were exposed to 2 Torr of ethylene vapor while being heated to 100 °C for 900 to 3600 s. Ethylene was used rather than propylene since the catalyst "activation" has been reported to occur at lower temperatures for this olefin,[23] although the resulting metathesis reaction cannot be observed by standard gas chromatographic detection (ethylene metathesis is degenerate). The tunneling spectrum that results from such a 900 s "activation" is shown in Figure 5C. None of the activation experiments provided any indication of hydrocarbon or carbene formation, as judged by the absence of C–H stretching modes in the 2800–3100-cm^{-1} region of the spectrum. Considering the rather severe conditions (400 °C and 1 atm of propylene) used to activate molybdenum(VI) oxide metathesis catalysts,[45] evidently our experimental conditions were insufficient to activate the decomposition product(s) of the molybdenum hexacarbonyl to the metathesis catalyst.

E. UV Exposure of Chemisorbed Molybdenum Hexacarbonyl. Photolysis of alumina-supported molybdenum hexacarbonyl by UV irradiation has been observed to produce CO and yield the proposed $Mo(CO)_3(ads)_3$ species.[36] We have attempted to prepare irreversibly adsorbed molybdenum hexacarbonyl by exposure to 366-nm radiation. Details of the experiment were given in section IIIE. The sample holder was oriented so that two junctions would be exposed to the light source and two junctions would be shielded. The resulting tunneling spectra for the exposed and unexposed junctions are shown in Figure 6, A and B. respectively. The similarity in the spectra indicates that the UV source was insufficiently intense to photolyze the carbonyl. Typically, light intensities of 4 mW/cm^2 (vs. 594 μW/cm^2 in our experiments) are used to initiate decomposition.[55] The observed weak ν(CH) modes are due to hydrocarbon contaminants from the solvent.

V. Summary

We have obtained the vibrational spectrum of a transient complex formed between molybdenum hexacarbonyl and a fully hydroxylated alumina surface. The spectrum shows significant similarities to the gas-phase or solid-state hexacarbonyl, and it is consistent with the carboxylic acid type intermediate (IV) proposed both by Burwell[31] and by Brown.[35] The complex is formed by the interaction of a surface hydroxyl group and a carbonyl from the molybdenum hexacarbonyl. Both the ease of desorption (~25 min at 22 °C) and the small perturbations from the gas-phase spectrum indicate relatively weak chemisorption on the surface. Attempts to dehydroxylate the surface partially or expose the adsorbed complex to ultraviolet irradiation proved insufficient to increase the reactivity of the carbonyl at room temperature. Heating the surface during the vapor exposure of molybdenum hexacarbonyl produced metallic molybdenum films at a temperature of 140 °C and a mixture of molybdenum suboxides and subcarbonyls at 100 °C. An attempt to react the molybdenum suboxides with ethylene to produce a molybdenum carbene species (the proposed metathesis catalyst) was unsuccessful. No evidence of hydrocarbon or carbene vibrational modes was observed.

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The Coadsorption of Hydrogen and Acetylene on the Ru(001) Surface

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Abstract: The adsorption of acetylene on Ru(001) surfaces with various coverages of preadsorbed hydrogen has been investigated by using high-resolution electron energy loss spectroscopy and thermal desorption mass spectrometry. The presence of a saturation coverage of dissociatively adsorbed hydrogen ($\theta_H \cong 0.85$) inhibits the subsequent adsorption of acetylene, reducing the fractional saturation coverage of chemisorbed acetylene at 80 K from approximately 0.25 to 0.11. Partial hydrogenation of the chemisorbed acetylene occurs as the surface is heated above 150 K, resulting in the formation of an η^2-$CHCH_2$ species. Further hydrogenation of η^2-$CHCH_2$ to ethylene occurs also, with 0.01 monolayer of ethylene desorbing at 175 K. The remainder of the chemisorbed acetylene is not hydrogenated to ethylene but undergoes carbon–hydrogen bond cleavage and formation to yield acetylide (CCH) and ethylidyne (CCH_3) above 230 K, as on clean Ru(001). The ratio of ethylidyne to acetylide is greater, however, on the hydrogen presaturated surface.

I. Introduction

The adsorption of acetylene has been studied on a number of single-crystalline transition-metal surfaces under ultrahigh vacuum (UHV) conditions,[1-15] both to gain insight into the interaction of alkynes with such surfaces and to isolate stable surface intermediates in order to make a connection with the bonding of similar ligands in organometallic complexes. In nearly all cases, acetylene adsorbs molecularly at low temperatures ($T \lesssim 250$ K) but with substantial rehybridization of the carbon–carbon triple bond occurring. We have recently reported the results of a study of acetylene adsorption and reaction on the hexagonally close-packed Ru(001) surface by using high-resolution electron energy loss spectroscopy (EELS) and thermal desorption mass spectrometry (TDMS).[16] It was found that acetylene chemisorbs molecularly on this surface below 230 K with rehybridization of

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the carbon atoms to nearly sp^3, as judged by a carbon–carbon stretching frequency of 1135 cm^{-1}.[17] The chemisorbed acetylene undergoes both carbon–hydrogen bond cleavage and bond formation when the surface is heated above 230 K, yielding two stable intermediates on the surface, namely acetylide (CCH) and ethylidyne (CCH_3). The acetylide and ethylidyne decompose below 400 K, leaving methylidyne (CH) and surface carbon, with desorption of H_2 centered at 375 K. The methylidyne decomposes below 800 K with further H_2 desorption between 480 and 800 K, leaving only carbon on the surface. The desorption of neither molecular acetylene nor any other hydrocarbons occurs.

An issue of fundamental importance in understanding alkyne hydrogenation reactions on transition-metal surfaces is the interaction of chemisorbed acetylene with coadsorbed hydrogen. The reactions of coadsorbed hydrogen and acetylene have been studied previously on the hexagonally close-packed Pt(111),[9] Pd(111),[6,7] Rh(111),[10] and Ni(111)[4] surfaces and also on the stepped $\text{Ni-}[5(111) \times (\bar{1}10)]$ surface.[4] Since the reactions of ethylene,[18,19] hydrogen,[20-22] and coadsorbed ethylene and hydrogen[23] on Ru(001) have all been studied previously with EELS and TDMS, this is an obviously desirable surface on which to conduct hydrogen and acetylene coadsorption experiments. We report here the results of such an investigation, also employing both EELS and TDMS, of acetylene coadsorption and reaction with preadsorbed hydrogen on Ru(001). These results provide unambiguous evidence for the hydrogenation of acetylene to ethylene under UHV conditions, and they yield additional information that permits important comparisons to acetylene and ethylene decomposition on clean Ru(001).

II. Experimental Procedures

The EEL spectrometer and the UHV chamber which houses it have been described in detail elsewhere.[24] The resolution of the spectrometer varied between 60 and 80 cm^{-1} (full-width at half-maximum), while maintaining a count rate of 2×10^5 counts per s in the elastically scattered beam with an incident electron beam energy of approximately 4 eV. All EEL spectra presented and discussed here were measured in the specular direction, which was 60° from the surface normal. The angle of acceptance of the electron energy analyzer was approximately 2°.

Thermal desorption mass spectrometric measurements were performed both in the EELS chamber and in a separate UHV chamber that has been described elsewhere.[25] This UHV chamber was equipped with a skimmer on the mass spectrometer in order to minimize the effects of desorption from the crystal edge (the area of which is approximately 8% of the oriented surface area) and the support leads. While most TDM spectra collected in the EEL chamber (including those in Figures 1 and 3) employed a temperature base, the TDM spectra in this second chamber were time base spectra with a computer algorithm for baseline subtraction, and this provided more accurate coverage determinations. All coverages reported in this paper are based on this more accurate method. The desorption peak temperatures reported here are accurate to within approximately ±5 K, and the heating rate was approximately 8 $K\text{-}s^{-1}$ in all cases.

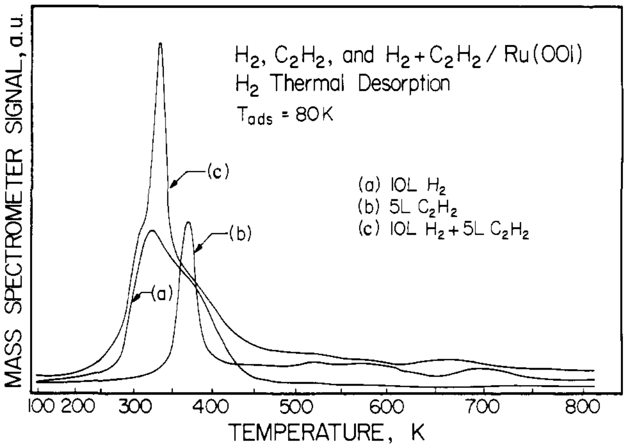

Figure 1. The H_2 thermal desorption spectra resulting after the Ru(001) surface at 80 K is exposed to (a) 10 L H_2, (b) 5 L C_2H_2, and (c) 10 L H_2 followed by 5 L C_2H_2. Note that the base line is not identical for the three cases and that the abscissa is nonlinear. The abbreviation a.u. denotes arbitrary units.

The Ru(001) crystals in both UHV chambers were cleaned by using standard techniques of Ar^+ sputtering and annealing in oxygen.[26] Surface cleanliness was monitored via EELS and TDMS in the EELS chamber and via Auger electron spectroscopy and TDMS in the second UHV chamber.

The H_2 and D_2 used in this study were obtained from Matheson with reported purities of 99.9995 and 99.5%, respectively. These gases were used without further purification, and their mass spectra gave no indication of any impurities. Previous studies of H_2 adsorption on Ru(001)[20-22] have shown that the adsorption is dissociative at all temperatures examined ($T \gtrsim 75$ K), with the hydrogen adatoms giving rise to very weak EELS loss features near 800 and 1150 cm^{-1}. In addition to the appearance of these loss features, hydrogen adsorption on clean Ru(001) resulted in an increase in the intensity of the elastically scattered peak (surface reflectivity) by about a factor of two, an effect which has been noted previously.[27]

The C_2D_2 (99 atom % deuteriated) was obtained from MSD Isotopes and used without further purification. The C_2H_2 was obtained from an industrial acetylene tank (95% purity) and was purified as described elsewhere.[16] Both the C_2H_2 and C_2D_2 showed mass spectral cracking patterns that were virtually identical with those reported in the literature,[28] and no impurities could be detected in either case. Thermal desorption measurements were performed with C_2D_4 in order to make a comparison with the observed desorption of ethylene following acetylene and hydrogen coadsorption on Ru(001). The C_2D_4 (99 atom % deuteriated) was also obtained from MSD Isotopes, and its purity was verified via mass spectrometry.

Gas exposures were effected by backfilling the UHV chambers through leak valves. The stainless steel vacuum lines leading to the leak valves were flushed several times with the relevant gas prior to the introduction of the gas into the UHV chamber. All reported exposures were measured with a Bayard–Alpert ionization gauge, uncorrected for relative ionization probabilities. Exposures are reported in units of Langmuirs, where 1 Langmuir $\equiv$ 1 L = 10^{-6} torr-s.

III. Results

A. Thermal Desorption Mass Spectrometry. Thermal desorption mass spectra were measured for acetylene adsorbed at 80 K on the Ru(001) surface with varying coverages of preadsorbed hydrogen. Similar to acetylene adsorption on the clean Ru(001) surface,[16] where hydrogen is the only thermal desorption product from chemisorbed acetylene, hydrogen is the principal thermal desorption product resulting from chemisorbed acetylene on the hydrogen precovered surface. There is no desorption, for example, of methane, ethane, benzene, or acetylene (other than the desorption of condensed acetylene multilayers at 95 K). However, in contrast to acetylene adsorption on clean Ru(001), small amounts ($\lesssim$0.01 monolayer) of ethylene are observed to

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desorb following acetylene adsorption on the Ru(001) surface with a sufficient concentration of preadsorbed hydrogen. This indicates clearly that chemisorbed acetylene and hydrogen adatoms can react on Ru(001) under these conditions.

1. Hydrogen Thermal Desorption. Figure 1 shows H_2 thermal desorption spectra for saturation exposures of both H_2 (a) and C_2H_2 (b) on Ru(001) and for a saturation exposure of C_2H_2 on a Ru(001) surface which had been presaturated with hydrogen (c). A saturation hydrogen exposure on Ru(001) gives rise to a broad thermal desorption peak centered at 325 K with a shoulder near 380 K, as shown in Figure 1a, and corresponds to a hydrogen adatom fractional surface coverage of 0.85,[20] i.e., 1.39×10^{15} atoms-cm^{-2}. The hydrogen adatoms occupy exclusively threefold hollow sites, and the peak splitting is due to adatom–adatom interactions.[22] As may be seen in Figure 1b, a saturation exposure of acetylene on Ru(001) gives rise to a sharp hydrogen desorption peak centered near 375 K, with a less intense and very broad feature between approximately 480 and 800 K which displays three weak maxima. The saturation fractional coverage of acetylene adsorbed on clean Ru(001) is 0.25 ± 0.03, as judged by the H_2 thermal desorption spectra. (Recall that only H_2 is observed to desorb from the Ru(001) surface on which acetylene is adsorbed.)

Comparison of spectra b and c of Figure 1 shows that the principal H_2 desorption peak is somewhat sharpened and downshifted by approximately 35 K, from 375 to 340 K, when the Ru(001) surface is presaturated with hydrogen. This peak corresponds to ethylidyne decomposition, which on the hydrogen precovered surface occurs at a slightly lower temperature than on the clean surface (see section III.B). On the clean surface, the peak at 375 K also involves a small contribution from hydrogen adatoms that are formed when acetylene decomposes to acetylide and that do not react further to form ethylidyne. On the hydrogen precovered surface, the peak at 340 K also involves substantial amounts of preadsorbed hydrogen adatoms. Clearly visible on both sides of the 340-K peak in Figure 1c are shoulders which are characteristic of hydrogen desorption from the clean surface and which result from the recombinative desorption of hydrogen adatoms that are not influenced significantly by the presence of coadsorbed hydrocarbon species. The leading edge of Figure 1c is downshifted slightly relative to that of Figure 1a due to the increased hydrogen adatom *density* in the former case.

Between 480 and 800 K, the H_2 thermal desorption spectra for both acetylene and acetylene with preadsorbed hydrogen show very broad peaks of low intensity. Since the desorption of hydrogen from the clean Ru(001) surface is complete below 500 K, these features clearly result from reaction-limited hydrogen desorption due to the decomposition of a surface hydrocarbon species. Our previous EELS results for acetylene decomposition on Ru(001) have shown that methylidyne is the only hydrocarbon species present on the surface above 400 K.[16] Consequently, hydrogen desorption above 480 K is necessarily due to methylidyne decomposition for acetylene adsorption on Ru(001). The fact that three desorption maxima are observed above 480 K for saturation acetylene coverages (only one maximum is observed for low coverages) and the broad temperature range for methylidyne decomposition results from variations in the local coverage of carbon and methylidyne. Similarly, EEL spectra for coadsorbed hydrogen and acetylene on Ru(001) demonstrate that methylidyne is the only hydrocarbon species on the surface above 400 K. Therefore, in this case also, hydrogen desorption above 480 K is due to methylidyne decomposition. The amounts of hydrogen that desorb between 480 and 800 K indicate that approximately 0.13 monolayer of methylidyne is formed for a saturation exposure of acetylene on clean Ru(001), while only about 0.04 monolayer of methylidyne is formed following a saturation exposure of acetylene on the hydrogen presaturated Ru(001) surface. The hydrogen thermal desorption peaks from the decomposition of methylidyne occur at somewhat lower temperatures for acetylene coadsorbed with hydrogen, similar to the case of lower acetylene coverages on the clean surface.[16] The higher desorption temperatures on the initially clean surface are probably due to a stabilization of methylidyne by the higher concentration of coadsorbed carbon adatoms, which block surface sites that are necessary for carbon–hydrogen bond cleavage and also hinder hydrogen–hydrogen recombination. The lower concentration of carbon adatoms in the case of coadsorbed acetylene and hydrogen is a consequence of the fact that preadsorbed hydrogen partially inhibits the adsorption of acetylene on Ru(001).

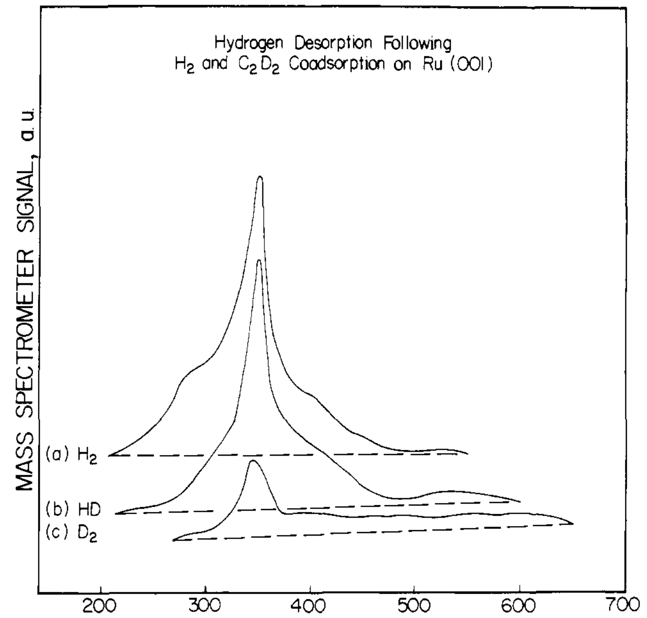

Figure 2. Thermal desorption spectra resulting after the Ru(001) surface at 80 K is exposed to 1 L H_2 followed by 1 L C_2D_2: (a) H_2, (b) HD, and (c) D_2. Dashed lines are approximate baselines for the three spectra.

By comparison to the amount of hydrogen that desorbs following a saturation exposure of H_2 on Ru(001), the amount of acetylene which adsorbs and decomposes to yield (eventually) H_2(g) and surface carbon on the hydrogen presaturated Ru(001) surface is estimated to be approximately 0.10 monolayer. To obtain this estimate, time integrated TDM spectra corresponding to Figure 1a are subtracted from similarly time integrated TDM spectra corresponding to Figure 1c, with no peak deconvolution required. Since the only other desorption product resulting from acetylene adsorption on hydrogen presaturated Ru(001) is 0.01 monolayer of ethylene (see section III.A.2), this indicates that approximately 0.11 monolayer of acetylene is chemisorbed on this surface. Thus, the presence of 0.85 monolayer of hydrogen adatoms on the Ru(001) surface inhibits acetylene chemisorption substantially, reducing the saturation acetylene coverage by approximately 60%.

Figure 2 shows H_2, HD, and D_2 thermal desorption spectra from a Ru(001) surface which has been exposed to 1 L of H_2 followed by a subsaturation exposure of 1 L of C_2D_2 at 80 K. A 1-L hydrogen exposure corresponds to 0.57 ± 0.05 monolayer of hydrogen adatoms, and the amount of C_2D_2 that adsorbs is approximately 0.11 monolayer. The equivalent coverages of the various hydrogen isotopes that desorb are approximately 0.22 monolayer of H_2, 0.12 monolayer of HD, and 0.05 monolayer of D_2. Thus the isotopic mixing of hydrogen and deuterium is not complete; a purely statistical distribution would be 0.21 monolayer of H_2, 0.16 monolayer of HD, and 0.03 monolayer of D_2. Several aspects of these thermal desorption spectra are noteworthy. The first is that no D_2 and only a trivial amount of HD desorb below 230 K, the temperature at which acetylene decomposition begins on both the clean and the hydrogen precovered Ru(001) surfaces. This indicates that virtually no H/D exchange occurs between the coadsorbed hydrogen adatoms and chemisorbed acetylene. Thus the reaction

$$\mathrm{DCCD(a) + H(a) \rightarrow HCCD(a) + D(a)}$$

is not facile on this surface. Second, small amounts of both H_2 and HD are desorbed between 480 and 600 K, indicating the decomposition of a CH methylidyne species. Thus, a small amount

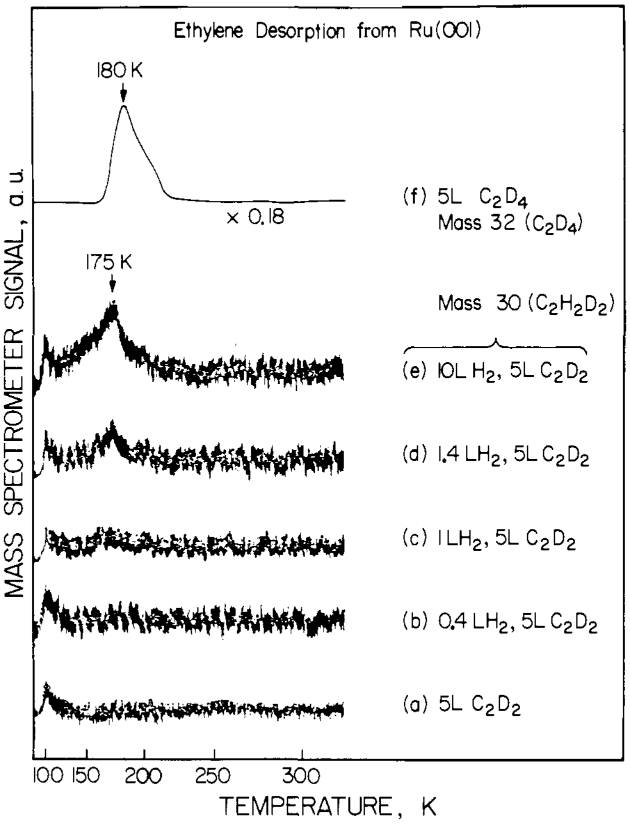

Figure 3. Thermal desorption spectra of CHDCHD (m = 30 amu) recorded after the Ru(001) surface at 80 K is exposed to (a) 5 L C_2H_2, (b) 0.4 L H_2 followed by 5 L C_2D_2, (c) 1 L H_2 followed by 5 L C_2D_2, (d) 1.4 L H_2 followed by 5 L C_2D_2, and (e) 10 L H_2 followed by 5 L C_2D_2. In spectra b–e the initial absolute hydrogen adatom coverages are approximately 0.35, 0.6, 0.75, and 0.85, respectively. Spectrum f shows the CD_2CD_2 (m = 32 amu) desorption that results following a 5 L C_2D_4 exposure at 80 K. The apparent peak just above 100 K in spectra a–e is a spectrometer effect and should be ignored. Note that the abscissa is nonlinear.

($\sim$0.01–0.02 monolayer) of the preadsorbed hydrogen adatoms have reacted with a hydrocarbon species below 480 K to become incorporated into the hydrocarbon adlayer and form eventually CH. It is also worth noting that methylidyne decomposition is complete below 700 K, consistent with the initial acetylene coverage of 0.11 monolayer.

2. Ethylene Thermal Desorption. Ethylene desorption following the coadsorption of hydrogen and acetylene on Ru(001) at 80 K was studied by using four combinations of hydrogen and acetylene isotopes, namely $H_2 + C_2H_2$, $H_2 + C_2D_2$, $D_2 + C_2H_2$, and $D_2 + C_2D_2$. Of these various combinations, $H_2 + C_2D_2$ and $D_2 + C_2H_2$ are the most useful since the presence of different hydrogen isotopes, in principle, allows different isotopes of ethylene to be desorbed. Consequently, the isotopes of ethylene that are observed to desorb provide mechanistic insight into the surface reaction (provided that desorption occurs at a temperature below which H/D exchange between adsorbed hydrogen and the adsorbed hydrocarbons is not important). The coadsorption of H_2 and C_2H_2 is the least useful for monitoring ethylene desorption, since any desorbed ethylene occurs at 28 amu (C_2H_4), and the presence of carbon monoxide (also at 28 amu) in the chamber background leads to a large, sloping background in the mass 28 thermal desorption spectra. This makes the detection of small amounts of C_2H_4 difficult.

Thermal desorption spectra of ethylene-d_2 ($C_2H_2D_2$) following the coadsorption of H_2 and C_2D_2 on Ru(001) at 80 K are shown in Figure 3a–e. The surface was exposed to various fluxes of hydrogen, as indicated, and then saturated with C_2D_2. The initial hydrogen coverages were calculated by comparing the amount of hydrogen desorbed following a given exposure on the clean Ru(001) surface to the amount desorbed following a saturation exposure on Ru(001). The C_2D_4 thermal desorption spectrum resulting from a saturation exposure of perdeuterioethylene on Ru(001) is shown in Figure 3f. Ethylene-d_2 is desorbed following H_2 and C_2D_2 coadsorption only for $\theta_H \gtrsim 0.6$. The peak desorption temperature of 175 ± 5 K is in excellent agreement with thermal desorption data for ethylene adsorbed on Ru(001) [cf. Figure 3f and ref 19], and the observations that the desorption peak temperature does not shift with increasing hydrogen adatom coverage and occurs at nearly the same temperature as ethylene desorption following ethylene adsorption on Ru(001)[19] suggest that this is a desorption-limited reaction with first-order desorption kinetics. Assuming a constant preexponential factor of the desorption rate coefficient of 10^{13} s^{-1}, an activation energy of desorption of approximately 10–11 kcal/mol is estimated.[29]

Comparison to the thermal desorption spectrum for a saturation exposure of chemisorbed C_2D_4 on Ru(001), where approximately 0.06 monolayer of ethylene desorbs molecularly at 180 K, allows the coverages of ethylene-d_2 that are desorbed to be estimated for various hydrogen precoverages (to within approximately a factor of two). For fractional hydrogen precoverages of 0.6, 0.75, and 0.85, approximately 0.002, 0.005, and 0.01 monolayer of $C_2H_2D_2$ are desorbed, respectively. Since approximately 0.10 monolayer of acetylene adsorbs and decomposes on Ru(001) which is presaturated with hydrogen, this indicates that approximately 9% of the chemisorbed acetylene is hydrogenated on this surface *and* desorbs as ethylene.

Ethylene-d_2 (at 30 amu) is the only isotope of ethylene which desorbs from Ru(001) following the coadsorption of H_2 and C_2D_2. No detectable desorption (i.e., <0.001 monolayer) is observed at 31 amu (C_2HD_3) or at 32 amu (C_2D_4), and only a very weak features is observed at 29 amu which is due to the C_2HD_2 cracking fragment of ethylene-d_2, rather than ethylene-d_1 (C_2H_3D). Thermal desorption spectra of coadsorbed D_2 and C_2H_2 on Ru(001) yield similar results: only ethylene-d_2 is observed as a desorption product. Thus, it is clear that the ethylene desorption at 175 K results from the reaction of chemisorbed molecular acetylene with two preadsorbed hydrogen adatoms and that the sequential addition of the two hydrogen atoms is irreversible.

B. Electron Energy Loss Spectroscopy. As noted in section I, hydrogen adsorption on Ru(001) has been investigated previously with EELS.[21,22] The observed loss features near 800 and 1150 cm^{-1}, due to the presence of hydrogen adatoms in threefold hollow sites, are extremely weak and are obscured by various hydrocarbon modes when either coadsorbed ethylene or acetylene is present.[16,19] The molecular chemisorption of acetylene on clean Ru(001) below 230 K produces a very nearly sp^3 hybridized species which is characterized by the following loss features in the case of C_2H_2 (C_2D_2): ruthenium–carbon stretching modes at 375 (350) and 520 cm^{-1} (not resolved for C_2D_2); CH (CD) bending modes at 765 (565) and 980 (715) cm^{-1}; a carbon–carbon stretching mode at 1135 (1085) cm^{-1}; and a CH (CD) stretching mode at 2940 (2210) cm^{-1}.[16] The EEL spectra for saturation exposures of C_2H_2 and C_2D_2 on Ru(001), corresponding to approximately 0.25 monolayer of chemisorbed acetylene, are shown in Figure 4a and b. The spectra in Figure 4 also show loss features due to small amounts (<0.01 monolayer) of CO adsorbed from the chamber background. It has been found previously that these small and varying amounts of CO do not affect the EEL spectra of chemisorbed acetylene or its decomposition products.[16]

Also shown in Figure 4 are EEL spectra of C_2H_2 adsorbed on a hydrogen presaturated Ru(001) surface (c) and of C_2D_2 adsorbed on a deuterium presaturated Ru(001) surface (d). The major difference between these spectra and those of Figure 4a and b is the appearance of a new vibrational mode, which occurs at 1440 cm^{-1} for coadsorbed H_2 and C_2H_2 and at 1175 cm^{-1} for coadsorbed D_2 and C_2D_2. The frequency of this mode is in the range characteristic of a CH_2 (CD_2) scissoring vibration, and the observed frequency shift upon deuterium substitution [δ (CH_2)/δ (CD_2) = 1.23] confirms this assignment. This indicates that a new surface species has been formed containing a CH_2 group,

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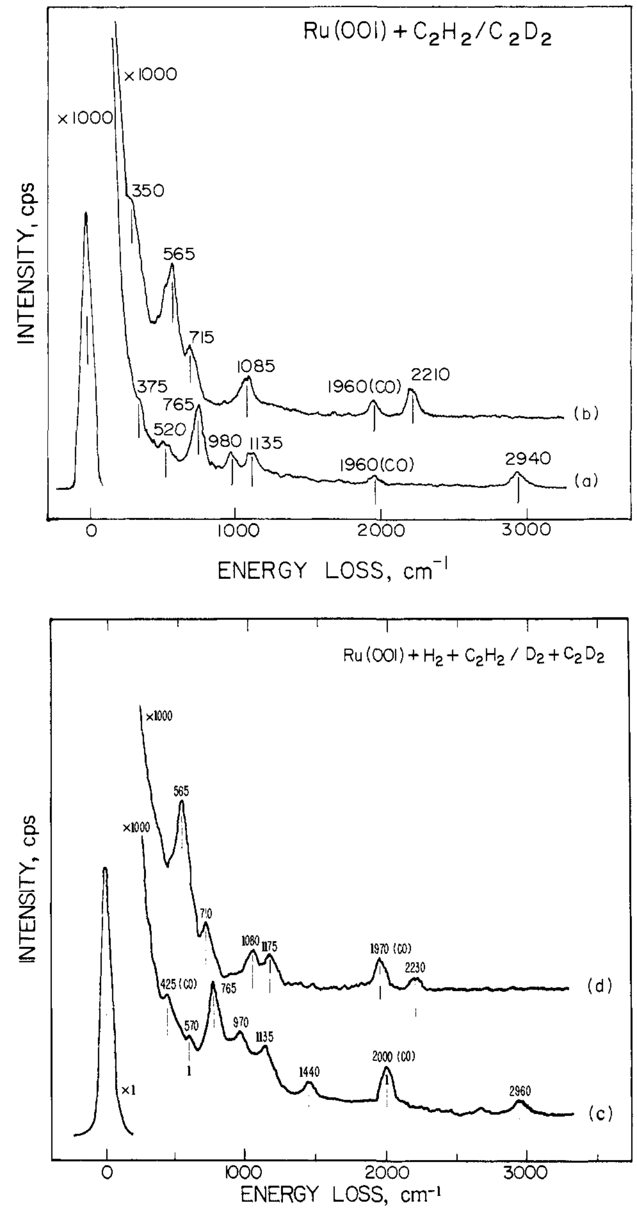

Figure 4. The EEL spectra that result when the Ru(001) surface at 80 K is exposed to (a) 5 L C_2H_2, (b) 5 L C_2D_2, (c) 10 L H_2 followed by 5 L C_2H_2, and (d) 10 L D_2 followed by 5 L C_2D_2 and then annealed to 150 K and recooled to 80 K prior to spectral collection. Spectra a and b are characteristic of molecularly chemisorbed acetylene, while spectra c and d show features characteristic both of chemisorbed acetylene and $CHCH_2$ ($CDCD_2$). In spectra c and d, the low-frequency metal–carbon modes are not resolved due to the somewhat poorer cutoff of the elastic peak. The apparent shift of the high-frequency metal–carbon mode in spectrum c compared to spectrum a is not very reproducible and may also be due to the poorer elastic peak cutoff.

which is in agreement with our TDMS results showing ethylene desorption at 175 K. However, the EEL spectra of Figure 4c and d are not due to chemisorbed ethylene (or a combination of chemisorbed ethylene and acetylene), as judged by a comparison with previous studies of ethylene adsorption on Ru(001).[18,19] The CH_2 scissoring mode is thus assigned to an η^2-$CHCH_2$ species, the logical intermediate in the hydrogenation of acetylene to ethylene. (The η^2 designation indicates that both carbon atoms of the $CHCH_2$ species are bonded directly to the surface but does *not* imply nearly equal metal–carbon bond lengths or anything else regarding the structure of $CHCH_2$.) An η^1-$CHCH_2$ species containing a carbon–carbon double bond (vinyl) is ruled out due to the lack of a carbon–carbon stretching mode above 1500 cm^{-1}. Other CH_2-containing species such as η^2-CCH_2 or CH_2 (methylene), that require the breaking of carbon–hydrogen or carbon–carbon bonds of acetylene in order to be formed, are excluded in view of the observed lack of H/D exchange below 230 K, the fact that CH bonds of chemisorbed acetylene are not broken below 230 K on clean Ru(001), and the observed lack of carbon–carbon bond cleavage below 340 K.

Since the modes characteristic of chemisorbed acetylene are still present in Figure 4c and d, the surface contains a mixture of chemisorbed acetylene and η^2-$CHCH_2$ after annealing to 150 K. This observation is in agreement with previous results for hydrogen and acetylene coadsorption on the stepped Ni[5(111) × ($\bar{1}$10)] surface, where the appearance of a δ (CH_2) mode at 150 K was taken as evidence for the formation of a mixed overlayer of $CHCH_2$ and chemisorbed acetylene.[4] The η^2-$CHCH_2$ should also give rise to CH_2 wagging, twisting, and rocking modes, which would be expected, respectively, near 1150, 900, and 775 cm^{-1}, based on a comparison to chemisorbed ethylene on Ru(001).[19] These modes are not resolved due to overlap with various modes of chemisorbed acetylene (or, in some cases, perhaps because they are intrinsically weak). However, spectra c and d of Figure 4 do exhibit slight changes in the frequencies and relative intensities of some modes compared to spectra a and b, and these differences are no doubt due at least partially to the presence of additional modes of η^2-$CHCH_2$ that are not well-resolved. This may very well also be the reason for the relatively poorer resolution in the 750–1150 cm^{-1} region of spectrum c, compared to spectrum a.

Further hydrogenation of η^2-$CHCH_2$ and desorption of ethylene occurs between 150 and 250 K, as indicated by the thermal desorption results of Figure 3. EEL spectra show that a small amount of η^2-$CHCH_2$ is present on the surface at 200 K, but that it is completely gone by 250 K. Molecularly chemisorbed acetylene decomposes near 230 K, as on the clean surface, and the surface species present from 250 to 340 K are acetylide (which is stable to nearly 400 K) and ethylidyne, as in the case of acetylene adsorbed on clean Ru(001).[16] The acetylide is characterized primarily by a strong CH bending mode at 750 cm^{-1}, while ethylidyne is characterized by modes of nearly equal intensity at 1140 [ν(CC)] and 1360 [δ_s (CH_3)] cm^{-1}. The decomposition of acetylene on the hydrogen presaturated Ru(001) surface differs, however, from the decomposition of acetylene on clean Ru(001) in that the ratio of ethylidyne to acetylide is increased on the hydrogen presaturated surface. On the clean surface, there is slightly more acetylide than ethylidyne (as judged from both EELS and TDMS); while on the hydrogen precovered surface, the ratio of ethylidyne to acetylide is approximately 3:2, as estimated from EEL spectra which are virtually identical with those resulting from ethylene decomposition for saturation ethylene coverages on clean Ru(001).[19] In addition, the ethylidyne decomposes at a slightly lower temperature on the hydrogen precovered surface, where EELS features due to this species have disappeared by 350 K. On the other hand, some ethylidyne is stable to at least 360 K when acetylene decomposes on the clean Ru(001) surface.

When C_2H_2 (C_2D_2) is adsorbed on Ru(001) and the surface is annealed between 400 and 700 K, a methylidyne species is formed that is characterized by the following vibrational modes: a ruthenium–carbon stretch at 440 (415), a CH(CD) bend at 800 (615), and a CH(CD) stretch at 3010 (2255) cm^{-1}. When C_2H_2 is adsorbed on a hydrogen presaturated Ru(001) surface and the surface is annealed to these same temperatures, the same CH species is formed in smaller concentrations, as discussed in section III.A.1. The coadsorption of H_2 and C_2D_2 or D_2 and C_2H_2, followed by annealing to over 400 K, leads to the production of both hydrogenated (CH) and deuteriated (CD) methylidyne on Ru(001), although CD predominates in the former case and CH in the latter. This mixing of hydrogen isotopes in the methylidyne is in agreement with our thermal desorption results, and provides unequivocal evidence for the incorporation of preadsorbed hydrogen into the hydrocarbon adlayer. The mechanisms of the incorporation of preadsorbed hydrogen into various hydrocarbon species will be discussed in a subsequent publication.[30]

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IV. Discussion

All the TDMS and EELS results reported here are consistent with the partial hydrogenation of acetylene on a hydrogen presaturated Ru(001) surface to produce low concentrations of a $CHCH_2$ species and ethylene. The $CHCH_2$ is a stable intermediate in the synthesis of ethylene, and the ethylene formed desorbs near 175–180 K, as does ethylene that desorbs following ethylene adsorption. Furthermore, the data prove that the formation of both $CHCH_2$ and ethylene results from the reaction of preadsorbed hydrogen with chemisorbed acetylene and not from a disproportionation reaction involving hydrogen adatoms that originate from acetylene decomposition. (This is not surprising since neither $CHCH_2$ nor ethylene is observed via EELS or TDMS in the absence of preadsorbed hydrogen, and because chemisorbed acetylene is stable on the clean surface to 230 K.) Acetylene that is not hydrogenated to ethylene decomposes to acetylide and ethylidyne near 230 K as on the clean Ru(001) surface, although the ratio of ethylidyne to acetylide is increased. The data also indicate that H/D exchange does not occur to an appreciable extent between chemisorbed acetylene and preadsorbed hydrogen on this surface, but that such exchange does occur for at least one of the decomposition products of acetylene. The formation of detectable amounts of ethylene that desorb below 200 K after hydrogen and acetylene coadsorption on Ru(001) under UHV conditions is significant in view of the lack of precedent for this reaction on other metal surfaces.

Coadsorbed hydrogen and acetylene react near room temperature to form ethylidyne on the Pt(111),[9] Pd(111),[6,7] and Rh(111)[10] surfaces. Ethylidyne is also produced, along with acetylide, as a decomposition product of acetylene on both Pd(111)[7] and Ru(001).[16] The reactions of coadsorbed acetylene and hydrogen below 200–250 K, however, have received somewhat less attention. On Ni(111), coadsorbed hydrogen and acetylene do not react below 250 K.[4] Experiments performed on Pt(111) are somewhat inconclusive. A recent TDMS study has reported ethylene desorption at 250 K following H_2 and C_2H_2 coadsorption on this surface,[31] whereas a previous EELS study reported that coadsorbed hydrogen and acetylene do not react on Pt(111) below 280 K, at which temperature ethylidyne is formed.[9]

Hydrogenation of acetylene to $CHCH_2$ has been observed with EELS, however, for coadsorbed hydrogen and acetylene at 150 K on the stepped Ni[5(111) × ($\bar{1}$10)] surface.[4] Adsorption of acetylene on this hydrogen presaturated surface produces a mixture of chemisorbed molecular acetylene and a $CHCH_2$ species similar to the case of Ru(001), as discussed in section III.B. The ruthenium and nickel surfaces differ markedly, however, in the extent of H/D exchange observed between the adsorbed hydrocarbon species and the preadsorbed hydrogen at low-surface temperatures. While little exchange occurs on Ru(001) below 230 K, exchange is facile on Ni[5(111) × ($\bar{1}$10)] at 150 K. This difference may be correlated with the ability of the two surfaces to dehydrogenate acetylene. On the clean nickel surface, acetylene has been found to dehydrogenate partially even at 150 K,[4] while chemisorbed acetylene is stable to 230 K on Ru(001). Unfortunately, no thermal desorption data are available for the nickel surface, so it is not known whether any ethylene is formed and desorbed from this surface. Given the dehydrogenation ability of this nickel surface, however, ethylene desorption would seem to be unlikely.

Although it is apparent that the ethylene formed from acetylene hydrogenation on Ru(001) is produced via a $CHCH_2$ intermediate, the bonding and hybridization of this intermediate are less obvious. Since only the δ (CH_2) mode of the $CHCH_2$ is distinguished clearly from the modes of coadsorbed molecular acetylene in the EEL spectra, conclusions concerning the hybridization of the carbon atoms in $CHCH_2$ are not easily drawn. The $CHCH_2$ species formed in Ni[5(111) × ($\bar{1}$10)] was assigned, on the basis of a CH_2 stretching mode at 3050 cm^{-1}, as being sp^2 hybridized, although no ν(CC) mode was identified.[4] A $CHCH_2$ ligand has been identified in the organometallic complex $Os_3(CHCH_2)(H)(CO)_{10}$ which is σ-bonded to one osmium atom with a π-bond to a second osmium atom.[32] The carbon atoms of the $CHCH_2$ ligand are intermediate between sp^3 and sp^2 hybridization with strongly coupled ν (CC) and δ (CH_2) modes at 1310 and 1476 cm^{-1}. Although these precedents might suggest a $CHCH_2$ species with at least some double bond character, we believe that the $CHCH_2$ species formed on Ru(001) is more nearly sp^3 hybridized. The lack of any carbon–hydrogen stretching mode above 3000 cm^{-1} or any carbon–carbon stretching mode above 1200 cm^{-1} is suggestive of sp^3 hybridization, although this is not conclusive because these modes could be too weak to be detected. More significantly, both chemisorbed acetylene and ethylene on Ru(001) are essentially sp^3 hybridized, and since $CHCH_2$ is an intermediate in the conversion of acetylene to ethylene, it would be expected to have a similar structure. Such an η^2-$CHCH_2$ species would have both carbon atoms bonded directly to the surface, with the carbon–carbon bond either parallel or (more likely) slightly skewed with respect to the surface plane.

As stated previously, the decomposition products of chemisorbed acetylene are the same on the hydrogen presaturated Ru(001) surface as on the clean surface, namely ethylidyne and acetylide. As would be expected, the presence of surface hydrogen shifts the ratio of these two decomposition products toward more ethylidyne, the product that contains more hydrogen atoms. This is evident both in EEL spectra measured after annealing to 250–300 K and in the TDM spectra which show a smaller amount of methylidyne [which forms primarily (or exclusively) from acetylide, rather than ethylidyne, decomposition[16,19]] decomposing on the hydrogen precovered surface. Another difference between the clean and hydrogen presaturated surfaces is the slightly higher decomposition temperature of ethylidyne on the clean surface, which is evident in both EEL and TDM spectra. This is due to the lower concentration of hydrocarbon species on the hydrogen presaturated surface.

V. Conclusions

The adsorption of acetylene on Ru(001) with preadsorbed hydrogen has been studied by using high-resolution electron energy loss spectroscopy and thermal desorption mass spectrometry. The principal conclusions of this work may be summarized as follows.

1. The dissociative adsorption of hydrogen on Ru(001) inhibits the subsequent adsorption of acetylene. The reduction in the saturation coverage of acetylene is approximately 60% if the surface is saturated with hydrogen (from 0.25 monolayer on the initially clean surface to 0.11 monolayer on the hydrogen presaturated surface with $\theta_H = 0.85$).

2. Hydrogen thermal desorption spectra following the adsorption of acetylene on the hydrogen presaturated Ru(001) surface show features that are characteristic of hydrogen and acetylene adsorbed separately, although the major H_2 desorption peak resulting from acetylene decomposition is downshifted by 35 K from 375 to 340 K. This is the result of a slightly lower decomposition temperature for ethylidyne (one of the two major decomposition products of acetylene) on the hydrogen presaturated surface.

3. Thermal desorption spectra of H_2, HD, and D_2 from coadsorbed H_2 and C_2D_2 on Ru(001) indicate that some of the preadsorbed hydrogen is incorporated into surface hydrocarbon species, since both H_2 and HD are observed to desorb well above the temperature at which they desorb following adsorption on either the clean Ru(001) surface or the Ru(001) surface with various coverages of carbon adatoms. Electron energy loss spectra show that the stable hydrocarbon species leading to H_2 and HD desorption above 480 K is methylidyne. No D_2 and only a trivial amount of HD desorb from the surface below 230 K where acetylene decomposition begins, indicating that H/D exchange between chemisorbed acetylene and preadsorbed hydrogen is not facile. Thus hydrogen is incorporated into surface hydrocarbon species by H/D exchange between preadsorbed hydrogen and one or more of the decomposition products of acetylene.

4. Following saturation acetylene exposures on hydrogen presaturated Ru(001), approximately 0.01 monolayer of ethylene

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desorbs from the surface at 175 K. Thus, ethylene desorption accounts for approximately 9% of the chemisorbed acetylene under these conditions. Furthermore, the coadsorption of H_2 and C_2D_2 shows that the desorbed ethylene consists entirely of mass 30, i.e., CHDCHD, implying that ethylene formation results from the reaction of two preadsorbed hydrogen adatoms with molecularly chemisorbed acetylene. Ethylene formation and desorption is observed only if the initial coverage of hydrogen adatoms exceeds approximately 70% of saturation (about 0.6 monolayer). No other hydrocarbons desorb from Ru(001) following hydrogen and acetylene coadsorption at 80 K (except for condensed multilayers of acetylene).

5. Electron energy loss spectra show that at 150 K the hydrocarbon adphase is a mixture of molecularly chemisorbed acetylene and a CH_2-containing species that is inferred to be $CHCH_2$ (for H_2 and C_2H_2 coadsorption). In addition to the ethylene desorption at 175 K, annealing the surface to 230 K causes the decomposition of chemisorbed acetylene. The two decomposition products, ethylidyne and acetylide, are the same as in the case of acetylene decomposition on the initially clean surface, although the ratio of ethylidyne to acetylide is increased.

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Reaction of Scandium Ions with Ethane. First and Second Hydride–Scandium Ion Bond Energies

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Abstract: Reactions of atomic scandium ions with ethane (d_0, *1,1,1*-d_3, and d_6) are examined by using guided ion beam mass spectrometry. The present results for ethane-d_0 are in qualitative agreement with the previous work of Tolbert and Beauchamp.[1] Although the dominant reaction at low energies is exothermic dehydrogenation, this is inefficient. Strong inter- and intramolecular isotope effects suggest that this inefficiency results from the need for a triplet–singlet surface crossing. At low energies, dehydrogenation forms a Sc^+–ethene complex, while at higher energies, the product is Sc^+–ethylidene. Double dehydrogenation of ethane has two components: an exothermic one and an apparent endothermic one. Several possible explanations are discussed for this unusual result. The results are analyzed to yield both the first and second metal hydride bond energies, $D^\circ_{298}(Sc^+–H) = 56.2 \pm 2$ and $D^\circ_{298}(HSc^+H) = 59.3 \pm 3.7$ as well as $D^\circ_{298}(Sc^+–CH_3) = 59.0 \pm 3$ and $D^\circ_{298}(Sc^+–CH_2) \geq 93.4 \pm 2.5$, all in kcal/mol.

Extensive progress in understanding the activation of carbon–hydrogen and carbon–carbon bonds by transition-metal system has been made recently. Studies not only include condensed phase chemistry but also investigations of such processes by atomic transition-metal ions in the gas phase.[2] While the relationship between these highly idealized systems and systems of true catalytic interest is unclear, gas-phase studies can provide quantitative thermochemistry as well as insight into the periodic trends of reactivity. Recently, Tolbert and Beauchamp published the first study of the reactions of Sc^+ with hydrocarbons.[1] They found that the electron deficiency of Sc^+ makes it one of the most reactive atomic metal ions studied. As a consequence, it behaves differently than any other first-row transition-metal ion. Most striking was the unprecedented observation of MR_2^+ species where M = Sc, R = H and alkyl radicals. A detailed knowledge of such species is extremely important to an understanding of oxidative addition–reductive elimination processes. Unfortunately, they were unable to obtain any thermodynamic data regarding these species although they did estimate such data.

Another aspect of Sc^+ chemistry which has taken on increasing importance since Tolbert and Beauchamp's study is as the focus for a number of ab initio theoretical calculations. The reason for this is clear: Sc^+, having only two valence electrons, is the simplest transition-metal ion. As such, electron correlation effects are at a minimum while there are still sufficient electrons to bind several ligands. Detailed calculations have now been performed for the monohydride ion, ScH^+,[3-5] the dihydride ion, ScH_2^+,[4,5] and $ScCH_x^+$, $x = 1–3$.[4] In addition, detailed potential energy surfaces for the activation of H_2 by Sc^+ have been calculated.[5] Such calculations are of direct relevance to the similar processes of C–H and C–C bond activation.

In the present paper, we provide a detailed study of the reaction of Sc^+ with ethane. Ethane is of special interest because it is the simplest saturated hydrocarbon with both C–H and C–C bonds. It thus provides a model for more complex hydrocarbon chemistry while still being small enough to be tractable to detailed theoretical and experimental studies. Previous studies of the reaction of metal ions with ethane have been carried out under single collision conditions for Sc^+,[1] Ti^+,[6] V^+,[7,8] Cr^+,,[9] Mn^+,[9] Fe^+,[6,10] Co^+,[10,11] and Ni^+ [10] and under high-pressure conditions for the entire first transition series.[12] Here, the mechanism of the Sc^+–ethane

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