

A DFT-BASED COMPUTATIONAL STUDY ON HYDROGEN TUNNELING PHENOMENON IN THE ISOMERIZATION OF METHYLHYDROXYCARBENE

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2 A DFT-BASED COMPUTATIONAL STUDY ON HYDROGEN TUNNELING PHENOMENON IN THE ISOMERIZATION OF METHYLHYDROXYCARBENE

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Abstract. A recent research has found methylhydroxycarbene to be capable of transforming into acetaldehyde even when isolated in an inert argon matrix. It underwent the reaction producing acetaldehyde despite the classical TST-based preference towards the vinyl alcohol producing one. We have used DFT-based methods to predict the most possible one among these reactions considering the probability of hydrogen tunneling occurrence. We used B3LYP/6-31+G(d,p) and M08-SO/6-31+G(d,p) methods in all calculations using the GAMESS-US software and compared the results to Schreiner et al.'s. Our geometry optimization results of stable and transition molecules approximately agreed with those obtained by the CCSD/cc-pV6Z method in terms of molecular structure and energy. Both DFT methods also mapped out the ¹³C of each possible isomerization properly with the most noticeable difference being produced only by M08-SO/6-31+G(d,p). The tunneling analysis revealed that the isomerization into acetaldehyde, not vinyl alcohol, was the most possible one considering the possibility of tunneling occurrence.

Keywords: DFT, methylhydroxycarbene, hydrogen tunneling, isomerization

1. INTRODUCTION

Density functional theory (DFT) has long been regarded as a simpler alternative to wavefunction theory in calculating physical properties of a molecule and eventually predicting the most possible path of a chemical reaction. However, several researchers [1] have now found that most DFT methods are not suitable for molecular energy calculations due to their inaccuracy in predicting the structure and energetics of transition molecules. In spite of this fact, researches with exceptionally good results in support of DFT are constantly being conducted and published. Therefore, more DFT-based computational researches are necessary either to confirm or to reject the claim of DFT's systemic fault.

Schreiner et al. [2] have recently discovered a brand new understanding on the effect of quantum tunneling to a chemical reaction path. In the research, they tried to trap methylhydroxycarbene, a transition molecule produced from pyrolysis of pyruvate, in inert an argon matrix. However, the methylhydroxycarbene quickly transformed into acetaldehyde. This reaction is unusual in two aspects. First, it shouldn't have happened given that methylhydroxycarbene was trapped in an inert argon matrix. Second, classically, even if it happened, it shouldn't have produced acetaldehyde; it should have produced vinyl alcohol (ethenol) instead. Therefore, they concluded that not only does quantum tunneling make it possible for an inertly-trapped transition molecule to undergo a fast isomerization, it also determines the most preferable reaction path to undergo.

It is interesting to notice that Schreiner et al. didn't involve any DFT method in the research. It turns out that Schreiner [1] had stated that DFT methods, especially B3LYP,

are currently not reliable enough for comparative energy calculations. However, other researchers, namely Kiselev et al. [3] and Sirjean et al. [4], kept using DFT methods and published reliable results concerning them.

Kiselev et al. found that, for singlet-triplet energy gap of *trans*-hydroxycarbene, CCSD(T)/CBS gave more accurate results than the focal-point analysis used by Schreiner et al. in one of their research. They further stated that B3LYP/cc-pVTZ gave similar results with CCSD(T)/CBS for geometry optimization of all structures in one of the reactions studied. Given this result, Kiselev et al. used B3LYP/cc-pVTZ for geometry optimization of all remaining structures.

Meanwhile, Sirjean et al. found that B3LYP/6-311G(2d,d,p) agreed better with CBS-QB3 method than G3MP2B3 did when used in computing critical energies for H-atom shift in *n*-heptyl radicals at 0 K. They also stated that CBS-QB3 was more likely to be the more reliable one given its ability to accurately predict thermochemical and kinetic data for hydrocarbon combustion.

It is worth noting that both researches were meant for hydrogen tunneling cases in intramolecular isomerization, similar with Schreiner et al.'s research subject [2]. It is also interesting to find that in his review [1], Schreiner stated that for DFT, basis set deficiencies were less pronounced to contribute in energetic errors. In other words, when DFT happens to give reliable results, it is due to the theory level (i.e. B3LYP in the two researches) rather than the basis set completeness.

The novel cases of reaction path-governing hydrogen-tunneling deserve studies by all computational methods, including DFT. Confirming the reliability of DFT for hydrogen tunneling cases is also important considering the fact that DFT has been around since quite a long time ago and has been the method of choice for a wide range of chemical systems, from homogeneous solid-state materials to bulky medicinal compounds. Thus, this study was aimed at applying DFT methods to study the hydrogen tunneling phenomenon in methylhydroxycarbene isomerization to further confirm the reliability of DFT.

2. COMPUTATIONAL DETAILS

2.1 Electronic Structure Computation

All computations in this study were accomplished using GAMESS-US [5]. The visualization, whenever needed, was accomplished with the help of mainly WxMacMolPlt [6] and occasionally Avogadro. One hybrid-GGA functional and one hybrid meta-GGA functional, namely B3LYP and M08-SO respectively, were used in combination with 6-31+G(d,p) for each computation, including vibrational analysis. We chose the two methods based on the works of Kuwata et al. [7] and Zheng and Truhlar [8], respectively, in which each respective method was found to be reliable for intramolecular hydrogen-transfer reactions.

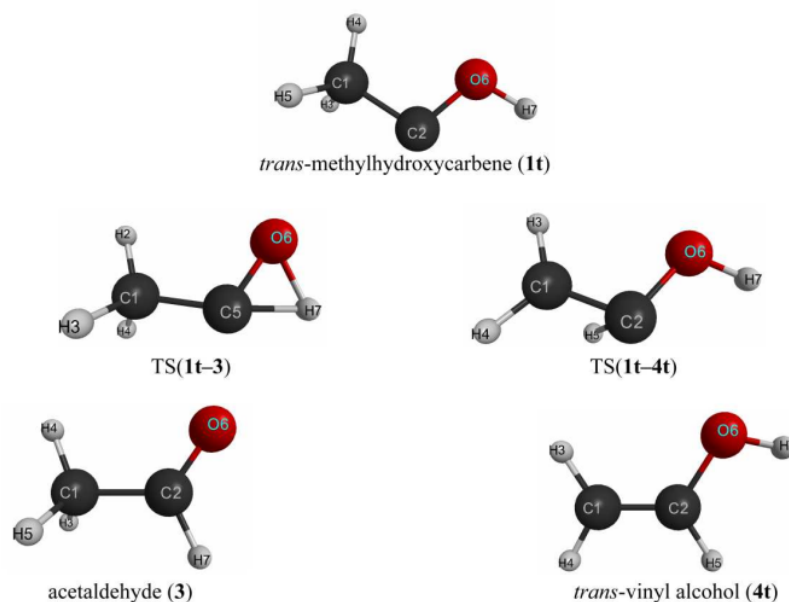


Figure 1. Optimized molecular structures of compounds involved in two major reaction paths of *trans*-methylhydroxycarbene isomerization

All structures optimized are shown in Fig. 1. These structures were involved in the isomerizations of **1t** according to Schreiner et al.'s experiment [2]. The first isomerization produced **3** while the second one produced **4t**. These two isomerizations were the major reactions of **1t** that occurred in the experiment and also the most likely to involve tunneling.

Stable molecular structures, i.e. **1t**, **3**, and **4t**, were optimized using restricted Hartree-Fock while the transition ones, i.e. TS(**1t-3**) and TS(**1t-4t**), using unrestricted Hartree-Fock. Transition state optimization was also conducted under stricter tolerance of 0.0001, instead of 0.001 as used for stable structure optimization, to ensure successful optimization, vibrational analysis, and IRC computation accomplishments.

2.2 Vibrational Analysis

Hessian calculation was conducted for each optimized transition state to accomplish vibrational analysis. A valid vibrational analysis indicates that the predicted transition state is indeed the stationary point in molecular PES. Transition state thermochemistry was computed with temperature parameter of 11 K given that the isomerization occurred under such condition in argon matrix isolation. All Hessian calculations were conducted using restricted Hartree-Fock. The Hessian data obtained from this analysis was then used to determine the intrinsic reaction coordinate of the corresponding reaction.

2.3 Tunneling Analysis

The tunneling probability $\kappa(\epsilon)$ of each possible path was calculated using the Wentzel-Kramers-Brillouin (WKB) formula [9]:

$$\kappa(\epsilon) = \frac{1}{1 + e^{2\theta(\epsilon)}} \dots \dots \dots (1)$$

where $\theta(\epsilon)$ is one-dimensional barrier penetration integrals obtained from the following equation:

$$\theta(\epsilon) = \int_{s_1}^{s_2} \sqrt{2[V(s) - \epsilon]} ds \dots \dots \dots (2)$$

where ϵ is collision energy and s_1 and s_2 are classical stationary points where $V(s) = \epsilon$. Schreiner et al. [2] further derived the equation above into this equation:

$$\theta(\epsilon) = \sqrt{\frac{m}{\hbar^2}} \left(\frac{\pi}{\sqrt{8}} \right) w(\epsilon) (\sqrt{V^* - \epsilon}) f(\alpha, \beta) \dots \dots \dots (3)$$

where $w(\epsilon)$ is the barrier width and V^* is the energy barrier height. The values of these variables were obtained from the IRC of each possible reaction path while $f(\alpha, \beta)$ is the constant for truncated parabolic barrier which has the value of 1.

3. RESULTS AND DISCUSSION

3.1 Geometry Optimization

Both B3LYP/6-31+G(d,p) and M08-SO/6-31+G(d,p) gave similar results with those of CCSD(T)/cc-pV6Z from Schreiner et al.'s work [2] in terms of energy and optimized structure. Table 1 shows the single-point energy of each structure given by these methods plus RHF, also from Schreiner et al.'s work. The single energies obtained from DFT calculations clearly show a far better agreement with those of CCSD(T)/cc-pV6Z compared to RHF/cc-pV6Z. The largest difference between B3LYP/6-31+G(d,p) results and CCSD(T)/cc-pV6Z is -0.1014 and between M08-SO/6-31+G(d,p) and CCSD(T)/cc-pV6Z is only -0.0715 while RHF with the same basis set as CCSD(T) gives about 0.6849. This is quite contrary to Schreiner's conclusion [1] that B3LYP performs only slightly better than HF theory.

The bond detection and bond-length determination of both DFT methods are also satisfying. From Table 2, it is obvious that both DFT methods can detect all the bonds in **1t** molecule and also determine the lengths accurately enough. This also works for all other structures. The bond lengths given by B3LYP/6-31+G(d,p) only differ very slightly from those of AE-CCSD(T)/cc-pCVQZ. Both DFT methods tend to give a slightly higher bond length compared to AE-CCSD(T)/cc-pCVQZ. This agrees with what Kuwata et al. concluded in their work [7] that DFT methods agree excellently with high-level *ab initio*

methods when the basis set used includes diffuse functions on non-hydrogen atoms. The basis set 6-31+G(d,p) meets such criteria.

Table 1. Single-point energies of each structure based on various methods

No.	Structure	Single-point energy			
		CCSD(T)/ cc-pV6Z [2]	B3LYP/ 6-31+G(d,p)	M08-SO/ 6-31+G(d,p)	RHF/ cc-pV6Z [2]
1	1t	-153.5727	-153.6735	-153.6442	-152.9137
2	3	-153.6533	-153.7542	-153.7214	-152.9893
3	4t	-153.6364	-153.7342	-153.7024	-152.9686
4	TS(1t-3)	-153.5214	-153.6228	-153.5910	-152.8365
5	TS(1t-4t)	-153.5330	-153.6340	-153.6037	-152.8598

Table 2. Bond lengths and orders detected in **1t** structure based on various methods.

No.	Atom	Pair	Method					
			B3LYP/ 6-31+G(d,p)		M08-SO/ 6-31+G(d,p)		AE-CCSD(T)/ cc-pCVQZ [2]	
			Bond Length (Å)	Bond Order	Bond Length (Å)	Bond Order	Bond Length (Å)	Bond Order
1	C1	C2	1.496	0.387	1.503	0.555	1.494	N/A
2	C1	H3	1.098	0.941	1.103	0.941	1.0915	N/A
3	C1	H4	1.100	0.936	1.104	0.932	1.0917	N/A
4	C1	H5	1.099	0.940	1.104	0.939	1.0915	N/A
5	C1	O6	2.280	-0.107	2.278	-0.110	N/A	N/A
6	C2	O6	1.325	1.349	1.320	1.329	1.318	N/A
7	O6	H7	0.970	0.813	0.971	0.803	0.963	N/A

Bond order threshold = 0.050.

3.2 Transition State Prediction

Both DFT methods correctly predicted all transition structures within the default value of optimization tolerance, i.e. 0.0001. However, when it came to predicting the correct structure for TS(**1t-4t**), M08-SO/6-31+G(d,p) failed at the first run. M08-SO/6-31+G(d,p) could predict it correctly only after preliminary optimization within 0.001 of tolerance.

Using the coordinate and Hessian data from this preliminary optimization as input, M08-SO finally gave the correct structure for TS(**1t-4t**). Given that B3LYP also used the same basis set, there was a strong indication that the failure was due to the high sensitivity of M08-SO.

As what Zhao and Truhlar [10] stated, M08-SO may be considered as an improved version of M06-2X. Like other hybrid meta-GGA functionals, the energy computation of M08-SO depends on the occupied orbitals through Hartree-Fock exchange terms and the non-interacting spin-component kinetic energy densities. Thus, M08-SO needs to take more factors than B3LYP does into account before it can find the correct energy. This results in a longer yet, according to Zhao and Truhlar, more reliable energy computation.

Vibrational analysis of each transition state under 11 K of temperature confirmed that all optimized transition states were properly on the molecular PES, vibrating the right atoms on the right directions connecting the respective reactant and product. Correct transition states are characterized by one imaginary frequency resembling vibration toward product formation. B3LYP/6-31+G(d,p) gave $-2012.0139 \text{ cm}^{-1}$ as the imaginary frequency for TS(**1t-3**) and $-1405.8900 \text{ cm}^{-1}$ for TS(**1t-4t**) while M08-SO/6-31+G(d,p) gave $-2126.5701 \text{ cm}^{-1}$ as the imaginary frequency for TS(**1t-3**) and $-1429.3500 \text{ cm}^{-1}$ for TS(**1t-4t**).

3.3 Intrinsic Reaction Coordinate

Due to the relatively low-capacity of the computer system used for this study, the IRC calculations were initially conducted at the less demanding STRIDE value of 0.3; it is the default value in GAMESS and is claimed to be reliable enough for GS2 method used in this study. B3LYP/6-31+G(d,p) gave proper IRC for each isomerization path as shown by Fig. 2. On the other hand, M08-SO/6-31+G(d,p) returned error every time the default STRIDE is used. The IRC computed using this method was obtained successfully only when the STRIDE value of 0.01 is used. This surely gave us a very smooth, seamless IRC plot (see Fig. 3) and visualization but demanded much resource, primarily processor's hard work, power supply, and GAMESS runtime, at the same time.

Interestingly enough, when compared to the relative energies from Schreiner et al.'s [2] focal point analyses as shown in Table 3, it is the resource-friendly B3LYP/6-31+G(d,p) that gives us the relative energies with closest resemblance to focal point analysis results. The highest relative energy difference between B3LYP/6-31+G(d,p) and focal point analysis is 1.8826 kcal/mol for **4t** while M08-SO/6-31+G(d,p) shows a larger difference of 3.4513 kcal/mol also for **4t**. It is interesting to notice that the relative energies for transition states show a good agreement between methods. Given that we optimized the stable (equilibrium) structures at a lower level of tolerance than the transition states, it is likely that the high relative energy difference between methods for **4t** are due to this fact.

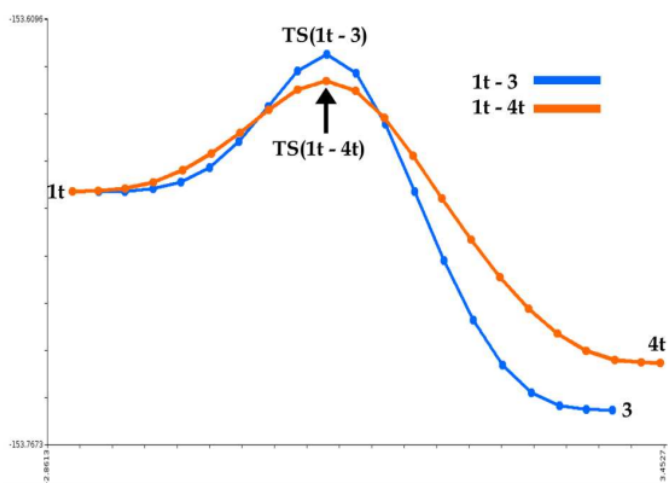


Figure 2. Intrinsic reaction coordinates of 1t - 3 isomerization and 1t - 4t isomerization obtained using B3LYP/6-31+G(d,p)

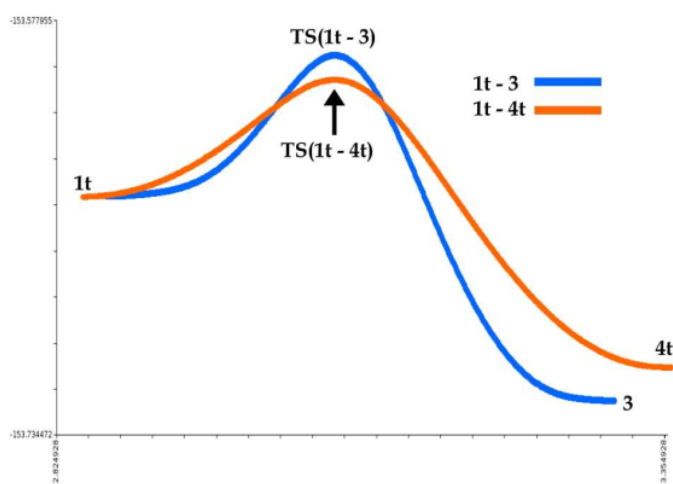


Figure 3. Intrinsic reaction coordinates of 1t - 3 isomerization and 1t - 4t isomerization obtained using M08-SO/6-31+G(d,p)

Table 3. Relative energies (in kcal/mol) of all structures based on various methods

No.	Structure	Relative Energy (in kcal/mol)		
		B3LYP/ 6-31+G(d,p)	M08-SO/ 6-31+G(d,p)	Focal Point Analysis [2]
1	1t	0.0000	0.0000	0.0000
2	3	-50.5632	-48.3669	-50.5005
3	4t	-38.0130	-36.4442	-39.8956
4	TS(1t - 3)	31.8916	33.4603	32.2680
5	TS(1t - 4t)	24.8635	25.4910	24.9889

3.4 Tunneling Analysis

Vibrational analysis of **1t** using B3LYP/6-31+G(d,p) revealed that **1t** underwent two possible collisions at the frequencies of 1332.22 cm⁻¹ and 734.81 cm⁻¹. The former directed **1t** to **3** with 1.9044 kcal/mol of collision energy while the latter directed **1t** to **4t** with 1.0504 of collision energy. Using the WKB formula, we found the tunneling probability of **1t - 3** reaction to be 3.2×10^{-19} while that of **1t - 4t** to be 2.38×10^{-23} .

Table 4. Values of key variables for finding tunneling probabilities

No.	Variables	Values					
		B3LYP/6-31+G(d,p)		M08-SO/6-31+G(d,p)		Schreiner et al. [2]	
		1t - 3	1t - 4t	1t - 3	1t - 4t	1t - 3	1t - 4t
1	Collision freq. (cm ⁻¹)	1332.22	734.81	1366.52	724.14	1346	736
2	Collision energy (kcal/mol)	1.90	1.05	1.95	1.04	1.92	1.05
3	Barrier height (kcal/mol)	31.89	24.86	33.46	25.49	29.99	23.94
4	Barrier width (amu ^{1/2} .bohr)	2.39	3.29	2.46	3.20	2.32	3.07
5	Effective barrier freq. (cm ⁻¹)	2012.01i	1405.89i	2126.57i	1429.35i	2031i	1443i
6	Barrier penetration integral	21.29	26.04	22.50	25.69	20.02	23.85
7	Tunneling probability	3.2×10^{-19}	2.38×10^{-23}	2.85×10^{-20}	4.87×10^{-23}	4.05×10^{-18}	1.90×10^{-21}

Vibrational analysis of **1t** using M08-SO/6-31+G(d,p) revealed that **1t** underwent two possible collisions at the frequencies of 1366.52 cm⁻¹ and 724.14 cm⁻¹. The former directed

1t to **3** with 1.9535 kcal/mol of collision energy while the latter directed **1t** to **4t** with 1.0352 of collision energy. Using the WKB formula, we found the tunneling probability of **1t** - **3** reaction to be 2.85×10^{-20} while that of **1t** - **4t** to be 4.87×10^{-23} .

Both DFT methods predicted the probability of hydrogen tunneling in **1t** - **3** isomerization to be higher than that of **1t** - **4t**. The overall results are quite similar with Schreiner et al.'s work [2] except that our DFT methods gave lower tunneling probability for both **1t** - **3** and **1t** - **4t**. Table 4 summarizes these results.

6. CONCLUSION

Geometry optimization, vibrational analysis, and IRC mapping have been successfully computed using two DFT methods, i.e. B3LYP/6-31+G(d,p) and M08-SO/6-31+G(d,p). All methods gave approximate results with Schreiner et al.'s work [2], except that the relative energies of **4t** given by the DFT methods differ quite significantly from focal point analysis. Using the data from IRCs, we found that the tunneling probability of isomerization into acetaldehyde was higher than that of isomerization into *trans*-vinyl alcohol. Therefore, the experimental preference toward acetaldehyde is very likely due to hydrogen tunneling.

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