

**COMPUTATIONAL INVESTIGATION INTO THE KINETICS, MECHANISM AND THERMODYNAMICS PROPERTIES OF THE GAS-PHASE THERMAL DECOMPOSITION OF 1-PHENYL ETHYL ACETATE****¹Timothy Oluwaseun ESAN, ²Babatunde Temitope OGUNYEMI, ³Oluwatoba Emmanuel OYENEYIN, ¹Oluwafemi Lawrence ADEBAYO, ⁴Isaiah Ajibade ADEJORO**¹Department of Chemical Sciences, Bamidele Olumilua University of Education Science and Technology, Ikere –Ekiti Ekiti State, Nigeria²Physical and Computational Unit, Department of Chemistry, Federal University Otuoke, Bayelsa State, Nigeria³Theoretical and Computational Chemistry Unit, Department Chemical Sciences, Adekunle Ajasin University, Akungba-Akoko, Ondo State, Nigeria⁴Department of Chemistry University of Ibadan, Ibadan Nigeria.*Corresponding authors' email: ogunyemibt@fuotooke.edu.ng**ABSTRACT**

Kinetics and thermodynamics of gas-phase thermal decomposition of 1-phenylethyl acetate to vinyl benzene and acetic acid (ethanoic) were carried out using the density functional theory (DFT) method at B3LYP/6-31++G**. Geometric parameters obtained include atomic charge distribution, dihedral angles, bond lengths, and bond angle for the ground state reactant (GS), transition state (TS), and the product (PRD) while the thermodynamic parameters such as a change in entropy change (ΔS), change in enthalpy ($\Delta H_{\text{reaction}}$) and free Gibbs energy were calculated at 623K with an interval of 25K. Kinetic parameters determined include activation energy (E_a), Pre-exponential Arrhenius factor ($\log A$) and rate (k). Geometric results revealed that the decomposition reaction is through asynchronous cleavage of α -ether oxygen bonds and β -carbon-hydrogen in the six-membered cyclic transition state: C₂-H₁ and C₅-O₇ bond breaking occurred first while the C₉-H₁ bond formation process is lagging behind in a single step. The ΔS (5.867 J/mol/K); $\Delta H_{\text{reaction}}$ (38.45 kcal/mol), ΔG (39.69 kJ/mol), E_a (43.7 kcal/mol), $\log A$ (12.70) and k ($6.1 \times 10^{-2} \text{ s}^{-1}$) compared well with the experimental available results in literature at 623K. The intrinsic reaction coordinate (IRC) on the TS structures shows that the reactant connects to the respective minima while the Wilberg bond index shows that the TS possesses 'an early' character closer to the reactant than the products. The theoretical calculation method can be used to study the thermodynamics, mechanism and kinetics of the thermal decomposition of acetates thus reducing the cost, laboratory experiments time and exposure to hazardous chemicals.

Keywords: Acetates, DFT, Olefins, Unimolecular reactions**INTRODUCTION**

The world has been encouraged to develop new chemistry that is eco-friendly, inexpensive and less time-consuming (Warren Hehre 2003). To achieve this mandate, the computational chemistry method which involves the use of computer algorithm to solve chemical problems becomes a focus. It uses the data obtained from theoretical calculations incorporated into efficient computer software to calculate the properties such as geometry of the constituent atom, absolute and relative energies, electronic charge distributions, dipole and vibrational energy of molecules and solids (Parr, 2001). The ability to calculate these properties allows theoretical chemists to solve problems of chemical importance. It should be noted that experimental methods used in explaining chemical reactions and structure-properties relationship of the new systems are often expensive and time-consuming. Advances in computer hardware, software, and theoretical chemistry have brought high-performance computing and graphic tools. Consequently, the use of theoretical methods has become a desirable approach to probe chemical reactions and overcome the disadvantages of trial and error of the experimental approach (Ogunyemi and Bosisade, 2020).

A large number of studied unimolecular reactions (thermal decomposition) in the gas phase apparently occurred through 4- and center cyclic activated complexes (Warren Hehre 2003; Blades, 1954; Hurd and Blunck, 1938; Saheb and Hosseini, 2013; Adejoro *et al.*, 2017). The mechanisms of ethyl acetate previously reported show that various pathways for the unimolecular reactions are possible [8-10]. All the pathways proposed have contributed immensely to the outcome of the

reaction. The most favourable pathway to this thermal decomposition through the experimental research has focused on pathways that give acetic acid and olefin [Chuchani *et al.*, 1981; Rosas *et al.*, 2010]. The first mechanism employed in the thermal decomposition of 1-phenyl ethyl acetate is based on the elimination pathway (Taylor 1983; Blades 1954; Hurd and Blunck, 1938). The gas-phase thermal decomposition reactions which are unimolecular in nature, seem to proceed through 4-centre and 6-centre cyclic activated complexes (O'Neal and Benson, 1967). According to experimental reports (Blades 1954), thermal decomposition of 1-phenylethyl acetate proceeds through a concerted six-membered cyclic transition state type of mechanism. The presence of a C_β-H on the alkyl side of organic esters, such as acetates, leads to elimination through a six-centered cyclic transition type of mechanism (Adejoro and Bamkole, 2005; Esan *et al.*, 2020; Brusco *et al.*, 2009; Adejoro *et al.*, 2013). The importance of the breaking of the carbon-hydrogen and carbon-oxygen single bonds aids the formation of olefinic bond stability of ester at higher yield. The vast majority of the six center reactions are carboxylic acid eliminations from the 1-phenylethyl acetate to produce olefins (Esan *et al.*, 2017; Adejoro and Bankole 2009). The reactions involve a non-synchronous break in the β -carbon-hydrogen and the α -ether oxygen bonds through a six-membered cyclic state. The aim of this research is to use computational modeling to investigate the kinetics and thermodynamic properties of acetate with electron donating group (phenyl) as substituent. This work therefore provides a guide to the thermal decomposition of organic compounds and helps in the

determination of other kinetic and thermodynamic properties that cannot be obtained through experimental method.

Computational Procedure Conformational Search

The molecules were set up for pre-optimization by searching for conformers with the least possible energy value. The molecular mechanics force field (MMFF), a model that has shown good ability for determining lowest conformer energy, was employed. Molecular mechanics force field has been chosen and efficient in conformational determination. Three conformers A, B and C (Figure 1) were obtained with their heat of formation recorded as 83.168kJ/mol, 89.253kJ/mol and 102.735kJ/mol, respectively. However, conformer A with

low energy and high stability was chosen for the study. Figure 2 shows the structures of the reactant and product.

Reaction path study

The optimized structures of 1-phenylethyl acetate were subjected to reaction path study. This was achieved by taking the C₂-H₁ bond length as the typical coordinate for the reaction. The value of the initial internal coordinate in the steady reactants was adjusted gradually to the fair accurate length in the product. 1-phenylethyl acetate for instance, was studied by setting the C₂-H₁ bond length gradually from 4.56Å in about 30 steps to 0.97Å, being the estimated value in the product.

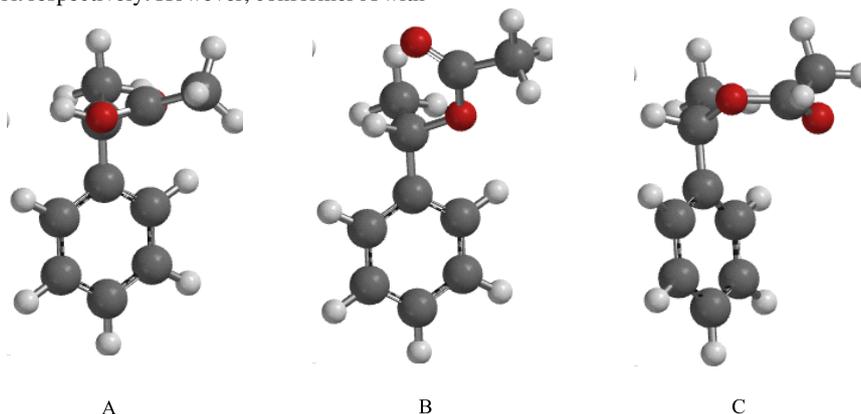


Figure 1: Conformer distribution of 1-Phenylethyl acetate

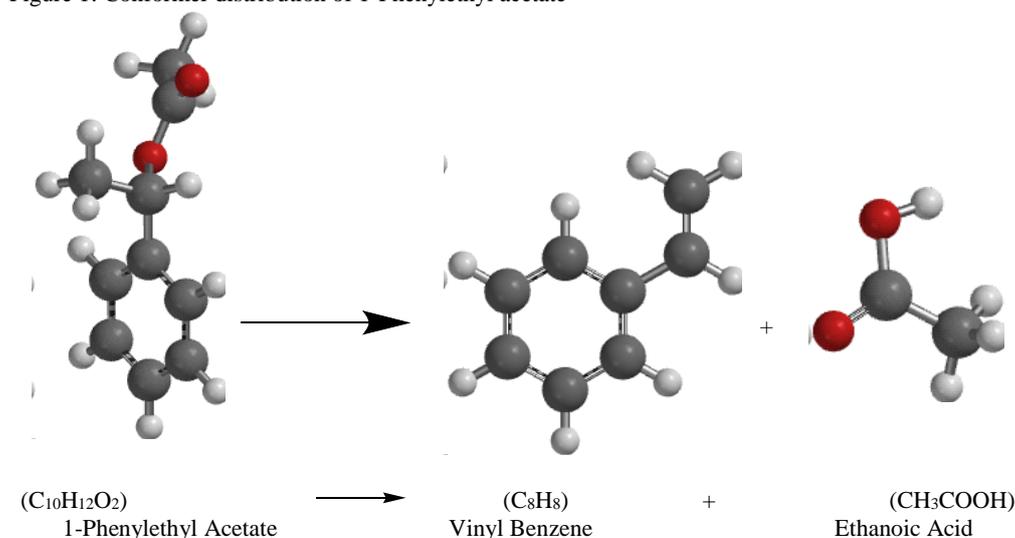


Figure 2: Structures of reactants and products

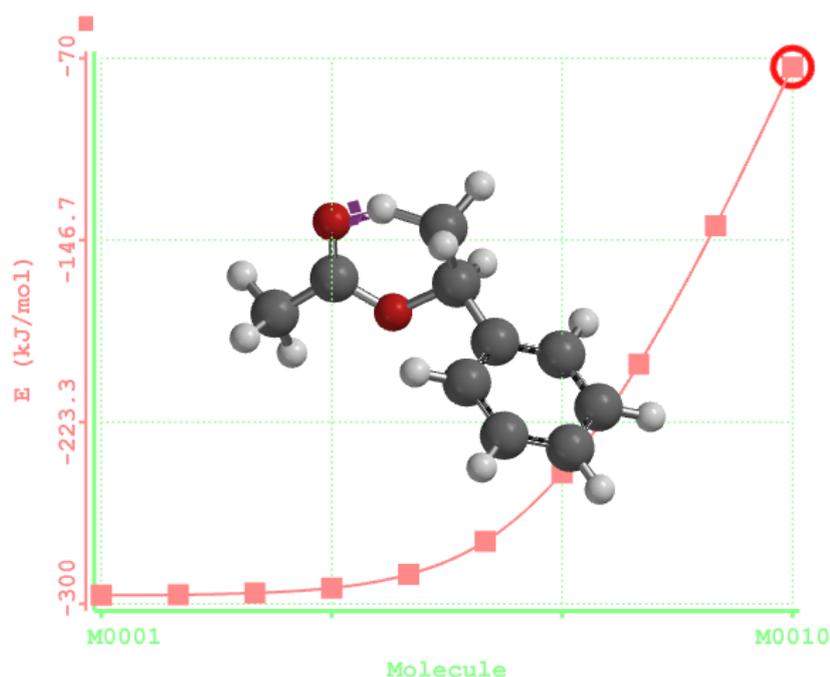


Figure 3: Pathway study of 1-phenylethyl acetate

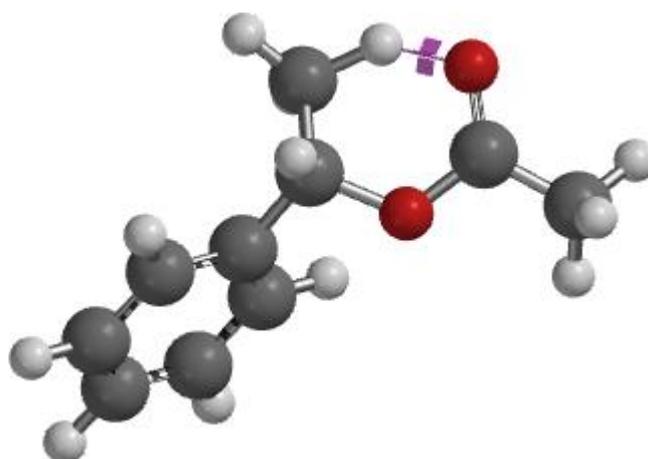


Figure 4: Structure of Transition state of 1-phenylethyl acetate.

Transition State Structure

The potential energy surface (PES) provides a fundamental knowledge of the relation between structures and stability of stable molecules to the minimal enthalpy the length side of the reaction path. In this case, the transition state (TS) geometry corresponds to energy maxima. The essential assumption is that stable molecules are linked together by an even pathway that passes through a sharp transition state. In order to overcome the challenge of locating the TS structure, the guess-TS structure provided by the suggested mechanism was optimized and put through the two-test needs. This is resourceful and pivotal in locating the saddle-point i.e. transition state. It also helps to show that the TS connect the reactants as well as the products, as shown in Figure 4.

Intrinsic Reaction Coordinate

During optimization, the molecules were subjected to a fixed point on the reaction path with the aid of intrinsic reaction coordinate (IRC). This method helps to affirm the transition states. The first IRC calculation, known as positive perturbation, was based on atomic coordinate directed towards a single negative frequency. The second, being negative perturbation, is done on the same typical coordinate.

Mechanism of decomposition of Acetate (Ester)

The reaction involves a non-synchronous cleavage of α -ether oxygen bonds and β -carbon-hydrogen (Figure 5) through a six-membered cyclic transition state.

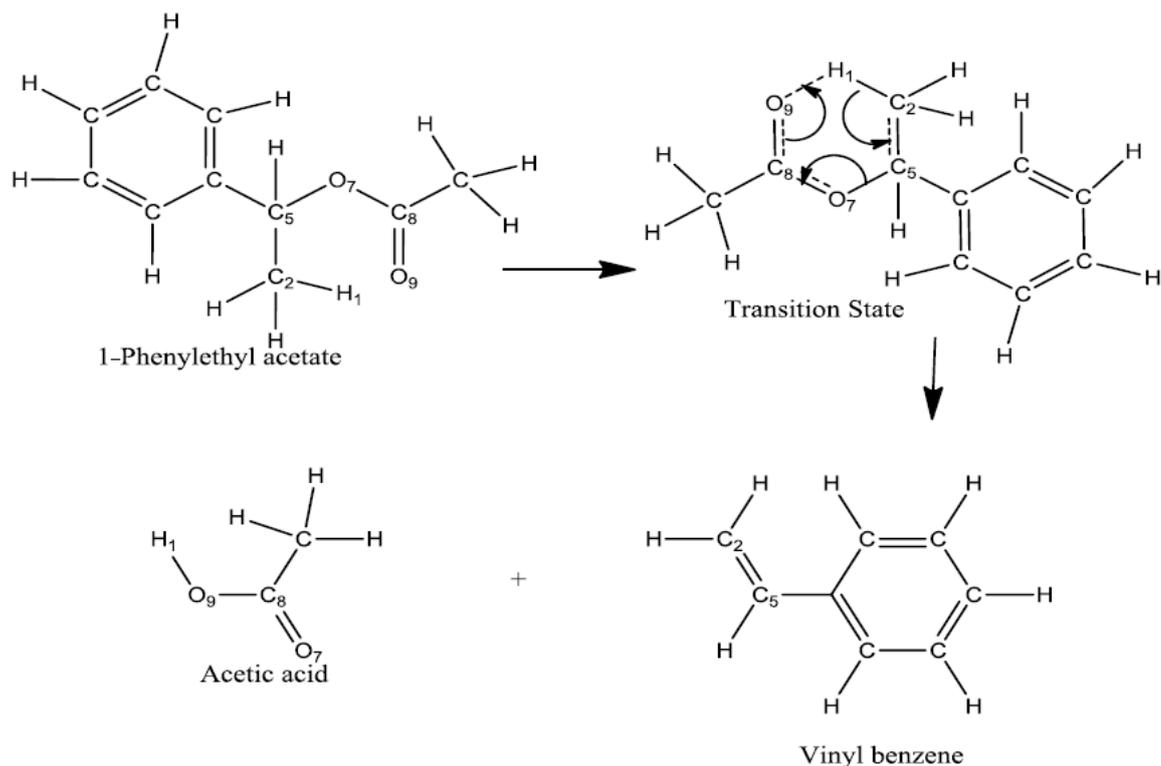


Figure. 5: Reaction mechanism of thermal decomposition of 1-phenylethylacetate

Kinetics and thermodynamic parameters

The thermodynamic parameters achieved for 1-phenylethyl acetate were calculated from the ground state (GS) optimized geometry, transition state (TS) and the products optimized structures. The statistically mechanistic premeditated enthalpy and the ground state energy (GSE) were summed up to obtain the approximate molecular energy. This was necessitated by the fact that high percentage of molecule's energy is domiciled in the bonds and physical geometry. The energy of a molecular entity is defined as;

$$H_i = GSE_i + H_i^{sm} \quad 1$$

SM denotes statistical mechanistically determined energy.

When substituted into initial description of enthalpy of reaction gives equation 2.

$$\Delta H_{rxn} = (GSE_p + H_p^{sm}) - (GSE_r + H_r^{sm}) \quad 2$$

The activation barrier, E_a , was determined in line with the transition state model for reaction involving one molecule at 623K;

$$E_a = \Delta H + RT \quad 3$$

The reaction entropy was evaluated by finding the difference between entropies of the products and that of the reactants.

$$\Delta S_{rxn} = \sum S_p - \sum S_r \quad 4$$

$$\Delta S^\ddagger = \sum S_{ts} - \sum S_r \quad 5$$

The Gibb's free energy was calculated by using the modify version the heat reaction equation knowing that $G = H - TS$;

$$\Delta G^* = \Delta H^* - T\Delta S \quad 6$$

The transition state theory (Bader and Bourns 1961) which proposes that the co-efficient of transition is unity, was employed to determine the first-order co-efficient k_r .

$$k_T = K \frac{T}{h} e^{-G^*/RT} \quad 7$$

ΔG^* represents change in Gibb's free energy between transition state and reactants while h and K are plank's constant and Boltzmann constant respectively.

The Arrhenius factor is expressed as;

$$A = K_B \frac{T}{h} e^{-\Delta S/R} \quad 8$$

By the use of the rate equation, Arrhenius rate is given as;

$$k_T = Ae^{-E_a/RT} \quad 9$$

Wiberg bond indices

Moyano *et al.*, (1989) termed the comparative disparity of the bond indices of the reactant, transition state and the product (∂B_i) for each bond i , associated with a chemical reaction as

$$\partial B_i = \frac{B_i^{ts} - B_i^r}{B_i^p - B_i^r} \quad 10$$

where r represented the reactant, ts represented transition state and p referred to product.

Percentage of evolution (%E_v) was calculated using equation 11.

$$\%E_v = 100\partial B_i \quad 11$$

As hypothesized by Taylor, C_α-O bond breaking ahead of C_β-H bond agrees with information available from experimental study for thermolysis (Blades 1954). This relies on the evidence that Hammett P-values of the α-carbon are higher than those for β-carbon. It can also be inferred that greater dissociation potential of C_α-O bond account for increased reaction rate. On the other hand, greater dissociation potential of C_β-H bond accounts for reduced rate of reaction.

The average value of the bond indices δB_{av} is calculated as

$$\partial B_{av} = \frac{1}{n} \sum \partial B_i \quad 12$$

“n” in the above equation represents number of bonds engaged in the reaction coordinate. It measures the level of progression of the transition state.

The values of δB_{av} show that there is difference between the two path ways of the Chugaev reaction.

The measure of how synchronous a chemical reaction is expressed as:

$$S_y = 1 - A \quad 13$$

Where “A” represents asynchronicity evaluated by using the proposal of Moyano *et al.*, (1989).

$$A = \frac{1}{(2n-2)} \sum \frac{|\partial B_i - \partial B_{av}|}{\partial B_{av}} \quad 14$$

Synchronicity ranges from 0 to 1, being the limit where all bonds along the reaction path are broken or formed at closely the same level in the transition states.

RESULT AND DISCUSSION

The pyrolysis of 1-phenylethyl acetate begins with a β-carbon hydrogen (H) atom connected to a α-carbon that is eliminated from the acetate's alkyl group, yielding vinyl benzene (C₈H₈) and ethanoic acid (CH₃COOH), as shown in Figure 6.

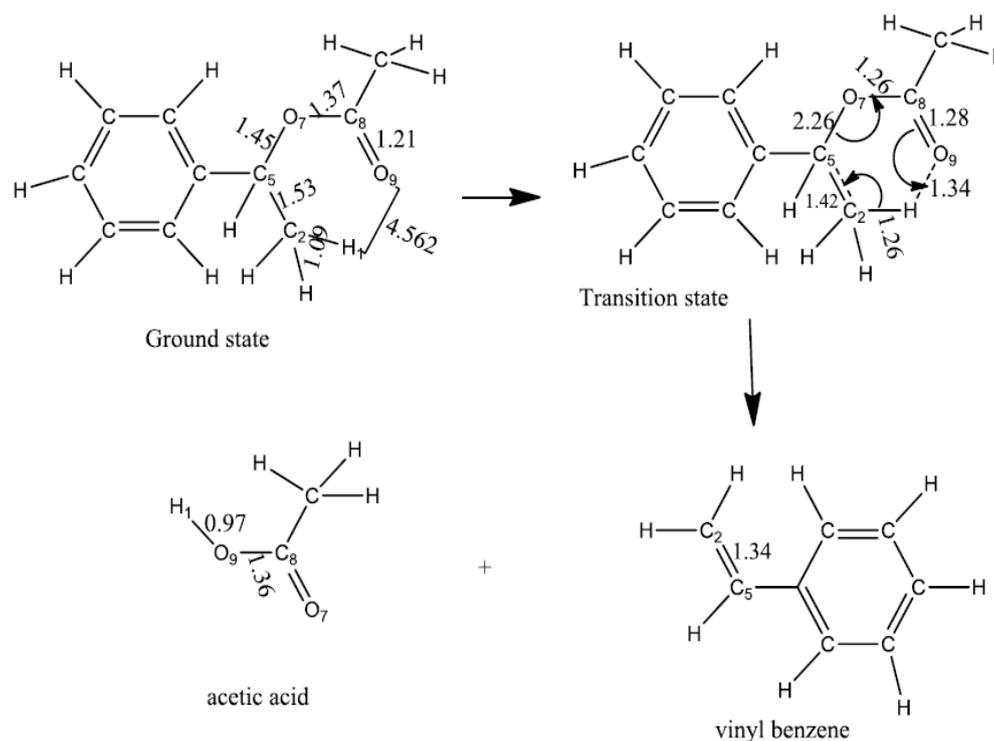


Figure 6: Geometry of ground state, transition state and the product

This decomposition also occurs through a concerted fragmentation via an E1 mechanism which includes a cyclic transition state with six-member ring as shown in Figure 3 that also involving C₅ – O₇ and C₂ – H₁ bond cleavages and a H₁ – O₉ bond making. The bond lengths are shown in Table 1. Noting a long bond length stretching between C₅ – O₇ in the ground state from 1.45 Å to 2.26 Å in the transition state, for C₂ – H₁ from 1.09 Å in the GS to 1.27 Å in the TS. The distance between (C₂ – C₅) in the ground state (GS) (1.53 Å) gives the length of a carbon-carbon single bond. At

the transition state, bond length (TS) is (1.42 Å). This same bond length reduced to 1.34 Å, changing form from the single bond to double bond in the product state. The 1.09 Å C₂-H₁ bond length at the reactant ground state stretched to 1.26 Å at the transition state. The absence of the same bond at the product shows the cleavage of the bond. The interatomic distance between hydrogen and oxygen is 4.56 Å before the formation of the new bond which was reduced to (1.34 Å) at the transition state where the bond length finally reduced to 0.94 Å and a new bond H₁-O₉ is formed. Furthermore, the

deformation that occurs during transformation of reactants into a transition state and finally into products resulted to the variation observed in bond length and dihedral angles as shown in tables 2 and 3 and figure 5 respectively.

Table 1: Geometry optimization at DFT/B3LYP/6-31++G**

Geometric parameters	State	Values
Bond length (Å)	GS	1.09
	TS	1.27
	PRD	-
	$\Delta d(\text{TS-GS})$	0.18
	GS	1.52
	TS	1.42
	PRD	1.34
	Δd	-0.1
	GS	1.45
	TS	2.26
Bond angle(°)	PRD	0.81
	Δd	0.79
	GS	1.37
	TS	1.26
	PRD	1.20
	Δd	-0.11
	GS	1.21
	TS	1.28
	PRD	1.36
	Δd	0.07
Dihedral angle (°)	GS	4.56
	TS	1.34
	PRD	0.97
	Δd	-3.22
	GS	58.97
	TS	-7.65
	PRD	-
	GS	105.36
	TS	105.88
	PRD	-
Dihedral angle (°)	GS	122.628
	TS	117.99
	PRD	-
	GS	118.29
	TS	118.77
	PRD	123.974
	GS	123.67
	TS	107.16
	PRD	124.506
	GS	123.35
TS	120.26	
PRD	111.520	
Dihedral angle (°)	GS	58.97
	TS	-7.65
	PRD	-
	GS	-158.99
	TS	27.35
	PRD	-

C ₅ - O ₇ - C ₈ - O ₉	GS	-174.34
	TS	-36.55
	PRD	-
H ₃ - C ₂ - C ₅ - O ₇	GS	-61.03
	TS	102.63
	PRD	-179.99

Note: GS = Ground State, TS = Transition State, PRD = Product

The Mulliken charges which provide simple and logical estimates of the atomic charges are very important to molecular systems. It affects molecular properties like polarizability, dipole moment and electronic structures. The atomic charge calculated from Mulliken charge distribution for the reactant, transition and product state are given in Table 4. The atomic charge calculated from Mulliken charge distribution for the reactant, transition and product state are given in Table 4. The atomic charge of H₁ (+0.195) has the leading charge population while C₂ (-0.146) has the least charge distribution. The reason for the increase in positive charge development on C₅ (+0.146) and C₈ (+0.007) carbon

atoms from (Table 4) causes a double bond formation which is as a result of charge polarization of the bonds between C₅ – O₇ and C₂ - H₁ which also causes the charge on oxygen atom O₉ (-0.119) to become more negative. In the activation, polarization of the C₅-O₇ and C₂-H₁ bonds causes positive charges on the carbon atom C₈ and Oxygen O₉ to become negative and causes C₂ atom to become more negative. The intermediate formation of methyl dithiocarbonates in the mechanism of the reaction in (Figure 5) is caused by the positive charge cloud on the β-hydrogen H₁ (+0.195) atom which attack ethyl vinyl carbon C₂ (-0.1) which is negatively charged shown in Table 4.

Table 2: Atomic charges (Mulliken) OF 1-phenylethyl Acetate

ATOMS	STATE	DFT/B3LYP/6-31++G**
H ₁	GS	+0.162
	TS	+0.357
	PRD	+0.407
	Δq(TS-GS)	+0.195
C ₂	GS	-0.441
	TS	-0.587
	PRD	-0.117
	Δq	-0.146
C ₅	GS	+0.055
	TS	+0.245
	PRD	-0.350
	Δq	+0.190
O ₇	GS	-0.455
	TS	-0.534
	PRD	-0.425
	Δq	-0.079
C ₈	GS	+0.597
	TS	+0.604
	PRD	+0.585
	Δq	+0.007
O ₉	GS	-0.440
	TS	-0.559
	PRD	-0.555
	Δq	-0.119

Note: Δq = Atomic charge in transition state (TS) – Atomic charge in the Ground State (GS)

Wiberg Bond Order of the pyrolysis of 1-phenylethyl acetate

Using Wiberg bond equations (Atkins & Friedman, 1997) variation of bond indices δB_i have been calculated and the percentage evolution of each bond has been obtained. The calculated percentage evolution of bond involved in the reaction coordinate is summarized in Table 5. The result obtained for the 1-phenylethyl acetate the formation of the bond O₉-H₁ with 100% is the most leading process

accompanied by the breaking of the bond (C₅-O₇) with 96.6%, also the transformation of (C₈=O₉) from double bond to single bond with a percentage evolution of 56% and also conversion of O₇-C₈ single from single bond of 42% to double bond. The simplest of the process is the formation of the C₂-C₅ double bond of 30.2% accompanied by the breaking of (C₂-H₁) bond at 37%. The evolution of bonds percentage listed above explained that formation of bond is the rate determining step followed by the breaking of bond (C₅-O₇).

Table 3: Wiberg bond indices for 1-phenylethyl acetate derived parameters

Compound	State	C ₂ -H ₁	C ₂ -C ₅	C ₅ -O ₇	O ₇ -C ₈	C ₈ =O ₉	O ₉ -H ₁
1-Phenyl	B_i^R	0.940	1.011	0.833	1.019	1.938	0.000
Ethyl	B_i^{TS}	0.592	1.279	0.028	1.414	0.140	0.303
Acetate	B_i^P	0.000	1.893	0.000	1.963	1.048	0.000
	δB_i	0.37	0.30	0.966	0.42	0.560	1.00
	%Ev	37	30	96.6	42	56	100
	δB_{av}	0.6027					
	A	0.097					
	Sy	0.9023					

The average value of bond indices (δB_{av}) measures the degree of progression of the transition state through the reaction path for 1-phenylethyl acetate which is 0.603 indicating that the transition state formed closer to the reactants than to the products. The synchronicity (Sy) value of the reaction for 1-phenylethyl acetate was 0.9023, which indicate that the compound 1-phenylethyl acetate corresponds to highly asynchronous processes indicating that formation of bonds comes before bond cleavage.

Thermodynamic and Kinetic studies

The thermodynamic and kinetics parameters estimations at 623 K were given in Table 7. These predicted parameters: ΔH^* (38.45 kJ/mol), E_a (39.69 kJ/mol), $\log A$ (12.70) and k

($2.93 \times 10^{-2} \text{ s}^{-1}$) agreed well with Blades' (1954) experimental reported results: ΔH^* (38.52 kJ/mol), E_a (43.70 kJ/mol), $\log A$ (12.8) and k ($2.8 \times 10^{-3} \text{ s}^{-1}$) at the same temperature condition. The value obtained for $\Delta H_{\text{reaction}}$ (+38.45 kJ/mol), indicates that the reaction is endothermic in nature. This endothermic nature of reaction was further confirmed using Hammond postulate: the TS energy of formation obtained (-1414053.375 kJ/mol) is closest to the product (-1414140.525 kJ/mol) than to the reactant (-1414213.50 kJ/mol). Positive entropy of activation (5.067 J/mol.K) suggests that the activation complex have significant amount of bond breakage to form two molecules (Sudhakar and Rajakumar 2014).

Table 4: Thermodynamics and Kinetics Parameters of the pyrolysis of 1-phenylethyl acetate

Parameters	Experimental Value	Theoretical Value
ΔH^* (kJ/mol)	38.52	38.45
ΔS (J/mol.K)	N/A	5.867
ΔG (kJ/mol)	N/A	39.69
E_a (kJ/mol)	43.70	39.69
LogA	12.80	12.70
k (S^{-1})	2.8×10^{-3}	2.93×10^{-2}

CONCLUSION

This research shows that theoretical calculations methods can be effectively used to study the thermodynamics, mechanism and kinetics of the thermal decomposition of 1-phenylethyl acetate in the gas phase as the results gotten agree with the experimental results. This methodology will help researchers to understand the reaction mechanism, thermodynamic and kinetic parameters prior to laboratory experiment thus reducing the cost, time and exposure to hazardous chemicals.

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