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Reactivity of Unsaturated Linear C_6 Hydrocarbons on Pd(111) and H(D)/Pd(111)

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The adsorption and reactivity of 1-hexene, 1,5-hexadiene, 1,3-hexadiene, and 1,3,5-hexatriene on clean Pd(111) and hydrogen (deuterium)-saturated/Pd(111) were investigated using temperature-programmed reaction spectroscopy. The low-temperature adsorption configuration for the linear C_6 hydrocarbons is proposed to be a weakly π-bonded species. The adsorbed molecules first desorb molecularly with a fraction converting to a more tightly bonded half-hydrogenated state, which either β-hydride eliminates to release the alkene or dehydrogenates completely to adsorbed carbon and hydrogen. Dehydrocyclization to benzene is observed on this surface, whereas it does not occur on Pd(100). Cyclization of 1,3,5-hexatriene to benzene occurs at temperatures as low as 333 K on Pd(111). Although hydrogenation of 1,3-hexadiene adsorbed on clean Pd(111) and of 1,3-hexadiene and 1,5-hexadiene adsorbed on H/Pd(111) to hexene was observed, and hexatriene was hydrogenated to hexadiene and hexene, hydrogenation of the alkenes to hexane was not observed for any of the unsaturated species. H–D exchange into all the adsorbed alkenes was observed. The exchange reaction is proposed to occur through the reversible C–H bond formation in a half-hydrogenated intermediate. © 1998 Academic Press

I. INTRODUCTION

Hydrogenation and reforming of relatively low molecular weight unsaturated hydrocarbons on metal catalysts are important processes in the chemical industry. The hydrogenation of polyenes to alkenes and cyclization of linear hydrocarbons to aromatics leads to starting compounds for largescale industrial processes. Modern investigational techniques assist the understanding of the molecular processes underlying these conversions by revealing the microscopic structure of the catalytic surface and permit identification of the reaction intermediates that are formed and interact with the surface in forming products (1). Studies on single-crystal surfaces under ultrahigh vacuum (UHV) are thus useful in lending insight into the complex mechanisms involved on catalytic surfaces.

Few studies have been reported on the hydrogenation of alkenes other than ethylene on transition metal surfaces under UHV conditions. Hydrogenation of ethylene of ethane has been shown to occur efficiently on Pt(111) (2) and Rh(111) (3). However, the production of ethane is not observed for ethylene adsorption on H-covered Ni(100) (4), Fe(100) (5), Pd(100) (6), or W(100) (7), even though coadsorption of CO weakens Fe–H bonds on Fe(100) (5, 8) and induces the formation of ethane. A recent study of higher alkenes on a H-covered Pd(100) surface (6) showed selective hydrogenation of allene, 1,3-butadiene, 1,5-hexadiene, and 1,3,5-hexatriene to the corresponding alkene but no further. Hydrogenation has also been observed for propene on Ir(111) and Ir(110)-(l × 2) (9) and for 1,3-butadiene on Pt(100), Pt(110) and Pt(111) (10, 11).

The mechanism for hydrogenation catalyzed by transition-metal surfaces was first proposed by Horiuti and Polanyi in 1934 (12). The process consist of four steps: (1) dissociation of H_2 to form metal-H bonds, (2) coordination of the alkene to the metal, (3) the migratory insertion reaction between H and the coordinated alkene to form a metal-bound alkyl, and (4) and reductive elimination reaction between H and alkyl to produce the alkane. The observation of H–D exchange reactions of adsorbed alkanes on metal surfaces (13, 14) and alkene isomerization by double-bond migration (15, 16) support this mechanism.

In hydrocarbons, C–H bonds are both broken as well as formed in reactions on transition metal surfaces. Several studies have been performed on the adsorption and decomposition of propene, butene, and 1,3-butadiene on Pt(111) (17–21). The alkenes and the polyene (butadiene) adsorb in a di-σ configuration at low temperatures (95–200 K). The alkenes undergo dehydrogenation, leading to the formation of the corresponding alkylidyne at ∼300 K. Upon further heating, the alkylidyne dehydrogenates and fragments at ∼400 K, eventually forming adsorbed carbon and hydrogen. On the clean Pd(100) surface, propene, 1-butene and 1,3-butadiene also dehydrogenate to adsorbed carbon and hydrogen (22). However, formation of the alkylidyne is not observed on Pd(100); the formation of this intermediate appears to be structure sensitive.

Dehydrogenation of ethylene has also been extensively studied and has been summarized by Sheppard (17). It has been inferred using vibrational spectroscopies that

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adsorption of ethylene occurs on many metal surfaces at low temperature (80–200 K) in a di-σ bonded configuration, π-bonded configuration or a mixture of both. The di-σ bonded complex has been determined to exist on the clean metal surfaces of Ni(111) (23, 24), Ni(100) (25–27), Ni(110) (28–30), Ru(001) (31), Pt(111) (32, 33), Pt(100) (34), and Fe(110) (35). The π-bonded species prevails on the clean metal surfaces of Cu(100) (36), Pd(111) (37, 38), Pd(100) (39), and Pd(110) (40). Few clean metal surfaces seem to prefer the π-complexes, but the few surfaces that have been studied with appreciable amounts of preadsorbed carbon or oxygen show that adsorbed ethylene reverts to π-bonding in the presence of these adsorbates (32, 34, 41–47). Clean metal surfaces that exhibit coexistence of π- and di-σ-bonded ethylene are Pd(100) (42), Ru(001) (48), and Fe(111) (47).

Upon heating the adsorbed ethylene to room temperature, ethylidyne forms on the close packed fcc (111) planes studied (31, 32, 34, 37, 38, 48–53). On surfaces without threefold symmetry, other intermediates form. Adsorbed acetylene appears on Pt(100) (34); vinylidene appears on Pt(100) (34) and Ru(001) with preadsorbed oxygen (48); vinyl is suggested to form on Ni(100) (26, 27). Further heating of these species causes fragmentation and eventual dehydrogenation to adsorbed carbon and hydrogen.

Reactions of alkenes and polyenes not only involve C–H bond breaking and formation but also C–C bond coupling. Adsorbed ethyne tricylizes to benzene on Pd(111) below 250 K, following an associative reaction mechanism (54–57, 59). Initially, there is coupling of two ethyne molecules leading to the formation of a C_4H_4 metallocycle intermediate (60, 61). Addition of the third C_2H_2 leads to benzene formation in a tilted configuration which desorbs at 250 K from its tilted configuration and 510 K from a flat lying species (62, 63). The tricyclization reaction is efficient on palladium and very sensitive to the surface structure. Production of significant amounts of benzene was observed only on the (111) surface of palladium (58). It has been suggested that tricyclization of ethyne is efficient on Pd(111) because the adsorbed molecules interact strongly with the surface so that they are still adsorbed at the temperatures necessary to form the essential intermediates, but that the intermediates are not too strongly hybridized so that cyclization is favored over fragmentation (58).

Cyclization reactions of higher hydrocarbons have also been observed on platinum containing surfaces (64–68). Dehydrocyclization of 1-hexene and 1,3,5-hexatriene were shown to occur on a $Cu_3Pt(111)$ surface leading to the formation of benzene (64–66). Hexane was observed to form both benzene and methylcyclopentane on platinum catalysts (67). Heptane was shown to dehydrocyclize and form toluene on several platinum single-crystal surfaces (68).

In this study, the reactivity of 1-hexene, 1,5-hexadiene, 1,3-hexadiene, and 1,3,5-hexatriene on Pd(111) and H(D)/Pd(111) surfaces were investigated under UHV conditions using temperature programmed reaction spectroscopy (TPRS). The adsorbed molecules desorbed molecularly with a fraction dehydrogenating to adsorbed carbon and hydrogen. Hydrogenation to hexane was not observed for any of the adsorbed molecules. Selective hydrogenation to hexene was observed for 1,3-hexadiene adsorbed on clean Pd(111) and for 1,3-hexadiene and 1,5-hexadiene adsorbed on H/Pd(111). Hexatriene adsorbed on the H/Pd(111) surface produced both hexadiene and hexene. The structure-sensitive dehydrocyclization pathway leading to the formation of benzene was also observed.

II. EXPERIMENTAL

The experiments were conducted in a UHV chamber that contained a quadrupole mass spectrometer, argon bombardment gun, and a retarding field analyzer used for both low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES). A chromel–alumel thermocouple spot-welded at the edge of the crystal was used to monitor temperature. The crystal was cooled by conduction through tantalum wires in thermal contact with a liquid-nitrogen-cooled copper block. These same wire supports were used to heat the crystal resistively.

The surface was initially cleaned by a series of Ar^+ ion bombardments at room temperature followed by annealing to 1000 K. Oxygen treatments at 1000 K followed by annealing to 1100 K were performed as necessary to remove the excess carbon. Cleanliness was monitored by titrations of carbon residue with oxygen; the surface was considered clean when no CO or CO_2 desorption was observed. The Pd(111) surface was verified to be well ordered using LEED.

The TPRS measurements were obtained with a UTI mass spectrometer interfaced to a desktop computer with the capability of multiplexing up to 150 masses. Usually 10 masses were monitored during each experiment. The mass spectrometer signal for each product formed during heating is directly proportional to the desorption rate. An approximately linear heating rate of 12 K/s was used for all the spectra presented here. In all cases the mass spectra were corrected for cracking, and the products were identified utilizing their cracking pattern which were determined in the UHV chamber used for these experiments. All TPRS spectra presented in this chapter are displayed using the same mass spectrometer signal scaling.

The 1-hexene (99%), 1,5-hexadiene (98%), 1,3-hexadiene (99%), and 1,3,5-hexatriene (97%) used were obtained from Aldrich Chemical Company. All four of these samples were put through freeze–pump–thaw cycles to remove N_2, O_2, CO_2, and H_2O. The gases were introduced into the chamber through a capillary array doser with the surface directly in front of the doser. To saturate the surface, but minimize the multilayer state, 1-hexene was adsorbed at 150 K, 1,5-hexadiene at 130 K, and 1,3-hexadiene and 1,3,5-hexatriene at 160 K. The multilayer states of 1-hexene, 1,5-hexadiene, 1,3-hexadiene, and 1,3,5-hexatriene desorbed at approximately 125, 130, 150, and 160 K, respectively. Hydrogen (or deuterium) was adsorbed by dosing H_2 (D_2) through a stainless steel doser, while the crystal cooled from ~300 to ~130 K. This procedure minimized the amount of background hydrogen adsorbed when studying the reactions of adsorbed deuterium and was adopted as standard procedure.

III. RESULTS

A. Reactivity of Unsaturated Linear C_6 Hydrocarbons on Clean Pd(111)

Following an exposure of 4.5 Langmuir at 150 K, hexene desorbed molecularly from well-defined states at 188 K and 254 K (Fig. 1). Self-hydrogenation to hexane was not observed. At higher temperatures, a fraction of the adsorbed hexene (0.10 ML) dehydrogenated to form adsorbed carbon and hydrogen. For comparison, TPD spectra obtained by Gdowski *et al.* (69) for H from Pd(111) showed a single desorption peak which shifted from 310 to 370 K from low to saturation coverages of H, which we separately confirmed. Therefore, we conclude that hydrogen is desorption-limited or reaction-limited depending on whether its desorption peak lies below or above 370 K. The hydrogen produced from hexene dehydrogenation evolved at 405 K is reaction-limited with a shoulder on the low-temperature side that is the result of a desorption-limited step. This feature contains 0.52 ML of hydrogen atoms and ~42% of the total desorbing hydrogen. Further heating leads to extensive dehydrogenation in a broad feature above 460 K consisting of 0.71 ML of hydrogen; a total of 0.10 ML of hexene was dehydrogenated.

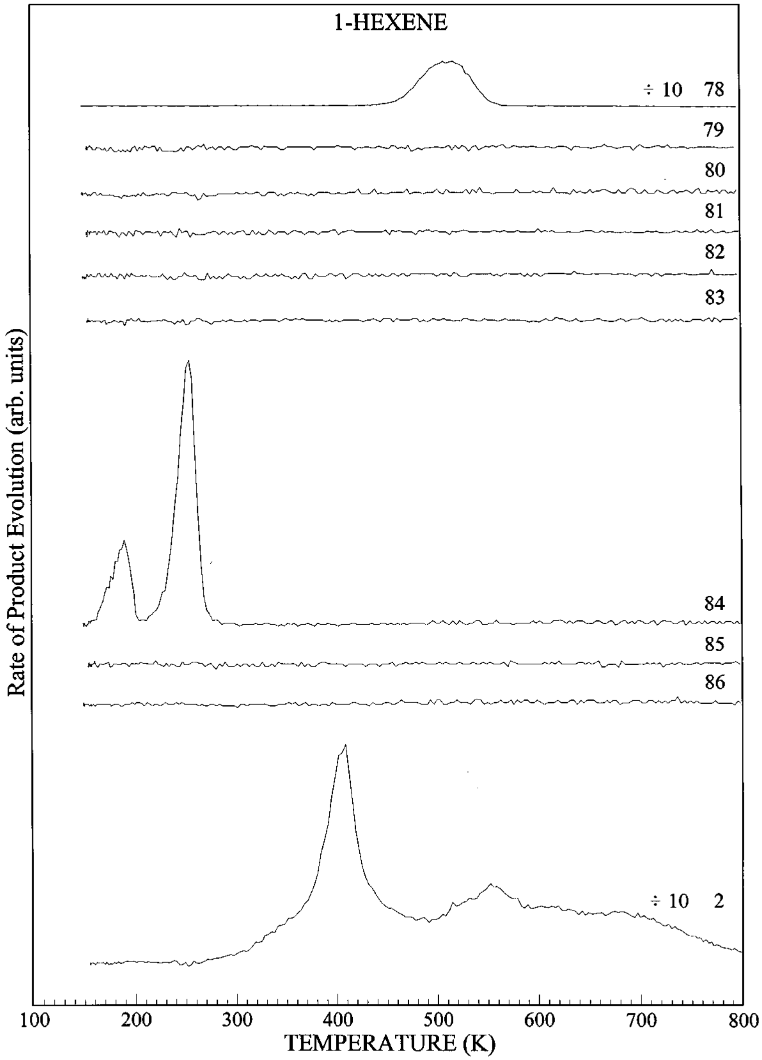

FIG. 1. TPR spectra of 1-hexene adsorbed at 150 K on Pd(111).

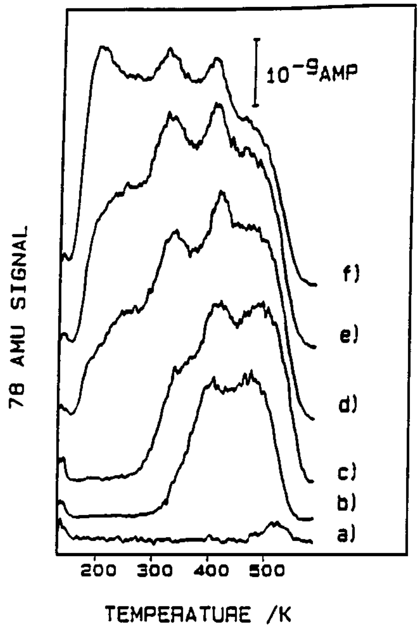

FIG. 2. Temperature programmed desorption of C_6H_6 chemisorbed on Pd(111) at 150 K as a function of C_6H_6 initial coverage. (a)–(f) refer to exposures of 0.25, 0.50, 0.75, 1.00, 1.40, and 10.00 Langmuirs, respectively (59). (Reproduced by permission.)

Benzene formed and desorbed at 513 K. For comparison, the complex TPD spectra obtained by Patterson and Lambert (59) for various exposures of benzene are shown in Fig. 2. As shown in the spectra, at low coverages benzene desorbs in a single state near 520 K. As the coverage increases, a number of peaks appear, with a reduction in the temperature for the onset of benzene desorption to below 200 K at saturation. In the experiments conducted in this study, the benzene formed by cyclization of 1-hexene evolved into the gas phase through a desorption-limited process.

Following an exposure of 2.3 Langmuir of 1,5-hexadiene at 130 K on the *clean* Pd(111) surface, hexadiene desorbed molecularly at 161 K (Fig. 3). Self-hydrogenation to hexene or hexane was not observed. A fraction of the adsorbed hexadiene dehydrogenated to adsorbed carbon and hydrogen. The hydrogen formed via the reaction-limited process at 405 K comprised 0.28 ML (25% of the total desorbing hydrogen); the remainder desorbed in a broad feature above ∼435 K (0.84 ML). Benzene desorption peaked at 500 K, and the amount was 1.8 times that generated by 1-hexene.

After an exposure of 2.3 Langmuir at 160 K and heating, 1,3-hexadiene desorbed molecularly at 176 K and 281 K (Fig. 4). In contrast to 1,5-hexadiene, a portion of the adsorbed 1,3-hexadiene self-hydrogenated, yielding hexene at 264 K; hexane was not observed. Dehydrogenation steps were observed at 384 K, yielding 0.26 ML of hydrogen (19% of the total desorbing hydrogen), and above 420 K (1.11 ML). A portion of the adsorbed hexadiene also cyclized to benzene, which desorbed in a sharp feature at 358 K followed by a broad peak at 424 K. The amount of benzene produced was approximately 3.9 times of that generated by 1-hexene.

Hexatriene showed similar interesting reactions. Molecular desorption of the adsorbed 1,3,5-hexatriene, dosed at an exposure of 2.3 Langmuir at 160 K, produced a sharp desorption feature at 177 K (Fig. 5). Hydrogenation to hexadiene, hexene, or hexane was not observed. The dehydrogenation processes were similar to those observed for 1,3-hexadiene. Hydrogen was produced in a sharp feature at 381 K, consisting of 0.17 ML (∼17% of the total desorbing hydrogen), overlapped by a broad feature above 410 K (0.83 ML). Cyclization of the adsorbed hexatriene to benzene also occurred, yielding two small overlapping desorption features at 333 and 358 K and a larger feature at 442 K. The amount of benzene produced was 2.8 times of that generated by 1-hexene. A summary of the relative amounts of the linear C_6 products desorbing from the *clean* surface is listed in Table 1. The amounts of benzene generated relative to that formed by 1-hexene on the *clean* surfaces are listed in Table 2.

B. Reactivity of Unsaturated Linear C_6 Hydrocarbons on Hydrogen-Saturated Pd(111)

As shown elsewhere (70), given a similar hydrocarbon exposure as the *clean* surface, less hydrocarbon adsorbs on the hydrogen-saturated surface. In the experiments on the hydrogen-saturated surface exposures similar to that used on the *clean* surface were utilized, and therefore, the

TABLE 1

Relative Amounts of the Linear C_6 Products Desorbing from the *Clean* and Hydrogen-Covered Pd(111) Surfaces

Products	1-Hexene		1,5-Hexadiene		1,3-Hexadiene		1,3,5-Hexatriene	
Reactants (exposure)	*Clean*	H	*Clean*	H	*Clean*	H	*Clean*	H
1-Hexene (4.5 Langmuir)	1.0	1.60	0.0	0.0	0.0	0.0	0.0	0.0
1,5-Hexadiene (2.3 Langmuir)	0.0	0.02	1.0	1.0	0.0	0.0	0.0	0.0
1,3-Hexadiene (2.3 Langmuir)	0.3	1.50	0.0	0.0	1.0	0.70	0.0	0.0
1,3,5-Hexatriene (2.3 Langmuir)	0.0	0.29	0.0	0.0	0.0	0.32	1.0	0.50

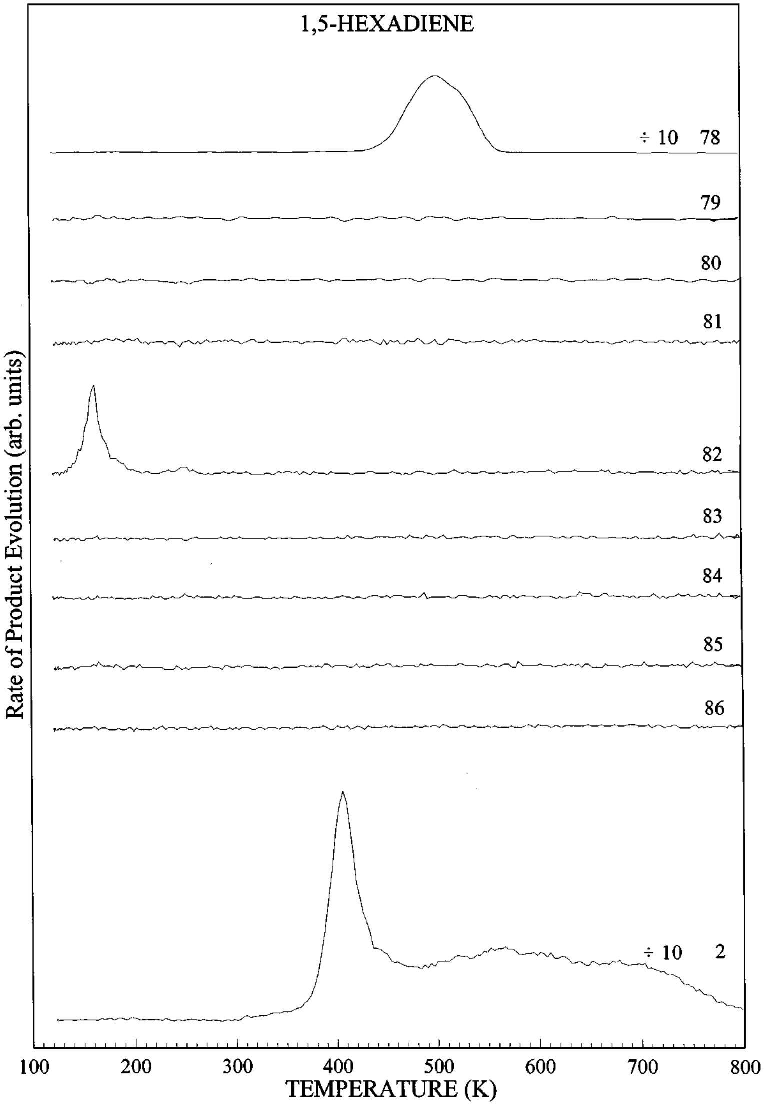

FIG. 3. TPR spectra of 1,5-hexadiene adsorbed at 130 K on Pd(111).

amount of the adsorbed hydrocarbon was less. Following adsorption, utilizing an exposure of 4.5 Langmuir on the H-presaturated surface [H/Pd(111)] at 150 K and heating, hexene desorbed molecularly in a sharp feature at 200 K with a small shoulder at ~232 K (Fig. 6). The amount of hexene *desorbing*, however, was 1.6 times that which desorbed following exposure on the *clean* surface. The preadsorbed hydrogen completely inhibited the formation of benzene. Hydrogenation to hexane was not observed, but approximately 0.06 ML of the adsorbed hexene did dehydrogenate to adsorbed carbon and hydrogen—a lower fraction than on the *clean* surface. The H_2 originating from the preadsorbed hydrogen and dehydrogenation is apparent in Fig. 6 as a peak at 336 K and shoulder at 392 K, respectively. Because hydrogen desorption from a H-saturated surface exhibits only a single peak (69), the two hydrogen states observed between 330 and 400 K clearly cannot both be caused by desorption-limited processes. The higher temperature peak must be caused by a reaction-limited step. The separation of these features gives further support to assigning the hydrogen evolution from the *clean* surface to reaction-limited processes. These overlapping features

TABLE 2

Relative Amounts of Benzene Formed from the Linear C_6 Molecules on the *Clean* and Hydrogen-Covered Pd(111) Surfaces

	Relative amounts of C_6H_6 formed	
Adsorbed molecule	Pd(111)	H/Pd(111)
1-Hexene	1.0	0.0
1,5-Hexadiene	1.8	0.0
1,3-Hexadiene	3.9	0.2
1,3,5-Hexatriene	2.8	2.2

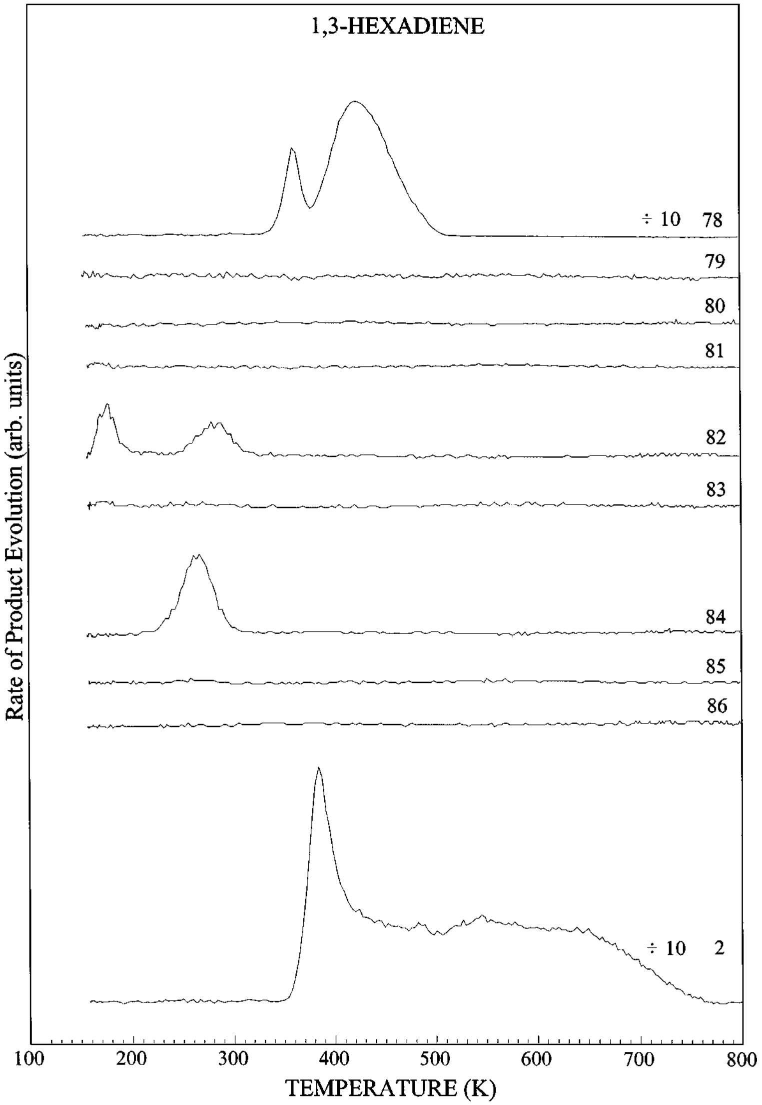

FIG. 4. TPR spectra of 1,3-hexadiene adsorbed at 160 K on Pd(111).

between 300 and 400 K consisted of 1.28 ML of hydrogen (59 and 12% of the total desorbing hydrogen, respectively). A broad reaction-limited feature caused by dehydrogenation appeared above ~460 K (0.53 ML).

1,5-hexadiene, initially adsorbed at an exposure of 2.3 Langmuir at 130 K on the H/Pd(111) surface desorbed molecularly at 184 K (Fig. 7). The amount of hexadiene desorbing was approximately equal to that desorbing from the clean surface. Only a very small amount of hydrogenation to hexene was observed at 189 K; no hexane was produced. As for hexene, the preadsorbed hydrogen and hydrogen from dehydrogenation produced two overlapping features at 329 and 387 K, which consisted of 1.12 ML (60 and 10% of the total desorbing hydrogen, respectively). A broad reaction-limited feature was also produced at 552 K (0.48 ML). Benzene formation was completely suppressed by the adsorbed hydrogen.

Adsorbed 1,3-hexadiene, dosed using an exposure of 2.3 Langmuir at 160 K, desorbed molecularly from H/Pd(111) at 186 K with a small shoulder at 216 K (Fig. 8). The amount of hexadiene desorbing was 0.7 times of that which desorbed from the *clean* surface. However, appreciable hydrogenation to hexene was observed at 221 K. The amount of hexene generated was 4.9 times of that produced on the *clean* surface. The ease of hydrogenation to hexene contrasts sharply with 1,5-hexadiene. Further hydrogenation to hexane did not occur. Hydrogen evolution produced two overlapping peaks at 321 and 363 K, which consisted of 0.96 and 0.17 ML (55 and 10% of the desorbing hydrogen), respectively. Dehydrogenation also produced a broad feature above ~425 K (0.61 ML). Benzene was formed and desorbed at 502 K. The amount of benzene produced was approximately 0.2 and 0.05 times that generated by 1-hexene and 1,3-hexadiene on the *clean* surface, respectively.

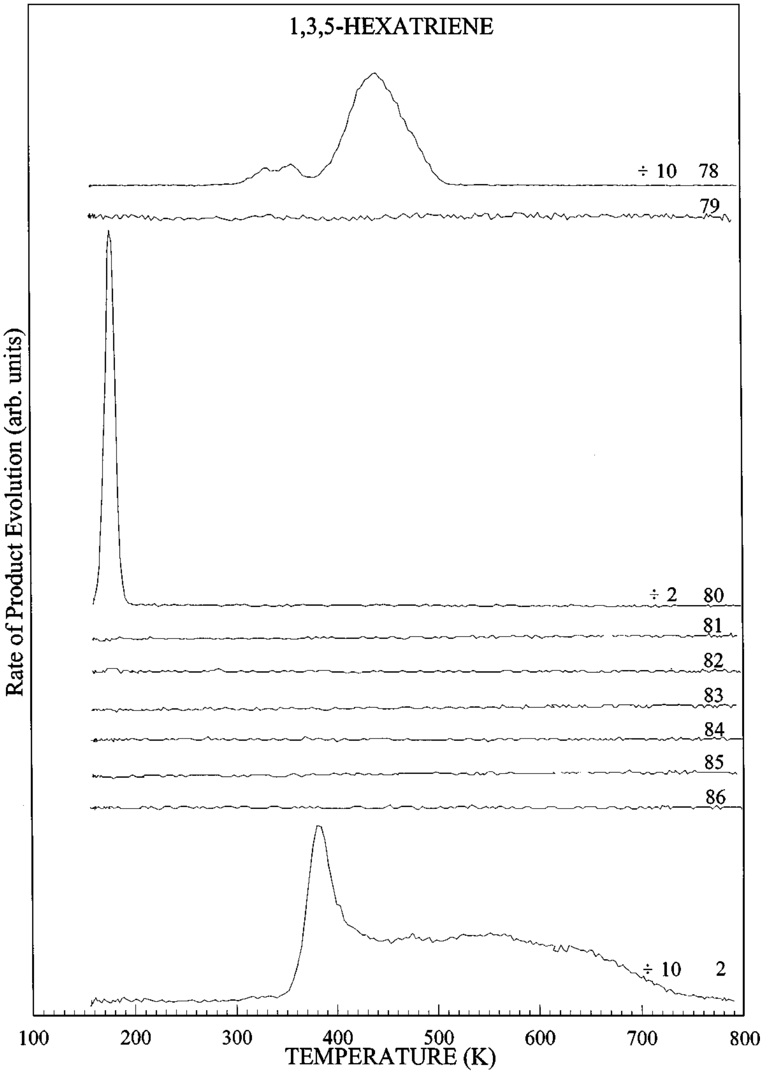

FIG. 5. TPR spectra of 1,3,5-hexatriene adsorbed at 160 K on Pd(111).

The reactions of 1,3,5-hexatriene on H/Pd(111) are the most complex of all the hydrocarbons studied. Following adsorption at 160 K, utilizing an exposure of 2.3 Langmuir and heating, hexatriene desorbed molecularly at 179 K (Fig. 9). The amount of hexatriene that desorbed was half of that which desorbed from the *clean* surface. Hydrogenation to hexadiene produced a feature at 189 K with a small shoulder at 160 K. Clearly hydrogenation is quite facile because it occurs at such a low temperature. Hexene was also observed at 239 K, but no hexane was produced. A summary of the relative amounts of the linear C_6 products desorbing from the hydrogen-covered surface is given in Table 1. Like the previous hydrocarbons studied, a fraction of the adsorbed hexatriene also dehydrogenated to adsorbed carbon and hydrogen, producing a reaction-limited H_2 feature at 370 K with a desorption-limited shoulder on the low temperature side; these features consist of 1.34 ML H. Because of the shapes of the two peaks, the exact amount of hydrogen in each feature is difficult to determine. A broad feature is also observed above ~425 K (0.61 ML). Benzene formation is only slightly suppressed compared to the *clean* surface and desorbs at 477 K. The amount of benzene produced was 2.2 and 0.8 times of that generated by 1-hexene and 1,3,5-hexatriene on the *clean* surface, respectively. The amounts of benzene generated relative to that formed by 1-hexene on the *clean* surface are listed in Table 2.

C. Reactivity of Unsaturated Linear C_6 Hydrocarbons on Deuterium-Saturated Pd(111)

To further clarify the details of the hydrogenation and cyclization reactions of the C_6 hydrocarbons on Pd(111), the reactions were studied on the deuterium-saturated surface. TPRS spectra for 1-hexene adsorbed on D/Pd(111)

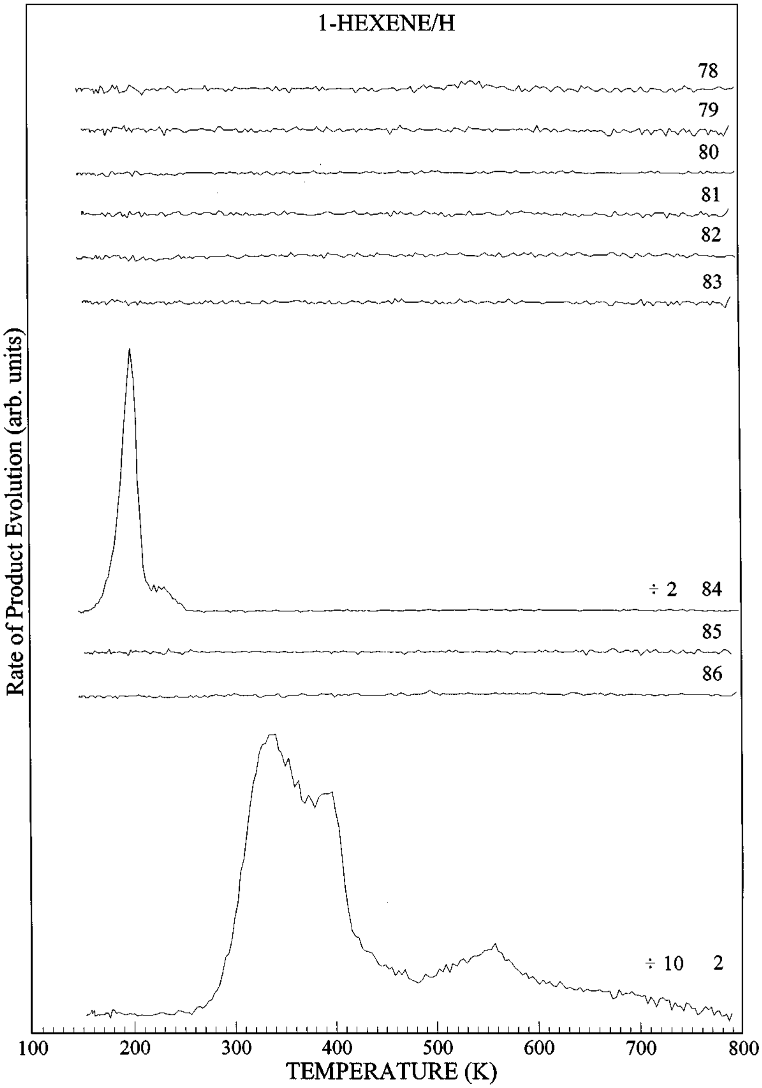

FIG. 6. TPR spectra of 1-hexene adsorbed at 150 K on a hydrogen presaturated Pd(111) surface.

at a surface temperature of 150 K are shown in Fig. 10. All mass spectra have been corrected for cracking. Hexene desorbed molecularly yielding a desorption feature at 200 K. In agreement with the studies on the H/Pd(111) surface, deuteration products were not observed. In addition, multiple H–D exchange reactions for up to three hydrogen atoms and possibly four occurred *below 237 K*. A fraction of the adsorbed hexene and of the exchange products dehydrogenated, yielding hydrogen and deuterium as well as adsorbed carbon, near 400 K. Deuterium evolved in a desorption-limited state at 331 K and a reaction-limited state at 396 K. Evolution of deuterium at higher temperature apparently arises from C–D bond cleavage of deuterium exchanged into the adsorbed hydrocarbon. Adsorbed hydrogen originating from exchange reactions and dehydrogenation processes produced features similar to the desorbing D_2. Scrambling of adsorbed hydrogen and deuterium lead to the desorption of HD, mimicking the desorption features of H_2 and D_2.

Similar to the behavior noted on the hydrogen-saturated surface, 1,5-hexadiene, when adsorbed at 130 K and heated, desorbed molecularly at 184 K (data not shown). A small amount of deuteration to hexene-d_2, expected on the basis of the reactions observed on the hydrogen covered surface, desorbed at 190 K. Neither deuteration of hexane-d_4 nor deuterium exchange were observed. A fraction of the adsorbed 1,5-hexadiene and exchange products dehydrogenated forming adsorbed carbon and H_2, D_2, and HD desorption features at 328, 394, and 563 K.

As on the H-saturated surface, the reactions of 1,3- hexadiene (Fig. 11) differed appreciably from 1,5-hexadiene on D/Pd(111). Extensive deuteration to hexene-d_2 (mass 86) was the dominant reaction, peaking at 232 K. The hexene produced exchanged up to four hydrogen atoms ($C_6H_6D_6$)

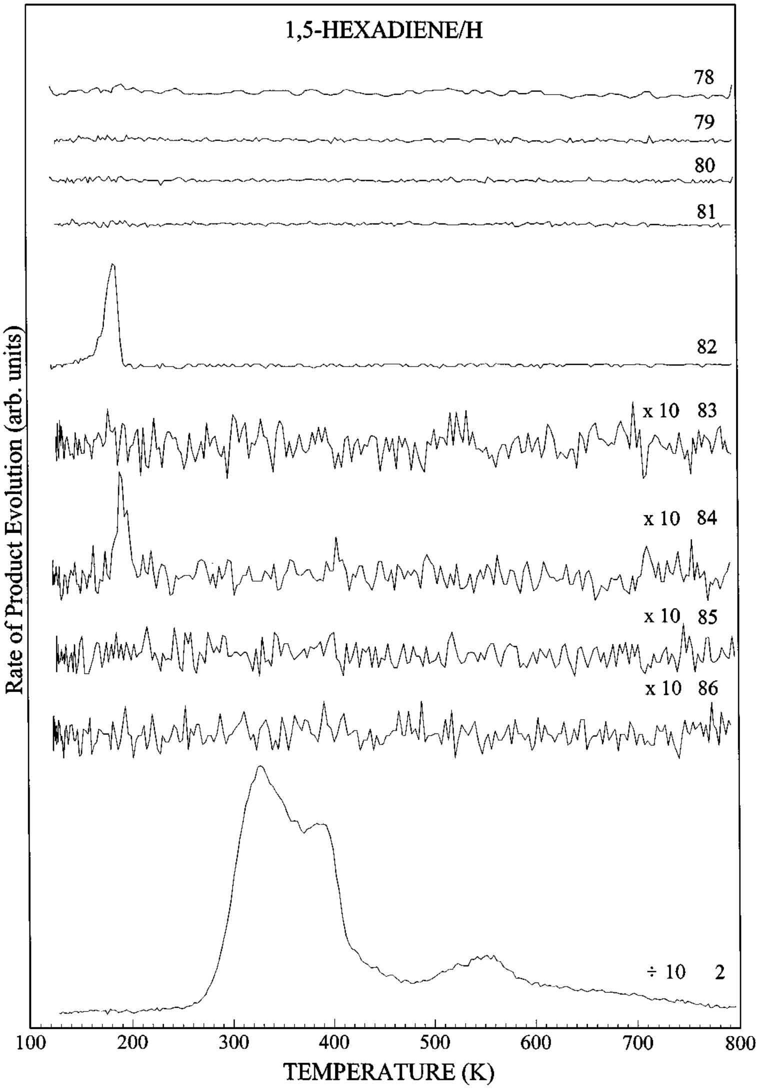

FIG. 7. TPR spectra of 1,5-hexadiene adsorbed at 130 K on a hydrogen presaturated Pd(111) surface.

below 266 K. Products with mass greater than 90 were not observed. Further deuteration to hexane-d_4 is not expected. Hydrogen which was available from dehydrogenation and exchange pathways hydrogenated the hexadiene to hexene-h_2 (mass 84). Hydrogenation/deuteration also occurred, leading to the evolution of hexene-h_1d_1 (mass 85). Hexene-h_2 and -h_1d_1 exchanged with adsorbed deuterium, but as observed from the hexene-d_2 produced in this experiment and the 1-hexene/D experiments previously mentioned, exchange only occurs to a limited extent. Figure 12 shows the reaction pathways followed by 1,3-hexadiene on the deuterium-covered surface. The preadsorbed deuterium and deuterium from dehydrogenation produced overlapping features at 354 and 405 K. A reaction-limited route to deuterium also appeared at 563 K. H_2 and HD originating from exchange and dehydrogenation processes produced features similar to the desorbing deuterium.

Benzene was produced from 1,3-hexadiene on the deuterated surface at 540 K, incorporating up to six deuterium atoms (data not shown). The mass spectrum showed a symmetrical distribution of exchanged products for benzene, with $C_6H_3D_3$ being dominant (Fig. 13). The isotope distribution formed from the isotope exchange at low coverages of benzene coadsorbed with deuterium on the D-saturated surface is shown for comparison in Fig. 13. The two distributions are entirely different; clearly the majority of H–D exchange found in the benzene formed from hexadiene occurs prior to benzene formation.

The products arising from the reaction of hexatriene (C_6H_8) on the deuterated surface also showed a complex combination of deuteration (hydrogenation), exchange, and dehydrocyclization. Molecular desorption of hexatriene (mass 80) occurred at 184 K (Fig. 14). The mass 84 feature desorbing at 196 K corresponds precisely in

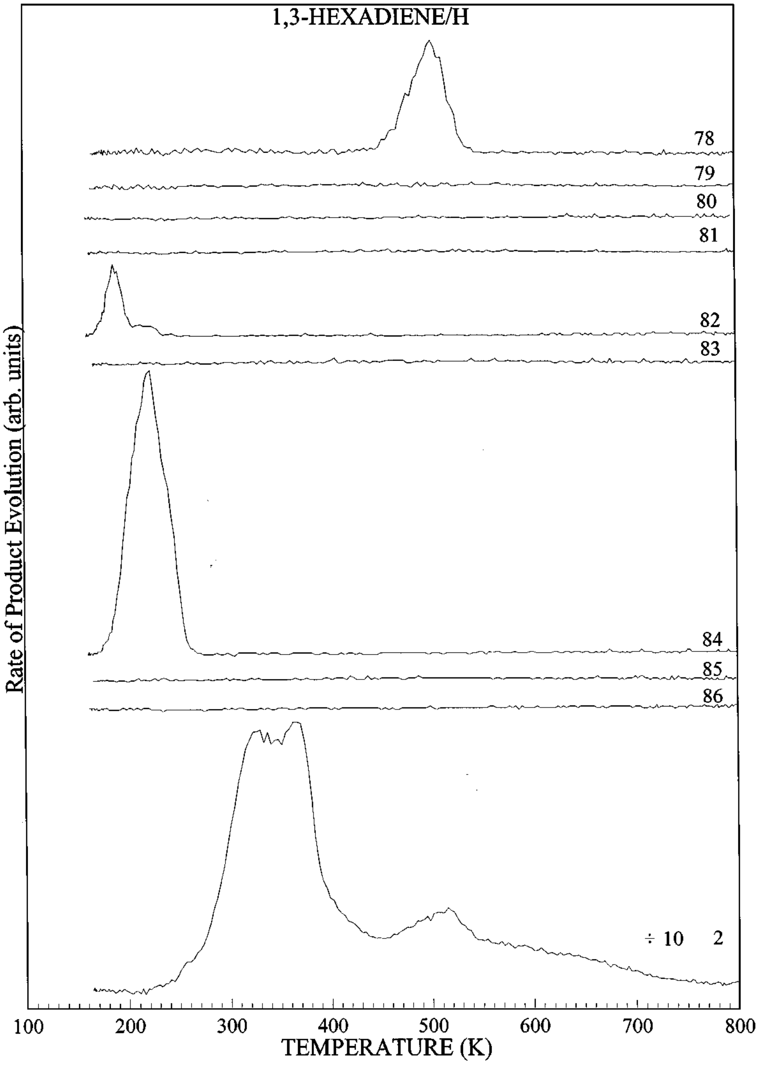

FIG. 8. TPR spectra of 1,3-hexadiene adsorbed at 160 K on a hydrogen presaturated Pd(111) surface.

temperature to the evolution of hexadiene produced by hydrogenation of 1,3,5-hexatriene on the H-saturated surface and is, therefore, attributed to deuteration of the hexatriene to $C_6H_8D_2$. Further exchange of this deuteration product was not observed. The mass 88 feature observed at 248 K is attributed to deuteration to hexene ($C_6H_8D_4$); the evolution temperature corresponds closely to that for hydrogenation of hexatriene to 1-hexene. Further, H–D exchange into $C_6H_8D_4$ up to $C_6H_6D_6$ was observed, leading to the evolution of products of mass 89 and 90. No products were observed above mass 90. Hydrogen which is made available by dehydrogenation and exchange pathways reacted with hexatriene to form hexadiene-h_2 (mass 82).

Hydrogenation/deuteration lead to the evolution of hexadiene-h_1d_1 (mass 83). The feature of mass 86 can originate either from hydrogenation of $C_6H_8D_2$ or deuteration of C_6H_{10} to $C_6H_{10}D_2$. Deuteration of $C_6H_9D_1$ and an H–D exchange of one of the hydrogen atoms in $C_6H_{10}D_2$ can generate $C_6H_9D_3$ (mass 87). Further exchange of $C_6H_9D_3$ can lead to contributions of higher masses. It is important to note that exchange occurs only to a limited extent, as illustrated by the exchange into 1-hexene adsorbed on the deuterium covered surface. Figure 15 shows the general pathway followed by 1,3,5-hexatriene on the deuterium-covered surface.

Like 1,3-hexadiene, the benzene produced from hexatriene showed incorporation of up to six deuterium atoms, the products being symmetrically disposed about $C_6H_3D_3$, the dominant product (Fig. 13). A fraction of the adsorbed hexatriene and exchange products dehydrogenated to form adsorbed carbon, hydrogen, and deuterium. The preadsorbed deuterium and deuterium from dehydrogenation produced a feature at 411 K with a shoulder on the low temperature side. A broad feature above 450 K was also

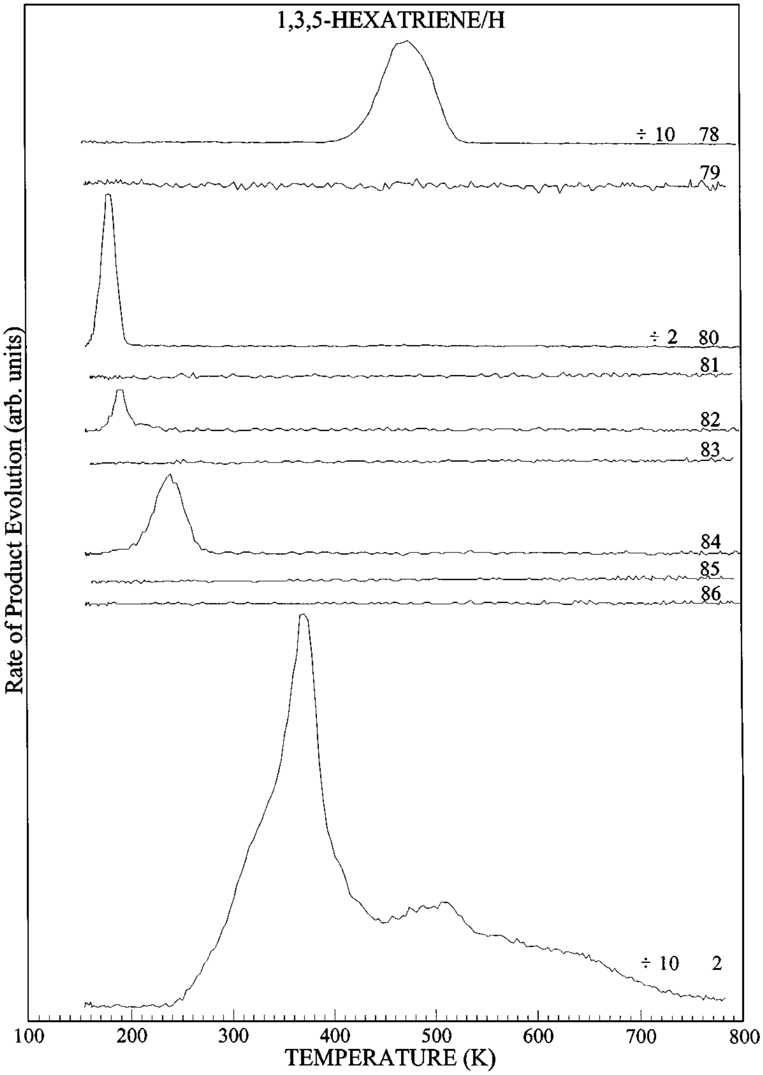

FIG. 9. TPR spectra of 1,3,5-hexatriene adsorbed at 160 K on a hydrogen presaturated Pd(111) surface.

observed. Hydrogen and HD desorbed with features similar to those of deuterium.

IV. DISCUSSION

The results can be summarized as follows. After adsorption onto Pd(111) or H(D)/Pd(111) surfaces, the linear, unsaturated C_6 hydrocarbons exhibit the gamut of reactivity, including molecular desorption, hydrogenation, dehydrogenation, hydrogen exchange, dehydrocyclization to benzene, or complete dehydrogenation. Self-hydrogenation on *clean* Pd(111) occurs only for 1,3-hexadiene, producing hexene. On the *hydrogen-covered* Pd(111) surface, 1,3-hexadiene hydrogenates to 1-hexene, hexatriene hydrogenates to hexadiene and hexene, and there is a very limited amount of hydrogenation of 1,5-hexadiene to hexene. In no case is hydrogenation to hexene observed. As would be expected from site-blocking considerations and/or simple mass arguments, on the hydrogen-covered Pd(111) surface, dehydrogenation is inhibited; correspondingly, dehydrocyclization to benzene from 1-hexene and 1,5-hexadiene is suppressed. However, for the conjugated molecules, 1,3-hexadiene and 1,3,5-hexatriene, which create “clean” surface by the incorporation of substantial amounts of the preadsorbed hydrogen into hydrogenation products, benzene formation *is* observed. H–D exchange between the surface and the alkenes occurs between 150 and 225 K. With the exception of the dehydrocyclization reaction leading to benzene, which is unique to the (111) surface, the pattern of reactivity of the C_6 hydrocarbons on the Pd(111) surface seen in this work corresponds well with the reactions on Pd(100) (6).

Insight into the bonding configuration upon adsorption of the C_6 hydrocarbons may be gained from previous

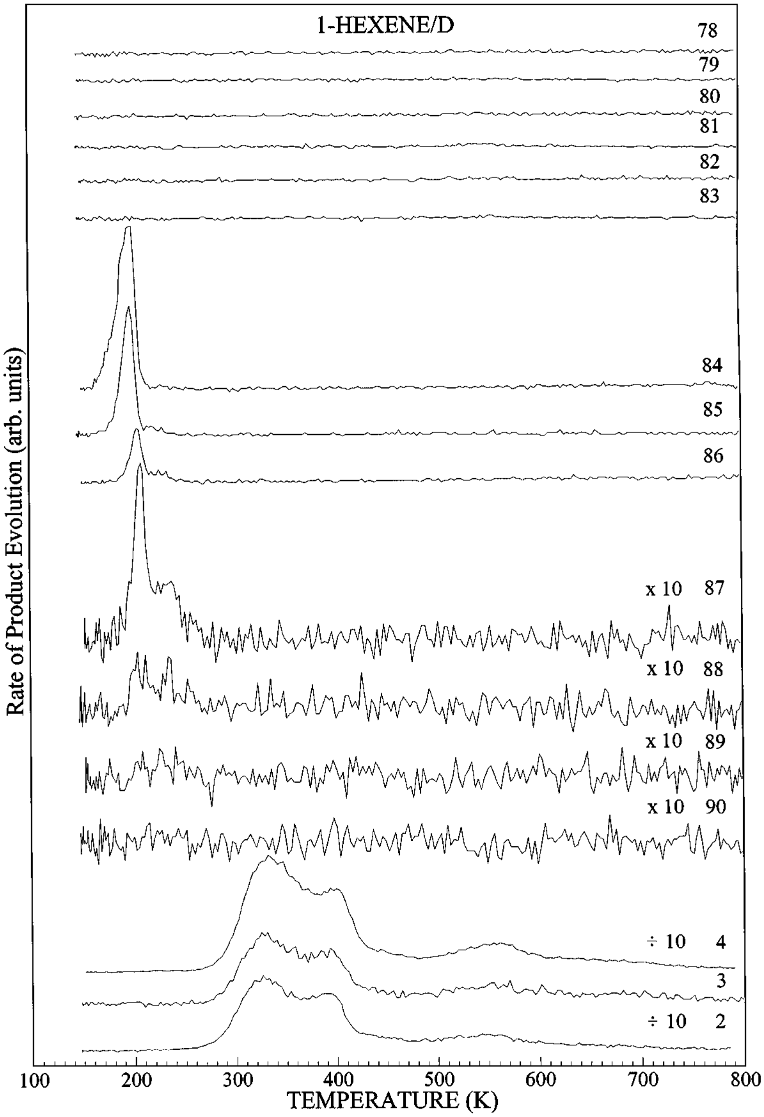

FIG. 10. TPR spectra of 1-hexene adsorbed at 150 K on a deuterium presaturated Pd(111) surface.

studies of alkene adsorption on Pd(111). High-resolution electron energy loss spectroscopy (HREELS) of the low-temperature adsorbed state of ethylene on Pd(111) indicates that ethylene is adsorbed in a π-bonded configuration (37, 38). Similarly, the near-edge X-ray adsorption fine structure (NEXAFS) of 1-butene and 1,3-butadiene adsorbed on Pd(111) at 95 K indicates that the intramolecular bonding in the species is not significantly modified by adsorption (20); 1-butene is π-bonded with its C=C plane parallel to the surface. 1,3-Butadiene, which is weakly bonded at 95 K, transforms into a more strongly di-π-bonded species at 300 K.

We also note that among these alkenes only hexene exchanges with deuterium in the low-temperature desorption state. These results suggest that the low-temperature desorption feature observed for all the C_6 hydrocarbons except 1-hexene originates from this weakly bound π-bonded state. A significant fraction of the π-bonded species, however, converts to a more strongly bound form which can subsequently exchange hydrogen with the surface, dehydrogenate, dehydrocyclize, or hydrogenate. The presence of the isotopically exchanged products of 1-hexene at 200 K (Fig. 10) indicate that this more strongly bound species is the only one giving rise to desorption of hexene near 200 K in the experiments reported here.

On Pd(111), adsorbed ethylene dehydrogenates to ethylidyne ($\equiv CCH_3$) at 300 K (37, 38). Between 400 and 500 K the ethylidyne decomposes to CH(a), which further dehydrogenates to adsorbed carbon and hydrogen. C–H bond breaking processes in 1-hexene adsorbed on clean Pd(111) first liberate hydrogen which begins to desorb near 300 K. As the temperature is increased to ~400 K, hydrogen

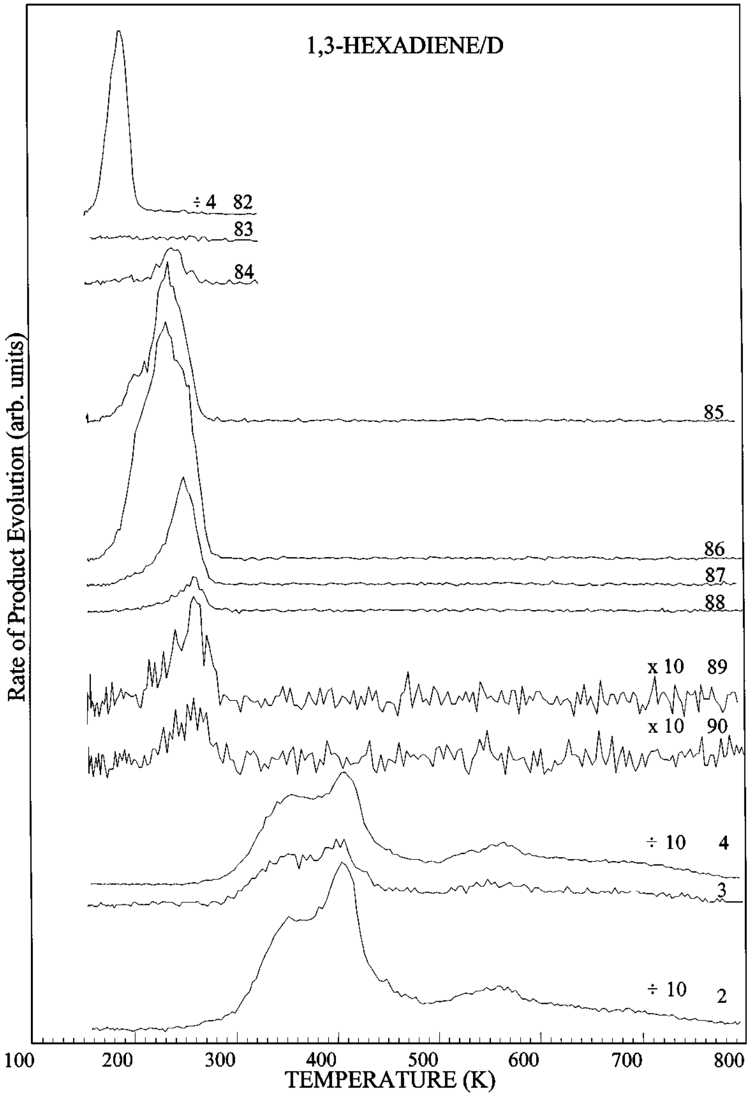

FIG. 11. TPR spectra of 1,3-hexadiene adsorbed at 160 K on a deuterium presaturated Pd(111) surface.

evolution increases caused by loss of hydrogen from the carbon backbone of the adsorbed species. For 1,3-hexadiene, the evolution of hexene at 265 K indicates that some hydrogen is available for hydrogenation at temperatures as low as 220 K, perhaps as the results to C—H bond cleavage. Heating above 400 K leads to further dehydrogenation of the hydrocarbon fragments formed.

On the hydrogen-covered surfaces the hydrocarbons are expected to dehydrogenate to a lesser extent resulting from site blockage by preadsorbed hydrogen; this is indeed observed (Table 3). However, dehydrogenation is evidenced by the hydrogen peak in the TPR spectra at a temperature slightly higher than the desorption-limited hydrogen. Apparently, adsorbed hydrogen does not eliminate binding sites for the more strongly held form of the hydrocarbon, which eventually dehydrogenates. The relative amounts of hydrogen evolved in the separate peaks of the TPRS do not indicate the formation of a stable alkylidyne, even for 1-hexene. Rather, it appears that most of the hydrogen is evolved in a reaction-limited step at 400 K, leaving highly dehydrogenated adsorbed fragments. Either the hexylidyne

TABLE 3

Amounts of Hydrogen Formed by Dehydrogenation of the Adsorbed Hydrocarbons on the *Clean* and Hydrogen-Covered Surfaces

	ML of hydrogen	
Adsorbed hydrocarbon	*Clean*	H-covered
1-Hexene	1.23	0.68
1,5-Hexadiene	1.12	0.59
1,3-Hexadiene	1.37	0.78
1,3,5-Hexatriene	1.00	0.89

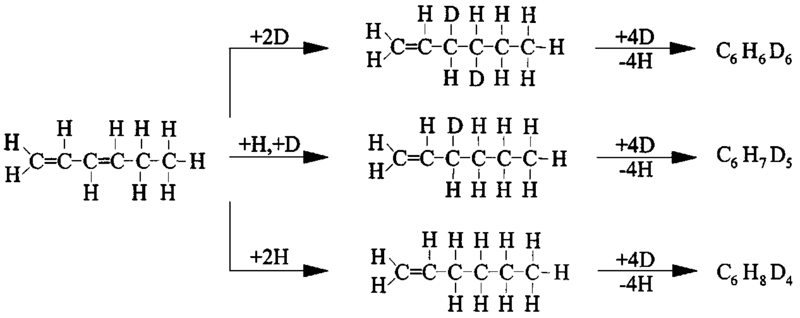

FIG. 12. Schematic of the general pathway followed by 1,3-hexadiene on a deuterium-covered Pd(111) surface.

is not very stable, or the initial dehydrogenation process is more complex and does not involve alkylidyne formation. We can conclude that the activation energy for the rate-limiting step for hydrogen evolution is similar for all the C_6 linear hydrocarbons studies because the peak temperatures and peak shapes for reaction-limited hydrogen near 400 K are nearly identical.

Dehydrocyclization to benzene competes with desorption and dehydrogenation to carbon and hydrogen. Recent studies reported by Guo and Madix (6) showed that adsorbed 1,3,5-hexatriene and 1,5-hexadiene do not dehydrocyclize to benzene on *clean* Pd(100), so this reaction is clearly structure sensitive. Similar structure sensitivity has been reported for the tricyclization reaction of acetylene to benzene on Pd, which occurs below 250 K via successive coupling reactions through a C_4H_4 metallocycle intermediate. The benzene desorbs at 250 K and/or 510 K, depending on coverage; the desorption features are attributed to

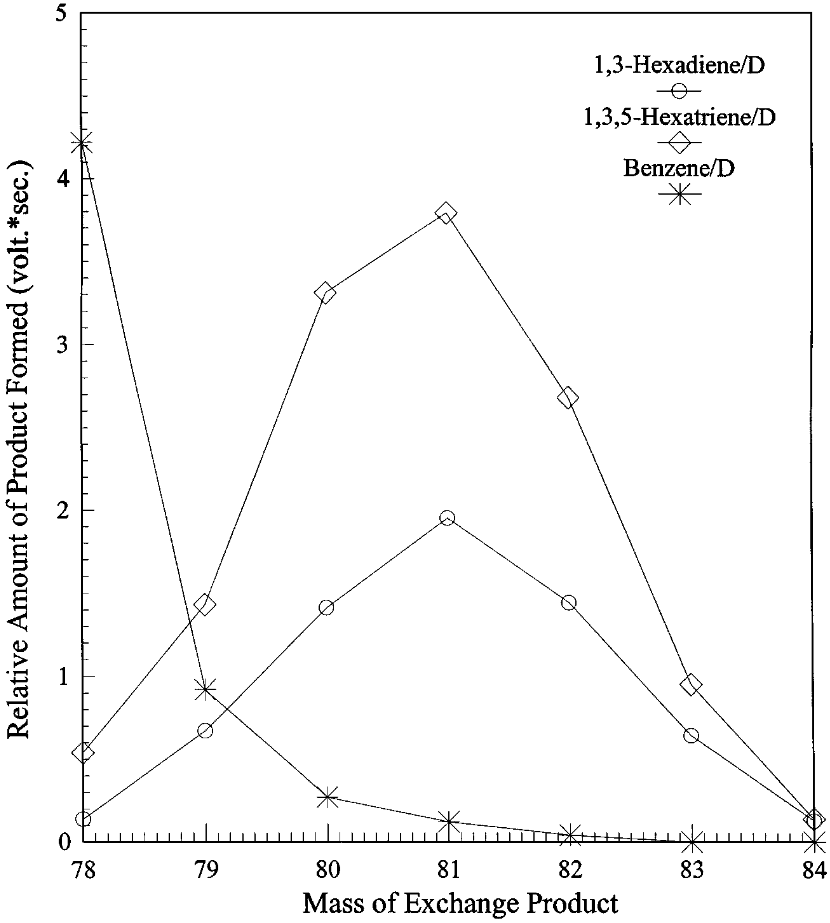

FIG. 13. Distribution of exchange products into benzene and in the benzene formed from 1,3-hexadiene and 1,3,5-hexatriene adsorbed on deuterium-covered surfaces. For the data collected, the same sensitivity factor was utilized.

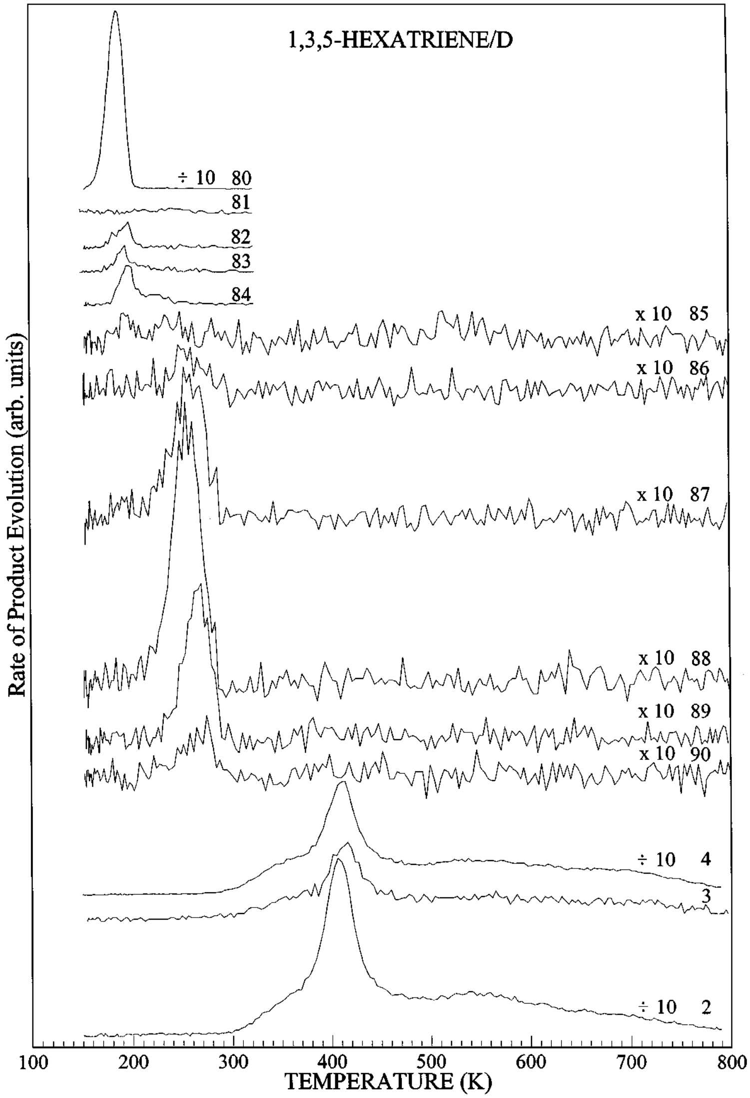

FIG. 14. TPR spectra of 1,3,5-hexatriene adsorbed at 160 K on a deuterium pre-saturated Pd(111) surface.

benzene adsorbed in a tilted (high coverage) or flat (low coverage) configuration, respectively (58).

Benzene formation from adsorbed 1-hexene and 1,3,5-hexatriene has also been observed on $Cu_3Pt(111)$ (64–66). For 1-hexene, the first step was suggested to be dehydrogenation ($T = 270$ K) to a planar C_6H_8 intermediate; cyclization occurs at 405 K, leading to the reaction-limited formation of benzene. On that surface, hexatriene also forms a similar C_6H_8 intermediate which produces both reaction-limited benzene and hydrogen at ~405 K. The rates of

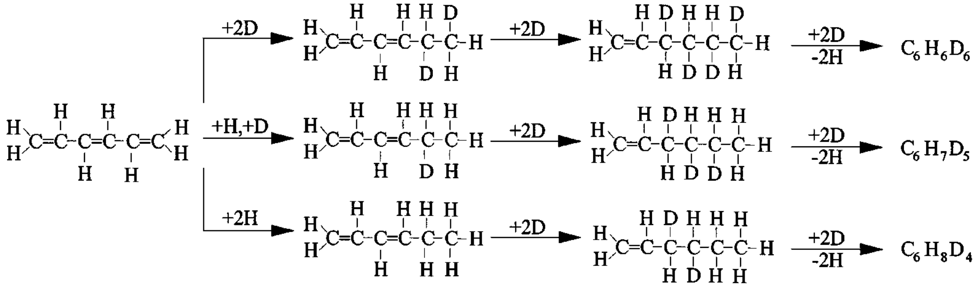

FIG. 15. Schematic of the general pathway followed by 1,3,5-hexatriene on a deuterium-covered Pd(111) surface.

benzene and hydrogen evolution from the aromatization of 1-hexene were comparable for cyclohexene, 1,3-cyclohexadiene and 1,4-cyclohexadiene, which suggests that the rate-determining step in the dehydrocyclization of 1-hexene is not the dehydrogenation step, but the cyclization step.

The patterns of reactivity observed for the linear hydrocarbons studied here support a similar mechanism on Pd(111). Clearly for both 1-hexene and 1,5-hexadiene, the carbon backbone of the adsorbed C_6 hydrocarbon species begins to dehydrogenate at temperatures below that at which benzene is evolved. This process apparently leads to the formation of an intermediate which carbon–carbon couples to form benzene. The benzene formed from both molecules evolves in a desorption-limited feature at ∼500 K with desorption characteristics similar to the desorption of benzene from Pd(111) at low coverage (Fig. 2). Furthermore, the more dehydrogenated species, 1,3-hexadiene and 1,3,5-hexatriene, produce more benzene than 1-hexene, underscoring the importance of dehydrogenation prior to cyclization. Also, the initial configuration of the double bonds in the diene is important for benzene formation, as observed 1,5-hexadiene produces substantially less benzene than 1,3-hexadiene.

Formation of benzene from 1,3-hexadiene and 1,3,5-hexatriene on the *clean* Pd(111) surface must occur at temperatures as low as 358 K, well below the temperature at which hydrogen desorption commences. The hydrogen that becomes available from the dehydrocyclization reaction to form benzene at 358 K is apparently utilized for hydrogenation to form hexene at 264 K. Additional dehydrocyclization produces hydrogen which contributes to the hydrogen desorbing at 384 K. For 1,3,5-hexatriene, a small amount of cyclization appears to occur at temperatures as low as 333 K. The benzene formed from both conjugated molecules desorbs in a fashion similar to that observed following the adsorption of benzene on Pd(111) at high coverage, but without the highest temperature state. It appears that this desorption route is inaccessible for the benzene produced from hexadiene and hexatriene, perhaps because adsorbed hydrocarbon fragments prevent the flat-lying configuration of benzene on the surface. This is an interesting case of the effect of reaction "spectators" on the kinetics of a complex surface reaction. Further, it is quite possible that dehydrocyclization of 1-hexene and 1,5-hexadiene occurs at similarly low temperatures, but the smaller amount of benzene formed dictates a higher desorption temperature because there are not sufficient lateral interactions among the adsorbed species to force the benzene into a more weakly held state at the very low coverages involved with 1,5-hexadiene.

Further, judging from the relative amounts of benzene produced (Table 2) by 1-hexene and the hexadienes, it might be expected that adsorbed hexatriene would produce the most benzene. Indeed, the triene might be envisioned as the perfect C_6H_8 intermediate leading to cyclization. However, this is not the case. Because the 1,3-hexadiene used was approximately 90% trans, and the 1,3,5-hexatriene was approximately a 50–50 mixture, isomerization to the cis form (which is presumably favorable for cyclization) does not appear to be a limiting factor. It is possible that the additional double bond of the triene tends to anchor the molecule to the surface in a configuration less favorable to benzene formation.

On the hydrogen-covered surfaces dehydrocyclization was completely suppressed for 1-hexene (Fig. 6) and 1,5-hexadiene (Fig. 7), but for the conjugated hydrocarbons, 1,3-hexadiene (Fig. 8) and 1,3,5-hexatriene (Fig. 9), the reaction persisted. It is likely that the dehydrocyclization channel for 1,3-hexadiene and 1,3,5-hexatriene becomes accessible as a result of the consumption of hydrogenation by extensive hydrogenation, which frees metal sites. Moreover, the benzene produced by 1,3-hexadiene was only 0.05 of that produced on the *clean* surface and desorbed at 502 K. The benzene formed from the hydrogen-precovered surface desorbed like benzene at low coverage adsorption on Pd(111). The high-temperature state may have been accessible because less dehydrogenation occurred in the presence of preadsorbed hydrogen, and there was a lower concentration of hydrocarbon fragments on the surface. For hexatriene, 0.8 of the benzene generated on the *clean* surface was evolved in the feature at 477 K. TPRS spectra were also obtained for the cyclic compounds, cyclohexene and 1,3-cyclohexadiene, adsorbed on the *clean* Pd(111) surface; in both cases, benzene was evolved in a desorption-limited step.

In no case, either on the Pd(111) or H/Pd(111) surface, was hydrogenation of the C_6 hydrocarbons to hexane observed. To understand the lack of alkane formation, it is necessary to look at a plausible hydrogenation reaction mechanism. Following the scheme proposed by Horiuti and Polanyi for ethylene hydrogenation, the hydrocarbon of interest adsorbs, forming an alkyl group through migratory insertion (12). The half-hydrogenated intermediate produced then reductively eliminates to form the alkane.

The observations for 1-hexene on the *clean* and hydrogen-covered surfaces (Figs. 1 and 6) indicate, however, that if the half-hydrogenated intermediate (alkyl) forms, it prefers hydride elimination to reform hexene. The dominance of the hexene-d_1 exchange product following adsorption of 1-hexene on the deuterium-covered surface (Fig. 10) further supports that an alkyl intermediate is involved. Furthermore, the temperature at which the d_1 exchange product is observed suggests that for 1-hexene adsorbed on the *clean* surface the desorption feature seen at 254 K is caused by hydride elimination of the alkyl species.

Up to four deuterium atoms are ultimately incorporated into hexene. It is possible to exchange three hydrogens atoms by several reversible cycles of hydrogenation and dehydrogenation at the initial double bond. Alkene H–D exchange with D_2 catalyzed by transition-metal complexes (71, 72) and supported catalysts (15, 16) is believed to follow a similar reaction scheme. However, to exchange more than the three deuterium atoms on the vinyl group, migration of the double bond must occur. Because relatively little exchange beyond three deuterium atoms is observed, bond migration is apparently **very** limited in these species. The same reversible reaction steps have been used to explain alkene isomerization via double-bond migration on both surfaces and in metalorganic complexes (16, 71, 72) where an internal alkyl must be involved.

There are some interesting differences in the hydrogenation behavior of the C_6 hydrocarbons. Neither 1-hexene nor 1,5-hexadiene self-hydrogenates on the *clean* surface, but on the hydrogen-covered surface a very limited amount of hydrogenation of 1,5-hexadiene to hexene does occur. The interaction of the second double bond must account for the limited hydrogenation. Initially, the hexadiene may form a half-hydrogenated intermediate with one double bond intact. Because of the stability conferred by the additional double bond, hydrogen can add to the intermediate to form hexene, which can either desorb or reform the alkyl species at the other double bond, which then undergoes hydride elimination.

For the conjugated molecule, 1,3-hexadiene, there is *substantial* hydrogenation to 1-hexene on both the clean and hydrogen-covered surfaces. Similar to 1,5-hexadiene, it is plausible that 1,3-hexadiene forms a half-hydrogenated intermediate through migratory insertion. Again, because of the presence of the additional double bond, the intermediate formed can then hydrogenate to 1-hexene. This half-hydrogenated intermediate can also hydride eliminate and reform hexadiene, which may be the origin of the desorption feature seen at 200 K on the *clean* surface. Upon formation from 1,3-hexadiene, 1-hexene can either desorb or form the alkyl species. Further insight into the reaction mechanism may be obtained from the TPRS results from the deuterium covered surface (Fig. 11). There is no incorporation of deuterium into the low-temperature desorption state of hexadiene, consistent with this state originating from a π-bonded species. Hydrogenation, deuteration, and exchange products were evolved. The exchange pathway is expected to be similar for that of 1-hexene adsorbed on the deuterium-covered surface. If the proposed mechanism using the half-hydrogenated intermediate is followed, 1,3-hexadiene would require the addition of three deuterium (hydrogen) atoms to form adsorbed hexyl. The subsequent reversible β-hydride elimination would be expected to favor formation of up to 1-hexene-d_5, resulting from the normal kinetic isotope effect expected in the elimination step (5). Further, to obtain masses greater than 89, there must be exchange into the hexene that has been produced by deuteration of the 1,3-hexadiene *and* double bond "migration" to obtain masses up to 90. Facile double-bond migration would lead to complete exchange, which is not observed, but limited migration could lead to exchange only through the 3-carbon, giving the observed result. In fact, the limit of four exchanged hydrogens in the deuteration product is identical to the behavior observed for 1-hexene. C–H bond breaking and formation steps appear to be faster than double bond migration.

An alternative pathway that may account for the limited amount of exchange is the formation of an allyl intermediate for both adsorbed 1-hexene and for the intermediate involved in deuteration of 1,3-hexadiene. If 1-hexene adsorption results in the formation of the allylic intermediate by loss of hydrogen at the 3-carbon, three allylic hydrogens can be readily exchanged with deuterium; the fourth deuterium added then results from deuteration of the allylic species to reform the hexene. In the deuteration of 1,3-hexadiene, the process may be more complex. Simple deuteration of the diene to 1-hexyl followed by exchange of the hydrogens on the 1 and 2 carbons, followed by β-hydride elimination would lead only to mass 89, if double-bond migration is assumed not to occur. However, formation of a conjugated system over 5-carbons by loss of a hydrogen at the 5-carbon would allow for exchange of hydrogens at the 1 and 5 positions, leading to incorporation of three deuterium atoms. Deuteration of this species to hexene would require another three deuterium atoms, yielding six deuterium atoms in the hexene product, mass 90, as observed. This process requires that the hexene formed not exchange further, given the ease of exchange into 1-hexene, this seems unlikely. Moreover, clearly 1-hexene-d_2 dominates the reactions with adsorbed deuterium, implying that deuteration is faster than exchange. If the conjugated species is formed, deuteration would require three deuterium atoms to form the hexene, and the dominant product would be 1-hexene-d_3; this is not the case. We therefore conclude that the half-hydrogenated intermediate is the most likely intermediate and that a limited amount of double-bond migration occurs.

The conjugated molecule, 1,3,5-hexatriene, also hydrogenates on the hydrogen-covered surface, forming 1,3-hexadiene and 1-hexene. On the *clean* surface, it prefers to dehydrogenate. It is expected that the hexatriene forms a half-hydrogenated intermediate through migratory insertion. Because of the presence of the additional double bond, the intermediate formed hydrogenates to 1,3-hexadiene. The hexadiene can then hydrogenate further to 1-hexene in a fashion similar to that envisioned for hexadiene. From the experiments on the deuterium-covered surface, it was observed that there was no incorporation of deuterium into the low-temperature desorption feature of the hexatriene, similar to adsorption of 1,3-hexadiene. This indicates that the low-temperature desorption feature is a π-bonded species. The mass 82 feature observed is from hydrogenation to 1,3-hexadiene-h_2, mass 83 is from hydrogenation/deuteration to 1,3-hexadiene-h_1d_1 and mass 84 is from deuteration to 1,3-hexadiene-d_2. It is also possible that contributions to masses 83 and 84 could come from exchange products from 1,3-hexadiene-h_2 and -h_1d_1. Masses observed equal to 86 and greater are the result of hydrogenation and deuteration of hexadiene to hexene, similar to the reaction scheme proposed for 1,3-hexadiene, and exchange products of hexene.

From the results of this work, it is clear that 1,5-hexadiene, 1,3-hexadiene, and 1,3,5-hexatriene can be hydrogenated selectively to 1-hexene. Also, the conjugated molecules, 1,3-hexadiene and 1,3,5-hexatriene are more easily hydrogenated than are the isolated double bonds found in 1,5-hexadiene. However, to hydrogenate the C_6 hydrocarbons to hexane, the intermediate species (alkyl) must go through reductive elimination. The strength of the bonding of the alkyl species or the adsorbed hydrogen atom to the surface or both may influence the rate of this step. Alkenes adsorbed on Pd(100) also do not hydrogenate to the alkane under similar conditions (6), though on Pt (2) and Rh (3) hydrogenation to the alkane is observed. The origin of the difference between these metals and Pd has been attributed to the strength of the metal–hydrogen bond because a distinctly different reaction mechanism is not likely (6). The occurrence of hydrogenation follows the trend in the H–metal binding energies.

V. SUMMARY

The adsorption and reactivity of 1-hexene, 1,5-hexadiene, 1,3-hexadiene and 1,3,5-hexatriene on clean Pd(111) and H(D)/Pd(111) were investigated using TPRS. The low-temperature adsorption configuration for the linear C_6 hydrocarbons appears to be a weak π-bonded species. Upon heating, a fraction of the π-bonded species bonds more tightly with the surface and can either desorb molecularly at higher temperatures through hydride elimination of a half-hydrogenated intermediate, dehydrogenate, dehydrocyclize, or selectively hydrogenate. Dehydrogenation to adsorbed carbon and hydrogen initiates through the loss of hydrogen from the carbon backbone of the adsorbed species at $\sim$400 K. Above 400 K, fragmentation of the adsorbed species and dehydrogenation of these fragments occurs. Structure-sensitive dehydrocyclization of the hydrocarbons leads to desorption-limited evolution of benzene; cyclization can occur as low as 333 K.

Hydrogenation to hexane was not observed for any of the adsorbed molecules. This lack of alkane formation is attributed to the strength of the H–Pd bond, which inhibits reductive elimination of the alkyl species formed. Selective hydrogenation to hexene was observed for 1,3-hexadiene adsorbed on clean Pd(111) and for 1,3-hexadiene and 1,5-hexadiene adsorbed on hydrogen-saturated Pd(111). Hexatriene adsorbed on the hydrogen-saturated surface produced hexadiene and hexene. Selective hydrogenation of the hexadienes and hexatriene is clearly related to the interaction of the additional double bonds with the surface which allows insertion of hydrogen into the half-hydrogenated intermediate produced.

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