gold are of lower and comparable reactivities.

Table I. Gas-Phase Acidities and Bond Dissociation Enthalpies

	$\Delta H^\circ_{\text{acid, gas}}$,[a] kcal mol^{-1}	$\Delta H^\circ_D(B-H)$,[b] kcal mol^{-1}
formic acid	345	112
acetylene	376	120
methanol	379	104
water	391	119
ethylene	416	108

[a] Reference 51. [b] Reference 52.

All three of the group 1B metals share the property that oxygen adatoms promote reactions on their surfaces. In this study oxygen adatoms were observed to induce oxidation of CH_3OH and C_2H_2 and create a more strongly bonded water state, possibly by hydrogen transfer to form hydroxyl groups. Oxygen adatoms also induce the same reaction on Ag(110) and enhance the reactivity of Cu(110) as well. This promotion of reactivity does not extend to ethylene on Au(110), which is the same result observed on Cu(110)[11] and Ag(110),[39] under UHV conditions. This pattern of reactivity correlates with the gas-phase acidity (eq 8) of the

$$HB_{(g)} \rightarrow H^+_{(g)} + B^-_{(g)} \qquad \Delta H_{\text{acid}} \qquad (8)$$

molecules involved. For example, Table I shows the gas-phase acidities of the molecules studied here with that of formic acid which also reacts with oxygen adatoms on Au(110).[25]

Ethylene, which has the largest positive value of $\Delta H^\circ_{\text{acid}}$, is the least acidic and does not react on any of the group 1B metals. Table I also shows that the reactivity does not follow the hydrogen bond dissociation energies which would erroneously predict that ethylene would be the second most reactive molecule. These observations indicate that the gas-phase acidity of a molecule is a useful criterion for predicting the susceptibility of a species toward hydrogen abstraction by oxygen adatoms on the Au(110) surface.

The oxidation mechanism for methanol on Au(110) is similar to that on copper and silver surfaces but differs in the products formed, at least at the coverages studied. Methanol oxidation

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(38) Stuve, E. M.; Madix, R. J.; Sexton, B. A. *Surf. Sci.* **1982**, *123*, 491.
(39) Barteau, M. A.; Madix, R. J. *Proc. ICSS-4, ECOSS-3, Cannes*, **1980**, 448.
(40) Avery, N. R. *J. Am. Chem. Soc.* **1986**, *108*, 6711.
(41) Klaua, M.; Madey, T. E. *Surf. Sci.* **1984**, *136*, L42.
(42) Bange, K.; Grider, D. E.; Madey, T. E.; Sass, J. K. *Surf. Sci.* **1984**, *136*, 38.
(43) Sass, J. K.; Richardson, N. V. *Surf. Sci.* **1984**, *139*, L204.
(44) Uy, P. S.; Bardolle, J.; Bujor, M. *Surf. Sci.* **1983**, *129*, 219; **1984**, *139*, L207.

is similar on all of the group 1B metals in that it is initiated by abstraction of the hydroxyl hydrogen and proceeds via a methoxy intermediate. Gold is unusual, however, in that gaseous formaldehyde is not produced. This is attributed to the low decomposition temperature of the methoxy intermediate, 250 K. Methoxy decomposes to form surface formaldehyde, but at this temperature formaldehyde is stable on oxidized gold surfaces so that it continues to react with methoxy or oxygen adatoms to form methyl formate or formate groups, respectively. Actually this behavior is simply an extension of that on copper and silver. For example, the methoxy decomposition temperature is the highest in the case of Cu(110), 375 K, so that the formaldehyde residence time is the shortest.[6,7] In this case, formaldehyde is observed to desorb rather than react to form methyl formate. On the Ag(110) surface, however, the formaldehyde is created at a lower temperature,[7] $\approx$300 K. The residence time for formaldehyde is therefore higher and, indeed, some methyl formate and formate groups are observed to form on Ag(110). As the temperature of the silver is raised, however, more formaldehyde is evolved at the expense of these other products. Thus, despite the differences in products from the various group 1B metals during methanol oxidation, the mechanisms appear to be similar.

Although methanol oxidation at higher pressures over gold catalysts produces predominately formaldehyde, the mechanism is probably similar to that outlined here. The difference in product distribution can be simply attributed to the difference in operating temperature. For the gold catalytic studies, the oxidation is conducted at approximately 600 K[45,46] at which temperature the lifetime of formaldehyde would be too short to react completely to form methyl formate. The lifetime of formaldehyde on the Au(110) surface is inversely related to the rate constant for desorption; this lifetime at 600 K is approximately 4×10^{-10} s. In contrast, the low pressures of this study require that the methoxy decomposition be studied near 250 K where formaldehyde is stable and thus can react to form methyl formate. Further supporting this hypothesis is the observation of methyl formate as one of the products under the catalytic conditions.[47]

The results of this study and two other recent studies[25,27] demonstrate that there are strong parallels in the reactivity of atomic oxygen adsorbed either as a Brønsted base or as a nucleophilic base. In this study atomic oxygen on the Au(110) surface has been shown to react like a Brønsted base by abstracting a hydrogen atom from acidic molecules. The same type of reaction has been observed on various copper and silver surfaces. This strongly suggests that a whole range of acid–base reactions which have been observed on silver and copper surfaces will also occur on gold. For example, oxygen adatoms are expected to promote reactions with alcohols, terminal acetylides, carboxylic acids, water, and other gas-phase Brønsted acids. Additionally, oxygen adatoms on the Au(110) surface have been observed to react like a nucleophilic base toward formaldehyde in a manner analogous to reactions observed on copper and silver surfaces.[25] Thus oxygen is also expected to promote reactions with molecules containing nucleophilic centers such as aldehydes, esters, sulfur dioxide, etc.

Although there are strong similarities in the reactivity of the three group 1B metals, there are some systematic differences in their behavior as well. As noted in the beginning of this Discussion the adsorption strength of several molecules on these metals follows the order Cu > Ag > Au. This same order is found in the metal–hydrogen bond strengths[25] and metal–oxygen bond strengths.[20] The stability of surface intermediates such as the methoxy examined in this study and formate[25] follows the opposite order, however. That is, formate and methoxy are most stable on copper and least stable on gold. This trend seems surprising, at first, since part of the driving force for the decomposition of the surface intermediates is the formation of metal–hydrogen and metal–oxygen bonds which are strongest on copper and least on gold. The reverse order for the decomposition of these surface intermediates suggests that their decomposition is not driven by product formation but instead by the stability of the reactants in the decomposition reaction, that is, the surface intermediates themselves.

Although the slight differences in reactivity of Au(110) vs. Cu(110) and Ag(110) are attributed to basic differences in the chemical reactivity of these elements, it should be pointed out that the Au(110) surface reconstructs to a different surface arrangement of atoms than occurs on Ag(110) or Cu(110). The Au(110) reconstruction has been studied by several techniques and can be roughly described as a (110) surface with missing alternate rows.[31-33] Despite the difference in the surface structure of Au(110), however, the reactions of the clean and oxidized surface observed here and previously[25,27] are similar to those on silver and copper. Furthermore, oxygen activation chemistry of copper and silver shows little dependence upon surface structure. For example, formic acid oxidation on both Cu(110)[2,4] and Cu(100)[1] surfaces proceeds through a formate intermediate, and methanol oxidation on both Ag(110)[6,7] and Ag(111)[8] proceeds through a methoxy intermediate. Thus surface crystallographic effects do not seem to be important in understanding the oxygen activation chemistry of group 1B metals.

5. Conclusions

Methanol, acetylene, water, and ethylene are weakly and molecularly adsorbed on the clean Au(110) surface. Methanol, acetylene, and water, but not ethylene, react with oxygen adatoms on the Au(110) surface. This pattern of reactivity parallels the gas-phase phase acidity of these molecules and follows behavior previously observed on Cu(110) and Ag(110) surfaces. This demonstrates the Brønsted base character of oxygen adatoms on all of the group 1B metals.

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Registry No. Atomic oxygen, 17778-80-2; Au, 7440-57-5; CH_3OH, 67-56-1; $CH\equiv CH$, 74-86-2; H_2O, 7732-18-5; $CH_2=CH_2$, 74-85-1.

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[45] Hodges, C. N.; Roselaar, L. C. *J. Appl. Chem. Biotechnol.* **1975**, *25*, 609.

[46] Hardy, J. G.; Roberts, M. W. *Chem. Commun.* **1971**, 494.

[47] Rao, V. N. *U.S. Patent* 4 219 198, 1983.

[48] *UTI 100C Mass Spectrometer Manual*; UTI, Inc.: Sunnyvale, CA, Appendix B.

[49] The spectra of Figure 2 were corrected to remove interference from the cracking of methyl formate and methanol. To perform this, the mass spectrum of methyl formate was obtained from ref 7, and the mass spectrum of methanol was measured to be *m/e* 32 (65%), 31 (100%), 30 (11%), 29 (81%), 28 (5.4%), 18 (22%), 2 (2.9%). The particular masses monitored for each product were *m/e* 31 for CH_3OH, *m/e* 60 for $HCOOCH_3$, *m/e* 44 for CO_2, *m/e* 18 for H_2O, and *m/e* 2 for H_2.

[50] The masses monitored for each product in Figure 3 were *m/e* 64 for $DCOOCD_3$, *m/e* 63 for $HCOOCD_3$, *m/e* 60 for $HCOOCH_3$, *m/e* 36 for CD_3OD, *m/e* 35 for CD_3OH, *m/e* 20 for D_2O, and *m/e* 18 for H_2O.

[51] Bartmess, J. T.; McIver, R. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: New York, 1979; Vol. 2, p 87.

[52] *Handbook of Chemistry and Physics*; Chemical Rubber Co.: Cleveland, 1985.