A and B) in favor of 11. As model D shows, however, maintenance of the relative amounts, calculated from MM2, of all possible conformers except No. 11 leads to only slightly poorer overall agreement than when the amounts of the conformers are allowed to refine freely. A more direct comparison of the experimental and theoretical results is obtained by transformation of the experimental compositions into steric energies. Since the experimental compositions provide only relative energies, it was necessary to scale them. This was done by use of the formula $E_s(\text{ED}) - E_s(\text{MM2}) = RT \ln [X(\text{ED})/X(\text{MM2})]$, where the X's are mole fractions. The results, given in Table I, are in very good agreement with those from the MM2 calculations; only the values for conformer AAA differ by more than the experimental uncertainty. All in all, we find no evidence in our experimental results that the MM2 energies are unreliable for those CB conformers incapable of hydrogen bond formation.

If it is assumed that the major difference between the MM2 and the experimental composition of the CB system is due to O–H⋯Cl hydrogen bonding, the difference provides a rough estimate of the energy of the hydrogen bond. Models A, B, and D have estimated steric energies for the hydrogen-bonded conformer $G^-G^+G^+$ that differ respectively by 6.7 ± 1.3, 7.1 ± 0.8, and 8.4 ± 0.4 kJ/mol from the MM2 result obtained with the assumption of no hydrogen bonding. Not surprisingly, these values are smaller

than the energies of such bonds to atoms more electronegative than chlorine. They are also smaller than the energy difference of 10.9 (+7.9, −3.3) kJ/mol between the gauche and anti forms of 2-chloroethanol.[3]

Since our investigation of CB made use of torsion-angle values for the various conformers calculated from MM2, the O⋯Cl distance in the hydrogen-bonded conformer, as in the other conformers, was restricted to a range determined by the uncertainties in the bond lengths and bond angles. This range is centered at about 3.4 Å (Figure 4), a value not much different from the 3.17 Å O⋯Cl distance found for the gauche conformer in 2-chloroethanol. It is not known how reliable the hydrogen-bonded O⋯Cl distance is because the parameters that determine it are highly correlated with its associated amplitude of vibration. Refinements designed to test the matter gave values over the approximate range 3.1–3.9 Å.

Selectivity of Proton Abstraction from Propyne on the Ag(110) Surface

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Abstract: Propyne reacts with oxygen atoms adsorbed on the Ag(110) surface via proton transfer to produce water. At 200 K this reaction is selective toward formation of stable surface methyl acetylides. At 300 K proton abstraction from the methyl group of propyne competes with methyl acetylide formation. Surface methyl acetylides were thermally stable to 500 K; surface propargyl species were unstable and could not be isolated before decomposing to deposit surface carbon. The activation energy difference for proton abstraction from the two ends of propyne was determined to be 3.2 kcal/mol based on results from XPS and TPD experiments. This difference is in good agreement with the calculated stabilities for methyl acetylide and propargyl anions and with the relative rates of proton abstraction in the gas phase. XPS spectra for adsorbed methyl acetylide species demonstrate greater polarization of the acetylenic π-orbitals than for adsorbed HC_2 species; these results support previous polarization models for alkyl substituent effects on gas-phase acidities.

I. Introduction

The unravelling of reaction mechanisms and the connection of surface chemistry to the physical and chemical properties of solids represent one of the great challenges in modern heterogeneous catalysis. In the absence of mechanistic information obtained by methods such as in situ spectroscopies or isotopic labeling, perhaps the most common approach to rationalization of heterogeneously catalyzed reactions is to borrow plausible mechanisms from homogeneous chemistry, both catalytic and noncatalytic. It is not surprising that these connections are most highly developed for some of the simplest reactions, e.g., proton-transfer reactions. The chemistry and product distribution of the heterogeneously catalyzed cracking of hydrocarbons, for example, appear to be well described by reactions observed in acid and superacid solutions.[1,2]

While it is tempting to apply the well-developed concepts of proton-transfer reactions in solution to the large number of hy-

drogen-abstraction reactions occurring on surfaces, particularly those of ionic solids, this approach may be both qualitatively and quantitatively misleading for certain reactions. For example, the relative acidities of organic acids in the gas phase are dramatically different from those in aqueous solution. It is not clear how such properties may change when these molecules are adsorbed on a solid surface, or how one can quantitatively relate the acid–base properties of a solid catalyst to those of an adsorbed indicator when the latter have been determined in solution. Likewise, although reactions such as the dehydration and dehydrogenation of alcohols are classic test reactions which have been used to characterize the acid–base properties of solid catalysts, recent studies have reported results (e.g., the production of ethylene from ethanol on basic MgO[3]) which suggest that the reaction selectivity may not be related straightforwardly to the mechanisms of acid and base catalysis usually postulated.

We have chosen the base-catalyzed isomerization of alkynes as a test reaction for the transferability of acid–base mechanisms from homogeneous media to solid surfaces. These isomerizations
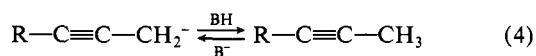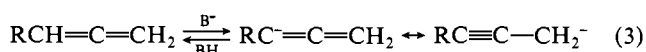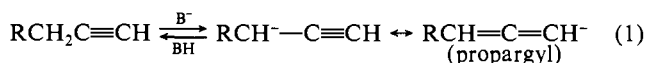
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have been studied for nearly a century since their discovery by Favorskii,[4] and their chemistry has been recently reviewed by Pines and Stalick.[5]   Indeed laboratory manuals are available which describe procedures for carrying out large numbers of isomerizations of acetylenes and allenes with basic reagents such as alcoholic KOH or sodium amide.[6]

In contrast, although they appear to be mechanistically similar to the commercially important class of allylic oxidations and oxidative dehydrogenations, the isomerization of alkynes with solid bases has received comparatively little attention. Jacobs[7] has shown, for example, that diaryl propynes are isomerized to diarylallenes over basic aluminas, while Kokes[8] reported the isomerization of propyne and allene over zinc oxide. These reactions have been rationalized by Kokes[9] in terms of the accepted mechanism for 1-alkyne isomerization via propargyl anions in basic solution.[5]   (For the simplest 1-alkyne, propyne, steps 3 and 4 are

$$RCH_2C\equiv CH \underset{BH}{\overset{B^-}{\rightleftharpoons}} RCH^-\text{---}C\equiv CH \leftrightarrow RCH=C=CH^- \quad (1)$$
$$\text{(propargyl)}$$

$$RCH=C=CH^- \underset{B^-}{\overset{BH}{\rightleftharpoons}} RCH=C=CH_2 \quad (2)$$

$$RCH=C=CH_2 \underset{BH}{\overset{B^-}{\rightleftharpoons}} RC^-=C=CH_2 \leftrightarrow RC\equiv C\text{---}CH_2^- \quad (3)$$

$$R\text{---}C\equiv C\text{---}CH_2^- \underset{B^-}{\overset{BH}{\rightleftharpoons}} R\text{---}C\equiv C\text{---}CH_3 \quad (4)$$

simply the reverse of steps 1 and 2, i.e., the only possible isomers are propyne and allene.) Cram[10] has reported that, in certain solvents, reactions of this type may proceed with greater than 80% intramolecular proton transfer and has suggested a "guided tour" mechanism whereby the proton migrates along the carbon backbone of the molecule. On the surfaces of ionic solids such as metal oxides, intramolecular proton transfer would probably not be required, since the surface would contain cations on which to stabilize the propargyl intermediates and since proton migration via surface hydroxyl groups would be expected to be rapid.

Some insight into the role of the surface in these isomerization reactions may be gained from considering the behavior of alkynes as acids in the absence of solvent. In gas phase ion cyclotron resonance experiments it has been shown that the acetylenic hydrogen of propyne is the most acidic,[11] i.e., the gas-phase heterolytic dissociation of propyne favors formation of acetylide rather than propargyl anions by ca. 6 kcal/mol.[12]   In contrast, for homolytic dissociation propargyl radicals may be estimated to be favored over acetylide radicals by >40 kcal/mol,[13] if one assumes comparable bond dissociation energies for the acetylenic C–H bonds in propyne and acetylene. The report of Kokes that propargyl species are the dominant intermediate on ZnO following propyne adsorption (since disputed by other workers[14]) is thus a surprising one if the surface species are ionic in character.

One of us has previously reported extensively on the basic properties of oxygen atoms on the Ag(110) surface[15–22] and on
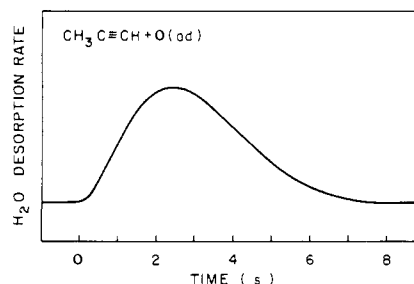

Figure 1. Water formation transient for reaction of CH_3CCH with $O(ad)$ at 210 K. The surface was initially exposed to 600 L of O_2 to produce an oxygen atom coverage of approximately one-third monolayer. At $t = 0$ the sample was rotated to face a steady beam of CH_3CCH. ($P_{C_3H_4} = 5 \times 10^{-9}$ torr out of beam, estimated at 5×10^{-7} torr in beam).

the applicability of the gas-phase acidity scale in describing proton-transfer reactions on this surface.[18,21] The present study is an examination of the reaction of propyne with oxygen atoms adsorbed on the Ag(110) surface in order to determine (1) if the selectivity for heterolytic dissociation in the gas phase is followed on this surface and (2) the role of the surface, in addition to proton abstraction, in promoting the propyne–allene isomerization. The results of this study are consistent with those of the previous investigation of propylene oxidation[22] in suggesting that zero-valent silver is incapable of stabilizing π-anion complexes.

II. Experimental Section

The temperature-programmed desorption (TPD) experiments in this study were carried out in a stainless steel vacuum chamber at typical base pressures of ca. 2×10^{-10} torr. The chamber was equipped with a single pass cylindrical mirror analyzer for Auger electron spectroscopy (AES), four-grid optics for low-energy electron diffraction (LEED), and a quadrupole mass spectrometer for monitoring gaseous products. The silver single crystal, oriented to expose the (110) surface, was suspended from a tungsten clip attached to a sample manipulator. Sample heating was provided by a planar tungsten filament suspended approximately 3 mm behind the sample. Cooling was provided via conduction through a copper braid connecting the sample manipulator to a flow-through liquid-nitrogen reservoir mounted on the manipulator flange. The sample temperature was monitored by means of a chromel–alumel thermocouple press fit in a hole in the side of the sample.

Following installation in the vacuum chamber, the sample was cleaned by argon bombardment until AES showed no measurable levels of carbon, oxygen, or sulfur; the crystal was then annealed to 1000 K to produce the sharp (1 × 1) LEED pattern characteristic of the clean surface. Oxygen (Matheson, 99.6%) was dosed onto the surface through a 0.16 cm diameter needle which extended to within 2 cm of the sample. The needle was connected to the external gas manifold via a variable leak valve. Propyne (Linde, 96%), propyne-d_1 (MSD 98 atom %), and acetic acid-d_1, (Chemical Dynamics 99.5 atom %) were dosed through a separate needle attached to a second gas manifold. The oxygen uptake as a function of oxygen exposure was found to be in excellent agreement with previous studies[23] which used a similar dosing arrangement.

Temperature-programmed desorption experiments following reaction of propyne with adsorbed oxygen were carried out by using the procedures of previous studies.[20] Surface carbon deposited by this reaction was removed by sequential oxygen exposures to form CO_2; this technique has been previously shown to provide a quantitative measure of the surface carbon present.

X-ray and ultraviolet photoelectron (XPS and UPS) spectra were obtained in a second vacuum chamber equipped with a double pass cylindrical mirror analyzer and photon sources: MgKα for XPS and He I 21.2 eV and He II 40.8 eV discharges for UPS. The silver sample was mounted on a resistively heated tantalum foil for these experiments; all

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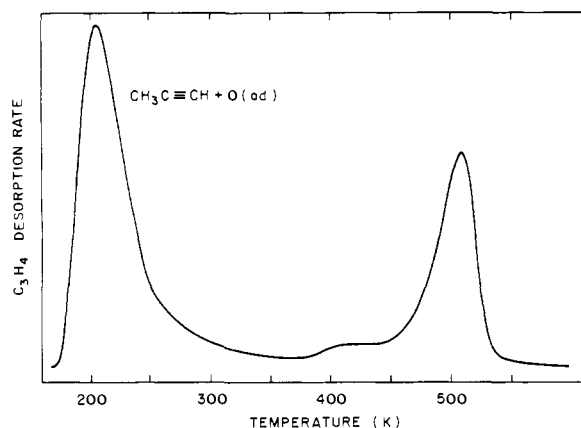(23) Barteau, M. A.; Madix, R. J. *Surf. Sci.* **1980**, *97*, 101.

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Figure 2. Temperature-programmed desorption spectrum following reaction of CH_3CCH with O(ad) at 200 K.

sample cleaning and reaction experiments were carried out in situ. All core-level binding energies were referenced to the Ag $3d_{5/2}$ peak at 367.9 eV; valence band spectra were referenced to the Fermi level of the silver surface.

III. Results

(1) Reaction of Propyne with O(ad) at 200 K. Propyne reacted with adsorbed oxygen atoms on the Ag(110) surface to form H_2O which desorbed during the propyne exposure for sample temperatures above 200 K. An example of the transient H_2O production for the reaction with one-third monolayer of preadsorbed oxygen atoms is shown in Figure 1. The shape of the H_2O transient is characterized by a delay of the order of seconds in reaching the maximum rate following the rapid rotation of the sample into a steady beam of propyne from the needle doser. Following attainment of the maximum rate of H_2O production, the transient exhibits an approximately exponential decay with time, reflecting the depletion of the preadsorbed oxygen layer. Such transient behavior has been previously observed for reaction of a number of Brønsted acids, including HCOOH,[16] CH_3COO-H,[17] and C_2H_2,[20] with oxygen atoms on the Ag(110) surface, and has been successfully modelled by the sequential reaction of two acid molecules with oxygen to form first hydroxyl species and then water.

The reaction of $CH_3C\equiv CH$ with O(ad) between 200 and 300 K was completed for propyne exposures of 20 langmuirs (1 langmuir = 10^{-6} torr·s) or less, as determined by the decay of the rate of H_2O production to zero. Following the cutoff of the propyne exposure and evacuation of the background gas, TPD experiments were conducted in order to examine the adsorbed species produced by this reaction. TPD data following reaction of propyne with oxygen at 200 K are shown in Figure 2. Perhaps most striking is the absence of products other than C_3H_4: no other volatile products were observed in these TPD experiments. The characteristic recombination and desorption of oxygen atoms near 600 K was not observed following exposure of the surface to propyne, indicating that the adsorbed oxygen atoms were completely consumed by this reaction. The absence of other oxygen-containing products suggests that oxygen is removed from the surface exclusively as water. In addition to the characteristic fragmentation pattern of propyne, mass fragments checked for but not found included m/e 2, 16, 26, 28, 29, 41, 56, and 78. The formation of products such as hydrogen, methane, ethane, ethylene, propylene, acrolein, benzene, and hexadiyne may be excluded on the basis of these negative results.

The desorption spectrum in Figure 2 for C_3H_4 following reaction of propyne with adsorbed oxygen contains two principal peaks: one near 225 K and the other at 500 K. In the absence of oxygen adsorption before exposure to propyne, only the 225 K peak was observed in the TPD spectrum. The 225 K peak was therefore assigned to the desorption of adsorbed propyne molecules and the peak at 500 K to the production of C_3H_4 from reaction of the hydrocarbon fragments deposited by reaction of propyne with adsorbed oxygen. Similar reactions of conjugate base species on

Ag(110) to reform the parent acids at higher temperatures than observed for simple molecular desorption have been reported previously, e.g.

$$2CH_3O(ad) \rightarrow CH_3OH(g) + H_2CO(g) \qquad (5)^{24}$$

$$2H\text{—}C\equiv C(ad) \rightarrow C_2H_2(g) + C_2(ad) \qquad (6)^{20}$$
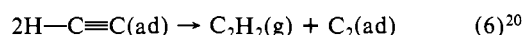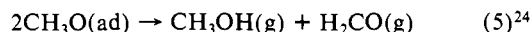
The C_3H_4 product evolved at 500 K was identified by comparison of the relative mass spectrometer signals for m/e 40, 39, 38, and 37 for this desorption peak with the mass spectrum obtained by introducing propyne directly into the vacuum chamber. The mass spectrum obtained (relative to mass 40 = 100%, mass 39 = 91%, mass 38 = 38%, mass 37 = 29%) was in excellent agreement with the literature.[25] The relative amounts of the desorption product fragments were equal to the above ratios to within the limits of reproducibility of the initial oxygen coverage (±10%). This agreement, while sufficient to identify most organic products, is insufficient to discriminate between propyne and allene, as these two molecules exhibit virtually identical mass spectra. Thus the possibility that some allene is evolved in the reaction of surface hydrocarbon intermediates cannot be ruled out. However, while the equilibrium propyne/allene ratio at this temperature is approximately 5:1,[26] no allene would be expected if the surface intermediate which decomposed at 500 K were a methyl acetylide rather than the propargyl. In addition, a small signal (4% of the m/e 40 signal) for m/e 27 was observed both in the propyne mass spectrum and in the spectra for the C_3H_4 desorbed at 225 and 500 K. This fragment could not be formed from allene unless significant protonation occurs in the ionizer of the mass spectrometer. For the purposes of the following discussion, it is therefore assumed that propyne is the sole hydrocarbon product in these TPD experiments.

The stoichiometry of the reaction of propyne with oxygen to form propyne plus water dictates that a more highly unsaturated hydrocarbon, or carbonaceous species, be produced. No other hydrocarbons were observed in this study; however, carbon was deposited on the surface following the evolution of propyne at 500 K in TPD experiments. Quantitative determination by AES of carbon coverages on silver is not possible due to the overlap of signals from the two elements. It has been previously shown[20] that the coverage of atomic carbon may be determined by the CO_2 evolved in a series of oxygen adsorption and thermal desorption cycles. The CO_2 TPD spectra for oxidation of carbon deposited from propyne were indistinguishable in shape from those for carbon from acetylene;[20] however, fewer oxygen cleaning cycles were required to clean off carbon from propyne than carbon from acetylene for the same initial oxygen coverage. Calibrated against the carbon deposited by reaction of acetylene with oxygen, which has been shown to be two carbon atoms per initially adsorbed oxygen atom, the carbon deposited from propyne was equal to 1.6 ± 0.2 carbon atoms per oxygen atom. This stoichiometry is consistent with that expected for the net reaction.

$$C_3H_4 + 2O(ad) \rightarrow 3C(ad) + H_2O \qquad (7)$$
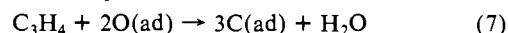
The slightly high value of the carbon coverage determined by cleanoff reactions may have been due to small amounts of propyne in the background gas which may also react during the cleanoff cycles.

In order to identify the surface intermediate which decomposes at 500 K, both TPD experiments with isotopically labeled propyne and acid–base titration reactions with labeled acetic acid were carried out. TPD spectra for reaction of propyne-d_1 with adsorbed oxygen atoms at 200 K are shown in Figure 3. These desorption spectra are identical with those obtained for reaction of propyne at 200 K, except for a m/e 41 peak at 225 K corresponding to molecularly adsorbed propyne-d_1. The relative peak areas for mass fragments m/e 40, 39, 38, and 37 in the 500 K desorption peak were again in excellent agreement with those reported for pro-

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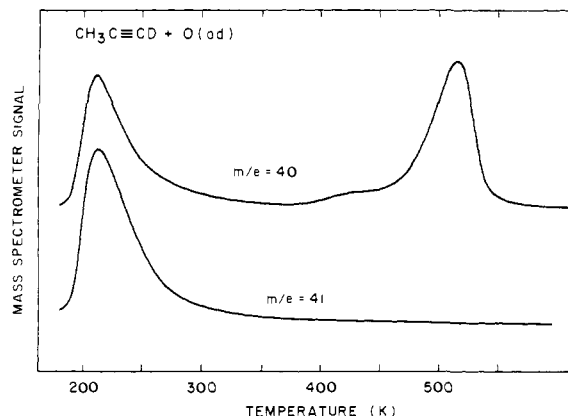(26) Cordes, J. F.; Gunzler, H. *Chem. Ber.* **1959**, *91*, 1055.

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Figure 3. TPD spectra for labeled and unlabeled propyne species following reaction of CH_3CCD with $O(ad)$ at 200 K.

Figure 4. TPD spectrum for titration of surface intermediates with CH_3COOD. The sequence of exposures was as follows: (1) sample exposed to 600 L of O_2 at 200 K; (2) $O(ad)$ consumed by reaction with CH_3CCH, sample heated to 300 K to desorb excess CH_3CCH; and (3) sample exposed to 20 L of CH_3COOD at 200 K and heated.

pyne.[25] The absence of a TPD peak at 500 K for m/e 41 following reaction of CH_3CCD clearly demonstrates that the acetylenic hydrogens of the reactant molecules are completely consumed by the initial reaction with $O(ad)$. In contrast to the formation of H_2O by reaction of CH_3CCH with $O(ad)$, neither H_2O nor D_2O production could be resolved during reaction of CH_3CCD with $O(ad)$ at 200 K. The absence of H_2O is not surprising if the reaction involves selective abstraction of the acetylenic hydrogens; D_2O evolution during adsorption could not be resolved from the m/e 20 signal of the CH_3CCD.

The absence of H_2O evolution during reaction of CH_3CCD and the absence of formation of deuterated propyne by reaction at 500 K strongly suggest that the adsorbed species formed by the initial reaction of propyne with oxygen is a methyl acetylide. In order to demonstrate that reaction of propyne with oxygen resulted in the removal of acetylenic hydrogens exclusively, acid–base titration reactions of the type previously performed for C_2H_2[20] and other Brønsted acids on the Ag(110) surface were carried out. In these experiments propyne was first reacted with adsorbed oxygen atoms at 200 K, the surface was then exposed to CH_3-OOD and heated in a TPD experiment. A typical desorption profile for such an experiment is shown in Figure 4. As in the titration of other adsorbed conjugate bases with stronger acids, the spectrum exhibits the characteristic desorption features associated with decomposition of the conjugate base of the stronger acid. Figure 4 contains both the characteristic peak for desorption of molecularly adsorbed acetic acid at 190 K and the characteristic peak for decomposition of surface acetate intermediates at 640 K.[17] The appearance of surface acetates (which may also be formed by direct reaction of acetic acid with adsorbed oxygen atoms) indicates that a proton transfer to the adsorbed species has occurred, as acetic acid does not dissociate on silver under the temperature and pressure conditions of these experiments.[17]

The proton acceptor in this case is the dehydrogenated intermediate formed by the initial reaction of propyne with oxygen; it is not surprising therefore that the hydrocarbon formed by titration is again propyne. More striking, however, is the isotopic composition of this product and the temperature at which it is evolved by titration vs. thermal decomposition. As shown in Figure 4, the deuterated product produced by titration was exclusively C_3H_3D which desorbed from the surface at 270 K (some C_3H_4 was also evolved at 270 K due to the presence of some CH_3COOH in the acetic acid sample). No evidence for mass fragments with $m/e \gtrsim 42$ was observed from the products desorbing at 270 K, thus no multiple deuteration and no hydrogenation to more highly saturated hydrocarbons occurred in the titration experiments. Further, there was no evidence for propyne formation at 500 K, indicating that titration with acetic acid resulted in complete displacement of the intermediates formed from propyne by surface acetate species. On the basis of these results it may be concluded that the reaction of propyne with adsorbed oxygen atoms at 200 K results in the abstraction of a single proton from each propyne molecule to form surface intermediates of stoichiometry C_3H_3.
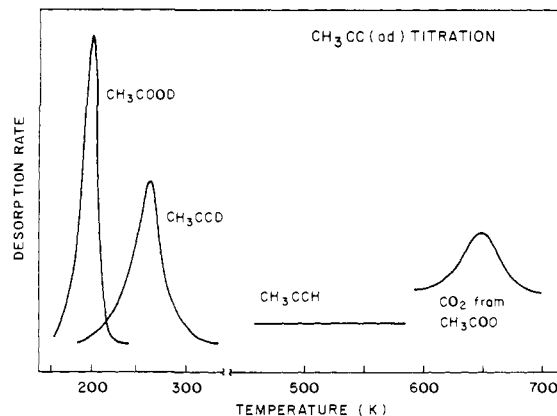
Furthermore, isotopic labeling experiments indicate that these intermediates are methyl acetylides rather than propargyls. The intermediates decompose at 500 K to form propyne and deposit the stoichiometric coverage of carbon atoms on the surface. If exposed to CH_3COOD, the adsorbed methyl acetylide may be stoichiometrically converted to C_3H_3D.

(2) Reaction of Propyne with O(ad) at 300 K. The reaction of propyne with oxygen on the Ag(110) surface at 300 K was qualitatively similar to that at 200 K, with an important quantitative difference. The TPD spectrum following reaction at 300 K exhibited the expected single peak for propyne at 500 K with no other volatile products. The magnitude of the 500 K propyne peak following reaction at 300 K was only 40 ± 4% of that observed following reaction at 200 K. The carbon deposited by reaction at 300 K and subsequent TPD was within 10% of that deposited by reaction at 200 K, as determined by CO_2 cleanoff.

These results suggest that at 300 K a second reaction channel is available which results in the oxidative dehydrogenation of propyne to surface carbon without formation of any stable surface intermediates. The methyl acetylide intermediate which decomposes at 500 K is still produced by the room-temperature reaction; however, its decomposition can account for only a fraction of the carbon ultimately deposited on the surface, which still follows the stoichiometry of eq 7.

Results of experiments with CH_3CCD also support the existence of an alternative to acetylide formation for oxidation of propyne at 300 K. Whereas the 500 K TPD was only 40% of its maximum height when CH_3CCH reacted with $O(ad)$ at 300 K, this peak was only 23% of its maximum height when CH_3CCD was oxidized at 300 K. Thus, the kinetic isotope effect reduces the rate of acetylide formation and allows other reaction channels to compete more effectively with acetylide formation at 300 K.

The most likely pathway competing with acetylenic proton abstraction is abstraction of other acidic protons from propyne, i.e., propargyl formation. As noted above, proton abstraction from the methyl position of propyne has been reported both on oxide surfaces and in the gas phase. In order to account for the lack of additional TPD peaks following reaction of propyne with oxygen at 300 K, propargyl species on the Ag(110) surface must be unstable, decomposing rapidly to deposit the stoichiometric coverage of carbon and liberate hydrogen to form water. This observation is consistent with previous results which demonstrated that stable allylic species were not formed in the reaction of propylene and oxygen on the Ag(110) surface;[22] these species were also presumed to decompose rapidly to deposit carbon on the surface. The thermochemistry of proton abstraction from propyne is discussed in detail below.

(3) Photoelectron Spectra of Adsorbed Species. The stable surface species $CH_3CCH(ad)$, $CH_3CC(ad)$, and $C(ad)$ were examined by XPS and UPS. The results of these experiments support the identification of adsorbed methyl acetylide interme-
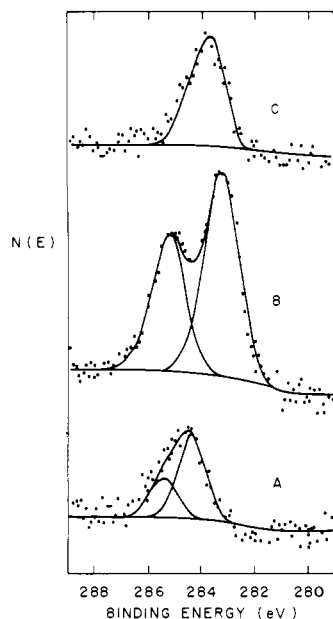
Figure 5. XPS spectra for adsorbed species: (A) CH$_3$CCH condensed on the clean Ag(110) surface at 110 K; (B) CH$_3$CC(ad) species formed by reaction of CH$_3$CCH with O(ad) at 200 K, sample heated to 300 K to desorb excess CH$_3$CCH; and (C) C(ad) following decomposition of methyl acetylides by heating the sample in B to 600 K.

Figure 6. UPS spectra for CH$_3$CC(ad) species formed as in Figure 5B: (a) clean surface spectrum; (b) surface containing CH$_3$CC(ad); and (c) (spectrum b − spectrum a) × 2 difference spectrum.

diates and confirm the reaction stoichiometries obtained from TPD studies.

The C(1s) spectra following adsorption of molecular propyne on the clean Ag(110) surface at 115 K (see Figure 5) consisted of an asymmetric peak at 284.5 eV, with the majority of the area located to the high binding energy side of the peak. This spectrum can be easily resolved into two peaks at 284.3 and 285.3 eV with an intensity ratio of 2:1. The spectrum is similar to that obtained by Cavell[27] for gas-phase propyne. In the gas phase the spectrum consists of two peaks in a 2:1 ratio at 290.7 and 291.7 eV, respectively. These peaks are shifted to lower binding energy by 6.4 eV for adsorbed propyne due to relaxation and final-state effects. A comparable relaxation shift for C$_2$H$_2$ (gas-phase C(1s) binding energy 291.2 eV,[27,28] adsorbate binding energy 285.6 eV[20]) has been noted previously on the Ag(110) surface. On the basis of estimated charge densities from CNDO/2 molecular orbital calculations[29,30] which showed the methyl carbon to be the most electron deficient carbon atom in propyne, Cavell assigned the high binding energy shoulder to the methyl carbon and the larger peak to the two acetylenic carbons.

More recent CNDO/2 calculations using an improved atomic orbital basis set[12] indicate that the methyl carbon is not the least negatively charged carbon in propyne. Rather, these calculations show that the least negatively charged carbon atom is the acetylenic carbon adjacent to the methyl group. Furthermore, the difference in the calculated charge densities between the two acetylenic carbons is approximately three times the difference between the methyl carbon and the H-bearing acetylenic carbon. These calculations seem to be more consistent with the observed XPS spectra for both gas-phase and condensed propyne and lead to the following peak assignments for the C(1s) spectrum of condensed propyne: the high binding energy shoulder located at 285.3 eV is due to the acetylenic carbon adjacent to the methyl group while the large peak centered at 284.3 eV consists of contributions from both the methyl carbon and the terminal acetylenic carbon.

The C(1s) spectrum observed for the adsorbed methyl acetylide formed by the reaction of propyne with O(ad) at 200 K was easily

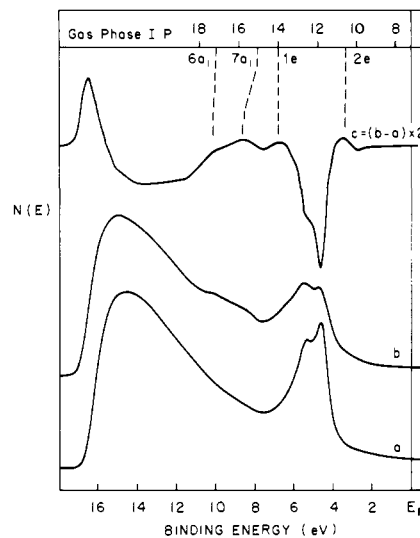distinguished from that for molecularly adsorbed propyne. Two distinct but overlapping peaks centered at 283.1 and 284.9 eV were observed. By curve resolving these two overlapping peaks, the area ratio of the peak at 284.9 eV to that at 283.1 eV was found to be 0.6. Although the spectrum is qualitatively similar to that for molecular propyne, both peaks are shifted to lower binding energy for the methyl acetylide, with an increase in the peak separation (1.8 vs. 1.0 eV for propyne). A previous study of acetylene on Ag(110)[20] found a 2-eV shift to lower binding energy for the C(1s) signal from the acetylenic carbon bound to the surface in an acetylide species (H—C≡C-) compared to the C(1s) binding energy of molecularly adsorbed acetylene. Assuming analogous behavior for propyne, one would expect the C(1s) signal from the terminal acetylenic carbon to shift to lower binding energy upon formation of methyl acetylide intermediate. The peak centered at 283.1 eV can be accounted for in part by the acetylenic carbon bound to the surface.

The assignment of the remaining contribution to the 283.1-eV peak to the methyl carbon, and that of the 284.9-eV peak to the acetylenic carbon adjacent to the methyl group, is consistent with previous XPS results for adsorbates on silver and copper surfaces. The C(1s) peaks for the two carbons in HC≡C(ad) are separated by 1.5 eV on the Ag(110) surface.[20] This separation is similar to that for the two peaks of the methyl acetylide and suggests that acetylenic carbons not bound to the surface should have higher binding energies than those which are bound to the surface. In addition, the binding energy shift of the methyl carbon (from 284.3 eV for adsorbed propyne to 283.1 eV for the methyl acetylide) is consistent with binding energy shift of methyl substituents upon dissociation of other Brønsted acids. The methyl group C(1s) energy decreases upon dissociation of CH$_3$COOH(ad) to CH$_3$COO(ad): this shift is 1.5 eV on Ag(110)[31] and 1.6 eV on Cu(110).[32]

When the surface containing C$_3$H$_3$(ad) was heated to 600 K to decompose this intermediate and deposit carbon on the surface, only a single C(1s) peak centered at 283.7 eV was observed. The ratio of the area of this peak to that observed for the adsorbed acetylide intermediate was found to be 0.28 ± 0.05. This ratio is consistent with the stoichiometry of the following overall reaction for the disproportionation of methyl acetylide species:

$$4C_3H_3(ad) \rightarrow 3C_3H_4(g) + 3C(ad) \qquad (8)$$
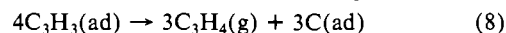
He I and He II UPS spectra were obtained for the adsorbed methyl acetylide intermediate. Both spectra were qualitatively similar; however, due to the higher intensity of the He I line,

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(29) Brownlee, R. T. C.; Taft, R. W. *J. Am. Chem. Soc.* **1970**, *92*, 7007.
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adsorbate bands were more easily identified at this photon energy. Therfore, only He I results are reported here. The He I UPS spectra of the clean silver surface and that containing adsorbed methyl acetylide species are shown in Figure 6. The UPS difference spectrum relative to the clean surface is also shown. The presence of methyl acetylide species caused considerable attenuation of the silver d bands as previously reported for a number of small molecules adsorbed on silver.[20,31,33] In addition to attenuation of the d bands, the difference spectrum also exhibited four new bands located 3.5, 7.0, 8.6, and 9.9 eV below the Fermi level. On the basis of the spectrum of gas-phase methyl acetylene[34] these features have been assigned to the 2e, 1e, 7a$_1$, and 6a$_1$ molecular orbitals, respectively. Assuming a constant extra molecular relaxation polarization shift, the gas-phase spectrum was aligned with the adsorbate spectrum by assuming no bonding shift in the 1e orbital of the adsorbate relative to that in the gas phase (the 1e orbital corresponds to the methyl group π orbital[35] and is assumed to be the orbital least involved in bonding to the surface). This gave a reasonably good fit between two of the remaining peaks; however, the 7a$_1$ orbital was found to shift by 0.6 eV to higher binding energy relative to the aligned gas-phase spectrum.
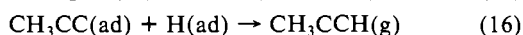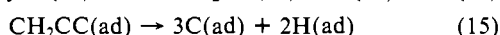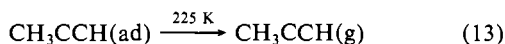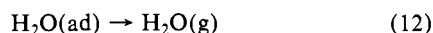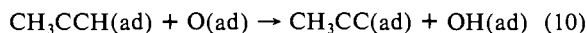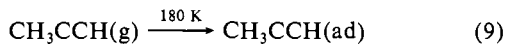
The UPS spectra also show that the adsorbed methyl acetylide caused a 0.2-eV decrease in the work function of the surface relative to that of the clean surface as determined from the cutoff of secondary electron emission. (Note the apparent positive peak in the difference spectrum near −17 eV.) This result is opposite to that obtained for O(a), HCOO(a), CH$_3$COO(ad), CO$_3$(ad), and C$_2$(ad) all of which increase the work function.[21] However, a similar result has been reported for C$_2$H(ad) which was found to decrease the work function by 0.4 eV.[20]

The UPS spectrum of the adsorbed carbon deposited on the surface after decomposition of the acetylide by heating to 600 K exhibited minor attenuation of the silver d bands, with no new adsorbate features. The work function was also found to revert back to that observed for the clean surface. The absence of adsorbate peaks for the adsorbed carbon indicates that no C–C bonds remain intact in the carbon deposited on the surface after completion of the reaction at 600 K.

IV. Discussion

The selectivity for formation of methyl acetylide species by reaction of propyne with adsorbed oxygen atoms is clearly incompatible with a homolytic model for dissociation of propyne. Typical C–H homolytic bond dissociation energies are of the order of 130 kcal/mol for acetylenic moieties, while that for removal of methyl hydrogen from propyne has been reported to be 89.4 kcal/mol.[13] The selective removal of acetylenic hydrogen from propyne by reaction with O(ad) at 200 K is instead characteristic of a proton-transfer reaction, consistent with previous observations of selective acid–base reactions involving oxygen atoms on silver.

The following reaction sequences describe the proton-transfer reactions of propyne and decomposition of the corresponding surface intermediates on the Ag(110) surface:

$$CH_3CCH(g) \xrightarrow{180\ K} CH_3CCH(ad) \qquad (9)$$

$$CH_3CCH(ad) + O(ad) \rightarrow CH_3CC(ad) + OH(ad) \quad (10)$$

$$CH_3CCH(ad) + OH(ad) \rightarrow CH_3CC(ad) + H_2O(ad) \quad (11)$$

$$H_2O(ad) \rightarrow H_2O(g) \qquad (12)$$

$$CH_3CCH(ad) \xrightarrow{225\ K} CH_3CCH(g) \qquad (13)$$

$$CH_3CC(ad) \xrightarrow{500\ K} CH_2CC(ad) + H(ad) \qquad (14)$$

$$CH_2CC(ad) \rightarrow 3C(ad) + 2H(ad) \qquad (15)$$

$$CH_3CC(ad) + H(ad) \rightarrow CH_3CCH(g) \qquad (16)$$

For reaction of propyne with oxygen atoms at 300 K, the following reactions compete with those above, depositing carbon on the surface directly.

$$CH_3CCH(ad) + O(ad) \rightarrow CH_2CCH(ad) + OH(ad) \quad (17)$$

$$CH_2CCH(ad) \rightarrow 3C(ad) + 3H(ad) \qquad (18)$$

$$H(ad) + OH(ad) \rightarrow H_2O(g) \qquad (19)$$

This surface reaction behavior for propyne can be explained to a great extent by the gas-phase thermochemistry for heterolytic dissociation of this molecule. Although the gas-phase acidity for propyne has been determined ($\Delta H°_{acid}$ for propyne is 4.1 kcal/mol greater than that for the acetylene[11] based on results from ion-cyclotron resonance experiments), the relative acidities of the acetylenic and methyl hydrogens within this molecule have not been clearly resolved. Bartmess and McIver[11] have noted that the methyl acetylide is the principal anion from propyne observed in the ICR at long times and there appears to be general agreement that the acetylenic hydrogen is the strongest acid site in the molecule. However, DePuy and co-workers[36,37] have observed that the reaction of propyne-d_1 with OH$^-$ and NH$_2^-$ in flowing afterglow experiments is not selective toward the thermodynamically preferred methyl acetylide anion; they have reported the following selectivities at 300 K:

$$OH^- + CH_3C{\equiv}CD \quad \begin{array}{c} \xrightarrow{\ 60\%\ } \ ^-CH_2C{\equiv}CD \ + \ H_2O \\[4pt] \xrightarrow{\ 40\%\ } \ CH_3C{\equiv}C^- \ + \ HOD \end{array} \qquad (20)$$

DePuy and co-workers have also reported selective formation of methyl acetylide anions in the gas phase by displacement reactions of fluoride ions with appropriately substituted silanes;[37,38] they have observed that the rate of reaction of methyl acetylide anion with molecular oxygen is about one-seventh the rate for the corresponding reaction of propargyl anion. This result has also been interpreted as evidence of the greater stability of the methyl acetylide.

Recent SCF–MO calculations by Hopkinson et al.[12] have shown that the methyl acetylide anion is more stable than the propargyl anion by 6.2 kcal/mol. These calculations yield a similar energy difference between the two possible resonance structures for the propargyl anion: CH$_2$=C=CH$^-$ was determined to be more stable than $^-$CH$_2$C≡CH by 6.6 kcal/mol. Thus the 6.2-kcal/mol difference above represents the minimum calculated acidity difference between the acetylenic and methyl hydrogens of propyne. In contrast, the facile abstraction by OH$^-$ of protons from either end of the molecule as reported by DePuy et al.[36] has led to the suggestion that the acidity difference is less than the theoretically determined value.[39]

The results of this present study help to reconcile this apparent discrepancy. The absence of evidence for methyl acetylide-propargyl interconversion and, indeed, for the formation of stable propargyl species indicates that the selectivity toward methyl acetylide species is controlled by the *kinetics* of proton transfer from propyne to O(ad), rather than by equilibrium. The difference in activation energies for proton transfer from the two acidic positions in propyne may be estimated from the change in reaction selectivity between 200 and 300 K. As noted above, following reaction at 300 K the coverage of surface acetylides was approximately 40% of the stoichiometric coverage based upon the initial oxygen concentration. If one assumes that the initial proton transfer is rate limiting, regardless of which proton is transferred, and if the propargyl species decompose rapidly once formed, then the initial abstraction of a methyl hydrogen results in consumption
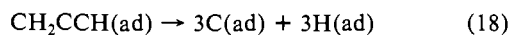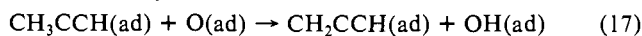
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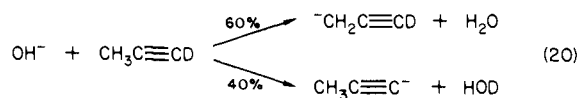
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(38) DePuy, C. H.; Bierbaum, V. M.; Flippin, L. A.; Grabowski, J. J.; King, G. K.; Schmitt, R. J.; Sullivan, S. A. *J. Am. Chem. Soc.* **1980**, *102*, 5012.

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of two oxygen atoms, while two acetylenic hydrogens are consumed per oxygen in the acetylide-forming reaction. Thus the relative rates of proton abstraction at 300 K may be estimated to be

$$\frac{r_{\text{acetylide formation}}}{r_{\text{propargyl formation}}} = \frac{40}{60/4} = 2.67 \qquad (21)$$

The relative rates of the reaction at 200 K may be estimated from the ratio of areas of the C(1s) peaks before and after thermal decomposition of the acetylide layer initially formed at 200 K. If no carbonaceous species other than the methyl acetylide were present before TPD, this ratio should be 0.25; the observed ratio of 0.28 is consistent with initial reaction of 3% of the propyne molecules via an unstable propargyl to form surface carbon directly at 200 K. Thus the rate of acetylide formation would be 33 times faster than that of propargyl formation at 200 K. This estimate is within the limit of these experiments in closing the stoichiometric balance for the propyne–oxygen reaction; it is therefore possible that this ratio is greater than 33 at 200 K. With this value as the lower limit, one can estimate the difference in activation energies for proton abstraction from the two ends of propyne to be 3.2 kcal/mol (with abstraction from the methyl position the more highly activated process). Even if one assumes that the ratio of abstraction rates at 200 K is 1000:1, the estimated difference in activation energies rises to only 7 kcal/mol. These estimated activation energy differences are in good agreement with estimates of the differences in heterolytic bond-dissociation energies.[12,39] Thus the reaction of alkynes with oxygen atoms on the Ag(110) surface is well described as a proton-transfer reaction; the kinetics of proton transfer appear to be consistent with the Brønsted relation ($k = k_0(K_a)^\alpha$) for proton transfer. Additional results which support this conclusion have been obtained from the reaction of weaker hydrocarbon acids with O(ad) on the Ag(110) surface. Ethylene[40] and propylene[22] react with O(ad) at lower rates than do acetylene or propyne, as expected on the basis of the relative gas-phase acidities of these molecules. The absence of evidence for stable surface vinyl or allyl species and the absence of isotopic scrambling in ethylene oxidation experiments at higher pressures indicate that the reaction of these molecules is limited by the rate of proton transfer rather than by the unfavorable equilibrium for heterolytic dissociation. The reaction of ethylene with oxide and hydroxide anions in the gas phase is likewise limited by the kinetics of proton transfer.[41,42]

From the relative amounts of the methyl acetylide species formed by reaction of CH$_3$CCH and CH$_3$CCD with O(ad) at 300 K (40% vs. 23% of the maximum concentration), the kinetic isotope effect for transfer of the acetylenic proton was estimated to be 2.2. (This estimate assumes that the rate of the competing proton abstraction from the methyl groups of these molecules is independent of isotopic substitution at the acetylenic position.) The magnitude of the kinetic isotope effect for transfer of acetylenic protons is in excellent agreement with the values ranging from 2.0 to 2.7 reported by Farneth and Brauman[43] for gas-phase transfer of allylic protons. Further, the relative rates of proton abstraction from the two ends of CH$_3$CCD are in good agreement with the flowing afterglow experiments of DePuy et al.[36] From the acetylide coverage following reaction on the Ag(110) surface at 300 K the ratio of rates for acetylenic deuteron vs. methyl proton transfer may be estimated to be 53:47; the corresponding ratio for reaction with gas-phase OH$^-$ is 40:60.[36] This agreement again points to the strong analogy between the thermochemistry of proton-transfer reactions in the gas phase and those on the Ag(110) surface.

XPS and UPS spectra of adsorbed anionic species such as the methyl acetylide provide insight into the electron distribution in these species; this information is generally not easily accessible for the free anions in the gas phase. The XPS spectra in Figure

5 suggest, for example, that the formation of methyl acetylide anion results in greater internal polarization of charge relative to propyne. While all three carbons exhibit a shift to lower binding energy upon heterolytic dissociation, the peak assigned to the terminal carbon atoms shifts further than that of the central carbon, thus increasing the separation of the two C(1s) peaks relative to molecular propyne.

These results provide novel experimental evidence in support of previous explanations of alkyl group effects on gas-phase acidities. In contrast to acidity trends observed in polar solvents, increasing the size of the alkyl group attached to an acidic center generally increases the gas-phase acidity. The effect of alkyl substitution for hydrogen is less straightforward. Substitution in ROH molecules increases the acidity monotonically through the series HOH, CH$_3$OH, C$_2$H$_5$OH, etc. For a number of other homologous series, alkyl substitution decreases the acidity relative to the unsubstituted parent, although the trend with alkyl size is as stated above, e.g., C$_2$H$_2$ > (CH$_3$CCH < C$_2$H$_5$CCH, etc.). Substitution of alkyl groups for hydrogens at other centers, including HS–, CH$_3$C(=O)–, and HOC(=O), results in gas phase acidity trends parallel to that of the alkynes.[44] Relative acidities within these series can be explained on the basis of polarization effects. In those species for which alkyl substitution results in net destabilization of the anion (i.e., reduction of the acidity), the π system of the alkyl group interacts with a relatively polarizable π system which, to a first approximation, bears the negative charge (e.g., C≡C$^-$, S$^-$, etc.). The net effect of this interaction is a repulsion between the filled π orbitals of the alkyl group and of the charged center, resulting in polarization of the electron density at the charged center away from the alkyl group.[44] Thus alkyl-for-hydrogen substitution in these series has a destabilizing effect upon the conjugate base anions. Substitution of large alkyl groups allows for greater delocalization of the alkyl π system, thus reducing the destabilizing interaction and increasing the acidity relative to the methyl-substituted homologue. For the alcohols, the oxygen center is considerably less polarizable, and the alkyl–oxygen interaction in the alkoxide is dominated by a net-stabilizing interaction of the unfilled alkyl π^* orbitals with the filled oxide π levels.[44,45] In such cases the acidity increases even upon substitution of a methyl group for hydrogen.

These trends are mirrored remarkably well in the XPS spectra for acetylenic species adsorbed on the Ag(110) surface. As noted above, dissociation of propyne results in greater polarization of the triple bond: there is a greater separation of C(1s) binding energies for the methyl acetylide species than for propyne. It is also evident by comparison with XPS spectra for HC≡C acetylide species that the polarization is greater for the methyl-substituted species: the separation of the C(1s) levels of the acetylenic carbons was 1.8 eV for CH$_3$C≡C but only 1.5 eV for HC≡C.[20] The polarization of the acetylide π-electron density and the destabilizing effect of alkyl substitution on the acetylide have often been discussed in terms of donation of π electrons from the alkyl group. As noted by Pellerite and Brauman,[44] this argument is somewhat misleading. There is little net charge transfer from the methyl group to the acetylide moiety, i.e., the effect of the alkyl group is to alter the shape of the acetylide π-electron distribution rather than the density of the distribution. This argument is supported by the XPS spectra of Figure 5; the C(1s) level of the methyl group exhibits a larger decrease upon propyne dissociation than does that of the central acetylenic carbon. The relative magnitudes of these shifts would be expected to be the opposite of those observed if there were a significant shift of electron density from the methyl group to the acetylenic portion of the methyl acetylide. At least a portion of the total shifts of the C(1s) levels can be attributed to greater final state relaxation due to the stronger interaction of methyl acetylide species than molecular propyne with the surface. The arguments above are therefore based upon

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the *relative* shifts of the C(1s) levels assigned to the various carbon centers. As noted above, the shift of the methyl group C(1s) binding energy by 1.2 eV between adsorbed propyne and adsorbed methyl acetylide species is typical for alkyl substituents on other Brønsted acids.

Given the unambiguous effects in the XPS spectrum of internal polarization of the methyl acetylide, it is perhaps surprising that the UPS spectrum from this species is not appreciably different from that of molecular propyne. If one aligns the gas-phase UPS spectrum of propyne[34] with that of the adsorbed methyl acetylide, the principal effect of dissociation is a 0.7-eV contraction of the separation between the $6a_1$ and $7a_1$ orbitals of propyne. This observation is not surprising since electron density on the acetylenic hydrogen in propyne can be largely assigned to these two orbitals; they become more nearly degenerate upon removal of the proton. In contrast the π orbitals (the 1e which is nearly localized on the methyl group and the 2e which is essentially the triple bond) appear to be nearly unperturbed by adsorption and proton abstraction from propyne. The photoemission from these orbitals of the methyl acetylide is somewhat more difficult to resolve owing to overlap with the emission from the silver d bands; however, any appreciable contraction of the separation between these levels should produce a noticeable distortion of the negative image of the d-band emission in the difference spectrum of Figure 6. Such distortion is not evident, and the separation of these levels appears to be equal to within 0.2 eV to that for gas-phase propyne. Since the interaction between the π orbitals is the principal basis for the thermochemical arguments advanced above, it is perhaps surprising that this interaction is not evident in the UPS spectrum for adsorbed methyl acetylides. It should be recalled, however, that one can only obtain relative shifts of orbital energies for adsorbed species, since the contribution of relaxation effects to total shifts relative to gas-phase spectra is difficult to quantify. Further, the gas-phase acidity difference between $CH_3C{\equiv}CH$ and $HC{\equiv}CH$ is less than 0.2 eV, and this value is comparable to the resolution of UPS spectra for adsorbed species. Finally, angle-integrated UPS has proven remarkably insensitive to rehybridization and rearrangement of hydrocarbon intermediates on metal surfaces;[46] it is therefore not surprising that it does not provide information about distortion of the electron distribution within the alkyne system with the increase of internal polarization upon proton removal.

One further parallel between this study and previous work on oxidation of hydrocarbons on the Ag(110) surface is the failure to observe stable π-carbanion complexes. While stable σ-bonded acetylides are formed by proton abstraction from alkynes, the allylic and propargyl species expected in the oxidations of propylene and propyne have not been observed, even at temperatures as low as 200 K. Since both propylene and propyne react with adsorbed oxygen atoms to form stiochiometric amounts of surface carbon, the decomposition of allyl and propargyl complexes must occur at rates which are rapid in comparison with the rates of

the initial proton abstraction reactions. Thus, in contrast to its interaction with a variety of other conjugate base species including acetylides, carboxylates, and alkoxides which are presumably σ bonded to the surface, silver does not appear to stabilize surface π-carbanion complexes. This characteristic distinguishes silver from the metal oxides typically utilized as catalysts for the oxidation of higher olefins. It is well established that π-allyl species are formed by the diss⸱ ʳiative adsorption of propylene on oxide materials ranging from ᵗʰe bismuth molybdates[47] to ZnO.[48] The charge on these surface complexes is less well defined; however, it is the ability to form such complexes which appears to be an essential property of effective olefin oxidation, oxidative dehydrogenation, and ammoxidation catalysts. It is not surprising, therefore, that silver is not an effective catalyst for the oxidation of propylene and higher olefins; it remains unique, however, as a heterogeneous catalyst for the epoxidation of ethylene. The unusual selectivity of silver for this reaction may be due to constraints, analogous to those observed here on formation of π-carbanion complexes, on the interactions between silver and ethylene, ethylene oxide, and the various intermediates in this catalytic reaction.

V. Conclusions

Propyne reacts with adsorbed oxygen atoms on the Ag(110) surface via proton transfer to form water plus adsorbed hydrocarbon species. At 200 K this reaction is selective toward formation of stable surface methyl acetylide intermediates via proton abstraction from the acetylenic position in propyne. At 300 K initial proton abstraction from the methyl group is also kinetically favorable; the propargyl intermediate formed by this reaction decomposes rapidly to deposit atomic carbon and to supply additional hydrogen for water production. The selectivities for proton abstraction from the two ends of propyne are in excellent agreement with estimates based on the thermochemistry of heterolytic dissociation in the gas phase. XPS and UPS results support polarization models for the destabilization of acetylides by alkyl substitution.

The methyl acetylide intermediate undergoes thermal decomposition at 500 K to produce propyne and to deposit the stoichiometric amount of surface carbon. No evidence for production of allene via the base-catalyzed isomerization of propyne was observed. The contrast of the thermal stabilities of methyl acetylide and propargyl species supports previous conclusions that silver does not stabilize π-carbanion complexes.

Registry No. CH_3CCH, 74-99-7; Ag, 7440-22-4.

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