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Chemistry of 1-Iodopropane on Cu(110): Formation, Bonding, and Reactions of Adsorbed Propyl Groups

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Abstract: The adsorption and thermal decomposition of 1-iodopropane on Cu(110) has been investigated under ultrahigh vacuum conditions using temperature-programmed desorption/reaction spectroscopy and reflection-absorption infrared spectroscopy. Adsorption is molecular at 100 K, but at 110 K the 1-iodopropane decomposes to form surface-bound propyl groups and coadsorbed iodine and the propyl groups assume an orientation such that the methyl group is upright. The subsequent chemistry of the propyl moieties is dominated by the evolution of propylene at 200–230 K and H_2 at 315 K. At higher coverages, in addition to molecular desorption, hexane evolution is observed at 130 K, propane forms at 220 K, and a pathway for propylene formation at 390 K opens up. Isotope labeling studies were used to confirm that β-H elimination is the mechanism for propylene formation.

1. Introduction

We present here the results of studies on the interaction of 1-iodopropane with Cu(110) and on the bonding and chemistry of adsorbed propyl groups formed by thermally dissociating the carbon–iodine bond of 1-iodopropane. The interest in alkyl species stems from the fact that alkyl moieties are postulated intermediates in many hydrocarbon conversion reactions[1-7] and that alkylcopper compounds are important reagents in organic synthesis.[8,9]

The practical utility of both organocopper reagents and copper catalysts derives from their selectivity. For instance, Cu/ZnO catalysts selectively hydrogenate CO to methanol without breaking the carbon–oxygen bond,[10,11] and arylcopper compounds react to form biaryls exclusively, without any scission of C–H or C–C bonds.[12] Organocopper compounds are also commonly used in reactions involving additions to C–C bonds, substitution reactions of organic halides, and oxidative dimerization reactions.[8] All of these cases illustrate the limited activity of both copper compounds and copper-based catalysts toward dissociating most chemical bonds. Copper does, however, readily dissociate carbon–halogen bonds, as evidenced by the Rochow process,[13,14] the Ullmann synthesis,[12] and recent ultrahigh vacuum studies of alkyl halides on Cu(100) and Cu(111) single crystal surfaces.[15-17] Additionally, C–H bond scission in alkylcopper compounds with β-hydrogens in solution has been reported by Whitesides, Kochi, and coworkers.[18-20] Understanding why copper is capable of dissociating certain chemical bonds such as C–I and β-C–H but not others is important for understanding the selectivity of copper reagents and catalysts.

In this paper we report studies of elementary C–I and C–H bond dissociation reactions for 1-iodopropane adsorbed on a single crystal Cu(110) surface under ultrahigh vacuum conditions. Both reactions were found to be extremely facile. Reflection–absorption infrared spectra indicate that C–I bond scission starts around 110 K to form adsorbed propyl groups and iodine atoms, while β-C–H bond scission in propyl groups occurs around 220 K to form mainly propylene and adsorbed hydrogen. Moreover, because copper interacts weakly with the hydrocarbon products, the rate of molecular desorption is fast compared with the rate of the surface reactions, and, as a result, it was possible to determine the kinetics and mechanisms for the surface reactions by temperature-programmed reaction experiments.

2. Experimental Section

The experiments were conducted in two ultrahigh vacuum (UHV) chambers. The first chamber, described elsewhere,[21] is equipped for ion sputtering, Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and temperature-programmed desorption/reaction (TPD/R) studies. The second chamber, also equipped for ion sputtering, AES, and LEED, includes a smaller chamber in which the reflection–absorption infrared spectroscopy (RAIRS) experiments were performed.[22]

Two Cu(110) single crystal surfaces were used in these studies. Both were 2-mm thick and 1 cm in diameter and were polished to a mirror finish before use. Different mounting schemes were used in the TPD/R and RAIRS studies. In the TPD/R experiments, the crystal was held flat against a 0.75-cm resistive molybdenum heating element using three small tantalum tabs spot-welded to a strip of platinum that had, in turn, been spot-welded around the heater. In the RAIRS experiments, the crystal was mounted on the manipulator using two 1-mm-thick tantalum wires bridged by two 0.25-mm tantalum wires wedged into grooves cut in the sides of the crystal. A chromel–alumel thermocouple inserted into a hole located on the side of each crystal was used for monitoring the temperature of the crystals, and liquid nitrogen was used to cool the crystals to temperatures as low as 115 K on the TPD/R chamber and below 100 K for the RAIRS experiments. The crystals were routinely cleaned by Ar^+ sputtering, first at 850–920 K and then at room temperature using a 2-kV, ~7-μA Ar^+ beam followed finally by annealing at 950 K until no impurities were detected by AES. Iodine was removed from the crystals between experiments by briefly annealing above 950 K.

The 1-iodopropane was obtained from Aldrich and was ≥99% pure. 2-Iodopropane (98%) was obtained from Alfa, and 1-iodopropane-*2,2*-d_2 (99 atom % D) was obtained from MSD Isotopes. After purification by filtration through a basic alumina column, the iodopropane samples were

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stored in glass ampules which were shielded from light. The 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. D_2 (99.5 atom % D) was obtained from Matheson, and a zeolite trap was used to remove water. Propane and propylene were also obtained from Matheson and used as received. Sample purities were routinely verified in situ by mass spectrometry.

For each TPD/R experiment, the compound of interest was adsorbed onto the crystal below 120 K. The crystal was then positioned ~2 mm in front of a 2-mm aperture located in line of sight to the ionizer of a differentially-pumped Vacuum Generators 0–300-amu quadrupole mass spectrometer. Experimenting with different crystal positions verified that only species that evolved from the center of the crystal were detected. The crystal was heated at a linear rate of 2.5 K/s in the TPD/R experiments by using a Eurotherm temperature programmer. The temperatures reported for the product evolution correspond to the TPD/R peak maxima. The relative product yields were determined by calibrating the mass spectrometer. Specifically, reference mass spectra were collected for each of the reaction products, and ion gauge sensitivity factors[23] were utilized to calculate the relative sensitivity factors for the different ion fragments of each compound.[24]

The RAIRS experiments were conducted using a Mattson Sirius 100 Fourier transform infrared (FT-IR) spectrometer. The infrared radiation was focused into the chamber through a NaCl window and was incident upon the crystal at an angle of 80 ± 3° with respect to the surface normal. The reflected light, after exiting the chamber through another NaCl window, passed through a wire-grid polarizer to select out the p-polarized light before being detected with a narrow-band mercury-cadmium-telluride (MCT) detector (1-mm^2 active area; ~2×10^{11} cm Hz$^{1/2}$ W^{-1} specific detectivity, D^*). The entire optical path was purged with H_2O- and CO_2-free air. The spectral resolution in these studies was 4 cm^{-1}, and each spectrum represents the signal ratio of 1000 scans with the adsorbate on the Cu(110) surface against 1000 scans taken with the surface clean. Each 1000-scan spectrum took less than 5 min to acquire, and all RAIRS spectra were taken at 100 K.

Specified exposures were achieved by backfilling the chamber in all cases and are reported in units of Langmuirs (L), where 1 L = 10^{-6} Torr·s; the reported exposures are uncorrected for differing ion gauge sensitivities. Because of the low dissociative adsorption probability for D_2 on copper surfaces,[25] deuterium atoms were dosed on the surface by backfilling the chamber with D_2 and then holding the crystal at 120 K while it was positioned in front of a hot tungsten filament.[21]

3. Results and Interpretation

The results are presented and interpreted in two parts. The first part describes the temperature-programmed experiments and Auger electron spectroscopy studies used to delineate the reaction products, and the second presents reflection-absorption infrared spectra of the adsorbed intermediates.

3.1. Temperature-Programmed Desorption and Reactions. Temperature-programmed desorption (TPD) profiles of 1-iodopropane (m/e = 170) desorbing from Cu(110) as a function of exposure are illustrated in Figure 1. No molecular desorption peaks are observed below 4 L, but at 4 L a peak at 160 K is visible in the spectrum which we attribute to molecular desorption from the monolayer. A second peak starts to grow at 140 K above 6 L, and it does not saturate even at 10 L; given its zeroth-order peak profile, we attribute it to condensed multilayers. On the basis of a leading edge Arrhenius analysis,[26] we find that the activation energy for multilayer desorption is 7.5 kcal/mol, which is consistent with the heat of sublimation for 1-iodopropane estimated from its heat of vaporization.[27]

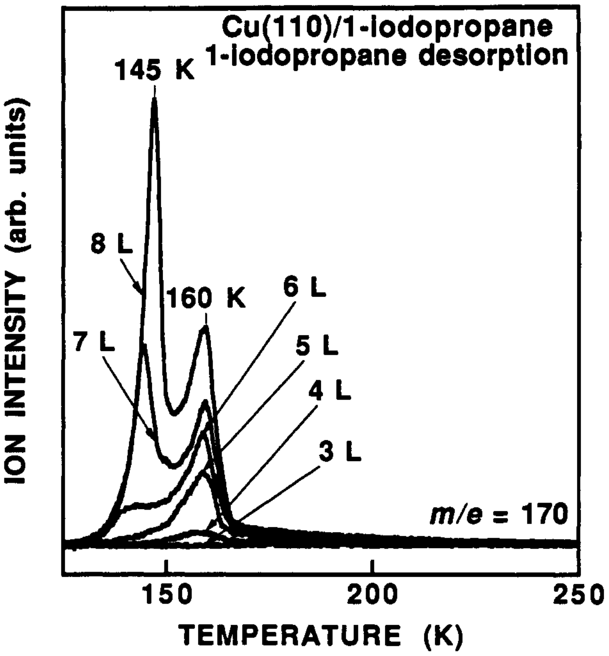

Figure 1. Temperature-programmed desorption spectra for 1-iodopropane (m/e = 170) adsorbed on a Cu(110) surface at 115 K. The heating rate was 2.5 K/s.

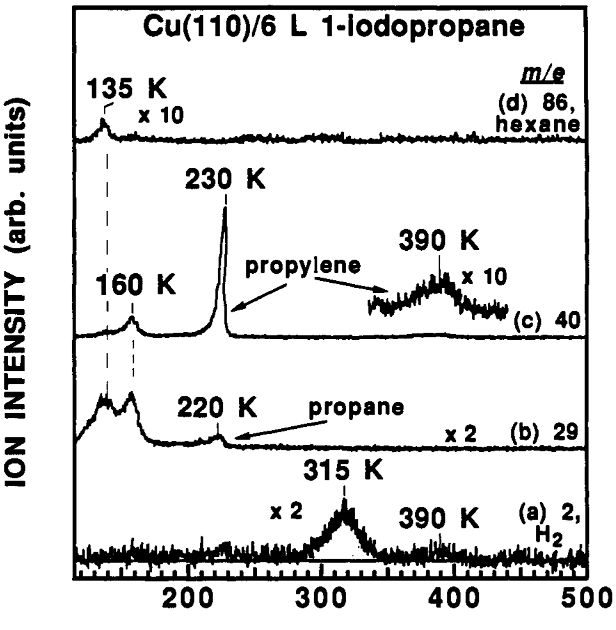

Figure 2. Temperature-programmed reaction spectra of the indicated ions after adsorbing 6 L of 1-iodopropane on Cu(110) at 115 K. The observed peaks are attributed to the following products: 135 K (hexane), 160 K (1-iodopropane), 220 K (propane), 230 K (propylene), 315 K (H_2), 390 K (propylene and H_2). The heating rate was 2.5 K/s.

The decomposition products for 6 L of 1-iodopropane on Cu(110) are shown in the various temperature-programmed reaction (TPR) spectra in Figure 2. The primary decomposition products are H_2 (m/e = 2, 315 K) and propylene (m/e = 40, 230 K), but small amounts of propane (m/e = 29, 220 K) and hexane (m/e = 86, 135 K) are also observed. In addition, small amounts of propylene and H_2 evolve jointly at 390 K. It is important to note that the low-temperature propylene evolution occurs below 200 K at low coverages and shifts to higher temperatures with increasing 1-iodopropane surface coverage (Figure 3). Propylene and propane were monitored by m/e = 40 ($C_3H_4^+$) and m/e = 29 ($C_2H_5^+$), respectively, because neither ion is common to the cracking pattern of the other. The small peaks seen at 160 K in Figure 2b and c are due to cracking fragments of 1-iodopropane desorbing from the monolayer, and the peak at 135 K in Figure 2b corresponds to the cracking of hexane. Other products checked for but not detected include propyl radicals, ethane, methane, and ethylene. Finally, Auger electron spectroscopy (AES) studies show that only iodine remains on the surface above 450 K, indicating that all carbon is removed from the surface by the products described above and that iodine leaves the surface above 950 K.

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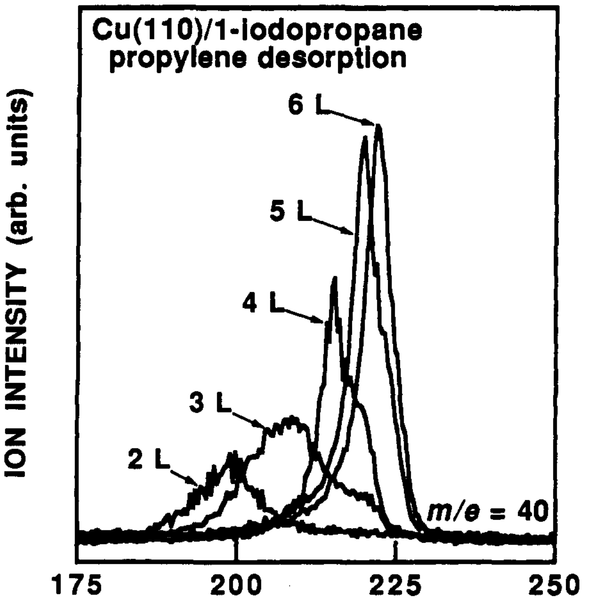

Figure 3. Temperature-programmed reaction spectra of propylene evolution ($m/e = 40$, $C_3H_4^+$) from 1-iodopropane adsorbed on Cu(110) at 115 K as a function of exposure. The heating rate was 2.5 K/s.

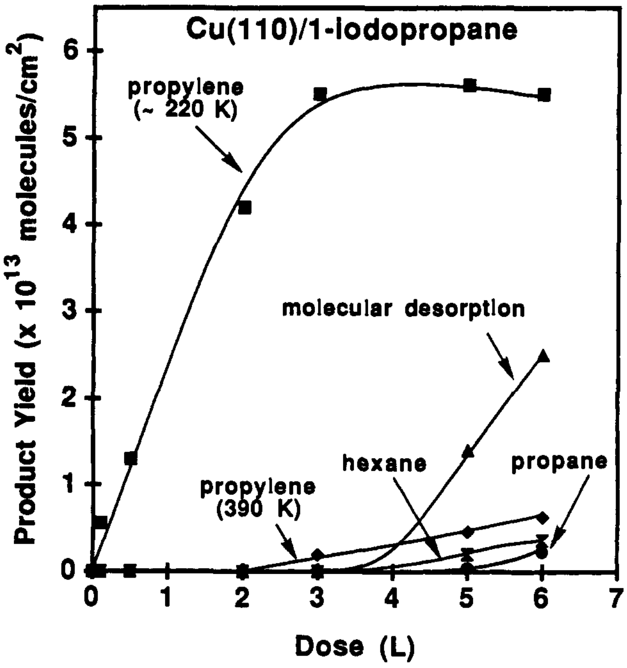

Figure 4. Absolute product yields as a function of 1-iodopropane exposure to Cu(110).

Attempts to observe iodine desorption as I, I_2, or CuI_x were unsuccessful; we attribute this to the configuration of our mass spectrometer. TPR studies reported elsewhere which involve a different spectrometer configuration show that iodine evolves from Cu(111) as I and CuI above 950 K;[28] the same products are presumably produced on Cu(110).

The absolute yields of the desorbing hydrocarbon products are shown in Figure 4 as a function of 1-iodopropane exposure. These yields were calibrated as follows: first, the absolute hydrogen yield was calculated by comparing the D_2 desorption peak area using labeled 1-iodopropane with that for a saturation coverage of D atoms adsorbed on Cu(110), for which $\theta_D = 0.5$ (where θ_D is the number of adsorbed D atoms relative to the number of surface copper atoms[29]) and by assuming that the exposures in these experiments correlate directly with those of the undeuterated 1-iodopropane. Second, according to mass balance arguments, the absolute propylene yield is given by $\sigma_H/(1 - \alpha)$, where σ_H is the absolute H atom coverage per unit area and α is the propane yield relative to that for propylene that is determined using the mass spectral calibrations described in the Experimental Section. Using this method, we were able to convert the TPD/R peak areas into absolute coverages and to determine that the 1-iodopropane coverage at 110 K for a saturation exposure (5 L) is $(8 \pm 2) \times 10^{13}$ molecules/cm^2 or $\theta = 0.07$. The results in Figure 4 show that propylene is the dominant hydrocarbon product from 1-iodopropane decomposition on Cu(110) and that propane, hexane, and 1-iodopropane evolution are observed only for exposures above 3 L. The relative percentages of the products at saturation (5 L) are as follows: 1-iodopropane, 18%; propylene (240 K), 73%; propylene (390 K), 6%; propane, 1%; hexane, 2%.

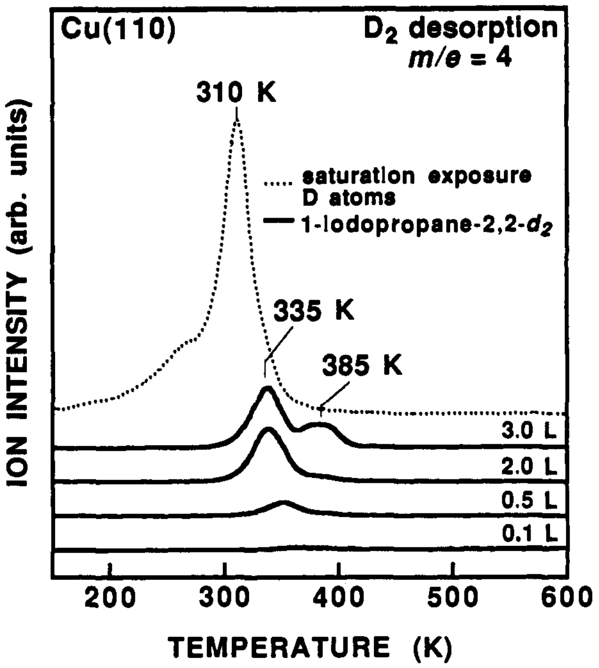

Figure 5. Temperature-programmed reaction spectra of D_2 evolution for the indicated doses of 1-iodopropane-2,2-d_2 on Cu(110) at 115 K. The TPR spectrum for a saturation exposure of D atoms is also shown as the dashed line for comparison. The heating rates were 2.5 K/s.

To determine the reaction pathways for the formation of propylene, hydrogen, and propane from 1-iodopropane on Cu(110), additional TPD/R experiments were conducted using 1-iodopropane-2,2-d_2. TPR spectra for D_2 evolved from 1-iodopropane-2,2-d_2 decomposition as a function of exposure are compared with those for a saturation exposure of D atoms in Figure 5. The peak temperature of 335 K for D_2 evolved after 1-iodopropane-2,2-d_2 decomposition is within 5 K of that for recombinative desorption of D atoms from clean Cu(110) for the same amount of D_2 evolved, and an analysis of the peak shape based on the method of Parker et al.[30] indicates that D_2 evolution is second order in the deuterium atom coverage. In addition, another D_2 peak is seen at higher temperature (385 K) for a 3-L exposure, which correlates with the evolution of a small amount of propylene-d at this same temperature, suggesting that both peaks result from the decomposition of a common adsorbed intermediate. Note, in particular, that this peak is at the same temperature, to within the experimental reproducibility of ±5 K, as the high-temperature evolution of propylene and H_2 observed for 1-iodopropane that was not deuterated (Figure 2a and c).

Three products predominate in the TPR of 1-iodopropane-2,2-d_2: propylene-d, propane-d_3, and D_2. A small amount of m/e

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Table I. Observed Vibrational Frequencies (in cm^{-1}) of 1-Iodopropane and 2-Iodopropane[a]

mode	1-iodopropane liquid[32-34]	3 L of 1-iodopropane on Cu(110)			2-iodopropane liquid[35]	2 L of 2-iodopropane on Cu(110)	
		100 K	110 K	165 K		100 K	170 K
$\nu_a(CH_3)$	2967	2951	2949	2950	2967	2970	2972
$\nu(CH_2)$	2938, 2846		2887	2927			
$\nu(CH)$					2951, 2920		2893
$\nu_s(CH_3)$	2876		2867	2865	2878 or 2861	2839	2880, 2843
$\delta_s(CH_3) + \rho(CH_3)$					2815	2817	2822
$\delta_a(CH_3)$	1458	1451	1451	1452	1449, 1459	1448, 1456 (sh)	
$\gamma(CH_2)$	1435	1408	1419				
$\delta_s(CH_3)$	1380	1380	1381, 1368	1372	1383	1382	
$\nu(CC) + \delta(CCC)$					1266	1259	
$\delta(CHI)$					1201	1188	
$\tau(CH_2)_\beta$, $\omega(CH_2)_\alpha$	1185	1171	1172	1179, 1212			
$\nu(CC) + \delta(CCI)$ or $\rho(CH_3)$					1141	1139	
$\nu(CC)$ or $\rho(CH_3)$	1090			1112	1113, 1148		1110
$\nu(CC)$	1020	1017			879		

[a] α denotes the CH_2 adjacent to iodine; β denotes the CH_2 next to the CH_3; sh stands for shoulder.

= 44 (propylene-d_2) was also observed, but it represented less than 10% of that for m/e = 43 (propylene-d) and appears to be attributable to an isotopic impurity in the 1-iodopropane-*2,2*-d_2 sample and to a fragment of propane-d_3 at high exposures. These results establish that propylene formation from 1-iodopropane on Cu(110) occurs via abstraction of both a hydrogen atom from the β-carbon and the iodine atom and that the small amount of propane formed at high coverage results, formally, from the replacement of the iodine atom from one molecule with a β-hydrogen atom from another.

Figure 6a and b compares the evolution of propylene (m/e = 42) and propylene-d (m/e = 43) after 2-L exposures of 1-iodopropane and 1-iodopropane-*2,2*-d_2, respectively; since no propane forms at this exposure, the molecular ions of both products were monitored in these experiments. Figure 6c and d shows the evolution of propane from 6-L exposures of 1-iodopropane and 1-iodopropane-*2,2*-d_2, respectively. Both the propylene and propane TPR peak areas obtained for the normal and the isotopically labeled iodopropanes are comparable, which is consistent with propylene-d and propane-d_3 being the only deuterated products formed from the labeled iodopropane. The peak shapes and temperatures of these peaks, however, differ significantly, an observation that reflects a kinetic isotope effect in which product desorption is not rate-determining. This is clearly the case for propane, which we have found desorbs below 135 K on Cu(110), and is partly true for propylene, as evidenced by the TPD/R results in Figure 7. For high exposures of 1-iodopropane and propylene (chosen such that about the same amount of propylene evolves), we find that propylene *desorption* occurs at a lower temperature than propylene *formation*, whereas for low exposures they are indistinguishable. We conclude that for exposures above 0.75 L the rate of propylene evolution from 1-iodopropane is determined by the rate of the surface reaction as opposed to desorption; the low-coverage behavior is due to adsorption on defect sites.[31]

3.2. Surface Vibrational Spectroscopy. In order to characterize the intermediates that form on the surface during the adsorption and the thermal decomposition of iodopropanes on Cu(110), reflection–absorption infrared spectroscopy (RAIRS) spectra were taken. In particular, the spectra of 1-iodopropane and 2-iodopropane are compared to confirm that C–H bond scission does not occur concurrently with C–I bond scission. If these reactions occur concurrently, then 1-iodopropane and 2-iodopropane will both produce propylene and have the same RAIRS spectrum. As is shown, they do not.

RAIRS spectra were taken as a function of surface temperature for a 3-L exposure of 1-iodopropane (Figure 8) and for a 2-L exposure of 2-iodopropane (Figure 9), exposures for which no molecular desorption is observed. The striking similarities between the monolayer RAIRS spectra and those for the corresponding liquid iodopropane[32-35] indicate that adsorption is molecular at

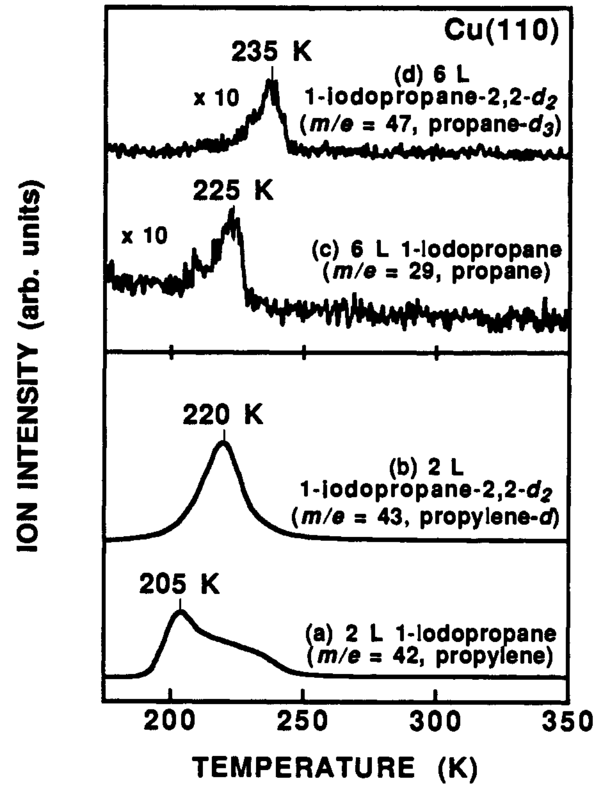

Figure 6. Temperature-programmed reaction spectra for the evolution of (a) propylene (m/e = 42) and (c) propane (m/e = 29) following the adsorption of 2 L and 6 L, respectively, of 1-iodopropane at 115 K and also of (b) propylene-d (m/e = 43) and (d) propane-d_3 (m/e = 47) following the adsorption of 2 L and 6 L, respectively, of 1-iodopropane-*2,2*-d_2 at 110 K.

low temperature (Table I). Moreover, the RAIRS spectrum of 2-iodopropane at 100 K (Figure 9a) shows peaks at 1139 and 1188 cm^{-1} which we tentatively identify with a ν(CC) + δ(CCI) combination and a δ(CHI) mode, respectively.[35] If our assignment is correct, it would indicate that the C–I bond in 2-iodopropane has not been broken, and, since the reported C–I bond strengths for 1-iodopropane and 2-iodopropane are similar (53 and 53.5 kcal/mol, respectively[35-37]), dissociation should occur at about

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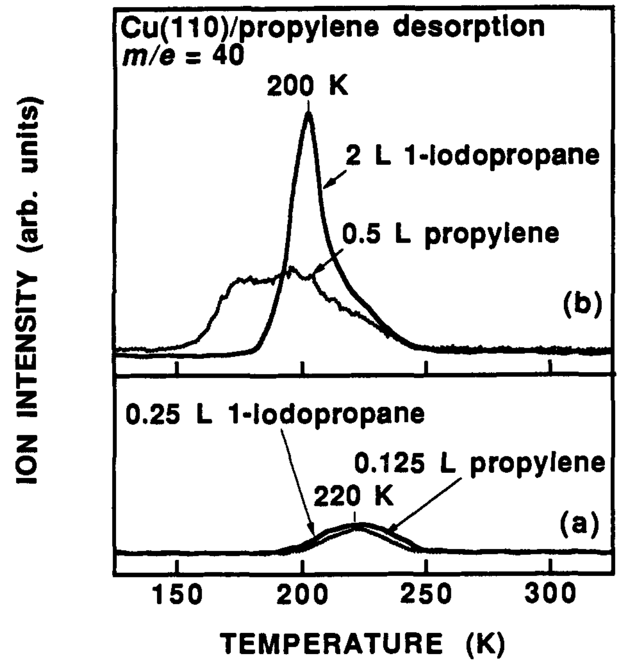

Figure 7. Temperature-programmed desorption/reaction spectra of propylene evolution (m/e = 40, $C_3H_4^+$) for the indicated exposures of propylene and 1-iodopropane to Cu(110) at 115 K. The exposures were chosen to yield approximately equivalent amounts of propylene. The heating rates were 2.5 K/s.

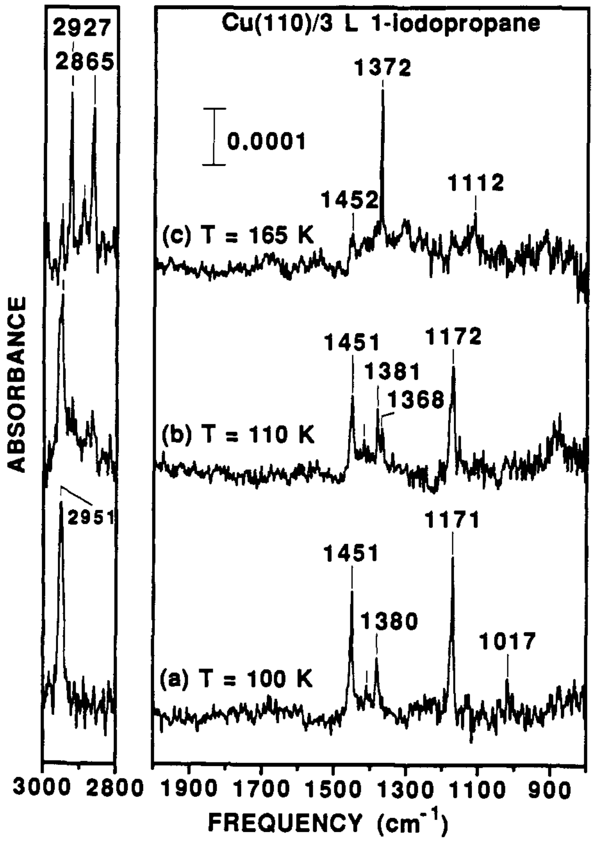

Figure 8. Reflection–absorption infrared spectra for 3 L of 1-iodopropane adsorbed on Cu(110) at (a) 100 K and after annealing at (b) 110 K and (c) 165 K.

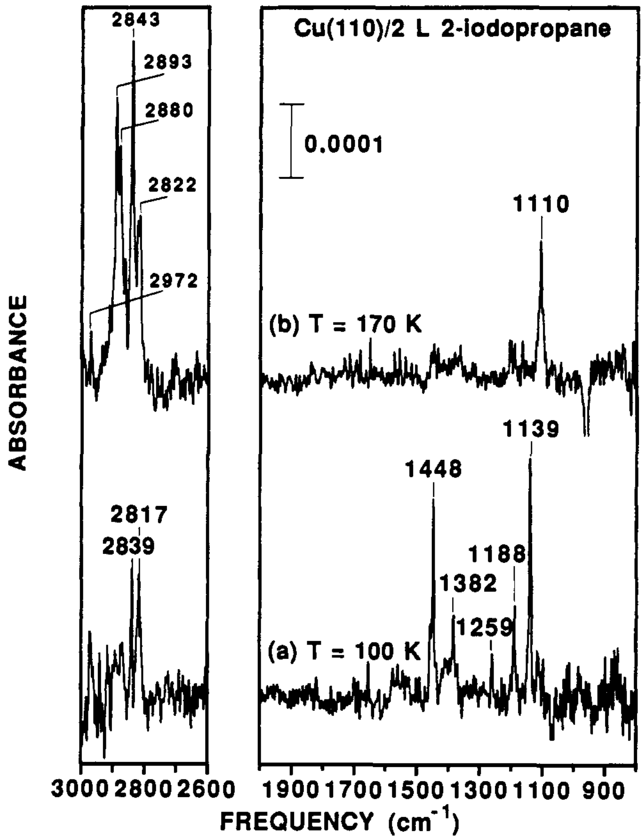

Figure 9. Reflection–absorption infrared spectra for 2 L of 2-iodopropane adsorbed on Cu(110) at (a) 100 K and after annealing at (b) 170 K.

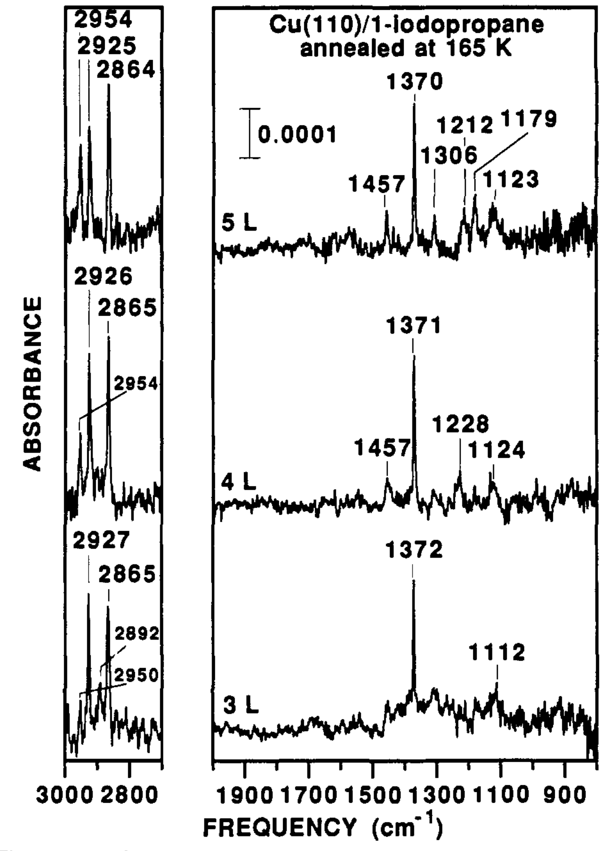

Figure 10. Reflection–absorption infrared spectra of specified exposures of 1-iodopropane adsorbed on Cu(110) at 100 K after annealing at 165 K.

the same temperature for 1-iodopropane as well.

Annealing both 1-iodopropane and 2-iodopropane on Cu(110) to above 165 K changes both RAIRS spectra completely; we attribute the new spectra to propyl (Figure 8c) and isopropyl (Figure 9b) groups that form upon C–I bond dissociation on Cu(110), respectively, and the spectrum at 110 K for 1-iodopropane (Figure 8b) to a mixture of 1-iodopropane and adsorbed propyl groups. The 165 K spectra are intriguing, since only one

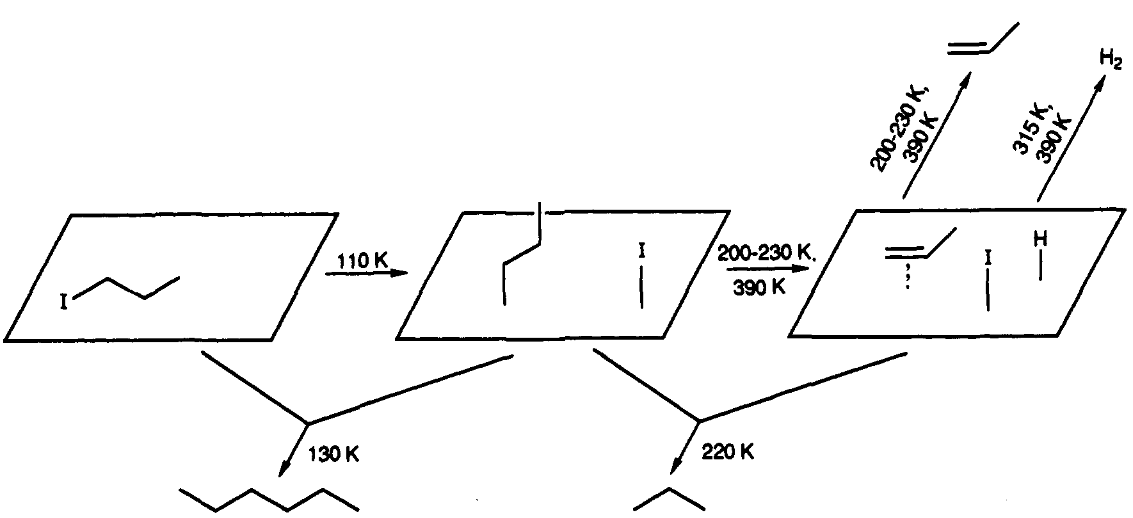

Figure 11. Surface reaction pathways for product formation from 1-iodopropane on Cu(110). The low temperatures for C–I and C–H bond scission are particularly noteworthy.

peak dominates the C–H deformation region in both cases. For propyl groups, the peak at 1372 cm^{-1} is attributed to the symmetric methyl deformation mode [$\delta_s(CH_3)$], which is seen at 1380 cm^{-1} in 1-iodopropane and whose dynamic dipole moment is parallel to the C_{3v} axis of the methyl group. Moreover, the peak corresponding to the antisymmetric methyl deformation mode, normally at about 1460 cm^{-1} and for which the dynamic dipole is perpendicular to the C_{3v} axis, is absent from our spectrum. On the basis of the dipole selection rule for RAIRS that states that modes with dynamic dipole moments parallel to the surface plane will not be observed,[38] these results imply that the C_{3v} axis of the methyl group is oriented along the surface normal. The absence or weakness of other peaks in the C–H deformation region of the RAIRS spectrum indicates that the rest of the vibrational modes have dynamic dipole moments that are either small or oriented parallel to the surface plane. Note, as shown in Figure 10, that some of these other modes do become detectable when the surface coverage is increased.

For isopropyl groups on Cu(110), the lone peak at 1110 cm^{-1} in the C–H deformation region (Figure 9b) correlates with either the 1148-cm^{-1} methyl rocking or the 1113-cm^{-1} carbon–carbon stretching mode in 2-iodopropane.[35] The former assignment is more reasonable, since the 38-cm^{-1} shift to lower frequency for adsorbed propyl groups can be easily explained by a softening of the α-CH bonds in the same way as that previously reported for the α-CH bonds in alkyl groups on Cu(100).[16] The prominence of the 1110-cm^{-1} peak in the RAIRS spectrum of 2-iodopropane on Cu(110), coupled with the absence of the $\delta_s(CH_3)$ mode, which is normally strongly absorbing when a methyl group is tilted away from the surface plane, suggests that, like *n*-propyl groups, the copper–carbon bond lies along the surface normal. The assignments of the reproducible RAIRS vibrational modes for all the moieties are given in Table I.

4. Discussion

The TPR and RAIRS results presented here establish that 1-iodopropane decomposes on Cu(110) by the pathways depicted in Figure 11. The scission of the carbon–iodine bond occurs around 110 K and results in the formation of adsorbed propyl groups and iodine atoms. These propyl groups are stable up to 200 K, at which temperature they decompose by β-H elimination to produce propylene and adsorbed hydrogen. For coverages below $\theta = 0.02$, the product propylene binds at surface defects until reaching the temperatures needed for its desorption, while at higher coverages β-H elimination is the rate-determining step in propylene evolution. The adsorbed hydrogen atoms formed on the surface as a result of the β-H elimination reaction combine and desorb at 315 K, the same temperature at which hydrogen recombination occurs on clean Cu(110). For high coverages, concurrent propylene and H_2 evolution occurs at 390 K as a result of the decomposition of alkyl groups that have been stabilized on the surface by high coverages of iodine.[31]

RAIRS experiments show that adsorption at low temperatures is molecular. As evidence, the spectra obtained for 1-iodopropane on Cu(110) at 100 K matches quite well with those obtained for the liquid state, and, in addition, the spectra obtained for 2-iodopropane at 100 K contain modes involving the C–I bond. Moreover, the relative intensities of the symmetric and antisymmetric methyl deformation modes indicate that the intact molecule is oriented with its methyl group tilted away from the surface normal. The details of the binding geometry of several small alkyl iodides on copper will be described elsewhere.[39]

The vibrational data also indicate that the C–I bond breaks around 110 K. Electron energy loss spectra on Cu(100) confirm that C–I bond scission of 1-iodopropane is completed by 120 K.[17] Given that the 110 K RAIRS spectrum (Figure 8b) is a mixture of dissociated and intact 1-iodopropane, C–I bond scission is slow but measurable at this temperature. Assuming a first-order preexponential factor of 10^{13} s^{-1}, the activation energy for C–I bond scission is approximately 7 kcal/mol. This value, which is 13% of the gas-phase bond energy of 54 kcal/mol, is comparable to the barrier found for C–I bond dissociation in alkyl iodides containing more than one carbon on Ag,[40] Al,[41] Ni,[42] and Pt surfaces.[22,43] The facility with which C–I bonds are cleaved on copper and other metals is not surprising, given the reaction thermodynamics. Based on typical bond strengths of 65, 35, and 55 kcal/mol for metal–iodine bonds, metal–carbon bonds, and gas-phase carbon–iodine bonds, respectively,[27,44,45] carbon–iodine bond dissociation on metal surfaces is exothermic by ~45 kcal/mol! In fact, even the formation of an adsorbed iodine atom and a gas-phase alkyl radical is exothermic, and although this reaction was not observed here, CH_3I dissociation on Cu(111)[46] and CH_3Br dissociation on potassium-promoted Ag(111)[47] do produce methyl radicals. It thus appears that carbon–iodine bond scission on copper surfaces is driven by formation of the copper–iodine bond at the expense of the carbon–iodine bond.

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The scission of the C–I bond results in the formation of a propyl group on the surface. The RAIRS spectra for this species display a strong peak due to the methyl umbrella mode, which lead us to propose an adsorption geometry in which the methyl group is oriented close to perpendicular to the surface. Additional evidence for the formation of propyl groups on Cu(110) comes from the fact that some propane is formed in the TPR experiments. It is clear that olefin formation does not take place below 165 K, because if that were the case, then the same molecule, propylene, would form from 1- and 2-iodopropane, and then the RAIRS spectra obtained for both molecules after annealing to 165 K would look identical. However, above 200 K, the propyl groups do go through a β-H elimination step to yield adsorbed propylene, as clearly shown by the predominance of propylene-*d* in the TPR experiments with 1-iodopropane-*2,2-d*$_2$. The deuterium isotope effect seen for the evolution of propylene implicates C–H bond breaking and/or formation in the rate-determining step of that reaction. Although the magnitude of the isotope effect cannot be determined with high accuracy because of the overlapping reaction-limited and desorption-limited peaks as well as uncertainties in the reaction order due to site-blocking, based on the peak temperatures and an assumed equivalence of the preexponential factors, we calculate a deuterium isotope effect (k_H/k_D) of 5 at 300 K. This is within the range normally measured for rate-determining C–H bond scission on transition-metal surfaces.[48]

While the facility of C–I bond scission in 1-iodopropane on Cu(110) is not surprising given the reaction thermodynamics, facile C–H bond scission is more surprising. C–H bonds are nearly twice as strong as C–I bonds, so C–H bond scission on metal surfaces is much closer to thermoneutral than C–I bond scission. Furthermore, copper catalysts are not known for activating hydrocarbon C–H bonds. Note, however, that the propyl/Cu(110) system is different from that typically encountered in hydrocarbon catalysis, in which molecular hydrocarbons react with the surface; propylene and propane have binding energies to copper of less than 10 kcal/mol and, as a result, desorb intact below the temperature required for C–H bond activation. Propyl groups bind more strongly to copper (Cu–C bond energy = 34 ± 6 kcal/mol[49]). Copper does not, however, bind propyl groups so strongly as to make the β-H elimination reaction unfavorable. In fact, because the binding energies of both the reactants (propyl groups) and products (propylene and H atoms) are relatively small compared with those on other metals, the reaction thermodynamics on copper ($\Delta H_{rxn} \approx 7$ kcal/mol[49]) are comparable to those for β-H elimination on Pt[50] and Fe.[48] It is thus not particularly surprising that β-H elimination occurs at ~200 K on all of these metals. By contrast, the ΔH for β-H elimination on Al surfaces is approximately 20 kcal/mol, and hydride elimination occurs at temperatures above 500 K.[41,51]

C–H bond scission of alkylcopper compounds with β-hydrogens in solution has been well-studied by Whitesides, Kochi, and coworkers,[18-20] who showed that such compounds decompose to give the corresponding alkene and alkane in roughly a 1:1 ratio. Two mechanisms have been proposed for alkene formation from these alkylcopper species. The first mechanism (1a and 1b) is stepwise

$$\mathrm{RCH_2CH_2Cu} \rightarrow \mathrm{RCH{=}CH_2} + \mathrm{CuH} \qquad (1a)$$

$$\mathrm{RCH_2CH_2Cu} + \mathrm{CuH} \rightarrow \mathrm{RCH_2CH_3} + 2\mathrm{Cu} \qquad (1b)$$

$$\mathrm{RCH_2CH_2Cu} + \mathrm{RCH_2CH_2Cu} \rightarrow \mathrm{RCH{=}CH_2} + \mathrm{RCH_2CH_3} + 2\mathrm{Cu} \qquad (2)$$

and involves the formation of an intermediate copper hydride species,[18] and the second (2) achieves direct disproportionation of an alkylcopper aggregate in a single step.[19] There is no question that copper hydride species are formed as a result of the β-hydride elimination of propyl groups in our adsorbed system. However, even though we believe that the stepwise pathway for the formation of propane in which propyl couples with a copper hydride is the most likely (as propane formation is only observed at high coverages), we cannot rule out the possibility that propane formation occurs as a result of direct abstraction of a β-hydrogen from another propyl molecule.

The formation of propane and hexane at high coverages of 1-iodopropane on Cu(110), while minor reaction channels, are also important because they imply C–H and C–C bond formation. The formation of propane is not unexpected on the basis of the chemistry of alkylcopper compounds mentioned above, in which alkanes are formed concurrently with alkenes. The hexane formation channel is also not surprising in the light of results by Ebert and Rieke, who found that by generating highly reactive Cu^0 in solution, alkyl halides containing β-hydrogens could be reacted to give the coupled product.[52] The unusual aspect of hexane formation from 1-iodopropane on Cu(110) is that the product evolves at very low temperatures; not only is the hexane peak observed at 135 K, but also this temperature, in fact, is approximately that expected for hexane desorption from Cu(110), suggesting that the reaction could occur even below 135 K. Recent analogous results on Cu(111) implicate a radical mechanism for these low temperature coupling pathways.[53]

Finally, concerning the effect of coadsorbed iodine atoms on the bonding and C–H bond breaking in adsorbed propyl groups, the peak shifts exhibited by the TPR results in Figure 3 provide some evidence for the blocking of surface sites by iodine.[54] The concurrent evolution of propylene and hydrogen at 390 K for high coverages of 1-iodopropane appears to result from the rate-determining decomposition of propyl groups that are trapped in "iodine cages" on the surface.[31]

5. Conclusions

The results we have presented here show that the chemistry of 1-iodopropane on Cu(110) is driven by the interaction of a number of processes that occur below 225 K. At 100 K, 1-iodopropane adsorbs on the surface intact. As the surface temperature is raised to 110 K, the 1-iodopropane starts to dissociate and to form adsorbed propyl groups which orient with the C_{3v} axis of the methyl group along the surface normal. These propyl groups subsequently react via β-H elimination as the temperature is raised further; propylene molecules not bound at defect sites immediately desorb, while those at the defects are bound more strongly and do not desorb until 220 K. The hydrogen atoms resulting from this hydride elimination step remain adsorbed on the surface until around 315 K, at which point they combine and desorb as H$_2$. At coverages exceeding 3 L a small amount of propane forms, and above 4 L some molecular desorption of iodopropane occurs and hexane formation is also observed. At high coverages, an additional amount of propylene evolves at 390 K as an effect of the coadsorbed iodine.[31] Iodine remains on the surface until above 950 K.

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