

THEORETICAL STUDY ON THE REACTION MECHANISM OF CO₂ FORMATION FROM ACYLOXY RADICALS

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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 CO₂ 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[•] 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 O₂, NO or hydroxyl radical OH[•]. The RCOO[•] 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.

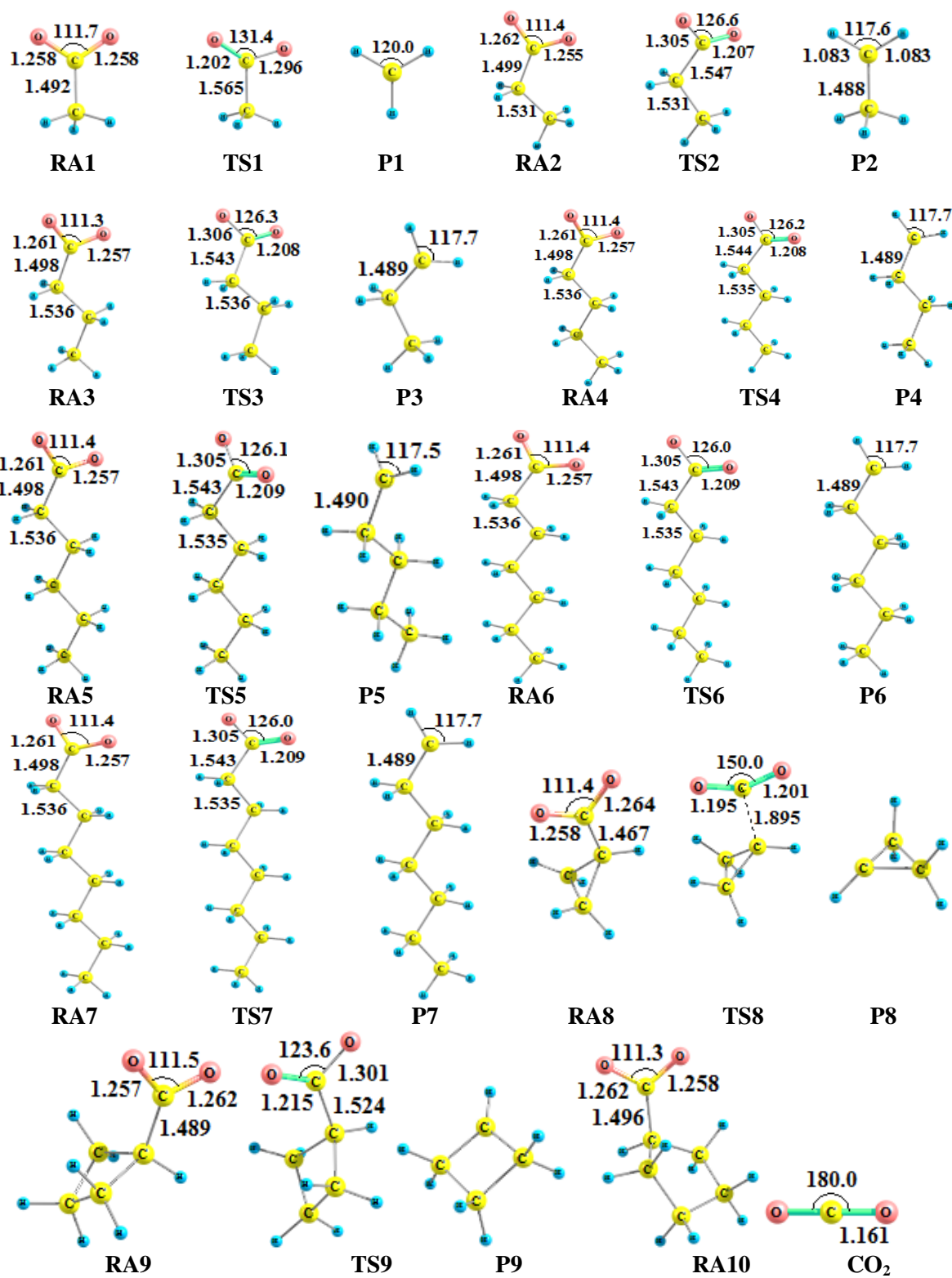
2. MATERIALS AND METHODS

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 $111-112^\circ$. 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 $1.250 - 1.260 \text{ \AA}$. 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 \AA while the other C-O bond is shortened down to about 1.200 \AA . The $\angle OCO$ bond angle is widened in order to facilitate the formation of a CO_2 molecule ($\angle OCO = 180^\circ$). 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 .



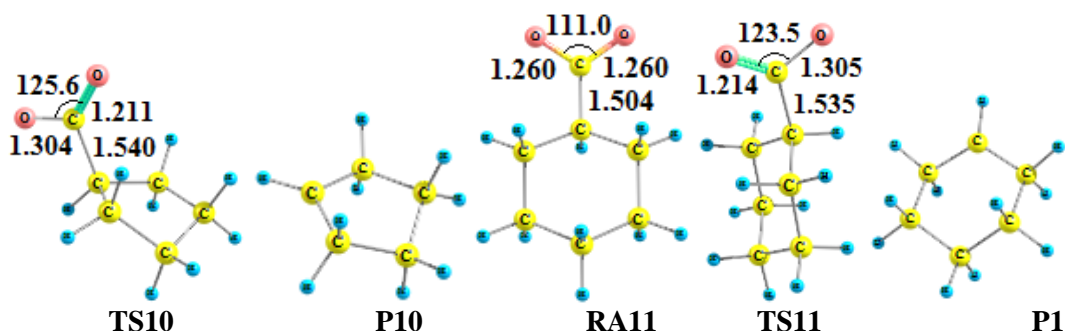


Figure 1. Optimized geometries of reactants, transition states, and products of decomposition of acyloxy free radicals at the B3LYP/6-311++G(d,p) level of theory. [Bond length in Å, bond angle in degrees].

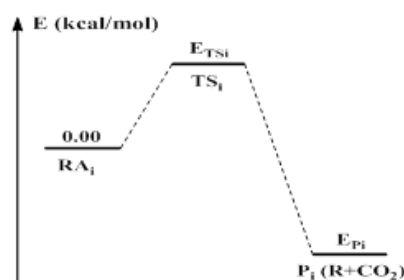


Figure 2. Energy diagram of decomposition of acyloxy radical of the i^{th} reaction pathway ($i = 1-7; 9-11$).

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 sp³ to sp² hybridization. The activation energies for the decomposition are lowest for the cases of forming cyclobutyl and cyclohexyl due to the spatial effect between the CO₂ group and neighboring hydrogen atoms.

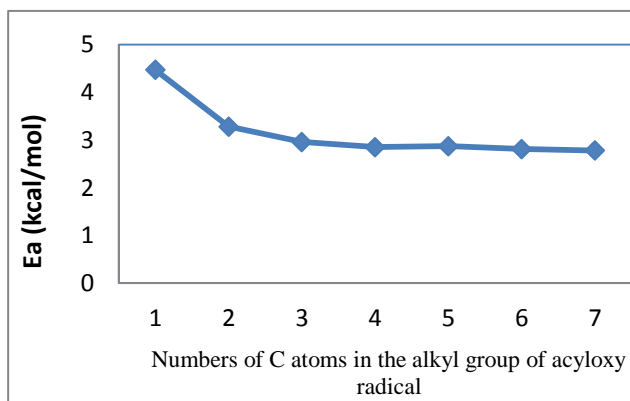


Figure 3: Graph represents the dependence of the activation energies on numbers of carbon atoms in the alkyl groups of the acyloxy radicals.

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°_{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°_{298} differ insignificantly. The formations of cyclopentyl and cyclohexyl radicals are the most kinetically favorable amongst the reactions concerned. The calculated results of enthalpy 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° (kcal/mol)	ΔH° (kcal/mol)	ΔH° (kcal/mol) (Experimental) [17]
1. CH ₃ CO ₂ → CH ₃ + CO ₂	-12.96	-4.96	-5.18 ± 1
2. C ₂ H ₅ CO ₂ → C ₂ H ₅ + CO ₂	-18.43	-8.32	-10.54 ± 1
3. C ₃ H ₇ CO ₂ → C ₃ H ₇ + CO ₂	-18.20	-8.28	-10.34 ± 1
4. C ₄ H ₉ CO ₂ → C ₄ H ₉ + CO ₂	-18.56	-8.25	
5. C ₅ H ₁₁ CO ₂ → C ₅ H ₁₁ + CO ₂	-18.52	-7.81	
6. C ₆ H ₁₃ CO ₂ → C ₆ H ₁₃ + CO ₂	-18.53	-8.22	
7. C ₇ H ₁₅ CO ₂ → C ₇ H ₁₅ + CO ₂	-18.41	-8.17	
8. cyc-C ₃ H ₅ CO ₂ → C ₃ H ₅ + CO ₂	-7.74	2.65	
9. cyc-C ₄ H ₇ CO ₂ → C ₄ H ₇ + CO ₂	-19.39	-8.57	
10. cyc-C ₅ H ₉ CO ₂ → C ₅ H ₉ + CO ₂	-22.53	-12.77	
11. cyc-C ₆ H ₁₁ CO ₂ → C ₆ H 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 $\text{C}_n\text{H}_{2n+1}$ ($n = 1-7$) and cycloalkyl groups $\text{C}_n\text{H}_{2n-1}$ ($n = 3-6$), 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.

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