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Effects of Surface Defects and Coadsorbed Iodine on the Chemistry of Alkyl Groups on Copper Surfaces: Evidence for a Cage Effect

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The effects of defect sites and coadsorbed iodine atoms on the chemistry of alkyl groups with two to four carbon atoms on copper surfaces have been studied by temperature-programmed reaction (TPR). The primary reaction pathway for the adsorbed alkyl group both in the presence and absence of defects and iodine atoms is β-hydride elimination. Because desorption is not (under most conditions) the rate-determining step in the evolution of the product from the surface, the rate of the surface β-hydride elimination reaction could be monitored by TPR. Neither surface defects nor low coverages of coadsorbed iodine significantly affect the β-elimination rate. For high coverages of iodine, however, the rate of β-elimination by 5–10% of the adsorbed alkyl groups is decreased by over five orders of magnitude (T_{rxn} = 385 K versus 230 K). The reaction kinetics together with observations from low-energy electron diffraction studies suggest that the dramatic inhibition of the β-elimination rate for high iodine coverages is due to cages of immobile iodine atoms that surround the alkyl groups and prohibit hydrogen transfer to the surface.

1. Introduction

Try as we may, no transition-metal single crystal is perfect. Scanning tunneling microscopy studies have shown that steps, kinks, adatoms, and vacancies are present at a fraction of a percent on even the most carefully prepared surfaces.[1] Because surface defects contain atoms that are coordinatively unsaturated relative to terrace plane atoms, reactivity at defect sites is often enhanced, leading to dramatic effects on surface reactions despite their small numbers. For example, polyolefin formation using Ziegler-Natta type catalysts is thought to occur exclusively at defect sites.[2] The important role of defect sites on surface reactions has recently been reviewed by Wandelt.[3]

Like surface defects, elemental coadsorbates can dramatically affect surface reactions. The promotion of the Haber process by alkali additions[4] and the poisoning of hydrocarbon reforming by small amounts of sulfur[5] are well-known examples. The chemical mechanisms for these effects remain controversial, and the question of whether steric (site-blocking) or electronic effects are dominant continues to be debated.[6]

In the present work, we examine the effects of surface defects and coadsorbed iodine atoms on alkyl dehydrogenation by β-hydride elimination on single-crystal copper surfaces using temperature-programmed reaction (TPR) experiments. TPR is particularly useful for this system, because the rate of dehydrogenation determines the rate of product evolution, i.e., for most conditions, desorption is not rate-determining. The rate of product evolution can thus be used to monitor the rate of the surface dehydrogenation reaction. Previous studies of this system have shown that linear alkyl iodides of two to four carbons in length dissociate below 150 K on copper surfaces to form adsorbed alkyl groups and iodine atoms.[7,8] As shown in Scheme 1, these alkyl moieties dehydrogenate by β-hyride elimination above 200 K to form adsorbed hydrogen atoms and the corresponding olefin, which desorbs from the surface.[8,9]

SCHEME 1: Primary Reaction Pathway on Copper Surfaces for the Decomposition of Alkyl Iodides Containing β-Hydrogen Atoms As Illustrated with 1-Iodopropane-2,2-d₂
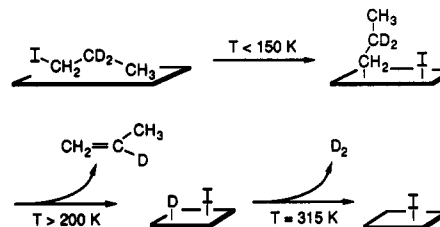
We will show in this paper that the primary effect of surface defects on the β-elimination reaction is to inhibit the rate of olefin desorption at low surface coverages. Defects do not appreciably promote or inhibit the β-hydride elimination reaction. Likewise, for low coverages of iodine (formed by up to 40% of an iodoalkane-saturated monolayer) there is no significant effect on the dehydrogenation rate. In contrast, high iodine adatom coverages produce a dramatic effect: 5–10% of the alkyl groups are stabilized so that the rate of dehydrogenation is decreased by over 5 orders of magnitude! Based on the results presented here this stabilization appears to be due to site-blocking by the iodine. In effect, the iodine atoms surround the alkyl groups and form "cages" that block hydrogen transfer from the alkyl groups to the surface analogous to cage effects in radical chemistry[10–12] and steric effects in inorganic chemistry.[13]

2. Experimental Section

The experiments that will be discussed were conducted in two ultra-high-vacuum chambers, both with a base pressure below 2 × 10⁻¹⁰ Torr. One apparatus is equipped with a scanning Auger electron spectrometer (Physical Electronics, 10-155), an ion sputter gun (Physical Electronics, 04-177), a 0-300 amu quadrupole mass spectrometer (Vacuum Generators, SXP300), and optics for low-energy electron diffraction (Physical Electronics, 15-120). The quadrupole mass spectrometer is differentially pumped with a 300 L/s Balzers (TPU 330) turbomolecular pump and is shielded from the chamber using a 304 stainless steel tube at the end of which is a skimmer with a 2 mm diameter aperture. Positioning the crystal ~2 mm from the skimmer's aperture ensured that the molecules detected in temperature-programmed

desorption/reaction (TPD/R) studies evolved from the sample rather than the sampler holder. Experimenting with different crystal positions verified that only species that evolved from the center of the crystal were detected. Likewise, the second chamber is equipped with an Auger electron spectrometer (Physical Electronics, 10-155) and a similar TPD/R setup.

Several different Cu(100) and Cu(110) single crystals were used in these experiments. These crystals were obtained from either Monocrystals Inc. or the Cornell Department of Materials Science. All were 2 mm thick and 0.6–1.0 cm in diameter and were polished to a mirror finish with 5-, 1.0-, and 0.3-μm alumina grits (Buehler) before use. Cleaning was accomplished by Ar$^+$ sputtering (generally 1–2 kV and 5–7 μA at 850 K for 45 min followed by 45 min while cooling the crystal) and annealing at 950 K for 15 min. Surface cleanliness was confirmed by Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED). Iodine could be removed from the crystals between experiments with iodoalkanes by briefly annealing above 950 K.

The crystals were mounted on a molybdenum resistive heating element (Spectra-Mat) using three small tantalum tabs spot-welded to a strip of platinum that had, in turn, been spot-welded to the heater; this arrangement allowed for heating to 1100 K. Heating was accomplished using a dc power supply (Hewlett-Packard, 6291A) which was controlled (Eurotherm 818P) to achieve a linear temperature ramp of 2.5 K/s during the TPR studies. The samples could be cooled to 110 K using liquid nitrogen. The temperature of the crystals was determined using a chromel–alumel thermocouple either inserted into a hole located on the side of each crystal or spot-welded onto a tab that held the crystal to the heating element. The latter arrangement, which was used for all the 1-iodobutane results shown, produces a thermocouple reading that is 20–25 K higher than the actual surface temperature as was found by comparing TPR data of 1-iodobutane using both methods.

For each TPR experiment, the compound of interest was adsorbed onto the crystal below 120 K by backfilling the chamber using precision sapphire leak valves. Doses are reported in units of langmuir, where 1 langmuir equals 1 × 10^{-6} Torr·s. Exposures are uncorrected for differing ion gauge sensitivities. Temperatures reported for the TPR studies are those of the TPR peak maxima.

The iodoalkanes were obtained from Aldrich with the exception of 1-iodopropane-*2,2-d$_2$* (99 atom % D), which was obtained from MSD Isotopes. After purification by filtration through an alumina column, the iodoalkane samples were stored in glass ampules which were shielded from light to prevent photodecomposition. The iodoalkane compounds underwent several freeze–pump–thaw cycles prior to their introduction into the chamber, and an in-line alumina plug was commonly used to remove any traces of HI. Reagent purities were routinely verified *in situ* by mass spectrometry.

3. Results and Analysis

Both copper surfaces studied [Cu(100) and Cu(110)] show the same dehydrogenation reactions for adsorbed alkyl groups (see Scheme 1), and a comparison shows that the dehydrogenation temperature differs by less than 20 K on these surfaces.[14] The effects of surface defects and coadsorbed iodine atoms on the dehydrogenation rate will be illustrated in the following sections, primarily with results from Cu(110).

3.1. Surface Defects. The effect of surface defects on the rate of evolution of olefins produced by β-H elimination of adsorbed alkyl groups on copper surfaces is demonstrated by comparing the chemistry of 1-iodobutane on sputtered versus annealed Cu-(110). We present first results for a Cu(110) surface which has been fully annealed, but which contains an adventitious number of surface defects. Figure 1 shows TPR spectra for butene evolution from β-hydride elimination in butyl groups on Cu(110)
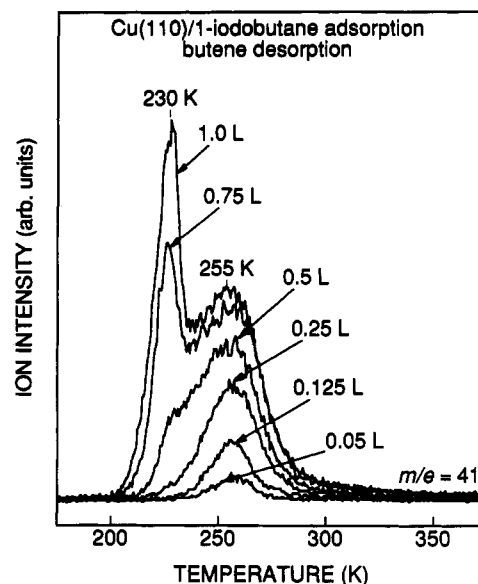

Figure 1. Evolution of butene during temperature-programmed reaction spectroscopy for low exposures of 1-iodobutane adsorbed on an annealed Cu(110) surface at 115 K. For reference, a 5-langmuir exposure is required to saturate the monolayer. Low-exposure spectra are shown to accentuate the effects of adventitious surface defects.
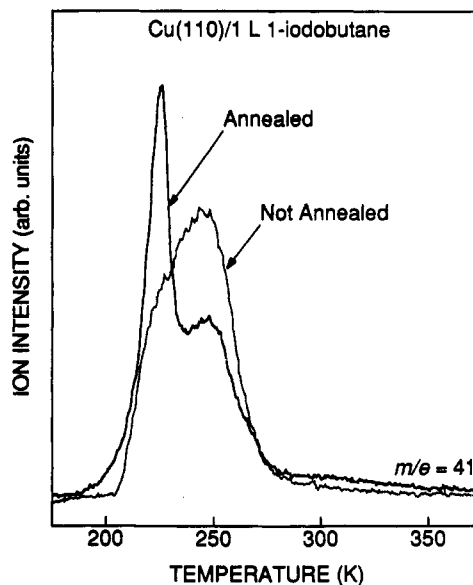

Figure 2. Temperature-programmed reaction spectroscopy for 1 langmuir of 1-iodobutane adsorbed on a Cu(110) surface that had been prepared by sputtering (dashed line) and sputtering + annealing (solid line). Not annealing the surface increases the number of surface defects.

at low exposures (up to 1 langmuir; a saturation exposure is 5 langmuirs) where the effects of defects are accentuated. Two peaks are evident for butene evolution in Figure 1. A higher temperature peak grows in first at 255 K followed by a peak at 230 K. The higher temperature peak saturates at 0.5 langmuir while the peak at 230 K continues to grow for exposures up to 5 langmuirs.

We attribute the higher temperature peak at low coverages to butene evolution from surface defects based on the sputter/anneal studies illustrated in Figure 2. This figure compares the rate of butene evolution after adsorbing 1 langmuir of 1-iodobutane on a Cu(110) crystal that has been (a) sputtered and annealed, and (b) sputtered but not annealed in order to produce a surface with a larger number of defects. The substantial increase in the yield of butene at high temperature from the unannealed surface suggests that the 255 K peak is attributable to surface defects. Another possible explanation for the change in the relative ratios
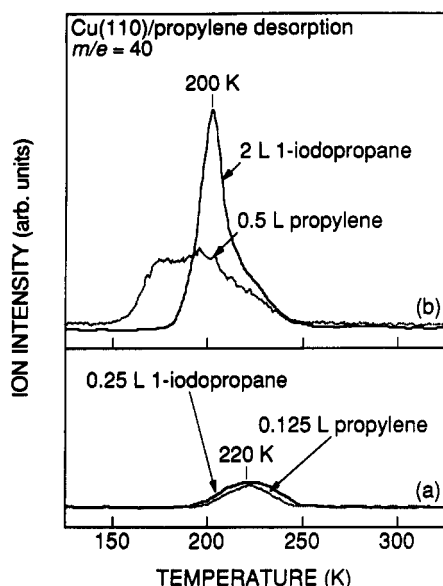
Figure 3. Temperature-programmed desorption/reaction spectra of propylene evolution (m/e = 40, $C_3H_4{}^+$) for the indicated exposures of propylene and 1-iodopropane to a fully annealed Cu(110) surface at 115 K. The exposures were chosen to yield approximately equivalent amounts of propylene.
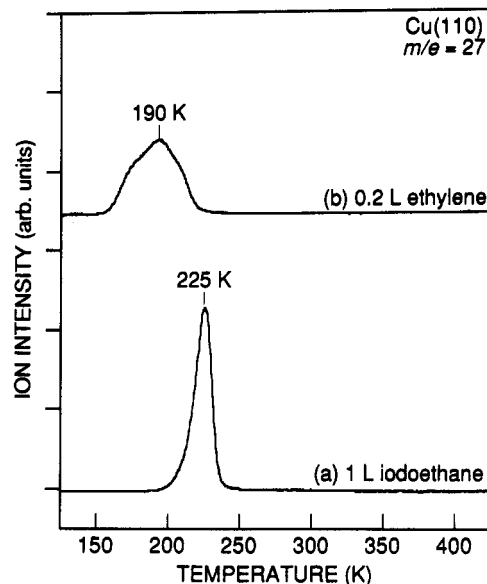

Figure 4. Ethylene evolution (m/e = 27, $C_2H_3{}^+$) after adsorbing (a) 1.0 langmuir of iodoethane and (b) 0.2 langmuir of ethylene onto Cu(110) at 115 K.

of the two peaks, however, is that sputtering increases the surface area by roughening the surface so that the same exposure produces a lower adsorbate density on the sputtered surface and that it is the adsorbate density which controls the relative heights of the two peaks. While no direct measurement of the surface areas (for example, by Xe adsorption) has been made for the two surfaces in Figure 2, other results indicate that changes in surface area are not responsible for this effect. For example, results presented in Figure 9 show that the relative size of the high-temperature peak varies between copper crystals for which the saturation exposure of iodobutane is the same. In other words, for the same surface density, the relative peak heights change. In addition, the two peaks are due to different rate-determining processes as shown by the results in Figure 3.

Figure 3 demonstrates that the higher temperature alkene peak is due to rate-determining desorption of the alkene product while the lower temperature peak is due to rate-determining β-hydride elimination by surface alkyl groups. Specifically, for a 0.25-langmuir exposure of 1-iodopropane on a fully annealed Cu(110) surface with adventitious defects, the propylene evolution temperature is coincident with that for a comparable coverage of propylene adsorbed on the surface. Thus, propylene desorption rather than β-hydride elimination presumably determines the kinetics of this peak. By contrast, for higher exposures as shown in Figure 3b, propylene desorbs from Cu(110) below the temperature where propylene is evolved by β-hydride elimination from propyl groups. Studies of propylene adsorption with iodine show that the effect of iodine is to lower, not increase, the olefin desorption temperature. Thus, olefin desorption is rate-determining at low coverages and β-H elimination is rate-determining at high coverages.

On the basis of the comparison in Figure 2 which shows increased olefin evolution from the surface under desorption-limited conditions for the rougher, unannealed surface, we conclude that the rate-determining olefin desorption at low coverage is due to bonding at defect sites. To summarize the results in the context of Figure 1 for butyl groups, for coverages <0.5 langmuir, β-hydride elimination occurs at or below 255 K and the butene product remains bound at surface defects until 255 K where it desorbs. At higher coverages, β-hydride elimination from butyl groups on the (110) terraces is the rate-determining step in butene evolution at 230 K.

From TPR studies of propyl and butyl groups on copper surfaces, it is not possible to determine the kinetics of β-hydride elimination for the alkene product evolved from defect sites because desorption is rate-limiting. We also cannot determine from our results whether it is the product butene or the reactant butyl groups that diffuse to the defects sites on the surface. We do know, however, that since all the butene product is associated with defect sites at low surface coverages (i.e., only the high-temperature peak is observed for exposures below 0.5 langmuir) butene and/or butyl groups diffuse to and bind preferentially at these defects. It is possible that β-hydride elimination by alkyl groups at defect sites is extremely facile and that the product alkene remains bound there until higher temperatures where it desorbs. This question can be directly addressed by studying ethyl groups, because β-hydride elimination of ethyl groups occurs at higher temperatures than for longer chain alkyls, and ethylene desorbs at lower temperatures than for the longer chain olefins. The results are shown in Figure 4. Figure 4a shows ethylene evolution after adsorbing 1 langmuir of iodoethane on Cu(110) while Figure 4b shows the rate of ethylene desorption for a comparable amount of adsorbed ethylene. It should be reemphasized that the peak temperatures in Figures 1 and 2 are 20–25 K too high because of the thermocouple mounting (see section 2); i.e., β-hydride elimination occurs at $\sim$20 K higher for ethyl groups than for propyl and butyl groups. It is clear from Figure 4 that β-hydride elimination is the rate-determining step in the evolution of ethylene from the majority of adsorbed ethyl groups and there is no evidence for a significant enhancement of the β-hydride elimination rate at surface defects.

The reason that defects can bind molecules more strongly to the surface and thus yield desorption at higher temperatures has been discussed by Serri et al.[15] The potential energy well at a defect site is deeper than at the terrace sites as a result of increased coordinative unsaturation which results in an increased barrier for desorption.[15] Note that this increased barrier is operative regardless of whether the adsorbate desorbs directly from the defect to vacuum or first diffuses out onto the terrace and then desorbs provided that the adsorbates are in equilibrium between the defect and terrace sites.

We conclude this discussion on the effect of surface defects on β-hydride elimination by illustrating how the combination of defects and an isotope effect can give rise to unusual TPR peak shapes and shifts upon deuteration. These effects are illustrated in Figure 5, a and b, for propylene and propylene-d evolution
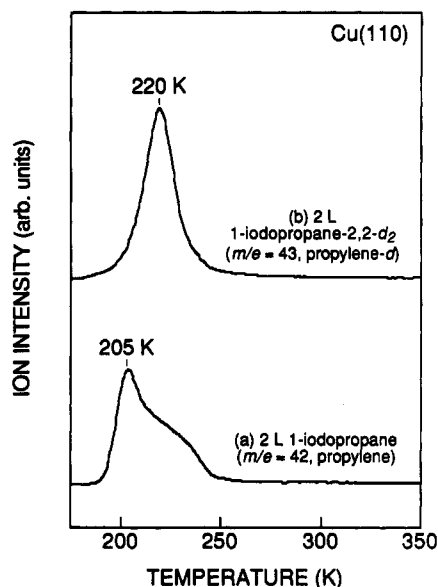
Figure 5. Temperature-programmed reaction spectra for the evolution of (a) propylene (m/e = 42) and (b) propylene-d (m/e = 43) following the adsorption of 2 langmuirs of 1-iodopropane and 1-iodopropane-$2,2$-d_2 at 110 K, respectively.
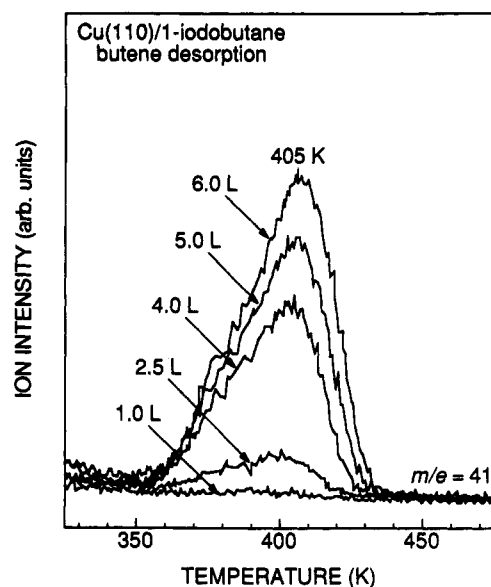

Figure 6. Partial temperature-programmed reaction spectra taken for the indicated exposures of 1-iodobutane adsorbed on Cu(110) at 115 K which show high-temperature (405 K) butene evolution (m/e = 41) for higher doses.

from propyl and propyl-$2,2$-d_2 groups, respectively. For propylene evolution in Figure 5a, surface defects produce the high-temperature shoulder of the TPR peak. For propylene-d evolution, however, the β-hydride elimination peak is shifted to higher temperature because of a deuterium isotope effect, but rate-determining propylene-d desorption from surface defects is relatively unaffected. Consequently, both peaks occur at approximately the same temperature and the peak shape in Figure 5b is dramatically different than that in Figure 5a.

3.2. Coadsorbed Iodine. To elucidate the effects of iodine on alkyl chemistry on Cu(110), two approaches have been taken: (1) adsorb alkyl radicals in the absence of iodine and (2) vary the coverage of coadsorbed iodine. To form ethyl and propyl radicals, azoethane ($C_2H_5N_2C_2H_5$) and azopropane ($C_3H_7N_2C_3H_7$) were synthesized. Gas-phase pyrolysis of these compounds produces ethyl and propyl radicals. These experiments, detailed elsewhere,[16] were unsuccessful in that the byproducts of the pyrolysis process were found to significantly affect the energetics of the β-elimination reaction. Nevertheless, these studies show that the β-hydride elimination pathway does not require coadsorbed iodine atoms.

The effect of iodine on the rate of β-hydride elimination was studied by adsorbing alkyl iodides onto a copper surface that had been partially precovered with iodine atoms. To our knowledge, these studies provide the first evidence for cage effect on solid surfaces.

While there is evidence for an iodine cage effect in all of the C_2–C_5 iodides that have been studied on Cu(100) and Cu(110), the experimental observations will be illustrated here using results for 1-iodopropane-$2,2$-d_2 and 1-iodobutane on Cu(110). The evidence for an iodine cage effect is a small yield of olefin and hydrogen at 380–420 K for high coverages of the alkyl iodide. This high-temperature peak, which is 150 K above where the majority of the alkyl groups decompose, is shown on an expanded scale for butene evolution from 1-iodobutane in Figure 6. Note that the high-temperature peak is not observed at low coverages. As shown below, this is because high coverages of adsorbed iodine are required to observe this peak.

First, however, we present results which show that the high-temperature evolution of alkene and hydrogen involves β-hydride elimination. Figure 7a–d shows temperature-programmed reaction spectra for propylene-d and D_2 evolution from a Cu(110) surface which has been exposed to 2 langmuirs and 6 langmuirs
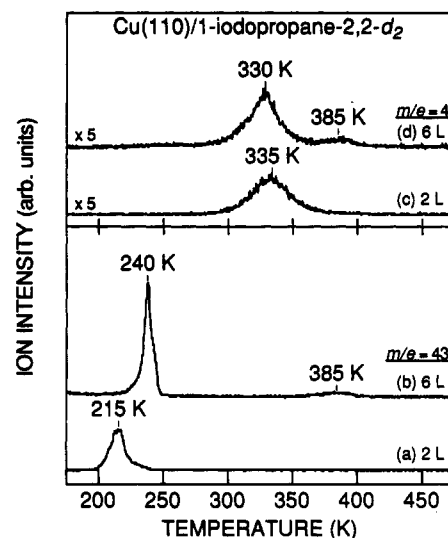
Figure 7. Temperature-programmed reaction studies of 1-iodopropane-$2,2$-d_2 adsorbed on Cu(110) at 115 K. In (a) and (b), m/e = 43 is followed, while in (c) and (d) m/e = 4 is detected for 2- and 6-langmuir exposures, respectively.

of 1-iodopropane-$2,2$-d_2, respectively. Compared to the 2-langmuir spectra, the higher dosage (6-langmuir) spectra in Figure 7b,d show, in addition to larger peak areas, new peaks at 385 K for both propylene-d and D_2. The new peaks at 385 K are attributed to β-deuterium elimination by adsorbed propyl groups. Note that consistent with propylene-d and D_2 being the only products detected at 385 K, the ratio of their peak areas is 1.6, which is the same to within experimental error as that for propylene-d and D_2 evolution at lower temperatures. Clearly, the surface reaction pathway at 385 K also involves β-deuterium elimination coupled with the deuterium recombination. However, for the 385 K peaks *no isotope effect is observed*, 1-iodopropane and 1-iodopropane-$2,2,d_2$ produce propylene and propylene-d at the same temperature. Furthermore, the hydrogen and olefin evolve at the same temperature in both cases. This latter result suggests that olefin and hydrogen evolution at 385 K involve a common rate-determining step.

Possible rate-determining steps include (1) dissociation of the carbon–iodine bond in 1-iodopropane, (2) β-hydride elimination by adsorbed propyl groups, and (3) a reaction of some other
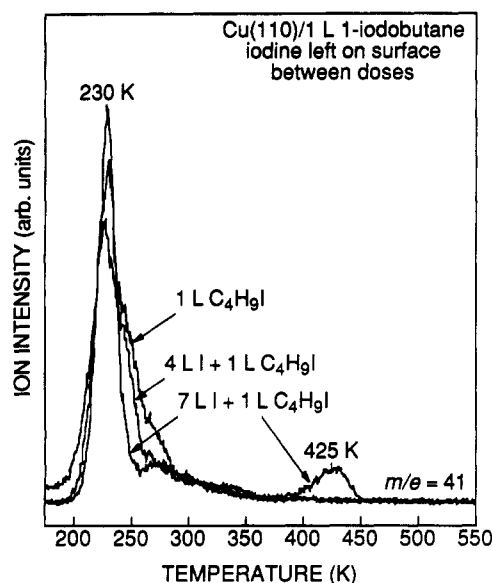
Figure 8. Temperature-programmed reaction studies of successive doses of 1-langmuir of 1-iodobutane on Cu(110). Between doses, the crystal was flashed to only 550 K, 400 K below the temperature at which iodine is removed from the surface so that the iodine would accumulate on the surface.
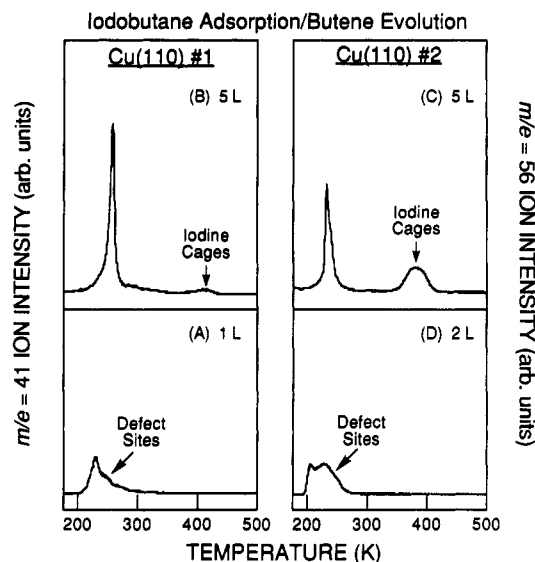

Figure 9. Temperature-programmed reaction studies of 1-iodobutane adsorbed at 115 K on two different Cu(110) crystals which have been fully annealed but which contain different concentrations of adventitious defects. In (a) and (b), $m/e = 41$ is followed for 1- and 5-langmuir exposures on the first crystal, respectively. In (c) and (d), $m/e = 56$ is followed for 2- and 5-langmuir exposures on the second crystal.

hydrocarbon fragment. The possibility of reaction by a hydrocarbon fragment other than propyl groups can be ruled out on the basis of both the lack of isotope scrambling in the partial deuteration experiments and the fact that H/D recombinative desorption occurs at 335 K on Cu(110), so rehydrogenation of the adsorbed fragment could not occur. On the other hand, dissociation of the C–I bond and β-hydride elimination (the other two possible rate-determining steps), occur at temperatures of <150[8] and ~230 K, respectively, for the majority of the propyl groups on the surface. The implication is that the rate of one or both of these steps is dramatically inhibited at high coverages. An additional requirement is that the reactant remain bound to the surface up to 385 K. On the basis of this latter requirement, we rule out dissociation of the C–I bond as the rate-determining step. There is no evidence that high coverages increase the binding energy of 1-iodopropane so that, instead of its normal desorption temperature of ~160 K,[8] it remains bound to the surface up to 385 K. By contrast, propyl groups could remain bound to the surface up to 385 K provided the β-hydride elimination channel, which normally occurs at ~230 K, is inhibited. The results below establish that this possibility is due to the coadsorbed iodine on the surface.

The role of iodine in product evolution at high temperature is demonstrated by the TPR spectra in Figure 8 for butene evolution from 1-iodobutane adsorbed on Cu(110). The spectra shown are for sequential TPR experiments for 1-langmuir exposures of 1-iodobutane in which the surface is only heated to 550 K during each experiment so that iodine accumulates on the surface (recall that iodine is not removed from the surface until 950 K). Note that even for a 1-langmuir exposure of 1-iodobutane the high-temperature peak is observed, but only when the surface has been precovered with iodine by seven sequential 1-langmuir exposure/anneal cycles ($\theta_{I/Cu} = 0.06$ or $\theta_{I/Imax} = 0.13$,[17,18]). The fact that the high-temperature butene peak occurs at 425 K, as opposed to 385 K for propylene from 1-iodopropane-2,2,d_2 in Figure 7, reflects differences in the degree of thermocouple contact with the crystal (see section 2).

The characteristics of iodine inhibition of β-hydride elimination in a small fraction of alkyl groups on the surface suggest a cage effect. Previous results indicate that β-hydride elimination requires the presence of an empty site adjacent to the alkyl group in order to occur.[19] If the alkyl groups are free to diffuse on the surface and are able to sample different sites in the monolayer,

then inhibition by site-blocking results in a gradual shift of the TPD peak to higher temperature.[19] On the other hand, if there are certain configurations in which all reactive sites are blocked by the coadsorbed iodine and consequently there is no path for diffusion to a new site, then the alkyl groups are caged in by the iodine atoms and reaction will be shut off until some iodine diffuses to open a path for alkyl diffusion and/or reaction. Such a scenario can explain why a small number of alkyl groups react at 385 K as opposed to 230 K and yet no reaction is ever observed at temperatures intermediate between 230 and 385 K. We note also that the temperature of this high-coverage pathway is the same to within experimental uncertainty for all of the alkyl iodides studied, and, as mentioned, that there is no deuterium isotope effect for β-elimination at this temperature. The only viable explanation we can offer for all of these results is that alkene evolution at 385 K is attributable to alkyl groups which are trapped in cages of iodine atoms and that the rate of reaction is controlled by the rate of iodine diffusion; this latter point is addressed below in section 3.3.

Surface defects may also play a role in alkene evolution at high temperatures. In particular, as shown in Figure 8, it is consistently observed that the 230–255 K alkene peak loses its high-temperature shoulder as the 425 K peak grows in. The correlation between the 425 K peak (due to iodine cages) and 255 K shoulder (attributable to surface defects) suggests that the iodine cages may be associated with defect sites on the surface. This may also explain, as illustrated in Figure 9, why the extent of caging, although always small and reproducible for a given crystal which has been fully annealed, differs from crystal to crystal. In other words, it appears that the number of adventitious defects on a crystal is largely determined by the surface preparation prior to insertion into the vacuum system (e.g., the exact crystal orientation and degree of perfection), and that the extent of argon sputtering once the surface is atomically clean has a relatively minor effect on the number of defects provided the crystal is fully annealed. Figure 9 shows results for the formation of butene from 1-iodobutane on two different Cu(110) crystals, one of which contained a particularly large number of adventitious defects. In comparing the two surfaces, we see that the amount of butene evolved from the iodine cages at saturation exposures of 5 langmuirs parallels the amount of butene evolved from the defect sites at low exposures and that the extent of the cage effect is
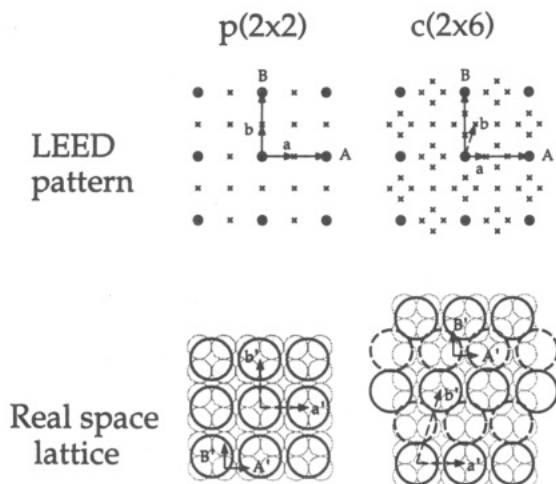
Figure 10. Low-energy electron diffraction (LEED) patterns and real space unit cells for the p(2×2) and c(2×6) structures observed for iodine on Cu(100). The bold circles correspond to the iodine atoms (with van der Waals radii of 2.2 Å) at the unit cell positions while the dashed circles indicate possible positions for additional iodine atoms required in the unit cell to be consistent with the relative I/C stoichiometries determined by Auger electron spectroscopy. The surface and overlayer unit cell vectors are indicated as A and B in the reciprocal lattice and as in a and b in the real space unit cells.

therefore larger on the crystal with a larger number of defects. Together with the results of Figure 8, these data show that the TPR peaks attributed to defect sites and the cage effect are correlated.

3.3. Low-Energy Electron Diffraction Studies. In order to examine the role of iodine diffusion on the β-H elimination pathway at ~400 K, low-energy electron diffraction (LEED) studies were conducted. Previous LEED studies of iodine on Cu(110) include a report by Citrin *et al.* in which they showed that no ordering is observed below $\theta_{I/Imax} = 0.5$ but at $\theta_{I/Imax} = 0.5$ a c(2×2) pattern abruptly emerges.[17] No studies of the temperature dependence of the iodine LEED patterns on copper have been reported in the literature. In our studies iodine atoms were generated on a *Cu(100)* surface by dosing 1-iodobutane *at 250 K*, a temperature where the alkyl groups (except for the minority species in iodine cages) are rapidly removed by β-hydride elimination. Two ordered iodine overlayers are observed: a p(2×2) structure for exposures of 5 langmuirs or less and a c(2×6) structure for exposures of 10-20 langmuirs. The LEED patterns and real space unit cells for these structures are shown in Figure 10. The number of iodine atoms shown per unit cell (1 for the p(2×2) and 4 for c(2×6)) are consistent with the 511 eV I/920 eV Cu peak-to-peak ratios in the derivative Auger electron spectra at normal incidence ($E_{primary}$ = 3 kV, modulation voltage = 4 eV peak-to-peak). Upon heating the surface, these LEED patterns for both structures disappeared between 300 and 500 K depending upon the exposure. These transformations are reversible upon cooling; the patterns reappear, but at slightly lower temperatures.

To quantify this temperature dependence under the conditions of the TPR experiments that produce the iodine cage effect, various exposures of 1-iodobutane were adsorbed at 110 K and the surface heated while monitoring the LEED pattern. By adsorbing at low temperatures, the maximum iodine coverage that can be achieved results in a p(2×2) pattern; although, a faint c(2×6) is sometimes observable for a 5-langmuir (or greater) exposure. Upon heating above 250 K, so that the alkyl groups are removed, it is found that the iodine overlayer spots disappear over a narrow temperature range of 340–395 K, with the onset temperature increasing as the exposure is increased. This temperature range is consistent with the onset temperature of the TPR peak for high-temperature β-H elimination. The suddenness of the transition argues against a Debye–Waller effect[20-22] and indicates that, at least by 370 K, iodine can diffuse on (or into[23]) the copper surface, consistent

with the hypothesized cage effect. For lower iodine coverages (i.e., 2 langmuirs of 1-iodobutane), where no cage effect is observed, the LEED overlayer spots disappear at 270 K.

4. Discussion

When alkyl groups are generated on copper surfaces by dissociatively adsorbing alkyl iodides, the iodine atoms remain coadsorbed with the alkyl group throughout the temperature range where the alkyl group reacts. The results in Figure 8 show that the rate of β-hydride elimination by the majority of the adsorbed alkyl groups is largely unaffected by the amount of preadsorbed iodine. The peak temperature for alkene evolution remains constant at 230 K, and the loss of the high-temperature shoulder for high iodine coverages can be attributed to blocking of the defect sites that give rise to this shoulder. For a small fraction of adsorbed alkyl groups, however, there is a dramatic decrease in the rate of β-hydride elimination, and alkene evolution is observed at 385 K when a large amount of iodine is preadsorbed on the surface. The concurrent evolution of propylene-d and D_2 at 385 K in Figure 7 for the decomposition of propyl groups deuterated at the β-position confirms the β-elimination mechanism, while the coverage dependence studies in Figure 8 show that this effect is attributable to high coverages of iodine. Assuming standard first-order preexponential factors of 10^{11} s^{-1} for these surface decomposition reactions,[24] this peak temperature difference corresponds to a difference in rate of ~10^6 at 300 K.

An unusual aspect of this high-temperature, iodine-correlated β-hydride elimination channel is that the TPR peak temperature is essentially independent of iodine coverage (see Figure 6). Inhibition of a surface decomposition reaction by blocking random sites on the surface results in a continuous shift of the TPR peak to higher temperature with increasing coverage of the site-blocker.[19] Similar effects are also typically observed with electronic interactions between adsorbed species.[25] The possibility of an iodine/alkyl complex of unusual thermal stability based on electronic interactions between the iodine and alkyl can be ruled out since the required attractive interactions would favor formation of such complexes at low coverages, which is not observed. We note also that, for the iodine coverages in these studies, the surface work function changes by a maximum of only 0.02 eV.[23]

We are thus led to propose that cages of immobile iodine atoms are responsible for inhibiting β-hydride elimination in 5–10% of the adsorbed alkyl groups. Inhibition of the β-hydride elimination rate by site-blocking is reasonable, since the reaction involves hydrogen transfer to the surface. Rate-determining iodine diffusion from the cage to exposed metal atoms adjacent to the alkyl groups is supported by the observations that (1) the product alkene and hydrogen are evolved at the same temperature, (2) there is no detectable deuterium isotope effect when the alkyl groups are deuterated in the β-position, and (3) LEED studies show evidence for iodine diffusion at about the temperature where alkyl decomposition is observed. (Note in connection with this last point that the LEED observations pertain to the iodine in ordered domains on the terrace planes and may not therefore be directly representative of iodine cages that appear to be associated with surface defects.) As for how the alkyl groups get into the iodine cages, an intriguing possibility is suggested by the observation that alkyl radical coupling and disproportionation products are observed concurrently with C–I bond scission for high alkyl iodide coverages.[8,26] Some of these alkyl radicals may diffuse on top of the iodine overlayer and become trapped in cage sites.

Several previous studies have addressed the effect of iodine in the chemistry of alkyl groups on metal surfaces, including a comparison of the chemistry of aluminum alkyls versus alkyl iodides adsorbed on aluminum single crystals,[27,28] and a comparison of methyl groups formed on Cu(100) from the thermal dissociation of iodomethane versus pyrolysis of azomethane.[29]

These results show that iodine has only minor effects on the resulting alkyl chemistry. In both studies, however, the alkyl groups decompose at temperatures above 400 K. Based on typical metal–iodine bond energies of 65 kcal/mol[30] and the general rule that activation energies for surface diffusion are ~20% of the desorption energy,[31] the rate of iodine diffusion is probably substantial at the alkyl decomposition temperature in these other studies. In other words, even if iodine can inhibit alkyl decomposition in these systems by blocking sites, a dramatic cage effect would not be observed. For alkyl groups on copper surfaces, the β-hydride elimination rate appears to be orders of magnitude faster than the rate of iodine diffusion. As a result, a cage effect is observed.

Finally, we address the question of why such a dramatic cage effect is not observed more often in surface reactions. A number of factors can be noted. First, the surface reaction must *not* be strictly first order in adsorbate coverage. (In the present case the rate of β-hydride elimination depends on both the adsorbed alkyl concentration and the number of adjacent empty surface sites since the H atom must be transferred to the surface.)[19] Second, as mentioned above, the adsorbed species forming the cage must be significantly less mobile than the reacting species. Third, the caged species must *not* have an alternate, facile reaction channel (e.g., molecular desorption). And fourth, the cage atoms must be unreactive with the caged species. All of these criteria must be met in order to achieve orders of magnitude effects such as those seen in the alkyl/iodine/copper system.

5. Conclusions

Because alkenes bond weakly to copper surfaces and desorb molecularly intact, it has been possible to utilize temperature-programmed reaction studies to address the effects of surface defects and coadsorbed iodine atoms on the rate at which adsorbed alkyl groups undergo β-hydride elimination to form alkenes. The effects are minor except for high coverages of iodine where the rate of β-hydride elimination for a small fraction of the adsorbed alkyl groups is slowed by over 5 orders of magnitude. A variety of experimental observations suggest that this strong inhibition of the β-hydride elimination rate is due to cages of immobile iodine atoms that surround the alkyl groups and block hydrogen transfer to the surface. The reaction eventually occurs when iodine diffusion breaks up the cage. There is also evidence that these iodine cages may be associated with defect sites on the surface.

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