Theoretical Studies of the Effect of α -methylation and β- methylation on the Gas - Phase Kinetics of Thermal Decomposition of AllylFormates.

K.K. Onyia[1], I.A Adejoro[2], C.U Ibeji[1*], E.O. Akintemi and E.O. Okpala

[1]Pure and Industrial Chemistry, University of Nigeria Nsukka, Enugu, Nigeria
[2]Department of Chemistry, University of Ibadan, Ibadan, Nigeria
Correspondence: ugochukwu.ibeji@unn.edu.ng

Abstract: The gas phase pyrolysis reaction of allylformate (I), its α-Methylated compound (II) and β- methylated (III) compound have been studied theoretically with PM3, HF/3-21G and DFT (B3LYP/6-31G) methods. The decomposition of these compounds proceeds by a concerted [1, 5] hydrogen shift through a six- centered transition state (TS) geometry. The overall result of calculations shows that the reactivity of the thermal decomposition increases as a result of steric releasing effect in the transition state by the methyl group in the α-position, hence it is rate enhancing while reactivity decreases upon β-methylation, hence decreases the rate of reaction. it is also found that rate enhancement due to C-O bond stretching in the formation of T.S is more significant as a rate determinant than the acidic nature of the formyl hydrogen eliminated.

Introduction

The gas-phase thermal decomposition of esters has been extensively studied experimentally [1-4] and theoretically [5-7], and the reaction is known to proceed in a concerted process through a six- centered transition state (TS) type of mechanism as described in reaction scheme 1.A number of studies have revealed that many simple esters containing non-vinylic β-hydrogen in the alkyl portion decompose to give one or more olefinic products with their corresponding carboxylic acid [8] following the six-membered transition state proposed by Hurd and Blunck [9].

Ground state (GS)   **Transition state (TS)**   **Products (PR)**
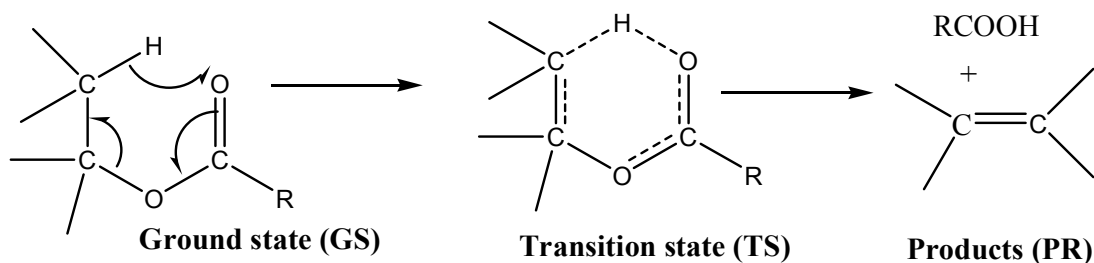
R= H or alkyl group
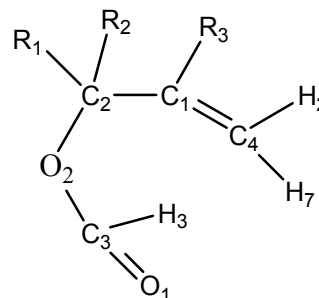
Scheme 1

Scheme II
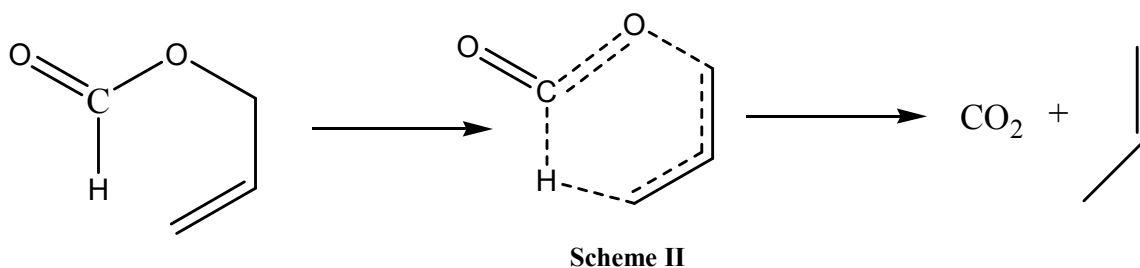
An interesting ester of formic acid is when the alkyl group is replaced with vinylic group that is allylformate, when pyrolyzed in static system, produced propene and carbon (II) oxide [10]. The elimination process is an intramolecular mechanism involving 1,5 transfer of the formyl hydrogen atom as shown in scheme II. The aim of this study is to use PM3, Hatree-Fock approximations and density functional computational approach in SPARTAN to predict the kinetics, thermodynamics and the mechanism of the pyrolysis allylformates and the effect of replacing an α and a β- hydrogen with a methyl group at the allyl portion of the compound.

Computational Details

The Semi-empirical PM3 and DFT (B3LYP/6-31G) procedures were used throughout in this work. Conformational search was carried out on the structures using Molecular Mechanics Force Field (MMFF) in aqueous medium which is quite successful in assigning low energy conformers and in providing quantitative estimates of conformational energy differences [11] to obtain the structure with the lowest energy value which is an indication of the stability of the molecule. Both allylformate and its α β-methylated compounds have nine conformers each with -278.62

kJmol^{-1}, -34.10 kJmol^{-1} and -25.45 kJmol^{-1} minimization energies respectively. The geometry optimization was performed on the ground state (GS), the transition state (TS) and the products (PR) to obtain the geometric parameters such as bond length, bond angle, dihedral, atomic charges and some thermodynamics parameters like enthalpy, entropy and Gibb's free energy of reaction.. The geometry of the allylformates is defined in scheme III; H_3 is the formyl hydrogen that will be transferred in a 1, 5 hydrogen shift mechanism.

Reactant Geometry; R_1, R_2 or R_3 =H or alkyl group
Scheme III

Table 1: Esters Studied in this Work

Designation	Non – hydrogen substituent	Nomenclature
I	-	Allylformate
II	R_1 or R_2 = CH_3	α – methylallylformate
III	R_3 = CH_3	β – methylallylformate

The transition state structures were located by using the guess-transition state in Spartan on the suggested mechanism of the transition state structure. The proposed structures were optimized and subjected to the two tests needs to be performed in order to verify that a practical geometry corresponds to a saddle point (transition structure) and that this saddle point corresponds to the reactants and products. The tests are: That the Hessian matrix of second – energy derivations with respect to coordinates yields one and only one imaginary frequency which will be in the range of 400 to 2000 cm^{-1} and the normal coordinates corresponds to the imaginary frequency smoothly corrects reactants and products.

Calculations

The thermodynamic calculations were obtained for allylformate and its α-methylated compound through calculation on the ground state (GS), Transition (TS) and the Product (PR). The enthalpy

calculated by the software is solely based on statistical mechanics and does not take into account the ground state energy which has significant contribution to the total energy of the molecule. However a function of the software is to calculate the ground state energy (GSE) using quantum mechanics. Therefore, we can simply take the sum of the enthalpy and the ground state energy equal to the overall energy of the molecules or total enthalpy and calculate the heat of reaction by taking the difference between the product and reactant overall energies.

According to Spartan Guide to calculations, the enthalpy of a compound will be defined as:

$$H = GSE + H^{sm} \qquad (1)$$

Where the superscript 'sm' is the statistical mechanically calculated enthalpy.

If the above equation is substituted into the initial definition of the heat of reaction, we have:

$$\Delta H_{rxn} = \left(GSE_{product} + H_{product}\right) - \left(GSE_{reactant} + H_{reactant}\right) \qquad (2)$$

The enthalpy of reaction was calculated at 710.5 k.

The enthalpy of activation ($\Delta H^{\neq}$) was obtained by subtracting the enthalpy of reactant at 710.5 k from the enthalpy of transition state at 710.5k.

$$\Delta H^{\neq} = (GSE_{transition} + H_{transition}) - (GSE_{reactant} + H_{reactant}) \qquad (3)$$

According to the transition state theory for a unimolecular reaction, activation energy (E_a) is given as:

$$E_a = \Delta H^{\neq} + RT \qquad (4)$$

The entropy of activation ($\Delta S^{\neq}$) was calculated at 710.5 k by taking the difference of transition state and reactant entropies that is:

$$\Delta S^{\neq} = S_{tsransition} - S_{reactant} \qquad (5)$$

$\Delta S^{\neq}$ value was used to calculate Arrhenius pre-exponential factor using the relation;

$$A = (e^m k_b T/h)\, exp\, \{(\Delta S^{\neq}/R)\} \qquad (6)$$

Where m is the molecularity of the reaction, k_b is the Boltzmann constant and h is the Planck constant.

The first order coefficient $k(T)$ was calculated using transition State theory (TST) [12] assuming that the transition coefficient is unity as shown in the following equation:

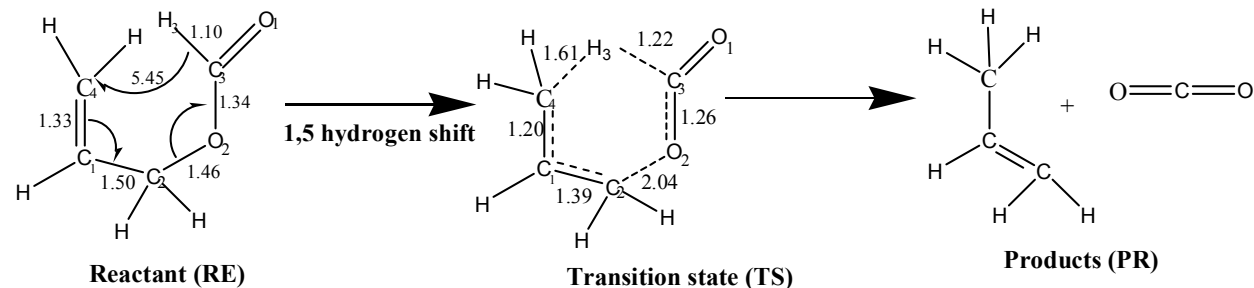$$k(T) = \frac{K_b T}{h} \exp\left[\frac{-\Delta G^{\neq}}{RT}\right] \qquad (7)$$

Where $\Delta G^{\neq}$ is the Gibbs free energy change between the reactant and the transition state, it was calculated using the following relation:

$$\Delta G^{\neq} = G_{transition} - G_{reactant} \qquad (8)$$

Arrhenius rate equation is given as:

$$k(T) = \frac{K_b T}{h} \exp\left[\frac{-E_a}{RT}\right] \qquad (9)$$

Results And Discussion

Using the semi-empirical method PM3 and Density Functional Theory (DFT) at 6-31G* level, the geometry of reactant (s), transition state (s) and product (s) are predicted and shown below in schemes IV and V. Experimental works reported by Hurd and Blunk [9], Depuy and King [13], Mcgreer and Chiu [14], suggested that the thermal decomposition of esters passes through a six-membered ring transition state if hydrogen of the alkyl substituent at the α-position is available for abstraction by acyl group.

Mechanism of decomposition of allylformate

The reaction pathway of allylformate is depicted in scheme IV in which the relevant atom numbering is also indicated. This study suggests that the gas-phase decomposition of allylformate to give propene and carbon (IV) Oxide occurs by a concerted asynchronous mechanism, that is, processes that led to the intermediate are concerted but the rate determining process is not synchronous but delayed [15].

From the mechanism below, two bonds that are breaking, that is, C_2-O_2 and C_3-H_3 are seen to stretch from $1.455A^0$ and $1.10A^0$ in the RE to $2.04A^0$ and $1.23\,A^0$ respectively in the TS (Table 3). In the transition state, C_4-H_3 bond is almost fully formed showing that this process is a two-stage reaction in which some changes in bonding took place mainly before, and some after the transition state.

Scheme IV

Geometry Parameters

Atomic charges are shown in Mulliken, according to Spartan calculation guide the Mulliken charges are preferred because it gives simple and reasonable estimates of atomic charges. As the reaction progress from reactant to product, the electron density at the carbonyl carbon C_3, decreases, C_3 becoming more positive for the substrates. The negative charge at carbon C_2 increases in the transition state as the O_2-C_2 bond breaks; this change is more

noticeable for allylformate (-0.102) and β-methylallylformate (-0.110) compared to α-methylallylformate (-0.051). However, charge at oxygen O_2 undergoes very small change for the substrates, from reactant to transition state, carbon C_2 and C_1 bearing the methyl substituent increase in electron density in transition state, implying donation of electron density from the αβ-methyl substituent. TABLES 2 and 3 are TABLES of selected optimized geometric parameters (bond lengths, bond angles and

dihedral angles) of reactants, transition states and products. It reveals that α- methylation of allylformate leads to greater O_2-C_2 stretch in the TS.

Particularly α- methylation of allylformate reflect on the charge density and bonds joined to the sites of substitution, that is charge density on C_2 and C_2-O_2 and C_1-C_2 bond lengths.

The methyl group has a positive (electron releasing) inductive effect, the C of the methyl group being partially negative. The α-methyl substitution should facilitate electron movement from C_2-O_2 bond into O_2-C_3 bond. The effect on C_1-C_2 bond length is to increase it ($1.496A^0$ to $1.501A^0$) and thereby lessening the developing double bond character.

REACTANT   **TRANSITION STATE**   **PRODUCTS**
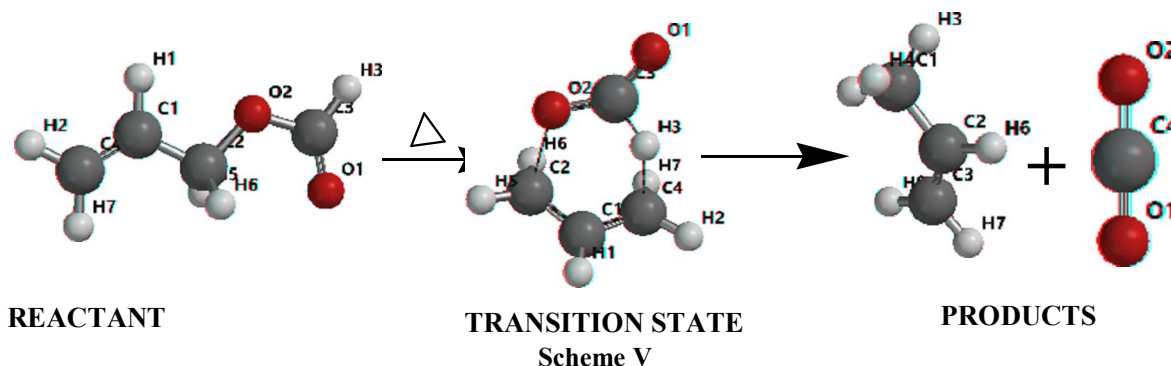
Scheme V

Table 2: Atomic charges (q) and Bond length (d in A^0) at selected atoms of reactant (RE), transition state (TS) and products (PR) for the decomposition of allylformates at DFT/B3LYP/6-31G* level.

Atom	Allylformate				α – methylallylformate				β – methylallylformate			
	RE	TS	PR	Δq^*	RE	TS	PR	Δq^*	RE	TS	PR	Δq^*
C_1	-0.057	-0.053	-0.489	0.004	-0.045	-0.060	-0.092	-0.051	0.211	0.197	0.219	-0.014
O_2	-0.415	-0.420	-0.370	-0.005	-0.427	-0.437	-0.365	-0.010	-0.417	-0.422	-0.367	-0.005
C_2	-0.095	-0.197	-0.341	-0.102	0.068	0.017	-0.092	-0.051	-0.115	-0.225	-0.400	-0.110
C_3	0.391	0.495	0.730	0.104	0.392	0.460	0.733	0.068	0.393	0.470	0.727	0.077
H_3	0.139	0.068	0.167	-0.071	0.136	0.068	0.164	-0.071	0.139	0.067	0.157	-0.072
C_4	-0.331	-0.370	-0.490	-0.039	-0.337	-0.368	-0.491	-0.031	-0.389	-0.400	-0.503	-0.011
Bond	RE	TS	PR	Δd^*	RE	TS	PR	Δd^*	RE	TS	PR	Δd^*
C_1-C_2	1.496	1.389	1.335	-0.107	1.501	1.395	1.337	-0.106	1.504	1.392	1.338	-0.112
C_1-C_4	1.332	1.202	1.502	-0.130	1.332	1.385	1.503	0.053	1.336	1.394	1.509	0.058
C_2-O_2	1.455	2.036	3.464	0.581	1.468	2.094	3.480	0.626	1.456	2.057	3.710	0.601
C_3-O_2	1.345	1.257	1.169	-0.085	1.341	1.212	1.169	-0.129	1.341	1.257	1.169	-0.084
C_3-H_3	1.101	1.226	3.690	0.125	1.101	1.212	3.565	0.111	1.101	1.226	4.122	0.216

$\Delta q^* = q^{(TS)} - q^{(RE)}$; $\Delta d^* = d^{(TS)} - d^{(RE)}$

Table 3: Optimized Bond and Dihedral angles for both reactant (RE) and transition state (TS) for allylformates at DFT/B3LYP/6-31G* level.

	Allylformate		α-methyallylformate		β-methyallylforsmate	
Bond angle (^{0})	RE	TS	RE	TS	RE	TS
C_1-C_2-O_2	107.90	102.57	106.14	100.02	108.34	101.50
C_2-O_2-C_3	115.48	113.91	116.68	115.05	115.58	113.50
H_3-C_3-O_2	108.93	109.81	108.72	109.23	108.95	109.27
H_3-C_3-C_4	128.93	17.33	40.83	148.73	129.27	17.54
Dihedral angle (^{0})						
C_2-O_2-C_3-O_1	-0.362	173.19	0.693	173.27	0.19	-174.45
C_2-O_2-C_3-H_3	179.65	-7.61	-179.12	-7.30	-179.90	6.40

Activation Energy Correlation

Methyl substitution at the α- carbon position of allylformate is to lower the activation energy (E_a) from 196.02kJmol^{-1} to 177.07kJmol^{-1}. This lowering of E_a is rate enhancing and the rate enhancement is generally ascribed to stabilization of C_2 bearing the methyl group by electron donating effect of the methyl group and steric acceleration of rate by the methyl group in TS. The explanation of the effect of α-methylation on the rate is that α-methyl substituent will tend to stabilize the six-membered transition state because of its polarity and substituents which are able to stabilize the growing charge centers of the activated complex, effect reductions in the activated energies

relative to the unsubstituted reactants. Also β-methylation increases the activation energy (E_a) from 196.02 kJmol^{-1} to 198.00 kJmol^{-1}, hence reduces the rate of reaction.

Because of the above reasons, it can therefore be concluded that rate enhancement due to C_2-O_2 bond stretching in the formation of the transition state is more significant as a rate determinant than the acidic nature of the hydrogen that is eliminated.

The results of the kinetic parameter found experimentally for allylformate are:

E_{act} = 43.15 ±0.66 kcalmol^{-1} (180.5 ± 2.9 kJmol^{-1}); log A = 10.0 ± 0.2 [17] and E_{act} = 43.0 ± 0.9

kcalmol^{-1} (179.9 ± 3.8 kJmol^{-1}); log = 10.1 ± 0.3 [18] while the calculated value for log A is 14.24, 14.21 and 14.15 respectively for PM3, HF/3-21G and DFT/B3LY/6-31G* levels.

It is important to note that the reported experimental values of log A of the allylicformates are rather low for a six-centered cyclic transition state structure. Estimation of Benson et al. [12] about the values of A-factor from transition state theory should approximately be around $10^{9.0}$-$10^{15.2}$ for six-membered cyclic transition state geometry.

Table 4: Effect of α – methylation on activation energy and reaction rate at 710.5k

Methods	Allylformate E_a(kJmol^{-1})	k (x10^{-1}) (S^{-1})	α-methylallylformate E_a(kJmol^{-1})	k (x10^1) (S^{-1})
PM3	194.57	8.81	174.98	2.23
HF/3-21G	194.70	7.91	174.37	1.63
DFT/B3LYP/6-31G*	196.02	5.53	177.07	0.99

Table 5: Effect of β – methylation on activation energy and reaction rate at 710.5k

Methods	Allylformate E_a(kJmol^{-1})	k (x10^{-1}) (S^{-1})	β-methylallylformate E_a(kJmol^{-1})	k (x10^{-1}) (S^{-1})
PM3	194.57	8.81	197.40	4.62
HF/3-21G	194.70	7.91	196.45	5.24
DFT/B3LYP/6-31G*	196.02	5.53	198.00	3.45

Table 6: Comparism of computed Arrhenius parameters and the experimental result for allylformate.

Methods	E_a(kJmol^{-1})	ΔH$^{\neq}$(kJmol^{-1})	LogA (S^{-1})
Experimental	180.75	174.84	10.00
PM3	194.57	188.66	14.24
HF/3-21G	194.70	188.79	14.21
DFT/B3LYP/6-31G*	196.02	190.11	14.15

Table 7: Activation Parameters and Arrhenius Parameters for the pyrolysis of Allylformate.

Methods	ΔH$^{\neq}$ (kJmol^{-1})	ΔG$^{\neq}$ (kJmol^{-1})	ΔS$^{\neq}$ (Jmol^{-1}K^{-1})	E_a(kJmol^{-1})	k (x10^{-1}) (S^{-1})	A (x10^{14}) (S^{-1})	LogA (S^{-1})
PM3	188.66	180.14	12.23	194.57	8.81	1.75	14.24
HF/3-21G	188.76	180.97	11.50	194.70	7.91	1.61	14.21
DFT/B3LYP/6-31G*	190.11	183.00	10.38	196.02	5.53	1.4	14.15

Table 8: Activation Parameters and Arrhenius Parameters for the pyrolysis of α – methlallylformate.

Methods	ΔH$^{\neq}$ (kJmol^{-1})	ΔG$^{\neq}$ (kJmol^{-1})	ΔS$^{\neq}$ (Jmol^{-1}K^{-1})	E_a (kJmol^{-1})	k (x10^{-1}) (S^{-1})	A (x10^{14}) (S^{-1})	LogA (S^{-1})
PM3	169.07	161.02	11.51	174.98	2.23	1.61	14.21
HF/3-21G	169.46	162.92	9.47	174.37	1.63	1.26	14.10
DFT/B3LYP/6-31G*	171.16	162.66	8.62	177.07	0.99	1.02	14.01

Table 9: Activation Parameters and Arrhenius Parameters for the pyrolysis of β – methlallylformate.

Methods	ΔH$^{\neq}$ (kJmol^{-1})	ΔG$^{\neq}$ (kJmol^{-1})	ΔS$^{\neq}$ (Jmol^{-1}K^{-1})	E_a(kJmol^{-1})	K (x10^{-1}) (S^{-1})	A (x10^{14}) (S^{-1})	LogA (S^{-1})
PM3	191.49	183.68	10.82	197.40	4.62	1.48	14.17
HF/3-21G	190.54	182.72	10.57	196.45	5.24	1.43	14.16
DFT/B3LYP/6-31G*	192.09	185.70	9.21	198.00	3.45	1.22	14.09

Conclusion

The gas-phase decomposition mechanisms of allylformate and α-methylallylformate were investigated by means of DFT, HF/3-21G and PM3 calculations. Available experimental data of reaction

were used to analyze the calculated parameters to propose a reasonable mechanism. The result shows that the reaction proceeds in a concerted non-synchronous six centered transition state mechanism. Thetheoretically results are in reasonable agreement

with the experimental result. Also reactivity of allylformate increases with methyl substitution at α-position and decreases upon β- methylationby electron donating effect of methyl group. This leads to steric acceleration of rate in TS for α-methylallylformate and a decrease in the rate for β-methylallylformate.

References
1. A.T. Blades, The kinetics of the pyrolysis of ethyl and isopropyl formates and acetates, Can. J. Chem. 32 (1954) 366–372.
2. A.T. Blades, H.S. Sandhu, The Arrhenius factors for some six-center unimolecular reactions, Int. J. Chem. Kinet. III (1971) 187–193.
3. R.F. Makens, W.G. Eversole, Kinetics of the thermal decomposition of ethyl formate, J. Am. Chem. Soc. 61 (1939) 3203–3206.
4. E. Gordon, S.J.W. Price, A.F. Trotman-Dickenson, The pyrolysis of tert.-butyl formate, J. Chem. Soc. (1957) 2813–2815.
5. (a) R. Taylor, The Chemistry of the Functional Groups, Supplementary Volume B. Acid Derivatives, ed., S. Patia, Wiley, London, (1979) p.880; (b) R. Taylor and M. P. Thorne, J. Chem. Soc., Perkin Trans. 2 (1976) 799; (c) R. Taylor, J. Chem. Soc., Perkin Trans. 2 (1972) 165; (d) S. de B. Norfolk and R.Taylor, J. Chem. Soc., Perkin Trans. 2 (1976).
6. N. Al-Awadi, R. F. Al-Bashir, and O. M. E. El-Dosouqui, J. Chem. Soc., Perkin Trans. 2 (1989) 576.
7. I.A. Adejoro, T.O. Bamkole, Semi-empirical quantum Mechanical, Molecular Orbital Method using MOPAC: Calculation of the Arrheniusparameters for the pyrolysis of some Alkyl Acetates J. Appl. Sci.5(9) (2005) 1559 - 1563.
8. R. Taylor, In chemistry of functional groups, Patai S (ed). Wiley: Chinchester (1986).
9. C.D. Hurd, F. HBlunck, The pyrolysis of esters. J. Am. Chem Soc.60(10) (1938) 2419-2425.
10. J.M. Venon, D. Waddington, Thermolysis of allylicformate. Journal of Chemical Communication 11(1969) 623-624.
11. J. H. Warren, A Guide to molecular Mechanics and Quantum Chemical Calculations. Irvine USA. P.399.
12. S.W. Benson, The Foundations of Chemical Kinetics. Mc-Graw-Hill: New York (1960).
13. C. H. DePuy, R.W. King, Pyrolyticcis eliminations. Chem. Rev., 60(5) (1960) 431-457.
14. D.A. Mcquarrie, Molecular Approach, Sausauto; University Science Books (1997).
15. I.A.Adejoro, O.T. Bamkole, Kinetics and Mechanism of elimination of ethyl acetate in the gas phase: A theoretical study. Afr. J. Pure Appl. Chem. 3:7 ((2009).
16. K.H. Leavel, E.S. Lewis, Rearrangement of esters in the gas phase, V. Gas phasethermolysis of allylicformates. Kinetics and isotope effects, Tetrahedron 28(1972) 1167–1171.
17. M. Szwarc, J. Watson Taylor, Pyrolyses of benzyl benzoate, acetate, andformate, J. Chem. Phys. 21 (1953) 1746–1749.
18. J.R. Mora, D. Perez, A. Maldonado, M. Lorono, G. Chuchani, Computational and theoretical chemistry 1019 (2013) 48-58.
19. Spartan Calculation Guide. www.engin.umich.edu/~cre/web_mod/quantum/topic03.htm

2/25/2018