# Correlation between the synchronicity and thermodynamic parameters based on Hammond-Leffler postulate in the decomposition reactions of cis-3,6-dicarboxyle-cyclohexa-1,4-diene and cyclohexa-1,4-diene

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**Abstract:** Decomposition of thecyclohexa-1,4-diene(1) and cis-3,6-dicarboxyle-cyclohexa-1,4-diene(2)to hydrogen molecule and their corresponding aromatic rings have been investigated at five different (300,400,500,600 and 700k) temperatures by means ofB3LYP and M06-2X methods with the 6-311+G** basis set on all atoms and natural bond orbital (NBO) interpretations.The rate constants fitted the Arrhenius equation.Two levels of theory showed that the calculated Gibbs free energy different between the transition and ground state structures ($\Delta G^{\ddagger}$) decrease from compound 1 to compound 2.the variation of the calculated$\Delta G^{\ddagger}$ values can justified by the decreaseof the advancement of transition state structures ($\delta B_{av}$)from compound 1 to 2 .Therefor the advancements of the transition state structures ($\delta B_{av}$)exothermic characters$\Delta[G_{product} - G_{react}]$associated withHammond-Leffler postulate.

## Introduction

The thermal decomposition ofcyclohexa-1,4-dienes(1,4 CHDN) proceed by molecular elimination of hydrogen that can be rationalized on the basis of Hoffman-Woodward rules[6]. Theoretical calculations have fairly consistently predicated a planar ($D_{2h}$) structure for 1,4CHDN. While minimal at the Hartree-Fock level have predicted a bout conformation, complete geometry optimization at the same level of the theory leads to a planar structure.All levels of theory agree with the wealth of experimental and theoretical information in predicting a planar conformationof the carbon framework in 1,4CHDN.
A brief investigation of the thermal decomposition of cyclohexa-1,4-dienes from 300 to 700 k, showed the reaction to be first order and predominantly homogenous [1-4].

Page and Coworkers performed ab initio multiconfiguration self-consistent field(MCSCF) was functions with 6-311G**basis sets to investigate the potential energy surface of thedecomposition reaction of compound **1** to benzene and hydrogen molecule [5].The result obtained by Page and Coworkerswell agrees with the suggestion of Cromwell andco-workers [4]. Although there are published experimental [1-4] and theoretical [5] data about the potential energy surfaces of the thermal decomposition reaction of cyclohexa-1,4-diene (**1**) to benzene and hydrogen molecule. There are no published in formation about the Synchronicities indices and so correlation between the advancements of the transition state structures ($\delta B_{av}$) and thermodynamic parameters[7-11].

The kinetic parameters activation energy($E_a$) the temperature dependent rate constant k(t) and Arrhenius(A factor) of the thermal decomposition reactions of compound 1 and 2 to hydrogen molecules

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and their corresponding aromatic compounds were calculated using the classical transition state theory(TST)[12-13].

## Results and discussion

### 1-*Thermodynamic parameters:*

The obtained Gibbs free energy, enthalpy and entropy differences (i.e, ΔG, ΔH and ΔS) for the ground, TSand product structures of the hydrogen molecule eliminations reactions of compounds 1and 4,from theB3LYP/6-311+G** and M06-2X/6-311+G** levels of theory in (**Table 2-6**). The

calculated Gibbs free energy differences between the ground and TS structures($\Delta G^{\ddagger}$)at five different temperatures (300, 400, 500, 600 and 700 K )decrease from compound **1** to compound **2**.TheGibbs energy profile for the thermal decomposition process of cyclohexa-1,4-dienes at 300 k, is presented in Scheme **1** and ΔG values of hydrogen molecule elimination reactions increase of compounds **1** to**2**.Accordinglythe exothermicity of the hydrogen molecule elimination reaction increase going from compound **1** to **2**.



Compound 1 ($\delta B_{av} = 0.4582$)        Compound 2 ($\delta B_{av} = 0.4215$)

X = H (1), COH (2*)*
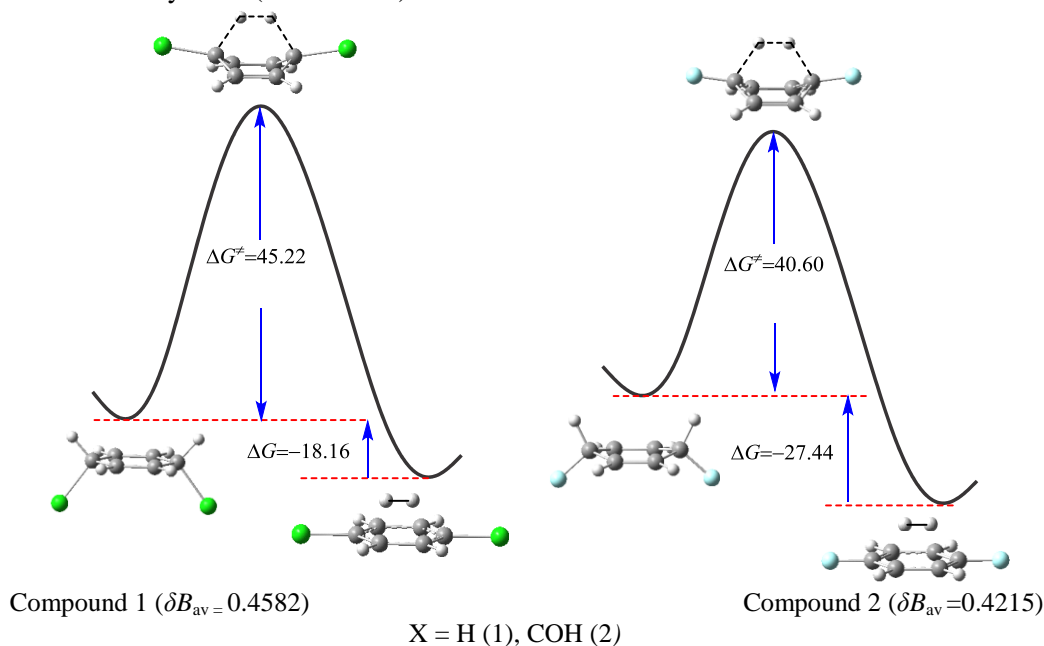
**Scheme 1:** B3LYP/6-311+G** calculated comparative potential energy profiles of the hydrogen molecule elimination reactions of compounds 1 and 2in connection with the Hammond-Leffler postulate. $\Delta G$, $\Delta G^{\ddagger}$ and $\delta B_{av}$ values are in kcal mol$^{-1}$

### 2-*Kinetic parameters:*

The classical transition state theory (*TST*) has been used to estimate the kinetic parameters of the hydrogen molecule elimination reactions of compounds **1**and **2**[12-13]. In order to estimate the temperature dependent rate constant [$k$(T)] of hydrogen molecule elimination reactions of compounds 1and 2, as expressed by the following relation as "Eyring-Polanyi equation (eq. 1):

$$k(T) = \frac{k_B T}{h} e^{\frac{-\Delta G^{\neq}(T)}{RT}}$$        (eq. 1)

where $k_B$, $R$ and $h$ are the Boltzmann constant, the Planck constantthe universal gas constant and, respectively, and the transmission coefficient wasassumed equal to unity. Based the reported experimental data, the hydrogen molecule elimination reaction of compound **1** occurs at 600 K [1-3]. Accordingly, we calculated the temperature-dependent rate constants [$k$(T)] of the hydrogen molecule elimination reactions of compounds **1**and **2**at five different temperatures (300, 400, 500, 600 and 700 K. All used methods in this work showed that the temperature-dependent rate constants [$k$(T)] of the hydrogen molecule elimination reaction of compoundthecis-3,6-dicarboxyle-cyclohexa-1,4-diene(2)is greater than compound cyclohexa-1,4-

diene(1) (**Tables 7-8**). Based on the results obtained, the rate constants of the hydrogen molecule elimination reactions of compounds **1**and **2**at 700 K are much greater than those values at the ambient temperature.

The unimolecular reactions ofthe importanceArrhenius *A* factors may be used to investigate the reality of the potential energy surfaces. The*A* factor valuesis acceptable within the range of $10^{11.5}$-$10^{14.5}$ sec$^{-1}$ for the unimolecular reactions [25].In order to estimate the magnitudes of the Arrhenius *A* factors of the hydrogen molecule elimination reactions of compounds **1**and **2**, we used the transition state theory (*TST*). The activation energy ($E_a$) and the Arrhenius *A* factors of the hydrogen molecule elimination reactions of compounds 1and 2have been calculated by the following equations, eqs. 2 and 3,respectively, derived from the TST theory:

$E_a = \Delta H^{\neq}(T) + RT$     (eq. 2)

$$A = \frac{ek_BT}{h} e^{\frac{\Delta S^{\neq}(T)}{R}}$$     (eq. 3)

The activation energy ($E_a$) for the hydrogen molecule elimination reactions of compounds **1**and **2**follow their corresponding activation Gibbs free energies. Also, the Arrhenius *A* factors of the hydrogen molecule elimination reactions of compounds 1and 2arearound $10^{12}$ that are within the range of $10^{11.5}$-$10^{14.5}$ sec$^{-1}$ (the acceptable values for the unimolecular reactions (table 7,8).

3-*The synchronicities and the advancements of the transition states ($\delta B_{av}$) of the hydrogen molecule elimination reactions of compounds 1and 2:*

In order to assess the applicability ofHammond-Leffler postulate in the unimolecular hydrogen molecule elimination reactions of compounds 1and 2, we examined their synchronicity indices by calculating the bond orders [Wiberg bond indices] of the ground states, transition states and products [7-11].

The synchronicity index (Sy) of the unimolecular hydrogen molecule elimination reactions of compounds 1and 2were examined to explore the nature and mechanisms of these reactions.To avoid the subjective aspect associated with the geometrical analysis of the TS, the reaction has been followed by means of the Wiberg bond indices $B_i$.The bond index between two atoms is a measure of the bond order , and hence, of the bond strength between these two atoms: thus if the evolution of the bond indices corresponding to the bonds being made or broken in a chemical

reaction is analyzed along the reaction path,a very precise picture of the timing and extent of the bond breaking and bond-forming processesat every point can be achieved.The synchronicity (sy) value of a reaction (eq. 4)can be obtained from it's a synchronicity index:

$Sy = 1 - ASy$     (eq. 4)

Where*ASy* is the asynchronicity (eq. 5):

$$ASy = \left(\frac{1}{2n-2}\right) \sum_{i=1}^{n} \frac{|\delta B_i - \delta B_{av}|}{\delta B_{av}}$$     (eq. 6)

where*n* is the bonds number involved in the reaction. $\delta B_i$ is the relative variation of the bond index for every bond (eq. 7) that is involved at the transition state (*TS*) structure in a chemical reaction:

$$\delta B_i = \frac{B_i^{TS} - B_i^R}{B_i^P - B_i^R}$$     (eq. 7)

TheB3LYP/6-311+G** and M06-2X/6-311+G** levels of theory usedin this work revealed that the lengthening of the $C_3$-$H_8$ and $C_6$-$H_{10}$ bonds with the initial migration of the $H_8$ and $H_{10}$atoms from $C_3$ and $C_6$and their bonding together ($H_8$-$H_{10}$), can be seen as the driving force for the reaction.:(Scheme **2**)
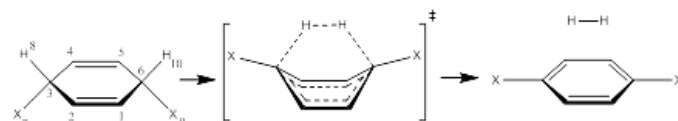


X = H (1), COH (2*)*
**Scheme 2**: Proposed mechanism for the thermal decompositioncyclohexane of compounds 1and 2

The degree of advancement of the transition state structures along the reaction paths could be estimated from the calculated $\delta B_i$ values. $\delta B_{av}$ is the average value (eq. 8) and is defined as:

$$\delta B_{av} = \frac{1}{n}\sum_{i=1}^{n} \delta B_i$$     (eq. 8)

The calculated bond orders (Wiberg bond indices, *WBI*), $\delta B_i$,$\delta B_{av}$, *ASy* and *Sy* values are given in Table **1**. Synchronicities vary between 0 and 1, which is the case when all of the bonds implicated in the reaction center have broken or formed at exactly the same extent in the TS. TheSY value calculated for the reaction studied is shown in table 1. Calculated synchronicity values (sy) for compound 1 and 2are 0.95 and 0.94, respectively. Calculated synchronicity values are very high, indicating that the mechanism is

**Table1.** NBO-B3LYP/6-311+G** bond orders (Wiberg Bond Index, WBI), $\delta B$ for the ground states, transition states and products of compounds 1 and 2 and also asynchronicity (Asy) and Synchronicity values for their hydrogen molecule elimination reactions.

| | 1 | | | 2 | | |
|---|---|---|---|---|---|---|
| | *GS* | *TS* | *P* | *GS* | *TS* | *P* |
| ***WBI*** | | | | | | |
| C1-C2 | 1.9229 | 1.6964 | 1.4380 | 1.006 | 1.1452 | 1.3625 |
| C2-C3 | 1.0340 | 1.2026 | 1.4380 | 1.9148 | 1.7349 | 1.4644 |
| C3-C4 | 1.0340 | 1.2026 | 1.4380 | 1.006 | 1.1466 | 1.3679 |
| C4-C5 | 1.9229 | 1.6964 | 1.4380 | 1.0059 | 1.1452 | 1.3625 |
| C5 –C6 | 1.0340 | 1.2026 | 1.4380 | 1.9220 | 1.7349 | 1.1644 |
| C6 –C1 | 1.0340 | 1.2026 | 1.4380 | 1.0128 | 1.1466 | 1.3679 |
| C3–H8 | 0.8986 | 0.4204 | 0.000 | 0.8597 | 0.4248 | 0.000 |
| C6-H10 | 0.8996 | 0.4204 | 0.000 | 0.8843 | 0.4248 | 0.000 |
| H8-H10 | 0.0035 | 0.4576 | 1.000 | 0.0027 | 0.4194 | 1.000 |
| $\delta B_i$ | | | | | | |
| $\delta B_{iC1\text{-}C2}$ | | 0.4671 | | | 0.3877 | |
| $\delta B_{iC2\text{-}C3}$ | | 0.4173 | | | 0.3994 | |
| $\delta B_{iC3\text{-}C4}$ | | 0.4173 | | | 0.3879 | |
| $\delta B_{iC4\text{-}C5}$ | | 0.4671 | | | 0.3906 | |
| $\delta B_{iC5\,–C6}$ | | 0.4173 | | | 0.4088 | |
| $\delta B_{iC6\,–C1}$ | | 0.4173 | | | 0.3767 | |
| $\delta B_{iC3–H8}$ | | 0.5326 | | | 0.5058 | |
| $\delta B_{iC6–H10}$ | | 0.5326 | | | 0.5196 | |
| $\delta B_{iH8–H10}$ | | 0.4556 | | | 0.4178 | |
| $\delta B_{av}$ | | 0.4582 | | | 0.4215 | |
| *ASy* | | 0.0421 | | | 0.0539 | |
| *Sy* | | 0.9559 | | | 0.9460 | |

**Table2**. B3LYP/6-311+G**andM06-2x/6-311+G** calculated thermodynamic parameters [$\Delta H$, $\Delta G$ (in kcal mol$^{-1}$),$\Delta S$ (in cal mol$^{-1}$ K$^{-1}$)] at 300K for the ground and transition states structures of the thermal decomposition reactions of compounds 1and 2.

| | B3LYP/6-311+G** | | | M06-2X/6-311+G** | | |
|---|---|---|---|---|---|---|
| | $\Delta H^a$ | $\Delta S^a$ | $\Delta G^a$ | $\Delta H^a$ | $\Delta S^a$ | $\Delta G^a$ |
| Geometries | | | | | | |
| **1**-*GS* | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| **1**-*TS* | 43.94 | -4.27 | 45.22 | 44.40 | -4.47 | 45.86 |
| | (43.8±0.4)$^a$ | | | | | |
| **1**-*Ps* | -10.14 | 26.91 | -18.16 | -6.36 | 25.31 | -13.91 |
| | (-6.5)$^a$ | | | | | |
| **2**-*GS* | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| **2**-*TS* | 38.70 | - 6.37 | 40.60 | 40.98 | -6.20 | 42.83 |
| **2**-*Ps* | -26.04 | 24.31 | -27.44 | -13.58 | 24.52 | -20.93 |

$^a$From mass spectrometry, UV spectroscopy, gas chromatography and pressure measurements, Ref. 2.

**Table 3**:.B3LYP/6-311+G**and M06-2x/6-311+G**calculated thermodynamic parameters [$\Delta H$, $\Delta G$ (in kcal mol$^{-1}$),$\Delta S$ (in cal mol$^{-1}$ K$^{-1}$)] at 400K for the ground and transition states structures of the hydrogen molecule elimination reactions of compounds 1and 2.

| | 400K | | | | | |
|---|---|---|---|---|---|---|
| | B3LYP/6-311+G** | | | M06-2X/6-311+G** | | |
| | $\Delta H^a$ | $\Delta S^a$ | $\Delta G^a$ | $\Delta H^a$ | $\Delta S^a$ | $\Delta G^a$ |
| Geometries | | | | | | |
| **1**-*GS* | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| **1**-*TS* | 43.80 | -4.718 | 45.68 | 44.38 | -4.91 | 46.34 |
| **1**-*Ps* | -9.76 | 28.01 | -20.97 | -5.79 | 26.39 | -16.54 |
| **2**-*GS* | 0.000 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| **2**-*TS* | 38.16 | -6.62 | 41.26 | 40.90 | -6.46 | 43.48 |
| **2**-*Ps* | -19.80 | 25.41 | -29.98 | -13.21 | 25.69 | -23.46 |

**Table 4**:B3LYP/6-311+G**andM06-2x/6-311+G**calculated thermodynamic parameters [$\Delta H$, $\Delta G$ (in kcal mol$^{-1}$),$\Delta S$ (in cal mol$^{-1}$ K$^{-1}$)] at 500K for the ground and transition states structures of the hydrogen molecule elimination reactions of compounds 1and 2.

| | 500K | | | | | |
|---|---|---|---|---|---|---|
| | B3LYP/6-311+G** | | | M06-2X/6-311+G** | | |
| | $\Delta H^a$ | $\Delta S^a$ | $\Delta G^a$ | $\Delta H^a$ | $\Delta S^a$ | $\Delta G^a$ |
| Geometries | | | | | | |
| **1**-*GS* | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| **1**-*TS* | 43.73 | -4.85 | 45.78 | 44.32 | -5.046 | 46.84 |
| **1**-*Ps* | -5.97 | 26.39 | -16.54 | -5.69 | 27.06 | -19.23 |
| **2**-*GS* | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| **2**-*TS* | 38.58 | -6.70 | 41.93 | 40.58 | -6.56 | 44.13 |
| **2**-*Ps* | -19.52 | 26.07 | -32.56 | -12.93 | 26.34 | -26.10 |

**Table 5**. B3LYP/6-311+G**andM06-2x/6-311+G**andcalculated thermodynamic parameters [$\Delta H$, $\Delta G$ (in kcal mol$^{-1}$),$\Delta S$ (in cal mol$^{-1}$ K$^{-1}$)] at 600K for the ground and transition states structures of the hydrogen molecule elimination reactions of compounds 1and 2.

| | 600K | | | | | |
|---|---|---|---|---|---|---|
| | B3LYP/6-311+G** | | | M06-2X/6-311+G** | | |
| | $\Delta H^a$ | $\Delta S^a$ | $\Delta G^a$ | $\Delta H^a$ | $\Delta S^a$ | $\Delta G^a$ |
| Geometries | | | | | | |
| **1**-*GS* | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| **1**-*TS* | 43.73 | -4.86 | 46.64 | 44.32 | -5.04 | 46.90 |
| **1**-*Ps* | -9.23 | 29.09 | -26.70 | -5.47 | -21.95 | 27.47 |
| **2**-*GS* | 0.000 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| **2**-*TS* | 38.58 | -6.70 | 42.60 | 40.85 | -6.57 | 44.79 |
| **2**-*Ps* | -19.33 | 26.42 | -35.21 | -12.73 | 26.70 | -28.76 |

**Table 6**. B3LYP/6-311+G** and  M06-2x/6-311+G**calculated thermodynamic parameters [$\Delta H$, $\Delta G$ (in kcal mol$^{-1}$),$\Delta S$ (in cal mol$^{-1}$ K$^{-1}$)] at 700K for the ground and transition states structures of the hydrogen molecule elimination reactions of compounds 1and 2.

| | 700K | | | | | |
|---|---|---|---|---|---|---|
| | B3LYP/6-311+G** | | | M06-2X/6-311+G** | | |
| | $\Delta H^a$ | $\Delta S^a$ | $\Delta G^a$ | $\Delta H^a$ | $\Delta S^a$ | $\Delta G^a$ |

| Geometries | | | | | | |
|---|---|---|---|---|---|---|
| **1**-*GS* | 0.00 | 0.00 | 0..00 | 0.00 | 0.00 | 0.00 |
| **1**-*TS* | 43.76 | -4.821 | 47.13 | 44.35 | -4.973 | 47.85 |
| **1**-*Ps* | -9.08 | 29.33 | -29.62 | -5.32 | -24.72 | 27.70 |
| | | | | | | |
| **2**-*GS* | 0.000 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| **2**-*TS* | 38.60 | -6.67 | 43.27 | 40.86 | -6.55 | 45.45 |
| **2**-*Ps* | -19.22 | 26.60 | -37.84 | -12.61 | 26.89 | -31.44 |

**Table 7.** B3LYP/6-311+G** calculated rate constants (in $s^{-1}$), Arrhenius A factors and activation energies of the hydrogen molecule elimination reactions of compounds 1and 2at 300, 400, 500,600 and 700 K.

| | 300 K | | | 400 K | | | 500 K | | |
|---|---|---|---|---|---|---|---|---|---|
| | $E_a$ | A | $k$ | $E_a$ | A | $k$ | $E_a$ | A | $k$ |
| **1**-*GS*→[*TS*]$^{\neq}$→**1**-*P* | 44.53 | $1.98\times10^{12}$ | $3.3410^{-21}$ | 44.59 | $2.136\times10^{12}$ | $7.44\times10^{-13}$ | 44.72 | $2.459\times10^{12}$ | $8.60\times10^{-8}$ |
| **2**-*GS*→[*TS*]$^{\neq}$→**2**-*P* | 39.29 | $6.88\times10^{11}$ | $8.32\times10^{-18}$ | 38.95 | $8.15\times10^{11}$ | $1.97\times10^{-10}$ | 39.57 | $9.53\times10^{11}$ | $4.1\times10^{-6}$ |

| | 600 K | | | 700 K | | |
|---|---|---|---|---|---|---|
| | $E_a$ | A | $k$ | $E_a$ | A | $k$ |
| **1**-*GS*→[*TS*]$^{\neq}$→**1**-*P* | 44.91 | $2.98\times10^{12}$ | $8.53\times10^{-5}$ | 45.14 | $3.54\times10^{12}$ | $2.1\times10^{-2}$ |
| **2**-*GS*→[*TS*]$^{\neq}$→**2**-*P* | 39.76 | $1.17\times10^{12}$ | $3.33\times10^{-3}$ | 39.98 | $1.39\times10^{12}$ | $4.0\times10^{-1}$ |

**Table 8.** M0X-2X/6-311+G** calculated rate constants (in $s^{-1}$), Arrhenius A factors and activation energies of the hydrogen molecule elimination reactions of compounds 1and 2at 300, 400, 500,600 and 700 K.

| | 300 K | | | 400 K | | | 500 K | | |
|---|---|---|---|---|---|---|---|---|---|
| | $E_a$ | A | $k$ | $E_a$ | A | $k$ | $E_a$ | A | $k$ |
| **1**-*GS*→[*TS*]$^{\neq}$→**1**-*P* | 44.99 | $1.79\times10^{12}$ | $1.12\times10^{-21}$ | 45.17 | $1.93\times10^{12}$ | $3.23\times10^{-13}$ | 45.31 | $2.25\times10^{12}$ | $2.95\times10^{-8}$ |
| **2**-*GS*→[*TS*]$^{\neq}$→**2**-*P* | 41.57 | $1.72\times10^{13}$ | $1.91\times10^{-19}$ | 41.69 | $8.77\times10^{11}$ | $1.19\times10^{-11}$ | 41.57 | $1.04\times10^{12}$ | $4.54\times10^{-7}$ |

| | 600 K | | | 700 K | | |
|---|---|---|---|---|---|---|
| | $E_a$ | A | $k$ | $E_a$ | A | $k$ |
| **1**-*GS*→[*TS*]$^{\neq}$→**1**-*P* | 45.50 | $2.71\times10^{12}$ | $6.84\times10^{-5}$ | 45.73 | $3.29\times10^{12}$ | $1.26\times10^{-2}$ |
| **2**-*GS*→[*TS*]$^{\neq}$→**2**-*P* | 41.76 | $1.25\times1\ 0^{12}$ | $5.24\times10^{-4}$ | 42.24 | $1.47\times10^{12}$ | $7.7\times10^{-2}$ |

correspond to a concerted and synchronous process. But there is no significant differentbetween compounds 1 and 2.

The unimolecular hydrogen molecule elimination reaction of compounds1and 2are exothermic, the shift of its transition state structure toward the reactant is expectable and the advancement of its transition state ($\delta B_{av}$) confirmed this expectation. Based on the results obtained, the exothermicity of the hydrogen molecule elimination reaction increase going from compound **1**($\Delta G$=*-18.16)* to compound **2**($\Delta G$=-27.44)(Scheme **2**). Therefore, one may expect the shifts of the transition states structures of the hydrogen molecule elimination reactions of compounds 1and2 toward their reactants,that the results of this work can be confirm this expectation. Surprisingly, $\delta B_{av}$ values of the hydrogen molecule elimination reactions decrease going from compound **1**($\delta B_{av}$=0.4582)to compound **2**($\delta B_{av}$=0.4215)and so their corresponding barrier heights decreasegoing from compound **1** to compound **2**(Scheme **2**). Accordingly, the variations between the advancements of the transition states ($\delta B_{av}$) and $\Delta G$ of compounds 1and 2agree with Hammond-Leffler postulate. (Scheme **2**).

## Conclusion

The B3LYP/6-311+G** and M06-2X/6-311+G** calculation reported above and NBOinterpretationprovideda reasonable image from energetic, bonding andmechanismof view on the thermal decomposition reactions (the hydrogen molecule elimination reactions) compounds 1and 2.The decrease of the potential energy surface barrier heights going from compound 1 to 2,well agreement withadvancements of the transition states ($\delta B_{av}$).The hydrogen molecule elimination reaction of compound 1 and 2are exothermic. The exothermic character of the hydrogen molecule elimination reactions increases from compound **1** to compound **2**. One may expect that the advancements of the transition state structures ($\delta B_{av}$) may increase with the decrease of their corresponding exothermic characters,accordingly this expectation observed for the hydrogen molecule elimination reactions of compounds 1 and 2. Based on the results obtained, $\delta B_{av}$ values of the hydrogen molecule elimination reactions decrease going from compound **1** to compound **2,**therefordecrease their corresponding barrier heights.Accordinglythe advancements of the transition state structures ($\delta B_{av}$) associated with exothermic characters ($\Delta G$). Revealingthat the hydrogen molecule elimination

reactions of compounds 1 and 2 obey the Hammond-Leffler postulate.

## Computational details

The NBO-B3LYP/6-311+G**(natural bond orbital interpretation)with the 5.G program was performed to investigate the bond orders (Wiberg bond indices, *WBIs*) of the ground states, transition states and products ofthe unimolecular hydrogen molecule elimination reactions ofcompounds 1and 2 [24].Electronic energies and thermodynamic functions were calculated by means of theMinnesota hybrid meta exchange-correlation functional (M06-2X) [14] and Becke, three-parameter, Lee-Yang-Parr) exchange-correlation functional (B3LYP) [15-17],theory based methods with 6-311+G** [18-21] basis set on all atoms with the GAMESS US package of programs [22,14].

The classical transition state theory (*TST*) has been used to estimate the kinetic parameters of the hydrogen molecule elimination reactions of compounds 1and 2[12-13]. The Kinetic parameters for the reaction studied have been calculated at the five temperatures, by means of ab initio molecular orbital theory (B3LYP/6-311+G**//M06-2X/6-311+G**).

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