Regioselectivity of Deuterium Atom Addition to Olefin Monolayers on Cu(100)

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The addition reaction of gas-phase D atoms to olefin monolayers adsorbed on a Cu(100) surface is studied, with a focus on the regioselectivity of deuterium addition onto monolayer 1-butene and 1-pentene molecules. Both 1- and 2-alkyl groups are generated from D atom additions to 2° and 1° carbons, respectively. The alkyl groups are separated based on a difference in their β-hydride elimination kinetics, with the rate of 2-alkyl groups losing β-hydrogens about 2 orders of magnitude faster than 1-alkyl groups on the copper surface. The results suggest that D addition to terminal (1°) carbon is favored by a factor of ∼3 for 1-butene and ∼4 for 1-pentene molecules adsorbed on the surface.

1. Introduction

Mechanistic studies of hydrogen atom addition to unsaturated compounds have become a popular topic in the past 50 years.[1−4] One of the simplest examples is hydrogen atom addition to alkene molecules, an interesting aspect of which is the regioselectivity of the addition, i.e., the position of H atom addition with respect to two inequivalent carbon atoms in the C=C double bond.

The vast majority of past studies were performed in the gas phase. Moore et al. examined hydrogen atom addition to propylene and 1-butene at 300 and 573 K.[5,6] Their results indicate that hydrogen atoms add predominately, if not exclusively, to the less substituted carbon atom of the C=C double bond. Isopropyl and 2-butyl radicals are the overwhelming products in H atom addition to propylene and 1-butene molecules, respectively. Additional studies indicate that there is a 5−7% possibility of nonterminal addition for H (D) atom addition to propylene and 1-butene,[1,5−8] and there is little isotope effect of the regioselectivity.[1] H atom addition to propylene has an activation energy of ∼1.3 kcal/mol,[9,10] with an activation energy difference of ∼1.5 kcal/mol between terminal and internal additions.[1,10]

The reaction of hydrogen atoms with olefin thin films condensed below 100 K was investigated by Klein and Scheer.[3,4] Similar to the gas-phase results, H atom adds predominately to the terminal carbon atom in propylene and 1-butene molecules. Based on the experimental results, an upper limit of ∼4% is determined for the nonterminal addition of H atom to a condensed propylene thin film. The reaction activation energy is 1.5 kcal/mol.[11]

We examine D atom addition to alkene monolayers adsorbed on a Cu(100) surface. It has been well documented in previous studies that hydrogen atoms impinging from the gas phase can, before equilibrating thermally with the substrates, react with monolayer olefin molecules adsorbed on metal surfaces.[12−18]

In particular, alkyl groups can be generated in a direct hydrogen atom addition to monolayer olefin molecules on copper.[12,14,17,18] In this paper, we report the regioselectivity of H (D) atom addition to 1-butene and 1-pentene monolayers adsorbed on Cu-(100) at 100 K. Both 1- and 2-alkyl groups are formed upon hydrogen atom addition to 2° and 1° carbons, respectively. During a subsequent heating of the sample, surface alkyl groups undergo β-hydride elimination to yield corresponding alkene molecules, which are liberated from the surface as soon as they are produced. The β-hydride elimination temperature is significantly different for 1- and 2-alkyl groups. This difference is exploited to quantify the surface coverage of 1-alkyl and 2-alkyl groups in a temperature ramp, en route to a determination of the regioselectivity of the addition reactions. Our experimental results indicate that terminal addition predominates in H (D) addition to monolayer 1-butene and 1-pentene molecules on Cu(100). However, there is a 20−25% nonterminal addition, which differs from the results obtained in gas-phase and condensed multilayer film experiments.[1,3−8] The regioselectivity difference is discussed in section 4.2.

2. Experimental Section

Experiments were performed in an ultrahigh-vacuum (UHV) chamber with a base pressure of 5×10^{-10} Torr. The system was equipped with an ion gun, an Auger electron spectrometer, a high-resolution electron energy loss spectrometer, an infrared spectrometer, and a differentially pumped mass spectrometer.[19] The Cu(100) crystal (Monocrystals Inc., 1 cm in diameter and 2 mm thick) was fastened to a molybdenum button heater by a chromel wire passed through slots on the edge of the crystal, and the button heater was mounted on the manipulator (Vacuum Generators, HPLT 305). The sample temperature was monitored by a chromel−alumel thermocouple junction wedged into a hole on the side of the crystal. The sample could be heated resistively to 1000 K and cooled with liquid nitrogen to 100 K. Heating was provided by a dc power supply (Hewlett-Packard, 6291A) and controlled by a temperature programmer (Eurotherm 818P). The copper crystal was cleaned by Ar⁺ sputtering followed by annealing in UHV at 980 K,[20] and surface cleanliness was confirmed by Auger electron spectroscopy. Temperature-programmed desorption (TPD) studies were conducted with the center of the crystal positioned 2 mm away

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from an aperture in front of a mass spectrometer to detect the species desorbing from the center of the crystal. The heating rate was 3 K/s. Unless otherwise specified, an electron impact ionization energy of 70 eV was utilized in the experiments.

With the exception of benzene (Fisher, 99%), all liquid compounds were purchased from Aldrich with a purity not lower than 99%. They were purified by several freeze−pump−thaw cycles before being introduced into the chamber. Gases, deuterium (Matheson, 99.5%) and 1-butene (Matheson, 99.9%), were used as supplied. The sample purities were monitored in situ by the mass spectrometer. Exposures were achieved by backfilling the chamber through leak valves and are reported in units of langmuirs (1 langmuir = 1 × 10^{-6} Torr s).

Deuterium atoms were generated by dissociation of deuterium molecules on a hot (∼1800 K) tungsten filament and were impinged onto the copper crystal positioned ∼2 cm line-of-sight in front of the filament. The electron irradiation from the tungsten filament to the Cu(100) surface is less than 10^{-7} A. The potential electron-induced dissociation/desorption (EID) of monolayer molecules on the Cu(100) surface is investigated. The electron dosage can be adjusted by time and a bias voltage applied on the copper surface. No variation of TPD/R profiles was observed for surface alkene/alkyl groups after different electron exposures. It indicates a negligible EID of alkene molecules and alkyl groups on the copper surface.[12]

Under a deuterium pressure of 1 × 10^{-6} Torr, deuterium atom exposures are proportional to the exposures of D_2 molecules to the filament. An exposure of ∼50 langmuirs of D_2 is required to saturate a clean Cu(100) surface with D atoms. The saturation coverage of deuterium is calibrated as 1.2 × 10^{15} D atoms/cm^2.[21] A lower limit of the D atom flux is estimated from a linear uptake of surface D atoms at very low coverages, assuming a sticking probability of unity for incoming D atoms and a negligible abstraction of surface D atoms. The calculated deuterium atom flux is 4.0 × 10^{13} atoms/(s cm^2) at a D_2 pressure of 1 × 10^{-6} Torr.

3. Results

Alkyl groups are the predominate products in a direct reaction of atomic hydrogen with monolayer alkene molecules adsorbed on copper surfaces.[12] The H atom addition is much faster than the competing H atom abstraction reaction.[12] If the two carbon atoms in a double bond are nonequivalent, two different alkyl groups can be produced depending on the position of H atom addition. For instance, a hydrogen atom reaction with 1-butene molecules can generate 1-butyl and 2-butyl groups, upon H addition to 2° (internal) and 1° (terminal) carbon atoms, respectively. Neither the precursor 1-butene molecules nor the surface butyl groups undergo isomerization reactions on the copper surface.[22] As a result, the ratio of surface 1- and 2-butyl groups reflects the regioselectivity of hydrogen addition to 1-butene molecules on Cu(100).

To quantify the regioselectivity of the hydrogen addition reaction, an effective approach should be developed to distinguish surface-bound 1- and 2-alkyl groups. Due to small difference in their electronic structures and vibrational frequencies, the two alkyl groups cannot be readily quantified by surface electronic and vibrational spectroscopies. In the present work, a separation between 1- and 2-alkyl groups is accomplished by exploiting the difference in their β-hydrogen elimination kinetics. It has been reported that alkyl groups are stable on the copper surface below 200 K. At a surface temperature above 200 K, alkyl groups undergo a β-hydrogen elimination reaction on single-crystal copper surfaces, forfeiting a hydrogen atom

to the surface and yielding corresponding alkene molecules.[22] Despite similarities in their overall reaction schematics, different alkyl groups have significantly different β-elimination temperatures on Cu(100), ranging from 155 K for cyclopentyl groups to 255 K for ethyl groups.[22] For small (<C_5) alkyl groups, the alkene molecules formed by the β-elimination reaction are released promptly from the surface. As a result, by ramping the surface temperature and monitoring alkene evolution in the gas phase, different surface alkyl groups can be identified from their characteristic β-hydrogen elimination temperatures.

We organize our experimental results as follows. β-Hydride elimination of 1-butyl and 2-butyl groups on Cu(100) is first discussed in section 3.1. Exploiting the difference in the β-hydrogen elimination kinetics of the two alkyl groups, the regioselectivity of hydrogen atom addition to monolayer 1-butene molecules is determined, as described in section 3.2. Finally, results for the H atom addition to 1-pentene molecules are presented in section 3.3.

3.1. β-Hydride Elimination Reactions of Primary and Secondary Alkyl Groups. The β-hydride elimination reactions of different alkyl groups are studied by temperature-programmed reaction/desorption (TPR/D). Parts a and b of Figure 1 present TPR/D spectra of butene (C_4H_8, m/e = 56) evolution from 1-butyl and 2-butyl groups, respectively. In the experiments, 1- and 2-butyl groups are prepared on Cu(100) by thermal dissociation of the corresponding butyl bromides. In each case, the butyl bromide exposure is 2 langmuirs, which is approximately 35% of a monolayer saturation. Previous studies have indicated that C−Br bond cleavage in butyl bromides occurs on Cu(100) below 180 K to form butyl groups and chemisorbed bromine atoms on the surface.[23] At low coverages, coadsorbed halogen (bromine) atoms do not have a substantial effect on β-hydride elimination kinetics of alkyl groups.[17]

From chemical intuition, we can anticipate the formation of 1-butene molecules from 1-butyl groups. The β-elimination product for 2-butyl groups, however, is less apparent. Since 1-butene and 2-butene molecules have practically indistinguishable cracking patterns in the mass spectrometer,[24] the β-hydride elimination product cannot be assigned unambiguously. We tentatively attribute it to 2-butene based on a recent systematic study of β-hydride elimination reactions on Cu(100), which suggests the formation of 2-alkene molecules from a β-hydride elimination reaction of 2-alkyl groups.[22] The results are also confirmed in our studies of D atom addition to pentene, as shown later in section 3.3.

A thermal desorption spectrum of a 1-butene monolayer from the surface is presented in Figure 2 as a reference. The thermal desorption spectrum of a 2-butene monolayer is very similar. A majority of monolayer 1-butene molecules are liberated from Cu(100) at ∼160 K. A small fraction of 1-butene molecules desorb at a higher temperature of ∼225 K, which can be assigned to desorption of butene from surface defect sites. This is supported by the observation that the 225 K peak is significantly enhanced for butene desorption from a surface intentionally roughened by ion bombardment.

As shown in Figure 1b, two features are observed for butene evolution from 2-butyl groups: a dominant peak at 197 K and a small peak at 225 K. Since the temperature of 197 K is substantially higher than the temperature of 160 K for butene molecular desorption from surface terrace sites, it should be assigned to a reaction-limited butene evolution upon β-hydrogen elimination of 2-butyl groups. The 225 K peak is attributable to a desorption of residual butene molecules from surface defect sites, as observed for butene molecular desorption in Figure 2.
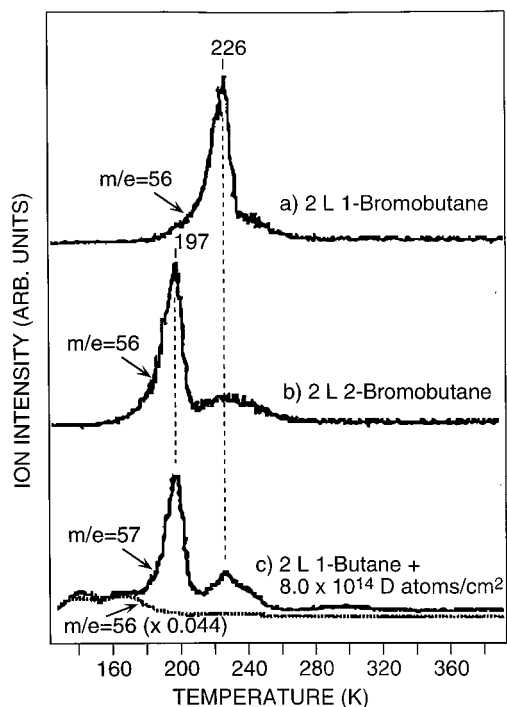
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Figure 1. Temperature-programmed reaction/desorption spectra of (a) butene ($m/e = 56$) evolution from 1-butyl groups; (b) butene ($m/e = 56$) evolution from 2-butyl groups; (c) butene-d_1($m/e = 57$) and butene-d_0 ($m/e = 56$, ×0.044) evolution after exposure of deuterium atoms to a Cu(100) surface precovered by 2 langmuirs of 1-butene at 100 K. In the experiments for (a) and (b), 1- and 2-butyl groups are generated on the Cu(100) surface by dissociation of the corresponding butyl bromides. In (c), butene-d_1 ($m/e = 57$) is evolved from butyl-d_1 groups formed in D atom addition to 1-butene on Cu(100). In the TPR/D experiments for both $m/e = 56$ and $m/e = 57$, the mass spectrometer was operated with an electron impact ionization energy of 15 eV to minimize the fragmentation of the molecular ions.
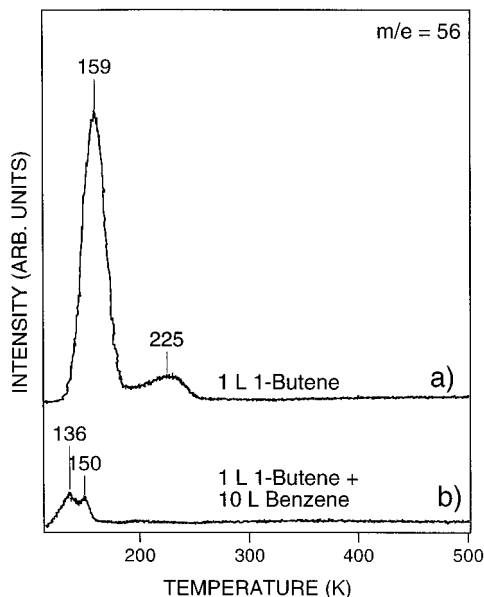

Figure 2. Temperature-programmed molecular desorption (TPD) spectrum of 1-butene on Cu(100).

The peak assignments are substantiated by complementary chemical displacement experiments, which will be discussed later in this section.

As evident in Figure 1a, butene evolution from 1-butyl groups is observed at 225 K. The peak area, which is proportional to the desorption yield, is significantly higher than that of butene

desorption from defect sites as shown in Figures 1b and 2. Hence, the butene desorption at 225 K cannot be attributed solely to desorption from surface defect sites. It should rather reflect the true butene formation temperature in the β-hydrogen elimination of 1-butyl groups. This conclusion is also confirmed in the chemical displacement experiments.

Chemical displacement is a phenomenon in which an adsorbate is displaced from the monolayer by another species that binds more strongly to the substrate.[25] It has been demonstrated that chemical displacement can be applied in surface reaction studies, especially in the determination of surface reaction temperatures. In the present work, we exploit the fact that monolayer butene molecules (weakly bound, physisorbed on Cu(100)) can be displaced by benzene molecules while butyl groups (strongly bound, chemisorbed on Cu(100)) remain intact on the surface. Benzene molecules undergo neither decomposition nor cross reaction with alkyl groups on the surface.

As shown in Figure 3a,b, in the presence of coadsorbed benzene molecules, butene evolution is evident at 234 K for 1-butyl and at 205 K for 2-butyl groups, respectively. These temperatures are similar to the main features of butene evolution in the absence of coadsorbed benzene molecules shown in Figure 1a,b. A notable difference, however, is the disappearance of the small 225 K peak in butene evolution from 2-butyl groups on benzene-covered surface. This observation again suggests that the original 225 K peak is due to butene desorption from surface defect sites, which are blocked effectively by coadsorbed and more strongly bonded benzene molecules.

3.2. Regioselectivity of D Atom Addition to Monolayer 1-Butene Molecules. Butyl groups are generated by H atom addition to monolayer 1-butene molecules on Cu(100) at 100 K. In a postreaction warm-up of the surface, butyl groups are converted back to butene via a β-hydride elimination. In an attempt to distinguish the butene evolution in the β-H elimination from the desorption of butene molecules unreacted during the H addition, we chose deuterium atoms in place of hydrogen atoms in the addition reaction. A deuterium atom addition to terminal (1°) carbon atoms generates 2-butyl-d_1 groups ($-CH(CH_2D)CH_2CH_3$), with one deuterium and four hydrogen atoms at the β-position. On the other hand, a deuterium atom addition to internal (2°) carbon atoms produces 1-butyl-d_1 groups ($-CH_2CHDCH_2CH_3$), with one D and one H atom at the β-position. In either case, due to the isotopic ratio at the β-position and an isotope effect of ~10 in favor of the hydrogen elimination,[14,18] butyl-d_1 groups forfeit predominately a β-H to yield butene-d_1. Butene-d_1 evolution in β-H elimination can be monitored by mass spectrometry with little interference from the desorption of butene-d_0 molecules that are unreacted in the D addition reaction. Figure 1c presents a TPR/D spectrum of butene-d_1 ($m/e = 57$) evolution after 8×10^{14} D atoms/cm^2 are exposed onto the surface precovered by 2 langmuirs of 1-butene molecules. Two small peaks at 140 and 165 K are observed in butene-d_1 evolution. They are attributable to the desorption of $M + 1$ isotopes of butene molecules unreacted in the D addition reaction. Such a contribution is shown in Figure 1c as a dotted line, which was obtained by recording the butene ($m/e = 56$) evolution and multiplying it by a factor of 4.4% for the natural abundance of ^{13}C in C_4H_8.[26] The difference between the solid and dotted lines in Figure 1b represents the butene-d_1 evolution from surface butyl-d_1 groups, which are formed in the D atom addition to 1-butene.

The cross section for D atom addition to 1-butene on Cu-(100) can be calculated from[12,17]

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$$S_r = \frac{d[C_4H_8D]/dt}{[C_4H_8]\Phi_D} \quad (1)$$

where Φ_D is the D atom flux, t is the D atom exposure time, and $[C_4H_8]$ and $[C_4H_8D]$ are the surface coverages of 1-butene-d_0 and butyl-d_1 groups, respectively. On the Cu(100) surface, butyl-d_1 (C_4H_8D) groups are transformed exclusively to butene-d_1 (C_4H_7D) in β-H elimination. For a low conversion of C_4H_8 in the D atom addition reaction (at the limit of a small deuterium atom exposure), eq 1 can be simplified to

$$S_r \approx \frac{[C_4H_7D]}{[C_4H_8]\Phi_D t}$$

where the reaction cross section S_r can be derived from the yields of butene-d_0 (C_4H_8, $m/e = 56$) and butene-d_1 (C_4H_7D, $m/e = 57$) in the TPR/D experiments. As shown in Figure 1c, the TPR/D peak area of butene-d_1 (C_4H_7D, $m/e = 57$) evolution is 19% of that of butene-d_0 (C_4H_8, $m/e = 56$). Notice that the $m/e = 56$ spectrum is multiplied by a factor of 0.044 in the plot. If we assume the same ionization probability for the two butene molecules, the ratio of the peak areas directly reflects the relative thermal desorption yields. The largest uncertainty in the calculation is the estimation of D atom flux. Using the lower limit of D atom flux calibrated in the Experimental Section, we obtain an upper limit of 2 Å^2 for the reaction cross section.

In comparison, the cross section for the gas-phase reaction at 295 K is estimated to be ~12 Å^2, based on a cross section of ~6 Å^2 for a hydrogen addition to *cis*-2-butene[27] and an approximate 2:1 ratio for the rates of H addition to 1-butene and *cis*-2-butene molecules.[2,28] The cross-section data for gas-phase and surface reactions are consistent within 1 order of magnitude. The difference can be probably attributed to the temperature difference and a possible isotope effect in the addition reaction.

As shown in Figure 1, the majority of butene-d_1 evolution from butyl-d_1 groups is observed at 197 K, with a minor peak evident at 226 K. The ratio of 197 K to 226 K peak areas is ~2.9:1. By comparing the TPR/D spectrum to the reference spectra in Figure 1a,b, the 197 K peak can be assigned to a butene evolution from 2-butyl-d_1 groups, while the 226 K peak can be attributed to a β-H elimination of 1-butyl-d_1 groups and/or a butene desorption from surface defect sites after its formation. Both 1-butene and 2-butene molecules, which are the possible β-hydride elimination products of butyl groups, have similar ionization probability and cracking pattern in our mass spectrometer. As a result, the ratio of 197 K to 226 K peak areas sets a lower limit on the ratio of 2-butyl-d_1 to 1-butyl-d_1 groups formed in D addition to 1-butene molecules. The predominate 2-butyl-d_1 group formation indicates a preference of a D atom addition to terminal carbon atoms in 1-butene molecules.

A quantitative determination of the regioselectivity can be obtained in chemical displacement experiments. As mentioned in section 3.1, coadsorbed benzene molecules eliminate the butene desorption from surface defect sites on Cu(100), while having little influence on the reaction kinetics of surface-bound butyl groups. Figure 3c presents a TPR/D spectrum of butene-d_1 ($m/e = 57$) evolution after the surface precovered with 1-butene is exposed to D atoms and then to 10 langmuirs of benzene. With benzene molecules displacing unreacted butene molecules and effectively blocking surface defect sites, the ratio of 197 K to 226 K peak areas in the butene-d_1 evolution is 3.1:1. This ratio is very close to the result (2.9:1) obtained from
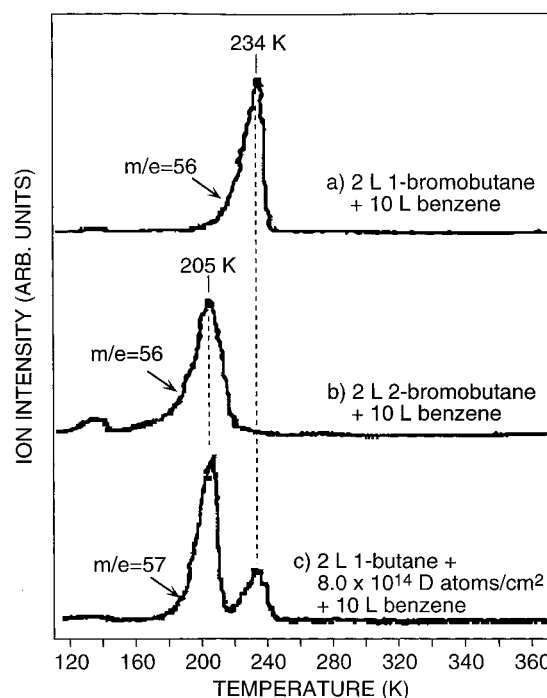

Figure 3. Application of chemical displacement reactions to analyze the regioselectivity in the reaction of atomic deuterium with 1-butene on Cu(100). (a) butene ($m/e = 56$) evolution from 1-butyl groups; (b) butene ($m/e = 56$) evolution from 2-butyl groups; (c) butene-d_1 ($m/e = 57$) evolution from butyl-d_1 groups formed by atomic deuterium addition to 2 langmuirs of 1-butene molecules physisorbed on Cu(100). In all three cases 10 langmuirs of benzene (~3 monolayers) was added to the surface as a displacing agent right before the temperature-programmed desorption experiments.

Figure 1c, which was collected in the absence of displacing agent on the surface. A 3:1 ratio in 2-butyl/1-butyl population corresponds to a 25% probability for the nonterminal addition of D atom to 1-butene molecules.

The regioselectivity of the D addition reaction is independent of the D atom exposure. As shown in Figure 4, the ratio of 2-butyl groups to 1-butyl groups produced in D addition reaction remains constant for a deuterium atom exposure up to 2×10^{15} D atoms/cm^2. At higher deuterium exposures, double addition and abstraction reactions become significant in the reaction scheme.

3.3. β-Hydride Elimination in 1- and 2-Pentyl Groups and D Atom Addition to Monolayer 1-Pentene Molecules on Cu-(100). In a similar fashion, we have also examined the regioselectivity of D atom addition to 1-pentene molecules on Cu(100). 1-Pentyl-d_1 and 2-pentyl-d_1 groups are formed from a D atom addition to internal and terminal carbon atoms, respectively. They are separated and quantified by a difference in their β-hydride elimination kinetics.

Figure 5 presents TPR/D spectra of pentene evolution from the β-elimination of 1- and 2- pentyl groups. The pentene molecules formed in the β-hydride elimination reaction can be readily identified using their characteristic cracking patterns in the mass spectra.[24] 1-Pentyl group yields exclusively 1-pentene in the β-H elimination, while 2-pentene is the product in 2-pentyl reactions. These results are consistent with a recent report.[23] As shown in Figure 5, pentene evolution was observed at 225 K for 1-pentyl groups and 202 K for 2-pentyl groups. Since the evolution temperatures are significantly higher than the thermal desorption temperatures of either 1-pentene or 2-pentene monolayer, pentene evolution from 1- and 2-pentyl groups is indicative of the kinetics of the β-H elimination reaction.

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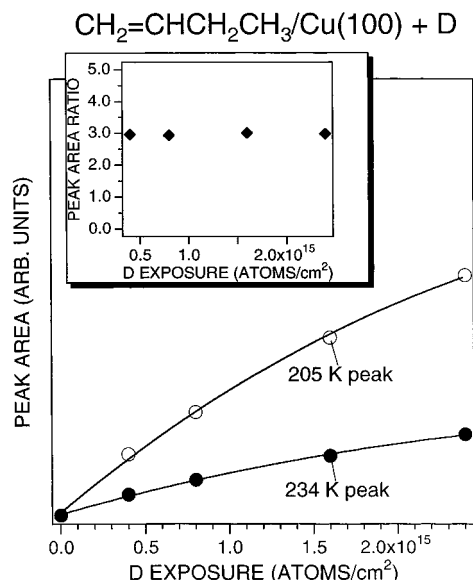*J. Phys. Chem. B, Vol. 102, No. 16, 1998* **2989**

Figure 4. 1-Butyl-d_1 (black circles) and 2-butyl-d_1 (open circles) yields in D atom addition to 2 langmuirs of 1-butene on Cu(100) as a function of deuterium atoms exposure. The 1-butyl-d_1 and 2-butyl-d_1 yields are determined from the area of ~205 and ~234 K peaks in butene-d_1 evolution collected in the presence of 10 langmuirs of benzene on surface as displacing agent.
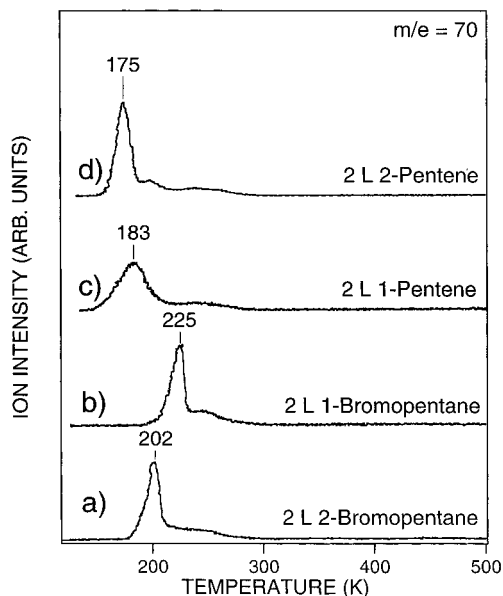

Figure 5. Pentene evolution from (a) 1-pentyl, (b) 2-pentyl, (c) 1-pentene, and (d) 2-pentene on the Cu(100) surface. Both 1- and 2-pentyl groups are generated on the Cu(100) surface by dissociation of the corresponding pentyl bromides.

The regioselectivity of D addition to 1-pentene on Cu(100) is determined in an approach similar to that for the reaction of D with 1-butene. As shown in Figure 6, pentene-d_1 evolution is observed at 204 and 228 K, which is attributable to β-H eliminations of 2- and 1-pentyl groups, respectively. The ratio of 204 K to 228 K peak areas is ~4:1 and is independent of the chemical nature of the displacing agents (in this case cyclohexene) on the surface. The ratio is very close to the ratio of ~3:1 determined in the D addition reaction to 1-butene molecules.

4. Discussion

4.1. Difference in β-Elimination Reaction Kinetics for Different Alkyl Groups.
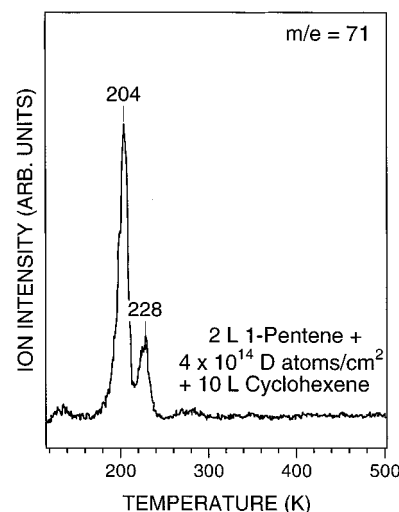Along with the previous studies,[22,23]

Figure 6. Temperature-programmed reaction/desorption spectra of pentene-d_1 ($m/e = 71$) evolution from pentyl-d_1 groups formed in D atom addition to 2 langmuirs of 1-pentene molecules. Cyclohexene (10 langmuirs) was placed on the surface as a displacing agent before the TPR/D experiment. The ratio of 204 and 228 K peak area is indicative of the regioselectivity of the D atom addition reaction.

our experimental results indicate a difference in the β-elimination reaction kinetics for primary and secondary alkyl groups. In particular, a difference of 30 K in β-elimination temperature is observed for 1- and 2-butyl groups in a linear temperature ramp with a heating rate of 3 K/s. This corresponds to a reaction rate difference of about 2 orders of magnitude at a common reaction temperature of 200 K.

In refs 23 and 22, the β-H elimination rates have been compared for a collection of alkyl and cycloalkyl groups on copper surfaces. Depending on the alkyl group structure, the β-H elimination temperature varies from 155 to 260 K on a Cu(100) surface.[22] This temperature difference is equivalent to about 6 orders of magnitude difference in the reaction rate at a common temperature of 200 K. The same studies also reported that the β-H elimination temperatures of secondary alkyl groups are lower than those of primary alkyl groups with the same chain length.[22]

4.2. Regioselectivity of H (D) Atom to Monolayer Alkene Molecules on Cu(100).
In the present work, we investigated D atom addition to monolayer 1-alkene molecules on Cu(100) at a surface temperature of 100 K. The predominate reaction product is 2-butyl groups, which are formed in a D addition to 1° carbons of surface-bound butene molecules.

The formation of 2-butyl radicals is thermodynamically favorable. Compared with 1-butyl radicals, 2-butyl radicals are thermodynamically more stable. Taking into account the heat of formation of 52 kcal/mol for H atom, 0.03 kcal/mol for 1-butene molecules, 18 kcal/mol for 1-butyl, and 15 kcal/mol for 2-butyl radicals,[26] the enthalpy change of H atom addition reaction to 1-butene is ~−34 and −37 kcal/mol for formation of 1- and 2-butyl radicals, respectively.

Although D atom addition to less substituted carbon atoms prevails, the probability of nonterminal addition is 20−25%, which is considerably higher than the selectivity in gas-phase and condensed layer reactions. In the gas phase[5,6] and in condensed layers,[3,4] terminal addition prevails in the H atom addition to 1-alkene molecules. For H (D) atom addition to propylene and 1-butene molecules, the ratio for nonterminal addition never exceeds 5−7% and shows little isotope effect.

Although a detailed study is necessary to address the difference in the reaction selectivity in different systems, we

would like to propose some possible explanations based on thermodynamic and steric considerations. For the sake of simplicity, we focus our discussion on the addition reaction of H atom to 1-butene.

The butyl group distribution likely depends on the extent of butyl radical exchange, which is related to the radical lifetime. It is evident that the lifetime of butyl radicals is different in the gas phase, in the condensed thin films, and on the Cu(100) surface. In the gas phase, butyl radicals decompose into methyl and propylene.[6] In the condensed 1-butene multilayer films, disproportionation and combination reaction products were observed.[3] On Cu(100), however, neither decomposition nor coupling products were detected. Butyl radicals, if they ever existed on the surface, were trapped on the surface at 100 K. It is thus predictable that the lifetime of butyl radicals is the shortest on the Cu(100) surface.

The regioselectivity difference between gas-phase and surface reactions might be attributed to a short lifetime of 1-butyl radicals on the surface, which inhibits a transformation of 1-butyl to 2-butyl radicals. An absence of 1-butyl to 2-butyl transformation is equivalent to a lack of 1,2 H shift in butyl radicals prior to their thermal accommodation to the surface. It has been reported that such a H (D) atom scrambling between two carbon atoms is absent upon a H (D) addition to monolayer ethylene molecules on Cu(100).[18]

The regioselectivity difference between gas-phase and surface reactions may also be attributed to a steric effect. In H atom addition to alkene molecules in the gas phase, H atoms strike alkene molecules from every incidence angle, and the apparent reaction probability is averaged over all the relative geometries of H atom and alkene molecules. However, H atom addition to monolayer alkene molecules on Cu(100) has a defined geometry. Surface vibrational spectroscopy[17] and X-ray absorption studies[29,30] indicate that monolayer alkene molecules lie with their double bonds nearly parallel to the copper surface. In our studies, H atoms are impinged onto the surface from normal incidence. An isotope labeling study of H atom addition to cyclohexene on Cu(100) suggests that H atom addition occurs exclusively from the top of a double bond, presumably upon direct impact of H atoms onto the alkene molecules.[17]

It is predictable that an H atom addition to a 2° carbon faces more spatial restraint introduced by the side alkyl groups. Compared with a random distribution of incidence angles of H atoms in gas phase and condensed layers, the defined geometry for H addition to monolayer 1-butene molecules on Cu(100) will likely reduce the steric hindrance of H atom addition to the internal (2°) carbon. As a consequence, the relative probability of H addition to the 2° carbon might be enhanced.

5. Summary

In this study, we examined the addition reaction of gas-phase H atoms to 1-butene and 1-pentene monolayers adsorbed on a Cu(100) surface at 100 K. The results suggest that, for both 1-butene and 1-pentene monolayers, H addition to terminal (1°) carbon predominates to generate 2-alkyl groups. The probability of nonterminal addition is 20−25%, which is significantly higher than previous reports in the gas phase and in condensed layer studies.

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