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# Interaction of D(H) atoms with physisorbed benzene and (1,4)-dimethyl-cyclohexane: Hydrogenation and H abstraction

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Benzene and (1,4)-dimethyl-cyclohexane monolayers were physisorbed on graphite covered Pt(111) surfaces. Exposure of benzene monolayers at 125 K to D atoms (1700 K) initially hydrogenates $sp^2$ hybridized C atoms with a cross section of ca. 8 Å$^2$ producing $C_6H_6D$ intermediates. Additional D atom reactions either transform this intermediate via a second hydrogenation reaction to cyclohexadiene-$d_2$, $C_6H_6D_2$, or restore benzene, $C_6H_5D$, via H abstraction. Once the aromaticity is broken, successive hydrogenation of the diene occurs rapidly generating the saturated cyclohexane-$d_6$, $C_6H_6D_6$. The $C_6H_5D$ reaction product can undergo further H/D exchange reactions and, at any level of deuteration, the benzene species might get hydrogenated. Monolayers of the saturated hydrocarbon (1,4)-dimethyl-cyclohexane (DMCH) that are exposed to D atoms produce deuterated DMCH via successive abstraction/hydrogenation reactions. Thermal desorption mass spectra revealed that H atoms at the ring were exchanged with an apparent cross section of 1.7 Å$^2$. Methyl groups H atoms were exchanged much more slowly than ring H atoms. It was also observed that D exposed molecules/radicals exhibit a tendency to desorb from the surface, which is ascribed to the exothermicity of the reactions which lead to these species. © *1996 American Institute of Physics.* [S0021-9606(96)00605-9]

## I. INTRODUCTION

The interaction of H(D) atoms with surfaces and adsorbates is a field of growing interest. Various examples have shown that H atoms adsorb at metal surfaces which exhibit a barrier towards hydrogen adsorption from molecular $H_2$.[1–4] H atoms impinging at Cl covered Au surfaces initiate HCl formation[5] with a subtle energy distribution of the products, indicative of Eley–Rideal and Langmuir–Hinshelwood branches in this atom/adsorbate reaction. H or D atoms directed at hydrocarbons adsorbed on metal surfaces react with these,[6,7] although the role of the metallic support is unclear.

Recently, we have shown that thermal D atoms impinging at the surfaces of ion beam deposited C:H films hydrogenate unsaturated $sp^2$ C centers to $sp^3$ at low temperature,[8] whereas at high temperatures H/D exchange due to thermally induced decomposition of a radical intermediate was observed.[9] D impact induced abstraction of H from saturated $sp^3$ $CH_n$ groups has been identified as an Eley–Rideal type process.[10] Hydrogenation and H abstraction was also observed at H covered diamond surfaces.[11] The interplay between hydrogenation, cross section $\sigma_H = 1.1$ Å$^2$, and H abstraction, cross section $\sigma_D = 0.05$ Å$^2$, causes a temperature dependent H impact induced erosion process of the C:H films.[12]

In an attempt to investigate whether these reaction mechanisms are also common to the interaction of thermal H atoms with adsorbed hydrocarbons, we have studied the reactions which proceed at physisorbed *p*-xylene under impact of D.[13] It was instrumental for this investigation that the influence of the metal substrate, a Pt(111) surface in the addressed study, was eliminated by covering the metal surface with a graphite monolayer prior to adsorption of *p*-xylene. It could be confirmed with TDS and HREELS methods that this Pt(111)/C substrate provided an almost ideal physisorption substrate for the hydrocarbon molecule.

Our study revealed that the interaction of D with physisorbed *p*-xylene is governed by H abstraction and hydrogenation reactions, with the important observation that radical intermediates generated by these reactions from molecular species exhibit some stability, at least at the temperature employed in the study, 135 K. This observation is a simple consequence from the fact that after sufficient atom exposure to the target species reaction products were detected in thermal desorption spectra which could only be formed via a radical intermediate.

The Pt(111)/C/*p*-xylene[13] study has also shown that the probabilities of the H impact induced hydrogenation and H abstraction reactions are affected by the stability of the intermediates and products generated by abstraction and hydrogenation, fully in line with the experience from the organic chemistry of these molecules.[14]

The present work presents a study of the interaction of thermal D and H atoms with physisorbed benzene and (1,4)-dimethyl-cyclohexane at Pt(111)/C. It will be shown that H abstraction and hydrogenation, stability of radical intermediates, and the role of favorable molecular structures govern this interaction.

## II. EXPERIMENT

The experiments were performed in a UHV chamber equipped with instrumentation for vibrational spectroscopy

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(HREELS), thermal desorption spectroscopy (TDS), Auger electron spectroscopy (AES) and low energy electron diffraction (LEED).

The substrates were clean Pt(111) single crystal surfaces and Pt(111) surfaces covered with a monolayer of graphite prepared by exposing Pt(111) surfaces to ethane at 900 K crystal temperature. LEED and Auger spectroscopy were used to characterize the clean and monolayer graphite covered surfaces. The graphitization procedure of Pt(111) surface used here is well established and characterized in the literature.[15]

Research grade benzene and (1,4)-dimethyl-cyclohexane (DMCH) were filled into a gas handling line and cleaned by several freeze cycles. The gases were admitted to the main chamber by backfilling the chamber. The exposures given below for benzene and DMCH in Langmuir units, $1\ \mathrm{L}=10^{-6}$ Torr s, are calculated from uncorrected ion gauge readings.

Deuterium or hydrogen atoms were produced in a heated Ta tube with an effusion hole (temperature 1700 K, pressure about 1 Pa). The H and D atom fluences are given in the present communication as monolayer (ML) equivalents relative to the graphite (0001) areal density, i.e., $1\ \mathrm{ML}=3.8\times10^{15}\ \mathrm{atoms/cm}^2$. The atom flux impinging the target surface was calculated from the tube temperature and in-tube $D_2$ ($H_2$) pressure. Typical atom fluxes were $1\text{–}2\times10^{13}\ \mathrm{atoms/s\ cm}^2$. The method used to produce atoms implies that they exhibit a Maxwellian velocity distribution, which for the present experiments has its maximum at 0.15 eV kinetic energy. As thermal atom sources cannot work at a dissociation efficiency of unity, it also implies that atom exposure is inevitably connected with simultaneous exposure of the respective molecules. These molecules, however, represent an unreactive background in the present experiments. Thermochemical data suggest that even vibrationally excited hydrogen molecules with 0.4 to 0.5 eV of vibrational energy can undergo only significantly endothermic reactions with the present reactant species.

HREEL spectra were recorded in specular direction at an electron impact energy of 7 eV. The resolution of the double pass monochromator/analyzer assembly was set at $35\ \mathrm{cm}^{-1}$.

TDS experiments were performed in the spectrum mode, in which a preselected mass range, typically 50 to 100 amu (for benzene) or 90 to 130 amu (for DMCH), was scanned by the quadrupole mass spectrometer simultaneously with the application of the temperature ramp, and the resulting signals were stored in a computer. This computer also controlled the linear temperature ramp applied to the crystal. Given the timing requirements of the quadrupole electronics/computer data exchange, at a heating rate of 1 K/s one spectrum could be collected every second. This data then allowed to construct accumulated mass spectra by summing up a series of spectra measured in a specific temperature range. Amu selected thermal desorption spectra could also be extracted from the original data set. The latter data were very useful for discrimination between background and sample signal. Alternatively, up to 9 masses could be preselected and multiplexed during the TDS runs. This method was used if it was clear prior to a TDS measurement which masses had to be followed.

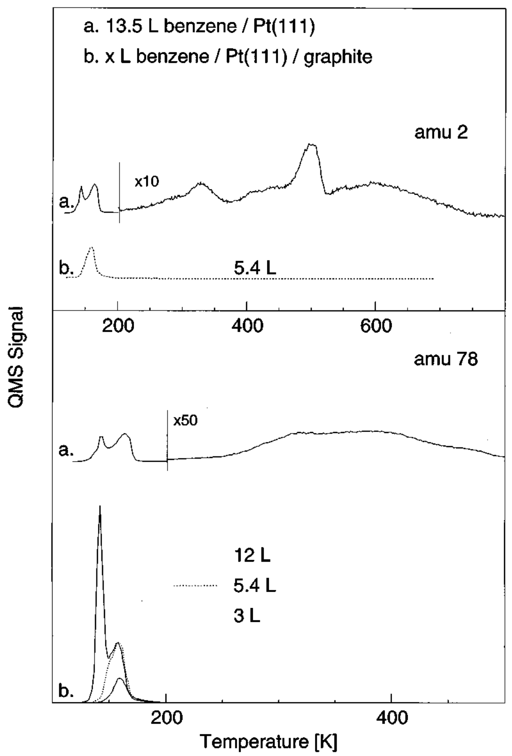

FIG. 1. Benzene (amu 78) and hydrogen (amu 2) thermal desorption spectra measured after adsorbing benzene at (a) Pt(111) and (b) Pt(111)/C surfaces at 125 K. Heating rate: 1 K/s.

In order to test their stability and reactivity, H and D atoms were directed at bare graphite monolayers on Pt(111) surfaces at 120 to 300 K surface temperature. That hydrogenation reactions had occurred was confirmed with TDS, but barely detectable in HREEL spectra. The fraction of hydrogenated C atoms of the graphite monolayer was only a few percent in the atom fluence range of significance here. Apparently, only at steps and other imperfections of the C monolayers hydrogenation reactions can proceed. It is therefore safe to assume that the C monolayer does not contribute to the observed reactions of atoms with adlayer species and the spectral changes induced by these reactions.

## III. RESULTS

### A. Benzene

Prior to the investigation of the reactions of D (H) atoms with monolayers of benzene at Pt(111)/C it was studied how monolayers of benzene had to be prepared and in which way the substrate/adsorbate chemistry was affected by the presence of a sandwiched graphite monolayer. For this, clean Pt(111) surfaces and Pt(111)/C surfaces were exposed to benzene at 125 K substrate temperature and the adsorption characteristics were studied with TDS and HREELS. Figure 1 shows amu 78 (molecular benzene) and amu 2 TD spectra for benzene exposures covering the monolayer and multilayer range at Pt(111). Three amu 78 desorption peaks at 370, 165, and 142 K can be correlated with first layer chemisorbed benzene, second layer physisorbed benzene and third and following layers of condensed benzene. The peak due to chemisorbed benzene is very broad and indicates a complicated desorption behavior affected by simultaneous decomposition of benzene. The adsorption/desorption characteristics observed in the present study are similar to previous results[16] and will be addressed in a separate paper.[17]

The TD spectrum recorded for amu 2 [upper panel, Fig. 1, spectrum (a)] exhibits a low temperature feature identical to that seen at amu 78 due to fragmentation of desorbed benzene in the mass spectrometer. Additional amu 2 features observed between 300 and 650 K are due to recombinative desorption of H atoms. The temperature dependence of these features is a function of the kinetics of benzene decomposition and the kinetics of hydrogen desorption. Accordingly, Auger spectra measured after desorption of chemisorbed benzene exhibit a carbon signal.

Benzene adsorbed at Pt(111)/C exhibits very different desorption features. Submonolayer and monolayer desorption peaks are seen around 158 K, at lower temperature than at Pt(111). These signals occur right at the descending edge of the multilayer signal which peaks at 142 K after 12 L benzene exposure. As expected, in Fig. 1 corresponding amu 2 fragmentation signals are observed but decomposition signals are absent.

The measured desorption spectra at Pt(111)/C are in accordance with weak bonding between benzene and the graphite monolayer. The observation that the monolayer signal almost overlaps with the multilayer peak indicates that adsorption of benzene at the C layer is similar to benzene adsorbed on a benzene layer, not too surprising in view of the structural similarities of graphite and benzene. This and the fact that benzene decomposition is eliminated indicates that the Pt(111) substrate is effectively shielded by the C layer.

It is seen in Fig. 1 that in desorption spectra the transition from the monolayer to the multilayer benzene at Pt(111)/C is smooth. Guided by the spectra shown in Fig. 1 the preparation of monolayers of benzene at Pt(111)/C was achieved by exposing 5.4 L of benzene to the substrate at 125 K. After this procedure, no multilayer desorption signal could be detected and the measured monolayer signals, as shown by the respective dotted desorption trace in Fig. 1, varied only by 5% between different experiments. The benzene coverage of a benzene monolayer expressed with respect to the C monolayer atom density is calculated as 0.07 [0.18 with respect to the Pt(111) surface atom density] from the amu 78 signal. The calibration of this signal in terms of coverage was performed with hydrogen desorption spectra measured at the saturation coverage of hydrogen at Pt(111) surfaces[18] and the mass spectrometer sensitivity factors for hydrogen and benzene, respectively. The benzene/C/Pt monolayer coverage obtained here is in good agreement with the value determined for benzene adsorbed at the basal plane of graphite.[19]

These TD results are fully supported by the HREEL spectra shown in Fig. 2. Here, vibrational spectra are displayed measured at benzene monolayer and multilayers at Pt(111), and at a benzene monolayer at Pt(111)/C prepared as noted above. The Pt(111) monolayer spectrum shows a strong out-of-plane CH bending mode at 830 $cm^{-1}$ whereas the multilayer and Pt(111)/C monolayer spectra exhibit this mode at 685 $cm^{-1}$. At increased sensitivity the benzene/Pt monolayer and multilayer spectra show in addition to that vibrational mode signals from excitation of other vibrations, even small signals from the $sp^2$ CH stretch mode at 2990 and 3050 $cm^{-1}$, respectively. The Pt(111)/benzene monolayer spectrum agrees very well with published data.[20]

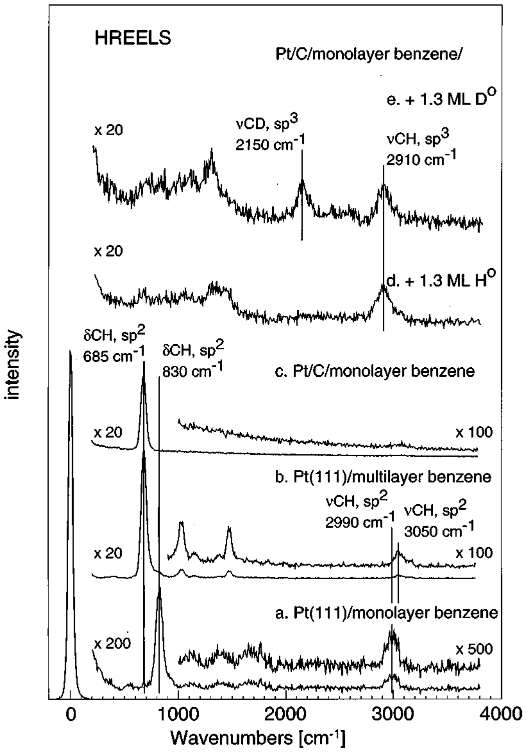

FIG. 2. Family of HREEL spectra measured at adsorbed and reacted benzene at 125 K. (a) chemisorbed benzene monolayer at Pt(111) after 3.5 L exposure, (b) benzene multilayers at Pt(111) after 250 L, (c) benzene monolayer at Pt(111)/C after 5.4 L, (d) after exposure of 1.3 ML H atoms to a benzene monolayer at Pt(111)/C, (e) after exposure of 1.3 ML D atoms to a benzene monolayer at Pt(111)/C.

A $sp^2$ CH stretch mode is virtually absent for benzene adsorbed at Pt(111)/C surfaces. The vibrational excitation selection rules operating in HREELS[21] require that benzene lies flat in that case. It is remarkable that within the precision of our experiment the CH out-of-plane mode frequencies of benzene in multilayers and a monolayer at Pt(111)/C are the same and very close to the gas phase value of 673 $cm^{-1}$.[22] This corroborates the statement made above on the bonding of benzene at this surface and supports the view that a graphite monolayer supplies an almost ideal substrate for physisorptive bonding.

Monolayers of benzene at Pt(111)/C were prepared in the above described manner and exposed to D and H atom fluxes at 125 K substrate temperature. Figure 2 includes HREEL spectra measured after 1.3 ML D or H atom expo-

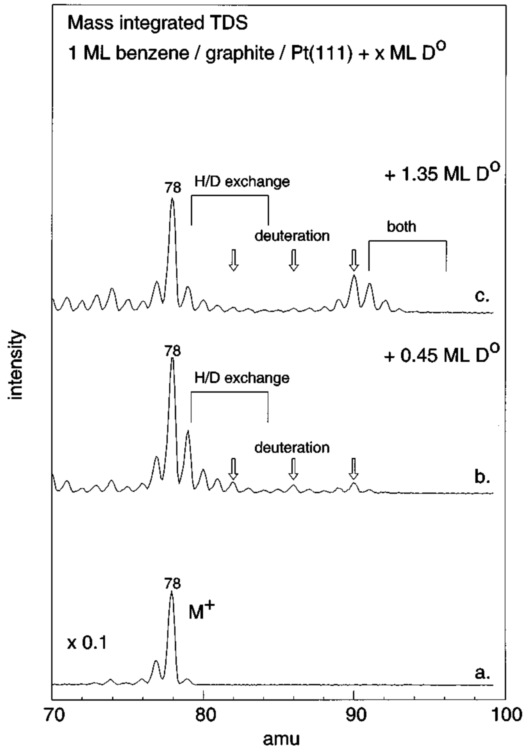

FIG. 3. Mass scan TD spectra measured after exposing D atoms to a benzene monolayer at Pt(111)/C at 125 K. Heating rate: 1 K/s. (a) Unexposed benzene, (b) 0.45 ML D, (c) 1.35 ML D. For easier identification the reaction paths are indicated. M$^+$ indicates the peak of the parent molecule ion.

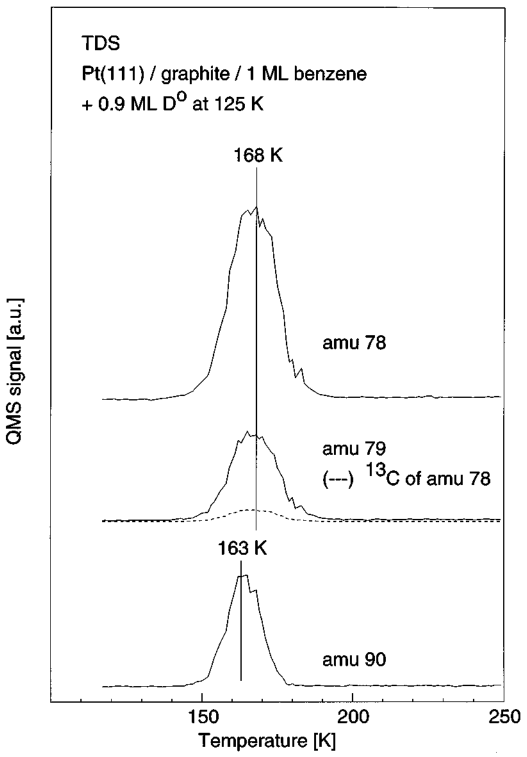

FIG. 4. Amu selected thermal desorption spectra extracted from mass scan TD spectra measured after exposing a benzene monolayer at Pt(111)/C to 0.9 ML D atoms at 125 K.

sure. It is seen that the vibrational spectrum is markedly changed as compared to a unexposed benzene layer. The occurrence of CD bending and stretching modes clearly indicate C–D bonding in reaction products after D exposure. These products are not simply deuterated (in the sense of H/D exchanged) benzene, as from the positions of the CH stretch band at 2910 cm$^{-1}$ and CD stretch band at 2150 cm$^{-1}$ it is clear that after reaction of D(H) with benzene H and D are bound to $sp^3$ hybridized C atoms. Apparently, these atoms undergo addition to the ring thereby transforming the $sp^2$ C center at which they have been added to $sp^3$. The occurrence of bending modes of $sp^3$ CHD groups in the range 500 to 1500 cm$^{-1}$ suggests that the reaction product does not lay flat at the Pt(111)/C surface. We note for completeness, that the same effects have been observed in HREELs spectra of D atom exposed benzene multilayers.

To identify the reactions in more detail, desorption spectra were measured after specific D atom fluences had been directed to benzene monolayers. In Fig. 3 spectra are displayed which illustrate the reactions induced by D exposure. Here, the sums of about 180 individual mass spectra accumulated between 120 and 300 K upon desorption of unexposed and D exposed benzene monolayers are shown. As expected, the spectral information of the unexposed monolayer contains the amu 78 signal from $^{12}$C benzene, fragmentation signals at smaller masses, and the amu 79 component from the $^{13}$C contribution to benzene. In contrast to this, the spectral signals of D exposed monolayers exhibit a sequence of peaks above amu 79, up to amu 94 after a 1.35 ML D atom dose. As already suggested from the HREEL spectra, these peaks give evidence for reactions between benzene and impinging D.

Further data analysis was performed based on amu selected TD spectra extracted from the series of individual mass scans the sum of which is shown in Fig. 3. Figure 4 gives examples for 78, 79, and amu 90 TD spectra extracted from a measurement done after 0.9 ML D atom exposure.

The amu 78 spectrum is that of the unreacted fraction of benzene. The amu 79 spectrum is composed of the $^{13}$C contribution of this signal, shown as a dashed line, plus a contribution from a reaction product, obviously $C_6H_5D$. This reaction product must exhibit the same adsorption energy at the Pt/C surface as $C_6H_6$ benzene and should therefore desorb with the same kinetics, as observed. In contrast to this, the TD spectrum of amu 90 exhibits a different peak temperature which excludes a H/D exchanged benzene as the desorbing species. As the desorption peak temperature has shifted downwards by 5 K with respect to the benzene peak, this species should be less aromatic than benzene. The amu value suggests fully hydrogenated (in the sense of D addition) benzene, i.e., cyclohexane $C_6H_6D_6$, as this species. In line with this assignment, mass spectrometer fragmentation products of cyclohexane were detected in mass scan TD spectra, each with an individual TD spectrum which reflects that cyclohexane is the parent molecule. In separate experiments with adsorbed cyclohexane it was confirmed that its desorption temperature is 163 K.

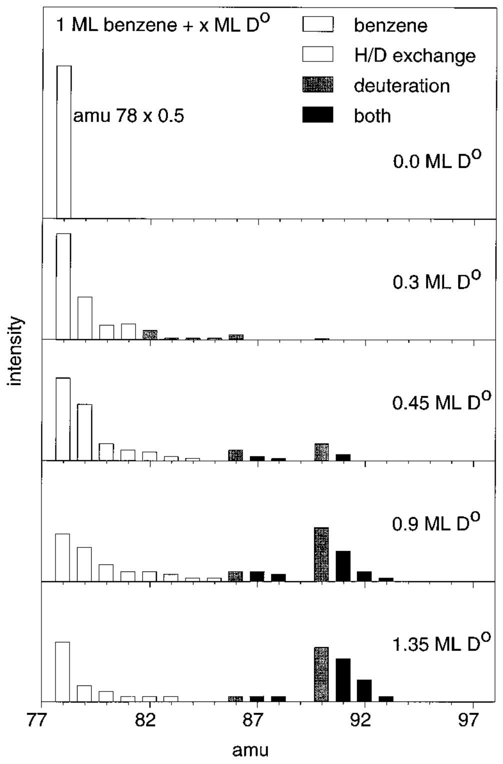

FIG. 5. Normalized reaction product distributions measured at D exposed benzene monolayers at Pt(111)/C.

It is seen in Fig. 3 that there are mass signals below amu 78, which could stem from other products than those mentioned, e.g., alkanes produced by ring-breaking reactions. The analysis, however, revealed that these signals in the integrated spectra are either mass spectrometer fragmentation products of heavier molecules or do not exhibit particular desorption peaks and are due to unidentified background species.

Figure 5 demonstrates the progress of exchange and deuteration reactions as a function of D atom exposure from 0 to 1.35 ML. Here, contributions to the mass integrated TDS by identified molecular species are represented by bars [e.g., the bar in the top panel of Fig. 5 represents the amu 78 peak from Fig. 3(a)]. The sums of the bar heights were normalized to the benzene signal obtained from an unreacted benzene monolayer (i.e., the bar height in the upper panel). These normalized signals were used instead of the measured raw data as it was observed that after D exposure the number of molecules collected in thermal desorption spectra had decreased. This loss of particles increased linearly with D atom fluence. As an example, after 1.35 ML D exposure, only about 10% of the molecules initially adsorbed as benzene could be detected as desorption species, benzene or reaction products. The origin of this phenomenon will be addressed in the discussion.

From the progression of mass distributions shown in Fig. 5 two reaction pathways can be identified which are indicated by differently shaded bars. The initial step for both pathways is D addition resulting in a radical intermediate, $C_6H_6D$, in which one ring $sp^2$ CH group is converted to $sp^3$ CHD. In the first pathway a further D impact induces H abstraction from this latter group accompanied by formation of HD which escapes into the gas phase. This leads to H/D exchanged benzenes like $C_6H_5D$, $C_6H_4D_2$, etc. In the second pathway the $C_6H_6D$ radical intermediate formed in the initiating step undergoes deuteration (in the sense of D addition) via cyclohexadiene-$d_2$ (amu 82) and cyclohexane-$d_4$ (amu 86) to cyclohexane-$d_6$ (amu 90) with the appropriate radical intermediates. As expected, products with amu values above 90 indicate that H/D exchanged benzenes generated by the first pathway can undergo hydrogenation by D as well, i.e., switch to the second pathway. In Fig. 10(a) the reaction steps are collected. If H atoms are used for the reaction, the abstraction pathway specified above should lead back to $C_6H_6$ benzene which cannot be distinguished in TD spectra from unreacted species. The H addition pathway was isolated using thermal H atoms. Analysis of the data from these experiments in conjunction with data from D atom experiments discussed previously yields cross sections for both abstraction from and addition to the $C_6H_6H$ (D) intermediate.

In order to check whether D atoms can abstract H from a saturated ring system, the above experiments were performed at monolayers of (1,4)-dimethyl-cyclohexane. This molecule was chosen instead of cyclohexane as it allowed to investigate the reactivity at ring and methyl C atoms towards atomic D in one experiment.

### B. (1,4)-Dimethyl-cyclohexane

For experiments with (1,4)-dimethyl-cyclohexane (DMCH), at first the proper monolayer preparation technique had to be established, and it had to be assured, that the Pt(111)/C substrate acts as a suitable unreactive carrier of the molecule, as was demonstrated for benzene.

Figure 6 displays thermal desorption spectra measured after adsorption of multilayers of DMCH at Pt(111) and Pt(111)/C. On Pt(111) surfaces DMCH (amu 112) exhibits complicated desorption features, very similar to those previously reported for the Pt(111)/cyclohexane system.[23] In addition to a multilayer peak at 154 K and a double-peaked monolayer structure at 245/260 K, a further sharp peak is observed at 192 K, which might stem from step sites in the monolayer which offer an increased adsorption energy in the second layer. The corresponding amu 2 desorption spectrum shows in addition to the mass spectrometer fragmentation signal hydrogen desorption above 280 K from decomposition of products left by decomposition of DMCH. At Pt(111)/C the situation is much less complicated. The peak at 200 K signals monolayer desorption and a multilayer/second layer peak is seen at 154 K. The respective amu 2 spectrum exhibits the expected fragmentation signals but no hydrogen desorption from decomposition reactions. This suggests that DMCH in the monolayer at Pt(111)/C is less strongly bound than at Pt(111) and that the sandwich C monolayer eliminates decomposition of DMCH molecules. The above conclusion on the action of the C layer for the molecule/substrate interaction therefore is confirmed with DMCH.

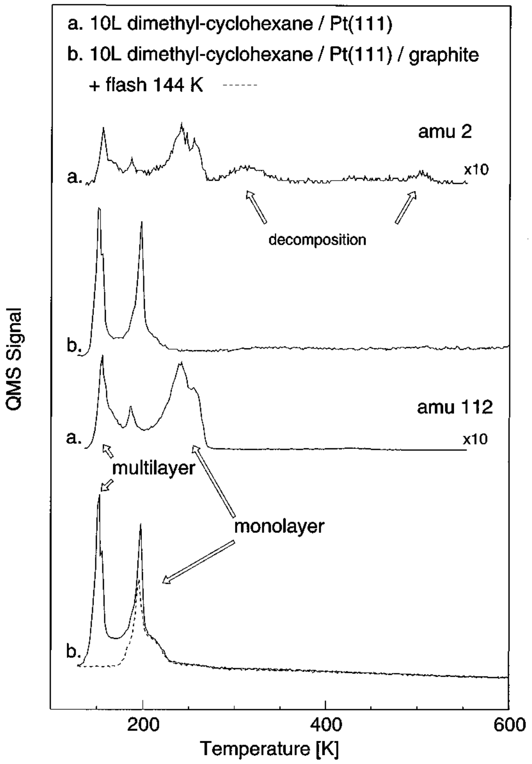

FIG. 6. (1,4)-dimethyl-cyclohexane (DMCH, amu 112) and hydrogen (amu 2) thermal desorption spectra measured after 10 L DMCH exposures at Pt(111) and Pt(111)/C surfaces.

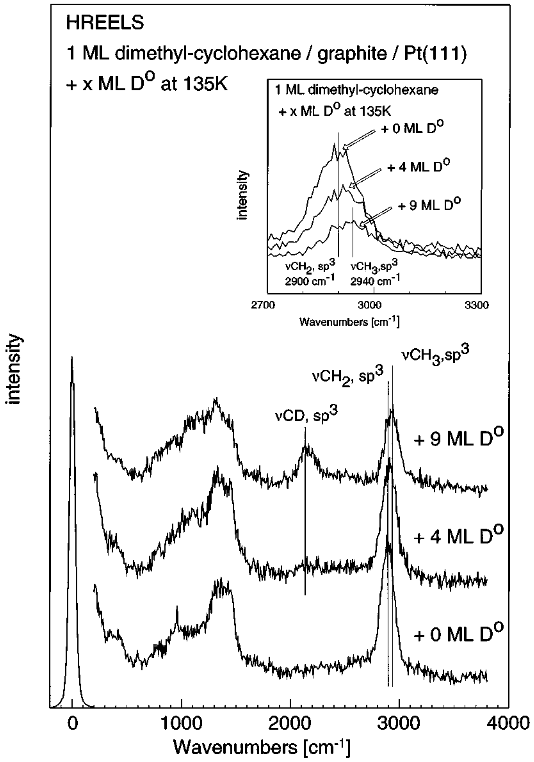

FIG. 7. HREEL spectra of unreacted and reacted DMCH monolayers at Pt(111)/C at 135 K. The inset shows the CH stretch region on an expanded scale.

Physisorbed DMCH monolayers could be prepared routinely by exposing 10 L of DMCH to Pt(111)/C followed by a flash to 144 K. A sample of corresponding monolayer desorption spectra is displayed in Fig. 6 as a dotted line. The coverage of a DMCH monolayer is estimated as 0.13 [relative to the Pt(111) atom density].

HREEL spectra recorded at a monolayer of DMCH at Pt(111)/C prior and subsequent to exposure to D atoms are shown in Fig. 7. The unexposed monolayer spectrum exhibits a CH stretch band around 2900 cm$^{-1}$ from $sp^3$ $CH_2$ and $CH_3$ groups at the ring and the methyl groups, respectively. In addition there are peaks due to bending modes in the fingerprint frequency region below 1500 cm$^{-1}$. D atom exposure to DMCH monolayers causes the occurrence of a $sp^3$ CD stretch mode peak at 2150 cm$^{-1}$ and a decrease of the CH band intensity, which is correlated with a shift of the band position towards the $sp^3$ $CH_3$ frequency value of 2940 cm$^{-1}$, emphasized in the inset of Fig. 7. The presence of a CD band clearly indicates that DMCH had reacted with D in H/D exchange reactions. The shift of the CH band peak suggests that H/D exchange had occurred at the ring $CH_2$ groups and not at the methyl groups. As was observed for benzene multilayers, HREEL spectra for D exposed DMCH multilayers exhibit the same features as the D exposed DMCH monolayers.

The results of TDS experiments at various stages of D atom exposure to adsorbed DMCH are displayed in Fig. 8. The integrated scan spectrum of unreacted DMCH exhibits the signal at amu 112 of the parent molecule and the leading fragment at amu 97 which occurs from methyl split-off upon ionization. Interaction with D reveals parent peaks at amu $112+x$ accompanied by the respective $112+x-15$ fragments. This observation corroborates the conclusion drawn from the HREEL spectra that H/D exchange proceeds at the ring. Completed H/D exchange at the ring leads to a amu 122 product. The spectrum measured after 5.9 ML of D had been exposed to adsorbed DMCH exhibits products which indicate that finally even the methyl H atoms get exchanged. As observed in the experiments with benzene, D atom exposure leads to loss of adsorbed species. Consequently, products from D atom exchange at the methyl group can only be observed at mass spectrometer sensitivities at which also contributions to the spectra from background species are present (e.g., signals below amu 97 in Fig. 8).

Results from the analysis of mass spectra measured upon reaction of DMCH with D are shown in Fig. 9. As with D exposed benzene the observed loss of particles was significant, about half of the particles were lost within the first monolayer of D exposure. Therefore, in Fig. 9 relative yields are plotted rather than absolute yields. A comparison of the D exposures noted in this bar graph with those shown in Fig. 5 suggests a less pronounced reactivity of DMCH as compared with benzene.

## IV. DISCUSSION

In full analogy to the investigation of D atom induced reactions at adsorbed $p$-xylene,[13] the present study with ben-

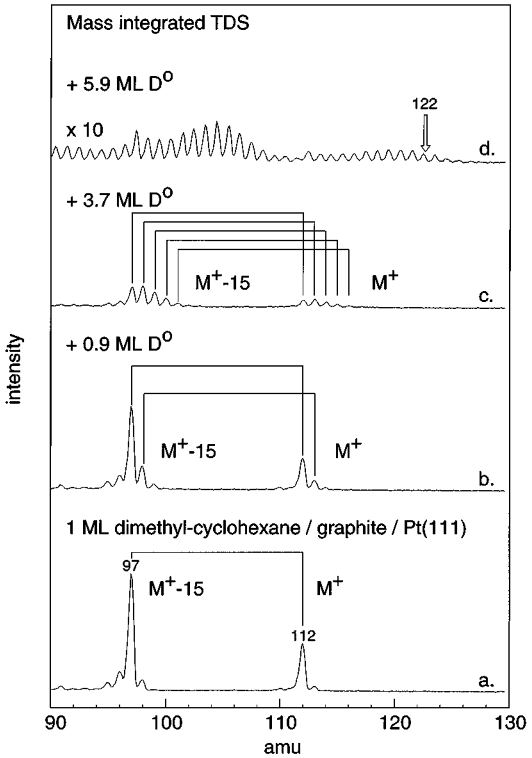

FIG. 8. Mass scan TD spectra measured after exposing D atoms to a DMCH monolayer at Pt(111)/C at 135 K. Heating rate: 1 K/s. (a) Unexposed DMCH, (b) 0.9 ML D, (c) 3.7 ML D, (d) 5.9 ML D. For easier reading the fragmentation correlations are indicated.

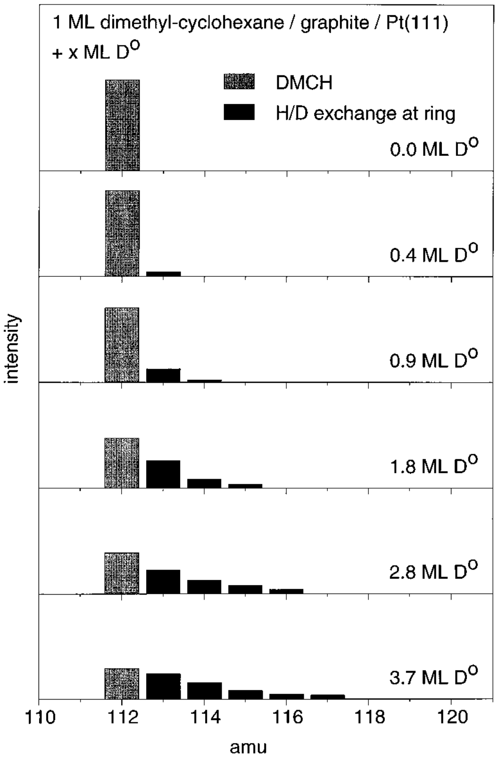

FIG. 9. Normalized reaction product distributions measured at D exposed DMCH monolayers at Pt(111)/C.

zene and DMCH shows that the ongoing reactions can be classified in the categories H abstraction via HD formation and hydrogenation (D addition). The reaction schemes displayed in Fig. 10 illustrate the processes identified and serves as a base for further discussion.

It is evident that all observed reactions are of the Eley–Rideal type, i.e., the reactions proceed upon impact of the D atoms at an adsorbed target molecule. Adsorbed D is not involved as it is not feasible that D adsorbs either at the C monolayer or at the target molecules.

All but one reaction steps included in Fig. 10 are exothermic. Consider first the reaction numbered as 1 in Fig. 10(a). The heat of reaction can be calculated from the corresponding heats of formation of the radicals H and $C_6H_7$ and the $C_6H_6$ molecule[24] as 103 kJ/mol. In contrast to this, reaction (2), H abstraction by D from benzene, is endothermic by 28 kJ/mol as the $C_6H_5$–H dissociation energy of 464 kJ/mol[24] has to be compared with the HD dissociation energy, 436 kJ/mol. Accordingly, in gas phase studies on H/benzene reactions this abstraction was negligible and occurs only under harsh conditions.[25] For the present case we therefore consider reaction (2) as not contributing. Reaction (3), the hydrogenation by D of a radical center, e.g., adjacent to the CHD group, is very exothermic. The gain of C–D binding energy is given by the full $C_6H_6D$–D dissociation energy, ca. 305 kJ/mol.[24] Similar energy gains are obtained by hydrogenation (by D) of the other radical species in Fig. 10(a).

Competitive to reaction (3) the restoration of benzene through reaction (4) is observed in the present study. The energy balance of this reaction is determined by the gain of HD dissociation energy, 436 kJ/mol, minus the $C_6H_5D$–H dissociation energy, 103 kJ/mol. Overall an energetically favorable reaction. An alternate pathway back to $C_6H_5D$ benzene would be the split-off of an H atom, which is not feasible at the given substrate temperatures. At elevated temperatures H split-off could occur via activation.[26]

Checking the numbers for all reactions in Fig. 10(a) it is confirmed that with the exclusion of H abstraction from benzene all reactions are considerably exothermic.

The present study cannot supply any information on the activation energies of the observed reactions. It is known from gas phase studies that the H/benzene and H/DMCH reactions are activated. The H abstraction from benzene, $H+C_6H_6 \rightarrow C_6H_5+H_2$, has a barrier of ca. 65 kJ/mol,[25] in line with the endothermicity mentioned above. The H addition to $C_6H_6$ has a barrier of only ca. 18 kJ/mol,[14] expected from its exothermicity. It is clear that the kinetic energy supplied by the high energy fraction of the 1700 K D atoms suffices to overcome this barrier. From the fact that the present reactions were performed at 125 K target molecule temperatures nothing can be concluded, of course.

The cross sections or reaction probabilities for the reactions in Fig. 10 can be roughly estimated from the present experiments as the kinetic data were obtained under pseudo-first-order conditions, i.e., constant H flux. Accordingly, the appropriate rate law can be formulated as

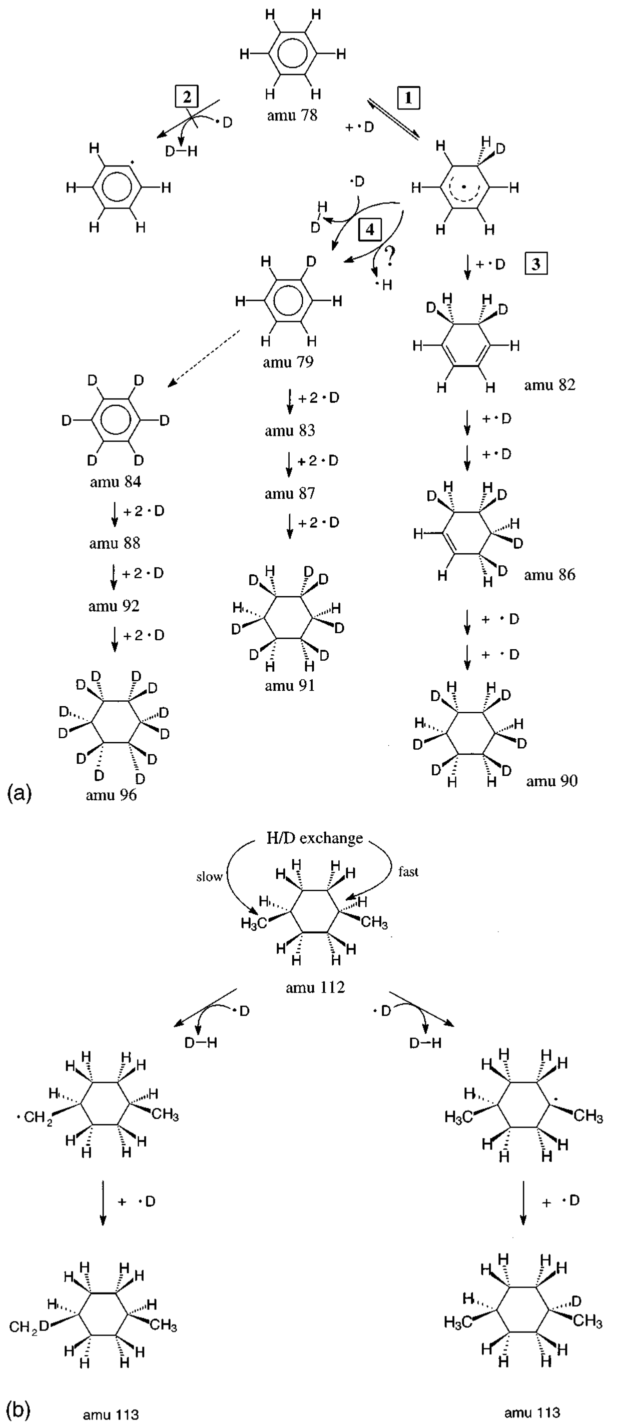

FIG. 10. Detailed map of reaction sequences identified upon reactions of thermal D atoms with adsorbed benzene (a) and DMCH (b).

$$\frac{-dc_t}{dt}=c_t{}^*\sigma^*\Phi$$

with $c_t$ as concentration of the target molecules, $\sigma$ as cross section, and $\Phi$ as flux of D atoms.

A logarithmic plot of the decrease of the relative target molecule concentration against atom fluence, as obtained from Fig. 5 and Fig. 9, should yield a straight line with the cross section as slope. Due to the above mentioned loss of particles raw data were used to get these numbers. This procedure implies that particles which were lost had reacted and are accounted for in the calculated cross section. The D reaction cross section obtained in this way are 8 Å$^2$ for benzene and 1.7 Å$^2$ for DMCH. The H/benzene cross section was determined at 4 Å$^2$, but one has to keep in mind that in the H/benzene reactions the H/D exchange reaction is not included. These numbers are in the range deduced by Bent *et al.* from his experiments on interaction of H with hydrocarbons adsorbed at Cu(111)[6,7] and corroborate the above statement that the reactions are of the Eley–Rideal type. It has to be observed, however, that the present experiments deal with energy distributed atoms and as the cross sections are expected to depend on the atom kinetic energy the given numbers are averages over the energies determined by the Maxwellian distribution delivered by our 1700 K source.

Ignoring this complication, the progression of amu values in Fig. 5 and Fig. 9 suggest the following characteristics. The bottleneck in the H(D)/benzene reaction is the initiating H(D) addition to the ring. Impact of a further atom with equal probabilities produces either the diene via addition or restores benzene via abstraction. These observations emphasize the strong tendency of the system to keep its aromatic character. If the aromaticity is broken, further addition reactions are fast, in particular those which occur at radical species. It might be of importance here to consider that the activation barrier for H(D) addition to nonaromatic $sp^2$ CH groups, e.g., cyclohexadiene: 6 kJ/mol,[27] cyclohexene: ca. 10 kJ/mol,[27] or ethylene: ca. 9 kJ/mol[28] is considerably lower as compared to 18 kJ/mol for benzene, with the consequence that more atoms from the thermal sources carry enough energy to add to the diene. Abstraction reactions at $sp^3$ CH groups of cyclohexane are less important due to the high activation barrier of ca. 39 kJ/mol.[29] The progression in Fig. 5 can be modeled numerically with sufficient agreement without considering their contributions.

The progression of products from reactions between DMCH and D atoms as shown in Fig. 9 and summarized in Fig. 10(b) suggests that abstraction of H from the ring carbon atoms is much more probable than from the methyl groups, in line with the lower C–H bond energy of secondary $CH_2$ groups in comparison with primary $CH_3$ groups.[24] The preferential H abstraction at secondary $CH_2$ groups was also observed for propane.[30] That abstraction from a methyl group is not necessarily improbable is, however, clear from our *p*-xylol study.[13]

It has to be observed, that even in the present study, as in our previous work on *p*-xylene, radical intermediates are stable at the Pt(111)/C surfaces. It is clear that the special structure of the present substrate is essential for this stability. An ideal graphite monolayer does not offer any sites for bonding of a radical or its dissociation species, only at imperfections this is feasible. This makes it also clear that the present results would have hardly been obtained at a reactive metal surface, as this offers plenty of sites for bonding of decomposition products of radical species.

Finally, we address the observed loss of particles. The same phenomenon has been observed by Bent *et al.*[6,7] There are two possibilities to consider. First the above mentioned imperfections at the graphite monolayer which could act as sinks of radicals. We do not think that this is of relevance in the present study as in that case at bigger atom exposures desorption spectra would exhibit increasing amounts of background species originating from these trapped radicals, which was not observed. Second, because many of the reaction steps depicted in Fig. 10 are extremely exothermic it is possible that dissipation of this energy via a desorption channel is competitive with dissipation into the substrate. This effect would lead to a continuous loss of particles, as observed. One expects that the ability to release excess reaction energy is connected with the adsorption energy of the respective species. From the small adsorption energy of the present hydrocarbon molecules at the graphite monolayers this mechanism is feasible to operate.

## V. SUMMARY AND CONCLUSIONS

The interaction of thermal D atoms with physisorbed benzene and (1,4)-dimethyl-cyclohexane proceed via the Eley–Rideal type reactions D addition and H abstraction. The initial step in D/benzene interaction is D addition to a $sp^2$ CH center. The radical intermediate exhibit stability and is either transferred back to singly deuterated benzene $C_6H_5D$ via H abstraction or to cyclohexadiene-$d_2$ $C_6H_6D_2$ via addition of a second D atom. Repetitive application of these reactions then leads to multiply deuterated cyclohexane. D atoms impinging at physisorbed dimethylcyclohexane induce overall H/D exchange at the ring C atoms via sequential H-abstraction/D-addition reactions. H/D exchange at the methyl groups is also observed, but less probable.

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