THEORETICAL STUDY ON THE REACTION MECHANISM OF CO$_2$ FORMATION FROM ACYLOXY RADICALS

Nguyen Thi Minh Hue[1,*] Pham Tho Hoan[2], Vu Hoang Phuong[3], Nguyen Trong Nghia[4], Ngo Tuan Cuong[1,*]

[1]Faculty of Chemistry and Center for Computational Science,
Hanoi National University of Education, 136 Xuan Thuy, Cau Giay, Ha Noi, Viet Nam

[2]Faculty of Information Technology and Center for Computational Science,
Hanoi National University of Education,136 Xuan Thuy, Cau Giay, Ha Noi, Viet Nam

[3]Sao Do University, 24 Thai Hoc 2, Chi Linh, Hai Duong, Viet Nam

[4]School of Chemical Engineering, Hanoi University of Science and Technology,
1 Dai Co Viet, Ha Noi, Viet Nam

[*]Email*: hue.nguyen@hnue.edu.vn*

ABSTRACT

The decomposition mechanism of acyloxy radicals has been studied by the Density Functional Theory (DFT) using B3LYP functional in conjunction with the 6-311++G(d,p) and 6-311++G(3df,2p) basis sets. The potential energy profiles for reaction systems were generally established. Calculated results indicate that the formation of products including hydrocarbon radicals and CO$_2$ molecule is energetically favored. The rate of decomposition increases with the number of carbon in non-cyclic saturated acyloxy radicals. Calculated enthalpies and Gibbs free energies of reactions well agree with experimental values. This study is a contribution to the understanding of the reaction mechanism of decomposition of acyloxy radicals in atmosphere and combustion chemistry.

Keywords: reaction mechanism, acyloxy radical, density functional theory.

1. INTRODUCTION

In chemical reactions of organic compounds free radicals play a crucial role [1-3]. They are involved in almost every reactions in fuel systems, and in the earth's atmosphere. In particular, reactions of the free acyloxyl radical RCOO$^\bullet$ has attracted much attention from both theoretical and experimental chemists [4-14]. These radicals are readily formed from thermal decompositions and photo-decompositions of diacyl peroxides due to the weakness of -O-O- bonds. In addition, they can be formed directly in the atmosphere from reactions between aldehydes and ketones with reagents such as O$_2$, NO or hydroxyl radical OH$^\bullet$. The RCOO$^\bullet$ free

radicals exist only for a very short time but are crucial for organic synthesis reactions. It has been proven experimentally that alkyl free radicals $R^\bullet$ and CO_2 are the products of decompositions of $RCOO^\bullet$ radicals [13], in which alkyl radicals $R^\bullet$ are important for the synthesis of hydrocarbons, and such complex natural products as interiorins, kadsulignans. However, to our knowledge there is no theoretical investigation on the mechanisms of decompositions of acyloxy free radicals, as well as a rule for these decompositions as the numbers of carbon atoms in the radicals increase. Therefore, a theoretical study on the mechanism of decompositions of acyloxy radicals $RCOO^\bullet$ is important.

2. MATERIALS AND METHODS

Geometrical structures of the reactants, intermediates, transition states and products considered are optimized by using the method of density functional theory at the B3LYP/6-311++G(d,p) level [15]. Transition states are confirmed by analyzing the vibrational frequency and intrinsic reaction coordinate (IRC) calculations. Relative energies are improved at higher level of calculation, being B3LYP/6-311++G(3df,2p). Geometrical structures, energies, thermodynamical parameters and energy diagrams for the systems are given in the following section. Calculations are performed using the Gaussian 09 package [16].

3. RESULTS AND DISCUSSION

We have investigated the decompositions of 11 acyloxy free radicals $RCOO^\bullet$ in which $R^\bullet$ is a unbranched alkyl radical C_nH_{2n+1} (n = 1-7) or a cycloalkyl C_nH_{2n-1} (n = 3-6) moiety. Reactants, intermediates and products of the *i*th reaction are denoted respectively as RA_i, TS_i, P_i, whose optimized geometries are illustrated in Figure 1. Relative energies of the species are evaluated and listed in Table 1. Each reaction pathway goes through a single transition state forming the products directly, *i.e.* the hydrocarbon radical $R^\bullet$ and CO_2 molecule. All the reaction pathways, except for the cyclopropyl-substituted reactant (8th channel), have quite similar trends and are shown in the energy diagram in Figure 2.

For the 8th reaction pathway the relative energy of product P8 is higher than that of the reactants due to the formation of a high-energy cyclopropyl radical. Generally, in the structures of reactants, the $\angle OCO$ bond angle is in between 111-112°. There is an unpaired electron delocalized amongst three atoms O-C-O, leading to a symmetric OCO structure with the O-C bond length of about 1.250 – 1.260 Å. Each of transition states has only one vibrational mode with an imaginary frequency corresponding to the cleavage of the C-C bond while forming the second C=O double bond. As a result, a C-O bond is lengthened to about 1.300 Å while the other C-O bond is shortened down to about 1.200 Å. The $\angle OCO$ bond angle is widened in order to facilitate the formation of a CO_2 molecule ($\angle OCO = 180°$). The unpaired electron which is delocalized amongst three atoms O-C-O gradually transfers onto the C atom of the alkyl group. The result is that this latter C atom switches from the sp^3 hybridization in the reactant to the sp^2 one in the hydrocarbon radical $R^\bullet$.
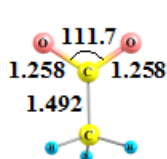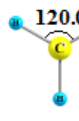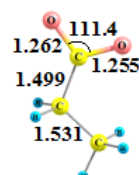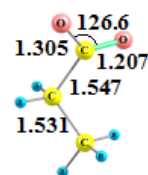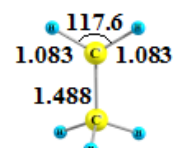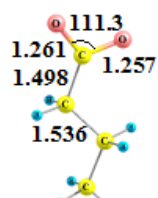
RA1   **TS1**   **P1**   **RA2**   **TS2**   **P2**
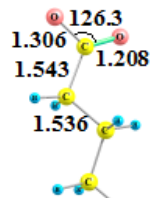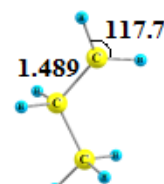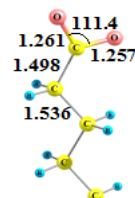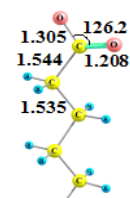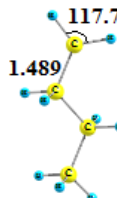
RA3   **TS3**   **P3**   **RA4**   **TS4**   **P4**
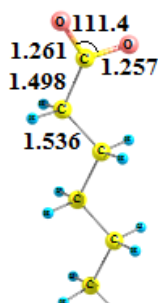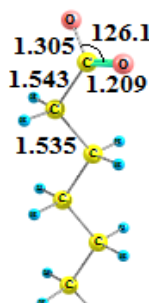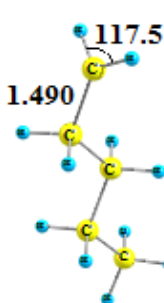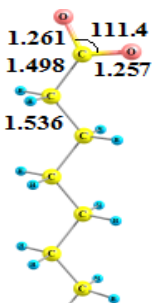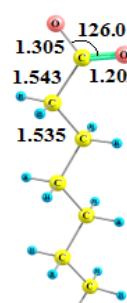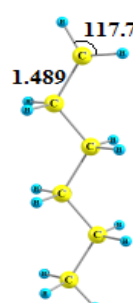
RA5   **TS5**   **P5**   **RA6**   **TS6**   **P6**
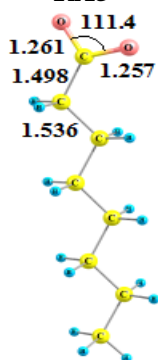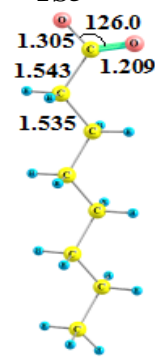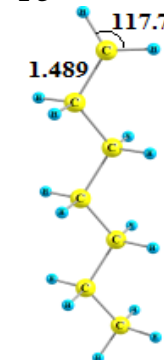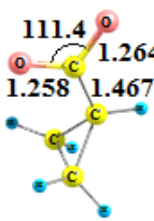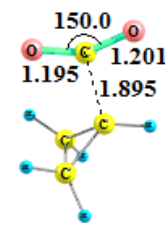
RA7   **TS7**   **P7**   **RA8**   **TS8**   **P8**
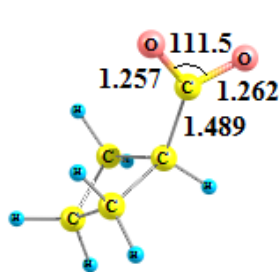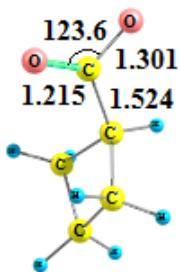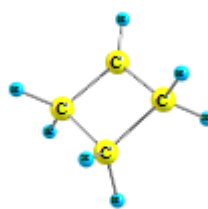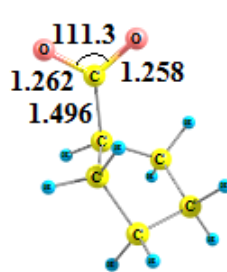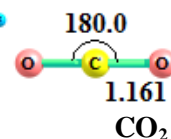
RA9   **TS9**   **P9**   **RA10**   **CO₂**
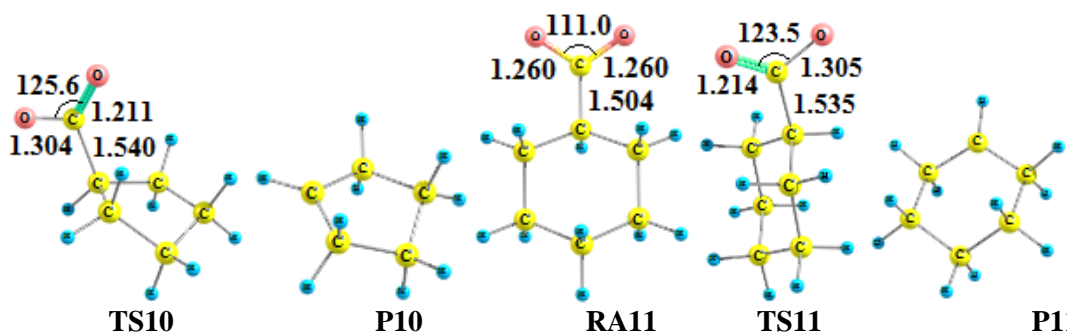
Figure 1. Optimized geometries of reactants, transition states, and products of decomposition of acyloxy free radicals at the B3LYP/6-311++G(d,p) level of theory. [Bond length in Å, bond angle in degrees].
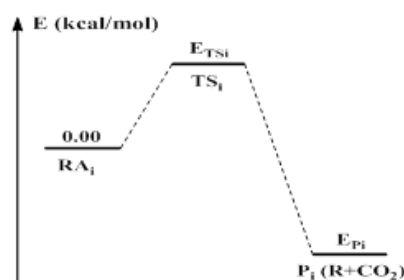
Figure 2. Energy diagram of decomposition of acyloxy radical of the ith reaction pathway (I = 1-7; 9-11).

From Table 1 showing relative energies of the species, we have plotted a graph which illustrates the dependence of the barrier heights - the relative energies between reactants and transition states - on the numbers of carbon atoms in the alkyl group in the decompositions of linear chain acyloxy radicals. The result is represented in Figure 3.

Table 1. Relative energy (ΔE) of the species available in the decomposition of acyloxy free radicals.

Species	ΔE (kcal/mol)	Species	ΔE (kcal/mol)	Species	ΔE (kcal/mol)	Species	ΔE (kcal/mol)
RA1	0.00	P3	-9.20	TS6	2.81	RA9	0.00
TS1	4.47	RA4	0.00	P6	-9.06	TS9	1.35
P1	-6.27	TS4	2.85	RA7	0.00	P9	-9.52
RA2	0.00	P4	-9.15	TS7	2.78	RA10	0.00
TS2	3.28	RA5	0.00	P7	-9.00	TS10	2.36
P2	-9.45	TS5	2.87	RA8	0.00	P10	-13.44
RA3	0.00	P5	-8.73	TS8	4.25	RA11	0.00
TS3	2.96	RA6	0.00	P8	1.82	TS11	1.73
						P11	-11.66

It can be seen from Figure 3 that in term of kinetics as the numbers of carbon atoms increase, the activation energies for the decompositions of straight chain acyloxy radicals decrease, though for the cases as radicals with more than 4 carbons the values of barrier heights differ insignificantly. This trend could be reasoned as follow: as the numbers of carbon atoms increase, the acyloxy radicals become bulky, less stable and more readily decomposable. For the reactions of cyclic

acyloxy radicals, the highest activation energy corresponds to the formation of cyclopropyl. This radical has a high energy of formation due to the ring strain arising when the radical carbon atom transforms from the sp^3 to sp^2 hybridization. The activation energies for the decomposition are lowest for the cases of forming cyclobutyl and cyclohexyl due to the spatial effect between the CO_2 group and neighboring hydrogen atoms.

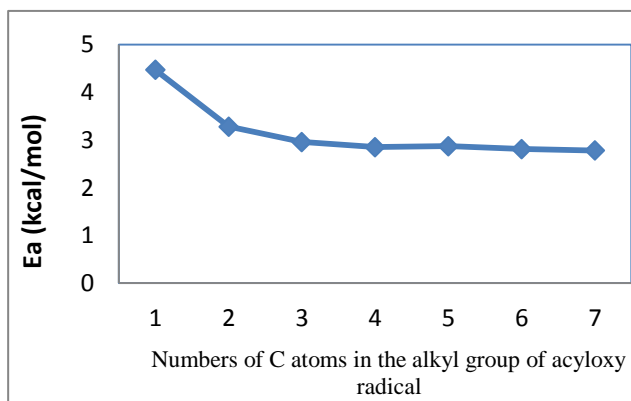*Figure 3*: Graph represents the dependence of the activation energieson numbers of carbon atoms in the alkyl groups of the acyloxy radicals.

Along with the relative energies, thermodynamical parameters of the decompositions are also calculated and arranged in Table 2. The results in this Table show that in terms of thermodynamics all the investigated reactions could occur spontaneously. Two reaction pathways which have highest energy barriers (the 1st pathway, 4.47 kcal/mol, and the 8th pathway, 4.25 kcal/mol) have the least negative free energy change ΔG^o_{298} (-12.96 and -7.74 kcal/mol, respectively) while for the formation of alkyl groups R (C_nH_{2n+1}; n = 2 - 7) the free energy change ΔG^o_{298} differ insignificantly. The formations of cyclopentyl and cyclohexyl radicals are the most kinetically favorable amongst the reactions concerned. The calculated results of elthanpy changes of 1st, 2nd and 3rd reactions are rather close to experimental values. This affirms that the results of our theoretical calculations are reliable.

Table 2. Thermodynamical parameters for the decomposition of acyloxy free radicals.

Reaction pathway	ΔG^o (kcal/mol)	ΔH^o (kcal/mol)	ΔH^o (kcal/mol) (Experimental) [17]
1. $CH_3CO_2 \rightarrow CH_3 + CO_2$	-12.96	-4.96	-5.18 ± 1
2. $C_2H_5CO_2 \rightarrow C_2H_5 + CO_2$	-18.43	-8.32	-10.54 ± 1
3. $C_3H_7CO_2 \rightarrow C_3H_7 + CO_2$	-18.20	-8.28	-10.34 ± 1
4. $C_4H_9CO_2 \rightarrow C_4H_9 + CO_2$	-18.56	-8.25	
5. $C_5H_{11}CO_2 \rightarrow C_5H_{11} + CO_2$	-18.52	-7.81	
6. $C_6H_{13}CO_2 \rightarrow C_6H_{13} + CO_2$	-18.53	-8.22	
7. $C_7H_{15}CO_2 \rightarrow C_7H_{15} + CO_2$	-18.41	-8.17	
8. cyc-$C_3H_5CO_2 \rightarrow C_3H_5 + CO_2$	-7.74	2.65	
9. cyc-$C_4H_7CO_2 \rightarrow C_4H_7 + CO_2$	-19.39	-8.57	
10. cyc-$C_5H_9CO_2 \rightarrow C_5H_9 + CO_2$	-22.53	-12.77	
11. cyc-$C_6H_{11}CO_2 \rightarrow C_6H_{11} + CO_2$	-21.03	-10.96	

4. CONCLUSION

Geometrical structures of intermediates in the decomposition of acyloxy free radicals $RCOO^{\bullet}$, in which R are alkyl groups C_nH_{2n+1} (n = 1-7) and cycloalkyl groups C_nH_{2n-1} (n = 3-6), have been determined. The potential energy surfaces of these processes have also been constructed. Generally, heights of energy barriers of the investigated reactions are quite small. A graph was plotted demonstrating the dependence of the activation energies on the number of carbon atoms in the acyloxy radicals. For larger unbranched acyloxy radicals, the decomposition proceeds more readily as the number of carbon atoms increase. Thermodynamical parameters of the reactions including Gibbs free energy changes, enthalpy changes have also been computed. All the investigated decompositions of acyloxy radicals are thermochemically favorable and the calculated enthalpy changes of the reactions are in good agreement with experimental values.

REFERENCES

1. March J. - Advanced Organic Chemistry: Reactions, Mechanisms, and Structure, 4th Edition, John Wiley& Sons, New York, (1992).

2. Herk L., Feld M., Szwarc M. J. - Studies of "Cage" Reactions, Am. Chem. Soc. **83** (1961) 2998.

3. Skell P. S., May D. D. J. – Ground- and excited-state carboxylate radical chain carriers. Radical chain substitution reactions with acyl hypohalites, Am. Chem. Soc. **105** (1983) 3999.

4. Ioffe A. I., Troyanskii É. I., Nikishin G. I. - Theoretical examination of the competitive decarboxylation and isomerization of acyloxy radicals, Bulletin of the Academy of Sciences of the USSR, Division of chemical science **36** (7) (1987) 1538-1540.

5. Skakovskii E. D., Lamotkin S. A., Tychinskaya L. Yu. - Lifetime of acyloxy radicals produced by decomposition of acetylpropionyl peroxide, Journal of Applied Spectroscopy **64** (3) (1997) 319-324.

6. Jousseaume B., Noiret N., Pereyre M., Frances, J. M. and Petraud M. - Stereochemistry of the thermal decomposition of (2-(acyloxy)alkyl) triorgano stannanes, Organometallics **11** (11) (1992) 3910-3914.

7. Fraind Turncliff R., Fox T., Salisbury B., Sodano J., Elabd A., Ryzhkov L. R. - Geminate reactions and the lifetimes of acyloxy radicals in thermal decomposition of symmetrical primary diacyl peroxides, Journal of Undergraduate Chemistry Research **6** (2) (2007).

8. Renaud P., Sibi M. P. - Radicals in Organic Synthesis, 1st Edition.; Wiley-VCH: Weinheim, 2001, pp. 1–2.

9. Zard S. Z. - Radical Reactions in Organic Synthesis; Oxford University Press: Oxford, 2003.

10. Crich D., Yao Q., Fredrick Filzen G. - Chemistry of beta-(Phosphatoxy) alkyl and beta-(Acyloxy)alkyl Radicals. Migration Reactions: Scope and Stereoselectivity of beta -

(Phosphatoxy)alkyl Rearrangement. Mechanism of beta-(Phosphatoxy)alkyl and beta-(Acyloxy)alkyl Migration, J. Am. Chem. Soc. **117** (46) (1995) 1455–11470.

11. Sibi M. P., Zimmerman J. - Pyrones to Pyrans: Enantioselective Radical Additions to Acyloxy Pyrones, J. Am. Chem. Soc. **128** (41) (2006) 13346–13347.

12. Pokidova T. S., Denisov E. T., Shestakov A. F. - Kinetic parameters and geometry of the transition state of decarboxylation reactions of carboxyl and formyl radicals, Petroleum Chemistry, Springer Science and Business Media, 2008, pp. 0965-5441.

13. Hilborn J. W., Pincock J. A. - Rates of decarboxylation of acyloxy radicals formed in the photocleavage of substituted 1-naphthylmethyl alkanoates, Journal of The American Chemical Society, **113**(7) (1991) 2683-2686

14. Zipse H. - Acyloxy-shifts in open and closed shell systems–intramolecular nucleophilic substitution reactions in disguise, J. Chem. Soc., Perkin Trans. **2** (1996) 1797-1800.

15. Jensen F. - Introduction to Computational Chemistry, Second edition, John Wiley & Sons, Ltd, 2007.

16. Frisch M. J., Trucks G. W., Schlegel H. B., Scuseria G. E., Robb M. A., Cheeseman J. R., Scalmani G., Barone V., Mennucci B., Petersson G. A., Nakatsuji H., Caricato M., Li X., Hratchian H. P., Izmaylov A. F., Bloino J., Zheng G., Sonnenberg J. L., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Vreven T., Montgomery J. A., Peralta J. E., Ogliaro F., Bearpark M., Heyd J. J., Brothers E., Kudin K. N., Staroverov V. N., Kobayashi R., Normand J., Raghavachari K., Rendell A., Burant J. C., Iyengar S. S., Tomasi J., Cossi M., Rega N., Millam J. M., Klene M., Knox J. E., Cross J. B., Bakken V., Adamo C., Jaramillo J., Gomperts R., Stratmann R. E., Yazyev O., Austin A. J., Cammi R., Pomelli C., Ochterski J. W., Martin R. L., Morokuma K., Zakrzewski V. G., Voth G. A., Salvador P., Dannenberg J. J., Dapprich S., Daniels A. D., Farkas O., Foresman J. B., Ortiz J. V., Cioslowski J., and Fox D. J. - GAUSSIAN 09, Revision A.02, Gaussian, Inc. Wallingford, CT, 2009..

17. Lide D. R. - CRC Handbook of Chemistry and Physics, Internet Version 2005.