

effect apparent in comparing the TDS dehydrogenation rates for C_6H_6 and C_6D_6 suggests that C-H bond cleavage is involved in the rate-determining step here.

V. Conclusions

Benzene adsorbs molecularly on Pt(111) up to 420 K. By 570 K, it has dehydrogenated to leave an adlayer of stoichiometry C_2H , which further dehydrogenates to graphitic carbon by 800 K. At high coverages, benzene desorbs molecularly in two peaks at 350 and 505 K. Experiments with perdeuterated benzene indicate a substantial primary kinetic isotope effect in the dehydrogenation

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of adsorbed benzene. Coadsorption of benzene with small amounts of Bi strongly influences the competition between dehydrogenation and desorption, in favor of desorption. This is interpreted in terms of site blocking by Bi_a and a large ensemble requirement for dehydrogenation, since the activation energies for desorption and dehydrogenation are not strongly effected in this coverage range. Benzene adsorbs very weakly on a close-packed Bi adlayer. Some evidence is presented for a minor pathway to dehydrogenation involving defect sites.

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Registry No. Bi, 7440-69-9; Pt, 7440-06-4; benzene, 71-43-2.

Probing Ensemble Effects in Surface Reactions. 3. Cyclohexane Adsorption on Clean and Bismuth-Covered Pt(111)

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The adsorption and chemistry of cyclohexane on clean and Bi-covered Pt(111) surfaces have been studied with thermal desorption mass spectroscopy (TDS), deuterium labeling, Auger electron spectroscopy (AES), and X-ray photoelectron spectroscopy (XPS). The thermal desorption experiments show that, on clean Pt(111), cyclohexane is adsorbed in three molecular states with desorption temperatures of ~ 236 (monolayer), ~ 181 (second monolayer), and ~ 154 K (multilayer). There is little isotopic exchange in the molecularly desorbing cyclohexane. Benzene is formed at ~ 236 K on the clean Pt(111) surface as a product of the dehydrogenation of adsorbed cyclohexane. This process is 13-fold slower for perdeuterated cyclohexane. The activation energy for this process (13.4 kcal/mol for C-H and 14.5 kcal/mol for C-D) is very close to that for molecular desorption (~ 13.9 kcal/mol). A small amount of deuterium can be incorporated into the adsorbed benzene formed by this process when deuterium is also present on the surface. An analysis of quantitative XPS data and the effect of Bi poisoning on the chemisorption of cyclohexane shows that an ensemble of about five Pt atoms is necessary to chemisorb C_6H_{12} . The dehydrogenation of adsorbed cyclohexane is poisoned at very low bismuth coverages ($\theta_{Bi} < 0.1$) according to a mechanism dominated by steric, site-blocking effects. Electronic effects of Bi are small in this low coverage range, as evidenced by the near invariance of TDS peak temperatures for desorption and dehydrogenation of the hydrocarbon and its products. Kinetic modeling of the results suggests that an ensemble of at least eight free Pt atoms (in addition to those five required for chemisorption) is required for the dehydrogenation of adsorbed cyclohexane ($C_6H_{12,a} \rightarrow C_6H_{6,a} + 6H_a$). The influence of coadsorbed Bi upon the C(1s) XPS spectra of adsorbed cyclohexane suggests that the carbon atoms of the hydrocarbon, like adsorbed xenon, reside almost outside the surface electrostatic potential barrier.

I. Introduction

The chemisorption and surface reactions of cyclohexane, C_6H_{12} , on metal surfaces have been extensively studied from the viewpoint of catalysis.^{1,2} Due to the rupture of its C-H and/or C-C bonds, cyclohexane can produce different compounds upon decomposition. One of these is benzene. The great practical importance of the dehydrogenation of cyclohexane to produce benzene on Pt catalysts has given rise to a great number of studies of the interaction of C_6H_{12} with Pt surfaces.¹⁻⁹ This present work is concerned with the chemisorption and surface reactions of cyclohexane on Pt(111). The adsorption and chemistry of C_6H_{12} on Pt(111) have been previously studied by using thermal desorption mass spectrometry (TDS),³ near-edge X-ray absorption fine structure (NEXAFS),^{4,5} low-energy electron diffraction (LEED),⁶ and high-resolution electron energy-loss spectroscopy (HREELS).⁷ From a theoretical point of view, Kang and Anderson,¹⁰ employing a modified version of extended Hückel calculations, studied the chemisorption of C_6H_{12} on Pt(111) and its dehydrogenation to produce benzene.

One main objective of the present work is to probe the number of sites that are required on the Pt(111) surface for adsorption of C_6H_{12} and for its dehydrogenation. To accomplish this, we

study in detail the chemisorption and dehydrogenation of C_6H_{12} on clean and bismuth-covered surfaces. The motivation for employing bismuth to probe site-size or ensemble requirements has been presented in detail in the accompanying paper.¹¹

II. Experimental Section

The chemisorption and dehydrogenation of C_6H_{12} on clean and

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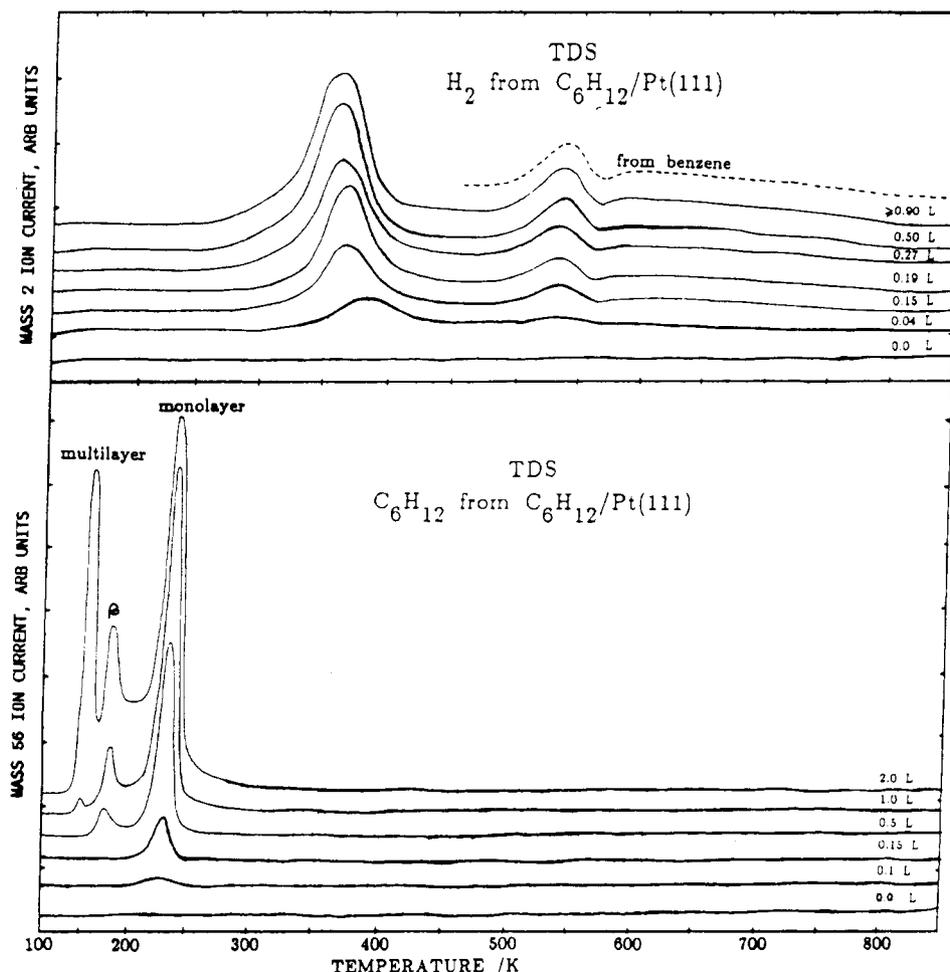


Figure 1. Representative thermal desorption spectra showing the evolution of H_2 (top) and molecular desorption of cyclohexane (bottom) following various C_6H_{12} exposures to clean Pt(111) at temperatures of ~ 100 K.

bismuth-covered Pt(111) surfaces were studied employing TDS, Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). The characteristics of the apparatus (together with its sample manipulator and Bi doser) and the procedure employed for the preparation and cleaning of the Pt(111) crystal were described in the accompanying paper,¹² as are other details of the experimental procedures and spectroscopic parameters.

The cyclohexane employed in the experiments was from Mallinckrodt, stated to be of greater than 99% purity. It was further purified by freeze/pump/thaw cycles, and its purity was proven in situ by mass spectroscopy. For dosing C_6H_{12} , we generally used a cosine-emitting pinhole doser such as described previously.¹² This was located ~ 8 cm from the sample and gave a small enhancement factor of ~ 1.5 compared to dosing only from the background pressure. This enhancement factor was taken into consideration in reporting the exposures here. Cyclohexane was usually dosed onto the surfaces at a sample temperature of ~ 100 K. In reporting exposures here, we used the ion gauge reading directly, without correction for the sensitivity factor for cyclohexane relative to N_2 . However, in calculating sticking coefficients, we used the reported relative ion gauge sensitivity factor of 6.0 for cyclohexane.¹³

Bismuth was vapor-deposited only onto the front face of the Pt(111) sample, usually at a sample temperature of ≤ 125 K. (See details of the Bi doser and dosing procedure in ref 12.) After each adsorption/desorption experiment, the sample was routinely cleaned of carbon and/or bismuth on the surface by sputtering at 1000 K followed by annealing briefly to ~ 1200 K. The

cleanliness of the surface was checked by using AES and XPS.

The TDS experiments were performed by using a feedback circuit in which the heating rate was held constant at 0.286 mV s^{-1} on the chromel-alumel thermocouple. This leads to a temperature rate of 11 to 7 K s^{-1} between 120 and 250 K and to a constant value of 7 K s^{-1} above 250 K. The typical temperature range monitored during the TDS experiments was between 100 and 860 K.

In this work, absolute coverages are reported with respect to the number of Pt(111) surface atoms, so that $\theta = 1.0$ corresponds to 1.505×10^{15} species cm^{-2} .

III. Results

A. Adsorption and Dehydrogenation of C_6H_{12} on Clean Pt(111). 1. Thermal Desorption Spectroscopy. A series of thermal desorption spectra for C_6H_{12} adsorbed on Pt(111) is shown in Figure 1. The top part of the figure displays the evolution of H_2 ($m/e = 2$) for different exposures of C_6H_{12} . In the bottom part, the thermal evolution of molecular C_6H_{12} is presented as a function of exposure. (We used $m/e = 56$ to monitor C_6H_{12} here, since it had the highest intensity in the cracking pattern of pure C_6H_{12} .)

For high exposures (≥ 1 langmuir), three molecular desorption states appear in the TDS spectra from C_6H_{12} /Pt(111). The first state that is populated desorbs at ~ 236 K and can be assigned to desorption of molecularly adsorbed C_6H_{12} on Pt(111) (monolayer desorption). This state saturates at an exposure of ~ 1.0 langmuir. The final state to be filled desorbs at ~ 154 K. It can be assigned to the desorption of the C_6H_{12} multilayer since it grows continuously with exposure without saturation. The intermediate (β) state at ~ 181 K will be assigned to desorption of C_6H_{12} from a state with an adsorption energy between that for cyclohexane bonded directly to Pt(111) and cyclohexane bonded to other

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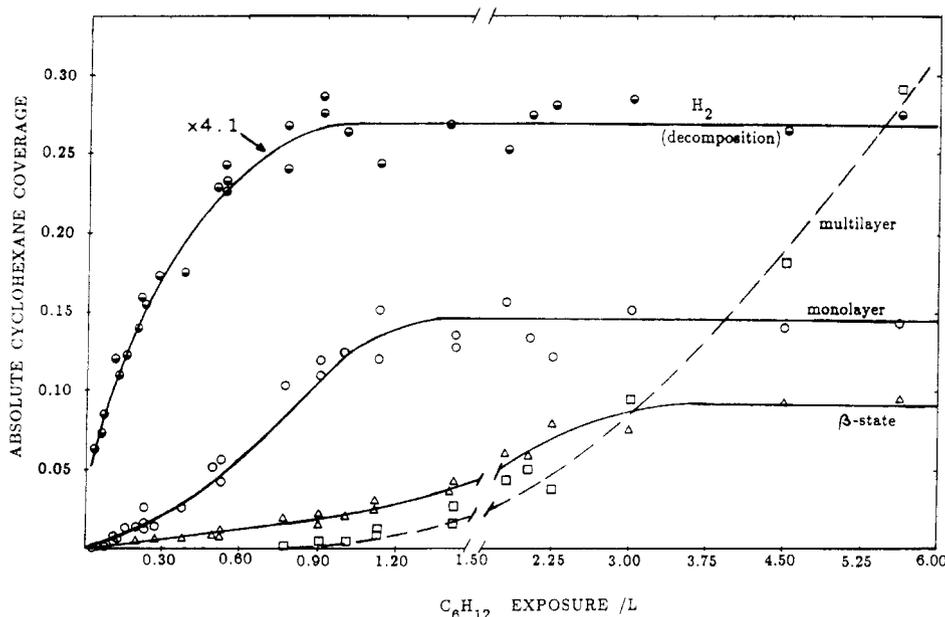
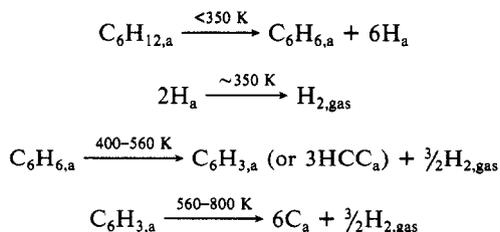


Figure 2. Variation of the coverage of the different desorption states seen in TDS with cyclohexane exposure on Pt(111) at ~ 100 K. Note that the H_2 (decomposition) curve has been multiplied by a factor of 4.1 to separate it from the other curves.

cyclohexane molecules. Thus, this species is still close enough to the Pt(111) substrate to partially feel its stabilizing influence. The molecular TDS spectrum of C_6H_{12} on Pt(111) presented here is similar to those reported for the same molecule on ruthenium surfaces.¹⁴⁻¹⁶

The thermal desorption spectra for H_2 evolution (Figure 1, top) are characterized by the presence of two clear peaks at approximately 365 and 536 K and a broad region of desorption between 563 and 805 K. The H_2 desorption peaks grow simultaneously with cyclohexane exposure until they saturate at ~ 0.75 langmuir. The desorption peak at ~ 365 K is rate-limited, probably by the associative desorption of adsorbed hydrogen atoms ($2H_a \rightarrow H_2$) rather than by C-H bond scission, since this peak is very similar in temperature and shape to that for H_2 desorption from hydrogen adatoms (deposited with H_2 gas) on Pt(111).^{17,21} The higher temperature peaks are rate-limited by scission of C-H bonds, since they occur well above the normal hydrogen desorption temperature (when deposited from H_2 gas). A quantitative analysis of the area below the spectra in the regions 240–395, 395–563, and 563–810 K showed that these areas are in ratio of $(6.24 \pm 0.17):(2.81 \pm 0.11):(2.95 \pm 0.09)$, and independent of exposure. (Many more spectra than those presented in the limited space here were averaged to obtain these values, and the error bars are at the 95% confidence limits.) Such proportions suggest that the H_2 desorption peaks are a consequence of reactions with the following overall stoichiometries:



It should be mentioned that these are overall stoichiometries and could potentially be a consequence of several different adsorbates in proper proportions. Measurements with XPS and AES showed a small amount of adsorbed graphitic carbon after the thermal

desorption experiments (see below), consistent with this mechanism.

The line shape of the H_2 TDS spectra observed between 480 and 810 K is identical with that reported for adsorbed benzene on Pt(111)¹² (see dashed curve in Figure 1, top), suggesting strongly that adsorbed benzene is formed in the first step above. As we will see below, adsorbed benzene is indeed formed in the first dehydrogenation step, which leads to desorption-limited H_2 evolution at ~ 350 K. However, during the experiments on clean Pt(111), no benzene was ever observed to desorb from the surface. This is due to the fact that the amount of benzene formed from cyclohexane is relatively small and it all decomposes on the surface during the heating process (see below). In our accompanying study of benzene adsorption on clean Pt(111), we also found that benzene coverages of this size always dehydrogenated completely.¹²

Figure 2 shows the uptake curve for C_6H_{12} on clean Pt(111). The figure displays the dependence of amounts of the three molecular desorption states (monolayer, β -state, multilayer) upon exposure. This dependence was directly obtained from the time-integrated TDS intensities (peak areas). The "decomposition" curve represents the variation of the total amount of C_6H_{12} that is dehydrogenated to evolve H_2 during TDS as a function of the exposure. The curve was obtained by using the area below the H_2 thermal desorption spectra and was scaled with respect to the other curves using the ratio of carbon-platinum XPS peak areas before and after desorption of a saturated monolayer (see below). As can be seen, dehydrogenation predominates at the lowest exposures but saturates already at ~ 0.8 langmuir. Below 0.2 langmuir, the ratio of the amount of C_6H_{12} which dehydrogenates to that which desorbs molecularly is approximately 2 (taken from the initial slopes of the curves in Figure 2). This ratio approximates the ratio of rate constants for dehydrogenation:desorption on clean Pt(111) at the desorption temperature (236 K). By 0.6 langmuir, desorption starts to predominate. This monolayer desorption state saturates by ~ 1.0 langmuir, after which the β -state grows and saturates. Finally, the multilayer state grows without saturation. Notice that the total amount of cyclohexane desorbing in the monolayer peak at 236 K is roughly twice that which dehydrogenates. It is interesting to point out that molecular desorption from the monolayer state starts to grow from the lowest exposures and saturates very soon after dehydrogenation, suggesting that C_6H_{12} is at first molecularly adsorbed on the surface, and, upon heating, there is a strong competition between desorption and dehydrogenation at around 236 K. The fact that the desorption temperature of hydrogen adatoms as H_2 (~ 350 K) is higher than the temperature of this first dehydrogenation step

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(~ 236 K) means that both the resultant hydrogen adatoms and the other decomposition product (adsorbed benzene) will remain on the surface well beyond the TDS peak temperature where desorption and dehydrogenation are in competition. As such, as this competition proceeds they will be on the surface to block sites for further dehydrogenation. Thus, the reaction is self-poisoning. Once the Pt sites start to be largely covered by adsorbed decomposition products (hydrogen and benzene), desorption of C_6H_{12} is favored due to the lack of empty sites required for dehydrogenation.

On the basis of the variation of the total amount of chemisorbed cyclohexane (the sum of all curves in Figure 2) with exposure, we were able to determine the sticking coefficient of C_6H_{12} on a clean Pt(111) surface at 100 K. (The gas temperature was 300 K.) The value was 0.24. It is interesting to point out that this value decreased by a factor of 3 after saturation of the first monolayer.

During the desorption experiments on clean Pt(111), neither benzene nor cyclohexane were detected with the mass spectrometer as desorption products from the surface, and all peaks seen in the ion gauge (total pressure) response could be attributed to H_2 and cyclohexane.

To determine the difference in activation energies between C_6H_{12} desorption and dehydrogenation to produce benzene, we studied the variation of the dissociative sticking coefficient with surface temperature. A small dose of 0.23 langmuir was given to the surface at temperatures between 236 and 400 K (higher than those for molecular desorption of C_6H_{12}), and the effect of dosing temperature on the area of the subsequent H_2 thermal desorption spectrum was observed. Only the region above 480 K was integrated to obtain this H_2 area, so that it is proportional to the amount of adsorbed benzene produced during the dose, which in turn is proportional to the total amount of dissociatively adsorbed cyclohexane. This area thus reflects the dissociative sticking probability of cyclohexane, as a function of temperature. The absolute (scaled) areas of the TDS peaks showed that the dissociative adsorption probability for cyclohexane was ~ 0.16 at 236 K. We found that this area decreased only $\sim 15\%$ with increasing adsorption temperature between 236 and 400 K, which indicates qualitatively that the activation energies for desorption and dissociation of C_6H_{12} are very similar. This is consistent with the fact that these processes have very similar rates (see above). Those data were quantitatively analyzed using a kinetic model described in the accompanying paper,²⁹ which assumes that the molecularly adsorbed state is the precursor to dissociation and that the sticking coefficient into the molecular state (0.24, see above) is independent of temperature. The dissociative sticking probability decreases below this value due to the competition between dissociation and desorption in the molecular state. The best fit to the decrease in the dissociative sticking probability with temperature for cyclohexane was provided by a model whereby the activation energy for dehydrogenation was 0.5 ± 0.1 kcal/mol smaller than that for molecular desorption, and its preexponential factor was a factor of ~ 1.5 smaller than that for molecular desorption. These parameters are also consistent with the ratio of rate constants for dehydrogenation:dissociation of ~ 2 at the desorption temperature, obtained from the low-coverage branching ratio in TDS (see above).

To test whether significant scrambling of hydrogen could be seen in the cyclohexane that desorbs molecularly from Pt(111), we performed TDS experiments after an exposure of 1.5 langmuirs of an equimolar mixture of C_6H_{12} and C_6D_{12} to the clean Pt(111) surface at ~ 100 K. In the molecular desorption peak at 236 K, there was no observable desorption of scrambling products ($\leq 1\%$) in the mass range from 85 to 95 (except that due to the cracking pattern characteristic of the original C_6H_{12}/C_6D_{12} mixture). The 84 and 96 mass peaks were the only observable molecular desorption products, and the ratio 84/96 had decreased slightly ($\sim 15\%$) compared to the original mixture. There was also no observable D_2 desorption ($< 1\%$). The HD desorption spectrum mimicked that of H_2 (see Figure 1), but it was a factor of 6.5 lower in intensity. This indicates that there is a large kinetic isotope

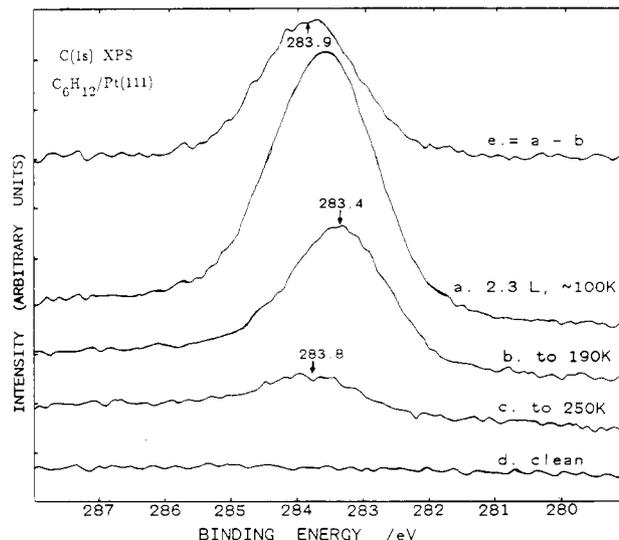


Figure 3. C(1s) peak position in the XPS spectrum of cyclohexane adsorbed on clean Pt(111): (a) after dosing 2.3 langmuirs of C_6H_{12} at 100 K; (b) after flashing this adlayer to 190 K (to remove everything beyond the first monolayer); (c) after flashing to 250 K to desorb molecularly chemisorbed C_6H_{12} or convert it to benzene and hydrogen on the surface; (d) clean surface; (e) difference spectrum representing the C(1s) spectrum of multilayer and β -state cyclohexane.

effect for the dehydrogenation of adsorbed cyclohexane, whereby the rate of dehydrogenation of C_6H_{12} is a factor of ~ 13 larger than that of C_6D_{12} . (This value is calculated from the ratio of the amounts of H and D desorbing: $6.5 \times 2 = 13$.) The low amount of C_6D_{12} dehydrogenation means that the amount of D_a on the surface at any time was very low compared to H_a , so that the absence of isotopically mixed species is not too surprising.

To further test whether any significant amount of the molecularly desorbing cyclohexane could undergo exchange with surface hydrogen prior to desorption, we coadsorbed pure C_6H_{12} with pure D_2 at ~ 100 K and performed TDS. In these experiments, 0.25–2-langmuir D_2 exposures were followed by 1-langmuir C_6H_{12} exposures. Again, in the subsequent TDS there were no observable scrambling products ($\leq 1\%$) in the mass range from 85 to 96 during the molecular desorption peak at 236 K. The D_a produced from the D_2 exposure almost all desorbed as D_2 and HD in the usual temperature range for hydrogen adatom desorption (300–400 K). The total atomic ratio of D:H that desorbed as H_2 , HD, or D_2 in this temperature range increased from 0.5 to 4 with increasing initial D_2 exposure. There was some observable HD in the hydrogen evolution peaks above 400 K, but the amount was very small ($\sim 7\%$ of the H_2 intensity in this temperature region). This suggests that a small amount of deuterium ($\sim 4\%$) is somehow incorporated into the adsorbed products of cyclohexane dehydrogenation. Whether this small amount of deuterium reflects scrambling within adsorbed cyclohexane or the adsorbed benzene product is not clear, since benzene is formed before all the deuterium desorbs. In general, hydrogen scrambling occurs much more readily in adsorbed benzene on Pt(111) than in cyclohexane.¹² When deuterium (D_2) and benzene (C_6H_6) were coadsorbed on Pt(111), the HD evolution peaks above 400 K were also $\sim 6\%$ of the H_2 peaks,¹² which suggests that the HD evolution from cyclohexane may be due to exchange within the benzene product.

2. X-ray Photoelectron Spectroscopy. Curve a of Figure 3 shows the C(1s) X-ray photoelectron spectrum after dosing 2.3 langmuirs of C_6H_{12} onto the clean Pt(111) surface at 100 K. Curves b–d show spectra obtained by briefly flashing this overlayer to the indicated upper-temperature limits to desorb the different individual adsorption states. This dose is sufficient to saturate the H_2 TDS peaks, the molecular monolayer peak, and the β molecular peak and to populate the equivalent of about one monolayer of the multilayer state (see Figures 1 and 2). Note that there are not huge differences in the position of the C(1s)

peak as successively higher temperature states are desorbed. The peaks always appear in the range between 283.4 and 284.2 eV.

The difference spectrum between curves a and b, which reflects mostly the cyclohexane multilayer (with some β -state), is shown as curve e. It is centered at 283.9 eV. Curve b, which reflects the saturated monolayer remaining after heating to 190 K to desorb the multilayer and β -states, is centered at 283.4 eV. Its peak width of 1.71 eV is almost indistinguishable from the instrumental resolution, consistent with the presence of a single adsorption state for cyclohexane in which the carbon atoms are in similar chemical environments. Upon heating to 250 K, the molecularly adsorbed cyclohexane state desorbs and a C(1s) peak centered at 283.8 eV remains (curve c). Further heating to 440 K to desorb the first H₂ state leaves a C(1s) peak of the same intensity, now centered at 284.1 eV (not shown). This peak position is very close to the value of 284.2 eV, reported in the accompanying paper¹² for molecularly adsorbed benzene on clean Pt(111) at about this same coverage. This further supports a mechanism where the product of the first dehydrogenation step is adsorbed benzene. Finally, heating the surface to >800 K (i.e., the completion of H₂ evolution) leaves a C(1s) peak of the same intensity, now centered at 283.8 eV (not shown). This is completely consistent with the position of 283.8 eV reported in the accompanying paper¹² for the graphitic residue remaining after complete dehydrogenation of adsorbed benzene and other hydrocarbons. As noted in the previous paper,¹² the C(1s) peak positions do not change much (<1 eV) with the nature of adsorbed hydrocarbons, and so they are only useful as supporting evidence in species identification. The major utility of XPS here is in quantitative analysis (see below).

Experiments such as shown in Figure 3 were repeated a number of times for initial cyclohexane exposures exceeding 1 langmuir, which were sufficient to saturate the molecular desorption state at 236 K and the H₂ evolution peaks. For these, the average integrated C(1s):Pt(4f) intensity ratio after flashing to 190 K to remove the multilayer and β -desorption states was 0.0172 ± 0.0005 . (See ref 12 for integration limits. We use 95% confidence limits on the mean here.) This reflects the saturation coverage of molecularly adsorbed cyclohexane on Pt(111). The average C/Pt XPS ratio after flashing to 250 K or higher was 0.00538 ± 0.00011 . This value reflects the maximum amount of dehydrogenation product that can be obtained in a TDS from adsorbed cyclohexane. These C/Pt XPS ratios can be scaled to absolute coverage units by using the value of 0.00779 ± 0.0001 for this ratio measured in this same instrument for saturation CO exposure at 260 K on Pt(111), which is known to give an absolute CO coverage of 0.58 ± 0.02 (per Pt surface atom).²⁰ Thus, the saturation coverage of molecularly adsorbed cyclohexane is 0.21 ± 0.01 molecules per Pt surface atom. The maximum amount of dehydrogenation product corresponds to an absolute carbon atom coverage of 0.40 ± 0.04 , or a maximum benzene coverage of 0.067. In our accompanying paper, we show that the saturation coverage of molecularly adsorbed benzene that can be formed by adsorbing benzene is 0.158, or roughly twice this large. One must remember, however, that in the present case each adsorbed benzene is associated with six adsorbed hydrogen atoms when it is produced. Each hydrogen adatom occupies about $1/0.8 = 1.25$ Pt surface atoms,²¹ so that roughly 50% of the surface sites are occupied with adsorbed hydrogen when the benzene is produced (~235 K). This explains most of the difference in maximum benzene coverage producible from cyclohexane dosing as compared to benzene dosing.

The absolute saturation coverages obtained above from XPS results were used as scaling factors for TDS data such as shown

in Figures 1 and 2. Thus, the saturation H₂ TDS peak area corresponds to an absolute cyclohexane coverage of 0.067, while the sum of saturation H₂ and molecular TDS peaks (when properly scaled) must correspond to a cyclohexane coverage of 0.21 (see above). The scaling factors obtained in this way were used to convert TDS peak areas to absolute coverage units in Figure 2 and throughout this paper.

B. Adsorption and Dehydrogenation of C₆H₁₂ on Bismuth-Covered Pt(111). One main objective of this work is to probe the number of active sites on the surface that are required for chemisorption and dehydrogenation of C₆H₁₂ on Pt(111). To address this issue, we vapor-deposited Bi on the surface and observed the decay in the adsorbate coverages and TDS reaction rates as the concentration of the Bi overlayer increased.

Previous experiments²² have shown that a close-packed monolayer of Bi on Pt(111) corresponds to an absolute coverage of 0.56. Our Bi coverages here will be reported relative to that value. We will refer to these scaled coverages as θ_{Bi}^* , and they thus refer to the fraction of a close-packed monolayer. The completion of a close-packed Bi monolayer was determined from the appearance of a multilayer Bi TDS peak at $\theta_{\text{Bi}}^* > 0.56$ ($\theta_{\text{Bi}}^* > 1.0$), as described previously.^{12,22} For all the experiments presented here, the Bi was deposited at a Pt temperature of <125 K. For submonolayer Bi coverages, Bi desorption begins only above 740 K,²² so that all of the TDS experiments described below are for constant Bi coverage.

1. Thermal Desorption Spectroscopy. Figure 4 shows the effect of Bi precoverage on the H₂ TDS ($m/e = 2$) for two different fixed exposures (0.23 and 0.75 langmuir) of C₆H₁₂. It is clear in Figure 4 that there is a drastic effect of the Bi coverage on the dehydrogenation of C₆H₁₂. The evolution of H₂ is almost completely suppressed already by $\theta_{\text{Bi}}^* = 0.2$. As we will see, the presence of Bi on the surface prevents the dehydrogenation of adsorbed C₆H₁₂ mostly because it blocks the additional Pt atoms that are necessary for this reaction.

Figure 5 shows the effect of Bi precoverage on the molecular desorption of C₆H₁₂ corresponding to the same experiments as shown in Figure 4 on clean Pt(111). At these exposures, there is not yet saturation of the monolayer on clean Pt(111) (see Figure 2). As the Bi coverage increases to $\theta_{\text{Bi}}^* = 0.15$ – 0.2 , the amount of C₆H₁₂ that desorbs molecularly at ~236 K increases, and there is a very slight (~5 K) decrease in the peak desorption temperature. The increase in molecular desorption in this low-coverage region is due to the fact that the dehydrogenation pathway for the adsorbed molecule is almost completely suppressed, and the molecule is now obliged to desorb. The minimal increase in desorption temperature shows that, for $\theta_{\text{Bi}}^* \leq 0.2$, there is only a very minor electronic influence of Bi on the chemisorbed cyclohexane molecules (see below). For high coverages of Bi ($0.7 \leq \theta_{\text{Bi}}^* \leq 1.0$), the cyclohexane molecules are bonded above the Bi adlayer, bound only to Bi atoms and not to Pt atoms. Here there is no dehydrogenation (Figure 4), and the molecular desorption temperature decreases to ~171 K. For adsorption of cyclohexane on a surface with $\theta_{\text{Bi}}^* = 2$, we found a temperature for molecular desorption of ~190 K. This value can be considered as characteristic for C₆H₁₂ adsorption on a pure Bi surface. The decrease in desorption temperature with respect to that on clean Pt(111) shows that C₆H₁₂ is much more strongly bonded to the Pt atoms than to the Bi atoms.

For the medium range of Bi coverages ($0.2 < \theta_{\text{Bi}}^* < 0.7$) the situation on the surface is very complex, and one can imagine from steric arguments alone that there is not enough room on the surface now for the cyclohexane molecules to bond entirely to Pt atoms as they did in the absence of Bi. It appears that the molecules find bonding sites on the surface where they can simultaneously bond to Pt and Bi adatoms. The presence of such species is reflected in the two distinct new TDS peaks for molecular cyclohexane at ~190 and ~215 K, intermediate in temperature between purely Pt- (~236 K) and Bi-bonded (~171 K) molecules.

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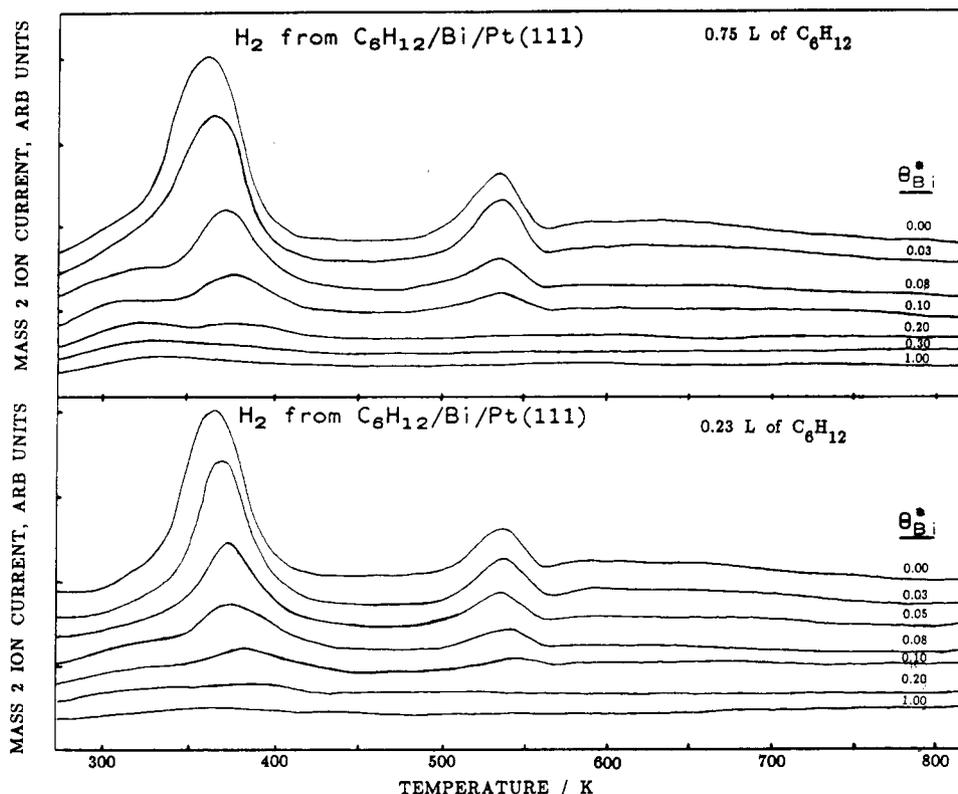


Figure 4. Effect of Bi precoverage on the dehydrogenation of C_6H_{12} on Pt(111): variations in H_2 -TDS spectra with θ_{Bi}^* for two fixed cyclohexane exposures at ~ 100 K.

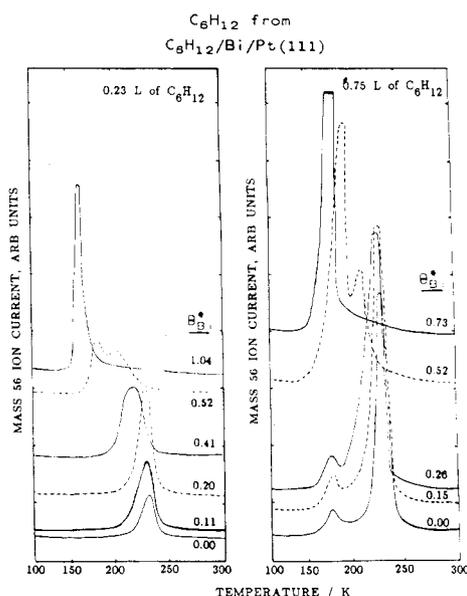


Figure 5. Effect of Bi precoverage on the desorption of C_6H_{12} from Pt(111): variations in C_6H_{12} TDS spectra with θ_{Bi}^* for the same two fixed cyclohexane exposures used in Figure 4.

Figure 6 summarizes the results of many TDS experiments such as shown in the representative spectra of Figures 4 and 5, with each region (A–C) of the figure corresponding to a fixed cyclohexane exposure at ~ 100 K. Here we show the areas of the various TDS peaks as a function of Bi coverage, scaled to absolute coverage units by using the procedure described for Figure 2, based on XPS intensities. Curve a in each case shows the total area below the H_2 TDS peaks and therefore represents the amount of dehydrogenation occurring during the TDS. Curves b–d represent the integrated areas below the molecular C_6H_{12} thermal desorption spectra between the following temperature limits: curves b = 273–210 K; curves c = 210–160 K; curves d = 160–119 K. Thus, curve b represents the desorption of C_6H_{12} bonded only to Pt atoms on the surface, and curve d the desorption of the C_6H_{12} multilayer.

(The latter is included only when present in significant amounts.) Curve c includes a small contribution from the β (second layer) state of clean Pt(111) and large contributions from C_6H_{12} bonded partially or entirely to Bi adatoms. Unfortunately, the β - and Bi-bonded TDS peaks occur at about the same temperature and cannot be separated. In Figure 6, curve e is the sum of curves a and b. We will assume here that all the C_6H_{12} that decomposes on the surface during the TDS was initially molecularly adsorbed at 100 K (see above). Thus, curves e in Figure 6 represent the total amount of molecularly adsorbed C_6H_{12} formed upon exposure at ~ 100 K, which is bonded only to platinum sites. Thus, for saturation exposure (1 langmuir) curve e shows the influence of Bi precoverage on the total capacity of the Pt(111) surface for cyclohexane chemisorption (to purely Pt sites).

The dehydrogenation data of Figure 6 are separately presented in Figure 7, which also includes the influence of Bi upon the H_2 TDS area for a fourth, lower exposure of C_6H_{12} (0.11 langmuir). The top two curves here are for C_6H_{12} exposures sufficient for saturation of the H_2 (dehydrogenation) peaks on a clean Pt(111) surface. Their decreases with increasing Bi coverage are essentially identical. For all the exposures, there is strong decrease in the dehydrogenation activity, which is suppressed by a factor of about 5 by $\theta_{Bi}^* = 0.1$. For $\theta_{Bi}^* \geq 0.4$, the H_2 TDS area reaches a small, nearly constant level, which, as can be seen in Figure 4, is due to a broad, structureless background H_2 pressure rise during sample heating. This background should not be attributed to the Pt(111) surface. Returning to Figure 6, parts A and B, for low C_6H_{12} exposures, we can see that as the dehydrogenation activity decays with θ_{Bi}^* , the amount of Pt-bonded molecular desorption correspondingly increases (curve b). Thus the total amount of chemisorbed cyclohexane on Pt sites (curve e) remains nearly constant at first. For high cyclohexane exposures where the Pt-bonded molecular desorption peak (curve b) is always saturated (Figure 6C), it remains constant as the dehydrogenation activity is suppressed, so that the total amount of Pt-bonded C_6H_{12} (curve e) decays with θ_{Bi}^* even at low θ_{Bi}^* . This largest cyclohexane exposure is the only one in Figure 6 that is sufficient for the saturation of C_6H_{12} chemisorption on a clean Pt(111) surface. In this case, the total chemisorption capacity of the surface for purely Pt-bonded C_6H_{12} (curve e) decreases almost linearly with

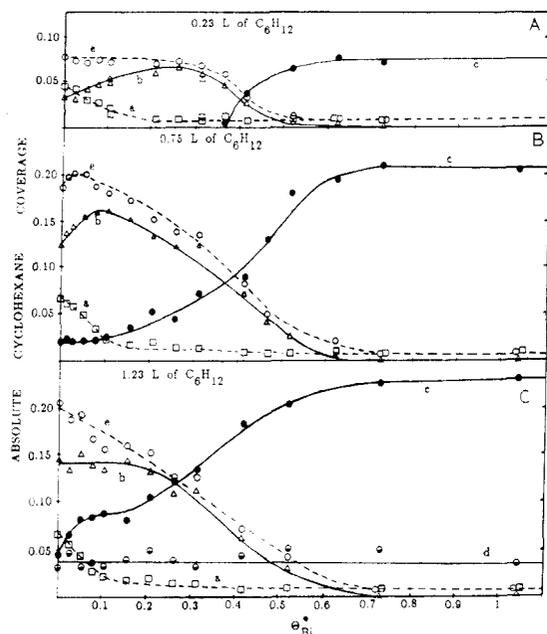


Figure 6. Effect of Bi precoverage upon the amounts of chemisorption and dehydrogenation of cyclohexane on Pt(111). The figure is divided in three sections, each one for a different C_6H_{12} exposure at ~ 100 K: A = 0.23 langmuir, B = 0.75 langmuir, and C = 1.23 langmuir. In each section, curve a (\square) refers to that part of adsorbed cyclohexane that dehydrogenates. Curve b (Δ) represents the amount of desorption of C_6H_{12} that was bonded only to Pt atoms on the surface, and curve d (\bullet) the desorption of the C_6H_{12} multilayer. Curve c (\bullet) represents "bismuth-bonded" cyclohexane. This curve includes a small contribution from the β -state of clean Pt(111) but is dominated by contributions from cyclohexane bonded partially or entirely to Bi adatoms. Curve e (\circ) represents the total amount of molecularly adsorbed C_6H_{12} , which is bonded only to Pt atoms. This figure was obtained by using the various TDS peak areas (see Figures 4 and 5) as a function of Bi precoverage, scaled to absolute coverage units employing the XPS intensities as described in the text.

Bi coverage. By $\theta_{Bi}^* \approx 0.6$, it is almost completely suppressed at all cyclohexane exposures. Comparison of curve e with Figure 7 shows that the effect of the Bi is much stronger on the dehydrogenation reaction than on the Pt chemisorption capacity. In Figure 6, we can also see that, as the chemisorption capacity of the surface for Pt-bonded cyclohexane (curve e) decays with θ_{Bi}^* , the Bi-bonded monolayer (curve c) increases so that the total amount of adsorbed cyclohexane (c + e) remains constant. This shows that the sticking coefficient of cyclohexane at 100 K is independent of Bi coverage.

2. X-ray Photoelectron Spectroscopy. Figure 8 displays typical X-ray photoelectron spectra after dosing 0.75 langmuir of C_6H_{12} onto the Pt surface pre dosed with various Bi coverages. Curves a–e were taken immediately after dosing C_6H_{12} at ~ 100 K. Comparison of these curves shows that there is an increase by almost 2 eV in the C(1s) binding energy of adsorbed cyclohexane as θ_{Bi}^* increases in the first monolayer.

Spectrum f in Figure 8 was taken after heating the surface which gave spectrum b ($\theta_{Bi}^* = 0.21$) to 245 K to allow desorption of all the nondissociated C_6H_{12} . For this case, it can be seen that there is almost no carbon remaining on the surface, consistent with nearly complete suppression of dehydrogenation activity by Bi. In contrast, at these conditions on a Bi-free Pt(111) surface, a much greater amount of residual carbon is observed (see spectrum c in Figure 3). This agrees with our TDS results, showing that the presence of Bi on the surface favors desorption over dehydrogenation, preventing in this way the evolution of H_2 and the deposition of carbon on the surface.

IV. Discussion

Our results show that for high exposures (> 1 langmuir) three different desorption states appear in the molecular thermal desorption spectra of C_6H_{12} on Pt(111). A similar characteristic

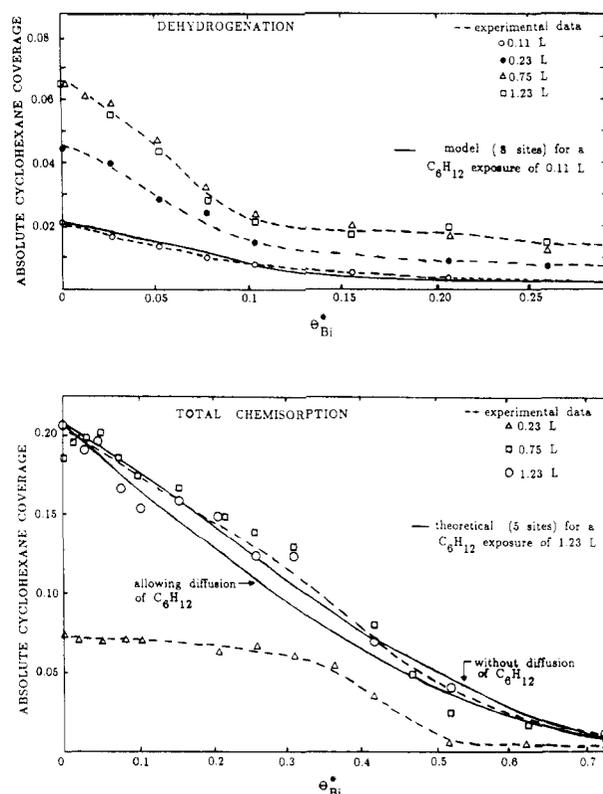


Figure 7. Variation of amount of dehydrogenation (top) and total chemisorption of cyclohexane (bottom) with respect to Bi precoverage. In the top part of the figure the solid line represents the kinetic model of ref 11, for an exposure of 0.11 langmuir. The model corresponds (see ref 11) to an ensemble size of eight Pt atoms for C_6H_{12} dehydrogenation. In the bottom part of this figure, the solid line refers to the theoretical values obtained with a Monte Carlo simulation,²⁶ assuming that Bi blocks two Pt sites on the surface and an ensemble size requirement of five sites for C_6H_{12} chemisorption. Note that both theoretical curves (with and without C_6H_{12} diffusion on the surface) are in good agreement with the experimental values for an exposure of 1.23 langmuirs.

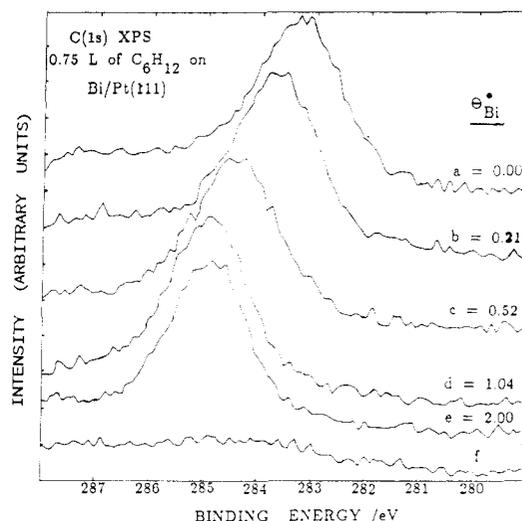


Figure 8. Effect of Bi precoverage upon the C(1s) XPS spectra of cyclohexane adsorbed on Bi-covered Pt(111). Spectra a–e were taken after dosing 0.75 langmuir of C_6H_{12} onto the surface at ~ 100 K. Spectrum f was taken after heating the surface that gave spectrum b to 245 K.

has been observed in the TDS spectra of cyclohexane on ruthenium surfaces.^{14–16} It is generally agreed to assign the peak at highest temperature (236 K) to desorption of the monolayer and the peak at lowest temperature (154 K) to multilayer desorption. The intermediate (β) peak has been assigned by some authors to C_6H_{12} desorption from the back or the edges of the crystal, and for others to a second state of molecularly adsorbed C_6H_{12} on the surface

that is not so strongly bonded as the monolayer peak.¹⁴⁻¹⁶ The second interpretation is preferred here since the state grows in intensity most rapidly just after completion of the monolayer peak. (See Figure 2.) Assuming first-order desorption and a typical preexponential factor of 10^{13} s^{-1} for all the states, a standard, first-order Redhead analysis²³ yields desorption activation energies of 8.9, 10.5, and 13.9 kcal/mol for the desorption peak temperatures of 154 (multilayer), 181 (β -state), and 236 K (monolayer), respectively. (For the multilayer peak, we used a coverage that gave a multilayer coverage of approximately one equivalent monolayer, so that this first-order treatment is fairly accurate for this peak. It eventually becomes zero order, with a constant leading edge.) The multilayer desorption energy is identical with the sublimation energy of pure cyclohexane (8.9 kcal/mol).²⁴ Since adsorption occurs readily at ~ 100 K and is apparently nonactivated, the activation energies for desorption listed above can be taken as good estimates of the heats of adsorption.

As was shown in section III.A.1, the activation energy for the dehydrogenation of adsorbed cyclohexane is ~ 0.5 kcal/mol less than the activation energy for its desorption (~ 13.9 kcal/mol). Thus, the activation energy for dehydrogenation is ~ 13.4 kcal/mol. If this activation energy is associated with a reaction coordinate that closely resembles a single C-H stretch, as might be expected, we can predict based upon the primary isotope effect that the activation energy for dehydrogenation of C_6D_{12} should be slightly larger, due to the difference in zero-point energies for C-H compared to C-D stretches of ~ 1.1 kcal/mol.¹⁸ (Here we have used the average C-H stretch frequency of $\sim 2700 \text{ cm}^{-1}$ reported for C_6H_{12} on Pt(111),⁷ and the reduced-mass estimation of this average for C-D.) Therefore, the activation energy for dehydrogenation of perdeuterated cyclohexane should be ~ 14.5 kcal/mol. Assuming the same preexponential factor, this difference in activation energies predicts that the rate constant for dehydrogenation of C_6H_{12} should be 11-fold higher than that for C_6D_{12} at the desorption temperature (~ 236 K). This agrees very well with the observed kinetic isotope effect, which indicated that this ratio is 13. (The accuracy of these measurements and the analysis are insufficient to distinguish between which of the two C-H stretching modes observed in HREELS may be involved in C-H bond cleavage.)

We measured here a sticking coefficient of 0.24 for cyclohexane adsorption on clean Pt(111) at 100 K. We found very similar values for cyclopentene (~ 0.2)²⁹ and benzene (0.25)¹² adsorption on this same surface, even at multilayer coverages. Our first impression of this result was that all these sticking coefficients were probably near unity (the commonly assumed value for condensation coefficients) and that our ion gauge was simply miscalibrated. However, we tested this point by measuring the sticking coefficient for CO adsorption on clean Pt(111) using the same method, which we found to be 1.2, very close to the known value of 0.9.¹⁹ In addition, we calculated very similar or even lower values for the sticking coefficients (≤ 0.25) for cyclohexane and benzene adsorption on Ru(0001) using data presented by Polta et al.¹⁶ Unfortunately few authors carefully state whether their exposures include corrections for ion gauge sensitivity factors, so comparison with other results is difficult. We are not aware of sufficiently accurate measurements of the sticking or condensation coefficients of these large nonpolar molecules to warrant any absolute expectation that these values must be closer to unity, so we have not made any corrections to our present results. It is possible, however, that pressure gradients in the vacuum chamber have caused some error here.

The thermal desorption spectra from cyclohexane adsorption on Pt(111) have not been previously presented, except in very qualitative terms.³ Tsai et al.³ claim a 273 K peak maximum for molecular desorption of cyclohexane after adsorption at ~ 250 K on Pt(111). This is considerably higher than the desorption peak temperature of 236 K we report here. They observed a very

low sticking coefficient for cyclohexane, which is probably due to the fact that they were trying to adsorb cyclohexane above its true desorption temperature. We see a sticking coefficient of 0.24 at a surface temperature of 100 K and a dissociative adsorption coefficient of ~ 0.15 between 236 and 400 K. The origin of their small 273 K molecular desorption peak is unknown. These authors also state that Pt(111) was either inactive or possessed a low activity for dehydrogenation at 293–373 K. This is also in some discrepancy with our present results, which show that heating a 1-langmuir dose of cyclohexane from 100 to 250 K is sufficient to saturate 92% of the surface with its dehydrogenation products (benzene + 6H_2).

Our results are in good agreement with those of Demuth et al.⁷ who interpret HREELS vibrational data on Pt(111) in terms of the complete conversion of adsorbed cyclohexane to benzene occurring above ~ 200 K. (These authors performed neither TDS nor quantitative surface analysis, so they were unable to report on the desorption of C_6H_{12} seen in the present study.) Our results refine this picture somewhat, showing that dehydrogenation occurs simultaneously and in competition with molecular desorption at 236 K (depending, of course, on the heating rate). In support of that HREELS evidence for benzene production are also our H_2 TDS and C(1s) line shapes above 350 K, which match perfectly those following the adsorption of benzene.¹² In addition our results are also in agreement with experiments with Fourier transform infrared spectroscopy²⁷ that show that cyclohexane dehydrogenates on Pt/ Al_2O_3 at 300 K to form benzene.

Finally, in a separate experiment,²⁵ we have completely confirmed the identity of the dehydrogenation product formed at 350 K by *postdosing* a cyclohexane adlayer that had been heated to 350 K with Bi to prevent the further dehydrogenation of the species. The species could then be quantitatively removed from the surface as benzene gas by further heating. Details of this result are presented elsewhere, together with other experiments that take advantage of "bismuth postdosing in thermal desorption mass spectroscopy" (BPTDS) for identifying adsorbed intermediates that otherwise prefer to decompose.²⁵ This method is reminiscent of the technique of displacement by trimethylphosphine adapted by the Muettterties group to show, for example, that traces of gaseous benzene could be seen thermally desorbing at ~ 450 K from Pt[6(111) \times (111)] following exposure first to cyclohexane and then to trimethylphosphine at 293 K.³

Blakely and Somorjai have shown that the catalytic dehydrogenation of cyclohexane to gaseous benzene at low pressure ($<10^{-6}$ Torr) is structurally sensitive on Pt surfaces, occurring readily only in the presence of steps and not on flat Pt(111).⁸ It is tempting to assume that the presence of steps and defects could have influenced our results and those of Demuth et al.,⁷ both of which indicate substantial dehydrogenation to benzene already at ≤ 236 K on Pt(111), in contrast to the work of Tsai et al.,³ who claim little or no dehydrogenation. We carefully checked the TDS spectra of CO from our crystal, which is a very sensitive probe for surface steps and defects.^{17,19} We found very perfect (111) CO desorption characteristics, with little possibility for defect sites ($<2\%$).¹² Further evidence that defect sites are not controlling the dehydrogenation kinetics here is presented in a related paper³⁸ where cyclopentane dehydrogenation was studied on this same clean Pt(111) crystal and on the surface after attempts to decorate any active sites with carbon residue. Given the extreme sensitivity of cyclohexane dehydrogenation to impurities on Pt(111) (see Figure 7), very minor impurities may have decreased the extent of dehydrogenation in the results of Tsai et al.³

Interestingly, we see here no direct evidence for significant adsorbed or gaseous cyclohexene production from cyclohexane, although it was the major dehydrogenation product observed by Gland et al. in the catalytic reaction of cyclohexane (8.3×10^{-8} Torr) with H_2 (4.2×10^{-7} Torr) at 423 K.⁹ These authors suggested σ -bonded C_6H_9 as the major species produced on Pt(111) at 293 K from cyclohexane. The above results show that adsorbed

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benzene is produced instead. Blakely et al.⁸ state that cyclohexene is an intermediate in cyclohexane dehydrogenation to benzene on Pt surfaces, although we see no evidence for that species here. This does not prove, however, that cyclohexene or σ -C₆H₉ are not formed as transient species during dehydrogenation to produce benzene. However, there is also no HREELS⁷ or XPS (see above) evidence for any intermediates formed in significant concentration as cyclohexane converts to benzene on Pt(111). Kang and Anderson¹⁰ have studied the dehydrogenation of C₆H₁₂ on Pt(111) to produce benzene using a modified version of extended Hückel theory. On the basis of their results, these authors propose a mechanism for dehydrogenation in which not all the six C-H bonds are broken simultaneously. The initial removal of a hydrogen atom from adsorbed cyclohexane is the slowest step in the dehydrogenation process, followed by the formation of a partially dehydrogenated intermediate, C₆H₉, which loses three more H atoms in a relatively easy way.

At low values of θ_{Bi}^* (<0.2), a very small shift (~ 5 K) toward lower temperature is observed for the peak position of the C₆H₁₂ monolayer in the molecular thermal desorption spectrum. This shift reflects a slight decrease in the activation energy for desorption (and therefore in the adsorption energy) of cyclohexane (~ 0.3 kcal/mol), according to the same analysis and assumptions as used above. The decrease in work function that is observed for Bi on Pt(111)²² and for C₆H₁₂ and similar cycloalkanes on metal surfaces³²⁻³⁴ suggests that both Bi and C₆H₁₂ form downward-pointing dipoles characteristic of the transfer of a small amount of electron density toward the surface when adsorbed on Pt(111). The decrease in adsorption energy is consistent with a model in which both cyclohexane and bismuth are partially positively charged when adsorbed on Pt(111), and these adsorption dipoles weakly repel each other. Quantum chemical calculations¹⁰ also suggest that, upon adsorption on Pt(111), C₆H₁₂ donates electron density to the Pt. As θ_{Bi}^* increases above 0.2, new, more dramatically influenced cyclohexane desorption states appear at temperatures of ~ 215 K, shifting to lower temperatures with increasing θ_{Bi}^* . In this coverage range the dipole repulsions mentioned above probably still contribute to this TDS peak shift, but the dominant effect now is related to the fact that some cyclohexane molecules are sterically prevented from finding free Pt sites for optimum bonding. These molecules are probably forced into new geometries that maximize their bonding to Pt atoms but where parts of the molecules are removed from the Pt surface, bonding mainly to Bi adatoms.

It is important to point out here that the dehydrogenation of cyclohexane was completely suppressed by a very low coverage of bismuth ($\theta_{\text{Bi}} \leq 0.2$). In this important low-coverage region, the TDS peak shifts are very small (< 5 K), and therefore the lateral repulsive interactions between Bi and cyclohexane that influence cyclohexane desorption are still very weak (≤ 0.3 kcal/mol).

The TDS results indicate cyclohexane molecular desorption temperatures of 171 and 190 K for one and two monolayers of Bi, respectively, where cyclohexane bonding is now clearly only to Bi atoms. Employing these temperatures and the same method that we used above to estimate the activation energies for C₆H₁₂ molecular desorption on clean Pt(111), we calculate activation energies for cyclohexane desorption of ~ 9.9 ($\theta_{\text{Bi}}^* = 1$) and ~ 11.0 kcal/mol ($\theta_{\text{Bi}}^* = 2$). This difference indicates that the first monolayer of Bi atoms are slightly electronically modified by their bonding to Pt. The temperature and activation energy for cyclohexane desorption at $\theta_{\text{Bi}}^* = 2$ can be taken as a good approximation to the expected values for C₆H₁₂ adsorbed on a pure bismuth surface.

Our XPS results indicate that the saturation coverage of molecularly adsorbed cyclohexane on Pt(111) is ~ 0.21 . Results of LEED,⁶ NEXAFS,^{4,5} and HREELS⁷ show that cyclohexane is adsorbed on Pt(111) with its molecular plane approximately parallel to the substrate. A model proposed to explain the LEED pattern of C₆H₁₂ on Pt(111),⁶ which is based on parallel adsorption, suggests a maximum cyclohexane coverage of $^{4/}_{21} = 0.19$. This value is close to our experimental value of 0.21 ± 0.01 obtained

by using XPS data. The small difference here may be due to the error inherent in using non-angular-integrated XPS intensities for quantitative XPS. These values indicate that about five Pt-(111) surface atoms are required to accommodate each adsorbed cyclohexane molecule.

We were also able to assess this ensemble size independently using the Bi site-blocking results of Figure 7, bottom. The data for the 1.23-langmuir (saturation) exposure there reflects the influence of Bi upon the total chemisorption capacity of the surface for Pt-bonded cyclohexane adsorption. We have previously presented statistical methods suitable for treating such data to extract the adsorption ensemble size, together with Monte Carlo simulations of several prototypical models.²⁶ We used a number of such simulated models to try to fit the data of Figure 7, bottom, at 1.23 langmuirs. All of our attempted models assumed that each Bi adatom blocks two Pt atoms on the surface. (This number is determined from the approximate area occupied by a Bi adatom at high coverages.²²) The best fits to the data assumed that each cyclohexane molecule requires four or five free Pt atoms on the surface, depending upon whether or not the cyclohexane molecules were allowed to diffuse on the Pt surface to maximize packing. The simulation for the five-atom model is shown as the solid curve through the data of Figure 7, bottom. This model allows cyclohexane diffusion at 110 K. The number of atoms in the chemisorption ensemble (four or five) determined in this way agrees well with the value (five) determined by quantitative XPS. This helps verify that Bi-site-blocking is a viable method for assessing ensemble requirements.

As indicated in the XPS of submonolayer cyclohexane on Bi/Pt(111) in Figure 8, the C(1s) peak increases in binding energy by about 1.5 eV with increasing Bi coverage within the first monolayer. It is interesting to note that the overall 1.5-eV increase in the C(1s) BE with θ_{Bi}^* is almost equal in magnitude to the decrease in work function caused by Bi adsorption (2 eV²²). This suggests that the C(1s) peak shifts may be explainable with the same model used by Wandelt to explain the photoemission of adsorbed xenon (PAX).²⁸ In this model, the adsorbed xenon resides spatially almost completely *outside* the surface electrostatic potential barrier or the surface dipole layer. Thus, changes in the work function of the surface are *directly* reflected as changes in the photoelectron binding energies when the latter are referenced to the Fermi level of the sample. This is due to the fact that the photoelectron is created in a region in space that is at a different electrostatic potential than the spectrometer. The magnitude of this potential difference *equals* the change in the (local) work function in the case of PAX.²⁸ A similar model is expected to pertain to the C(1s) spectrum of adsorbed cyclohexane since its carbon atoms are thought to reside ~ 3.5 Å above the topmost plane of Pt atoms,¹⁰ which is similar to the height of adsorbed xenon (~ 3.2 Å²⁸). In Figure 9, we show the position of the C(1s) peak of adsorbed cyclohexane, taken from Figure 8, plotted versus the decrease in work function of Pt(111) at that Bi coverage, taken from ref 22. One can see that there is a smooth increase in C(1s) binding energy with decreasing work function in the first Bi monolayer. For comparison, we show the C(1s) position versus Bi-induced work function for submonolayer adsorbed cyclopentene,²⁹ cyclohexene,³⁰ and benzene¹² on this same surface. Notice that the magnitude of the binding energy change is larger for cyclohexane than for benzene, which is consistent with the fact that the carbon atoms of benzene reside only ~ 2.1 Å from the top Pt plane³¹ and therefore partially within the surface po-

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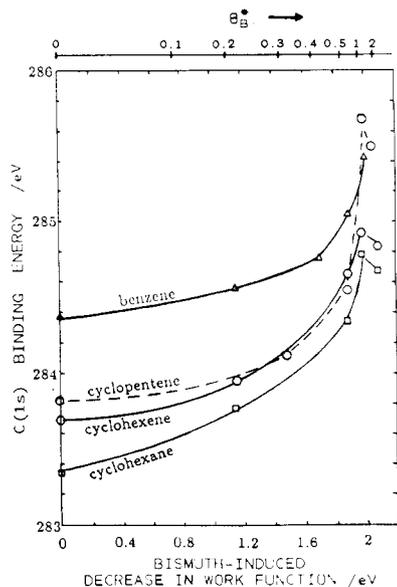


Figure 9. Correlation between the C(1s) peak position of adsorbed hydrocarbons and the decrease in work function of Pt(111) at the corresponding Bi precoverage. The hydrocarbon coverages here are cyclohexane = 65%, cyclohexene = 16%,³⁰ cyclopentene = 38%,²⁹ and benzene = 74%,¹² where the percentage is relative to a saturated monolayer on the bismuth-free surface.

tential barrier.²⁸ For all of the curves of Figure 9, the C(1s) binding energy starts out almost independent of the work function change at low θ_{Bi}^* and then accelerates at high θ_{Bi}^* . At low θ_{Bi}^* , the adsorbed hydrocarbons preferentially sit *beside* the Bi adatoms and bond in their usual geometry to the Pt site. They therefore feel the local potential of the Pt(111) plane. At high θ_{Bi}^* , they can only sit on top of the Bi adlayer and therefore feel the local electrostatic potential appropriate for the Bi adlayer, which has a lower work function. The corresponding increase in the C(1s) BE can be thought of as a destabilization of the core-hole final state due to the fact that it now resides in a region of lower electrostatic potential for electrons but *higher* electrostatic potential for cations. Thus, no chemical changes in the initial state energy of the molecules are needed to explain these shifts. Our results indicate that the C(1s) spectra of these adsorbed hydrocarbons, like spectra for adsorbed xenon, probe the local electrostatic potential (work function) of the surface sites. These hydrocarbons, however, are much larger than xenon so that the local region probed is much larger here. Notice that the hydrocarbon coverage is large in the case of cyclohexane, so that even at $\theta_{\text{Bi}}^* = 0.21$ some of the molecules are not bonded to Pt in their usual geometry (see Figure 6B). This can at least partially explain the small shift of the C(1s) peak in this case even at $\theta_{\text{Bi}}^* = 0.21$. (It should be remembered, however, that the XPS experiment at 110 K may probe a different population distribution of Pt- and Bi-bound molecules than is probed above 160 K in the TDS results of Figure 6B.)

The decrease in the dehydrogenation probability of cyclohexane during TDS with increasing Bi coverage (Figure 7) is kinetically

modeled in an accompanying publication.¹¹ In that work, data for several hydrocarbons are treated with a general kinetic expression, and trends in the kinetic parameters with hydrocarbon characteristics are discussed. The central parameter of that treatment is that the dissociation or dehydrogenation rate decreases with θ_{Bi} as

$$\text{rate} = k_{\text{dt}}(1 - n\theta_{\text{Bi}})^A \quad (1)$$

where A represents the number of additional vacant Pt atoms that are simultaneously required for dissociation of an (already) adsorbed cyclohexane molecule, and n is the number of Pt atoms blocked by a Bi adatom. Thus, A represents the ensemble size requirement for adsorbed cyclohexane to convert into dehydrogenation products. The dehydrogenation probability is determined by the competition between desorption and dehydrogenation near the desorption temperatures. We allowed for small electronic influences of Bi upon the rate constants for desorption and dehydrogenation in this treatment, as described in detail in ref 11. The magnitude of the electronic influence in this model was limited based upon our TDS data. For example, we allowed the activation energy for desorption of cyclohexane to decrease by up to 0.3 kcal/mol with increasing Bi coverage in the range $\theta_{\text{Bi}}^* \leq 0.2$, consistent with the 5 K decrease in the desorption peak temperature in this coverage range (see above). Acceptable fit to the low-exposure data of Figure 7 was provided only for $A \geq 8$, which indicates that an ensemble size of at least eight free Pt atoms is required for the dehydrogenation of adsorbed cyclohexane to proceed.¹¹ We should point out that this is *in addition* to the five Pt sites already required to accommodate the adsorbed cyclohexane molecule itself (see above).

We are not sure yet exactly what is implied by such an unexpectedly large ensemble requirement. It may indicate that several hydrogen atoms are abstracted from the cyclohexane and attach to the Pt sites in a single, concerted step or that rapid dehydrogenation/rehydrogenation reactions compete in a series of steps until the stable benzene intermediate is formed. A full discussion of these models is presented in the accompanying paper.¹¹ We hasten to point out that similarly large ensemble requirements (12–30 sites) have been determined in kinetic studies of related hydrocarbon conversion reactions over other bimetallic transition-metal catalysts.^{35–37} Our present results may help give confidence to those unexpectedly large values, since the present values were determined in experiments that were accompanied by actual surface analytical measurements to confirm the fraction of sites masked by the inert metal and the lateral distribution of the inert metal (at least initially). These, in fact, are the first experiments of this general type to appear where the inert metal was not clustered into two-dimensional islands.

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Registry No. Bi, 7440-69-9; Pt, 7440-06-4; cyclohexane, 110-82-7; benzene, 71-43-2.

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