COMPUTATIONAL DETERMINATION OF THE KINETICS, MECHANISMS AND THERMODYNAMICS OF THE DECOMPOSITION REACTION OF PYRUVIC ACID

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ABSTRACT

The gas phase decarboxylation of Pyruvic acid ($CH_3COCOOH$) yielded Hydroxyethylidene (CH_3COH). The kinetics, mechanism, and thermodynamics studies of pyrolysis of pyruvic acid at 623k was studied using semi-empirical(PM3) and DFT with B3LYP/6-31G* basis set. The reaction was found to be first order rate equation. The temperature dependence of the rate coefficients is given by the following Arrhenius equation: log $A(S^{-1})$ with PM3 = 12.60 and DFT/B3LYP at 6-31G* = 13.05. The calculation values for the energy of activation, entropy, Gibb's free energy and enthalpy of activation were predicted. The theoretical calculations suggest a molecular mechanism involving a concerted polar five membered cyclic transition state which involves O_3-H_3 and C_2-C_3 bond breaking and O_1-H_3 bond formed.

KEYWORDS: Pyruvic Acid, Kinetics, DFT Calculation, Semi-Empirical Calculation And Mechanisms.

INTRODUCTION

The hydroxyethylidene and carbondioxde are the products of pyrolysis of pyruvic acid. Pyruvic acid is colourless liquid with a smell, similar to acetic acid and miscible with water. It occurs naturally in the body and is end product of metabolism of sugar and starch. Pyruvic acid plays a significant role in biological system (Rita Kakkar, etal, 2006). Its anion, pyruvate ($CH3COCOO^-$), is also an important intermediate compound in the carbohydrate metabolism of living organisms.
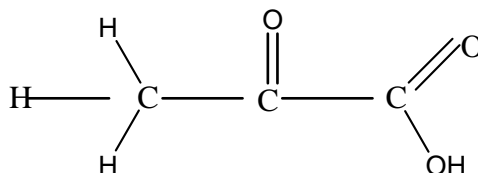

Figure 1.The geometry of pyruvic acid

The decarboxylation of organic acids such as pyruvic acid leads to a gas phase elimination through a five-centered cyclic transition state type of mechanism. A large number of gas-phase unimolecular reaction, which have been studied, appeared to take place by the ways of 4-centre, 5- Centre and 6-centre cyclic activated complex (O'Neal and Benson, 1967).

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The decarboxylation elimination from pyruvic acid to produce Hydroxyethylidene is usually five centred reaction. The main aim of the this study is to use semi-empirical and density functional computational approach in SPARTAN in order to estimate how it can successfully predict the kinetics, thermodynamics, and mechanisms of the decomposition reaction of pyruvic acid. The method is an adaptation of the work reported by Adejoro and Adeboye for ethyl bromide (I.A Adejoro et al, 2013)

COMPUTATIONAL METHOD AND MODEL

All the computations were performed with the Spartan 14 programs [Wareen J.H, 2003]. The geometries of all ground state (GS), Transition state (TS), and products were fully optimized at PM3 and DFT with the B3LYP functional at 6-31G* basis set. The kinetics for the gas-phase elimination decomposition reaction of $CH_3COCOOH$ into CH_3COH and CO_2 suggest a concerted mechanism.

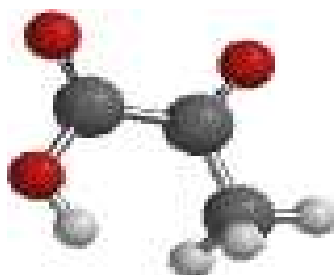**Figure 2.The optimized structure of Pyruvic acid using DFT at the B3LYP/6-31G* basis set level**

H_3 is the β-hydrogen to be eliminated. Reaction path calculations were performed on the optimized geometry of Pyruvic acid under the study using H_3-O_1 as the reaction coordinate. The internal coordinate was varied from its initial distance of 2.477Å in many small steps to the value of 1.382Å in the product molecule as show in figure 3.
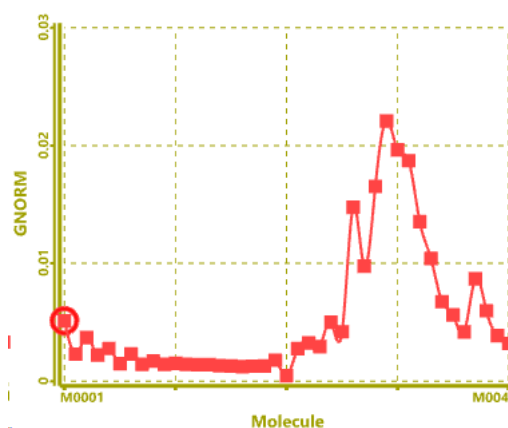

**Figure 3.A plot of energy against the number of molecules to depict the reaction path studies**

TRANSITION STATE

Potential energy surfaces provide a basis for understanding the relationship between molecular structure and stability. Stable molecules correspond to energy minima along the reaction coordinate. Transition states correspond to the energy maxima. The problem is that the diagram cannot be constructed that is cannot be visualized. However, the underlying principle is that stable molecules (energy minima) will be interconnected by smooth pathway passing through well − defined transition state remain the same. The only problem is to identify this special point (stable molecules/transition state). Using the guess-transition state in Spartan on the suggested mechanism of the transition state structure was optimized and was subjected

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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-1and the normal coordinates corresponds to the imaginary frequency smoothly corrects reactants and products. This could be achieved by animating the normal coordinate. The transition state was obtained by building the mechanism which follows Markovnikov's addition reaction mechanism; the transition state (TS) was confirmed by the single negative Eigen value in the Hessian matrix, intrinsic reaction coordinate

and by only one imaginary IR value at absorption band 2427cm-1with the intensity at 1482.95. The intrinsic reaction coordinates method was also used by optimizing the molecule subject to a fixed position along the reaction coordinate (Warren, 2003). The transition state was confirmed using the IRC method. Two IRC calculations were performed. The first one a positive perturbation was done by an initial perturbation on the atomic coordinates in the direction of the single negative frequency while the other one a negative perturbation performed along the same normal coordinates. The plot of energy against the intrinsic reaction coordinate to ascertain the transition state is as shown in Figure 4.
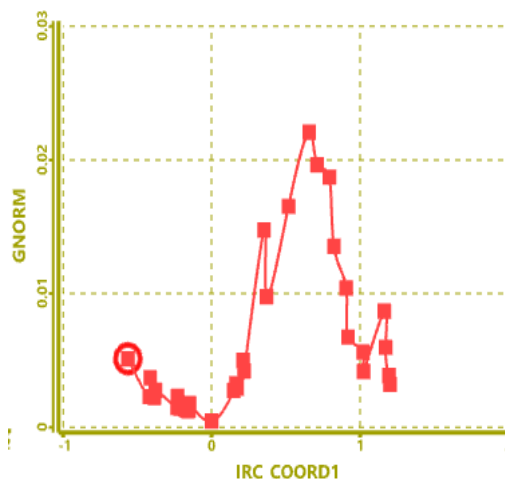
Figure 4.A plot show the intrinsic reaction coordinate

CALCULATION

Thermodynamic calculations were obtained for pyruvic acid through calculation on the ground state (GS), Transition state (TS) and products. The statistical mechanically calculated enthalpy and entropy were used which is not the true representative of the total energy of the molecule, knowing that large portion of enthalpy in molecule is contained in its bonds and conformation, hence, the sum of the ground state energy (GSE) and the statistical mechanically calculated enthalpy are used to get a closer approximation of the true energy of the

molecule. The enthalpy of the species will be defined as follow:

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

Where superscript 'sm' is the statistical mechanically calculated enthalpy. Then ΔH is equal to the sum, products minus reactants. $H_i = GSE_i + H_i^{sm}$,

$$\Delta H = (GSE_{products} + H^{sm}_{products}) - (GSE_{reactants} + H^{sm}_{reactants}). \tag{2}$$

The enthalpy of this reaction was calculated at 623K.

The entropy of the reaction was calculated by taking the difference of products and reactants entropies;

$$\Delta S_{reaction} = S_{products} - S_{reactants}. \qquad (3)$$

The Gibbs free energy was calculated using the modified version of the Heat of reaction equation:

$$G = H - TS.$$

$$\Delta G^* = \Delta H^* - T\Delta S \qquad (4)$$

Activation energy (Ea) was calculated according to transition state theory (TST) for a unimolecular reaction at 623K.

$$Ea = \Delta H + RT. \qquad (5)$$

The first order coefficient K (T) was calculated using transition state theory (TST)[Benson S.W,1960], assuming that the transition coefficient is unity as shown in the following equation.

$$K(T) = K'T/h \ exp(-\Delta G^*/RT). \qquad (6)$$

Where ΔG^* is the Gibbs free energy change between the reactant and transition state and K' and h are the Boltzmann and Planck's constant respectively.

Reaction rate constants are fitted to modified Arrhenius equation:

$$K(T) = A'T^n exp(-Ea/RT). \qquad (7)$$

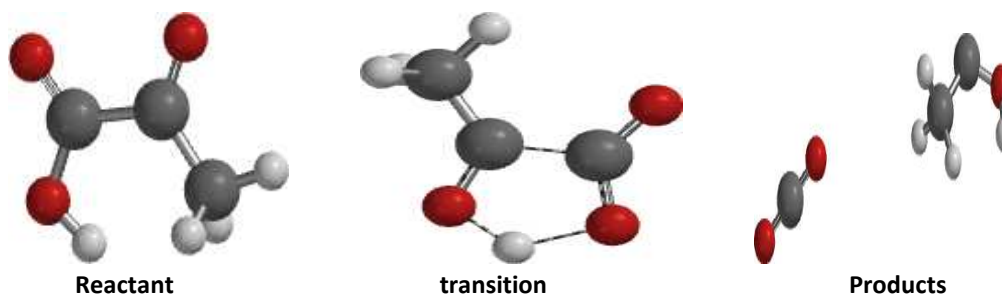Where A is the pre-exponential factor, Ea is the activation energy and n is unitless parameter.

Δs^* value was used to calculate Arrhenius pre-exponential factor using the relation:

$$A = e^m K'T/h \ exp(\Delta S^*/R). \qquad (8)$$

Where m is the molecularity of the reaction

RESULTS AND DISCUSSION

Theoretical studies suggest that the gas-phase elimination reaction of $CH_3COCOOH$ to give CH_3COH and CO_2 occur by a concerted mechanism. The geometry optimization was performed on the ground state (GS), Transition state (TS) and the products are predicted in figure 3, and to obtain the geometric parameters such as bond length, bond angle, dihedral and atomic charge, the data obtained were used to calculate the other thermodynamic parameters. Bond length, bond angle and atomic charges are shown in Table. 1, 2 and 3. The bond length and atomic charges are shown in Mulliken. The Mulliken charges are used because it gives simple and reasonable estimation of charges [Warren J. Henhre, 2003].charges in the TS: (Table 1), shown that C_1-C_2 and C_3-O_1 bond length are (0-994, 1.042 and 0.994) and (0.039, 1.969 and 0.039) respectively for Pyruvic acid. Some selected calculated and experimental structural parameters for Pyruvic acid are given in table 2. The CCO angle of the ground state of pyruvic acid calculated are (124.05° and 125.27°) are predicted. Charges in TS: (Table 3) show that C_3 (+0.377 and +0.722) has the largest charge development, but O_3 (-0.465and -0.485) has the least charge.

Reactant　　　　　**transition**　　　　　**Products**

Figure5.Structures of reactant (left) and transition state (right) optimized using DFT at the B3LYP with 6-31G* basis set level

The transition state found is late in the reaction coordinate in relation to the breaking of C_2-C_3 and O_3-H_3 bonds and formation of the O_1-H_3 bond.

The transition state geometry optimized is shown in fig.4.
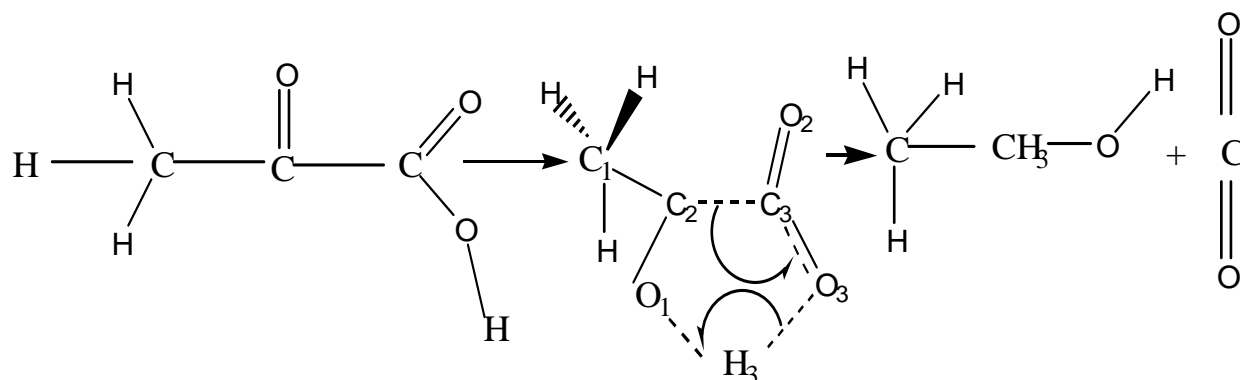

Figure 6.Mechanism of pyruvic acid for the formation of Hydroethylidene

Table 1.bond length of the species involved in elimination reaction for the ground state (GS), transition state (TS) and products (Mullikens)

BOND ORDER	STATE	PM3	DFT(6-31G*)
C1H1	GS	0.984	0.934
	TS	0.961	0.926
	PDT	-	0.916
C1H2	GS	0.349	-
	TS	0.341	0.925
	PDT	-	0.934
CIH4	GS	0.410	0.916
	TS	0.149	0.925
	PDT	-	0.916
C1H7	GS	-	0.916
	TS	-	-
	PDT	-	-
C1C2	GS	0.249	0.994
	TS	0.549	1.042
	PDT	-	0.994
C2C3	GS	1.888	0.867
	TS	1.709	-
	PDT	0.307	0.867
C2O1	GS	2.206	1.830
	TS	2.191	-
	PDT	-	1.830
C3O1	GS	0.193	0.039
	TS	0.189	1.969
	PDT	-	0.039
C3O2	GS	-	1.887
	TS	0.451	1.974
	PDT	0.029	1.886

C3O3	GS	-	1.100
	TS	-	-
	PDT	-	1.100
O1O2	GS	0.931	0.026
	TS	0.434	0.272
	PDT	-	0.039
O1H2	GS	0.032	0.085
	TS	0.054	-
	PDT	-	-

Table 2.Calculated and experimental ground state bond angle for pyruvic acid in degree

BOND ANGLE	PM3	DFT/B3LYP/6-31G*
C1C2C3	116.21	117.19
C1C2O1	124.05	125.27
C3O2O3	36.33	29.21
H3O3C3O3	-175.97	180.00

Table 3.Atomic charges of the species that involved in the elimination reaction for ground state (GS), transition state (TS) and products (mullikens)

ATOMS	STATE	DFT(6-31G*)	PM3
H1	GS	0.187	0.073
	TS	0.175	0.089
	PDT	0.202	-
	Δq(TS-GS)	-0.012	0.016
C1	GS	-0.524	-0.157
	TS	-0.519	-0.141
	PDT	-0.524	0.539
	Δq(TS-GS)	0.005	-0.253
H2	GS	0.433	0.084
	TS	0.176	0.094
	PDT	0.187	-
	Δq(TS-GS)	-0.257	0.01
H4	GS	0.201	0.076
	TS	0.146	0.089
	PDT	0.201	0.041
	Δq(TS-GS)	-0.055	0.013
C2	GS	0.384	0.266
	TS	0.08	0.23
	PDT	0.384	-0.248
	Δq(TS-GS)	-0.304	-0.036
C3	GS	0.549	0.301
	TS	0.722	0.377
	PDT	0.549	-0.017
	Δq(TS-GS)	0.173	0.076
O1	GS	-0.439	-0.288
	TS	-0.363	-0.229

	PDT	-0.439	-0.295
	Δq(TS-GS)	0.076	0.059
O2	GS	-0.432	-0.313
	TS	-0.359	-0.362
	PDT	-0.432	-0.233
	Δq(TS-GS)	0.073	-0.049
O3	GS	-0.561	-0.254
	TS	-0.485	-0.465
	PDT	-0.561	-0.098
	Δq(TS-GS)	0.076	-0.211

TOTAL ENERGY

The total energy calculated by quantum mechanical method is also a beneficial parameter. The total energy determines the occurrence or non-occurrence of chemical reactions and stereospecific paths in intra- and intermolecular processes [Fukuli F.K, 1982]. The total energy of a system is composed of the internal, potential, and kinetic energy. Hohenberg and Kohn [Faust W.L,1989] proved that the total energy of a system including that of the many body effects of electrons (exchange and correlation) in the presence of static external potential (for example, the atomic nuclei) is a unique functional of the charge density. The minimum value of the total energy functional is the ground state energy of the system. The electronic charge density which yields this minimum is then the exact single particle ground state energy. The total energy of pyruvic acid shows in table 4, PM3 (163.92KJ/mol) and DFT/B3LYP/6-31G*(-0.05KJ/mol).

Table 4.Heat of formation of reactant (GS), transition state (TS) and products, and the derived energetic, ΔE and ΔE* (KJ/mol)

	GS	TS	PDT	ΔE=(TS-GS)	ΔE*=(PDT-GS)
PM3	-538.48	-334.86	-374.56	203.62	163.92
DFT(6-31*)	-898797.38	-898593.30	-898797.43	204.08	-0.05

HOMO-LUMO ENERGY

The study of energies of HOMO and LUMO of molecules provide reliable and quantitative data for straightforward prediction of chemical and thermodynamic stabilities of molecules. It has been reported earlier that HOMO-LUMO energy gap (ΔE) is an important stability index [Pearson R.G, 1970]. A large energy gap implies higher stability and lower chemical reactivity and vice versa.
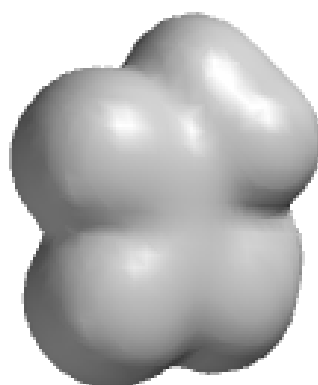
Figure 7.The density of Pyruvic acid using DFT at the B3LYP/6-31G* basis set level

From the calculations made for pyruvic acid at GS, TS, and Pdt (table 5) using semi-empirical PM3 gives EHOMO (-11.06eV, and -10.82, -8.98eV) and ELUMO (-0.66eV,-1.66eV and 0.54eV). DFT at the B3LYP/6-31G* basis set level, EHOMO (-7.38eV,-5.44eV,-7.38eV) and ELUMO (-2.47eV, -0.72eV, and -2.27eV).
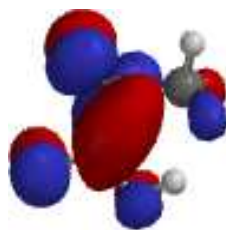

Figure 8.The lowest unoccupied molecular orbital (LUMO) density of pyruvic acid using DFT at the B3LYP/6-31G* basis set level.
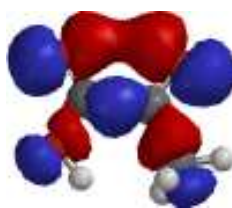

Figure 9.The highest occupied molecular orbital (HOMO) density of pyruvic acid using DFT at the B3LYP/6-31G* basis set level.

Table 5.HOMO and LUMO Energy (eV)

	PARAMETERS	GS	TS	PDT
PM3	E HOMO	-11.06	-10.82	-8.98
	E LUMO	-0.66	-1.66	0.54
DFT(6-31G*)	E HOMO	-7.38	-5.44	-7.38
	E LUMO	-2.47	-0.72	-2.27

DIPOLE MOMENT

Parameter that helps in the understanding of interaction between atoms in the same or different molecules is the dipole moment. It is a measure of the net molecular polarity, which is the magnitude of charge (/Q/) at the either ends of the molecular dipole time the distance between the charges. Dipole moment increases with increase in electronegativity of atoms [11]. Chemical reactivity usually increases with increase in dipole moment. The use of dipole moment to probe chemical reactivity according to our theoretical study suggests that transition state of pyruvic acid is of higher dipole moment (table 6).

Table 6.Dipole moment for ground state, transition state (TS) and products. (Debye)

	GS	TS	PDT
PM3	2.32	5.50	3.28
DFT(6-31G*)	2.38	0.97	2.38

Table 7.Arrhenius and Thermodynamics parameter @ 623K

METHOD	Ea(KJ/mol)	ΔH*(KJ/mol)	ΔS*(J/mol)	ΔG*(KJ/mol)	Log A(S^{-1})	K(S^{-1})
PM3	189.85	184.67	-9.85	190.81	12.60	1.30×10^{-3}
DFT(6-31G*)	192.33	193.03	-1.13	193.73	13.05	7.36×10^{-4}

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Calculated activation parameters at 298.15k for semi-empirical PM3, and DFT at the B3LYP/6-31G* basis set level as shown in Table 7 for PM3, Ea(189.85KJ/mol), Log A(12.60S^{-1}) and K(1.30×10^{-03}S^{-1}.) and with DFT/B3LYP/6-31G*, Ea (192.33kJ/mol), Log A (13.05S^{-1}) and K(7.36×10^{-04}S^{-1}) were predicted.

SPECTROSCOPIC INVESTIGATION

Results obtained from theoretical calculation at DFT at the B3LYP/6-31G* basis set level, of electronic absorption wavelength and vibrational frequencies of pyruvic acid at ground state, transition state and the products are shown in figures 10-11.
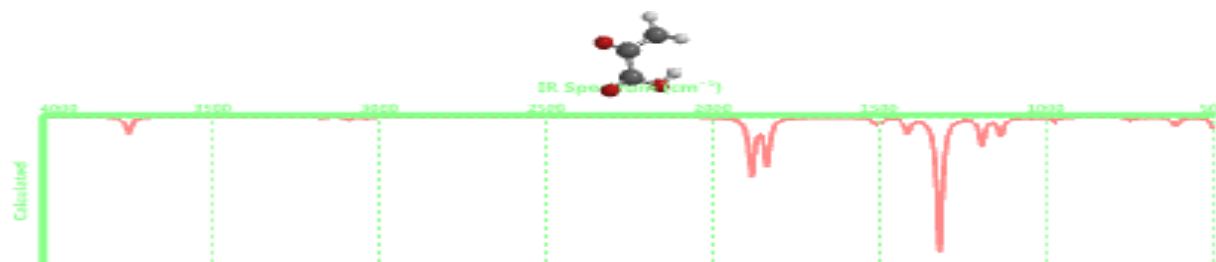

Figure 10.Infra red for pyruvic acid at ground state (GS)
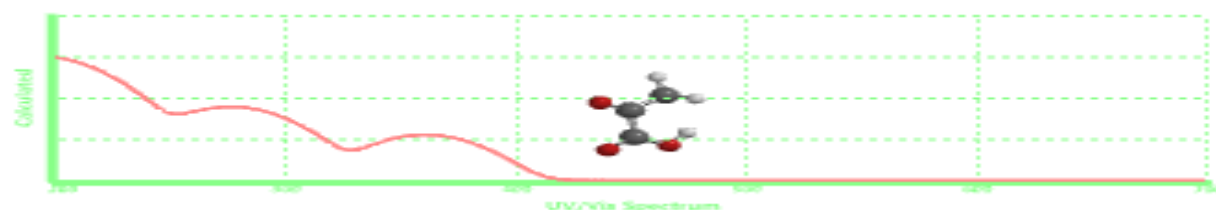

Figure 11.Ultra violet for pyruvic acid at transition state (GS)

CONCLUSION

It is observed that both semi-empirical and ab-initio methods could effectively predicts the kinetics, mechanism and activated parameters of pyruvic acid. The thermodynamics computed at 623K was predicted.

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