Reaction of Deuterium Atoms with Cyclohexane on Cu(111): Hydrogen Abstraction Reactions by Eley-Rideal Mechanisms

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Cyclohexane desorbs molecularly intact from Cu(111) and does not react with deuterium atoms that are preadsorbed on the surface. By contrast, when deuterium atoms formed on a hot tungsten filament are impinged onto a Cu(111) surface precovered with cyclohexane, *dehydrogenated* products (cyclohexene, cyclohexadiene, and benzene) are evolved when the surface is heated in a subsequent temperature-programmed reaction (TPR) experiment. These D-atom-induced dehydrogenation products provide strong evidence for an Eley-Rideal mechanism where D atoms abstract hydrogen from cyclohexane prior to thermal accommodation with the surface. The kinetics of cyclohexene evolution indicate that both single and sequential H-atom abstractions occur by this mechanism. The cross section for abstraction is on the order of $0.5 \text{ Å}^2/\text{cyclohexane}$, about an order of magnitude smaller than that for D-atom addition to π -bonds, consistent with the relative cross sections for these reactions in the gas phase. In addition to these Eley-Rideal-type reactions, there is evidence for Langmuir-Hinshelwood hydrogenation and dehydrogenation reactions during the TPR experiment. Product distributions in the desorbing flux were quantified by mass spectrometry using an electron-impact ionization energy of 15 eV to accentuate the molecular ions.

1. Introduction

Bimolecular reactions at surfaces have been classified according to two basic types of mechanisms: reaction between two adsorbed species (Langmuir–Hinshelwood mechanism) and reaction of an adsorbate with a species incident from the gas phase (Eley–Rideal mechanism).¹ While Langmuir–Hinshelwood mechanisms dominate in thermal processes, a number of recent studies have provided evidence for Eley–Rideal mechanisms when atoms, ions, and radicals are reacted with adsorbate-covered surfaces.²⁻⁹

In the present work, we are concerned with the Eley-Rideal reaction of hydrogen or deuterium atoms with adsorbate-covered surfaces. Previous studies by Lykke and Kay have shown that when hydrogen atoms are impinged onto a chlorine-precovered Au(111) surface at 300 K, HCl is observed in the gas phase.² On the basis of the internal state distribution of the evolved HCl, it was suggested that at least portion of the products (vibrationally excited HCl in v = 1) may be formed by an Elev-Rideal mechanism where the incident H atoms abstract Cl prior to thermal accommodation with the surface.² Studies by Cheng et al. have shown evidence for an analogous process in the reaction of H atoms with Si(100) covered with halogens (Cl, Br, and I). In this case, Br was removed from the surface at temperatures as low as 300 K, 420 K below where adsorbed H and Br react by a Langmuir-Hinshelwood mechanism to evolve HBr into the gas phase.³ More recently, Rettner has provided convincing dynamical evidence for an Eley-Rideal mechanism in H abstraction of D atoms (and vice versa) from a Cu(111) surface at 100 K.9

Given the reaction energetics, these H-atom abstraction reactions by Eley-Rideal mechanisms are not particularly surprising. In the case of Cl/Si(100), ΔH for reaction with H atoms to form HCl is estimated to be -13 kcal/mol, based on a typcial Si-Cl bond strength of 90 kcal/mol.¹⁰ For Cl/Au(111), abstraction to form HCl is exothermic by ~50 kcal/mol for a Au-Cl bond energy of 53.3 kcal/mol,² while for H/Cu(111), H₂ formation has a ΔH of -48.4 kcal/mol on the basis of a Cu-H bond energy of 55.3 kcal/mol.⁹ If one views these processes as atom-transfer reactions, i.e., transfer of the H or Cl atom from the surface to the incident D atom, then comparison with

Here, we present evidence for a different type of H-atom abstraction reaction on a Cu(111) surface: abstraction of a hydrogen atom from a physisorbed hydrocarbon. In particular, we show that D atoms abstract hydrogen from C-H bonds in cyclohexane adsorbed on a Cu(111) surface. This system is of practical significance as a model for the reaction of hydrogen atoms in plasmas with organic polymer films in microelectronics processing. The advantage of this model system is that the surface reactions can be monitored by thermally desorbing the products and identifying them with mass spectrometry. This system is also ideal for studying Eley-Rideal abstraction reactions, since cyclohexane does not dehydrogenate on either clean Cu(111) or Cu(111) precovered with a partial monolayer of D atoms. Thus, the formation of dehydrogenation products when D atoms are impinged onto a Cu(111) surface precovered with cyclohexane provides strong evidence for an Eley-Rideal mechanism.

2. Experimental Section

Details of the ultrahigh vacuum (UHV) chamber and the experimental procedures have been described previously.12 Briefly, the Cu(111) crystal (Monocrystals, 99.999%) was cleaned by cycles of Ar⁺ sputtering and annealing. Reactants, cyclohexane (Fisher, 99.8%), cyclohexene (Aldrich, 99%), 1,3-cyclohexadiene (Aldrich, 98%), 1,4-cyclohexadiene (Aldrich, 97%), and bromocyclohexane (Aldrich, 95%), were dosed onto clean Cu(111) by backfilling the chamber via leak valves. In the experiments reported here, H and D atoms were generated in situ by dissociating H₂ (Matheson, 99.9995%) and D₂ (Matheson, 99.5 atom % D) with a hot tungsten filament that is resistively heated to ~1800 K.¹³ The crystal was held 3 cm away from the filament during H/D atom dosing. All exposures are given in langmuirs (1 langmuir = 1×10^{-6} Torr-s) and are uncorrected for differing ion gauge sensitivities. In the temperature-programmed reaction (TPR) studies, the heating rates were 4 K/s. Up to three masses were monitored simultaneously in these experiments, and a differentially-pumped shield with a 2-mm-diameter aperture ensured that only those species evolved from the center of the Cu(111) crystal were detected by the mass spectrometer. To

exothermic gas-phase atom-transfer reactions¹¹ shows that energy barriers of only a few kilocalories per mole or less are to be expected for these Eley–Rideal reactions.

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Figure 1. Temperature-programmed desorption spectra of cyclohexane adsorbed on Cu(111) at 110 K. The heating rates were 4 K/s. The inset shows the TPD peak area as a function of cyclohexane exposure.

obtain mass spectra of the products evolved, integrated desorption mass spectroscopy (IDMS)¹⁴ experiments were performed. In this technique, entire mass spectra are rapidly acquired and summed over the temperature range where products of interest desorb from the surface. Throughout this study, an electron energy of 15 eV^{15} was used for ionization in the mass spectrometer in order to reduce product fragmentation. The advantages of using such a low ionization energy for identifying and quantifying product mixtures have been demonstrated in previous studies.⁴

3. Results and Discussion

3.1. Cyclohexane and Cyclohexane + D Atoms. The adsorption/desorption behavior of cyclohexane on the Cu(111) surface was studied by temperature-programmed desorption (TPD). Figure 1 shows TPD spectra for molecular cyclohexane (m/e =84) as a function of exposure. At low exposures, a single peak is observed at 175 K. With increasing exposure this peak increases, shifts slightly to higher temperature, and finally saturates with a peak temperature of 180 K for exposures between 3.0 and 4.0 langmuirs. For exposures above 4 langmuirs, an additional peak appears at 135 K. The leading edges of both peaks show typical zero-order desorption behavior,¹⁶ and similar results have been observed previously for cyclohexane desorbing from Ni(111).¹⁷ No additional features were observed in the TPD spectra even for exposures of up to 15 langmuirs. The amount of molecularly desorbing cyclohexane as derived from the TPD peak area is plotted versus cyclohexane exposure in the inset of Figure 1. The linear increase in the cyclohexane yield from the surface to above one monolayer coverage is consistent with the fact that no decomposition products are detected in TPD and that there is no carbon deposition on the surface as monitored by Auger electron spectroscopy. These observations indicate reversible adsorption/ desorption behavior for cyclohexane on Cu(111).

Analysis of the TPD spectra using zeroth-order kinetics as suggested by the alignment of the leading edges of TPD peaks¹⁶ shows that the desorption energies for the two cyclohexane TPD peaks on Cu(111) are 10 kcal/mol for the 180 K peak and 9 kcal/mol for the 140 K peak. This latter value is consistent with the heat of sublimation for cyclohexane (8.94 kcal/mol¹⁸), and we attribute this peak to desorption of multilayers. The 1 kcal/ mol larger heat of adsorption for the higher temperature peak is consistent with desorption from the monolayer. Zebisch et al. found that cyclohexane desorbs from Ni(111) in three TPD peaks.¹⁷ These peaks were attributed to desorption from the first layer, second layer, and multilayers. Further investigation is needed to determine why we do not observe a similar splitting of the low-temperature peak on Cu(111) into second and multilayer peaks.

Before presenting the results on the reaction of cyclohexane with H (D) atoms, the adsorption/desorption behavior of hydrogen (deuterium) on Cu(111), which has been studied quite thoroughly, $^{9,19-22}$ is briefly reviewed. While molecular hydrogen



Figure 2. TPR spectra following m/e = 82, 84, and 85 from Cu(111) after the following exposures at 110 K: (A) 3.0 langmuirs of C₆H₁₂, (B) 3.0 langmuirs of C₆H₁₂ followed by exposure to the hot tungsten filament for 100 s, and (C) 30 langmuirs of D atoms ($\theta = 0.2$) followed by 3.0 langmuirs of C₆H₁₂. The heating rates were 4 K/s.

has very low dissociative sticking probability, H atoms can be readily adsorbed onto the surface. Adsorbed hydrogen atoms recombine and desorb from Cu(111) between 240 and 400 K.²¹ Because the absolute flux of atomic hydrogen generated in our apparatus by using a hot tungsten filament to dissociate background H₂ is not accurately known, the exposures of hydrogen atoms are reported as the exposure of H_2 to the filament. For reference, an 80-langmuir hydrogen exposure is required to saturate the Cu(111) surface. This result indicates that the H atom flux is $\sim 1 \times 10^{13}$ (atoms/cm²)/s at $P_{\rm H_2} = 1 \times 10^{-6}$ Torr. If we assume that the H atoms (in our studies) and the translationally hot H_2 molecules (in the work of Anger et al.²¹) produce the same saturation coverage of H on the surface, then the results in ref 21 imply that the saturation coverage of H atoms in our studies is $\theta = 0.5$ (number of hydrogen atoms per surface copper atom). This assumption is not unreasonable, since the dissociative adsorption of H_2 will be inhibited by site-blocking, while the H-atom coverage via H-atom dosing is limited by concurrent H-atom abstraction. In particular, we have found that H atoms will abstract preadsorbed deuterium atoms from the Cu(111) surface during dosing at 120 K. The kinetic energies and angular distribution for the HD formed by this reaction have been reported by Rettner.9 Analogous low-temperature abstraction reactions have been observed previously on $Si(100)^3$ and $Au(111)^{23}$ surfaces, and there is evidence that these processes occur by Eley-Rideal mechanisms; i.e., the incident H atom abstracts the D atom prior to thermal accommodation with the surface.

In order to determine the possible effects of electrons emitted from the hot tungsten filament on adsorbed cyclohexane, the TPR spectra of cyclohexane taken before and after exposure to the filament are compared in parts A and B of Figure 2. Figure 2A shows spectra of cyclohexane without exposure to the filament. The intensities of m/e = 85 and m/e = 82, which track that for the molecular ion at m/e = 84, are due to the M + 1 ion of cyclohexane and to a small amount of cracking in the mass spectrometer despite the low electron impact ionization energy of 15 eV. Unlike benzene on Cu(111), where there is evidence for electron-stimulated desorption,⁴ cyclohexane is unaffected as evidenced by comparing parts A and B of Figure 2. The possibility of electron-induced dissociation can be ruled out since no new products are detected. For example, m/e = 82, which is the molecular ion of cyclohexene [the β -hydride elimination product of surface cyclohexyl groups (ref 24, see below)], is unchanged by exposure to the hot filament (compare parts A and B of Figure 2). Thus, there is no detectable electron-induced C-H bond dissociation to produce cyclohexyl groups. This fact is not too surprising given that the total number of electrons incident onto



Figure 3. Integrated desorption mass spectra of the products from a Cu(111) surface over the temperature range 120-280 K after the indicated exposures at 110 K. Each D-atom dose corresponded to a 100-s exposure at the required chamber pressure. All the spectra were taken with an electron impact ionization energy of 15 eV as described in the text. The inset spectrum corresponds to that in (C) after subtracting the contributions of the M + 1 ions and M - 1 ions from molecules with m/e = 84, 82, 80, and 78.

the surface from the hot tungsten filament during the 100-s exposure is only 2×10^{12} based on the measured current of 3.2×10^{-9} A from the crystal to ground. This number is at least 1 order of magnitude smaller than the number of cyclohexane molecules on the surface.

Cyclohexane is also unreactive with *preadsorbed* deuterium atoms on Cu(111). The TPD spectra for cyclohexane from a Cu(111) surface precovered with 30 langmuirs of deuterium ($\theta_D \sim 0.2$) are shown in Figure 2C. The m/e = 82, 84, and 85 spectra display the same shape and peak temperature as those from the clean surface. There is no evidence for H,D exchange or H-atom abstraction on the basis of the 84/85 and 84/82 intensity ratios. We therefore conclude that cyclohexane does not react with coadsorbed deuterium atoms that are thermally accommodated with the surface.

Cyclohexane does react with deuterium atoms incident from the gas phase. The effects of deuterium exposure on the cyclohexane/D atom reaction have been studied by integrated desorption mass spectrometry (IDMS). Selected results for the reaction of 3.0 langmuirs of adsorbed cyclohexane (75% of monolayer saturation) with variable amounts of deuterium atoms are shown in Figure 3. All the spectra were acquired between 120 and 280 K, a temperature range that includes all products detected by TPR. The IDMS spectrum in Figure 3A is for pure cyclohexane, and two points are particularly noteworthy. First, because the mass spectrometer ionizer is operated at 15 eV, virtually all cracking of cyclohexane to m/e = 83 has been eliminated and the spectrum is dominated by m/e = 84. Second, the intensity ratio of 0.07 for m/e = 85 (M + 1) to m/e = 84(M) is consistent with the theoretical value of 0.067 based on the 1.1% natural abundance of ¹³C. By comparison of this spectrum with the spectra in parts B-D of Figure 3 for increasing D-atom exposure, it is evident that products of lower as well as higher molecular weight are formed! In other words, exposing adsorbed cyclohexane to D-atom flux at 120 K gives rise to dehydrogenated products as well as D-atom incorporation products in the subsequent TPR experiment.





Figure 4. H abstraction reaction product distribution after 2.5 langmuirs of cyclohexane was reacted with 2000 langmuirs of H atoms: (A) raw mass spectrum over the temperature range 120-180 K after background subtraction, (B) spectrum after correcting for the contributions of M + 1 and M - 1 ions, and (C) product distribution after taking into account the detection efficiency of the mass spectrometer for the indicated products.

Because the total reaction cross section is small and the required D_2 exposures to the filament source are quite large (up to 2000) langmuirs in the experiments of Figure 3), it is possible that an impurity at the percent level in the H_2 or D_2 source, which has a large reaction cross section, accounts for the reaction products observed. To test this possibility, control experiments with potential contaminants in the D_2 source have been performed. Matheson quotes the following impurity levels in their D_2 : O_2 = 3 ppm; $N_2 < 3$ ppm; other impurities below detection limits. Mass spectrometry in our apparatus confirms that the upper limits for the contaminates are less than 1%; Ar and H₂O, however, are also detected at the percent level (presumably displaced from the ion pump and chamber walls). Control experiments in which a cyclohexane-covered surface is exposed to 300 langmuirs of Ar, 300 langmuirs of CH₄, and 200 langmuirs of air with the tungsten filament on showed virtually no dehydrogenation products. With 500 langmuirs of H_2O , the total yield of dehydrogenated products is comparable to that with 2000 langmuirs of D_2 , but the product mass spectra are substantially different. With H_2O , some m/e= 76 and 77 are observed in addition to m/e = 78-85. Since the gas exposures used in the control experiments are at least 1 order of magnitude larger than the maximum possible levels of contamination introduced with D_2 or H_2 , we rule out abstraction by impurities as the source of the D-atom-induced products in Figure 3.

3.2. Hydrogen Abstraction Products. Identification of these D-atom-induced dehydrogenation products is straightforward since the mass spectra in Figure 3 are dominated by the molecular ions. If no H,D exchange occurs and there is no fragmentation in the mass spectrometer, then only even-mass ions are expected, since all stable hydrocarbon molecules have an even molecular weight. In particular, the dominant ions at m/e = 82, 80, and78 in Figure 3B-D can be attributed to cyclohexene, cyclohexadiene, and benzene, respectively. These products have been confirmed by H-atom experiments, where only abstraction and addition (not H,D exchange) are possible. Figure 4 shows the IDMS results for reaction between 2.5 langmuirs of cyclohexane and 2000 langmuirs of H atoms. The raw ion intensities after background subtraction are shown in Figure 4A, while Figure 4B presents the product mass spectrum after correcting for the M+ 1 and M - 1 ions (the major ions besides the molecular ion at 15 eV) attributable to cyclohexane, cyclohexene, cyclohexadiene, and benzene. The M + 1 correction was based on the 1.1% natural abundance of ¹³C, while the M - 1 cracking fragments were accounted for by using calibration mass spectra taken at 15 eV. For reference, the M - 1 daughter ion yields at this ionization energy in our mass spectrometer are 6%, 9%, 43%, and 3% of the molecular ion intensities for cyclohexane, cyclohexene, 1,3cyclohexadiene, and benzene, respectively. As expected, the odd mass ion intensities in Figure 4A are effectively eliminated when M + 1 and M - 1 ion contributions are taken into account. To determine the relative yields of the dehydrogenation products, the relative ionization and detection efficiencies for the molecules at 15-eV ionization energy must also be considered. These values were determined by acquiring reference mass spectra at a given pressure and utilizing ion gauge sensitivity factors from the literature.²⁵ (The values for cyclohexene and cyclohexadiene, which are not in literature, were estimated by interpolating between the values for cyclohexane and benzene.) Taking these ion gauge sensitivity factors into account, the relative ionization/ detection efficiencies for the molecular ions in the mass spectrometer relative to 1 for cyclohexane are 1.2 (cyclohexene), 2.6 (cyclohexadiene), and 3.9 (benzene). The resulting product yields are shown in Figure 4C.

It is clear from the product yields in Figure 4C that most of the adsorbed cyclohexane is unreacted despite a 2000-langmuir H-atom exposure (25 times the exposure required to saturate a clean surface with H atoms). The dominate dehydrogenation product is cyclohexene, although measurable amounts of cyclohexadiene and benzene are also formed. Significantly, the yield of benzene is comparable to that for cyclohexadiene, and the relative yields of these two products are approximately independent of the H-atom exposure. This conclusion is also evident in the D-atom results presented in Figure 3; i.e., the relative ion intensities at m/e = 78-81 are independent of D-atom exposure. If we assume that m/e = 78, 80, 82, and 84 are due solely to perhydro products and not partially-deuterated compounds, then correction for M + 1 and M - 1 ions yields the inset spectrum in Figure 3C. The small but measurable ion intensities at the odd mass ions are attributable to monodeuterated products.

Since cyclohexane does not dehydrogenate on clean Cu(111) or Cu(111) precovered with H or D atoms, the formation of dehydrogenated products in Figures 3 and 4 indicates that H and D atoms from the gas phase initiate cyclohexane dehydrogenation. On the basis of the gas-phase chemistry of saturated hydrocarbons with H atoms, the logical conclusion is that D atoms initiate dehydrogenation by abstracting an H atom from cyclohexane to form a cyclohexyl group, which remains adsorbed, and HD, which desorbs undetected in our experiments. Such a gas/surface reaction is supported by the observation that the yield of dehydrogenation products continues to increase for H/D atom exposures 10–30 times that required to saturate a clean Cu(111) surface. Analogous Eley–Rideal-type mechanisms have recently been proposed for a variety of other radical/adsorbate reactions.²⁻⁷

With respect to the mechanism(s) for forming dehydrogenation products from cyclohexyl groups, two possibilities should be distinguished: sequential H abstraction at the adsorption temperature of 120 K and dehydrogenation upon heating the surface in the TPR experiment. The TPR spectra provide evidence for both types of mechanisms, and the results are most definitive for the case of cyclohexene formation. Figure 5A shows TPR spectra for cyclohexene (m/e = 82) evolved after reacting 3.0 langmuirs of cyclohexane with 700 langmuirs of D atoms at 120 K. Two peaks are observed: one at 190 K and the other at 225 K. The peak at 190 K results from rate-determining desorption of adsorbed cyclohexene formed by two sequential D abstractions at 120 K, while the peak at 225 K is attributable to β -hydride elimination by adsorbed cyclohexyl species. Support for this interpretation comes from the reference TPR spectra in parts B and C of Figure 5. Figure 5B shows the molecular desorption spectrum for 2.0 langmuirs of cyclohexene on Cu(111), while Figure 5C shows evolution of cyclohexene after rate-determining



Figure 5. TPR spectra monitoring cyclohexene (m/e = 82) evolved from Cu(111) after adsorbing (A) 3.0 langmuirs of cyclohexane followed by 700 langmuirs of D atoms, (B) 2.0 langmuirs of cyclohexene, and (C) 1.0 langmuir of bromocyclohexane. The heating rates were 4 K/s.



Figure 6. TPR spectra monitoring benzene (m/e = 78) evolved from Cu(111) after adsorbing (A) 3.0 langmuirs of cyclohexane followed by 200 langmuirs and 1000 langmuirs of D atoms and (B) 2.5 langmuirs of benzene and cyclohexane from a 1:8 (volume ratio) mixture. The heating rates were 4 K/s.

 β -hydride elimination by cyclohexyl groups formed from dissociative adsorption of C₆H₃Br. (The formation of surface alkyl groups from alkyl halides and their decomposition by β -hydride elimination on copper surfaces has been discussed extensively elsewhere.²⁴) We conclude that both single and sequential H abstraction reactions occur at 120 K when cyclohexane is exposed to D atoms. These mechanisms are illustrated in the top panel of Figure 8.

The mechanisms for forming more highly dehydrogenated products are less clear. Multiple dehydrogenation at 120 K is required since cyclohexyl (C_6H_{11}) does not dehydrogenate past cyclohexene on clean or D-atom-precovered Cu(111). But whether cyclohexadiene and benzene are formed at 120 K or upon heating the surface in the TPR experiments cannot be determined from the TPR results. For example, Figure 6A shows TPR results for benzene (m/e = 78) evolution after exposing 3.0 langmuirs of C_6H_{12} on Cu(111) to 200 and 1000 langmuirs of D atoms, respectively. The shift in the benzene peak temperature from 250 to 210 K between these two spectra is typical of benzene desorption from Cu(111), where the desorption peak temperature is highly sensitive to the benzene coverage and to coadsorbed species.²⁶ Furthermore, a peak temperature of 210–240 K is quite reasonable for benzene desorption when coadsorbed with



Figure 7. TPR spectra monitoring (A) cyclohexane- d_1 (m/e = 85) after adsorbing 3.0 langmuirs of cyclohexane followed by 500 langmuirs and 1000 langmuirs of D atoms and (B) cyclohexane (m/e = 84) after adsorbing 2.5 langmuirs cyclohexane followed by 800 langmuirs of H atoms. The hydrogen or deuterium doses corresponded to a 100-s exposure at the required chamber pressure.

cyclohexane as shown by the reference spectrum in Figure 6B. However, since this temperature range is also comparable to that for β -hydride elimination (C–H bond scission) on Cu(111),²⁴ it is possible that dehydrogenation occurs during the TPR experiment. Likewise, we cannot determine from the TPR results whether cyclohexadiene is formed during H/D atom dosing at 120 K or during the subsequent TPR experiment.

Several observations suggest a common adsorbed intermediate that reacts during the TPR experiment to form cyclohexadiene and benzene. We note in particular that the relative yield of these products is roughly independent of H/D atom exposure and that the yield of benzene is comparable to that for cyclohexadiene. Sequential H abstractions at 120 K would produce a dose-dependent product distribution. On the other hand, dehydrogenation of an adsorbed intermediate whose coverage increases with increased H,D-atom exposure could produce a product distribution that is independent of H,D-atom dose. Furthermore, selective removal of specific H atoms from cyclohexane to form a particular intermediate would not be surprising given that the well-known conformations for six carbon rings may orient selected C-H bonds for preferential reactivity.27,28 We note also that a C_6H_9 species has been documented as a particularly stable intermediate in the dehydrogenation of cyclohexane to benzene on Pt(111).^{27b,c}

3.3. Deuterium Incorporation Products. The ions at odd m/e values (79, 81, 83, and 85) in the mass spectra of the cyclohexane/ D-atom reaction products (Figure 3) indicate that besides H abstraction, deuterium incorporation occurs during this reaction. The small intensity of these ions relative to those at even m/e values (78, 80, 82, and 84) indicates that dehydrogenation predominates.

As with H-atom abstraction, D-atom incorporation can occur either during D-atom dosing or while heating surface in the TPR experiment. In actuality, both probably occur. For example, we have shown previously that D atoms efficiently add, by Eley-Rideal mechanisms, to the π -bonds in ethylene and benzene adsorbed on Cu(111).⁴ Analogous D-atom addition to cyclohexene formed in the experiments here by two sequential H abstractions on cyclohexane produces cyclohexyl- d_1 . β -Hydride elimintion during the TPR experiment then produces cyclohexene d_1 . This mechanism is illustrated in Figure 8. Alternatively, cyclohexene- d_1 could be formed by deuterium addition during the TPR experiment to a triply-dehydrogenated surface fragment.



Figure 8. Postulated H abstraction and D incorporation reaction pathways for the reaction of deuterium atoms incident onto a cyclohexane-covered Cu(111) surface at 110 K. Gas-phase products are indicated by the vertical arrows, and D additions/abstractions by Eley-Rideal mechanisms are indicated by curved arrows.

Such hydrogenation reactions at high surface coverages of hydrogen have precedence in the chemistry of *n*-alkyl groups on Cu(110).²⁴

Deuterium incorporation during the TPR experiment is also supported by the formation of cyclohexane- d_1 (m/e = 85). The absence of this peak in the H-atom experiments of Figure 4 confirms that this product results from H,D exchange. The TPR spectra for m/e = 85 after D-atom exposure to cyclohexane are shown in Figure 7A, and two peaks are observed. The small peak at 180 K is the M + 1 ion from molecular desorption of cyclohexane (compare Figure 7B), while the larger peak at 225 K can be attributed to rate-determining addition of adsorbed deuterium to cyclohexyl groups to form cyclohexane- d_1 . When the experiment is performed with H atoms, as shown in Figure 7B, cyclohexane is formed and evolved at 10 K lower temperature, the isotope effect being consistent with a rate-determining hydrogenation reaction. This mechanism is shown schematically in Figure 8. Note that m/e = 85 could also result from ring-opening D-atom addition to cyclohexane to form n-hexyl- d_1 , which undergoes β -hydride elimination during the TPR experiment to evolve *n*-hexene- d_1 (m/e = 85). The argument against this pathway is that no isotope effect is expected in comparing the reactions of H and D atoms.

3.4. Mechanistic Implications and Comparison to Gas-Phase Reactions. The key inferences from the results above on the D-atom-induced dehydrogenation and exchange reactions of cyclohexane on Cu(111) are summarized in Figure 8. The absence of these reactions when D atoms are coadsorbed with cyclohexane indicates, as shown, that the reactions are initiated by hydrogen abstraction via an Eley-Rideal-type mechanism to form HD (which is not detected in our experiments) and adsorbed cyclohexyl groups. While we cannot determine from our results whether H abstraction occurs by a direct gas/surface collision or rather involves several bounces of the D atom across the surface prior to reaction, it is clear that the cross section for reaction is quite small. On the basis of the relative yields of cyclohexene and cyclohexane in Figure 3B and an approximate D-atom flux of 1 $\times 10^{13}$ (atoms/cm²)/s, the cross section for H atom abstraction is 0.5 $Å^2$ per cyclohexane. Because of the large uncertainty in the D-atom flux, this value is only order of magnitude. The nominal value for the cross section, however, is an order of magnitude smaller than that determined previously for the same D-atom flux for D-atom addition to π -bonds on Cu(111) by an Elev-Rideal mechanism.

The large difference between the cross sections for H atom addition to π bonds and abstraction from cyclohexane is not surprising, given the energetics for these processes in the gas phase. H-atom addition to gas-phase ethylene is exothermic by 37 kcal/mol^{18} and has a reaction barrier of $\sim 2 \text{ kcal/mol}^{29}$ while H-atom abstraction from cyclohexane is only slightly exothermic $(\Delta H = -8.7 \text{ kcal/mol}^{18})$ and has a barrier of ~9 kcal/mol.³⁰ If we assume that the H/D atoms from the tungsten filament in our experiments have kinetic energies consistent with a Maxwell distribution at the filament temperature of 1800 K, then 17% of the hydrogen atoms have kinetic energy in excess of the reaction barrier for H abstraction from alkanes compared with 77% for addition to π -bonds. Besides these energy requirements, the cross sections for H abstraction and addition for energies above the barrier may also differ. For example, in the gas phase, the cross section for H addition to ethylene is 3.34 ± 0.74 Å² for a collision energy of 20 kcal/mol,³¹ while that for H abstraction from cyclohexane- d_6 is only 0.098 \pm 0.017 Å²/C–D bond for collision energies of 24-48 kcal/mol.³⁰ Consequently, for energies above the reaction barrier, the ratio of the cross sections for H addition to ethylene and H abstraction from cyclohexane is ~ 34 . A similar calculation for these molecules physisorbed on Cu(111) using the results here and in ref 4 gives a ratio of \sim 90 after accounting for the fraction of H atoms whose energies exceed the gas-phase reaction barriers. Note that by taking the ratio of cross sections the large uncertainty in the hydrogen atom fluxes is removed and the relative cross sections for addition and abstraction on the surface and in the gas phase are found to be quite similar.

Potential differences between gas/surface and gas-phase H abstraction/addition reactions should also be noted. For example, in the gas-phase addition of H atoms to ethylene, the nascent ethyl radical with 37 kcal/mol of internal energy will decompose to ethylene and H in about a nanosecond if it cannot dissipate the extra energy by collisions. This process substantially lowers the measured cross section for forming C_2H_5 under collision-free conditions.²⁹ In the gas/surface reaction, the surface can act as an effective third body, and the effect of recrossing the dividing surface between reactant and products is assumably unimportant. On the other hand, concurrent metal-carbon bond formation on the surface makes the reaction even more exothermic (E_{Cu-C} in $C_2H_5/Cu(100) = 34 \pm 6 \text{ kcal/mol}^{32}$, so more energy must be dissipated. It remains to be demonstrated which factor dominates in the case of H addition reactions on the surface.

For H abstraction on the surface, there is also the possibility that concurrent copper-carbon bond formation can substantially increase the reaction cross section by lowering the reaction barrier, which is ~ 9 kcal/mol in the gas phase. On the basis of the copper-alkyl bond strength of 34 ± 6 kcal/mol, the overall process becomes exothermic by 43 kcal/mol, as opposed to \sim 9 kcal/mol in the gas phase. Conformational constraints, however, probably prohibit concerted C-H bond scission and Cu-C bond formation. In particular, a number of surface spectroscopy studies indicate that cyclohexane adsorbs in a chair conformation on metal surfaces.²⁸ In this conformation, three axial and three equatorial hydrogens are directly accessible to a deuterium atom incident on the surface, but forming a metal-carbon bond at any one of these sites requires inversion of the configuration at the carbon atom. On this basis, it seems unlikely that copper-carbon bond formation assists the hydrogen abstraction, thereby justifying the use of gas-phase processes as models for this gas/adsorbate abstraction reaction.

4. Conclusions

IDMS. Cyclohexane, which desorbs molecularly intact from Cu-(111), is found not to react with deuterium atoms that are preadsorbed on the surface. By contrast, if deuterium atoms are impinged onto a Cu(111) surface precovered with cyclohexane, dehydrogenated products (cyclohexene, cyclohexadiene, and benzene) are evolved when the surface is heated. The kinetics of product evolution during the TPR experiments suggest that the adsorbed cyclohexyl groups form cyclohexene by either a second D-induced abstraction reaction at the adsorption temperature or β -hydride elimination during the TPR experiment. Deuterium addition during the TPR experiment to form cyclohexane- d_1 is also observed.

Acknowledgment. Financial support from the National Science Foundation (Grant DMR-89-57236), the A. P. Sloan Foundation, and the Joint Services Electronics Program through the Columbia Radiation Laboratory (Contract DAAL03-91-C-0061) is gratefully acknowledged.

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