

## MECHANISTIC STUDY OF THE CONVERSION FROM DMDFC TO DOHE IN THE LEVULINIC ACID FORMATION PROCESS BY THEORETICAL APPROACHES

Ze Wang, Weigang Lin, and Wenli Song

A reaction route accounting for the formation of levulinic acid from 5-hydroxymethylfuran-2-carbaldehyde was deduced on the basis of the mechanism previously offered by Horvat, to match the steps with more details. A newly deduced reaction route was proposed between two intermediate products within this mechanism, and the probabilities of the two mechanisms were compared by Gaussian 03 software. It was found that the conversion from the intermediate 2,3-dihydroxy-5-methyl-2,3-dihydro-furan-2-carbaldehyde (DMDFC) to 2,5-dioxo-hex-3-enal (DOHE) in the original mechanism has a lower net energy barrier than that in the newly deduced mechanism, and thus should be more preferred. The mechanism indicates that DMDFC is first protonized, followed by a proton shift process, and thereafter an OH<sup>-</sup> ion is added, completing the hydration process. Thereafter, an intramolecular H-shift reaction proceeds, leading to conversion to the intended intermediate product DOHE by the consecutive processes of isomerization and dehydration.

*Keywords: Levulinic acid; Mechanism; Transition state*

*Contact information: State Key Laboratory of Multi-Phase Complex System, Institute of Process Engineering, Chinese Academy of Sciences, Beijing, China, 100190; wangze@home.ipe.ac.cn*

### 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), as a versatile building block for the 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), 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). The composition of the liquid product is rather complex and varies severely with reaction conditions, such as temperature, content of solvent, reaction time, and acidity of the environment. This makes control of the reaction very complicated and hard to understand. So a theoretical study is important to explain factors affecting the reaction and even to have better control of the final composition. The content of LA is typically condition-dependant as well, and therefore a deep understanding on the LA formation mechanism has potential to improve the synthesis process.

The mechanism is rather difficult to be determined experimentally due to the complexity of the thermal conversion process, since thermal conversion always generates

too many products simultaneously. Presently, just a brief formation route from 5-hydroxymethylfuran-2-carbaldehyde (HMFCFA) to levulinic acid has been put forward by Horvat et al. (1985), while the conversion details were not presented therein and are still not quite clear as of now. In this paper, a more detailed conversion route is deduced on the basis of this mechanism, and another possible reaction route between two intermediate products within this mechanism is put forward. The probabilities of the two mechanisms are compared by the enthalpy values of transition states by Hartree-Fock (HF) method in Gaussian 03 software 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 Deduced by Horvat et al.

The mechanism from HMFCFA (A) to levulinic acid deduced by Horvat et al. (1985), denoted mechanism-O, is shown in Fig. 1. The mechanism indicates that the reactant A was successively transferred through the intermediate products of B, C, D, E, F, G, to the final product of levulinic acid (H). The compounds in the brackets were not detected by experiment, as shown in Fig. 1. In other words, F was the only detected intermediate product. It can be seen from Fig. 1 that most of the conversions between two intermediates are not one-step processes, so a more detailed formation route is necessary. In this paper, the route from C to F in mechanism-O is at issue.

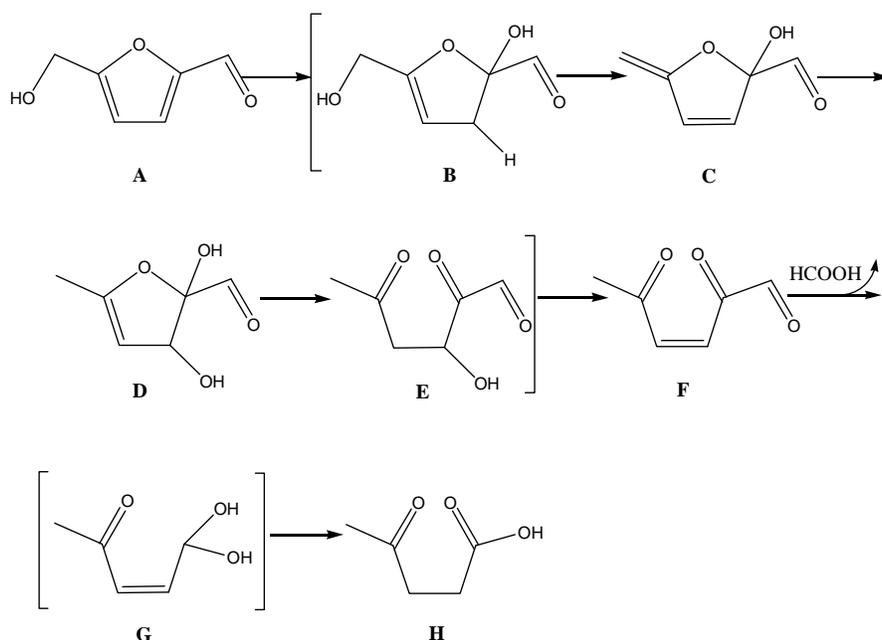
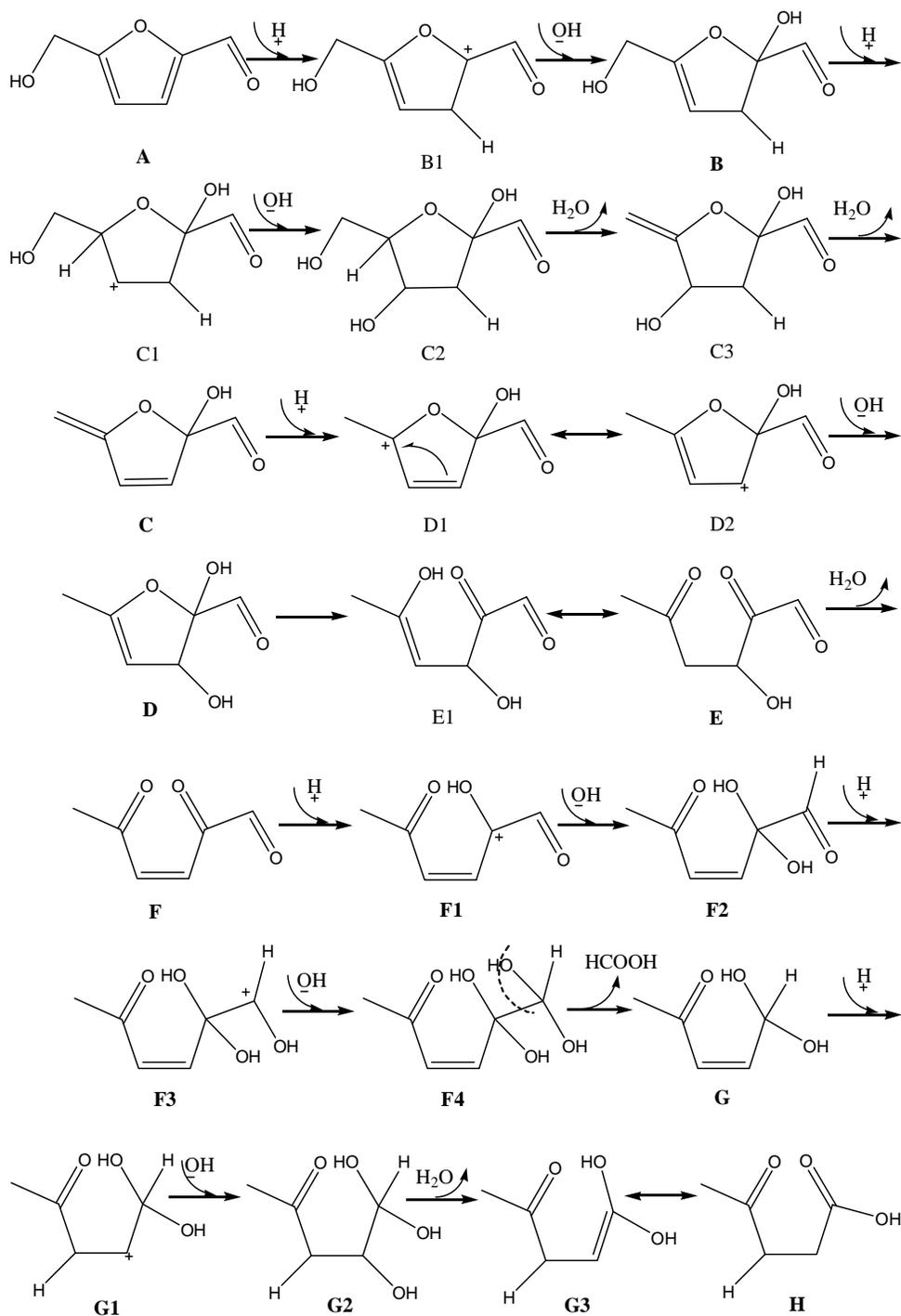


Fig. 1. Mechanism-O deduced by Horvat et al. (1985)

### Deduced Reaction Route with More Details to Match with the Steps in Mechanism-O from A to H

The more detailed reaction route, denoted mechanism-I from **A** to **H** on the basis of mechanism-O was deduced as shown in Fig. 2.



**Fig. 2.** Mechanism-I deduced from **A** to **H** with more details on the basis of Mechanism-O

This mechanism is deduced just to conform to every step in mechanism-O. It can be seen from Fig. 2 that **A** is originally protonized to form **B1** and then combines with  $\text{OH}^-$ , forming the intermediate **B**; **B** repeats the  $\text{H}^+$  and  $\text{OH}^-$  addition process, forming **C2**; and then two  $\text{H}_2\text{O}$  molecules are released from **C2** to form **C3** and **C** successively; **C** further reacts with  $\text{H}^+$ , forming **D1**, and then an intramolecular ion transfer within **D1** takes place to form **D2**; thereafter **D2** combines with  $\text{OH}^-$ , forming the intermediate product **D**; subsequently an isomerization of **D** takes place to form **E1** by an intramolecular H-shifting process, and then **E1** changes to the more stable form of **E** by keto-enol tautomerization; thereafter **E** dehydrates to the intermediate **F**. **F** is further hydrated by addition of two  $\text{H}_2\text{O}$  molecules to form **F4**, and then a  $\text{HCOOH}$  molecule is released from **F4** forming the intermediate **G**. **G** converts to **G3** by a consecutive  $\text{H}_2\text{O}$  addition and elimination process. Finally, the intended product **H** is generated by the keto-enol tautomerization reaction from **G3**.

### Newly Deduced Reaction Route from **C** to **F**

It can be seen from Fig. 2 that in mechanism-I the intermediate **C** is first hydrated to form **D**, and then **D** is further converted to **E1** through an intramolecular H-shifting process. It is interesting to consider whether the intramolecular H-shifting reaction must proceed after the hydration of **C**, and whether it is possible that **C** could be directly converted to **D3** through the intramolecular H-shifting reaction without an early hydration process. Based on such an assumption, **D3** may be further converted to **F** by keto-enol tautomerization. The newly deduced mechanism from **C** to **F** can be written as shown in Fig. 3.

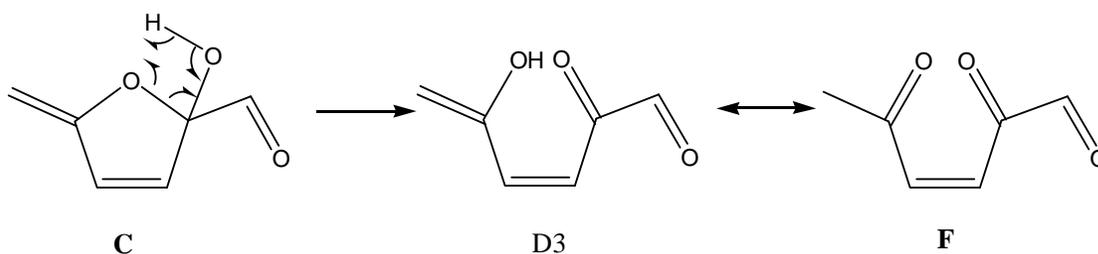


Fig. 3. Mechanism-II deduced from **C** to **F**

### Comparison of the Routes from **C** to **F** between Mechanism-I and Mechanism-II

To make an evaluation on the probability between the mechanism-I and mechanism-II, the enthalpies of the transition states in the process from **C** to **D3** and from **D** to **E1** were compared. The structures of **C**, **D3**, **D**, and **E1** were first optimized, and then the transition state of **TS-C** between **C** and **D3**, and the transition state of **TS-D** between **D** and **E1** were obtained by the qst2 approach with the  $\text{HF}/6\text{-}31\text{G}^*$  method by Gaussian 03 software (Frisch et al. 2003). Through the search for transition state, it was found that in the conversion process from **D** to **E1**, **D** first conforms to the most stable state of conformation-1 and then proceeds to the less stable state of conformation-2, and

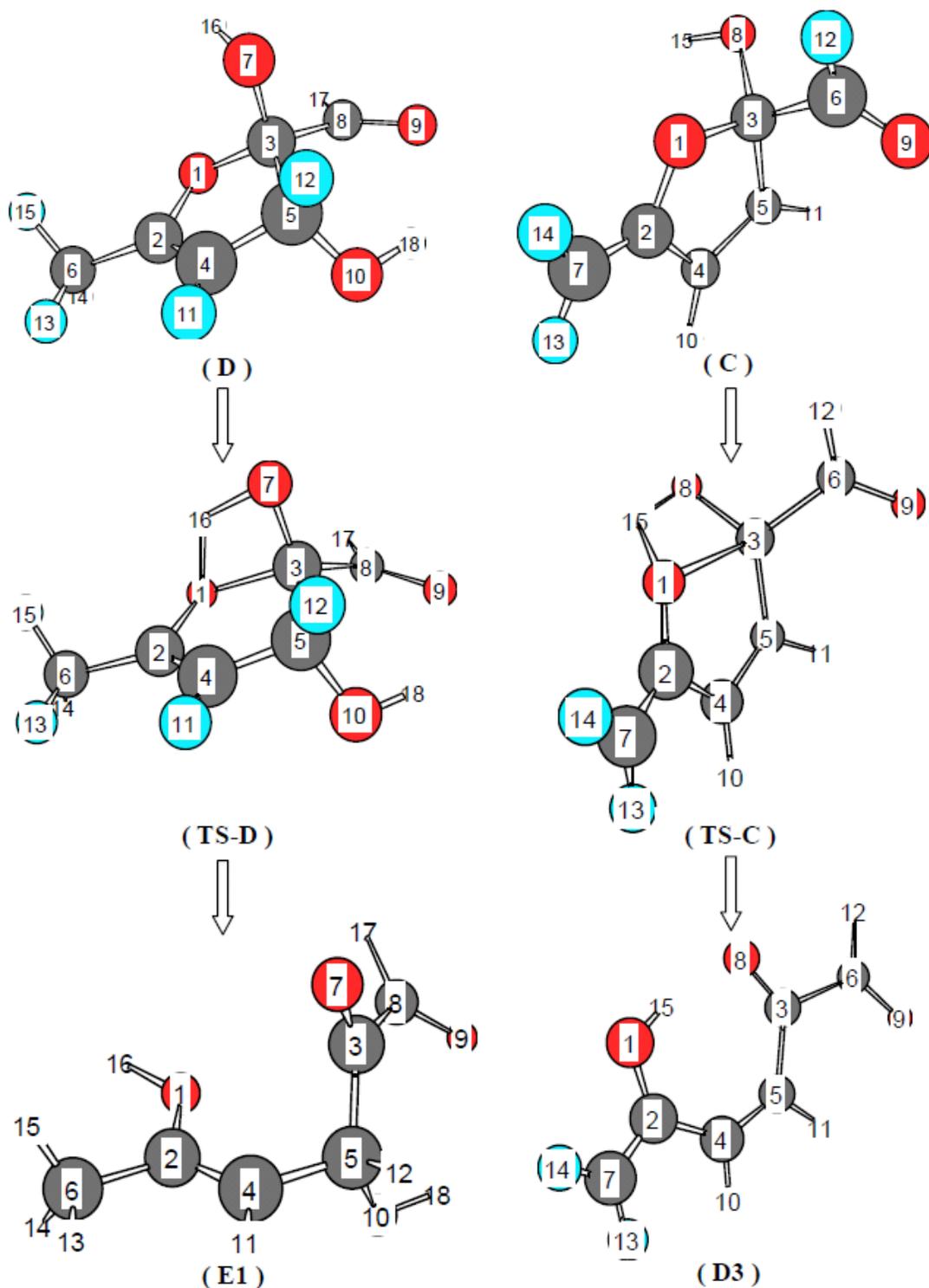
then to the intermediate product **E1** in the less stable state of conformation-2 through the transition state of **TS-D**; then **E1** further conforms to the most stable state of conformation-1. The enthalpies of the molecules from **C** to **F** mentioned in the two mechanisms, including the two obtained transition states are listed in Table 1, and the geometric converting processes from **C** to **D3** and from **D** to **E1** through the corresponding transition states are shown in Fig. 4.

**Table 1.** Enthalpies (Hartree/Particle) of the Reactant, Intermediates, Products, and Transition states

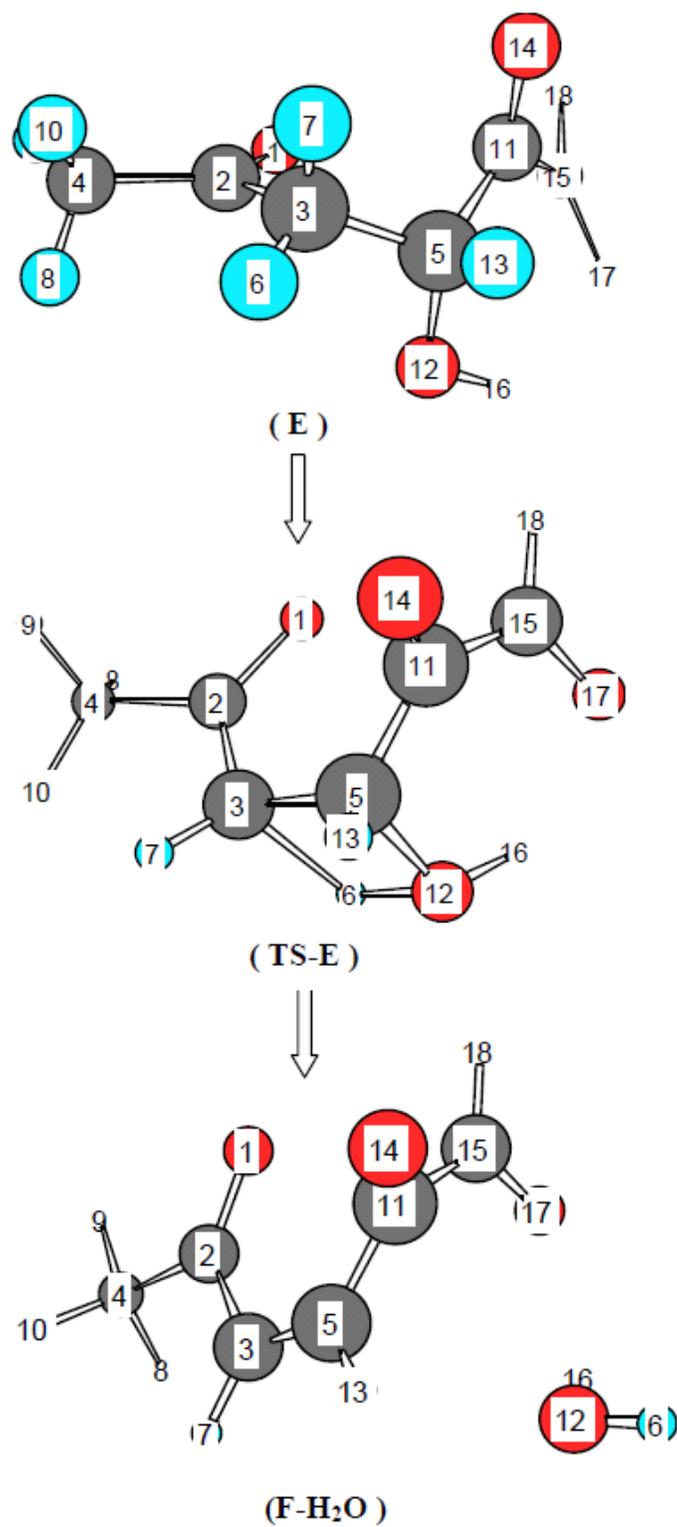
Mechanism-I		Mechanism-II	
Molecule	Enthalpies	Molecule	Enthalpies
H <sub>2</sub> O	-75.983994	H <sub>2</sub> O	-75.983994
C	-455.10332	C	-455.10332
D1	-455.449241	C+H <sub>2</sub> O	-531.087314
D2	-455.449241		
D	Conformation-1		-531.113339
	Conformation-2	TS-C	-455.007631
TS-D	-531.020794	TS-C+H <sub>2</sub> O	-530.991625
E1	Conformation-2		-531.095908
	Conformation-1	D3	-455.09859
E	-531.136127	D3+H <sub>2</sub> O	-531.082584
TS-E	-531.023353		
F	-455.120469	F	-455.120469
F+H <sub>2</sub> O	-531.104463	F+H <sub>2</sub> O	-531.104463

As can be seen from Table 1, the enthalpy of the transition state of **TS-D** is -531.020794 Hartree/Particle, which is lower than the sum of the enthalpies of **TS-C** and H<sub>2</sub>O of -530.991625 Hartree/Particle, indicating that **TS-D** is more stable than **TS-C**, and thus **TS-D** should be more easily generated. From the viewpoint of kinetics, the conversion from **C** to **D3** through **TS-C** must overcome a higher energy barrier than the barrier from **D** to **E1** through **TS-D**, so the route from **D** to **E1** should be more preferred than the route from **C** to **D3**.

On the other hand, in mechanism-I, the dehydration step from **E** to **F** may overcome another energy barrier, and its value may influence the prevalence between the two mechanisms, so the transition state of **TS-E** between **E** and **F-H<sub>2</sub>O** was also calculated by the same method of qst2 and basis of HF/6-31G\*, where **F-H<sub>2</sub>O** was first optimized under a constant C-OH<sub>2</sub> bond distance. The obtained enthalpy of **TS-E** is also listed in Table 1, and the geometric converting process from **E** to **F-H<sub>2</sub>O** through **TS-E** is shown in Fig. 5.



**Fig. 4.** Conversion processes from D to E1 and from C to D3 through transition states of TS-D and TS-C respectively



**Fig. 5.** Conversion process from **E** to **F-H<sub>2</sub>O** through transition states of **TS-E**

It can be seen from Table 1 that the enthalpy of **TS-E** is a little bit lower than that of **TS-D**, generally in similar level, so the route from **E** to **F** is not the determinative step in mechanism-I, and thus will not change the former estimation on the prevalence of the two mechanisms. Figure 6 shows the enthalpy changes along the reaction routes in the two mechanisms, and it can be clearly seen that the enthalpies of **TS-D** and **TS-E** are both lower than that of **TS-C+H<sub>2</sub>O**, indicating the greater stability and lower energy requirement in mechanism-I, so the route from **C** to **F** as shown in mechanism-I is more preferred than the newly deduced mechanism-II. Though the enthalpy difference between **TS-E** and **E**, i.e. the energy barrier, is higher than that between **TS-C** and **C**, the energy needed in the process from **E** to **TS-E** can be offered by the step from **TS-D** to **E**, so the net energy required in the route from **C** to **F** should be taken as the enthalpy difference between **TS-D** and **C**, which is lower than the energy required in the step from **C** to **TS-C**.

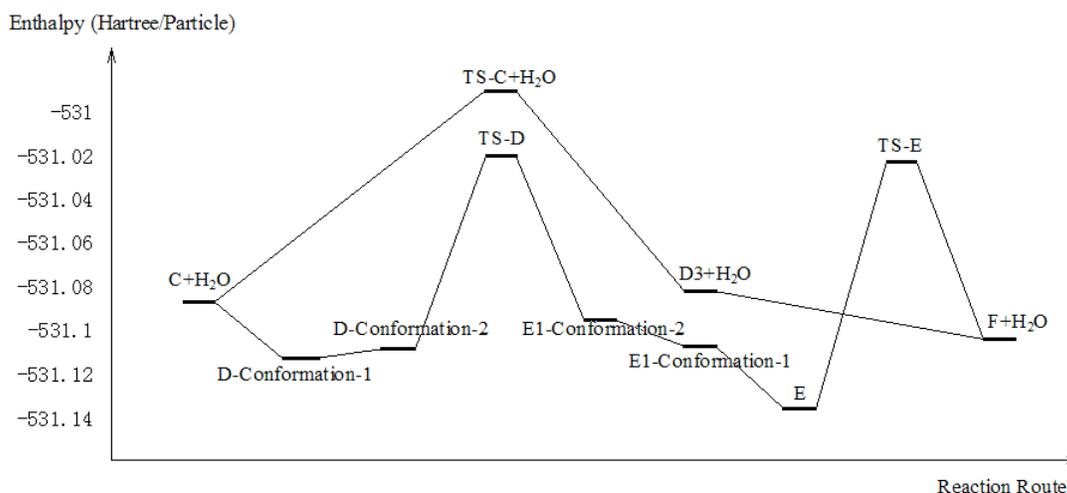


Fig. 6. Enthalpy changes along the reaction routes

## CONCLUSIONS

A more detailed reaction route to account for the formation of levulinic acid from 5-hydroxymethylfuran-2-carbaldehyde was deduced on the basis of the mechanism previously offered by Horvat et al. (1985). Another deduced reaction route between two intermediates within this mechanism was put forward, and the probabilities of the two mechanisms were compared based on the enthalpies of transition states, using Gaussian 03 software. It was found that the original mechanism in the conversion from the intermediate 2,3-dihydroxy-5-methyl-2,3-dihydro-furan-2-carbaldehyde (DMDFC) to 2,5-dioxo-hex-3-enal (DOHE), has a lower net energy barrier level, and should be more preferred than the newly deduced one. That is, DMDFC (**C**) is first protonized, followed by a proton shift process, and thereafter an OH<sup>-</sup> ion is added, forming the intermediate product of 2,3-dihydroxy-5-methyl-2,3-dihydro-furan-2-carbaldehyde (**D**); this intermediate (**D**) then is converted to 3,5-dihydroxy-2-oxo-hex-4-enal (**E1**) by an intramolec-

ular H-shift process; and finally the intermediate (**E1**) is further converted to the intended intermediate product DOHE (**F**) by two consecutive processes of isomerization and dehydration.

## ACKNOWLEDGMENTS

The authors are grateful for support by the National Natural Science Fund (No. 0202017127).

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Article submitted: December 16, 2010; Peer review completed: April 1, 2011; Revised version received and accepted: April 7, 2011; Published: April 8, 2011.