J. Am. Chem. Soc. **1998,** *120,* 2421−2427

Metallacyclobutane and Cyclopropyl Species on Cu(111) and Cu(110)

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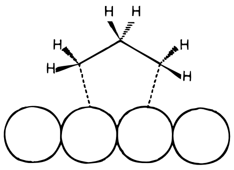
Received July 10, 1997

Abstract: Low-energy electron bombardment of cyclopropane submonolayers was used to prepare cyclopropyl and metallacyclobutane species on Cu(110) and Cu(111) surfaces. The thermal chemistry of both species was monitored over the 90−450 K range by taking high-resolution electron energy loss (HREELS) and temperature-programmed desorption (TPD) measurements. Cyclization of the metallacyclobutane species, to eliminate cyclopropane, was found to occur at 205 K. The metallacyclobutane species was characterized by CH stretching losses at 2806 and 2839 cm^{-1} for Cu(110) and Cu(111), respectively. The cyclopropyl species was found to undergo ring opening to yield a propene desorption product at 290 K. The observed surface chemistry of both of these cyclic C_3 species is compared with data from the organometallic, catalysis, and surface science literature.

Introduction

Cyclopropane[1−3] and alkyl-substituted cyclopropanes[4] serve as probe molecules in studies of hydrocarbon transformation reactions on metal catalysts. Questions related to selectivity and reaction mechanisms may be addressed since, for example, c-C_3H_6 undergoes hydrogenation to propane, partial hydrogenolysis to ethane, or complete hydrogenolysis to methane depending on the metal employed.[5] In parallel, there is a rich literature dealing with organotransition metal complex mediated ring opening and isomerization of cyclopropanes.[6] Studies of the reaction of cyclopropane with metal ion beams[7−9] and with argon matrix isolated metal atoms[10] have also been reported. Species **1**−**4** are possible intermediates in the reaction of cyclopropane with metals, and in particular, metallacyclobutane (**2**) and π-allyl (**4**) species are featured in the analysis of many of the above-mentioned studies.



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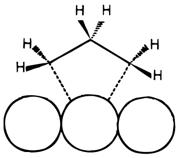

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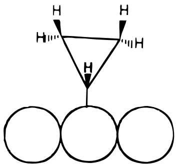

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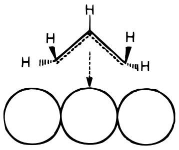

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While there is no direct spectroscopic evidence for adsorbed species derived from cyclopropane, there is indirect evidence for the identity of reaction intermediates in cyclopropane transformations on metal catalysts. For example, a detailed reaction kinetics study of the hydrogenation of cyclopropane to propane and propylene on Ir(111) revealed a hydrogen pressure dependence consistent with the role of a common π-allyl intermediate.[11] Similarly, rate law data for the hydrogenolysis of cyclopropane to methane and ethane on the same surface were interpreted in terms of the facile formation of a metallacyclobutane intermediate.[11] The results of an early catalysis study of the reaction between deuterium and cyclopropane on metal films were interpreted in terms of the participation of metallacycle (on Pt, Ni, Rh, and Fe) and cyclopropyl (**3**) (on W) species.[12] More recently, product distributions for cyclopropane hydrogenation over supported Pt and Ir catalysts were discussed in terms of the reactivity of a range of species including metallacycle and allyl surface complexes.[1] The organotransition metal literature provides many examples relating to the reaction chemistry of C_3 ligands such as **1**−**4.**[13−15] The interest in the study of metallacyclobutane species, in particular, extends far beyond that related to

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S0002-7863(97)02301-9 CCC: $15.00

the chemistry of cyclopropane, as they are believed to be implicated in many catalytic processes. These include alkane isomerization,[16] olefin metathesis,[17] and olefin polymerization reactions.[18]

Surface science studies of the interaction of cyclopropane with clean single-crystal metal surfaces have been reported for Ru(0001),[19−21] Ru(11$\bar{2}$0),[21] Ni(100),[22] Pt(111),[23] Cu(110),[24] Cu(111),[25] Ir(111),[11,26,27] and the reconstructed Ir(110)-(1×2) surface.[11,26,27] Cyclopropane dissociates on the latter surface below 100 K, but desorbs molecularly from the remaining surfaces in the 125−150 K range. The present HREELS (high-resolution electron energy loss spectroscopy) and TPD (temperature-programmed desorption) study shows that cyclopropane desorbs molecularly from Cu(111) and Cu(110) at 125 K. Hence, adsorption of cyclopropane onto these surfaces in a UHV (ultrahigh vacuum) experiment is not a feasible method for preparing adsorbed species such as **1**−**4**. Different strategies for the preparation of at least some of these species may, however, be adopted. For example, Carter et al.[28] used allyl chloride to prepare allyl species on Ag(110). Similarly, Bent *et al.*[29] used 1,3-diiodopropane to prepare structure **1** on Al(100). HREELS measurements were used in both cases to characterize the adsorbed species. The procedure of using 1,3-dihalopropanes was also adopted by White *et al.*[30] and Zaera *et al.*[31] in thermal desorption studies of Ag(111) and Ni(100), respectively. In both cases they observed low-temperature reaction-limited desorption of cyclopropane, which they attributed to the reactivity of surface metallacycle groups. The approach adopted in this study is to generate chemisorbed species through energy-resolved electron beam induced dissociation of weakly adsorbed cyclopropane. The use of low-energy electrons to prepare catalytically interesting surface species, or to modify surfaces, is well documented.[32−36]

Experimental Section

The experiments were performed in an ultrahigh vacuum chamber using Auger spectroscopy, thermal desorption measurements, and HREELS. Dispersion compensation (DC)−HREELS spectrometers,[37] such as the one used in this study, permit the delivery of high current to the sample while retaining the ability to measure high-resolution vibrational spectra. Typical values for the current on the sample and for the overall resolution were 10 nA and 8 meV, respectively. The DC−HREELS spectrometer was operated in two distinct modes in order to sequentially use it as a relatively high-intensity monoenergetic electron source and as a high-resolution (HREELS) vibrational spectrometer. In the electron gun mode of operation, the resolution was degraded to 135 meV in order to increase the current on the sample to a space charge limited value of 70 nA/cm^{-2}. Thus, the high current throughput and high-resolution capabilities intrinsic to DC−HREELS spectrometers were used to sequentially electron bombard and vibrationally analyze a given region of the surface. Electron irradiation of the surface using the spectrometer acted on an approximately 0.02 cm^2 area of the surface. Vibrational analysis was then performed in a 0.015 cm^2 area centered within the irradiated area. This capability was assured by placing an aperture at the entrance to the analyzer lens. The above approach was convenient for HREELS analysis but problematic for TPD experiments since the total (front face) surface area of the copper crystal was 0.5 cm^2. Hence, the TPD measurements were combined with nonmonoenergetic electron bombardment using a simple filament, so as to irradiate all of the surface. Calibration HREELS measurements were used to establish that electron irradiation at 10 eV with respect to the center of the simple filament induced the same surface modification as that achieved using the spectrometer beam at 10 eV. Thus, the TPD/electron filament irradiation results may be correlated with the HREELS spectra/HREELS gun irradiation results.

The Cu(110) and Cu(111) samples were cleaned by cycles of Ne$^+$ sputtering at room temperature and flash heating to 900 K. The cleanliness of the surface was monitored using AES and HREELS measurements before each experiment. Cyclopropane (Aldrich, 99% pure) was further purified using freeze, pump, and thaw cycles as verified by in situ measurements using the mass spectrometer.

Results

Experiments were performed on Cu(110) and Cu(111) crystals, and apart from a relatively minor difference in the ν(CH) stretching frequency region of the HREELS spectra, the results obtained for both surfaces were essentially identical. Molecular desorption from both single-crystal surfaces takes place at 125 K, and the integrated desorption signal saturates at an exposure of approximately 2 langmuirs. Application of the Redhead approximation,[38] assuming a preexponential factor of 10^{13} s^{-1}, gives a desorption energy of $\sim$9 kcal/mol. The weak copper−cyclopropane interaction determined by the TPD measurements is consistent with the HREELS data in that the loss frequencies are invariant as a function of surface coverage and are only weakly shifted with respect to those for gas-phase cyclopropane.[39] Loss energies for cyclopropane on Cu(111) are listed in Table 1. The shoulder at 759 cm^{-1} is a CH_2 twisting mode.

Low-energy electron bombardment may be used to break bonds in adsorbed molecules.[24,32−36] In the particular case of

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Table 1. HREELS Vibrational Peak Assignments for Cyclopropyl and Cyclopropane on Cu(111)

	frequency (cm^{-1})					
approximate description[25] of vibrational modes	infrared data for gas-phase cyclopropane[39]	cyclopropane monolayer on Cu(111) at 90 K	10 eV electron irradiated c-C_3H_6/Cu(111)	bromo-cyclopropane[46]	bicyclopropyl[45]	cyclopropyl complexes[49]
CH stretching	3024−3101	3064	3033 2839	3008−3102	3002−3076	2864−3070
CH_2 deformation	1438−1479	1451	1435	1417−1444	1416−1471	1412−1461
ring breathing	1188	1177	1173	1196	1185−1196	1175−1191
asymmetric ring deformation	1028	1032	981	927	962	
symmetric ring deformation	868	839	827	852−864	870−883	808−895

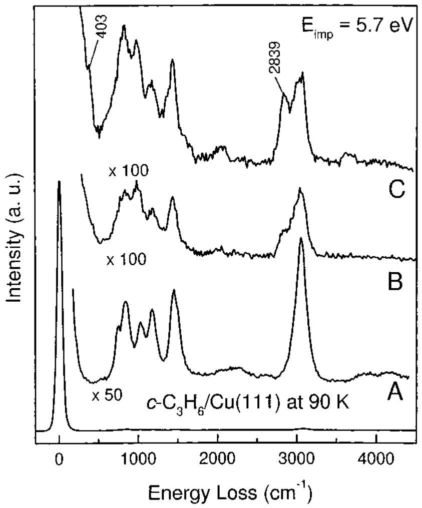

Figure 1. HREELS spectra displaying the replacement of adsorbed cyclopropane by chemisorbed species resulting from the 10 eV irradiation of cyclopropane on Cu(111) at 90 K: (A) reference spectrum of nonirradiated cyclopropane; (B) spectrum of the irradiated adlayer at 90 K; (C) irradiated adlayer following a brief anneal to 145 K to remove residual cyclopropane.

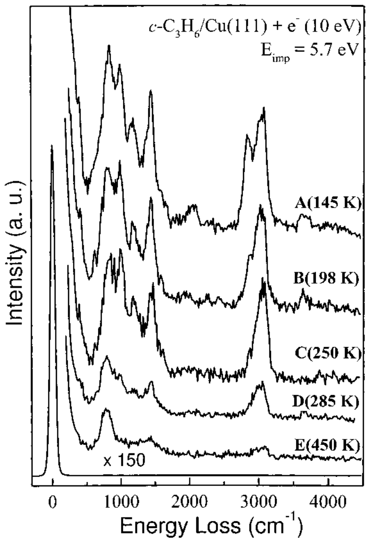

Figure 2. HREELS spectra related to the reaction chemistry of the species produced by 10 eV electron irradiation of cyclopropane on Cu(111): (A) same as spectrum 1C; (B) spectrum acquired following a brief anneal to 198 K; (D) annealed to 285 K; (E) annealed to 450 K. Spectrum C was acquired in a separate experiment following an anneal to 250 K.

cyclopropane on Cu(111) and Cu(110) surfaces, a dissociative electron attachment (DA) resonance[40] is detected at approximately 10 eV.[41] HREELS data demonstrating DA dissociation of cyclopropane at 90 K on Cu(111) are presented in Figure 1. Spectrum 1A is for the nonbombarded cyclopropane adlayer, and thus serves as a reference for the interpretation of spectra B and C. Spectrum B is for the electron-bombarded surface at 90 K, and thus displays features due to both cyclopropane and electron beam generated surface species. Two new losses are resolved in spectrum C, one at 2839 cm^{-1} and the other at 403 cm^{-1}. The latter feature may be readily attributed to a metal−carbon stretching vibration, and thus suggests that 10 eV electron irradiation causes bond breaking in cyclopropane, and that the hydrocarbon dissociation fragments form a bond to the surface. Such a conclusion is borne out by a comparison of spectra A−C which shows that an anneal to 145 K is not sufficient to clean off the copper surface, despite the fact that cyclopropane desorbs at 125 K. Heating to 145 K does not, however, create new surface species, since no new losses are produced by the anneal from 90 to 145 K. It is important to note that although the relative intensities of the losses are modified, the fingerprint structure characteristic of cyclopropane (the ring deformation and breathing modes, as well as the CH_2 deformation mode, in the 700−1500 cm^{-1} region) remains at 145 K despite the removal of cyclopropane. There is, however, a small difference in that the postirradiation spectra display a loss at 977 cm^{-1} whereas adsorbed cyclopropane displays one at 1032 cm^{-1}. The retention of the cyclopropane fingerprint structure suggests that the surface species present at 145 K are also C_3-cyclic species.

HREELS measurements as a function of anneal temperature were used to explore the thermal chemistry of the electron beam induced surface species. The first major change in the vibrational spectrum occurs on heating to 190−205 K. Data for Cu(111) are shown in Figure 2. In particular, spectrum 2B shows that the relatively intense ν(CH) loss feature at 2839 cm^{-1}, which appears following 10 eV irradiation, is almost completely removed on annealing to 198 K. Nevertheless, despite the removal of this band, spectrum 2B retains the c-C_3 fingerprint structure similar to that displayed by cyclopropane (spectrum 1A). In contrast, as may be seen from spectrum 2D, the c-C_3 fingerprint structure is removed on annealing to 285 K. Additional measurements show, however, that the c-C_3 fingerprint structure is present at temperatures up to at least 260 K. An example of such a measurement is included as spectrum 2C. Spectrum 2E shows that a hydrocarbon residue remains on the surface at 450 K.

Electron bombardment of cyclopropane on Cu(110) at 90 K gives rise to a carbon−metal vibration at 419 cm^{-1} and a new ν(CH) loss at 2806 cm^{-1}. HREELS spectra taken as a function of anneal temperature for a 10 eV electron-bombarded cyclopropane adlayer on Cu(110) are shown in Figure 3. In particular, a comparison of spectra 3C and D show that annealing to 205 K causes the removal of the low-frequency

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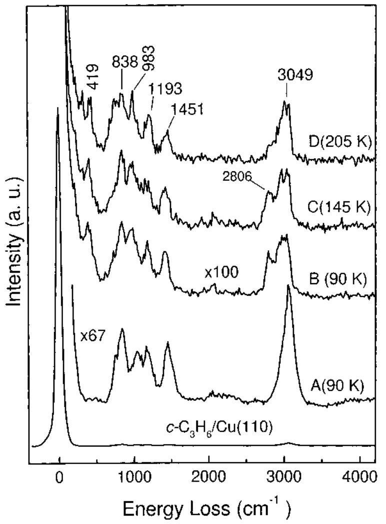

Figure 3. HREELS spectra for cyclopropane (A) and 10 eV electron irradiated cyclopropane on Cu(110). Spectra C and D were recorded following a brief anneal to 145 and 205 K, respectively.

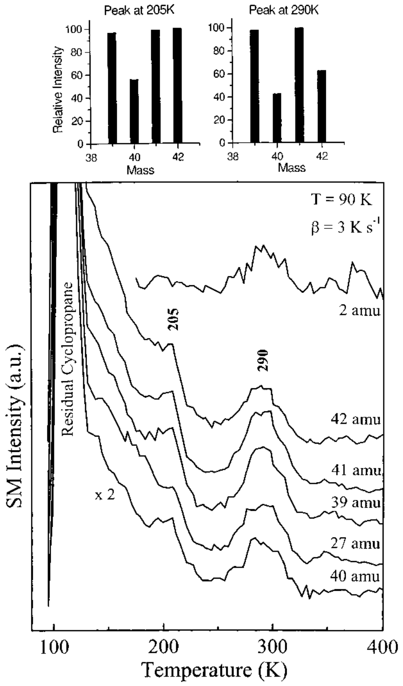

Figure 4. Thermal desorption data for 10 eV electron irradiated cyclopropane on Cu(110). The electron dose was 1.1 × 10^{17} e cm^{-2}. Signal intensities for the propene and cyclopropane desorption peaks are included in histogram form.

(2806 cm^{-1}) ν(CH) loss. As is observed for Cu(111), the c-C_3H_6 fingerprint structure is also retained above 205 K.

The modification of the adlayer effected by electron irradiation at 10 eV was also studied by performing TPD measurements. The TPD data in Figure 4, for Cu(110), display three desorption peaks in addition to the molecular desorption at 125 K. The high-temperature tail of the latter peak is due to the large volume of the chamber occupied by the bulky mμ-metal-shielded DCEELS spectrometer. Two of the new peaks are due to simultaneous hydrogen and propene desorption at 290 K. The third peak, which appears as a shoulder at 205 K, is attributed to reaction-limited cyclopropane desorption. The identification of propene and cyclopropane as desorption products, as well as the differentiation between the two products, is based on the relative intensities of the m/e = 42, 41, 40, and 39 peaks as calibrated using our mass spectrometer, and by comparison with the cracking pattern for the cyclopropane desorption peak at 125 K. The ratio of the m/e = 41 to the m/e = 42 peak intensities (1:1 at 205 K and 1.4:1 at 290 K) is consistent with the desorption of cyclopropane at 205 K and the desorption of propylene at 290 K. The areas of the cyclopropane and propene desorption peaks were calculated and corrected for the respective sensitivity factors, yielding a cyclopropane/propene desorption ratio of approximately 1:4. No other desorption products were detected. In particular, m/e = 27 measurements show that the desorption of ethylene can be ruled out. As described in a separate publication,[41] detailing the DA mechanism, the HREELS data were used to estimate the cross section for the process leading to the formation of the species yielding the new low-frequency ν(CH) losses. An estimate of 0.8 × 10^{-17} cm^2 was obtained for cyclopropane on Cu(110). Such a low cross section means that only a small quantity of new surface species may be created on the surface in a period of time consistent with keeping the surface clean. As a result, the reaction-limited TPD features at 205 and 290 K are weak compared to the molecular desorption peak at 125 K.

Discussion

Electron bombardment, at 10 eV impact energy, of cyclopropane on both Cu(110) and Cu(111) induces bond breaking and leads to the replacement of weakly adsorbed cyclopropane with more strongly adsorbed molecular fragments. Whereas molecular cyclopropane desorbs at 125 K, the electron beam generated species remain on the surface and may be isolated by heating from 90 to 145 K. These cyclopropane-derived species evolve to yield reaction-limited cyclpropane and propene desorption peaks at 205 and 290 K, respectively. Before the chemistry at the origin of the formation of cyclopropane and propene desorption products is discussed, it is necessary to consider the electron-induced dissociation processes which occur at 90 K. One possible process is the generation of cyclopropyl fragments, as in eq 1, through CH scission caused by a

$$\text{c-}C_3H_6 + e(10\text{ eV}) \rightarrow [\text{c-}C_3H_6^-]^* \rightarrow \text{c-}C_3H_5^{\bullet} + H^- \quad (1)$$

dissociative attachment (DA) core-excited resonance.[40] The asterisk denotes a core-excited resonance, that is, a process involving electron capture into an electronically excited parent state. A detailed discussion of the dissociative process, including the measured cross section, is given in a separate publication.[41]

The cyclopropyl radical and hydride ion produced in the submonolayer may either stick to the surface or escape into vacuum. Excess energy is evidently deposited in the dissociation fragments, since the DA resonance energy is approximately 6 eV greater than that required to break the CH bond. The probability for escape depends on the value of the kinetic energy acquired in the dissociation process relative to the escape threshold imposed by the polarization field (E_{pol}) due to the adsorbate-covered substrate.[42,43] For example, consider the escape probability for H^-, taking the upper limit case where all of the excess energy (~6 eV) acquired in the DA process is channeled into kinetic energy of the fragments. Given the very different ratios of the masses of the fragments with respect to the parent molecule, almost all (the fraction equal to 1 − 41/

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42) of the kinetic energy is partitioned to hydride ion.[43] However, the kinetic energy threshold for escape must be greater than $E_{pol}/\cos^2 \theta$ where θ is the ejection angle relative to the normal to the surface.[42] Taking 2.0 eV as a reasonable upper limit[44] for the polarization potential, it follows that only H^- ejected along directions for which θ is less than approximately 55° can escape. If internal excitation of the cyclopropyl fragment is factored in, then the conditions for H^- ejection become more stringent. Attraction between the transient negative ion intermediate and its image charge in the metal may possibly play a role in the dynamics of the process leading to cyclopropyl capture by the metal.[35b] The important point, with respect to the subsequent chemistry of the adsorbed dissociation fragments, is that the DA process given by eq 1 could create an adsorbed layer that contains a nonstoichiometric (alkyl rich) mixture of alkyl and atomic hydrogen. The further removal of some of this hydrogen coverage through recombination close to room temperature should also be taken into account in TPD experiments on the electron beam generated surface species.

The identification of the electron beam prepared precursors to propene and cyclopropane desorption, as given below, is made on the basis of the correlation between the HREELS and the TPD data. HREELS spectra recorded on annealing the electron-irradiated cyclopropane adlayer to 145 K show clear evidence for the presence of $Cu-C_3$ cyclic surface species since, for example, spectrum 1C retains the essential features of the cyclopropane spectrum, 1A. In particular, the ring breathing mode (at ~1166 cm^{-1} in c-$C_3H_{6\ ads}$) and the symmetric ring deformation mode (at ~843 cm^{-1} in c-$C_3H_{6\ ads}$) are present in both spectra. Data for a whole range of molecules containing cyclopropyl groups,[45-49] including bromocyclopropane[45] and bicyclopropyl[46] and cyclopropyl complexes,[49] display a ring breathing mode at 1183-1205 cm^{-1} and a symmetric ring deformation mode in the 784-887 cm^{-1} region. Hence, a comparison of loss frequencies in spectra 1C and 2C with the literature infrared data for cyclopropyl groups listed in Table 1 strongly suggests the presence of cyclopropyl on the surface. Even the observation that adsorbed cyclopropane displays a loss at 1032 cm^{-1}, whereas the postirradiated adlayer displays one at 977 cm^{-1}, indicates the presence of cyclopropyl groups. The latter losses may be attributed to the asymmetric ring deformation/CH_2 wag modes, with the lower frequency being more characteristic of cyclopropyl (Table 1).

The HREELS data, however, also show that 10 eV electron irradiation creates *more than one* chemisorbed hydrocarbon species on the surface. In particular, Figure 3C shows that the irradiated c-C_3H_6/Cu(110) system displays a ν(CH) stretching mode at 2806 cm^{-1} which is *selectively* removed on heating to 205 K. Similarly, Figure 2B shows that the corresponding loss (at 2839 cm^{-1}) for the irradiated c-C_3H_6/Cu(111) system is selectively attenuated on heating to 198 K. These two peaks may be reasonably attributed to the presence of metallacyclobutane species. For example, matrix-isolated nickel-metallacyclobutane[10b] (Ni-$(CH_2)_3$) displays a band at 2850 cm^{-1}, and bisallyl-Mo and W-metallacylcobutane complexes[6d,50] display characteristic bands at 2775 and 2786 cm^{-1}. The fact that, as shown below, metallacyclobutane is the minority hydrocarbon surface species explains why the deformation region is dominated by the intense cyclopropyl bands. Hence, spectra recorded on annealing to 205 K differ from those taken on annealing to 145 K essentially only with respect to the CH stretching region of the spectrum. Although annealing above 200 K removes the loss attributed to metallacyclobutane, cyclopropyl species still remain on the surface. The results are thus consistent with the presence of both cyclopropyl and metallacyclobutane species on the surface at 145 K, and the selective removal of the latter species at approximately 205 K. The absence of loss peaks at approximately 1380 and 1600 cm^{-1} may be used to rule out the presence of propyl[51,52] or alkenyl[29] species. The spectra are also not consistent with published HREELS spectra of propene [51] on Cu(111) or η_{-3}-allyl (π-bonded allyl) on Ag(110).[28] Additional justification for the presence of both cyclopropyl and metallacyclobutane is given below in the relation to the observed reaction-limited desorption chemistry.

First, we consider if the reaction-limited desorption of cyclopropane at 205 K is consistent with either the hydrogenation of cyclopropyl or the cyclization of metallacyclobutane. Since the present study shows that c-$C_3H_{5\ ads}$ is stable in the presence of coadsorbed atomic hydrogen (produced as in eq 1) to at least 260 K, the hydrogenation of cyclopropyl may be ruled out. The latter conclusion provides support for the observation that the hydrogenation of cyclopropyl groups does take place, in cyclopropane/deuterium reactions, on supported Pt catalysts.[1] In contrast, the organotransition literature provides ample support for the elimination of cyclopropane from metallacyclobutane intermediates.[6b] Similarly, a number of gas-phase metal ion studies, involving the reactions of Fe^+ or Co^+ with cyclopropane or cyclobutanone, provide clear evidence for the reductive elimination of cyclopropane from metallacylobutane intermediates.[7-9] Both the organotransition and metal ion studies show, in fact, that metallacyclobutanes can undergo decomposition via three principal reaction pathways.[6d] These are, as follows, (i) reductive elimination of cyclopropane through the cyclization of metallacyclobutane, (ii) β-dehydrogenation to form a hydrido-metal-allyl complex (hydrogenation of the allyl species then yields propene; α-elimination is observed for platinacyclobutanes[15]), and (iii) CC bond scission to yield a carbene-metal-ethylene complex. Since ethylene desorption is observed in the present study, we do not consider channel iii in any detail. Channel ii is also improbable, since only cyclopropane desorption correlates with the removal of the loss attributed to metallacyclobutane. In contrast, reductive elimination (channel i) is a strong possibility since the HREELS data (spectra 2B and 3D) show that cyclopropane formation coincides with the removal of loss features at 2839 and 2806 cm^{-1} on Cu(111) and Cu(110), respectively.

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The reductive elimination of cyclopropane from metal ion metallacyclobutanes is often referred to as a thermoneutral reaction. The analogous reaction on copper surfaces is also either thermoneutral or exothermic. The CC bond energy for cyclopropane is approximately 69 kcal/mol,[53] and the formation of the relatively weak CC bond is offset by approximately 9 kcal/mol[53] through the fact that the CH bonds of cyclopropane are uniquely strong for an alkane.[54] Cu−alkyl bond energies are on the order of ∼30 kcal/mol,[55] and bond dissociation energies on the order of 40 kcal/mol have been estimated for neutral Ni and Rh metallacyclobutane complexes.[56] Furthermore, the strain energies for the reactant and product are not expected to differ by more than about 10 kcal/mol since Th,[57] Co,[9] and Fe[9] metallacyclobutanes are reported to display strain energies in the 17−22 kcal/mol range, as compared to 27.5 kcal/mol for cyclopropane.[54] The latter point is central to our attribution of the surface metallacycle to a metallacyclobutane rather than a pentanuclear (strucure **1**) species. The metallacyclobutane is much closer, both energetically and structurally, to a likely transition state for transformation to the cyclopropane product. Seigbahn and Blomberg have previously pointed out, on the basis of quantum chemical model studies, that the calculated small activation barrier for reductive elimination of cyclopropane from palladocyclobutane may be rationalized in terms of the highly strained metal−carbon bonds in the metallacyclobutane.[58] In contrast, it is difficult to envision the efficient formation of cyclopropane at 205 K from structure **I**, since such a reaction would involve breaking two metal−alkyl bonds and the formation of a highly strained molecule. This line of reasoning finds support in the HREELS/TPD study by Bent et al. of a structure **1** C_3-metallacycle prepared on Al-(100) through the thermal decomposition of 1,3-diiodopropane,[29] in that they observed decomposition to yield propene at 500 K but no cyclopropane formation. It is also useful to compare the present data with temperature-programmed reaction results for three 1,3-haloiodopropanes on Cu(100) published in a thesis from Bent's group.[59] The iodo−carbon bond breaks on Cu(100) at 125 K. Data for 1-chloro-, 1-bromo-, and 1-iodo-3-iodopropanes were interpreted[59] in terms of a true branching mechanism leading to cyclopropane and propene formation. Cyclopropane formation, the dominant pathway, took place in each case at the temperature of scission of the second halo−carbon bond (125, 165, and 240 K for the diiodo, iodobromo, and iodochloro compounds, respectively). This result was interpreted in terms of an intramolecular radical trapping reaction.[59] The minor pathway leading to propene formation at 315 K was attributed to the decomposition of a metallacycle species formed by radical trapping by the copper surface.[59]

The present experiment allows the chemistry specific to cyclopropyl species to be isolated, since the HREELS data acquired on annealing to 205 K show that removal of the metallacyclobutane species leaves cyclopropyl on the surface. Additional experiments[60] on the decomposition of bromocyclopropane on Cu(111) confirm that spectrum 2C is indeed characteristic of adsorbed cyclopropyl groups. The spectrum characteristic of cyclopropyl persists to at least 260 K, and its absence at 300 K may be reasonably linked with the reaction-limited desorption of propene at 290 K. Although examples of cyclopropyl to allyl transformations have been reported in the organometallic literature,[13a] no direct spectroscopic evidence was obtained for surface allyl species in the present study. The propene desorption peak is, however, consistent with the hydrogenation of such a species, since Gurevich et al.[61] have shown that preadsorbed hydrogen reacts with π-allyl on Cu(100), to give a propene desorption peak at 250 K as the sole desorption product. In contrast, they observed that, in the absence of surface hydrogen, allyl groups desorbed at 415 K with approximately 85% selectivity, the other desorption product being propene. The surface hydrogen involved in the formation of propene in our experiment partly results from the DA resonance process described in eq 1. However, spectrum 4E shows that a hydrocarbon residue remains on the surface following the desorption of propene. This indicates that partial dehydrogenation, driven by strain energy release, occurs during cyclopropyl ring opening. Such an interpretation finds significant support in the fact that hydrogen desorption occurs simultaneously to propene desorption. The release of hot hyrogen atoms during the highly exothermic ring opening of cyclopropyl serves both to scavenge hydrogen adatoms and to hydrogenate surface allyl species.

A number of implications with respect to possible reaction mechanisms for cyclopropane transformations on metal surfaces emerge from this work. First, the reductive elimination of cyclopropane from metallacyclobutane is shown to be a facile reaction, occurring on copper surfaces at 205 K. Thus, cyclization of surface metallacyclobutane intermediates may be competitive with β-dehydrogenation, hydrogenation, and hydrogenolysis channels. In particular, β-dehydrogenation can occur at low temperatures.[62] The hydrogenation of cyclopropane to propane takes place on alumina-supported platinum catalysts at temperatures as low as 235 K.[1] Similarly, β-elimination of propyl groups from Cu(110) occurs at 200−230 K in TPD experiments.[63] The selectivity toward reductive elimination of cyclopropane may thus decrease, from right to left across the transition metal group, as the metal−C_3H_6 metallacyclobutane bond stength increases. A different reaction chemistry, excluding facile cyclization, is expected for pentanuclear C_3-metallacycle (structure **1**) surface species. In agreement with the work of Brown and Kemball[1] our study shows that the hydrogenation of cyclopropyl to cyclopropane is unlikely to be a major reaction pathway. In contrast, isomerization of cyclopropyl to surface allyl may be possibly involved in the formation of propene from cyclopropane/H_2 mixtures in cases where the metal is able to break one of the strong CH bonds of cyclopropane.

Conclusions

Energy-resolved electron bombardment of submonolayer cyclopropane on copper(111) and -(110) surfaces was used to prepare a mixture of adsorbed cyclopropyl, atomic hydrogen, and metallacyclobutane. The two C_3 hydrocarbon fragments were prepared at 10 eV and identified by comparing the

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HREELS data to IR data for cyclopropyl and metallacyclobutane complexes. Thermal desorption and temperature-dependent HREELS data were used to show that the metallacyclobutane species undergoes facile cyclization to eliminate cyclopropane at 205 K. The metallacyclobutane species were characterized by a CH stretching mode loss at 2806 and 2839 cm^{-1} on Cu(110) and Cu(111), respectively. The cyclopropyl species evolved to yield a propene desorption peak at 290 K. Although no spectroscopic evidence for an allyl intermediate was obtained, it is likely that propene formation occurs by hydrogenation of a transient allyl species resulting from ring opening of the cyclopropyl species.

Acknowledgment. Financial support from NSERC and FCAR is gratefully acknowledged. R.M. acknowledges the receipt of an FCAR postgraduate scholarship.

JA972301N