Hydrogenation of Weakly Rehybridized Ethylene on Fe(100)−H: Ethyl Group Formation

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Abstract: The bonding and reactivity of ethylene on hydrogen presaturated Fe(100) has been investigated using temperature programmed reaction spectroscopy (TPRS) and electron energy loss spectroscopy (EELS). Hydrogen preadsorbed on Fe(100) limits the extent of electron back-donation to coadsorbed ethylene, resulting in weak rehybridization relative to adsorption on clean Fe(100). Adsorption at 100 K leads to rehybridization intermediate between the sp^2 gas phase species and the nearly sp^3 di-σ bound ethylene on clean Fe(100), as indicated by $\pi\sigma$ parameters of 0.58 (0.53 for C_2D_4). Migratory insertion of coadsorbed hydrogen into this adsorbed ethylene occurs below 170 K; vibrational spectroscopy positively identifies the intermediate formed as surface ethyl groups.

Introduction

Previous observation of CO-promoted formation of ethane from ethylene on hydrogen-covered Fe(100) (Fe(100)−H) has prompted us to use vibrational spectroscopy to positively identify the intermediate involved. Ethylene adsorption and decomposition on clean Fe(100) has been studied extensively.[1−3] Ethylene adsorbs with di-σ bonding and, upon heating, evolves H_2 while forming ethynyl and methylidyne, which further decompose to evolve the remaining hydrogen, leaving carbon on the surface. Preadsorbed hydrogen inhibits the decomposition. EELS measurements demonstrate that the hydrogen adsorbs within the 4-fold hollows,[4] the site of decomposition proposed by Hung and Bernasek.[3]

Burke and Madix reported extensive temperature programmed reaction spectroscopy (TPRS) studies of the reactivity of ethylene on Fe(100)−H.[1] Ethylene evolves in desorption states at 150 and 225 K. These studies suggested the competitive desorption and reaction of ethylene to form adsorbed ethyl groups. Further heating of this surface results in the *reaction limited* desorption of ethylene. Since the reaction of ethylene-h_4 with coadsorbed deuterium showed isotopic mixing for the high temperature state to form ethylene-d_1, and the kinetic isotope effect indicated that C−H(D) bond breaking is the rate limiting step liberating ethylene from this state, vinyl and vinylidene were eliminated as possible intermediates. However reactions of either ethyl or ethylidyne intermediates could be conceived to be the precursor to ethylene formation.

Three arguments were advanced against ethylidyne as the intermediate leading to ethylene formation at 225 K. First, based on the patterns observed on other metal surfaces, ethylidyne is not normally expected to form on a surface of 4-fold symmetry.[5−9] Second, on all surfaces where it is formed, ethylidyne decomposes at much higher temperatures. Third, in the presence of coadsorbed CO, this intermediate hydrogenates to evolve ethane at 165 K;[10] no ethane is formed without the addition of CO. Adsorbed ethyl is the intermediate most consistent with these observations.

Several features of the CO-promoted hydrogenation reaction are notable. Weakening of the Fe−H bond is readily apparent in the temperature programmed desorption of hydrogen in the presence of coadsorbed CO. Further, the rate limiting step in the evolution of ethane appears to be the formation of the intermediate when CO is coadsorbed with ethylene at 100 K. EELS measurements also demonstrate perturbation of the Fe−H bond[4] by coadsorbed CO and show the site conversion[11] of CO from atop or bridge bonding to 4-fold hollow as hydrogen vacates this site in forming both the intermediate and ethane.[12] The site conversion of CO appears to contribute to the driving force of the hydrogen transfer reactions.

The bonding of ethylene to the surface is undoubtedly related to its propensity for hydrogenation. Bonding of ethylene in organometallic complexes can be described by the Dewar−Chatt−Duncanson (DCD) model[13,14] —a combination of donation from the filled ethylene p orbitals to empty metal orbitals and donation from filled metal orbitals to unfilled ethylene π^* orbitals. Wong and Hoffmann have investigated the bonding of ethylene on metal surfaces by an approximate molecular orbital method (extended Hückel calculations within a tight binding formalism).[15] Interaction of ethylene π and π^* orbitals dominate the bonding to the surface, analogous to the DCD model. According to this treatment, antisymmetric combinations of metal s and p orbitals dominate the bonding interaction with the π and π^* orbitals of ethylene. The dominance of s and p orbitals in the bonding arises because the d orbitals (although strongly interacting) combine to form *occupied* bonding *and* antibonding states for little net bonding.

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(1) Burke, M. L.; Madix, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 3675.
(2) Benziger, J. B.; Madix, R. J. *J. Catal.* **1980**, *65*, 49.
(3) Hung, W.-H.; Bernasek, S. *Surf. Sci.* **1995**, *339*, 272.
(4) (a) Merrill, P. B.; Madix, R. J. *Surf. Sci. in press.* (b) Merrill, P. B. Ph.D. Thesis, Stanford University, 1995; Chapter 2.
(5) Steininger, H.; Ibach, H.; Lehwald, S. *Surf.* **1982**, *Sci. 117*, 685.
(6) Koel, B. E.; Bent, B. E.; Somorjai, G. A. *Surf. Sci.* **1984**, *146*, 211.
(7) Gates, J. B.; Kesmodel, L. L. *Surf. Sci.* **1983**, *124*, 68.
(8) Marinova, T. S.; Kostov, K. L. *Surf. Sci.* **1987**, *181*, 573.
(9) Hills, M. M.; Parmeter, J. E.; Mullins, C. B.;Weinberg, W. H. *J. Am. Chem. Soc.* **1986**, *108*, 3554.
(10) Burke, M. L.; Madix, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 1475.
(11) Merrill, P. B.; Madix, R. J. *Surf. Sci.* **1992**, *271*, 81.
(12) EELS measurements demonstrate a decrease in atop νCO which correlates to an increase in 4-fold νCO; bridge νCO are prominent before and after the conversion.[11] However, these studies cannot distinguish between (1) direct conversion of CO from atop to 4-fold sites and (2) conversion from bridge to 4-fold sites along with simultaneous conversion from atop to bridge sites.
(13) Dewar, J. S. *Bull. Soc. Chim. France* **1951**, *18*, C71.
(14) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939.
(15) Wong, Y.-T.; Hoffmann, R. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 4083.

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Vibrational spectroscopy has been utilized to determine the bonding of ethylene and its reactivity in several organometallic complexes[13,14,16] and on various metal surfaces,[17−20] demonstrating a wide variety of binding and reaction pathways. Perhaps the most straightforward method for determining the state of rehybridization of ethylene complexes, vibrational spectroscopy generally reveals a reduced C−C stretching frequency relative to gas phase ethylene. However, these shifts of νCC are minor in comparison to the νCC shifts for C−C bonds in sp^1 $C_2H_{2(g)}$ (1974 cm^{-1}), sp^2 $C_2H_{4(g)}$ (1623 cm^{-1}), and sp^3 $C_2H_{6(g)}$ (993 cm^{-1}).[21] Generally, ethylene binds on metal surfaces with π- or di-σ binding; the differences mainly result from the extent of back-donation from the metal to the ethylene π^* orbital. Organometallic analogues for both types of binding exist. Zeise's salt, or $K^+[(C_2H_4)PtCl_3]^-$, contains π-bound ethylene,[16] whereas di-σ bonding of ethylene is found in $(C_2H_4)Os_2(CO)_8$.[22] Di-σ bound ethylene species have been reported for several surfaces,[3,5,23−28] indicative of strong interactions with the metal surface. Conversely, π-bound complexes have been reported for surfaces where back-bonding is limited.[7,29−31] Many surfaces exhibit π-binding of ethylene with coadsorbed oxygen;[3,5,27,30,32−34] in such cases, electron withdrawal by the coadsorbates may limit metal electron availability to participate in back donation with the ethylene. The reactions of ethylene adsorbed on metal surfaces largely involves decomposition upon heating. Intermediates such as ethylidyne, acetylene, vinylidene, and vinyl have all been reported to be observed in the decomposition.[3,5,27,35]

We report here the first studies of coadsorbed ethylene and hydrogen on Fe(100) by vibrational spectroscopy. These studies demonstrate the isolation of surface ethyl groups, formed via the migratory insertion of hydrogen into ethylene on Fe(100)−H. The reactivity of ethyl groups can thus be understood; β-hydride elimination of ethyl groups leads to evolution of ethylene at 225 K. Conversely, reductive elimination of the ethyl groups to evolve ethane is facilitated at 165 K by coadsorbed CO.

Experimental Section

Experiments were performed in a stainless steel ultrahigh vacuum chamber described previously[4] with a base pressure of 3×10^{-11} Torr capable of low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), temperature programmed reaction spectroscopy (TPRS), and high-resolution electron energy-loss spectroscopy (HREELS) measurements. The temperature of the Fe(100) crystal, mounted on a rotatable manipulator with three degrees of freedom, could be controlled from 100 K to over 1000 K. The sample was cooled by thermal conduction from a liquid nitrogen reservoir. Resistive heating was accomplished with current flow through the tantalum support. Temperature was monitored with a chromel-alumel thermocouple spot-welded to the crystal. HREELS was conducted with a double-pass 127° cylindrical sector monochrometer and a single-pass analyzer. The typical full width at half maximum (FWHM) for elastically scattered electrons was about 70 cm^{-1}. Most gases were used as supplied from Matheson without further purification; they included argon (prepurified; 99.998% min), ethylene (C.P.; 99.5% min), hydrogen (prepurified; 99.99% min), and deuterium (C.P.; 99.7% min). Ethylene-d_4 (Cambridge Isotope Labs, 99% D) contained acetone impurities, which were eliminated from the sample with an ethanol/ice trap on the dosing lines. Mass spectrometer measurements assured purity of all gases admitted into the UHV system and utilized in these experiments. Dosing of hydrogen, deuterium, and ethylene was directed from capillary array dosers at close distances; the saturation exposures were easily reproduced, and chamber pressures were kept to a minimum.

Details of the preparation and initial cleaning of the Fe(100) crystal are given elsewhere.[36] Routine cleaning was accomplished with argon ion bombardment. First the crystal was heated to 923 K and sputtered for 10 min; the crystal was then allowed to cool to 105 K before sputtering for another 10 min. Following evacuation to 10^{-10} Torr, the crystal was then annealed at 723 K for 5 min. AES and EELS were used to evaluate surface cleanliness. A c(2×2) random $C_a + O_a$ overlayer resulting from the dissociation of CO_a[37] was used for AES calibration; XPS studies report dissociation of 0.24 mL of CO yield this state.[38] This cleaning procedure very efficiently eliminated surface carbon (0.00−0.01 mL by AES) (none detected by EELS) but was not always completely successful in removing oxygen as indicated by M−O losses[39] detected by EELS. Prolonged heating above 727 K brings dissolved oxygen from the Fe(100) bulk to the surface if any exists.[39] Excessive oxygen impurities were removed with ethylene titrations, as was necessary after exposure of the crystal to atmospheric pressures for routine maintenance or in cases where very large quantities of O_a accumulated on the surface, and the routine sputtering procedure yielded little progress. However residual carbon, a product of the reaction, then needed to be sputtered away. At low concentrations O_a could be titrated off at the expense of C_a. With these procedures, the O_a impurities could be greatly reduced (0.01−0.03 mL by AES).

All EELS spectra were recorded at 100 K following tuning of the spectrometer. Cleaning and repreparation of the surface was not necessary between collection of spectra for hydrogen saturated surfaces, ethylene adsorption at 100 K, or formation of the intermediate upon annealing.

Thus, for each set of reactants, the clean surface was prepared, cooled to 100 K, saturated with hydrogen, and EELS was performed; ethylene was dosed on this surface, and the EELS spectrum was once again collected. Finally, this surface was annealed to 170 K and recooled, and the final EELS spectrum was recorded. Vibrational spectra were examined for evidence of H_2O (1300 cm^{-1}) and CO adsorption (νCO at 1200 cm^{-1} and/or 2000 cm^{-1}).[11] Spectra recorded for the direct preparation of ethylene on Fe(100)−H and ethyl on Fe(100) (without EELS collection prior to preparation) showed no differences from the spectra recorded successively as described above.

Results and Discussion

The EELS spectrum for a saturated hydrogen adlayer on Fe(100) is presented in Figure 1(a). Hydrogen adsorption and binding on Fe(100) has been discussed elsewhere.[4] Briefly, hydrogen dissociatively adsorbs on Fe(100) at 100 K binding

(16) Powell, D. B.; Scott, J. G. V.; Sheppard, N. *Spectrochim. Acta* **1972**, *28A*, 327.
(17) Stuve, E. M.; Madix, R. J. *J. Phys. Chem.* **1985**, *89*, 3183.
(18) Bent, B. E.; Mate, C. M.; Kao, C.-T.; Slavin, A. J.; Somorjai, G. A. *J. Phys. Chem.* **1988**, *92*, 4720.
(19) Bent, B. E. Ph.D. Thesis, University of California, Berkeley, 1982.
(20) Sheppard, N. *Ann. Rev. Phys. Chem.* **1988**, *39*, 589.
(21) Herzberg, G. *Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules*; Van Nostrand Reinhold Company: New York, 1945.
(22) Bandy, B. J.; Chesters, M. A.; James, D. I.; McDougall, G. S.; Pemble, M. E.; Sheppard, N. *Philos. Trans. R. Soc. London Ser. A* **1986**, *318*,141.
(23) Lehwald, S.; Ibach, H. *Surf. Sci.* **1979**, *89*, 425.
(24) Lehwald, S.; Ibach, H.; Steininger, H. *Surf. Sci.* **1982**, *117*, 342.
(25) Anson, C. E.; Bandy, B. J.; Chesters, M. A.; Keiller, B.; Oxton, I. A.; Sheppard, N. *J. Electron. Spectrosc. Rel. Phenom.* **1983**, *29*, 315.
(26) Barteau, M. A.; Broughton, J. Q.; Menzel, D. *Appl. Surf. Sci.* **1984**, *19*, 92.
(27) Hatzikos, G. H.; Masel, R. I. *Surf. Sci.* **1987**, *185*, 479.
(28) Erley, W.; Baro, A. M.; Ibach, H. *Surf. Sci.* **1982**, *120*, 273.
(29) Nyberg, C.; Tengstal, C. G.; Andersson, S. *Chem. Phys. Lett.* **1982**, *87*, 87.
(30) Stuve, E. M.; Madix, R. J. *J. Phys. Chem.* **1985**, *89*, 105.
(31) Chesters, M. A.; McDougall, G. S.; Pemble, M. E.; Sheppard, N. *Appl. Surf. Sci.* **1985**, *22/23*, 369.
(32) Backx, C.; de Groot, C. P. M.; Biloen, P. *Appl. Surf. Sci.* **1980**, *6*, 256.
(33) Kostov, K. L.; Marinova, T. S. *Surf. Sci.* **1987**, *184*, 359.
(34) Seip, U.; Tsai, M.-C.; Kuppers, J.; Ertl, G. *Surf. Sci.* **1984**, *147*, 65.
(35) Zaera, F.; Fischer, D. A.; Carr, R. G.; Gland, J. L. *J. Chem. Phys.* **1988**, *89*, 5335.
(36) Burke, M. L; Madix, R. J. *Surf. Sci.* **1990**, *237*,20.
(37) Ho, W.; Willis, R. F.; Plummer, E. W. *Phys. Rev. Lett.* **1978**, *40*, 1463.
(38) Cameron, S. D.; Dwyer, D. J. *Langmuir* **1988**, *4*, 282.
(39) Lu, J.-P.; Albert, M. R.; Bernasek, S. L. *Surf. Sci.* **1989**, *215*, 348.

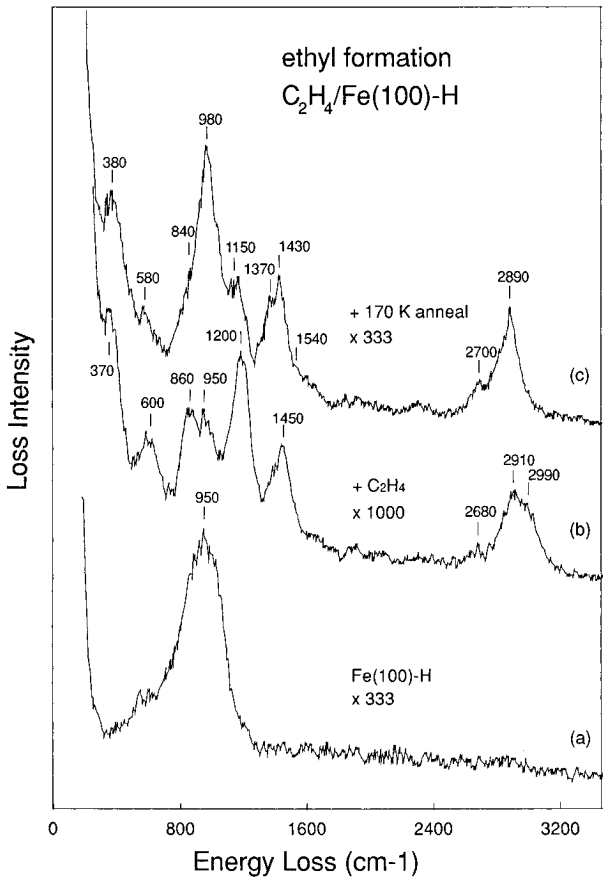

Figure 1. EELS: (a) saturation coverage of $H_{(a)}$ on Fe(100) at 100 K, (b) Fe(100)−H with saturation exposure of C_2H_4 at 100 K, and (c) surface intermediate at 100 K following anneal to 170 K.

Table 1. Vibrational Assignments for Ethylene on Clean and Hydrogen-Saturated Fe(100)[a]

mode description	C_2H_4/Fe(100)−H (C_2D_4/Fe(100)−D)		ν_H/ν_D	C_2H_4/Fe(100)[3] (C_2D_4/Fe(100))		ν_H/ν_D
$\nu CH_{2(a)}$	2990	(2230)	1.34	2985	(2220)	1.33
$\nu CH_{2(s)}$	2910	(N.R.)				
νFe−HC	2680	(2040)	1.31	2720	(2040)	1.33
$\delta CH_2/\nu CC \rightarrow (\delta CD_2)$	1450	(950)	1.53	1395	(900)	1.55
$\nu CC/\delta CH_2 \rightarrow (\nu CC)$	1200	(1270)	0.94	1095	(1160)	0.95
νFeH	950	(700)	1.36			
CH_2wag	860	(640)	1.31	860	(645)	1.33
$\nu FeC_{(s)}$	600	(N.R.)	560			
$\nu FeC_{(a)}$	370	(400)	0.93	380	(410)	0.93

[a] N.R. = not resolved.

within the 4-fold hollows up to a saturation coverage of 1 mL, yielding the broad peak at 950 cm^{-1}.

Dosing C_2H_4 upon the hydrogen-saturated surface at 100 K leads to the EELS spectrum of Figure 1(b). Assignments of the losses are summarized in Table 1. Asymmetric and symmetric CH_2 stretches (νCH_2) are observed at 2990 and 2910 cm^{-1}, respectively. Carbon−carbon stretching (νCC) and CH_2 scissors modes (δCH_2) of the same symmetry lead to two mixed modes at 1200 and 1450 cm^{-1}. The frequencies of the pure modes are unknown. Also observed are the CH_2 wag at 860 cm^{-1} and the metal−carbon stretch (νFeC) at 370 cm^{-1}. Intensity of the νFeH loss at 950 cm^{-1} is greatly attenuated by coadsorbed ethylene; dipole screening is expected from the p-orbitals of ethylene. Similar attenuation was noted with the coadsorption of CO and H in a mixed adlayer.[4,11] A weak loss due to CH

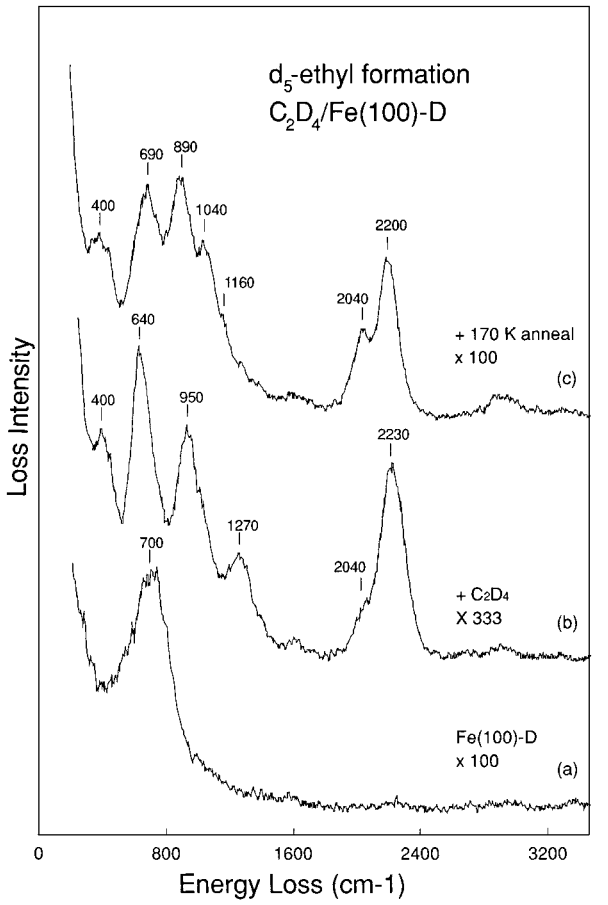

Figure 2. EELS: (a) saturation coverage of $D_{(a)}$ on Fe(100) at 100 K, (b) Fe(100)-D with saturation exposure of C_2D_4 at 100 K, and (c) surface intermediate at 100 K following anneal to 170 K.

mode softening is observed at 2680 cm^{-1}; such features are greatly enhanced in latter spectra and are discussed below.

Phase separation of the post-dosed ethylene and hydrogen-saturated adlayer does not occur. Hung and Bernasek have reported the EELS spectra of C_2H_4 on clean Fe(100).[3] We reproduced these results in independent experiments. Comparison of Figure 1(b) with clean surface spectra demonstrate significant shifts of the ethylene vibrational modes. Table 1 includes vibrational frequencies for ethylene on clean Fe(100) for comparison.[3] Ethylene νCC and δCH_2 modes at 1095 and 1395 cm^{-1} on the clean surface are significantly lower than values of 1200 and 1450 cm^{-1} observed on the hydrogen presaturated Fe(100) surface. As discussed below, this redshift indicates a weakened C−C bond strength on the clean surface resulting from an increased ethylene−metal interaction. The dominance of modes different from those characteristic of adsorption on clean iron mitigates against the occurrence of phase separation.

Deuterated analogs were utilized to aid assignments of vibrational modes. Figure 2(a),(b) show deuterium on the Fe(100) surface and subsequent adsorption of C_2D_4 at 100 K. Assignments and isotopic shifts for C_2H_4 (C_2D_4) on H- (D-) saturated Fe(100) are included in Table 1 with comparison to clean Fe(100).[3] With these assignments, the expected[40] isotopic shifts, ν_H/ν_D are observed for the CH/CD stretching and wagging modes. Given the substantial redshift expected for the scissors mode in adsorbed C_2D_4, the loss at 1270 cm^{-1} is predominantly νCC (although not pure), while the 950 cm^{-1} mode is attributed to δCD_2.

Further understanding of the νCC and δCH_2 modes can be gained from a consideration of the normal mode vibrations in

correlation tables of C_2H_4 and *gauche*-$C_2H_4Br_2$. Bent *et al.* have presented correlation tables for the perhydrido and perdeutero forms.[18] Upon bonding with a surface, the νCC (A_g), δCH_2 (A_g), and CH_2wag (B_{1g}) modes of ethylene converge to the same symmetry (A); complex mixing is expected. However, mixing of the νCC mode is minimized considerably in the perdeutero species. Isotopic shifts of pure δCH_2 and δCD_2 modes should yield a ν_H/ν_D of 1.33, while the ν_H/ν_D of νCC should be approximately 1.07. The highly mixed modes of perhydrido ethylene, when compared to those of perdeutero ethylene, yield *apparent* ν_H/ν_D values which differ from those expected; deviations from these values result from mixing of the pure modes in the perhydrido species, which is reduced upon isotopic substitution. Using the correlation tables of Bent et al., the 1270 cm^{-1} loss for C_2D_4 on the deuterium-presaturated surface would suggest that in the perhydrido species, the "pure" δCH_2 and νCC modes can be expected near 1325 cm^{-1} (the midpoint of the observed bands).

Since determination of νCC for ethylene is complicated by mixing with the δCH_2 mode of similar symmetry, Stuve and Madix have proposed a $\pi\sigma$ parameter as a measure of rehybridization which combines the percentage shift to lower frequency of both the δCH_2 and νCC modes upon adsorption.[17] The parameter is normalized to zero for gas-phase ethylene and unity for 1,2-dibromoethane, which represent the extremes of rehybridization. The organometallic compound $K[(C_2H_4)PtCl_3]$[16] (Zeise's salt), in which ethylene is bound with intermediate rehybridization to the Pt atom (π-bonding),[41] exhibits a $\pi\sigma$ parameter of 0.38 (0.35 for deuterated Zeise's salt). C_2H_4 adsorption on Pt(111) shows the largest rehybridization on surfaces with $\pi\sigma$ parameter of 0.92 (0.88) and can be characterized as di-σ bonding. Very weakly bound and weakly rehybridized species exist in complexes such as $Ag(C_2H_4)BF_4$,[16] ($\pi\sigma = 0.12$), and on surfaces such as oxygen-precovered Ag(110)[32] ($\pi\sigma$ parameter $= 0.14$).

Bent et al. have suggested that the deuterated $\pi\sigma$ parameter is the more reliable measure of rehybridization,[18] since the νCC is less coupled with the δCD_2 mode, thus yielding a parameter more simply related to the extent of rehybridization. The $\pi\sigma$ parameter for deuterated species scales from 0 to 0.78 (not unity); however there is only good agreement between the perhydrido- and perdeutero- $\pi\sigma$ parameters up to 0.4. Therefore, for ease of comparison between perhydrido and perdeutero ethylene, especially with highly rehybridized species, Bent et al., propose the application of a DCD parameter which considers only the νCC for deuterated ethylene complexes.[19] This should be the only mode in the 1100 to 1550 cm^{-1} range and be relatively free of coupling with the δCD_2 mode. The DCD parameter scales from 0 to 1 throughout the entire rehybridization range of C_2D_4 complexes.

Table 2 presents $\pi\sigma$ and DCD parameters for ethylene on several transition metal surfaces in comparison to $C_2H_{4(g)}$, $C_2H_4Br_{2(g)}$, and Zeise's salt. Based on our results, ethylene adsorption at 100 K on Fe(100)−H exhibits $\pi\sigma$ parameters of 0.58 (0.53) and a DCD parameter of 0.66. EELS data for C_2H_4 and C_2D_4 on the clean Fe(100) surface yield $\pi\sigma$ parameters of 0.89 (0.86) and a DCD of 0.95.[3] These results indicate that ethylene is less strongly rehybridized on the hydrogen-presaturated Fe(100) surface than on the clean surface. Hydrogen presaturation of the surface appears to reduce back donation from metal orbitals into the π^* orbitals of ethylene compared to the bonding of ethylene on the clean surface. This result is consistent with the reactivity of C_2H_4 on the different iron surfaces. Ethylene decomposes on all low index clean iron surfaces, (100), (110), and (111),[3,28,34] whereas the Fe(100)−H surface affects no decomposition.

Table 2. Extent of Rehybridization as Indicated by $\pi\sigma$ and DCD Parameters

species/substrate	$\pi\sigma$ C_2H_4 (C_2D_4)		DCD
$C_2H_{4\,(g)}$[44]	0	(0)	0
Cu(100)[29]	0.21	(0.27)	0.25
Pd(110)[31]	0.38	(0.38)	0.38
zeise's salt[16]	0.38	(0.35)	0.43
Fe(100)−H	0.58	(0.53)	0.66
Ru(001)[26]	0.85	(0.78)	0.8
Fe(100)[3]	0.89	(0.86)	0.95
Pt(111)[5]	0.92	(0.85)	0.96
$C_2H_4Br_{2\,(g)}$[44]	1.00	(0.78)	1

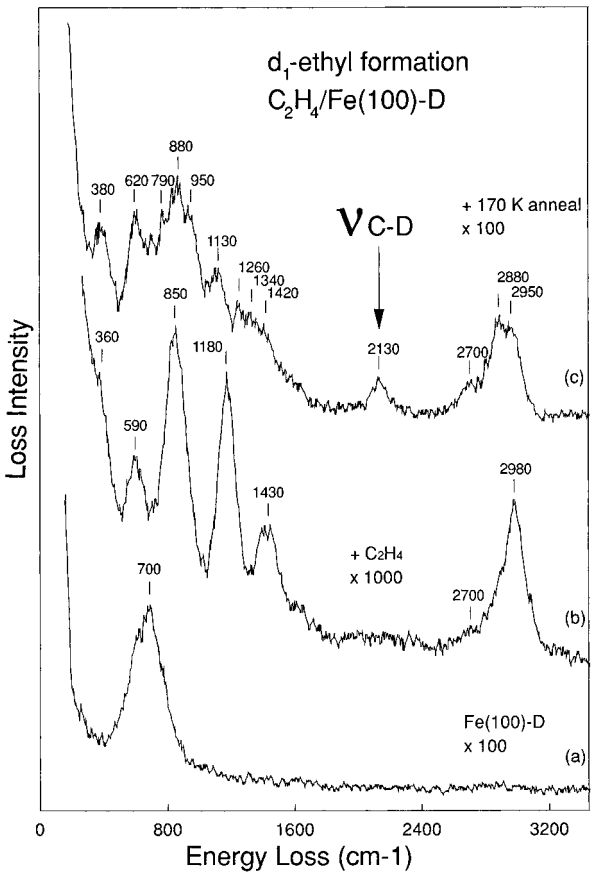

Figure 3. EELS: (a) saturation coverage of $D_{(a)}$ on Fe(100) at 100 K, (b) Fe(100)-D with saturation exposure of C_2H_4 at 100 K, and (c) surface intermediate at 100 K following anneal to 170 K.

EELS spectra for the intermediate formed and isolated by annealing C_2H_4 (C_2D_4) on the H (D) presaturated Fe(100) surface to 170 K are presented in Figures 1(c) and 2(c). As previously noted, formation of such an intermediate was indicated by previous TPRS experiments,[1] which were reproduced here. Comparison of these vibrational spectra with Figures 1(b) and 2(b) clearly indicate an intermediate different from the π-bonded ethylene.

Mixed isotope experiments with C_2H_4 adsorption on Fe(100)−D were performed. Figure 3 shows the EELS spectra for adsorption at 100 K followed by annealing to 170 K. The anneal leads only to evolution of pure C_2H_4 into the gas phase

(40) Lowry, T. H.; Richardson, K. S. *Mechanism and theory in organic chemistry*, 2nd ed.; Harper & Row: New York, 1981.

(41) Molecular calculations of electron density in ethylene π and π^* orbitals demonstrate limited, but finite back-bonding in Zeise's salt.[15] Thus, as a model of π bonding, Zeise's salt represents the organometallic analog with *weak* back−back bonding; however, it is not an example of *pure* π bonding.

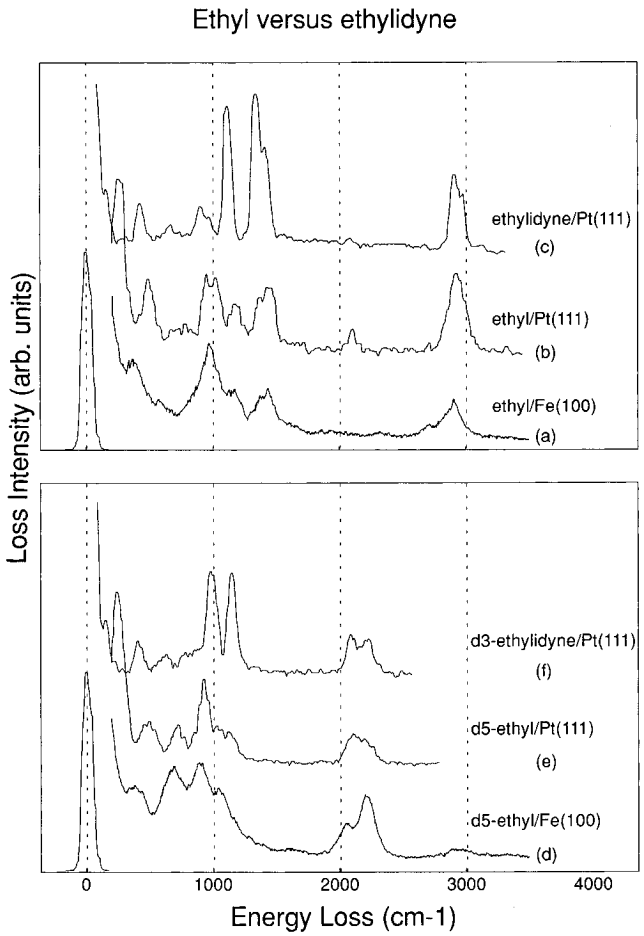

Figure 4. EELS: comparison of perhydrido- and perdeutero- ethyl intermediates formed on Fe(100) with ethyl[42] and ethylidyne[5] species isolated on Pt(111); (a) ethyl/Fe(100)−H, (b) ethyl/Pt(111), (c) ethylidyne/Pt(111), (d) ethyl-d_5/Fe(100), (e) ethyl-d_5/Pt(111), (f) ethylidyne-d_3/Pt(111).

at 170 K—no deuterated species evolved. Upon further heating of the intermediate, ethylene-d_1 is evolved at 225 K. Observation of νCD at 2130 cm^{-1} following the anneal to 170 K clearly indicates the formation of C−D bonds (Figure 3(c)). No such features were observed in Figure 3(b), indicating formation of the intermediate occurs above the adsorption temperature of 100 K and below 170 K.

The vibrational spectra of Figures 1(c), 2(c), and 3(c) mitigate against ethylidyne (CCH_3) as the intermediate. Ethylidyne intermediates have been isolated on Ru(001),[9] Rh(111),[6] Pd(111),[7] Ir(111),[8] and Pt(111).[5] Spectra in all cases are characterized by a pair of very intense modes (νCC and δCH_3) between 1000 and 1400 cm^{-1} which dominate the spectral region at frequencies below the νCH_3 modes. The vibrational spectrum of the intermediate on hydrogen-saturated Fe(100) is inconsistent with ethylidyne; losses below 1000 cm^{-1} dominate. Figure 4 shows the vibrational spectra for perhydrido- and perdeutero-ethylidyne and ethyl groups on Pt(111)[5,42,43] along with the spectra of Figures 1(c) and 2(c). The similarity of these spectra strongly suggest that the intermediate produced by the 170 K anneal is surface-bound ethyl.

Vibrational assignments for the ethyl intermediate on Fe(100)−H are presented in Table 3 with comparison to analogous ethyl species on Pt(111)[42] and gas phase $C_2H_5Cl_{(g)}$.[44] As expected, the ethyl groups exhibit a significantly reduced νCC frequency at 980 cm^{-1}. Other prevalent modes include CH stretching at 2890 cm^{-1}, CH_3 deformation at 1430 cm^{-1}, CH_2 wagging at 1150 cm^{-1}, and CH_3 rocking near 840 cm^{-1}. The 980 cm^{-1} loss of Figure 1(c) is intensified by poor resolution between the νCC, νFeH, and CH_3 rocking modes on the hydrogen-covered surface. The spectrum of Figure 2(c) exhibits increased intensity in two modes due to overlap of the CD_3 rock and νFeD and overlap of νCC and CD_2 wag modes. Hydrogenic modes exhibit the expected isotopic shifts. Excellent agreement with $C_2H_5Cl_{(g)}$ and ethyl/Pt(111) are indicated by Figure 4 and Table 3.

Table 3. Vibrational Assignments for Ethyl on Fe(100)−H with Comparison to $C_2H_5Cl_{(g)}$[44] and Ethyl on Pt(111)[42] [a]

mode	C_2H_5/Fe	C_2D_5/Fe	ν_H/ν_D	$C_2H_5Cl_{(g)}$	C_2H_5/Pt	C_2D_5/Pt	ν_H/ν_D
$\nu CH_{2(s)}$				2967		2205	1.32
$\nu CH_{3(a)}$	2890	2200	1.31	2946	2918	2264	1.29
$\nu CH_{3(s)}$				2881		2154	1.35
νFe−HC	2700	2040	1.32				
CH_2sciss	1540	1160	1.33	1448	1450	1130	1.28
$CH_3def_{(a)}$	1430	1040	1.38	1448	1430	1071	1.34
$CH_3def_{(s)}$	1370			1385	1376	1024	1.34
CH_2wag	1150	890	1.29	1289	1173	929	1.26
νCC	980	890	1.10	974	1022	929	1.10
CH_2twist				1251	894		
CH_3rock	840	690	1.22	974	941	729	1.29
νMC	380	400	0.95		484	480	1.01
νPtCl					252	248	

[a] Contributions to the vibrational spectra of Figures 1(c) and 2(c) also arise from coadsorbed hydrogen (νFeH = 950 cm^{-1}) and deuterium (νFeD = 700 cm^{-1}).

Assignment of the losses in Figure 3(c) is complicated by isotopic effects resulting from insertion of a single D atom into the $C_2H_{4(a)}$ species. The aforementioned 2130 cm^{-1} loss is attributed to CD stretching in the methyl end of the ethyl-d_1 intermediate. Loss of symmetry affects the CH_3 deformation (near 1340 cm^{-1}) and the CH_3 rock (near 880 cm^{-1}). The CH_2 wag appears relatively unperturbed at 1130 cm^{-1}. CH stretching modes are still prevalent in the ethyl-d_1 species as evidenced by νCH_2 at 2880 cm^{-1} and νCH_2D at 2950 cm^{-1}.

The ethyl groups on Fe(100)−H exhibit softened CH(CD) modes at 2700 cm^{-1} (2040 cm^{-1}). The frequencies of these features are too low to be attributed to symmetric CH stretches. Unusually low frequency (softened) C−H vibrational modes have been reported for several hydrocarbons on transition metal surfaces. For example, cyclohexane demonstrates significantly lowered CH stretching frequencies on Ru(001) (404 cm^{-1}),[45] Pt(111) (310 cm^{-1}),[46] and Ni(111) (180 cm^{-1});[46] softened C−H and C−D stretches have been observed for methyl on Ni(111)[47] and Cu(111)[48] and for ethyl and propyl on Cu(111).[48]

Many examples exist in organometallic clusters where C−H groups interact with the metal via a two-electron three-center, "agostic" bond, producing a marked effect on molecular and electronic structure and thus on the reactivity of the molecule.[49] Several relevant examples of such bonds exist, including methyl and ethyl hydrogens, and iron centers are prevalent in this body of work. This bonding can occur by donation of electrons from

(42) Lloyd, K. G.; Roop, B.; Campion, A.; White, J. M. *Surf. Sci.* **1989**, *214*, 227.

(43) Thermal treatment of ethylene on clean Pt(111) leads to the formation and isolation of ethylidyne,[5] whereas photolysis of $C_2H_5Cl_{(a)}$ produces ethyl intermediates coadsorbed with $Cl_{(a)}$.[42]

(44) Shimanouchi, T. *Tables of Molecular Vibrational Frequencies Consolidated Volume I*; U.S. Dept. of Commerce, NSRDS-NBS, 1972.

(45) Hoffmann, F. M.; Felter, T. E.; Thiel, P. A.; Weinberg, W. H. *Surf. Sci.* **1983**, *130*, 173.

(46) Demuth, J. E.; Ibach, H.; Lehwald, S. *Phys. Rev. Lett.* **1978**, *40*, 1044.

(47) Yang, Q. Y.; Maynard, K. J.; Johnson, A. D.; Ceyer, S. T. *J. Chem. Phys.* **1995**, *102*, 7734.

(48) Lin, J.-L.; Bent, B. E. *Chem. Phys. Lett.* **1992**, *194*, 208.

(49) Brookhart, M.; Green, M. L. H. *J. Org. Chem.* **1983**, *250*, 395.

C−H bonding orbitals to the metal or by donation of electron density from the metal to antibonding C−H orbitals. With these species, the C−H−M bond contributes to satisfying the valence of the metal center, thus stabilizing the complex. In our case, available interactive sites may be made available by the hydrogen atoms that add to ethylene to form ethyl. However, electronic structure calculations and the vibrational information we have obtained cast doubt on such an interpretation, at least to the extent that this bonding contributes to the reactivity of the adsorbed ethyl group.

Yang and Whitten[51] find that methyl groups in their lowest energy configuration exhibit no sign of metal−hydrogen bonding interactions, and, indeed, *repulsive* interactions were found between hydrogen and nickel. Lowering of C−H stretching frequencies *was* observed when the methyl group was moved to an assymetric binding site and the methyl group was tilted so that one of the hydrogen atoms resided above one nickel atom; the energetic cost of this displacement was 1.6 kcal/mol. In this configuration there was a net charge gain on all three hydrogens as well as on the nickel atom below the hydrogen and a net charge loss on the carbon atom. For Ti(0001), Cr-(110), and Co(0001) Zheng et al.[51] found the M−H interactions with adsorbed methyl to be slightly antibonding in the energetically favorable atop sites, but weak M−H interactions were reported for bonding of the methyl group in the 3-fold hollow. Hoffmann et al.[52] explain mode softening in cyclic hydrocarbons on Ru(001) in terms of proximity of the hydrogen with the surface; however, their electronic structure calculations indicated the origin of the frequency shift is not attractive interactions between the hydrogen and metal atoms (hydrogen bonding) but rather Pauli exchange repulsions that increase as the CH bond approaches the surface in the most stable bonding geometry of the ligand. These repulsions tend to increase the CH bond length and thus manifest themselves in decreased stretching frequencies. Similarly, Schüle et al. report reduction of the C−H stretching frequencies for methyl on Ni(111) in the lowest energy binding site (3-fold hollow) and attribute this effect to charge donation from the metal into the C−H antibonding molecular orbitals.[53] It is noteworthy, however, that they state that their results are in agreement with Hoffmann et al. and that this interaction in *not* a precursor to dehydrogenation. To test the relationship between C−H bond softening and the presence of H-bonding to the surface, Hoffmann et al. determined the binding energies of several C_nH_{2n} ($n = 3-6, 8$) cyclic hydrocarbons on Ru(001); they found no correlation between the surface-molecule binding energies and the appearance of mode softening; i.e., in this case there appear to be no "H-bonding" interactions with the surface, even though the vibrational frequencies are lowered.[52] Raval and Chesters, on the contrary, suggest that there is a significant correlation between C−H bond softening and either the surface binding energy or the propensity for dehydrogenation in adsorbed cyclohexane on metal surfaces.[54]

It is indeed tempting to associate the β-H elimination from ethyl on Fe(100)−H with the mode softening observed in this work. However, the EELS spectra indicate that the mode softening is associated with the α-carbon, not the β-carbon, of the ethyl group. When adsorbed ethyl is formed by reaction of preadsorbed deuterium with perhydrido ethylene, the deuterium is expected to reside in the methyl group. In that case (Figure 3) there is no sign of C-D bond softening. For comparison, the isolated C−D stretching frequency in singly deuterated, adsorbed methoxy on Ni(100) is 2152 cm^{-1}.[55] This behavior is identical to that observed for ethyl groups on copper for which mode softening occurs at the α-carbon, even though this species reacts by β-elimination.[48] In that case mode softening is attributed to charge donation from the metal into the C−H antibonding orbitals; a similar explantion of the C−H bond softening in methyl on Ni(111) has been offered.[47] However, these interpretations are based on the recent electronic structure calculations discussed above, and there seems to be some ambiguity in the theoretical interpretations. Most importantly, however, the mode softening we observe is appears not to be associated with the β-elimination reaction on Fe(100)−H.

If this reduction in frequency is associated with C−H bond weakening, it is notable that it does not produce reaction by α-elimination. It could of course be argued that α-elimination would lead to decomposition of the ethyl group to carbon and hydrogen, but, when heated, the only species which desorb that desorb from the mixed layer of ethyl groups and hydrogen are ethylene and hydrogen, and no detectible carbon accumulates on the surface. Thus, if this mode softening *is* the result of weakening of the C−H bond by a type of "agostic" bonding, the transition state for α C−H bond rupture must still lie energetically above that for β-elimination. Alternatively, the explanation of Hoffman et al. may account for the mode softening, and there may be no weakening of the C−H bond. At this time this issue cannot be resolved.

In summary, the identification of the ethyl intermediate is based on the nearly identical spectra of Figure 4(parts a-b and d-e) in conjunction with the chemical evidence obtained in previous work.[1] Specifically, the vibrational spectra reported here are consistent with ethyl groups and inconsistent with the vibrational spectra reported for ethylidyne. Further, incorporation of deuterium in the intermediate is clearly revealed in mixed isotope experiments. All vibrational losses for the intermediate isolated upon heating ethylene on the hydrogen- presaturated Fe(100) surface are assigned to vibrational modes of surface ethyl groups, and isotopic shifts for the perdeutero ethyl species are consistent with these assignments. Such vibrational modes cannot arise from surface ethylidyne.

Conclusions

Hydrogen preadsorbed on Fe(100) limits the extent of electron back-donation to ethylene, resulting in rehybridization intermediate between the gas phase species (sp^2) and the di-σ bonded species adsorbed on the clean Fe(100) surface. Insertion of coadsorbed hydrogen occurs into adsorbed ethylene, leading to the formation of ethyl groups on Fe(100)−H. Upon heating the ethyl, β-hydride elimination occurs at 225 K to evolve ethylene, whereas coadsorbed CO facilitates reductive elimination at 170 K to evolve ethane.

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(50) Yang, H.; Whitten, J. L. *J. Am. Chem. Soc.* **1991**, *113*, 6442.
(51) Zheng, C.; Apeliog, Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1988**, *110*, 749.
(52) Hoffmann, F. M.; Upton, T. H. *J. Phys. Chem.* **1984**, *88*, 6209.
(53) Schüle, J.; Siegbahn, P.; Wahlgren, U. *J. Chem. Phys.* **1988**, *89*, 6982.
(54) Raval, R.; Chesters, M. A. *Surf. Sci.* **1988**, *219*, L505.
(55) Huberty, J.; Madix, R. J. *Surf. Sci.*, in press.