THE THEORETICAL STUDY OF TEMPERATURE- AND PRESSURE-DEPENDENT REACTIONS KINETIC FOR UNIMOLECULAR ISOMERIZATION REACTIONS OF C_2H_5O RADICAL

Nguyen Ngoc Tri[1,2], Nguyen Ngoc Ha[1*]

[1]*Faculty of Chemistry-Hanoi National University of Education*

[2]*Faculty of Chemistry-Quy Nhon University*

Abstract

Minimum energies for the C_2H_5O radical, products and transition states of reactions on the potential energy surface were obtained at the MP2/6-311++G(3df,2pd) high level of theory, and single-point energies were refined at the CCSD(T)/6-311++G(3df,2pd) level of theory for all stationary points. Isomerization reactions of C_2H_5O radical take place via two proton migration mechanisms: $C_2H_5O \rightarrow CH_3CHOH$ (1,2-H shift) **(1)** and $C_2H_5O \rightarrow CH_2CH_2OH$ (1,3-H shift) **(2)**. Temperature and pressure-dependent rate constants of the two reactions **(1)** and **(2)** were calculated by using transitional state theory (TST) and Rice-Ramsperger-Kassel-Marcus (RRKM) theory. Obtained results show that the reaction rate constants were: $k_\infty^{TST}(T)$ **(1)** $= 1.978.10^{10}.T^{0.428} \exp(-13530.4/T)$, $k_\infty^{TST}(T)$ **(2)** $= 3.077.10^{10}.T^{0.403} \exp(-14347.2/T)$; $k_\infty^{RRKM}(T)$ **(1)** $= 1.664.10^{12}.T^{0.204} \exp(-15465.0/T)$, $k_\infty^{RRKM}(T)$ **(2)** $= 1.183.10^{12}.T^{0.147} \exp(-15927.1/T)$ using TST and RRKM theory, respectively. The pressure-dependent rate constants of isomerization reactions being analysed and solved by RRKM theory and master equation (ME) method were $k(T,P)$ **(1)** $= 9.110.10^7.P^{0.815} \exp(-4959.3/T)$ and $k(T,P)$ **(2)** $= 1.382.10^7.P^{0.850} \exp(-5009.5/T)$. Our results suggest that, rate constants of both **(1)** and **(2)** depend linearly on pressure in the low-temperature and pressure ranges, or in the high-temperature range. Conversely, rate constants of both **(1)** and **(2)** are nearly not depending on pressure in the low-temperature and high-pressure ranges.

Keywords. Potential energies surface, isomerization reactions, Rice-Ramsperger-Kassel-Marcus theory.

1. INTRODUCTION

Alkoxy radicals are important intermediate species in hydrocarbon combustion and atmospheric processes [1-3]. Among alkoxies, ethoxy (C_2H_5O) is a simple and important radical. Ethoxy is formed from combination reactions i.e. C_2H_4 + OH, C_2H_5 + O,..., or decomposition reactions of C_2H_5OH, C_2H_5OOH, C_2H_5ONO,...[3, 4]. In recent years, many studies have focused on unimolecular reactions such as decomposition or isomerization reactions by using TST and RRKM theory [5]. Within these studies, decomposition reactions of ethoxy radical were investigated based on both experimental and theoretical aspects. All results showed that products formed from these decomposition reactions are important aldehydes such as HCHO, CH_3CHO [2,6]. In addition, the isomerization reaction with H atom migration in C_2H_5O molecule is more interested. However, the pressure-dependent rate constant for these reactions has not been surveyed in detail [1, 4, 6, 7]. In present paper, we used TST and RRKM theory to investigate the dependence of isomerization reaction rate constant of ethoxy radical on both temperature and pressure, taking the quantum tunneling effect by Wigner into account [8].

2. COMPUTATIONAL METHOD

Optimized geometries and the vibration frequencies for the reactant, products and transition states were performed at the MP2/6-311++G(3df,2pd) high-level of theory. Single point energy of species was calculated at the CCSD(T)/6-311++G(3df,2pd), a very high-level of theory, with optimized geometry structures carried out at MP2/6-311++G(3df,2pd) level. All thermodynamic parameters and reactions kinetic parameters were calculated by the Gaussian 03 and Chemrate programs [9, 10]. Gas-phase rate constants for reactions were calculated in the temperature range of 200-2500K based on TST and RRKM theory incorporating the quantum tunneling effect by Wigner [8]. Pressure-dependent rate constant was calculated by using RRKM theory and the ME

method [11, 12]. In the present work, pressure is taken in the range from 0.01 to 100 atms. The Leonard-Jones parameters for C_2H_5O radical and He buffer gas used as collision particle are taken from previous literature [13] (He: σ = 2.55 Å, ε/kT = 10K; C_2H_5O: σ = 4.53Å, ε/kT = 326.6K, the energy transfer per collision $\langle \Delta E_d \rangle = 200 \, cm^{-1}$).

3. RESULTS AND DISCUSSION

3.1. Geometry structures of reactant, products and transition states

Using the MP2/6-311++G(3df,2pd) high-level of theory, we obtained stable geometry structures of C_2H_5O radical, CH_3CHOH, CH_2CH_2OH products and **TS-1**, **TS-2** transition states for the isomerization reactions with the 1,2-H and 1,3-H

shifts, and results were shown in figure 1.

Calculated results show that geometry parameters of C_2H_5O radical are close to experimental data, in which the deviation of length just ranges from 0.003 to 0.014Å, and of angle ranging from 0.02 to 0.31^0 [14]. In addition, the structure of transition states found in this study is in good agreement with previously reported results [1, 6 ,7]. Specifically, the lengths of O-H, C-H and C-O bonds in **TS-1** and **TS-2** transition states in the previous studies were in the range of 1.205-1.216 Å (O-H); 1.234-1.274 Å (C-H) and 1.381-1.390 Å (C-O) for **TS-1**; 1.255-1.264 Å (O-H); 1304-1.353 Å (C-H) and 1.428-1.477 Å (C-O) for **TS-2**, respectively. Furthermore, imaginary frequencies in transition states estimated in this study are in good agreement with those of the previous ones [4, 6, 7].
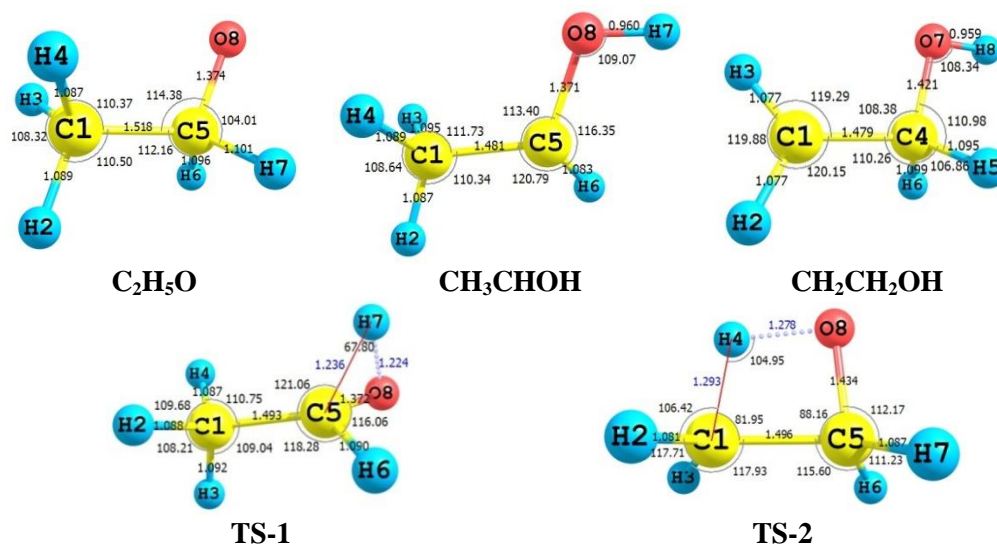

Figure 1: Optimized geometries of C_2H_5O radical, products and transition states (length: Å; angle: degree ^{o})

Table 1: The vibrational frequencies for C_2H_5O radical, products and transition states

Species	Frequencies
C_2H_5O	240.97, 406.35, 555.18, 885.87, 923.62, 1077.01, 1111.82, 1266.93, 1377.95, 1413.12, 1419.81, 1504.20, 1517.16, 2993.68, 3052.32, 3078.13, 3170.59, 3182.74
CH_3CHOH	195.03, 379.77, 415.28, 623.60, 944.67, 1035.99, 1070.29, 1224.48, 1278.06, 1400.33, 1465.61, 1486.30, 1509.09, 3034.27, 3123.85, 3174.11, 3193.45, 3896.31
CH_2CH_2OH	127.85, 264.47, 401.96, 454.03, 883.98, 980.35, 1082.03, 1135.36, 1241.59, 1273.76, 1436.16, 1486.73, 1517.97, 2987.38, 3043.22, 3218.00, 3343.35, 3897.88
TS-1	2042.24i, 199.19, 434.42, 644.78, 917.29, 932.67, 1086.12, 1132.15, 1226.48, 1379.85, 1417.14, 1491.75, 1501.38, 2569.44, 3061.88, 3119.19, 3150.13, 3188.85
TS-2	2245.20i, 397.01, 745.45, 833.19, 959.37, 1021.10, 1113.17, 1138.93, 1174.72, 1243.06, 1314.90, 1439.24, 1548.25, 2102.47, 3103.95, 3164.49, 3171.83, 3290.03

3.2. Thermodynamic parameters for isomerization reactions of C_2H_5O radical

The general reaction pathways of the investigated system and the corresponding potential energy barriers calculated at MP2/6-311++G(3df,2pd) were shown in figure 2.

Isomerization reactions of C_2H_5O radical can be divided into two categories as $C_2H_5O \rightarrow CH_3CHOH$ (1,2-H shift) (**1**) and $C_2H_5O \rightarrow CH_2CH_2OH$ (1,3-H shift) (**2**). Thermodynamic parameters for each reaction pathway were calculated at the MP2/6-311++G(3df,2pd) and CCSD(T)/6-311++G(3df,2pd) high levels of theory and shown in table 2.
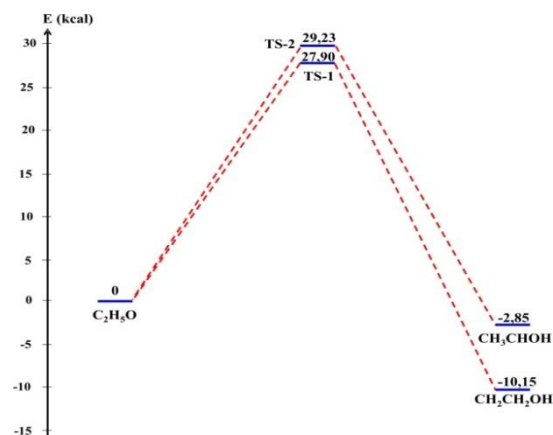

Figure 2: Potential energy surface for reactions at MP2/6-311++G(3df,2pd) level

Table 2: Thermodynamic parameters for reactions (kcal.mol^{-1}) ($^\#$for transition state)

Reaction	ΔE^0	ΔE_{ZPE}	ΔH^0_{298}	ΔG^0_{298}	$\Delta E^\#$	$\Delta H^\#$	$\Delta G^\#$
(**1**)	-10.54	-10.15	-9.95	-10.26	27.90	27.88	27.89
(**2**)	-2.27	-2.85	-2.40	-3.29	29.23	28.90	29.53

As shown in Table 2, reaction energies (ΔE^0, ΔE_{ZPE}) as well as Gibbs free energy at 298K (ΔG^0_{298}) of reactions (**1**) and (**2**) are quite negative. Therefore, (**1**) and (**2**) are likely to occur at 298K thermodynamically. In particular, energy values of ΔE^0, ΔE_{ZPE} and ΔG^0_{298} of (**1**) are greater than those of (**2**), so the reaction (**1**) takes places easily as compared to the (**2**). In addition, reaction enthalpy calculated at 298K (ΔH^0_{298}) for these reactions is negative, implying that those are exothermic reactions. Also, as shown in Figure 2, the potential energy for the α-C-H bond dissociation reaction (**1**) is smaller than that in β-C-H bond dissociation reaction (**2**), so reaction (**1**) is likely to happen as compared to reaction (**2**). Remarkably, our obtained results are compared to calculated results at different levels of theory in the previous studies. Accordingly, in the previous reported results, ΔE, $\Delta E^\#$ and $\Delta H^\#$ values for (**1**) reaction are about -9.69, in the range of 26.17-27.58 and about 26.58 kcal.mol^{-1}, respectively; ΔE, $\Delta E^\#$ and $\Delta H^\#$ for (**2**) reaction are about -2.77, in the range of 27.7-29.08 and about 20.27 kcal.mol^{-1}, respectively [1-4, 6]. Thus, the thermodynamic parameters estimated in this study are in good agreement with the aforementioned results.

3.3. The temperature- and pressure-dependent rate constant for isomerization reactions of C_2H_5O radical

Using TST and RRKM theory with the quantum tunneling correction by Wigner, at the high level of theory, we computed rate constant for isomerization reactions of C_2H_5O radical, and all results were shown in figure 3 and table 3.
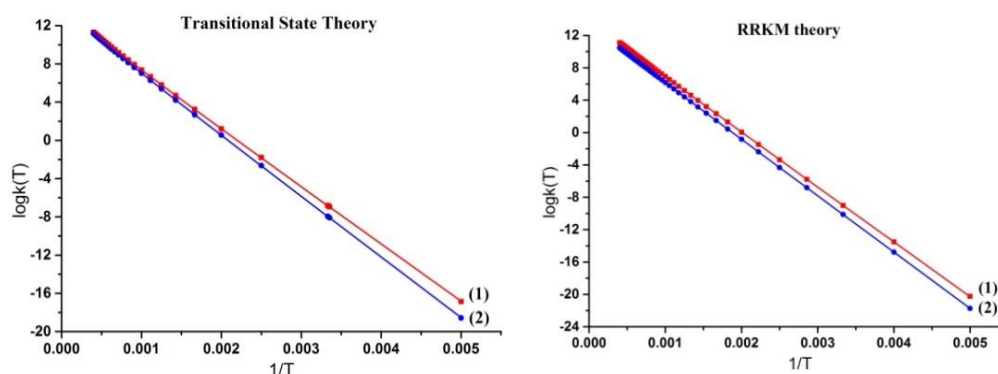

Figure 3: The temperature-dependent rate constant k(T) for (**1**) and (**2**) reactions by using TST and RRKM theory

Table 3: The temperature-dependent rate constant for (**1**) and
(**2**) reactions obtained at the MP2/6-311++G(3df,2pd) level

Reaction	Using TST	Using RRKM theory
(**1**)	$k_\infty(T) = 1.978.10^{10}.T^{0.428} \exp(-13530.4/T)$	$k_\infty(T) = 1.664.10^{12}.T^{0.204} \exp(-15465.0/T)$
(**2**)	$k_\infty(T) = 3.077.10^{10}.T^{0.403} \exp(-14347.2/T)$	$k_\infty(T) = 1.183.10^{12}.T^{0.147} \exp(-15927.1/T)$

Analyzing rate constants of reactions following three parameters Arrhenius expression $k_\infty(T) = A^{'}.T^n \exp(-E_a/RT)$ in the range of temperature 200-2500K, we obtained results shown in Table 3. Data on Table 3 shows that rate constants based on TST and RRKM theory for (**1**) and (**2**) reactions are close together. Our results show that the rate constant $k(T)$ depend highly linearly on the temperature T.

As a result, when the temperature increases, the reaction rate constant increases fast.

Pressure-dependent rate constants of reactions (**1**) and (**2**) calculated at the MP2/6-311++G(3df,2pd) level based on RRKM theory using He buffer gas as collision particle are shown in Figure 4.
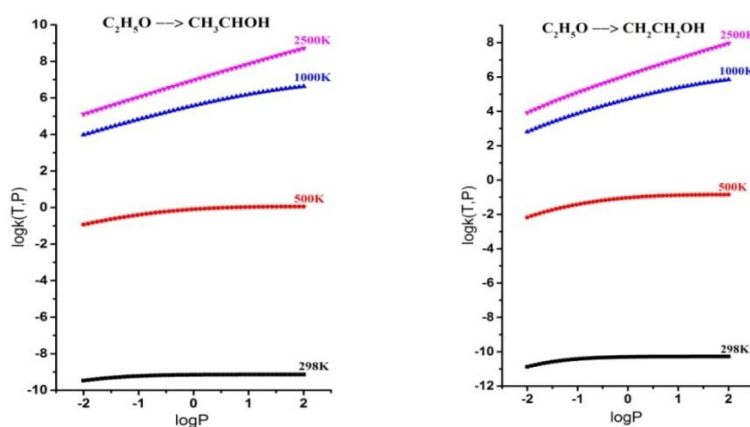

Figure 4: The pressure-dependent rate constants at different temperatures

The result in figure 4 shows that, the pressure-dependent rate constants of (**1**) are greater than those of (**2**) at different temperatures. The temperature- and pressure-dependent rate constants for the two reactions are obtained as followed: $k(T,P)$ (**1**) = $9.110.10^7.P^{0.815} \exp(-4959.3/T)$ and $k(T,P)$ (**2**) = $1.382.10^7.P^{0.850} \exp(-5009.5/T)$. This result indicates that (**1**) occurs faster than (**2**). Additionally, figure 4 shows that in the low temperature range (200-500 K), rate constants of reactions (**1**) and (**2**) depend linearly on pressure at low pressure (smaller than 1 atm), and being nearly independent on pressure at high pressure range (about 100 atm). Interestingly, rate constants of the two reactions depend nearly linearly on pressure at the high temperature range (1000-2500 K).

Unfortunately, we have not found any experimental data for these reactions. However, the analyzed results of reaction rate constants in this work calculated at MP2/6-311++G(3df,2pd) agree well with theoretical results in the previous studies. Thus, according to Zhang et al [1], the μVT/Eckart

rate constants of (**1**) and (**2**) reactions at QCISD(T)/aug-cc-pVTZ//MPW1K/6-31+G(d,p) level were $k(T)$ (**1**) = $3.90.10^{-31}.T^{12,4} \exp(-2130/T)$ s^{-1} and $k(T)$ (**2**) = $2.83.10^{-29}.T^{11.9} \exp(-2240/T)$ s^{-1}; according to Hoyermann et al. [4], those calculated by RRKM theory at the MP2/6-311+G**//MP2/6-31G* level were $k(T)$ (**1**) = $7.94.10^{12} \exp(-14830.4/T)$ s^{-1} and $k(T)$ (**2**) = $5.01.10^{13} \exp(-13579.5/T)$ s^{-1}; according to Viskolcz et al. [7], at QCISD(T)/6-311+G(3df,2p) level by using TST at 298, 500 and 750 (K) temperatures those were $6.41.10^{-8}$, $1.39.10^1$, $2.04.10^5$ for reaction (**1**), respectively and $7.57.10^{-12}$, $3.30.10^{-2}$, $2.11.10^3$ for reaction (**2**), respectively.

4. CONCLUSIONS

Stable structures of C_2H_5O radical, CH_3CHOH, CH_2CH_2OH products and transition states were optimized at the MP2/6-311++G(3df,2pd) high level of theory. Single point energy of species was calculated at the CCSD(T)/6-311++G(3df,2pd)

level. As a result, **(1)** and **(2)** reactions were likely to occur at 298K and 1 atm, thermodynamically. Rate constants for isomerization reactions of C_2H_5O radical were calculated based on the transition state theory and RRKM theory. As a result, the expressions of the temperature-dependent rate constants for **(1)** and **(2)** were: $k_\infty(T)$ **(1)** = $1.978.10^{10}.T^{0.428}$ exp(-13530.4/T), $k_\infty(T)$ **(2)** = $3.077.10^{10}.T^{0.403}$ exp(-14347.2/T) by using TST and $k_\infty(T)$ **(1)** = $1.664.10^{12}.T^{0.204}$ exp(-15465.0/T), $k_\infty(T)$ **(2)** = $1.183.10^{12}.T^{0.147}$ exp(-15927.1/T) by using RRKM theory, respectively. In addition, we obtained highly linear expressions of the temperature- and pressure-dependent rate constants for two reactions **(1)** and **(2)** as following: k(T,P) **(1)** = $9.110.10^7.P^{0.815}$ exp(-4959.3/T) and k(T,P) **(2)** = $1.382.10^7.P^{0.850}$ exp(-5009.5/T), respectively. Our results suggest that, the **(1)** reaction occurs more strongly than **(2)** reaction does. Also, at the low temperature (200-500 K), the rate constants of **(1)** and **(2)** are linearly dependent on pressure (within the small pressure range) and almost not depending on the pressure (in the range of high pressure). In the range of high temperature (1000-2500 K), rate constants for the two reactions are linearly dependent on pressure.

REFERENCES

1. Zhang Y., Zhang S., Li Q. S. *Ab initio calculations and mechanism of two proton migration reactions of ethoxy radical*, Chem. Phys., **308**, 109 (2005).

2. Poad B. L., Ray A. W. and Continetti R. E. *Dissociative Photodetachment of the Ethoxide Anion and Stability of the Ethoxy Radical CH_3CH_2O*, J. Phys. Chem. A, **117(46)**, 12035-12041 (2013).

3. Choi H., Bise R. T. and Neumark D. M. *Photodisociation Dynamics of the Ethoxy Radical C_2H_5O*, J. Phys. Chem. A, **104**, 10112-10118 (2000).

4. Hoyermann K., Olzmann M., Seeba J. and Viskolcz B. *Reactions of C_2H_5 Radical with O, O_3, NO_3: Decomposition Pathways of the Intermediate C_2H_5O Radaical*, J. Phys. Chem. A, **103**, 5692-5698 (1999).

5. Wright M. R. *An Introduction to Chemical Kinetics*, John Wiley & Sons Ltd, England (2004).

6. Xu Z. F., Xu K. and Lin M. C. *Ab initio Kinetics for Decomposition/Isomerization Reactions of C_2H_5O Radicals*, Chem. Phys. Chem., **10**, 972-982 (2009).

7. Hippler H. and Viskolcz B. *Addition complex formation vs. direct abstraction in the OH + C_2H_4 reaction*, Phys. Chem. Chem. Phys., **2**, 3591-3596 (2000).

8. Matus M. H., Nguyen M. T. and Dixon D. A. *Theoretical Prediction of the Heats of Formation of C_2H_5O Radicals Derived from Ethanol and of the Kinetics of β-C-C Scission in the Ethoxy Radical*, J. Phys. Chem. A, **111**, 113-126 (2007).

9. Frisch M. J. et al. *Gaussian 03 (Revision B.04),* Gaussian, Inc.: Wallingford, CT (2003).

10. Mokrushin V., Bedanov V., Tsang W., Zachariah M. and Knyazev V. *ChemRate. NIST*, Gaithersburg, MD, 1996-2002.

11. Barker J. R. and Golden D. M. *Master Equation Analysis of Pressure-Dependent Atmospheric Reactions*, Chem. Rev., **103**, 4577-4591 (2003).

12. Pritchard H. O. *The quantum theory of unimolecular reactions*, Cambridge University Press, UK (1984)

13. Caralp F., Devolder P., Fittschen C., Gomez N., Hippler H., Mereau R., Rayez M. T., Striebel F. and Viskolcz B. *The thermal unimolecular decomposition rate constants of ethoxy radicals*, Phys. Chem. Chem. Phys., **1**, 2935-2944 (1999).

14. http://webbook.nist.gov/chemistry/ and http://cccbdb.nist.gov/

Corespoinding author: **Nguyen Ngoc Ha**
Faculty of Chemistry
Hanoi National University of Education
136 Xuan Thuy, Cau Giay, Hanoi
E-mail: nguyenhalvt@yahoo.com, Telephone: 0989133436.