



The mechanisms of isobutene hydration yielding *tert*-butanol catalyzed by a strong mineral acid (H₂SO₄) and Lewis-Brønsted superacid (HF/SbF₅)



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ABSTRACT

The mechanism of the (CH₃)₂CCH₂+H₂O→(CH₃)₃COH reaction catalyzed by two strong acids (H₂SO₄ and HSBF₆) was investigated theoretically using the ab initio MP2 and CCSD(T) methods and the aug-cc-pVDZ/LANL2DZ and aug-cc-pVTZ/LANL2DZ basis sets. The effects of surrounding solvent molecules were approximated by employing the polarized continuum solvation model. The most important findings include the observation that both acids are capable of catalyzing isobutene hydration but the reaction is predicted to proceed faster when the HSBF₆ superacid plays the catalyst role.

1. Introduction

Due to their wide range of applications, alcohols continue to arouse great interest in scientific community. Along with ethanol (commonly obtained in fermentation process) and methanol (synthesized primarily from synthesis gas), *tert*-butanol remains among the most popular alcohols used both in industry and laboratory. (CH₃)₃COH is utilized either directly as gasoline additive (where it acts as oxygenate, i.e., the substance facilitating complete combustion) or as a starting compound in synthesis of other oxygenates (such as methyl *tert*-butyl ether or ethyl *tert*-butyl ether) [1]. Apart from being used as a solvent [2], *tert*-butanol is also utilized to prepare potassium *tert*-butoxide which is a strong non-nucleophilic base used in Williamson ether synthesis [3] and has to be prepared *in situ* due to its high reactivity.

The hydration of alkenes is a prominent method for preparation of secondary and tertiary alcohols. Addition of water to alkenes can potentially lead to two products, one Markovnikov and one anti-Markovnikov. Primary laboratory method in which the main product is consistent with the Markovnikov's rule is the oxymercuration-reduction reaction (highly toxic mercury (II) acetate is used as a catalyst in this process) [4]. The most common laboratory way to obtain anti-Markovnikov product of alkene hydration is performing the Brown hydroboration [5]. This reaction, however, requires the use of extremely flammable and explosive borane as a catalyst. Alternative method of obtaining alcohols via hydration that is widely utilized in the industry (as it involves relatively safe catalyst) is the hydration of alkenes catalyzed by the acidic systems [6]. At present, H₃PO₄/SiO₂ catalysts are used in

this type of synthesis, however, major disadvantages of such processes include the relatively low alkene-to-alcohol conversion and the requirement of high purity of the alkene substrates [7]. Therefore, the use of sulfuric acid as a catalyst in alkene hydration reactions may still be considered reasonable. In 1965, Schubert and Lamm studied the mechanism of acid-catalyzed hydration of styrene and showed that the protonation of alkene is the rate determining step of this reaction [8]. This finding suggested that utilizing strong acids as catalyst should render the hydration of alkenes more efficient. Indeed, several experiments conducted in the last few decades confirmed this assumption [9, 10].

The addition of water to isobutene leading to *tert*-butanol has been the subject of many considerations. In 1934, Lucas and Eberz found that the reaction rate of isobutene hydration performed at constant ionic strength depends linearly on the concentration of isobutene and the concentration of nitric acid [11]. Two decades later, Taft Jr demonstrated that the rate of isobutene hydration catalyzed by a mineral acid (HNO₃ or H₂SO₄) is proportional to the Hammett acidity function (*H*₀) of the catalyst employed [12] (Deckwer et al. arrived at similar conclusions while evaluating the rate constants of hydration of isobutene catalyzed by sulfuric acid) [13]. The Bielański group used H₄SiW₁₂O₄₀ (dodecatungstosilicic acid) as a catalyst in the conversion of isobutene to *tert*-butanol performed in the gas phase [14], whereas Nakagawa, Tajima, and Hirao calculated heights of the energy barriers (spanning the 25–28 kcal/mol range) for the hydration of ethene catalyzed by H₃PO₄, H₂SO₄, and HClO₄ acids [15].

As vaguely indicated above and demonstrated in many earlier reports, strong acids (and superacids in particular) can act as catalysts in many

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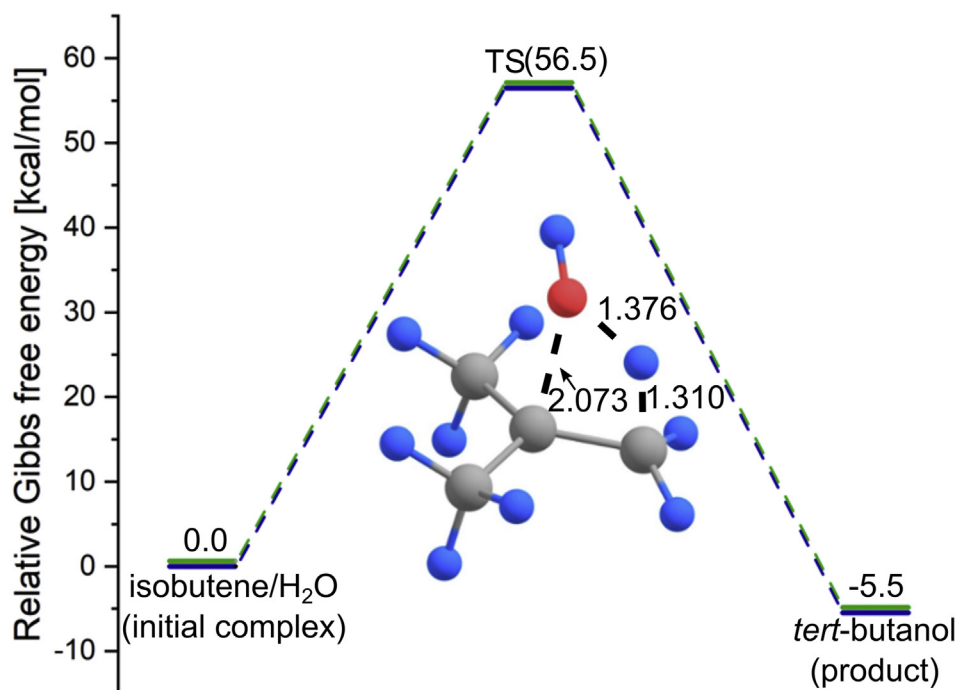


Fig. 1. The Gibbs free energy profile of the uncatalyzed $(\text{CH}_3)_2\text{CCH}_2 + \text{H}_2\text{O} \rightarrow (\text{CH}_3)_3\text{COH}$ reaction in the liquid phase and the structure of the corresponding transition state. The relative Gibbs free energies of the stationary points obtained for the H_2O solvent (green) and HF solvent (brown) differ by less than 0.05 kcal/mol whereas the geometrical parameters of the corresponding transition states (TS) differ by less than 0.001 Å (for bond lengths) and 0.01° (for angles). Relative Gibbs free energies (obtained at $T = 298.15\text{K}$) are given in kcal/mol, selected bond lengths in Å.

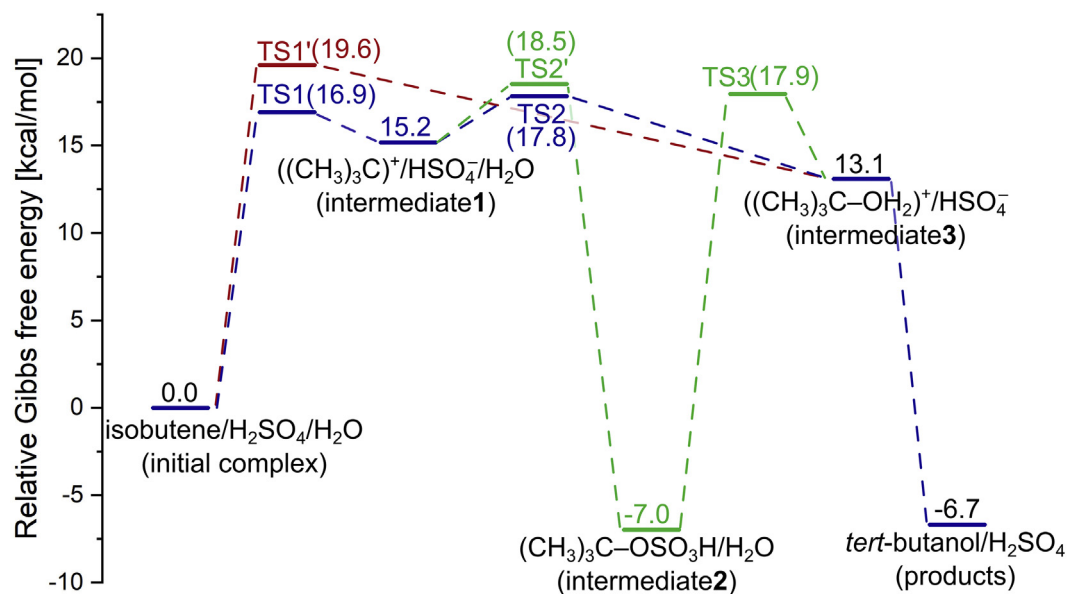


Fig. 2. The Gibbs free energy profile of the isobutene hydration catalyzed by H_2SO_4 . The relative Gibbs free energies (at $T = 298.15$) of the stationary points are obtained for the H_2O solvent. Relative Gibbs free energies are given in kcal/mol.

chemical reactions [16, 17, 18, 19]. Recently, our research group contributed to these studies by providing the mechanism of acid-catalyzed carbon monoxide hydrogenation yielding formaldehyde [20, 21] and predicting the ethanol-based $(\text{C}_2\text{H}_5\text{OH}_2)^+(\text{SbF}_6)^-$ salt formation resulting from acetaldehyde hydrogenation in the presence of HSbF_6 superacid [22]. In this contribution, we present our results and conclusions concerning the mechanism of isobutene hydration catalyzed either by a representative strong mineral acid (H_2SO_4) or by the fluoroantimonic superacid.

2. Methods

The structures of isobutene interacting with water molecule in the

presence of either H_2SO_4 or HSbF_6 catalyst were obtained by applying the second-order Møller-Plesset (MP2) perturbational method [23, 24, 25] with the aug-cc-pVDZ basis sets (for C, O, F, S, and H) [26] and with the Los Alamos National Laboratory (LANL) effective core potentials (ECP) with the appropriate valence basis set of double zeta quality (denoted LANL2DZ) for Sb [27, 28, 29]. The harmonic vibrational frequencies characterizing the stationary points were evaluated at the same theory level to assure that all the obtained structures correspond to true minima or first order saddle points on the potential energy surface. The intrinsic reaction coordinate (IRC) procedure [30, 31, 32, 33] (during which the reaction path is followed in both directions away from the transition state) was employed to confirm the corresponding minima for each transition structure.

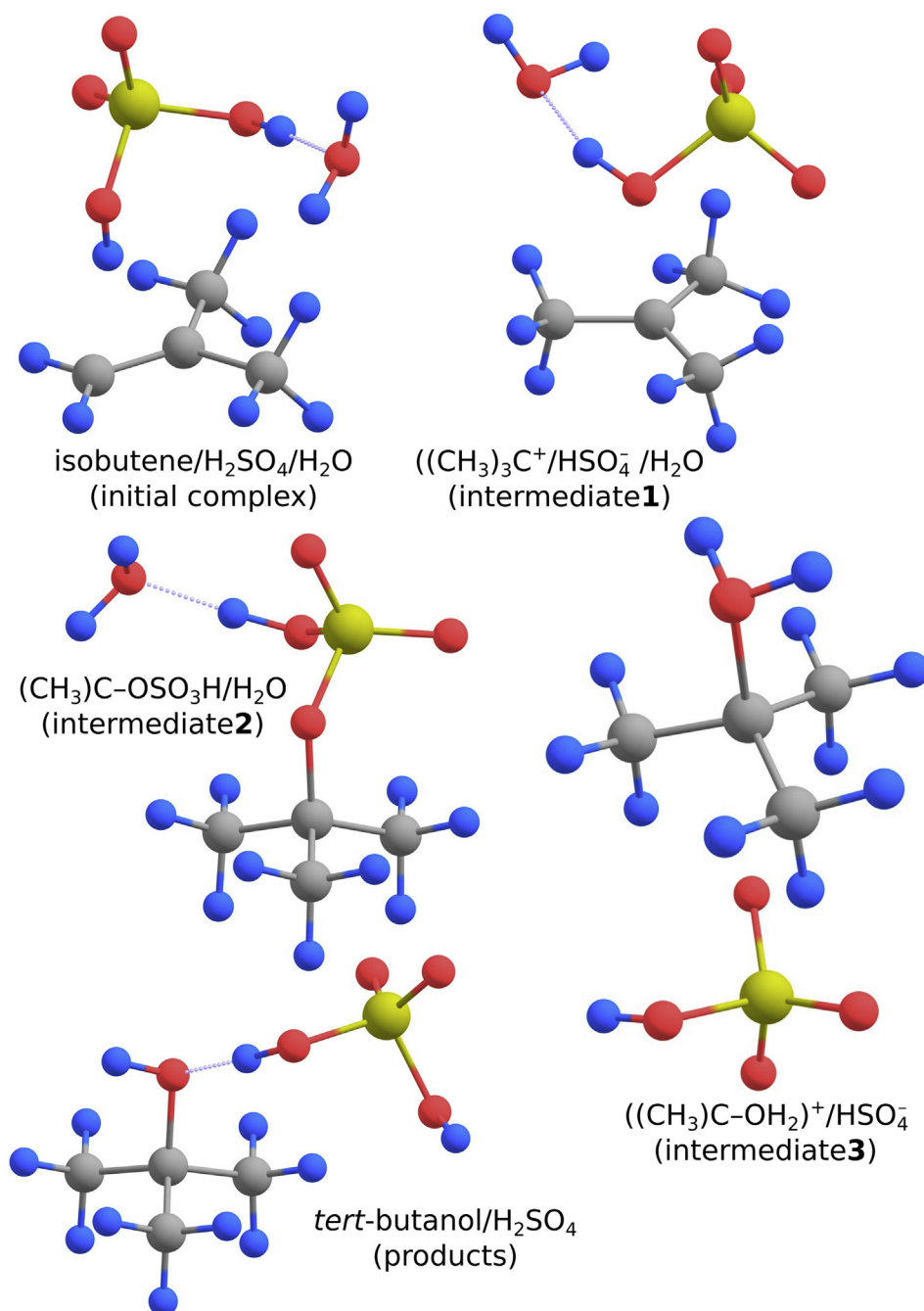


Fig. 3. The MP2/aug-cc-pVDZ equilibrium structures of the initial complex, intermediate products and final products predicted for the isobutene hydration catalyzed by H₂SO₄.

The electronic energies of all stationary points were obtained by using a compound method, namely, by computing single point MP2 energies with the triple zeta aug-cc-pVTZ basis set for each structure previously optimized at the MP2/aug-pVDZ level, and then by adding the differences between the MP2/aug-pVDZ and CCSD(T)/aug-pVDZ energies (where CCSD(T) stands for the coupled-cluster method with single, double, and non-iterative triple excitations [34, 35, 36, 37]). Finally, the Gibbs free energies were obtained by combining such calculated electronic energies of the stationary points and the thermal and zero-point energy corrections as well as the entropy contributions (at $T = 298.15\text{K}$) computed at the same level of theory.

The reaction mechanisms were investigated in the liquid phase and the effects of surrounding solvent molecules (H₂O or HF) were approximated by employing the polarized continuum solvation model (PCM)

[38, 39, 40] within a self-consistent reaction field treatment, as implemented in the GAUSSIAN09 program (the default options for PCM and the dielectric constant of 78.36 and 84.20 were used for water and hydrogen fluoride, respectively) regarding to all structures investigated.

The partial atomic charges were evaluated by the Natural Bond Orbital (NBO) analysis scheme [41, 42, 43, 44, 45]. All calculations were performed using the GAUSSIAN09 (Rev. A.02) package [46].

Cartesian coordinates of all stationary point structures and their electronic energies and Gibbs free energies are gathered in the Supplementary Materials.

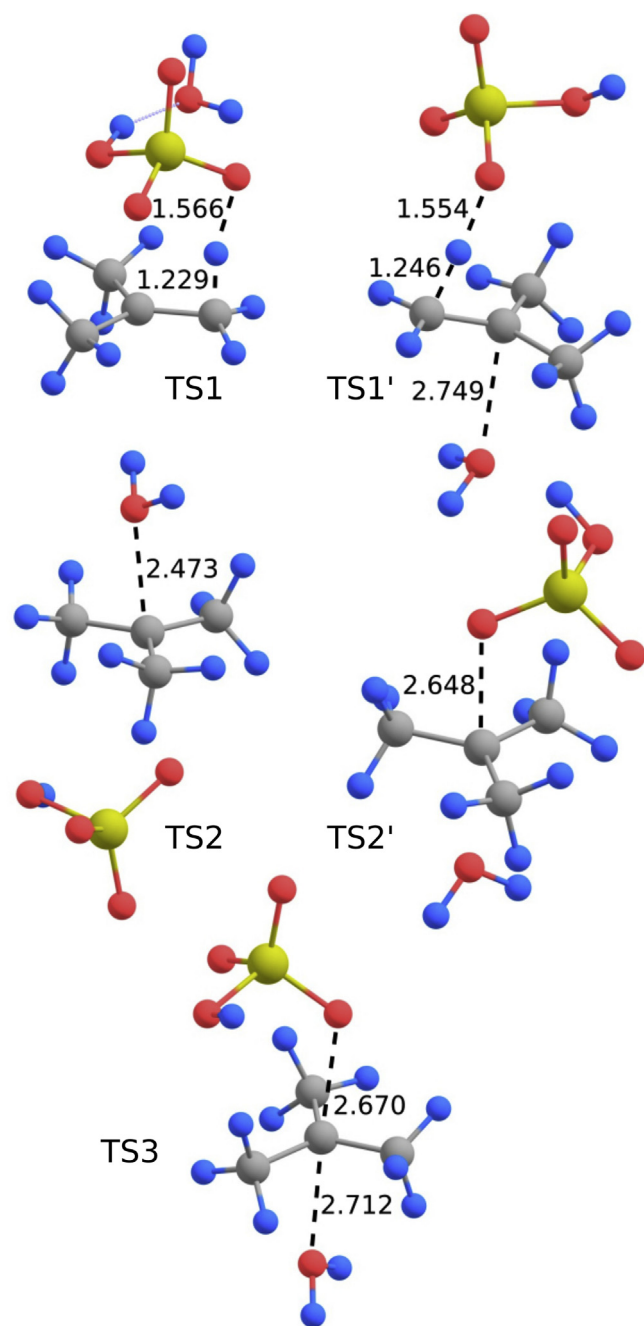


Fig. 4. The MP2/aug-cc-pVDZ structures of the transition states predicted for the isobutene hydration catalyzed by H_2SO_4 . Selected bond lengths are given in Å.

3. Results

3.1. The uncatalyzed hydration of isobutene

In order to verify the performance of acidic catalysts in the hydration of isobutene, the activation barrier for the uncatalyzed $(\text{CH}_3)_2\text{CCH}_2 + \text{H}_2\text{O} \rightarrow (\text{CH}_3)_3\text{COH}$ reaction has to be determined for comparison. Hence, we investigated the direct H_2O molecule attachment to isobutene (in the absence of any catalyst) in the liquid phase represented by two solvents, namely, water and hydrogen fluoride (as the H_2SO_4 and HSbF_6 acids were selected to play the catalyst role in this process, see the forthcoming sections). Since our Gibbs free energy profiles for the uncatalyzed hydration of isobutene reveal that the relative energies of

the stationary points (i.e., initial complex, transition state, and product) are nearly identical regardless the solvent considered (see Fig. 1), in this section we discuss our results jointly for these two solvents.

The initial complex (consisting of the $(\text{CH}_3)_2\text{CCH}_2$ and H_2O reactants) and the $(\text{CH}_3)_3\text{COH}$ product are connected through a single transition state (TS) whose structure is depicted in Fig. 1. The imaginary vibration (1870 i cm^{-1}) found for this TS corresponds to the simultaneous H–OH stretching (the H–O bond elongates to 1.376 Å) and formation of the C–O and C–H bonds. The partial atomic charges resulting from the NBO population analysis performed for this transition state structure confirm that the mechanism of this process can be considered an electrophilic addition as the partial charges on the OH fragment (i.e., nucleophilic agent) sum up to $-0.558e$, the partial charge on the H atom (i.e., electrophilic agent) that is being attached to isobutene was calculated to be $+0.419e$ whereas the charges on two carbon atoms involved were found to be $+0.260e$ (for the tertiary carbon which is the target of the electrophilic attack) and $-0.757e$ (for the carbon atom which is the target of the nucleophilic attack).

The height of the kinetic barrier for the uncatalyzed $(\text{CH}_3)_2\text{CCH}_2 + \text{H}_2\text{O} \rightarrow (\text{CH}_3)_3\text{COH}$ reaction is rather large (56.5 kcal/mol , see Fig. 1) which indicates that such a process should not be considered plausible. Since other evaluations of this barrier are not available in the literature, we compare our estimation to the barrier predicted for the H_2O attachment to ethylene and reported by Nakagawa et al. [15] who obtained (at the BLYP/6-31G(d) theory level) a similar value of 46.1 kcal/mol .

Taking into account a significant height of the activation barrier for the uncatalyzed reaction, one may conclude that the formation of *tert*-butanol by combining isobutene and H_2O , although thermodynamically favorable by 5.5 kcal/mol (as evaluated at the theory level employed), should not proceed at any noticeable rate in the absence of catalysts.

3.2. The hydration of isobutene catalyzed by the H_2SO_4 acid

The mechanism of the isobutene hydration might be changed by the introduction of a catalyst. Since the sulfuric acid is commonly used to catalyze hydration reactions of various alkenes, we chose the H_2SO_4 molecule to play the catalyst role while investigating the mechanism of the $(\text{CH}_3)_2\text{CCH}_2 + \text{H}_2\text{O} \rightarrow (\text{CH}_3)_3\text{COH}$ process.

The Gibbs free energy profile corresponding to the H_2SO_4 -catalyzed hydration of isobutene yielding *tert*-butanol is presented in Fig. 2, whereas the equilibrium structures of all stationary points are depicted in Fig. 3 (initial complex, intermediate products, and final product) and Fig. 4 (transition states). The reaction begins with formation of the initial complex consisting of mutually interacting (yet structurally intact) isobutene, H_2SO_4 , and H_2O molecules.

Next, the reaction path bifurcates as the initial complex might evolve either to the $((\text{CH}_3)_3\text{C})^+/\text{HSO}_4^-/\text{H}_2\text{O}$ intermediate product (labeled intermediate1 in Figs. 2 and 3) or to the $((\text{CH}_3)_3\text{C}-\text{OH}_2)^+/\text{HSO}_4^-$ intermediate product (labeled intermediate3 in Figs. 2 and 3). The former path involves the protonation of isobutene by H_2SO_4 and proceeds through the transition state labeled TS1 in Figs. 2 and 4 whereas the latter path consists of simultaneous isobutene protonation and H_2O molecule attachment to the central carbon atom and proceeds via the transition state labeled TS1' in Figs. 2 and 4. The kinetic barrier that has to be surmounted to form the $((\text{CH}_3)_3\text{C}-\text{OH}_2)^+/\text{HSO}_4^-$ intermediate product was found to be 19.6 kcal/mol while the barrier for the formation of $((\text{CH}_3)_3\text{C})^+/\text{HSO}_4^-/\text{H}_2\text{O}$ (intermediate1) was predicted to be smaller (16.9 kcal/mol), see Fig. 2. Once the $((\text{CH}_3)_3\text{C}-\text{OH}_2)^+/\text{HSO}_4^-$ (intermediate3) is formed, it should spontaneously (i.e., through a negligibly small kinetic barrier) evolve to the final products (*tert*-butanol and regenerated H_2SO_4 catalyst, see the equilibrium structure of the $(\text{CH}_3)_3\text{COH}/\text{H}_2\text{SO}_4$ complex in Fig. 3).

Alternatively, when the intermediate1 is formed after passing the TS1 saddle point, the reaction path bifurcates once again as the $((\text{CH}_3)_3\text{C})^+/\text{HSO}_4^-/\text{H}_2\text{O}$ complex might evolve either to the $(\text{CH}_3)_3\text{C}-\text{OSO}_3\text{H}/\text{H}_2\text{O}$

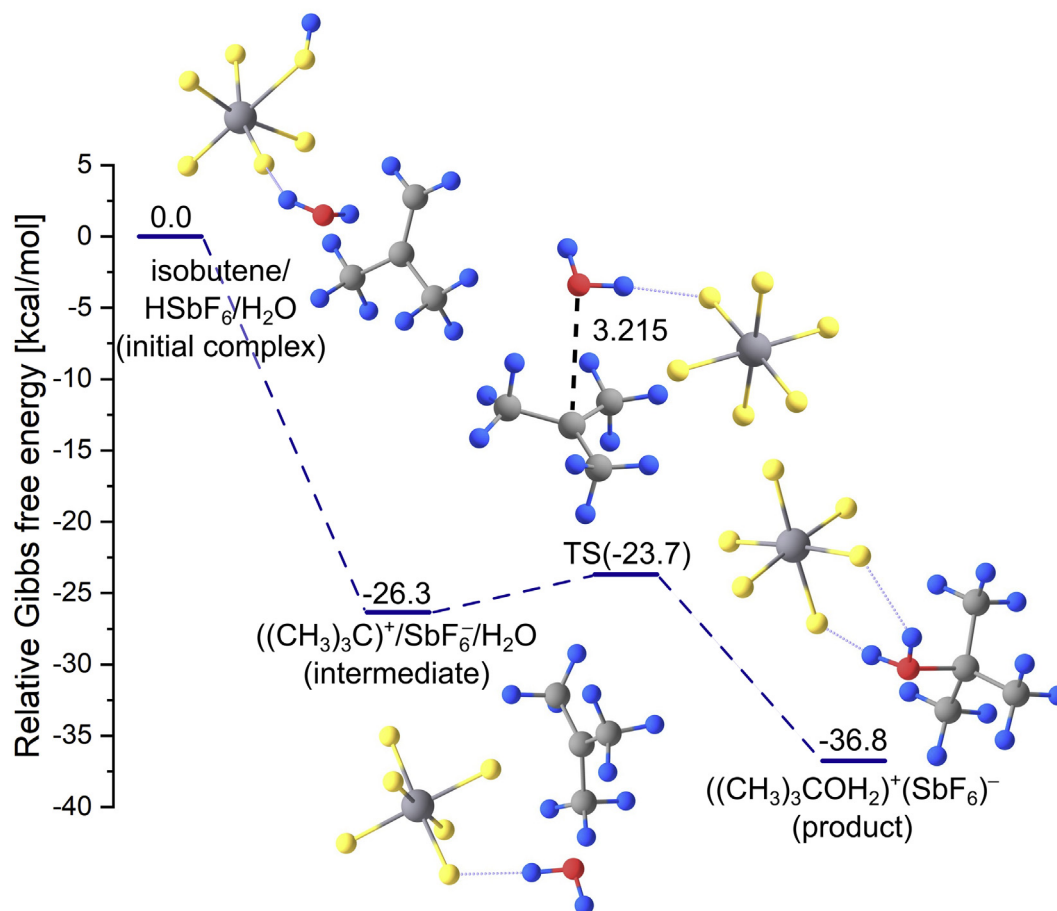


Fig. 5. The Gibbs free energy profile of the isobutene hydration catalyzed by HSbF_6 . The relative Gibbs free energies (at $T = 298.15$) of the stationary points are obtained for the HF solvent. Relative Gibbs free energies are given in kcal/mol.

complex (consisting of the *tert*-butyl carbocation neutralized by the HSO_4^- anion attached to it, labeled intermediate2 in Figs. 2 and 3) or to the $((\text{CH}_3)_3\text{C}-\text{OH}_2)^+/\text{HSO}_4^-$ (intermediate3) described above. The kinetic barriers for the transformation of intermediate1 to intermediate2 (through the TS2') or to intermediate3 (via the TS2) are very similar (3.3 kcal/mol and 2.6 kcal/mol, respectively) despite the structural differences in the corresponding saddle points. As explained above, the formation of the intermediate3 is followed by its immediate (due to the negligibly small kinetic barrier) evolution to the final products consisting of *tert*-butanol and regenerated H_2SO_4 . By contrast, the intermediate2 represents a very stable complex whose relative energy approaches that of the final reaction products, hence its transformation to $(\text{CH}_3)_3\text{COH}/\text{H}_2\text{SO}_4$ might be problematic. In addition, the evolution from $(\text{CH}_3)_3\text{C}-\text{OSO}_3\text{H}/\text{H}_2\text{O}$ to $((\text{CH}_3)_3\text{C}-\text{OH}_2)^+/\text{HSO}_4^-$ requires passing relatively large kinetic barrier (via TS3, see Figs. 2 and 4) of 24.9 kcal/mol. Once this barrier is overcome, the $((\text{CH}_3)_3\text{C}-\text{OH}_2)^+/\text{HSO}_4^-$ (intermediate3) is generated and then the formation of the $(\text{CH}_3)_3\text{COH}/\text{H}_2\text{SO}_4$ final product follows.

Summing up, our calculations confirm that sulfuric acid effectively reduces the kinetic barrier that has to be surmounted to transform isobutene into *tert*-butanol. As we demonstrated, this conversion might be accomplished by following a few different reaction paths each of which involves the isobutene protonation as the initial step (that may or may not be associated with the simultaneous H_2O attachment). Also, our results indicate that if the $(\text{CH}_3)_3\text{C}-\text{OSO}_3\text{H}/\text{H}_2\text{O}$ complex is formed along the reaction path, the overall process should become slower as the conversion of this intermediate product into *tert*-butanol becomes the rate limiting step.

3.3. The hydration of isobutene catalyzed by the HSbF_6 superacid

The mechanism of isobutene hydration catalyzed by HSbF_6 superacid is much simpler than the mechanism involving H_2SO_4 as a catalyst and described in the preceding section. As demonstrated in the Gibbs free energy profile shown in Fig. 5, the reactants form the initial complex (consisting of nearly non-deformed isobutene, HSbF_6 , and H_2O systems stabilized mainly by the intermolecular hydrogen bonds).

Once the isobutene/ $\text{HSbF}_6/\text{H}_2\text{O}$ initial complex is formed, it spontaneously converts to the intermediate product due to negligibly small (<0.5 kcal/mol) kinetic barrier separating $(\text{CH}_3)_2\text{CCH}_2/\text{HSbF}_6/\text{H}_2\text{O}$ from $((\text{CH}_3)_3\text{C})^+/\text{SbF}_6^-/\text{H}_2\text{O}$. This first reaction step involves the protonation of isobutene by the HSbF_6 superacid and the energy of such generated intermediate product (consisting of tertiary $((\text{CH}_3)_3\text{C})^+$ carbocation interacting with the SbF_6^- anion and water molecule) is lower by 26.3 kcal/mol than that of the initial complex. Next, a small kinetic barrier of 2.6 kcal/mol has to be surmounted (see Fig. 5 for the corresponding transition state structure labeled TS) to form the reaction product. During this step, H_2O molecule is being attached via its oxygen atom to the tertiary carbon atom of $((\text{CH}_3)_3\text{C})^+$ carbocation. Hence, the final product of the isobutene hydration catalyzed by HSbF_6 represents the $((\text{CH}_3)_3\text{COH}_2)^+(\text{SbF}_6)^-$ ionic compound rather than the complex of *tert*-butanol and regenerated acid catalyst, see Fig. 5. However, one should recall that superacid-catalyzed reactions very often lead to ionic salts instead of desired covalent products and their further transformation into preferred products requires proper quenching (usually performed by utilizing Na_2CO_3 or $\text{NaHCO}_3/\text{H}_2\text{O}$) [47].

It seems important to notice that choosing the HSbF_6 superacid to play the catalyst role in the hydration of isobutene yielding *tert*-butanol is

predicted to proceed very fast because the only kinetic barrier on the reaction path is very small (2.6 kcal/mol).

4. Conclusions

On the basis of our *ab initio* calculations carried out using the CCSD(T) and MP2 methods with the aug-cc-pVDZ/LANL2DZ and aug-cc-pVTZ/LANL2DZ basis sets (including the effects of surrounding solvent molecules approximated by employing the polarized continuum solvation model) performed to study the mechanism of the $(\text{CH}_3)_2\text{CCH}_2 + \text{H}_2\text{O} \rightarrow (\text{CH}_3)_3\text{COH}$ reaction catalyzed by either the H_2SO_4 or HSbF_6 acid, we arrive at the following conclusions:

- (i) The uncatalyzed isobutene hydration yielding *tert*-butanol might proceed according to the electrophilic addition mechanism but the activation barrier predicted for this reaction is very large (56.5 kcal/mol in the liquid phase) which renders this process highly unlikely.
- (ii) The use of the sulfuric acid effectively reduces the kinetic barrier that has to be surmounted to transform isobutene into *tert*-butanol. H_2SO_4 -catalyzed $(\text{CH}_3)_2\text{CCH}_2 + \text{H}_2\text{O} \rightarrow (\text{CH}_3)_3\text{COH}$ reaction might proceed along a few different paths involving the isobutene protonation as the initial step. Possible formation of the $(\text{CH}_3)_3\text{C}-\text{OSO}_3\text{H}/\text{H}_2\text{O}$ complex as the intermediate product is predicted to decrease the rate of the overall process as its further conversion to *tert*-butanol requires overcoming a large kinetic barrier of ca. 25 kcal/mol.
- (iii) The isobutene hydration is predicted to proceed very fast when catalyzed by the HSbF_6 superacid as only one small kinetic barrier of ca. 3 kcal/mol has to be surmounted along the reaction path.

Declarations

Author contribution statement

Jakub Brzeski: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data.

Piotr Skurski: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

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