the mising energy can all be attributed to formation energy of the radical pair.

Measuring a series of benzophenone/0.3 M aniline samples in EtOH, we observe the slope, $|V|/E_pA$ in Figure 5 corresponding to $\Phi_{nr} = 0.43 \pm 0.06$. The heat of reaction is then just $(1 - \Phi_{nr})h\nu_{exc} = 46 \pm 5$ kcal/mol. The error in the absolute value of the reaction heat results mostly from uncertainty in the calibration curve of Figure 5. Although the error in the absolute value is quite substantial, the internal consistency of our data allows us to assign relative nonradiative yields to better than 0.01.

The measured value of heat of reaction to the radical pair, 46 ± 5 kcal/mol, is in good agreement with the enthalpy of reaction deduced from the thermodynamic cycle of Scheme II.[14] Since the system being studied is not at equilibrium the value that we obtain experimentally is not rigorously the thermodynamic enthalpy of reaction. However, the photoacoustic wave does not significantly alter the pressure of the system; the experiment is performed at nearly constant pressure. Thus, we would expect to obtain good agreement between our measured value and the calculated enthalpy change.

Conclusions

In this paper we report the first direct measurement of the heat of reaction of a metastable photochemical intermediate, the radical pair produced by the reaction of triplet benzophenone with aniline. The pulsed photoacoustic technique used to measure nonradiative energy deposition is both simple and inexpensive. We have demonstrated both theoretically and experimentally that one can obtain quantitative calorimetric information directly by discriminating between heat deposited by long-lived ($\nu\tau \gg 1$) and short-lived ($\nu\tau \ll 1$) transients. In principle, both dynamic and calorimetric information can be obtained in the true point source limit. We have shown, however, that it is not necessary to design experiments to conform to this limit in order to retain calorimetric information.

In addition to the study of solution-phase calorimetry of other metastable species, extension of this work to the study of energy-transfer processes and gas-phase reactions is in progress. We have already used a two-color version of this experiment to measure the intensity-dependent quantum yields and the cross sections for stimulated emission of coumarin dyes.[15]

Acknowledgment. This work is supported by a grant from the National Science Foundation CHE-8117519, and the Camille and Henry Dreyfus Foundation.

Registry No. Aniline, 62-53-3; benzophenone, 119-61-9; fluorenone, 486-25-9; tetraphenylethylene, 632-51-9; anthracene, 120-12-7; rhodamine 6G, 989-38-8; *p*-bis(*o*-methylstyryl)benzene, 13280-61-0.

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Adsorption and Hydrogenation of Acetylene on Cu(110) and Cu(110)–O Surfaces

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Abstract: The chemistry of acetylene adsorbed at a temperature of 170 K on Cu(110) surfaces has been studied as a function of C_2H_2 and oxygen coverage using TPD, TPRS, X-ray PES, UV PES, isotope exchange reactions, AES, and LEED. Acetylene was largely nondissociatively adsorbed on clean Cu(110) with acetylene desorption peaks at 280, 340 and 375 K. Some ethylene formation was detected with a desorption maximum occurring at 340 K. Approximately 11% of the carbon initially adsorbed in the acetylene remained on the surface following ethylene desorption as determined using X-ray PES. Coadsorption of surface hydrogen atoms and acetylene on the Cu(110) surface increased the amount of ethylene formed, and the C_2H_2 which normally desorbed at 340 and 375K was completely hydrogenated to ethylene in the presence of excess surface hydrogen. The C_2H_2 temperature-programmed desorption spectrum obtained following adsorption on the Cu(110)–O surfaces was qualitatively the same as on the clean Cu(110) surface. The extent of acetylene dehydrogenation was greater on the oxidized surface by a factor of 3, indicating that oxygen facilitated acetylene dissociation. Indeed X-ray PES results showed a strong interaction between adsorbed oxygen and acetylene, whereas no such interaction was observed in the X-ray PES of C_2H_4 and $O_{(ads)}$. Water was formed by reaction of $C_2H_{2(a)}$ with $O_{(a)}$ in the temperature range of 200–400 K, and no ethylene formation was detected on the Cu(110)–O surfaces, since the surface hydrogen was removed by adsorbed oxygen to form water.

Introduction

The determination of the adsorption properties of hydrocarbons on clean and chemically modified transition metal surfaces may lead to a fundamental understanding of catalytically important surface processes. Basic ultra-high-vacuum studies may identify important surface intermediates in hydrocarbon reactions and the role of surface impurities in catalytic processes. Acetylene is one of the most widely studied cases of hydrocarbon adsorption and reaction on transition metal surfaces. Acetylene has been a molecule of choice because of its relative structural simplicity and the richness of its catalytic chemistry. To date, acetylene adsorption has been primarily studied on clean transition metal surfaces. Acetylene adsorption on nickel, palladium, and platinum surfaces has been studied with a wide range of ultra-high-vaccum techniques, including UV PES,[1-5] TDS,[1,4-6] EELS,[7-10] and

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LEED.[5,11] On these metals acetylene nondissociatively adsorbs at low temperatures.[1,2] On the other hand, reactions are observed at higher temperatures.

A wide range of chemistry involving CH bond breakage occurs on Ni, Pt, Pd, and Ag. Acetylene is completely dehydrogenated near 300 K[1,3] on nickel surfaces. There is no agreement as to the structure of the surface intermediate formed in the dehydrogenation; CCH, CH_2, and CH have been proposed. There is no evidence for rehydrogenation of the acetylene-derived intermediate under ultra-high-vacuum conditions. However, on Pt(111) and Pd(111) partial hydrogenation to form a CCH_3 species has been proposed on the basis of LEED[11] and EELS[7-10] measurements. Finally, on clean Ag(110), acetylene adsorbs nondissociatively with a desorption temperature of 195 K.[12]

The effect of oxygen adatoms on the surface chemistry of acetylene has been investigated on Ni(111)[5] and Ag(110).[12] In the case of nickel it was suggested that the oxygen pretreatment induced formation of a CH species on the surface[5] on the basis of UV PES, LEED, and TPRS. On oxygen-pretreated Ag(110), acetylene is dehydrogenated below 250 K to form a CCH surface species which subsequently disproportionate to form $C_{2(ads)}$ and gaseous acetylene at 270 K.[12] In both cases, the presence of oxygen adatoms significantly alters the chemistry associated with adsorbed acetylene.

In this work, the reaction and adsorption of acetylene on clean and oxygen-pretreated Cu(110) surfaces were studied. Previous studies of acetylene adsorption on copper surface have been limited in scope. UV PES data are available for acetylene adsorbed on polycrystalline[13] copper at 110 K and Cu(100)[14] at 80 K. These studies considered only the low-temperature nondissociated acetylene phase and did not probe for surface reactions. Here we have utilized a combination of surface techniques to study further the chemistry of acetylene on Cu(110) and Cu(110)–O. Also, the hydrogenation of acetylene to form ethylene was studied and a mechanism is discussed below.

Experimental Section

All experiments were performed in a stainless steel, ultra-high-vacuum system (PHI), with a base pressure of 2×10^{-10} torr, equipped with the capability for X-ray PES, UV PES, AES, LEED, and TPRS described in detail previously.[16]

The X-ray photoelectron spectra were obtained using a Mg-anode X-ray source and a double-pass cylindrical mirror electron energy analyzer. Each spectrum was repeatedly scanned for 40 min, and data were accumulated in a 250-channel multichannel analyzer. Binding energies were measured relative to the $Cu(2p_{3/2})$ peak at 932.2 eV with a precision of ±0.2 eV. Coverages were estimated by comparison to the p(2×1) oxygen structure which was assumed to correspond to a coverage of 0.50 monolayer. This structure was obtained by dosing 100 L of O_2 at 300 K. Further exposure to O_2 did not increase the area of the O(1s) peak. Carbon coverages were estimated relative to the p(2×1) oxygen state using the theoretical cross-section ratio of O/C = 2.85.[16]

Research purity oxygen, ethylene, hydrogen, and deuterium were all obtained from Matheson. The C_2D_2 (99+% D) was obtained from Merck. All gases were used without further purification. Acetylene (99.6% purity, Matheson) was passed over a trap maintained at 195 K to remove the acetone stabilizer. In order to obtain a significant coverage of adsorbed H or D atoms on the Cu surface, hydrogen and deuterium molecules were atomized using the filament of the mass spectrometer while maintaining a H_2 or D_2 background pressure of 5×10^{-9} torr. All gas exposures were carried out at a crystal temperature of 170 K except for oxygen which was dosed at 300 K.

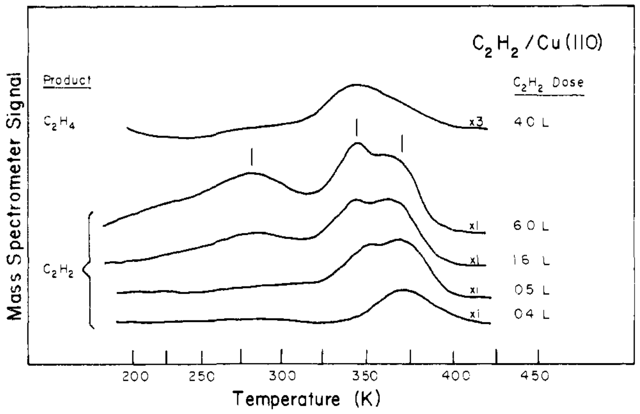

Figure 1. Mass 26 thermal desorption spectra obtained as a function of acetylene exposure. The top spectrum is the ethylene produced from a saturation acetylene dose. The heating rate was approximately 10 K/s. Exposures are accurate only to about a factor of 2.

Results and Discussion

Clean Cu(110). The mass 26 TDS profile obtained for acetylene adsorbed on clean Cu(110) consisted of three desorption maxima with peak positions that were coverage invariant at temperatures of 280, 340, and 375 K (Figure 1). The 375-K peak appeared initially, followed by growth of the 340-K peak as the acetylene coverage was increased. At high acetylene coverage, the two higher temperature desorption peaks were of approximately equal intensity, and the 280-K peak appeared in the spectrum. Isotopic exchange experiments performed with coadsorbed C_2H_2 and C_2D_2 yielded no significant C_2HD in the thermal desorption spectrum. No ordered LEED patterns were observed for adsorbed acetylene in the temperature range of 170–700 K.

The combined results of TPD and isotopic exchange experiments suggest that acetylene adsorbed as a rehybridized C_2H_2 species which was the intermediate in the primary reaction pathway for ethylene formation on the Cu(110) surface. First, when separately adsorbed, ethylene itself desorbed at 210 K with no evidence of reaction. This desorption temperature is characteristic of weak, electron-donor bonding (13 kcal/gmol). Clearly, the high-temperature C_2H_2 desorption states reflect a significantly stronger bond of copper to acetylene (22 kcal/gmol). Second, following acetylene adsorption ethylene also formed by a surface-reaction rate-limiting step with a maximum rate at approximately 340 K. No detectable H_2, CH_4, or C_2H_6 was formed, and no other products were examined. This result indicates that some of the adsorbed acetylene is readily hydrogenated. In order to examine the mechanism of ethylene formation, hydrogen atoms and acetylene were coadsorbed on the Cu(110) surface. As the hydrogen atom coverage was increased, the amount of ethylene formed increased at the expense of the two *higher temperature acetylene desorption peaks*. No H_2 desorbed from the surface in TPRS experiments with coadsorbed hydrogen atoms and acetylene as long as these acetylene desorption peaks were still present. When surface hydrogen was adsorbed in excess of that needed to hydrogenate the adsorbed acetylene, molecular hydrogen was desorbed from the surface, and *all* of the acetylene desorbing in the 340- and 375-K peaks was hydrogenated to form ethylene. In order to further clarify the mechanism, hydrogenation experiments were performed with excess surface deuterium atoms and adsorbed C_2H_2. The predominant isotope of ethylene formed was $C_2D_2H_2$. The relative amount of each isotope formed was $C_2D_2H_2 > C_2D_3H, C_2DH_3 > C_2D_4, C_2H_4$. The absolute amount of each ethylene isotope was dependent on the initial deuterium atom and acetylene coverages. Because of the extent of overlap in the mass spectra of the various ethylene isotopes, no attempt was made to quantify the isotopic distribution. The relevance of these observations to C_2H_2 bonding on copper is discussed below.

The X-ray PES results of a surface initially dosed with acetylene at 170 K and progressively heated also reflected the surface

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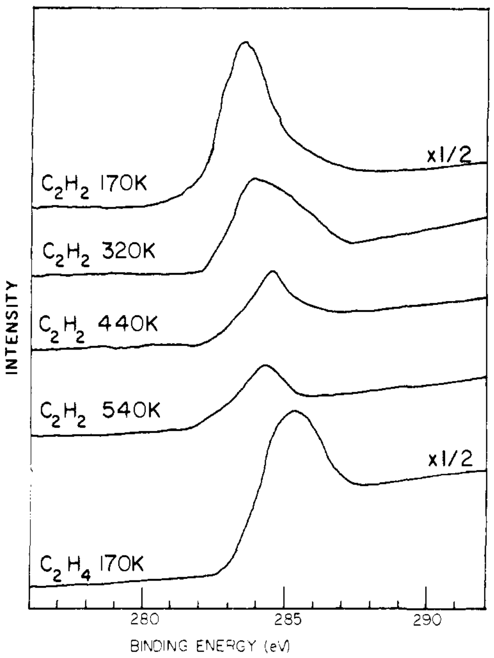

Figure 2. The C(1s) emission in the X-ray PES for C_2H_2 and C_2H_4 on clean Cu(110).

Table I. X-ray PES Data for C_2H_2 Adsorbed on Cu(110)[a]

temp (K)	C(1s) BE (eV)	fwhm (eV)	θ_C
170	283.6	2.1	0.9
320	284.0	2.8	0.3
440	284.5	1.6	0.1
540	284.3	1.8	0.1

[a] X-ray PES data obtained following adsorption of acetylene on clean Cu(110) at 170 K are summarized in the table. The initial acetylene exposure was 7 L. Spectra were taken following heating of the acetylene overlayer to the indicated temperatures. The values at 320 K represent partial desorption of the high-temperature acetylene peaks.

reactions. Changes in the chemical environment of the carbon atoms due to hydrogen-transfer reactions were evident in the X-ray PES (Table I and Figure 2). At 150 K adsorbed acetylene showed a somewhat broadened C(1s) peak at 283.6 eV. At 320 K two-thirds to the acetylene had desorbed, and the C(1s) peak broadened further and shifted toward higher binding energy owing to the presence of reaction intermediates. At temperatures above 420 K acetylene desorption was complete, and the C(1s) X-ray PES peak showed a binding energy of 284.5 eV and was reduced to approximately 11% of its initial intensity. The binding energy of the carbon present above 420 K corresponded to the value of 284.3 eV ascribed previously to atomic carbon on Cu(110).[19] The value of the fwhm of 1.6 eV at 420 K indicated that there was only one type of carbon remaining on the surface following desorption of the acetylene. The nature of this carbon is of chemical interest, since a C_2 species was identified from the reaction of acetylene on an oxidized Ag(110) surface by Barteau and Madix[12] by means of surface titration experiments. Unfortunately, it was not possible to determine if the C–C bond was intact on Cu(110) by either X-ray PES or titration methods. Furthermore, the carbon remaining on the Cu(110) surface following the desorption experiment could not be rehydrogenated to form C_2H_2 or C_2H_4, indicating that rehydrogenation of the residual atomic carbon did not significantly contribute to either acetylene or ethylene formation.

The UV PES data are in agreement with previous work on polycrystalline copper[13] and Cu(100)[14] surfaces. The UV PES of gaseous acetylene was studied by Turner et al.[15] and showed features centered at 11.5, 16.8, and 18.7 (weak) eV, which were assigned to the $1\pi_u$, $3\sigma_g$, and $2\sigma_u$ orbitals, respectively. The He I UV PES of C_2H_2 adsorbed on Cu(110) at 170 K is shown in Figure 3. Upon adsorption the acetylene orbitals have lower binding energies due to a shift in energy reference from vacuum to the Fermi level and due to final state relaxation effects. The ionization feature at 8.6 eV below the Fermi level is assigned as the $3\sigma_g$ acetylene molecular orbital, and the emission centered at 5.35 eV below E_F is attributed to the $1\pi_u$ orbitals with their degeneracy lifted by the Cu(110) surface. Thus, the $1\pi^a$ orbitals are shifted closer to the $3\sigma_g$ orbital by approximately 2.0 eV compared to the gas phase, suggesting a significant amount of interaction of the π orbitals with the metal. These are the same assignments made by Demuth[14] for acetylene adsorbed on Cu(100) at 80 K and are indicative of an adsorbed C_2H_2 species. As noted above, the ethylene desorption temperature was 210 K, corresponding to E_d = 13 kcal/mol,[21] the order of magnitude of the desorption energy expected from simple π-interaction with the Cu surface. Vibrational studies on Cu(100) also suggest that C_2H_4 is bound via the π system with the C–C bond vector essentially parallel to the metal surface.[20] On the other hand, the acetylene desorption temperature of 340–375 K corresponds to a desorption energy of approximately 22 kcal/mol, significantly higher than that obtained for ethylene, indicating a stronger bond with the surface. This conclusion is corrorborated by UV PES results which show that the π orbitals shifted to higher binding energy with respect to the σ level by 1.0 eV for ethylene and 2.0 eV for acetylene[13] in bonding to the surface, indicating a larger degree of bonding for acetylene. It is possible that there is bonding to the metal via one or more π orbitals with some extent of σ interaction with the metal. In addition, the C_2H_2 may be distorted from the gas-phase geometry with the hydrogen atoms bending away from the metal-surface plane. The details of the bonding geometry cannot be determined on the basis of the available data. The ease of hydrogenation of acetylene observed here, in contrast to the absence of ethylene hydrogenation, is suggestive of bond rehybridization involving carbon–metal σ bonds.

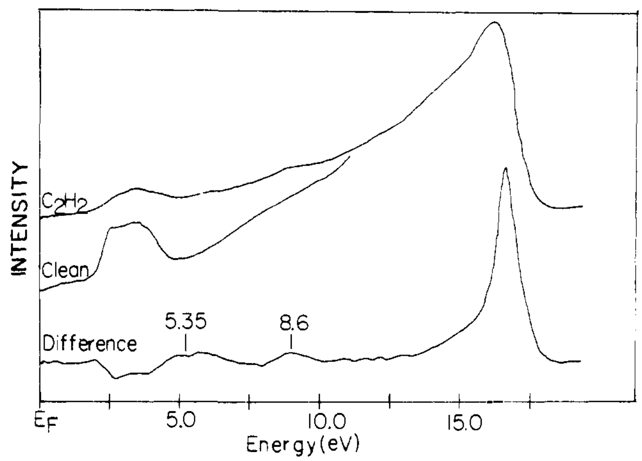

Figure 3. He I UV PES results for acetylene adsorbed on clean Cu(110) at 170 K. The two upper profiles correspond to the actual electron emission from the C_2H_2-covered and clean surfaces. The bottom spectrum is the difference between the acetylene-covered surface and the clean surface.

All of the desorption and spectroscopic evidence is consistent with the following scheme for acetylene desorption and reaction on Cu(110):

$$C_2H_{2(g)} \rightleftharpoons C_2H_{2(a)} \quad (1)$$

$$C_2H_{2(a)} \rightleftharpoons C_2H_{(a)} + H_{(a)} \quad (2)$$

$$C_2H_{2(a)} + H_{(a)} \rightleftharpoons C_2H_{3(a)} \quad (3)$$

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$$C_2H_{(a)} \rightarrow 2C_{(a)} + H_{(a)} \quad (4)$$

$$C_2H_{3(a)} + H_{(a)} \rightarrow C_2H_{4(g)} \quad (5)$$

$$2H_{(a)} \rightleftharpoons H_{2(g)} \quad (6)$$

The lack of H–D exchange between coadsorbed C_2H_2 and C_2D_2 does not prohibit the reversibility of step 2, provided steps 3 and 5 proceed much faster. In such a case, step 2 proceeding forward would provide a source of surface hydrogen which would be consumed by steps 3 and 5 to produce mixed ethylenes. To explain the CD_4 evolved from coadsorbed C_2H_2 and D, either step 3 is reverisble or the reverse of step 2 becomes apparent only at higher deuterium atom coverages. Step 5 is irreversible, based on the lack of H–D exchange when C_2H_4 was coadsorbed with deuterium. Step 4 must be irreversible because the carbon residue from a flash desorption terminated at the completion of C_2H_2 desorption could not be rehydrogenated. Step 6 must be slow with respect to steps 3 and 5 since H_2 formation is observed only when excess hydrogen is coadsorbed with acetylene. This is a rather surprising observation, as H_2 desorption from the clean surface occurs near 350 K and would be expected to compete with acetylene hydrogenation.

Oxygen-Pretreated Cu(110) Surfaces. The product desorption spectrum for C_2H_2 adsorbed on *oxygen-pretreated* Cu(110) surfaces was qualitatively the same as on the clean surface. Mass 26 desorption maxima were observed at 280, 340, and 375 K. Water was the only other detectable product in the spectrum, appearing as a broad desorption feature in the temperature range of 200–400 with maxima at 330 and 370 K. Water evolution above 300 K was reaction limited, given that molecular water desorbs at 140 K[18] and that water formed from reaction of adsorbed OH and H or from hydroxyl recombination desorbs below 300 K.[18,22] Thus a significant amount of acetylene reacted with the adsorbed oxygen above 300 K. No ethylene was evolved from the oxygen predosed surface. Also, when molecular ethylene was dosed onto the Cu(110)–O surface at 210 K, it did not react with the oxygen. Thus none of the H_2O resulted from ethylene which formed and then reacted with the surface oxygen. Clearly, any hydrogen atoms formed from acetylene decomposition reacted preferentially with adsorbed oxygen atoms to form H_2O. All three of the acetylene desorption peaks were temperature invariant as a function of C_2H_2 and oxygen coverage. As in the case of clean Cu(110), the two higher temperature peaks grew in at lower acetylene exposures followed by the appearance of the 280-K desorption feature at high C_2H_2 exposures. No significant H–D exchange was observed in the acetylene desorbed from a coadsorbed layer of C_2H_2 and C_2D_2. The relative intensity of the 340- and 375-K peaks compared to the 280-K acetylene desorption decreased as a function of oxygen coverage as shown in Figure 4. The decrease in the desorption of acetylene at higher temperatures was accompanied by an increase in the amount of H_2O that desorbed from the surface at temperatures greater than 300 K, indicating a greater extent of oxidation relative to acetylene desorption as the oxygen coverage was increased. This was also reflected by a larger deposition of residual carbon. At higher oxygen predoses (>1.0 L) the desorption of both water and high-temperature acetylene decreased because of a decrease in the amount of C_2H_2 that could be adsorbed.

The X-ray PES results obtained for C_2H_2 coadsorbed with atomic oxygen indicated a hydrogen-bonding interaction (Table II). The O(1s) binding energy following oxygen adsorbed on the Cu(110) surface was 529.6 eV in agreement with the results obtained on the Cu(111) surface.[17] The O(1s) binding energy shifted to 531.0 eV when C_2H_2 was adsorbed at 170 K. This shift is not due to adsorbed H_2O or OH since the bulk of the water desorbs above 300 K and its formation is reaction limited; however, acetylene hydrogen-bonded to the surface oxygen may be expected to yield a similar O(1s) chemical shift. For comparison, no shift in the O(1s) binding energy was detected for C_2H_4 adsorbed on the Cu(110)–O surface. The C(1s) binding energy at low temperature was 283.7 eV with a fwhm of 2.0 eV, the same (to within experimental error) as the binding energy on the clean surface. This result indicates that C_2H_2 is adsorbed intact on the surface without appreciable hydrogen transfer to adsorbed oxygen, supporting the conclusion that the O(1s) shift was due to H-bonding. At higher temperature, the C(1s) peak broadened, indicating that more than one type of carbon was formed on the surface, and the O(1s) binding energy shifted to 529.8 eV. Corresponding to this downward shift in binding energy to the value of adsorbed atomic oxygen, water desorbed and the oxygen coverage decreased. There was apparently little interaction between the remaining acetylenic residue and the oxygen. At 660 K the C(1s) binging energy was 284.2 eV, assigned to adsorbed atomic carbon. The increase in the C(1s) binding energy between 440 and 660 K suggests that the residue may not be fully dissociated at 440 K, similar to the behavior on Ag(110).[12]

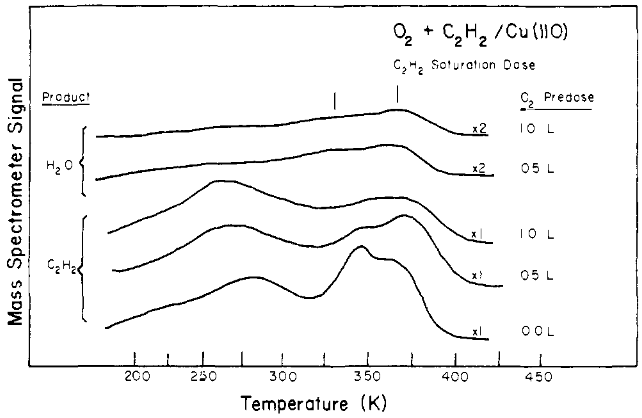

Figure 4. The TPRS for water and acetylene desorption from oxygen pretreated Cu(110) obtained as a function of oxygen exposure. The heating rate was 10 K/s. for cases shown.

Table II. X-ray PES Data for C_2H_2 Adsorbed on Cu(110)–O[a]

temp (K)	C(1s) BE (fwhm) (eV)	θ_C	O(1s) BE (eV)	θ_C
170	283.7 (2.0)	0.4	531.0	0.3
320	283.6 (2.5)	0.4	529.8	0.15
440	283.8 (2.5)	0.3	529.8	0.15
660	284.2 (2.25)	0.3	529.8	0.15

[a] This table presents X-ray PES data collected for C_2H_2 adsorbed on an oxygen-pretreated Cu(110) surface at 170 K. The oxygen exposure was 0.75 L and was carried out at 300 K. Sequential spectra were obtained following annealing of the overlayer at the indicated temperature.

The He I UV difference spectra obtained as a function of temperature are shown in Figure 5. The low-temperature (200 and 280 K) spectra for C_2H_2 adsorbed on the oxygen-pretreated surface were essentially identical with those on clean Cu(110) with the ionization feature 9.0 eV below the Fermi level assigned as the $3\sigma_g$ acetylene molecular orbital, and that centered at 5.2 eV below E_F as the $1\pi_u$-derived orbitals with the degeneracy lifted by the metal surface. At a temperature of 725 K, the ionization features attributable to molecular C_2H_2 disappeared, but the work function decreased with respect to the clean and oxidized surface, indicating the presence of residual carbon.

To summarize, acetylene adsorbed at 170 K largely without dissociation on oxygen-pretreated Cu(110), similarly to the clean Cu(110) surface, though evidence for C_2H_2–oxygen interaction was observed. Based on the UV PES data the acetylene binds via the π orbitals on the preoxidized surface. Some degree of σ-bonding and distortion of the C_2H_2 from its gas-phase geometry is also possible. The oxygen appears to play a dual role in the adsorbed and reaction of acetylene on the Cu(110) surface. Initially, surface oxygen interacts directly with the adsorbed acetylene, most likely via hydrogen bonding. This interaction probably accounts for the increase in the degree of C_2H_2 decomposition on the oxygen-dosed surfaces. The oxygen also scavenges surface

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[22] M. Bowker and R. J. Madix, *Surf. Sci.*, **95**, 190 (1980).

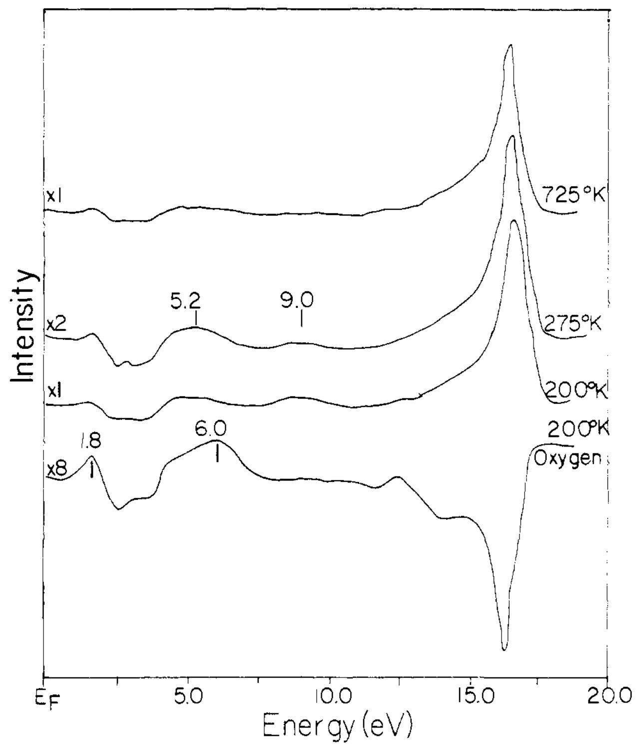

Figure 5. He I UV difference spectra for oxygen and acetylene adsorbed on Cu(110). The bottom spectrum corresponds to atomic oxygen on Cu(110) at 200 K. The upper traces are those obtained for coadsorbed acetylene and oxygen as a function of temperature.

hydrogen to form water, and thus prevents hydrogenation of C_2H_2 to ethylene on Cu(110)–O surfaces.

Conclusion

The investigation of the chemistry of acetylene adsorbed on clean and oxygen-pretreated Cu(110) surfaces has yielded some surprising results. The formation of ethylene on clean Cu(110) is the first reported example of hydrogenation of acetylene under ultra-high-vacuum conditions. It is a very efficient reaction as shown by the TPRS results where all of the acetylene is hydrogenated to ethylene in the presence of excess hydrogen. Two key factors contribute to this unique chemistry. First, the desorption energies of acetylene and molecular hydrogen on Cu(110) are relatively high in comparison with Ag(110).[12] Second, as shown by the isotope-exchange experiments, C_2H_2 is primarily nondissociatively adsorbed on Cu(110), in contrast to the cases of nickel and platinum. The two above observations are suggestive of a C_2H_2 species bound to the copper surface such that the C–C bond order is significantly reduced. This may be the result of strong σ-bonding or possibly σ- and π-interaction. In this model, the C_2H_2 may be distorted such that the hydrogen atoms are bent away from the metal surface, yielding a surface intermediate that may be more readily hydrogenated than adsorbed C_2, C_2H, or undisturbed acetylene. Of equal importance is the fact that the desorption energies of H_2 and C_2H_2 are relatively high such that the surface species have a significant coverage in a temperature range where there is sufficient thermal energy to allow the hydrogenation to proceed. Therefore, the Cu(110) surface is ideally suited for the hydrogenation of acetylene, the limiting factor being adsorption of a sufficient amount of atomic hydrogen on the surface.

The results on Cu(110)–O surfaces may be contrasted to the chemistry of acetylene adsorbed on Ag(110)–O. In the copper case, no significant reversible C–H bond cleavage was *observed*. The C_2H_2 either completely dehydrogenated or desorbed as molecular acetylene. There is no evidence for the parital dehydrogenation to form a metastable C_2H species and subsequent disproportionation to form $C_{2(ads)}$ and gaseous C_2H_2 as in the case of Ag(110)–O. The fraction of acetylene that reacts with the Cu(110)–O surface is significantly smaller than on Ag(110)–O. In the case of copper, the dehydrogenation is a competing process with desorption. This suggests that the interaction between the acetylenic hydrogen atoms and the adsorbed oxygen is weaker on copper than on silver.

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