of the putative knot is inconclusive proof of its identity, because relative mobility is a function of gel concentration. Sedimentation velocity offers a direct physical measurement of the relative compactness of a molecule. Figure 3 shows the results of a sedimentation experiment illustrating that the new species sediments faster than the circle of the same sequence under denaturing conditions.[10]

The knot molecule formed here is the first of a series of knots that appear constructable from synthetic single-stranded DNA or RNA. Nucleic acid knots have the virtue that it is easy to make circular structures from the same molecule, thus providing a baseline structure for determining the physical properties[18] of these unusual molecular topologies. The A–B–A′–B′ motif used here will result in more complex knots if longer double-helical segments are used; more complex motifs and other strategies will generate additional knots.

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Alkyl Iodide Decomposition on Copper Surfaces: α-Elimination and β-Hydride Elimination from Adsorbed Alkyls

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While many studies have addressed carbon–hydrogen bond activation at the α and β positions in metal–alkyl compounds,[1-3] little is known about the analogous processes on transition-metal surfaces.[4] We report here mechanistic studies of C–H bond activation in alkyls generated on a Cu(110) single crystal surface by dissociative adsorption of alkyl iodides. Our results enable us to compare the rates of β-hydride elimination and α-elimination on copper surfaces. Specifically, we find that the rate of β-hydride elimination from linear alkyls is over 6 orders of magnitude faster than the rate of α-elimination from adsorbed methyl groups.

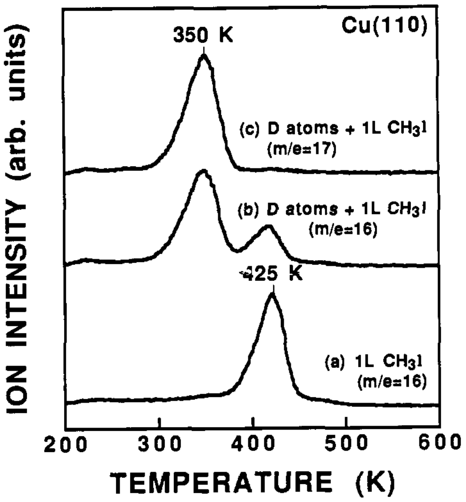

Figure 1. Thermal evolution of methane and partly deuterated methane after adsorption of CH_3I on Cu(110) at 110 K with and without coadsorbed deuterium atoms: (a) desorption of m/e = 16 (CH_4^+) after adsorption of 1.0 L of CH_3I; (b and c) desorption of m/e = 16 (CH_4^+, CH_2D^+) and m/e = 17 (CH_3D^+) respectively after preadsorption of deuterium atoms generated using a hot tungsten filament followed by 1.0 L of CH_3I. The D/CH_3I ratio on the surface in these experiments is 4. The heating rate is 2.5 K/s.

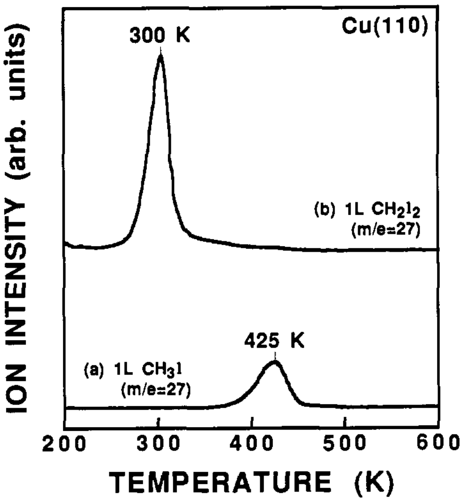

Figure 2. Thermal evolution of ethylene [monitoring m/e = 27 ($C_2H_3^+$)] after the adsorption of (a) 1.0 L of CH_3I and (b) 1.0 L of CH_2I_2 on Cu(110) at 110 K. The heating rate is 2.5 K/s.

The experiments were performed in two ultrahigh vacuum systems equipped with low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), quadrupole mass spectrometry, and high-resolution electron energy loss spectroscopy (HREELS).[5] Using these techniques; we have found that, analogous to other metal surfaces,[4,6-9] alkyl iodides thermally dissociate on copper surfaces below 200 K to form alkyl groups

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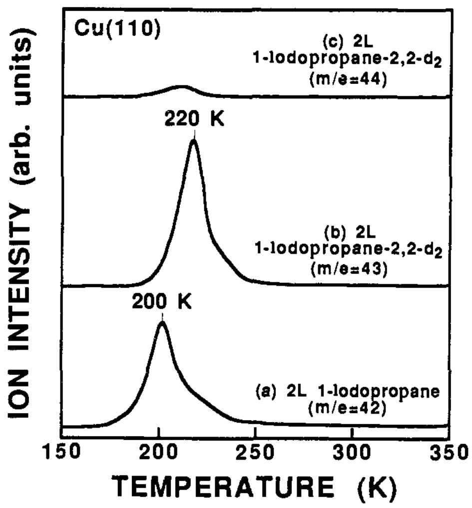

Figure 3. Thermal evolution from Cu(110) of (a) propylene ($m/e = 42$) after adsorption of 2.0 L of 1-iodopropane at 110 K and (b,c) propylene-*d* ($m/e = 43$) and propylene-d_2 ($m/e = 44$), respectively, following the adsorption of 2.0 L of 1-iodopropane-*2,2*-d_2 at 110 K. The high-temperature shoulders are due to surface defects.[5b] The heating rate is 2.5 K/s.

and iodine atoms. In addition, studies in which the iodine coverage is varied show that, at least for the low coverages discussed in this paper, the alkyl reaction products and kinetics are not significantly affected by the coadsorbed iodine. These results are discussed in detail elsewhere.[5,10] We report here on the mechanisms and rates of the C–H bond breaking reactions that occur subsequent to C–I bond scission. This chemistry is illustrated with results from studies with iodomethane and 1-iodopropane.

Methyl groups formed by CH_3I dissociation on Cu(110) are stable until temperatures above 400 K as evidenced by the lack of H_2 desorption at 330–360 K, the temperature range for hydrogen recombination on iodine-covered Cu(110). Above 400 K, methyl groups react to form methane and ethylene, and as shown in Figures 1a and 2a, both products evolve at 425 K. These results are consistent with data previously reported without mechanistic interpretation for the photolysis and thermal annealing of CH_3Br monolayers on copper films.[9] Coverage-dependence studies as well as analyses of the peak shapes indicate first-order reaction kinetics, suggesting that unimolecular C–H bond breaking in the methyl group is rate limiting. Consistent with this inference, studies with CD_3I yield a deuterium isotope effect of 3.1 ± 0.8 at 400 K.[5a] In addition, calibrated mass spectrometry shows that the methane/ethylene ratio is 2, while AES studies indicate that all detectable carbon is removed from the surface by these two products. Taken together, these observations suggest that methane and ethylene are formed by the following coupled reactions:

$$CH_3(a) \xrightarrow[\text{step}]{\text{rate-determining}} CH_2(a) + H(a) \qquad \alpha\text{-elimination}$$

$$CH_3(a) + H(a) \longrightarrow CH_4(g) \qquad \text{reductive elimination}$$

$$CH_2(a) + CH_2(a) \longrightarrow C_2H_4(g) \qquad \text{methylene coupling}$$

We have confirmed that α-elimination is rate determining by studying the subsequent reductive elimination and methylene coupling reactions separately. In particular, as shown in parts b and c of Figure 1, when Cu(110) is precovered with a partial monolayer of deuterium atoms, reductive elimination to form methane-*d* occurs at temperatures as low as 350 K. Similarly, as shown in Figure 2b, the coupling of methylene groups, formed by thermal dissociation of CH_2I_2, produces ethylene with a peak temperature, T_p, of 300 K.

While α-elimination from methyl groups occurs above 400 K, β C–H bond scission in longer alkyls occurs below 250 K. For example, as shown in parts a and b of Figure 3, 1-iodopropane decomposes to produce propylene ($T_p = 200$ K), while 1-iodopropane-*2,2*-d_2 decomposes to produce propylene-*d* ($T_p = 220$ K). The other product at low coverage is correspondingly H_2 or D_2 ($T_p = 335$–360 K). The lack of significant propylene-d_2 ($m/e = 44$) formation from 1-iodopropane-*2,2*-d_2, as illustrated in Figure 3c, confirms the β-elimination pathway, while the deuterium isotope effect evident in parts a and b of Figure 3 implicates C–H bond breaking as the rate-determining step. Consistent with this conclusion, it is found that propylene adsorbed on Cu(110) thermally desorbs below 200 K.[5b]

Applying several methods for extracting kinetic parameters from thermal desorption spectra,[11] we find that the ratio of the rate of β-elimination from propyl groups to the rate of α-elimination from methyl groups at 300 K on iodine-covered Cu(110) is $\sim 10^{10}$. Even if one assumes preexponential factors as low as 10^7 s^{-1}, this ratio is still 10^6. This observation is particularly interesting in light of recent results for the decomposition of alkyl halides on Pt(111) where α-elimination from methyl groups[12] and β-hydride elimination from ethyl groups[4c-f] occur at quite similar temperatures (260 K vs 200 K). Furthermore, since β-hydride elimination on both Pt(111) and Cu(110) occurs at about 200 K, the major difference between platinum and copper is the differing rate of α-elimination on these metals. Studies are in progress to address this issue.

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Unambiguous Demonstration of Vacant-Site Inversion in a *cis*-$P_2M(CO)_3$ Intermediate

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Ligand substitution reactions of octahedral metal carbonyl complexes have been intensely studied over the past 25 years. A wealth of evidence suggests the formation of reactive five-coordinate intermediates in these reactions.[1] Matrix isolation studies and elegant kinetic and flash photolysis studies by Dobson indicate rapid solvolysis of these species even in poorly coordinating solvents such as toluene.[2] Collapse of the nonsolvated five-coordinate intermediates to fluxional TBP species is often proposed to account for isotopic scrambling of ^{13}CO observed in these substitution reactions.[1] It has also been noted that many ligand substitution

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