



# The desorption and reaction of 1-alkenes and 1-alkynes on Cu(111) and copper foils



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## ARTICLE INFO

### Article history:

Received 15 March 2013

Accepted 19 April 2013

Available online 25 April 2013

### Keywords:

Copper foils

Cu(111)

1-Alkenes

Temperature-programmed desorption

## ABSTRACT

The adsorption of a series of 1-alkene and 1-alkynes is examined both on Cu(111) single crystals and a polycrystalline copper foil in order to explore the influence of low-coordination sites expected to be present on the copper foil on the chemistry of 1-alkenes. The 1-alkene desorption temperatures increase linearly with the number of carbon atoms in the 1-alkene due to van der Waals' interaction between the n-alkyl chain and the surface. However, 1-alkenes desorb at temperatures from 60 to 100 K higher on the polycrystalline copper foil than the Cu(111) single crystal due to the presence of low-coordination sites on the foil. In contrast, 1-alkynes up to 1-octyne desorb at ~345 K from both the polycrystalline foil and Cu(111), while 1-nonyne and 1-decyne desorb between 400 and 430 K. This is ascribed to the strong rehybridization of 1-alkynes on copper surfaces that causes the n-alkyl group to move away from the surface, except for 1-nonyne and 1-decyne, where the termini of the alkyl chains are proposed to be able to access the surface. The stabilization of 1-alkenes on the polycrystalline foil allows them to dehydrogenate to form the corresponding 1-alkyne. This effect is ascribed to the presence of low-coordination sites on the polycrystalline sample that stabilize the 1-alkene allowing surface reactions to occur.

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## 1. Introduction

Ethylene adsorbs rather weakly and reversibly on low-Miller-index surfaces of copper [1–5]. However, low-coordination sites present on a stepped Cu(410) surface have been shown to induce the complete thermal decomposition of ethylene to carbon, which then decorates the step edges inhibiting further reaction [6–8]; ethylene decomposition is favored on the low-coordination step sites [7,8], while molecular desorption is favored on low-Miller-index surfaces.

Studies of n-alkanes on surfaces reveal that their desorption activation energies increase with chain length on metals [9–13] and graphite [14,15] due to van der Waals' interactions between the alkyl chains and the surface. Their adsorption and desorption have been explored using density functional theory (DFT) [16] and molecular dynamics (MD) simulations [17,18], and an increase in desorption activation energy of ~6 kJ/mol per methylene group has been found for n-alkanes on Au(111) [9]. Scanning tunneling microscopy (STM) reveals the formation of lamellar structures on gold [19].

This implies that functionalizing alkenes with n-alkyl chains should stabilize them due to the additional van der Waals' interactions with the surface. This idea is borne out experimentally since the desorption activation energies for 1-alkenes on Cu(100) increase by ~6.3 kJ/mol per methylene group [20], similar to the adsorption energy increase per methylene group found for n-alkanes. Since the

decomposition of ethylene on stepped copper surfaces arises from a balance between the rate of desorption and decomposition, lowering the desorption rate by increasing the length of the n-alkyl chain may lead to a greater extent of dehydrogenation. This idea is explored in the following by measuring the desorption kinetics and reactions of a range of 1-alkenes on a Cu(111) single crystal as well as on an annealed polycrystalline copper sample. It has been demonstrated previously that annealed polycrystalline copper shows (100) facets in low-energy electron diffraction (LEED) measurements after cleaning and annealing cycles are carried out in ultrahigh vacuum (UHV) [21]. The sample will, nevertheless have defects at the grain boundaries between the (100)-oriented crystallites, while the coverage of defects (steps, edges etc) will be lower, on the Cu(111) single crystal.

## 2. Experimental

The equipment used for these experiments has been described in detail elsewhere [22]. Briefly, temperature-programmed desorption (TPD) data were collected in a UHV chamber operating at a base pressure of  $\sim 1 \times 10^{-10}$  Torr following bakeout. The system was equipped with a UTI quadrupole mass spectrometer interfaced to a computer that allowed up to seven masses to be sequentially monitored in a single experiment. The sample was placed about 2 mm from the front of the mass spectrometer ionizer before each TPD experiment, and data were collected using a heating rate of 4 K/s. The surface temperature was measured with a thermocouple (K-type) inserted into a

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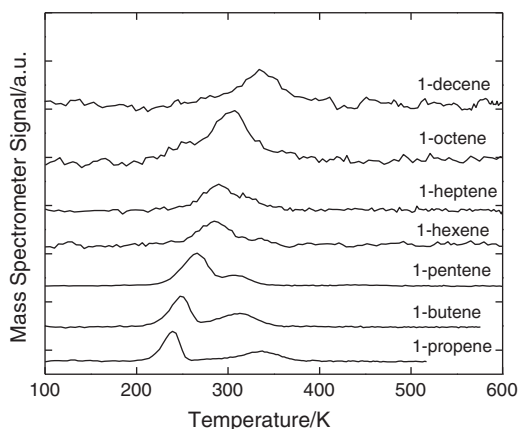
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pinhole located at the edge of the copper samples, which could be cooled to  $\sim 80$  K by thermal contact to a liquid-nitrogen-filled reservoir, and resistively heated to  $\sim 1000$  K. The polycrystalline copper sample (Alfa Aesar, 99.99% purity, 1 mm thick) was polished to a mirror finish using 1  $\mu\text{m}$  diamond paste and then rinsed with deionized water and ultrasonically degreased in acetone. Once in UHV, the polycrystalline copper and Cu(111) samples were cleaned using a standard procedure that consisted of Argon ion bombardment ( $\sim 1$  kV,  $\sim 2$   $\mu\text{A}/\text{cm}^2$ ) and annealing cycles up to  $\sim 850$  K. The cleanliness of the samples was monitored using Auger spectroscopy.

The 1-alkenes and 1-alkynes (Aldrich, 99.0% purity) were transferred to glass bottles and attached to the gas-handling system of the UHV chamber, where they were subjected to several freeze-pump-thaw cycles. The purity of the 1-alkenes and 1-alkynes was monitored using mass spectroscopy.

### 3. Results

The desorption and reaction of a number of 1-alkenes (propene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene and 1-decene) were explored on a Cu(111) single crystal and a polycrystalline copper foil to measure the desorption temperatures and to search for possible reaction products. The desorption spectra for low coverages of selected alkenes on a polycrystalline foil are displayed in Fig. 1. In all cases, the measured masses for the 1-alkenes were selected based on their mass spectrometer ionizer fragmentation patterns measured using the same mass spectrometer. Also indicated in the caption are the exposures (in Langmuirs,  $1 \text{ L} = 1 \times 10^{-6} \text{ Torr s}$ ) used for each 1-alkene along with the exposures required to saturate the surface. Propene desorbs from the foil in a state centered at  $\sim 240$  K with a weaker, broad peak at  $\sim 340$  K. The temperature of the major desorption peak from polycrystalline copper ( $\sim 240$  K) is substantially higher than that found for Cu(111) (see below) and Cu(100) ( $\sim 140$  K) [20]. As noted above, the polycrystalline sample exhibited a LEED pattern that indicates that (100) facets have formed on the surface [21]. The difference between the propene desorption temperatures from polycrystalline copper and the single crystals is therefore ascribed to the presence of a substantial number of defects on the surface that stabilize propene compared to the single crystal, in accord with the well known stabilizing effect of low-coordination sites [23]. The desorption peak temperature increases with increasing

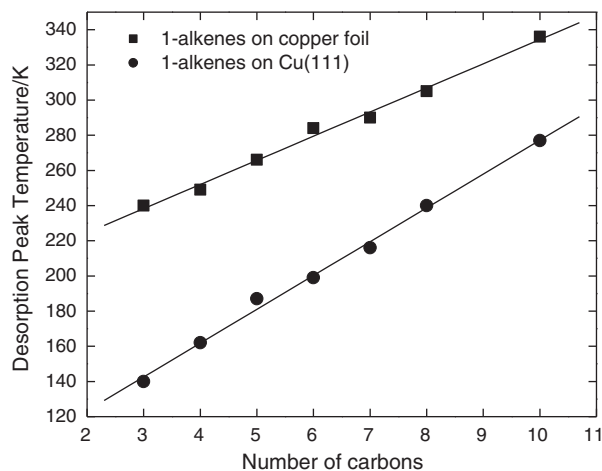


**Fig. 1.** TPD profiles of 1-alkenes on a copper foil showing desorption of low coverages of 1-propene (41 amu, exposure, 0.05 L, saturation exposure, 0.75 L), 1-butene (56 amu, exposure, 0.02 L, saturation exposure, 0.9 L), 1-pentene (70 amu, exposure, 0.09 L, saturation exposure, 1.0 L), 1-hexene (84 amu, exposure, 0.18 L, saturation exposure, 1.1 L), 1-heptene (98 amu, exposure, 0.15 L, saturation exposure, 1.2 L), 1-octene (43 amu, exposure, 0.2 L, saturation exposure, 1.3 L) and 1-decene (70 amu, exposure, 0.23 L, saturation exposure, 1.4 L). 1-Alkene desorption was confirmed by comparing the desorption intensities at various masses with the mass spectrometer ionizer fragmentation pattern.

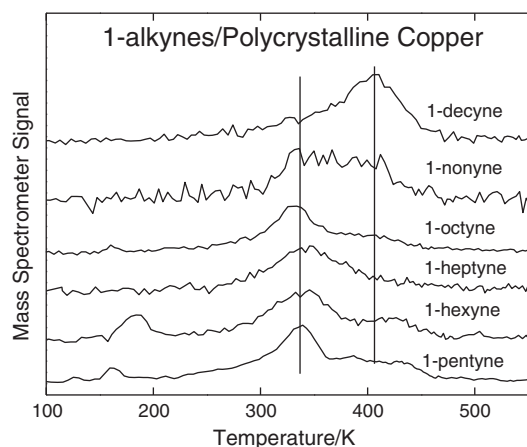
length of the alkyl chain, so that the main feature for 1-butene is at  $\sim 250$  K with a weaker feature at  $\sim 310$  K, increasing to  $\sim 265$  K for 1-pentene, with a smaller feature at  $\sim 310$  K. This trend continues for higher homologs, so that 1-decene desorbs with a peak at  $\sim 335$  K.

The variation in desorption peak temperature for 1-alkenes on Cu(111) was also explored as a function of the number of carbon atoms (data not shown). The peak temperatures found for propene, 1-butene, 1-pentene and 1-hexene were in excellent agreement with previous results for 1-alkenes on Cu(100) surfaces [20]. The resulting variation in peak desorption temperature with the number of carbon atoms for 1-alkenes on a polycrystalline copper sample (■) and a Cu(111) single (●) crystal is compared in Fig. 2. This reveals a linear increase in desorption temperature with increasing molecular weight on both surfaces even up to the highest 1-alkene studied ( $\text{C}_{10}$ ). However, both the slopes and intercepts are different. In the case of Cu(111) surfaces (Fig. 2, (●)), the slope of the line is  $19.2 \pm 0.6$  K/methylene group and the intercept is  $85 \pm 4$  K. For polycrystalline copper at low coverages (Fig. 2 (■)), the slope of the line is  $13.7 \pm 3.5$  K/methylene group and the intercept is  $197 \pm 4$  K.

The desorption behavior of 1-alkynes was also explored on Cu(111) and polycrystalline copper in order to gain insights into the rate-limited steps in the dehydrogenation reaction (see below), and to explore whether they undergo any additional reactions. The desorption spectra for low coverages of a number of 1-alkynes on polycrystalline foils are displayed in Fig. 3. Again, the measured masses for 1-alkynes were selected based on their mass spectrometer ionizer fragmentation patterns using the same mass spectrometer. All spectra, with the exception of 1-decyne, display a feature at  $\sim 340$  K, with a much weaker, broad desorption state at  $\sim 430$  K for 1-pentyne and 1-hexyne. However, in the case of 1-nonyne, the desorption profile consists of two features, one at  $\sim 340$  K and another at  $\sim 400$  K. 1-Decyne, desorbs in a single state at  $\sim 410$  K. Similar experiments were performed for 1-alkynes on Cu(111) (data not shown) and similar trends were found. The resulting peak desorption temperatures for various 1-alkynes are summarized in Fig. 4, which plots the peak desorption temperatures as a function of the number of carbon atoms for Cu(111) (●) and polycrystalline copper (■). The trend is completely different from that found for the 1-alkenes, which showed a linear variation in desorption temperature with the number of carbon atoms (Fig. 2). In the case of 1-alkynes, the desorption peak temperature remains rather constant up to 1-octyne, where the 1-alkynes desorb at  $\sim 340$  K from the polycrystal and at slightly higher temperatures (by  $\sim 10$  K) from Cu(111). For higher homologs (1-nonyne and 1-decyne) the desorption temperature rises on Cu(111) by around 30 to 40 K per additional methylene group. A



**Fig. 2.** Plot of the peak desorption temperatures in TPD of low coverages of 1-alkenes on a Cu(111) single crystal (●) and on a copper foil (■) as a function of the number of carbon atoms in the corresponding 1-alkene.



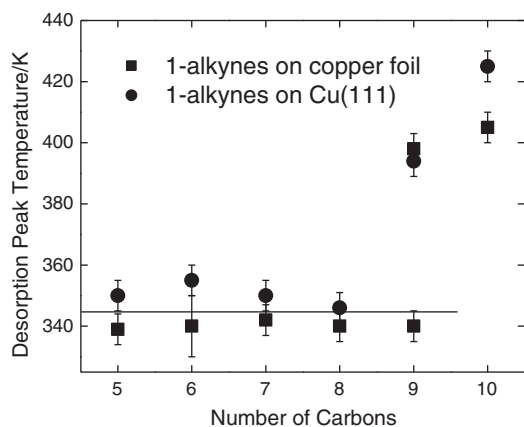
**Fig. 3.** TPD profiles of 1-alkynes on a copper foil showing the desorption of low coverages of 1-pentyne (67 amu), 1-hexyne (53 amu), 1-heptyne (81 amu), 1-octyne (81 amu), 1-nonyne (81 amu) and 1-decyne (67 amu). 1-Alkyne desorption was confirmed by comparing the desorption intensities at various masses with the mass spectrometer ionizer fragmentation pattern.

similar trend is seen on polycrystalline copper except that 1-nonyne has two desorption states at  $\sim 340$  and  $398$  K.

In the case of higher 1-alkenes, substantial dehydrogenation to 1-alkynes also occurs on copper foils as illustrated by the TPD data in Figs. 5 and 6. In the case of 1-hexene (Fig. 5(a)), both 1-hexene and 1-hexyne have significant intensities at 54 amu. It was shown that the low-temperature state is due to 1-hexene desorption (see Fig. 2), while the high-temperature state was attributed to 1-hexyne by comparing the desorption intensities at various masses with the mass spectrometer ionizer fragmentation pattern of 1-hexyne measured using the same mass spectrometer. 1-hexene desorbs between  $\sim 270$  and  $290$  K depending on coverage, while 1-hexyne desorbs between  $325$  and  $340$  K, also depending on coverage.

The corresponding results for 1-heptene on a polycrystalline copper sample (Fig. 5(b)) show desorption of molecular 1-heptene (70 amu) between  $\sim 280$  and  $300$  K depending on coverage. The clear formation of 1-heptyne is evidenced by 67 amu signals between  $\sim 335$  and  $350$  K. The 67 amu feature is relatively intense in the mass spectrometer fragmentation pattern of 1-heptyne, but there is also a very weak, yet detectable fragment of 1-heptene at this mass. However, the 81 amu fragment occurs only for 1-hexyne thus confirming its formation (data not shown).

Similar results are shown for 1-octene on polycrystalline copper in Fig. 6(a). 1-Octene is monitored at 43 amu and desorbs between



**Fig. 4.** Plot of the peak desorption temperatures in TPD at low coverages for 1-alkynes on a Cu(111) single crystal (●) and on a copper foil (■) as a function of the number of carbon atoms in the 1-alkyne.

$\sim 305$  and  $330$  K depending on coverage. The most intense fragment of 1-octene (41 amu) has significant intensity in the 1-octene mass spectrum and two desorption states are thus detected at 41 amu. The lower-temperature state is due to 1-octene and the higher-temperature state is due to the formation of 1-octyne, which desorbs at  $\sim 350$  to  $\sim 370$  K depending on coverage.

Finally, the data for 1-decene on polycrystalline copper are shown in Fig. 6(b). Molecular 1-decene (70 amu) desorbs between  $\sim 350$  and  $375$  K depending on coverage, while relatively intense 1-decyne signals (67 amu) are detected at  $\sim 375$  K, with a lower-temperature state appearing at  $\sim 280$  K at higher exposures. All the desorption spectra show 1-alkyne desorption as well as molecular desorption of the corresponding 1-alkene.

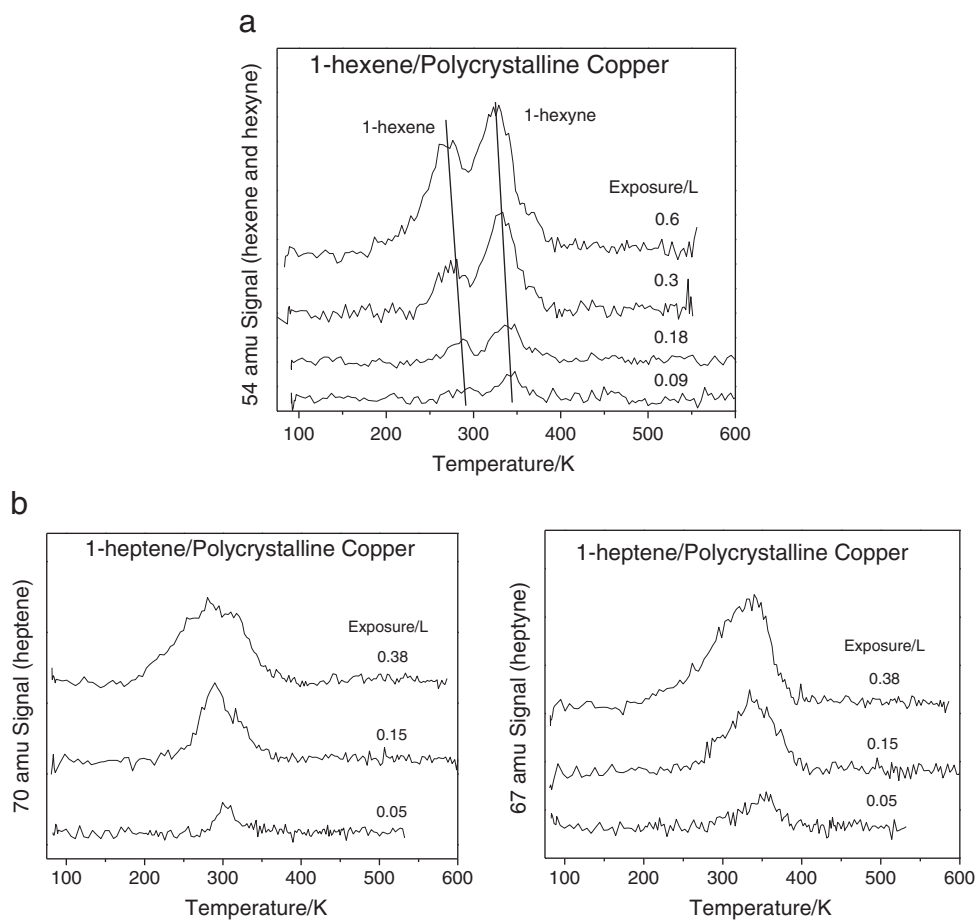
Lastly, experiments were carried out to search for 1-alkynes forming from 1-alkenes on a Cu(111) single crystal and no significant 1-alkyne formation was found (data not shown), in accord with results found on single crystal Cu(100) [20].

#### 4. Discussion

The linear trend in the desorption peak temperature found for 1-alkenes adsorbed on Cu(111) (Fig. 2, ●) is in accord with previous results on Cu(100) [20] where the desorption peak temperatures on Cu(100) are very close to those for 1-alkenes up to  $C_6$  measured here on Cu(111). In addition, the measured change in peak desorption temperature of  $\sim 19$  K/methylene group (Fig. 2) is similar to that found for alkyl chlorides [24] and alcohols [25]. Assuming a typical pre-exponential factor for a first-order desorption process of  $1 \times 10^{13} \text{ s}^{-1}$  [26], the measured variation in peak temperature with chain length for 1-alkenes on Cu(111) (Fig. 2) yields an increase in desorption activation energy of  $5.6 \pm 0.2$  kJ/mol/methylene group. However, a discussion of the origin of the intercept found for a plot of alkane desorption activation energy from metal and graphite surfaces as a function of chain length [12] suggested that a variation in desorption pre-exponential factor with chain length was the most plausible explanation for its appearance. Analyses of alkane desorption from surfaces have suggested that this occurs with a higher value of pre-exponential factor of  $\sim 1 \times 10^{16} \text{ s}^{-1}$  [17,18]; using this value results in a slightly increased desorption energy change of  $6.7 \pm 0.2$  kJ/mol/methylene. Extrapolating the data in Fig. 2 predicts an ethylene desorption temperature of  $\sim 120$  K, which is in good agreement with the value of  $\sim 140$  K for ethylene on Cu(100) [27], and  $\sim 120$  K on Cu(111) [4].

The behavior of the 1-alkenes on polycrystalline copper is similar to that on Cu(111) (Fig. 2, ■). However, the slope of the plot of desorption temperature versus carbon chain length is somewhat lower on the foil than on Cu(111), and corresponds to an increase in desorption activation energy of between 4.7 and 5.6 kJ/mol/per methylene group, depending on the choice of pre-exponential factor. In this case, however, extrapolating the curve suggests a  $C_2$  desorption peak temperature of  $\sim 220$  K, higher than the value of  $\sim 140$  K measured on Cu(100) [27], although values as high as 190 K have been reported [28]. However, while the foil sample does contain (100) facets as indicated by LEED [21], the higher desorption temperatures found for the annealed polycrystalline sample implies that there are sufficient low-coordination sites to bind the  $C=C$  bond more strongly to the surface. Note that ethylene desorbs at  $\sim 240$  K from steps on Cu(410) [7,8] consistent with stronger vinyl group bonding to low-coordination sites on the foil.

The results suggest that the alkyl and vinyl groups in 1-alkenes can simultaneously interact with the surface. For a  $\pi$ -bonded  $CH_2$ -CHR molecule on the surface, the alkyl group would be coplanar with the vinyl group allowing a facile interaction of the alkyl group with the surface. However, the picture may be somewhat more complicated since the NEXAFS results suggest that the double bond in 1-hexene is oriented at  $\sim 24^\circ$  to the plane of a Cu(100) substrate



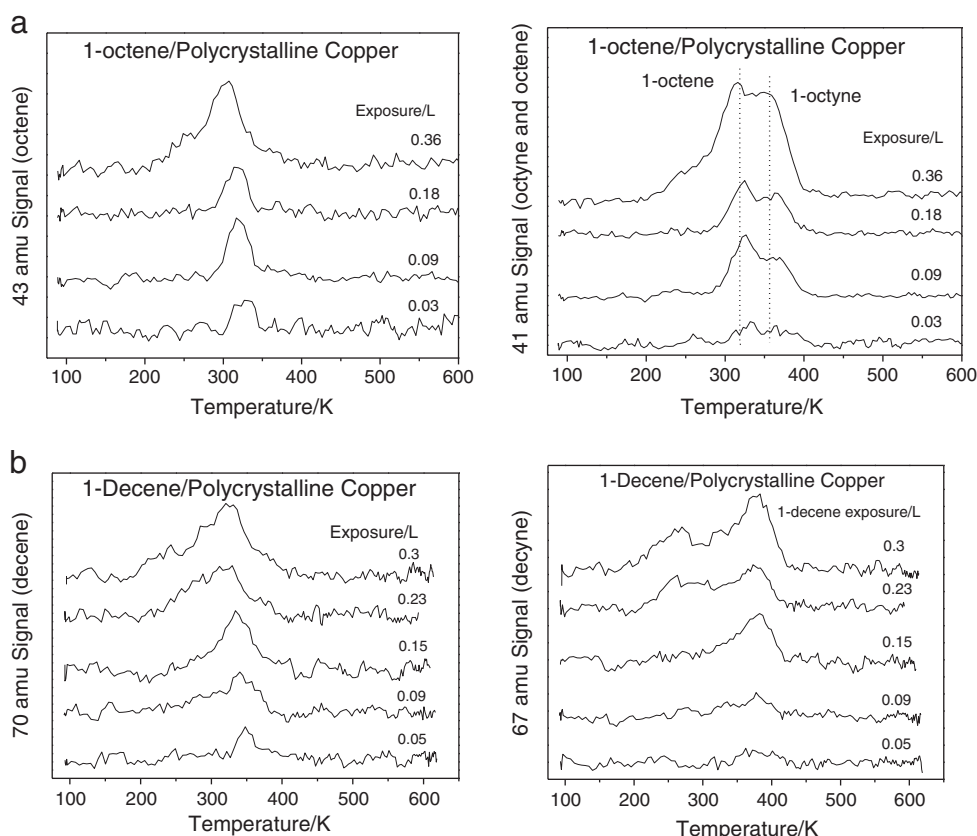
**Fig. 5.** TPD profiles as a function of exposure for 1-alkenes on a polycrystalline copper foil following (a) the adsorption of 1-hexene monitoring 54 amu (1-hexene and 1-hexyne), and (b) the adsorption of 1-heptene monitoring 70 amu (1-heptene) and 67 amu (1-heptyne). The 1-alkene exposures (in Langmuirs,  $1 \text{ L} = 1 \times 10^{-6} \text{ Torr s}$ ) are indicated adjacent to the corresponding profiles.

[20]. Nevertheless, the linear increase in desorption temperatures of 1-alkenes with increasing chain length implies that all of the methylene groups in the alkyl chain can interact with the surface. In addition to an increased strength of the C=C bond to the surface of the polycrystalline foil compared to the Cu(111) single crystal, the interaction energy per methylene group on the foil is slightly lower than on Cu(111) and Cu(100). It may be that the low-coordination sites present on the foil prevent close interaction between the alkyl groups with the surface. However, stronger surface bonding is also likely to cause some rehybridization of the vinyl group compared to bonding on low-Miller-index surfaces, which could move the alkyl group away from the surface.

Such an effect is seen for 1-alkynes, both on the polycrystalline copper foil and the Cu(111) single crystal (Fig. 4), where the variation in desorption energy with chain length is completely different from that found for 1-alkenes (Fig. 2). In this case, the peak desorption temperatures for 1-alkynes at low coverages are relatively independent of chain length up to 1-octyne. The 1-alkynes desorb between ~340 and 350 K, both from Cu(111) and the polycrystalline copper foil, except for 1-nonyne and 1-decyne. Studies of acetylene on copper surfaces reveal that it reacts to form benzene and cyclooctatetraene [29,30], although no evidence for cyclization reactions was found here for the higher 1-alkynes, although the resulting masses would be sufficiently large that their parent ions would be out of the range of our mass spectrometer. Studies of propyne on Cu(110) [31] found it to be significantly rehybridized and that it thermally desorbed at ~340 K, in good agreement with the desorption temperature in this work for the higher 1-alkynes. Thus, 1-alkynes

are strongly rehybridized on copper due to a strong bonding interaction between the acetylene group and the surface [32–35]. The resulting  $\sim sp^2$ -hybridized carbons cause the plane of the resulting vinyl-like group to be oriented perpendicularly to the surface, thus forcing the alkyl groups to be oriented away from it. Such restructuring accounts for the minimal variation in 1-alkyne desorption temperature as a function of alkyl chain length (Fig. 4) since adsorption is dominated by the interaction between the rehybridized acetylene group and the surface with minimal interactions between the alkyl group and the surface. However, as the *n*-alkyl side group becomes longer ( $\geq C_8$ ), it appears to be able to access the surface allowing van der Waals' interactions to occur between a portion of the alkyl group and the surface. Assuming that the desorption temperature increase per methylene group is similar for 1-alkynes and 1-alkenes implies that between 2 and 3 methylene groups can interact with the surface for 1-nonyne, and between 3 and 4 for 1-decyne. It appears that the termini of the alkyl chains of only a portion of the adsorbed 1-nonyne can interact with the surface, while the remainder are unable to do so leading to a desorption peak at ~340 K (Fig. 3). Presumably the alkyl chains must bend by forming gauche defects for their termini to access the surface. Analysis of the desorption peak temperatures for a wide range of *n*-alkanes from graphite suggests that this energy is ~6.2 kJ/mol per carbon–carbon bond [14] and is therefore of the same magnitude as the energy gained by the termini of the 1-nonyne chains interacting with the surface. The activation energy to form the gauche defects will presumably be higher, so that access of the end of the alkyl chain in 1-nonyne may also be kinetically limited.





**Fig. 6.** TPD profiles as a function of exposure for 1-alkenes on a polycrystalline copper foil following the adsorption of (a) 1-octene monitoring 43 amu (1-octene) and 41 amu (1-octene and 1-octyne), and (b) the adsorption of 1-decene monitoring 70 amu (1-decene) and 67 amu (1-decyne). The 1-alkene exposures (in Langmuirs,  $1 \text{ L} = 1 \times 10^{-6} \text{ Torr s}$ ) are indicated adjacent to the corresponding profile.

It is interesting that, while the behavior of 1-alkenes on polycrystalline copper and Cu(111) are completely different (Fig. 2), the desorption temperatures of the 1-alkynes are similar for both surfaces. One possible explanation for this effect is that the 1-alkynes are already substantially rehybridized, even on low-Miller-index surfaces [25] so that the presence of low-coordination sites on the foil causes little additional distortion.

The results in Figs. 5 and 6 clearly indicate that 1-alkenes dehydrogenate on polycrystalline copper to form the corresponding 1-alkyne. This is ascribed to the presence of defects and low-coordination sites on the copper foil that facilitate the reaction. This result is based on the observation that ethylene decomposes on stepped Cu(410) surfaces [6–8] to form carbonaceous deposits that decorate the steps and ultimately passivate the surface to further reaction with ethylene. The 1-alkynes must have formed at temperatures lower than the 1-alkene desorption temperature. This likely occurs in a step-wise dehydrogenation reaction to form a vinyl group from the  $\text{C}_2$  ethylenic carbon. Vinyl groups have been identified on Cu(100) [36], where they dimerize to form 1,3-butadiene with 100% selectivity, although no evidence of dimerization products was found in this work; however, their high molecular weights would make the products difficult to detect unequivocally. Some 1-alkene always desorbs from the surface, as well as forming 1-alkyne, so that not all of the adsorbed 1-alkene dehydrogenates to 1-alkyne, in agreement with the reaction occurring on particular surface sites. Based on the work with ethylene on Cu(410), these are most likely to be low-coordination sites present on the copper foil. If the dehydrogenation reaction occurs below the 1-alkene desorption temperature, the resulting 1-alkyne should, in principle, be desorption-rate limited and desorb at the same temperature as the corresponding 1-alkyne adsorbed on the surface. This appears to be the case for the 1-alkynes produced by 1-hexene and

1-heptene dehydrogenation. 1-Hexyne is reactively formed by 1-hexene dehydrogenation between 325 and 340 K (Fig. 5(a)) and desorbs from the foil at  $340 \pm 10 \text{ K}$  (Fig. 4); 1-heptyne forms from 1-heptene between 335 and 350 K (Fig. 5(b)), while it desorbs from the copper foil at  $340 \pm 5 \text{ K}$  (Fig. 4).

However, differences are seen for longer-chain hydrocarbons. Thus, 1-octyne is reactively formed from 1-octene and desorbs between  $\sim 350$  and  $370 \text{ K}$  (Fig. 6(a)), while 1-octyne adsorbed on the copper foil desorbs at  $340 \pm 5 \text{ K}$ . However, these differences may not be so large as to be significant. There are, however substantial differences in the case of 1-decyne formation, where 1-decyne is reactively formed from 1-decene at  $\sim 375 \text{ K}$ , while 1-decyne desorbs from the polycrystalline foil at  $\sim 405 \text{ K}$  (Fig. 4). In addition, some 1-decyne seems to appear at lower temperatures ( $\sim 280 \text{ K}$ , Fig. 6(b)), not seen in the other 1-alkyne desorption profiles. The higher desorption temperature of 1-decyne compared to the lower-molecular-weight alkynes was attributed to the end of the longer alkyl chain being able to access the surface. It appears that fewer methylene groups can access the surface for reactively formed 1-decyne that leads to a lower desorption temperature.

## 5. Conclusions

The desorption activation energies of 1-alkenes on a Cu(111) single crystal and a polycrystalline foil increase linearly with the number of carbons in the alkyl chain due to van der Waals' interactions between the alkyl chains and the copper surface. The increase in desorption activation energy per methylene group on Cu(111) is identical to that found previously on Cu(100), while the value on the copper foil is lower. This is ascribed either to the chain being able to interact less strongly with an atomically rougher foil surface, or to some

rehybridization of the more strongly bound C=C group on low-coordination sites on the surface. In contrast, 1-alkynes adsorbed both on the foil and a Cu(111) single crystal show similar behavior to each other with a desorption activation energy that is independent of the length of the alkyl chain, except for 1-nonyne and 1-decyne. This observation is consistent with the proposed adsorption geometry of 1-alkynes on copper, where it is substantially rehybridized, which would have the effect of moving the alkyl group away from the surface. It appears that the ends of the longer chains in 1-nonyne and 1-decyne can still access the surface.

It is also found that 1-alkenes undergo relatively facile dehydrogenation on copper foils due to the presence of low-coordination surface sites to produce a relatively large proportion of the corresponding 1-alkyne. In the majority of cases, the resulting reactively formed 1-alkyne desorbs at the same temperature as the 1-alkyne adsorbed on the surface, indicating that product formation is desorption-rate limited. The exception is the formation of 1-decyne from 1-decene. In this case, the desorption temperature of 1-decyne is higher than the rest of the 1-alkynes, possibly due to the interaction of a portion of the alkyl chain with the surface.

### Acknowledgments

We gratefully acknowledge the Chemistry Division of the National Science Foundation under grant number CHE-9213988 and the Office of Naval Research for support of this work.

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