The first-principle study on the stability of trans-HCOH in various solvents

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Abstract. We attempt to study about the solvent effects of the stability of trans-HCOH molecules using the density-functional theory. Experimentally, trans-HCOH rearranges to H₂CO with half-life of two hours [1] which we theoretically proved that it occurs through quantum tunneling [2]. In this work, we calculate the rearrangement rate of the molecules in various solvents. The solvents are selected based on their dielectric constant values, from lower to higher ones; they are benzene, dichloroethane, benzaldehyde, acetone, methanol, ethanediol, dimethylsulfoxide, formic acid, water, and formamide. We use polarizable continuum to model the solvents (PCM). We begin from determining the reaction path from trans-HCOH to H₂CO and its corresponding energy barrier using intrinsic reaction coordinate calculation with PCM. Then, we use Wentzel-Kramers-Brillouin (WKB) approximation to calculate the rearrangement rates. The calculation results showed a general trend in which there were rearrangement rate was decreasing inversely proportional to dielectric constant value.

1. Introduction
The existence of the trans-HCOH had been theoretically predicted since 1974, but it was isolated for the first time in 2008 by Schreiner et al. He found that trans-hydroxymethylene rearranges naturally to formaldehyde (H₂CO) through a mechanism called as quantum tunneling [1]. Our two previous studies have proved that the rearrangement of the molecules occurs through quantum tunnelling. The first study was based on the value of the molecule’s half-life [2], and the second study was based on the monodeuteriation effects on the molecule [3].

This study reports our continuous study on the stability of trans-HCOH. The aim of this study is to see whether or not the solvents could alter the rearrangement rate of trans-HCOH to H₂CO. Our theoretical investigation is conducted based on the rearrangement path of the molecules. We use density-functional theory and Wentzel-Kramers-Brillouin (WKB) approximation [4] to obtain the rearrangement rate of the molecules under the effect of solvents.

2. Computational details
Our previous study showed that our calculation method is proper for the rearrangement of trans-HCOH by comparing the results to the experimental data [2]. Thus, we continue using 6-31G(d,p) basic set and B3LYP exchange-correlation functional to perform our calculations for this study [2]. We perform the calculations with trans-HCOH and H₂CO as our molecule models which are shown in Fig. 1.
Fig. 1. Molecular geometry of (a) trans-HCOH (b) H2CO. Symbol 1H means hydrogen atom number 1, and symbol 2H means hydrogen atom number 2.

We selected ten solvents based on their dielectric constant values [5] from lower to higher ones; they are benzene, dichloroethane, benzaldehyde, acetone, methanol, ethanediol, dimethylsulfoxide (DMSO), formic acid, water, and formamide. The solvents and their respective dielectric constant values are listed in Table 1.

Table 1. These are ten selected solvents and their respective dielectric constant values. We notate the solvents as written in the second column of this table.

| solvents     | notation | ε   |
|--------------|----------|-----|
| (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 ground spin state electronic structure of trans-HCOH and H2CO inside those solvents using polarizable continuum model (PCM) calculation.

We predicted the transition state structure using STQN method coupled with PCM calculation [6]. We confirmed the existence of imaginary frequency through the frequency calculation.

We performed IRC calculation [7] with fifteen numbers of points and 10 bohr. $\sqrt{\text{amu}}$ of step sizes to map out the reaction path of trans-HCOH which rearranges to H2CO under the effect of solvents. In order to ensure that we get the true minimum energy of the final structure along the reaction path, we added the calculated energy of the optimized H2CO through optimization calculation. Then, we combined it with the IRC calculation data. We found a fitting function which best fits with our IRC calculation data. The fitting function would act as a potential barrier function. Hence, we would be able to calculate the probability of quantum tunneling which was given by WKB approximation with

$$T \cong \exp\left[-\frac{4\pi}{\hbar} \int_{x_i}^{x_f} \sqrt{2(V_b(x) - E_{sp})}dx\right].$$
where $h$ was Planck constant, and $m$ was the particle’s mass which tunneled through the energy barrier, $V_b(x)$ was the energy barrier as a function of position, and $E_{zp}$ was zero-point energy (ZPE). We performed the integration within the initial position ($x_i$) to the final position ($x_f$).

We obtained the rearrangement rate with

$$\nu T,$$

(2)

In which $\nu$ was the rearrangement rate, $v$ was the vibrational frequency, and $T$ was the probability of quantum tunneling. Finally, we would obtain the half-life ($\tau_{1/2}$) with

$$\tau_{1/2} = \frac{\ln(2)}{k}.$$

(3)

The DFT, frequency, PCM, and IRC calculations were performed by using Gaussian09 suite program.

3. Results and discussions

3.1 The comparison between the molecules inside the solvents and those in the gas phase

Our DFT calculation coupled with PCM obtained the geometric structure parameters of trans-HCOH and H$_2$CO inside ten solvents which were shown in Table 2 and Table 3. The results showed that the ground state electronic structures in solvents were not significantly different. The difference was in order of $10^{-6}$eV. It implied that the solvents did not affect the geometric structures.

Table 2. Geometric structure parameters of trans-HCOH in singlet spin state configuration from our DFT calculation under the effects of ten solvents.

| Parameter       | solvents          |
|-----------------|-------------------|
|                 | {0} | {1} | {2} | {3} | {4} | {5} | {6} | {7} | {8} | {9} | {10} |
| dielectric constant | 1.000 | 2.271 | 11.09 | 18.220 | 20.493 | 32.613 | 40.245 | 46.826 | 51.100 | 78.355 | 108.940 |
| $\angle$OCH (degree) | 101.3 | 101.6 | 101.9 | 102.0 | 102.0 | 102.0 | 102.0 | 102.0 | 102.0 | 102.0 | 102.0 |
| C-O distance (Å) | 1.320 | 1.316 | 1.313 | 1.312 | 1.312 | 1.312 | 1.312 | 1.311 | 1.311 | 1.311 | 1.311 |
| C-H distance (Å) | 1.124 | 1.124 | 1.125 | 1.125 | 1.125 | 1.126 | 1.126 | 1.126 | 1.126 | 1.126 | 1.126 |
| O-H distance (Å) | 0.973 | 0.980 | 0.991 | 0.993 | 0.993 | 0.994 | 0.994 | 0.995 | 0.995 | 0.995 | 0.995 |

Table 3. Geometric structure parameters of H2CO in singlet spin state configuration from our DFT calculation under the effects of ten solvents.

| Parameter       | solvents          |
|-----------------|-------------------|
|                 | {1} | {2} | {3} | {4} | {5} | {6} | {7} | {8} | {9} | {10} |
| dielectric constant | 2.271 | 10.125 | 18.220 | 20.493 | 32.613 | 40.245 | 46.826 | 51.100 | 78.355 | 108.940 |
| $\angle$HCH (degree) | 115.4 | 115.6 | 115.7 | 115.7 | 115.7 | 115.7 | 115.7 | 115.7 | 115.7 | 115.7 |
| C-O distance (Å) | 1.209 | 1.212 | 1.212 | 1.212 | 1.212 | 1.212 | 1.212 | 1.212 | 1.212 | 1.212 | 1.212 |
| C-H distance (Å) | 1.110 | 1.109 | 1.109 | 1.109 | 1.109 | 1.109 | 1.109 | 1.109 | 1.109 | 1.109 | 1.109 |

Besides the molecular geometry, we obtained the vibrational frequency of trans-HCOH inside the solvents as it was shown at Fig.2. The results showed that there was no significant difference in the vibrational frequency.

We obtained six vibrational modes of the molecules. There were two out of six vibrational modes which involved atom 2H (see Fig. 1) in its vibration. Based on our previous study, we chose the vibrational mode based on its type of motion and its probability to occur. We chose the second vibrational mode of the molecule in each solvent. We used this vibrational frequency to calculate the rearrangement rate of the molecules.

3.2 Energy barrier

After we studied about trans-HCOH and H$_2$CO inside solvents separately, we predicted the transition state structure inside the solvents followed by the reaction path for each reaction which is shown in Fig. 3.
Based on the result of IRC calculation, we obtained the molecule’s energy in each coordinate reaction. The results showed that the increasing dielectric constant value affected the height of the energy barrier: the higher that the dielectric constant was, the higher that the energy barrier was.

Fig. 2. Vibrational frequencies of trans-HCOH normal modes inside benzene (1), methanol (5), and water (9) as the result of frequency calculation. The mode which is enclosed by red circle is the chosen normal mode that contributes to the rearrangement of trans-HCOH.
Fig. 3. Potential energy curves are the reaction path of the rearrangement inside (a) benzene, (b) methanol, (c) water. The energy of trans-HCOH is set as a reference point. The orange line represents zero-point energy (ZPE) which corresponds to the rearrangement of trans-HCOH. The blue line is the fitted function which acts as energy barrier.
We fitted some trial functions to our IRC calculation data and we found the best fitting function was the eight-degree polynomial function. Then, the fitted function acted as the energy barrier function of the rearrangement.

The energy barrier function determined the probability of quantum tunneling. We integrated the energy barrier function from $x_i$ to $x_f$ (see equation (1)) and resulted in the probabilities of quantum tunneling which are shown in the following Table 4. The results showed that the perturbation coming from solvents lowered the probability of quantum tunneling.

| $\varepsilon$ | Probability of Quantum Tunneling |
|--------------|----------------------------------|
| {0}          | 2.100E-18                        |
| {1}          | 8.101E-19                        |
| {2}          | 3.048E-19                        |
| {3}          | 2.672E-19                        |
| {4}          | 2.621E-19                        |
| {5}          | 2.428E-19                        |
| {6}          | 2.401E-19                        |
| {7}          | 2.084E-19                        |
| {8}          | 2.332E-19                        |
| {9}          | 2.233E-19                        |
| {10}         | 2.122E-19                        |

3.3 Rearrangement rate under the effect of solvent
The probability of quantum tunneling led us to acquire the rearrangement rate of the molecules in each solvent. Based on equation (2), we obtained the rearrangement rates of the molecules for ten solvents with mode 2 as the consideration mode which initiated the rearrangement. The results are shown in Table 5.
Table 5. Rearrangement rate in gas phase ({0}) [2] and in ten selected solvents ({1}–{10})

| ε   | Rearrangement rate |
|----|-------------------|
| {0} | 7.640E-05         |
| {1} | 2.942E-05         |
| {2} | 1.107E-05         |
| {3} | 9.704E-06         |
| {4} | 9.517E-06         |
| {5} | 8.816E-06         |
| {6} | 8.718E-06         |
| {7} | 7.567E-06         |
| {8} | 8.469E-06         |
| {9} | 8.107E-06         |
| {10}| 7.706E-06         |

Compared to the rearrangement rate of our previous study which resulted in $7.640 \times 10^{-5}$ in the gas phase (see Table 4), the perturbation from solvents has decreased the rearrangement rate of the molecules: the higher that the dielectric constants value was, the lower that the rearrangement rate was. It indicated that the stability of trans-HCOH was increasing due to the existence of solvents. The trend of the decreasing rearrangement rate is shown in Fig. 4.

![Fig. 4. The decreasing rearrangement rate of the molecules in the gas phase ($\varepsilon = 1$) and in each solvent based on dielectric constant values.](image)

4. Conclusion

This study reports that the perturbation coming from solvents increases the energy barrier of the rearrangements. Hence, it lowers the rearrangement rates of the molecules. We have obtained the rearrangement rate of the molecules under the effect of solvents, which are lower than those in the gas phase.
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