A first-principles study on the quantum tunneling of methylhydroxycarbene isomerization in various solvents

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Abstract. Quantum tunneling phenomenon allows a high-barrier reaction to occur even though thermal energy is not sufficient to surmount the barrier. The phenomenon has been suggested to exist in the isomerization of methylhydroxycarbene which occurred at 11 K. Here we study the quantum tunneling that occurred in the isomerization of methylhydroxycarbene to acetaldehyde and to vinyl alcohol based on density functional calculations. The isomerization pathways are determined under the effect of various solvents which are modeled by polarizable continuum model (PCM). We use Wentzel-Kramers-Brillouin (WKB) approximation to calculate the tunneling probability (T) and extend the usefulness of T into isomerization rate. The results show that the solvents give a significant effect on the isomerization rate of methylhydroxycarbene to acetaldehyde but an insignificant one on the isomerization rate to vinyl alcohol.

1. Introduction

Quantum tunneling commonly occurs in subatomic particles, such as nucleons and electrons. The example of quantum tunneling phenomenon is alpha decay which is explained by Gamow theory [1]. Quantum tunneling is difficult to occur in the molecular scale because of its dependence on the size of the particle [2]. However, previous studies have proven the existence of quantum tunneling in molecular reaction [3, 4].

The quantum tunneling phenomenon has successfully explained the isomerization of trans-HCOH to H\textsubscript{2}CO occurs through quantum tunnelling experimentally [3] and theoretically [5, 6]. The phenomenon also occurs in the isomerization of methylhydroxycarbene to acetaldehyde with the half-life being one hour [4]. It is worthwhile to mention that the isomerization of trans-HCOH, the simplest hydroxycarbene, is solvent-dependent [7]. The perturbation coming from solvents decreases the isomerization rate of trans-HCOH.
In this study, we report the effect of solvent on the quantum tunneling of methylhydroxycarbene isomerization based on density functional calculations. We calculate the quantum tunnelling probability using Wentzel-Kramers-Brillouin (WKB) approximation [2] to get the half-life of methylhydroxycarbene in the solvents.

2. Computational detail

We model the isomerization as the following figure:

![Figure 1. The isomerization model of methylhydroxycarbene (Me), acetaldehyde (Ac), and vinyl alcohol (Vi).](image)

We considered the trans and the cis isomer of both Me and Ac. We employed routines of calculation based on density functional theory (DFT) to determine the ground and the transition states of our system of interest. Our previous study showed that the quantum tunneling probability increases as the increment of basis set size [8]. Therefore, in this study, we opted B3LYP/6-311+G(d,p) as the exchange-correlation functional/basis set integrated in Gaussian 09 software [9]. We coupled the DFT calculations with polarizable continuum model (PCM) to model the solvent environment. We listed the notations of the solvents and the corresponding dielectric constant value (SCRF) [10] in table 1.

| Phase            | Notation | Dielectric constant (\(\varepsilon\)) |
|------------------|----------|--------------------------------------|
| Gas phase        | {0}      | 1.000                                |
| Benzene          | {1}      | 2.271                                |
| Dichloroethane   | {2}      | 10.125                               |
| Benzaldehyde     | {3}      | 18.220                               |
| Acetone          | {4}      | 20.493                               |
| Methanol         | {5}      | 32.613                               |
| Ethanediol       | {6}      | 40.245                               |
| DMSO             | {7}      | 46.826                               |
| Formic acid      | {8}      | 51.100                               |
| Water            | {9}      | 78.355                               |
| Formamide        | {10}     | 108.940                              |

We determined the reaction pathway: Me \(\rightarrow\) \([\text{TS}_{\text{Me-Ac}}]\) \(\rightarrow\) Ac and Me \(\rightarrow\) \([\text{TS}_{\text{Me-Vi}}]\) \(\rightarrow\) Vi using intrinsic reaction coordinate (IRC) calculation. To calculate the probability of the quantum tunneling, we used WKB approximation [2],

\[
T \approx \exp \left( -\frac{4\pi}{\hbar}\int_{x_i}^{x_f} \sqrt{2[V_b(x) - E_{ZP}]^2} \, dx \right),
\]

where \(\hbar\) is Planck constant, \(V_b(x)\) is the potential barrier represented by the fitted function of the reaction pathway, and \(E_{ZP}\) is zero-point energy (ZPE). Then, we calculated isomerization rate with,

\[
k = \nu T,
\]

where \(k\) is the isomerization rate, \(\nu\) is the vibrational frequency, and \(T\) is the quantum tunneling probability.
3. Results and discussion

3.1 The ground state
Table 2 lists the geometrical parameters of Ac in the gas phase and in the solvent from our calculations (Calc.) and the experiment (Expr.) [11]. The notations used to describe the parameters refer to figure 1. The value of “Δ” for all parameters is within the accuracy of limits according to Young [12]. It implies that B3LYP/6-311+G(d,p) is appropriate for studying the isomerization of Me.

We compare the geometrical parameters of Ac in the gas phase and in the solvent. For clarity, we only display the result of our calculation in the solvent with the highest dielectric constant {10}. Based on our results, we found that there are no significant changes in the structure of Ac after being introduced into the solvent. It implies that the presence of solvents did not affect the geometrical structure of molecules.

Table 2. Geometrical parameters of Ac in the gas phase and in the solvent {10} from our calculation (Calc.) and the experiment (Expr.) [10]. “Δ” is Calc. {0} minus Expr.

| Parameters          | Calc.   | Expr.   | Δ       |
|---------------------|---------|---------|---------|
| Bond Length (Å)     |         |         |         |
| C1-C2               | 1.504   | 1.496   | 1.515   | -0.011 |
| C2-O1               | 1.206   | 1.214   | 1.210   | -0.004 |
| C1-H1               | 1.096   | 1.095   | 1.107   | -0.011 |
| C1-H2               | 1.090   | 1.090   | 1.107   | -0.017 |
| C1-H3               | 1.096   | 1.095   | 1.107   | -0.011 |
| C2-H4               | 1.112   | 1.108   | 1.128   | -0.016 |
| Bond Angle (°)      |         |         |         |
| H1-C1-H2            | 110.1   | 110.3   | 109.8   | 0.305  |
| C1-C2-O1            | 124.8   | 124.9   | 124.1   | 0.726  |
| C1-C2-H4            | 115.1   | 115.3   | 115.3   | -0.211 |

Figure 2 shows the energy level diagram (ELD) of our molecules of interest in the gas phase (black line) and in the solvent (blue line). The ELD shows that Ac is the most stable molecule compared to Me and Vi which agrees with the experimental result [4]. Together with the results in table 1, the ELD shows that the selected exchange-correlation and basis set are appropriate for this study.

The ELD in figure 2 shows that the order of the molecules’ stability in the gas phase is same with the one in the solvent. It indicates that the presence of solvents did not affect the stability of molecules.
The ELD in figure 2 also shows that trans-Me is more stable than cis-Me; cis-Vi is more stable than trans-Vi. It means that energetically, Me prefer the trans-isomer, while Vi prefer the cis-isomer. Therefore, we only focus on trans-Me and cis-Vi for the rest of the manuscript.

3.2 The transition state

Figure 3 shows the isomerization reaction pathways of trans-Me to form either Ac or Vi in the gas phase (black line) and in the solvent (blue line). It is clear from the reaction pathway in figure 3 that each isomer are separated by TS. All the TS are characterized by one imaginary frequency and are ensured to connect them to the desired molecules as it shown in figure 1 through IRC calculations. Energetically, trans-Me tends to undergo isomerization into Vi rather than Ac due to the lower energy barrier. Trans-Me is possible to form Vi either in cis or trans isomer. The energy barrier of trans- to cis- isomerization is less than 0.2 which is very small; the isomerization can be occurred through thermal energy. Meanwhile, trans-Me undergo isomerization into Ac through quantum tunneling mechanism experimentally [4].

The isomerization reaction pathways in figure 3 also show that the order of molecules’ stability in both environment is same. However, the $V_b$ of each isomerization with respect to each corresponding initial state is slightly different when in the gas phase and in the solvent.

![Figure 3](image1.png)

**Figure 3.** The isomerization reaction pathway of initial (trans-Me), transition, and final ((a) Ac and (b) cis-Vi) states in the gas phase (black line) and in the solvent [10] (blue line). The total energy of trans-Me in the gas phase is used as reference point.

Figure 4 shows the reaction path of the isomerization of trans-Me to Ac in the gas phase and in the solvent. We fitted a function to our IRC calculation data which are a combination of gaussian and exponential function for trans-Me $\rightarrow$ Ac and Eckart model [13] for trans-Me $\rightarrow$ trans-Vi. The black dots represent the potential energy with its corresponding reaction coordinate for the isomerization of trans-Me to Ac and cis-Vi. The red line represents the fitted function. And the blue line represents ZPE.

![Figure 4](image2.png)

**Figure 4.** The reaction path of the isomerization of trans-Me to Ac in the (a) gas phase and (b) solvent [10].
Table 3 shows the quantum tunneling probability of trans-Me $\rightarrow$ Ac and trans-Me $\rightarrow$ trans-Vi. The results show that the perturbation coming from solvents give lower the quantum tunneling probability. The quantum tunneling probability of trans-Me $\rightarrow$ Ac is higher than that of trans-Me $\rightarrow$ trans-Vi. It indicates that trans-Me isomerization prefers to go towards Ac rather than towards trans-Vi. It also supports the experiment that the isomerization of trans-Me to Ac occurs through quantum tunneling mechanism.

Table 3. The quantum tunneling probability of the isomerization of trans-Me to Ac and trans-Vi in the gas phase and in ten selected solvents.

| Dielectric Constant ($\varepsilon$) | Quantum tunneling probability (T) |
|------------------------------------|----------------------------------|
|                                    | trans-Me $\rightarrow$ Ac   | trans-Me $\rightarrow$ trans-Vi |
| [0]                                | $3.25 \times 10^{-19}$       | $1.25 \times 10^{-21}$       |
| [1]                                | $1.42 \times 10^{-19}$       | $8.60 \times 10^{-22}$       |
| [2]                                | $6.36 \times 10^{-20}$       | $1.63 \times 10^{-21}$       |
| [3]                                | $5.79 \times 10^{-20}$       | $1.52 \times 10^{-21}$       |
| [4]                                | $5.52 \times 10^{-20}$       | $1.52 \times 10^{-21}$       |
| [5]                                | $5.26 \times 10^{-20}$       | $1.48 \times 10^{-21}$       |
| [6]                                | $5.14 \times 10^{-20}$       | $1.48 \times 10^{-21}$       |
| [7]                                | $5.14 \times 10^{-20}$       | $1.45 \times 10^{-21}$       |
| [8]                                | $5.02 \times 10^{-20}$       | $1.45 \times 10^{-21}$       |
| [9]                                | $5.02 \times 10^{-20}$       | $1.45 \times 10^{-21}$       |
| [10]                               | $4.90 \times 10^{-20}$       | $1.45 \times 10^{-21}$       |

3.3 Isomerization rate

Figure 5 shows the trend of the decreasing isomerization rate of trans-Me $\rightarrow$ Ac (blue line) and trans-Me $\rightarrow$ trans-Vi (orange line). The results show that the perturbation coming from solvents has decreased the isomerization rate of the molecules. The solvents give a significant effect on the isomerization rate of trans-Me to Ac but an insignificant one on the isomerization rate to trans-Vi.

The isomerization rate in figure 5 also shows that the trend of the decreasing isomerization rate in methylhydroxy carbene and trans-HCOH [7] is the same. It indicates that the result from previous study is also applicable to more complex carbene molecule, methylhydroxycarbene.

Figure 5. The isomerization rate of trans-Me $\rightarrow$ Ac (blue line) and trans-Me $\rightarrow$ trans-Vi (orange line) in the gas phase and in ten selected solvents.
4. Conclusion
We have reported the effect of solvents on the isomerization of trans-Me $\rightarrow$ Ac, trans-Me $\rightarrow$ trans-Vi, and trans-Vi $\rightarrow$ cis-Vi via quantum tunneling. The perturbation coming from solvents increases the energy barrier of the isomerization of trans-Me $\rightarrow$ Ac and trans-Vi $\rightarrow$ cis-Vi by 0.08 eV and 0.03 eV respectively, but decreases the energy barrier of trans-Me $\rightarrow$ trans-Vi by 0.01 eV. The effect is significant on the isomerization of trans-Me $\rightarrow$ Ac, but is insignificant on the isomerization of trans-Me $\rightarrow$ trans-Vi. However, the perturbation did not affect the geometrical structure and the stability of the individual molecules. Finally, we suggest considering the effect of solvents when studying isomerization via quantum tunneling.

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