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ARTICLE

Theoretical Investigation into Thermodynamics and Kinetics of Tautomerization of 2-Aminopropenal

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ABSTRAK

2-amino propenal merupakan salah satu molekul paling sederhana yang memiliki 2 gugus fungsi yang memungkinkan reaksi tautomerisasi. Reaksi tautomerisasi sudah umum dikenal, kinetika dan termodinamika untuk molekul ini menjadi perhatian karena dapat digunakan sebagai model untuk reaksi yang lebih kompleks. Perhitungan dilakukan dengan menggunakan metode AM1 dengan perangkat lunak Orca 4.2.1. Algoritma CI-NEB-TS digunakan untuk menentukan tingkat energi optimum pada jalur reaksi. Hasil perhitungan menunjukkan bahwa bentuk keto lebih stabil daripada bentuk enol, dan bentuk keadaan transisi (TS) memiliki tingkat energi tertinggi. Jarak N-O berkurang seiring berjalannya reaksi, mencapai minima pada TS dan meningkat seiring terbentuknya produk, mengindikasikan bahwa proses transfer proton lebih menyerupai proses serah terima dibandingkan proses transfer sederhana. Bentuk HOMO dan muatan parsial mendukung interpretasi ini karena proton yang ditransfer pada bentuk TS memiliki kerapatan elektron yang sangat rendah akibat berada diantara dua atom yang sangat elektronegatif.

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Kata Kunci : DFT/TD-DFT, Grafena, DIbenzokoronena, Efek doping

ABSTRACT

Compound 2-aminopropenal is one of the simplest molecules that has 2 functional groups that allows for tautomerization reaction. The tautomerization reaction is while quite well known, the kinetics and thermodynamics of this specific molecule is quite interesting because it can be used as model compound for more complex reaction. The calculation of the process was performed using AM1 method employing Orca 4.2.1 software. CI-NEB-TS search algorithm was used to compute the minimum energy pathway. Calculation results show that the keto form is more stable that that of enol form, with transition state (TS) form having the higher energy. The N-O distance decrease as the reaction happen, reached a minimum at TS, and increase as the product started to form, indicating that the proton transfer process was closer to a hand-off than a simple transfer. HOMO moiety as well as partial charges support this conclusion by showing that proton at TS form had a very low electron density due to the proximity of both O and N thus depleting H atom of its electron.

Keywords: *DFT/TD-DFT, Graphene, Dibenzocorronene, Doping effect*

INTRODUCTION

Most – if not all – chemical reactions in general can be classified into either addition, elimination, substitution, or rearrangement. Rearrangement reactions are particularly interesting type of reaction because the number of atoms in the main structure tend to be constant due to the fact that the reaction only moves atoms around or swapped them with nearby molecule. One such reaction is tautomerization reaction. Tautomerization is the reaction between a pair of btautomers, in which a proton is move from one atom to another. Tautomerization reaction in most cases would change the functional group of the molecules. These changes include keto-enol, imine-enamine, nitroso-oxime, as well as several other types of tautomer pairs [1-2].

Thermodynamically, one of the tautomers tend to dominate the form due to the fact that one of them is more stable. This can be observed especially in keto-enol and imine-enamine pairs, in which keto and enamine pairs tend to be more stable than their tautomer. However, it is possible to construct a molecule that combined more than one functional group, thus making the forms stability less predictable. One of the simplest molecules that include more than one functional group is 2-aminopropenal [3-6].

The structure of 2-aminopropenal includes both a keto group and an amino group. Its cis isomers can undergo tautomerization between keto/enamine form to enol/imine via intramolecular proton transfer from the -NH2 group to the C=O group. This also introduces the necessity to study the kinetics of the tautomerization. While both aspect of the process have been this reaction have been explored before, we aim to take another look onto this process and see how the electronic structure as well as the dynamics of the process is related to the thermodynamics and kinetics aspects of this reaction.

COMPUTATIONAL DETAILS

The calculations were performed on the structure of 2-aminopropenal on both the keto and enol forms, as well as the transition state using Austin Model 1 (AM1) Semiempirical Quantum Chemistry method. The structure of both keto and enol were both optimized at several temperature to obtained the thermodynamics, molecular structures, and electronic structure of the system. The structure of the transition state was calculated using Climbing Image-Nudge Elastic Band Transition State (CI-NEB TS) search at room temperature. The resulting structure was recalculated using OptTS method at several temperature to obtained the thermodynamics, molecular structures, and electronic structure of the system [7-9].

All calculations were conducted using Orca version 4.2.1 for Windows. Avogadro 1.2.0 were employed to construct the initial structure as well as visualizing calculation results including 3D structure and orbitals moiety [10-11]

RESULT AND DISCUSSION

The structure of keto, enol, and TS all calculated at their most optimized energy, due to the fact that statistically lower energy structure is more favoured than structures with higher energy. The optimization results for keto and enol structure were confirmed by the fact that there is no imaginary (negative) frequency on the vibrational spectrum. Optimization result for TS calculation were confirmed by the presence of exactly one imaginary frequency at -2156.13 cm^{-1}, which correspond to hydrogen shifting between O and N. The structure of molecules is given in Figure 1.

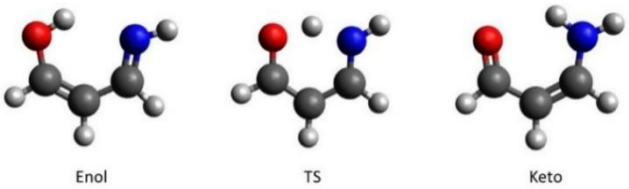

Figure 1. Structure of Enol, TS, and Keto form of the molecule

The structure of the molecule in all forms are planar and is not affected by the temperature. The position of the transferred proton is shifting from being bonded to O in enol form, to almost exactly in between O and N in TS form, and bonded to N in the enol form. From Figure 1 it can be also observed that during the transfer process not only the proton shifting from O to N, the position of O and N itself also shifting. This indicate the transfer process should be closer to hand off in which O move the proton and at some points it is closer to N and the electron from NH group start to envelope the transferred proton. This explanation is further supported by the orbital moiety of the molecule and the partial charges of the most involved atoms.

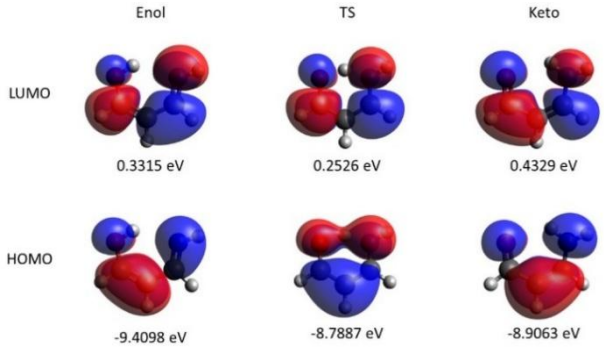

Figure 2. Frontier molecular orbital of the molecule

Table 1. Partial Charges of N, O, and H Involved in the Transfer in Proton Charge Unit

Atom	Enol	TS	Keto
H	0.3255	0.4134	0.2992
O	-0.5449	-0.5290	-0.3766
N	-0.3968	-0.4315	-0.3200

Figure 2 show the orbital moiety at HOMO and LUMO. At ground level, essentially HOMO is the occupied one. It can be seen that on enol and keto form the moiety only part on

O, N and 2 of the carbon atoms. However, at TS, the orbital moiety includes O-H-N with while the bottom part includes all of the carbon atoms. The orbital moiety on TS, while its envelope the proton, it also did not seem to be very significant. This is supported by the fact the partial charge of H on TS form is actually the highest indicating low electron density surrounding it.

Energetics

The energetics of the reaction is calculated at 290, 295, 300, 305, and 310 K. These calculations can be used to show the effect of temperature on the thermodynamics and kinetics of the reaction. This is especially useful to calculate the activation energy and the ac The relative energy of each form of the molecule at various temperature is given at Table 2.

Table 2. Relative Energy of the Molecule at Various Temperature in eV

Temperature (K)	enol	TS	keto
290	0.0000	0.7320	-0.4701
295	0.0038	0.7353	-0.4661
300	0.0076	0.7386	-0.4621
305	0.0114	0.7420	-0.4581
310	0.0153	0.7455	-0.4540

From Table 2 it can be seen that the energy of all the molecule increases as temperature increase, which are simply due to the fact that higher temperature correlate to higher internal energy. However, the increase happened at different rates, causing the reaction energy change (E_{rx}) to increase while the reaction activation energy (E_a) to decrease as temperature increase.

$$E_{rx} = E_{keto} - E_{enol}$$

$$E_a = E_{TS} - E_{enol}$$

Using harmonic transition state theory and E_a as function of temperature, the reaction rate constant can be calculated using this following equation

$$k = \frac{k_B T}{h} \frac{Q_{TS}}{Q_{keto}} \exp\left(-\frac{E_a}{k_B T}\right)$$

where k_B is the Boltzmann constant, h, is the Planck's constant, Q_{TS} and Q_{keto} is the harmonic partition function that can be calculated using

$$Q = \prod_{n=1}^{3N-6} \left[1 - \exp\left(-\frac{h\nu_n}{k_B T}\right)\right]$$

where ν_n are the frequency of the n-th real vibrational modes. The reaction rate constant and the activation energy from these calculations are shown in Table 2 and Figure 3.

Table 2. Kinetics Parameters from Harmonic Transition State Theory

Temperature (K)	Activation Energy (eV)	Reaction rate constant ($\times 10^{12}$ s^{-1})
290	1.2021	1.5437
295	1.2014	1.5703
300	1.2008	1.5969
305	1.2002	1.6235
310	1.1995	1.6501

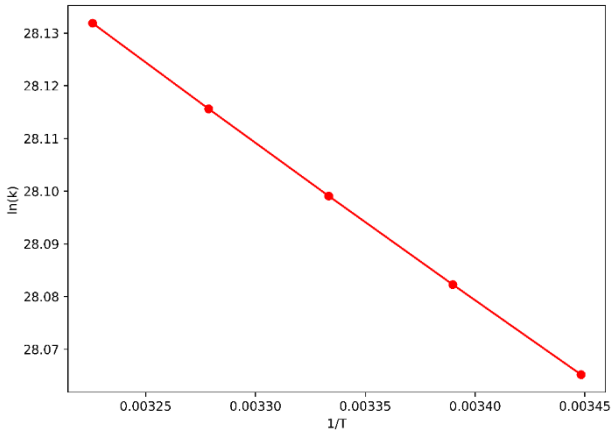

Figure 3. Arrhenius Plot from Harmonic Transition State Theory.

This result show that the Harmonic Transition State Theory is consistent with the simpler model from Arrhenius equation, indicating the viability of this model to be applied for chemical reaction modelling.

Minimum Energy Pathways

Minimum Energy Pathway (MEP) is the pathway on Potential Energy Surface that pass through the saddle point in between the reactant state and the product state. This saddle point usually corresponds to the transition state of the reaction. In mathematical sense MEP can be considered as geodesic on PES, and the horizontal projection of MEP line segment could be considered as the reaction coordinate.

The physical interpretation of this pathway on the other hand could be considered to be more straightforward as it is basically the most efficient way for the reaction happened in the state space. While it is not directly equivalent, it is quite similar to dynamic process for reaction in real space. The structural changes of 2-aminopropenal from enol form to keto form provided in Figure 4.

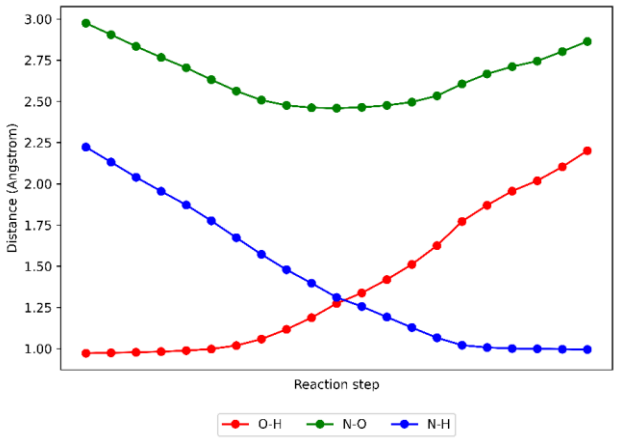

Figure 4. Atomic Distance as Reaction Moves Forward

From Figure out it can be seen that not only the proton that move in this tautomerization reaction, but also N and O. In the reaction process the O-N distance decrease first while O-H distance stays relatively the same. N-H distance decrease was merely due to the fact that H is being carried by O. At N-O distance approximately 2.70 Å the N-H distance has become quite close to significantly attract proton from O to N, thus the O-H distance started to increase quite significantly while N-H distance decrease. At the middle point which correspond to the TS structure, N-O distance was at minimum while O-H and N-H distance is at similar value.

The distance data consistency with optimization results was further supported by MEP energy values

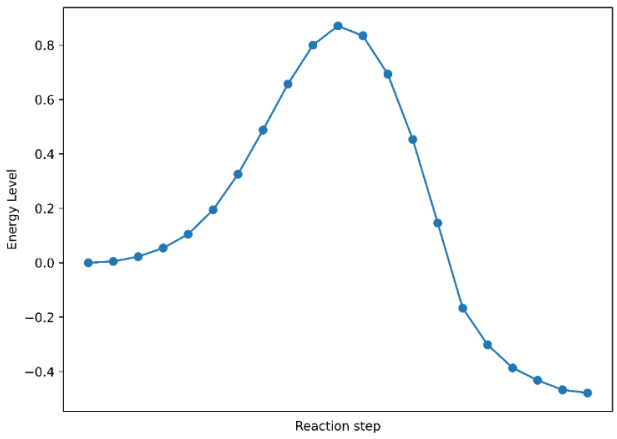

Figure 5. Energy Levels of the Minimum Energy Pathway

The energy level of the molecule increases as the reaction steps increase and reach a maximum at the middle and then decrease as the product started to formed. Due to the fact that keto form is more stable than its enol form, the energy of the product is lower than that of the reactant which further supported the viability of optimization/NEB-TS calculation to model this reaction process as the calculation results are self-consistent and the results also in good agreement with previous results.

CONCLUSION

Optimization calculation results in the form of structure and energetics indicate that the proton transfer process in 2-aminopropenal tautomerization reaction indicate that the proton transfer did not simply happen by moving the proton from O to N but more similar to moving OH group to the point that NH group are strong enough to accept it. HOMO moiety as well as H partial charge also shows that the proton has very low density at TS form.

The MEP of the reaction further supported this interpretation by showing that up to a point that the O-H atomic distance stays relatively the same until N-O distance become close enough for N to attract the proton

AUTHOR CONTRIBUTION

HAA, HH, FK, and YS all involved in the conceptualization of the paper. HAA performed the calculation and writing.

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