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Hydrogenation and H-D Exchange Reactions of C_3-C_6 Substituted Alkenes on Fe(100)

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Abstract: The adsorption and reaction of propylene, 1-butene, isobutene, *cis*- and *trans*-2-butene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene were studied on H-saturated Fe(100) (designated Fe(100)-H). Molecular desorption of both propylene and 1-butene occurs below 200 K, without incorporation of deuterium on Fe(100)-D. However, there are reaction pathways that form alkenes above 200 K and readily incorporate deuterium. These reactions are attributed to the β-hydride elimination of stable alkyls. Some alkane is formed from propylene and 1-butene, but the yield from β-hydride elimination to form the alkenes is much greater. The extent of H-D exchange in the alkene indicates that the surface alkyls formed are predominantly terminal. Multiple H-D exchange into the alkenes occurs to a minor extent and is attributed to surface defects; apparently internal alkyls (secondary, tertiary) form only at defect sites. Isobutene forms surface alkyls to a much lesser extent than does 1-butene, presumably due to additional steric hindrance about the carbon-carbon double bond. However, isobutyl groups appear to have a much greater propensity for alkane formation than do propyl and *n*-butyl. The internal alkenes *cis*-2-butene, *trans*-2-butene, and 2-methyl-2-butene yield less alkane than does 1-butene, and the sterically hindered tetrasubstituted 2,3-dimethyl-2-butene does not hydrogenate to a measurable extent.

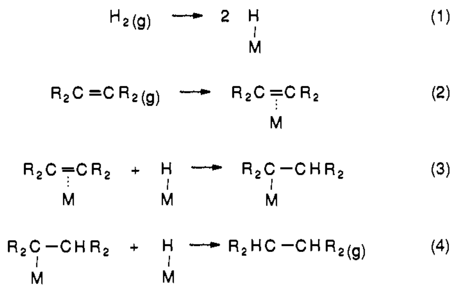
Introduction

Hydrogenation of alkenes is one of the most well-studied reactions catalyzed by transition metals in both homogeneous and heterogeneous systems.[1] The accepted hydrogenation mechanism in both regimes generally consists of four steps (Scheme I): (1) dissociation of H_2 to form M-H bonds, (2) coordination of alkene to the metal, (3) the migratory insertion reaction between H and the coordinated alkene to form an alkylmetal, and (4) the reductive elimination reaction between H and alkyl to produce alkane.

The ordering of steps 1 and 2 in the reaction sequence may be reversed for various catalytic systems, and the rate-limiting step may also vary among different systems. However, these four steps are well established for alkene hydrogenation catalyzed by several transition-metal complexes, including Wilkinson's catalyst, $RhCl(PPh_3)_3$,[2-4] and $[(diphos)Rh]^+$.[2,3,5] For the latter complex, the alkyl hydride intermediate has been directly observed.[3,5] These four steps for alkene hydrogenation catalyzed by transition-metal surfaces were first proposed by Horiuti and Polanyi in 1934,[6] and their existence is strongly supported by a variety of results (see ref 1 for a recent review). First, the H-D exchange of alkanes on metal surfaces is consistent with the formation of a surface alkyl, followed by repeated steps of β-hydride elimination and migratory insertion, terminated by the elimination of alkane.[7,8] Second, alkene isomerization by double-bond migration[9,10] is also consistent with the formation of an alkyl intermediate (step 3) followed by β-hydride elimination from a carbon other than that which gained the H atom in the insertion step. Last, the stereochemistry of alkane products from alkene hydrogenation indicates that predominantly cis addition of the two H atoms occurs, which is consistent with the stepwise addition of H atoms via an alkyl intermediate.[11] However, surface alkyl intermediates have yet to be directly observed in heterogeneous catalytic systems, and much remains unknown about the kinetics of individual steps.

An alternative mechanism for the heterogeneous catalytic hydrogenation of alkenes has been proposed that relies on the transfer of H atoms from adsorbed hydrocarbon fragments to adsorbed alkene.[12-15] Specifically for ethylene hydrogenation on a Pt(111) crystal near atmospheric pressure, the proposed mechanism involves addition of hydrogen to stable surface ethylidyne fragments ($\equiv CCH_3$) to form ethylidene ($=CHCH_3$).[13-15] A concerted reaction between gas-phase ethylene and two ethylidene fragments would then yield ethane and regenerate ethylidyne. Beebe and Yates, however, have found this mechanism inoperative for the hydrogenation of ethylene catalyzed by Pd particles supported on Al_2O_3.[16]

Scheme I



Previous studies on single crystals of transition metals under ultrahigh vacuum (UHV) have focused primarily on modes of decomposition of ethylene, as we have summarized elsewhere.[17] The only substantial mechanistic study of ethylene hydrogenation is for Pt(111).[14] In this case, an alkyl intermediate was not directly identified, but the kinetics of ethane formation were accurately modeled by assuming a rapid equilibrium between adsorbed ethylene and an ethyl intermediate. The rate-determining step

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in ethane formation was inferred to be the reductive elimination of H adatoms and ethyl groups; the proposed pathway is that depicted by Scheme I.

Very little work has been reported regarding the hydrogenation of larger alkenes under UHV conditions. It has been found that propylene will *not* self-hydrogenate on Rh(111),[18] Ir(111) and Ir(110)-(1*x*2),[19] Ni(100),[20] and Pt(111).[21] No studies have been reported for the coadsorption of propylene and hydrogen. For 1-butene, some self-hydrogenation occurs on Mo(100) and the butane yield is enhanced by preadsorbed hydrogen.[22] In contrast, *cis*- and *trans*-2-butene do not self-hydrogenate on Mo(100) but do hydrogenate when H or D adatoms are preadsorbed. All three linear butenes neither self-hydrogenate nor hydrogenate on Re(0001).[23] Additional null results have been reported for the self-hydrogenation of 1-butene on Ni(100),[20] of *cis*-2-butene on Fe(100),[24] and of 1-butene, isobutene, and 1-pentene on Pt(111).[21] However, Pd(111) and (100) have been found to be quite active for a variety of hydrogenation reactions,[25,26] forming ethane from ethylene, norbornane from norbornadiene, and cyclohexane from benzene on the hydrogen precovered surfaces.

We have recently reported evidence for the validity of Scheme I for the hydrogenation of ethylene on hydrogen-presaturated Fe(100) (designated Fe(100)-H).[17,27] Evidence of formation of the ethyl intermediate includes (1) the facile incorporation of deuterium into ethylene on Fe(100)-D and (2) the primary kinetic isotope effects observed in the reactions of deuterium-substituted ethylene, which are consistent with a rate-limiting β-hydride (D) elimination reaction that yields ethylene from the surface.[17] Direct hydrogenation of this intermediate to ethane is induced by the postadsorption of CO,[27] completing the pathway outlined in Scheme I and lending support to the existence of the ethyl intermediate. The stability of the ethyl intermediate on Fe(100)-H allowed us to evaluate the rate constants for the migratory insertion reaction to form ethyl groups and the β-hydride elimination reaction to yield ethylene.[17]

In the work reported here we have extended the study of alkene H-D exchange and hydrogenation reactions on Fe(100)-H to several C_3-C_6 alkenes; the primary technique used was temperature-programmed reaction spectroscopy (TPRS) with isotope-exchange reactions. With the exception of 1-butene, the molecules studied here were methyl-substituted ethylenes.

Experimental Section

All experiments were performed in a stainless steel ultrahigh vacuum chamber with a base pressure of 1 × 10^{-10} Torr. TPRS experiments utilized a quadrupole mass spectrometer (UTI 100C) modified with a collimating orifice approximately 0.8 cm in diameter. A chromel-alumel thermocouple was spotwelded to the Fe(100) sample, and the mass spectrometer and thermocouple signals were interfaced to a computer. The mass spectrometer signal was multiplexed to monitored up to eight masses in a single experiment. A liquid nitrogen cooling system allowed sample temperatures as low as 110 K to be reached. Two capillary array dosers were used so that contamination of a given adsorbate sample by other gases being used was minimized. Surface elemental composition was determined by Auger electron spectroscopy (AES), and long-range ordering of adsorbates was monitored with use of low-energy electron diffraction (LEED).

Details of the preparation and initial cleaning of the Fe(100) crystal are given elsewhere.[28] Routine cleaning was achieved by Ar ion bombardment with a sample temperature of 700 K. This temperature was high enough to allow diffusion of impurities from the bulk, but low enough that carbon preferentially resided at the surface rather than in the bulk, so it could be sputtered away more effectively. After each bombardment, the crystal was annealed at 1020 K for 30 s. This resulted in a sharp p(1×1) LEED pattern. The bulk impurity levels were low enough so that impurity segregation to the surface did not occur at the high temperatures reached during a TPRS scan. Surface cleanliness was determined by AES with absolute coverages of carbon, oxygen, and sulfur calibrated in correlation with LEED patterns: Carbided and sulfided Fe(100) each display a c(2×2) pattern at the adatom saturation coverages of 0.5 ML, where 1 ML equals the Fe(100) surface atom density of 1.22 × 10^{15} atom/cm^2. A c(2×2) pattern is also formed by saturation of the CO dissociative state, resulting in surface coverages of 0.25 ML each for carbon and oxygen. Our cleaning procedures resulted in surface carbon levels of approximately 0.03 ML, with oxygen levels of 0.01-0.02 ML.

Table I. Calibrated Mass Spectrometer Sensitivities Relative to Ethylene (*m*/*q* 28)

molecule	*m*/*q*	correction factor
ethylene	28	1.0
propylene	42	2.2
propane	29	0.73
1-butene	56	3.4
cis-2-butene	56	2.9
trans-2-butene	56	3.0
n-butane	43	0.80
isobutene	56	3.0
isobutane	43	0.71
2-methyl-2-butene	70	4.1
2-methyl-butane	57	2.9
2,3-dimethyl-2-butene	84	6.0
2,3-dimethyl-butane	71	6.6

TPRS experiments were performed by dosing reactants with the Fe sample at 110 K and by desorbing species through the collimator directly into the mass spectrometer. Gases were dosed directly by placing the crystal approximately 0.5 cm in front of the doser. Absolute exposures of hydrogen were calibrated via a combination of background and direct doses as described previously.[28] The saturation coverage of H atoms on Fe(100) was determined to be 1.0 monolayer.[28] Alkenes and CO have high sticking probabilities as well as large enhancement factors for direct dosing, the sum of which results in a large uncertainty in experimental values of the exposure. Absolute alkene and CO exposures therefore were not determined.

Absolute coverages of hydrocarbons evolved during TPRS were estimated by calibrating the sensitivity of the mass spectrometer for each product relative to ethylene. The procedure has been detailed elsewhere[27] and involved the experimental determination of mass spectral cracking patterns for ethylene as well as for identified TPRS products. Cracking patterns were corrected for ionization probabilities, mass spectrometer gain, and quadrupole transmission efficiency. The resulting correction factors for each molecular product identified in this work are listed in Table I. The same mass spectrometer was used for the calibration as was used in TPRS experiments. Absolute coverages of ethylene evolved during TPRS were estimated by a hydrogen and deuterium balance in the H-D exchange reaction of C_2H_4 on D-saturated Fe(100).[17] No decomposition of ethylene occurs on this surface, and the only gas-phase products evolved are hydrogen, ethylene, and their isotopes. The coverages of H adatoms deposited in this reaction thus must equal the D atom content of the desorbing ethylene. The TPRS traces of deuterated ethylenes were deconvoluted to correct for mass spectral fragmentation. With use of the hydrogen saturation coverage of 1.0 ML as a calibration standard along with the hydrogen-deuterium balance, the ethylene coverage/TPRS area ratio was determined. The accuracy of this ratio is ±20%.[17] To estimate other hydrocarbon product yields, the integrated TPRS area for a given product is multiplied by the (surface coverage)/(integrated TPRS area) ratio found for ethylene and by the correction factor for the mass spectrometer sensitivity relative to ethylene (Table I). However, since our collimated mass spectrometer detects products directly as they desorb, in a line-of-sight configuration, and since the signals reflect gas-phase molecular densities and not fluxes (see, e.g., ref 29), a $T^{1/2}$ correction was applied to the relative amounts of desorbing species, against the 220 TPRS state as the reference. This correction is based on the assumptions that the translational energy of desorbing

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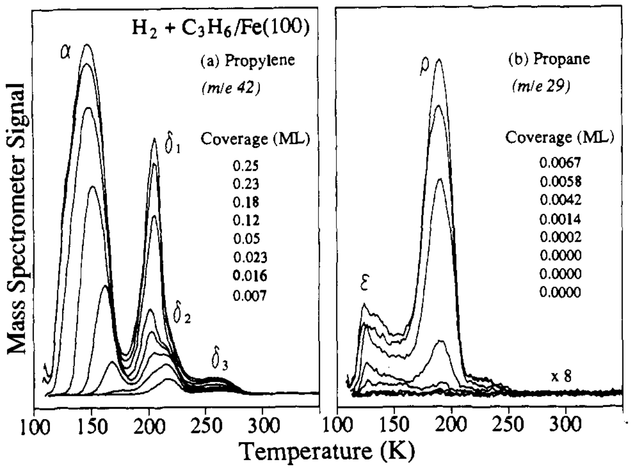

Figure 1. Temperature-programmed reaction spectra of (a) propylene and (b) propane after deposition of propylene on Fe(100)-H. Heating rates are approximately 10 K/s.

molecules scales with the temperature of the surface during desorption and that angular profiles of all desorbing species are the same. Absolute coverages of hydrocarbons reported here have an uncertainty of approximately 30% due to the uncertainties in the coverage of the ethylene standard and in the calibration of correction factors for the mass spectrometer sensitivity. Errors are also introduced by possible differences in product angular distributions and by possible deviations in the product translational energies from those expected on the basis of surface temperature. Parent ions were monitored to determine product yields for all alkenes, and the parent minus a methyl group (parent − 15) for all alkanes (Table I). Without exception, this led to optimal signal/noise for the species monitored, with minimal interference from the mass spectral cracking fragments of other species. The parent ion was identified for all alkane products, even though it is a minor fragment for large alkanes.

Results

1. Propylene on Fe(100)-H. Propylene desorbs from the H-saturated Fe(100) surface in four states (Figure 1), two of which saturate at total coverages below 0.02 ML. The features are nearly identical with those found for ethylene on this surface;[17] a minor state at 220 K (δ_2) saturates at low coverages before the α and δ_1 states grow in together. The total saturation coverage of propylene in all states is estimated to be 0.25 ML.

Since the α state does not incorporate deuterium when C_3H_6 is adsorbed onto Fe(100)-D, this state of propylene is attributed to desorption of molecularly adsorbed alkene. Furthermore, the δ_1 state is attributed to β-hydride elimination of surface-bound propyl groups (C_3H_7) (i.e., the reverse of step 3 in Scheme I), because the pattern of isotopes formed by C_3H_6 on Fe(100)-D and the kinetics of evolution mimic those seen for β-hydride elimination of ethylene. The minor δ_2 state of propylene was also seen for ethylene desorption,[17] but the δ_3 state has no counterpart in TPRS spectra for ethylene on Fe(100)-H. Due to their low amounts, these states may originate at surface defects, but the possibility cannot be ruled out that an intermediate other than an alkyl is formed in small quantity. A surface allyl, for instance, could be formed by propylene, whereas no analogous species would arise from ethylene adsorption. Regardless of the identity of the δ_3 surface intermediate, because of the small population of this state at saturation, we do not discuss it further.

A very small amount of propane is evolved during the temperature-programmed reaction of propylene on Fe(100)-H (Figure 1b), in contrast to the results for ethylene adsorption, in which no ethane was formed.[17] Propane is evolved in two states, ϵ and ρ, at 130 and 185 K, respectively. In separate desorption experiments, molecular propane desorption was determined to occur at 130 K; the kinetics of the ϵ state thus are governed by molecular desorption of propane (i.e., it is desorption-limited). A small propane impurity in the sample could easily lead to adsorbed molecular propane of this quantity. The kinetics of the ρ state, however, appear to be determined by the reductive elimination reaction between H adatoms and surface propyl groups; i.e., the ρ state is reaction-limited. The population of the δ_1 state indicates that propyl groups form readily. The simultaneous growth of the α and δ_1 states with propylene exposure suggests that molecular desorption of propylene and propyl formation are competing reactions. By analogy to the nearly identical, but more thoroughly studied, ethylene/Fe(100)-H system, the migratory insertion to form propyl groups probably occurs during heating in the same temperature range where propylene molecularly desorbs—ca. 160 K. The high product yield ratio of δ_1-propylene to ρ-propane of approximately 10/1 indicates that the slow step in the evolution of propane at 185 K is the reductive elimination reaction between H adatoms and propyl groups rather than the initial formation of propyl groups. In addition, the formation of propane does not compete effectively with the β-hydride elimination but occurs to a lesser extent suggests that the reductive elimination occurs only on a small fraction of the surface. The small yield of ρ-propane we attribute to the adsorption of CO from the background, since CO coadsorption with C_2H_4[27] or propylene on Fe(100)-H promotes hydrogenation. With ethylene, no hydrogenation occurs unless CO is coadsorbed.[27] The surface coverage of CO arising from adsorption of background gas was approximately 0.004 ML in these experiments. There is no significant difference in the propane product peak temperature or peak shape between the "CO-free" surface and an Fe(100)-H surface on which 0.03 ML of CO has been adsorbed before propylene adsorption (Figure 2). The amount of propane evolved is approximately 3 times greater when this small amount of CO is coadsorbed.[30]

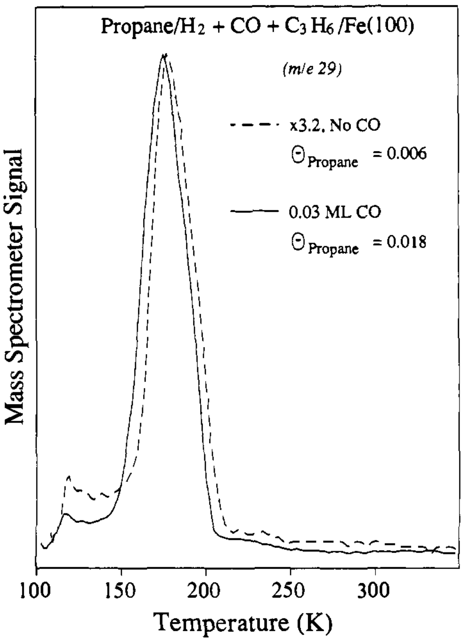

Figure 2. Temperature-programmed reaction spectra of the propane product evolved following the absorption of a saturation coverage of propylene on Fe(100)-H at 110 K. The dashed line has been multiplied by 3.2 and reflects the formation of propane in the absence of coadsorbed CO; the propane yield is 0.006 ML. The solid line illustrates propane formation when 0.03 ML of CO is adsorbed onto Fe(100)-H before propylene adsorption, with a propane yield of 0.018 ML.

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(30) The signal for m/q 29 for the propane products in Figure 2 should be influenced little by fragmentation of propylene since the ratio of m/q 29 to m/q 42 in our experimental propylene cracking pattern is 0.01. Even for the small amount of propane evolved when no CO is coadsorbed, the contribution of propylene to the total integrated signal in m/q 19 is at most 14%. Subtraction of this contribution does not change the m/q 29 peak temperature; only the signal level between the ϵ and ρ states is lowered slightly. Furthermore, an identical propane peak shape was recorded at m/q 44; the natural abundance of ^{13}C is 1%, which would lead to a propylene contribution of only 6% of the total integrated signal in m/q 44. The peak shapes and temperatures in m/q 29 and m/q 44 thus appear to reflect the kinetics of propane evolution.

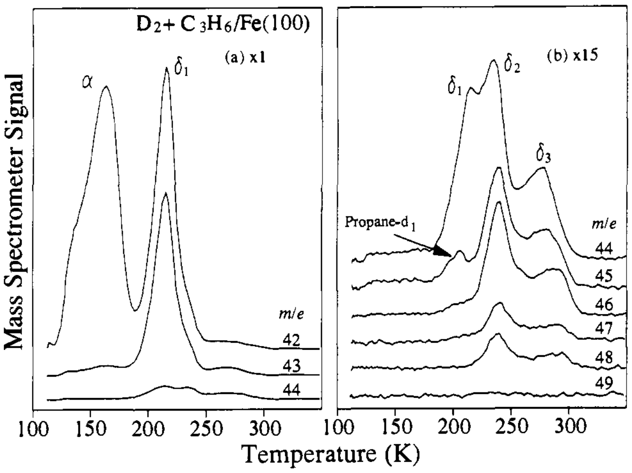

Figure 3. Temperature–programmed reaction spectra of deuterated propylene following propylene adsorption onto Fe(100)-D at 110 K. The heating rate is approximately 10 K/s.

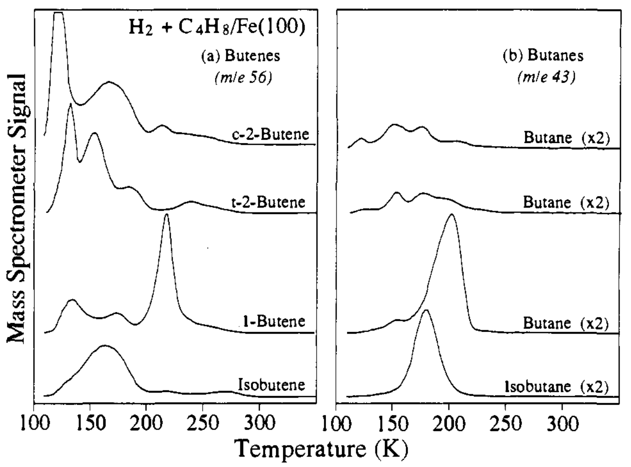

Figure 4. Temperature-programmed reaction spectra of (a) butenes and (b) butanes following the adsorption of each butene isomer on Fe(100)-H. Heating rates are approximately 10 K/s.

Table II. Alkane and Alkene Temperature-Programmed Reaction Yields for Alkenes Adsorbed on Fe(100))-H[a]

	alkene yield (ML)				
alkene	total[b]	from alkyl	alkane yield (ML)	carbon deposited (ML)	total alkene adsorbed[c] (ML)
propylene	0.25	0.08	0.008	0.01	0.27
1-butene	0.30	0.19	0.030	0.04	0.35
isobutene	0.18	0.02	0.016	0.09	0.22
cis-2-butene	0.23	0.04	0.006	0.04	0.25
trans-2-butene	0.20	0.07	0.009	0.05	0.23
2-methyl-2-butene	0.14	0.03	0.008	0.05	0.16
2,3-dimethyl-2-butene	0.10	0.00	0.000	0.14	0.13

[a] Each value is the average of results for three TPRS experiments. [b] Multilayer desorption was excluded from the estimate of the total amount of alkene evolved during TPRS. [c] The total alkene coverage was estimated by the sum of alkene and alkane yields plus $\Delta\theta_C/n$, where $\Delta\theta_C$ is the coverage of carbon deposited from alkene decomposition and n is the number of carbon atoms in the alkene.

2. Propylene on Fe(100)-D. When propylene is adsorbed onto the D-presaturated Fe(100) surface, no H–D exchange occurs in the α state, while up to six deuterium atoms are incorporated in the δ propylene states (Figure 3). Only 4% of the total integrated signal in m/q 48 can be attributed to ^{13}C impurities due to the natural abundance of ^{13}C in propylene products containing fewer than six D atoms. Thus, it appears that all the hydrogen atoms in propylene can be exchanged, even if only to a limited extent. These H–D exchange results support our assignment of the α state to the desorption of molecularly adsorbed propylene and indicate that the δ states arise from a surface intermediate that has either gained or lost hydrogen. As mentioned above, we assign the δ states to β-hydride elimination of surface propyl groups, based the similarity of the results for propylene with those of ethylene,[17] for which extensive studies were conducted. The amount of m/q 44 in the small δ_1 state can be attributed to ^{13}C impurities in propylene-d_1; no detectable formation of propylene-d_2 occurs in the δ_1 state. This result contrasts with H–D exchange in ethylene, where up to three (and possibly four) D atoms are incorporated in the δ_1 state due to reversible formation of a chemisorbed ethylene intermediate during the β-hydride elimination of ethyl groups. However, the peak shapes, temperatures, and populations of the α and δ_1 states of propylene are nearly identical with those of ethylene. This similarity suggests that the kinetics for the elementary steps of molecular desorption of alkene, migratory insertion to form alkyl, and β-hydride elimination of the alkyl do not differ significantly between the two. The absence of multiple H–D exchange in the δ_1 state of propylene indicates that only primary alkyls are formed and only the central carbon of propylene is available for H–D exchange. The lack of multiple exchanges in δ_1-propylene and the dominance of the δ_1 state thus imply that propylene forms terminal, but not internal, alkyls on the defect-free surface terraces, since the δ_1 state is the only alkyl state that is not clearly attributable to defects.

H–D exchange in the δ_2 and δ_3 states yields full deuteration of propylene. As stated above, the intermediate giving rise to the δ_3 state is unknown, but we suggest that the δ_2 state arises from β-hydride elimination of propyl groups bound at defect sites. At defects such as steps there is less steric constraint, and the terminal carbons of propylene may become available for H–D exchange, with repeated D incorporation and β-hydride elimination occurring before the propylene product desorbs. Furthermore, that different surface sites are involved for the δ_2 state is at least consistent with its higher temperature relative to δ_1.

Only a small state attributable to propane is formed following propylene adsorption on Fe(100)-D (Figure 3). Less propane is formed relative to that for the Fe(100)-H surface. This result is consistent with either less CO desorption from the background or a normal kinetic isotope effect for the addition of a D adatom to the propyl group to form propane, which reduces the rate of reductive elimination to that of β-hydride elimination of propyl-d_1 groups, so the yield of propane is reduced.

3. Butenes on Fe(100)-H. The desorption of butene isomers adsorbed on Fe(100)-H suggests that the formation of surface alkyls followed by β-hydride elimination is significant only for 1-butene. The butene desorbed for isobutene and *cis*- and *trans*-2-butene arises predominantly from molecular desorption (Figure 4). Like propylene and ethylene, 1-butene exhibits a sharp peak in the temperature-programmed reaction spectrum attributable to β-hydride elimination of a surface alkyl at 220 K; this state also undergoes H–D exchange to yield predominantly butene-d_1. Butene containing up to eight D atoms, however, is formed in small states in the high-temperature tail of the β-hydride elimination region; these states clearly originate from a different reaction pathway. The possible influence of defects in their case cannot be eliminated. The 1-butene states below 200 K do not undergo H–D exchange and thus arise from molecular desorption. Following a saturation exposure of 1-butene, 0.30 ML of butene desorbs, 0.19 ML of which is evolved at 220 K (Table II).

A saturation exposure of 1-butene on Fe(100)-H also yields 0.030 ML of butane at 210 K. The butane peak cuts off sharply at the high-temperature edge as the rate of the competing β-hydride elimination becomes rapid. A residual carbon coverage of approximately 0.04 ML remains following the reaction. As

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(31) The TPRS traces in Figure 3 for propylene-d_n are uncorrected with regard to mass spectral fragmentation. Our measured mass spectral cracking pattern of propylene shows that the ratio of the signals for the ion at m/q 41 to the parent ion at m/q 42 is 1.6; the ratio for m/q 42 to m/q 43 in the δ states is 1.5 in the H–D exchange experiments, suggesting that the signal in m/q 42 for the δ states in Figure 3 is nearly entirely due to fragmentation of propylene-d at m/q 43.

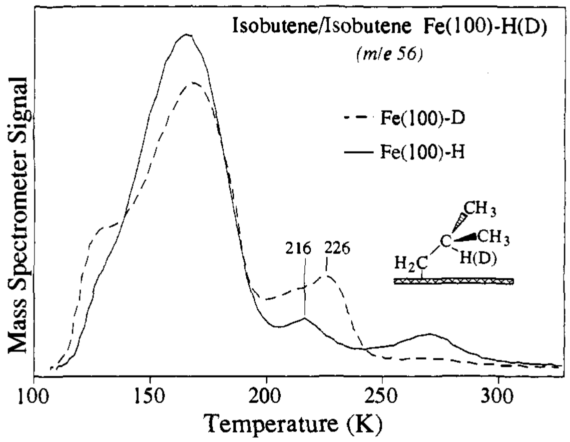

Figure 5. Temperature-programmed reaction of isobutene adsorbed at 110 K onto Fe(100)-H (solid line) and Fe(100)-D (dashed line). The small peak at 216 K on the hydrogen-covered surface is shifted up by 10 K on the deuterium-covered surface. This kinetic isotope effect suggests that this pathway involves the β-hydride(D) elimination of the depicted isobutyl group, $CH_2CH(D)(CH_3)_2$.

was observed for propylene, the amount of H_2 liberated during TPRS is greater than the amount of hydrogen initially adsorbed; more surface hydrogen is formed from butene decomposition than is consumed in butane formation. This general result applies to all of the C_4–C_6 hydrocarbons studied. The total coverage of alkene was estimated to be the sum of alkene and alkane TPRS yields plus the amount of alkene decomposing. The total coverage of 1-butene adsorbed is estimated to be 0.35 ML (Table II).

Alkane yields from ethylene and propylene are strongly dependent on the CO coverage. Since the alkane yield from 1-butene is consistently much greater than that from propylene, and the conditions of the experiment were otherwise identical, we believe that background CO adsorption is *not* responsible for the formation of butane. Coadsorbed CO thus does not appear to be *required* for alkene hydrogenation to occur, but we cannot rule out possible contributions from minor amounts of coadsorbed CO ($\leq$0.005 ML, section 1). The origin of this difference is unclear.

Isobutene provides an interesting contrast to 1-butene, since only a small state is attributable to alkyl β-hydride elimination (Figures 4 and 5). The peak for isobutene at 170 K is entirely attributable to molecular desorption, based on the absence of H–D exchange following isobutene adsorption on Fe(100)-D. However, the peak shape is altered somewhat for desorption from the D-covered surface; this effect has also been observed for ethylene and may be due to coupling of kinetics for the competing reactions of desorption and alkyl formation, with a kinetic isotope effect in alkyl formation leading to altered desorption features. The peak temperature and shape of the 170 K isobutene desorption state are also similar to the molecularly adsorbed states of ethylene, propylene, and 1-butene on Fe(100)-H.

Because the temperature is nearly identical with that observed for alkene formation via β-hydride elimination for ethylene, propylene, and 1-butene, the evolution of isobutene at 220 K is attributed to β-hydride elimination of adsorbed $-CH_2CH(CH_3)_2$ (Figure 5). As further evidence of this reaction, this state does *not* exhibit H–D exchange into isobutene since as expected for a primary alkyl any H(D) added to the tertiary carbon of isobutene to form the alkyl is lost to the surface in the β-hydride(D) reaction to liberate isobutene. Furthermore, a kinetic isotope effect is observed. The peak temperature is shifted upward by 10 K on the D-covered surface (Figure 5), which indicates that C–D bond cleavage occurs on Fe(100)-D and C–H bond cleavage on Fe(100)-H, as expected for this species. The population of this state is higher on Fe(100)-D, which may be due in part to reduced alkane formation. Isobutane-d_2 is clearly formed (MW 60) on Fe(100)-D, and there is no evidence for other isotopes.

From one to four D atoms, however, were incorporated into the isobutene product evolved at 270 K; more than four deuterium atoms may have been incorporated, but the yield of isobutene drops sharply with increasing deuterium content and the mass spectrometer signal falls to the noise level at m/q values $\geq$61. This minor reaction path is attributed to the same pathways associated with multiple exchange in propylene and 1-butene. The amount of isobutene desorbing at saturation is roughly two-thirds that of 1-butene, and the total yield of isobutene, which may be the result of β-hydride elimination at 220 and 270 K, is only 0.02 ML (Table II).

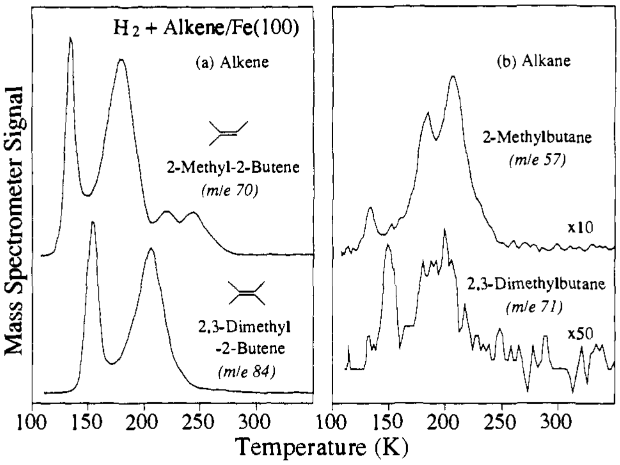

Figure 6. Temperature-programmed reaction spectra of (a) alkenes and (b) alkanes following the adsorption of 2-methyl-2-butene and 2,3-dimethyl-2-butene on Fe(100)-H. Heating rates are approximately 10 K/s.

Isobutane is evolved in a single state at 180 K following a saturation exposure of isobutene on Fe(100)-H. Formation of the alkane product is reaction-limited, since the isobutane molecular desorption temperature at 140 K on Fe(100)-H. The alkane yield is 0.016 ML, and 0.09 ML of carbon is left following reaction (Table II). The saturation coverage of isobutene is estimated as 0.22 ML.

The states for *cis*- and *trans*-2-butene below 175 K are attributed to molecular chemisorption, since they undergo no H–D exchange. Both the *trans*-2-butene state at 180 K and an unresolved state for *cis*-2-butene at the same temperature (Figure 4) give a small amount of butene-d_1 following adsorption of the perhydroalkene on Fe(100)-D. Thus, internal alkyls may be forming and undergoing β-hydride(D) elimination to a limited extent. The lower temperature of these states relative to the β-hydride elimination states of the terminal alkyls formed from propylene, 1-butene, and isobutene indicates that they may be destabilized by steric interactions with the surface. Excluding the multilayer states, the maximum yields of *cis*- and *trans*-2-butene are 0.23 and 0.20 ML, respectively (Table II). For *trans*-2-butene, 0.07 ML desorbs in states above 175 K; these states may involve an alkyl intermediate. At least 0.04 ML desorbs in similar states for *cis*-2-butene. Alkane yields are 0.006 and 0.009 ML, respectively, for *cis*- and *trans*-2-butene, with carbon coverages of 0.07 and 0.05 ML, respectively, remaining after temperature-programmed reaction; the respective saturation coverages are 0.25 and 0.23 ML.

Butane is formed from *cis*- and *trans*-2-butene in several states; a desorption-limited state occurs at 150 K along with reaction-limited states above 170 K. Small amounts of butane are displaced into the butene multilayer state for both molecules. The desorption-limited butane does not appear to originate from alkane impurities in the butene sample, since our in situ mass spectral determination of sample impurity indicates that the upper limit of the butane concentration is 0.15% of the butene. Regardless, butane evolved in reaction-limited peaks must arise from the hydrogenation of butene, since no similar peaks are seen following the adsorption of butane on Fe(100) or Fe(100)-H. The lower limit for the butane, which is 0.004 ML for both butene isomers.

4. Tri- and Tetrasubstituted Alkenes. 2-Methyl-2-butene possesses even greater steric hindrance about the carbon–carbon double bond than do *cis*- and *trans*-2-butene. However, the resulting alkene desorption spectra from Fe(100)-H are qualitatively

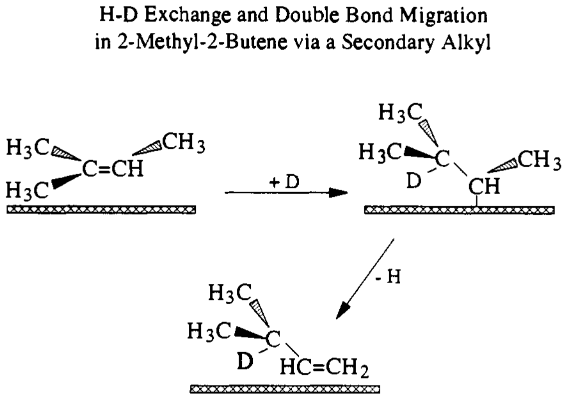
H-D Exchange and Double Bond Migration in 2-Methyl-2-Butene via a Secondary Alkyl

Figure 7. Possible reaction pathway of 2-methyl-2-butene on Fe(100)-D whereby deuterium incorporation and double-bond migration occur via a secondary alkyl intermediate.

similar. Multilayer desorption occurs at 140 K, and a broad *molecular* desorption state is observed at 180 K (Figure 6). Minor states at 220 and 245 K appear to arise from alkyl β-hydride elimination, since the 220 K state incorporates predominantly one deuterium on the Fe(100)-D surface, and alkene products containing up to at least six deuterium atoms were identified as products of the 245 K reaction pathway. The incorporation of more than six deuterium atoms may also occur, but detection of higher levels of isotopic substitution was limited by signal/noise levels. A secondary alkyl is likely to be responsible for the 220 K state, formed by the addition of a deuterium atom to the disubstituted carbon (Figure 7). The subsequent loss of a hydrogen from the methyl group in the β position results in double-bond migration and retention of the deuterium atom. The resulting alkene could incorporate up to three more deuterium atoms via the formation of terminal and secondary alkyls, but this does not occur in the 220 K state. However, since more than four deuteriums are incorporated in the 245 K pathway, a tertiary alkyl accompanied by double-bond migration appears to be involved in H-D exchange for 2-methyl-2-butene, assuming that exchange occurs via alkyl formation and β-hydride elimination. The amount of alkene formed via these two routes is very small. Only 0.14 ML of 2-methyl-2-butene desorbs at saturation, excluding the multilayer (Table II). The states at 220 and 240 K, which may arise from alkyl formation, account for 0.03 ML.

The amount of C_5 alkane formed is only 0.008 ML, reflecting the low propensity for alkyl formation (Figure 6, Table II). The two pathways for alkane formation at 185 and 210 K appear to be reaction-limited since the desorption temperature of 2-methylbutane on Fe(100)-H is 140 K. The small C_5 alkane state at 135 K is desorption-limited, and some product may have been displaced into the alkene multilayer. Alkene decomposition results in a residual carbon coverage of 0.05 ML following temperature-programmed reaction of 2-methyl-2-butene. Only 0.01 ML of the alkene needs to decompose to yield this carbon coverage. Adding the apparent alkene decomposition yield to the alkene and alkane TPRS yields results in an alkene saturation coverage of 0.16 ML.

The tetrasubstituted alkene 2,3-dimethyl-2-butene desorbs in multilayer and molecular states at 155 and 205 K, respectively, which are similar to those of 2-methyl-2-butene (Figure 6). There is a small unresolved state at around 220 K, however, that incorporates from one to four deuterium atoms following adsorption on Fe(100)-D; the possible formation of products containing more than four deuterium atoms is masked by the noise level of the mass spectrometer. The 220 K state may arise from tertiary alkyl formation at defect sites followed by double-bond migration similar to that depicted in Figure 7 for 2-methyl-2-butene. The monolayer state of 2,3-dimethyl-2-butene has a saturation population of 0.10 ML (Table II).

No hydrogenation of the tetrasubstituted alkene is apparent; the mass spectrometer signal for the C_6 alkane mirrors that of the alkene regardless of the fragment monitored. Even for the parent ion of the C_6 alkane at m/q 86 the mass spectrometer signal mirrors that for alkene desorption. The ratio of m/q 86 to m/q 84 of approximately 0.004 indicates that the m/q 86 signal may be attributed to ^{13}C impurities (natural abundance of 1%) in the alkene. A residual carbon coverage of 0.14 ML remains following temperature-programmed reaction of 2,3-dimethyl-2-butene on Fe(100)-H, indicating that approximately 0.02 ML of the alkene decomposed, and thus the saturation coverage is approximately 0.13 ML.

Discussion

1. Reaction Mechanisms of Hydrogenation and H-D Exchange. Our results suggest that the steps illustrated in Scheme I, with an alkylmetal intermediate in the path toward alkane formation, applies generally to alkene hydrogenation on Fe(100)-H. The strong evidence for a stable ethyl intermediate formed from ethylene on Fe(100)-H[17] and its hydrogenation in the presence of CO[27] is foremost among our evidence in support of Scheme I. Furthermore, the reactivity displayed by propylene and 1-butene on Fe(100)-H is quite similar to that of ethylene. The stepwise addition of hydrogen atoms thus appears responsible for the observed hydrogenation of propylene and 1-butene on Fe(100)-H, with stable surface alkyls formed as intermediates. These steps are general features of alkene hydrogenation on Fe(100)-H.

The H-D exchange reactions observed for alkenes on Fe(100)-D are consistent with the reversible formation of an alkyl intermediate. Alkene H-D exchange with D_2 catalyzed by transition-metal complexes[32,33] and supported catalysts[9,10] is belived to occur via steps 1-3 and their reverse. The same reversible reaction steps have been used to explain alkene isomerization via double-bond migration for both surfaces and complexes[9,10,33] where an internal alkyl must be involved. We have no direct evidence that alkenes evolved from Fe(100)-H have been isomerized. However, double-bond migration may explain the incorporation of deuterium into alkenes on Fe(100)-D at carbon atoms removed from the original site of unsaturation; such behavior has been observed for all of the alkenes studied here. Our results thus suggest that the hydrogenation and H-D exchange of alkenes on Fe(100) occur via a mechanism analogous to that for mononuclear complexes.

2. Effects of Molecular Structure on Reactivity. Rates of alkene hydrogenation catalyzed by transition-metal complexes are quite sensitive to alkene structure; steric hindrance about the carbon-carbon double bond typically reduces the hydrogenation rate. For Wilkinson's hydrogenation catalyst, $RhCl(PPh_3)_3$, the relative order of reactivity is $RCH{=}CH_2 > R_2C{=}CH_2 >$ *cis*-$RCH{=}CHR >$ *trans*-$RCH{=}CHR > R_2C{=}CHR$.[2] Tetrasubstituted alkenes do not react. A similar result has been found to hold for a supported Ni catalyst, with only the ordering of $R_2C{=}CH_2$ and *cis*-$RCH{=}CHR$ reversed.[34] Steric constraints imposed by the metal center determine the magnitude of the reactivity change upon the introduction of substituents on the alkene. The PPh_3 ligands in Wilkinson's catalyst result in a bulky metal center; thus, reactivity is greatly reduced upon increased hindrance at the alkene. In contrast, however, the catalyst $[Ir(PCy_3)(Py)]^+$, where Py is pyridine and Cy is cyclohexyl, is much less hindered and will hydrogenate even tetrasubstituted alkenes rapidly.[2,35] Supported catalysts may also be active in the hydrogenation of tetrasubstituted alkenes,[11] although the molecular level structure of the catalytic site is unknown.

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(36) The data values are the mean of three experimental determinations, and the error ranges reflect the full range of experimental values: error range = (max − min)/2. The alkyl yield was estimated as the sum of alkane yield and the yield of alkene in pathways attributable to β-hydride elimination of alkyl groups. Alkyl yields were estimated both with and without the carbon deposited in the experiment attributed to alkyl groups; both values for each experiment are included in the data value and error range.

Table III. Absolute and Relative Alkane and Alkyl Yields[a]

molecule	alkane yield (ML)	alkyl yield (ML)	alkane/ alkyl ratio
propylene	0.0083 (4)	0.088 (7)	0.094 (9)
1-butene	0.030 (7)	0.227 (7)	0.13 (3)
isobutene	0.016 (2)	0.048 (14)	0.35 (10)
cis-2-butene	0.0065 (34)	0.052 (18)	0.12 (5)
trans-2-butene	0.0091 (11)	0.087 (20)	0.11 (3)
2-methyl-2-butene	0.0079 (14)	0.044 (10)	0.18 (3)
2,3-dimethyl-1-butene	0.0	0.012 (12)	0.0

[a] Values reported to two significant figures, or three where appropriate. Numbers in parentheses are the error ranges on the last digit(s).[36]

On Fe(100)-H the highest alkane yield results for 1-butene, reflecting the ease of alkyl formation from terminal alkenes (Table III). The lower alkane yield for the more hindered isobutene appears to arise from its lower propensity to form alkyl groups, since isobutyl groups appear to have the greatest hydrogenation propensity among the intermediates studied here. This enhanced alkane/alkyl ratio appears to arise predominantly from a reduction of the barrier to alkane formation, possibly due to steric destabilization of the adsorbed isobutyl species by the methyl at the β-carbon. Although propylene is structurally similar to 1-butene, its hydrogenation yield is lower than either 1-butene or isobutene. Desorption of alkene and conversion to the alkyl appear to compete,[17] so that the weaker binding of molecular propylene than 1-butene to Fe(100) may result in a lower alkyl yield relative to 1-butene.

3. Comparison to Previous UHV Studies. Compared to the number of studies for ethylene there have been very few studies reported regarding the reactions of propylene and larger alkenes on single-crystal transition-metal surfaces. Even fewer studies exist on the coadsorption of hydrogen with the alkene. As indicated in section 1, alkene self-hydrogenation has not been generally observed. In no case has the formation of alkyl intermediates from alkenes been verified. However, several relevant mechanistic results have been reported.

Our results for Fe(100) are in qualitative agreement with the reduced propensity for hydrogenation of internal alkenes on Mo(100),[22] supported nickel catalysts,[34] and Wilkinson's catalyst.[2] On Mo(100), 1-butene both decomposes and self-hydrogenates, whereas *cis*- and *trans*-2-butene do not self-hydrogenate on the same surface.[22] The butane yield from 1-butene self-hydrogenation on Mo(100) is enhanced by small carbon precoverages, and a maximum butane yield is obtained at $\Theta_C = 0.2$. In the presence of preadsorbed hydrogen, however, all three of butenes will hydrogenate. Evidence that hydrogenation may proceed through an alkyl is the evolution of 2-butene following 1-butene adsorption on a partially carbided surface.[22] By lowering the electron energy of the mass spectrometer from 70 to 27 eV, Kelly et al. report that they were able to distinguish between 1-butene and 2-butene desorption products. The butene TPRS product formed by the adsorption of 1-butene on partially carbided Mo(100) was found to be mainly 2-butene (85 ± 13%). One possible mechanism for this isomerization is the formation of an internal alkyl by the addition of an H adatom to adsorbed 1-butene, with β-hydride elimination leading to 2-butene formation; the required H adatoms would be generated by the decomposition of some 1-butene on the partially carbided surface.

Ethylene has been found to hydrogenate readily on Pt(111) in the presence of preadsorbed hydrogen,[14,37] but no direct evidence for an alkyl intermediate via hydrogenation was reported. Ethyl groups produced on Pt(111) from ethyl halides have been reported.[38] On Pd(100) and Pd(111) a variety of hydrogenation reactions occur readily,[25,26] but mechanistic studies have not been reported. This study on Fe(100) thus gives the most firm evidence to data for the stepwise addition of H adtoms in the hydrogenation of alkenes on single-crystal transition-metal surfaces.

Summary

Propylene adsorbed on Fe(100)-H forms stable alkyl groups that lead to small amounts of propane formation but that primarily undergo β-hydride elimination to yield propylene. Propylene readily undergoes H–D exchange on Fe(100)-D via surface propyl groups; the yield of propylene-d_n with $n > 1$ is low, however, and implies that internal alkyls do not form readily. The dominance of propylene-d_1 at 220 K is strong evidence for the adsorbed propyl intermediate. The polydeuterated propylene products are evolved in only the highest temperature pathways and may involve defect sites that are less sterically hindered than the flat terraces. Hydrogenation to yield propane is a minor pathway, but as with ethylene,[27] alkane formation is promoted by the coadsorption of CO.

Adsorption of 1-butene leads to reactions similar to those of propylene, except the alkyl and alkane yields are greater by a factor of approximately 3 and 4, respectively. The higher temperature for molecular desorption of 1-butene compared to propylene appears to favor alkyl formation. The ratio of alkane to alkyl formed, is virtually identical for both propylene and 1-butene. In contrast, isobutene forms alkyls to a much lesser extent than does 1-butene, probably due to steric hindrance. However, the isobutyl intermediate appears to have a high propensity to form alkane, rather than undergo β-hydride elimination; this difference may arise from a reduced barrier to alkane formation compared to a linear alkyl due to steric destabilization introduced by the methyl group at the β-carbon of the alkyl. The yield of alkenes from the internal alkenes *cis*-2-butene, *trans*-2-butene, and 2-methyl-2-butene is low, consistent with steric hindrance around the carbon–carbon double bond. The tetrasubstituted alkene, 2,3-dimethyl-2-butene may form alkyls to a limited extent based on a small yield of H–D exchange products, but there is no sign of hydrogenation to the alkane. As with propylene, minor pathways of all other alkanes studied lead to the multiple incorporation of deuterium atoms following alkene adsorption on Fe(100)-D. The maximum number of deuterium atoms incorporated in each case is greater than that which could result from the exchange of hydrogens bound only to the olefinic carbons. This result suggests that double-bond migration may occur in these minor pathways. Highly deuterated alkenes were only evolved in small amounts in the highest temperature pathways for each alkene and thus may arise from reactions at defect sites.

The observed reactivity of alkenes on Fe(100) offers strong evidence in favor of alkane formation via the stepwise addition of hydrogen atoms, with stable surface alkyls formed as intermediates. The trends in reactivity with molecular structure suggest that both alkyl formation and alkyl hydrogenation steps are sensitive to steric influences. Internal surface alkyls may form more readily at defect sites than on the first surface terraces; thus, the selectivity of hydrogenation, isomerization, and H–D exchange of alkenes may be greatly effected by the concentration of defects on other surfaces.

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Registry No. D, 7782-39-0; propylene, 115-07-1; 1-butene, 106-98-9; isobutene, 115-11-7; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; 2-methyl-2-butene, 513-35-9; 2,3-dimethyl-2-butene, 563-79-1.

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