Ethanol

1,3-butadiene

Catalytic conversion of ethanol to 1,3-butadiene on MgO: a comprehensive mechanism elucidation using DFT calculations

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Abstract

In this work, we performed periodic Density Functional Theory calculations and explored reactive pathways of ethanol catalysis to catalytically form 1,3-butadiene on undoped MgO surface. We have identified critical reactive intermediates, as well as thermodynamic and kinetic barriers involved in the overall reactive landscape. The overall free energy surface was explored for the highly debated reaction mechanisms, including Toussaint's aldol condensation mechanism, Fripiat's Prins mechanism and mechanism based on Ostromislensky's hemiacetal rearrangement. Thermodynamics and kinetics data calculated showed four rate limiting steps in the overall process. In particular, ethanol dehydration to form ethylene possessed lower energy barrier than dehydrogenation to yield acetaldehyde suggesting competing reactive pathways. C-C bond coupling to form acetaldol (3-hydroxybutanal) is preceded with 16 kcal/mol forward reaction barrier. Direct reaction of ethylene and acetaldehyde proceeds with a free energy barrier of 29 kcal/mol suggesting that Prins condensation is an alternative route. Finally, thermodynamic stability of 1-ethoxyethanol prevents further reaction via hemiacetal rearrangement. The results here provide a first glimpse into the overall 1,3-butadiene formation mechanism on undoped MgO reactive sites in light of the vast literature discussing variety of the proposed mechanistic pathways mostly based on conventional homogenous organic chemistry reactions.

Keywords: ethanol; 1,3-butadiene; DFT; MgO catalyst

1. Introduction

Since the rapid expansion of coal industry in the 18th century World has relied on non-renewable sources for organic chemicals [1]. Currently, petroleum and natural gas are the main feedstocks of relatively inexpensive carbon source [2]. Biomass can serve as a sustainable and renewable carbon source to generate chemicals and bio derived ethanol catalytic upgrading has been proposed as a viable route for biomass valorization [3,4]. In particular, ethylene, propylene, ethyl acetate, n-butanol and isobutene are some of the high value chemicals that can be derived from ethanol [5–14]. Furthermore, 1,3-butadiene, the most important monomer for synthetic rubber, has been produced via catalytic processing of ethanol during World War II in USSR and USA, using Lebedev and Ostromislensky processes, respectively [15]. The former utilized catalytic conversion of ethanol to 1,3-butadiene via one-step on MgO/SiO₂ catalysts [16], while the latter utilized a two-step process with the first step ethanol dehydrogenation to acetaldehyde over Cu/SiO₂ catalysts [3,17] followed by acetaldehyde and ethanol coupling to 1,3-butadiene over a tantalum-based catalyst. Catalysts for the one-step process were reported to have achieved ~50-60% yield [18,19], while the two-step process could attain over 60% yield, with purity of about 98-99% at 300-350°C. Recent abundance of shale gas resulted in a different catalytic cracker product distribution dominated by ethylene [3]. This caused a worldwide shortage of C₄ hydrocarbons, such as 1,3-butadiene. Since ethanol can be produced using variety of biomass sources including fermentation and gasification, it recently emerged as the green route to catalytically form 1,3-butadiene [3,4].

The biggest obstacle in ethanol catalysis to form 1,3-butadiene is relatively low selectivity and the resulting yields of the desired product. Angelici *et al.* reported 74% conversion with 49% selectivity on CuO/MgO-SiO₂, while Makshina *et al.* described a similar catalyst that attained 97.5% conversion with 58.2% selectivity [18,20]. Most recently, a CuO/HfO/ZnO catalyst was reported to have achieved 99% conversion with 71.1% selectivity, e.g. ~70% yield [19]. In general, doped-MgO supported on silica [18,20–29] (Lebedev's catalyst) or mixed (supported) oxides [16,19,30–36] were used. Various transition metal dopants (Zn, Cu, and Ag) were used to improve MgO/SiO₂ catalyst performance, as well as different synthesis methods and composition of MgO/SiO₂ were investigated, such as Kvisle's wet kneading method [26] and the utilization of clay and sepiolite as the support [21,28]. However, multitude of byproducts, including ethylene,

C4 oxygenates and olefins, diethyl ether, acetaldehyde and even acetone are still detected implying high separation. This lack of the kinetic control over the ethanol-to-1,3-butadiene catalytic process and poor understanding of the fundamental mechanistic steps involved have hindered the development of catalysts with reasonable performance. The generally accepted one-step catalytic mechanism involves dehydrogenation of ethanol to acetaldehyde which then undergoes C-C coupling via aldol condensation mechanism to yield crotonaldehyde. Crotonaldehyde is further hydrogenated via MPV (Meerwein-Ponndorf-Verley) reduction with ethanol and the resulting crotyl alcohol is dehydrated to give butadiene [37,38] as shown in **Figure 1a**. In addition, Fripiat and Ostromislensky proposed two other possible reaction pathways [39,40]. Fripiat suggested Prins-like mechanism involving both dehydration and dehydrogenation reactions producing ethylene and acetaldehyde, as shown in **Figure 1b**. The C=O group is hydroxylated in the presence of Brønsted acid and reacts with ethylene opening the double bond. The resulting 3-buten-2-ol is then dehydrated to yield 1,3-butadiene [40]. Ostromislensky's version of the reaction mechanism shown in **Figure 1c** involves the hemiacetal rearrangement between ethanol and acetaldehyde to yield 1-ethoxyethanol that later converts to butane-1,3-diol [3]. Two computational studies by Chieragato *et al.* [41] and Zhang *et al.* [42] attempted to unravel the overall reaction mechanism. Zhang *et al.* performed calculations using density functional generalized gradient approximation (GGA) and focused on the very first step of the mechanism, e.g. dehydrogenation of the alcohol. Stepped MgO surface was predicted to have lower energy barrier than flat surface for this reaction [42]. Chieragato *et al.*, on the other hand, proposed an entirely different mechanism using cluster type calculations and Gaussian basis set. They ruled out crotonaldehyde and crotyl alcohol as possible intermediates and concluded that acetaldehyde would react with a carbanion resulting from ethanol C-H cleavage. In this work we performed ethanol catalytic coupling to 1,3-butadiene using a kink Mg atom at a step-edge MgO (100) as a model catalyst surface in accordance with the recent works that suggest MgO as a bifunctional catalyst [43–53]. The energetics and structure of key reactive intermediates, e.g. acetaldehyde, crotonaldehyde, and crotyl alcohol, for Lebedev's reaction [16] based on the proposed mechanism by Toussaint *et al.* [38,54], as well as the proposed Fripiat's Prins and Ostromislensky mechanistic pathways were explored to determine the kinetic limitations of ethanol catalytic coupling to 1,3-butadiene on MgO.

2. Computational Details

2.1 Electronic structure calculations.

Periodic DFT calculations have been performed using the VASP code [55–58]. The Kohn–Sham equations have been solved variationally in a plane-wave basis set using the projector-augmented-wave (PAW) method of Blochl [59], as adapted by Kresse and Joubert [59]. The exchange-correlation energy was described by the PBE generalized gradient approximation [60]. Brillouin-zone was sampled using 2x2x1 k-point mesh. The plane-wave cutoff was set to 400 eV. The convergence criterion for the electronic self-consistency cycle, measured by the change in the total energy between successive iterations, was set to 10^{-6} eV/cell.

2.2 Structural optimization calculations.

Transition states have been identified using the DIMER method [61], as improved by Heyden *et al.* [62]. Atomic positions were considered to be relaxed if all forces acting on the atoms were smaller than 0.005 eV/Å. Transition states were proven to be first-order saddle points of the potential energy surface using vibrational analysis. The intrinsic reaction coordinates [63,64] (IRCs) for the forward and backward reaction steps were identified using the damped velocity Verlet algorithm [65]. The structures corresponding to potential energy minima along the IRC were further relaxed using a conjugate-gradient algorithm such as to satisfy the same optimization criterion as for transition states. Vibrational analysis was performed to ensure that the relaxed structures correspond to true potential energy minima. This procedure guarantees that reactant and product states are linked by a path with a single transition state.

The Gibbs free-energy calculations have been performed using the harmonic/rigid rotor approximation to the transition state theory [66] for the temperature of 723 K. The detailed calculations for the Gibbs energy estimations are provided in **Section 1** of the Supplementary Material, including **Table S1**. All relative energies were referenced to the sum of the relaxed MgO slab, and three molecules of gas phase ethanol. The first-order reaction constants were computed using:

$$k(T) = \frac{k_B T}{h} e^{-\frac{\Delta G_A(T)}{RT}} \quad (1)$$

where $k_B = 1.380662 \times 10^{-23}$ m² kg/s² K¹, $T = 723$ K, $h = 6.626176 \times 10^{-34}$ m² kg/s, $R = 1.987$ cal/K mol, and $\Delta G_A(T)$ is molar Gibbs free-energy of activation defined for the forward and reverse reactions as follows:

$$\Delta G_{A,forward} = G_{TS} - G_{IS} \quad (3)$$

$$\Delta G_{A,reverse} = G_{TS} - G_{FS} \quad (4)$$

with subscripts TS, FS and IS representing transition state, final state, and initial state, respectively. Similarly, the reaction free energy (ΔG_{Rx}) is defined as follows:

$$\Delta G_{Rx} = G_{FS} - G_{IS} \quad (5)$$

The rate constants for the forward and reverse reaction steps are labelled as k_f and k_r , respectively.

2.3 Structural model.

Under normal conditions, MgO crystallizes in the rocksalt crystal structure, with (001) being the most prominent surface. For the specific reaction of ethanol to 1,3-butadiene, the original working catalyst is MgO/SiO₂ [3,26]. The addition of MgO to SiO₂, regardless of the methods used to synthesize the catalysts, does not result in the formation of MgSiO₄ solid solution [23,25,26,42]. It was found that MgO crystalline phase was the only phase found on the amorphous surface. In contrast, a study by Angelici *et al.* [67] claims that MgSiO₄ phase was indeed formed and it was suggested to be responsible for the aldol condensation of the acetaldehyde intermediates. The authors argued that FTIR shows the presence of a hydroxyl group which coincides with that found in talc. This statement contradicts their previous study, in which the presence of the silicate was not confirmed by XRD [20]. The addition of MgO to amorphous silica combined with increased surface area of the catalyst is also known to create more defects on the MgO itself, which clearly contributes to the higher activity and selectivity of the catalyst. The unsaturated surface oxygen atoms, e.g. corner and edge O, are unfavorable energetically leading to the tendency to release an electron and to turn into O⁻ species. Hence these unsaturated oxygen atoms act as donors of an electron pair, i.e. as Lewis bases [68]. Cube corners [49], terraces, steps, corners, and reverse corners were studied extensively [48].

Periodic three layer slab of MgO consisting of 8 x 6 x 3 primitive cells was used throughout all the calculations. Previous investigations have identified defect sites of MgO catalysts, most notably the three- and four-fold coordinated surface atoms (Mg²⁺_{3C} O²⁻_{4C}), as the active sites [45–48,50,52] whereas atoms at surface terraces were found to be relatively unreactive [69]. The positions of atoms in the bottommost layer were fixed while remaining atoms were relaxed. PBE

lattice parameter of 4.255 Å was used to construct the slab. This value is similar to values of 4.261 (PBE) and 4.186 Å (experimental).[70] In this work we considered the Mg₃C coordinated to O_{4C} in the form of stepped kink, as the active sites for the reaction. The large slab is used to accommodate several intermolecular reactions that might include interactions of C2 and C4 intermediates and also to avoid significant interaction between molecules in the neighboring unit cells. The MgO slab used is depicted in **Figure 2** whereas **Figure 3** depicts all intermediates and transition state (TS) structures optimized in this work. Relevant geometrical parameters are provided in Supplementary Material **Table S2**. The corresponding electronic and free energy values at 0 K and at 723 K respectively are tabulated in **Table 1**.

3. Computational results

3.1. Reaction Pathways

3.1.1. Ethanol Dehydrogenation and Dehydration

We begin with the first step of ethanol catalytic transformation into acetaldehyde or into ethylene for which the computed free-energy profiles are shown in **Figure 4**. States 1A-1C and 5A-5C in **Figure 3** demonstrate the reaction pathways for ethanol dehydrogenation and dehydration to form acetaldehyde and ethylene, respectively. The corresponding TSs are labelled as 1B(TS) and 5B(TS). In both cases the reaction starts from the structures formed upon spontaneous dissociative adsorption of ethanol whereby proton is abstracted either by the edge or terrace oxygen atoms. The calculated relative free energies for the configurations 1A and 5A are -13.5 and -10.5 kcal/mol, respectively, at 450 °C. In 1B TS, the surface bound proton becomes coordinated to the proton leaving α -carbon atom. The H...H distance is 0.84 Å, which is 0.07 Å longer than the equilibrium H-H bond distance in hydrogen molecule in 1C. Compared to 1A, the distance between the hydrogen atom and lattice O_{4C} has significantly increased from 0.98 Å to 1.61 Å. Furthermore, acetaldehyde is coordinated to Mg_{3C} via oxygen atom while also accepting some electron density from in the terrace O_{5C} resulting in a distorted chemisorbed structure. During the dehydration step hydrogen atom is adsorbed on terrace oxygen atom as shown in Fig.3 (5A). During the reaction over transition state 5B one of the β -hydrogen atoms becomes oriented towards O_{4C} with C-H and O_{4C}-H of 1.45 and 1.22 Å, respectively. The final state 5C results in two hydroxyl groups formed on the MgO surface with ethylene molecule

loosely coordinated to the surface. Relative electronic energies at $T=0$ K and the corresponding free energy values at 450°C for the reaction profile shown in **Figure 4** are provided in **Table 1**. In particular, at 450°C the forward free-energy barrier for the reaction $1\text{A} \rightarrow 1\text{C}$ is 39.6 kcal/mol while the barrier for the reverse barrier is only 20.5 kcal/mol suggesting that the acetaldehyde formation is endergonic. Ethylene formation via $5\text{A} \rightarrow 5\text{C}$ has barrier 33.5 kcal/mol but the reverse barrier is higher with 38.3 kcal/mol. While both acetaldehyde and ethylene are typically observed as reaction byproducts of ethanol catalytic coupling [18,20,22–25], the stability of ethylene vs acetaldehyde is intriguing but not surprising. Ethanol is known to undergo intramolecular dehydration in the presence of acidic and basic surface sites [71], while acetaldehyde formation in general needs redox metals [72]. Hence for undoped MgO catalyst ethylene generation is expected and preferred over acetaldehyde.

The reaction pathways of ethanol dehydration and dehydrogenation products further proceed via two main reaction mechanisms discussed in detail in Sec.3.1.2 and 3.1.3: aldol condensation and Prins condensation reaction. The aldol condensation pathway entails acetaldehyde transformation into its enolate form followed by the reaction with the molecular acetaldehyde to form a C-C bond. The resulting C4 intermediate then undergoes several steps of intermolecular proton transfer with the surface and ethanol to yield 1,3-butadiene. Prins condensation entails C-C bond formation via reaction of acetaldehyde and ethylene followed by proton transfer steps. In these mechanisms, the proton diffusion through the surface leads to water release from the surface.

3.1.2. Aldol condensation

Classical aldol condensation mechanism requires one of the acetaldehyde molecules to be in its enolate state.[73] In this work the enolate state 2C (see Fig. 3) was obtained via proton transfer of β -hydrogen to terrace atom $\text{O}_{5\text{C}}$ yielding a hydroxyl group via low energy barrier 2B TS from the initial stable strongly adsorbed acetaldehyde molecule in 2A with free-energy of -8.5 kcal/mol relative to the reference state. The forward barrier for the reaction step $2\text{A} \rightarrow 2\text{C}$ is 16 kcal/mol as shown in **Figure 5**. This mechanism is facilitated by the C=O bond elongated from 1.21 Å[74] to 1.43 Å due to strong interaction with the surface oxygen atoms. In TS configuration, one of hydrogen atoms from the methyl group establishes a hydrogen bond with surface oxygen atom causing an elongation of the corresponding C-H bond from 1.10 to 1.29 Å.

State 2C represents a stable configuration with sp^2 hybridized carbon enolate atoms and surface hydroxyl group.

For the aldol condensation to take place, the hydrogen atom bound to the surface needs to be in a close proximity to the enolate molecule requiring it to diffuse to the edge O_{4C} atom. This transition proceeds via transition state structure 2D with the forward barrier of only 3 kcal/mol. The next step is the physisorption of a second acetaldehyde molecule on the surface in 2F, preceding the C-C bond formation via aldol condensation (2F-2H). The TS for this step (the structure 2G) shows the coordination between enolate and acetaldehyde with the reactive β -carbon of enolate and the α -carbon of acetaldehyde adsorbed on surface site Mg_{3C} establish a C-C bond of length of 2.07 Å. The forward IRC analysis for this reaction shows the formation of C-C bond between the two reactive carbon atoms. The length of the latter bond in the stable structure 2H is 1.64 Å. Formation of the acetaldol (3-hydroxybutanal) in 2H is preceded with forward reaction barrier of 16.1 kcal/mol.

Once 3-hydroxybutanal is formed, the aldol needs to lose a hydrogen atom to the surface to undergo dehydration to yield crotonaldehyde. For this step to take place, a reactive O_{4C} is required. Assuming transient proton diffusion between O_{4C} and O_{5C} atoms, proton abstraction takes place followed by the transformation of the trans isomer, as depicted in 2I, into 2J via aergonic steps. The activation energy from cis- to trans-crotonaldehyde reported is ~13 kcal/mol [75]. The molecule subsequently loses hydrogen atoms to the MgO surface via step 2J→2L ($\Delta G_{A,forward} = 5.9$ kcal/mol) and desorbs from the surface after breaking the C-O bond via sequence 2L→2M(TS)→2O ($\Delta G_{A,forward} = 24$ kcal/mol) yielding the structure 2O with a newly formed surface site O_{3C} which under reactive conditions can recombine with protons to form H_2O reforming the original Mg_{3C} site.

Formation and desorption of crotonaldehyde in 2N-2O agrees very well with the occasional gas phase byproduct observations [22,37]. Formation of the O_{3C} surface site in 2O is followed by the water molecule formation, which is another product of ethanol coupling reactions. The next step in the overall mechanism is the MPV reduction of crotonaldehyde by ethanol (3A→3C) to form adsorbed acetaldehyde in 3C followed by its desorption and proton transfer to the surface (3C→3G) to form 1,3-butadiene. The corresponding free-energy profile (2H → 2O → 3A → 3G) is shown in **Figure 6**. The highest barrier that we determined within this sequence was that

of proton transfer to the surface in 3E TS with 27.6 kcal/mol. Reduction of the unsaturated aldehyde by hydrogen was assumed not to take place as confirmed by the measured hydrogen content in the reaction products [30] and due to the gas-phase thermodynamic calculation which favors the reduction by ethanol [3]. Dissociation of hydrogen on the defected MgO surface itself is a non-spontaneous process with a relatively low activation barrier of 2.8 kcal/mol [76] whereas ethanol dissociation on Mg_{3c} is spontaneous as shown in Figure 4. Additionally, the heterolytic dissociation can only be stabilized on a high density of 3-coordinated sites which suggests small amount of surface hydrogen [77].

Alternatively, the 1,3-butadiene formation mechanism proposed earlier by Ostromislensky (also *vide infra*) involves the hemiacetal rearrangement [39]. It was argued that ethanol can react with acetaldehyde to form 1-ethoxyethanol which will then undergo rearrangement to butane-1,3-diol and further dehydrate to 1,3-butadiene. However, this mechanism has been rebuffed by Quattlebaum *et al.* [37]. The formed C-O-C bond, if it is to be rearranged to make C-C bond, would lead to its dissociation. The identified butane-1,3-diol, however, could be formed when acetaldol is reduced by ethanol, as shown in **Figure 6** 4A-4C. State 4C is effectively dissociated (adsorbed) butane-1,3-diol which is formed via series of exergonic steps 2J-4A-4B TS-4C with a very low forward free-energy barrier of 9.8 kcal/mol. The resulting adsorbed butane-1,3-diol can further undergo several steps of proton transfer to yield 1,3-butadiene (4C-4K). In this situation, there are three competing processes with transition states 4E, 4G, and 4J. The reaction channel with TS 4G breaks a C-O bond of the adsorbed butane-1,3-diol. The reaction 4F→4H is extremely exergonic with very low free-energy of activation (~2 kcal/mol). It is preceded by the 4E TS and the free-energy of activation of 26.2 kcal/mol, which is a typical value to that of sp^3 proton transfer to the reactive surface O4c atoms. The last step of this condensation mechanism is the simultaneous C-O bond breaking and proton transfer to the surface (4I→4K). Fig. 3 (4J) depicts a transition state where the 1,3-butadiene is desorbing from the surface. Interestingly, the two different MPV reduction steps yield two different conformations of 1,3-butadiene. MPV reduction of crotonaldehyde gives s-trans conformation, while that of acetaldol results in s-cis conformation (structures 3G and 4K, respectively, see Fig. 3). The stable conformation is, however, trans 1,3-butadiene, which makes an additional step for acetaldol reduction necessary. This last step will be cis/trans isomerization to trans 1,3-butadiene with rather low free-energy of activation of only ~4 kcal/mol [78].

3.1.3. Prins condensation

Our data shown in Figure 4 suggest that on undoped MgO the ethylene formation from ethanol will compete with that of acetaldehyde. Prins condensation is among the early proposed mechanisms for ethanol reaction to 1,3-butadiene [40]. The explicit ethanol reaction mechanism on MgO via Prins mechanism is studied in this work and the corresponding results are presented in this section. The corresponding structures are shown in **Figure 3** (6A-6E) whereas the free-energy reaction profiles are displayed in **Figure 7**. The Prins condensation pathway is the formation of C-C bond by opening the double C=C and C=O bonds of both ethylene and acetaldehyde, respectively (6A-6C). 6B TS represents the double bond opening of C=O with the oxygen coordinated between two surface Mg atoms (Mg_{4C} and Mg_{3C}). This charge transfer to the MgO surface makes the α -carbon susceptible to attack by the sp^2 carbon molecule. The intermolecular C-C distance is now 1.90 Å, while that of the aldehyde C-O bond is elongated by 0.1 Å. The double bond opening results in a C4 structure bound to the surface, as shown in Fig. 3 (6C). The corresponding forward free-energy barrier is 28.8 kcal/mol. This C-C coupling step is then followed by the proton transfer to the surface atom O_{5c} and the simultaneous C-O_{lattice} bond breaking (see Fig. 3 (6C-6E)) followed by another proton transfer from the terminal sp^3 carbon to the O_{4c} surface atom (see Fig. 3 (6E-6G)). The free-energy barriers for these steps are of 38.7 and 34.1 kcal/mol, which are typical values for proton transfer reactions considered in this work. The structure 6H represents the desorbed structure of 1,3-butadiene.

An alternative pathway for transformation of the structure 6E is that via transition state 6E i leading to the product 6E ii (see Fig. 3). Here instead of the subsequent proton transfer from the terminal carbon (as in the reaction 6E→6G) the surface proton diffuses from planar surface atom O_{5c} to a nearby edge atom O_{4c} via low forward barrier of 2.9 kcal/mol. The terminal proton transfer then takes place, as depicted in Fig. 3 (6E iii, 6E iii 1, 6iii 2) and the computed free-energy of activation (32.9 kcal/mol) is comparable to that for steps alternative pathway (6C→6E and 6E→6G). Interestingly, a cyclic TS can also be established in another variant of this mechanism, see Fig. 3 (6E iv). This mechanism yields a physisorbed molecule as a product, which is similar to methylethyl ketone (MEK) shown in Fig. 3 (6E v). However, this step has rather large forward activation energy of 71.6 kcal/mol.

3.1.4. 1-ethoxyethanol formation

Final major reaction mechanism considered in this study is the Ostromislensky's hemiacetal rearrangement which will be discussed in this section. The very first step in this case is the reaction of ethanol and acetaldehyde to yield 1-ethoxyethanol, which was further postulated to undergo a molecular rearrangement to form butane-1,3-diol. The very first step was investigated and it was found to proceed via stationary structures 7A to 7E shown in **Figure 3**. The free-energy profile for these steps is shown in **Figure 8**. The initial structure 7A contains an ethoxy species formed during the chemisorption of ethanol, as well as a molecule of acetaldehyde physisorbed to the MgO surface. The C-O bond formation to yield 1-ethoxyethanol (via transition state 7B) has a forward barrier of 28.9 kcal/mol with several nearly isoexergonic molecular rearrangements followed by the stabilized 7E structure with former aldehyde C-O that is still coordinated to the surface atom Mg_{3c}. It is apparent from **Figure 8** that reverse barrier for the 1-ethoxyethanol formation is almost zero. In this case 1-ethoxyethanol can behave as a thermodynamical sink that would form in a transient fashion before reacting via other discussed pathways to form 1,3-butadiene. Surprisingly, the free energy computed for the structure 7C, which is a minimum on potential energy surface (PES), is slightly higher than that for the structure 7B – TS that is a first-order saddle point on PES. This unexpected result is clearly due to a failure of the harmonic approximation used in this work to determine free-energies. This level of theory implies that the positions of stationary points on PES and on the free-energy surfaces are identical which is generally not true (see Ref.[79] for discussion of the limitations of harmonic transition state theory). Furthermore, this level of theory is unsuitable to describe soft degrees of freedom such as hindered molecular rotations or long-wave lattice vibrations which contribute to harmonic free-energies more than the hard ones. In our case, the free energy for the first-order saddle point structure 7B is 28.9 kcal/mol higher than that for the minimum 7A and, importantly, the reaction coordinate for the whole sequence 7A→7E consists of hindered rotations of the CH₃CH₂O- and CH₃CHO- groups with the imaginary frequencies for the TS structures 7B and 7D that are smaller than 100 cm⁻¹. We note, however, that the free-energies for the sequence of structures between two stable configurations 7A and 7E (i.e. the structures 7B, 7C and 7D) are all within 4 kcal/mol and this number is relatively small compared to the free-energy difference with respect to the stable structure 7A. As the configuration 7D is the one with the highest free-energy on the sequence of steps 7A→7E, we consider the difference G(7D)-G(7A)=32.8 kcal/mol as the effective free-energy barrier for the whole process 7A→7E.

3.2. Details of the Free-energy profiles

Three particular steps will be discussed here, namely elimination/redox reactions of ethanol, C-C bond formation, and proton transfer.

Elimination/redox reaction of ethanol

Elimination reaction takes place when a substituent leaves the molecule, e.g. water leaving ethanol, while redox reaction is defined as a reaction where a molecule loses or gains hydrogen. [80] Dehydrogenation reaction of ethanol (redox) is the first and foremost reaction step in all mechanisms proposed for the 1,3-butadiene formation. This oxidation step yields hydrogen as a byproduct while also transforming ethanol into acetaldehyde, a more reactive intermediate. The transformation 1A→1C shows a rather high free-energy barrier, 39.6 kcal/mol, while the reaction itself is endergonic in nature, with $\Delta G_{\text{Rx}}=20.5$ kcal/mol. On the other hand, ethanol dehydration to ethylene has slightly lower activation barrier, 33.5 kcal/mol, and it is slightly exergonic with $\Delta G_{\text{Rx}}=-4.9$ kcal/mol. Comparison of both reactions shows that ethanol is more likely to lose water than hydrogen on undoped MgO catalyst surface, which means that ethylene should be produced in higher amounts than acetaldehyde. This is in agreement with the experimental reports where small amounts of Ag, Cu or Zn are typically incorporated into the lattice structure to enhance acetaldehyde formation [23,67,81–86].

C-C bond formation

Two C-C bond formation pathways are presented in this study. Namely, aldol condensation and Prins condensation. The pathway 2F→2H possesses a favorable activation energy, lower than that of Prins, 16.1 v 28.8 kcal/mol. However, this reaction is thermodynamically limited, as shown by the endergonic nature of the reaction, with $\Delta G_{\text{Rx}}=12.9$ kcal/mol. This suggests that aldol condensation step is kinetically favored on undoped MgO samples, with arguably one of the most favorable steps in the whole reaction landscape, while the exergonic nature of the Prins mechanism makes it thermodynamically favored. The activation energy of the latter is also similar to the energetic barrier to other steps, comparable to that of ethylene formation, and even lower than the activation energy of ethanol dehydrogenation. However, the overall picture is more complex since ethylene formed is only physisorbed onto the surface and adsorption of both reactants, i.e. ethylene and acetaldehyde, is only -0.2 kcal/mol lower in free-energy than the reference state suggesting that both molecules can desorb as byproducts. In accord with

implications of these results, both ethylene and acetaldehyde have been seen as byproducts of ethanol catalytic coupling to form 1,3-butadiene.[18,20,22–25]

Proton transfer

Proton transfer steps can be further subdivided into three categories. The proton transfer steps of the first category are those that take place between the organic molecule and the surface, e.g. 2J→2L, 3D→3F, 4D→4F, 4I→4K, 6C→6G. The second type of proton transfer reactions is the MPV reduction taking place between two organic molecules, e.g. 3A→3C and 4A→4C. The last type is the proton diffusion from one site of the MgO surface to another, e.g. 6E→6E i→6E ii, 2C→2E, and also the understated proton diffusion steps between 2H and 2I.

The first type of proton transfer typically exhibits moderate activation energy. Most of the cases have $\Delta G_{A,forward} = \sim 30$ kcal/mol with only one case, i.e. 2J→2L, possessing very low activation energy of ~ 6 kcal/mol, possibly due to the very saturated nature of the organic C4 compound. In the case of the MPV reduction, hydrogen atom moves from an alcohol α -carbon to open up the C=O bond of a molecule. This reduction reaction does not have a typical activation energy but rather it depends on the nature of the C=O containing molecule itself. The values computed for crotonaldehyde and acetaldol are ~ 12 kcal/mol and ~ 10 kcal/mol, respectively. Finally, the last type of the proton transfer reaction is proton diffusion from one MgO surface site to another. This reaction has typically very low activation energy of ~ 3 kcal/mol which suggests that the water formation and desorption are easily facilitated by the MgO catalyst.

4. Discussion

Adsorption of ethanol on both perfect and defect sites of MgO surface had been studied previously using cluster calculation [47]. It was shown that ethanol dissociated on defect sites but not on the perfect surface. Moreover, the adsorption energy decreased with the coordination number of the adsorption site [47]. This finding also aligns well with our calculations which show two modes of ethanol dissociation on the defect sites, i.e. 1A and 5A. In the state 1A, adsorbed molecules are coordinated on Mg_{3C} (corner) and O_{4C} (edge), while in the configuration 5A the ethanol molecule is chemisorbed on Mg_{3C} and O_{5C} (terrace). The energy of the former is lower than the latter (both electronic energy and Gibbs' free energy), indicating the difference in

stability of both states. The lower coordination O_{4C} is very reactive and hence the spontaneous chemisorption of ethanol [45,52]. **Figure 3** structure 5A, however, depicts the adsorption of ethanol on the same Mg atoms (Mg_{3C} and Mg_{5C}), but proton adsorbing on O_{5C} . The highly-coordinated O_{5C} does not possess similar deprotonation ability to its lower-coordinated counterparts, as it is already stabilized by coordination with the neighboring atoms [45,50]. This situation causes the ethoxy oxygen to interact less strongly with the surface in **Figure 5A**, resulting in a relatively more unstable state compared to **Figure 3** structure 1A. Similarly, two new hydroxyl groups are formed during the dehydration process and only weakly bound acetaldehyde and molecular hydrogen during the dehydrogenation process in **Figure 3** structures 5C and 1C, respectively, with the former being more stable.

A study by Zhang *et al.* showed a peculiar finding where ethanol dissociated on both perfect and defected sites with energy barriers of 1.63, 1.42, and 1.30 eV, for terrace, kink, and edge, respectively [42]. Surprisingly, the molecule needed to surpass higher barrier for kink which consisted of two low coordinated ions ($Mg_{3C}-O_{3C}$), than for stepped $Mg_{4C}-O_{4C}$. This is in contrast to findings reported in this work and those of Branda where strong dissociation on the defect sites takes place without any barrier [47]. Finally, Chierigato *et al.* [41] showed that ethanol dehydrogenation over corner site of the MgO surface had an energetic barrier of 44.7 kcal/mol on Mg_{3C} site, as determined using cluster B3LYP/6-31++G(d,p) DFT calculations. Furthermore, the reaction was also postulated to be slightly exergonic with respect to the gas phase reference components, with ΔE of -1.4 kcal/mol. Our periodic calculations, on the other hand, predict that ethanol to acetaldehyde has a rather high energetic barrier, and it essentially represents rate-limiting step in the overall mechanism. The free-energy barrier, based on our calculation was 39.6 kcal/mol at 450°C. The ΔG_{Rx} for this reaction is also calculated to be +19.1 kcal/mol, which is highly endergonic.

The free-energy values for the profiles presented in **Figure 4-8** are listed in **Table 2**, along with the computed reaction rate constants. Based on the results presented in **Figure 4**, ethylene is more likely to be produced than acetaldehyde due to the lower activation energy and the exergonic nature of the reaction. As depicted in **Figure 5** only one TS structure has barrier higher than the desorption energy of the molecules in the reference state, namely that for enolate formation (2A-2C). In the subsequent step C-C bond coupling takes place between the enolate

and the physisorbed acetaldehyde (2F-2H). This transition state (2G) is facilitated by enol, acetaldehyde as well as the resulting C-C product bonded by low-coordinated Mg atoms.

The resulting acetaldol, after several steps of proton diffusion and isomerization to *cis* conformer, can either lose proton to the surface or undergo MPV reduction, as shown in **Figure 6** for steps 2J→2L and 2J→4C, respectively. The two different pathways show that MPV reduction of acetaldol can be more favorable with a sharp decrease in its energy when ethanol is adsorbed, i.e. ethanol adsorption is much more favorable than a proton transfer from acetaldol to the surface. One should note that the overall MPV reduction pathway of acetaldol is below the reference state, which means that all the reaction steps are more favorable than the desorption of any adsorbates. State 4D, which results from the subsequent acetaldehyde desorption from state 4E, is essentially an adsorbed butane-1,3-diol. This is the basis of Ostromislensky's reaction mechanism supported by our calculations, although the rearrangement step from 1-ethoxyethanol to this diol has been previously rejected.[39] As mentioned before, MPV reduction of acetaldol pathway would require an additional step to convert the *cis*-1,3-butadiene to *trans*-1,3-butadiene ($\Delta G_{\text{Rx}} = \sim 4 \text{ kcal/mol}$), which is the more stable molecule.

The adsorption of crotonaldehyde on the defected surface shows that the C=O bond is now lengthened from 1.25 Å (gas-phase) to 1.27 Å. This bond lengthening, also noticed by Boronat, *et al.*, is attributed to the back-donation of the surface antibonding orbital $\pi^*(\text{CO})$ of crotonaldehyde [87]. These authors calculated three main pathways for MPV reduction of cyclohexanone by 2-butanol over a tin-zeolite catalyst and reported the most favorable pathway ($\Delta G_{\text{A,forward}} = \sim 15 \text{ kcal/mol}$) proceeding via formation of alkoxy species on the surface, although their calculation was carried out on a single metal center model [87]. Furthermore, both direct MVP and H-transfer facilitated by metal hydride formation have been reported with the former taking place over alkali-catalysts while the latter over transition metal catalysts [88,89]. A direct MPV reduction mechanism was also reported to take place during the 5-HMF reduction by methanol on $\text{Mg}_{3\text{c}}$ site of MgO cluster model, as reported by Pasini, *et al.* [88] with electronic energy of 27.5 kcal/mol.

Free-energy profile for the Prins pathway is depicted in **Figure 7**. Both acetaldehyde and ethylene (6A) have rather low adsorption energies, i.e. the two C2 species can easily desorb from the surface before going to the anticipated TS (6B). Notably, all transition states in this

mechanism have positive relative energy with respect to the reference state. The blue pathway indicates a Prins mechanism that includes proton diffusion which results in a slightly lower free energy of the last transition state (6E iii 1) compared to the original red pathway, of which last transition state has a higher free energy (6F). The final state in both variants of Prins mechanism is *trans*-1,3-butadiene detached from the surface. Another step considered within the discussion of Prins mechanism is the formation of highly energetically unfavorable cyclic TS (6E iv). Not only does it have a large activation barrier, but it also goes to another minimum (6E v) which has a slightly higher relative energy than the initial state (6E iii).

The Prins mechanism was originally suggested by Gruver *et al.* [40]. The authors used aluminated sepiolites (both ammonium-exchanged and silver-exchanged) for the butadiene production from ethanol. On the silver exchanged catalyst, the production of ethylene and 1,3-butadiene increased exponentially with increasing contact time, while acetaldehyde production was linear [40]. The adoption of the same mechanism for MgO can be attributed to the fact that both catalysts possess almost exclusively Lewis acid sites [90] as Prins is a mechanism that mostly takes place on Lewis acid sites [91]. The reason that this mechanism has not been considered viable was the postulated step of ethylene protonation, which was supposed to result in a highly unstable carbocation [3]. As shown in this work, there is another type of intermediate/transition state for Prins mechanism which does not require protonation of ethylene. This intermediate was also identified by Yamabe, *et al.* [92]. In their theoretical work, propylene and formaldehyde were reacted via a novel C4 intermediate. Finally, other evidences of reaction between olefin and aldehyde were shown in US Patent no 2377025 A for 1,3-butadiene production, albeit through an acetylene intermediate, on alumina-silver and Cr- and Mo-oxide catalyst [93], isobutylene and pentenes with formaldehyde on KU-2 cation exchanged resin to make dioxanes [94] and 1,3-butanediol production via reaction of propylene and formaldehyde over ceria catalysts that contain mostly Lewis acid sites [95].

Work presented here for the enol formation step also shows a much lower free-energy barrier, compared to ethanol dehydrogenation, with a much more negative ΔG_{R_x} of reaction, 16 and -11.8 kcal/mol, respectively. Chiericato *et al.* suggested a novel mechanism with ethanol releasing a proton from its β -carbon and yielding a carbanion with ~33-36 kcal/mol forward barrier and negligible reverse barrier. This carbanion would then react with either ethanol or acetaldehyde to yield 1-butanol or crotyl alcohol, respectively, which subsequently dehydrate to produce 1,3-

butadiene [41]. The carbanion has an interesting configuration in which the ethanol is not deprotonated, rather the hydroxyl group is interacting with a proton detached from β -carbon. From their overall mechanism, the rate-limiting step was predicted to be the reaction of acetaldehyde and carbanion with the electronic energy barrier of 11.4 kcal/mol with respect to the adsorbed reactants. The reaction to form C4 hydrocarbons is exergonic. Our attempt on cleaving the proton from β -carbon, however, lead to another pathway, namely to dehydration to form ethylene in 5A, 5B TS and 5C in **Figure 3** ($\Delta G_{A,forward} = 33.5$ kcal/mol, $\Delta G_{Rx} = -4.9$ kcal/mol). The unstable carbanion situation that would lead to C-O bond scission was not encountered in the case of diol transformation to 1,3-butadiene (Figure 4D-4K). As a result, Figure 4F shows a C4 molecule with two oxygen atoms bound to the surface. The terminal carbon, however, is in distorted sp^2 configuration and thus, represents a carbanion. Similarly, on the investigated Prins mechanism, a stabilized C4 carbanion, which leads to the desorption of 1,3-butadiene, is also observed in Figure 6G and 6E iii 2.

Interesting observation stemming from our work was that the Prins mechanism for C-C bond formation was thermodynamically more favorable than aldol C-C coupling step, and with the calculated barrier of 28.8 kcal/mol, i.e. ~ 10 kcal/mol lower than ethanol dehydrogenation. The activation energy is, however, still larger than that of aldol condensation (16.1 kcal/mol). Another fact complicating our conclusions further is that adsorption of both C2 intermediates on the surface is almost unfavorable thermodynamically (adsorption free energy (ΔG_{Ads}) = -0.2 kcal/mol), and the transition state is located above the reference state. This step was similar to the carbanion/acetaldehyde reaction, which is also a double bond opening of two sp^2 carbon atoms in acetaldehyde and ethylene. The suggested carbanion/acetaldehyde reaction involved butane-1,3-diol as an intermediate which subsequently deprotonates, as opposed to but-3-en-2-ol (state 5C) suggested by our calculation. 1,3-butanediol, however, still appears in our mechanism as a product of MPV reduction on the resulting acetaldol from aldol condensation.

5. Conclusion

A complex reactive mechanism of ethanol to form 1,3-butadiene was explored using periodic quantum chemical methods. Overall free energy surface was explored for the highly debated reaction mechanisms, including Toussaint's aldol condensation mechanism, Fripiat's Prins

mechanism and mechanism based on Ostromislensky's hemiacetal rearrangement. Based on the thermodynamic and kinetic data determined within this study we identified four rate limiting steps in the overall process. In particular, ethanol dehydration to form ethylene possessed lower energy barrier than dehydrogenation to yield acetaldehyde suggesting competing reactive pathways. Aldol condensation step to form acetaldol is preceded with forward free-energy barrier of 16.1 kcal/mol but limited thermodynamically with endergonic reaction free energy of 12.9 kcal/mol. This calculation also offers another viable route in the form of Prins condensation, which has a free energy barrier of 28.8 kcal/mol with exergonic reaction free energy of -22.7 kcal/mol. Finally, thermodynamic stability of 1-ethoxyethanol prevents further reaction via hemiacetal rearrangement. The results presented here provide a first glimpse into the 1,3-butadiene formation mechanism on undoped MgO reactive sites in light of the vast literature discussing variety of the proposed mechanistic pathways mostly based on conventional homogenous organic chemistry reactions. While the surface model employed in this work utilized most reactive MgO site, presence of H₂O as a reaction product suggests that other surface sites, based on reactive hydroxyls, can also affect the overall reactive pathways and will be the focus of the future studies. However, based on the present calculations alone several mechanisms appear possible. Reactivity experiments are needed to discriminate between the different hypothesis, and we hope that our calculations will stimulate such studies.

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Tables

Table 1

State	Electronic energy (kcal/mol)	Referenced free energy (kcal/mol)	State	Electronic energy (kcal/mol)	Referenced free energy (kcal/mol)
1A	-40.6	-13.5	4F	-45.3	-8.1
1B	3.9	26.2	4G	-43.2	-6.1
1C	-16.6	5.6	4H	-52.0	-46.2
2A	-14.3	-8.5	4I	-37.8	-37.7
2B	4.1	7.4	4J	-5.5	-5.3
2C	-22.2	-20.3	4K	-18.7	-24.0
2D	-17.7	-17.3	5A	-39.9	-10.5
2E	-26.2	-28.8	5B	-2.6	23.0
2F	-22.5	-23.7	5C	-32.0	-15.3
2G	-15.9	-7.6	6A	11.6	-0.2
2H	-19.4	-10.8	6B	25.6	28.6
2I	-12.5	-1.6	6C	-34.8	-22.9
2J	-11.4	-1.6	6D	3.7	15.8
2K	-6.2	4.2	6E	-26.8	-18.9
2L	-15.4	-8.2	6F	9.5	15.3
2M	9.3	15.7	6G	-6.0	-0.7
2N	2.2	3.2	6H	-4.4	-2.9
2O	6.8	-18.2	6E i	-21.8	-16.0
3A	-24.1	-18.8	6E ii	-30.5	-27.2
3B	-14.6	-6.8	6E iii	-32.5	-27.3
3C	-19.8	-15.2	6E iii 1	2.2	5.6
3D	-27.3	-27.8	6E iii 2	-13.8	-9.6
3E	-1.3	-0.2	6E iii 3	-11.5	-12.7
3F	-15.4	-15.4	6E iv	43.9	44.3
3G	-15.6	-20.4	6E v	-21.4	-25.4
4A	-53.1	-14.6	7A	-51.2	-26.4
4B	-52.5	-4.8	7B	-30.6	2.5
4C	-64.4	-22.1	7C	-33.4	3.9
4D	-68.3	-32.0	7D	-30.5	6.4
4E	-42.5	-5.8	7E	-44.8	-8.7

Table 2

Reaction	ΔG_A (kcal/mol)		K (s ⁻¹)	
	Forward	Reverse	Forward	Reverse
1A $\rightarrow$ 1C	39.6	20.5	15.9	$9.37 \cdot 10^6$
2A $\rightarrow$ 2C	16.0	27.7	$2.26 \cdot 10^8$	$6.26 \cdot 10^4$
2C $\rightarrow$ 2E	3.0	10.5	$1.84 \cdot 10^{12}$	$9.93 \cdot 10^9$
2F $\rightarrow$ 2H	16.1	3.2	$2.04 \cdot 10^8$	$1.60 \cdot 10^{12}$
2J $\rightarrow$ 2L	5.9	12.5	$2.52 \cdot 10^{11}$	$2.59 \cdot 10^9$
2L $\rightarrow$ 2N	24.0	12.5	$8.66 \cdot 10^5$	$2.44 \cdot 10^9$
3A $\rightarrow$ 3C	12.1	8.5	$3.35 \cdot 10^9$	$4.17 \cdot 10^{10}$
3D $\rightarrow$ 3F	27.6	15.3	$6.88 \cdot 10^4$	$3.67 \cdot 10^8$
4A $\rightarrow$ 4C	9.8	17.3	$1.69 \cdot 10^{10}$	$8.74 \cdot 10^7$
4D $\rightarrow$ 4F	26.2	2.4	$1.77 \cdot 10^5$	$2.86 \cdot 10^{12}$
4F $\rightarrow$ 4H	2.1	40.2	$3.57 \cdot 10^{12}$	11.0
4I $\rightarrow$ 4K	32.5	18.8	$2.26 \cdot 10^3$	$3.18 \cdot 10^7$
5A $\rightarrow$ 5C	33.5	38.3	$1.15 \cdot 10^3$	38.9
6A $\rightarrow$ 6C	28.8	51.5	$3.07 \cdot 10^4$	$4.11 \cdot 10^{-3}$
6C $\rightarrow$ 6E	38.7	34.7	29.6	$4.93 \cdot 10^2$
6E $\rightarrow$ 6G	34.1	2.3	$7.45 \cdot 10^2$	$3.14 \cdot 10^{12}$
6E $\rightarrow$ 6E ii	2.9	11.3	$2.00 \cdot 10^{12}$	$6.00 \cdot 10^9$
6E iii $\rightarrow$ 6E v	71.6	69.7	$3.43 \cdot 10^{-9}$	$1.26 \cdot 10^{-8}$
6E iii $\rightarrow$ 6E iii2	32.9	15.2	$1.76 \cdot 10^3$	$3.92 \cdot 10^8$
7A $\rightarrow$ 7E	32.8	15.1	$1.86 \cdot 10^3$	$4.24 \cdot 10^8$

Figures

Figure 1. Reaction mechanisms proposed for ethanol to 1,3-butadiene; (a) Toussaint's aldol condensation mechanism, (b) Fripiat's Prins mechanism, (c) mechanism based on Ostromislensky's hemiacetal rearrangement.

Figure 2. Periodic MgO slab used throughout the calculations. The highlighted bottom layer indicates frozen atoms during calculations.

Figure 3. All stable intermediates and transition states calculated following the reaction pathways. (1A-1C): ethanol dehydrogenation to acetaldehyde; (2A-2O): acetaldehyde aldol condensation to 3-hydroxybutanal (acetaldol) followed by proton transfer to crotonaldehyde; (3A-3G): MPV (Meerwein–Ponndorf–Verley) reduction of crotonaldehyde to 1,3-butadiene; (4A-4K): acetaldol MPV reduction to butadiene; (5A-5C): ethanol dehydration to ethylene; (6A-6E iii 3): Prins condensation of acetaldehyde and ethylene; (7A-7E): ethanol and acetaldehyde nucleophilic addition reaction (Ostromislensky's hemiacetal rearrangement).

Figure 4. Free-energy profiles for (a) ethanol dehydrogenation to form acetaldehyde and (b) ethanol dehydration to ethylene.

Figure 5. Free-energy profile for aldol condensation pathway.

Figure 6. Free-energy profiles for the MPV reduction of the resulting molecule from aldol condensation. Red pathway indicates subsequent proton transfer of acetaldol followed by MPV reduction of the crotonaldehyde; Blue pathway shows the direct MPV reduction of the resulting acetaldol.

Figure 7. Free-energy profiles for the Prins condensation between ethylene and acetaldehyde. Red pathway indicates a typical route of Prins condensation; Blue pathway shows an additional proton diffusion step in between the reaction steps; Black pathway shows the unlikely formation of MEK.

Figure 8. Free-energy profiles for ethanol and acetaldehyde nucleophilic addition reaction via Ostromislensky's hemiacetal rearrangement.

(a)

(b)

(c)

Figure 1. Reaction mechanisms proposed for ethanol to 1,3-butadiene; (a) Toussaint's generally accepted mechanism, (b) Fripiat's Prins mechanism, (c) Ostromislensky's hemiacetal rearrangement.

Figure 2. Periodic MgO slab used throughout the calculations. The whited out bottom layer indicates the atoms whose positions were kept frozen during calculations.

4J (TS)	4K

6A	6B (TS)	6C	6D (TS)

6E	6F (TS)	6G	6H

6E i (TS)	6E ii	6E iii	6E iv (TS)

6E v	6E iii 1 (TS)	6E iii 2	6E iii 3

Figure 3. All stable intermediates and transition states calculated following the reaction pathways. (1A-1C): ethanol dehydrogenation to acetaldehyde; (2A-2O): acetaldehyde aldol condensation to 3-hydroxybutanal (acetaldol) followed by proton transfer to crotonaldehyde; (3A-3G): MPV (Meerwein–Ponndorf–Verley) reduction of crotonaldehyde to 1,3-butadiene; (4A-4K): acetaldol MPV reduction to butadiene; (5A-5C): ethanol dehydration to ethylene; (6A-6E iii 3): Prins condensation of acetaldehyde and ethylene; (7A-7E): ethanol and acetaldehyde nucleophilic addition reaction (Ostromislensky's hemiacetal rearrangement).

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Figure 8. Free-energy profile for ethanol and acetaldehyde nucleophilic addition reaction.