

## Interaction of Acetylene with the Ru(001) Surface

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**Abstract:** The adsorption and decomposition of acetylene on the hexagonally close-packed Ru(001) surface has been studied by using high-resolution electron energy loss spectroscopy and thermal desorption mass spectrometry. Below 230 K, acetylene is molecularly adsorbed on this surface with rehybridization of the acetylenic carbon atoms to nearly  $sp^3$  occurring. Between 230 and 250 K, the acetylene undergoes both dehydrogenation and hydrogenation reactions, resulting in the formation of two stable surface intermediates, ethylidyne ( $CCH_3$ ) and acetylide ( $CCH$ ). Both the ethylidyne and the acetylide decompose near 350 K, accompanied by hydrogen desorption and leaving only methylidyne ( $CH$ ) and carbon adatoms on the surface. The methylidyne decomposes with hydrogen evolution into the gas phase between approximately 480 and 700 K.

## I. Introduction

The interaction of unsaturated hydrocarbon molecules with a variety of low Miller index single-crystalline transition-metal surfaces has been the focus of much research in surface science recently.<sup>1</sup> These studies are of obvious importance both in quantifying the relationships between the bonding of hydrocarbon ligands to multinuclear homogeneous complexes and their bonding to surfaces and in view of the role that such hydrocarbons play in industrial, heterogeneous catalytic processes. The application of modern, sophisticated experimental techniques to the study of hydrocarbon adsorption and decomposition on metals has led to the identification of a number of surface species which may act as intermediates in these catalytic surface reactions and which have been observed in organometallic cluster compounds. Perhaps the most useful technique in understanding the structure and bonding of adsorbates on metal surfaces has been vibrationally inelastic electron scattering which is usually termed high-resolution electron energy loss spectroscopy (EELS), especially when employed in combination with thermal desorption mass spectrometry (TDMS). Recently, the results of two different EELS and TDMS studies of ethylene adsorption on the hexagonally close-packed Ru(001) surface have been reported.<sup>2,3</sup> As a natural extension of this work, we report here a similar investigation of the adsorption and decomposition of acetylene on Ru(001).

Acetylene adsorption has been studied previously with EELS on a wide variety of metal surfaces, including Cu(111),<sup>4</sup> Cu(100),<sup>5</sup> Cu(110),<sup>5</sup> Ag(110),<sup>6</sup> Ni(111),<sup>7</sup> Ni(110),<sup>4</sup> Pd(111),<sup>8,9</sup> Pd(100),<sup>9,10</sup> Pd(110),<sup>4</sup> Pt(111),<sup>11</sup> Rh(111),<sup>12</sup> Fe(110),<sup>13</sup> Fe(111),<sup>14</sup> W(110),<sup>15</sup> W(111),<sup>16</sup> and W(100).<sup>17</sup> With the exception of the Ag(110) surface, on which the adsorption is weak and reversible below 160 K, acetylene is adsorbed molecularly, but with the molecule strongly distorted from its gas-phase structure, in all the cases where adsorption below 200 K has been reported. Typically, the molecularly adsorbed acetylene is stable at temperatures below approximately 250–350 K. The single most important spectroscopic indication of the degree of rehybridization of molecular acetylene upon adsorption is the carbon–carbon stretching frequency, which is  $1974\text{ cm}^{-1}$  in gas-phase acetylene.<sup>18</sup> However, a large number of metal surfaces, including Cu(111), Cu(100), Cu(110), Pd(111), Pd(110), Ni(110), and Pt(111), on which acetylene is adsorbed molecularly, exhibit carbon–carbon stretching frequencies in the  $1300\text{--}1400\text{-cm}^{-1}$  range, indicative of a rehybridization of the carbon atoms to between  $sp^2$  and  $sp^3$  and an approximate carbon–carbon bond order of 1.5. On other surfaces, even more extensive rehybridization of the acetylene molecule occurs, resulting in still lower carbon–carbon stretching frequencies. These surfaces include Fe(110) ( $\nu_{CC} = 1240\text{ cm}^{-1}$ ), Ni(111) ( $\nu_{CC} = 1220\text{ cm}^{-1}$ ), Pd(100) ( $\nu_{CC} = 1210\text{ cm}^{-1}$ ), and Fe(111) ( $\nu_{CC} = 1145\text{ cm}^{-1}$ ). Further insight into the degree of distortion that the molecule experiences upon adsorption is given by the reduction of the carbon–hydrogen stretching frequencies

in going from the gas phase to the chemisorbed phase. Finally, the relative intensities of the carbon–hydrogen bending and carbon–carbon stretching modes may serve to delimit the geometry and the binding site of the adsorbed species.<sup>4</sup> It is both to investigate these issues and to quantify the connection with ethylene adsorption that we have undertaken this study of acetylene adsorption on Ru(001).

The mechanism by which molecularly adsorbed acetylene decomposes on metal surfaces is also of great interest. The initial dissociation step may be either carbon–carbon bond cleavage to produce methylidyne ( $CH$ ) or carbon–hydrogen bond cleavage and formation which may result in a number of different adsorbed hydrocarbon intermediates. Initial cleavage of the carbon–carbon bond has been reported on Ni(111) at 400 K<sup>7</sup> and on Fe(110) at approximately 320 K<sup>13</sup> to form surface methylidyne. Initial cleavage of carbon–hydrogen bonds occurs on the Pt(111), Pd(100), and Pd(111) surfaces. On Pt(111), formation of a  $CCH_2$  species via hydrogen transfer has been proposed as the initial step in acetylene decomposition.<sup>11</sup> On Pd(100), a hydrogen atom is abstracted from the molecularly adsorbed species by the surface between 300 and 450 K, resulting in the formation of an acetylide ( $CCH$ ).<sup>9</sup> The Pd(111) surface exhibits interesting and complex behavior, with the formation of both acetylide and ethylidyne ( $CCH_3$ ) above 300 K.<sup>9</sup> These species dehydrogenate thermally at higher temperatures, possibly via methylidyne intermediates. In view of the recent identification of both ethylidyne and methylidyne as decomposition products of ethylene on Ru(001),<sup>2,3</sup> a similar study of the decomposition of acetylene on this surface is of obvious importance.

In this paper, we first discuss thermal desorption measurements

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after acetylene adsorption on Ru(001) and then EEL spectra of both multilayer and chemisorbed molecular acetylene on this surface. The EEL spectra provide evidence for a highly distorted, nearly  $sp^3$ -hybridized, molecularly adsorbed acetylene in the chemisorbed overlayer at temperatures below approximately 230 K. We then turn to a discussion of the thermal decomposition of acetylene, which leads to the formation of both acetylide and ethylidyne between approximately 230 and 350 K. These species decompose below 400 K to yield methylidyne and surface carbon.

## II. Experimental Procedures

The EEL spectrometer used in these studies, as well as the ultra-high-vacuum (UHV) chamber in which it is contained, has been described in detail elsewhere.<sup>19</sup> Briefly, the stainless steel UHV chamber is pumped by a 220 L/s Varian ion pump and a titanium sublimation pump, and base pressures below  $5 \times 10^{-11}$  torr are obtained routinely. The home-built EEL spectrometer is of the Kuyatt-Simpson type, with  $180^\circ$  hemispherical deflectors serving as the energy dispersing elements in both the monochromator and the analyzer. The monochromator is spatially fixed, but the analyzer is rotatable to allow off-specular spectra to be measured. All spectra presented and referred to in this paper were collected in the specular direction unless otherwise noted. The impact energy of the incident electron beam was approximately 4 eV in all cases, and the beam was incident on the Ru(001) crystal at an angle of  $60^\circ$  with respect to the surface normal. The instrumental energy resolution in these studies, defined as the full-width at half-maximum of the elastically scattered beam, varied from 60 to  $80 \text{ cm}^{-1}$ , while count rates in the elastic peak varied from  $1.5 \times 10^5$  to  $3 \times 10^5$  cps.

The Ru(001) crystal was cooled by using liquid nitrogen, and temperatures as low as 80 K were obtained routinely. Crystal cleaning was achieved by using the well-established techniques of argon ion sputtering and heating the crystal in a background of oxygen.<sup>20</sup> The cleanliness of the surface was verified with EELS. Some of the EEL spectra presented in section III show a small amount of CO contamination (below 1–2% of a monolayer) due to adsorption from the background. Not surprisingly, it was found that these varying and low concentrations of coadsorbed CO did not affect the EEL spectra of acetylene and its decomposition products.

Thermal desorption mass spectrometry was performed in a separate UHV chamber also containing a Ru(001) crystal and equipped with a quadrupole mass spectrometer (UTI 100C) with a skimmer to discriminate between desorption from the crystal surface and desorption from the crystal edges and support leads, as well as an Auger electron spectrometer for verifying surface cleanliness. Heating rates between 5 and 20 K/s were used in the TDMS experiments. Crystal cooling and cleaning were accomplished as in the EELS chamber.

The  $C_2H_2$  used in these studies was obtained from an industrial acetylene tank (95% purity) and was purified as it was introduced into a glass flask by passage through a dry ice/methanol slurry. The main purpose of this procedure was to remove acetone, which is always added to prevent explosions when acetylene is stored under high pressures. The  $C_2D_2$  (99 atom % deuterated) was obtained from MSD Isotopes. The stainless steel leak lines through which the acetylene was introduced into the UHV chamber were flushed several times with  $C_2H_2$  or  $C_2D_2$ , in order to passivate them toward acetylene decomposition, before any acetylene was introduced into the UHV chamber. Mass spectra of the  $C_2D_2$  and  $C_2H_2$  which were admitted into the UHV chamber showed no traces of any impurities. Multilayer EEL spectra also showed no detectable impurities.

## III. Results and Discussion

**A. Thermal Desorption Mass Spectrometry.** Thermal desorption measurements after acetylene adsorption on Ru(001) at 80 K were performed for acetylene exposures in the range of 0.2–10 langmuir (1 langmuir =  $10^{-6}$  torr s). The only desorption products detected in the temperature range between 80 and 800 K were molecular acetylene and hydrogen. Benzene, ethylene, ethane, and methane were specifically looked for and were not detected under any circumstances.

Molecular acetylene desorbs only in a sharp peak at 95 K. Since this peak appears only for acetylene exposures greater than 5 langmuir and does not saturate for increasing exposures above 5 langmuir, it may be assigned unambiguously as the desorption of a multilayer state. No molecular acetylene desorbs from the

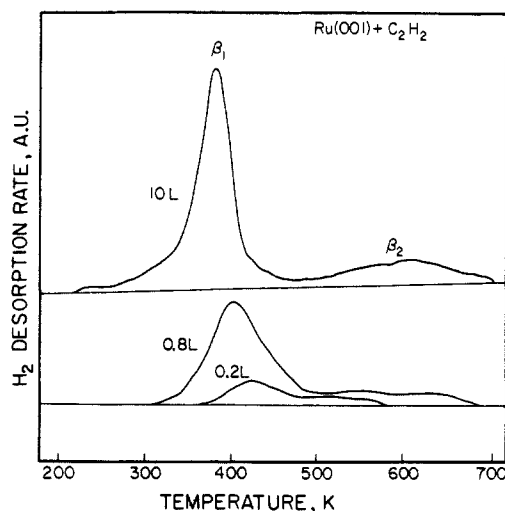


Figure 1.  $H_2$  thermal desorption spectra resulting after the Ru(001) surface at 80 K is exposed to 0.2, 0.8, and 10 langmuir of  $C_2H_2$ . The heating rate used in recording these spectra is approximately  $20 \text{ K s}^{-1}$ .

chemisorbed monolayer state of acetylene on the Ru(001) surface.

The hydrogen thermal desorption spectra that result after 0.2-, 0.8-, and 10-langmuir acetylene exposures on Ru(001) at 80 K are shown in Figure 1. The 0.2- and 0.8-langmuir exposures correspond, respectively, to approximately 20% and 70% of saturation acetylene coverage, and the 10-langmuir exposure, as the results discussed above suggest, is more than sufficient to saturate the monolayer. Indeed, hydrogen thermal desorption spectra are identical for all acetylene exposures greater than 5 langmuir, confirming that a 5-langmuir exposure corresponds to saturation coverage of chemisorbed acetylene on Ru(001) and that the hydrogen thermal desorption features shown in Figure 1 correspond to the decomposition of these chemisorbed species. The spectra in Figure 1 reveal two main desorption features, a low-temperature ( $\beta_1$ ) peak and a broad, high-temperature ( $\beta_2$ ) peak. The  $\beta_1$  peak is centered at 425 K for a 0.2-langmuir acetylene exposure and shifts downward to 380 K for saturation acetylene exposures. This behavior is characteristic of second-order desorption kinetics. The  $\beta_2$  peak is quite broad, extending from about 480 to 580 K for 0.2-langmuir acetylene exposures and from 480 to 700 K for saturation exposures.

As will be shown from the EELS results, the only hydrocarbon species resulting from acetylene decomposition on Ru(001) above 400 K is methylidyne. Thus, the high-temperature  $\beta_2$  desorption peak of hydrogen results from methylidyne decomposition to yield carbon adatoms and  $H_2(g)$ . The  $\beta_1$  desorption peak of hydrogen results from surface hydrogen that is formed from the dehydrogenation of ethylidyne (and to a lesser degree from acetylene decomposition to acetylide), as will be discussed later. For initial acetylene exposures of 0.4 langmuir or more, the ratio of the  $\beta_1$ -to- $\beta_2$  peak areas is 3:1 within experimental error, indicating that one-fourth of the hydrogen initially present in the chemisorbed acetylene is eventually present in methylidyne. For 0.2-langmuir acetylene exposures, the ratio of the  $\beta_1$ -to- $\beta_2$  peak areas is more difficult to determine due to peak overlap, but it is approximately 2:1, indicating that one-third of the hydrogen atoms initially present in the acetylene are eventually present in methylidyne. Thus, relatively more methylidyne is formed for low initial acetylene exposures.

Since neither monolayer acetylene nor other hydrocarbons desorb molecularly from Ru(001), all of the chemisorbed acetylene decomposes on the surface to yield eventually  $H_2(g)$  and carbon adatoms. Thus, there is a one-to-one correspondence between the amount of acetylene adsorbed in the monolayer and the total amount of hydrogen desorbing in the  $\beta_1$  and  $\beta_2$  thermal desorption peaks. Consequently, the total amount of hydrogen desorbing following an acetylene exposure may be compared to the amount of hydrogen desorbing from the clean Ru(001) surface following a saturation exposure to  $H_2$ ,<sup>21</sup> and this may be used to calculate

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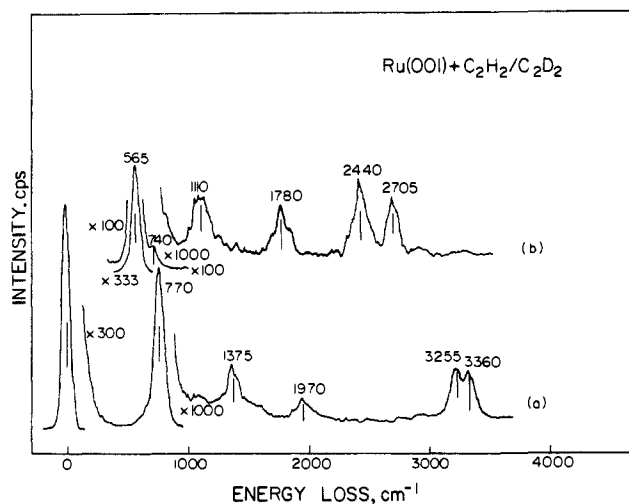


Figure 2. EEL spectra that result from 10-langmuir exposures of (a)  $C_2H_2$  and (b)  $C_2D_2$  to the Ru(001) surface at 80 K. These spectra are characteristic of condensed acetylene multilayers.

Table I. Vibrational Frequencies ( $cm^{-1}$ ) for  $C_2H_2$  and  $C_2D_2$  in Gas and Crystalline Phases and for  $C_2H_2$  and  $C_2D_2$  Multilayers on Ru(001) at 80 K

mode	gas <sup>18</sup>	crystalline IR <sup>22a</sup>	multilayers on Ru(001)
$C_2H_2$			
CH s bend ( $\nu_4$ )	612		605 <sup>b</sup>
CH a bend ( $\nu_5$ )	729	761, 769	770
CC stretch ( $\nu_2$ )	1974		1970
CH a stretch ( $\nu_2$ )	3287	3226	3255
CH s stretch ( $\nu_1$ )	3374		3360
$C_2D_2$			
CD s bend ( $\nu_4$ )	505		545 <sup>b</sup>
CD a bend ( $\nu_5$ )	539	562, 568	565
CC stretch ( $\nu_2$ )	1762		1780
CD a stretch ( $\nu_3$ )	2439	2393	2440
CD s stretch ( $\nu_1$ )	2701		2705

<sup>a</sup> Crystalline IR data at 63 K. <sup>b</sup> Estimated from frequency of  $\nu_4 + \nu_5$  combination band. s = symmetric, a = asymmetric.

the acetylene coverage. This yields a saturation fractional coverage of approximately 0.27 for acetylene adsorption on Ru(001).

**B. Electron Energy Loss Spectroscopy. 1. Multilayer State.** As indicated above, exposing the Ru(001) surface at 80 K to approximately 5 langmuir or more of  $C_2H_2$  or  $C_2D_2$  results in the condensation of molecular multilayers of acetylene on the surface. The EEL spectra of  $C_2H_2$  and  $C_2D_2$  multilayers on the Ru(001) surface are shown in Figure 2, and the observed vibrational frequencies are listed in Table I, together with data for both gas-phase and crystalline acetylene. These multilayer spectra are useful as a supplement to TDMS data, both in verifying the purity of the acetylene used in these experiments and in determining when saturation coverage of chemisorbed acetylene is obtained. For both  $C_2H_2$  and  $C_2D_2$ , all fundamental modes are clearly resolved except  $\nu_4$ , the Raman-active carbon-hydrogen symmetric bending mode, which is obscured by the intense, IR-active asymmetric bending mode,  $\nu_5$ . As in the case of gas-phase IR spectra of acetylene,<sup>18</sup> the frequency of the  $\nu_4$  mode may be estimated from the observed  $\nu_5 + \nu_4$  combination band, which occurs at 1375  $cm^{-1}$  for  $C_2H_2$  multilayers and 1110  $cm^{-1}$  for  $C_2D_2$  multilayers. Not surprisingly, the IR-active modes of the acetylene multilayers are close in frequency to both those of crystalline acetylene<sup>22</sup> and those of gas-phase acetylene.<sup>18</sup> The feature near 740  $cm^{-1}$  in Figure 2b is probably due to a small amount of  $C_2H_2$  in the deuterated acetylene. This impurity is on the order of 1% or less.

**2. Molecularly Chemisorbed Acetylene.** Annealing the Ru(001) surface on which acetylene multilayers are present to above 95

Table II. Vibrational Modes of Molecularly Adsorbed Acetylene on Ru(001) in the Temperature Range 80–230 K, with Corresponding Frequencies from the Cobalt Compounds  $Co_2(CO)_6(C_2H_2)^{24}$  and  $Co_4(CO)_{10}(C_2H_2)^{26}$  Presented for Comparison. All Frequencies Are Reported in  $cm^{-1}$

mode <sup>a</sup>	Ru(001)			$Co_2(CO)_6-$ ( $C_2H_2$ )	$Co_4(CO)_{10}-$ ( $C_2H_2$ )
	$C_2H_2$	$C_2D_2$	$\nu(C_2H_2)/$ $\nu(C_2D_2)$		
CH a stretch	2940	2210	1.33	3116	3020
CH s stretch				3086	2993
CC stretch	1135	1085	1.05	1403	1199
CH bend	980	715	1.37	894	983, 1120
CH bend	765	585	1.35	768	837, 922
MC a stretch	520	obscured		605	619
MC s stretch	375	350	1.07	551	?

<sup>a</sup> s = symmetric, a = asymmetric.

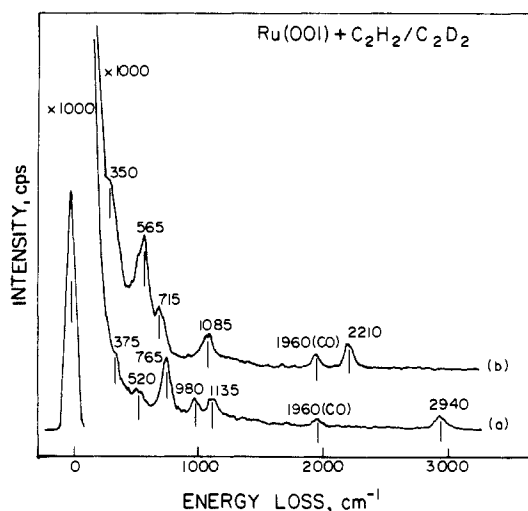


Figure 3. EEL spectra that result when the Ru(001) surface at 80 K is exposed to 5 langmuir of (a)  $C_2H_2$  and (b)  $C_2D_2$  and heated to 150 K. The spectra were recorded at 80 K. These spectra are characteristic of chemisorbed acetylene.

K, or exposing the Ru(001) surface to less than 5 langmuir of acetylene at 80 K, results in the formation of a surface species which is stable to approximately 230 K. This chemisorbed species is identified easily as molecularly adsorbed acetylene which has undergone extensive rehybridization upon adsorption. The observed vibrational modes for  $C_2H_2$  and  $C_2D_2$  are listed together with their assignments in Table II, and the relevant EEL spectra are presented in Figure 3. For comparison, the vibrational data for acetylene in two organometallic cobalt compounds are listed also in Table II. These data will be discussed below in relation to possible bonding geometries for acetylene on Ru(001).

The mode assignments follow in a straightforward fashion from a comparison of the spectra of hydrogenated and deuterated acetylene. The loss feature at 2940 (2210)  $cm^{-1}$  for  $C_2H_2$  ( $C_2D_2$ ) is clearly due to a carbon-hydrogen (carbon-deuterium) stretching vibration. In both cases, the symmetric and asymmetric stretching modes are not resolved. The intense mode at 765  $cm^{-1}$ , which shifts down to 565  $cm^{-1}$  upon deuteration, is assigned to a carbon-hydrogen bending mode, as is the less intense mode which shifts from 980 to 715  $cm^{-1}$  upon deuteration. The feature which appears at 1135  $cm^{-1}$  in the  $C_2H_2$  spectrum and at 1085  $cm^{-1}$  in the  $C_2D_2$  spectrum clearly does not shift sufficiently to be a hydrogenic mode and is thus assigned as the carbon-carbon stretching vibration. Modes at 520 and 375  $cm^{-1}$  in the  $C_2H_2$  spectrum are assigned, respectively, to the asymmetric and symmetric metal-carbon stretching modes of adsorbed acetylene. The latter mode occurs at 350  $cm^{-1}$  for  $C_2D_2$ , while the asymmetric metal-carbon stretch in the deuterated species is obscured by the carbon-deuterium bending mode that is centered at 565  $cm^{-1}$ . There is no other set of mode assignments that consistently ac-

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counts for the observed spectra.

Off-specular EEL spectra indicate that the carbon-carbon stretching vibration at  $1135\text{ cm}^{-1}$  in  $\text{C}_2\text{H}_2$  and the carbon-hydrogen bending vibration at  $765\text{ cm}^{-1}$  are principally dipolar excited modes, while the carbon-hydrogen stretching vibration at  $2940\text{ cm}^{-1}$  and the carbon-hydrogen bend at  $980\text{ cm}^{-1}$  are excited primarily by nondipolar mechanisms.<sup>23</sup> These data suggest that the carbon-hydrogen bend at  $765\text{ cm}^{-1}$  involves motion of the hydrogen atoms largely perpendicular to the surface, while the carbon-hydrogen bend at  $980\text{ cm}^{-1}$  involves motion of the hydrogen atoms largely parallel to the surface. However, without detailed knowledge of the surface binding site of chemisorbed acetylene, assignment of these bending modes as "in-plane" or "out-of-plane" is not possible. No additional vibrational modes are observed in off-specular spectra.

The observed carbon-carbon stretching frequency of  $1135\text{ cm}^{-1}$  for chemisorbed  $\text{C}_2\text{H}_2$  corresponds to a carbon-carbon bond order nearly equal to one, with the carbon atoms being nearly  $\text{sp}^3$  hybridized. This may be seen by comparison to the gas-phase carbon-carbon stretching frequencies of ethane ( $\nu_{\text{CC}} = 995\text{ cm}^{-1}$ ) and ethylene ( $\nu_{\text{CC}} = 1623\text{ cm}^{-1}$ ).<sup>18</sup> Although this is the lowest carbon-carbon stretching frequency which has heretofore been observed for chemisorbed acetylene on any transition-metal surface, it is quite close to the value of  $1145\text{ cm}^{-1}$  which has been observed for  $\text{C}_2\text{H}_2$  on  $\text{Fe}(111)$ .<sup>14</sup> The carbon-hydrogen stretching frequency of  $2940\text{ cm}^{-1}$  is also consistent with carbon atoms that are nearly  $\text{sp}^3$  hybridized; typical values for  $\nu_{\text{CH}}$  are  $2800\text{--}3000\text{ cm}^{-1}$  for  $\text{sp}^3$ -hybridized carbon atoms and  $2950\text{--}3100\text{ cm}^{-1}$  for  $\text{sp}^2$  hybridized carbon atoms.<sup>18</sup>

A comparison of the carbon-carbon stretching frequency of  $1135\text{ cm}^{-1}$  for acetylene chemisorbed on  $\text{Ru}(001)$  to the carbon-carbon stretching frequencies of the acetylene ligands in the cobalt compounds listed in Table II suggests that such a low value of  $\nu_{\text{CC}}$  is not at all unreasonable for acetylene adsorbed on a metal surface. The decrease in frequency of  $204\text{ cm}^{-1}$ , from  $\nu_{\text{CC}} = 1403$  to  $1199\text{ cm}^{-1}$ , in going from a two-cobalt atom cluster to a four-cobalt atom cluster suggests that a further decrease in  $\nu_{\text{CC}}$  might be expected as the metal "cluster" becomes infinitely large (i.e., a metal surface). This should be especially true of the surfaces of the relatively more reactive iron group metals, as opposed to surfaces of the nickel-palladium-platinum triad on which acetylene adsorption has been studied more extensively.

Based on the EELS data alone, any conclusions regarding the nature of the adsorption site for acetylene on  $\text{Ru}(001)$  must be somewhat speculative. It has been suggested<sup>4</sup> that adsorbed  $\text{C}_2\text{H}_2$  species exhibiting strong carbon-hydrogen bending modes in the  $670\text{--}770\text{ cm}^{-1}$  region, together with relatively weak carbon-carbon stretching modes, are the result of a "di- $\sigma + \pi$ "-bonding structure in which the plane of a  $\text{cis M}-\text{CH}=\text{CH}-\text{M}$  complex is tilted significantly with respect to the surface normal through the interaction of the  $\text{C}=\text{C}$  bond with a third metal atom. Such a model accounts successfully for the dipolar enhancement of the intense carbon-hydrogen bending mode in these surface complexes, assigned as the  $\gamma_{\text{CH}}$  out-of-plane bend. Such species occur when acetylene is adsorbed on  $\text{Ni}(110)$ ,  $\text{Pd}(111)$ ,  $\text{Pd}(110)$ ,  $\text{Rh}(111)$ , and  $\text{Pt}(111)$ . However, on all of these surfaces, the adsorbed acetylene is characterized by a carbon-carbon stretching frequency between  $1300$  and  $1400\text{ cm}^{-1}$ . Consequently, it is not clear that the same structure should apply to  $\text{C}_2\text{H}_2$  on  $\text{Ru}(001)$ . Indeed, the low carbon-carbon stretching frequency of  $1135\text{ cm}^{-1}$  argues against any model which invokes  $\pi$ -bonding between the carbon-carbon bond and the surface. Possible alternative bonding geometries are suggested by the organometallic compounds listed in Table II. In the compound  $\text{Co}_2(\text{CO})_6(\text{C}_2\text{H}_2)$ ,<sup>24</sup> the plane containing the  $\text{C}_2\text{H}_2$  group bisects the cobalt-cobalt vector and is perpendicular to it. A similar bonding configuration could be obtained for acetylene on  $\text{Ru}(001)$  if the carbon atoms of acetylene

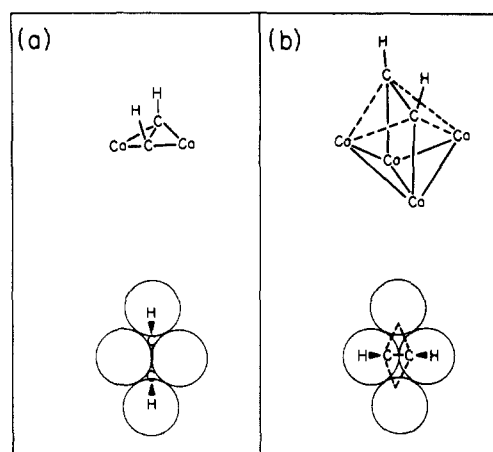


Figure 4. (a) Metal-acetylene structure of the organometallic compound  $\text{Co}_2(\text{CO})_6(\text{C}_2\text{H}_2)$ ,<sup>24</sup> and an analogous bonding configuration for acetylene on the  $\text{Ru}(001)$  surface. (b) Metal-acetylene structure of the organometallic compound  $\text{Co}_4(\text{CO})_{10}(\text{C}_2\text{H}_2)$ ,<sup>26a</sup> and an analogous bonding configuration for acetylene on the  $\text{Ru}(001)$  surface.

occupy adjacent, inequivalent threefold hollow sites on the surface (Figure 4a). Since these adjacent adsites are separated by  $1.56\text{ \AA}$  on this surface,<sup>25</sup> slightly farther apart than the length of a carbon-carbon single bond in a hydrocarbon molecule ( $1.54\text{ \AA}$ ), it is probable that the carbon atoms would not be centered directly above the threefold sites if such a bonding geometry were to occur. In the compound  $\text{Co}_4(\text{CO})_{10}(\text{C}_2\text{H}_2)$ ,<sup>26</sup> the carbon-carbon bond of the acetylene ligand lies parallel to a cobalt-cobalt bond, with each carbon atom being  $\sigma$ -bonded to one of these two cobalt atoms and with a four-centered,  $\mu$ -type bond between the carbon atoms and the remaining two cobalt atoms. An analogous bonding situation on  $\text{Ru}(001)$  would be achieved if the two carbon atoms of the acetylene are  $\sigma$ -bonded to nearest-neighbor ruthenium atoms and with a four-centered bond between the carbon atoms and the two ruthenium atoms on either side of this carbon-carbon bond (Figure 4b). It should be emphasized that the observation of a dipolar-enhanced carbon-carbon stretching mode in specular EEL spectra does not rule out such bonding models in which the carbon-carbon bond lies very nearly parallel to the surface, since charge coupling between the adsorbed acetylene and the metal may result in a substantial dynamic dipole being associated with the  $\nu_{\text{CC}}$  vibration.<sup>27</sup>

In summary, molecularly adsorbed acetylene on  $\text{Ru}(001)$  exhibits vibrational frequencies characteristic of essentially a carbon-carbon single bond and  $\text{sp}^3$ -hybridized carbon atoms. Although we have discussed two possible bonding configurations based on a comparison with organometallic cobalt complexes, we stress that this is speculative and feel that additional studies of the vibrational spectra of acetylene in cluster compounds and additional measurements with other surface-sensitive techniques are necessary before firm conclusions concerning the nature of the binding site on  $\text{Ru}(001)$  may be drawn.

**3. Thermal Decomposition of Chemisorbed Acetylene.** When the  $\text{Ru}(001)$  surface is heated with molecularly chemisorbed acetylene to temperatures in the range of  $250\text{--}350\text{ K}$ , marked changes occur in the EEL spectra. Figure 5a shows the EEL spectrum that results when the surface represented in Figure 3a of adsorbed  $\text{C}_2\text{H}_2$  is annealed to  $300\text{ K}$ . The most obvious changes are the disappearance of the carbon-hydrogen bending mode of molecularly adsorbed acetylene at  $980\text{ cm}^{-1}$  and the appearance of a new mode at  $1360\text{ cm}^{-1}$ , which is comparable in intensity to the mode at  $1140\text{ cm}^{-1}$ . In addition, the strong carbon-hydrogen bending mode which occurs at  $765\text{ cm}^{-1}$  for molecularly adsorbed

(25) This distance is calculated easily from the nearest-neighbor separation of  $2.71\text{ \AA}$  in bulk ruthenium; see: Kittel, C. *Introduction to Solid State Physics*; 5th ed.; Wiley: New York, 1976.

(26) Gervasio, G.; Rossetti, R.; Stanghellini, P. L. *Organometallics* 1985, 4, 1612.

(27) Reference 23, pp 171-172.

(23) For a discussion of EELS scattering mechanisms, see: Ibach, H.; Mills, D. L. *Electron Energy Loss Spectroscopy and Surface Vibrations*; Academic: New York, 1982.

(24) Iwashita, Y.; Tamura, F.; Nakamura, A. *Inorg. Chem.* 1969, 8, 1179.

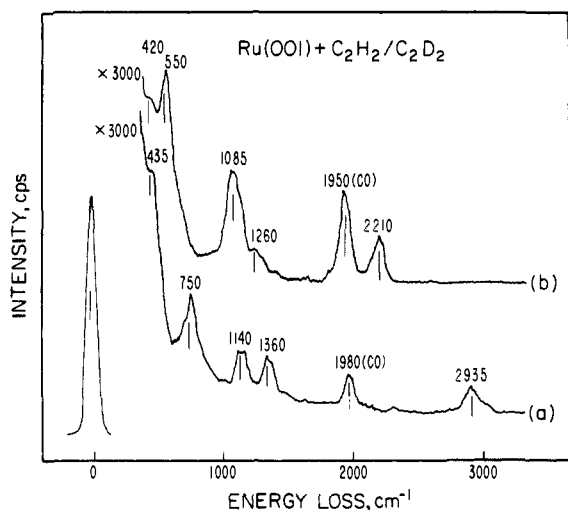


Figure 5. EEL spectra that result when the Ru(001) surface at 80 K is exposed to 5 langmuir of (a)  $C_2H_2$  and (b)  $C_2D_2$  and heated to 300 K. These spectra were recorded at 80 K and show the characteristic features of acetylide and ethylidyne.

acetylene shifts down slightly ( $\sim 15\text{ cm}^{-1}$ ) in frequency. Finally, the metal-carbon stretching modes of adsorbed acetylene at 375 and  $520\text{ cm}^{-1}$  are no longer present but are replaced by a new mode at  $435\text{ cm}^{-1}$ .

Spectra of deuterated acetylene on Ru(001) which has been annealed to 300 K (Figure 5b) show similar changes. The intense carbon-deuterium bend of molecularly adsorbed  $C_2D_2$  shifts downward slightly from 565 to  $550\text{ cm}^{-1}$ , the carbon-deuterium bend at  $715\text{ cm}^{-1}$  is greatly reduced in intensity or completely absent, and a new mode appears at  $420\text{ cm}^{-1}$ . In addition, a relatively broad feature appears between 1080 and  $1120\text{ cm}^{-1}$ , and a weaker feature appears at  $1260\text{ cm}^{-1}$ .

These observed changes that occur in the EEL spectra when the surface is annealed to temperatures above 250 K might be accounted for in two different ways. One possibility is that acetylene remains molecularly chemisorbed on the surface under these conditions but has undergone a change in molecular orientation or adsorption site such that the observed spectral changes result. The second possibility is that a surface reaction has taken place, resulting in the formation of one or more new surface species. The first of these two possibilities is most unlikely in view of the previously discussed thermal desorption spectra. The fact that the low temperature tail of the  $\beta_1$  hydrogen thermal desorption peak extends to below 250 K for saturation acetylene coverages indicates that some carbon-hydrogen bond cleavage has occurred by this temperature. Furthermore, attempting to rationalize the EEL spectra observed after heating to 300 K in terms of molecularly adsorbed acetylene would require assigning the  $1360\text{-cm}^{-1}$  peak in the  $C_2H_2$  spectra to a carbon-hydrogen bending mode, which is inconsistent with all existing vibrational data for acetylene adsorbed on surfaces or as a ligand in organometallic compounds.<sup>28</sup> In addition, the bands at 1140 and  $1360\text{ cm}^{-1}$  in Figure 5a disappear at a slightly lower temperature than the band at  $750\text{ cm}^{-1}$ . Hence, these two modes cannot be assigned as belonging to the same surface species that gives rise to the  $750\text{-cm}^{-1}$  mode. The possibility that the EEL spectra in Figure 5 correspond to some altered form of molecularly chemisorbed acetylene may therefore be ruled out unambiguously.

Consequently, it must be concluded that the EEL spectra shown in Figure 5 are characteristic of at least two different reaction products that result from the thermally activated decomposition of acetylene on Ru(001). Indeed, the observed vibrational modes

(28) To our knowledge, no CH bending mode above  $1000\text{ cm}^{-1}$  has been identified previously for acetylene in an organometallic complex. The only CH bending frequency identified previously for chemisorbed acetylene which lies above  $1150\text{ cm}^{-1}$  is one of  $1415\text{ cm}^{-1}$  on Fe(110), a surface species for which all four possible acetylene CH bending modes were observed in specular EEL spectra.<sup>13</sup>

Table III. Vibrational Modes Observed for Ethylidyne and Acetylide Present on the Ru(001) Surface in the Temperature Range 250–350 K due to Acetylene Decomposition. All Frequencies Are Given in  $\text{cm}^{-1}$

CCH <sub>3</sub> (ethylidyne)			
mode	C <sub>2</sub> H <sub>3</sub>	C <sub>2</sub> D <sub>3</sub>	$\nu(C_2H_3)/\nu(C_2D_3)$
CC stretch	1140	$\sim 1150^a$	0.98
$\delta_s(CH_3)$	1360	$\sim 1030^a$	1.30
CH stretch <sup>b</sup>	$\sim 2935$	$\sim 2210$	1.33
$\delta_a(CH_3)^c$	1440		
$\rho(CH_3)^c$	990	800	1.24
CCH (acetylide)			
mode	C <sub>2</sub> H	C <sub>2</sub> D	$\nu(C_2H)/\nu(C_2D)$
CH bend	750	550	1.36
CC stretch	observed	1260	
CH stretch <sup>b</sup>	$\sim 2935$	$\sim 2210$	1.33
RuC stretch	435	420	1.04

<sup>a</sup>These two modes overlap in the deuterated spectra, and the frequencies given are best estimates based on several different spectra. <sup>b</sup>The CH and CD stretching modes of the acetylide and ethylidyne species are not well resolved. <sup>c</sup>These modes are observed mainly in off-specular spectra; they are very weak or absent in specular EEL spectra.

may be explained easily in terms of two species, namely acetylide and ethylidyne. Mode assignments for both species are listed in Table III. Ethylidyne has previously been isolated and identified as a product of ethylene decomposition on Ru(001),<sup>2,3</sup> and modes of approximately equal intensity at  $1140\text{ cm}^{-1}$  (carbon-carbon stretch) and  $1360\text{ cm}^{-1}$  [ $\delta_s(CH_3)$ ] are characteristic of this species. To confirm further the identity of this species, off-specular EEL spectra were measured which showed additional vibrational modes at  $990\text{ cm}^{-1}$  [ $\rho(CH_3)$ ] and  $1440\text{ cm}^{-1}$  [ $\delta_a(CH_3)$ ], as is the case for ethylidyne formed by ethylene decomposition. The remaining vibrational modes in Figure 5 may be assigned to the acetylide species. The  $750\text{-cm}^{-1}$  mode is a carbon-hydrogen bend, and the  $435\text{-cm}^{-1}$  mode is a metal-carbon stretch. The latter is far too intense to be attributed solely to the metal-carbon stretch of coadsorbed CO, and since a mode of this intensity was not observed in the case of ethylidyne formed from ethylene on Ru(001), we attribute it mainly to the acetylide species. It is possible, however, that the symmetric metal-carbon stretch of ethylidyne, which occurs at  $480\text{ cm}^{-1}$  for ethylidyne formed from ethylene decomposition,<sup>3</sup> also contributes to the intensity of this mode. As may be seen in Table III, deuterated spectra are consistent with these assignments. The feature at  $1085\text{ cm}^{-1}$  in the  $C_2D_2$  spectrum is due to the overlap of the carbon-carbon stretch and the  $\delta_s(CD_3)$  mode of deuterated ethylidyne. In addition, the weak mode which appears at  $1260\text{ cm}^{-1}$  in the deuterated spectra may be assigned to the carbon-carbon stretch of the acetylide. This frequency is too high to be due to any sort of carbon-deuterium vibration, since no modes (except the carbon-hydrogen stretch) appear above  $1360\text{ cm}^{-1}$  in the specular spectra of acetylide and ethylidyne. The corresponding mode for acetylide is expected to be upshifted slightly (it appears at  $1290\text{ cm}^{-1}$  for acetylide formed from ethylene decomposition) and is thus obscured by the  $\delta_s(CH_3)$  mode of ethylidyne. Finally, it should be noted that the carbon-hydrogen (carbon-deuterium) stretching frequencies of the acetylide and the ethylidyne are not well resolved and therefore must be at approximately the same frequency.

Since ethylidyne has a larger hydrogen-to-carbon atom ratio than acetylene, it is obvious that not all of the molecularly adsorbed acetylene on Ru(001) may be converted to ethylidyne when the surface is heated. This is consistent with the observation that ethylidyne is formed only when acetylide is formed simultaneously. Thus, the overall chemical conversion which results in ethylidyne formation may be written as the self-hydrogenation reaction



This is not meant to imply, however, that acetylide and ethylidyne

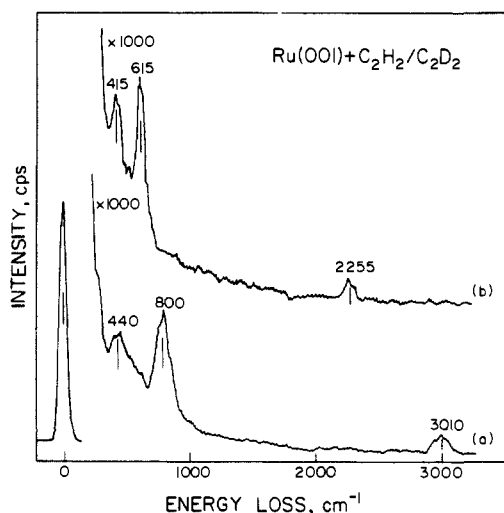
**Table IV.** Vibrational Frequencies ( $\text{cm}^{-1}$ ) of the Carbon-Hydrogen Bending and Stretching Modes of Methylidyne in Two Organometallic Compounds and on Several Metal Surfaces

	$\text{Co}_3(\mu_3\text{-CH})\text{-(CO)}_9^{34}$	$\text{Ru}_3(\text{CO})_9\text{H}_3\text{-(}\mu_3\text{-CH)}^{35}$	$\text{Fe(111)}^{14}$	$\text{Ni(111)}^{30}$	$\text{Pd(111)}^{31}$	$\text{Pt(111)}^{32}$	$\text{Rh(111)}^{33}$	$\text{Ru(001)}$ (this work)
CH bend	850	894	795	790	762	850	770	800
CH stretch	3041	2988	3015	2980	3002	3100	3025	3010

are formed in a ratio of 1:1, since it is obvious that acetylide formation may occur without ethylidyne formation. As written, this reaction says nothing concerning the mechanism of acetylide and ethylidyne formation from acetylene, an issue of obvious fundamental importance. We have not been able to isolate spectroscopically a  $\text{CCH}_2$  species or any other intermediate in the formation of ethylidyne under these conditions. Coadsorption experiments with acetylene and hydrogen on Ru(001) are currently in progress, which may shed light on the mechanism of acetylide and ethylidyne formation.<sup>29</sup>

The ethylidyne that is formed on Ru(001) has been discussed in detail in previous studies of ethylene adsorption<sup>2,3</sup> and, consequently, will not be considered further here. However, since we have not previously described the acetylide species in detail, a discussion of this species is in order. Very few acetylide species have been identified previously on metal surfaces. On Ag(110) with preadsorbed oxygen, an acetylide has been identified as the result of acetylene decomposition.<sup>6</sup> However, since the carbon atoms in this species retain an sp hybridization, as evidenced by a carbon-hydrogen stretching frequency of  $3250\text{ cm}^{-1}$ , this species is clearly not closely related to the acetylide that is formed on Ru(001). Acetylene decomposition on Pd(100) and Pd(111),<sup>9</sup> however, leads to the formation of an acetylide which is very similar to the one that is observed on Ru(001), the former being characterized by an intense carbon-hydrogen bend at  $750\text{ cm}^{-1}$ , a weak carbon-carbon stretch at  $1340\text{ cm}^{-1}$ , and a rather weak carbon-hydrogen stretch at  $3000\text{ cm}^{-1}$ . From these data it was suggested that the acetylide on the palladium surfaces has both carbon atoms bonded to the surface, with the carbon-carbon bond axis either parallel or slightly skewed relative to the surface plane. This is consistent with a weak carbon-carbon stretching vibration and an intense carbon-hydrogen bending vibration, in accordance with the surface dipole selection rule for EELS.<sup>23</sup> The same conclusions very likely apply to the acetylide on Ru(001), and the somewhat lower carbon-carbon ( $1260\text{ cm}^{-1}$  for CCD) and carbon-hydrogen ( $\sim 2935\text{ cm}^{-1}$ ) stretching frequencies on the ruthenium surface suggest a slightly lower carbon-carbon bond order than occurs in the acetylide on palladium, although in both cases the bond order is clearly between one and two. This slightly lower carbon-carbon bond order may be related to the lower decomposition temperature of acetylide on Ru(001). On this surface the acetylide has decomposed entirely by 400 K, while on Pd(100) at least some acetylide remains on the surface to 650 K. Finally, we note that it is quite reasonable that the carbon-carbon stretching frequency of adsorbed acetylide is somewhat higher than that of chemisorbed acetylene on Ru(001), since the former may have some double bond character due to the additional electron no longer involved in a carbon-hydrogen bond.

Annealing the Ru(001) surface to temperatures of 400 K or higher causes the decomposition of both the acetylide and the ethylidyne, and a new surface species appears which is characterized by vibrational modes at 440 (415), 800 (615), and  $3010\text{ (2255)}\text{ cm}^{-1}$  in the case of  $\text{C}_2\text{H}_2$  ( $\text{C}_2\text{D}_2$ ). The vibrational spectra for the hydrogenated and deuterated forms of this species are shown in Figure 6. Based on the previous studies of ethylene decomposition on Ru(001), and comparison to vibrational data for a number of previously identified surface species<sup>14,30-33</sup> and analogous organometallic compounds,<sup>34,35</sup> the vibrational modes



**Figure 6.** EEL spectra that result after the Ru(001) surface at 80 K is exposed to 5 langmuir of (a)  $\text{C}_2\text{H}_2$  and (b)  $\text{C}_2\text{D}_2$ , annealed to 400 K, and recooled to 80 K. These spectra are characteristic of a methylidyne species.

of this new species are identified easily, respectively, as the metal-carbon stretch, the carbon-hydrogen (carbon-deuterium) bend, and the carbon-hydrogen (carbon-deuterium) stretch of a surface methylidyne. The carbon-hydrogen modes are listed in Table IV and compared to those for other methylidyne species on surfaces and in the organometallic compounds  $\text{Ru}_3\text{-(CO)}_9\text{H}_3(\mu_3\text{-CH})$  and  $\text{Co}_3(\mu_3\text{-CH})(\text{CO})_9$ . A significant feature of the methylidyne spectra is the complete lack of any vibrational features between 1000 and 2000  $\text{cm}^{-1}$  which might have been associated with a carbon-carbon stretching vibration. Note that the frequency of the carbon-hydrogen bend of methylidyne is approximately  $50\text{ cm}^{-1}$  higher than, and thus quite distinct from, the carbon-hydrogen bend of the acetylide which exists at lower temperatures and that the carbon-hydrogen stretch is also up-shifted by about  $70\text{ cm}^{-1}$ . It should be pointed out that, in addition to methylidyne, there must be a rather large concentration (approximately 0.4 monolayer) of carbon adatoms on the Ru(001) surface at 400 K, since the thermal desorption spectra indicate that a large fraction of the hydrogen initially present in the acetylene has desorbed from the surface by this temperature. Heating the surface to slightly over 700 K desorbs the remaining hydrogen, and EEL spectra measured at 800 K verify that all spectral features due to methylidyne have disappeared. All that remains is a weak loss feature near  $600\text{ cm}^{-1}$ , which may be attributed to the presence of carbon adatoms.

Both chemical intuition and the structures of the organometallic complexes listed in Table IV suggest that the most likely coordination site for methylidyne on Ru(001) is one in which the carbon atom occupies a threefold hollow site. Indeed, the observed carbon-hydrogen bending and stretching modes of methylidyne on Ru(001) resemble most closely those of methylidyne on the hexagonally close-packed Ni(111) surface, on which a structure has been proposed in which the carbon atom occupies a threefold hollow site, and the carbon-hydrogen bond axis is tilted slightly with respect to the surface normal. The latter allows the carbon-hydrogen bending mode to become dipolar active and could

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(30) Demuth, J. E.; Ibach, H. *Surf. Sci.* **1978**, *78*, L747.

(31) Gates, J. A.; Kesmodel, L. L. *Surf. Sci.* **1983**, *124*, 68.

(32) Reference 23, Chapter 6.

(33) Dubois, L. H.; Somorjai, G. A. *Am. Chem. Soc., Symp. Ser.* **1980**, *32*, 1.

(34) Howard, M. W.; Kettle, S. F.; Oxtun, I. A.; Powell, D. B.; Sheppard, N.; Skinner, P. J. *Chem. Soc., Faraday Trans. 2*, **1981**, *77*, 397.

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account for its relatively high intensity in the methylidyne spectra on Ru(001). Spectra taken  $10^\circ$  off-specular do indeed indicate a marked reduction in the intensity of the carbon-hydrogen bending mode on Ru(001), which suggests that this mode is dipolar enhanced in specular EEL spectra and that the carbon-hydrogen bond axis may be tilted slightly with respect to the surface normal. These conclusions are in agreement with those of Barteau et al.<sup>2</sup> for methylidyne formed from ethylene decomposition on Ru(001).

Two closely related issues remain to be addressed regarding acetylene decomposition on Ru(001). The first is the relative concentrations of acetylide and ethylidyne formed upon decomposition of molecularly chemisorbed acetylene between 230 and 250 K. Unfortunately, neither the EELS nor the TDMS results discussed here can provide an unambiguous answer to this question. Clearly, stoichiometry requires that unless some acetylene is dehydrogenated completely to  $C_2$  dimers below 250 K, a possibility which seems unlikely and for which there is no spectroscopic evidence, no more than half of the chemisorbed acetylene may be converted to ethylidyne, while the rest decomposes to acetylide. Taking into account the saturation acetylene coverage of 0.27 monolayer, this places an upper limit of approximately 0.14 monolayer on the total concentration of the ethylidyne produced. A suitable lower limit is not so easily derived. Since the desorption of hydrogen begins slightly below 250 K for a saturation exposure of acetylene, it is obvious that not all of the hydrogen that results from acetylide formation contributes to ethylidyne formation. Rather, an overall reaction such as

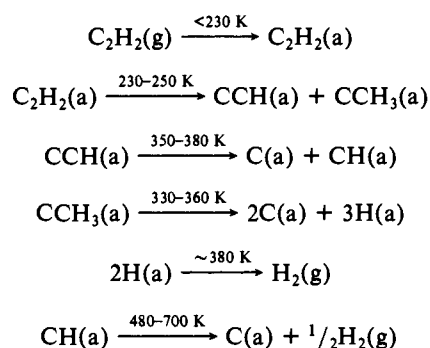


also occurs to some extent. Consequently, the surface concentration of acetylide is greater than that of ethylidyne, although the exact ratio is not known.

The second remaining question involves the mechanism of methylidyne formation; i.e., is the methylidyne formed via carbon-carbon bond cleavage of acetylide, via decomposition of ethylidyne, or via a combination of both of these mechanisms? Since acetylide and ethylidyne decompose in very similar temperature ranges, the former between approximately 350 and 380 K and the latter between approximately 330 and 360 K (as judged both from this acetylene study and our previous ethylene study<sup>3</sup>), EEL spectra are of little use in answering this question. However, some information may be gleaned from the fact that the ratio of the areas of the  $\beta_1$ -to- $\beta_2$  hydrogen thermal desorption peaks is less for low initial acetylene exposures compared to higher exposures. This implies that relatively more methylidyne is formed from acetylene decomposition at low initial coverages of the latter. In our study of ethylene decomposition on Ru(001),<sup>3</sup> it was found that the ratio of acetylide to ethylidyne formed upon ethylene decomposition was larger at lower initial ethylene coverages relative to higher initial coverages, and it would be expected that this is true in the case of acetylene as well. This is in accord with the fact that ethylidyne occupies only one site on the surface, while an acetylide and two hydrogen adatoms occupy at least three sites. Consequently, the former should be favored at higher initial coverages of acetylene. Therefore, a relatively greater amount of acetylide formation leads to a relatively greater amount of methylidyne formation, and it follows that acetylide must have a greater tendency to decompose to yield methylidyne than does ethylidyne. Thus, the dominant mechanism of acetylide decomposition appears to be carbon-carbon bond cleavage to give C(a) and CH(a), while the dominant mechanism of ethylidyne decomposition is to two C(a) and three H(a). This is in agreement with the more conclusive EELS results for ethylene decomposition on Ru(001),<sup>3</sup> which show more clearly the decomposition of ethylidyne prior to the decomposition of acetylide and with little or no methylidyne formation accompanying the ethylidyne decomposition.

Further evidence that methylidyne is formed largely from acetylide decomposition was provided by adsorbing acetylene at 350 K. A subsequent hydrogen thermal desorption spectrum showed that the area of the  $\beta_2$  desorption peak (from methylidyne) is enhanced by approximately a factor of 2 compared with that observed after a saturation exposure of acetylene at 80 K. Since the desorption of surface hydrogen is rapid at 350 K, the probability of ethylidyne formation under these conditions is negligible. On the other hand, acetylide is stable at 350 K, and its surface concentration was found to be enhanced relative to adsorption at 80 K, followed by annealing. This enhancement in the surface concentration of acetylide correlated with the enhancement in the surface concentration of methylidyne that was observed strongly implicating acetylide as the major source of methylidyne. However, the possibility that a small amount of ethylidyne decomposes to give methylidyne or that a small amount of acetylide decomposes to  $2C(a) + H(a)$  rather than to C(a) and methylidyne cannot be ruled out completely.

In summary, the overall mechanism of acetylene decomposition on Ru(001) may be written as



#### IV. Conclusions

The principal conclusions of this work may be summarized as follows:

1. Molecularly adsorbed acetylene on Ru(001) is stable below 230 K and is characterized by a carbon-carbon stretching frequency of  $1135\text{ cm}^{-1}$ , corresponding to carbon atoms that are very nearly  $sp^3$  hybridized. This is the lowest carbon-carbon stretching frequency yet observed for molecularly adsorbed acetylene on a transition-metal surface. The saturation coverage of molecularly adsorbed acetylene on Ru(001) is approximately 0.27 monolayer.
2. Molecularly adsorbed acetylene does not desorb intact from Ru(001) but rather is an intermediate to dehydrogenation and hydrogenation which occurs between 230 and 250 K, yielding acetylide and ethylidyne.
3. The acetylide and ethylidyne decompose near 350 K, leaving methylidyne as the only hydrocarbon species on the surface by 400 K, along with carbon adatoms. The decomposition of ethylidyne (and perhaps to some degree the decomposition of acetylide) produces surface hydrogen, which recombines and desorbs as  $H_2(g)$ . This desorption occurs at 425 K for very low initial coverages of acetylene and at 380 K for a saturation coverage of chemisorbed acetylene.
4. The methylidyne decomposes between 480 and 700 K, yielding  $H_2(g)$  and leaving only carbon on the surface.

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**Registry No.**  $C_2H_2$ , 74-86-2; Ru, 7440-18-8;  $CCH_3$ , 67624-57-1; CCH, 29075-95-4; CH, 3315-37-5.