# H and D Atom Addition to Ethylene on Cu(100): Absence of Ethyl H/D Shift and Decomposition

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The addition of gas phase H and D atoms to unsaturated hydrocarbons physisorbed on metal surfaces is a viable synthetic route to partially-deuterated alkyl groups on the surface (Jenks, C. J.; Xi, M.; Yang, M. X.; Bent, B. E. J. Phys. Chem. 1994, 98, 2152–2157). Because these processes are exothermic by  $\sim 60$  kcal/ mol, the possibility of alkyl decomposition and/or rearrangement prior to thermal accommodation with the surface (a possibility not explicitly addressed in prior studies) should be considered. In the studies here, these decomposition and rearrangement possibilities have been investigated by studying H and D atom addition to variously-deuterated ethylenes physisorbed on a Cu(100) surface. Ethyl decomposition by C-H, C-D, or C-C bond scission has been addressed and shown not to occur by comparison with results from previous studies of the surface species that would be formed by these bond scission processes. H/D shift between the two carbons of the ethyl groups has been addressed by heating the surface to induce  $\beta$ -hydrogen or  $\beta$ -deuterium elimination. The resulting alkene product ratios are compared with those for  $\beta$ -elimination from selectivelydeuterated ethyl groups formed by an independent route, i.e., the dissociative adsorption of a labeled bromoethane. The results show that the extent of H/D shift, if it occurs at all, is <5%. On the basis of this finding and the product ratios, it is determined that the kinetic isotope effect  $(k_{\rm H}/k_{\rm D})$  for  $\beta$ -hydrogen/ $\beta$ -deuterium elimination is 9.5  $\pm$  0.4 at ~260 K on Cu(100). No secondary isotope effect of D for H substitution at the  $\alpha$ -carbon is detected to within the experimental uncertainty. These results demonstrate, at least for a Cu-(100) surface, the feasibility of synthesizing selectively-labeled surface alkyl groups from H and D atom addition to alkenes.

#### 1. Introduction

Extensive studies have been carried out on the addition of atomic hydrogen to unsaturated  $\pi$  systems in the gas phase.<sup>1</sup> More recently, it has also been reported that gas phase hydrogen atoms add to unsaturated molecules adsorbed on surfaces.<sup>2–8</sup>

The addition of gas phase H atoms to unsaturated hydrocarbons on surfaces<sup>2,4</sup> is of interest not only for generating and isolating adsorbed hydrocarbon fragments which are of catalytic relevance and which are difficult to prepare by other methods9 but also as a means to generate, via deuterated hydrocarbons and/or deuterium addition, selectively-deuterated surface fragments. A common feature of these addition reactions is that they are highly exothermic and that they occur by direct or quasi-direct mechanisms (Elev-Rideal mechanisms) in which the H or D atoms react with the unsaturated hydrocarbon prior to thermally accommodating with the surface.<sup>2,4</sup> As a result of the reactions' exothermicities and the direct nature of these process, the possibility of product rearrangement and/or decomposition prior to accommodation to the surface must also be considered.<sup>10</sup> These rearrangement/decomposition possibilities have important implications with respect to the generation and isolation of selectively-labeled surface fragments.

In this paper, the issue of product rearrangement and/or decomposition is addressed for the addition of H and D atoms to an adsorbed ethylene monolayer on copper surfaces at 110 K. Previous studies<sup>2,3</sup> have documented that it is H (and D) atoms that have not thermally equilibrated with the surface that react with adsorbed ethylene to form ethyl groups. It is also clear that this is a highly exothermic process. As shown in

Scheme 1, two extremes (both very exothermic) may be envisioned for the nascent product of this reaction: i.e. hot ethyl radicals or hot surface ethyl groups. The thermochemical cycle presented in Scheme 2 shows that the enthalpy change for formation of ethyl radicals (neglecting any radical-surface interaction) is given by

$$\Delta H_1 = E_{\rm des} + \Delta H_{\rm gas} \tag{1}$$

where  $E_{\text{des}}$  is the desorption activation energy of ethylene from Cu(100) and  $\Delta H_{\text{gas}}$  is the enthalpy change in the gas phase for H addition to ethylene under standard conditions. Given that the activation energy for ethylene desorption from Cu(100),  $E_{\text{des}}$ , is  $8 \pm 2 \text{ kcal/mol}^3$  and that the gas phase reaction enthalpy is -36.5 kcal/mol on the basis of the heats of formation of ethyl radicals (28.0 kcal/mol),<sup>11</sup> ethylene (12.5 kcal/mol),<sup>12</sup> and H atoms (52 kcal/mol),<sup>13</sup> the enthalpy change for formation of surface ethyl radicals,  $\Delta H_1$ , is  $\sim -28 \text{ kcal/mol}$ . In fact, the actual energy that the nascent ethyl radicals possess could be even larger, since the H atoms in our studies have a translational energy of 5-6 kcal/mol.

The other extreme in the D + physisorbed ethylene reaction, i.e. direct formation of surface ethyl groups, is even more exothermic than formation of ethyl radicals, since the carbon-metal bond energy for ethyl groups adsorbed on Cu(100) is 33  $\pm$  6 kcal/mol.<sup>3</sup> Thus, as indicated in Scheme 2, formation of surface ethyl groups is accompanied by an enthalpy change of  $\Delta H_2 = \Delta H_1 - E_{M-C} = -61$  kcal/mol.

Since the exothermicity of this addition reaction is significantly larger than the activation energies for a number of coppercatalyzed ethyl decomposition reactions, one might expect not only ethyl rearrangement by H/D shifts but also ethyl decomposition by C–H and C–C bond scission processes. These

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**SCHEME 1** 



possibilities along with a preview of the conclusions from the present work are shown in Scheme 1. In prior studies<sup>2,3</sup> of this system, it was assumed that the rearrangement and decomposition pathways in Scheme 1 did not occur, and one of the objectives of the current study is to determine whether or not this is a valid assumption. The second objective is to provide highly accurate determinations of the deuterium kinetic isotope effect for  $\beta$ -hydride elimination by ethyl groups on Cu(100).

The focus of the studies here is H and D atom addition to variously-deuterated ethylenes physisorbed on a Cu(100) surface at 100 K. The isotope distribution in the resulting ethyl groups has been determined by measuring the isotopic composition of the ethylene produced by  $\beta$ -H or  $\beta$ -D elimination from the surface ethyl groups. To access kinetic isotope effects, the results are compared with the ethylene product ratio from  $\beta$ -H ( $\beta$ -D) elimination from labeled ethyl groups formed by dissociative adsorption of BrCD<sub>2</sub>CD<sub>2</sub>H. The results indicate that little or no rearrangement occurs in ethyl groups upon their formation from H or D addition to ethylene on Cu(100). The results also substantiate previous conclusions concerning the kinetic isotope effect ( $k_{\rm H},k_{\rm D}$ ) for  $\beta$ -elimination by ethyl groups on Cu(100).<sup>3</sup>

#### 2. Experimental Section

Details of the ultrahigh vacuum (UHV) chamber and the experimental procedures have been described previously.<sup>14</sup> The Cu(100) crystal (Monocrystals, 99.999%) was mounted on a molybdenum heating button that can be heated resistively to 1100 K and cooled by liquid nitrogen to 110 K. The sample temperatures were measured by a chromel–alumel thermocouple inserted into a hole drilled into the side of the crystal. The surface was cleaned by cycles of Ar<sup>+</sup> sputtering and annealing, and the cleanliness of the surface was confirmed by Auger electron spectroscopy.

Temperature-programmed desorption (TPD) and temperatureprogrammed reaction (TPR) studies were performed using a shielded and differentially-pumped quadrupole mass spectrometer with an electron impact ionization energy of 15 eV to eliminate most of the fragmentation of the molecular ions.<sup>3</sup> The heating rates were 3 K/s, and up to three ion intensities were monitored simultaneously by computer-controlled multiplexing of the mass spectrometer.

Hydrogen (deuterium) atoms were produced by dissociation of hydrogen molecules on a hot ( $\sim$ 1800 K) tungsten filament. During dosing, the crystal was positioned line-of-sight  $\sim$ 2 cm in front of the filament. The H (D) atom exposures indicated correspond to the exposures of H<sub>2</sub> (D<sub>2</sub>) molecules to the filament. For reference, an exposure of  $\sim 30$  L of H<sub>2</sub> or  $\sim 50$  L of D<sub>2</sub> is required to saturate a clean Cu(100) surface with H or D atoms. Also for reference, the average thermal energy for a Maxwellian distribution at 1800 K is 5.4 kcal/mol. However, previous time-of-flight studies indicate that a beam of H atoms generated from thermal dissociation of hydrogen molecules in a tungsten tube at 2300 K has an energy  $\sim 8.2$  kcal/mol, which is slightly higher than the expected thermal energy of 6.9 kcal/mol, <sup>15</sup> so the average thermal energy on our hot wire source at 1800 K may be slightly higher than expected for a Maxwell distribution.

Dosing was achieved by backfilling the chamber via precision sapphire leak valves. Exposures are reported in units of Langmuirs (L), where 1 L equals to  $1 \times 10^{-6}$  Torr•s. H<sub>2</sub> (Matheson, 99.9995%), D<sub>2</sub> (Matheson, 99.5%), C<sub>2</sub>D<sub>4</sub> (MSD isotopes, 99 atom % D) and *trans*-CDH=CDH (from Prof. R. Bersohn's group; unknown original source) were used without further purification. Bromoethane-1,1,2,2-d<sub>4</sub> and iodoethane-2,2,2-d<sub>3</sub> (Cambridge Isotope Laboratory, 98 atom % D) were purified by several freeze-pump-thaw cycles. Sample purities were verified *in situ* by mass spectrometry.

Since quantification of isotopic purity is critical for the kinetic isotope effect results presented in section 3, several comments on the in situ mass spectra of the variously deuterated compounds are warranted. In the case of iodoethane- $2, 2, 2-d_3$ (Cambridge Isotope Laboratory, 98 atom % D), the detected m/e = 158 signal is ~2.5% of that for m/e = 159 (molecular ion of  $C_2D_3H_2I$ ). While cracking of the molecular ion could in principle account for part of the m/e = 158 intensity, for the 15 eV electron impact ionization energy used in these studies, no cracking contribution is expected at this mass. More probably, the m/e = 158 intensity is due to impurity C<sub>2</sub>D<sub>2</sub>H<sub>3</sub>I, and the 2.5% relative intensity of this ion places an upper limit on the amount of this species. For bromoethane- $1, 1, 2, 2-d_4$  (C/D/N, 99.3 atom % D), m/e = 111 (probably C<sub>2</sub>D<sub>3</sub>H<sub>2</sub>Br) has an intensity ~0.6% of that for m/e = 112 (parent C<sub>2</sub>D<sub>4</sub>HBr). For  $C_2D_4$  (MSD isotopes, 99 atom % D) small amounts of m/e =31 (probably C<sub>2</sub>D<sub>3</sub>H), m/e = 30 (probably C<sub>2</sub>D<sub>2</sub>H<sub>2</sub>), and m/e =28 (probably  $C_2H_4$  or  $N_2$ ) are observed. The latter two masses are not an issue for the study here, but the C<sub>2</sub>D<sub>3</sub>H (m/e = 31) impurity is significant for the experiments. The intensity of this ion is 4.5% of that for m/e = 32. In order to confirm that m/e = 31 is due to ethylene- $d_3$ , TPD studies of m/e = 31 and m/e = 32 evolution after C<sub>2</sub>D<sub>4</sub> adsorption were performed. In these studies, both m/e = 31 and 32 showed the same peak temperatures, and the ion ratio was the same as that measured in the mass spectra of the dosing gas. On the basis of these results we can safely conclude that all m/e = 31 intensity is due to  $C_2D_3H$ . trans-CDH=CDH (m/e = 30) has small intensities at m/e = 26, 27, 28, and 29. The level of m/e = 29(probably ethylene- $d_1$ ) is ~5.0% of that of C<sub>2</sub>D<sub>2</sub>H<sub>2</sub>, and this factor is taken into account in the analysis of the results presented in section 3.3.

#### 3. Results and Interpretation

The experimental results are presented as follows. Section 3.1 briefly reviews the results of D atom addition to ethylened<sub>0</sub> to exclude the possibility of C-C and/or C-H bond dissociation concurrent with D addition. The thermal chemistry of BrCD<sub>2</sub>CD<sub>2</sub>H on the surface is then used in section 3.2 to determine the kinetic isotope effect for  $\beta$ -hydride elimination by surface ethyl groups. Finally, this isotope effect is used, together with the results of D atom addition to *trans*-CHD=CHD and H atom addition to CD<sub>2</sub>=CD<sub>2</sub>, to determine the extent of H/D shift between the two carbon atoms during the H/D addition reaction.

3.1. D Atom Addition to Ethylene: Absence of C-H(D) and C-C Bond Scission. As mentioned in the Introduction and shown in Scheme 1, possible reactions for excited ethyl radicals (groups) formed by D addition to ethylene on Cu(100) include copper-catalyzed C-H (D) and C-C bond scission. On the basis of previous studies, it is known that the activation energies for these various processes are comparable to or less than the exothermicity of the ethyl formation, which is at least 30 kcal/mol (see Introduction). For example, previous studies have shown the surface ethyls undergo  $\beta$ -hydride elimination on Cu(100) to yield ethylene and a chemisorbed H atom with a reaction barrier of only  $14.5 \pm 2$  kcal/mol.<sup>16,17</sup> By contrast, the activation energy for  $\alpha$ -hydrogen elimination by methyls is 27  $\pm$  2 kcal/mol on copper surfaces.<sup>14,18</sup> No C-C bond dissociation by alkyl groups has been reported on Cu(100), but previous studies have indicated an energy barrier of  $39 \pm 14$ kcal/mol for ethyl group C–C bond cleavage on Cu(110).<sup>14</sup>

The possibility of these various copper-catalyzed C-H and C-C bond scission reactions after H addition to ethylene but prior to thermal accommodation of the ethyl product with the Cu(100) surface at the 100 K surface temperature of reaction has been addressed by TPR studies of the  $D + C_2H_4$  reaction. For example, if  $\beta$ -hydride elimination by the nascent ethyl intermediate were to occur at the D addition reaction temperature of 110 K, then both the kinetic isotope effect for elimination  $(k_{\rm H}/k_{\rm D} \sim 10$ , see sections 3.2 and 3.3) and the H:D ratio of 2:1 at the  $\beta$ -carbon [This ratio assumes that there is no rearrangement by 1,2 H or D shift of the ethyl species formed by D addition-an assumption which is confirmed by studies presented in section 3.3. Note that if rearrangement were to occur, the average H:D ratio at the  $\beta$ -carbon would be  $\geq 2$ .] would favor  $\beta$ -H elimination over  $\beta$ -D elimination. As a result, some ethylene- $d_1$  would be generated on the surface at the addition reaction temperature of 110 K. In subsequent heating of the surface, ethylene- $d_1$  evolution would be observed at the ethylene molecular desorption temperature of <140 K. Note that we treat the possibility that the D atom added to the C=C bond is preferentially eliminated (because the C-D bond formed is vibrationally excited) as equivalent to a lack of D addition.

The experimental results regarding the possibility of  $\beta$ -H elimination at the D addition temperature of 110 K are presented in Figure 1, which dislays TPD spectra taken after dosing "5 L" D (10% of clean surface saturation) onto a Cu(100) surface precovered by 1 L of  $C_2H_4$  (~40% of monolayer saturation). As shown, unreacted ethylene (m/e = 28) has a molecular desorption peak only at <140 K. Ethylene- $d_1$  (m/e = 29), however, shows a peak at ~258 K, which, as previously documented, is due to  $\beta$ -hyrdide elimination by surface ethyl groups ( $CH_2CH_2D$ ) formed in the D addition reaction. The lack of an appreciable ethylene (m/e = 28) peak at 250 K reflects the absence of detectable  $\beta$ -D elimination by surface ethyl- $d_1$ groups, which can be attributed to a combination of the large kinetic isotope effect for reaction and the stoichiometry in the ethyl group (H:D = 2:1 in the  $\beta$  position [This ratio assumes that there is no rearrangement by 1,2 H or D shift of the ethyl species formed by D addition-an assumption which is confirmed by studies presented in section 3.3. Note that if rearrangement were to occur, the average H:D ratio at the  $\beta$ -carbon would be  $\geq 2$ .]). The key feature of these studies with respect to  $\beta$ -H elimination during D addition at 110 K is that no ethylene- $d_1$  evolution is detected at <140 K. The intensity of the very small m/e = 29 peak at 132 K in Figure 1 is 2.4  $\pm$ 0.4% of that of m/e = 28 peak and is entirely attributable to the 2.2% natural abundance of <sup>13</sup>C in C<sub>2</sub>H<sub>4</sub>. An upper limit for the percent of ethyl groups that could undergo  $\beta$ -hydride



**Figure 1.** Temperature-programmed reaction spectra of m/e = 18 (CH<sub>2</sub>D<sub>2</sub>), 28 (C<sub>2</sub>H<sub>4</sub>), 29 (C<sub>2</sub>H<sub>3</sub>D), and 30 (C<sub>2</sub>H<sub>2</sub>D<sub>2</sub>) after impinging 5 langmuirs (L) of D atoms onto a surface precovered with a 1.0 L exposure of C<sub>2</sub>H<sub>4</sub>. The spectra were obtained with a surface heating rate of 3 K/s and an electron impact ionization energy of 15 eV.

elimination before thermal accommodation to the substrate and still be consistent with the data here is 2%.

Given that  $\beta$ -H elimination is the most facile copper-catalyzed ethyl reaction pathway, the absence of  $\beta$ -hydride elimination suggests that significant  $\alpha$ -hydride elimination and C—C bond dissociation before ethyl thermal accommodation to the surface are unlikely. These predictions are confirmed by experiments. For example, suppose that C<sub> $\alpha$ </sub>—H bond dissociation occurs to form ethylidene-2- $d_1$  (CH<sub>2</sub>DCH=) on the surface. Studies presented elsewhere<sup>19</sup> have shown that the excess surface D atoms (generated from D atom dosing) would scavenge these ethylidene groups to form ethyl-1,2- $d_2$  (CH<sub>2</sub>DCHD—) groups, which would then form ethylene-1,2- $d_2$  (m/e = 30) via  $\beta$ -hydride elimination at ~255 K. As shown in Figure 1, the absence of an ethylene- $d_2$  (m/e = 30) peak at ~255 K excludes the possibility of  $\alpha$ -hydride elimination by the ethyl groups formed at 110 K on Cu(100).

Finally, the possibility of C-C bond cleavage can be addressed on the basis of what is known about the surface reactions of methylene (CH<sub>2</sub>=) and methyl- $d_1$  (CH<sub>2</sub>D-) groups on Cu(100). Specifically, it is known from prior studies that at  $\sim$ 240 K methylene (CH<sub>2</sub>=) reacts by one of three pathways on Cu(100): coupling with other CH<sub>2</sub> groups to form ethylene $d_0$ , coupling with surface methyl groups to form ethyl- $d_1$  (CH<sub>2</sub>-DCH<sub>2</sub>-), and/or coupling with surface D atoms to form methyl $d_1$  (CH<sub>2</sub>D–) groups.<sup>20</sup> Mass balance implies that, unless all of the CH<sub>2</sub> groups recombine with CH<sub>2</sub>D groups to reform ethyl $d_1$  (highly unlikely in the presence of surface D<sup>14</sup>), then regardless of the relative yields of the three possible processes, there must be methyl- $d_1$  (CH<sub>2</sub>D-) groups left on the surface at temperatures > 250 K. Furthermore, it is known that surface methyl groups readily combine with surface D atoms at  $\sim$ 350 K to form methane, and in this case the product would be methane- $d_2$  (CH<sub>2</sub>D<sub>2</sub>, m/e = 18).<sup>14</sup> As shown in Figure 1, the absence of both methane $-d_2$  (m/e = 18) evolution at ~350 K and ethylene- $d_0$  (m/e = 28) evolution from CH<sub>2</sub> coupling at  $\sim$ 240 K indicate that no detectable C–C bond cleavage occurs during D addition to physisorbed ethylene at 110 K on Cu-(100).

3.2. Thermal Chemistry of Bromoethane- $1,1,2,2-d_4$ : Determination of the Kinetic Isotope Effect for  $\beta$ -Elimination from Surface Ethyl Groups. As will be elaborated in section



**Figure 2.** Evolution of  $C_2D_4$  (m/e = 32) and  $C_2D_3H$  (m/e = 31) after adsorption of 1.0 L of CD<sub>2</sub>HCD<sub>2</sub>Br on Cu(100) at 110 K. The spectra were obtained with a surface heating rate of 3 K/s. The inset schematics show the origin of the observed ion intensities.

3.3,  $\beta$ -hydride elimination together with isotope labeling has been applied to investigate the extent of H/D shift between the two carbon atoms in ethyl groups formed by H/D addition to physisorbed ethylene. An important value required in these studies is the deuterium kinetic isotope effect for  $\beta$ -hydride elimination. In the present section, we present a determination of this isotope effect from studies of the thermal chemistry of bromoethane-1,1,2,2-d<sub>4</sub>. The idea is that bromoethane-1,1,2,2d<sub>4</sub> dissociates on Cu(100) to generate labeled ethyl groups (CD<sub>2</sub>-CD<sub>2</sub>H) and that the relative rates at which CD<sub>2</sub>CD<sub>2</sub> and CD<sub>2</sub>CDH are formed by  $\beta$ -H/ $\beta$ -D elimination from this species in a TPR experiment provide the kinetic isotope effect.

Bromoethane monolayers on Cu(100) partially dissociate to yield ethyl groups and bromine atoms on the surface. In the absence of H or D shift during this dissociative adsorption reaction (an assumption to be verified below), bromoethane- $1, 1, 2, 2-d_4$  generates ethyl- $1, 1, 2, 2-d_4$  groups on the surface. The results of  $\beta$ -hyrdide elimination by these ethyl-1,1,2,2-d<sub>4</sub> groups are presented in Figure 2, which shows the evolution of  $CD_2=CD_2$  and  $CD_2=CDH$  as a result of  $\beta$ -H and  $\beta$ -D elimination, respectively. (Previous studies have established that the coadsorbed halogen (bromine) atoms do not have a substantial effect on the  $\beta$ -hydride elimination rate.<sup>3</sup>) The isotope effect for  $\beta$ -hydride elimination ( $k_{\rm H}/k_{\rm D}$ ) is given by twice the ratio of the H and D elimination rates, where the factor 2 accounts for the D/H ratio in the  $\beta$ -position of the ethyl group. Seven measurements were conducted in which both m/e = 32 $(C_2D_4)$  and m/e = 31  $(C_2D_3H)$  evolution were monitored simultaneously. (It is worth emphasizing again that the mass spectrometer is operated with an electron impact ionization energy of 15 eV throughout the studies reported here, so the molecular ion intensities represent more than 98% of the total ion intensity in the cracking patterns.) Neglecting for a moment the temperature dependence of  $k_{\rm H}/k_{\rm D}$ , an average value (determined by integrating the TPR peaks) of  $4.7 \pm 0.1$  is found for the ratio of the H-elimination and D-elimination yields. After correcting for the 0.6% impurity of bromoethane- $d_3$  in bromoethane-1,1,2,2- $d_4$  (see section 2) and taking into account the 2:1 D:H ratio at the  $\beta$ -carbon, this result corresponds to a kinetic isotope effect of 9.5  $\pm$  0.4 for  $\beta$ -hydride elimination over the 247–265 K temperature range of the TPR peak.

The results in Figure 2 also allow determination of the temperature dependence of the kinetic isotope effect for  $\beta$ -hyr-



**Figure 3.** Temperature dependence of the kinetic isotope effect  $(k_{\rm H}/k_{\rm D})$  for  $\beta$  elimination for CD<sub>2</sub>HCD<sub>2</sub>- groups on Cu(100). The isotope effect is given by twice the ratio of the H and D elimination rates in the TPR spectra shown in Figure 2. Different symbols represent data from different experiments. The solid and dotted lines (which are essentially indistinguisable because of overlap) represent curve-fitting results assuming that the  $k_{\rm H}/k_{\rm D}$  ratio is of the form  $A \exp(-E/RT)$ . The fitting parameters are A = 1.17, E = 1.08 kcal/mol for the solid line and A = 1.00, E = 1.16 kcal/mol for the dotted line, as discussed in the text.

dide elimination. Since the TPR peak heights are directly proportional to the rates of product evolution, if we make the reasonable assumption that CD<sub>2</sub>CD<sub>2</sub> and CD<sub>2</sub>CDH have the same detection sensitivities in the mass spectrometer, than the temperature dependence of the isotope effect can be determined from twice the ratio of the CD<sub>2</sub>CD<sub>2</sub> and the CD<sub>2</sub>CDH peak heights. After correcting for the 0.6% impurity of bromoethane $d_3$  in bromoethane-1,1,2,2- $d_4$  (see section 2), the results are shown in Figure 3, where different symbols are used to represent data from independent experiments. The temperature range is limited to 247-265 K on the basis of the signal-to-noise ratio in the data. Although the temperature range is limited, there appears to be a temperature dependence to the  $k_{\rm H}/k_{\rm D}$  ratio. The  $k_{\rm H}/k_{\rm D}$  ratio decreases with increasing temperature, indicating that H elimination has a lower energy barrier. Further discussion of the temperature dependence is deferred to section 4.2.

The isotope effect determination above is based on the assumption that no H or D shift occurs in ethyl groups during thermal dissociation of the carbon-bromine bond, so that the ethyl groups formed on the surface are exclusively ethyl- $1,1,2,2-d_4$ . To investigate the possibility of H/D shift during the thermal dissociation of carbon-halogen bonds in ethyl halides, the dissociative adsorption of ethyl iodide-2,2,2- $d_3$  has been studied on Cu(100). In the absence of H/D shift, thermal dissociation of the C-I bond generates ethyl-2,2,2-d<sub>3</sub> (CD<sub>3</sub>-CH<sub>2</sub>-) groups, which will form exclusively  $CD_2$ =CH<sub>2</sub> by  $\beta$ -D elimination. However, either D shift upon C-I bond dissociation or reversible formation of ethyl from  $CH_2 = CD_2 + D$  would produce some ethyl-1,1,2- $d_3$  (CH<sub>2</sub>DCD<sub>2</sub>-) groups on the surface, which would eliminate a  $\beta$ -H to form CD<sub>2</sub>=CDH. Figure 4 presents the results of C–I dissociation and  $\beta$ -elimination for a 1 L exposure ethyl iodide- $2, 2, 2-d_3$ . The evolution of H-elimination (m/e = 31) and D-elimination (m/e = 30) products are monitored simultaneously. The results show an m/e = 31(CD<sub>2</sub>=CDH) intensity, which is ~5.0% of the m/e = 30(CD<sub>2</sub>=CH<sub>2</sub>) signal. Taking into account the 1.1% natural abundance of  ${}^{13}C$  in CD<sub>2</sub>=CH<sub>2</sub>, we can conclude that the extent of H/D shift upon C-I bond dissociation is less than 2.8%. In fact, the degree of H/D shift is probably negligible, and the 2.8% of C<sub>2</sub>D<sub>3</sub>H is probably attributable to either some reversibility in the  $\beta$ -elimination reaction (which has been previously demonstrated for higher surface coverages<sup>3</sup>) or impurities (such as ethyl iodide- $1, 2, 2-d_3$  in the ethyl iodide- $2, 2, 2-d_3$  sample.



**Figure 4.** Evolution of  $C_2H_2D_2$  (*m/e* = 30) and  $C_2D_3H$  (*m/e* = 31) after adsorption of 1.0 L of CD<sub>3</sub>CH<sub>2</sub>I on Cu(100) at 110 K. The spectra were obtained with a surface heating rate of 3 K/s and an electron impact ionization energy of 15 eV.

#### **SCHEME 3**



**3.3.** H Addition to Ethylene- $d_4$  and D Addition to *trans*-CHD=CHD: Extent of H/D Shift. As shown in Scheme 1, a possible reaction for the nascent ethyl radical/group intermediate is H or D atom shift between the two carbon atoms. While calculations indicate that the barrier for a 1,2 H atom shift in gas phase ethyl radicals is ~84 kcal/mol,<sup>21,22</sup> the possibility of a surface-promoted H shift with a barrier less than the 30–60 kcal/mol exothermicity of the addition reaction cannot be ruled out.

Using the results from sections 3.1 and 3.2, the possibility of H/D atom shift upon ethyl radical/group formation from hydrogen atom addition to ethylene on Cu(100) has been studied by two different isotopic variations of the reaction. The first is H addition to CD<sub>2</sub>=CD<sub>2</sub>, and the second is D addition to trans-CDH=CDH. As shown in Scheme 3, in the absence of any H/D shift, H addition to ethylene- $d_4$  (CD<sub>2</sub>=CD<sub>2</sub>) yields ethyl- $1,1,2,2-d_4$  (CD<sub>2</sub>HCD<sub>2</sub>-), and D addition to ethylene- $1,2-d_2$ (CDH=CDH) forms ethyl- $1, 2, 2-d_3$  (CD<sub>2</sub>HCDH-). In other words, both reactions produce ethyl groups with one hydrogen and two deuterium atoms at the  $\beta$  position. On the other hand, if H and/or D shifts occur, then the two nascent ethyl groups generated by these addition reactions can convert to other structural isomers. In the case of CD<sub>2</sub>HCD<sub>2</sub>-, only one other structural isomer (CD<sub>3</sub>CDH-) is possible, while, for CD<sub>2</sub>-HCDH-, both CDH<sub>2</sub>CD<sub>2</sub>- and CD<sub>3</sub>CH<sub>2</sub>- can be formed. As a result, different H and D populations will be present at the  $\beta$ -carbons in the ensemble of surface ethyl groups if H or D shifts occurs. The extent of rearrangement can be quantified by comparing the relative yields of the H and D elimination



**Figure 5.** Evolution of  $C_2D_4$  (m/e = 32) and  $C_2D_3H$  (m/e = 31) after impinging 5 L of H atoms onto a surface precovered with a 1.0 L exposure of  $C_2D_4$ . The spectra were obtained with a surface heating rate of 3 K/s and an electron impact ionization energy of 15 eV.

products with the yields determined in the control experiments utilizing the labeled ethyl halides in section 3.2.

Figure 5 shows TPR spectra taken after exposing a Cu(100) surface precovered with a partial monolayer of C<sub>2</sub>D<sub>4</sub> (about 40% of monolayer saturation) to 5 L of H atoms. As will be discussed further in section 4.1, the extent of rearrangement is expected to be independent of the absolute coverage of ethyl groups formed in the addition reaction. The TPR experiments in Figure 5 were carried out using an electron impact ionization energy of 15 eV, so that the ion intensities at m/e = 32 and 31 in Figure 5 accurately represent the evolution of ethylene- $d_4$ and ethylene- $d_3$ , respectively. Notice that the  $\beta$ -hydride elimination peaks are observed at 258 K, which is the same to within the  $\pm 5$  K experimental reproducibility as the peak temperature of 261 K for  $\beta$ -elimination by the ethyl-1,1,2,2-d<sub>4</sub> groups generated from the thermal dissociation of ethyl bromide, as presented in section 3.2 (Figure 2). (The higher temperature of 273 K for  $\beta$ -elimination by ethyl-2,2,2-d<sub>3</sub> groups in Figure 4 reflects the deuterium isotope effect for this reaction.) As in the studies of Figure 2, the average H to D elimination reaction yield ratio (yield-H/yield-D) over the 240-270 K temperature range of the studies of Figure 5 can be determined by comparing the m/e = 32 (ethylene- $d_4$ ) and m/e = 31 (ethylene- $d_3$ ) peak areas. On the basis of three sets of experiments, the product yield ratio is  $4.2 \pm 0.2$ . After correction is made for the 4.2%  $C_2D_3H$  impurity in the  $C_2D_4$  source (see section 2), the value is  $5.1 \pm 0.3$ . A complete discussion of the procedure for this correction can be found in ref 3.

Figure 6 presents TPR results from the reaction of "5 L" D (~10% of saturation) with a Cu(100) surface precovered by 1 L of *trans*-CHD=CHD (~40% of monolayer saturation). The ion intensities at m/e = 31 and 30 represent the evolution of ethylene- $d_3$  and ethylene- $d_2$  from  $\beta$ -H and  $\beta$ -D elimination. Again, the relative yields of H and D elimination (yield<sub>-H</sub>/ yield<sub>-D</sub>) can be determined from the results by comparing the peak areas for ethylene- $d_3$  and ethylene- $d_2$  evolution. On the basis of ten separate measurements, the yield ratio is  $4.1 \pm 0.2$ . After a correction is made for the 4.0% ethylene- $d_1$  impurity in the ethylene- $d_2$  source (see section 2), the value for the H to D elimination reaction yield ratio (yield<sub>-H</sub>/yield<sub>-D</sub>) is  $4.9 \pm 0.3$ .

These results for H addition to ethylene- $d_4$  and for D addition to ethylene- $1,2-d_2$  will be discussed in the following section,



**Figure 6.** Evolution of  $C_2D_3H$  (m/e = 31) and  $C_2H_2D_2$  (m/e = 30) after impinging 5 L of D atoms onto a surface precovered with a 1.0 L exposure of *trans*-CDH=CDH. The spectra were obtained with a surface heating rate of 3 K/s and an electron impact ionization energy of 15 eV.

where it is shown that little or no H/D shift occurs during ethyl group formation.

### 4. Discussion

4.1. Extent of H/D Shift. In order to quantify the extent of H/D shift from the reaction kinetics data presented in section 3.3, we evaluate first the changes in the  $\beta$ -H(D) populations that would be expected as a function of the extent of H/D shift. In both of the experiments described  $(H + CD_2 = CD_2 \text{ and } D + CD$ CHD=CHD), the nascent ethyl groups formed by addition have two D atoms and one H atom at the  $\beta$ -carbon. Note that even if the energy released upon H or D addition to the double bond is not rapidly randomized within the ethyl fragment, so that there is a preferential shift of the H or D atom that was just added, this shift does not affect the isotope distribution in the ethyl groups, since both ethylene molecules in these studies have the same isotope composition at either end of the molecule. In other words, immediate transfer of the added H or D to the adjacent carbon is equivalent to initial addition at the adjacent carbon, and the species formed by addition at either carbon are equivalent with respect to isotope composition at the  $\alpha$  and  $\beta$ positions. For the purposes of the discussion that follows, we assume that all  $\beta$ -hydrogen atoms have the same shift rate ( $r_{\rm H}$ ) and that all  $\beta$ -deuterium atoms have the same shift rate ( $r_{\rm D}$ ). We consider first the effects of H and D shift on H addition to  $C_2D_4$ .

(*i*) *H* Addition to  $CD_2=CD_2$ . The nascent ethyl group formed by H atom addition to  $CD_2=CD_2$  is ethyl-1,1,2,2-d<sub>4</sub> ( $CD_2$ -HCD<sub>2</sub>-). Note that a 1,2 hydrogen shift maintains the lone hydrogen atom at the  $\beta$  position, but a 1,2 deuterium shift converts  $CD_2HCD_2$ - to its structural isomer  $CD_3CDH$ -, which has no hydrogen atom at the  $\beta$  position. These two structural isomers, which are the only two possible without intermolecular exchange, are interconverted only by D transfer between carbons, and this interchange process can be written as

$$CD_2CD_2H \xrightarrow{2r_D}_{3r_D} CDHCD_3$$
 (2)

where  $r_D$  is the rate constant for exchange of a single D atom. The coverages of the two ethyl structural isomers can be related



**Figure 7.** Time evolution of the fractional surface coverages of the two ethyl structural isomers (CD<sub>2</sub>HCD<sub>2</sub>- and CD<sub>3</sub>CDH-) possible for C<sub>2</sub>D<sub>4</sub>H stoichiometry as a function of the number of H/D shifts between the two carbon atoms for three different relative rates of deuterium and hydrogen shift ( $r_{\rm H}/r_{\rm D}$ ): (A) fast hydrogen shift ( $r_{\rm H} = 10r_{\rm D}$ ); (B) equal rate for deuterium and hydrogen shift ( $r_{\rm D} = r_{\rm H}$ ); (C) fast deuterium shift ( $r_{\rm D} = 10r_{\rm H}$ ). The initial coverages were taken as 1 for CD<sub>2</sub>HCD<sub>2</sub>- and 0 for CD<sub>3</sub>CDH- to correspond to the experimental results for H atom addition to C<sub>2</sub>D<sub>4</sub> on Cu(100).

to the rate of change of coverage of either isomer by

$$-\frac{\mathrm{d}\theta_{\mathrm{CDHCD}_3}}{\mathrm{d}t} = \frac{\mathrm{d}\theta_{\mathrm{CD}_2\mathrm{CD}_2\mathrm{H}}}{\mathrm{d}t} = 3r_{\mathrm{D}}\theta_{\mathrm{CDHCD}_3} - 2r_{\mathrm{D}}\theta_{\mathrm{CD}_2\mathrm{CD}_2\mathrm{H}}$$
$$= r_{\mathrm{D}}(3\theta_{\mathrm{CD}_2\mathrm{CD}_2\mathrm{H}}^\circ - 5\theta_{\mathrm{CD}_2\mathrm{CD}_2\mathrm{H}})$$

where  $\theta^{\circ}_{CD_2CD_2H}$  is the initial coverage of  $CD_2CD_2H$  formed upon H atom addition to  $CD_2=CD_2$  and

$$\theta_{\rm CD_2CD_2H} + \theta_{\rm CDHCD_3} = \theta_{\rm CD_2CD_2H}^{\circ}$$

The time evolution of two isomers is therefore given by

$$\theta_{\mathrm{CD}_{2}\mathrm{CD}_{2}\mathrm{H}} = \theta_{\mathrm{CD}_{2}\mathrm{CD}_{2}\mathrm{H}}^{\circ} \left(\frac{3}{5} + \frac{2}{5}\mathrm{e}^{-5r_{\mathrm{D}}t}\right)$$
$$\theta_{\mathrm{CDHCD}_{3}} = \theta_{\mathrm{CD}_{2}\mathrm{CD}_{2}\mathrm{H}}^{\circ} \left(\frac{2}{5} - \frac{2}{5}\mathrm{e}^{-5r_{\mathrm{D}}t}\right) \tag{3}$$

Figure 7 shows representative examples for the evolution of the surface concentrations of the two isomers as a function of the "number of H and D shifts" for three different relative rates of deuterium and hydrogen shift ( $r_D/rH$ ). Because we have no experimental measure of the relative rates of H and D transfer, the plots in Figure 7 show the effects of an orders of magnitude change in the relative rates. One "shift", as indicated on the *x* axis in Figure 7, is defined by the time constant  $1/(2r_D + r_H)$ . For the case in Figure 7B, where there is no isotope effect for H/D transfer and  $r_D = r_H = r$ , this time constant is 1/3r, and this value reflects the average time per 1,2 shift event per ethyl group, where a shift event is defined as a single exchange of an H or D atom between the two carbon atoms. In the cases where there is a deuterium kinetic isotope effect for the 1,2 shift ( $r_D \neq r_H$ , as in Figure 7A and C), the value of  $1/(2r_D + r_H)$   $r_{\rm H}$ ) reflects the average time per shift event per ethyl only in the limit of zero time, where there are one hydrogen and two deuterium atoms at the  $\beta$  position of all surface ethyl groups.

As shown in Figure 7 and by eq 3, for small times  $(t \rightarrow 0)$ ,

$$\frac{\mathrm{d}\theta_{\mathrm{CD}_{2}\mathrm{CD}_{2}\mathrm{H}}}{\mathrm{d}t} = -2r_{\mathrm{D}}\theta_{\mathrm{CD}_{2}\mathrm{CD}_{2}\mathrm{H}}^{\circ}$$
$$\frac{\mathrm{d}\theta_{\mathrm{CDHCD}_{3}}}{\mathrm{d}t} = 2r_{\mathrm{D}}\theta_{\mathrm{CD}_{2}\mathrm{CD}_{2}\mathrm{H}}^{\circ}$$

and deuterium atom transfer in CD<sub>2</sub>HCD<sub>2</sub>- to form CD<sub>3</sub>CDHoccurs at a rate of  $2r_D\theta^{\circ}_{CD_2CD_2H}$ , where  $\theta^{\circ}_{CD_2CD_2H}$  is the initial coverage of CD<sub>2</sub>CD<sub>2</sub>H assuming that all CD<sub>2</sub>CD<sub>2</sub>H species are formed simultaneously. On the other hand, for infinite times  $(t \rightarrow \infty)$ , the two structural isomers reach equilibrium, with

$$\theta^{\infty}_{\text{CD}_2\text{CD}_2\text{H}} = \frac{3}{5}\theta^{\circ}_{\text{CD}_2\text{CD}_2\text{H}}$$
$$\theta^{\infty}_{\text{CDHCD}_3} = \frac{2}{5}\theta^{\circ}_{\text{CD}_2\text{CD}_2\text{H}}$$
(4)

Note that this is the result expected for a statistical distribution of one H and four D atoms between the two  $\alpha$  and three  $\beta$ positions in an ethyl group. The implication of the results in Figure 7 for the experimentally-measured  $\beta$  elimination product ratio is given by

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$$\frac{\text{yield}_{-H}}{\text{yield}_{-D}} = \frac{\frac{K_{\text{iso}}}{2 + K_{\text{iso}}} \theta_{\text{CD}_2 \text{CD}_2 \text{H}}}{\frac{2}{2 + K_{\text{iso}}} \theta_{\text{CD}_2 \text{CD}_2 \text{H}} + \theta_{\text{CDHCD}_3}}$$
(5)

where yield<sub>-H</sub>/yield<sub>-D</sub> indicates the yield of the hydrogen elimination product (CD<sub>2</sub>=CD<sub>2</sub>) relative to the yield of the deuterium elimination product (CD<sub>2</sub>=CDH) and  $K_{iso}$  is the isotope effect ( $k_{\rm H}/k_{\rm D}$ ) for the  $\beta$ -hydride elimination reaction. Notice from eqs 3 and 5 that the relative yields of H and D elimination products are a function of only the shift rate constant and the isotope effect for  $\beta$ -hydride elimination and are independent of the initial coverage of CD<sub>2</sub>CD<sub>2</sub>H formed in the H atom addition reaction. Using the results in Figure 7 and the  $K_{iso}$  of 9.5 determined in section 3.2, the product yield ratio is plotted as a function of number of shifts for various relative H and D scrambling rates in Figure 9 (open circles). Further comments on these results will be made after discussing the analogous possibilities for the D + CHD=CHD experiment.

(*ii*) D Addition to CHD=CHD. D atom addition to trans-CHD=CHD forms initially ethyl-1,2,2- $d_3$  (CD<sub>2</sub>HCDH-). In this case, deuterium shift between carbons does not change (at least initially) the ethyl structural isomer, but hydrogen shift converts CD<sub>2</sub>HCDH- to CDH<sub>2</sub>CD<sub>2</sub>-. This new isomer can then be either transformed back to CD<sub>2</sub>HCDH- through a hydrogen shift or converted to a third species CD<sub>3</sub>CH<sub>2</sub>- via a deuterium atom shift. The final possibility is conversion of CD<sub>3</sub>-CH<sub>2</sub>- back to CD<sub>2</sub>HCDH- through a deuterium shift. The entire reaction system can be summarized as

$$CDHCD_{2}H \xrightarrow{r_{H}} CD_{2}CDH_{2}$$
$$CD_{2}CDH_{2} \xrightarrow{r_{D}} CH_{2}CD_{3}$$

where  $r_{\rm H}$  and  $r_{\rm D}$  are the rate constants for hydrogen and deuterium shift per C<sub> $\beta$ </sub>-H and C<sub> $\beta$ </sub>-D bond, respectively. The

rates of population change for two of the three structural isomers are given by

$$\frac{\mathrm{d}\theta_{\mathrm{CDHCD_{2}H}}}{\mathrm{d}t} = 2r_{\mathrm{H}}\theta_{\mathrm{CD_{2}CDH_{2}}} - r_{\mathrm{H}}\theta_{\mathrm{CDHCD_{2}H}}$$
$$= r_{\mathrm{H}}(2\theta_{\mathrm{CDHCD_{2}H}}^{\circ} - 3\theta_{\mathrm{CDHCD_{2}H}} - 2\theta_{\mathrm{CH_{2}CD_{3}}})$$

$$\frac{\mathrm{d}\theta_{\mathrm{CH}_{2}\mathrm{CD}_{3}}}{\mathrm{d}t} = r_{\mathrm{D}}\theta_{\mathrm{CD}_{2}\mathrm{CDH}_{2}} - 3r_{\mathrm{D}}\theta_{\mathrm{CH}_{2}\mathrm{CD}_{3}}$$
$$= r_{\mathrm{D}}(\theta_{\mathrm{CDHCD}_{2}\mathrm{H}}^{\circ} - \theta_{\mathrm{CDHCD}_{2}\mathrm{H}} - 4\theta_{\mathrm{CH}_{2}\mathrm{CD}_{3}})$$
(6)

where  $\theta_{\text{CDHCD}_2\text{H}} + \theta_{\text{CD}_2\text{CDH}_2} + \theta_{\text{CH}_2\text{CD}_3} = \theta_{\text{CDHCD}_2\text{H}}^\circ$  and  $\theta_{\text{CDHCD}_2\text{H}}^\circ$  is the initial coverage of ethyl-*1,2,2-d*<sub>3</sub> (CD<sub>2</sub>HCDH) formed by D addition to CDH=CDH. Equations 6 above represent a system of two linear first-order differential equations with two variables for which the general solution has the form

$$\theta_{\text{CDHCD}_{2}\text{H}} = C_0 + C_1 e^{-r_1 t} + C_2 e^{-r_2 t}$$
$$\theta_{\text{CH}_2\text{CD}_3} = C'_0 + C'_1 e^{-r_1 t} + C'_2 e^{-r_2 t}$$

Determination of the time constants  $r_1$  and  $r_2$  and the coefficients  $C_0$ ,  $C_1$ ,  $C_2$ ,  $C'_0$ ,  $C'_1$ , and  $C'_2$  from the constraints imposed by eqs 6 gives the time evolution for each of the three structural isomers as

 $\theta_{\rm CDHCD,H} =$ 

$$\theta^{\circ}_{\text{CDHCD}_{2}\text{H}}\left(\frac{3}{5} + \frac{5}{5} \frac{r_{\text{H}} - 2r_{2}}{(r_{1} - r_{2})} e^{-r_{1}t} + \frac{5}{5} \frac{r_{\text{H}} - 2r_{1}}{(r_{2} - r_{1})} e^{-r_{2}t}\right)$$

 $\theta_{\rm CD,CDH_2} =$ 

$$\theta_{\text{CDHCD}_{2}\text{H}}^{\circ} \left( \frac{3}{10} + \frac{3 r_{2} - 10 r_{\text{H}}}{10 (r_{1} - r_{2})} e^{-r_{1}t} + \frac{3 r_{1} - 10 r_{\text{H}}}{10 (r_{2} - r_{1})} e^{-r_{2}t} \right)$$

 $\theta_{\mathrm{CH}_2\mathrm{CD}_3} =$ 

$$\theta_{\text{CDHCD}_2\text{H}}^{\circ} \left( \frac{1}{10} + \frac{r_2}{10(r_1 - r_2)} e^{-r_1 t} + \frac{r_1}{10(r_2 - r_1)} e^{-r_2 t} \right)$$
(7)

where

$$r_{1} = \frac{3r_{\rm H} + 4r_{\rm D} + \left[(3r_{\rm H} - 4r_{\rm D})^{2} + 8r_{\rm H}r_{\rm D}\right]^{1/2}}{2}$$
$$r_{2} = \frac{3r_{\rm H} + 4r_{\rm D} - \left[(3r_{\rm H} - 4r_{\rm D})^{2} + 8r_{\rm H}r_{\rm D}\right]^{1/2}}{2}$$

The curves in Figure 8 show the evolution of the surface coverages of the three ethyl structural isomers as a function of the extent of rearrangement for different relative rates of D and H shifting. As for Figure 7, the "number" of shifts is defined by  $1/(2r_D + r_H)$ , where a value of 1 corresponds to an average of one shift per ethyl in the absence of any isotope effects.

As shown in Figure 8 and by eqs 6 and 7, as  $t \rightarrow 0$ ,

$$\frac{\mathrm{d}\theta_{\mathrm{CDHCD_{2}H}}}{\mathrm{d}t} = -r_{\mathrm{H}}\theta_{\mathrm{CDHCD_{2}H}}^{\circ}$$
$$\frac{\mathrm{d}\theta_{\mathrm{CD_{2}CDH_{2}}}}{\mathrm{d}t} = r_{\mathrm{H}}\theta_{\mathrm{CDHCD_{2}H}}^{\circ}$$



**Figure 8.** Time evolution of fractional surface coverages of the three ethyl structural isomers (CD<sub>2</sub>HCDH<sup>-</sup>, CDH<sub>2</sub>CD<sub>2</sub><sup>-</sup>, and CD<sub>3</sub>CH<sub>2</sub><sup>-</sup>) possible for C<sub>2</sub>D<sub>3</sub>H<sub>2</sub> stoichiometry as a function of number of H/D shifts between the two carbon atoms for three different relative rates of deuterium and hydrogen shift ( $r_{\rm H}/r_{\rm D}$ ): (A) fast hydrogen shift ( $r_{\rm H} =$  $10r_{\rm D}$ ); (B) equal rate for deuterium and hydrogen shift ( $r_{\rm D} = r_{\rm H}$ ); (C) fast deuterium shift ( $r_{\rm D} = 10r_{\rm H}$ ). The initial coverages were taken as 1 for CD<sub>2</sub>HCDH<sup>-</sup> and 0 for CDH<sub>2</sub>CD<sub>2</sub><sup>-</sup> and CD<sub>3</sub>CH<sub>2</sub><sup>-</sup> to correspond to the experimental results for D atom addition to CDH=CDH on Cu-(100).

$$\frac{\mathrm{d}\theta_{\mathrm{CH}_2\mathrm{CD}_3}}{\mathrm{d}t} = 0$$

In other words, 1,2-hydrogen shift initially transforms CD<sub>2</sub>-HCDH— to CDH<sub>2</sub>CD<sub>2</sub>—, but the coverage of CD<sub>3</sub>CH<sub>2</sub>—remains zero. At equilibrium  $(t \rightarrow \infty)$ , the populations of the three structural isomers are given by

$$\theta_{\text{CDHCD}_{2}\text{H}}^{\infty} = \frac{3}{5} \theta_{\text{CDHCD}_{2}\text{H}}^{\circ}$$
$$\theta_{\text{CD}_{2}\text{CDH}_{2}}^{\infty} = \frac{3}{10} \theta_{\text{CDHCD}_{2}\text{H}}^{\circ}$$
$$\theta_{\text{CH}_{2}\text{CD}_{3}}^{\infty} = \frac{1}{10} \theta_{\text{CDHCD}_{2}\text{H}}^{\circ}$$
(8)

which is consistent with a statistical distribution of two H and three D atoms between two  $\alpha$  and three  $\beta$  positions. From an ensemble of these three different structural isomers, two  $\beta$ -hydride elimination products can be formed: ethylene-d<sub>3</sub> and ethylene-d<sub>2</sub>. The relative yield of hydrogen elimination product (ethylene-d<sub>3</sub>) vs deuterium elimination product (ethylene-d<sub>2</sub>) is given by

$$\frac{\text{yield}_{C_{2}D_{3}H}}{\text{yield}_{C_{2}D_{2}H_{2}}} = \frac{\frac{K_{\text{iso}}}{2 + K_{\text{iso}}}\theta_{\text{CDHCD}_{2}H} + \frac{2K_{\text{iso}}}{1 + 2K_{\text{iso}}}\theta_{\text{CD}_{2}\text{CDH}_{2}}}{\frac{2}{2 + K_{\text{iso}}}\theta_{\text{CDHCD}_{2}H} + \frac{1}{1 + 2K_{\text{iso}}}\theta_{\text{CD}_{2}\text{CDH}_{2}} + \theta_{\text{CH}_{2}\text{CD}_{3}}} (9)$$



**Figure 9.** Relative  $\beta$ -H and  $\beta$ -D elimination yields as a function of the extent of H/D shift for three different relative rates of deuterium and hydrogen shift ( $r_{\rm H}/r_{\rm D}$ ). Open circles represent the relative product yields for H atom addition to C<sub>2</sub>D<sub>4</sub>. Solid circles represent the relative product yields for D atom addition to CDH=CDH. The zero time value of 4.7 in all cases reflects the isotope effect measured for H and D elimination from CD<sub>2</sub>HCD<sub>2</sub>- groups formed by dissociative adsorption of CD<sub>2</sub>HCD<sub>2</sub>Br.

Notice again that the relative yield of the two reaction products is independent of the initial coverage of CDHCD<sub>2</sub>H formed by D addition to CHD=CHD.

(iii) Implications of the Experimental Results. As illustrated above, in both H addition to C<sub>2</sub>D<sub>4</sub> and D addition to CDH=CDH, H/D shift in the nascent product ethyl group will change the H and D population at the  $\beta$  position and consequently the ratio of H and D elimination reaction yields. Given the deuterium kinetic isotope effect,  $K_{iso} = k_H/k_D$ , of 9.5 determined in section 3.2, the relationship between the relative H and D elimination reaction yields and the extent of H/D shift can be predicted from eqs 5 and 9. Figure 9 presents these relationships for both H addition to ethylene- $d_4$  and D addition to ethylene- $1,2-d_2$  for three different relative rates of H and D shift ( $r_D/r_H$ ).

The general characteristics of the plots in Figure 9 can be understood as follows. In the case of H addition to ethylene $d_4$ , the nascent product is ethyl-1,1,2,2- $d_4$  (CD<sub>2</sub>HCD<sub>2</sub>-). With no D shift, one hydrogen and two deuterium atoms are present at the  $\beta$  position, and on the basis of the bromoethane studies in section 3.2, the expected yield ratio for H and D elimination, yield<sub>-H</sub>/yield<sub>-D</sub>, is 4.7. This value is the point at x = 0 for all three plots in Figure 9. In the case of D shift, the CD<sub>2</sub>HCD<sub>2</sub>group coverage decreases, accompanied by an increase in the CD<sub>3</sub>CDH- group coverage, as shown in Figure 7. Thus, the H population at the  $\beta$  position steadily decreases, resulting in a monotonic decrease in the H elimination yield, as shown by the open circles in all three plots of Figure 9.

On the other hand, D addition to ethylene-1,2- $d_2$  forms ethyl-1,2,2- $d_3$  (CD<sub>2</sub>HCDH-), and for short times (t  $\rightarrow$  0), the initial decrease in the CD<sub>2</sub>HCDH- coverage as a result of H shift is mirrored by an increase in the CDH<sub>2</sub>CD<sub>2</sub>- coverage while the CD<sub>3</sub>CH<sub>2</sub>- coverage remains zero. Thus, the average H population at the  $\beta$  position increases, which results in a slight increase in the  $\beta$ -H elimination yield relative to the value of 4.7 for no rearrangement. This increase is, however, less significant for a faster relative D shift rate, since D shift transforms  $\text{CDH}_2\text{CD}_2$ — to  $\text{CD}_3\text{CH}_2$ —, which has no H population at the  $\beta$  position. The limiting value for yield<sub>-H</sub>/yield<sub>-D</sub> for a statistical distribution of the three structural isomers (see Figure 8) and for a  $k_{\text{H}}/k_{\text{D}}$  ratio of 9.5 (see section 3.2) is 3.5 (see Figure 9).

The results in Figure 9 can be used to interpret the experimental results as follows. As presented in section 3.3, the ratio of H and D elimination product yields is  $5.1 \pm 0.3$  after H addition to ethylene- $d_4$  and  $4.9 \pm 0.3$  after D addition to trans-ethylene- $1,2-d_2$ . Comparing these results with the plots presented in Figure 9, we can conclude that the extent of rearrangement by 1,2 H or D shift in ethyl groups formed by H or D addition to physisorbed ethylene on Cu(100) is immeasurably small. On the basis of the experimental uncertainties, we can place an upper limit on the extent of rearrangement at 5%.

4.2. Kinetic Isotope Effect for  $\beta$ -Hydride Elimination. Having established that there is no detectable 1,2 H or D shift in partially deuterated ethyl groups formed by H or D addition to ethylene on Cu(100), we can use the relative rates measured for  $\beta$ -H and  $\beta$ -D elimination from these selectively labeled alkyls to determine the kinetic isotope effect(s) for  $\beta$  elimination. In the case of H addition to  $C_2D_4$  to form  $CD_2HCD_2-$ ,  $k_H/k_D$ for  $\beta$  elimination is determined from the studies in section 3.3 to be  $10.3 \pm 0.7$  over the temperature range 245–265 K. To within the experimental uncertainty, this value is the same as that of 9.5  $\pm$  0.4 determined for  $\beta$  elimination from CD<sub>2</sub>HCD<sub>2</sub>groups generated by dissociative adsorption of bromoethane- $1, 1, 2, 2-d_4$ . Thus, while previous studies have shown that the presence of coadsorbed bromine does not significantly affect the rate of  $\beta$ -hydride elimination, the studies here show that bromine also does not significantly affect the deuterium kinetic isotope effect for this reason.

The possibility of secondary kinetic isotope effects can be addressed by comparing the results above with those for  $\beta$ elimination from CD<sub>2</sub>HCDH— groups generated by D addition to CHD=CHD. These latter studies show a kinetic isotope effect of 9.8 ± 0.6 for the temperature range 245–265 K. To within the experimental uncertainty, this isotope effect is the same as that measured for CD<sub>2</sub>HCD<sub>2</sub>— groups, as described above. We conclude that there is no measurable 2° isotope effect for  $\beta$  elimination as a result of D for H substitution at the  $\alpha$ -carbon. This result is not surprosing given that studies by Madix and Telford of methoxy decomposition by  $\beta$  elimination on Cu(110) have shown that there is no measurable 2° isotope effect for this reaction despite H,D substitution at the  $\beta$ -carbon.<sup>23</sup>

The possible role of tunneling in the ethyl  $\beta$ -hydride elimination reaction on Cu(100) can be addressed using the temperature-dependence measurements in Figure 3 for  $k_{\rm H}/k_{\rm D}$ elimination from CD<sub>2</sub>HCD<sub>2</sub>-. As discussed in refs 23–26, two diagnostics for tunneling are the relative activation energies and the relative prefactors in the Arrhenius rate constants for the isotopic variants of the reaction. These values can be determined from the results in Figure 3. In particular, if we make the reasonable assumptions that Arrhenius expressions can be used to represent the temperature dependences of the rate constants and that the  $\beta$ -H and  $\beta$ -D elimination rates have the same dependences on surface coverage, then the relative rates of H and D elimination are given by

$$\frac{\text{rate}_{-\text{H}}}{\text{rate}_{-\text{D}}} = \frac{A_{\text{H}} \exp(-E_{\text{H}}/RT)}{A_{\text{D}} \exp(-E_{\text{D}}/RT)} = \frac{A_{\text{H}}}{A_{\text{D}}} \exp(-(E_{\text{H}} - E_{\text{D}})/RT)$$

where the A's and E's are the Arrhenius prefactors and activation energies for H and D elimination. A fit of this function to the results in Figure 3 gives the solid line shown and the following fit parameters:  $A_{\rm H}/A_{\rm D} = 1.17$  and  $E_{\rm H} - E_{\rm D} = -1.08$  kcal/mol.

As discussed in refs 24 and 25, the issues with respect to the possibility of tunneling are the extent to which the prefactor ratio deviates from 1 and the magnitude of the action energy difference with respect to the difference in zero-point energies for the "reactive vibrational modes" in the reactants or products. In the present system, the experimentally-determined zero-point energy difference of 1.08 kcal/mol for  $\beta$ -H vs  $\beta$ -D elimination is quite similar to the difference in zero-point energies for C–H and C–D bond stretching, which are expected to be the reactive coordinates. Specifically, the reported values of 2935 and 2153 cm<sup>-1</sup> for C–H and C–D bond stretching in ethyl groups on Cu(111) correspond to an energy difference of 1.12 kcal/mol.<sup>27</sup>

In the case of the prefactor ration, transition state theory predicts the following:

$$\frac{A_{\rm H}}{A_{\rm D}} = \frac{Y_{\rm H}}{Y_{\rm D}} \frac{\kappa_{\rm H}}{\kappa_{\rm D}} \frac{Q_{\rm H}^{+}Q_{0,\rm D}}{Q_{\rm D}^{\dagger}Q_{0,\rm H}}$$

where Y is a correction factor for tunneling,  $\kappa$  is the transmission coefficient,  $Q^{\dagger}$  is the partition function for the transition state (excluding the critical vibrational mode in the reaction coordinate), and  $Q_0$  is the partition function for the reactant. Since in the studies here,  $\beta$ -H and  $\beta$ -D elimination both occur from the same reactant,  $Q_0$  is the same for the two reactions. Furthermore the difference in  $Q^{\ddagger}$  for the two reactions corresponds (assuming that the reaction coordinate is C-H/C-D stretching) simply to  $Q_{\text{vib}(\text{C}-\text{D})}/Q_{\text{vib}(\text{C}-\text{H})} = 1 - e^{-h\nu_{\text{C}-\text{H}}/k\text{T}}/(1 - e^{-h\nu_{\text{C}-\text{H}}/k\text{T}})$  $e^{-h\nu_{C-D}/kT}$ ). This ratio is a function of temperature, ranging from 1.00 at 0 K to  $v_{C-H}/v_{C-D}$  at infinite temperature. At 260 K, this ratio is 1.00. Assuming  $\kappa_{\rm H}/\kappa_{\rm D} = 1$ , the nominal experimental  $A_{\rm H}/A_{\rm D}$  ratio of 1.17 is >1 and indicative of tunneling corrections. However, we estimate an experimental uncertainty of at least  $\pm 0.2$  in the measured value of 1.17 on the basis of the dashed line fit to the data in Figure 3 for a prefactor ratio of 1.00 and an activation energy difference of 1.16 kcal/mol. Thus, while tunneling cannot be ruled out, one need not invoke tunneling to account for the experimental results. Similar conclusions have been reached previously for other C-H bond scission processes at metal surfaces.23,26

4.3. Competition between Alkyl Group Decomposition/ **Rearrangement and Energy Dissipation to the Substrate.** The absence of any detectable ethyl group decomposition/rearrangement in H atom addition to ethylene at 110 K on Cu(100) indicates that the nascent ethyl radicals/groups dissipate substantial amounts of energy (30-60 kcal/mol) and accommodate to the surface prior to the occurrence of these processes. In the case of ethyl rearrangement by 1,2-hydrogen shift, the absence of reaction is probably attributable to a high barrier for reaction. Specifically, if one views the 1,2 shift as occurring while the ethyl species exists as a free radical prior to forming a metal-carbon bond, then the energetics of the process are probably similar to those for a 1,2 shift in gas phase ethyl groups, where a barrier of 84 kcal/mol is determined from the potential energy surface calculated for the  $H + CH_2 = CH_2$ system.<sup>11,21</sup> On the other hand, if the 1,2 shift were to occur



**Figure 10.** Unimolecular rate constant for ethyl  $\beta$  elimination of Cu-(100) as a function of total energy available and the number of classical oscillators, *s*, over which the energy is statistically distributed. As described in the text, the reaction rate has been determined using RRK theory for a unimolecular  $\beta$  elimination reaction with an energy barrier,  $E_0$ , of 15 kcal/mol.

after formation of the metal-carbon bond, then the shift process would require metal-carbon scission, which has a barrier of  $33 \pm 6$  kcal/mol. In either case, the expected energy barrier is larger than that for a number of ethyl decomposition processes which are also not observed.

The absence of ethyl decomposition is interesting, particularly since the activation energy for  $\beta$  elimination is 14.5  $\pm$  2 kcal/ mol on Cu(100),16,17 which is only one quarter of the overall addition reaction exothermicity and less than half the energy released by forming the copper-carbon bond. To address whether or not this result is surprising given what is known about the rates of energy dissipation from adsorbates to surfaces, we consider first the rate expected for  $\beta$  elimination as a function of the ethyl internal energy. Assuming that the internal energy of the ethyl group is randomized and that the internal energy available is significantly larger than the barrier for reaction (a reasonable assumption in this case until significant energy has been dissipated to the substrate), then the probability that the critical oscillator along the reaction coordinate contains energy greater than or equal to the energy required for reaction is given by Rice-Ramsperger-Kassel (RRK) theory as

$$\left(\frac{E-E_0}{E}\right)s-1$$

where *E* is the energy available,  $E_0$  is the barrier for reaction, and *s* is the number of oscillators over which the energy is statistically distributed. The unimolecular rate constant is simply this probability multiplied by the vibrational frequency of the critical oscillator. As an upper limit to the rate constant, we choose the highest frequency mode associated with the  $C_{\beta}$ -H bond being broken, i.e. the  $C_{\beta}$ -H stretch, as the critical oscillator. Note that this is also the only mode which, in the absence of tunneling, can account quasi~classically for the large kinetic isotope measured for  $\beta$ -hydride elimination (see Figure 3). This mode has a vibrational frequency of 9.0 × 10<sup>13</sup> s<sup>-1</sup>.

Given this value, Figure 10 presents the RRK unimolecular reaction rate constant for  $\beta$ -hydride elimination by ethyl groups on Cu(100) as a function of the total energy available and as a function of the number of oscillators over which the energy is distributed. If we neglect energy dissipation into the copper lattice to determine an upper limit for the rate, then the number of oscillators over which the energy is distributed for adsorbed ethyl groups (note that adsorption converts rotations and translations to hindered rotations and translations) is 21. In this extreme case, if the total energy available is the full 60 kcal/

mol exothermicity for formation of adsorbed ethyl groups, then the half-life for ethyl groups on the surface is  $\sim 10$  ps. On the other hand, if only the 30 kcal/mol of energy released upon formation of the copper-carbon bond is available for reaction, then the half-life is >10 ns.

While no measurements have been made of energy transfer between hot alkyls and surfaces, measurements of energy relaxation for vibrationally excited carbon monoxide on metals indicate energy transfer on the picosecond time scale. For example, the lifetime for CO in v = 1 has been determined to be  $\sim$ 3 ps on Pt(111)<sup>28</sup> and  $\sim$ 1.2 ps on Cu(100).<sup>29</sup> The lifetime for intra-adsorbate energy transfer in the case of the symmetric CH<sub>3</sub> stretching mode in CH<sub>3</sub>S on Ag(111) is also only  $\sim$ 3 ps, but adsorbate to surface energy transfer in this system occurs on a much longer time scale with a time constant of  $\sim 5$  ns.<sup>29</sup> In the case of ethyl formation from H + ethylene on Cu(100), adsorbate-substrate energy transfer is probably significantly faster than in the  $CH_3S/Ag(111)$  system, since formation of the copper-carbon bond places energy directly in the mode that couples the adsorbate to the substrate. Thus, on the basis of the expected adsorbate-substrate energy transfer on the order of picoseconds and a statistical reaction rate of >10 ns for internal energies <30 kcal/mol, the lack of  $\beta$  elimination by ethyl groups during the H + ethylene reaction on Cu(100)appears conceptually reasonable.

Despite the predominance of quenching over reaction in the ethyl/Cu(100) system, there is evidence from other studies that "hot" adsorbates can have chemically-significant lifetimes on surfaces. For example, O atoms produced by photodissociation of  $O_2$  on Pt(111) have been shown to react with coadsorbed species prior to thermal accommodation with the surface.<sup>30-32</sup> There are also reports of analogous reactions by hot atoms and radicals produced by the thermal dissociation of adsorbates, 33-39 and in the case of  $O_2$  dissociation on Al(111) there is evidence from STM that hot O atoms produced by dissociative adsorption of  $O_2$  diffuse ~80 Å across the surfaces at 300 K with a lifetime of >1 ps prior to thermal accommodation.<sup>40,41</sup> While these results provide evidence for a range of interesting phenomena, further studies are needed to assess the relative rates of reaction and quenching in excited adsorbate systems and to determine the extent to which statistical theories are applicable for predicting reactivity.

#### 5. Conclusions

The addition, at 110 K, of gas phase H and D atoms to physisorbed ethylenes on a Cu(100) surface has been studied. The results show that, despite the 60 kcal/mol exothermicity of this reaction, there is no detectable C—C or C—H bond dissociation in the nascent ethyl products. Studies of H addition to C<sub>2</sub>D<sub>4</sub> and D atom addition to CDH=CDH also show that the extent of H/D shift between two carbon atoms of the product ethyl prior to thermal accommodation with the surface is negligible. These results demonstrate the potential of such H atom addition reactions for the synthesis of surface alkyl groups. The results also demonstrate the potential of isotope labeling for forming selectively-deuterated fragments on the surface, and in the present studies, selectively-labeled ethyl groups have been utilized to measure the deuterium kinetic isotope effect for  $\beta$ -hydride elimination on Cu(100).

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