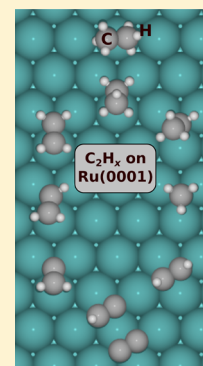


First-Principles Investigation of C–H Bond Scission and Formation Reactions in Ethane, Ethene, and Ethyne Adsorbed on Ru(0001)

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S Supporting Information

ABSTRACT: We have studied all possible elementary reactions (including isomerization reactions) involved in the interaction of CH₄ (methane), CH₃CH₃ (ethane), CH₂CH₂ (ethene), and CHCH (ethyne) with the Ru(0001) surface using density functional theory based first-principles calculations. Site preference and adsorption energies for all the reaction intermediates and activation energies for the elementary reactions are calculated. From the calculated adsorption and activation energies, we find that dehydrogenation of the adsorbates is thermodynamically favored in agreement with experiments. Dehydrogenation of CH (methylidyne) is the most difficult in the dehydrogenation of CH₄ (methane). CH₃CH₃ (ethane), CH₂CH₂ (ethene), and CHCH (ethyne) dehydrogenate through the CH₃C (ethylidyne) intermediate. Of the five possible pathways for the production of CH₃C (ethylidyne), the CH₂CH (ethenyl)–CH₂C (ethenylidene) pathway is the most dominant. In the case of ethene, the ethenyl–ethenylidene pathway is also the dominant pathway on Pt(111). Comparison of α and β -C–H bond scission reactions, important for the Fischer–Tropsch process, shows that alkenes should be the major products compared to the formation of alkynes. Dehydrogenation becomes slightly favorable at lower coverages of the hydrocarbon fragments while hydrogenation becomes slightly unfavorable. In addition to resolving the dominant pathways during decomposition of the above hydrocarbons, the activation energies calculated in this paper can also be used in the modeling of processes that involve the considered elementary reactions at longer length and time scales.



■ INTRODUCTION

C–H scission and formation reactions play an important role in a wide variety of industrial processes ranging from hydrogenation of unsaturated fats to the conversion of CO and H₂ to higher alkanes in the Fischer–Tropsch process.¹ In the Fischer–Tropsch process, hydrogenation and dehydrogenation reactions play an important role in the chain growth steps and also determine the final product distribution in terms of the amounts of various hydrocarbons.^{2,3} Among known Fischer–Tropsch catalysts, Ru is one of the most active. An in-depth knowledge of elementary C–H bond scission and formation reactions on its surface is therefore a welcome addition to existing knowledge.

In addition to the significance of C–H bond scission and formation reactions in traditional catalytic processes, they are also turning out to be important in thin film growth by atomic layer deposition (ALD). ALD is increasingly used to grow thin films at the nanometer scale with very good conformity even on complex structures. Among ALD of a variety of materials, noble metal ALD (Ru, Pt, Pd, etc.) finds uses in a number of applications ranging from microelectronics, clean energy, and catalysis to anticorrosion.^{4–9} It has recently been shown that after the initial nucleation of the noble metal film, the film itself catalyzes the decomposition of the precursor. In this light, achieving ultimate control over ALD of noble metals therefore requires a good understanding of precursor decomposition at the catalytic surface. This is still lacking.¹⁰ A number of

precursors used are organometallic in which various organic (and inorganic) ligands bond to a metal center (for example, RuCp₂, Ru(EtCp)₂, (CpMe)RuEt(CO)₂). The organic ligands are usually cyclic or aliphatic hydrocarbons like CH₃ (methyl), CH₃CH₂ (ethyl), Cp (cyclopentadienyl), CpMe (methyl cyclopentadienyl), and so forth. The decomposition of these organic ligands clearly involves C–H bond scission reactions. Thus, both traditional catalytic processes, like the Fischer–Tropsch process and precursor decomposition on noble metal surfaces, can benefit from the study of C–H bond scission and formation reactions. (Note: Names of all the hydrocarbon fragments used in this paper are derived from the names of the gas phase molecules: CH₄ (methane), CH₃CH₃ (ethane), CH₂CH₂ (ethene), and CHCH (ethyne). For a fragment derived from one of the gas phase molecules and short of 1 H, -ane (-ene, -yne) is modified to -yl (-enyl, -ynyl). If the molecule is short of 2 H atoms, -ane (-ene, -yne) is modified to -ylidene (-enylidene, -ylidene). And finally, if the molecule is short of 3 H atoms, -ane is modified to -ynyl. CH₂CH₂ (ethene), CHCH (ethyne), CH₂CH (ethenyl), and CH₂C (ethenylidene) are also commonly known as ethylene, acetylene, vinyl, and vinylidene, respectively.)

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Although the final objective would be to study the decomposition of the complete precursor, in this paper, as a first step, we restrict ourselves to the decomposition of CH_3 (methyl) and CH_3CH_2 (ethyl) groups on Ru(0001). Since CH_3 (methyl) and CH_3CH_2 (ethyl) groups are just one H atom short of CH_4 (methane) and CH_3CH_3 (ethane), we include the latter also in the present study. Since the elementary reactions in CH_4 (methane) are obvious, the decomposition pathway for CH_3CH_3 (ethane) on the Ru(0001) surface, including all the intermediates, is shown in Figure 1.

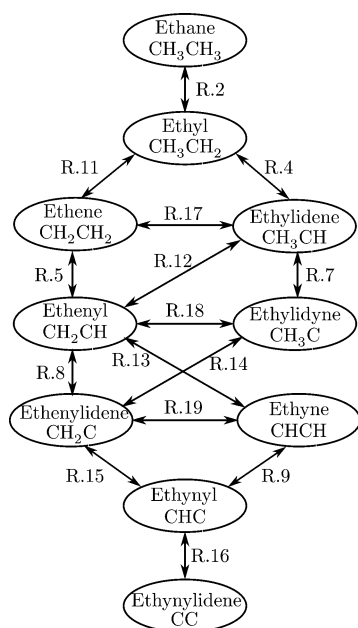


Figure 1. Dehydrogenation pathways for CH_3CH_3 (ethane), CH_2CH_2 (ethene) and CHCH (ethyne) including isomerization reactions. Possible mechanisms for the formation of ethylidyne, one of the key intermediates during dehydrogenation (M: mechanism, R: reaction) are M.2: (R.5, R.18), M.3: (R.17, R.7), M.4: (R.5, R.8, R.14, M.5: R.5, R.12, R.7), M.6: (R.11, R.4, R.7).

In the present paper, we study all the elementary C–H bond reactions going from CH_3CH_3 (ethane), CH_2CH_2 (ethene), and CHCH (ethyne) to surface carbon—including 1,2-H-transfer (isomerization) reactions (Figure 1). We calculate adsorption geometries and energies of all the intermediates. Furthermore, we also calculate the transition state geometries and activation energy barriers for all the elementary reactions (Figure 1). The knowledge gained from the study of these elementary reactions is used to identify the most favorable reaction pathways during the interaction of CH_4 (methane), CH_2CH_2 (ethene), and CHCH (ethyne) with the Ru(0001) surface. It will be shown that a number of stable intermediates, which are also observed experimentally, result from the interaction of these hydrocarbons with Ru(0001). Therefore, we also identify the pathways that lead to the occurrence of these stable intermediates. Further, we classify the C–H bond reactions into α and β C–H bond reactions to utilize the knowledge obtained in the present study in the context of Fischer–Tropsch catalysis. The β -C–H bond scission is especially relevant for the Fischer–Tropsch process as it leads to the formation of alkenes and determines product distribution.

To the best of our knowledge, no studies have been done on the interaction of CH_3CH_3 (ethane), CH_2CH_2 (ethene), and CHCH (ethyne) with the Ru(0001) surface using first-principles calculations. However, recently first-principles investigations have been carried out on the interaction of CH_2CH_2 (ethene) with Pd, Pt, Rh, and Ni (111) surfaces;¹¹ kinetic Monte Carlo simulations have also been carried out on the Pd and Pt (111) surfaces.¹² As in the present study, the ethenyl–ethynylidene mechanism is also calculated to be the most favorable pathway for the formation of CH_3C (ethylidyne) in the case of CH_2CH_2 (ethene) on both Pd and Pt(111) surfaces.¹² The interested reader is referred to ref 11 for more references related to first-principles calculations on Pd, Pt, Rh, and Ni.

METHODOLOGY

Computational Details. We used six layer 2×2 and 3×3 surface supercells for calculating the adsorption and activation energies. The cell parameters of a fully relaxed $2 \times 2 \times 2$ hexagonal unit cell of Ru were used in building the surface supercell. A vacuum of about 15 Å is used to separate the slabs to minimize interactions via periodic boundary conditions. The three bottom layers of Ru atoms were kept fixed during all relaxations. For the supercells considered, the adsorbate coverage is equivalent to 25% (0.25 ML) and 11% (0.11 ML), respectively.

We used the generalized gradient approximation (GGA) to density functional theory (DFT)^{13,14} and a plane-wave basis with a kinetic energy cutoff of 400 eV. The Kohn–Sham equations were solved using the Vienna ab initio simulation package (VASP, v 5.2.12).^{15–18} The valence electron and core interactions were described using the projector augmented wave method (PAW).^{19,20} The first-order Methfessel–Paxton method was used with a smearing width of 0.05 eV along with the Perdew–Burke–Ernzerhof (PBE) exchange correlation functional.^{21,22} Structural relaxations were considered converged when the energy in two consecutive ionic relaxation steps differed by less than 10 μeV . Integrations in reciprocal space employed a dense $16 \times 16 \times 1$ evenly spaced k -point grid with Monkhorst–Pack sampling²³ centered on the gamma point. Both the k -point density and energy cutoff were verified to give total energy convergence of 1 meV/supercell or better. Spin of the isolated fragments was taken into consideration by using the spin-polarized version of the GGA approximation. All energies correspond to 0 K. The transition states were found first using the nudged elastic band (NEB) method²⁴ and were later refined using the dimer method²⁵ as implemented into VASP using the VTST tool set.²⁶ The transition state was assumed to be found when the force on the dimer was less than 0.01 eV/Å.

Adsorption Energies. We calculate three different adsorption energies with different reference energies: $E_{\text{ads,iso}}$, $E_{\text{ads,far}}$, and $E_{\text{ads,near}}$. $E_{\text{ads,iso}}$ (eq 1) is the adsorption energy of the CH_x or C_2H_x fragments with respect to isolated gas phase fragments. $E_{\text{ads,far}}$ (eq 2) is the adsorption energy of the fragment with respect to all the disassociated H adsorbed in separate supercells and the gas phase molecule. Finally, $E_{\text{ads,near}}$ (eq 3) is the same as $E_{\text{ads,far}}$ except that 1 H atom is adsorbed along with the fragment and the rest are adsorbed in separate supercells (Figure 2).

The adsorption energy of a gas phase fragment CH_x , or C_2H_x on the bare Ru surface is given as

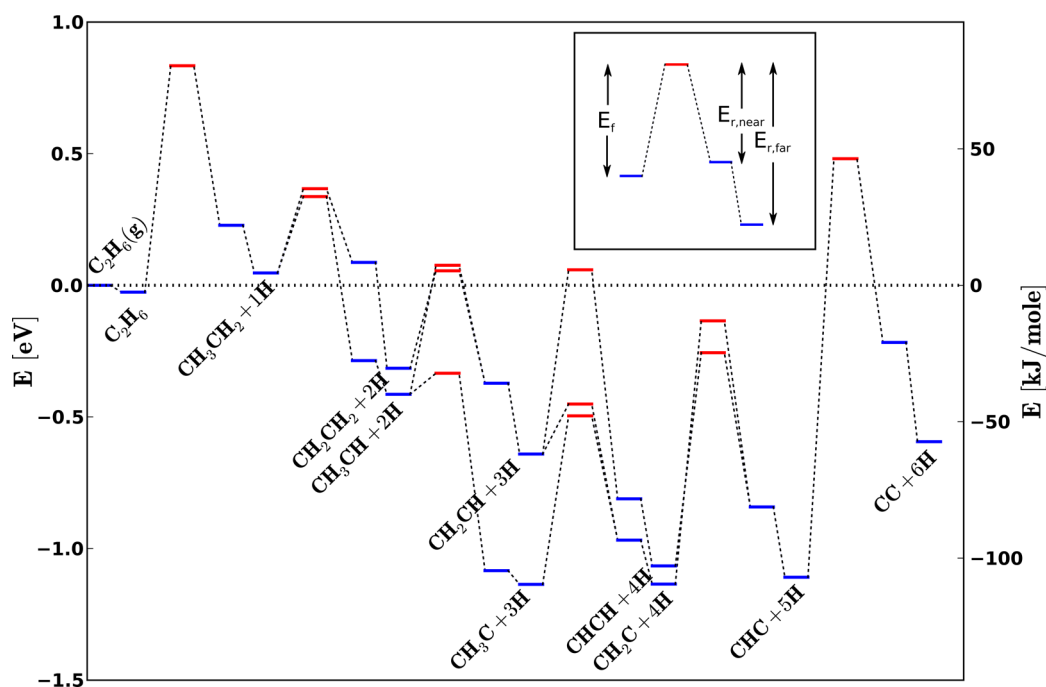


Figure 2. Reaction energy diagram for the dehydrogenation of CH_3CH_3 (ethane) on Ru(0001) surface with respect to gas phase ethane. Reactant/product states are in blue and activation energies are in red. The two levels for the products (see inset for clarity) represent 1 H coadsorbed in the same supercell with the rest of the H atoms each adsorbed in a separate supercell (left) and all H atoms each adsorbed in separate supercells (right), respectively.

$$E_{\text{ads,iso}} = E_{\text{surf+fragment}} - E_{\text{surf}} - E_{\text{fragment}} \quad (1)$$

E_{surf} is the total energy of the bare surface, E_{fragment} is the total energy of the isolated gas phase fragment, and $E_{\text{surf+fragment}}$ is the total energy of the fragment adsorbed on the surface.

The adsorption energy of a C_2H_x fragment with respect to all H atoms adsorbed in separate supercells and gas phase CH_3CH_3 (ethane), $E_{\text{ads,far}}$ is calculated as

$$E_{\text{ads,far}} = E_{\text{surf}} + \text{C}_2\text{H}_x + (6 - x)(E_{\text{surf+H}} - E_{\text{surf}}) - E_{\text{surf}} - E_{\text{C}_2\text{H}_6(\text{g})} \quad (2)$$

Along similar lines, the adsorption energy of a C_2H_x fragment, $E_{\text{ads,far}}$ with respect to 1 H atom coadsorbed with the fragment and the rest of the H atoms in separate cells, $E_{\text{ads,near}}$ is calculated as

$$E_{\text{ads,near}} = E_{\text{surf+C}_2\text{H}_x+\text{H}} + (6 - x - 1)(E_{\text{surf+H}} - E_{\text{surf}}) - E_{\text{surf}} - E_{\text{C}_2\text{H}_6(\text{g})} \quad (3)$$

Similarly, the adsorption energy of CH_4 dissociating into a one carbon fragment of the form CH_x is calculated as

$$E_{\text{ads,far}} = E_{\text{surf+CH}_x} + (4 - x)(E_{\text{surf+H}} - E_{\text{surf}}) - E_{\text{surf}} - E_{\text{CH}_4(\text{g})} \quad (4)$$

and

$$E_{\text{ads,near}} = E_{\text{surf+CH}_x+\text{H}} + (4 - x - 1)(E_{\text{surf+H}} - E_{\text{surf}}) - E_{\text{surf}} - E_{\text{CH}_4(\text{g})} \quad (5)$$

For example, consider the dissociation reaction $\text{CHCH} \rightarrow \text{CHC} + \text{H}$. The CHC fragment and the H atom can be considered to occupy either the same supercell or two different

supercells. $E_{\text{ads,near}}$ is applicable to the case in which CHC and H are considered in the same supercell while $E_{\text{ads,far}}$ is applicable when they are considered in different supercells. Since the reference gas phase molecule is CH_3CH_3 (ethane)—with a total of 6 H atoms—in both the cases, the other 4 H atoms, not involved in the reaction considered, are assumed to be adsorbed in separate supercells.

Our sign convention for the adsorption energies is that negative adsorption energies mean that the adsorption reaction is energetically favorable. In other words, more negative adsorption energies mean stronger binding. Finally, our nomenclature is that the carbon atom with the least number of H atoms attached is called the α -C atom and is the closest C atom to the surface. In cases where both the C atoms have equal numbers of H atoms (CH_3CH_3 (ethane), CH_2CH_2 (ethene), and CHCH (ethyne)) the C atom where the bond scission or formation happens is the α -C atom and is the closest C atom to the Ru surface. The other C atom is the β -C atom and is the farthest C atom from the surface. In the same way, H atoms attached to the α -C (β -C) atom are called α -H (β -H) atoms.

Activation Energies. As a consequence of the two different adsorption energies defined above, two different reverse activation energies, where two adsorbed fragments combine to form a single fragment, can be defined: $E_{\text{r,near}}$ and $E_{\text{r,far}}$. In our case, $E_{\text{r,near}}$ refers to the case when one H atom is coadsorbed along with the CH_x or the C_2H_x fragment and the rest occupy different supercells. $E_{\text{r,far}}$ refers to the case where all the H atoms are adsorbed on different supercells (Figure 2). The difference in the two activation energies is equal to the difference between the corresponding adsorption energies. It is clearly seen from Figure 2 that, while the reverse activation energy in the two cases can be different, the forward activation energy E_{f} in both cases is identical. Unless otherwise

Table 1. Adsorption Energies with Respect to Different Reference Energies ($E_{\text{ads,iso}}$, $E_{\text{ads,near}}$, and $E_{\text{ads,far}}$), Distance between the Top Layer Ru Atoms and the Closest C Atom ($r_{\text{Ru-C}}$), the C–C Bond Distance in Adsorbed Fragments in Adsorbed C_2H_x Fragments ($r_{\text{C-C}}$), and the Adsorption Geometry of the Fragments α -C ($-\beta$ -C)^a

fragment	$E_{\text{ads,iso}}$ [eV]	$E_{\text{ads,near}}$ [eV]	$E_{\text{ads,far}}$ [eV]	$r_{\text{Ru-C}}$ [Å]	$r_{\text{C-C}}$ [Å]	adsorption geometry
CH_4	−0.02	—	−0.02 −0.03 ^b	4.13	—	—
CH_3	−2.05	0.01	−0.20 −0.16 ^b −0.06b	1.75	—	hcp
CH_2	−2.19 ^d −4.33	−0.12	−0.39 −0.33 ^b −0.11 ^c −0.64 ^d	1.37	—	hcp
CH	−4.32 ^d −6.83	−0.84	−0.95 −0.87 ^b −0.58 ^c −1.14 ^d	1.20	—	hcp
C	−6.69 ^d −7.54	−0.57	−0.72 −0.68 ^b −0.22 ^c −0.89 ^d	1.05	—	hcp
H	−7.14 ^d −2.87 −2.96 ^d	—	—	—	—	fcc
CH_3CH_3	−0.03	—	−0.03	3.82	1.52	—
CH_3CH_2	−1.58 −1.76 ^e	0.23	0.05	1.76	1.54	hcp-ontop
CH_3CH	−3.96 −4.12 ^e	−0.29	−0.41	1.41	1.53	hcp
CH_3C	−5.91 −6.00 ^e	−1.08	−1.14	1.24	1.51	hcp
CH_2CH_2	−0.87 −0.95 ^e	0.09	−0.31	1.75	1.45	hcp-ontop
CH_2CH	−3.20 −3.30 ^e	−0.37	−0.64	1.43	1.43	hcp-ontop
CH_2C	−4.70 −4.67 ^e	−0.97	−1.14	1.26	1.41	hcp-fcc
CHCH	−2.67 −2.76 ^e	−0.81	−1.07	1.43	1.43	hcp-fcc
CHC	−5.76 −5.86 ^e	−0.84	−1.11	1.27	1.38	hcp-fcc
CC	−7.65	−0.22	−0.59	1.31	1.36	hcp-fcc

^a $E_{\text{ads,iso}}$: adsorption energy with respect to isolated fragment (eq 1). $E_{\text{ads,near}}$: adsorption energy with respect to 1 H atom co-adsorbed in the same supercell and ($n-1$) H atoms each adsorbed in a separate supercell (eq 3). $E_{\text{ads,far}}$: adsorption energy with respect to n H atoms each adsorbed in a separate supercell (eq 2) ($n = 4$ and 6 for CH_4 (methane) and CH_3CH_3 (ethane) respectively). ^bRef 27 for a 3×3 supercell. ^cRef 28. ^dRef 29. ^eRef 32.

mentioned, we use $E_{\text{r,far}}$ in all our discussions below. This would correspond to a situation where the H atom would have to reach the reaction site from a distance.

RESULTS

Adsorption Geometries and Energies. CH_x Fragments. Adsorption energies $E_{\text{ads,iso}}$, $E_{\text{ads,near}}$, and $E_{\text{ads,far}}$ as calculated from eqs 1, 4, and 5 are given in Table 1 along with results from previous first-principles studies. The geometries of all the adsorbed fragments and transition states are presented graphically and as coordinates within the supercell in the Supporting Information (SI).

CH_4 (methane) adsorbs very weakly on Ru(0001) with an adsorption energy of about 20 meV. Of the four possible adsorption sites on the Ru(0001) surface (bridge, fcc, hcp, and

ontop), CH_x ($x = 1$ or 2) fragments and C adsorb preferentially on a hcp site. The adsorption of the remaining fragment, CH_3 (methyl), is slightly more favorable on an fcc site. These observations are in good agreement with previous calculations^{27–29} and experiments.^{30,31} Considering $E_{\text{ads,iso}}$ (Table 1), the adsorption energy increases almost linearly with decreasing hydrogen content with atomic C having the highest adsorption energy.

Although the values of $E_{\text{ads,far}}$ that we obtain are higher than those reported in ref 27, the trends in the adsorption energies are the same; CH (methyldiene) adsorbs the most strongly, followed by C, CH_2 (methyldiene), CH_3 (methyl), and CH_4 (methane) in that order. $E_{\text{ads,near}}$ also reflects the same trend. Considering the difference $E_{\text{ads,near}} - E_{\text{ads,far}}$, lateral interactions of about 100–300 meV can be seen between the coadsorbed H

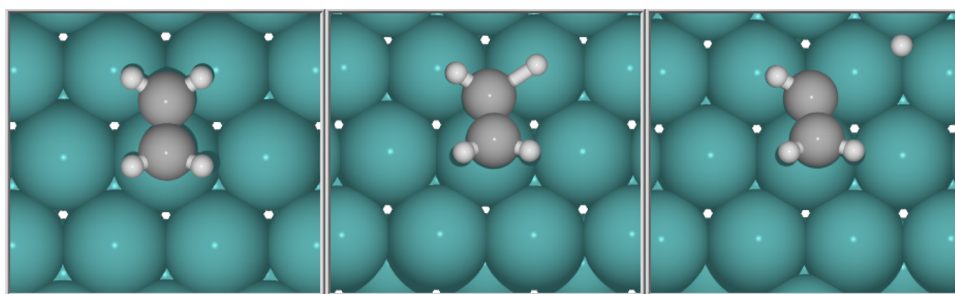


Figure 3. Top view of the α -C-H scission reaction: $\text{CH}_2\text{CH}_2 \rightarrow \text{CH}_2\text{CH} + \text{H}$ R.S on Ru(0001). From left to right: Reactant, transition, and product states. Cyan = Ru, gray = C, and white = H.

and the organic fragment. In other words, up to 300 meV is gained when a coadsorbed hydrogen atom diffuses away from an organic fragment.

C_2H_x Fragments. Similar to CH_4 (methane), CH_3CH_3 (ethane) also adsorbs very weakly with an adsorption energy of about 30 meV. Adsorption energies of the C_2H_x fragments are in good agreement with previous first-principles calculations³² (Table 1). All the C_2H_x ($0 \leq x \leq 6$) fragments are more stable with the α -C atom on the hcp adsorption site than on any of the other sites; the β -C atom is either on the fcc site or the ontop site depending on the fragment. The preference for the hcp site with respect to the next most stable site, fcc, increases as the amount of hydrogen in the fragment decreases. While CH_2CH_2 (ethene) adsorbs in the well characterized di- σ configuration³⁰ (Figure 3), CHCH (ethyne) adsorbs with one C atom on a hcp site and another on an fcc site (Supporting Information Figure S14). In both cases, the C–C bond length is about 1.45 Å, which is between the C–C bond length in CH_3CH_3 (ethane) and CH_2CH_2 (ethene). The lengthening of the bond with respect to the gas phase molecules implies significant bonding with the surface (Table 1). In all the fragments that are derived from CH_2CH_2 (ethene) or CHCH (ethyne), the C–C bond length is greater than the bond length of gas phase CH_2CH_2 (ethene) implying significant bonding to the surface (Table 1). The mean distance between the top layer of Ru atoms and the C atom closest to the surface varies from 3.82 Å for CH_3CH_3 (ethane) to 1.24 Å in CH_3C (ethylidyne) (Table 1). In general, the fragments move closer to the surface as the number of H atoms decreases indicating increased bonding with the surface. For fragments with the same number of H atoms (e.g., CH_3CH , CH_2CH_2 ; CH_3C , CH_2CH ; CH_2C , CHCH), the fragments with fewer α -H atoms are closer to the surface.

With the number of β -H atoms fixed and the number of α -H atoms increasing, the angle that the C–C bond makes with the plane of the surface decreases. For example, while CH_3C (ethylidyne), with no α -H atoms, is perpendicular to the surface (Supporting Information Figure S13), the C–C bond in CH_3CH_2 (ethyl) makes an angle of about 55° with the surface (Supporting Information Figure S7). In contrast, with a fixed number of α -H atoms and increasing number of β -H atoms, the C–C bond angle with the surface increases. For example, while CHCH (ethyne) is almost parallel to the surface (about 3°) (Supporting Information Figure S14) and CH_3CH (ethylidene) makes an angle of 70° with the surface (Supporting Information Figure S9).

Going from a stable gas-phase molecule (CH_3CH_3 (ethane), CH_2CH_2 (ethene), or CHCH (ethyne)) to a surface species completely dehydrogenated of the α -H atoms (CH_3C (ethyl-

idyne), CH_2C (ethenylidene), or CHC (ethynyl)), the binding energy increases linearly with decreasing number of H atoms. In other words, fragments with less α -H bind more strongly with the surface.

Irrespective of which adsorption energy is considered— $E_{\text{ads,near}}$ or $E_{\text{ads,far}}$ —the fragments CH_3C (ethylidyne), CH_2C (ethenylidene), CHC (ethynyl), and CHCH (ethyne) are the most stable. Considering only $E_{\text{ads,far}}$, the binding energies of all the fragments in increasing order of stability are CH_3CH_2 (ethyl) $\approx \text{CH}_3\text{CH}_3$ (ethane) < CH_2CH_2 (ethene) < CH_3CH (ethylidene) < CC (ethynylidene) = CH_2CH (ethenyl) < CHCH (ethyne) = CHC (ethynyl) = CH_2C (ethenylidene) = CH_3C (ethylidyne). When the total hydrogen content in the fragments is equal, the fragment with lesser number of α -H atoms has a larger binding energy (CH_2CH_2 (ethene) < CH_3CH (ethylidene), CH_2CH (ethenyl) < CH_3C (ethylidyne), CHCH (ethyne) < CH_2C (ethenylidene)). It is interesting to note that while $E_{\text{ads,far}}$ for CH_3C (ethylidyne) and CH_2C (ethenylidene) is almost equal, $E_{\text{ads,near}}$ of CH_3C (ethylidyne) is lower than $E_{\text{ads,far}}$. This could imply that CH_3C (ethylidyne) is more stable than CH_2C (ethenylidene) on a surface with coadsorbed H.

The lateral repulsion between coadsorbed H and C_2H_x fragments is slightly higher compared to the case of one carbon fragment. For example, in the case of CH_2CH_2 (ethene) and CC (ethynylidene), the lateral repulsion is as high as 400 meV. This is expected on steric grounds as the number of atoms in the surface supercell is almost twice that of the CH_x fragments.

Transition State Geometries and Activation Energies.

We classify the C–H bond reactions into two types: α and β . C–H bond scission at the α -C (closest to the surface) is called an α -C–H bond scission reaction and that at β -C (farthest from the surface) is called β -C–H bond scission. They are also called α and β -hydrogen abstraction reactions in some of the literature. It is instructive to consider these scission reactions as happening at RCH_x groups. This will enable us to use this knowledge in the context of the Fischer–Tropsch process where longer carbon chains (>2) are encountered. Obviously, given the reaction energy, the activation energy calculated for the bond scission reaction can be used to calculate the activation energy for the reverse reaction, i.e., bond formation. Therefore, these findings are equally applicable to the reverse, C–H bond formation reactions.

Geometries. The transition state geometries can be classified into three types: (1) In all the α -C–H scission reactions from the groups CH , RCH_2 , and RCH ($\text{R} = \text{H}$, CH_3 , CH_2), the α -C atom is on the hcp site with the leaving α -H atom activated to the closest atop site (Figure 3). (2) In the β -C–H scission

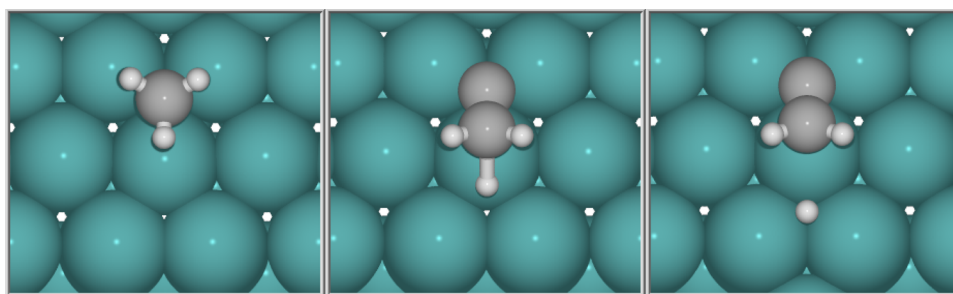


Figure 4. Top view of the dissociation reaction: $\text{CH}_3\text{C} \rightarrow \text{CH}_2\text{C} + \text{H}$ R.14.

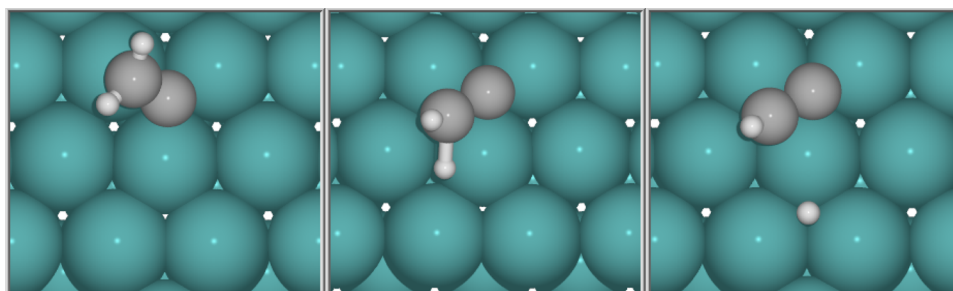


Figure 5. Top view of the dissociation reaction: $\text{CH}_2\text{C} \rightarrow \text{CHC} + \text{H}$ R.15.

Table 2. Forward Activation Energy (E_f) and Reverse Activation Energies ($E_{r,\text{near}}$ and $E_{r,\text{far}}$) for C–H Bond Scission and Isomerization Reactions for CH_4 (Methane) and CH_3CH_3 (Ethane) Adsorbed on the Ru(0001) Surface^a

		reaction		E_f [eV]	$E_{r,\text{near}}$ [eV]	$E_{r,\text{far}}$ [eV]	$r_{\text{C-H}}^{\text{TS}}$ [Å]
C–H scission							
R.1	CH_4	\rightleftharpoons	$\text{CH}_3 + \text{H}$	0.86	0.82	1.04	1.56
				0.88 ^b	0.79 ^b	0.94 ^b	
R.3	CH_3	\rightleftharpoons	$\text{CH}_2 + \text{H}$	0.65	0.57	0.83	1.70
				0.51 ^b	0.32 ^b	0.56 ^b	
R.6	CH_2	\rightleftharpoons	$\text{CH} + \text{H}$	0.16	0.62	0.73	1.57
				0.17 ^b	0.51 ^b	0.63 ^b	
R.10	CH	\rightleftharpoons	$\text{C} + \text{H}$	1.06	0.67	0.83	1.68
				1.12 ^b	0.51 ^b	0.76 ^b	
				0.37–0.75 ^c	$\approx 0.26^c$		
R.2	CH_3CH_3	\rightleftharpoons	$\text{CH}_3\text{CH}_2 + \text{H}$	0.86	0.59	0.77	1.60
R.4	CH_3CH_2	\rightleftharpoons	$\text{CH}_3\text{CH} + \text{H}$	0.29	0.62	0.75	1.57
				0.37 ^d	0.64 ^d	0.80 ^d	
R.11	CH_3CH_2	\rightleftharpoons	$\text{CH}_2\text{CH}_2 + \text{H}$	0.32	0.37	0.77	1.50
R.5	CH_2CH_2	\rightleftharpoons	$\text{CH}_2\text{CH} + \text{H}$	0.37	0.42	0.69	1.60
R.7	CH_3CH	\rightleftharpoons	$\text{CH}_3\text{C} + \text{H}$	0.08	0.75	0.80	1.51
R.12	CH_3CH	\rightleftharpoons	$\text{CH}_2\text{CH} + \text{H}$	0.49	0.45	0.72	1.55
				0.23 ^d	0.08 ^d	0.33 ^d	
R.8	CH_2CH	\rightleftharpoons	$\text{CH}_2\text{C} + \text{H}$	0.19	0.52	0.69	1.57
R.13	CH_2CH	\rightleftharpoons	$\text{CHCH} + \text{H}$	0.70	0.87	1.12	1.39
R.14	CH_3C	\rightleftharpoons	$\text{CH}_2\text{C} + \text{H}$	0.64	0.48	0.65	1.61
R.9	CHCH	\rightleftharpoons	$\text{CHC} + \text{H}$	0.81	0.59	0.85	1.64
R.15	CH_2C	\rightleftharpoons	$\text{CHC} + \text{H}$	1.00	0.71	0.98	1.50
R.16	CHC	\rightleftharpoons	$\text{CC} + \text{H}$	1.59	0.70	1.07	1.66
Isomerization							
R.17	CH_3CH	\rightleftharpoons	CH_2CH_2	1.78	1.68	–	1.30
R.18	CH_3C	\rightleftharpoons	CH_2CH	1.80	1.30	–	1.33
R.19	CH_2C	\rightleftharpoons	CHCH	2.24	2.17	–	1.33

^a $r_{\text{C-H}}^{\text{TS}}$ is the bond C–H bond length in the transition state between the C atom and the dissociating H atom according to the present work. ^bRef 28. ^cRef 42. ^dRef 34.

reactions from the groups RCH_2 , RCH , and RC ($\text{R} = \text{CH}_3$), the α -C atom is on the hcp site while the β -C atom is activated to an atop site with the leaving β -H atom pointing toward the

closest hcp site (Figure 4). (3) In the β -C–H scission reactions from the groups RCH , RC ($\text{R} = \text{CH}_2$ or CH), the α -C atom is on the hcp site while the β -C atom is activated to an fcc site

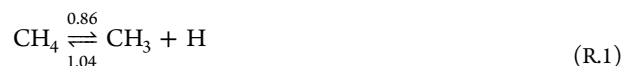
with the β -H activated toward the closest hcp or atop site (Figure 5).

In the majority of the transition states, the C–H bond length between the dissociating H and the C atom is in the range of 1.50 to 1.70 Å (Table 2). No clear correlation is found between the bond length in the transition state and the activation energy. From visual inspection (see Supporting Information) it can be seen that the C–H bond dissociation reactions have a late transition state. That is, the transition state is closer to the product state than to the reactant state.

Activation Energies. The activation energies E_f , $E_{r, \text{near}}$, and $E_{r, \text{far}}$ for all the C–H bond scission reactions are listed in Table 2. As mentioned before, we refer to $E_{r, \text{far}}$ below. Although the activation energies range from 0.1 to 1.6 eV depending on the reaction, they fall into three distinct groups (considering both forward and reverse reactions): (i) reactions with E_f between 0.1 and 0.4 eV (7 reactions), (ii) reactions with E_f between 0.6 and 0.9 eV (17 reactions), and (iii) reactions with E_f above 1 eV (7 reactions). As can be seen, the majority of the reactions have activation energies closely spaced in the range of 0.6–0.9 eV.

Results of α -C–H reactions where the α -C group is fixed and the β -C group changes are presented first, followed by β -C–H reactions. Since C_1 fragments do not have a β -C atom, they will all be considered under α -C–H reactions.

The RCH_3 group ($R = H, CH_3$) can undergo two possible α -C–H reactions:



The numbers above and below the arrows are forward and reverse activation energies E_f and $E_{r, \text{far}}$, respectively (Table 2). These scission (forward) and formation (reverse) reactions are equivalent to alkane activation and alkane formation reactions, respectively. The activation energies for the scission of the C–H bond in CH_4 and C_2H_6 are very similar (both 0.86 eV). Considering the opposite, hydrogenation of the CH_3CH_2 (ethyl) group has a smaller activation energy compared to that of the CH_3 (methyl) group. As we will see later, the magnitude of these activation energies indicates that these are relatively slow processes.

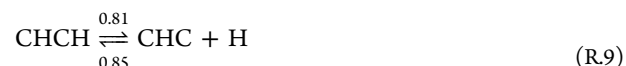
There are three α -C–H reactions of adsorbed RCH_2 ($R = H, CH_3, CH_2$):



The activation energies indicate that dehydrogenation of an CH_3CH_2 (ethyl) group can occur substantially faster than that of a CH_3 (methyl) group (0.29 vs 0.65 eV). Going from $R = CH_3$ to $R = CH_2$, the activation energy for dehydrogenation increases slightly (0.29 vs 0.37 eV), that is, CH_3CH_2 (ethyl) dehydrogenation is more facile than CH_2CH_2 (ethene) dehydrogenation. The activation energies indicate that CH_3CH_2 would rapidly dehydrogenate after the initial slow

activation of the CH_3CH_3 (ethane) molecule ($E_f = 0.86$ eV, R.2).

For α -C–H bond reactions of adsorbed RCH ($R = H, CH_3, CH_2$, or CH) there are four possibilities:



Excluding the dehydrogenation of $CHCH$ (ethyne), the dehydrogenation of the RCH ($R = H, CH_3, CH_2$) group is found to be the most facile among all the dehydrogenation reactions (all activation energies less than 0.2 eV). This implies that the dehydrogenation of CH_3CH (ethylidene), CH_2CH (ethenyl), and CH_2 (methylidene) to CH_3C (ethylidyne), CH_2C (ethenylidene), and CH (methylidyne) groups, respectively, happens readily even at low temperature. It is noteworthy that the resulting RC fragments are also the most stable fragments observed on the Ru(0001) surface. Consistent with this, in all the reactions except R.9, the reverse hydrogenation reactions have a much higher barrier (0.7–0.9 eV) than the dehydrogenation reactions.

Now, considering the first dehydrogenation reaction of adsorbed alkanes, alkenes, and alkynes ($E_f = 0.86, 0.37$ vs 0.81 eV, respectively), it can be seen that dehydrogenation is most facile for alkenes.

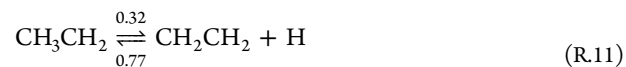
Finally, α -C–H bond scission from the RC group ($R = H$) group can be written as



Among all the α -C–H bond scission reactions described so far, this reaction has the highest activation energy (1.06 eV). This explains the persistence of CH groups on the Ru surface^{30,31} even at relatively high temperatures.

Our activation energies for the reactions R.1, R.3, R.6, and R.10—dehydrogenation reactions in methane—agree well with previous first-principles results²⁸ (Table 1).

There are six possible β -C–H bond reactions for C_2H_x ($1 \leq x \leq 5$):



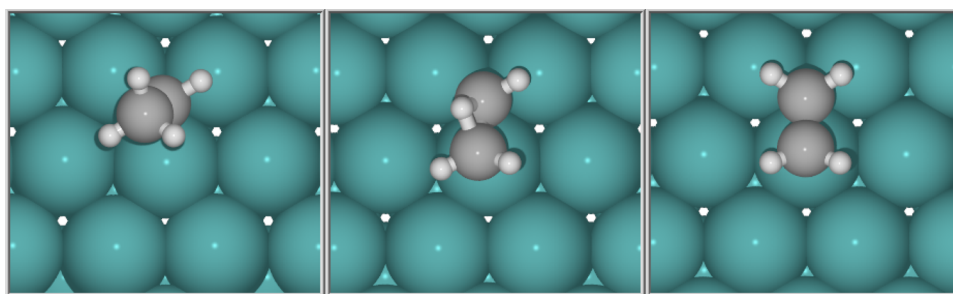


Figure 6. Top view of the isomerization reaction: $\text{CH}_3\text{CH} \rightarrow \text{CH}_2\text{CH}_2$ R.17

β -C–H scission is the most facile from the β -methyl groups of CH_3CH_2 (ethyl) (0.32 eV) and CH_3CH (ethylidene) (0.49 eV) followed by higher activation energies in CH_3C (ethylidyne) (0.64 eV) and CH_2CH (ethenyl) (0.70 eV). The highest activation energies occur for dehydrogenation from CH_2C (ethenylidene) (1.00 eV) and CHC (ethynyl) (1.59 eV). The activation energies thus increase in the order: CH_3CH_2 (ethyl) < CH_3CH (ethylidene) < CH_3C (ethylidyne) < CH_2CH (ethenyl) < CH_2C (ethenylidene) < CHC (ethynyl). Again, it is noteworthy that CH_2C (ethenylidene) and CHC (ethynyl), whose dehydrogenation is the hardest, are also the most stable fragments on the Ru(0001) surface (Table 1). In light of this, it is interesting that although CHC (ethynyl) has been spectroscopically identified in experiments, CH_2C (ethenylidene) has not been identified on bare Ru(0001). However, it has been identified on O-covered Ru(0001).³³

Ciobîcă et al. calculated the activation energies for the reactions R.4, an α -C–H scission reaction, and R.12, a β -C–H scission reaction.³⁴ While our results agree well (to within 5 meV) with the activation energy for the α -C–H scission reaction, they do not compare equally well (differ by up to 40 meV for $E_{r,\text{near}}$ and $E_{r,\text{far}}$) with the activation energy for the β -C–H scission reaction (Table 2). Although it is hard to point out exactly where the origin of this difference lies, it could be, among other reasons, due to the different exchange–correlation potentials used (PBE in this paper vs PW91), different treatment of the core–valence electrons (PAW vs pseudopotentials), different plane-wave energy cut-offs, or the different k -point meshes. But, more importantly, it could be an artifact of using adsorption on both sides of a 4-layer surface model with no fixed surface atoms—we use a 6-layer model with single side adsorption with the three bottom layers held fixed. Our thicker slab with bulk constrained bottom layers may therefore be a more reliable model. Moreover, our transition states have been refined using dimer method while this is not the case with Ciobîcă et al.

Isomerization by H-1,2-Shift Reaction. Intramolecular 1,2-H-shift reactions are possible in three of the fragments: CH_3CH (ethylidene), CH_3C (ethylidyne), and CH_2C (ethenylidene). They are



In the transition state, the H atom involved in the transfer is roughly equidistant from the two carbon atoms and away from

the surface (Figure 6). In CH_3CH (ethylidene) and CH_3C (ethylidyne) the CH_3 group is activated to an atop site and in CH_2C (ethenylidene) the CH_2 group is activated to an fcc site. The lowest activation energy for isomerization is observed in $\text{CH}_2\text{CH} \rightarrow \text{CH}_3\text{C}$ (1.3 eV, R.18); the others are substantially higher. Therefore, all the intramolecular isomerization reactions, compared to all the reactions considered so far, will be relatively slow and can be neglected as possible reactions during the dehydrogenation of CH_3CH_3 (ethane), CH_2CH_2 (ethene), or CHCH (ethyne). Alternative pathways for the isomerization via hydrogenation–dehydrogenation reactions involving the surface show much lower activation energies. For example, for the isomerization reaction $\text{CH}_2\text{CH} \rightarrow \text{CH}_3\text{C}$ R.18, with an activation barrier of 1.3 eV, an alternative reaction pathway via the mechanism $\text{CH}_2\text{CH} \xrightarrow{-\text{H}} \text{CH}_2\text{C} \xrightarrow{+\text{H}} \text{CH}_3\text{C}$ R.8, R.18 is available and the highest barrier in the latter multistep pathway (0.65 eV) is only half the activation energy of the former.

The activation energies that we obtained for C–H bond scission in CH_4 on Ru(0001) and its reverse reaction are also in good agreement with those reported in ref 28 (Table 2).

DISCUSSION

In this section, we first present a brief overview of the knowledge gained from previous experimental research on the interaction of CH_4 (methane), CH_2CH_2 (ethene), and CHCH (ethyne) with the Ru(0001) surface; to the best of our knowledge, there is no report on the interaction of CH_3CH_3 (ethane). In addition, experiments which isolate some of the stable intermediates observed will also be discussed. Then, we discuss how our results relate to what has been experimentally observed. This includes the dominant reaction pathways available to the hydrocarbons during the interaction with the Ru(0001) surface, pathways leading to the stable intermediates and their decomposition. All the discussion below is based on the 2×2 supercell calculations with the effect of increasing supercell size discussed at the end.

Previous Research. Interaction of CH_4 (methane) with the Ru(0001) surface ultimately leads to complete dehydrogenation above 700 K. Below 700 K, CH (methylidyne) and CH_2C (ethenylidene) are observed as stable intermediates.³⁵ Since CH_4 (methane) is a C_1 fragment, the CH_2C (ethenylidene) fragments obviously result from C–C coupling reactions. Although we have not considered C–C coupling of C_1 fragments in the present paper, various elementary C–C coupling reactions have been considered in the past—both on stepped and flat Ru surfaces.^{34,36,37}

CH_2CH_2 (ethene) adsorbs molecularly on a Ru(0001) surface at least up to 120 K; further increase in temperature leads to the onset of dehydrogenation. Using HREELS, it is seen that between 150 and 280 K, CH_3C (ethylidyne) is the

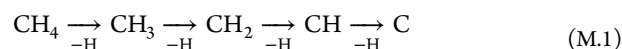
most stable intermediate.^{30,38,39} At temperatures above 400 K further dehydrogenation of CH₃C (ethylidyne) occurs and CHC (ethynyl) is observed. At even higher temperatures C–C bond scission occurs and leads to the formation of CH (methylidyne) on the surface. Increasing the temperature further leads to complete dehydrogenation and surface carbon.^{30,38,39}

CHCH (ethyne) adsorbs horizontally with a significant amount of hybridization on the C atoms bound to Ru(0001) up to a temperature of about 230 K. Above this temperature, experiments show that it dehydrogenates and forms CHC (ethynyl) and CH₃C (ethylidyne) at temperatures below 350 K.^{39,40}

It is clear from the above summary that, as surface temperature is increased, interaction of all three hydrocarbons with the Ru(0001) surface leads to complete dehydrogenation and surface C via the occurrence of stable intermediates. Our results also clearly show that this should be the case. A reaction energy diagram showing all the dehydrogenation reactions going from CH₃CH₃ (ethane) to surface carbon is shown in Figure 2. It is clear that after the initial activation of CH₃CH₃ (ethane), CH₂CH₂ (ethene) or CHCH (ethyne) dehydrogenation is thermodynamically favorable and should lead to one of the stable intermediates CH₃C (ethylidyne), CH₂C (ethenylidene), or CHC (ethynyl). Since the adsorption energies of these intermediates is almost equal to that of CH (methylidyne), C–C bond cleavage in any of these fragments should lead to the formation of CH (methylidyne), another stable intermediate observed in all the above studies before complete dehydrogenation occurs. It can also be seen that once the stable intermediates form, it is thermodynamically uphill for further dehydrogenation. This explains why dehydrogenation of the stable intermediates happens only when the temperature is increased to greater than 400 K.

While CH₂C (ethenylidene) and CH (methylidyne) occur as stable intermediates in the case of CH₄ (methane), CH₃C (ethylidyne), CHC (ethynyl), and CH (methylidyne) occur in the case of CH₂CH₂ (ethene) and CHCH (ethyne). It is interesting that CH₂C (ethenylidene) occurs in the interaction of CH₄ (methane) but not during the interaction of CH₂CH₂ (ethene) or CHCH (ethyne). Moreover, CH₂C (ethenylidene) also occurs during the interaction of CH₂CH₂ (ethene) with a O-covered Ru(0001) surface.⁴¹ Below, we will discuss the most favorable dehydrogenation reaction pathways leading to the formation of stable intermediates and their further dehydrogenation to surface C.

CH₄ (Methane). The dehydrogenation pathway for CH₄ (methane) is straightforward:



Dehydrogenation of CH (methylidyne) R.10 has the highest activation energy and thus would be the rate-determining step (Table 2) for complete dehydrogenation of CH₄ (methane) once it is activated, R.1. Among the four CH_x fragments, CH is the most stable fragment on the Ru(0001) surface ($E_{\text{ads, far}}$, Table 1). Thus, both the adsorption energy and the activation energy for its dehydrogenation corroborate previous experimental evidence about the formation of CH (methylidyne) as a stable intermediate during dehydrogenation of CH₄ (methane)³⁵ (and also of CH₂CH₂ (ethene) and of CHCH (ethyne)^{30,31,35,38,40}). Besides being isolated in dehydrogenation experiments, CH (methylidyne) has also been directly

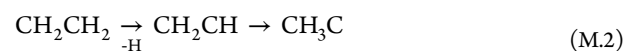
synthesized on a Ru(0001) surface by hydrogenation of surface C, R.10.^{31,42} Shimizu et al. used scanning tunneling microscopy at 100 K to directly follow this reaction.⁴² However, the activation energy proposed by Shimizu et al. (0.26 eV) is almost four times lower than the one reported by Barteau et al. (0.95 eV). We report an activation energy of about 0.83 eV (Table 2, R.10) which is close to the value of Barteau et al., and the discrepancy could be due to the different initial coverages in the experiments. Our calculations at 25% coverage resemble the experiments of Barteau et al. more closely than those of Shimizu et al.

CH₃CH₃ (Ethane). Since the activation energies for both CH₄ (methane) and CH₃CH₃ (ethane) activation are very similar and CH₄ (methane) has been observed experimentally to interact with Ru(0001),³⁵ one can expect that CH₃CH₃ (ethane) would also interact with the Ru(0001) surface. But to the best of our knowledge, there is no report of experimental/theoretical study of the dehydrogenation of CH₃CH₃ (ethane) on Ru(0001). In the event that CH₃CH₃ (ethane) is activated on the surface, R.2, further dehydrogenation can occur either to form CH₂CH₂ (ethene), R.11, or CH₃CH (ethylidyne), R.4. While the activation energies for these dehydrogenation reactions are very similar (they differ only by about 30 meV), the formation of CH₃CH (ethylidyne), R.4, is thermodynamically slightly more favorable (Figure 2). Hence, the formation of CH₃CH (ethylidyne) should be more favorable than the formation of CH₂CH₂ (ethene) on the surface. The CH₃CH (ethylidyne) can then easily dehydrogenate to one of the most stable stable fragments on the surface, CH₃C (ethylidyne) (E_f = 0.08 eV, Table 2, R.7). The dehydrogenation of CH₃C (ethylidyne) is described below.

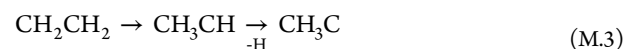
CH₂CH₂ (Ethene). Since in a number of studies of CH₂CH₂ (ethene) interacting with Ru(0001), CH₃C (ethylidyne) and CHC (ethynyl) have been observed, in this section we describe all possible dehydrogenation pathways that lead to CH₃C (ethylidyne). Later, we will describe how CH₃C (ethylidyne) dehydrogenates further to CHC (ethynyl).

There are five possible pathways for the formation of CH₃C (ethylidyne) from CH₂CH₂ (ethene) (Figure 1):

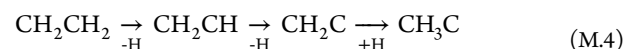
via CH₂CH (ethenyl) and 1,2-H-shift:



via 1,2-H-shift and CH₃CH (ethylidyne):



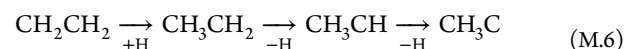
via CH₂CH (ethenyl) and CH₂C (ethenylidene):



via CH₂CH (ethenyl) and CH₃CH (ethylidyne):



via CH₃CH₂ (ethyl) and CH₃CH (ethylidyne):



Mechanisms involving isomerization (M.2 and M.3) can be immediately excluded as the activation energies are too high compared to alternative pathways (Table 2). The ethenyl–ethenylidene mechanism M.4 will be compared to both the ethenyl–ethylidyne M.5 and the ethyl–ethylidyne mechanisms M.6. In both cases, it will be shown that the ethenyl–ethenylidene M.4 mechanism will be the dominant mechanism.

First, we will compare the ethenyl–ethenylidene mechanism M.4 with the ethenyl–ethylidene mechanism M.5. While the first step is identical in both mechanisms, R.5, the second reaction R.8 in the ethenyl–ethenylidene mechanism M.4 is more favorable ($E_f = 0.19$ eV), both kinetically (about 10^3 times more likely to occur at 450 K) and thermodynamically (Figure 2) compared to the second reaction R.12 in the ethenyl–ethylidene mechanism M.5 ($E_{r,\text{near}} = 0.45$ eV); (note: the rate r of a reaction can be approximated as $A \exp(-E_a/k_B T)$ where E_a is the activation energy, T is the temperature of the reaction and A is the prefactor of the reaction). Given two competing reactions with activation energies E_{a1} and E_{a2} , the relative rates of the two reactions, assuming the same prefactor, will be given as $r_1/r_2 = \exp[-(E_{a1} - E_{a2})/k_B T]$. Also, the second reaction in the ethenyl–ethenylidene mechanism M.4 leads to the formation of the CH_2C (ethenylidene) intermediate which is one of the most stable species on the surface ($E_{\text{ads,far}}$, Table 1, Figure 2). The conversion between CH_2C (ethenylidene) and CH_3C (ethylidyne) can then be understood as surface mediated hydrogenation–dehydrogenation reactions. These arguments show that the ethenyl–ethenylidene mechanism M.4 will be dominant over the ethenyl–ethylidene mechanism M.5 in the formation of both the CH_2C (ethenylidene) and CH_3C (ethylidyne) surface species.

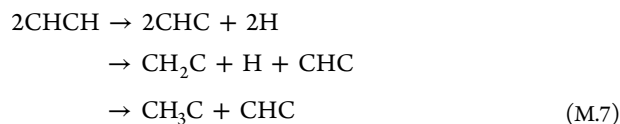
Next, comparing the ethenyl–ethenylidene mechanism M.4 to the ethyl–ethylidene mechanism M.6, the ethenyl–ethenylidene mechanism M.4 is again more favorable. The first reaction R.5 in the ethenyl–ethenylidene mechanism M.4 is either kinetically equivalent or more favorable compared to the first reaction in the ethyl–ethylidene mechanism M.6 depending on the chosen activation energy for the hydrogenation step R.11 of the ethyl–ethylidene mechanism M.6. Considering $E_{r,\text{near}}$ the first reactions in both mechanisms are kinetically equivalent, but considering $E_{r,\text{far}}$ the first reaction in the ethenyl–ethenylidene mechanism is clearly more favorable. In addition, the first reaction R.5 in the ethenyl–ethenylidene mechanism M.4 is thermodynamically more favorable as it leads to the formation of a more stable CH_2CH (ethenyl) species compared to the CH_3CH_2 (ethyl) species. Additionally, dehydrogenation of the CH_2CH (ethenyl) species ($E_a = 0.19$ eV) is kinetically more facile compared to the dehydrogenation of the CH_3CH_2 (ethyl) species ($E_a = 0.29$ eV). These arguments show that the ethenyl–ethenylidene mechanism M.4 is more likely than the ethyl–ethylidene mechanism M.6.

Combining the two comparisons above, it can be seen that the ethenyl–ethenylidene mechanism M.4 will be the dominant mechanism in the dehydrogenation of CH_2CH_2 (ethene) on Ru(0001). Previous first-principles studies show that the same mechanism is also favored on Pt(111) surfaces.¹²

Although no experiments have reported the occurrence of CH_2C (ethenylidene) on the surface, according to activation energies obtained in our calculations, CH_2C (ethenylidene) should exist in at least a narrow window of temperature between the onset of dehydrogenation in CH_2CH_2 (ethene) and the observation of CH_3C (ethylidyne) on the surface. Once CH_2CH_2 (ethene) is activated via R.5 ($E_f = 0.37$ eV), it should immediately convert to CH_2C (ethenylidene) as the activation energy for the dehydrogenation of CH_2CH (ethenyl), R.8, is quite low (0.19 eV). The conversion of CH_2C (ethenylidene) to CH_3C (ethylidyne), R.14, has an appreciably higher activation energy ($E_{r,\text{near}} = 0.48$ eV). So, in the temperature window corresponding to this difference in activation energies,

one can expect the existence of the CH_2C (ethenylidene) surface fragment. Also, CH_2C (ethenylidene) and the CH_3C (ethylidyne) surface species are almost equally stable on the surface, and hence there is no thermodynamic reason why one should be favored over the other. Of course, this only holds if we assume that there are no systematic errors from the exchange-correlation functional. It is possible that coverage effects (of adsorbed carbon fragments, hydrogen, or other adsorbates like oxygen) alter the activation energies for this interconversion. This can play an important role in determining the exact composition of the surface. In addition, the position of the equilibrium will also depend on the availability of surface H. These points need to be investigated further.

CHCH (Ethyne). Although dehydrogenation of CHCH (ethyne) leads to the occurrence of CH_3C (ethylidyne) and CHC (ethynyl) as surface intermediates, CH_2C (ethenylidene) has not been experimentally observed as an intermediate during dehydrogenation on the bare Ru(0001) surface.³³ Based on the absence of CH_2C (ethenylidene) as intermediate on the Ru(0001) surface in experiments and our calculated activation energies, we propose the following reaction for the formation of CHC (ethynyl) and CH_3C (ethylidyne):



Essentially, we propose that two CHCH (ethyne) molecules first undergo dehydrogenation to two CHC (ethynyl) and then one of these CHC (ethynyl) is hydrogenated to form CH_3C (ethylidyne). Since the rate-limiting step for the conversion is the hydrogenation of CHC (ethynyl) to CH_2C (ethenylidene), at temperatures where this reaction can readily happen, CH_2C (ethenylidene) should readily convert to CH_3C (ethylidyne).

CH_3C (Ethylidyne), CH_2C (Ethenylidene), and CHC (Ethynyl). The dehydrogenation of CH_3C (ethylidyne) can happen directly via CH_2C (ethenylidene), R.14, and CHC (ethynyl), R.15, or with an intermediate conversion of CHC (ethynyl) to CHCH (ethyne). The CHCH (ethyne) intermediate can possibly occur as the activation energy for the hydrogenation of CHC (ethynyl) (R.9, $E_{r,\text{far}} = 0.85$ eV) is lower than the activation energy for further dehydrogenation of CHC (ethynyl) (R.16, $E_f = 1.59$ eV) to CC. The same sequence also explains the dehydrogenation of CH_2C (ethenylidene) to CHC (ethynyl). Finally, CHC (ethynyl) can either first undergo C–C bond scission to C and CH (methylidyne) or, alternatively, completely dehydrogenate and then undergo C–C scission to give two surface C atoms.

Fischer–Tropsch Process. Role of Isomerization Reactions. Three major chain propagation steps are thought to happen during the Fischer–Tropsch process: (i) Brady–Pettit alkyl mechanism,⁴³ (ii) Maitlis alkenyl mechanism,⁴⁴ and (iii) Gaube alkylidene mechanism.⁴⁵ H-transfer reactions have been proposed to happen in the Gaube and Maitlis mechanisms. The high activation energies that we obtain here for 1,2-H-transfer suggest that (at least in the case of Ru(0001)) intramolecular H-transfer reactions (R.17, R.18, and R.19) can be precluded from happening. Obviously, this does not exclude the possibility that surface mediated isomerization can happen (see M.7).

α vs β Dehydrogenation Reactions. α and β C–H bond scission reactions play an important role in the selectivity of a

number of catalytic processes including the Fischer–Tropsch process.⁴⁶ Among the three C_2H_x species where both α and β C–H bond scission are possible (CH_3CH_2 (ethyl) R.4, R.11), CH_3CH (ethylidene) (R.7, R.12), and CH_2CH (ethenyl) (R.8, R.13), α -H abstraction is always more facile. However, in the CH_2CH (ethenyl) case, the activation energy for α and β C–H bond scission are within 0.1 eV (the difference in the other two C_2H_x species is more than 0.4 eV). Thus, it is clear that β -H abstraction from an RCH_2 ($R = CH_3$) species is more facile than the dehydrogenation from RCH ($R = CH_2$) or $RC(R = CH)$ groups on Ru(0001). This implies that the probability of forming an α -olefin is much higher than that of forming an alkyne.

Supercell Size Effects. In addition to the calculations on 2×2 supercells, on which the above discussion is based, we also carried out calculations on 3×3 supercells to see the effect of supercell size. Since increase in the supercell size translates to lower coverage of the surface species, we can also draw conclusions on the effect of surface coverage. E_f and $E_{r,near}$ calculated using a 3×3 supercell indicate that dehydrogenation is more favorable (by ≤ 20 meV). In contrast, hydrogenation becomes slightly unfavorable by about the same amount. This implies that as the coverage of the hydrocarbon species on the surface decreases, dehydrogenation becomes slightly more favorable while hydrogenation becomes slightly unfavorable.

CONCLUSIONS

In conclusion, we have studied the site preference, adsorption energies, and activation energies for C–H bond reactions in CH_4 (methane), CH_3CH_3 (ethane), CH_2CH_2 (ethene), and $CHCH$ (ethyne) on the Ru(0001) surface at 0.25 and 0.11 ML coverage (2×2 and 3×3 supercells, respectively) using density functional theory (DFT) based first-principles calculations. In all the fragments except CH_4 (methane), CH_3CH_3 (ethane), and CH_3 (methyl), the α -C adsorbs on the hcp site; depending on the fragment, the β -C is either on an atop or an fcc site. Adsorption energies show that CH_3C (ethylidyne), CH_2C (ethenylidene), CHC (ethynyl), and CH (methylidyne) are the most stable fragments on the Ru(0001) surface. The activation energies for the C–H bond cleavage reactions range from 0.1 to 1.6 eV, with the majority of them closely spaced between 0.6 and 0.9 eV. Dehydrogenation from CH_2CH (ethenyl) is the most facile, while dehydrogenation from CHC (ethynyl) is the hardest. 1,2-H-shift isomerization reactions, considered to happen in the Fischer–Tropsch process, can be ruled out, as their activation energies are too high. In intermediates where either α and β C–H scission is possible, the α scission is always more favorable and terminal alkenes have a much higher probability to form than alkynes.

The reaction energy diagram derived from the calculated adsorption and activation energies clearly shows that dehydrogenation is thermodynamically favorable on Ru(0001) for all the considered hydrocarbons in agreement with previous experiments. Additionally, the calculated activation energies of the elementary reactions were used to determine the most dominant pathways for the dehydrogenation of all the hydrocarbons and their stable intermediates. Dehydrogenation of CH (methylidyne) has the highest activation energy in the dehydrogenation of the multiple steps in the dehydrogenation of CH_4 (methane). CH_3CH_3 (ethane) is shown to dehydrogenate via CH_3C (ethylidyne). Both experiments and our results show that CH_2CH_2 (ethene) also dehydrogenates via the CH_3C (ethylidyne) intermediate.

Among five possible pathways for the formation of CH_3C (ethylidyne) from CH_2CH_2 (ethene), the ethenyl–ethenylidene pathway is the most dominant. This is similar to what happens on the Pt(111) surface. Although CH_2C (ethenylidene) has not been observed spectroscopically, so far, our calculations indicate a small temperature window where it might be observed. However, since the reaction barriers on which its occurrence depends are very closely spaced, coverage effects and coadsorbates can alter this conclusion. Based on previous experiments and our results, we propose that dehydrogenation of $CHCH$ (ethyne) proceeds via CHC (ethynyl), a fraction of which then undergoes hydrogenation to CH_3C (ethylidyne). CH_3C (ethylidyne) dehydrogenates via CH_2C (ethenylidene) to CHC (ethynyl), which further dehydrogenates to surface carbon, possibly via C–C bond cleavage which leads to CH (methylidyne) on the surface. Finally, we would like to comment that the activation energies for some of the competing reactions are so close that it is difficult to quantify the exact contribution of each reaction to the overall mechanism without a detailed analysis. A microkinetic model employing these activation energies could yield more information about the exact reaction pathways and also provide a handle to see how coverage would affect the reaction pathways.

ASSOCIATED CONTENT

Supporting Information

Structural information on the adsorbed fragments, reactant, product, and transition states is provided. Additionally, graphical representations of all the elementary reactions are provided. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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