Justification on cyclopropene to propyne isomerization pathway based on vibrational calculations

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Abstract. We report a density-functional coupled with vibrational calculation on justifying the isomerization pathway of cyclopropene to propyne. The idea is to present the pathway in energy level diagram which the transition state is ensured by tracking a particular mode that supports the cyclic bond breaking and triple bond formation to occur. This mode decreases along the pathway and disappears at the transition state. To verify the designed pathway, the activation energy of the isomerization is used to find the rate constant with respect to experimental data at 500 K and 700 K by using transition state theory (TST). At those temperatures, TST predicts the rate constant at the same order of magnitude with the experimental result. It shows that the trend between calculation and experimental data is qualitatively in a good agreement, which implies that the designed pathway is justified. Furthermore, this study can be used as a guide if one needs to construct an isomerization pathway.

1. Introduction

An isomerization is the simplest chemical reaction. It involves only one molecule; hence, it is called a unimolecular reaction. Kinetically, it is a first-order reaction; consequently, the unit of its rate constant is 1/sec [1]. In most cases, isomerizations can occur in the gas phase and do not require a catalyst [2,3]. Even though it is simple, the mechanism of isomerization is not always straightforward. An isomerization commonly requires energy from the heat to begin. However, it not always the case, such as in isomerization of trans-HCOH to formaldehyde [4]. In this case, the isomerization occurs even without enough heat (at very low temperature, 11 K). The computational study revealed that the isomerization happens via quantum tunneling [5,6]. Therefore, experimental and computational studies are required to understand the isomerization mechanism.

One of the interesting isomerization to study computationally is cyclopropene to propyne. The reason is because this isomerization involves a C-C cyclic bond breaking and a C-C triple bond formation. The bond breaking and formation, in this case, hardly occur because of quantum tunneling, such as the case of trans-HCOH isomerization. Therefore, the isomerization is mostly due to the heat. Consequently,

there must be at least one vibrational mode that supports the bond breaking and formation to occur. Furthermore, this cyclopropene isomerization occurs in the gas phase and without catalyst [7]. It implies the isomerization is straightforward, but yet the mechanism is not necessarily simple.

2. Computational detail

2.1. Energy and structure calculations

We designed an isomerization pathway of cyclopropene to propyne as illustrated in the following scheme as shown in figure 1.

$$H_2C1 — C3H \qquad\qquad H_3C1 — C2 \equiv C3H$$

Cyclopropene   Propyne
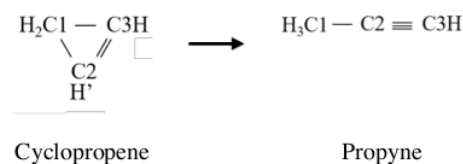
Figure 1. Initial and final states of cyclopropene isomerization in Kekule's structure.

We performed routine of ground state calculation [8] on initial and final structures. By tracking the vibrational mode, we predicted the transition state (TS) structure. For the TS structure, we applied TS optimization routine of calculation [8]. We constructed energy level diagram for all states based on density-functional calculations. We employed B3LYP as exchange-correlation functional and 6-311+G(d,p) as basis set that integrated in the Gaussian09 software.

2.2. Thermochemistry and chemical kinetics calculations

We calculated the standard enthalpy of reaction ($\Delta_r H°$) using the following formula,

$$\Delta_r H° = H°_{TS} - \Delta G°_{IS} \tag{1}$$

with IS and TS are the initial and the transition state, respectively. We calculated activation energy based on electronic energy (E_B), transition state theory (E_a) and Gibbs energy ($\Delta^{\ddagger} G°$) using the following formula [1]

$$E_B = E_{TS} - E_{IS} \tag{2}$$

$$E_a = \Delta^{\ddagger} H° + RT \tag{3}$$

$$\Delta^{\ddagger} G° = \Delta G°_{TS} - \Delta G°_{IS}. \tag{4}$$

We also calculated pre-exponential factor (A) using transition state theory as follows [1]:

$$A = \frac{e k_B T}{h c°} exp\left[-\frac{\Delta^{\ddagger} S°}{R}\right]. \tag{5}$$

The quantities in equation (1), (3), (4) and (5) are temperature dependence which calculated at room temperature. We performed the vibrational calculations at 500 K and 700 K to determine the rate constants which mathematically described as [1]

$$k(T) = \frac{k_B T}{h c°} exp\left[-\frac{\Delta^{\ddagger} G°}{RT}\right], \tag{6}$$

which k_B, h, R are the constant of Boltzman, Planck and molar gas. $c°$ is the molecule's concentration from the reactant to the transition state (which assume to be 1) [1], and T is the temperature. Then, we compared all these calculation results with experimental data to justify the designed pathway.

3. Results and discussion

3.1. Isomerization pathway design

Figure 2 shows the designed isomerization pathway of cyclopropene to propyne. The isomerization involves C-C cyclic bond breaking and a C-C triple bond formation. We design our pathway by displacing a hydrogen atom (labeled with H' in scheme 2, State A). The displaced H' to C1 causes the C-C cyclic bond between C1 and C3 is broken (State B). Then, the triple bond is formed (State C). Finally, the expected product in the final state is formed (State D).
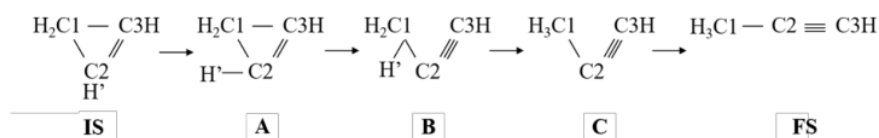

Figure 2. The designed isomerization pathway of cyclopropene to propyne.

3.2. Ground and transition states

Table 1 presents the geometrical parameters from DFT calculations (Calc.) and experiment (Expr.) [9]. Delta (Δ) in Table 1 is the discrepancy between our calculation results and the experimental value. The values of Δ in table 1 are within the accuracy limit according to Young [10]. It implies the selected exchange-correlation and basis set B3LYP/6-311+G(d,p) are suitable to study ground state of the molecules of interest.

Table 1. The selected geometrical parameters of cyclopropene (initial state) and propyne (final state) [9].

State		Bond Length				Bond Angle		
		C1-C2	C2-C3	C1-H	C3-H	C_1C_2H	C_1C_3H	HC_3H
Initial	Calc.	1.510	1.291	1.091	1.076	149.8		113.7
	Expr.	1.505	1.293	1.085	1.072	150.0		114.3
	Δ	0.005	-0.002	0.006	0.004	-0.2		-0.6
Final	Calc.	1.457	1.202	1.094	1.062		110.9	
	Expr.	1.459	1.206	1.105	1.056		110.2	
	Δ	-0.002	-0.004	-0.011	0.006		0.7	

Table 2 resumes the comparison between the initial state and state A which are the value of relative energy, E_r; selected vibrational frequency, v_1; geometrical parameters: bond length (R) and bond angle (A). Energetically, the initial state is more stable than state A, which is as expected. The v_1 is the deduced as the one which triggers the isomerization as illustrated in figure 3.

Table 2. Some parameters of initial state and state A.

Parameter	Unit	IS	A
E_r	eV	0.00	1.50
v_1	1/s	781	-244
R C1-C2	Å	1.510	1.873
A C1C2H'	°	149.8	71.9
A C1C2C3	°	64.7	50.4

The mode fulfills the requirement of our designed isomerization pathway (figure 2): the frequency decreases along the pathway and eventually becomes an imaginary number at state A. The imaginary frequency of State A indicates that structure in State A is close enough with the one in the transition state (TS). Therefore, the structure in State A is called as precursor geometry. The precursor geometry becomes our initial guess to do the TS optimization routine of calculation. Figure 4 illustrates the optimized TS geometry and the corresponding transition state.
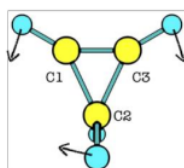

Figure 3. The illustration motion of selected vibrational v_1 of cyclopropene.
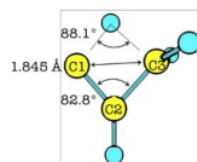
Figure 4. Optimized geometrical structure of transition state with $v_1 = -927$ 1/s.

3.3. Energy level diagram
Figure 5a and b show the energy level diagram (ELD) of the isomerization. Figure 5a is based on electronic energy, while figure 5b is after thermal corrections: enthalpy and Gibbs free energy. These ELDs give us three interesting facts: First, thermal corrections do not change the trend of ELD (there is one transition state which indicates a one-step reaction mechanism). Second, the negative value of $\Delta_r H°$ indicates an exothermic reaction, which agrees with an experimental fact (expr. = 92.2kJ/mol) [6]. Third, the comparison between E_B, TST (E_a), and $\Delta^\ddagger G°$, with experimental data ($E_{a\ expr.}$ =147 kJ/mol) shows that $\Delta^\ddagger G°$ gives the most accurate prediction to the activation energy.
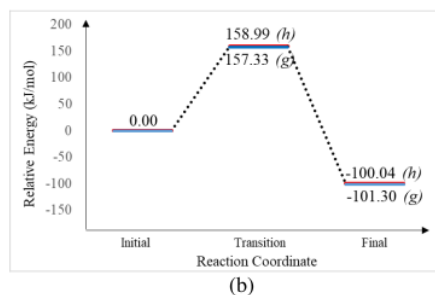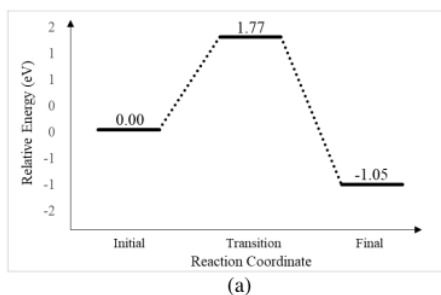
Figure 5. Energy level diagrams of the isomerization (a) based on electronic energy and (b) after thermal correction at room temperature (298.15K). The red and blue line in Figure 5(b) is for enthalpy (labeled with *h*) and Gibbs free energy (labeled with *g*), respectively. The value of $\Delta^\ddagger H°$ plus RT factor is 161 kJ/mol (the activation energy, E_a based on TST).

3.4. Chemical kinetics quantities
Table 3 presented the kinetic quantities based on TST and experimental results [1]. The Δ is the discrepancy between our calculation results and the experimental value. The value of Δ shows that calculation based on TST gives a value that agrees with the experiment. However, the calculation does not give a good prediction for the natural logarithmic of the pre-exponential factor, ln(A). The prediction of A depends on the vibrational frequency: the higher bond order of C-C, the higher the error of the calculated C-C vibrational frequency [11]. In this case, the isomerization involves single C-C cyclic bond breaking and C-C triple bond formation. Therefore, the error in the vibrational frequency calculations of the isomerization leads to error in the calculated ln(A).

Table 3. The values of Arrhenius parameter and rate constant from TST (Calc.) and experiment (Expr.) [1].

Reac. Quantities	Unit	Expr.	Calc.	Δ
E_a	kJ/mol	147	161	14
$ln(A)$	1/s	27.9	30.7	2.8
$k(500K)$	1/s	5.67E-04	6.98E-04	same order
$k(700K)$	1/s	1.35E+01	4.49E+01	same order

Table 3 shows that the calculated rate constants are in the same order of magnitude with the experimental data. It indicates that the obtained TS geometry, and consequently our designed isomerization pathways (scheme 2) are correct. Also, v_1 is the vibrational frequency that initiates the isomerization. Accordingly, we have successfully explained the mechanism of isomerization via vibrational movement. Furthermore, this study can be used as a guide if one needs to construct an isomerization pathway.

4. Conclusion

We have successfully justified the constructed isomerization pathway of cyclopropene to propyne based on vibrational calculations. We calculated activation energy in terms of E_B, E_a (based on TST), and $\Delta^{\ddagger}G°$, with $\Delta^{\ddagger}G°$ as the most accurate one. Furthermore, the comparison between the calculated rate constants is in the same order of magnitude with experimental data ($\sim 10^{-4}$ 1/s at 500 K and $\sim 10^1$ 1/s at 700 K). It implies that the constructed pathway is the correct mechanism of cyclopropene to propyne isomerization. Finally, this study can be used as a guide if one needs to construct an isomerization pathway based on vibrational calculation.

Acknowledgements

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