

# Thermal Chemistry of C<sub>4</sub> Hydrocarbons on Pt(111): Mechanism for Double-Bond Isomerization

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The thermal chemistry of a number of C<sub>4</sub> hydrocarbons (1,3-butadiene, 1-bromo-3-butene, 1-bromo-2-butene, *trans*-2-butene, *cis*-2-butene, 1-butene, 2-iodobutane, 1-iodobutane, and butane) was investigated on clean and hydrogen- and deuterium-predosed Pt(111) single-crystal surfaces by temperature-programmed desorption and reflection–absorption infrared spectroscopy. A combination of rapid  $\beta$ -hydride eliminations from alkyls to olefins and the reverse insertions of those olefins into metal–hydrogen bonds explains the hydrogenation, dehydrogenation, and H–D exchange products that desorb from the surface. A preference for hydrogenation at the end carbons and dehydrogenation from the inner carbons also explains the extent of the isotope exchange and the preferential isomerization of 1-butene to 2-butene observed on this Pt(111) surface. The reactions of more dehydrogenated C<sub>4</sub> species is also discussed.

## 1. Introduction

The conversion of hydrocarbons on transition metals is one of the oldest but still one of the most widely used catalytic processes.<sup>1–3</sup> Extensive mechanistic studies were carried out in the early years using conventional catalytic kinetic techniques,<sup>4–7</sup> but only with the advent of new surface-sensitive techniques has it been possible to interrogate the reaction details directly at a molecular level.<sup>8,9</sup> Much fundamental research work has been carried out since, in particular on the prototypical conversion of ethylene on the close-packed (111) surface of platinum,<sup>10–13</sup> and most of the basic ideas proposed by the pioneer investigators have been corroborated. These include the rehybridization of the C=C double bond to a di- $\sigma$  state upon adsorption,<sup>14–17</sup> the rapid interconversion between the alkene and the alkyl as a way of exchanging hydrogens for deuteriums,<sup>18,19</sup> and the stepwise hydrogenation of the olefin to the alkane.<sup>20,21</sup> Of particular importance was the isolation of the facile  $\beta$ -hydride elimination step from alkyl surface moieties back to an adsorbed alkene.<sup>16,22</sup> However, the new studies have also revealed some unforeseen complications, in particular the rapid and irreversible conversion of the alkene to alkylidyne on clean metal surfaces<sup>23–25</sup> and the passivating and hydrogen-storing roles that the resulting carbonaceous layer play during hydrocarbon catalytic conversions under realistic conditions.<sup>17,26–31</sup>

The initial studies with ethylene have been extended to larger hydrocarbons, where a larger degree of chemical complexity is possible.<sup>32–38</sup> In particular, a new H–D exchange mechanism starting with a dehydrogenation step at the highly labile allyl position is in principle possible in olefins with three or more carbons.<sup>39</sup> However, recent studies in our laboratory with C<sub>3</sub> species have ruled this possibility out: the hydrogenation (deuteration) to alkyl surface intermediates still prevails in those systems.<sup>40–44</sup> In this report, we extend our past studies to address the surface chemistry of C<sub>4</sub> species in order to check on the generality of that conclusion and to complement previous work by others.<sup>32,33,36,45–49</sup> Particular emphasis is placed here on the understanding of double-bond isomerization reactions. It is shown that, as with the C<sub>3</sub> hydrocarbons, the surface chemistry

of C<sub>4</sub> species is dominated by a rapid interconversion between the adsorbed olefin and the corresponding alkyl intermediates, and that allyl formation only plays a minor (if any) role in hydrogenation, H–D exchange, or isomerization processes. In addition, the preference for  $\beta$ -hydride elimination from the central carbons of the alkyl species is indicated, and the consequent selective formation of olefins with inner double bonds, 2-butenes in this case, is accordingly justified. A discussion of the chemistry of more dehydrogenated species, butadiene in particular, is also provided.

## 2. Experimental Section

All temperature-programmed desorption (TPD) and reflection–absorption infrared spectroscopy (RAIRS) experiments were performed in a two-tier ultrahigh vacuum (UHV) chamber cryo-pumped to a base pressure below  $8 \times 10^{-11}$  Torr.<sup>50,51</sup> The main stage of this chamber is used for the TPD experiments, which are performed by using a computer-controlled quadrupole mass spectrometer (UTI 100C) with an extendible nose cone ended in a 5-mm diameter aperture that can be placed within 1 mm of the single crystal for the selective detection of molecules desorbing from the front surface. A constant heating rate of 10 K/s was used in all TPD runs, and a bias of  $-100$  V was applied to the crystal in order to avoid any chemistry induced by stray electrons from the ionizers of the ion gauge or the mass spectrometer.<sup>40</sup>

The second, smaller stage is accessible with a long-travel manipulator, and is used for the RAIRS experiments. The IR beam from a FT-IR spectrometer (Bruker Equinox 55) is passed through a polarizer and focused through a NaCl window onto the platinum crystal at a grazing ( $\sim 85^\circ$ ) incidence. The reflected beam that escapes from the UHV chamber through a second NaCl window is then refocused onto a narrow-band mercury–cadmium–telluride (MCT) detector. The entire beam path is enclosed in a sealed box purged with dry air purified by using a scrubber (Balston 75-60) for CO<sub>2</sub> and water removal. All spectra were taken at a resolution of  $4\text{ cm}^{-1}$  by averaging over 2000 scans, a process that takes about four minutes per experiment, and ratioed against spectra from the clean sample acquired before gas dosing. The sample condition and IR beam alignment were checked routinely by comparing IR spectra for a saturation coverage of CO with those reported in the literature.<sup>52,53</sup>

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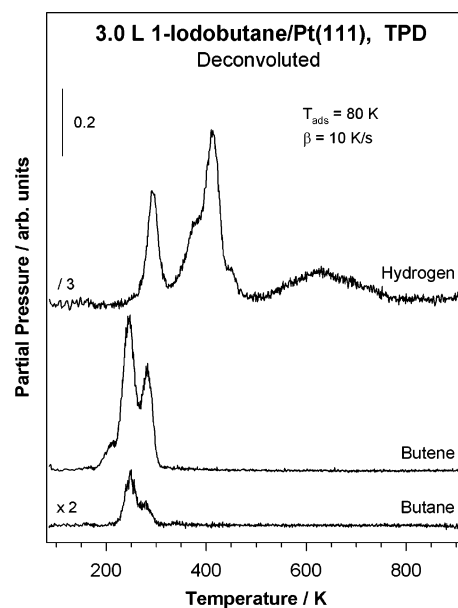
The platinum (111) single crystal, a disk 8 mm in diameter and 2 mm in thickness, is mounted on the sample holder via spot-welding to two tantalum wires attached to two copper electrical feedthroughs. With this arrangement, it is possible to cool the sample to below 80 K using a continuous flow of liquid nitrogen through hollow tubes connected to the nonvacuum side of the copper feedthroughs and to heat the crystal resistively to up to 1100 K. The surface temperature is measured with a chromel–alumel thermocouple spot-welded to the side of the crystal, and set to within  $\pm 1$  K of any given value by using a homemade temperature controller also employed to ramp the temperature linearly for the TPD experiments. The sample was regularly cleaned by cycles of oxidation in  $5 \times 10^{-7}$  Torr of oxygen at 700 K and annealing in a vacuum at 1100 K.  $\text{Ar}^+$  ion sputtering followed by annealing at 1100 K was used as needed but sparingly to avoid the creation of surface defects.

1,3-Butadiene (>99% purity), *cis*-2-butene (>95% purity), *trans*-2-butene, (>95% purity), 1-butene (>99% purity), butane (>99% purity), and deuterium (>99.5% atom purity) were all purchased from Matheson, and hydrogen (>99.995% purity) was obtained from Liquid Carbonic. All those gases were used as supplied, but their purities were frequently checked by mass spectrometry. 1-Iodobutane (99% purity), 2-iodobutane (99% purity), 1-bromo-2-butene (85% purity, 1:5 mixture of *cis* and *trans* isomers, main impurity: 3-bromo-1-butene), and 1-bromo-3-butene (97% purity) were obtained from Aldrich and purified by a series of freeze–pump–thaw cycles before dosing; their purities were also checked daily using the mass spectrometer in our UHV chamber. Dosing of the liquids was achieved by using their vapors, by backfilling of the vacuum chamber using leak valves, and is reported in Langmuirs ( $1 \text{ L} \equiv 10^{-6}$  Torr), not corrected for differences in ion gauge sensitivities. All dosings were carried out at 80 K unless otherwise indicated.

### 3. Results

**3.1. TPD Survey.** Figure 1 shows typical TPD spectra for one of the  $\text{C}_4$  hydrocarbons studied in this project, 1-iodobutane, adsorbed on Pt(111). The data correspond to an exposure of 3.0 L, which leads to monolayer saturation. Here, as in most of the cases investigated, the most prominent desorption products observed were hydrogen (2 amu), butene (56 amu), and butane (58 amu). No heavier molecules were detected indicative of C–C bond formation (alkyl coupling), and no lighter species from C–C bond scission were seen either. The butene and butane TPD traces reported in Figure 1 (and in Figures 3–7) were deconvoluted from the original data to remove the contributions from the cracking pattern of the other species, even though it was determined that in none of the cases reported here those interferences were significant.

Hydrogen desorption from 1-iodobutane decomposition occurs in several stages, with peaks at 300, 380, 410, 450, and 640 K. The feature between 220 and 340 K is in general attributed to the recombinative desorption of adsorbed hydrogen atoms on Pt(111),<sup>54</sup> either from background adsorption and/or from facile dehydrogenation steps. In the case of 1-iodobutane,  $\beta$ -hydride elimination from the 1-butyl species formed after C–I bond scission is the likely source of this feature.<sup>55,56</sup>  $\beta$ -H elimination leads to butene formation, some of which desorbs between 200 and 300 K, but the hydrogen released from that step is also available for the hydrogenation of some surface 1-butyl species to the butane that desorbs in the same temperature range. The similarity of the TPD peak shapes and temperatures for butene and butane desorption suggests a disproportionation process starting with a rate-limiting  $\beta$ -H elimination step followed by a rapid reductive elimination of

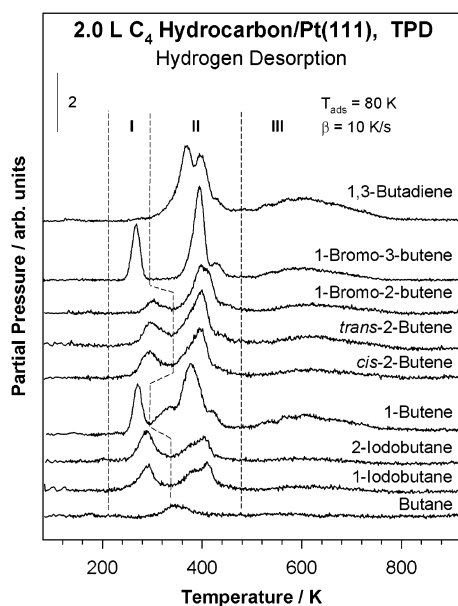


**Figure 1.** Hydrogen (2 amu), butene (56 amu), and butane (58 amu) TPD traces for 3.0 L of 1-iodobutane adsorbed on a Pt(111) single-crystal surface at 80 K. The 1-butyl intermediate produced via thermal activation of the C–I bond on the surface initially disproportionates to butane and butene, which desorb in several stages starting around 180 K. Further dehydrogenation takes place in a stepwise manner, and leads to the formation of butylidyne at  $\sim 300$  K and other more dehydrogenated surface species at higher temperatures. No other products were detected in these TPD experiments.

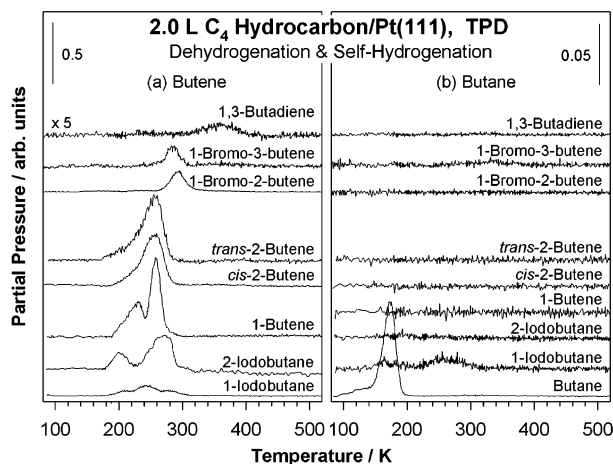
some of the surface butyl groups with the resulting hydrogen. All this has been well documented for other surface alkyls.<sup>16,42,55,57,58</sup> Additional reaction-limited hydrogen desorption from the hydrocarbon surface species produced by 1-iodobutane decomposition is observed in several stages between 340 and 480 K and then in a broad feature between 500 and about 750 K.

**3.2. Hydrogen Desorption.** Survey TPD experiments were performed for all the  $\text{C}_4$  compounds listed in the Experimental Section, starting with saturation coverages, on the Pt(111) surfaces. The results for hydrogen desorption are displayed in Figure 2 and those for butene and butane in Figure 3. Hydrogen desorption can be roughly divided in three regions, below or around 300 K (region I), between  $\sim 300$  and 500 K (region II), and above 500 K (region III). Almost all  $\text{H}_2$  TPD traces in Figure 2 showed at least one peak in each of those temperature regions. Only the dehydrogenation of 1,3-butadiene starts via two close but distinct steps in region II. Also, the TPD spectra of butane only show one small feature about 350 K, the same as with low coverages of the other compounds. Most of the adsorbed butane desorbs molecularly about 175 K (Figure 3), so perhaps this small  $\text{H}_2$  production is the result of decomposition on defect sites.

On the basis of the integrated areas of the  $\text{H}_2$  TPD peaks in Figure 2, the estimated average stoichiometries of the  $\text{C}_4$  hydrocarbons that form on the surface at the different stages of dehydrogenation are listed in Table 1. Caution must be exercised when interpreting those data because: (a) they only represent average values; and (b)  $\text{H}_2$  adsorption from background gases may alter the calculated yields. Nevertheless, some general observations can be highlighted. In particular, the stoichiometry of the surface species that form after the first dehydrogenation in region I is approximately  $\text{C}_4\text{H}_6$  in all cases except 1-butene, which is believed to convert directly to butylidyne ( $\text{Pt}_3\equiv\text{CCH}_2\text{CH}_2\text{CH}_3$ ),<sup>33</sup> and butadiene. Also, some butene desorption usually



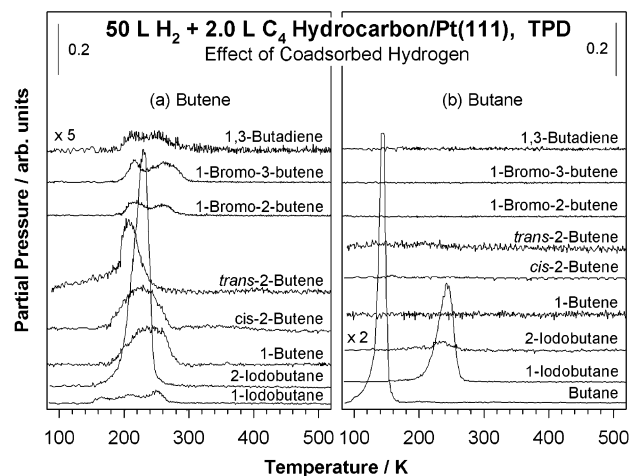
**Figure 2.** Hydrogen TPD traces for 2.0 L of each of the C<sub>4</sub> hydrocarbons studied here (1,3-butadiene, 1-bromo-3-butene, 1-bromo-2-butene, *trans*-2-butene, *cis*-2-butene, 1-butene, 2-iodobutane, 1-iodobutane, and butane) adsorbed on Pt(111) at 80 K. The 2.0 L exposures were chosen to ensure near-monolayer saturation. Broadly, three desorption regimes can be identified with most of the reactants, namely, around room temperature, between ~300 and 500 K, and above 500 K. The boundaries among those correspond to the formation of intermediates with average stoichiometries of C<sub>4</sub>H<sub>6</sub> and C<sub>4</sub>H<sub>2</sub> (Table 1).



**Figure 3.** Butene (a) and butane (b) TPD traces for the same C<sub>4</sub> hydrocarbons as in Figure 2. Butane desorption is only seen from butane and 1-iodobutane. Butene, on the other hand, is produced by all. Note the similarities between the traces of the two 2-butenes and also between 1-bromo-2-butene and 1-bromo-3-butene.

precedes the first hydrogen TPD peak (compare Figures 2 and 3). In fact, the temperature of the peak maximum for the (first) butene desorption often coincides with the onset of the H<sub>2</sub> evolution. Finally, further dehydrogenation in region II leads to new surface species, typically with C<sub>4</sub>H<sub>2</sub> average compositions.

**3.3. Hydrogenation/Dehydrogenation.** Figures 3 and 4 show TPD traces for butene (left panel) and butane (right panel) desorption from the various C<sub>4</sub> hydrocarbons studied here after adsorption on clean (Figure 3) and 50 L H<sub>2</sub>-predosed (Figure 4) Pt(111). On the clean surface, butene desorption is in most cases observed between 200 and 280 K. However, 1-bromo-3-butene and 1-bromo-2-butene display butene desorption features only at temperatures close to 300 K, and with 1,3-butadiene, C<sub>4</sub>H<sub>8</sub> production starts above 320 K and peaks at ~360 K, indicating



**Figure 4.** Butene (a) and butane (b) TPD traces for the C<sub>4</sub> hydrocarbons adsorbed on 50 L hydrogen-predosed Pt(111). More butane production is seen with the iodobutanes, but, surprisingly, a larger butene yield is also seen here with 2-iodobutane than on the clean surface. The butene TPD traces for all three butenes are now different, and those for the bromobutenes show two peaks, both at lower temperatures than the one seen on clean Pt(111).

**TABLE 1: Average Stoichiometries for the Surface Species that Form after Thermal Dehydrogenation of Different C<sub>4</sub> Hydrocarbons Adsorbed on Pt(111), as Calculated by Integration of the Areas of the Hydrogen (2 amu) TPD Peaks in Figure 2**

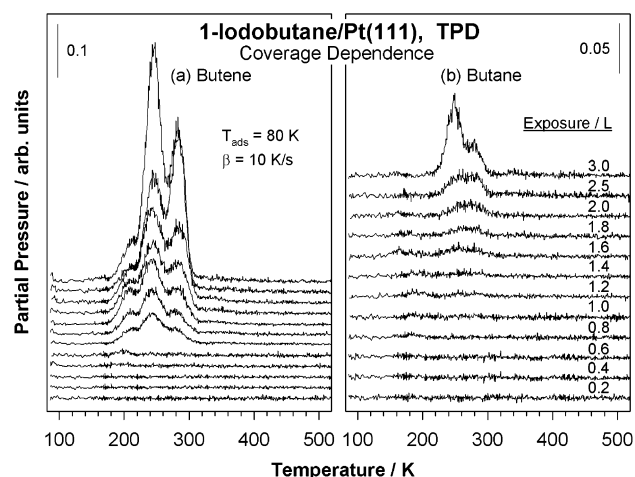
	after first H <sub>2</sub> desorption	at 480 K
1,3-butadiene (C <sub>4</sub> H <sub>6</sub> )	C <sub>4</sub> H <sub>4.2</sub>	C <sub>4</sub> H <sub>2</sub>
1-bromo-3-butene (C <sub>4</sub> H <sub>7</sub> Br)	C <sub>4</sub> H <sub>5.6</sub>	C <sub>4</sub> H <sub>2</sub>
1-bromo-2-butene (C <sub>4</sub> H <sub>7</sub> Br)	C <sub>4</sub> H <sub>6.2</sub>	C <sub>4</sub> H <sub>2.7</sub>
<i>trans</i> -2-butene (C <sub>4</sub> H <sub>8</sub> )	C <sub>4</sub> H <sub>6.4</sub>	C <sub>4</sub> H <sub>2</sub>
<i>cis</i> -2-butene (C <sub>4</sub> H <sub>8</sub> )	C <sub>4</sub> H <sub>6.4</sub>	C <sub>4</sub> H <sub>2</sub>
1-butene (C <sub>4</sub> H <sub>8</sub> )	C <sub>4</sub> H <sub>7.2</sub>	C <sub>4</sub> H <sub>3.5</sub>
2-iodobutane (C <sub>4</sub> H <sub>9</sub> I)	C <sub>4</sub> H <sub>6.1</sub>	C <sub>4</sub> H <sub>2</sub>
1-iodobutane (C <sub>4</sub> H <sub>9</sub> I)	C <sub>4</sub> H <sub>6.1</sub>	C <sub>4</sub> H <sub>2</sub>

the formation of more stable surface intermediates. Butane desorption was observed only in the case of 1-iodobutane (and butane).

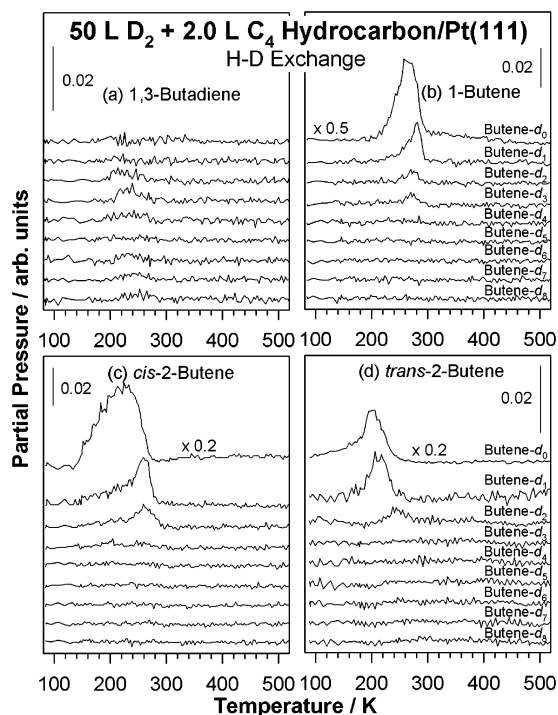
The effect of coadsorbed hydrogen on the desorption of both butene and butane is highlighted by the data in Figure 4. As expected, hydrogenation to butane is enhanced in the case of 1-iodobutane by the predosed hydrogen, as indicated by both the lower peak temperature (245 vs 270 K) and the larger peak area in the corresponding traces in Figure 4 vs Figure 3. A minor amount of C<sub>4</sub>H<sub>10</sub> is also detected with 2-iodobutane on the H<sub>2</sub>-predosed surface at about 240 K, but no significant butane desorption is observed with any of the other hydrocarbons. The changes in the butene TPD are subtle and depend on the particular molecule being considered. Significant decreases in peak temperatures are seen for most, and a large increase in yield is observed with 2-iodobutane, a behavior that we do not completely understand.

More detailed TPD studies were carried out for each compound as a function of initial coverage. Figure 5 shows the results for the case of 1-iodobutane. No C<sub>4</sub> species desorbs after exposures below 1.0 L; only hydrogen is detected at those low coverages (data not shown). This behavior is common to all the C<sub>4</sub> hydrocarbons and means that the adsorbed species decompose rapidly during thermal activation to surface carbon and hydrogen gas. On the basis of similar observations with other hydrocarbons,<sup>40,43,44</sup> it may be concluded that at low coverages the hydrocarbons adsorb flat and display a strong interaction with the metal surface, which facilitates extensive





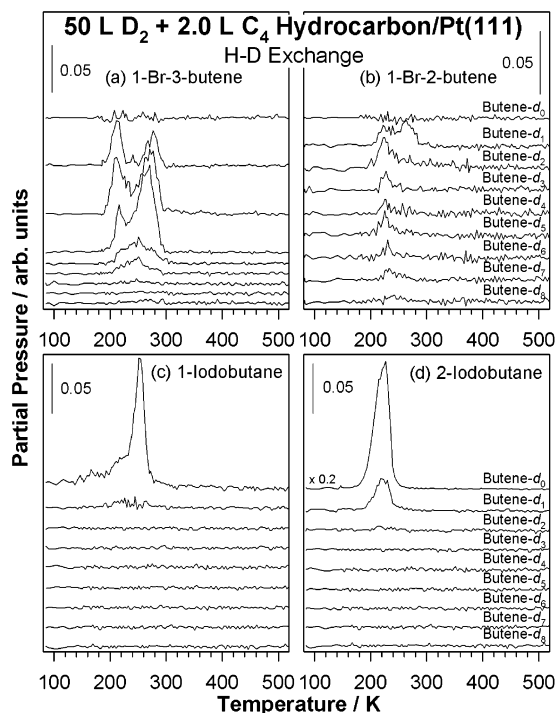
**Figure 5.** Butene (a) and butane (b) TPD traces for 1-iodobutane on Pt(111) as a function of initial exposure. Butene and butane desorption start only above 1.0 and 1.5 L, respectively; only total decomposition to  $H_2$  and surface carbon is seen at low coverages (data not shown).



**Figure 6.** TPD traces for all possible deuterated butene- $d_x$  products from thermal activation of 1,3-butadiene (a), 1-butene (b), *cis*-2-butene (c), and *trans*-2-butene (d) on 50 L deuterium-predosed Pt(111). Only butene- $d_0$ , - $d_1$ , and - $d_2$  are detected with both 2-butenes, presumably because only the inner hydrogens can be exchanged. The butene- $d_3$  produced with 1-butene can be interpreted as evidence for its initial isomerization to 2-butene. Butadiene produces very little butene, but what desorbs does so at reasonably low ( $\sim 250$  K) temperatures, and after extensive isotope scrambling.

dehydrogenation. On the other hand, production of butene and butane can be seen above 1.0 and 1.5 L, respectively, with yields that increase with increasing doses up to about 3.0 L, just before monolayer saturation. In all cases, the major product between 200 and 300 K is always butene.

**3.4. H–D Exchange.** In the presence of coadsorbed deuterium, the thermal activation of  $C_4$  hydrocarbons chemisorbed on Pt(111) not only leads to deuteration to butene and/or butane but also to multiple H–D exchange. Figures 6 and 7 show the TPD spectra of the different deuterated butenes- $d_x$  obtained for all the  $C_4$  hydrocarbons adsorbed on 50 L  $D_2$ -predosed Pt(111)

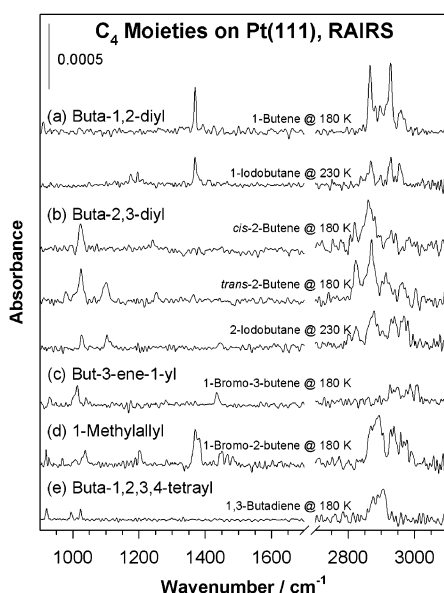


**Figure 7.** TPD traces for all possible deuterated butene- $d_x$  products from thermal activation of 1-bromo-3-butene (a), 1-bromo-2-butene (b), 1-iodobutane (c), and 2-iodobutane (d) on 50 L deuterium-predosed Pt(111). A small amount ( $\sim 10\%$ ) of H–D exchange is seen with 2-iodobutane but not with 1-iodobutane. 1-Bromo-2-butene produces butene in two peaks, indicating two adsorption configurations, a  $\eta^1$  species that deuterates directly to butene- $d_1$  around 260 K and a  $\eta^3$ -allylic species that shows extensive scrambling before hydrogenating (deuteration) to butene about 230 K. The reaction of 1-bromo-3-butene with coadsorbed deuterium occurs in three temperature regimes leading to exchange of a maximum of either three and five hydrogen atoms, presumably at the  $C_1$  and  $C_2$  positions.

surfaces. In the case of 1,3-butadiene (Figure 6a), all butene- $d_2$  to - $d_8$  were detected, even if only in very small amounts. On the other hand, only up to three D substitutions were detected in reactions with 1-butene, and only up to two with the 2-butenes (parts b, c, and d of Figure 6). This implies a preference for  $\beta$ -hydride elimination and exchange at the inner carbons. Also, the kinetics of butene- $d_0$  desorption is quite different (faster) than those for the production of the other isotopomers. Sometimes different kinetics are also seen in the butene- $d_1$  trace.

1-Bromo-3-butene and 1-bromo-2-butene both react with deuterium starting at around 215 K, and extensive deuterium incorporation is seen in both cases, up to butene- $d_5$  and butene- $d_8$ , respectively (parts a and b of Figure 7). However, no butene- $d_0$  is made with either hydrocarbon. It seems that in the case of 1-bromo-3-butene the double bond is kept intact during the H–D exchange, and that the deuterated butenes are produced via cycles of  $\beta$ -hydride elimination and deuterium incorporation at the  $C_1$  and  $C_2$  carbons exclusively. In the case of 1-bromo-2-butene, on the other hand, all possible deuterated butanes are formed, suggesting rapid and extensive H–D exchange within the initial allyl surface intermediate produced by elimination of the bromine atom.

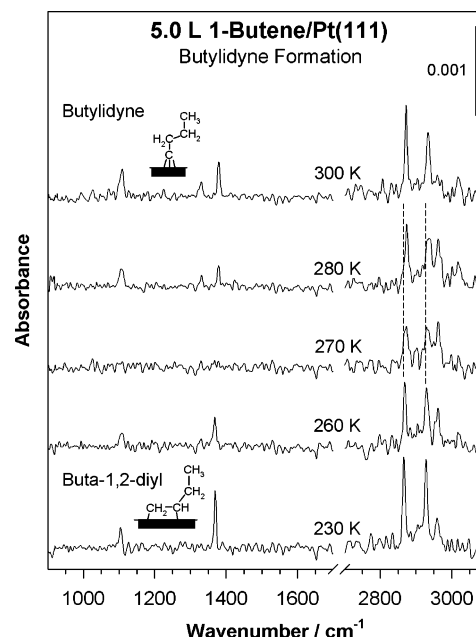
As mentioned before, only butene- $d_0$  is produced in the reaction of 1-iodobutane with deuterium (Figure 7). The maximum number of deuterium incorporated in the accompanying desorbing butane in that case is two (the yields for butane- $d_0$ :- $d_1$ :- $d_2$  follow  $\sim 0.47$ : $0.48$ : $0.05$  proportions, data not shown). This indicates the occurrence of only one single H–D exchange cycle on the 1-butyl species, a  $\beta$ -hydride elimination to 1-butene



**Figure 8.** RAIRS for the moieties obtained by adsorption of the different C<sub>4</sub> compounds on Pt(111) around 180–230 K. Evidence is provided for the formation of buta-1,2-diyl from 1-iodobutane (a), buta-2,3-diyl from 2-iodobutane (b), but-3-ene-1-yl from 1-bromo-3-butene (c), 1-methylallyl from 1-bromo-2-butene (d), and 1,2,3,4-tetra-yl from 1,3-butadiene (e). Tentative vibrational assignments are listed in Table 2.

followed by two sequential deuterium incorporations.<sup>22,42,57</sup> The fact that this cycle does not repeat a second time indicates that the new intermediate after the first deuterium addition is a 2-butyl (not 1-butyl) surface species. In fact, in the case of 2-iodobutane, which yields surface 2-butyl directly after iodine elimination, the production of about 10% of butene-*d*<sub>1</sub> is detected. Also, the butene resulting from 2-iodobutane desorbs at lower temperatures than with 1-iodobutane, at 225 vs 255 K, indicating a faster  $\beta$ -H elimination. This elimination is likely to occur at the inner (C<sub>3</sub>) carbon atom, and to lead to the formation of 2-butene.

**3.5. Reaction Intermediates.** RAIRS data for the key reaction intermediates produced by annealing the main C<sub>4</sub> adsorbates on Pt(111) at 180–230 K are displayed in Figure 8. These include buta-1,2-diyl, buta-2,3-diyl, but-3-ene-1-yl, 1-methylallyl, and buta-1,2,3,4-tetra-yl. Tentative vibrational assignments are listed in Table 2. Notice in particular that di- $\sigma$  bonded intermediates are proposed for the 1- and 2-iodobutanes after mild (230 K) thermal activation, following C–I bond scission and



**Figure 9.** RAIRS spectra for 1-butene on Pt(111) as a function of annealing temperature. These data provide clear evidence for the conversion of the initial di- $\sigma$  adsorbed olefin (the buta-1,2-diyl surface intermediate) to butylidyne around room temperature.

$\beta$ -H elimination.<sup>22,55,59</sup> This is based on the similarities of their spectra with those of adsorbed 1-butene and 2-butene, respectively.

As an example of the thermal chemistry that takes place at higher temperatures, the RAIRS data for 1-butene adsorbed on Pt(111) at a few preselected adsorption temperatures are displayed in Figure 9. The most prominent features in the low-temperature range are the carbon–carbon single-bond stretching [ $\nu$ (CC)] and the methyl symmetric deformation [ $\delta$ (CH<sub>3</sub>)] modes, at 1106 and 1369 cm<sup>−1</sup> respectively, of the di- $\sigma$  bonded olefin. Both those modes disappear at 270 K but grow back at higher temperatures, albeit on the higher-frequency side of the spectra. Moreover, a new peak is seen at 1331 cm<sup>−1</sup> above 280 K, indicative of a CH<sub>2</sub> wagging mode. The methyl symmetric stretching [ $\nu$ <sub>s</sub>(CH<sub>3</sub>)] and the CH<sub>2</sub> asymmetric stretching [ $\nu$ <sub>s</sub>-(CH<sub>2</sub>)] modes also shift upon heating to ~280 K, from 2866 and 2928 to 2872 and 2933 cm<sup>−1</sup>, respectively. Finally, the methyl asymmetric stretching mode [ $\nu$ <sub>a</sub>(CH<sub>3</sub>)] at about 2960 cm<sup>−1</sup> almost disappears. All these changes indicate a conversion

**TABLE 2: Vibrational Assignments for the RAIRS Data of the C<sub>4</sub> Moieties Prepared by Heating Adsorbed 1-Butene (1B), 1-Iodobutane (1IB), *cis*-2-Butene (c2B), *trans*-2-Butene (t2B), 2-Iodobutane (2IB), 1-Bromo-3-butene (1B3B), 1-Bromo-2-butene (1B2B), and 1,3-Butadiene (13BD) Adsorbed on Pt(111) at 180–230 K, as Shown in Figure 8<sup>a</sup>**

	buta-1,2-diyl		buta-2,3-diyl			but-3-ene -1-yl	$\eta^3$ 1-methyl allyl	buta-1,2 ,3,4-tetra yl
modes	1B	1IB	c2B	t2B	2IB	1B3B	1B2B	13BD
$\nu_s(=CH_2)$						2987 (m)		
$\nu_a(CH_3)$	2960 (m)	2955 (m)		2964 (m)	2967 (w)		2958 (m)	
$\nu(CH)$						2949 (w)		
$\nu_a(CH_2)$	2928 (s)	2929 (s)				2926 (w)	2937 (m)	
$\nu(CH)$				2913 (m)	2937 (s)			2907 (s)
$\nu_s(CH_3)$	2866 (s)	2868 (s)	2861 (m)	2871 (m)	2877 (s)		2868 (s)	
$\delta_a(CH_3)$							1455 (m)	
$\gamma(CH_2)$						1435 (m)	1450 (w)	
$\delta_s(CH_3)$	1369 (s)	1369 (s)		1364 (w)			1369 (s)	
$\omega(CH)$			1242 (w)	1252 (w)			1202 (m)	
$\gamma(CH)$				1102 (m)	1103 (m)			
$\rho(CH_3)$			1023 (s)	1025 (s)	1026 (m)	1040 (w)	1037 (m)	
$\nu(CC)$						1013 (m)	1008 (w)	1023 (m)
$\omega(CH), \omega(CH_2)$						930 (w)	969 (w), 919 (m)	995 (m), 920 (m)

<sup>a</sup> Frequencies are reported in cm<sup>−1</sup>, and relative intensities are given in parentheses: s = strong, m = medium, w = weak.





Steric effects also appear to play a key role in defining the relative rates for the alkyl–olefin interconversion, and with that the selectivity among the hydrogenation–dehydrogenation and isomerization processes. For instance, the large TPD peak seen at 225 K for the butene production from 2-butyl in the presence of coadsorbed hydrogen (Figure 4) attests to the facile nature of the  $\beta$ -hydride elimination step from those groups. On the other hand, only a small amount of butene is made from 1-butyl, and that desorbs mainly around 250 K. Also, while the reaction of 1-butyl with coadsorbed deuterium only produces butene-*d*<sub>0</sub> (at 260 K), implying no H–D exchange, 2-butyl dehydrogenation does produce about 10% of butene-*d*<sub>1</sub> (about 220 K), the result of one H–D exchange cycle (Figure 7). Clearly,  $\beta$ -hydride elimination is much faster from 2-butyl than from 1-butyl, but, in addition, the reverse insertion of the resulting olefin into a metal–hydrogen bond is even faster with 2-butene (where it competes with the dehydrogenation) than with 1-butene (where olefin desorption is dominant).

It can be concluded from the preceding discussion that, while hydrogenation (reductive elimination) is favored at the terminal carbons of adsorbed alkyl species, dehydrogenation ( $\beta$ -hydride elimination) prevails at the inner carbons. Note that the RAIRS data in Figure 8 shows that the dehydrogenation of the 2-butyl surface species leads to the exclusive formation of adsorbed 2-butene. Also, only two (presumably internal) hydrogens are exchanged during the H–D exchange in 2-butene. With 1-butene a maximum of three isotope exchanges is observed, because in that case an initial deuteration to 2-butyl is required before the same rapid  $\beta$ -hydride elimination/butene insertion into a Pt–D bond cycle that account for inner hydrogen exchange in 2-butene can occur. A corollary from this observation is the fact that 1-butene isomerizes rapidly to the more stable 2-butene on the Pt(111) surface. A comparative analysis of the data for *cis*- vs *trans*-2-butene also suggests that the latter can be converted into the former more easily than the other way around (Figure 6). On the basis of the desorption temperatures of the molecular olefins, their adsorption energies are estimated to follow the sequence *cis*-2-butene < *trans*-2-butene < 1-butene, at least on hydrogen-precovered surfaces (Figures 4 and 6).

The surface decomposition of the C<sub>4</sub> species studied here takes place in several temperature regimes, as indicated by the data in Figure 2, and leads to the formation of several partially dehydrogenated surface intermediates. Interestingly, most of the hydrogen TPD traces, in particular those from the alkyls and 2-butenes, are quite similar (Figure 2). This suggests the formation of a common surface intermediate around 300 K with C<sub>4</sub>H<sub>6</sub> stoichiometry, previously identified as adsorbed 2-butyne.<sup>33</sup> Butadiene behaves differently, but the same C<sub>4</sub>H<sub>6</sub> species appears to form from activation of the methylallyl species prepared by thermal activation of 1-bromo-2-butene. This may be understood in terms of a previous hydrogenation of the allyl intermediate to butene, some of which in fact desorbs even in the absence of coadsorbed hydrogen (Figure 3); a similar reaction sequence was reported by us with C<sub>3</sub> species.<sup>43,44</sup> The exception to this behavior is 1-butene, which converts directly to butylidyne (Pt<sub>3</sub>≡CCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>),<sup>33</sup> as evidenced directly by the RAIRS data in Figure 9. Butylidyne formation most likely occurs via an unstable butylidene (Pt=CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>) intermediate.<sup>25</sup> It could also be inferred that the but-3-ene-1-yl surface species prepared with 1-bromo-3-butene may form but-3-ene-1-ylidyne (Pt<sub>3</sub>≡CCH<sub>2</sub>CH=CH<sub>2</sub>), although the stoichiometry obtained from the H<sub>2</sub> TPD data is somewhat higher than what would be expected in that case.

Both 1-bromo-2-butene and 1-bromo-3-butene display similar behavior in terms of the production of butene, which desorbs about 300 K from clean platinum (Figure 3) and in two stages about 220 and 270 K on surfaces preadsorbed with hydrogen (Figure 4). Virtually no butene desorbs from butadiene on clean Pt(111) (a small amount is in fact seen around 360 K), which means that at least some of the eneyl species produced from the bromobutenes may not dehydrogenate extensively to butadiene, but rather hydrogenate at the alkyl position to yield the corresponding butenes. This most likely implies adsorption of some of the allyl intermediate in a  $\eta^1$  configuration, at least at saturation. Indeed, the butene that desorbs around 260 K in the TPD experiments with 1-bromo-2-butene coadsorbed with deuterium contains only one deuterium atom (Figure 7), indicating direct hydrogenation (deuteration) of the  $\eta^1$ -but-2-ene-1-yl intermediate to 2-butene. On the other hand, the extensive H–D exchange observed at 230 K must come from a  $\eta^3$ -butenyl. Again, all this parallels what was reported for propenyl surface species.<sup>43</sup> The small amount of butene produced from butadiene + deuterium also comes off the surface as a mixture of all possible isotopologues, up to perdeuterobutene (Figure 6, the data are somewhat noisy, but the features between 200 and 300 K are reproducible). On the basis of these observations, we propose that in both cases an interconversion of  $\eta^3$ -butenyl and buta-1,2,3,4-tetrayl may be responsible for the complete isotope exchange at the two terminal methyl moieties and that such exchanged allylic species may then be hydrogenated (deuterated) to buta-2,3-diyl, which can further exchange its inner hydrogens before desorbing as 2-butene.

The case of 1-bromo-3-butene is particularly curious. The  $\eta^1$ -but-3-ene-1-yl surface species produced by early scission of the C–Br bond is expected to undergo facile  $\beta$ -hydride elimination to a new moiety with the same stoichiometry as 1,3-butadiene. However, the butene TPD traces from clean and H- and D-predosed Pt(111) for 1-bromo-3-butene are all significantly different from those for 1,3-butadiene (Figures 3, 4, and 7). It may be that the butadiene that forms from the eneyl species bonds to the surface in a di- $\sigma$  configuration (but-3-ene-1,2-diyl) rather than via the tetra- $\sigma$  interaction (buta-1,2,3,4-tetrayl) identified for butadiene by RAIRS (Figure 8). We speculate that, since 1-bromo-3-butene surface saturation is achieved before any  $\beta$ -hydride elimination takes place (because that step requires heating), the surface may be too crowded to accommodate a multiple coordination species. 1,3-Butadiene, by contrast, has ample time to accommodate into its most stable bonding configuration as it is dosed on the surface.

Following this proposal, a rapid sequence of hydrogenation–dehydrogenation reversible steps at the second carbon (via an interconversion between the but-3-ene-1,2-diyl and the original but-3-ene-1-yl intermediates) followed by final deuteration at the C<sub>1</sub> position of the butenyl may explain the three deuterium substitutions seen in the butene TPD peaks at 210 and 270 in Figure 7. A slower exchange sequence at the C<sub>1</sub> carbon involving a but-3-ene-2-yl intermediate would account for the butene-*d*<sub>4</sub> and -*d*<sub>5</sub> seen as broad peaks about 255 K. It is interesting to note that the extensive H–D exchange seen with the 1-bromo-3-butene is not paralleled by that observed with 1-iodobutane, even though both are proposed to follow similar mechanisms. It is quite possible that the particular lability of the allyl hydrogen in the but-3-ene-1-yl species allows for the  $\beta$ -hydride elimination step to compete favorably with reductive elimination reactions. 1-Butyl, on the other hand, prefers to incorporate a hydrogen at the C<sub>1</sub> position and form butane directly. This high reactivity at the allylic position may also

explain the slight preference for the formation of but-3-ene-1-yl over but-3-ene-2-yl upon hydrogenation of but-3-ene-1,2-yl, although the former involves an inner carbon and the latter a terminal one.

The hydrogen TPDs for 1-bromo-3-butene and 1,3-butadiene do start resembling each other above 380 K, at which point the average stoichiometry of the adsorbed species is  $C_4H_4$ . We suggest that this may correspond to the formation of a metallacyclic species, perhaps  $CH(Pt)CH=CHCH(Pt)$ . Similar intermediates have been isolated on other metals starting from butadiene<sup>61</sup> and are also known in the organometallic literature.<sup>16</sup>

Both the selective hydrogenation of 1,3-butadiene and the hydrogenation and isomerization of polyunsaturated olefins are central catalytic processes in the oil reforming and food industries.<sup>3,62–64</sup> The activity and selectivity of those reactions have been shown to depend on subtle ways on both the nature of the catalyst and the conditions used.<sup>65–67</sup> It can be seen from the data reported here that the selectivities in particular can vary significantly upon small changes in relative rates for the competing surface steps available (hydride and reductive eliminations, olefin insertions) to key alkyl, diyl, and enyl intermediates.<sup>13,68</sup> This may be tuned by preparing catalysts with optimized structural and electronic properties.

## 5. Conclusions

The thermal reactions of  $C_4$  moieties adsorbed on Pt(111) were investigated by TPD and RAIRS.  $H_2$  TPD data indicate stepwise dehydrogenation, and IR spectra confirm the formation of key surface species such as alkyls, di- $\sigma$  bonded olefins,  $\eta^1$ - and  $\eta^3$ -allyls, other eneyls, and metallacycles. Interconversion among those intermediates occurs in a stepwise manner and involves surface elementary steps such as  $\beta$ -hydride and reductive eliminations and olefin insertions into Pt–H bonds. Steric effects play an important role in defining reaction selectivities, with dehydrogenation steps dominating at the inner carbon atoms of the hydrocarbon chain and hydrogenation competing favorably in many reactions involving terminal carbons.

The general observations summarized above help explain some specific observations from our experiments with the various  $C_4$  hydrocarbons. For instance, while 1-butyl groups prepared by surface thermal decomposition of 1-iodobutane can be easily hydrogenated to butane, 2-butyl (from 2-iodobutane) mostly yields butene instead, even if hydrogen or deuterium is preadsorbed on the platinum surface. On Pt(111) precovered with deuterium, only a maximum of two H–D exchanges is possible in adsorbed 2-butene, presumably at the inner carbon atoms, but up to three isotope replacements are seen in 1-butene, most likely because of its initial conversion to the more favored 2-butene via an initial deuteration to a 2-butyl intermediate. Finally, 1-bromo-2-butene produces a series of  $\eta^1$  and  $\eta^3$  allylic intermediates, while 1-bromo-3-butene initially forms a  $\eta^1$ -bonded enyl species capable of exchanging up to five deuterium atoms in three different temperature regimes by interconverting with an enediyl surface moiety. The latter dehydrogenates further at higher temperatures and eventually follows the same surface chemistry as 1,3-butadiene.

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