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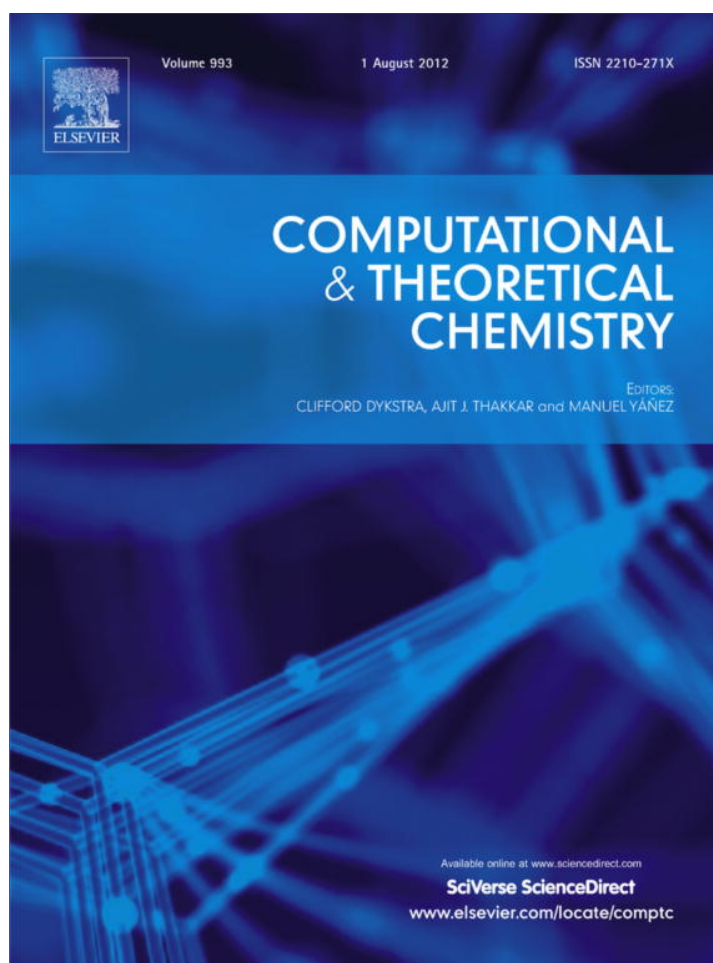**99** PUBLICATIONS **256** CITATIONS

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Quantum chemical calculations of the thermal isomerization of 2-methyl-4,5-dihydrofuran

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ABSTRACT

The mechanism for the thermal isomerization reactions of 2-methyl-4,5-dihydrofuran was investigated using quantum chemical calculations at B3LYP/6-31G(d,p), B3LYP/6-31++G(d,p), MPW1PW91/6-31G(d,p), MPW1PW91/6-31++G(d,p), and [PBE/6-31G(d,p), PBE/6-31++G(d,p)] levels of theory. It was found that 2-methyl-4,5-dihydrofuran isomerizes to acetylcyclopropane, and by a parallel reaction a slower isomerization to give 3-pentene-2-one. The acetylcyclopropane formation occurs through unimolecular electrocyclic mechanism. The 3-penten-2-one formation also takes place through electrocyclic mechanism, involving [1,2] hydrogen migration. The isomerization reaction of acetylcyclopropane to 3-penten-2-one occurs by step-wise mechanism, with the formation of an intermediate product 2-hydroxy-2,4-pentadiene, which subsequently isomerizes to the keto form, 3-penten-2-one. The step-wise acetylcyclopropane isomerization to 3-penten-2-one has lower energy of activation than the direct conversion of 2-methyl-4,5-dihydrofuran to 3-penten-2-one. Reasonable agreement was found between experimental and calculated energies of activation using B3PW91/6-311G(d,p) and MPW1PW91/6-311G(d,p) methods. Results suggest that both isomerization reactions pathways are possible under the experimental conditions reported. However, the lower energy of activation of the rate determining step of the step-wise mechanism favors this process over the single step mechanism.

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1. Introduction

The thermal reaction of the substrate 2-methyl-4,5-dihydrofuran, using the shock tube method at the temperature range of 800–1030 K, was found to give an irreversible isomerization to acetylcyclpropane, together at a low rate a direct isomerization to 3-pentene-2-one (reaction (1)) [1].
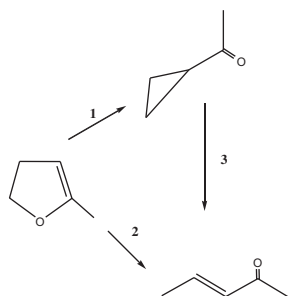
(1)

The Arrhenius expressions of the three processes described in reaction (1) were found as follows: 2-methyl-4,5-dihydrofuran to acetylcyclopropane (**Via 1**), $\log k_1$ (s^{-1}) = 15.4 − 237.6 kJ/mol $(2.303 \, RT)^{-1}$; 2-methyl-4,5-dihydrofuran to 3-penten-one (**Via 2**), $\log k_2$ (s^{-1}) = 15.7 − 266.0 kJ/mol $(2.303 \, RT)^{-1}$; acetylcyclopropane to 3-penten-2-one (**Via 3**), $\log k_3$ (s^{-1}) = 14.4 − (243.9) kJ/mol $(2.303 \, RT)^{-1}$. In spite of the sound experiments carried out in this work, the authors [1] could not suggest a rational mechanism of this isomerization process.

This interesting thermal isomerization of 2-methyl-4,5-dihydrofuran led us to inquire a reasonable mechanism of this process by examining the potential energy surface (PES) at DFT levels of theory. In this respect, we expect to obtain the kinetic and thermodynamic parameters for the theoretical reaction paths to contrast with the experimental parameters and propose a more likely mechanism. The estimations of the kinetics and thermodynamic parameters in the elucidation of this isomerization mechanism were followed as reported in previous theoretical calculations [2–5]. In the present work, we have studied the possible mechanism for 2-methyl-4,5-dihydrofuran thermal isomerization in the gas-phase, involving pericyclic reactions and leading to the observed reaction products. The proposed pathways are discussed contrasting the experimental kinetic and thermodynamic

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parameters. Even though many pericyclic reactions have been studied, to our knowledge the isomerization reaction mechanism of 2-methyl-4,5-dihydrofuran has not been reported. This work is aimed at understanding this isomerization reaction mechanism, to provide additional information on this interesting non-polar reaction type, which are possible in the gas-phase, where no solvent is involved, and help to understand other gas-phase processes.

2. Computational methods and models

The electronic structure calculations were carried out at the density functional theory (DFT). Becke's three-parameter formulation from functional Lee, Yang and Parr [B3LYP/6-31G(d,p), B3LYP/6-31++G(d,p) [6–8], Perdew–Wang 1991 correlation functional [MPW1PW91/6-31G(d,p), MPW1PW91/6-31++G(d,p)] [9], and Perdew, Burke, and Ernserhof [PBE/6-31G(d,p), PBE/6-31++G(d,p)] [10] have been used to elucidate a reasonable mechanism of the elimination kinetics of 2-methylbenzyl chloride in the gas phase. The calculations have been performed in Gaussian 03 [11]. The Berny analytical gradient optimization routines were used, with convergence on the density matrix was 10^{-9} atomic units, threshold value for maximum displacement 0.0018 Å, and maximum force of 0.00045 Hartree/Bohr. The nature of the stationary points was determined by using frequency calculations for the minimum energy structures and for the transition states. The quadratic synchronous transit (QST) protocol was used to locate the transition state (**TS**) structures. The identification of the **TS** structures was obtained through the normal-mode analysis by having a single imaginary frequency and the corresponding transition vector (TV). In order to confirm the transition state structures associating the reactant and products in the minimum energy path, Intrinsic Reaction Coordinate (IRC) calculations were made.

The thermodynamic values of zero-point vibrational energy (ZPVE), temperature corrections ($E(T)$) and absolute entropies ($S(T)$), were achieved from frequency calculations. Temperature corrections and absolute entropies were obtained considering ideal gas behavior from the harmonic frequencies and moments of inertia by standard methods [12] at average temperature and pressure values within the experimental range. Scaling factors for frequencies and zero point energies were cited from the literature [13,14].

3. Results and discussion

3.1. Mechanisms of the isomerization reaction

To explain the product formation in the isomerization of 2-methyl-4,5-dihydrofuran, e.g. acetylcyclopropane and 3-penten-2-one described on [reaction (1)], we have studied the possible mechanisms illustrated in Scheme 1.

At first site, one may assume that the thermal elimination of the substrate 2-methyl-4,5-dihydrofuran undergoes a cleavage at the oxygen atom, assisted by the H atom of the CH$_3$ group as in alkyl ethers, where the O atom is attached to a tertiary C atom [reaction (2)] [15]. However, this mechanistic consideration must be discarded since 2,4-dipenten-1-ol was not experimentally obtained as a final product.

$$(2)$$
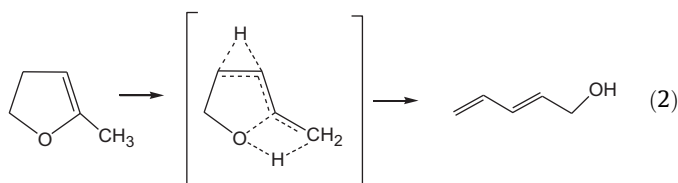
Because of the improbable reaction (2), it appears that in hydrogen competitions, the allylic H may be more labile than the H of the CH$_3$ group, and thus may assists the cleavage of the O atom for what it seems to be a more favorable a mechanism as depicted in reaction (3). This process leads to the formation of the final product 3-penten-2-one.

$$(3)$$
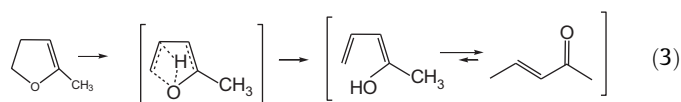
The proposed mechanism in Scheme 1, involves two pathways. First, **Via 1** considers the isomerization of 2-methyl-4,5-dihydrofuran to acetylcyclopropane (**P1**) through four-electron electrocyclic reaction mechanism. This reaction is thermally disallowed in suprafacial or disrotarory fashion, and should take place in antarafacial or conrotatory manner. **P1** continues to isomerize to an intermediate product, 2-hydroxy-2,4-pentadiene (**I**), which tautomerizes through thermally-allowed 1,5-hydrogen migration, to the keto form 3-penten-2-one (**P2**) under the reaction conditions. **Via 2** considers the direct isomerization of 2-methyl-4,5-dihydrofuran to 3-penten-2-one (**P2**) through electrocyclic reaction with 1,2-hydrogen migration. For each path the reactant and products were optimized prior to the QST search to locate the transition state, **TS**.

Calculated parameters from frequency calculations carried out on the optimized structures are shown in Table 1. Description of the transition state geometries is given in the following sections.

For **Via 1** mechanism, steps 1 and 2 have comparable energy of activation, with the first step leading to the formation of acetylcyclopropane being slightly more facile than the second step, by about 7 kJ/mol. The thermally-allowed tautomerization step, through **TS3**, occurs with a smaller barrier compared to steps 1 and 2, as expected. The calculated energy of activation, and consequently the enthalpy of activation of step 1, are close to the experimental values for B3PW91/6-31G(2d,2p), with 3.9 kJ/mol departure, and MPWPW91/6-311G(d,), 4.6 kJ/mol off the experimental value.

The mechanism in **Via 2** has a higher energy of activation than both steps 1 and 2 in **Via 1**. The calculated energy and enthalpy of activation of this process is very close to the experimental values at B3PW91/6-31G(2d,2p), MPW1PW91/6-31++G(d,p) and MPW1PW91/6-311G(d,p); within 0–1 kJ/mol.

Regarding calculated entropies of activation we found significant departure from experimental values in **Via 1** and **Via 2;** in general, calculated entropies of activation were less positive. Because of the presence of low-frequency modes, which are highly un-harmonic, we performed also anharmonic frequency calculations to determine the impact of the use of the harmonic approximation in the entropy calculations. The results revealed that the anharmonic contributions produced no significant change in the entropies of activation (Supplementary information, Table 1b). The differences observed when comparing to the experimental values of entropies of activations may be related to the method of experiment performed, e.g. the shock tube. For example, the entropy value of 32 J/K mol reported for step 1, **Via 1,** and 38 J/K mol for **Via 2,** suggest an ionic reaction as opposed to a molecular reaction in the gas phase.

3.2. Transition state and mechanisms

The optimized structure of the species involved in the reactions shown in Scheme 1, Via 1 and **Via 2,** are shown in Figs. 1–4. The transition state of step 1, **Via 1**, is four-centered cyclic structure (Fig. 1, **TS1** Scheme 2). The transition state geometry of step 2 is shown in Fig. 2, and **TS2** Scheme 2. The tautomerization step transition state **TS3** is a cyclic six-centered structure; shown in Fig. 3 and Scheme 2, and implies the hydrogen transfer from oxygen O$_3$
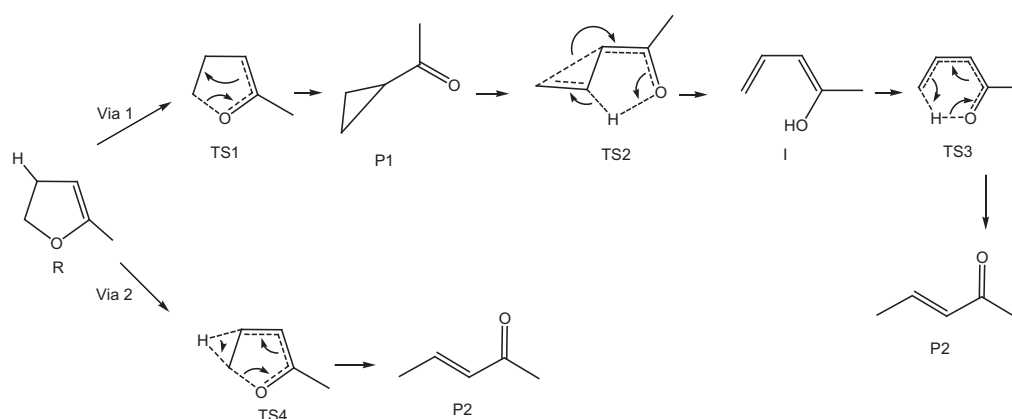
Scheme 1.

Table 1
Thermodynamic and Arrhenius parameters calculated for the isomerization of 2-methyl-4,5-dihydrofuran at 917.15 K.

Method	E_a (kJ/mol)	$\log A$ (s^{-1})	$\Delta H^{\neq}$ (kJ/mol)	$\Delta S^{\neq}$ (kJ/mol)	$\Delta G^{\neq}$ (kJ/mol)
Via 1/TS1					
Experimental	**237.6**	**15.4**	**230.1**	**32.2**	**200.6**
B3LYP/6-31++G(d,p)	224.5	14.2	216.9	8.4	209.2
B3PW91/6-31G(2d,2p)	241.6	14.0	233.9	6.3	228.2
B3PW91/6-311G(d,p)	233.6	14.2	226.0	8.5	218.2
MPW1PW91/6-31++G(d,p)	242.4	14.2	234.8	8.8	226.7
MPW1PW91/6-311G(d,p)	242.3	14.2	234.6	8.5	226.9
PBEPBE/6-31G(2d,2p)	212.7	14.2	205.1	10.0	196.0
Via 1/TS2					
Experimental	**243.9**	**14.4**	**236.3**	**13.1**	**224.3**
B3LYP/6-31++G(d,p)	244.2	13.5	236.6	−4.4	240.6
B3PW91/6-31G(2d,2p)	259.2	13.5	251.6	−3.8	255.1
B3PW91/6-311G(d,p)	256.2	13.4	248.6	−5.2	253.3
MPW1PW91/6-31++G(d,p)	263.4	13.4	255.7	−5.1	260.4
MPW1PW91/6-311G(d,p)	266.6	13.4	259.0	−5.9	264.4
PBEPBE/6-31G(2d,2p)	222.3	13.4	214.7	−4.1	218.4
Via 1/TS3					
B3LYP/6-31++G(d,p)	67.6	12.6	60.0	−21.3	79.3
B3PW91/6-31G(2d,2p)	59.6	12.7	52.0	−18.2	69.0
B3PW91/6-311G(d,p)	62.7	12.7	55.1	−19.5	73.0
MPW1PW91/6-31++G(d,p)	63.5	12.6	55.9	−20.8	75.0
MPW1PW91/6-311G(d,p)	65.1	12.7	57.5	−19.4	75.3
PBEPBE/6-31G(2d,2p)	43.1	12.8	35.4	−17.0	51.0
Via 2/TS4					
Experimental	**266.0**	**15.7**	**258.5**	**38.0**	**223.6**
B3LYP/6-31++G(d,p)	263.3	14.4	255.6	12.3	244.3
B3PW91/6-31G(2d,2p)	267.3	14.1	259.7	7.4	252.8
B3PW91/6-311G(d,p)	258.2	14.4	250.5	12.6	239.0
MPW1PW91/6-31++G(d,p)	267.1	14.3	259.5	12.1	248.3
MPW1PW91/6-311G(d,p)	266.1	14.2	258.5	9.8	248.1
PBEPBE/6-31G(2d,2p)	236.1	14.4	228.5	14.0	215.7

Experimental kinetic parameters were taken from Ref. [1], while the thermodynamic parameters have been estimated in this work.

to carbon C_2. The transition state of **Via 2, TS4,** shown in Fig. 4 and **TS4** Scheme 2, has a five-centered geometry.

Further description and analysis of the nature of the transition states and the stable species involved in these reactions, in terms of geometrical parameters, NBO charges and bond orders is given in the following sections.

Verification of the transition states in the reactions described in **Via 1** and **Via 2** was carried out by Intrinsic Reaction Coordinate (IRC) calculations, Figs. 5 and 6.

3.3. Geometrical parameters

Table 2 summarizes the geometrical parameters of reactant, transition states and products of the reactions **Via 1** and **Via 2**. For **Via 1,**

TS1, the most significant change is the increase in distance C_2–O_3, from 1.44 Å to 2.33 Å in the transition step indicating the breaking of this bond. The C_1–C_2 distance decreases from 1.54 Å to 1.44 Å, illustrating the change in bond order, while the distance C_2–C_5 shortens from 2.34 Å to 2.17 Å. The imaginary frequency is associated with a rocking motion mainly involving atoms C_2 and O_3 to open the cycle.

TS2 is characterized by a significant decrease in O_3–H_6 distance from 2.60 Å to 1.49 Å and an increase in H_6–C_1 distance from 1.08 Å to 1.23 Å in the transition state, indicating the hydrogen transfer to form the enol intermediate 2-hydroxy-2,4-pentadiene. The imaginary frequency is mainly associated with the hydrogen transfer from C_1 to O_3.

For the tautomerization of 2-hydroxy-2, 4-pentadiene to 3-penten-2-one, step 3, **TS3** demonstrates the transfer of the hydrogen
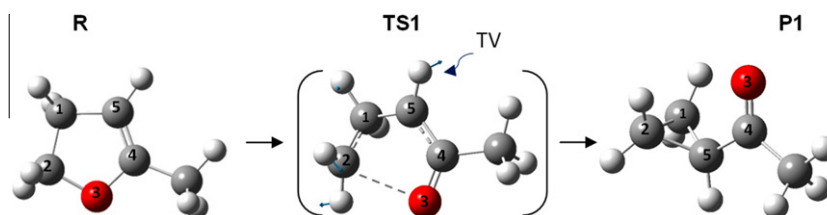
Fig. 1. Optimized structures for reactant **R**, transition state **TS1**, and product acetylcyclopropane **P1**, in the isomerization of 2-methyl-4,5-dihydrofuran at MPW1PW91/6-311G(d,p) level.
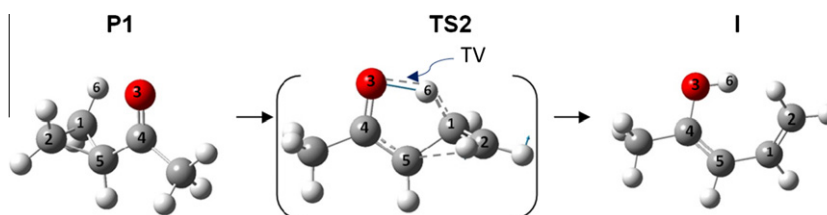

Fig. 2. Optimized structures for the product **P1**, transition state **TS2**, and intermediate **I**, in the isomerization of acetylcyclpropane to 2-hydroxy-2,4-pentadiene at MPW1PW91/6-311G(d,p) level.
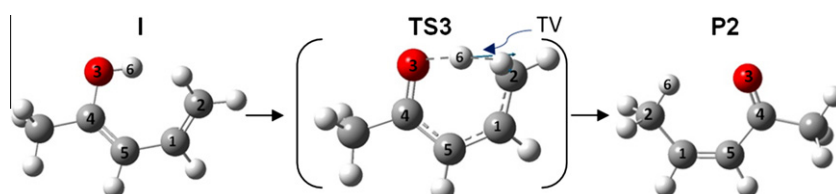

Fig. 3. Optimized structures for the intermediate **I,** transition state **TS3**, and product **P2,** in the tautomerization of 2-hydroxy-2,4-pentadiene to 3-pentene-2-one at MPW1PW91/6-311G(d,p) level.
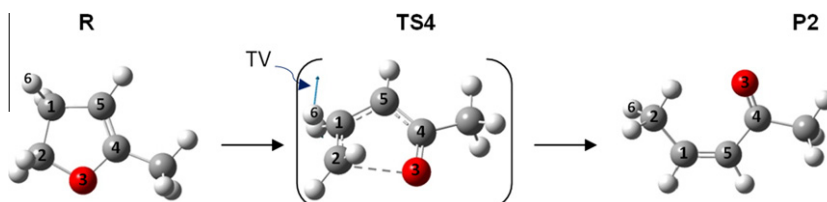
Fig. 4. Optimized structures for reactant **R**, transition state **TS4**, and product **P2**, in the isomerization of 2-methyl-4,5-dihydrofuran to 3-penten-2-one at MPW1PW91/6-311G(d,p) level.
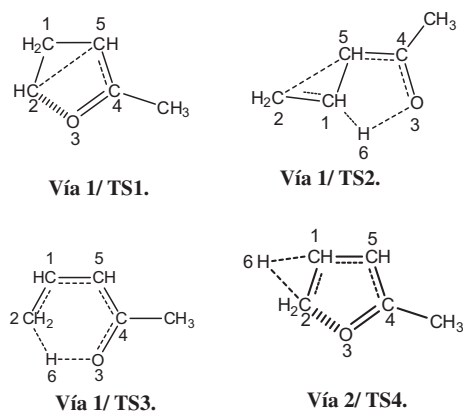
Scheme 2.

H_6, from O_3 to C_2, by the elongation of H_6–O_3 distance from 0.97 Å to 1.25 Å, and the decrease in C_2–H_6 distance from 2.28 Å to 1.38 Å in the transition state. The vibration illustrated by the imaginary frequency is mainly linked to the hydrogen transfer.

The mechanism in **Via 2** through **TS4** shows an important decrease in H_6–C_2 distance from 2.19 Å to 1.49 Å in the transition state, accompanied by an increase in C_1–H_6 distance from 1.09 Å to 1.23 Å in the transition state, together with a significant elongation of C_2–O_3 bond from 1.43 Å to 2.27 Å. The imaginary frequency vibration shows a rocking movement and the displacement of hydrogen between carbon C_3 and C_4.

3.4. NBO charges

Changes in electron density along the reaction coordinate can be described by NBO charges in the reactant, transition state and products. The NBO charges for the relevant atoms in the possible
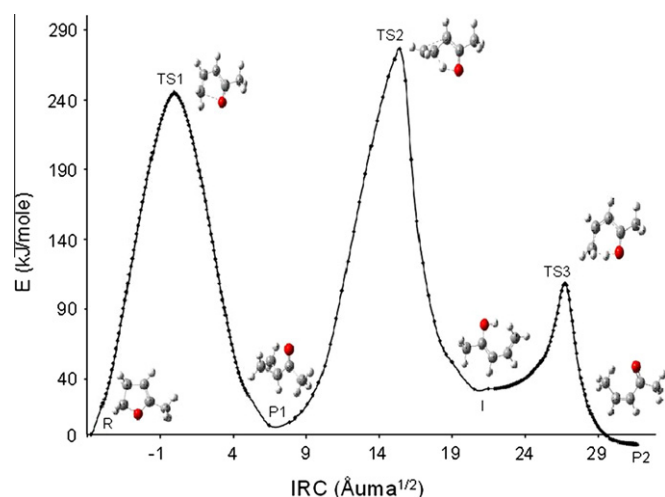
Fig. 5. Reaction profile for the isomerization of 2-methyl-4,5-dihydrofuran to 3-penten-2-one (**Via 1**) at MPW1PW91/6-311G(d,p) level of theory.
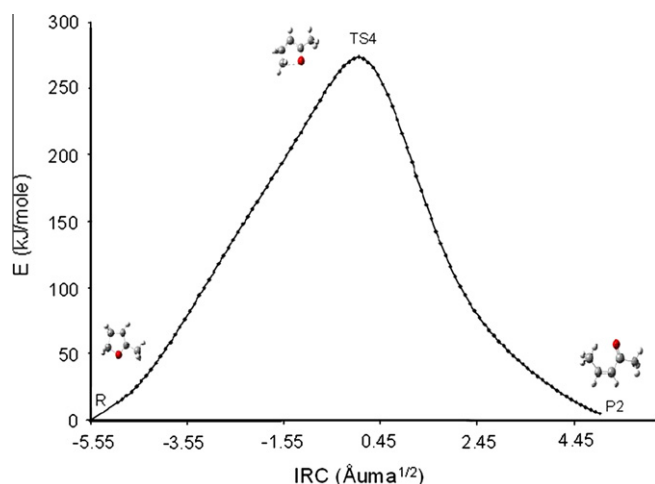
Fig. 6. Reaction profile for the isomerization of 2-methyl-4,5-dihydrofuran to 3-penten-2-one (**Via 2**) at MPW1PW91/6-311G(d,p) level of theory.

reaction pathways for the isomerization of 2-methyl-4,4-dihydrofuran are shown in Table 3. Atom numbers are shown in Scheme 2.

In the first step **Via 1,** leading to the formation of acetylcyclopropane, the transition state is characterized by augmentation on the negative charge at O_3; while C_4 becomes more positive. The negative charge increase at C_1 and C_2 suggest electron delocalization.

For step 2 **Via 1,** the **TS** is described by significant changes in electron density in all atoms involved in the reaction changes with noteworthy increase in negative charge at C_1 and decrease in electron density at C_2.

The tautomerization step in **Via 1,** step 3, is described by important decrease in negative charge at C_1 and increase in negative charge at C_2; changes in electron density at other atoms also occur, however in lesser amount.

In **Via 2** the **TS** shows important changes in electron density at all atoms involved in the reactions, implying important rearrangement if the molecular structure.

To obtain better description of the molecular changes in the reaction pathways, NBO bond order calculations were performed. The results are presented in the following section.

Table 2
Structural parameters of reactant (**R**), transition state (**TS**) and products (**P**) for the isomerization of 2-methyl-4,5-dihydrofuran (917.15 K) at MPW1PW91/6-311G(d,p) level of theory.

Via/TS	Interatomic lengths (Å)	R	TS	P
Via 1/TS1	C1–C2	1.536	1.439	1.482
	C2–O3	1.439	2.328	2.903
	O3–C4	1.366	1.249	1.210
	C4–C5	1.332	1.397	1.489
	C5–C1	1.505	1.519	1.515
	C2–C5	2.340	2.165	1.515
	Angles (degrees)			
	C1–C2–O3–C4	37.153	C4–C5–C1–C2	53.551
	C2–O3–C4–C5	−7.637	C5–C1–C2–O3	−42.492
	O3–C4–C5–C1	−24.038		
	Imaginary frequency (cm^{-1})		−587.501	
Via 1/TS2	C1–C2	1.482	1.391	1.340
	C2–C5	1.515	2.285	2.509
	C5–C4	1.489	1.393	1.347
	C4–O3	1.210	1.266	1.350
	O3–H6	2.596	1.492	0.966
	H6–C1	1.082	1.233	2.452
	Angles (degrees)			
	C1–C5–C4–O3	−5.762	O3–H6–C1–C5	−8.185
	C5–C4–O3–H6	1.400	H6–C1–C5–C4	6.694
	C4–O3–H6–C1	5.593		
	Imaginary frequency (cm^{-1})		−1123.32	
Via 1/TS3	C1–C2	1.340	1.408	1.488
	C2–H6	2.280	1.373	1.095
	H6–O3	0.966	1.246	2.238
	O3–C4	1.350	1.275	1.213
	C4–C5	1.347	1.405	1.483
	C5–C1	1.454	1.391	1.339
	Angles (degrees)			
	C1–C2–H6–O3	48.916	O3–C4–C5–C1	−12.801
	C2–H6–O3–C4	−43.351	C4–C5–C1–C2	22.406
	H6–O3–C4–C5	14.191	C5–C1–C2–H6	−27.532
	Imaginary frequency (cm^{-1})		−1645.15	
Via 2/TS4	H6–C2	2.187	1.485	1.095
	C2–O3	1.437	2.272	2.996
	O3–C4	1.366	1.255	1.213
	C4–C5	1.332	1.410	1.483
	C5–C1	1.505	1.425	1.339
	C1–C2	1.536	1.427	1.488
	C1–H6	1.093	1.233	2.123
	Angles (degrees)			
	C2–O3–C4–C5	−2.109	C6–C2–O3–C4	18.417
	O3–C4–C5–C1	−15.990	C5–C6–H6–C2	−105.862
	C4–C5–C1–C2	34.510	C1–H6–C2–O3	48.288
	C5–C1–C2–O3	−38.404		
	Imaginary frequency (cm^{-1})		−1164.37	

3.5. Bond order analysis

Further analysis of the changes in the reaction coordinates along the minimum energy pathways, was carried out using bonds orders of the reactant, **TS** and products [16–18]. Wiberg bond indexes [19] were computed using the natural bond orbital NBO program [20] implemented in Gaussian 03 W. Bond breaking and making process involved in the reaction mechanism are monitored by means of the Synchronicity (Sy) concept proposed by Moyano et al. [21] defined by the expression:

$$Sy = 1 - \left[\sum_{i=1}^{n} |\delta B_i - \delta B_{av}|/\delta B_{av} \right]/2n - 2$$

n is the number of bonds directly involved in the reaction.

The calculated bond index is B_i, and the relative variation of the bond index is obtained from:

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$$\delta B_i = [B_i^{\mathbf{TS}} - B_i^{\mathbf{R}}]/[B_i^{\mathbf{P}} - B_i^{\mathbf{R}}]$$

where the superscripts **R, TS, P,** represent reactant, transition state and product respectively.

The average value is calculated from:

$$\delta B_{ave} = 1/n \sum_{i=1}^{n} \delta B_i$$

The synchronicity parameter in concerted reactions varies from 1 for synchronic processes, to 0, for non-synchronous. Wiberg bonds indexes B_i, shown in Table 4, were calculated for the bonds undergoing changes in the reactions.

Table 3
NBO charges for reactant (**R**), transition state (**TS**) and products (**P**), at MPW1PW91/6-311G(d,p) level of theory.

Via/TS	Átom	R	TS	P
Via 1/TS1	C1	−0.430	−0.480	−0.367
	C2	−0.016	−0.075	−0.367
	O3	−0.552	−0.622	−0.578
	C4	0.345	0.463	0.593
	C5	−0.329	−0.359	−0.335
Via 1/TS2	C1	−0.367	−0.525	−0.190
	C2	−0.367	−0.116	−0.436
	O3	−0.578	−0.631	−0.685
	C4	0.593	0.442	0.403
	C5	−0.335	−0.349	−0.381
	H6	0.228	0.358	0.480
Via 1/TS3	C1	−0.190	−0.037	−0.055
	C2	−0.436	−0.693	−0.641
	O3	−0.685	−0.641	−0.567
	C4	0.403	0.502	0.557
	C5	−0.381	−0.406	−0.342
	H6	0.480	0.394	0.217
Via 2/TS4	H6	0.205	0.299	0.217
	C2	−0.017	−0.194	−0.641
	O3	−0.554	−0.632	−0.567
	C4	0.347	0.476	0.557
	C5	−0.330	−0.465	−0.342
	C1	−0.432	−0.341	−0.055

Table 4
Wiberg bond index of reactant (**R**), transition state (**TS**) and products (**P**) for the isomerization of 2-methyl-4,5-dihydrofuran (917.15 K) at MPW1PW91/6-311G(d,p) level of theory.

Via/TS	Bond	$B_i^{\mathbf{R}}$	$B_i^{\mathbf{TS}}$	$B_i^{\mathbf{P}}$	% E_v	Sy
Via 1/TS1	C2–O3	0.892	0.267	0.023	71.9	0.91
	O3–C4	0.983	1.477	1.775	62.3	
	C4–C5	1.786	1.345	1.017	57.4	
	C5–C2	0.009	0.417	0.944	43.7	
Via 1/TS2	C1–C2	1.024	1.386	1.881	42.26	0.86
	C1–H6	0.923	0.561	0.004	39.42	
	H6–O3	0.004	0.220	0.735	29.58	
	O3–C4	1.775	1.388	1.037	52.52	
	C4–C5	1.017	1.416	1.694	58.95	
	C5–C2	0.944	0.327	0.026	67.18	
Via 1/TS3	C1–C2	1.881	1.400	1.066	59.00	0.94
	C1–H6	0.004	0.427	0.926	45.91	
	H6–O3	0.735	0.353	0.000	52.08	
	O3–C4	1.037	1.354	1.755	44.09	
	C4–C5	1.694	1.355	1.054	53.03	
	C1–C5	1.117	1.432	1.834	43.96	
Via 2/TS4	H1–C6	0.9217	0.533	0.0049	42.40	0.80
	C6–C5	1.0241	1.1975	1.834	21.41	
	C5–C4	1.7859	1.3585	1.0544	58.43	
	C4–O3	0.9819	1.4539	1.7548	61.07	
	O3–C2	0.8915	0.2622	0.0067	71.12	
	C2–H1	0.0031	0.2998	0.9189	32.40	

While global synchronicity Sy is a general concept, analysis of bond order in the different reaction coordinates describe the extension to which any particular bond involved in the reaction is formed or broken in the **TS**. With this concept a reaction can be described more advanced in some reaction coordinates than others.

The reaction **Via 1,** step 1, is dominated by the breaking of C_2–O_3 bond, 72% in the **TS**, and the C_3–C_4 bond order change from single to double, 62%, other reaction coordinates show less progress. The Sy value of 0.91 suggests a moderate asynchronous process. The step 2 of **Via 1,** is more asynchronous than the preceding step 1; for **TS2** Sy = 0.86 with more progress in the breaking of C_5–C_2, 67% in the transition step.

The tautomerization step through **TS3**, is more synchronic, Sy = 0.94, showing an intermediate progress in several reaction coordinates, however, the C_1–C_2 bond order change form double to single bond is more advanced, 59% in **TS3**.

The mechanism **Via 2,** is more asynchronous, Sy = 0.80, and is dominated by the C_5–C_4 bond order change, from double to single bond.

4. Conclusions

In the present study we investigated the possible mechanisms for the isomerization of 2-methyl-4,5-dihydrofuran. We have considered two pathways. The stepwise mechanism, **Via 1,** involves the formation of an intermediate product, acetylcyclopropane, in four-electron electrocyclic reaction. The acetylcyclopropane latter decomposes to 2-hydroxy-2,4-pentadiene which tautomerizes to 3-penten-2-one in low-activation energy [1,5]-hydrogen migration process, as expected. Higher activation energy is observed for the thermally-disallowed suprafacial four-electron electrocyclic reaction; e.g. the reaction occurs in antarafacial fashion, requiring higher energy, as anticipated.

The alternate pathway, **Via 2,** is a single step concerted process, in which 2-methyl-4,5-dihydrofuran isomerizes to 3-penten-2-one; the mechanism involves electrocyclic rearrangement and [1,2]-hydrogen migration. This pathway has higher activation energy than the rate determining step in **Via 1,** consequently, both isomerization reaction pathways are possible; however, the lower energy of activation of the rate determining step of the step-wise mechanism favors the step-wise mechanism over the single step mechanism.

Theoretical calculations allowed to propose a reasonable mechanism for the isomerization reaction of 2-methyl-4,5-dihydrofuran in the gas-phase, between two proposed pathways. Pericyclic reactions are observed in the gas-phase where polar processes are hammered due to the lack of solvent to stabilize charged species. The "forbidden" electrocyclic reaction in the mechanism occurs with higher energy of activation, compared to the thermally allowed step, as anticipated. This study may help to improve the knowledge of this type of reaction in the gas-phase. The study was carried out using several density functional methods. Thermodynamic and Arrhenius parameters were calculated and compared with the experimental values. Reasonable agreement between calculated and experimental energies and enthalpies of activation was found using B3PW91/6-311G(d,p) and MPW1PW91/6-311G(d,p); nevertheless, deviation of the entropy of activation occurred, which are not attributed to the use of the harmonic approximation. Calculated geometrical parameters, NBO charges and bond orders allowed the characterization of the species involved in the reaction pathway; **Via 2** mechanism is more asynchronous than the steps involved in **Via 1**.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.comptc.2012.05.032.

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