

Supporting Information for "Monomolecular mechanisms of isobutanol conversion to butenes catalyzed by acidic zeolites: alcohol isomerization as a key to the production of linear butenes"

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SI. List of animations

In this section we provide a list of file names and short descriptions of animations for each elementary step uploaded in mp4 format as a part of Supporting Information.

dh1.mp4	Isobutanol to isobutene (DH1)
dh1-anti-a.mp4	Isobutanol to tert-butyl cation intermediate (DH1-anti-a) (first step of E1 elimination mechanism)
dh1-anti-b.mp4	Tert-butyl cation to isobutene (DH1-anti-b) (second step of E1 elimination mechanism)
dh2.mp4	Tert-butanol to isobutene (DH2)
dh2-anti-a.mp4	Tert-butanol to tert-butyl cation intermediate (DH2-anti-a) (first step of E1 elimination mechanism)
dh3-cis.mp4	Butan-2-ol to <i>cis</i> -but-2-ene (DH3-cis)
dh3-trans.mp4	Butan-2-ol to <i>trans</i> -but-2-ene (DH3-trans)

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dh4.mp4	Butan-2-ol to but-1-ene (DH4)
dh5.mp4	Butan-1-ol to but-1-ene (DH5)
dh5w.mp4	Butan-1-ol to but-1-ene (water mediated) (DH5w)
dha1-a.mp4	Isobutanol to isobutoxide (DHA1-a)
dha1-b.mp4	Isobutoxide to isobutene (DHA1-b)
dha5.mp4	Butan-1-ol to n-butoxide (DHA5)
dhi1-cis.mp4	Butan-1-ol to <i>cis</i> -but-2-ene (DHI1-cis)
dhi1-trans.mp4	Butan-1-ol to <i>trans</i> -but-2-ene (DHI1-trans)
dhi2.mp4	Isobutanol to but-1-ene (DHI2)
i1.mp4	Isobutanol to tert-butanol (I1)
i2.mp4	Isobutanol to butan-2-ol (I2)
ia2-a.mp4	Isobutoxide to secondary butoxide (IA2-a)
ia2-b-cis.mp4	Secondary butoxide to <i>cis</i> -but-2-ene (IA2-b-cis)
ia2-b-trans.mp4	Secondary butoxide to <i>trans</i> -but-2-ene (IA2-b-trans)
ia3-b.mp4	Secondary butoxide to but-1-ene (IA3-b)
r-a_r-b_r-c.mp4	Three step rotation of isobutanol (R-a, R-b, R-c)

SII. Notation used to label elementary steps

Path	Description
DH1	Dehydration of isobutanol to isobutene via <i>syn</i> E2 elimination
DH2	Dehydration of tert-butanol to isobutene via water-assisted <i>syn</i> E2 elimination
DH3-cis	Dehydration of butan-2-ol to cis-but-2-ene via <i>syn</i> E2 elimination
DH3-trans	Dehydration of butan-2-ol to trans-but-2-ene via <i>syn</i> E2 elimination
DH4	Dehydration of butan-2-ol to but-1-ene via <i>syn</i> E2 elimination
DH5	Dehydration of butan-1-ol to but-1-ene via <i>syn</i> E2 elimination
DH1-anti-a	First step of dehydration of isobutanol to isobutene involving tert-butyl cation via <i>anti</i> E1 elimination
DH2-anti-a	First step of dehydration of tert-butanol to isobutene involving tert-butyl cation via <i>anti</i> E1 elimination
DH1-anti-b	Second step of dehydration of isobutanol and tert-butanol involving tert-butyl cation via <i>anti</i> E1 elimination
DH5w	Dehydration of butan-1-ol to but-1-ene via water-assisted syn E2 elimination
DHI1-cis	Synchronous isomerization and dehydration of butan-1-ol to cis-but-2-ene via E2 + H shift
DHI1-trans	Synchronous isomerization and dehydration of butan-1-ol to trans-but-2-ene via E2 + H shift
DHI2	Synchronous isomerization and dehydration of isobutanol to but-1-ene via water-assisted E2 + methyl shift
I1	Isomerization of isobutanol to tert-butanol via OH/H exchange
I2	Isomerization of isobutanol to butan-2-ol via OH/methyl exchange
DHA1-a	Formation of isobutoxide from isobutanol via SN2 substitution
DHA1-b	Water-assisted formation of isobutene from isobutoxide
DHA5	Formation of n-butoxide from butan-1-ol via SN2 substitution
IA2-a	Formation of secondary butoxide from isobutoxide via H/methyl exchange
IA2-b-cis	Water-assisted formation of cis-but-2-ene from secondary butoxide
IA2-b-trans	Water-assisted formation of trans-but-2-ene from secondary butoxide
IA3-b	Water-assisted formation of but-1-ene from secondary butoxide

SIII. Free energy calculations

The thermodynamic calculations presented in this work have been performed using a static approach based on the harmonic oscillator, rigid rotor and ideal gas approximations to vibrational, rotational, and translational degrees of freedom, respectively. Here we briefly summarize all the working equations, a more detailed presentation can be found in standard textbooks on computational chemistry, such as Ref. [S1] For the given stable or transition state i , the partition function is expressed as follows:

$$q_i = q_{i,el} \cdot q_{i,vib} \cdot q_{i,rot} \cdot q_{i,trans}. \quad (S1)$$

The electronic partition function ($q_{i,el}$) writes

$$q_{i,el} = g_0 e^{-E_{DFT}/k_B T} \quad (S2)$$

where g_0 is the electronic degeneracy, E_{DFT} is the electronic ground state energy as obtained in a DFT calculation and k_B is the Boltzmann constant. We note that all electronic ground states considered in this work were singlets with $g_0=1$.

The vibrational partition function has been obtained as

$$q_{i,vib} = \prod_{i=1}^{N_{vib}} \frac{e^{\frac{-h\nu_i}{2k_b T}}}{1 - e^{\frac{-h\nu_i}{k_b T}}} \quad (S3)$$

where summation runs over all N_{vib} vibrational modes with real frequencies ($3N_{at} - 3$ and $3N_{at} - 6$ for a stable periodic and a molecular system consisting of N_{at} atoms, respectively, and $3N_{at} - 4$ for transition states created in a periodic system), h is the Planck constant, and ν_i is the harmonic frequency of the vibrational mode i . We emphasize that vibrational frequencies have been always computed for the full system whereby we always ensured (by means of energy minimization (line minimization) along the artificial unstable eigenvector direction) that the correct eigen spectrum (with exactly zero and one

imaginary frequency for a stable and transition state, respectively) has been used. Importantly, no *ad hoc* manipulation of computed values, such as removal or replacement of values under a certain threshold, has been done and hence our computed data fully rely on transparent and well defined physical model without attempting to mask any of its deficiencies.

The rotational partition function for a non-linear gas phase molecule writes

$$q_{i,rot} = \frac{\sqrt{\pi}}{\sigma} \left(\frac{8\pi^2 k_B T}{h^2} \right)^{3/2} \sqrt{I_1 I_2 I_3} \quad (S4)$$

with I_1 , I_2 , and I_3 being the momenta of inertia and σ is the symmetry index set to 2 in the case of the water, isobutene, *cis*- and *trans*- but-2-ene and to 1 in the case of isobutan-1-ol and but-1-ene molecules.

Finally, the translational partition function for a gas phase molecule is defined as

$$q_{i,trans} = \left(\frac{2\pi k_B T M}{h^2} \right)^{3/2} \frac{k_B T}{p} \quad (S5)$$

with M being the total mass of the molecule and p being the external pressure set to 101325 Pa.

The Gibbs free energies, enthalpies and entropies are then determined via defining equations:

$$G_i = k_B T \left(\frac{\partial \log(q_i)}{\partial \log(V)} - \log(q_i) \right), \quad (S6)$$

$$H_i = k_B T \left(\frac{\partial \log(q_i)}{\partial \log(V)} + \frac{\partial \log(q_i)}{\partial \log(T)} \right), \quad (S7)$$

and

$$S_i = \frac{H_i - G_i}{T}. \quad (S8)$$

Note that we assumed in our calculations that the volume dependence of the partition function of the substrate before and after adsorption of small amount of molecular adsorbates is approximately identical, i.e., the change of the $pV = k_B T \frac{\partial \log(q_i)}{\partial \log(V)}$ term of the substrate due to adsorption can be neglected.

SIV. Rotational isomers of reactant, product and intermediate states

In this section we provide information about energies of all rotational isomers (rotamers) of molecules created at different stages of reactions (note that only molecules forming more than one rotamer are discussed here). Those rotamers that are specifically required as reactants or are formed as products in some elementary steps are also identified here.

SIV.1. *Isobutanol*

Three rotamers of isobutanol can be formed by varying the dihedral angle O1-C2-C3-C4 (τ) shown in Fig. S1, with the potential energy minima located at $\tau \approx -60^\circ$, 60° , and 180° . Two of these isomers ($\tau \approx 60^\circ$ and $\tau \approx 180^\circ$) are symmetrically equivalent and can occur in chemical reactions interchangeably. All the rotamers are nearly energy degenerate as they differ in energy by less than 2.5 kJ mol^{-1} . Since the barriers separating the individual rotamers are within 23.0 kJ mol^{-1} , the transformations between the rotamers can be considered as a relatively fast process compared to other reactions studied in this work.

Isobutanol plays the role of reactant in the elementary steps DH1, I1, DH12, and I2, whereby the former three reactions involve the rotamer $\tau \approx 60^\circ$ (or, equivalently 180°) while the latter one the rotamer $\tau \approx -60^\circ$.

SIV.2. *Butan-2-ol*

In analogy to isobutanol, butan-2-ol forms three rotational isomers differing in the value of dihedral angle O1-C2-C3-C4 (τ) shown in Fig. S2, with the potential energy minima located at $\tau \approx -60^\circ$, 60° , and 180° . The computed potential energies of all rotamers are very similar (differences within 4.0 kJ mol^{-1}). Similar to isobutanol, the barriers separating the individual rotamers are within 22.0 kJ mol^{-1} , justifying the neglect of the rotamers' transformations in our analysis of reaction kinetics. When created as product in I2, butan-2-ol forms the isomer with $\tau \approx 180^\circ$. When acting as reactant, the specific value of τ is decisive for the skeletal arrangement of the product. Thus, the elementary steps DH3-trans starts from the rotamer $\tau \approx 60^\circ$ and leads to formation

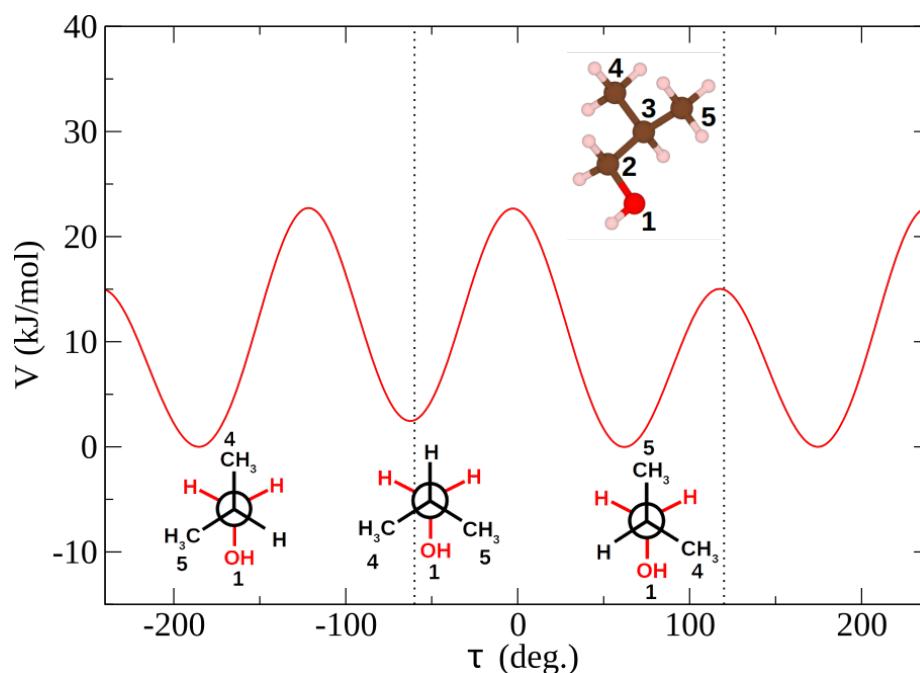


Figure S1: Potential energy profile of isobutanol along the torsional angle (τ) O1-C2-C3-C4. The dotted lines delimit the asymmetric part of the profile. Diagrams depicting the three stable rotamers viewed in direction perpendicular to the rotational axis (C2-C3) are shown in the inset.

of *trans*-but-2-ene, DH3-cis starts from the rotamer $\tau \approx -60^\circ$ and leads to formation of *cis*-but-2-ene, and DH4 starts from the rotamer $\tau \approx 180^\circ$ and yields *trans*-but-1-ene as product.

SIV.3. But-1-ene

The molecule of but-1-ene forms three isomers accessible via variation of the dihedral angle C1-C2-C3-C4 (τ) shown in Fig. S3. The corresponding potential energy minima are located at $\tau \approx -120^\circ$, 0° , and 120° . Two of these isomers ($\tau \approx -120^\circ$ and $\tau \approx 120^\circ$) are symmetrically equivalent and they can occur in chemical reactions interchangeably. All the rotamers are nearly energy degenerate as they differ in energy by less than 1.0 kJ mol^{-1} . The barriers separating the individual rotamers are only 10.0 kJ mol^{-1} suggesting a very

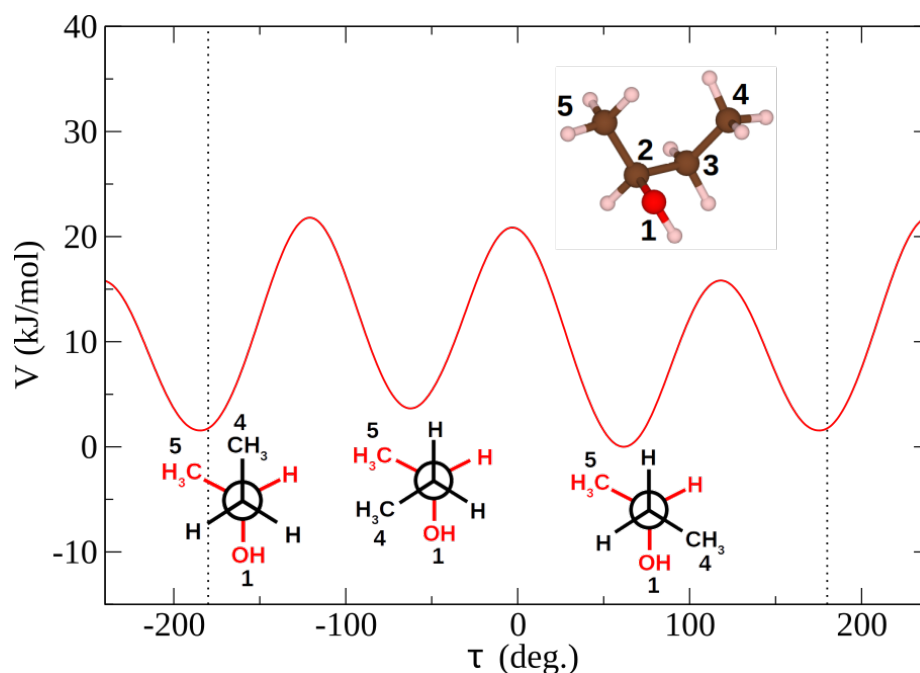


Figure S2: Potential energy profile of butan-2-ol along the torsional angle (τ) O1-C2-C3-C4. The dotted lines delimit the asymmetric part of the profile. The dotted lines delimit the asymmetric part of the profile. Diagrams depicting the three stable rotamers viewed in direction perpendicular to the rotational axis (C2-C3) are shown in the inset.

rapid interconversion between rotamers at the thermodynamic conditions considered in this work.

All three paths yielding but-1-ene (DH4, DHI2 and IA3-b) result in formation of rotamers $\tau \approx \pm 120^\circ$.

SIV.4. But-2-ene

Unlike the other molecules discussed in this section, but-2-ene forms two stable isomers (*cis* and *trans*) separated by a very high potential energy barrier of 353 kJ mol^{-1} (see Fig. S4), which is the reason why these isomers are treated as two separate products and the corresponding transformation paths (DH3-*trans* and DH3-*cis*) are labeled accordingly. The potential energy computed for

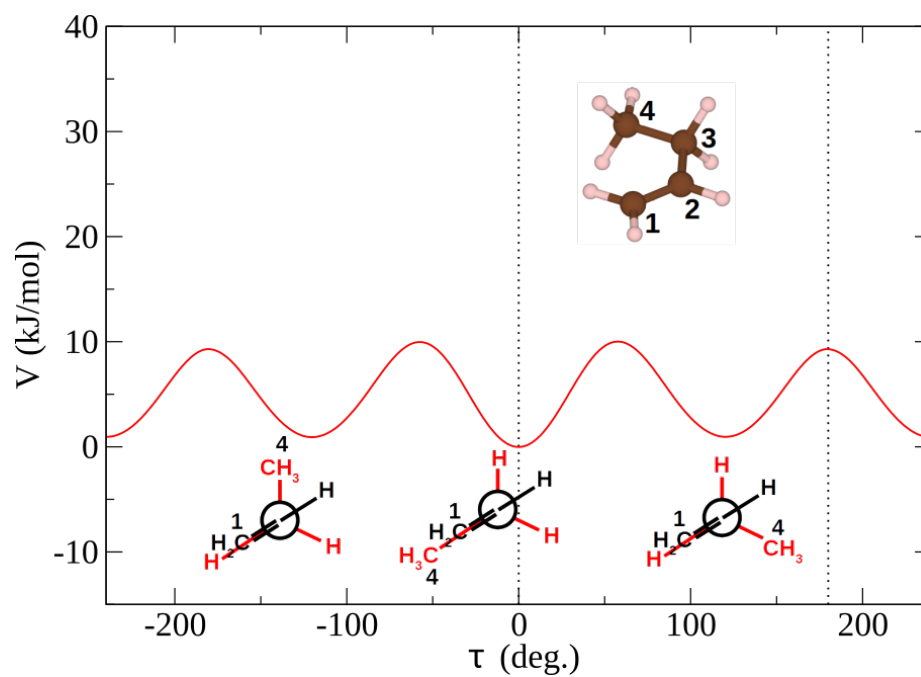


Figure S3: Potential energy profile of but-1-ene along the torsional angle (τ) C1-C2-C3-C4. The dotted lines delimit the asymmetric part of the profile. The dotted lines delimit the asymmetric part of the profile. Diagrams depicting the three stable rotamers viewed in direction perpendicular to the rotational axis (C2-C3) are shown in the inset.

the *trans* isomer is marginally (3 kJ mol^{-1}) lower than that for the isomer *cis*.

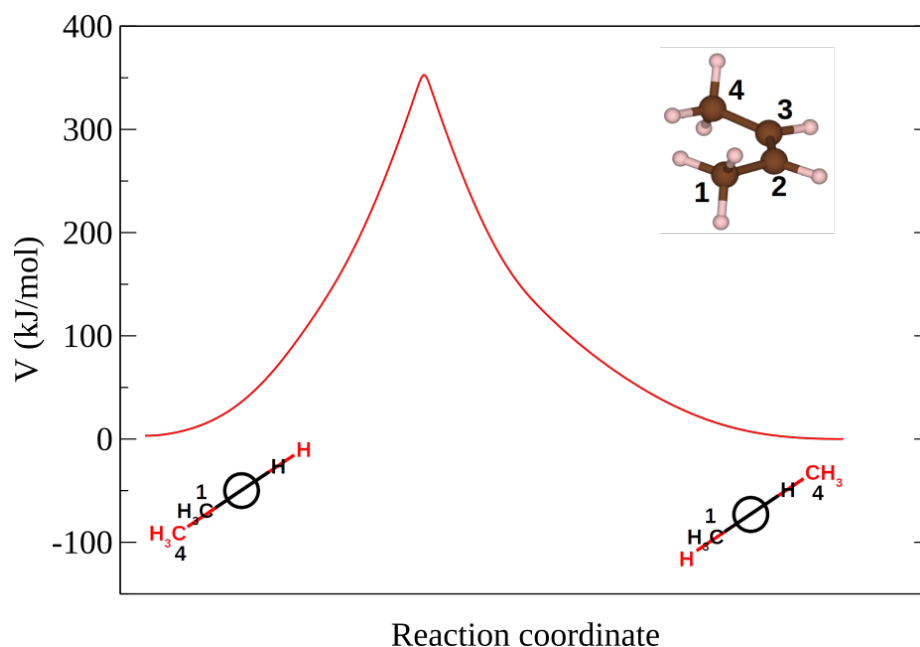
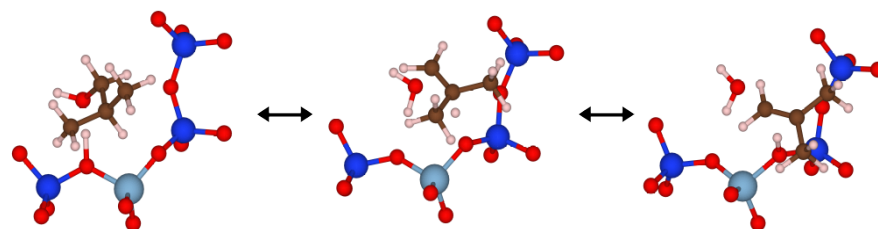


Figure S4: Potential energy profile of but-2-ene along the intrinsic reaction coordinate for the conversion between the isomers *cis* (inset left) and *trans* (inset right).

SV. Additional figures of reactant, transition state, and product molecular structures

In this section, we provide additional figures of reactant, transition state, and product molecular structures identified by IRC procedures for transformations catalyzed by bridging OH group and transformations involving alkoxide intermediates. The drawings of the structures presented here were created using the program VESTA [S2]. The color code used throughout this document to distinguish the type of atom is as follows: silicon in dark blue, aluminium in light blue, oxygen in red, hydrogen in white, and carbon in brown.

DH1

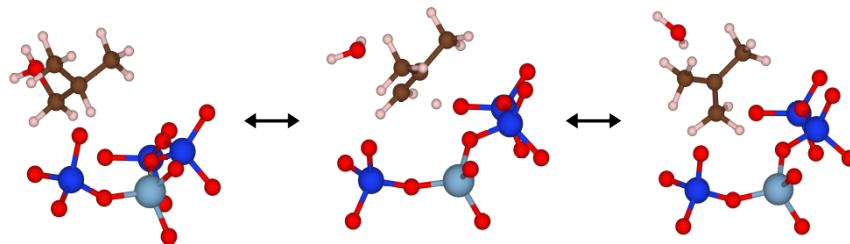


R

TS

P

DH1-anti-a

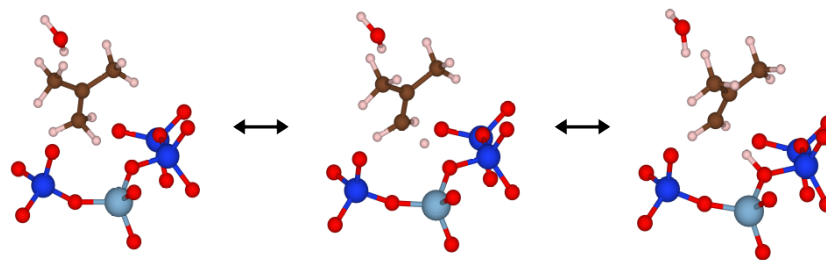


R

TS

P

DH1-anti-b



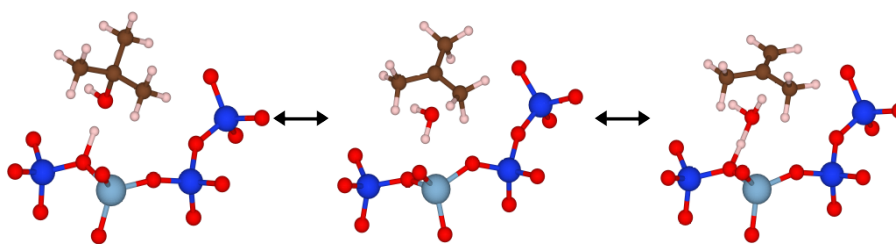
R

TS

P

Figure S5: Reactant, transition state and product molecular structures of conventional E2 elimination mechanism of isobutanol to isobutene (DH1) transformation, and two-step E1 elimination mechanism of isobutanol to isobutene via tert-butyl cation intermediate (path DH1-anti-a followed by path DH1-anti-b) catalyzed by bridging OH group in CHA.

DH2

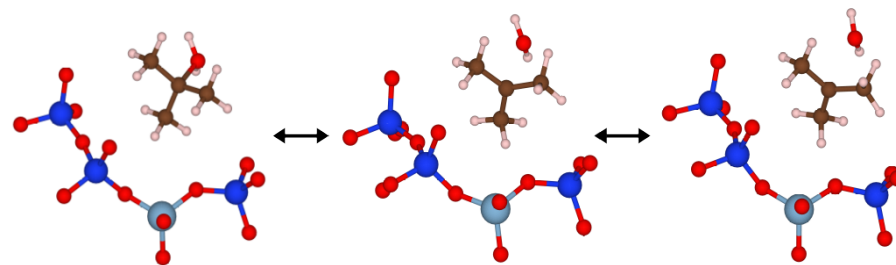


R

TS

P

DH2-anti-a

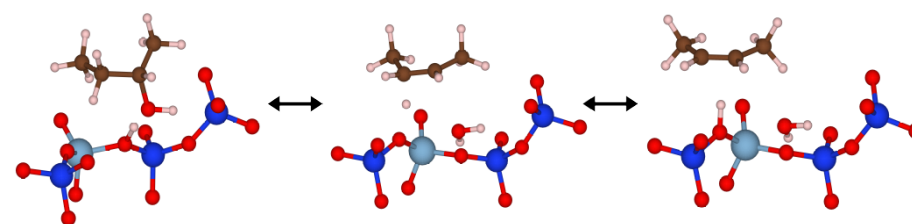


R

TS

P

DH3-cis



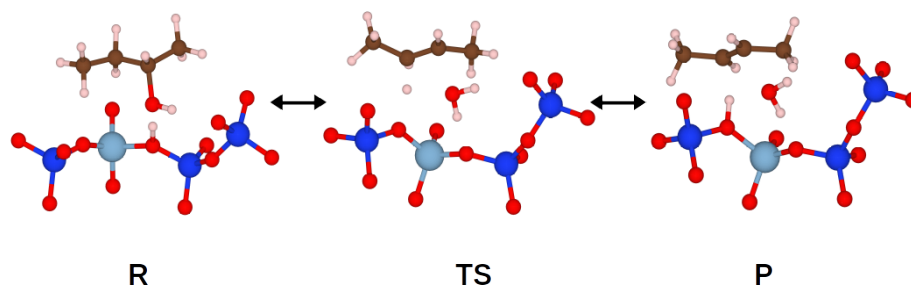
R

TS

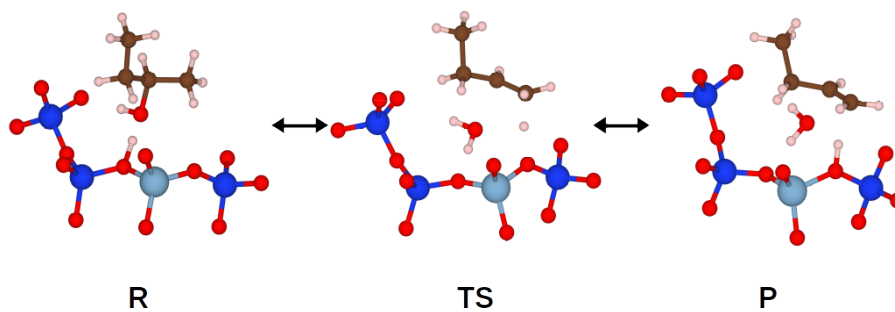
P

Figure S6: Reactant, transition state and product molecular structures of E2 elimination of tert-butanol to isobutene (DH2), E1 elimination of tert-butanol to tert-butyl (DH2-anti-a), and E2 elimination of butan-2-ol to *cis*-but-2-ene (DH3-cis) catalyzed by bridging OH group in CHA.

DH3-trans



DH4



DH5

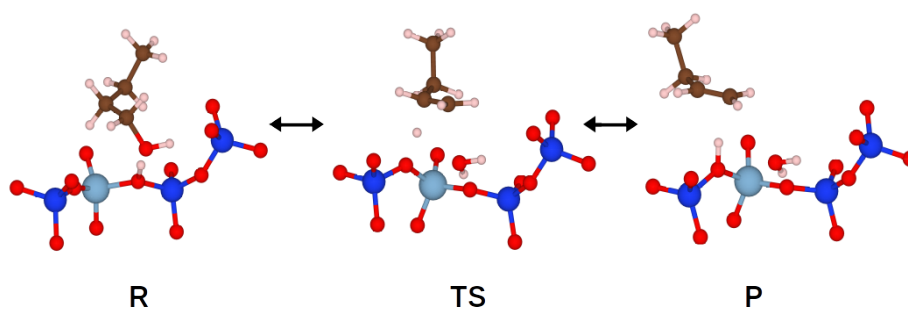


Figure S7: Reactant, transition state and product molecular structures of E2 elimination of butan-2-ol to *trans*-but-2-ene (DH3-trans), butan-2-ol to but-1-ene (DH4), and butan-1-ol to but-1-ene (DH5) catalyzed by bridging OH group in CHA.

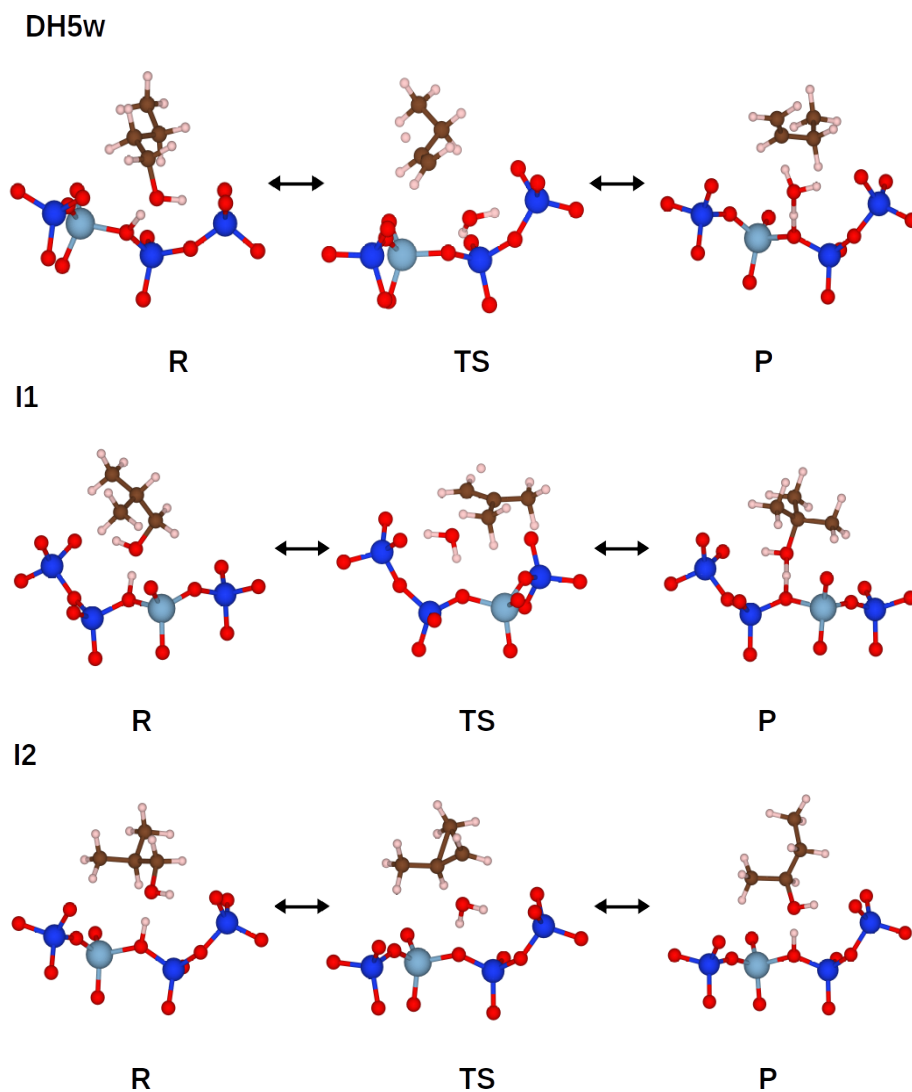


Figure S8: Reactant, transition state and product molecular structures of water mediated butan-1-ol to but-1-ene transformation (DH5w), and isomerizations of isobutanol to tert-butanol (I1) and isobutanol to butan-2-ol (I2) catalyzed by bridging OH group in CHA.

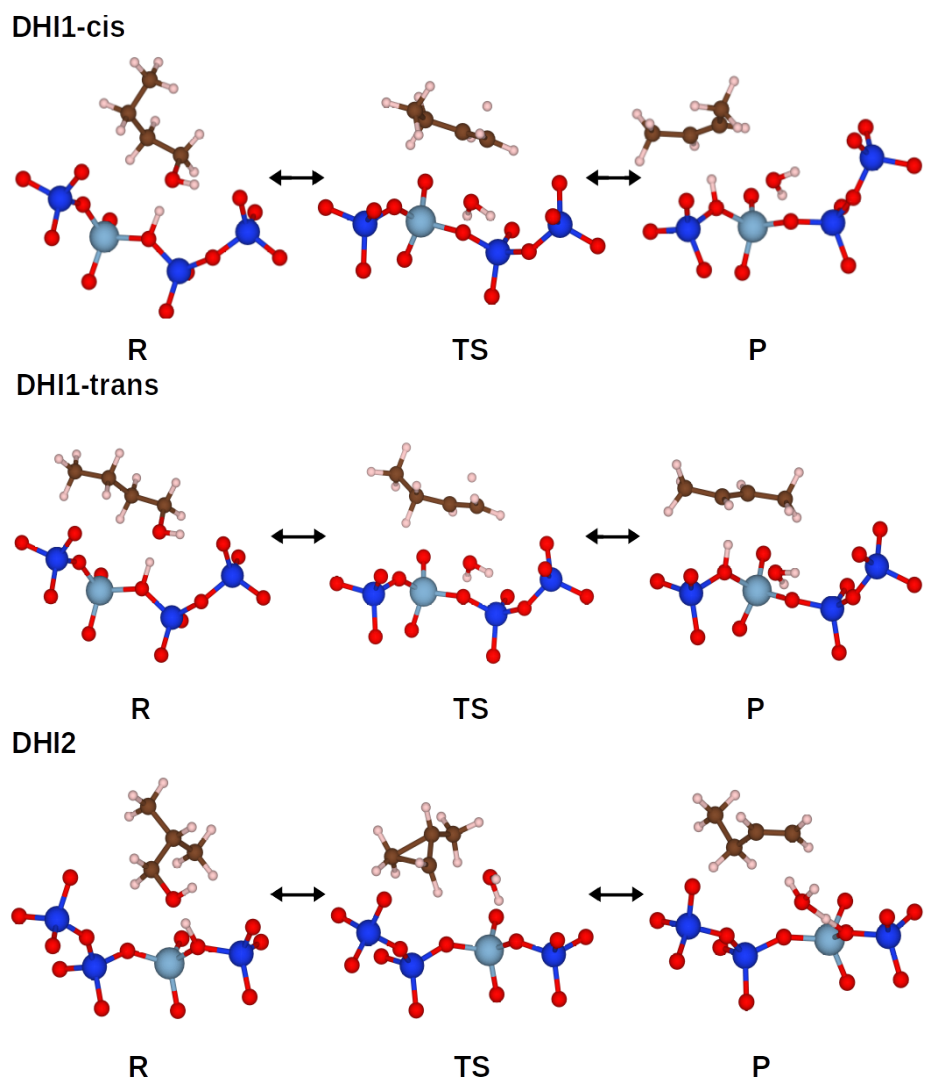


Figure S9: Reactant, transition state and product molecular structures of butan-1-ol to *cis*-but-2-ene (DHI1-cis), butan-1-ol to *trans*-but-2-ene (DHI1-trans), and isobutanol to but-1-ene (DHI2) transformations catalyzed by bridging OH group in CHA.

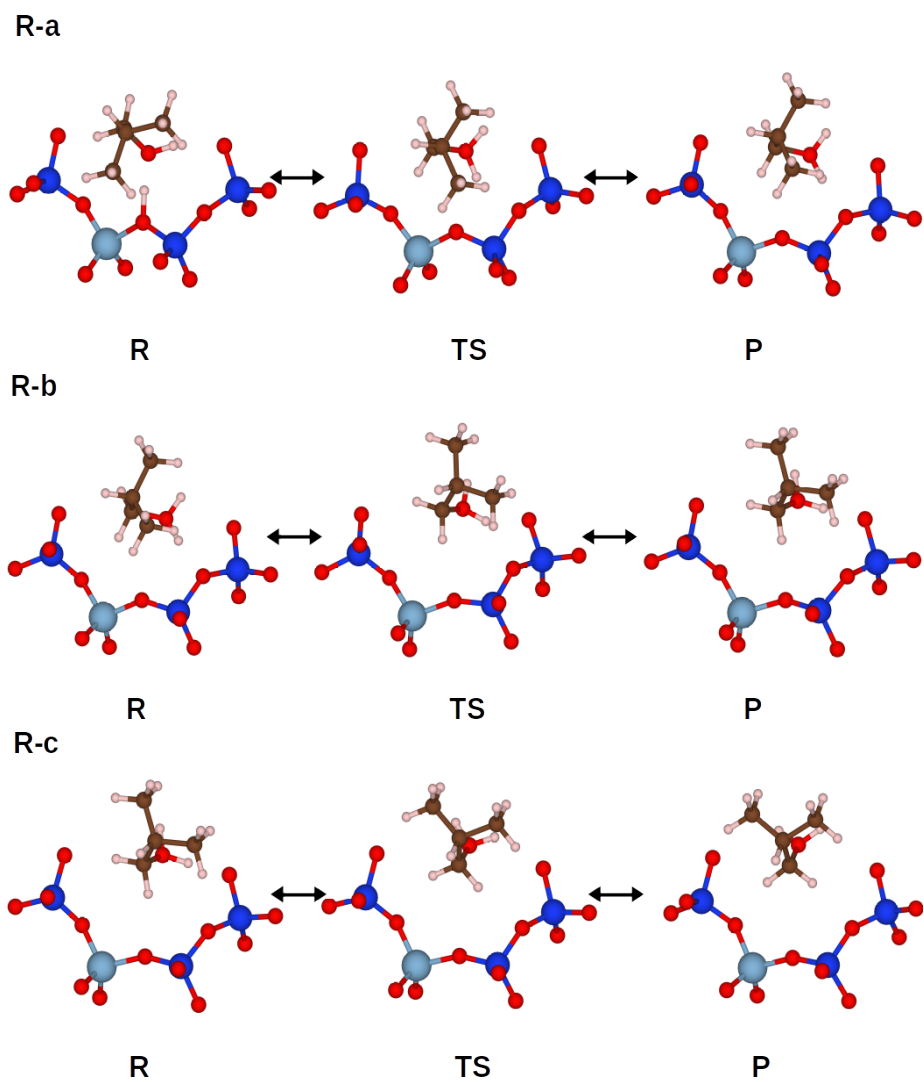
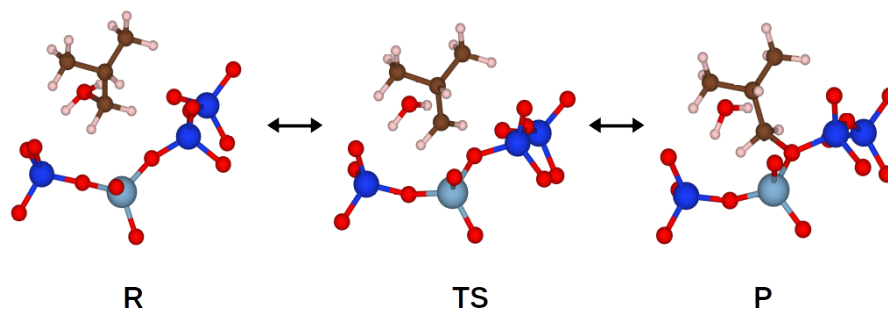
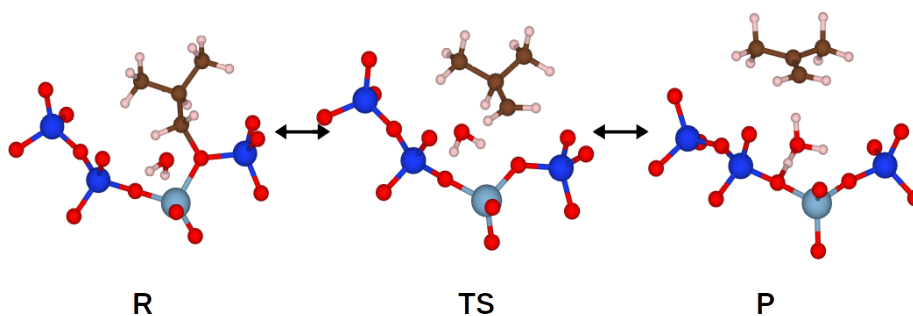


Figure S10: Reactant, transition state and product molecular structures of three step rotation of isobutanol from position of R state in DH1 to position of R state in DHA1-a catalyzed by bridging OH group in CHA.

DHA1-a



DHA1-b



IA2-a

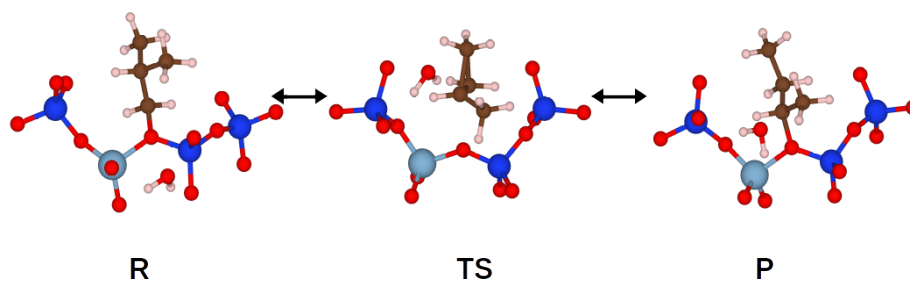
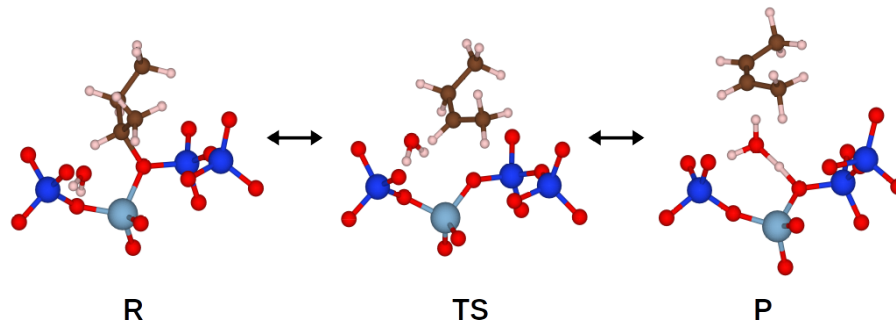
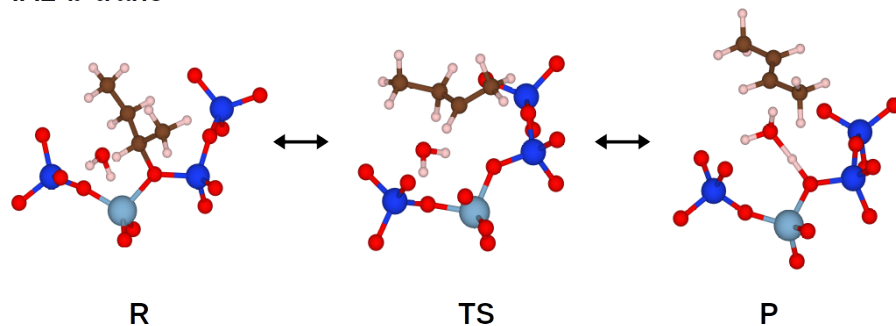


Figure S11: Reactant, transition state and product molecular structures of isobutanol to isobutoxide (DHA1-a), isobutoxide to isobutene (DHA1-b), and isobutoxide to secondary butoxide (IA2-a) transformations catalyzed by bridging OH group in CHA.

IA2-b-cis



IA2-b-trans



IA3-b

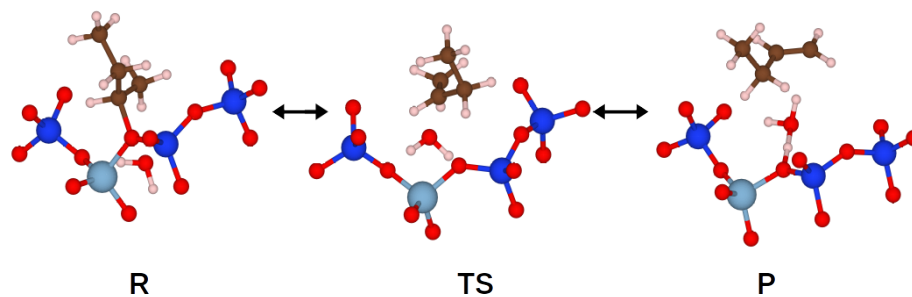


Figure S12: Reactant, transition state and product molecular structures of secondary butoxide to *cis*-but-2-ene (IA2-b-cis), to *trans*-but-2-ene (IA2-b-trans), and to but-1-ene (IA3-b) transformations catalyzed by bridging OH group in CHA.

DHA5

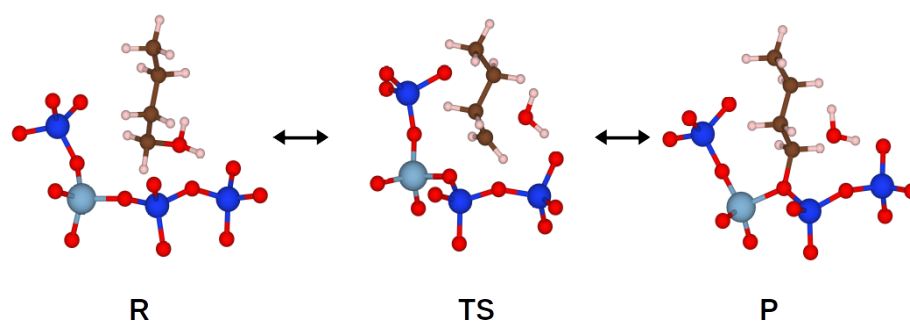


Figure S13: Reactant, transition state and product molecular structures of butan-1-ol to n-butoxide (DHA5) transformation catalyzed by bridging OH group in CHA.

SVI. IRC profiles

In this section, the potential energy profiles along the intrinsic reaction coordinates (IRC) are presented. For each path, the energies are referenced to the energy of the corresponding transition state.

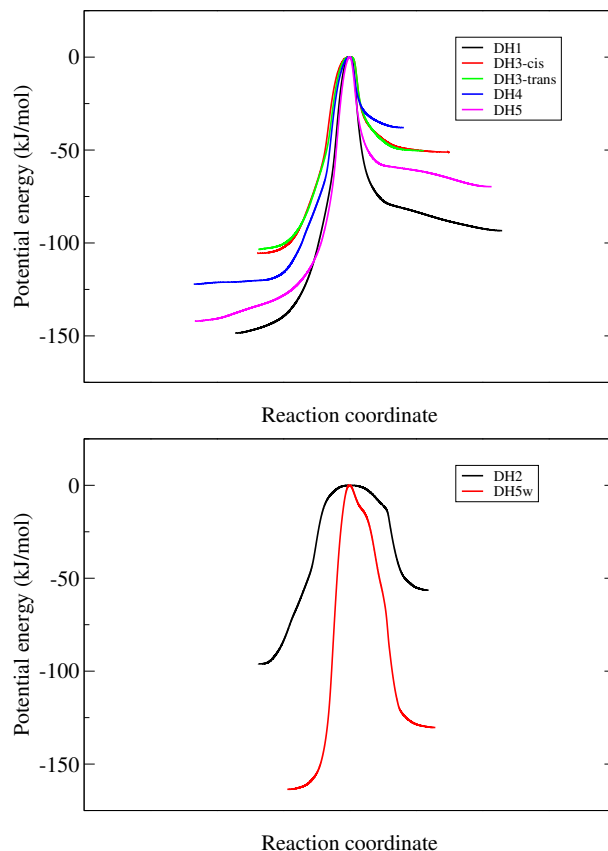


Figure S14: Potential energy profile along the intrinsic reaction coordinate for conventional dehydration reactions (top): isobutanol to isobutene (DH1), butan-2-ol to *cis*-but-2-ene (DH3-cis) and to *trans*-but-2-ene (DH3-trans), butan-2-ol to but-1-ene (DH4), and butan-1-ol to but-1-ene (DH5); and for unconventional dehydration reactions (bottom): tert-butanol to isobutene (DH2), and butan-1-ol to but-1-ene water mediated (DH5w) catalyzed by bridging OH group in CHA.

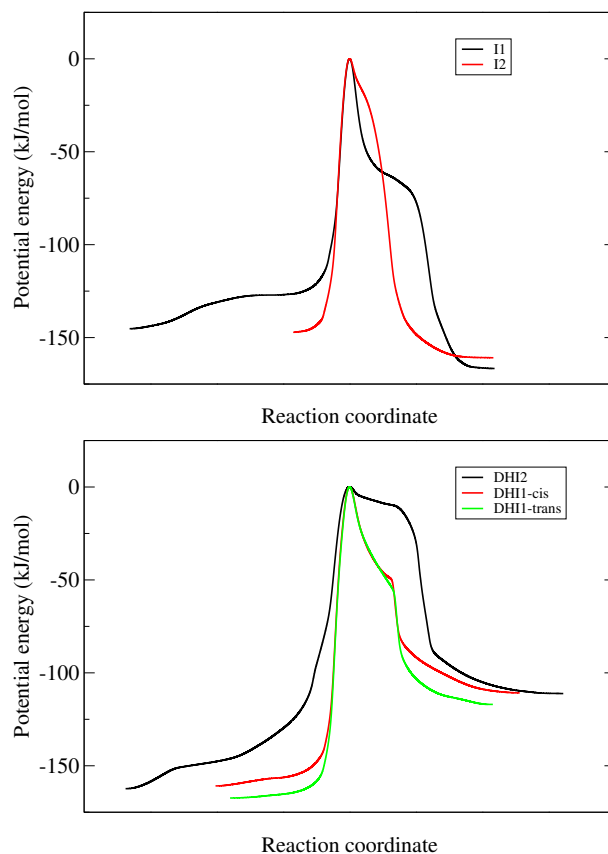


Figure S15: Potential energy profile along the intrinsic reaction coordinate for the alcohol isomerization reactions (top): isobutanol to tert-butanol (I1), and isobutanol to butan-2-ol (I2); and synchronous alcohol dehydration plus isomerization (bottom): butan-1-ol to *cis*-but-2-ene (DHI1-*cis*) and to *trans*-but-2-ene (DHI1-*trans*), and isobutanol to but-1-ene (DHI2) catalyzed by bridging OH group in CHA.

SVII. Effect of temperature on energy span

Here we analyze the temperature dependence of energy spans (ΔG_{ES}) for transformations of isobutanol to butene products. The spans have been determined for the temperature range between T_{min} and T_{max} with an increment of $\Delta T = 5$ K. The upper limit, T_{max} , has been set to 900 K while the lower limit, T_{min} has been chosen as a temperature for which the given reaction begins to

be exergonic (240 K, 350 K, 285 K, and 255 K for transformations to isobutene, but-1-ene, *cis*- and *trans*-but-2-ene, respectively).

The T -dependent energy spans for the transformations of isobutanol into isobutene are shown in Fig. S16. For the one-step reaction mechanism (path DH1) between 240 and 685 K, we identified the transition state of the path DH1 as TDTS and the adsorbed reactant as TDI. TDI changes at 690 K to the desorbed reactant state (isobutanol molecule in the gas phase and clean CHA). For the two-step reaction mechanism (path I1 followed by DH2, see Fig. 9 in the main text), the transition state of path I1 was identified as TDTS and the product of I1 (tert-butanol) as TDI below 420 K. At 420 K, TDI changes to the reactant of path I1 (isobutanol), and at 650 K, TDI changes to the desorbed reactant state. In a five-step transformation (paths R-a, R-b, R-c, DHA1-a, DHA1-b) of isobutanol to isobutene via an isobutoxide intermediate, a sudden change of increasing trend appears at 705 K, when TDI is changed from the reactant in path R-a (isobutanol) to the desorbed reactant state. The transition state of the path DHA1-b was identified as TDTS for the whole range of temperatures considered here. Thus, the most favorable transformation mechanisms emerging from the energy span concept are the one-step mechanism (for the temperature range between 240 and 330 K) and the two-step mechanism ($T > 300$ K), see Fig. 13 in the main text.

The T -dependent energy spans for the transformation of isobutanol into but-1-ene are shown in Fig. S17. In the low- T regime (350-725 K) of the one-step transformation (path DHI2), the transition state of DHI2 was identified as TDTS and the reactant state in DHI2 as TDI. At a temperature of 725 K, the TDI changes to the reference reactant state, which is, as in the case of transformation to isobutene, reflected in a steep increase of ΔG_{ES} with T . In the case of the two-step transformation (path I2 followed by DH4), the transition state of I2 was identified as TDTS and the product state of I2 as TDI (butan-2-ol) for temperatures between 350 and 525 K. From 530 K to 655 K, TDI changed to the reactant state from path I2 (isobutanol). At $T = 660$ K, the TDI eventually changed to the reference reactant state. The energy span for the six-step trans-

formation via alkoxy intermediates (paths R-a, R-b, R-c, DHA1-a, IA2-a, IA3-b) at temperatures up to 700 K is given by the free energy difference between the TS of DHA1-a and reactant from path R-a (isobutanol). At 705 K, TDI changed to the desorbed reactant state. The span for the sequence involving alkene isomerization (DH1, -DH1-b, IA2-a, IA3-b) is given by TDTS corresponding to TS of -DHA1-b and TDI corresponding to reactant from path DH1 (isobutanol) for temperatures of 350-645 K. From 650 K to 695 K, TDI is reactant from path -DHA1-b (isobutene) and then at $T > 700$ K TDI is the desorbed reactant state. Altogether, the preferred mechanisms for but-1-ene formation for low (350-405 K) and high (> 405 K) temperatures are the six-step transformation mechanism and the two-step mechanism, respectively.

The T -dependent energy spans for transformations of isobutanol into *cis*- and *trans*-but-2-ene are shown in Fig. S18 and S19, respectively. In both cases, three sequences of reactions are discussed. The transition state of I2 is, regardless of temperature, identified as TDTS of the two-step transformations leading to *cis*-but-2-ene (path I2 followed by path DH3-*cis*) and to *trans*-but-2-ene (path I2 followed by path DH3-*trans*). The product of path I2 (butan-2-ol) is identified as TDI for the transformation to *cis*-but-2-ene within the temperature range of 285-445 K, and for the transformation to *trans*-but-2-ene within the range of 255-410 K. In both cases, the TDI then changes to the reactant state of I2 (isobutanol) and, when T reaches 660 K, to the desorbed reactant state. The six-step transformation leading to *cis*-but-2-ene (paths R-a, R-b, R-c, DHA1-a, IA2-a, IA2-b-*cis*) initially involves the transition state of the path IA2-a as TDTS and the product state of the path IA2-b-*cis* (*cis*-but-2-ene) as TDI. At a temperature of 305 K, the TDTS changes to the transition state of DHA1-a, and at 345 K TDI changes to the reactant state of the path R-a. At 705 K, the TDI changes to the desorbed reactant state. Similarly, the six-step transformation leading to *trans*-but-2-ene (paths R-a, R-b, R-c, DHA1-a, IA2-a, IA2-b-*trans*) involves the transition state of the path IA2-a as TDTS and the product state of the path IA2-b-*trans* (*trans*-but-2-ene) as TDI in the low- T regime. At 290 K, TDI is changed to the reactant state of the R-a path. Up to the temperature of 305 K, the ΔG_{ES}

versus T dependence has a decreasing trend, but it increases at higher temperatures due to the change of TDTS to the transition state of the DHA1-a path. As in the case of but-1-ene formation, the formation of products via a sequence involving alkene isomerization (DH1, -DH1-b, IA2-a, IA3-b) proceeds via TDTS corresponding to the TS of -DHA1-b. At temperatures 255-260 K, the TDI for *trans*-but-2-ene formation was identified as product of IA2-b-*trans* path, and TDI for formation of *cis*-but-2-ene at 285-320 K was found to be the product of path IA2-b-*cis*. Then, as in the case of but-1-ene formation, for the rest of the low- T regime (<650 K) TDI was identified as reactant of path DH1, which then changed at 650 K to reactant of -DHA1-b path, and at high- T to the desorbed reactant. The six-step mechanism of transformation of isobutanol to but-2-enes via alkoxide intermediates is preferred for lower temperatures, in the range of 285-350 K (*cis*) and 255-330 K (*trans*). Above these T ranges, the preferred mechanisms corresponds to the two-step transformations.

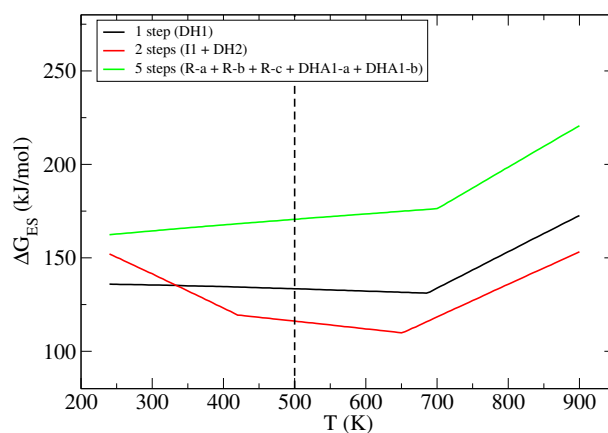


Figure S16: Effect of temperature on the values of energy span (ΔG_{ES}) determined for transformation of isobutanol to isobutene via a one step mechanism (path DH1), via tert-butanol intermediate (path I1 and DH2), and via isobutoxide intermediate (paths R-a, R-b, R-c, DHA1-a, DHA1-b). The corresponding free energy profiles for the temperature of 500 K (indicated by a vertical dashed line) are shown in Fig. 9.

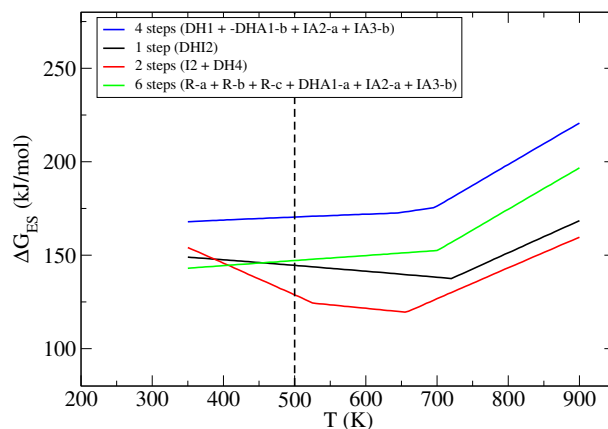


Figure S17: Effect of temperature on the values of energy span (ΔG_{ES}) determined for transformation of isobutanol to but-1-ene via isobutene isomerization (paths DH1, -DHA1-b, IA2-a, IA3-b), via one step mechanism (path DH12), via butan-2-ol intermediate (path I2 and DH4), and via secondary butoxide intermediate (paths R-a, R-b, R-c, DHA1-a, IA2-a, IA3-b). The corresponding free energy profiles for the temperature of 500 K (indicated by a vertical dashed line) are shown in Fig. 10.

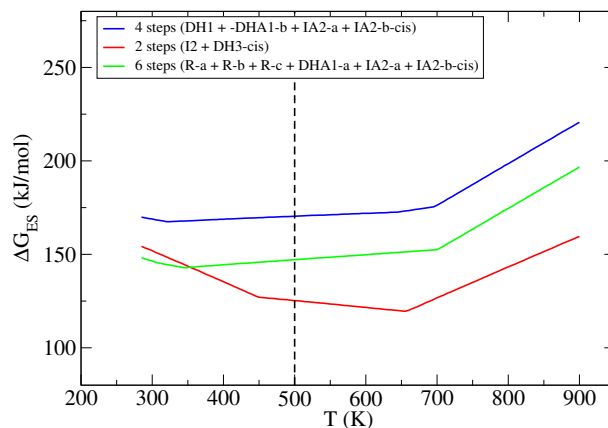


Figure S18: Effect of temperature on the values of energy span (ΔG_{ES}) determined for transformation of isobutanol to *cis*-but-2-ene via isobutene isomerization (paths DH1, -DHA1-b, IA2-a, IA2-b-cis), via butan-2-ol intermediate (path I2 and DH3-cis), and via secondary butoxide intermediate (paths R-a, R-b, R-c, DHA1-a, IA2-a, IA2-b-cis). The corresponding free energy profiles for the temperature of 500 K (indicated by a vertical dashed line) are shown in Fig. 11.

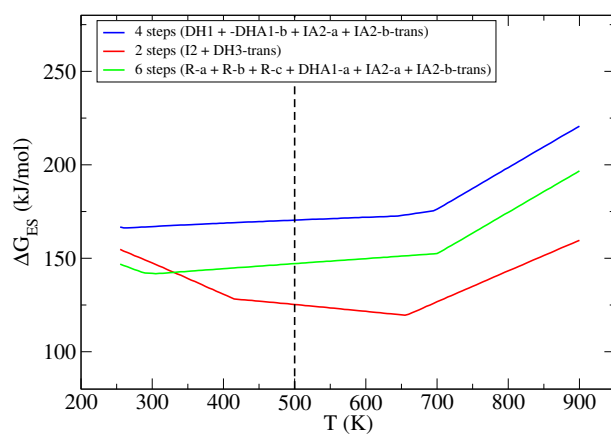


Figure S19: Effect of temperature on the values of energy span (ΔG_{ES}) determined for transformation of isobutanol to *trans*-but-2-ene via isobutene isomerization (paths DH1, -DHA1-b, IA2-a, IA2-b-trans), via butan-2-ol intermediate (path I2 and DH3-trans), and via secondary butoxide intermediate (paths R-a, R-b, R-c, DHA1-a, IA2-a, IA2-b-trans). The corresponding free energy profiles for the temperature of 500 K (indicated by a vertical dashed line) are shown in Fig. 12.

SVIII. Additional tables

In this section, additional tables are presented. Table S1 shows the free energies, enthalpies, entropies, and electronic contributions to the free energies of all relaxed reactants, transition states, and products that were obtained by IRC analysis, relative to the state with isobutanol in the gas phase and clean CHA. The quantities of activation and reaction for transformation paths involving alkoxide intermediates are compiled in Table S2 and S3, respectively. Finally, Table S4 contains thermodynamic data for reactant and product states desorbed from the catalyst, and Table S5 provides comparison of experimental and theoretical differences in formation enthalpies, Gibbs free energies and entropies for gas phase molecular systems.

Table S1: Free energies (ΔG), enthalpies (ΔH), entropies (ΔS), and electronic contributions to free energies (ΔG_{el}) of all relaxed reactant (R), transition state (TS) and product (P) structures at 500 K. All values are referenced to the state with isobutanol in the gas phase and clean CHA. Bold font is used to distinguish the alcohol to alkene from other transformations.

Path	State	ΔG (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	ΔG_{el} (kJ mol ⁻¹)
DH1	R	-39.5	-146.5	-214	-147.0
	TS	94.0	-7.0	-202	1.5
	P	-14.0	-91.0	-155	-92.0
DH1-anti-a	R	55.0	-41.0	-193	-46.5
	TS	99.0	-4.0	-206	3.5
	P	3.0	-68.0	-142	-65.5
DH1-anti-b	R	2.5	-68.0	-141	-65.5
	TS	-4.0	-73.5	-139	-61.5
	P	-4.5	-76.5	-145	-78.5
DH2	R	-60.5	-170.0	-219	-167.5
	TS	8.5	-79.5	-177	-71.5
	P	-60.0	-133.0	-146	-128.0
DH2-anti-a	R	7.5	-87.0	-190	-90.5

	TS	7.0	-72.0	-158	-66.0
	P	1.5	-69.5	-142	-67.0
DH3-cis	R	-29.0	-136.5	-216	-138.0
	TS	53.0	-42.0	-189	-32.5
	P	-9.5	-81.5	-145	-83.5
DH3-trans	R	-27.0	-137.5	-222	-139.5
	TS	46.5	-44.5	-183	-36.0
	P	-12.5	-85.0	-145	-86.0
DH4	R	-46.5	-153.5	-215	-153.5
	TS	52.0	-41.5	-187	-31.5
	P	1.5	-67.5	-138	-69.5
DH5	R	-26.5	-138.0	-224	-140.0
	TS	91.0	-8.5	-199	2.0
	P	4.5	-65.0	-139	-67.5
DH5w	R	-34.0	-143.5	-220	-145.0
	TS	100.0	12.0	-177	18.5
	P	-38.5	-115.0	-153	-112.0
I1	R	-33.5	-144.5	-223	-146.0
	TS	82.5	-8.0	-182	-1.0
	P	-61.5	-170.0	-217	-167.5
I2	R	-32.5	-136.5	-209	-139.5
	TS	93.0	6.5	-172	8.0
	P	-59.5	-153.0	-187	-153.0
DHI1-cis	R	-32.5	-130.5	-196	-132.5
	TS	91.0	20.5	-141	28.0
	P	-5.5	-81.0	-151	-82.5
DHI1-trans	R	-25.5	-133.5	-217	-135.5
	TS	107.5	24.5	-167	32.0
	P	-10.0	-83.5	-147	-85.0
DHI2	R	-46.0	-151.5	-211	-152.0

	TS	98.5	8.5	-180	10.0
	P	-31.5	-103.0	-144	-101.0
R-a	R	-40.0	-140.0	-201	-141.5
	TS	27.0	-84.5	-224	-86.0
	P	19.5	-87.5	-214	-92.5
R-b	R	21.5	-87.5	-218	-92.5
	TS	33.0	-67.5	-201	-71.0
	P	29.0	-82.5	-223	-88.5
R-c	R	25.5	-83.5	-217	-89.0
	TS	43.5	-64.0	-215	-67.5
	P	44.5	-69.5	-228	-76.0
DHA1-a	R	44.5	-64.5	-219	-71.5
	TS	107.5	-6.0	-227	-9.0
	P	70.5	-37.5	-217	-47.5
DHA1-b	R	50.0	-52.0	-204	-60.5
	TS	131.0	16.0	-230	21.0
	P	-33.5	-121.0	-175	-115.0
IA2-a	R	28.5	-81.0	-218	-89.5
	TS	96.0	12.5	-167	13.5
	P	32.5	-64.5	-194	-74.0
IA2-b-cis	R	52.5	-38.5	-182	-47.0
	TS	81.0	-15.0	-191	-7.0
	P	-58.5	-129.0	-141	-124.5
IA2-b-trans	R	31.5	-64.5	-192	-73.5
	TS	94.5	-5.0	-199	1.0
	P	-54.5	-131.5	-155	-128.5
IA3-b	R	22.0	-69.5	-184	-78.5
	TS	69.5	-24.5	-188	-19.0
	P	-39.5	-119.5	-160	-115.5
DHA5	R	45.5	-72.0	-235	-79.5

	TS	124.5	23.0	-203	16.0
	P	19.5	-72.0	-183	-81.0

Table S2: Free energies of activation (ΔG^\ddagger), enthalpies of activation (ΔH^\ddagger), entropies of activation (ΔS^\ddagger), and electronic contributions to free energies of activation (ΔG_{el}^\ddagger) for reactions proceeding via the alkoxy paths, and for rotation of isobutanol (paths R-a, R-b, R-c) which precedes the step DHA1-a. Temperature of 500 K has been considered in simulations.

Transformation Path	ΔG^\ddagger (kJ mol ⁻¹)	ΔH^\ddagger (kJ mol ⁻¹)	ΔS^\ddagger (J mol ⁻¹ K ⁻¹)	ΔG_{el}^\ddagger (kJ mol ⁻¹)
R-a	67.0	55.5	-23	55.5
R-b	11.5	20.0	17	21.5
R-c	18.0	19.5	3	21.5
DHA1-a	63.0	58.5	-9	62.0
DHA1-b	81.0	68.0	-26	82.0
IA2-a	67.5	93.0	51	103.0
IA2-b-cis	28.5	23.5	-10	40.0
IA2-b-trans	63.5	59.5	-7	74.5
IA3-b	47.0	45.0	-4	59.5
DHA5	79.5	95.0	31	95.5

Table S3: Free energies of reaction ($\Delta G_{R \rightarrow P}$), enthalpies of reaction ($\Delta H_{R \rightarrow P}$), entropies of reaction ($\Delta S_{R \rightarrow P}$), and electronic contributions to the free energies of reaction ($\Delta G_{el,R \rightarrow P}$) for reactions that proceed through alkoxy paths, and for rotation of isobutanol (paths R-a, R-b, R-c) that precedes the DHA1-a path. Temperature of 500 K has been considered in simulations.

Transformation Path	$\Delta G_{R \rightarrow P}$ (kJ mol ⁻¹)	$\Delta H_{R \rightarrow P}$ (kJ mol ⁻¹)	$\Delta S_{R \rightarrow P}$ (J mol ⁻¹ K ⁻¹)	$\Delta G_{el,R \rightarrow P}$ (kJ mol ⁻¹)
R-a	59.0	52.5	-14	49.0
R-b	7.5	5.0	-5	4.0
R-c	19.0	13.5	-11	13.0
DHA1-a	26.0	27.0	2	24.0
DHA1-b	-83.5	-69.0	29	-54.5
IA2-a	4.5	16.5	24	16.0
IA2-b-cis	-111.0	-90.5	41	-77.5
IA2-b-trans	-85.5	-67.0	37	-54.5
IA3-b	-61.5	-50.0	23	-37.0
DHA5	-26.0	0.0	52	-1.5

Table S4: Free energies (ΔG), enthalpies (ΔH), entropies (ΔS), and electronic contributions to free energies (ΔG_{el}) of all relaxed reactant and product states involving non-interacting gas phase alkene molecules and a clean catalyst (CHA). All values are referenced to the initial reactant state (isobutanol in gas phase and clean CHA). Temperature of 500 K has been considered.

Desorption complex	ΔG (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	ΔG_{el} (kJ mol ⁻¹)
isobutanol + CHA	0.0	0.0	0	0.0
isobutene + H ₂ O + CHA	-39.5	36.0	150	47.5
<i>cis</i> -but-2-ene + H ₂ O + CHA	-34.0	44.0	156	54.5
<i>trans</i> -but-2-ene + H ₂ O + CHA	-39.0	40.0	158	51.5
<i>cis</i> -but-1-ene + H ₂ O + CHA	-22.0	53.5	151	64.0
<i>trans</i> -but-1-ene + H ₂ O + CHA	-23.5	54.5	156	65.0

Table S5: Comparison of experimental [S3, S4] (Exp.) and theoretical (DFT) differences in standard formation enthalpies ($\Delta_f H^\circ$), Gibbs free energies ($\Delta_f G^\circ$) and entropies ($\Delta_f S^\circ$) for the gas phase molecular systems appearing as reactants, reaction intermediates, or products in transformations of alcohols to alkenes. All values are referenced to the quantities of formation of isobutanol. The standard state corresponds to $T=298.15$ K and $p=100000$ Pa.

System	$\Delta_f H^\circ$ (kJ mol ⁻¹)		$\Delta_f G^\circ$ (kJ mol ⁻¹)		$\Delta_f S^\circ$ (J mol ⁻¹ K ⁻¹)	
	Exp.	DFT	Exp.	DFT	Exp.	DFT
isobutan-1-ol ^a	0.0	0.0	0.0	0.0	0.0	0.0
isobutan-2-ol ^a	-27.0	-25.5	-20.0	-23.5	-22	-7
butan-2-ol ^a	-7.0	-9.0	-10.0	-8.5	11	-1
butan-1-ol ^a	10.5	8.0	6.5	7.5	15	1
isobutene+H ₂ O ^b	25.5	34.5	-15.0	-9.0	136	148
but-1-ene+H ₂ O ^b	43.5	54.0	0.0	7.5	145	155
<i>trans</i> -but-2-ene +H ₂ O ^b	32.0	39.5	-9.0	-7.0	137	156
<i>cis</i> -but-2-ene +H ₂ O ^b	37.0	43.0	-5.5	-2.5	142	154

^a Experimental data from Ref. [S5]

^b Experimental data from Ref. [S6, S7]

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