

THEORETICAL STUDY OF THE CONVERSION FROM 5-HYDROXYMETHYLFURAN-2-CARBALDEHYDE TO 2-HYDROXY-5-METHYLENE-2,5-DIHYDRO-FURAN-2-CARBALDEHYDE IN THE LEVULINIC ACID FORMATION PROCESS

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A novel reaction route was proposed from 5-hydroxymethylfuran-2-carbaldehyde (HMFCa) to 2-hydroxy-5-methylene-2,5-dihydro-furan-2-carbaldehyde (HMDFC) on the basis of the mechanism previously offered by Horvat, to account for the formation mechanism of levulinic acid. The probabilities of the two mechanisms were compared by Gaussian 03 software. It was found that the conversion from HMFCa to HMDFC in the newly deduced mechanism has a lower net energy requirement than that in the original mechanism, and thus should be more preferable. The mechanism indicates that HMFCa is initially protonized by H^+ addition at the position 5 of the furan ring, and then combines with OH^- , thereby completing the hydration process after isomerization. Finally, an H_2O molecule is released, forming the intended intermediate product of HMDFC.

Keywords: Levulinic acid; Mechanism; Transition state

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INTRODUCTION

Biomass is an important source for energy and for chemicals due to its carbon neutrality and renewable characteristics (Bridgwater 2003; Mohanet et al. 2006; Serrano-Ruiz et al. 2010). Levulinic acid (LA) is a major product obtained by hydrothermal treatment of biomass (Amarasekara and Ebede 2009; Cha and Hanna 2002; Chang et al. 2007; Girisuta et al. 2006; Hegner et al. 2010) and is broadly used as a versatile building block for synthesis of various organic compounds (Bozell et al. 2000; Guo et al. 2008; Iskanderet et al. 2009; Martin and Prather 2009; Patel et al. 2010; Saito et al. 2004). The composition of the liquid product is very complex and varies severely with reaction conditions. The content of LA is typically condition-dependant as well. This makes control of the reaction complicated and hard to understand. So, a theoretical study is important for a deep understanding on the LA formation mechanism, and even for the improvement of the LA productivity.

A brief formation route from 5-hydroxymethylfuran-2-carbaldehyde (HMFCa) to LA has been put forward by Horvat et al. (1985), while the conversion details were not presented therein. We have studied the conversion details from the intermediate product

of 2-hydroxy-5-methylene-2,5-dihydro-furan-2-carbaldehyde (HMDFC) to 2,5-dioxo-hex-3-enal (DOHE) in the LA formation process (Wang et al. 2011). In this paper, a novel reaction route from HMFCFA to HMDFC was put forward on the basis of the mechanism offered by Horvat. The probabilities of the novel and the original mechanism are compared by the Hartree-Fock (HF) method, using Gaussian 03 software (Frisch et al. 2003) to evaluate the more preferred mechanism. The HF method is frequently used in equilibrium structure and transition-state optimizations (Boronat et al. 1996; Viskolcz et al. 1996) and also applied herein.

RESULTS AND DISCUSSION

Mechanism-I (a): Reaction Route with More Details in Match with the Steps in the Horvat Mechanism

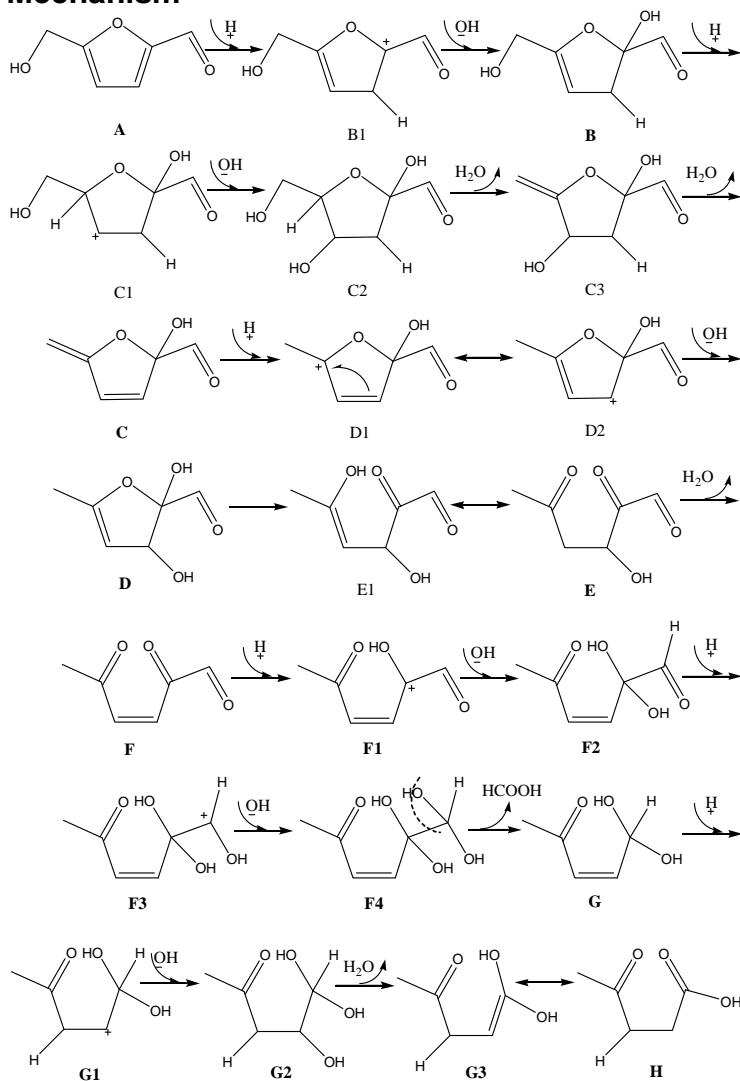


Fig. 1. Mechanism-I (a) deduced with more details on the basis of the Horvat mechanism (Wang et al. 2011)

On the basis of the mechanism offered by Horvat (1985), a more detailed reaction route, denoted as mechanism-I (a), has been deduced to conform to every step in the Horvat mechanism as shown in Fig. 1; the reaction details from **C** (HMDFC) to **F** (DOHE) have been discussed in a previous report (Wang et al. 2011). In this paper, the reaction from **A** (HMFCa) to **C** (HMDFC) is discussed.

Mechanism-I (b): Another Reaction Route from C2 to C on the Basis of Mechanism-I (a)

It can be seen from Fig. 1 that the hydroxymethyl group at position 5 of the furan ring of **C2** firstly dehydrates to **C3**, and then **C3** further converts to **C** by dehydration at position 4. Besides this case, there is another probability, i.e. the two dehydration steps may proceed in a reverse order that the dehydration at position 4 may proceed ahead, as shown in Fig. 2. To make an evaluation on the two cases, the energy barriers as the enthalpy difference between the transition state and the corresponding reactant in the two routes are compared.

The structures of the molecules were optimized, by the HF method with 6-31G* basis, by Gaussian 03 software. The calculated enthalpies are listed in Table 1. The transition state of **TS-C2toC3** between **C2** and **C3-H₂O**, **TS-C3toC** between **C3** and **C-H₂O**, **TS-C2toB4** between **C2** and **B4-H₂O**, and **TS-B4toC** between **B4** and **C-H₂O** are obtained by qst2 approach (Peng et al. 1993; 1996) and HF/6-31G* method. The enthalpies of the transition states are also listed in Table 1. The geometric conversions from **C2** to **C3** and from **C3** to **C** are shown in Fig. 3, and the conversions from **C2** to **B4** and from **B4** to **C** are shown in Fig. 4.

Table 1. Enthalpies (Hartree/Particle) of the Reactants, Intermediate Products, and Transition States in Mechanism-I(a), Mechanism-I(b), and Mechanism-II

Mechanism-I		Mechanism-II (in Fig.5)			
Mechanism-I(a) (in Fig.1)		Mechanism-I(b) (in Fig.2)			
H ₂ O	-75.983994	H ₂ O	-75.983994	H ₂ O	-75.983994
OH	-75.314776	OH	-75.314776	OH	-75.314776
A+2H ₂ O	-607.082092	A+2H ₂ O	-607.082092	A+2H ₂ O	-607.082092
B1+OH+H ₂ O	-606.707728	B1+OH+H ₂ O	-606.707728	B2+OH+H ₂ O	-606.728406
B+H ₂ O	-607.087006	B+H ₂ O	-607.087006		
C1+OH	-606.704461	C1+OH	-606.704461	B3+OH+H ₂ O	-606.725371
C2	-607.109541	C2	-607.109541		
TS-C2toC3	-606.964774	TS-C2toB4	-606.975402		
		B4(conformation-I) +H ₂ O	-607.090676	B4(conformation-I) +H ₂ O	-607.090676
C3+H ₂ O	-607.093863	B4(conformation-II) +H ₂ O	-607.081584	B4(conformation-II) +H ₂ O	-607.081584
TS-C3toC+H ₂ O	-606.958993	TS-B4toC+H ₂ O	-606.94054	TS-B4toC+H ₂ O	-606.94054
C+2H ₂ O	-607.071308	C+2H ₂ O	-607.071308	C+2H ₂ O	-607.071308

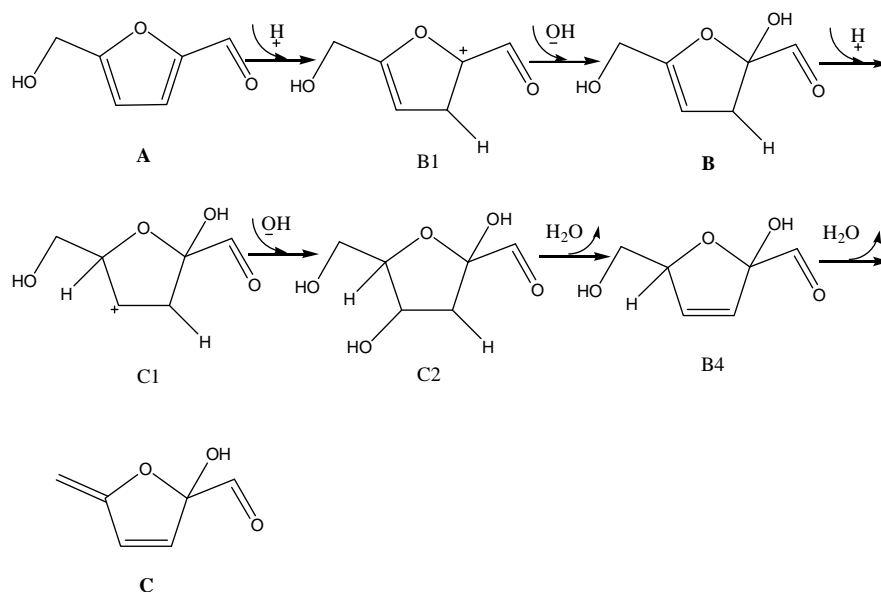


Fig. 2. Mechanism-I (b) deduced from **A** to **C2** to **B4** to **C** on the basis of Mechanism-I (a)

In the route from **B4** to **C**, **B4** is found to conform firstly from the most stable state of conformation-I to the less stable state of conformation-II, and then further converts to **C** through the transition state of **TS-B4toC**. It can be seen from Table 1 that the enthalpy of **TS-C2toB4** is lower than that of **TS-C2toC3**, indicating that **B4** may be more easily generated than **C3**. The enthalpy of **TS-B4toC** is higher than that of **TS-C3toC**, and even higher than the enthalpy values of all the other three transition states, indicating that the conversion from **B4** to **C** has a higher energy barrier to overcome. Therefore, the route from **C2** to **C3** to **C**, as shown in Fig. 1, should be more preferable than the route from **C2** to **B4** to **C** seen in Fig. 2.

Novel Reaction Route from **A** to **C**

In **mechanism-I**, two H_2O molecules are needed for the conversion from **A** to **C**, on the precondition that H^+ is initially added to the position 1 of molecule **A**. This precondition is set to match the steps in the Horvat mechanism. While this is interesting, it would also be worth investigating what happens if H^+ is added to another position of molecule **A**. Herein, the novel mechanism is deduced as follows: H^+ is initially added to the position 5 of the furan ring forming **B2**, and then **B2** isomerizes to **B3**, **B3** then combines with OH^- forming **B4**, and then **B4** releases an H_2O , forming the intermediate **C**. In this process from **A** to **C**, nominated as **mechanism-II** as shown in Fig. 5, only one H_2O molecule is added and then released, instead of two H_2O molecules like that in **mechanism-I**.

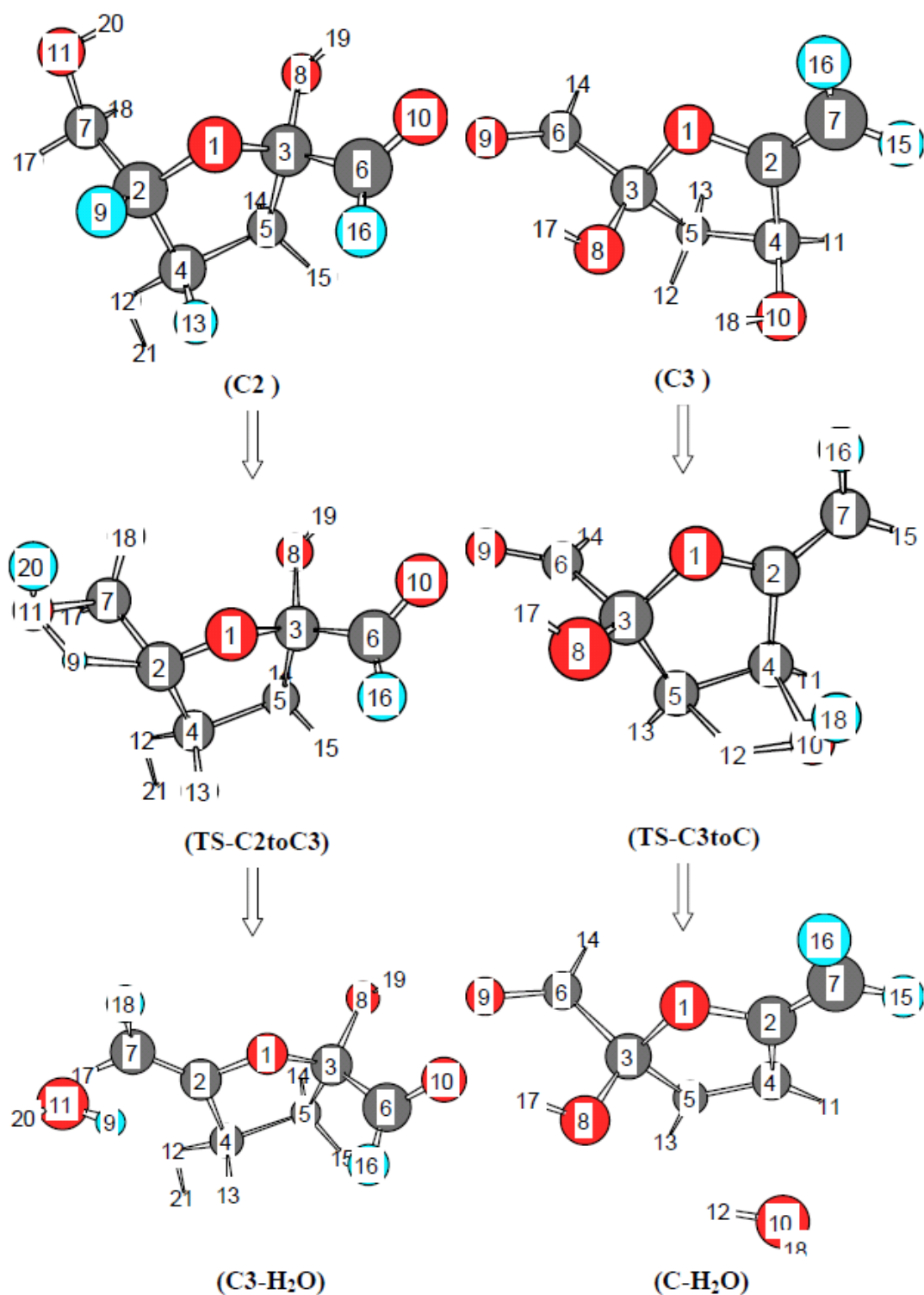


Fig. 3. Geometric converting process from C2 to C3-H₂O and from C3 to C-H₂O through the transition states of TS-C2toC3 and TS-C3toC

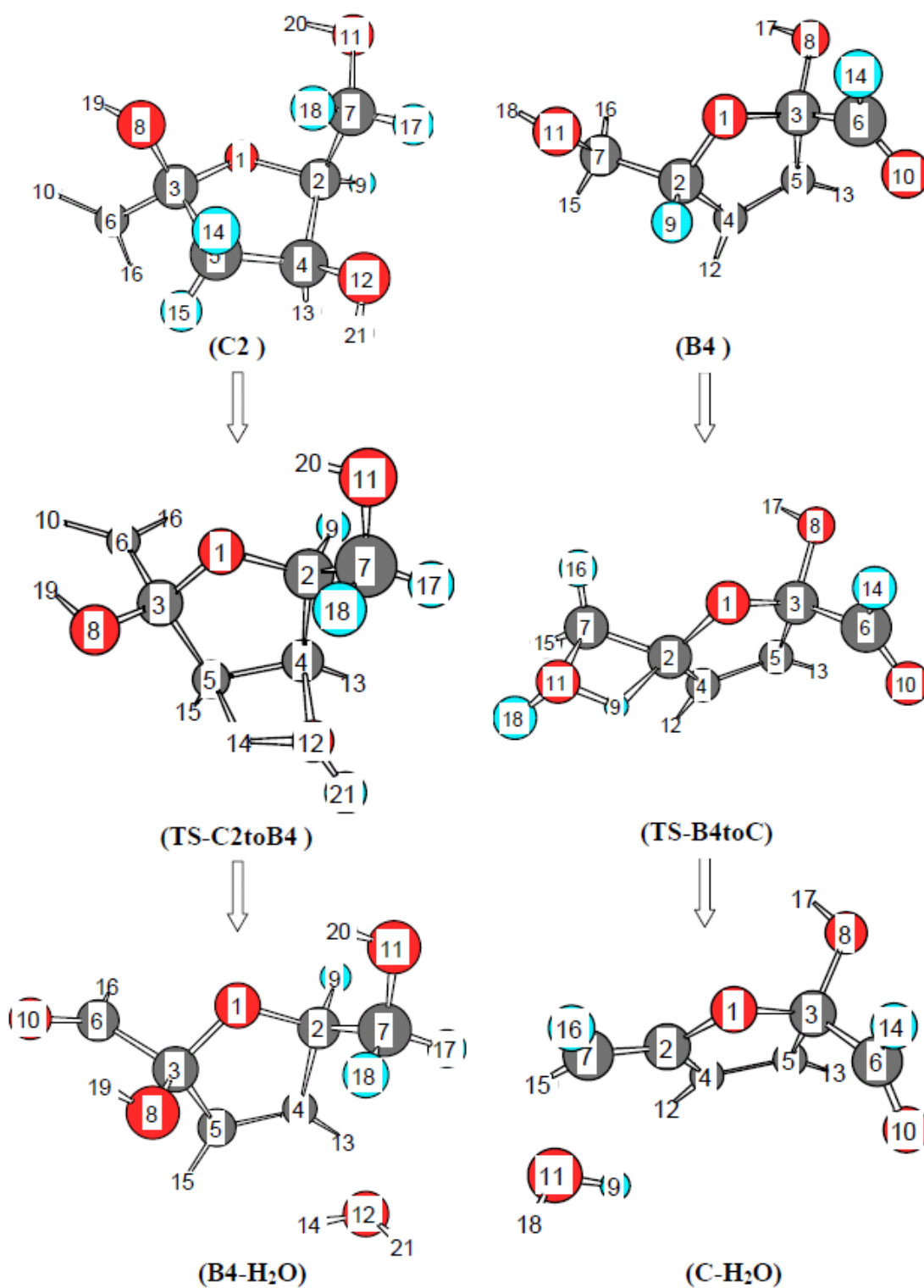


Fig. 4. Geometric converting process from **C2** to **B4-H₂O** and from **B4** to **C-H₂O** through the transition states of **TS-C2toB4** and **TS-B4toC**

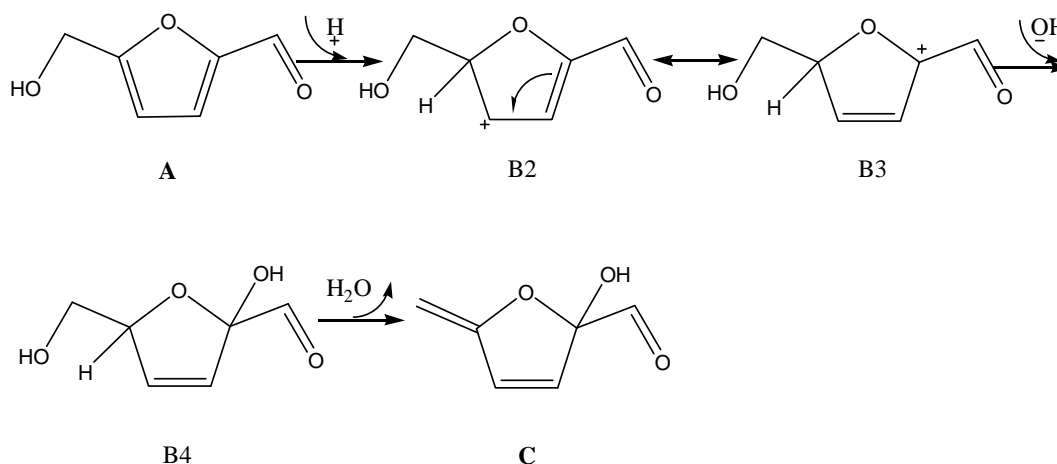


Fig. 5. Mechanism-II deduced from **A** to **C**

The structures of the molecules in **mechanism-II** are optimized by the same HF/6-31G* method, and the calculated enthalpies are listed in Table 1. The enthalpy changes along the reaction routes from **A** to **C** are shown in Fig. 6. It can be seen from Table 1 that the enthalpy of **B2** is distinctly lower than that of **B1**, indicating that **B2** is more stable than **B1**, and thus should be more easily generated. As more **B2** is generated the conversion of **B2** increases, thereby increasing the production of species derived from **B2**. From this kinetic point of view, **mechanism II** should be more preferable than **mechanism I** in the route from **A** to **C**.

As can be seen from Table 1 and Fig. 6, the enthalpy value of **B3+OH+H₂O** is the highest value in **mechanism-II**. It is slightly higher than that of **B2+OH+H₂O**, but much higher than the enthalpy value of **B4+H₂O**, **TS-B4toC+H₂O** or **C+2H₂O**, all in same atom numbers. It indicates that the formation of **B2** or **B3** is the rate determinative step in the whole reaction path.

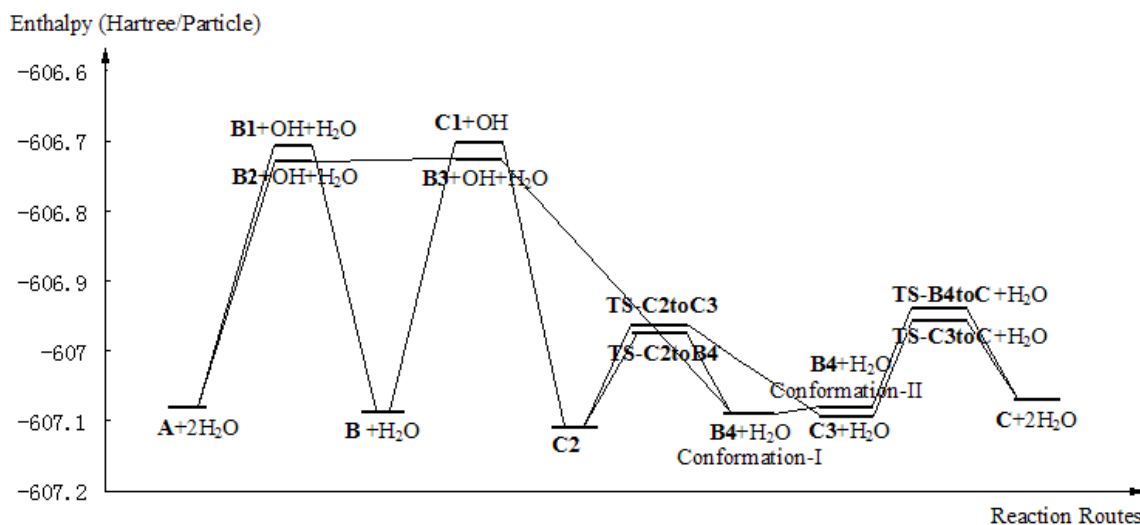


Fig. 6. Enthalpy changes along the reaction routes from **A** to **C**

The highest enthalpy value of **B3+OH+H₂O** in **mechanism-II** is distinctly lower than that of **C1+OH** in **mechanism-I** with the same atom number, so the net energy requirement in **mechanism-II** is lower than that in **mechanism-I**. Therefore, **mechanism-II** should be more preferred from the viewpoint of energy demand, although the enthalpy of **TS-B4toC** is higher than that of **TS-C3toC** in the non-determinative step from **B4** or from **C3** to **C**.

CONCLUSIONS

A novel reaction mechanism between 5-hydroxymethylfuran-2-carbaldehyde (HMFCA) and 2-hydroxy-5-methylene-2,5-dihydro-furan-2-carbaldehyde (HMDFC) was put forward, on the basis of the levulinic acid formation mechanism previously offered by Horvat. The probabilities of different reaction mechanisms were compared through energy-barrier comparisons by Gaussian 03 software. It was found that the conversion from HMFCA to HMDFC in the newly deduced mechanism has a lower net energy requirement than that in the original mechanism, and thus should be more preferred. The mechanism indicates that HMFCA is initially protonized by H⁺ addition at position 5 of the furan ring, and then combines with OH⁻, thereby completing the hydration reaction after isomerization. Finally, an H₂O molecule is released, forming the intended intermediate product HMDFC.

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