

transition-metal ion chemistry. Also interesting is the reaction of  $\text{Ni}(\text{CO})_3^-$  with benzophenone which appears to involve formation of  $\text{Ni}(\text{C}_6\text{H}_5)_2(\text{CO})_2^-$  as a result of two oxidative additions. The second oxidative addition in this process is activated by the attractive interaction between the reacting ion and a neutral collision partner.

Outright charge transfer when exothermic competes with ligand substitution and oxidative addition in the case of  $\text{Ni}(\text{CO})_3^-$ , but only tetracyanoethylene reacts by outright charge transfer with  $\text{Cr}(\text{CO})_5^-$  and  $\text{Fe}(\text{CO})_4^-$ . This difference is consistent with the fact that  $\text{Cr}(\text{CO})_5$  and  $\text{Fe}(\text{CO})_4$  have significantly higher electron affinities than  $\text{Ni}(\text{CO})_3$ .

## The Metal-Alkyl Bond Energy of the Fe(100)-Hydrogen-Ethyl Surface Complex

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**Abstract:** A thermochemical cycle has been constructed for the reactions of ethylene on H-presaturated Fe(100); this cycle has been used to accurately determine Fe-C<sub>2</sub>H<sub>5</sub> and Fe-H surface bond energies of  $38 \pm 4$  and  $59.5 \pm 2$  kcal/mol, respectively. The Fe-C<sub>2</sub>H<sub>5</sub> bond energy is considerably smaller than that measured in the gas phase. Both values are similar to those expected for mononuclear transition metal complexes, provided that the complex contains a first or second row transition metal and is not sterically crowded.

### 1. Introduction

With the overall goal of comparing and contrasting transition metal surface reactivity to that of mononuclear complexes and clusters, we have recently undertaken detailed studies of alkene hydrogenation on an Fe(100) surface.<sup>1-3</sup> This particular system was chosen because of the wealth of information available for alkene hydrogenation catalyzed by complexes and by the generally high catalytic activity of iron for all degrees of nuclearity.

As a product of this research we have been able to accurately determine the strength of the Fe-C<sub>2</sub>H<sub>5</sub> (ethyl) bond on the hydrogen-saturated Fe(100) surface; to our knowledge this is the first determination of a metal-alkyl bond energy for a transition metal surface. Considerably more is known about metal-alkyl bond energetics in complexes, however; we thus have compared our results (for Fe-H as well as Fe-C<sub>2</sub>H<sub>5</sub> bonds) to those for complexes to discern similarities and differences between a single metal atom and an extended surface.

The Fe-C<sub>2</sub>H<sub>5</sub> bond energy was calculated by constructing a thermochemical cycle using kinetic data from studies of the forward and reverse reactions of ethylene on hydrogen-saturated Fe(100), whereby an ethyl intermediate is formed. Kinetic studies were performed using the techniques of temperature programmed desorption and temperature programmed reaction spectroscopy (TPD/TPRS).

### 2. Experimental Section

All experiments were performed in a stainless steel ultrahigh vacuum (UHV) chamber with a base pressure of  $1 \times 10^{-10}$  Torr. TPD/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 so up to eight masses could be monitored 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 gas 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 using low energy electron diffraction (LEED).

Details of the preparation and initial cleaning of the Fe(100) crystal are given elsewhere.<sup>4</sup> Routine cleaning was achieved by Ar ion bom-

bardment with a sample temperature of 700 K. This temperature was high enough to allow diffusion of impurities from the bulk, but low enough to preferentially segregate carbon 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 anneal resulted in a sharp  $p(1 \times 1)$  LEED pattern and ensured that bulk impurity levels were low enough that impurity segregation to the surface would 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  $c(2 \times 2)$  pattern at the adatom saturation coverages of 0.5 ML, where 1 ML equals the Fe(100) surface atom density of  $1.22 \times 10^{15}$  atom/cm<sup>2</sup>. A  $c(2 \times 2)$  pattern is also formed by saturation of the CO dissociative state, resulting in surface coverages of 0.25 ML each for carbon and oxygen.

TPD/TPRS experiments were performed by dosing gases while the Fe sample was held at its base temperature of 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.

### 3. Results

**3.1. Formation and Reaction of Ethyl Groups on Fe(100)-H.** Recently we have reported that ethylene has been found to reversibly form ethyl groups (C<sub>2</sub>H<sub>5</sub>) on an Fe(100) surface which has been presaturated with 1 ML of hydrogen.<sup>1</sup> (Hereafter the H-saturated Fe(100) surface will be referred to as Fe(100)-H.) Ethylene adsorbs molecularly at 110 K, with a saturation coverage of  $0.25 \pm 0.05$  ML. Upon heating the crystal the desorption of molecular ethylene at ca. 160 K competes with the migratory insertion to form adsorbed ethyl. The maximum yield of ethyl groups in this reaction is  $0.12 \pm 0.03$  ML. Ethyl groups undergo  $\beta$ -H elimination at ca. 220 K to regenerate adsorbed ethylene, which rapidly desorbs, and H adatoms. Desorption of hydrogen becomes significant only at temperatures above 250 K; thus the surface remains covered with H adatoms throughout the reactions of ethylene and ethyl.

Our evidence for the formation of C<sub>2</sub>H<sub>5</sub> includes H-D exchange reactions and both primary and secondary kinetic isotope effects in the  $\beta$ -H(D) elimination reaction. Specifically, C<sub>2</sub>H<sub>4</sub> adsorbed on Fe(100)-D incorporates deuterium into the ethylene product

- (1) Burke, M. L.; Madix, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 3675.
- (2) Burke, M. L.; Madix, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 1475.
- (3) Burke, M. L.; Madix, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 4151.
- (4) Burke, M. L.; Madix, R. J. *Surf. Sci.* **1990**, *237*, 20.

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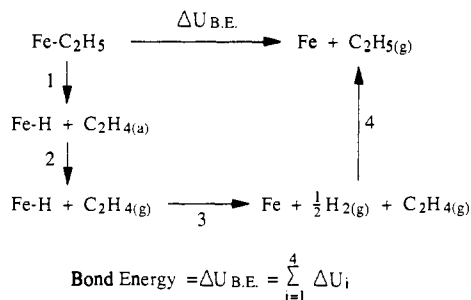


Figure 1. A thermochemical cycle constructed to determine the Fe-C bond strength for ethyl groups on Fe(100)-H.

Table I. Activation Energies Used To Determine Bond Strengths<sup>1</sup>

step	reaction	activation energy (kcal/mol)
1	$\beta$ -H elimination of C <sub>2</sub> H <sub>5</sub>	13.2 ± 0.6
-1	migratory insertion of C <sub>2</sub> H <sub>4</sub> + H	6 ± 1
2	desorption of C <sub>2</sub> H <sub>4</sub>	8 ± 1.5
2-(-1)		1.8 ± 0.3 <sup>a</sup>
-2	adsorption of C <sub>2</sub> H <sub>4</sub>	0
3	desorption of 1/2 H <sub>2</sub>	8.4 ± 0.3
-3	adsorption of 1/2 H <sub>2</sub>	1 ± 1

<sup>a</sup> See footnote 6.

of  $\beta$ -H(D) elimination. Kinetic studies of  $\beta$ -H elimination of (a) C<sub>2</sub>H<sub>5</sub> and (b) CD<sub>2</sub>CHD<sub>2</sub> and  $\beta$ -D elimination of (c) C<sub>2</sub>D<sub>5</sub> yield  $k_H/k_D$  values at 219 K of 1.9 ± 0.2 for the secondary ( $k_a/k_b$ ), 4.9 ± 0.5 for the primary ( $k_b/k_c$ ), and 9.4 ± 1.1 for the total ( $k_a/k_c$ ) kinetic isotope effects.

Additional evidence for the formation of C<sub>2</sub>H<sub>5</sub> from ethylene is the observation that coadsorbed CO induces the formation of ethane from ethylene on Fe(100)-H;<sup>2</sup> no ethane is formed without the addition of CO.<sup>1</sup> Ethane formation in the presence of CO is quite facile, with an evolution temperature of approximately 165 K when CO is coadsorbed with the isolated C<sub>2</sub>H<sub>5</sub> intermediate. The ease of ethane formation suggests that the isolated intermediate is directly involved in ethane formation and supports our identification of the intermediate as C<sub>2</sub>H<sub>5</sub> rather than another species, e.g., vinyl (CHCH<sub>2</sub>) or ethylidyne (CCH<sub>3</sub>). Furthermore, the coadsorption of CO with ethylene at 110 K on Fe(100)-H yields ethane at the higher temperature of 170 K; thus ethane is not formed until after the intermediate is created.

**3.2. Evaluation of the Fe-C<sub>2</sub>H<sub>5</sub> Bond Energy.** Parameters obtained from extensive kinetic studies allow an accurate estimate for the Fe-C<sub>2</sub>H<sub>5</sub> bond energy to be made using a thermochemical cycle (Figure 1, Table I). Cleavage of the Fe-C bond of a surface ethyl group is reconstructed in four steps, with the sum of the internal energy changes ( $\Sigma \Delta U_i$ ) for these steps assigned to the bond energy. The  $\Delta U_i$  values are derived from experimentally determined activation energies ( $E_i$ ), with  $\Delta U_i$  for step  $i$  equal to the difference between forward and reverse internal energies of activation,  $\Delta U_i^\ddagger - \Delta U_{-i}^\ddagger$ . In the precise terms  $E_i = \Delta U_i^\ddagger + RT$  for an isothermal reaction,<sup>5</sup> but since forward and reverse rate parameters will be used, the  $RT$  terms cancel for each step; thus  $\Delta U_i = E_i - E_{-i}$ .

The first two steps in the thermochemical cycle consist of  $\beta$ -H elimination from ethyl groups to yield C<sub>2</sub>H<sub>4(a)</sub> and H<sub>(a)</sub> followed by desorption of ethylene into the gas phase. The total internal energy change for these steps is equal to the activation energy for  $\beta$ -H elimination,  $E_1$ , plus that for ethylene desorption,  $E_2$ , minus that for C<sub>2</sub>H<sub>5(a)</sub> formation from H<sub>(a)</sub> + C<sub>2</sub>H<sub>4(a)</sub>,  $E_{-1}$ . We observed a high sticking probability for ethylene on Fe(100)-H; thus ethylene adsorption appears to be nonactivated, i.e.,  $E_{-2} = 0$ . We thus estimate  $\Delta U_1 + \Delta U_2$  to be  $E_1 + (E_2 - E_{-1})$  or 13.2 + 1.8 = 15.0 ± 0.9 kcal.<sup>6</sup>

(5) Levine, I. N. *Physical Chemistry*; McGraw-Hill: New York, 1978; Chapter 23.

Table II. Metal-Alkyl Bond Energies for Complexes

system	R	bond energy (kcal/mol)	ref
R-Fe(100)-H	C <sub>2</sub> H <sub>5</sub>	38	this work
R-Co(PMe <sub>2</sub> Ph)(DH) <sub>2</sub>	CH(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub>	24 <sup>a</sup>	10
R-Co(PEtPh <sub>2</sub> )(DH) <sub>2</sub>	CH(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub>	19	10
R-Co(PPh <sub>3</sub> )(DH) <sub>2</sub>	CH(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub>	17	10
R-Mn(CO) <sub>5</sub>	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	29	9
	CH <sub>3</sub>	44	9
R <sub>2</sub> -Ir(Cp*)(PMe <sub>3</sub> )	CH <sub>3</sub>	56 <sup>b</sup>	9
R <sub>2</sub> -W(Cp) <sub>2</sub>	CH <sub>3</sub>	50 <sup>b</sup>	9
R-Rh(H)(Cl)(PH <sub>3</sub> ) <sub>2</sub>	C <sub>2</sub> H <sub>5</sub>	35 <sup>c</sup>	9

<sup>a</sup>(DH)<sub>2</sub> = dimethylglyoxime. <sup>b</sup> Mean value. <sup>c</sup> Calculated value.

Recombinative desorption of hydrogen constitutes the third step in the cycle. An activation energy of 16.8 kcal has been measured for H<sub>2</sub> desorption at high H adatom coverages,<sup>4</sup> and the upper limit of the barrier to H<sub>2</sub> adsorption was found to be 2 kcal/mol by assuming that an activation barrier to adsorption is solely responsible for reduction of the sticking probability of H<sub>2</sub> from its maximum possible value of 1 to its measured value of 0.05.<sup>4</sup> The value of  $\Delta U_3$  is thus (16.8 - 2)/2 or 7.4 ± 1.3 kcal/mol.

The  $\Delta U$  for step four is derived from gas phase enthalpies of formation at 300 K of 26.5 ± 1 kcal/mol for C<sub>2</sub>H<sub>5</sub>, 0 for H<sub>2</sub>, and 12.5 kcal/mol for C<sub>2</sub>H<sub>4</sub>;<sup>7</sup> the resulting value for  $\Delta H_4$  is 14.0 ± 1 kcal/mol at 300 K. This is converted to the  $\Delta U_4$  value of 14.3 ± 1 by subtracting  $\Delta nRT$ , with  $\Delta n$  being the change in gas phase molecules, or -1/2.

Finally, to make the process isothermal at 300 K, corrections must be made for internal energy changes of the system between 300 K and the temperatures at which activation energies were measured. It is assumed that all vibrational contributions to internal energy in the thermodynamic cycle will cancel, and thus it is only the ideal gas translational and rotational terms which contribute.<sup>8</sup> For these terms  $\Delta U = C_V \Delta T$ , where  $C_V$  is the constant volume heat capacity, 3R for nonlinear and 5R/2 for linear molecules, i.e., C<sub>2</sub>H<sub>4</sub> and H<sub>2</sub>, respectively, where R is the gas constant. The internal energy required to take ideal gas products from their evolution temperature (C<sub>2</sub>H<sub>4</sub> at 160 K and 1/2 H<sub>2</sub> at 290 K) to 300 K is 0.8 kcal/mol. Summing the  $\Delta U_i$  and error values then results in an Fe-C<sub>2</sub>H<sub>5</sub> bond strength of 38 ± 4 kcal/mol at 300 K.

**3.3. Evaluation of the Fe-H Bond Energy.** The Fe-H bond energy at 300 K is obtained much more simply, but in a similar fashion as for Fe-C<sub>2</sub>H<sub>5</sub>. The above assumption for the barrier to adsorption of approximately 2 kcal for H<sub>2</sub> is kept as is the correction for taking the gas phase product from its evolution temperature to 300 K. For Fe-H, the binding energy is then the sum of the internal energy change for desorption of 1/2 H<sub>2</sub>, (16.8 - 2)/2 kcal/mol, plus the heat of formation of a gaseous H atom from 1/2 H<sub>2</sub>, 52.1 kcal. The correction for taking gas phase H<sub>2</sub> from 290 K to 300 K is negligible. The result is an Fe-H bond of 59.5 ± 2 kcal/mol at 300 K.

#### 4. Discussion

In an attempt to further the understanding of how transition metal bonding varies upon increasing the degree of metal nucleation, we compare our Fe-C<sub>2</sub>H<sub>5</sub> and Fe-H bond strengths to those of mononuclear transition metal complexes. Since to the

(6) Kinetic simulations of the branched reaction involving ethylene desorption and migratory insertion to form ethyl allow the quantity  $E_2 - E_{-1}$  to be determined more accurately than the sums of uncertainties on the individual parameters.

(7) Benson, S. W. *Thermochemical Kinetics* 2nd ed.; Wiley: New York, 1976.

(8) The only vibrational contributions to  $\Delta U$  which may not be negligible are those of the (unknown) low frequency modes of the ethyl surface complex. These contributions would occur in a step cooling the surface alkyl from 300 K to ca. 200 K where activation energies were measured. The contribution would be smaller than, and of opposite sign to, the  $\Delta U$  for warming the gas phase ethylene product back to 300 K. We thus have neglected these surface vibrations and have included the 0.8 kcal/mol contribution from heat capacities of gas phase products in our error limits.

best of our knowledge no other metal-alkyl bond strengths are known for surfaces or cluster complexes, the comparison of our value of  $38 \pm 4$  kcal/mol for the Fe-C<sub>2</sub>H<sub>5</sub> bond strength is necessarily restricted to mononuclear complexes.

**4.1. Metal-Alkyl Bond Strengths.** Quantitative values for transition metal alkyl bond strengths are difficult to obtain, but recently more have appeared in the literature. A review by Stoutland et al.<sup>9</sup> incorporates recent results; values referred to here are listed in Table II. The bulk of the work has been conducted by Halpern and co-workers for sterically crowded octahedral Co-alkyl complexes.<sup>10,11</sup> The cobalt-alkyl bond energies have been found to be quite low, ranging from 17 to 25 kcal/mol. Steric interaction is a critical factor in the metal-alkyl bond energy, with a remarkable decrease in bond energy occurring as the either the alkyl or the ligands become bulkier. This is exemplified by variations in Co-CH(CH<sub>3</sub>)C<sub>6</sub>H<sub>5</sub> bond energies as bulkier substituents are added to the tertiary phosphine ligand located trans to the alkyl; along the series from PMe<sub>2</sub>Ph (where Me = CH<sub>3</sub> and Ph = C<sub>6</sub>H<sub>5</sub>) to PPh<sub>3</sub>, the Co-CH(CH<sub>3</sub>)C<sub>6</sub>H<sub>5</sub> bond energy drops continuously from 24 to 17 kcal/mol.

Considerably higher M-C bond energies are found for alkyl complexes with less steric crowding. For example, energies of 29 and 44 kcal/mol are reported for the Mn-CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> (benzyl) and Mn-CH<sub>3</sub> (methyl) bonds in MnR(CO)<sub>5</sub>; metal-benzyl bonds are among the weakest and metal-methyl bonds are usually among the strongest of metal-alkyl bonds.<sup>12</sup> Values determined for H<sub>2</sub>Ir(Cp\*)PMe<sub>3</sub>, however, are considerably higher, as is the mean W-CH<sub>3</sub> bond energy of W(CH<sub>3</sub>)<sub>2</sub>(Cp)<sub>2</sub>, with energies in the range of 48-58 kcal/mol. (Here and elsewhere Cp = η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub> and Cp\* = η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>.) The high M-alkyl bond energies for both W and Ir exemplify the inherently higher bond strengths for third row transition metals; this phenomenon has been attributed to relativistic effects.<sup>13</sup> For these complexes the Cp ligands reduce steric interactions with the alkyl in that they occupy three coordination sites and thus occupy less space than three individual ligands would. In terms of calculated bond energies we refer to those for a simplified model of Wilkinson's hydrogenation catalyst.<sup>14</sup> For the alkyl hydride intermediate HRh(C<sub>2</sub>H<sub>5</sub>)Cl(PH<sub>3</sub>)<sub>2</sub>, the Rh-C bond energy has been calculated to be 35.5 kcal/mol.

The 38 kcal/mol bond strength for ethyl groups bound to Fe(100)-H falls exactly in the range expected for a first row transition metal complex; there thus appears to be no unusual enhancement in the bond strength for this metal-carbon σ bond on the extended surface. In fact, the bond energy is much less than that reported for gas phase Fe<sup>+</sup>-C<sub>2</sub>H<sub>5</sub> (52 kcal/mol), though the bond strength for the neutral may be lower.<sup>15</sup> It might seem the bond energy to Fe(100)-H should be higher since a surface can accommodate modes of bonding not available in complexes, i.e., coordination to several metal atoms at 2-fold bridge and 4-fold hollow sites. This appears not to be the case. The advantage of coordination to several metal atoms, indeed, appears to be greatest for π rather than σ bonding; calculations for CO adsorbed on Ni, Pd, and Pt surfaces indicate that the extent to which the CO π\* orbital interacts with the surface increases as the number of metal atoms CO is coordinated to is increased.<sup>16,17</sup> However, the σ bonding interaction between the CO 5σ orbital and the surfaces of Pd and Pt is greatest for CO binding to a single metal atom.<sup>17</sup>

(9) Stoutland, P. O.; Bergman, R. G.; Nolan, S. P.; Hoff, C. D. *Polyhedron* **1988**, *7*, 1429.

(10) Halpern, J. *Inorg. Chim. Acta* **1985**, *100*, 41.

(11) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 238.

(12) Excellent correlations between metal-alkyl and H-alkyl bond energies have been obtained for several transition metal complexes (ref 9 and ref 24 therein). The strong H-methyl and weak H-benzyl bonds (104 and 85 kcal/mol, respectively) suggest that metal-methyl (-benzyl) bonds should be among the strongest (weakest) metal-alkyl bonds.

(13) Ziegler, T.; Tschinke, V.; Becke, A. *J. Am. Chem. Soc.* **1987**, *109*, 1351.

(14) Daniel, C.; Koga, N.; Fu, X. Y.; Morokuma, K. *J. Am. Chem. Soc.* **1988**, *110*, 3773.

(15) Schultz, R. H.; Elkind, J. L.; Armentrout, P. *J. Am. Chem. Soc.* **1988**, *110*, 411.

(16) Sung, S.-S.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 578.

(17) Anderson, A. B.; Awad, Md. K. *J. Am. Chem. Soc.* **1985**, *107*, 7854.

Table III. Metal-H Bond Energies for Complexes

system	bond energy (kcal/mol)	ref
Fe(100)-H	59	this work
H-Mn(CO) <sub>5</sub>	65	18
H-Co(CO) <sub>4</sub>	57	18
H <sub>2</sub> -Fe(CO) <sub>4</sub>	<65 <sup>a</sup>	18
H <sub>2</sub> -Rh(Cl)(PAr <sub>3</sub> ) <sub>3</sub>	58 <sup>a,b</sup>	18
H <sub>2</sub> -W(Cp) <sub>2</sub>	73 <sup>a</sup>	18
H <sub>2</sub> -Os(CO) <sub>4</sub>	78 <sup>a</sup>	9
H <sub>2</sub> -Ir(Cp*)(PMe <sub>3</sub> )	74 <sup>a</sup>	9

<sup>a</sup> Mean value. <sup>b</sup> Ar = *p*-tolyl.

We recognize that our Fe-C<sub>2</sub>H<sub>5</sub> bond energy is not for a bare metal surface but for a surface extensively covered with H adatoms. Even though ethyl groups were formed on a surface initially saturated with H adatoms, a vacancy for Fe-C<sub>2</sub>H<sub>5</sub> binding is created in the C<sub>2</sub>H<sub>4(a)</sub> + H<sub>(a)</sub> insertion reaction. Thus there should not be direct competition between C<sub>2</sub>H<sub>5(a)</sub> and H<sub>(a)</sub> for binding sites so the Fe-C<sub>2</sub>H<sub>5</sub> bond energy should not be drastically reduced from the bare surface value. However, there may be some repulsion between C<sub>2</sub>H<sub>5(a)</sub> and H adatoms, and the H adlayer undoubtedly affects the electronic character of the Fe-C<sub>2</sub>H<sub>5</sub> bond; the metal-alkyl bond may thus be somewhat stronger on a bare surface. The presence of H adatoms on the surface in our experiments creates a "ligated" environment for C<sub>2</sub>H<sub>5(a)</sub> similar to a coordinatively saturated transition metal complex, yet without large steric interactions. Comparison of our results with those for unhindered, coordinatively saturated metal-alkyl complexes is thus appropriate.

**4.2. Metal-H Bond Strengths.** The metal-H bond energy at H saturation on Fe(100) of 59.5 kcal/mol estimated above is close to metal-H bond strengths for mononuclear transition metal complexes which have been determined to be remarkably uniform at approximately 60 kcal/mol (Table III).<sup>10,18</sup> The values for several third row metal dihydride complexes stand out as having unusually strong M-H bonds; these bond energies are 73 kcal/mol for H<sub>2</sub>W(Cp)<sub>2</sub>,<sup>18</sup> 78 kcal/mol for H<sub>2</sub>Os(CO)<sub>4</sub>,<sup>9</sup> and 74 kcal/mol for H<sub>2</sub>Ir(Cp\*)PMe<sub>3</sub>.<sup>9</sup> The strong M-H bonding in these complexes is consistent with the strong M-alkyl bonds found for complexes of third row metals (section 4.1). Calculations for M-H bond energies in carbonyl complexes also reflect these intrinsically high energies for the third row hydrides and, as noted above, have been attributed to relativistic effects.<sup>13</sup>

For surfaces in general, transition metal-H binding energies decrease from left to right along a given row in the periodic table, with little variation down a particular column.<sup>19</sup> As in complexes the M-H bond energies are relatively constant in the range of 60-70 kcal/mol. However, the values can vary considerably as a function of hydrogen coverage with lower bond energies at high coverages indicative of adatom-adatom repulsion, possibly mediated through the metal electronic states.<sup>20,21</sup> The Fe-H bond energy of 59.5 kcal/mol was found at a high H adatom coverage; thus as for our Fe-C<sub>2</sub>H<sub>5</sub> bond energy it is appropriate to compare this value to M-H bond energies found for coordinatively saturated complexes.

**4.3. Fe-Ethylene Bond Strength.** We have also extracted an M-C<sub>2</sub>H<sub>4</sub> bond energy of approximately 8 kcal/mol for Fe(100)-H. However, ethylene is binding on top of a saturated adlayer of H in our experiments (as opposed to ethyl groups where vacancies in the H-adlayer are created during their formation); there is thus direct competition between C<sub>2</sub>H<sub>4(a)</sub> and H<sub>(a)</sub> for binding sites which may prohibit ethylene from binding in its preferred site. In a sense the surface is coordinatively saturated before the adsorption of ethylene. The unknown structural constraints cannot be deconvoluted from other factors which influence binding, such as electronic structure of the surface and its modification by H

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(19) Norlander, P.; Holloway, S.; Norskov, J. K. *Surf. Sci.* **1984**, *136*, 59.

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(21) Ruchenstein, E.; Halachev, T. *Surf. Sci.* **1982**, *122*, 422.

adatoms. We have thus refrained from comparing this bond energy to those of complexes. Note, however, that the weak bond energy for  $C_2H_4$  on Fe(100)-H does not reflect the possible enhancement of metal-adsorbate  $\pi$  interactions for a surface relative to a single metal atom. That ethylene readily decomposes on clean Fe(100)<sup>22-24</sup> but not on Fe(100)-H<sup>1</sup> at least reflects the altered reactivity for the H-presaturated surface, if not the interaction strength.

### 5. Summary and Conclusions

Previously we have reported the reaction pathways and kinetics for ethylene on H-presaturated Fe(100). The formation of ethyl groups and their decomposition to regenerate ethylene was demonstrated using H-D exchange reactions and kinetic isotope effects.

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(23) Brucker, C.; Rhodin, R. *J. Catal.* **1977**, *47*, 214.

(24) Rhodin, T. N.; Brucker, C. F.; Anderson, A. B. *J. Phys. Chem.* **1978**, *82*, 894.

A thermochemical cycle has been constructed for these reactions and has been used to accurately determine Fe-C<sub>2</sub>H<sub>5</sub> and Fe-H bond energies on this surface of  $38 \pm 4$  and  $59.5 \pm 2$  kcal/mol, respectively. It is the first instance we know of where a metal-alkyl bond strength has been determined for a transition metal surface.

Comparison of our Fe-C<sub>2</sub>H<sub>5</sub> and Fe-H bond energies to those of mononuclear transition metal complexes shows that the values on the Fe surface are precisely in the range expected for a sterically unhindered complex containing a first or second row transition metal. That both bond energies should follow the same trend with degree of metal nucleation is reasonable since they are both of  $\sigma$  character. Our results suggest that the extended surface does not lead to a bond strength appreciably greater than expected in mononuclear complexes.

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## Rare Gas-Metal Carbonyl Complexes: Bonding of Rare Gas Atoms to the Group VI Pentacarbonyls

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**Abstract:** Transient infrared spectroscopy has been used to study reactions of  $M(CO)_5$  generated by 355-nm photolysis of  $M(CO)_6$  where  $M = Cr, Mo,$  and  $W$ . At 298 K,  $M(CO)_5$  reacts with CO with bimolecular rate constants of  $(1.4 \pm 0.2) \times 10^{-10}$ ,  $(1.5 \pm 0.1) \times 10^{-10}$ , and  $(1.4 \pm 0.1) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for Cr, Mo, and W, respectively.  $M(CO)_5$  also reacts with Xe with bimolecular rate constants of  $(0.9 \pm 0.4) \times 10^{-10}$ ,  $(0.9 \pm 0.4) \times 10^{-10}$ , and  $(2.6 \pm 0.2) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for Cr, Mo, and W, respectively. Infrared absorptions attributed to  $M(CO)_5Xe$  and  $W(CO)_5Kr$  were observed. The rate of dissociative loss of the Xe atom from the  $M(CO)_5Xe$  complexes was determined by the observation of the rate of regeneration of  $M(CO)_6$  in a reaction mixture consisting of  $M(CO)_5$ , CO, and Xe. The bond dissociation energy for the loss of the Xe atom from  $M(CO)_5Xe$  for all three metals is the same within experimental error and has an average value of 8.5 kcal/mol. A bond dissociation energy was estimated for the loss of Kr from  $W(CO)_5Kr$ , and an upper limit can be estimated for the bond dissociation energy for loss of Ar from  $W(CO)_5Ar$ .

### I. Introduction

Time resolved infrared spectroscopy (TRIR) has been employed to observe coordinatively unsaturated organometallic species in real time, monitor their kinetic behavior, and generate infrared spectra of these short lived species.<sup>1</sup> One conclusion of this body of work is that coordinatively unsaturated organometallic species can be extraordinarily reactive, with rate constants often approaching the gas kinetic limit. It has recently been shown that these species can even bind "poor" ligands such as N<sub>2</sub>O and CF<sub>2</sub>Cl<sub>2</sub>.<sup>2</sup> Reports also exist of coordination of coordinatively unsaturated organometallics with normally inert solvents on a picosecond time scale.<sup>3</sup>

The rate constants for and energetics of solvation of coordinatively unsaturated species have potential ramifications for a host of organometallic systems.<sup>4</sup> If the rate constant for solvent

coordination by the coordinatively unsaturated species is comparable to the rate constant for reaction of the other ligand(s) present in the system and the bond energy of the coordinated solvent molecule is comparable to the bond energy of the other ligands present, then the solvent molecule is in effect competing with the other potential ligands for the open site(s) on the coordinatively unsaturated organometallic species. Since the solvent is typically present in far greater concentration than added ligands, the kinetics of competitive binding can be biased toward the solvent. Thus the solvent could affect the measured rate constant or potentially even the pathway of a solution-phase chemical reaction.

The gas phase is the phase of choice for studying ligand interactions (including potential reactions with solvent molecules) via TRIR because the interaction between potential ligands and isolated nonsolvated coordinatively unsaturated species can be studied in detail in real time using the technique employed in ref 2. It has been shown that the bond energy between a weakly bound ligand (solvent molecule) and the coordinatively unsaturated organometallic can be determined by monitoring the rate of dissociative loss of the ligand (solvent) from the  $M(CO)_xS$  species as a function of temperature. Additionally, the infrared spectrum of the complex formed from the coordinatively unsaturated organometallic complexed with a solvent molecule can give clues to the nature of the solvent bond by monitoring the carbonyl

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