

# Dehydrogenation of Methylcyclohexane on Pt(111)

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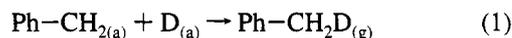
The mechanism of the dehydrogenation of methylcyclohexane (MCH) on Pt(111) has been studied using HREELS, TPD, and BPTDS. Upon warming a monolayer of MCH dosed at 100 K,  $\approx 55\%$  desorbs and  $\approx 45\%$  dehydrogenates to a  $\pi$ -allylic species at  $\approx 240$  K. This  $\pi$ -allylic intermediate dehydrogenates further to a benzyl species at  $\approx 310$  K. Adsorbed benzyl is stable up to  $\approx 450$  K on Pt(111), but at higher temperatures further dehydrogenation occurs.

## 1. Introduction

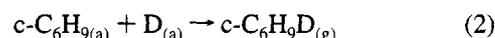
As a prototypical hydrocarbon conversion reaction, the adsorption of cyclohexane on transition metals has been extensively studied in the past<sup>1–13</sup> using surface science techniques. The adsorption of methylcyclohexane (MCH), however, had not been studied under ultrahigh-vacuum (UHV) conditions until a recent TPD study was carried out in our group,<sup>14</sup> and much remains to be learned about this system. From a scientific point of view, we are interested in how the introduction of a methyl group onto the cyclohexane ring (and thus the creation of a weaker, tertiary C–H bond) influences the dehydrogenation of MCH compared to cyclohexane. Many studies of MCH reactions over supported Pt catalysts at high pressure are present in the literature.<sup>15</sup> The major product of MCH dehydrogenation in these studies was found to be toluene. Thus, fundamental studies of the mechanism of the conversion of MCH to toluene are of interest. In this paper we report our HREELS and BPTDS studies of the adsorption and reaction of methylcyclohexane on the Pt(111) surface.

Bismuth postdosing thermal desorption mass spectroscopy (BPTDS) is a useful complement to HREELS, especially concerning hydrocarbon reactions where vibrational assignments are often difficult to make. The details of BPTDS are discussed at length elsewhere.<sup>16,17</sup> Briefly, BPTDS operates by allowing adsorbed molecules to desorb intact, whereas in the absence of Bi they would not usually do so but would instead dissociate. In the case of intermediate species that are molecular fragments and have no stable gas phase analog, the basic experiment is augmented by adsorption of D<sub>a</sub> before the Bi dose (i.e., “D<sub>2</sub>-BPTDS”). This allows intermediates that are deficient in only one H (D) atom to be deuterated to form a species that can be desorbed. Once a species is desorbed it is detected by mass spectrometry, and so both a quantitation of the surface concentration and chemical identity of the species can be derived.

Two previous D<sub>2</sub>-BPTDS results are of particular relevance to this paper.<sup>16b–d</sup> These have demonstrated the presence of adsorbed benzyl (Ph-CH<sub>2(a)</sub>) from the dehydrogenation of toluene<sup>16d</sup> and a  $\pi$ -allylic-c-C<sub>6</sub>H<sub>9(a)</sub> species from the dehydrogenation of cyclohexane or cyclohexene<sup>16b,c</sup> on Pt(111). Identification and quantitation of these species was based on the following reactions that occur with  $\approx 100\%$  yield during D<sub>2</sub>-BPTDS:



and



These reactions yield *d*<sub>1</sub>-toluene and *d*<sub>1</sub>-cyclohexene, respectively, in the gas phase at  $\approx 200$  K.

One intent in the experiments described in the current communication was to discover whether dehydrogenation of methylcyclohexane on Pt(111) results in the formation of similar species. In the case of the benzyl moiety, this has been predicted to be the case.<sup>18</sup>

## 2. Experimental Methods

The experiments were performed in two ultrahigh-vacuum chambers. The system base pressures of both chambers were  $\leq 8 \times 10^{-11}$  Torr. The HREELS chamber was equipped for Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), temperature-programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), and high-resolution electron energy loss spectroscopy (HREELS).<sup>19</sup> The HREELS spectrometer contains single 127° cylindrical sectors in both the monochromator and analyzer. All HREELS data were taken in the specular reflection geometry with  $\Theta_{\text{in}} = \Theta_{\text{out}} = 65^\circ$ , with a typical resolution of 85 cm<sup>-1</sup>.

The BPTDS chamber has been described elsewhere<sup>16b,c,17</sup> and is equipped for BPTDS, AES, LEED, and TPD.

TPD measurements in both systems were made using a quadrupole mass spectrometer in line-of-sight with the sample surface and using a linear heating rate of 4–5 K/s. For the TPD experiments in the BPTDS chamber, the cracking patterns for desorbed molecules were determined directly using the Inficon QMS when possible or estimated by correcting tabulated reference cracking patterns<sup>20</sup> for the ion transmission function of our QMS. For the Inficon QMS, this function decreases rapidly, but smoothly, as the *m/e* ratio increases. The mass spectrometer cracking patterns measured in our instrument are very similar to those reported in the literature,<sup>20</sup> except for a more rapid decrease in intensity with an increasing *m/e* ratio. The mass spectral cracking patterns for several C<sub>6</sub>, C<sub>7</sub>, C<sub>8</sub>, and C<sub>14</sub> hydrocarbons were determined by flowing a pure sample of each hydrocarbon through the chamber. The measured spectrum was compared to a reference spectrum<sup>20</sup> in

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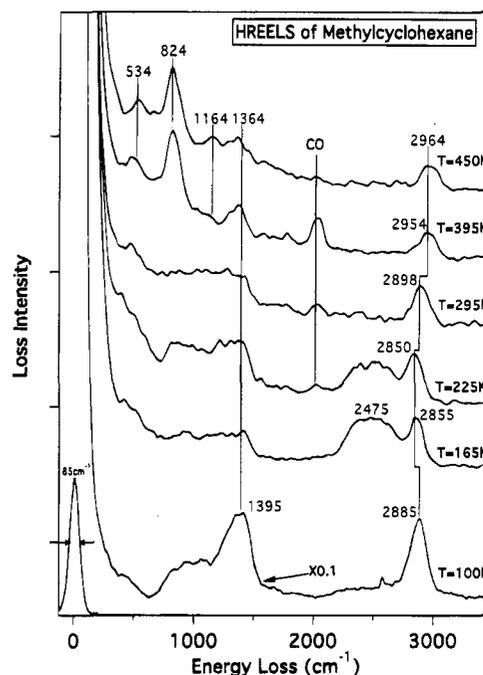
each case by normalizing the spectral intensities near  $m/e = 39$  to 1.00. The ratio of intensities of all other observed peaks to that in the reference cracking pattern was plotted versus the  $m/e$  ratio, and this was found to decrease smoothly but rapidly with mass. The plot included numerous hydrocarbons and all masses up to 200. It was fit well by the function  $4 \exp(-0.04 m/e)$ , with the error within the scatter of the data or the reproducibility of reference cracking patterns. (Different cracking patterns reported in the literature for the same molecule often give relative intensities that differ by a factor of up to 2.) This steep function reflects the poor transmission function of our mass spectrometer at high masses. We have used it routinely in other studies to correct reference cracking patterns for the transmission function of our mass spectrometer, and the resulting spectra agree well with what we measure. Even though the upper mass limit performance specification of the mass spectrometer is 200 amu, this function sets the practical upper mass limit of our mass spectrometer in TPD applications for sub-monolayer amounts of hydrocarbons at about  $m/e = 100-150$ , depending on the intensity of the signal. Intensities for higher masses are often at the noise level with small amounts of desorbing molecules.

The Pt(111) crystal was cooled to 95 K using liquid nitrogen or resistively heated to 1200 K. The temperature was measured by a chromel–alumel thermocouple spot-welded to the side of the crystal. The Pt(111) crystal was cleaned using a standard procedure as previously reported.<sup>21</sup> After TPD measurements, the surface was contaminated with carbon, which was easily removed by heating the sample in  $2 \times 10^{-8}$  Torr of  $O_2$  at 800 K, or sputtering, and then annealing in UHV to 1200 K. In all of the annealing experiments reported in this paper, the sample was briefly flashed to the anneal temperature and not held at that temperature for any appreciable amount of time.

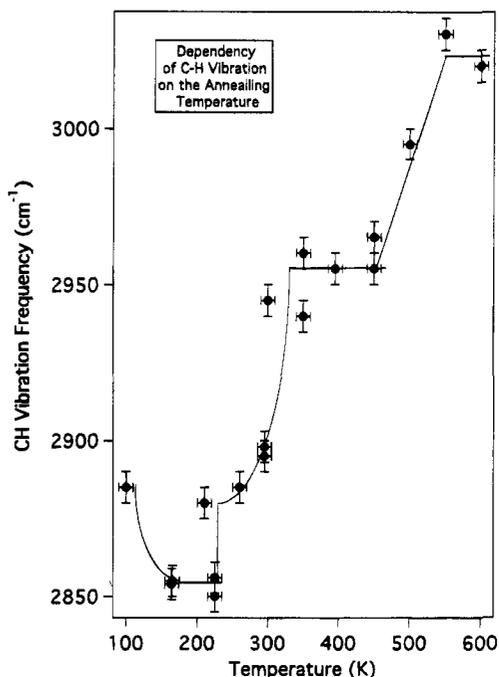
Methylcyclohexane was purified by freeze–thaw cycles while pumping. The purity was checked with gas chromatography (GC) and in-situ by mass spectroscopy.

### 3. Results

**3.1. HREELS Data.** In these studies of the dehydrogenation of MCH using HREELS, various spectra were taken in two manners: (i) after dosing MCH on Pt(111) at 100 K followed by annealing the sample to specified temperatures and (ii) after dosing MCH on Pt(111) at elevated temperatures. Figure 1 shows a typical annealing series taken after dosing to produce 3–4 layers of MCH at 100 K. From bottom to top, the sample was annealed to (b) 165, (c) 225, (d) 295, (e) 395, and (f) 450 K. The spectrum at 100 K, curve a, has its main contribution from physisorbed MCH in the multilayer. A peak due to C–H vibrations is observed at  $2885 \text{ cm}^{-1}$ . Two broad peaks between 700 and  $1600 \text{ cm}^{-1}$  represent the contributions of various unresolved C–C and C–H vibrations. A very weak, broad peak near  $2475 \text{ cm}^{-1}$  is also seen. Upon annealing the surface to 165 K, the multilayer desorbs, leaving the surface covered with a monolayer of MCH according to the TPD results. A noticeable change occurs between 700 and  $1600 \text{ cm}^{-1}$  and between 2800 and  $3100 \text{ cm}^{-1}$ . The intensities of the peaks in both ranges decrease. In contrast, the broad peak near  $2475 \text{ cm}^{-1}$  remains at a similar intensity. This broad peak is attributed to softened C–H vibrations resulting from their hydrogen-bonding interaction with the Pt surface. Similar softening has been observed previously for the adsorption of cyclohexane on many transition metals.<sup>16c,22</sup> Further annealing to 225 K introduces no major changes in the HREELS spectrum. However, after annealing the surface to 295 K, the broad peak centered at  $2475 \text{ cm}^{-1}$  disappears completely. A significant



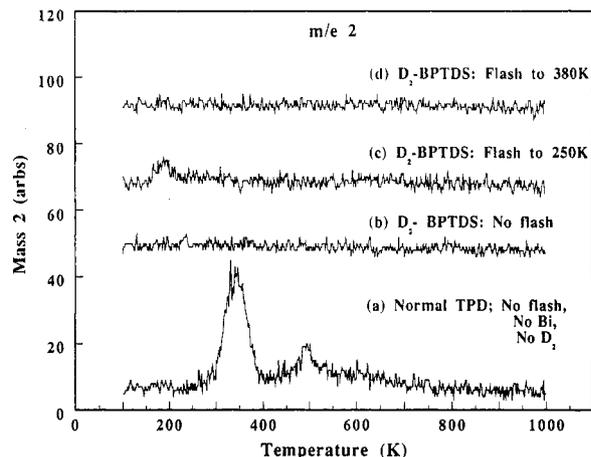
**Figure 1.** HREELS spectra following MCH adsorption on Pt(111) at 100 K. The spectra show the effects of increasing annealing temperature from bottom to top.



**Figure 2.** Affect of the annealing temperature on the C–H stretching vibrational frequency derived from Figure 1.

shift of the peak at  $2850 \text{ cm}^{-1}$  by  $50 \text{ cm}^{-1}$  to  $2900 \text{ cm}^{-1}$  is also observed. Further annealing to 395 K causes this peak to shift again to  $2960 \text{ cm}^{-1}$ . At this temperature, the most interesting change occurs between 800 and  $1200 \text{ cm}^{-1}$ . Instead of two broad peaks, three well-resolved sharp peaks develop. The sharp peak at  $825 \text{ cm}^{-1}$  is characteristic of an aromatic ring (as in chemisorbed benzene), and the high intensity of this peak is an indication of a molecular geometry with the ring plane of this species parallel to the Pt surface plane.<sup>23</sup>

Since the frequency of the C–H vibration is closely related to the extent of dehydrogenation, we show in Figure 2 the energy dependence of the C–H vibration near  $2900 \text{ cm}^{-1}$  on the annealing temperature. The chemisorbed MCH layer shows a reduced C–H vibrational frequency compared to that of the

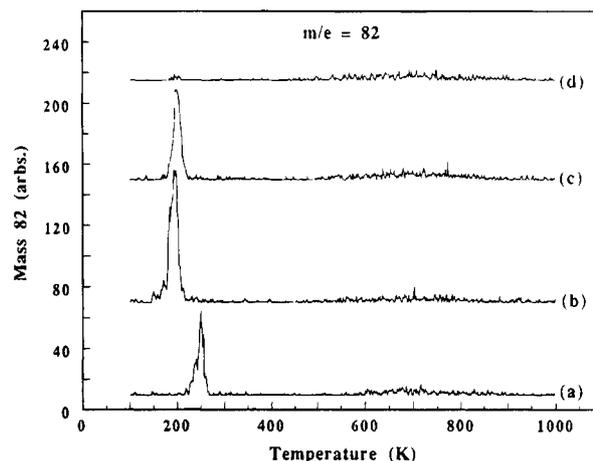


**Figure 3.** TPD and  $D_2$ -BPTDS spectra obtained monitoring the  $m/e = 2$  mass spectrometer signal from an initial monolayer of MCH adsorbed on Pt(111) at 100 K. Each spectrum corresponds to a different experimental history as follows: (a) TPD of approximately one monolayer of MCH adsorbed on a clean Pt(111) surface; (b) as in (a) but with the addition of  $D_2$  and then a monolayer of Bi after the MCH dose at 100 K; (c) as in (b) but with the MCH adlayer heated quickly to 250 K and then rapidly cooled to 100 K before dosing  $D_2$  and Bi; and (d) as in (c) but with rapid heating of the MCH adlayer to 380 K.

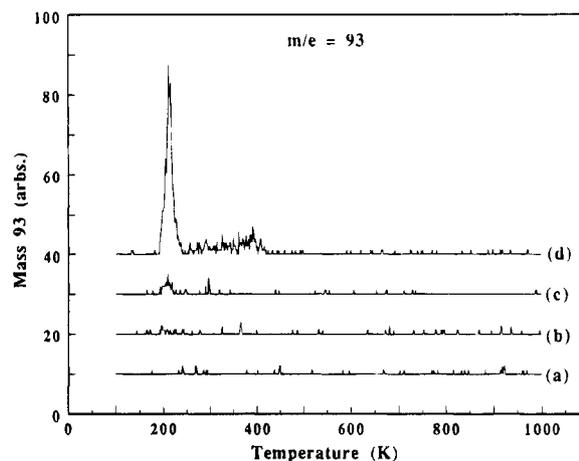
multilayer due to the chemisorption interaction with the Pt surface. The C–H stretching frequency of the chemisorbed MCH layer increases stepwise with increasing annealing (surface) temperature due to sequential dehydrogenation steps producing distinct hydrocarbon intermediates on the surface.

**3.2. BPTDS Results.** The  $D_2$ -BPTDS experiments carried out here are a variation of normal BPTDS and were performed as follows.<sup>17</sup> The clean Pt(111) sample was dosed with an amount of MCH that had been determined to give  $\approx 1$  monolayer coverage of MCH at 100 K. (Here a monolayer is defined as the amount required to just saturate the monolayer TPD peaks, before the onset of the multilayer MCH TPD peak. The MCH monolayer coverage was previously determined to be  $2.1 \times 10^{14}$  molecules of MCH  $cm^{-2}$  from absolute sticking coefficient measurements.<sup>14</sup>) After waiting 8–10 min to allow the background pressure of MCH to return to its base line, the sample was heated rapidly to a predetermined temperature and then rapidly cooled. The surface was then exposed to a dose of  $\approx 2 \times 10^{-8}$  mbar of  $D_2$  for 210 s. (This dose was performed with a directed doser so it actually corresponds to a  $\approx 3$ -fold higher exposure than these numbers suggest. This dose had previously been determined to saturate the surface with  $D_{(a)}$ .) Subsequently, Bi was dosed to the surface in an amount that was known to deposit a monatomic layer of Bi over the whole crystal surface. This complex surface was then subjected to rapid heating while the products of desorption were monitored using the QMS multiplexed to follow signals at 6 mass/charge ratio ( $m/e$ ) values every  $1/6$  s.

Figures 3–6 show results obtained from TPD and  $D_2$ -BPTDS experiments following MCH adsorption on Pt(111). Each figure corresponds to a specific  $m/e$  signal from the QMS. Each spectrum within the figures corresponds to a different experimental history. Spectra are shown for 2, 82, 93, and 98 amu. Mass 98 is the MCH molecular (M) ion and the only mass solely attributable to MCH. Mass 93 is the molecular (M) ion for  $d_1$ -toluene. Mass 82 is a fragmentation product ( $M - 15$ ) of  $d_1$ -methylcyclohexene but is also seen in the mass spectrum of MCH. A number of other mass spectrometer signals were also monitored in these and identical experiments. These signals included additional features of the mass spectrum of MCH (98, 97, 96, 92, 91, 89, 83, 82, 81, 80, 78, 69, 67, 55, 54 amu),

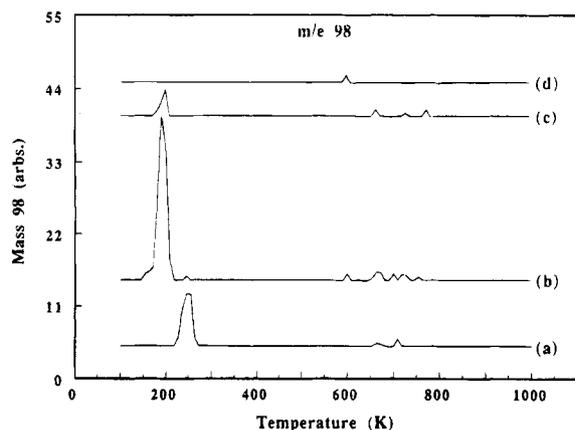


**Figure 4.** TPD and  $D_2$ -BPTDS spectra that accompany Figure 3 obtained by monitoring an  $m/e = 82$  mass spectrometer signal: (a) TPD of approximately one monolayer of MCH adsorbed on a clean Pt(111) surface; (b) as in (a) but with the addition of  $D_2$  and then a monolayer of Bi after the MCH dose at 100 K; (c) as in (b) but with the MCH adlayer heated quickly to 250 K and then rapidly cooled to 100 K before dosing  $D_2$  and Bi; and (d) as in (c) but with rapid heating of the MCH layer to 380 K.



**Figure 5.** TPD and  $D_2$ -BPTDS spectra that accompany Figure 3 obtained by monitoring the  $m/e = 93$  mass spectrometer signal: (a) TPD of approximately one monolayer of MCH adsorbed on a clean Pt(111) surface; (b) as in (a) but with the addition of  $D_2$  and then a monolayer of Bi after the MCH dose at 100 K; (c) as in (b) but with the MCH adlayer heated quickly to 250 K and then rapidly cooled to 100 K before dosing  $D_2$  and Bi; and (d) as in (c) but with rapid heating of the MCH adlayer to 380 K.

$d_1$ -toluene (98, 93, 92, 91, 89, 78, 77, 83, 82, 69, 65, 55, 54 amu), and  $d_1$ -methylcyclohexene (98, 97, 96, 93, 92, 91, 89, 83, 82, 69, 67, 55, 54 amu). The tracking of these masses and comparisons to known mass spectrometer cracking patterns further reinforces our species identification, though for clarity and brevity they are not shown here. The mass spectral cracking patterns for methylcyclohexane, toluene, benzene, and bibenzyl were measured as described in section 2. The patterns for methylcyclohexene and toluene- $d_1$  were estimated from those reported in the reference literature<sup>20</sup> after correction for the known decrease in transmission function versus mass in the Inficon QMS. Even though we could not observe the parent masses for bibenzyl and stilbene, it was a straightforward matter to distinguish the species of greatest interest here based on their fragmentation patterns in the mass range below 150 (see ref 16e, for example). The species we particularly considered in trying to fit the observed BPTDS data were  $H_2$ , MCH, methylcyclohexene, toluene, benzene, bibenzyl, and stilbene.



**Figure 6.** TPD and  $D_2$ -BPTDS spectra that accompany Figure 3 obtained by monitoring the  $m/e = 98$  mass spectrometer signal: (a) TPD of approximately one monolayer of MCH adsorbed on a clean Pt(111) surface; (b) as in (a) but with the addition of  $D_2$  and then a monolayer of Bi after the MCH dose at 100 K; (c) as in (b) but with the MCH adlayer heated quickly to 250 K and then rapidly cooled to 100 K before dosing  $D_2$  and Bi; and (d) as in (c) but with rapid heating of the MCH adlayer to 380 K.

(See ref 16d–e for some of their observed cracking patterns for our system.) The masses we followed in these experiments included  $m/e = 2, 51–53, 55, 65, 69, 76–79, 82–83, 88–93, 98$ . When deuterium was also present we also considered the deuterated analogs of these values.

The desorption spectra shown in Figures 3–6 reveal a number of aspects of the surface chemistry. The lowest spectrum (curve a) in each case is simply that for normal TPD of  $\approx 1$  monolayer of MCH adsorbed at 100 K. This has already been reported<sup>14</sup> for masses 55 and 2. Briefly, a molecular MCH desorption state is seen at  $\approx 250$  K. Beyond this only  $H_2$  desorption is seen in three separate features at higher temperatures. The  $H_2$  desorption spectrum is consistent with the dehydrogenation of the adsorbed hydrocarbon to a strongly bound aromatic species. This species does not desorb under ordinary TPD conditions and subsequently dehydrogenates on the surface to eventually form “graphitic”  $C_{n(a)}$  and  $H_2$ . It should be noted that no 93 amu signal derived from  $d_1$ -toluene is observed during this experiment and that the relative desorption intensities of all the signals above  $m/e = 2$  follow well those obtained from the gas phase mass spectrum of MCH in our UHV system.

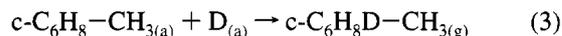
The addition of Bi to the surface before TPD caused profound changes in the desorption spectra (not shown, but the spectra were essentially identical to curves b shown in Figures 3–6). The most noticeable change was a downward shift in the desorption peak temperature for all signals. This is always seen in BPTDS and is, in part, why the technique works. This decrease in the desorption temperature is due to the disruption of the adsorbate–substrate bonding by the adsorbed Bi.<sup>17</sup>

The  $D_2$ -BPTDS spectra for the “as-dosed” MCH monolayer at 100 K is presented in spectra b of Figures 3–6. No  $H_2$  or HD (not shown) desorption occurs. This immediately indicates that dehydrogenation of the molecularly adsorbed MCH species does not occur on clean Pt{111} at 100 K and that dehydrogenation in the subsequent heating of the sample is completely suppressed by Bi. The intensities at 98, 82, and 55 amu are all dramatically increased relative to the normal TPD case (curves a) but retain the ratios they had in the molecular MCH desorption peak from the clean surface. Comparison of the absolute intensities for each of the signals due to MCH in spectra and b shows that  $\approx 55–65\%$  of the MCH monolayer initially adsorbed desorbs molecularly from the clean surface. This compares well to the results of Jiang et al.,<sup>14</sup> who estimated

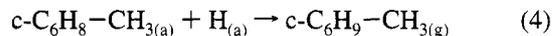
this percentage to be  $\approx 65\%$  via comparison of the hydrogen desorption from the clean surface TPD to that from one monolayer of toluene adsorbed on Pt(111). It should be noted that again there is no desorption signal at 93 amu.

The  $D_2$ -BPTDS spectra following heating the sample to 250 K (spectra c in Figures 3–6) reveal larger changes in the product desorption spectra. A small  $H_2$  desorption feature reappears at  $\approx 180$  K, indicating that the flash to 250 K has initiated dehydrogenation. The  $H_{(a)}$  released does not desorb from the clean Pt(111) surface at 250 K and remains on the surface until it is desorbed subsequently in  $D_2$ -BPTDS. Quantification of how much dehydrogenation this actually represents is difficult from the 2 amu signal alone. To do this requires that  $m/e = 3$  (HD) must be followed since most of the surface hydrogen is expected to desorb as HD due to the high levels of  $D_a$  present on the surface in the  $D_2$ -BPTDS experiment. Much of the MCH adsorbed on the surface has undergone dehydrogenation since the intensity of the desorption feature at 98 amu (the molecular ion of MCH) is severely attenuated to less than 10% of its value in curve b where all the MCH desorbs molecularly. Indeed, since that part (55–65%) of the original MCH monolayer that desorbs from the clean surface has already done so by this temperature (see spectra a), most of the rest must have already dehydrogenated. The 82 amu signal, however, maintains  $\approx 70\%$  of the intensity it had in the absence of this thermal treatment. This clearly indicates that *another species must now be contributing to the 82 amu intensity*.

Thus, a large proportion of the molecular MCH remaining on the surface after the flash to 250 K has been converted to a new species. This was clearly observed in HREELS taken after a similar thermal treatment, though no specific identification can be made on the basis of those HREELS data alone. Major cracking fragments of singly deuterated methylcyclohexenes (i.e.,  $c-C_6H_8D-CH_3$ )<sup>20</sup> are expected at 82, 55, and 69 amu (not shown). These three masses are all observed in our  $D_2$ -BPTDS experiments in ratios similar to those expected from the desorption of  $d_1$ -methylcyclohexene along with some of its perhydro analog. The latter is produced in  $D_2$ -BPTDS since at these temperatures the hydrogen removed from the parent molecule remains on the surface as  $H_{(a)}$  that can add to any molecular fragments present in competition with the adsorbed deuterium. By analogy with reaction 2 above, we therefore assign these  $d_1$  and  $d_0$  methylcyclohexene signals to the following reactions, occurring during BPTDS:



and



The precise amount of each product formed will be a function of how much dehydrogenation had occurred in the thermal pretreatment and also the magnitude of any kinetic isotope effect present in the subsequent hydrogenation. For similar reactions at the temperatures in question, hydrogenation has been found to be around 3 times faster than deuteration.<sup>16b–d,17</sup>

A small but detectable feature at 93 and 92 amu (not shown) can also be seen in curve 5c after the 250 K flash. These signals are expected for the M and M – 1 ion, respectively, of  $d_1$ -toluene. The  $d_1$ -toluene has been shown to be the product, formed with  $\approx 100\%$  yield, in  $D_2$ -BPTDS from the surface benzyl species formed from thermal treatment of adsorbed toluene on Pt(111)<sup>16d</sup> (see eq 1). Therefore, by 250 K under our heating and cooling conditions, further dehydrogenation of MCH(a) to benzyl is also possible, although it is still very slow.

This dehydrogenation product of MCH was hypothesized in ref 14 on the basis of the H<sub>2</sub> TPD spectra that correspond to Figure 3a.

The top spectra d in Figures 3–6 show the result of a thermal flash of the adlayer to 380 K. By this temperature the desorption profiles show that all the surface MCH has been fully converted to the benzyl species. Again, this is evidenced by the *m/e* = 92 and 93 signals detected in the D<sub>2</sub>-BPTDS due to desorption of *d*<sub>1</sub>-toluene from eq 1. The tiny signal at ≈200 K for 82 amu is probably due to readsorption from the gas phase of molecular MCH (the concentration must be so small that the molecular ion cannot be detected) or possibly from a trace amount of the  $\pi$ -allylic *c*-C<sub>6</sub>H<sub>8</sub>-CH<sub>3(a)</sub> species. There is no H<sub>2</sub> desorption, and the only other signals detected are at 93 and 92 amu and other appropriate *m/e* values due to the desorption of *d*<sub>1</sub>-toluene derived from adsorbed benzyl.

At the flash temperature of curves d, 380 K, the hydrogen liberated in the conversion of MCH to benzyl desorbs from the surface during the thermal pretreatment. The lack of any hydrogen desorption in this D<sub>2</sub>-BPTDS trace therefore confirms the isotopic purity of the D<sub>2</sub>. The lack of any other desorption products indicates that conversion of irreversibly adsorbed MCH to benzyl via a  $\pi$ -allylic intermediate is likely to be close to 100%. No other species are present in significant concentration on the Pt(111) surface after the 380 K flash. Also, the amount of toluene-*d*<sub>1</sub> is seen in Figure 5d was compared with the signal intensity from known coverages of adsorbed toluene. This allows us to conclude that >70% of the MCH that does not desorb molecularly has converted to adsorbed benzyl.

After the large peak at ≈200 K for 93 amu in Figure 5d there also appears to be some weak, broad desorption between 300 and 400 K. This is also seen for 92 amu, though not in the expected ratio for *d*<sub>1</sub>-toluene. We show elsewhere<sup>24</sup> that when high levels of benzyl are present at the bismuth-postdosed surface, dimerization can occur to produce a bibenzyl species. It is this bibenzyl species that gives rise to this intensity, although small amounts of benzyl radical and toluene seem to be included in this peak.<sup>24</sup>

#### 4. Discussion

Methylcyclohexane and cyclohexane dehydrogenation are two prototypical reactions for studying selective dehydrogenation catalysis. Of these two, cyclohexane has been much more extensively studied, both catalytically and from a molecular viewpoint in surface science. The adsorption of cyclohexane on transition metal surfaces has been extensively probed using various surface science techniques including HREELS.<sup>1–13</sup> Furthermore, there is general agreement regarding the mechanism of cyclohexane dehydrogenation on Pt(111).<sup>12,16c,25</sup> We expect that MCH will behave chemically very similarly to cyclohexane, and we will utilize the previous cyclohexane results as benchmarks regarding MCH dehydrogenation. Since this is the first HREELS study of MCH adsorption on the Pt(111) surface, and one of only a few surface science investigations of this chemistry,<sup>14</sup> we will interpret our HREELS results with regard to this previous work on cyclohexane chemisorption and reaction on Pt(111) and make use of the valuable complementary information available from BPTDS experiments.

Molecular adsorption of MCH occurs on Pt(111) at 100 K. The adsorption of a chemisorbed MCH layer is differentiated from the multilayer phase by the broad peak at 2475 cm<sup>-1</sup> that is attributed to the softened C–H vibrations due to the direct interaction of MCH with the Pt surface. The high intensity of this peak and the similarity of the HREELS spectra of MCH to that of cyclohexane suggest that MCH is also adsorbed with

hydrogen bonds between the surface and the three axial hydrogens that are directed toward the Pt surface. This also implies that the MCH is adsorbed with the ring plane more or less parallel to the surface, as was shown to occur with cyclohexane also.<sup>25</sup>

Annealing to 295 K removes the broad peak at 2475 cm<sup>-1</sup> completely due to a loss of hydrogen-bonding interactions with the surface. The shift of the C–H stretching vibration at 2850–2900 cm<sup>-1</sup> indicates that some additional dehydrogenation occurs. However, the aromatic ring has not formed yet at this temperature because of the absence of a strong C–H bending mode near 800 cm<sup>-1</sup> that would be present for an aromatic ring. These results indicate that a stable reaction intermediate for MCH dehydrogenation has been formed on the Pt(111) surface over this temperature range. A very similar reaction intermediate has also been found in a HREELS study of cyclohexane dehydrogenation on Pt(111) conducted at different annealing temperatures. In this case, this species was assigned to be a *c*-C<sub>6</sub>H<sub>9</sub>  $\pi$ -allyl species by HREELS<sup>25</sup> and D<sub>2</sub>-BPTDS.<sup>16c</sup> This species was also predicted by semiempirical theory<sup>18</sup> and suggested as an intermediate in cyclohexane dehydrogenation by LITD-FTMS<sup>12</sup> and by quantitative hydrogen analysis.<sup>26</sup> Therefore, we assign a reaction intermediate for MCH dehydrogenation to be a *c*-C<sub>6</sub>H<sub>8</sub>-CH<sub>3</sub> species, bonded in a similar  $\pi$ -allylic manner to Pt(111). From Figure 2, we can see that this species is found on the surface at 230–240 K and is stable up to a surface temperature of 300–320 K.

Heating the surface to 395 or 450 K dehydrogenates the surface species formed from MCH further, as indicated by the shift of the C–H stretching vibration from 2900 to 2960 cm<sup>-1</sup>. The appearance of an intense peak at 825 cm<sup>-1</sup> indicates that an aromatic intermediate has been formed on the surface in this temperature range. On the basis of a comparison of these spectra to those obtained by Avery<sup>27</sup> from thermal treatment (heating to 350 K) of toluene on Pt(111) to form adsorbed benzyl, we assign this intermediate to be chemisorbed benzyl. Figure 2 shows again that the benzyl species is stable on the Pt(111) surface over the temperature range 350–480 K. Further heating the surface to 550–660 K shifts this C–H mode from 2960–3020 cm<sup>-1</sup>, indicating the decomposition of benzyl species. This is also consistent with a gradual disappearance of the C–H bending mode near 825 cm<sup>-1</sup>. (HREELS spectra for this temperature range were collected but are not shown in this paper.)

The D<sub>2</sub>-BPTDS technique provides strong support for the identification and thermal stabilities of these surface intermediates and reveals several additional results. By 250 K, a facile dehydrogenation process is active in dehydrogenating the surface-bound MCH to an adsorbed *c*-C<sub>6</sub>H<sub>8</sub>-CH<sub>3</sub> species. It seems likely that this species is a major contributor to the complex HREELS spectrum derived from heating an adlayer of MCH to 250 K. However, BPTDS reveals that up to three other species are present in smaller amounts and contributing to the HREELS spectrum. These are MCH<sub>(a)</sub>, H<sub>(a)</sub>, and benzyl<sub>(a)</sub>. The relative proportions of these species will depend on the precise nature of the heating and cooling schedules. At higher surface temperatures, both the MCH<sub>(a)</sub> and *c*-C<sub>6</sub>H<sub>8</sub>-CH<sub>3(a)</sub> have been completely replaced by the adsorbed benzyl species, Ph-CH<sub>2(a)</sub>. The lack of any high-temperature H<sub>2</sub> desorption or any other desorption products other than those due to *d*<sub>1</sub>-toluene indicates that at this temperature the MCH that does not desorb molecularly is quantitatively converted to adsorbed benzyl and that no other processes such as C–C bond cleavage or isomerization are occurring to any significant degree at 380 K.

As a final comment, the sequential dehydrogenation mechanism that occurs for MCH on Pt(111) can be compared to

simple predictions from examining the C–H bond strengths in the molecule. The weakest C–H bond is the tertiary C–H, which probably breaks first. When two other ring hydrogens are lost, the  $c\text{-C}_6\text{H}_8\text{-CH}_{3(a)}$  species results. The methyl group in this species is left intact since the C–H bonds in this group are stronger than the ring C–H bonds. Dehydrogenation of one H from each of the three remaining ring  $\text{CH}_2$  groups and one hydrogen from the methyl group are required to form the chemisorbed benzyl species. It is interesting to note that the initial dehydrogenation reaction occurs at similar temperatures (within  $\approx 20$  K) for both cyclohexane and MCH on Pt(111), showing little effect on this elementary step due to the presence of the tertiary C–H bond in MCH.

## 5. Conclusion

The adsorption of MCH on the Pt(111) surface has been studied with BPTDS and HREELS. MCH is adsorbed on the surface with the ring plane roughly parallel to the surface, with three axial hydrogens directed toward the surface. This bonding interaction produces a strong softening of the C–H vibration. Two metastable dehydrogenation intermediates are identified on the Pt(111) surface: a  $\pi$ -allylic  $c\text{-C}_6\text{H}_8\text{-CH}_{3,a}$  species and chemisorbed benzyl ( $\text{Ph-CH}_{2,a}$ ). These species are present over the temperature ranges 235–310 and 350–480 K, respectively.

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