Theoretical and kinetic assessment of the mechanism of ethane hydrogenolysis on metal surfaces saturated with chemisorbed hydrogen

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1. Introduction

Hydrogenolysis of C–C bonds on metals is the reaction of choice for decreasing the chain length of acyclic molecules and for opening rings in cyclic hydrocarbons [1–12]. It is also responsible, however, for yield losses during hydrocarbon reforming and isomerization [13,14], making mechanistic models of hydrogenolysis reactivity and selectivity useful in practice [15]. C–C bond rupture has been widely used to probe the effects of cluster size [9,10,16–26], elemental identity, and alloying [27–37] in catalysis. Early studies recognized that hydrogenolysis requires the progressive weakening of C–C bonds through the formation of unsaturated intermediates that replace C–H bonds with C-metal bonds on surfaces [9,11,16,38–41]. The structure and degree of unsaturation of these species on metal surfaces have been inferred indirectly from measured effects of H2 pressure on hydrogenolysis rates [29,38–40] and from isotopic exchange data [42–44], because they lack distinguishable spectroscopic signatures required for their direct interrogation and, therefore, can only be assessed using theoretical methods [35,45–48].

Our recent studies have addressed the enthalpic and entropic barriers that govern reactivity and selectivity in hydrogenolysis of C7–C10 n-alkanes [49] and isoalkanes [50] on supported Ir clusters. Here, we combine hydrogenolysis turnover rates and their kinetic interpretation on Ir clusters saturated with chemisorbed hydrogen (H+) with density functional theory (DFT) treatments on the Ir(111) surface in order to infer mechanistic details for the hydrogenolysis of ethane. This study shows that C–C bond cleavage occurs via a specific reactive intermediate (‘CHCH’) that...
forms by the loss of four H-atoms (as H₂) through the sequential dehydrogenation of adsorbed ethane molecules. These findings and the DFT-derived activation barriers agree well with measured turnover rates and activation energies on Ir clusters. They confirm the essential role of unsaturation in the cleavage of C–C bonds in ethane [45,46,48] and, by inference, in larger n-alkanes, iso-alkanes, and cycloalkanes [78,16,35,47], for which similar kinetic dependencies and activation barriers have been observed. The identification of the reactive species that cleave C–C bonds shows also how their concentrations depend on H₂ pressures and temperatures and can, therefore, inform the choice of reaction conditions and catalysts for processes that deliberately, or inadvertently, involve hydrogenolysis reactions.

2. Methods

2.1. Synthesis and characterization of Ir–SiO₂

Ir–SiO₂ (3.0 wt.%) was prepared by incipient wetness impregnation using reported methods [49]. Samples were heated to 393 K at 0.017 K s⁻¹ in flowing dry air (Praxair, 99.99%, 5.0 cm³ g⁻¹ s⁻¹) and held for 8 h and subsequently heated at 0.033 K s⁻¹ to 1123 K and held for 12 h. The sample was cooled to ambient temperature and then heated at 0.033 K s⁻¹ to 1173 K in flowing 50% H₂/He (Praxair, 99.999%, 1.0 cm³ g⁻¹ s⁻¹) and held for 8 h. The sample was again cooled to ambient temperature and passivated in flowing 0.5% O₂/He (Praxair, 99.99%, 1.0 cm³ g⁻¹ s⁻¹) for 3 h. The number of exposed Ir atoms (Irₐ) was determined from volumetric uptakes of H₂, O₂, and CO at 298 K [49,51] and the mean Ir cluster diameter (dₘ) was estimated by assuming hemispherical crystallites and the atomic density of bulk Ir (70.7 atoms nm⁻³) [52,53]. Ir fractional dispersions from H₂, O₂, and CO chemisorption were 0.13, 0.15, and 0.13, respectively, the average of which indicates that the mean diameter of the Ir clusters was 7 nm. Distribution of cluster sizes was determined by transmission electron microscopy (TEM) in bright-field mode (Philips, CM200F) using samples applied as a fine dust onto lacey carbon-coated Cu grids. Surface-averaged cluster diameters were calculated using the following:

< dₘ > = \frac{\sum_n n d_n^3}{\sum_n n d_n^2} (1)

where nᵢ is the number of clusters with a diameter dᵢ (1029 clusters) [54]. Values of < dₘ > (14.4 nm) and < dₘ > (7 nm) indicate that the majority of the Ir exists in aggregates of ~10⁴ atoms. We must conclude that, in this case, distributions of detected cluster sizes overestimate the mean cluster diameter because TEM does not detect a significant number of small (< 0.6 nm) clusters that are represented in chemisorption experiments. Thus, we conclude that the chemisorption measurements most accurately represent the average size of the clusters, 7 nm, and the corresponding number of Irₐ is used to calculate hydrogenolysis turnover rates. The Ir content was measured by inductively-coupled plasma optical emission spectroscopy (Gallbraith Laboratories, Inc.). The Supporting Information summarizes the synthesis and characterization of the 7 nm Ir–SiO₂ catalyst (Table S1) and contains a representative TEM image and cluster size distribution for the Ir–SiO₂ catalyst (Fig. S1).

2.2. Ethane hydrogenolysis rate measurements

Ethane hydrogenolysis rates were measured in a flow packed-bed stainless steel tubular reactor (3/8” O.D.) with plug-flow hydrodynamics from 553 to 663 K with ethane ((C₂H₆)) and hydrogen ((H₂)) pressures from 10 to 80 kPa and from 0.6 to 1.8 MPa, respectively. The reactor was placed within a three-zone resistively-heated furnace, and the bed temperature was measured with a type K thermocouple held within a 1/16” stainless steel sheath aligned axially along the bed. The Ir–SiO₂ catalyst was mixed with additional SiO₂ (Cab–O–Sil HS-5, washed with deionized water and treated in flowing dry air at 793 K for 5 h) to avoid any axial or radial temperature gradients. Pressure was controlled using a dome-loaded regulator (Mity-Mite, S91XX). The catalyst was treated in flowing H₂ (Praxair, 99.999%) at ambient pressure (50 cm³ g⁻¹ s⁻¹) by heating to 673 K at 0.083 K s⁻¹ and holding for 2 h. The composition of the reactant stream was set using electronic mass flow controllers (Parker, 201) to meter the flow rates of H₂ (Praxair, 99.999%), and ethane (5% ethane, 10% Ar, 85% He, Praxair, certified-grade). CH4 and C₂H₆ effluent concentrations were measured by gas chromatography (Agilent GC, 5890) using a methyl silicone capillary column (HP-1, 50 m x 0.32 mm x 1.05 μm) and a flame ionization detector. No other hydrocarbons were detected. All rates are reported at differential conversions (<5%) to avoid consequential axial gradients in reactant concentrations. Turnover rates are reported as moles of ethane consumed per unit time normalized by the number of surface metal atoms determined by chemisorption, and reported uncertainties represent two-standard deviations (95% confidence intervals).

2.3. Computational methods

Periodic plane-wave DFT calculations were performed using the Vienna ab initio simulation package (VASP) [55–58]. The plane-waves were constructed using projector augmented-wave (PAW) potentials with an energy cutoff of 396 eV [59,60]. The revised Perdew–Burke–Ernzerhof (RBE) form of the generalized gradient approximation (GGA) was used to determine exchange and correlation energies [61–63]. Calculations of gaseous species were computed using 18 × 18 × 18 Å unit cells. The catalyst surface was modeled as a 4 × 4 Ir(111) closed-packed periodic lattice with a lattice parameter of 3.84 Å; it consists of four layers in the z-direction with the bottom two layers fixed in their bulk positions and the other two allowed to relax to their minimum energy structures. Wavefunctions were converged to within 10⁻⁶ eV and forces were computed using a fast Fourier transform (FFT) grid with a cutoff of twice the plane-wave cutoff and a 3 × 3 × 1 Monkhorst–Pack sampling of the first Brillouin zone (k-point mesh) [64]. For optimizations, the structures were relaxed until the force on unconstrained sampling was <0.05 eV/Å. After geometric convergence, a single-point calculation with a 6 × 6 × 1 k-point mesh was performed to optimize energy minima of reactant, product, and transition states. Transition state (TS) structures were obtained for each elementary reaction by using the nudged elastic band (NEB) method [65,66] and the dimer method [67]. The NEB method was carried out using 16 images, and wavefunctions were converged to within 10⁻⁴ eV using a 3 × 3 × 1 k-point mesh and an FFT grid size of 1.5 times the plane-wave cutoff. The maximum force on each atom was converged to <0.3 eV/Å. These protocols provided an estimate of the reaction path and a starting point for the structure and the reactive vibrational mode for each transition state. The dimer algorithm was then used with wavefunctions converged to within 10⁻⁶ eV using a 3 × 3 × 1 k-point mesh and an FFT grid size of 2 times the plane-wave cutoff. For dimer calculations, the maximum force on each atom was converged to <0.05 eV/Å. As with optimizations of reactant and product states, the energy of the TS was then determined using a single-point calculation with 6 × 6 × 1 k-point mesh. Zero-point energy and thermal corrections were implemented using vibrational frequencies for reactants, transition states and products involved in each elementary step to estimate enthalpies and entropies of each state (details in Supporting information). For transition states, these frequency
analyses confirmed the transition state mode and the presence of a single negative frequency.

3. Results and discussion

Scheme 1 shows a sequence of elementary steps that account for measured rates for the hydrogenolysis of ethane [38–40,45,48,68], and which are analogous to steps for larger n-alkanes [17,49,69,70], and isoalkanes [17,27,50]. These steps are examined here by combining experimental rate data and DFT calculations. These elementary steps are consistent with the previously observed dependence of n-alkane hydrogenolysis rates on temperature and pressure. The reactive species (‘\( \text{C}_2\text{H}_y \)) cleave C–C bonds at rates proportional to their respective surface concentrations:

\[
r_y = k_{CC,y} [\text{C}_2\text{H}_y]\]

where \( r_y \) is the rate of C–C cleavage of species with \((6-y)\) H-atoms. The reactive species (‘\( \text{C}_2\text{H}_y \)) can plausibly contribute to measured ethane hydrogenolysis rates. Some of these quasi-equilibrated intermediates will preferentially contribute to the products formed, because C–C bonds weaken as C–H bonds are replaced by C-metal bonds, in a process that transfers electron density from the C–C bond to the surface metal atoms [73]. Consequently, measured hydrogenolysis rates and their dependence on temperature and hydrogen pressure (\((\text{H}_2)\)) reflect the appropriately averaged degree of unsaturation of the intermediate pool and the stability of the respective transition states that lead to C–C bond cleavage in each of these intermediates.

Fig. 1 shows \( \text{C}_2\text{H}_6 \) hydrogenolysis turnover rates as a function of \( \text{C}_2\text{H}_6 \) (Fig. 1a) and \( \text{H}_2 \) (Fig. 1b) pressures on Ir clusters of 7 nm mean diameter. Hydrogenolysis rates are proportional to \( \text{C}_2\text{H}_6 \) pressure ((\( \text{C}_2\text{H}_6 \)) \( \text{mol}^{-1} \)) and show an inverse dependence on \( \text{H}_2 \) pressure ((\( \text{H}_2 \)) \( \text{MPa}^{-1} \)). Measured \( \text{C}_2\text{H}_6 \) hydrogenolysis rates \( (r_{\text{obs}}) \) represent the combined rates of C–C bond cleavage for quasi-equilibrated reactive C\(_2\)-intermediates with each value of \( y \):

\[
r_{\text{obs}} = \sum_{y=0}^{6} r_y
\]

where \( r_y \) is the rate of C–C cleavage of species with \((6-y)\) H-atoms.

Scheme 1 includes \( \text{H}_2 \) dissociation (1.1), molecular \( \text{C}_2\text{H}_6 \) adsorption (1.2), and dehydrogenation of adsorbed \( \text{C}_2\text{H}_6 \) (\( \text{C}_2\text{H}_y^+ \)) via sequential C–H bond cleavage to form a quasi-equilibrated pool of dehydrogenated chemisorbed surface intermediates with \( y \) H-atoms removed from the ethane reactants (‘\( \text{C}_2\text{H}^{y-}_x \)) where \( 1 \leq y \leq 6 \) and ‘·’ denotes an intermediate bound to two vicinal metal atoms; (1.3–1.5)). C–C bond rupture may occur in any of these ‘\( \text{C}_2\text{H}^{y-}_x \)’ intermediates, which differ in both the number of H-atoms removed from ethane and the location from which they are removed. The presence of equilibrated mixtures of isobutane–isobutene [50] and cycloalkane–arene mixtures during hydrogenolysis on Ir [50,71] (and Pt, Ru, and Rh [72]) and the equilibrated nature of H/D exchange reactions during ethane hydrogenolysis on Pt [42], suggest that \( \text{H}_2 \) and ethane dissociation steps (steps 1.1–1.5) are indeed quasi-equilibrated, making C–C bond cleavage the sole kinetically-relevant step. Each surface intermediate (‘\( \text{C}_2\text{H}_y^+ \)) cleaves C–C bonds with a rate constant that reflects, in part, the stability of the transition state that mediates that reaction event; thus, any of these unsaturated species (‘\( \text{C}_2\text{H}_y^+ \)) can plausibly contribute to measured ethane hydrogenolysis rates. Some of these quasi-equilibrated intermediates will preferentially contribute to the products formed, because C–C bonds weaken as C–H bonds are replaced by C-metal bonds, in a process that transfers electron density from the C–C bond to the surface metal atoms [73]. Consequently, measured hydrogenolysis rates and their dependence on temperature and pressure ((\( \text{H}_2 \)) \( \text{mol}^{-1} \)) reflect the appropriately averaged degree of unsaturation of the intermediate pool and the stability of the respective transition states that lead to C–C bond cleavage in each of these intermediates.

**Scheme 1.** Proposed sequence of steps and intermediates in ethane hydrogenolysis on Ir clusters. ‘·’ denotes an unoccupied surface site; ‘·’ an intermediate bound to two vicinal metal atoms; \( k_x \) and \( k_{y+r} \) are kinetic constants for each forward and reverse step.

- \( \text{H}_2 + 2^* \xrightarrow{k_{H2}} 2 \text{H}^* \) (1.1)
- \( \text{C}_2\text{H}_6 + ^* \xrightarrow{k_{\text{C}_2\text{H}_6}} \text{C}_2\text{H}_y^* \) (1.2)
- \( \text{C}_2\text{H}_y^* + ^* \xrightarrow{k_{\text{C}_2\text{H}_y^*}} \text{C}_2\text{H}_y^+ + \text{H}^* \) (1.3)
- \( \text{C}_2\text{H}_y^* + 2^* \xrightarrow{k_{\text{C}_2\text{H}_y^*}} ^*\text{C}_2\text{H}_y^+ + \text{H}^* \) (1.4)
- \( ^*\text{C}_2\text{H}_y^{(y-1)}^* + ^* \xrightarrow{k_{\text{C}_2\text{H}_y^{(y-1)}^*}} ^*\text{C}_2\text{H}_y^{(y-1)}^* + \text{H}^* \) (1.5)
- \( ^*\text{C}_2\text{H}_y^{(y-1)}^* \xrightarrow{k_{\text{C}_2\text{H}_y^{(y-1)}^*}} \text{CH}_x^* + \text{CH}_x^* \) (1.6)
- \( \text{CH}_x^* + x\text{H}^* \xrightarrow{k_{\text{CH}_x^*}} \text{CH}_x + (x+1)^* \) (1.7)
In this case, the rate equation derived from elementary steps in Scheme 1, taken together with the assumption of quasi-equilibrated molecular adsorption and dehydrogenation steps (steps 1.1–1.5) [49], becomes:

\[
\begin{equation}
\tau_y = k_{\text{CC}} \cdot \prod_{n=1}^{y} K_{\text{CH,n}} \cdot K_{\text{CH6}} \cdot (C_2H_6)^{\cdot \cdot [L]} \cdot \gamma \cdot (C_2H_4)^{\cdot \cdot}
\end{equation}
\]

Here, \(K_{\text{HH}}\) and \(K_{\text{CH,n}}\) are the equilibrium constants for adsorption of \(H_2\) and \(C_2H_6\), respectively and \(\prod_{n=1}^{y} K_{\text{CH,n}}\) represents the product of the equilibrium constants for the sequential C–H bond ruptures that occur as \(C_2H_6\) dehydrogenates before C–C bond cleavage in each intermediate. This equation is consistent with measured hydrogenolysis turnover rates, which are proportional to \((C_2H_4)\) (Fig. 1a) and decrease with increasing \(H_2\) pressure (Fig. 1b). The value of \(\gamma\) (3.3 ± 0.2, from the data in Fig. 1b) in Equation (4) reflects the combination of the number of H-atom desorb from the surface \(\gamma\) to accommodate the reactive intermediate (reverse of step 1.1) and the number of H-atoms lost from \(C_2H_6\) to form reactive species that cleave C–C bonds \((y. 1.3–1.5)\) [49] according to the equation:

\[
y + \gamma = 2\lambda
\]

where \(\lambda\) must be multiplied by a factor of two because \(\lambda\) represents the number of \(H_2\) molecules while \(y\) and \(\gamma\) are the number of H-atoms. The chemical interpretation of \(\gamma\) values is identical on H-covered surfaces of other metal clusters (e.g., 0.7 nm Ir, 3.0 ± 0.2 [49]; 0.9 nm Rh, 3.0 ± 0.2 [49]; 0.6 nm Pt, 2.3 ± 0.2 [49]; and 1.0 nm Ru, 3.0 ± 0.2 [72]). These values show that C–C bonds are cleaved in deeply dehydrogenated intermediates derived from \(C_2H_6\) on metal cluster catalysts. This conclusion is consistent with previous findings that have shown that multiple H-atoms are lost from \(C_2H_6\) before the C–C bond cleaves on metal surfaces [28,38,74]. The chemical significance of the dependence of rates on \((H_2)\) is less clear for \(C_2H_6\)-covered surfaces (hydrocarbons as MAS) or surfaces containing both free sites and \(C_2H_2\)-species [28,38], because the average H-content of the surface intermediates and the H-content of the reactive intermediates are both unknown [49].

Ethane hydrogenolysis rates show that an average of 6.6 ± 0.4 H-atoms evolve as \(H_2\) during the formation of the reactive intermediates that undergo C–C bond cleavage on 7 nm Ir clusters (Fig. 1b). The non-integer nature of the reactivity-averaged value of \(y\) would indicate that several intermediates, with different H-contents (Eq. (2), e.g., ‘CHCH’ and ‘CHC’), have transition states with similar stability, thus cleaving C–C bonds at comparable rates. Non-integer \(\gamma\) values would show that multiple pairs of exposed Ir atoms, distinct in their H-coverage, contribute to measured rates. For example, ensembles that include edge and corner atoms, can bind more than one H-atom (H/Ir > 1) [75–77], and would give a different \(\gamma\) than ensembles containing only terrace sites, which bind a single H-atom. Alternatively, the rates could be dominated by C–C bond rupture that occurs entirely on ensembles of terraces (hydrocarbons as MASI) or surfaces containing both free sites and \(C_2H_2\)-species [28,38,74]. In these simulations, C–C cleavage can occur via interactions of \(C_2H_6\) with ‘**’ site pairs to form two \(CH_2\) fragments \((H_{\text{act}} = 200 \text{kJ mol}^{-1})\) but, oxidative metal–atom insertion into the C–H bond to form adsorbed ethyl \((CH_2CH_2)\) and \(\gamma\) involves a much smaller barrier \((H_{\text{act}} = 99 \text{kJ mol}^{-1})\). After this initial C–H activation step, \(CH_2CH_2\) can react with an unoccupied site to cleave the C–C bond and form \(CH_3CH_2\) and \(CH_2\) \((H_{\text{act}} = 136 \text{kJ mol}^{-1})\), but its dehydrogenation to form \(CH_3CH_2\) \((H_{\text{act}} = 29 \text{kJ mol}^{-1})\) or \(CH_2CH_2\) \((H_{\text{act}} = 46 \text{kJ mol}^{-1})\) or its hydrogenation by \(H^+\) to re-form \(CH_2CH_2\) \((H_{\text{act}} = 18 \text{kJ mol}^{-1})\) are more facile. Differences between the barrier to cleave the C–C bond and to form or cleave C–H bonds (>90 kJ mol−1) indicate that \(CH_3CH_2\) formation is quasi-equilibrated during ethane hydrogenolysis.

\[
H_{\text{xn}} \text{ and } H_{\text{act}} \text{ for C–C and C–H bond cleavage were calculated for all surface intermediates from C}_2H_2 \text{ to } ‘C_2’ \text{ (Fig. 2, and SI, Figs.}
\]
S2–S11]. Table 1 lists the ΔH‡ and ΔG‡ values, calculated from Eq. (7) and Eq. (10), respectively, for C–C bond cleavage in each of the 10 C2-intermediates. The formation and cleavage of C–H bonds is favored by >50 kJ mol⁻¹ over C–C bond cleavage for all "C2H₆, y" species, except "CHCH" intermediate. C–C bond cleavage in this "CHCH" intermediate shows a much lower activation barrier (Hact = 105 kJ mol⁻¹) than for its further dehydrogenation (Hact = 185 kJ mol⁻¹), indicating that "CHCH" is the dehydrogenated intermediate predominantly responsible for measured ethane hydrogenolysis turnover rates. Hact values for its hydrogenation steps to re-form C2H6 are lower than its Hact for C–C bond cleavage by >25 kJ mol⁻¹, consistent with quasi-equilibrated "CHCH" formation from C2H6. These conclusions are consistent with measured hydrogenolysis rates (Fig. 1) and with the rate equation Eq. (4), and its chemical interpretation [49].

The formalism of transition state theory [79] dictates that the gas-phase C2H6 and two H-atoms exist in quasi-equilibrium with the transition state that cleaves the C–C bond ("C2H₆, y") and the product H₂:

\[
\text{C}_2\text{H}_6 + y \cdot \text{H} \overset{K_1}{\rightleftharpoons} \text{C}_2\text{H}_6,y + y \cdot \text{H}_2
\]

where \(K\) is the equilibrium constant describing the overall equilibrium between these reactants and products. Hydrogenolysis rates for each reactive intermediate (Table 1) are calculated at 20 kPa C2H6, 1.8 MPa H2, and 593 K using the functional form of the rate expression derived from transition state theory:

\[
\frac{r}{[I]} = \frac{k_B T}{h} \exp \left(\frac{-\Delta G^\ddagger}{RT}\right) \left(\frac{\text{C}_2\text{H}_6}{\text{H}_2}\right)^y
\]

(12)

Here, \(k_B\) and \(h\) are the Boltzmann and Planck constant, respectively, and \(\Delta G^\ddagger\) and \(\lambda\) have values that depend on the intermediate (Table 1). Turnover rates reflect the reactivity of multiple intermediates only when their C–C bonds rupture at comparable rates Eq. (12). DFT-derived barriers (Table 1) show that the enthalpy barrier for cleaving C–C bonds in "CHCH" (ΔH‡ = 218 kJ mol⁻¹) is 13 kJ mol⁻¹ smaller than for the next most reactive intermediate (CH₃CH₃, ΔH‡ = 231 kJ mol⁻¹). Differences in ΔG‡ values for different reactive intermediates, which determine rate constants, also reflect the significant entropy gained from gas-phase H₂ formed by quasi-equilibrated dehydrogenation of C₂H₆ and desorption of H° from the surface [49]. As a result of entropy differences, it is far more favorable to cleave the C–C bond in "CHCH" (ΔG‡ = 137 kJ mol⁻¹) rather

![DFT-derived reaction enthalpy diagram for ethane hydrogenolysis on an Ir(111) surface at 593 K. Dashed lines show barriers for unfavorable C–C and C–H bond activation transition states. The intermediates CH₃C and ‘CHC’ are omitted for clarity, but are shown in SI (Figs. S8 and S10).](image-url)
than in CH₃CH⁺ (ΔG° = 229 kJ mol⁻¹) or any other intermediate (Table 1), because more deeply dehydrogenated intermediates produce a larger number of gaseous H₂ molecules, giving larger entropy gains (Table 1), which decrease ΔG° (Eq. (10)). Calculated barriers for C–C bond cleavage in ‘CHCH₊’ (ΔH° = 218 kJ mol⁻¹, ΔG° = 137 kJ mol⁻¹) agree within 10 kJ mol⁻¹ with measured barriers for C₃H₆ hydrogenolysis (ΔH° = 213 ± 2 kJ mol⁻¹, ΔG° = 130 ± 5 kJ mol⁻¹, Table 1); these experimental barriers were determined from changes in hydrogenolysis turnover rates with temperature (Fig. 3) on surfaces of 7 nm Ir clusters, which predominantly consist of close-packed (1 1 1) terraces [78]. The predicted rates for C–C bond cleavage in all possible reactive intermediates (Table 1) show that differences in ΔG° lead to much higher C–C bond cleavage rates in ‘CHCH’ (3.7 × 10⁻⁴ C₃H₆ Ir⁻¹ s⁻¹) than for any other species in the quasi-equilibrated pool of unsaturated intermediates (e.g., CH₃CH⁺, 5.2 × 10⁻¹¹ C₃H₆ Ir⁻¹ s⁻¹) (20 kPa C₃H₆, 1.8 MPa H₂, 593 K). These computational and experimental results, summarized in Fig. 4, show that measured hydrogenolysis turnover rates predominantly reflect C–C bond rupture in a single intermediate, ‘CHCH’, at the experimental conditions. Thus, the value of γ in Eq. (5) is equal to four.

DFT calculations show that measured hydrogenolysis rates reflect C–C cleavage rates in ‘CHCH’, therefore, four of the 6.6 ± 0.4 H-atoms that desorb come from dehydrogenating C₃H₆. This requires that the other 2.6 ± 0.4 H-atoms desorb from the catalyst surface (i.e., γ = 2.6 ± 0.4; Eq. (5)). This fractional value of γ indicates that H⁻-coverages are not uniform at all sites on 7 nm Ir clusters. A plausible interpretation involves ensembles of surface atoms that require either two or three H⁻ to desorb depending on the coordination of exposed atoms on non-uniform Ir clusters. Edge and corner atoms of Ir nanoparticles have larger H/Ir ratios than terraces at all H⁻-coverages, as shown by our DFT calculations on Ir₂₀₁ cubo-octahedral nanoparticles (1.6 nm in diameter, Fig. S2), DFT calculations on <1 nm Pt clusters [76], and experiments with Ir, Rh, and Pt clusters (<1.5 nm in diameter) [77]. The agreement between measured and DFT-derived ΔG° values (Table 1) and turnover rates (Fig. 4) indicates that hydrogenolysis occurs predominantly via the ‘CHCH’ reactive intermediate and that fractional γ values are likely to reflect differences between the H/Ir₁ among distinct active site ensembles on Ir clusters.

C₃H₆ hydrogenolysis rates on H⁻-covered Ir clusters and their kinetic dependence on reactant pressure and temperature and DFT-derived energy and free energy barriers for C–H and C–C bond cleavage on Ir(111) indicate that C–C cleavage occurs predominantly in a single reactive intermediate because of C–H and C–C bond activation barriers that vary with the H-content of C₂-species. Chemical similarities between alkanes suggest that hydrogenolysis rates for a given C–C bond in larger n-alkanes [49], isoalkanes [50], and cycloalkanes [50,71] will also arise from the rupture of a C–C bond within a small fraction of all unsaturated surface intermediates. The quasi-equilibrated nature of the intervening adsorption and dehydrogenation steps provide opportunities to control the position of C–C bond cleavage in larger alkane reactants by controlling H₂ pressures, which concomitantly change the relative coverages of intermediates with different degrees of unsaturation. Differences between C–H and C–C activation barriers will change with the elemental identity of metal clusters and cause the H-content of reactive intermediates to differ among catalysts [27–37]. In spite of this, even very small differences in ΔG° at typical temperatures for hydrogenolysis will cause C–C bond cleavage to occur predominately in a single unsaturated species [9,11,16,38–41].

### 4. Conclusions

Overall activation parameters (ΔH°, ΔS°, ΔG°) to cleave the C–C bond in ethane-derived C₂ surface intermediates were calculated by DFT and compared to measurements that reflect the composition of the reactive species and the ΔG° for the dominant reaction pathway. This comparison was possible because hydrogenolysis turnover rates were measured in the limit of well-defined coverages (H⁻ as MASI) on 7 nm Ir particles for which the predominant surfaces are similar to the (1 1 1) plane modeled in simulations. Results from DFT confirm that C₃H₆ undergoes quasi-equilibrated dehydrogenation steps, forming a pool of dehydrogenated intermediates prior to C–C bond cleavage. Each C₂-intermediate can undergo irreversible and kinetically-relevant C–C activation to form C₁ intermediates which are then rapidly hydrogenated to form CH₄. The rates at which each intermediate cleaves its C–C bond de-

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**Fig. 3.** Change in ethane hydrogenolysis turnover rate with reciprocal temperature on hydrogen-covered surfaces of 7 nm Ir–SiO₂ clusters at 20 kPa C₃H₆, 1.8 MPa H₂, 553–633 K.

**Fig. 4.** Turnover rates (logarithmic scale) for C–C bond rupture in all C₄-intermediates, calculated from Eq. (12), using ΔG° from DFT calculations for the Ir(111) surface, and experimentally measured turnover rate at these conditions on 7 nm Ir clusters (dashed line) at 20 kPa C₃H₆, 1.8 MPa H₂, 593 K.
hypothesis and /C3/C3/C3/C3 hydrogenolysis on large clusters of Ir, yet it establishes a methodology to effectively combine experiment and theory in order to study hydrogenolysis of complex alkanes and other reactants on metal clusters of different elements and sizes.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2013.11.026.

References