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β-Hydride Elimination from Alkyl and Cycloalkyl Groups on a Cu(100) Surface: Ring Strain and Planarity of the Transition State

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Abstract: Alkyl (C_5-C_6), cycloalkyl (C_4-C_7), and 2-bicyclo[2.2.1]heptyl (norbornyl) groups have been generated on a Cu(100) surface by the dissociative adsorption of their bromo derivatives. All these groups decompose by a *β*-hydride elimination reaction upon heating the surface, and the product alkenes which are evolved from the surface were detected by mass spectrometry. Studies in which cyclohexyl-d_1 groups were generated on the surface by reacting D atoms with physisorbed cyclohexene show that the coadsorbed bromine atoms in the bromoalkane studies do not have a significant effect on the rate or mechanism of these reactions. A particularly interesting finding from these studies is that the rates of *β*-hydride elimination for these structurally similar alkyl groups vary by 6−7 orders of magnitude if one extrapolates the rates to a common reaction temperature of 200 K. Assuming a common, first-order preexponential factor of 10^{13} s^{-1} gives the following relative rate scale (normalized to 1 for the transformation cyclohexyl → cyclohexene): cyclobutyl (0.6) < cyclohexyl (1) < norbornyl (300) < 3-hexyl (3×10^4) ≈ 3-pentyl (5×10^4) < cycloheptyl = cyclopentyl (10^6). Thermodynamic differences between these reactions, as qualitatively addressed by differences in strain energy between reactant and product, may play a role in the 20-fold difference in rate between cyclopentyl and 3-pentyl, but thermodynamics cannot account for the ~4 order of magnitude larger rate for 3-hexyl relative to cyclohexyl. We suggest that the dramatic rate difference between these two secondary alkyls is due to the different free energy changes required to achieve a planar geometry in the transition state, i.e., a dihedral angle of 0° between the substituents on α- and *β*-carbons.

1. Introduction

One of the most common reaction pathways for alkyl groups bound to metal centers is *β*-hydride elimination. As shown in Scheme 1 for the case of a selectively deuterated ethyl group bound to a metal surface, this reaction involves, formally, the transfer of a hydrogen atom from the *β*-carbon of the alkyl group to the metal with concurrent formation of an alkene.

Scheme 1

From a practical standpoint, *β*-hydride elimination by alkyl groups is important as (1) one of the elementary steps in the catalytic dehydrogenation of paraffins to alkenes,[1,2] (2) one of the pathways for chain termination in polymerization processes such as Ziegler−Natta catalysis[3,4] and the Fischer−Tropsch synthesis,[5−7] (3) the rate-determining step in organometallic chemical vapor deposition processes for the deposition of metal films,[8−10] and (4) an undersirable side reaction in catalytic olefin hydrogenation[11] and organometallic transmetalation.[12,13] The reverse of *β*-hydride elimination by a metal alkyl (olefin insertion into the metal−hydrogen bond) is the important initiating step in such processes as olefin hydrogenation,[14,15] olefin isomerization,[16] olefin H/D exchange,[11,17] and possibly also Ziegler−Natta catalysis.[3,18]

The focus of this paper is *β*-hydride elimination by alkyl groups bound to a single crystal copper surface. The issue addressed is the effect of alkyl conformation on the rate of *β*-hydride elimination. As will be shown below, simply the difference between five-membered and six-membered carbon rings (cyclopentyl vs cyclohexyl) has a dramatic effect on the

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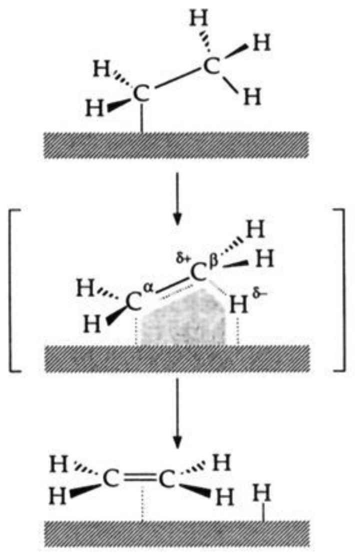

Figure 1. Schematic diagram of the transition state proposed for β-hydride elimination on a surface.

rate of β-hydride elimination. To place this work in context, a few comments regarding the nature of β-hydride elimination from alkyls are warranted.

β-hydride elimination is a predominant reaction pathway for alkyl groups bound to metal centers in organometallic compounds[19,20] and on surfaces[21] under both gas and solution phase conditions. Interestingly, the thermodynamics and kinetics for this reaction have been shown to be quite similar in these different environments.[21-26]

There is also evidence for similar transition states in these β-elimination processes. Previous studies of β-elimination by aluminum alkyls in the gas phase[23] and of the reverse olefin insertion reaction in rhodium complexes in solution[27] have shown significant effects on the rate of elimination (insertion) upon addition of electron-withdrawing and electron-donating substituents to the β-carbon. Studies of β-hydride elimination by alkyl groups on copper surfaces[28] have supported the hypothesis that the transition state for this reaction is hydride-like as shown by the $C^{\delta+}\cdots H^{\delta-}$ charge separation in Figure 1. (It should be noted, however, that the extent to which the β-elimination transition state is hydride-like is system dependent.[29,30]) In addition, a *cyclic* transition state (syn elimination) is supported by the negative entropies of activation that have been measured for this type of reaction in other systems.[31] The stereochemistry of the reaction is also consistent with a syn elimination involving a cyclic transition state,[32] and calculations suggest a planar transition state for the reaction, i.e., a geometry where the two carbon atoms, the β-hydrogen, and the metal atom involved are coplanar.[33]

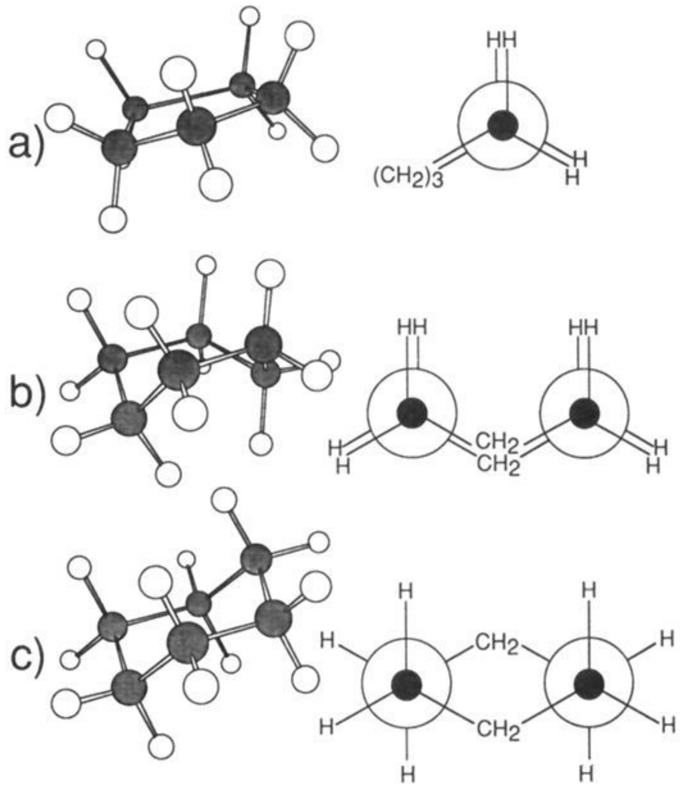

Figure 2. Comparison of the gas phase conformations of cyclopentane and cyclohexane: (a) cyclopentane in its envelope conformation, (b) cyclohexane in its boat conformation, (c) cyclohexane in its chair conformation.

Such a planar geometry, which is a central issue in the current study, is a general feature of elimination reactions—both syn (like the β-elimination processes considered here) and anti.[34] A planar geometry allows the p-orbitals involved in forming the C−C double bond to maximize their overlap (and leads directly to a planar product olefin), and this criterion appears to be a dominant factor in determining the transition state geometry. Experimental support for such a planar geometry in syn elimination reactions comes from studies of the rates of elimination from cyclic alkyls where the molecular conformations are constrained by the cyclic nature of the molecule (see below).

For example, it is found that the rate of elimination from cyclopentyl species is up to several orders of magnitude (depending on the experimental conditions) faster than from cyclohexyl derivatives.[34,37] This large difference in rate has been attributed to differences in conformational constraints between these molecules. Cyclohexyl groups can achieve a conformation (the chair conformation) where hydrogens on adjacent carbons are all staggered, as shown in Figure 2c.[38] On the other hand, in cyclopentyl compounds, hydrogens on adjacent carbons are constrained by the ring to be in an eclipsed position for the case of the envelope conformation (Figure 2a) or a nearly eclipsed configuration for the case of the half-chair conformation. Furthermore, pseudorotation in this system[39,40] means that the cyclopentyl conformers can interconvert with a barrier less than 0.1 kcal/mol in the gas phase, so little energy is required for two adjacent C−H bonds to attain eclipsed positions. For

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cyclohexene, a boat conformation (Figure 2b), which is at ~5.5 kcal/mol higher energy than the chair conformation, is required to achieve eclipsed C−H bonds on adjacent carbons.[41−44] One might thus view the lowest energy conformation of cyclopentane with its near-eclipsed interactions as being ~5.5 kcal/mol closer to the transition state for a planar elimination reaction relative to the chair conformation of cyclohexane where all interactions are staggered.[45] We note that a 5.5 kcal/mol difference in the activation energy for two reactions with the same preexponential factor at 300 K corresponds to a difference of ~4 orders of magnitude in rate, but effects such as ring strain must also be considered; e.g., the "strain energy" in cyclopentane is 6.2 kcal/mol higher than that in cyclohexane which is virtually strainless.[46]

In the present work, we investigate whether similar conformational effects and effects arising from differences in strain energy are observed in β-hydride elimination from a spectrum of secondary alkyl and cycloalkyl groups bound to a Cu(100) single crystal surface. The alkyl and cycloalkyl groups in these studies were generated on the surface by the oxidative addition of their bromo derivatives. Specifically, submonolayer coverages of the bromoalkanes were condensed on the surface at ~100 K, a temperature which is low enough so that the compounds remain molecularly intact. The surface was then warmed to temperatures above 130 K, where the carbon−bromine bonds are selectively broken to generate the adsorbed alkyl groups. Further warming of the surface induces the β-hydride elimination reaction, and the product alkene desorbs into the gas phase where it is detected by a mass spectrometer. The bromine remains bound to the surface throughout this reaction but has no significant effect on either the reaction mechanism or rate. This assertion is proven by studies in which adsorbed cyclohexyl-d_1 groups are generated on the surface in the absence of bromine by reaction of cyclohexene with deuterium atoms.

The significant finding from these studies is that there is an about 6 kcal/mol difference in the free energy of activation between the fastest and the slowest alkyl β-hydride elimination processes. This difference corresponds to a difference of 6−7 orders of magnitude in rate if the rates are extrapolated to a common reaction temperature of 200 K. Much of this difference can be rationalized by conformational effects if we presume that the reaction proceeds through a planar transition state; however, differences in strain energy between the reactants and the products also appear to play a role.

2. Experimental Section

The experiments were performed in two ultrahigh vacuum chambers with base pressures of ~5 × 10^{-10} Torr. One is equipped with a LEED (low-energy electron diffraction) instrument, an Auger electron spectroscopy instrument, and a mass spectrometer;[47] the second is equipped with a HREELS (high-resolution electron energy loss spectroscopy), IR (infrared spectroscopy) instrument, an Auger electron spectroscopy instrument, a mass spectrometer, and a Kelvin probe for measuring changes in the surface work function.[21a]

The Kelvin probe, which has not been previously described, was a model KP-5000 from McAllister Technical Services. It was used to measure the surface work function changes as a function of temperature. The probe consists of a vibrating electrode of known work function which can be positioned near (~0.5 mm from) the surface to be studied, forming a parallel plate capacitor. The work function difference between the reference and the sample appears as a difference in potential between the two surfaces. As the reference electrode vibrates, the capacitance varies periodically with time, and the derivative of the charge becomes a measurable ac current, whose amplitude can be adjusted to null by applying a dc voltage to compensate the related potential.[48] Detailed reviews of work function change measurements by this approach are given in refs 49 and 50.

Two Cu(100) single crystals were obtained from Monocrystals Inc. as circular disks (1 cm diameter and 2 mm thickness) polished to a mirror finish on both (100) surfaces. The crystals were attached to heating elements, which were mounted on manipulators with capabilities for heating the surface to 1100 K resistively and cooling to 100 K with liquid nitrogen. Chromel−alumel thermocouples, which were wedged into holes in the sides of the crystals, were used to measure the surface temperature. Heating was provided by a dc power supply (Hewlett-Packard, 6291A), controlled by a temperature programmer (Eurotherm 818P) to achieve a linear temperature ramp. A temperature ramp of 3 K/s was used in the majority of these studies; for the heating rate variation studies to determine activation energies, the heating rate was varied from 0.1 to 7 K/s.

The single crystal surfaces were cleaned by Ar^+ sputtering[51] (20 min at 915 K and 5 min at 450 K) and annealing in UHV at 980 K to free the surface of carbon, sulfur, and oxygen as confirmed by Auger electron spectroscopy.

The following reagents were purchased from the indicated sources: bromocyclobutane (Aldrich, 97%), bromocyclopentane (Aldrich, 99%), bromocyclohexane (Aldrich, 98%), bromocycloheptane (Aldrich, 97%), *exo*-2-bromonorbornane (Aldrich, 98%), iodobenzene (Aldrich, 98%), diiodomethane (Aldrich, 99%), cyclopentene (Aldrich, 99%), cyclohexene (Aldrich, 99+%), norbornylene (Aldrich, 99%), 2-pentene (Aldrich, 99%), 1-hexene (Aldrich, 99+%), benzene (Fisher, 99+%), cycloheptene (Janssen Chimica, 99+%), 3-bromohexane (Lancaster, 97%), 1,3-butadiene (Matheson, 99.8%), and 1-butene (Matheson, 99.9%). All liquid reagents were purified by at least three freeze−pump−thaw cycles before introduction into the chambers, and the purity of each sample was verified *in situ* by mass spectroscopy. Molecules were adsorbed onto the copper surfaces by back-filling the chambers.

Atomic deuterium was produced by dissociation of D_2 (Matheson, 99.9999%) on a hot (~1800 K) tungsten filament.[52] The Cu(100) crystal was held 3 cm from the filament during dosing, and exposures are reported as the D_2 exposure to the filament, since the atomic flux is not accurately known.

All the exposures are reported in langmuirs, where 1 langmuir is 10^{-6} Torr·s; the pressures have not been corrected for different ion gauge sensitivities of the compounds. For the alkenes and bromoalkanes used in the studies described here, exposures of 3−5 langmuirs are required to form an adsorbed monolayer at a surface temperature of 110 K. A ~100 langmuir exposure is required to saturate a clean copper surface with D atoms.

3. Results and Interpretation

The alkyl groups which have been studied in this work are cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, norbornyl, 3-pentyl, and 3-hexyl. They can be subdivided into two classes on the basis of whether the β-hydride elimination reaction occurs above or below the temperature at which the product olefin desorbs from the Cu(100) surface. The former are much simpler to study because the rate at which the product alkene evolves from the surface is the same as the rate for β-hydride elimination

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by the adsorbed alkyl group. This behavior is illustrated with results for bromocyclohexane in section 3.1.

By contrast, alkyl groups such as cyclopentyl undergo β-hydride elimination to produce alkenes at a temperature close to that of C−Br bond dissociation in bromoalkanes and below that for alkene molecular desorption from Cu(100). As a consequence, chemical displacement studies as well as work function change measurements were applied, as illustrated in section 3.2 for cyclopentyl groups, to establish the temperatures for C−Br bond dissociation and for β-hydride elimination. The spectator role of adsorbed bromine in the β-hydride elimination reaction is established in section 3.3 using the reaction of D atoms with physisorbed cyclohexene to generate adsorbed cyclohexyl-d_1 in the absence of coadsorbed bromine.

The chemical behavior of the other bromoalkanes is similar to that of either bromocyclohexane or bromocyclopentane, and the results are summarized in section 3.4. Finally, section 3.5 describes the approach for determining the free energy of activation from the thermal desorption results.

3.1. Bromocyclohexane on Cu(100). Temperature-programmed desorption (TPD) and reaction (TPR) studies of bromocyclohexane on a Cu(100) surface monitoring $m/e = 162$ (^{79}Br isotope) show that no molecular desorption occurs for exposures below 4 langmuirs. The main product of the reaction of bromocyclohexane with the Cu(100) surface in this submonolayer exposure regime is cyclohexene, as was determined by monitoring masses 54, 67, and 82 (the most intense and diagnostic masses in the cracking pattern of cyclohexene). The relative intensities of these masses (75:100:40, respectively) are very close to the literature data for cyclohexene (77:100:41, respectively).[53] Only a small amount of cyclohexane, the hydrogenation reaction product (<10%, as determined by methods described in ref 54), and no coupling reaction product (cyclohexylcyclohexane, molecular mass 158) were detected. These results lead to the conclusion that the predominant reaction for bromocyclohexane decomposition on a Cu(100) surface is, formally, 1,2-elimination of H and Br to form cyclohexene.

On the basis of previous results for haloalkanes on copper surfaces, it is clear that this formal 1,2-elimination of HBr is a two-step process, involving first C−Br bond dissociation to generate an adsorbed alkyl and second β-hydride elimination. For example, vibrational spectroscopy studies show that carbon−bromine bond dissociation occurs at ~180 K for 1-bromopropane and 1-bromobutane on a Cu(111) surface to form stable, adsorbed alkyl groups which subsequently undergo β-hydride elimination at ~220 K to produce the corresponding alkene.[47] While analogous vibrational spectroscopy studies have not been performed here for bromocyclohexane, work function change measurements and chemical displacement studies for bromocyclo*pentane* presented in section 3.2 establish that analogous two-step chemical transformations occur for these cyclic compounds on Cu(100).

The fact that hydrogen elimination from cyclohexyl groups occurs at higher temperature than the temperature of molecular desorption of cyclohexene is evidenced in Figure 3 by the comparison of the cyclohexene evolution kinetics from bromocyclohexane with the kinetics for cyclohexene desorption from Cu(100). The 26 K higher peak temperature (239 K vs 213 K) for cyclohexene evolution from bromocyclohexane indicates that the β-hydride elimination rate is slower than the rate of cyclohexene desorption. This inference assumes that the β-hydride elimination step is effectively irreversible under the conditions of these experiments, i.e., that there is no alkyl/alkene equilibration prior to alkene desorption. This assumption has been substantiated by studies in which D atoms (<0.5 monolayer) are coadsorbed with bromocyclohexane: no deuterium is incorporated in the product alkene.

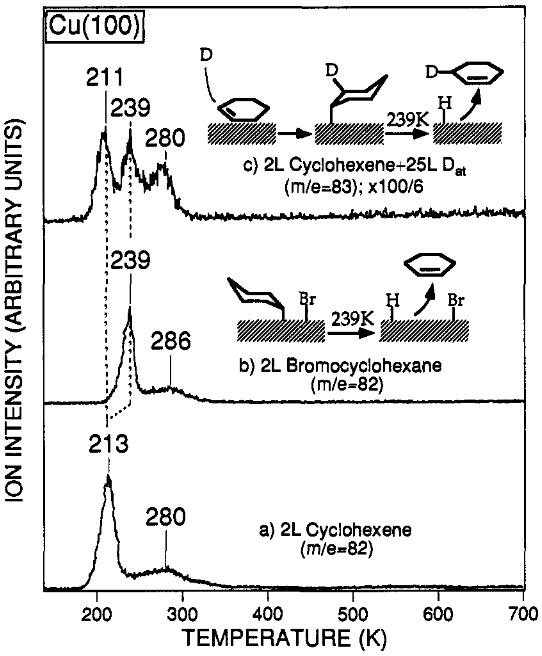

Figure 3. TPR experiments to determine the temperature of the β-hydride elimination temperature in cyclohexyl on Cu(100): (a) monitoring $m/e = 82$ after a 2 langmuir exposure of cyclohexene; (b) monitoring $m/e = 82$ after a 2 langmuir exposure of bromocyclohexane; (c) monitoring $m/e = 83$ after reaction of atomic deuterium with preadsorbed cyclohexene. The deuterium atom exposure reflects the D_2 exposure to the hot tungsten filament used to generate D atoms (the actual D atom exposure to the surface is much less). See section 3.3 for a discussion of the results in (c).

The two-peak structure seen in Figure 3b for cyclohexene evolution from bromocyclohexane on Cu(100) is typical of β-hydride elimination by alkyl groups on copper surfaces. Comparison with the alkene TPD spectrum (e.g., Figure 3a) shows that the smaller high-temperature peak (286 K for cyclohexene evolution from bromocyclohexane) is also observed in alkene desorption. Studies of sputtered vs annealed surfaces[55] show that this high-temperature alkene peak is due to desorption from surface defect sites (steps, kinks, etc.) which have a significantly higher alkene binding energy than the sites of an ideal (100) surface.[56] Consistent with the finding that alkenes desorb at 60−80 K higher temperature from low coordination number defect sites on Cu(100), we have found (studies not presented here) that cyclopentene desorbs at ~60 K higher temperature from the corrugated Cu(110) surface compared with Cu(100).

In summary, cyclohexyl groups on the Cu(100) terraces undergo β-hydride elimination at 240 K which is above the temperature for cyclohexene desorption from these sites, and so the product is immediately evolved from the surface. By contrast cyclohexyl groups associated with defect sites on the surface produce cyclohexene which remains bound to these sites until almost 290 K, where the thermal energy is sufficient for desorption.

Since the predominant cyclohexene TPR peak at 239 K in Figure 3b reflects the kinetics of β-hydride elimination by

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adsorbed cyclohexyl groups on (100) terrace sites, the kinetic parameters for this reaction can be determined by TPR methods.[57] Both a heating rate variation method[58] (heating rate was varied from 0.1 to 7 K/s) and a leading edge (or Habenschaden–Kuppers) method[59] give an activation energy of 15.5 ± 0.6 kcal/mol for this process. The corresponding first-order preexponential factor is $(1.4 \pm 1.2) \times 10^{14}$ s^{-1}.[60]

While both methods of analysis give similar results, it should be noted that these procedures assume that (1) the kinetic parameters are independent of surface coverage and (2) the reaction is first order. There is evidence that neither of these assumptions is strictly valid,[61] but deviations from this idealized behavior are not expected to affect the measured activation energy by more than 2 kcal/mol.

3.2. Bromocyclopentane on Cu(100). 3.2.a. Product Identification. As in the case of bromocyclohexane, when studying bromocyclopentane on Cu(100), several reaction pathways were checked including β-hydride elimination, coupling, hydrogenation, and decomposition. Auger electron spectroscopy studies showed that no carbon remained on the surface after heating to 500 K, which rules out a decomposition pathway that deposits carbon on the surface. No coupling reaction product (cyclopentylcyclopentane, molecular mass 138) and only a very small amount (<1%) of the hydrogenation product (cyclopentane, molecular mass 70) were detected.

The major pathway for bromocyclopentane evolution on a Cu(100) surface is the same as for bromocyclohexane: a formal 1,2-elimination of HBr to produce cyclopentene. The cyclopentene product was identified from TPR spectra monitoring masses 68, 67, and 53 (the most intense and diagnostic ions in the cracking pattern of cyclopentene). The ratio of the peak areas at these three masses is 44:100:25, respectively, which is close to the literature data for cyclopentene of 43:100:23, respectively.[53] The TPR spectrum for one of these ions (*m*/*e* = 68) is shown for a 2 langmuir exposure of bromocyclopentane in Figure 4 along with a TPD spectrum taken while monitoring the same ion after adsorbing 2 langmuirs of cyclopentene.

3.2.b. Kinetics of Cyclopentene Formation. Unlike cyclohexyl on Cu(100), where β-hydride elimination is the rate-determining step in alkene evolution from the surface, cyclopentene evolution from bromocyclopentane occurs at the same temperature as for molecular desorption of cyclopentene from Cu(100), as shown in Figure 4. This result indicates that both H and Br elimination from bromocyclopentane occur either at or below the temperature for molecular desorption of cyclopentene.

To determine the temperature at which cyclopentene is formed, we have employed a technique which we call chemical displacement and which is described in the citations of ref 62. The basic idea is that stable molecules which are weakly interacting with a surface can be chemically displaced from the monolayer to a physisorbed second layer by adsorbates which bind more strongly to the surface. Because the displaced molecules are even more weakly bound in a physisorbed second layer, they can be desorbed at still lower temperature and detected by mass spectrometry. In connection with the present studies, chemical displacement is applied as follows. A displacing agent such as 1-hexene is added to bromocyclopentane monolayers which have been heated to various temperatures. If cyclopentene has been formed by heating bromocyclopentane, then it will be displaced by 1-hexene to the second layer, and in a subsequent TPR experiment cyclopentene is evolved at ~140 K. If no cyclopentane has been formed, then cyclopentene is not evolved in the TPR until 200 K (the same temperature as in Figure 4). As reported in ref 62a, cyclopentene can be displaced from a Cu(100) surface by unsaturated compounds such as 1-hexene, cyclohexene, and benzene, and our studies here show that these reagents do not displace cyclopentyl groups bound to a copper surface. It is also important to note that these C_6 compounds do not displace molecularly adsorbed bromocyclopentane as proven by monitoring the molecular ion of bromocyclopentane (*m*/*e* = 148, ^{79}Br isotope) after depositing 10 langmuirs of a displacing agent on a submonolayer coverage of bromocyclopentane at 100 K.

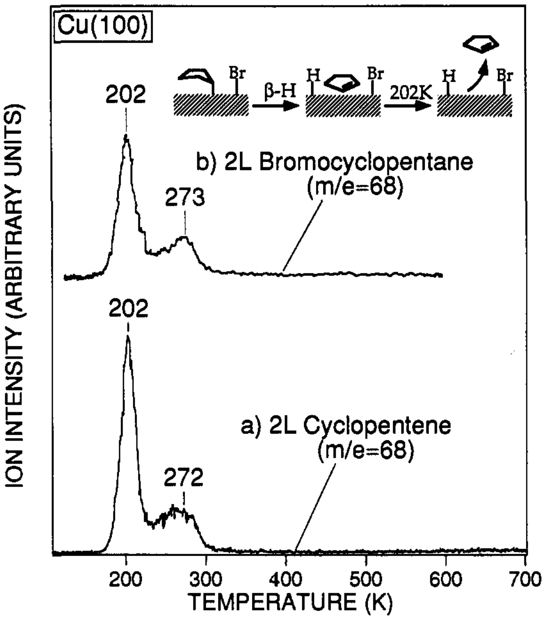

Figure 4. TPR experiments to compare cyclopentene evolution from cyclopentyl groups on the Cu(100) surface with the molecular desorption of cyclopentene: (a) monitoring *m*/*e* = 68 after a 2 langmuir exposure of cyclopentene; (b) monitoring *m*/*e* = 68 after a 2 langmuir exposure of bromocyclopentane.

As shown in Figure 5, the scheme of the experiment for determining the temperature at which cyclopentene is formed from bromocyclopentane on Cu(100) was as follows: cool the single crystal surface to at least 110 K; deposit 1 langmuir (about 25% of a monolayer) of bromocyclopentane on the surface; heat the surface to temperature *T*′; cool the surface back to 110 K; deposit 10 langmuirs (about two monolayers) of the displacing agent (1-hexene, cyclohexene, benzene, or iodobenzene); take a TPR spectrum tracing mass 68 (the molecular ion of cyclopentene).

As shown in Figure 6 for the case where 1-hexene was used as the displacing agent, the TPR spectrum shows two peaks: one at 140 K and another at 196 K. The ratio of the areas of these peaks depends on the temperature (*T*′) to which we heat the surface before adding the displacing agent. The low-temperature peak (140 K) corresponds to cyclopentane which was formed during a heating to *T*′ and which was displaced from the monolayer by 1-hexene. As is evident in Figure 6, this peak first grows with increasing *T*′ and then decreases as *T*′ approaches the temperature for molecular desorption of cyclopentene from Cu(100). The high-temperature peak (196 K) corresponds to cyclopentene which is formed from bromocyclopentane during the TPR experiment. This cyclopentene

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[62] (a) Kash, P. W.; Yang, M. X.; Teplyakov, A. V.; Bent, B. E. Manuscript in preparation. (b) Rodrigues, J. A.; Campbell, C. T. *J. Phys. Chem.* **1989**, *93*, 826–835. (c) Domagala, M. E.; Campbell, C. T. *Langmuir* **1994**, *10*, 2636–2639. (d) Tsai, M.-C.; Muetterties, E. L. *J. Phys. Chem.* **1982**, *86*, 5067–5071. (e) Tsai, M.-C.; Muetterties, E. L. *J. Am. Chem. Soc.* **1982**, *104*, 2534–2539.

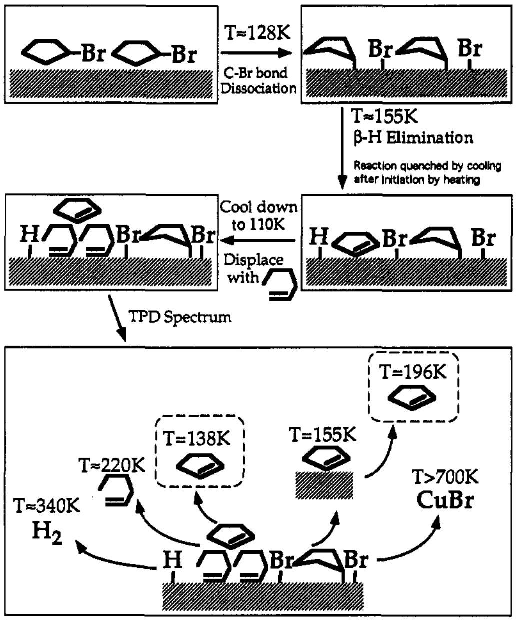

Figure 5. Schematic diagram of the experimental protocol used to determine the β-hydride elimination temperature in cyclopentyl on Cu(100).

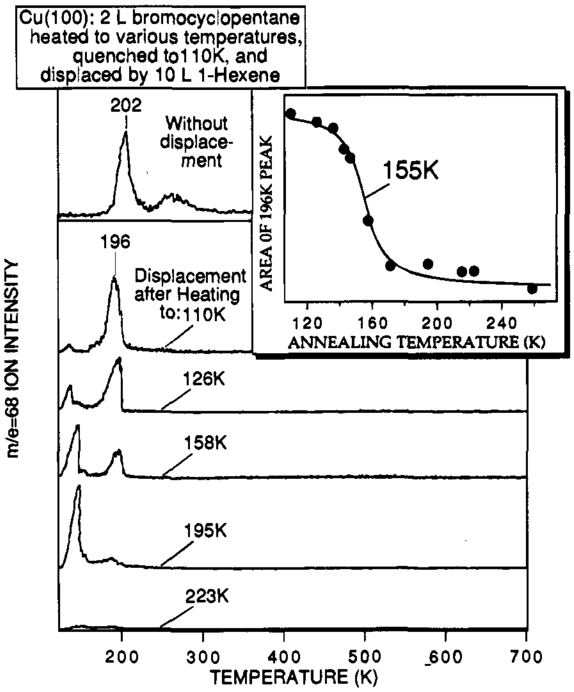

Figure 6. Determination of the β-hydride elimination temperature in cyclopentyl on a Cu(100) surface according to the scheme in Figure 5. Two langmuirs of bromocyclopentane was deposited on Cu(100), heated to various temperatures, and quenched by cooling to 110 K, and any product cyclopentene was displaced from the first monolayer by 10 langmuirs of 1-hexene. The TPD spectra were obtained using an electron impact ionization energy of 9 eV while monitoring $m/e = 68$ (molecular ion). The inset shows the area of the high-temperature (196 K) peak plotted versus the annealing temperature. The inflection point indicates the value equivalent to the peak temperature for β-hydride elimination in a TPR experiment.

remains bound to the surface until the temperature of molecular desorption from the monolayer on Cu(100) because, by the time it is formed, any second-layer 1-hexene which could potentially displace the cyclopentane as it is formed has already desorbed. It should be noted that the total area (sum of the peaks at 140 and 196 K) remains the same (within 10%) up to the temperature of molecular desorption of cyclopentene. During this experiment the electron energy of the mass spectrometer was set to 9 eV to avoid interference from the cracking pattern of 1-hexene. (Nine electronvolts was the electron energy setting on the ionizer potentiometer; previous studies[54] have suggested that the true electron impact energy is slightly higher.)

Plotting the area of the high-temperature peak versus T', we obtain a curve which decreases with increasing temperature as shown in the inset to Figure 6. Differentiation of this curve gives the rate of cyclopentene evolution from bromocyclopentane, which has a maximum at 155 K. Experiments with cyclohexene, benzene, and iodobenzene as displacing agents were performed, and the results were the same: maximum rate at 155 ± 5 K. The same result is also obtained by differentiating the increasing part of the plot of the low-temperature (140 K) peak area versus T'.

Although the anneal/quench/displace experiments described above do not provide a highly accurate temperature/rate profile for the β-hydride elimination reaction by cyclopentyl, if we assume that the preexponential factor for this reaction is the same as that for cyclohexyl → cyclohexene conversion, then we can estimate, using the method of Redhead,[60] that the activation energy for β-hydride elimination in cyclopentyl groups on Cu(100) is 10.0 ± 0.6 kcal/mol (heating rate taken as 0.1 K/s; see Figure 9 and explanation to Table 1). The assumed value for the prefactor for cyclopentyl β-hydride elimination translates to an experimental uncertainty of 1 kcal/mol in activation energy assuming that the actual preexponential factor for β-hydride elimination in cyclopentyl may differ by an order of magnitude.

3.2.c. C−Br Bond Dissociation Kinetics. The extremely low temperature for cyclopentene formation from bromocyclopentane on Cu(100) raises the question of whether C−Br bond dissociation occurs concurrently with the loss of a β-H atom in bromocyclopentane. Since the C−Br bond is difficult to detect by HREELS and IR, chemical displacement was applied to determine the C−Br dissociation kinetics. A compound which displaces physisorbed bromocyclopentane from the first monolayer on Cu(100) is CH_2I_2. The fact that displacement of bromocyclopentane by CH_2I_2 is complete is based on the following evidence. For *submonolayer* exposures of bromocyclopentane, there is no molecular desorption in the absence of a displacing agent. However, when *submonolayer* exposures of bromocyclopentane are displaced by 10 langmuirs of CH_2I_2, there is a linear increase in peak area with bromocyclopentane exposure and the rate of increase is the same (within 5%) as that for multilayers.

The procedure for determination of the dissociation temperature for bromocyclopentane on Cu(100) was therefore as follows: cool the surface to 110 K; deposit 1 langmuir of bromocyclopentane; heat to temperature T''; cool the surface back to 110 K; deposit 10 langmuirs of CH_2I_2; take a TPD spectrum (Figure 7) tracing mass 148 (molecular mass with ^{79}Br isotope). The TPD spectrum shows one peak at ~185 K whose area decreases as T'' increases. Plotting the area of this peak versus T'' and differentiating the curve, we obtain 128 K as the dissociation temperature, i.e., the maximum rate of dissociation, for bromocyclopentane on Cu(100). This result shows that dissociation does not affect the β-hydride elimination process which occurs at 27 K higher temperature.

3.2.d. Comparison of the Results of Displacement Experiments with Measurements of the Surface Work Function Change. The temperatures determined above by chemical displacement and TPR for C−Br bond dissociation (128 K), β-hydride elimination (155 K), and cyclopentene desorption (202 K) are also apparent as inflection points in a plot of the surface work function change, $\Delta\Phi$, versus temperature. As presented in Figure 8, the work function change of a Cu(100) surface

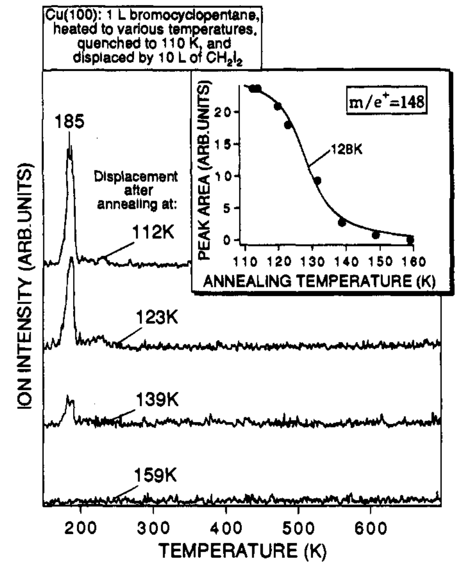

Figure 7. Determination of the C−Br bond dissociation temperature in bromocyclopentane on Cu(100). Two langmuirs of bromocyclopentane was deposited on Cu(100), heated to various temperatures, and quenched by cooling the crystal to 110 K, and any undissociated bromocyclopentane then displaced from the first monolayer by 10 langmuirs of CH_2I_2. The TPD spectra were obtained monitoring *m/e* = 148 (molecular ion for bromocyclopentane). The inset shows the area of the TPD peak plotted versus the annealing temperature to determine the temperature of C−Br bond dissociation.

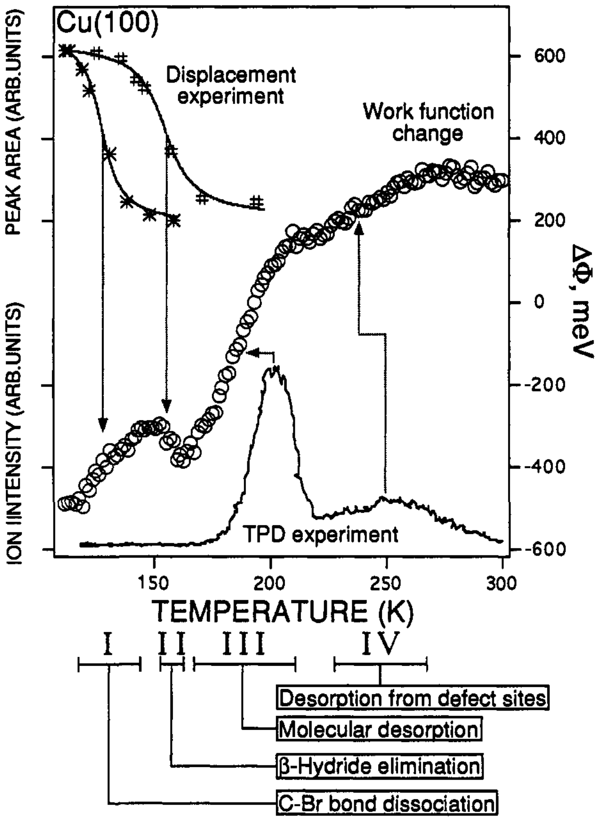

Figure 8. Comparison of the surface work function change with data obtained by conventional TPD experiments (see Figure 4) and displacement methods (see Figures 6 and 7). The work function change was measured after deposition of 2 langmuirs of bromocyclopentane on Cu(100). The heating rate in these studies was 0.1 K/s.

covered with 2 langmuirs of bromocyclopentane shows four features. The two highest temperature features correspond to molecular desorption of cyclopentene from the (100) face and from defect sites, respectively. Since the heating rate in these studies was only 0.1 K/s, compared with 3 K/s in the TPR experiment, the TPR peak temperatures are about 10−15 K higher than the inflection points of the corresponding parts of the ΔΦ plot. C−Br bond dissociation and β-hydride elimination are evident in the ΔΦ plot in Figure 8 as an increase at 130 K and a decrease at 155 K. The fact that these inflection point temperatures agree quite well with the chemical displacement results implies that the anneal/quench protocol in the displacement studies is equivalent to a surface heating rate of ~0.1 K/s. It is also of interest to note that the decrease in the surface work function upon bromocyclopentane adsorption and the increases in ΔΦ upon C−Br bond dissociation and alkene desorption are consistent (in both magnitude and direction) with results in the literature for analogous processes.[47] The decrease in the surface work function upon β-hydride elimination is interesting, since, to our knowledge, this is the first measurement of the work function change for a β-hydride elimination process which is not directly coupled to alkene desorption.

3.3. Effect of Coadsorbed Bromine. The presence of bromine atoms on the surface does not significantly affect the β-hydride elimination temperature as evidenced by experiments with atomic deuterium. When reacted with preadsorbed cyclohexene on the Cu(100) surface, atomic deuterium attacks the double bond[63] and forms a cyclohexyl group bound to the surface analogous to the species formed by dissociation of bromocyclohexane. When this cyclohexyl-d_1 group undergoes β-hydride elimination, the product [deuterated cyclohexene (*m/e* = 83)] can be detected by TPR. As seen from Figure 3c, this mass shows a distinctive three-peak spectrum. The peak at 211 K corresponds to the A + 1 peak of unreacted cyclohexene (due to the 1% natural abundance of ^{13}C; compare Figure 3a and note the expansion factor); the second peak (at 239 K) has the same temperature as the main peak in the experiment with bromocyclohexane (Figure 3b) and corresponds to cyclohexene-d_1 evolution after β-hydride elimination by cyclohexyl-d_1 groups;[63] the peak at 280 K is due to the desorption of cyclohexene and cyclohexene-d_1 from surface defect sites.

The fact that the 239 K peak for cyclohexene-d_1 in Figure 3c in the absence of surface bromine matches the 239 K peak for cyclohexene evolution from bromocyclohexane where bromine is coadsorbed with cyclohexyl groups indicates that coadsorbed bromine does not have a significant effect on the rate of cyclohexyl β-hydride elimination on Cu(100). Similar results for ethyl groups on Cu(111) in the presence and absence of coadsorbed iodine are presented in ref 63.

3.4. Bromocyclobutane, *exo*-2-Bromobicyclo[2.2.1]heptane (*exo*-2-Bromonorbornane), 3-Bromohexane, 3-Bromopentane, and Bromocycloheptane on Cu(100). These compounds, like bromocyclopentane (section 3.2) and bromocyclohexane (section 3.1), undergo C−Br bond dissociation followed by β-hydride elimination on Cu(100). The main differences among these compounds are in the relative surface reaction rates which were determined using the methods described above for bromocyclopentane and bromocyclohexane. These various alkyl groups were chosen because they represent a spectrum of properties such as ring strain and relative conformational stabilities. At the same time, the electronic stuctures of all these secondary alkyl groups are similar. The results are summarized in Figure 9, which compares TPR spectra for alkene evolution from the β-hydride elimination reaction with TPD spectra for molecular desorption of the product alkene from Cu(100). The interpretation of these results is given briefly below by compound.

3.4.a. Bromocyclobutane. This compound was studied to investigate the effect of ring strain in cyclic alkyls on the rate of β-hydride elimination. Cyclobutane has 26.5 kcal/mol of

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(63) Xi, M.; Bent, B. *J. Vac. Sci. Technol., B* **1992**, *10*, 2440−2446.

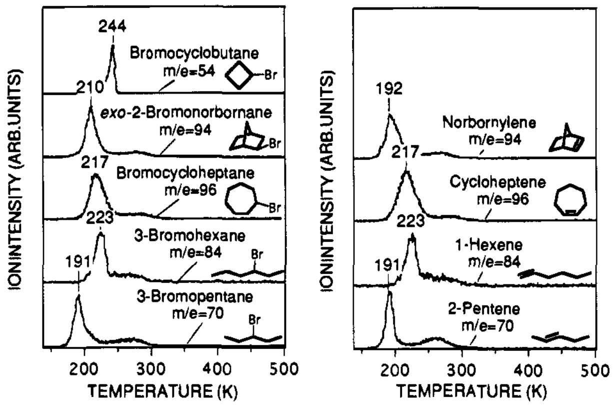

Figure 9. Comparison of TPR results for alkene evolution from β-hydride elimination [after a 2 langmuir exposure of the indicated bromoalkanes on Cu(100)] with molecular desorption studies of 2 langmuirs of the alkenes. Because of availability, 1-hexene was used instead of 2- or 3-hexene to compare with β-hydride elimination by 3-hexyl; cyclobutene molecular desorption was not studied.

strain energy compared with 6.2 for cyclopentane and 0.0 for cyclohexane.[46]

As for bromocyclohexane, β-hydride elimination in cyclobutyl occurs above the temperature for cyclobutene desorption from Cu(100), so the β-hydride elimination kinetics can be determined directly from the cyclobutene TPR spectrum (monitoring mass 54) as shown in Figure 9. This conclusion presumes that, by the 244 K peak temperature for cyclobutene evolution, the C−Br bond has already dissociated and that the temperature of molecular desorption of cyclobutene lies below 220 K. The first assumption is consistent with the measured C−Br bond dissociation below 200 K for other bromoalkanes,[47,64,65] and the second assumption is reasonable on the basis of studies of the molecular desorption of various hydrocarbons from the Cu(100) surface: 1-butene desorbs molecuarly at about 170 K, and cyclobutene would be expected to desorb at a similar temperature since there is no significant difference in the temperature of molecular desorption between 2-pentene and cyclopentene on Cu(100). The possibility of isomerization of the product cyclobutene to 1,3-butadiene appears unlikely on the basis of a comparison of the mass 54 TPR spectrum for bromocyclobutane with the TPD results for molecular desorption of 1,3-butadiene. Both spectra show peaks near 240 K, but the substantial tailing to higher temperature for 1,3-butadiene argues against a common reaction product.

The activation energy for β-hydride elimination by cyclobutyl on Cu(100) was determined by heating rate variation studies (see section 3.1) to be 16.3 ± 0.5 kcal/mol. The Arrhenius factor corresponding to this energy is $(3.0 \pm 2.3) \times 10^{14}\ s^{-1}$.[60]

3.4.b. *exo*-2-Bromonorbornane. This compound is of interest to compare with bromocyclopentane. Similar to bromocyclopentane, the substituents on the 2- and 3-carbon centers (i.e., the Br-substituted carbon and the adjacent CH_2 group) of norbornyl are nearly eclipsed, and this group would thus be expected to undergo β-hydride elimination at low temperature from the point of view of a planar transition state. On the other hand, unlike for the C_5 system, one expects a significant increase in ring strain in transforming norbornyl to norbornylene (4.8 kcal/mol for norbornane → norbornylene in the gas phase[46]).

The results in Figure 9 show that, after 4 langmuirs of *exo*-2-bromonorbornane was deposited on the Cu(100) surface, the *m*/*e* = 94 (molecular mass of the product norbornylene (bicyclo[2.2.1]heptene)) TPR spectrum has two peaks: a primary peak at 210 K and a smaller peak at 270 K. The 210 K peak is 18 K higher in temperature than the temperature of molecular desorption of norbornylene (see adjacent panel in Figure 9). The 270 K peak is due to rate-determining product desorption from surface defect sites (see section 3.1 for the explanation).

As in the case of the cyclohexyl → cyclohexene reaction on Cu(100), the rate of norbornylene evolution from the surface corresponds to the rate of β-hydride elimination, and the activation energy for this conversion, as determined by the heating rate variation method, is 16.9 ± 0.6 kcal/mol. The corresponding prefactor is an unexpectedly large $(4.7 \pm 4.2) \times 10^{17}\ s^{-1}$.[60] It is possible that the coverage independence of the kinetic parameters which is assumed in this method is not valid for this reaction, and this value should be treated with appropriate caution.

3.4.c. Bromocycloheptane on Cu(100). Cycloheptyl is of particular interest for comparison with cyclopentyl. Not only is the increase in strain energy on converting the C_5 and C_7 alkanes to the corresponding alkenes quite similar,[46] but also the conformational energy differences in these cyclic alkanes are quite similar to one another and much smaller than those in cyclohexane. Not surprisingly, the rate of β-hydride elimination from cycloheptyl on Cu(100) is similar to that for cyclopentyl and orders of magnitude faster than that for cyclohexyl (see below). In reaching this conclusion, it is assumed that, as for bromocyclopentane, C−Br bond dissociation in bromoheptane occurs at temperatures below 160 K and consequently does not affect the temperature of β-hydride elimination.

Chemical displacement was used to determine the temperature of β-hydride elimination in cycloheptyl since the temperature of cycloheptene evolution from cycloheptyl is the same as the temperature of the molecular desorption of cycloheptene. A useful displacement agent for this situation was found to be *o*-xylene. However, this displacing agent desorbs from the second layer at ~180 K on Cu(100), which means that it remains on the surface as a second layer long enough to displace the alkene as soon as it is formed by β-hydride elimination in the first layer. As a result, *o*-xylene displaces cycloheptene to the second layer as it is formed by β-hydride elimination from cycloheptyl. The β-hydride elimination temperature determined by this method is ~155 K. It should be noted, however, that the high coverages of displacing agents present during the β-hydride elimination reaction in these studies may have had some effect on the reaction kinetics as a result of, for example, site-blocking. For all other systems studied (for reasons which are not yet understood) this approach of immediate displacement by a physisorbed second-layer molecule did not work; the product alkene could not be displaced from the first monolayer as it was formed, even if the displacing agent did displace the alkene in control experiments and had a large enough heat of adsorption to remain on the surface as a second layer until the temperature of the β-hydride elimination.

3.4.d. 3-Bromohexane and 3-Bromopentane. Studies of 3-pentyl and 3-hexyl provide an opportunity to compare β-hydride elimination in acyclic compounds with their cyclic counterparts. As shown in Figure 9, β-hydride elimination in these alkyls occurs at or below the temperature of molecular desorption of the product alkenes.

Studies of 3-bromopentane show that the temperature of C−Br bond dissociation in this *acyclic* bromoalkane is 128 K (the same as for bromo*cyclo*pentane) as was found in experiments analogous to that described in section 3.2.c for bromocyclopentane with CH_2I_2 as a displacing agent. The temperature of β-hydride elimination by the 3-pentyl groups generated on a surface by C−Br bond dissociation was determined by chemical displacement. *o*-Xylene was used as the displacing agent, and the displacing ability of this compound was verified by

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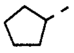
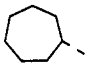
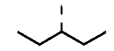
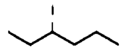
(64) Lin, J.-L.; Bent, B. E. *Chem. Phys. Lett.* **1992**, *194*, 208−212.
(65) Lin, J.-L. Dissertation, Columbia University, 1993.

Table 1. β-Hydride Elimination Temperatures and Corresponding Kinetic Parameters for the Indicated Alkyl Groups on Cu(100)

alkyl group	β-H elimination temperature,[a] K	k,[b] s^{-1}	$\Delta G^{\ddagger}$,[c] kcal/mol	E_a (heating rate var)	E_a (Redhead method)			relative rate at 200 K[d]
					$\nu = 10^{11}$	$\nu = 10^{13}$	$\nu = 10^{15}$	
	244	0.091	15.3	16.3 ± 0.5	12.6	14.9	17.1	~0.6
	155[e]	~0.1	9.6		7.9	9.3	10.7	~10^6
	239	0.065	15.1	15.5 ± 0.5	12.3	14.5	16.7	1
	155[e]	~0.1	9.6		7.9	9.3	10.7	~10^6
	210	0.191	12.8	16.9 ± 0.6	10.8	12.7	14.7	~300
	175[e]	~0.1	10.8		8.9	10.5	12.1	~5×10^4
	177[e]	~0.1	11.0		9.0	10.6	12.2	~3×10^4

[a] Peak temperature from TPR experiments; the surface heating rate is 3 K/s. [b] First-order rate constant at the temperature given in column 2; see section 3.5 for a discussion of the method of calculation. On the basis of an estimated absolute accuracy of ±10 K in the surface temperature measurements and an assumed coverage and temperature independence of the kinetic parameters, we estimated that these parameters are accurate to within at least an order of magnitude. The values associated with the temperatures indicated by footnote *e* have slightly higher uncertainties due to the experimental method (see footnote *e*). [c] Uncertainty based on 1 order of magnitude uncertainty in the rate constant (see footnote *b*) is about ±1 kcal/mol. [d] Common first-order preexponential factor of 10^{13} s^{-1} used. [e] Temperature determined by chemical displacement and/or work function change measurements (these temperatures are approximately equivalent to what would have been determined in TPR experiments with heating rates of ~0.1 K/s).

displacement experiments in which 2-pentene was adsorbed and displaced by *o*-xylene. The identity of the product (distinguishing 1-pentene and 2-pentene is possible by mass spectrometry) was determined by monitoring characteristic peaks in its mass spectrum. The results show that the temperature of β-hydride elimination is 175 K.

A procedure directly analogous to that described above was also followed to determine the β-hydride elimination temperature for 3-hexyl. *o*-Xylene (or iodobenzene) was used as displacing agent, and the temperature of β-hydride elimination for 3-hexyl was found to be 177 K.

3.5. Reaction Rate Constants and Free Energies of Activation. TPD/TPR experiments are generally not sufficient to determine accurately (or at least unambiguously) the activation energies and preexponential factors for surface reactions.[57] The simultaneous changes in coverage and temperature in these experiments coupled with the often significant coverage dependences of the kinetic parameters do not allow a unique determination of the activation energy and prefactor. However, if the kinetic order for reaction is known, the surface reaction rate constant at any specified temperature where there is a measurable signal in a TPD/TPR experiment can be determined to within the accuracy to which the absolute surface coverage is known. While absolute surface coverages are often difficult to determine with accuracy at the percent level, even accuracy to within a factor of 2 (which is not difficult to obtain) is sufficient, as we show below, to determine free energies of activation to within kT of the accurate value, i.e. within 1 kcal/mol for a temperature of 300 K.

For example in the case of a first-order reaction (which is a reasonable approximation for the rate of β-hydride elimination by alkyl groups at low coverages on Cu(100), the reaction rate can be expressed as

$$\text{rate} = -(\mathrm{d}\theta/\mathrm{d}T)\beta = k_1\theta \qquad (1)$$

where k_1 is the first-order rate constant (s^{-1}), θ is the absolute surface coverage of reactants (molecules/cm^2), T is the surface temperature (K), and β is the surface heating rate (K/s). To determine the reaction rate constant at any specified temperature, one first determines the proportionality constant relating the TPD signal to the absolute rate by equating the absolute initial surface coverage to the TPD peak area (integrated vs time). The rate constant for any particular temperature, T', is then determined from the relation

$$k_1(T') = \text{rate}(T')/\theta(T') \qquad (2)$$

In the β-hydride elimination studies here, the rate constants at the TPR peak temperatures have been determined assuming first-order kinetics and using the procedure described above. (Given the possibility of a non-first-order process, this assumption introduces an experimental uncertainty of up to a factor of 2 for the coverages at the TPR/D peak maximum.) The absolute surface coverages have been estimated by equating the monolayer saturation coverage with the maximum surface density possible based on the van der Waals size for the alkyl groups and bromine atoms which were packed on the surface in orientations which maximize dispersion interactions with the surface. On the basis of the literature data, this procedure can be expected to give results which are accurate to within about a factor of 2, which when combined with the uncertainty in the reaction order gives an accuracy to within a factor of 4.

The results of these rate constant determinations are summarized in Table 1. Note that all rate constants are quite similar at the TPR peak temperatures. This is to be expected. For a given heating rate, reactions which have the same reaction order and prefactor will have similar peak height to area ratios, i.e., similar peak shapes.[66] Redhead has shown that the ratio of these proportionality constants is almost the same for all first-order reactions if the ratio is evaluated at the same extent of the reaction, for example, at the peak temperature.[60] Thus, for first-order reactions with a common preexponential factor, the rate constant, as determined by eq 2 above, will always be ~0.1 s^{-1} when evaluated at the various TPR peak maxima. It should be emphasized, however, that the different reactions will have very different rate constants if a common reaction temperature is chosen.

The second point to note in connection with Table 1 is that, for the values associated with temperatures indicated by footnote

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(66) Yang, M. X. Manuscript in preparation.

e, the uncertainty is larger than a factor of 4 because the surface heating rate is not accurately known. Specifically, for these alkyl groups, the rate of β-hydride elimination was monitored by chemical displacement or work function change methods where the surface reaction was repeatedly initiated (by heating) and quenched (by cooling). The studies in connection with Figure 9 suggest that this initiate/quench procedure is equivalent to a surface heating rate of 0.1 K/s, but we estimate that an uncertainty of up to a factor of 2−3 is introduced by this approximation. When combined with the uncertainty in surface coverage and reaction order, this gives a total uncertainty of a factor of 10 in the rate constant.

Within the framework of transition state theory, the free energies of activation can be uniquely determined from the rate constants in Table 1 using the following relations:

$$k_1(T_p) = kT_p/h \exp(-\Delta G^{\ddagger}/RT_p) \qquad (3)$$

$$\Delta G^{\ddagger} = -RT_p \ln(k_1 h/kT_p) \qquad (4)$$

where k is Boltzmann's constant, h is Planck's constant, and T_p is the TPR peak temperature. The uncertainties in $\Delta G^{\ddagger}$ are $RT_p \ln a$ where a is the uncertainty in the rate constant. Thus, an uncertainty of a factor of 10 in the rate constant translates to ~1 kcal/mol for these β-hydride elimination reactions which occur at 150−250 K.

4. Discussion

Table 1 summarizes the kinetic parameters that were determined from the thermal desorption, chemical displacement, and work function change studies described above. While there is some uncertainty in the kinetic parameters (particularly the activation energies and preexponential factors), all of the standard methods of analysis show that there is a dramatic variation in the rates of β-hydride elimination across this series of alkyl groups on Cu(100). For example, if one extrapolates the rates to a common temperature of 200 K using activation energies determined *assuming a common preexponential factor of* 10^{13} s^{-1}, then one finds (see last column of Table 1) that the rates vary by about 7 orders of magnitude.

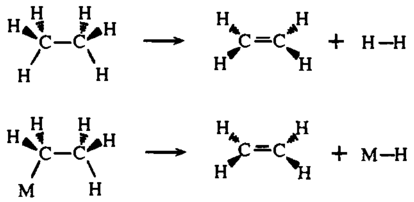
These dramatic rate differences are not unexpected on the basis of what is known about elimination reactions. As mentioned in the Introduction, there are numerous examples where 1,2-eliminations from C_5 rings are orders of magnitude faster than the corresponding eliminations from C_6 rings.[34,37] This result is analogous to what is found here for β-hydride elimination for cyclopentyl vs cyclohexyl. Also, Kemball[67] and Burwell[68] have reported that catalytic H/D exchange around one face of cyclopentane on metal catalysts can be much faster than H/D exchange around one face of cyclohexane. Since this process presumably involves alkyl/olefin equilibration on the surface via β-hydride elimination, it is not surprising that β-hydride elimination is significantly faster in a C_5 vs C_6 alkyls.

4.1. Rationalizing Relative Rates: Entropy vs Enthalpy and Possible Thermodynamic Effects. We turn now to the reason for the dramatic rate variations between these structurally similar alkyls—all of which are bound to the surface through a secondary carbon atom and all of which have single alkyl substituents on both the α- and β-carbons. No doubt, differences in both the enthalpy and entropy of activation play some role; however, to account for the dramatic effects observed, enthalpy effects must be dominant. Minimum and maximum entropies of activation expected for a cyclic four-center transition state like that expected for β-hydride elimination are −4 and 0 eu, respectively.[69] While these limits are for the gas phase elimination reactions, freezing additional rotations in a surface process would be expected to contribute at most 8 eu. Using this upper limit, the rate constant (and rate) varies by ~1.5 orders of magnitude, which is much less than the 7 orders of magnitude observed.

In addressing why the enthalpies of activation might be different in these systems, it is useful to distinguish between changes in the *enthalpies of reaction* (which would also be expected to show up to some extent as changes in the enthalpies of activation) and changes in *the enthalpy of activation* without a corresponding change in the reaction thermodynamics. Unfortunately, Δ*H* for these β-hydride elimination reactions is unknown. Δ*H* for β-hydride elimination by ethyl groups on Cu(100) has been determined to be 6.5 ± 4 kcal/mol,[70] but the procedure used to derive this value (i.e., measuring the activation energy for the reaction in the forward and reverse directions) was not possible for the systems described here where no significant reverse reaction was detectable. It should be noted, however, that the lack of reverse reaction simplifies the kinetic analysis, since one does not have to worry about the enthalpy change from an alkyl/alkene preequilibrium contributing to the activation energy for reaction. In other words, the absence of any preequilibrium has already been assumed in Table 1 by equating the activation energies measured for β-hydride elimination coupled with alkene desorption to the activation energies of β-hydride elimination.

4.2. An Assessment of ΔΔ*H* for β-Hydride Elimination on Surfaces. While the *surface* reaction thermodynamics for these various systems are unknown, we believe that a reasonable estimate of differences between the surface reaction enthalpies, i.e., ΔΔ*H*, can be made on the basis of the *gas phase* values of ΔΔ*H* for the dehydrogenation of alkanes to alkenes. The basis for this comparison is the formal analogy given in Scheme 2

Scheme 2



where M refers to the metal surface. Clearly the enthalpy changes for the two systems in Scheme 2 are quite different, but one might expect similarities among the ΔΔ*H* values for a series of structurally similar alkanes/alkenes in these two systems if it is differences in the hydrocarbon portion of the system which dominate ΔΔ*H*. In the gas phase there is indeed evidence that this is the case. If one replaces an H in the alkane (at the site adjacent to the incipient π-bond) with a CH_3 group to form a methylated alkane, one finds that the ΔΔ*H* values for loss of CH_3−H from the methylated alkane are quite similar to those for loss of H−H from the corresponding alkane. Whether or not the same is true for loss of M−H has not been demonstrated, but it is reasonable to assume that steric and electronic effects of the metal (while different for the reactant and product) would be similar among the structurally-related hydrocarbon systems studied here and therefore while affecting Δ*H* would not contribute significantly to ΔΔ*H*.

Since ΔΔ*H* values for alkane dehydrogenation are essentially equivalent to what are known as "olefin strain energies", it is the commonly tabulated olefin strain energies which are given

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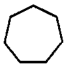
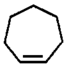
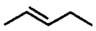
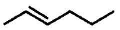
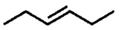
[67] Kemball, C. *Adv. Catal.* **1959**, *11*,

[68] Burwell, R. L., Jr.; Shim, B. K. C.; Rowlinson, H. C. *J. Am. Chem. Soc.* **1957**, *79*, 5142−5148.

[69] O'Neal, H. E.; Benson, S. W. *J. Phys. Chem.* **1967**, *71*, 2903−2921.

[70] Jenks, C. J.; Xi, M.; Yang, M. X.; Bent, B. E. *J. Phys. Chem.* **1994**, *98*, 2152−2157.

Table 2. Comparison of $\Delta\Delta G^{\ddagger}$ for β-Hydride Elimination by Surface Alkyl Groups (Relative to Cyclopentyl) with Olefin Strain Energy and the Minimum Energy (ΔE) Required To Achieve Planarity between the Substituents on α- and β-Carbons for the Indicated Alkane−Alkene Pairs in the Gas Phase

alkane	alkene	olefin strain energy,[a] kcal/mol	ΔE,[b] kcal/mol	$\Delta\Delta G^{\ddagger}_{\mathrm{B-H}}$, kcal/mol
		−2.1	~0	0
		−2.7	~0 (3.4[c])	0
		−1.1	3.5	1.2
		1.5	3.5	1.4
		−1.7	3.5	
		4.8	~0	3.2
		−0.3	5.6	5.5
		1.9	1.4	5.7

[a] In the case of acyclic alkyls, we have used $\Delta\Delta H$ of olefin dehydrogenation[72] (normalized to cyclohexene olefinic strain equal −0.3 kcal/mol) as a measure of the olefin strain energy (see text section 4.2). Values given are for trans isomers; cis isomers will be ~0.5 kcal/mol less negative. [b] ΔE is the difference in energy between the most stable alkane conformation and the lowest energy alkane conformation (not necessarily stable) having eclipsed interactions between C−H bonds on adjacent carbons. [c] Two values are given for cycloheptane because ΔE in this system depends on which pair of carbon atoms we focus; i.e., depending on the conformation and the point of attachment of cycloheptyl to the surface, one expects either an existing adjacent eclipsed interaction or a significant energy barrier to achieve one.

in Table 2. Before discussing the implications of these olefin strain energies for β-hydride elimination on Cu(100), we comment briefly on the meaning of olefin strain. Olefin strain energy is a measure of the differences in the amount of "strain" inherent in the alkene and corresponding alkane. This strain arises from a complex combination of factors such as bond angle distortion, bond extension or compression, torsional angle distortions, and nonbonded repulsions.[46] It should be emphasized that while the hydrocarbons listed in Table 2 have a wide range of strain, the important aspect with respect to the reaction thermodynamics is the difference in the amount of strain between reactant and product, and this quantity is the olefin strain energy.

4.3. Possible Correlation between Olefin Strain Energy and $\Delta\Delta G^{\ddagger}$ for β-Hydride Elimination. Using olefin strain energy (OSE)[46] as a measure of $\Delta\Delta H$ for β-hydride elimination among the alkyls in Table 2, we see that many of the trends in $\Delta\Delta G^{\ddagger}$ can be rationalized. In other words, there appears to be some correlation between changes in the reaction thermodynamics (as qualitatively assessed by OSE) and changes in the reaction kinetics (as quantitatively measured by $\Delta\Delta G^{\ddagger}$). For example, cyclopentene and cycloheptene have similar amounts of olefin strain energy, and the corresponding alkyls have virtually identical free energies of activation. Cyclobutene with about 4 kcal/mol more olefin strain energy has a free energy of activation which is ~5 kcal/mol larger.

However, one clue that changes in the reaction thermodynamics cannot completely account for the differences in rate is the fact that one generally expects only part of $\Delta\Delta H$ for reaction to show up as a change in activation energy. For example, in the empirical Ogg−Polanyi relationship[71] for structurally analogous reactions

$$E_a = E_a' = \alpha(\Delta H - \Delta H')$$

the value of α is generally between 0 and 1. On the other hand, if one takes the $\Delta\Delta G^{\ddagger}$/OSE correlation literally, then α is in some cases even greater than 1 for the systems given in Table 2. For example, the OSE ($\Delta\Delta H$) for cyclohexene is 1.8 kcal/mol larger than that for cyclopentene, yet $\Delta\Delta G^{\ddagger}(\Delta E_a)$ for the corresponding alkyl β-elimination reactions differs by 5.5 kcal/mol. The reverse situation exists for norbornyl. $\Delta G^{\ddagger}$ is much smaller than expected on the basis of the OSE. In the case of norbornyl, we suspect that the correlation may fail because of the extremely rigid conformational constraints and the large steric bulk of this alkyl group. It is probable that the amount of steric hindrance between the alkyl and the surface is significantly larger than for the other alkyls, while similar differences are probably not operative for the product alkene which is only weakly coordinated to the surface;[56] the net effect is that the reactant alkyl may be destabilized relative to the other alkyl groups, thereby giving rise to the significantly lower $\Delta G^{\ddagger}$ than one would expect on the basis of the increase in strain during the reaction. On the other hand, the structural similarities among cyclohexyl, cycloheptyl, and cyclopentyl suggest that factors other than sterics are necessary to account for the lack of correlation between OSE and $\Delta\Delta G^{\ddagger}$. The predominant effect, we believe, is relative conformational stabilities and the necessity of planarity in the transition state as discussed below.

4.4. Evidence for a Planar Transition State for β-Hydride Elimination. One possible kinetic explanation for the dramatic effect of alkyl structure on the β-elimination rate is the inductive effect of substituents on the α- and β-carbon atoms. It has been shown in the literature[28] that inductive electronic effects can have order of magnitude effects on the rates of β-hydride elimination. In the studies here, however, all of the alkyls studied are bonded to the surface through a secondary carbon and each has a single alkyl substituent at both the α- and β-positions. One would thus expect similar inductive electronic effects. Furthermore, one would also expect these structurally similar alkyls to have similar steric interactions with the surface.

A more likely explanation is that alkyl conformation plays an important role. The relative conformational energies in cyclic and acyclic compounds vary significantly, and as discussed in the Introduction, both theory and experiment suggest that a planar transition state (i.e., a specific conformation) is required in concerted 1,2-elimination reactions which convert hydrocarbons to olefins. Conceptually, a planar transition state can be rationalized as necessary in order to maximize the overlap between the p-orbitals in the incipient π-bond in these elimination reactions.

The results here are consistent with the idea that a similar conformational geometry is also important for surface β-hydride elimination reactions. The strongest experimental evidence is the dramatic differences in rate for cyclohexyl vs cyclopentyl and cycloheptyl−differences which do not appear to correlate with changes in the surface reaction thermodynamics. These differences can be rationalized on the basis of the very different energies required to achieve a conformation where the $M-{}^{\alpha}C$ and ${}^{\beta}C-H$ bonds lie in the same plane. While these energies are not known on the surface, the gas phase values for achieving an eclipsed conformation of adjacent C−H bonds in the

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[71] This relation was firstly published by M. G. Evans and M. Polanyi (*Trans. Faraday Soc.* **1938**, *34*, 11−29) but the "Ogg−Polanyi" descriptor was used by J. C. Polanyi (*Chem. Phys. Lett.* **1967**, *1*, 421−423).

[72] Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermodynamical Data of Organic Compounds*; 2nd ed.; Chapman and Hall: London, 1986; p 792.

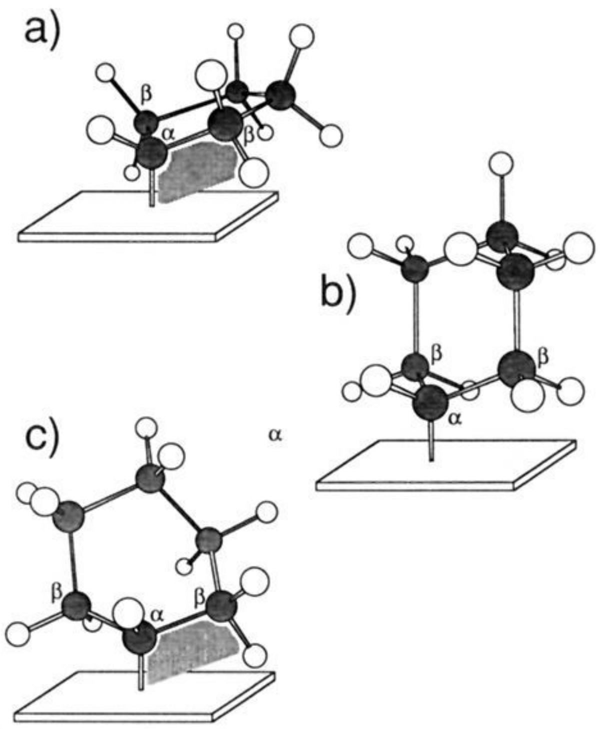

Figure 10. Accessibility of the planar transition state for β-hydride elimination in cyclopentyl and cyclohexyl groups on a surface: (a) cyclopentyl (envelope conformation); (b) cyclohexyl (chair conformation); (c) cyclohexyl (boat conformation).

corresponding alkanes are given in Table 2. It is clear from these values that, unless things change dramatically on the surface, achieving an eclipsed conformation in cyclohexyl requires significantly more energy than for the C_5 and C_7 cyclic alkyls. In fact, if the 5.5 kcal/mol difference for the gas phase were to show up in $\Delta\Delta G^{\ddagger}$ for the surface β-elimination reactions, then the rate for cyclohexyl would be a factor of 10^6 smaller than that for cyclopentyl, which is close to what is observed experimentally. Schematic representations of the relevant structures are shown in Figure 10. Similarly, for the other alkyls (except norbornyl, which we believe to be an exception as discussed above), the values for achieving an eclipsed conformation between adjacent C$-$H bonds are consistent with the relative rates observed.

One final note: On the surface, defining a planar transition state in terms of the M$-^{\alpha}$C bond can be ambiguous depending on the alkyl adsorption site and the points on the surface to which one assumes that the alkyl group is bonded. A rigorous definition of a transition state geometry which maximizes p-orbital overlap in the incipient π-bond is that the dihedral angle between the substituents on the α- and β-carbon atoms should be zero.

5. Conclusions

The results here show that a series of secondary alkyl bromides react thermally on a Cu(100) surface by formal 1,2-elimination of HBr to evolve the corresponding alkene at temperatures below 250 K. These elimination reactions occur by a two-step process involving first C$-$Br bond dissociation and subsequently β-hydride elimination. The H and Br atoms produced by these reactions remain adsorbed on the Cu(100) surface up to temperatures of 300 and 930 K, respectively. While the rates of C$-$Br scission are quite similar among these alkyls, the rates of β-hydride elimination (when extrapolated to a common temperature) vary by orders of magnitude. Comparison of the measured free energies of activation with qualitative assessments of the reaction thermodynamics and with the expected conformational requirements for the reaction provides evidence for the important role of ring strain and planarity in the transition state.

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