Quantum chemical reactivity investigation on ism methyl acetate through dft studies

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Abstract

The reliability of the product that will arise from the millions of reactions that are taking place in interstellar medium is dependent on the analysis of the rate constant. The current investigation is a chemical modelling research performed with Density Functional Theory (DFT) studies utilizing a foundation set of B3LYP 6-311++ G (d, p). The hydrolysis of methyl acetate in the interstellar medium is described using the quantum chemical parameters E_{HOMO} (highest occupied molecular orbital energy), E_{LUMO} (lowest unoccupied molecular orbital energy), energy gap (ΔE), chemical potential (μ), hardness (η), softness (S), the absolute electronegativity (χ), nucleophilicity index (N) and the electrophilicity index (ω). In order to study the probable reactive sites of the interstellar chemical methyl acetate in the ISM condition, the local reactivity descriptors Fukui function, NBO, and MEP were analysed in depth. The thermo chemical investigation contributed to the improvement of the chemical reaction mechanism and the calculation of the rate constant of the species under investigation results in the analysis of feasibility of the reaction under study.

Keywords: Interstellar chemistry, Quantum chemical parameters, NBO, MEP, ISM condition, Thermo chemical analysis, Feasibility, Fukui function.

1 Introduction

There is a tremendous variety of molecules in the interstellar medium. It is largely made up of so-called interstellar clouds of gas and dust, which can range in density from dense clouds that can appear dark against the sky to somewhat wispy diffuse clouds that are impenetrable to background light. It is necessary to conduct research into the complex interstellar chemistry, which consists of an abundance of space molecules and generates brand-new molecules every fraction of a second, in order to comprehend the process of new star formation and the development of this process. More than 250 molecules like H_2O, CH^+, CN, H_2S …. etc have been identified in interstellar and circumstellar clouds[1], with most interstellar sources having molecules in the gas phase. Both gas-phase activities and reactions on the surfaces of dust grains take place in interstellar clouds, with the latter taking place primarily on and in the water-dominated ice mantles of cold clouds. Some of these processes are extremely unusual by terrestrial standards, particularly when they occur at low temperatures [2].

In the past few decades, calculations based on quantum chemistry have found applications in a variety of chemical fields, such as the analysis of reaction pathways. This is a result of developments in theory, particularly improvements in the accuracy of functionals based on density functional theory (DFT).

Complex organic molecules and stars are born in the dark and dense environs of the interstellar medium (ISM), which includes everything between stellar systems. In these regions, dust grains covered in H_2O-ice provide the surface necessary for the formation of many organic molecules [3].

In the year 1982, the ISM NaOH is discovered in the interstellar medium. This detection represents the first proof of a grain reaction generation mechanism for simple metal hydroxides[4].Galactic centre source SgrB2 outside has been found to contain methyl acetate[5].The Atacama Large Millimeter /submillimeter Array (ALMA) has discovered the chemical compound methyl alcohol (methanol) in the TW Hydrae protoplanetary disc. It has never been discovered in a nascent planet-forming disc. The only complex organic compound that clearly originates from an ice state that has been found in discs so far is methanol. Its discovery aids astronomers in their understanding of the chemical processes involved in the formation of planetary

systems, which ultimately result in the production of the building blocks for life [6]. Using the Berkeley-Illinois-Maryland Association (BIMA) Array and the Caltech Owens Valley Radio Observatory (OVRO) Millimeter Array, the acetic acid (CH_3COOH) in the Sgr B2 Large Molecule Heimat source was discovered [7]. The IRAM 30 m radio telescope in Orion has recently detected methyl acetate CH_3COOCH_3, albeit its deuterated isotopomers have not yet been verified to be present. Acetyl CH_3CO and methoxy CH_3O radicals may combine with one another to produce methyl acetate. Using a gas-grain chemical network, we can estimate the abundances of CH_3COOCH_3, its two singly deuterated isotopomers, and its two isomers (ethyl formate and hydroxy acetone), as well as their two isomers [8,9].

This work employs Density Functional Theory and quantum chemical reactivity descriptors to investigate the hydrolysis of methyl acetate (ISM). We identified a knowledge gap in the DFT-based quantum chemical descriptor. Hydrolysis of interstellar molecules is the focus of the current research, which use B3LYP coupled with the 6-311++ G basis set to examine the process (d, p).

2 Experimental

The reaction mechanism of ISM methyl acetate was investigated in the ISM temperature and pressure using quantum chemical parameters. The experimental rate constant were studied using the rate law linking the concentrations of the reacting species with the rate of the hydrolysis of methyl acetate.

2.1 Materials

All the quantum chemical calculations have been performed at the B3LYP level of theory using Gaussian 16 series of programs.

2.2 Methods

In recent years, there has been a rise in the quantity of publications that are concerned with theoretical calculations in the areas of spectroscopic assignments, the investigation of electronic states and structures, and the clarification of reaction mechanism.

Geometry optimization is the first derivative of energy with respect to atomic location. When the geometry depends on either Cartesian or internal molecule

coordinates, the goal of geometry optimization is to locate the minimum of the corresponding mathematical function. For ISM methyl acetate, HOMO-LUMO values, Mulliken atomic charges, and thermochemistry ideas are provided by a successful geometry optimization utilising Functional Density Function Theory (DFT) with B3LYP connected with basis set 6-311++ G (d, p) at 0 **atmospheric** pressure and 15K temperature [10]. Quantum chemical calculations of ISM ethanol may be found using the Gaussian 16 software.

2.2.1 Frontier Molecular Orbital Studies

The frontier molecular orbital theory (FMO) of chemical reactivity states that, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the interacting species interact to cause the transition of the electron [11]. The capacity of a molecule to donate and accept electrons is used to define the HOMO and LUMO [12]. The study of molecular electronic characteristics relies heavily on the values of molecular orbitals. Chemical properties like an electrophilicity, hardness, and nucleophilicity are calculated using HOMO and LUMO energies.

Ionization potential (I), electron affinity (A), electronegativity (χ), global hardness (η) , and softness (S), Electrophilicity index(ω), Nucleophilicity index(N), can all be expressed in terms of HOMO and LUMO energy, according to **Koopman's** theorem [13].

The energy needed to remove an electron from a molecule is known as the ionisation potential (I). Equationally, it is connected to the of HOMO.

$$\text{Ionization energy, I} = -E_{\text{Highest Occupied Molecular Orbital}} \tag{1}$$

The energy released when a proton is introduced to a system is known as electron affinity (A). E_{LUMO} is connected to it via the following equation.

$$\text{Electron Affinity, A} = -E_{\text{Lowest Unoccupied Molecular Orbital}} \tag{2}$$

The ability of an atom or collection of atoms to draw electrons to itself is measured by the electronegativity, which may be calculated using the formula.

$$\text{Electro negativity, } \chi = \frac{Ionisation\ energy + Electron\ affinity}{2} \tag{3}$$

Chemical hardness (η) is a measure of an atom's resistance to a charge transfer. It is calculated using the following equation.

Chemical hardness, $\eta = \dfrac{Ionisation\ potential - Electron\ Affinity}{2}$ \hfill (4)

Chemical potential is a measure of the capability of a substance to cause either a chemical (or) electrochemical reaction in its environment, due to its internal energy (or) external energy.

Chemical potential, μ= - (Electro negativity) \hfill (5)

Chemical softness (S) is a measure of an atoms or group of atoms ability to accept electrons and is calculated using the equation

Softness, $S = \dfrac{1}{\eta}$ \hfill (6)

A reactivity descriptor called electrophilicity index a quantitative classification of a molecule's overall electrophilic nature on a relative scale. The electrophilicity index was described as follows.

Electrophilicity index, $\omega = \mu^2 / 2\eta$ \hfill (7)

The nucleophilicity N index is a measure of the nucleophilicity of complex organic molecules displaying nucleophilic behaviors.

Nucleophilicity index, $N = 1/\omega$ \hfill (8)

2.2.2 Fukui Function

With the use of the Fukui function, one can investigate the molecule's reactivity in relation to that of other molecules. It is a representation of the change in external potential in relation to the change in chemical potential when the number of electrons remains the same [14]. The greatest values of Fukui functions point to the areas of the molecular surface that are the most reactive. Atoms in a molecule that have the highest possible value of fk- indicate the electrophilic attacking centre, whereas atoms with the highest possible value of fk+ represent the nucleophilic attacking centre. Therefore, the Fukui function can be utilised to accurately predict the majority of the nucleophilic and electrophilic sites present in the molecule. The finite difference approximation can be used to calculate the nucleophilic f_k^+ and electrophilic f_k^- Fukui functions, which represent the change in electron density [15].

$$f_k^+ = q_{N+1} - q_N \qquad (9)$$

$$f_k^- = q_N - q_{N-1} \qquad (10)$$

2.2.3 Molecular Electrostatic Potential Analysis

The Molecular Electrostatic Potential of the surface provides an illustration of the three-dimensional charge distribution of the molecule. The MEP surface can glow as a map of areas with an excess of electrons and areas with an electron deficit. The MEP is utilised to recognise patterns of positive and negative potentials that are distinctive of a certain system. The potential energy interaction between proton and electron fields is categorised from high frequency (blue) region to higher wavelength (red) region, which identifies the charge dislocation between electrophilic and nucleophilic boundaries. The blue region has a higher frequency than the red region.

2.2.4 Non-Bonding Orbital Analysis

Natural Bond Orbital (NBO) investigation of ISM methyl acetate is carried out at the B3LYP/6-311++G (d, p) level for the purpose of obtaining information on hybridization as well as the electronic structure of the molecule [16].

2.2.5 Investigation of Reaction Mechanism -Thermochemical Analysis

The favourable energy conditions along with spontaneity studies provided the flow of energy to analyse the pathway in which the Interstellar reaction takes place.

2.2.5.1 Energetics of Reaction

For a reaction to be considered endothermic, the products must offer a net benefit to energy terms that are greater than those offered by the reactants. On the other hand, for an exothermic reaction, the reactants need to be more energetically favourable than the products. This is a prerequisite for an exothermic reaction.

$$E_{reaction} = E_{product} - E_{reactant}$$
$$(11)$$

2.2.5.2 Spontaneity of the reaction

According to **thermodynamics, free** energy means available energy which is used to do useful **work. This** free energy is released during spontaneous **reaction. A**

spontaneous reaction is one which favoured the product formation in condition in which it take place. Using the reaction's enthalpy and entropy values, Gibb's equation may determine whether the reaction is spontaneous or non-spontaneous. Negative free energy reactions are those that may proceed without spending any more energy.

$$\Delta_r H^0 = \Sigma \left[(\varepsilon_0 + H_{corr})_{products} \right] - \Sigma \left[(\varepsilon_0 + H_{corr})_{reactants} \right]$$

$$(12)$$

$$\Delta_r G^0 = \Sigma \left[(\varepsilon_0 + G_{corr})_{products} \right] - \Sigma \left[(\varepsilon_0 + G_{corr})_{reactants} \right]$$

$$(13)$$

2.6 Rates of Reaction

The key equation for calculating reaction rate is

$$k_{(15K)} = \frac{K_B \, T \, e^{-\Delta G0/RT}}{h \, C^0}$$

$$(14)$$

3 Results & Discussions

3.1 Structure optimization

Utilizing B3LYP/6-311++G, an optimization of the interstellar molecular structure of ISM methyl acetate Fig. 1 was carried out at a temperature of 15K and a pressure of 0 **atmosphere** (d, p).

ISM methyl acetate's HOMO Fig.2 and LUMO Fig.3 structures, computed using the B3LYP/6-311++G method d, p).

3.2 Reactivity Parameters Derived from Frontier Molecular Orbitals

The electrophilicity index is used to categorise electrophiles into three different strength levels: **weak (ω < 1.50 eV), moderate (1.50 > ω > 0.86 eV), and strong (ω >1.50 eV).** The nucleophiles can be broken down into three different categories: moderate (N >3.00 eV), marginal (N < 2.00 eV), and strong (N >3.00 eV) [17]. According to this categorization, the ISM methyl acetate act both as an electrophile as well as a nucleophile of significant strength.

Its strong nucleophilic nature in the ISM medium suggests that its chemical reactivity can donate electron density. It exists in the interstellar medium (ISM). Interstellar methyl acetate's chemical behaviour can be analysed by considering the energy gap between its HOMO and LUMO states. Both the chemical and kinetic stability of the molecule can be described here. It also reveals details about the molecular excitation type. For ISM methyl acetate, the energy gap between the HOMO and LUMO states is -0.27615 kJ/mol. Given these factors, it is reasonable to assume that ISM methyl acetate is highly reactive and less stable [18]. Therefore, the photochemical activation of isopropyl methyl acetate (ISM) is a simple process.

In this regard, the global electronegativity (χ), the chemical potential (μ), the global hardness (η), the global softness (S), and the electrophilicity index (ω) all have a high degree of success in forecasting the feasibility and character of reaction in the ISM medium. The global softness index and the global electrophilicity index are both calculated by making use of the energy of the border molecular orbitals EHOMO and ELUMO. This is done with the assistance of Koopmans' theorem.

3.3 Fukui functions Derived from Mulliken charges

The findings of the study on the local selectivity [19] indicate that ISM methyl acetate have the capacity to carry out the functions of both an electrophile and a nucleophile. It is anticipated that carbon 8 will be the site of most electrophilic attacks on ISM methyl acetate molecules. The carbon atom at position C3 of methyl acetate in the ISM possesses a nucleophilic attacking centre. It **was observed** from this that methyl acetate in the ISM can go through both electrophilic and nucleophilic processes. To explore the local reactivity, chemical reactivity and site selectivity associated with the ISM methyl acetate, the Fukui function and local electrophilicity/nucleophilicity have been used. By these calculations, it was observed that ISM methyl acetate **undergoes** hydrolysis in presence of water in the Interstellar medium. The 8C atom of ISM methyl acetate molecules contain higher electrophilicity than other hydrogen and carbon atoms. By global and local descriptors, the values of 7O and 3C atoms demonstrate that atom 7O would be the most favourable reaction site and atom 3C atom preferably attacks atom **7O** and, as a further step, 8C and 7C get attached, to form methanol in the interstellar medium. The highest values of 3C confirms that

most **favourable** reaction site for nucleophilic attack which leads to the formation of acetic acid in the **interstellar medium.**

3.4 Interpretation of Relative Polarity- MEP

The colour red indicates a positive extreme (lowest electrostatic potential, which reveals an electrophilic attacking centre) in the MEP figure of ISM methyl acetate, while the colour blue indicates a positive extreme (highest electrostatic potential, which shows a nucleophilic attacking centre) [20]. As a result of this work, the electrophilic centre of the oxygen atom in ISM methyl acetate is confirmed.

3.5 Analysis of Maximum Electron Density with NBO

Second order perturbation analysis confirms that the stabilization energy of **42. 41** kcal/mol corresponds to conjugative interaction from donor LP (2) of O_3 to $\boldsymbol{\pi^*C_1\text{-}O_2}$ and stabilization energy of **33. 13 kcal**/mol corresponds to conjugative interaction from donor LP (2) of O_2 to $\boldsymbol{\sigma^*C_1\text{-}O_3}$which confirms that ISM methyl acetate has three possible resonance **structures**.

Step I: The loan pair electron on LP (1) O_2 in ISM methyl acetate is transferred to protonated water molecule which initiate hydrolysis mechanism by forming first **intermediate (Protonation step).**

Step II: The lone pair electron on oxygen atom in water is attacking carbonyl carbon in methyl acetate which is confirmed by transition from π $C_1\text{-}O_2$ to $\pi^*C_1\text{-}O_2$ corresponds to energy 0.68 **K. Cal/mol (Nucleophilic addition).**

Step III: Proton transfer occurs between another molecule of water and second intermediate.

Step IV: ISM Methanol molecule is eliminated which is confirmed by LP (2) O_3 to $\sigma^*C_8\text{-}H_{10}$ and $\sigma^*C_8\text{-}H_{11}$ transition corresponds to energy 5.24 kcal/mol**. Further** transition from LP (2) O_3 to $\pi^*C_1\text{-}O_2$ having energy 42.41 K. Cal/mol also confirms that ISM methanol molecule is eliminated in this step.

Step V: ISM acetic acid is formed in this **step. Once** methanol is eliminated in the step IV, it forms carbocation which undergoes internal electron transfer forming double bond between $C_1$to O_2.

3.6 Kinetics of catalytic hydrolysis of methyl acetate

The value of the first order rate constant, k for the acid catalytic hydrolysis of methyl acetate obtained through experimentation is determined to be 2.3 x 10^{-2} s^{-1} (Table 5). The current theoretical investigation at temperature 15K and $\Delta_r G^0$ = 3.48205 kcal/mol suggests the rate constant**, k as 3.1254 X 10 ^{11} e $^{-116.83}$ s^{-1}** (Table 4) which corresponds to the experimental value except the theoretical study being done in the gas phase and ISM circumstances exhibiting little alteration in results.

3.7 Energetics of Reaction

Molecules are always broken (hydrolysed) through an endothermic process because it always requires energy to break bonds. An endothermic reaction must have an overall increase in the amount of energy present in the end products when compared to the reactants. **It is known that** the activation energy required to hydrolyse ISM methyl acetate into molecules of ISM acetic acid and methanol is 24.4472 kcal/mol based on the findings of the studies that were previously discussed. The endothermic nature of hydrolysis under the ISM condition is demonstrated graphically and supported by experimental values [22]. The energy values suggest that the final product of every reaction step has lower energy than the Reactant and TS is formed after crossing the potential barrier. All the calculations suggest the high feasibility of acetic acid and methanol formation in the ISM. The calculations for global and local reactivity descriptor are performed at B3LYP/6–311G (d, p) and are expressed in Table 1 and Table 2. These values indicate the formation of methanol and acetic acid through the soft-soft interaction in methyl acetate. The reaction mechanism for hydrolysis of methyl acetate reaction path is displayed in Fig. 6.

3.8 Spontaneity of a reaction

The change in entropy may be calculated by considering both the change in Gibb's free energy and the change in enthalpy values [23]. It has been shown that ΔG is positive for the hydrolysis of ISM methyl acetate. Because of this, it has been shown that the hydrolysis that occurs in the interstellar medium is not a spontaneous response. This hydrolysis is only capable of taking place in the presence of ISM acids or bases. There is evidence to support the viability of interstellar reactions with potential barriers greater than 60 kcal/mol [24]

4 Conclusion

Using chemical simulation technologies based on DFT methods, the hydrolysis of Interstellar molecule methyl acetate was explored in the ISM condition. Calculations were done to determine the energy levels of the HOMO and LUMO orbitals of the optimised ISM methyl acetate. It was observed that the HOMO-LUMO gap in ISM methyl acetate has a low energy level, which made it easy for electrons to transfer, as confirmed by the NBO analysis of the molecule. The $\Delta_r H^0$ and $\Delta_r G^0$ of hydrolysis reactions of ISM methyl acetate was also calculated. Using these values, it was confirmed that hydrolysis of ISM methyl acetate is non-spontaneous reaction in the interstellar medium. Energetics of reaction investigations confirmed that hydrolysis of ISM methyl acetate is endothermic in the interstellar medium. Kinetics of catalytic hydrolysis of methyl acetate is proven to be first order experimentally. Theoretical calculation of hydrolysis of ISM methyl acetate is likewise found to be first order in kinetics. Experimental and theoretical research have both shown that the rate of hydrolysis is solely dependent on the concentration of methyl acetate and is unrelated to the presence of water in the reaction mixture. Because of this, the hydrolysis of ISM methyl acetate can take place in the ISM medium.

Using quantum chemical techniques, it has been investigated whether the interstellar molecule CH_3COOCH_3 may produce acetic acid and methyl acetate. The B3LYP theory's quantum chemical calculations showed that the likelihood of their formation combines with the earlier statement. The proposed reaction pathways have large potential barriers, but it is still possible for reactants to pass over the barriers by thermal hopping or quantum tunnelling. The research showed that the synthesis of methanol and acetic acid in the ISM is effective both in the gas phase and in the ice grains. When some energy is available from cosmic and UV rays in the hot core of Sgr B2, the observed energetic study of the hydrolysis of ISM methyl acetate can penetrate. Therefore, there is a high likelihood that methyl acetate will be hydrolysed in ISM.
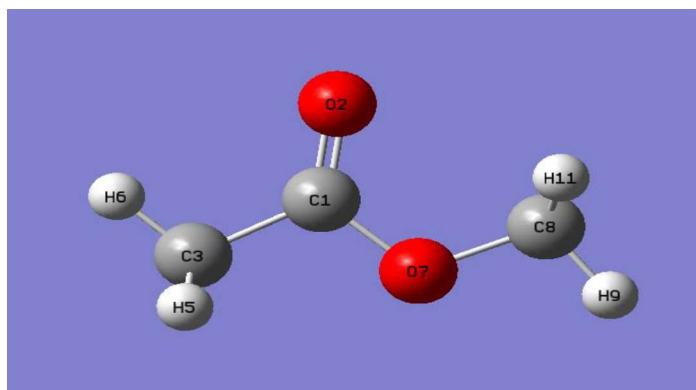
Figures:

Fig. 1 Optimized structure of ISM Methyl acetate
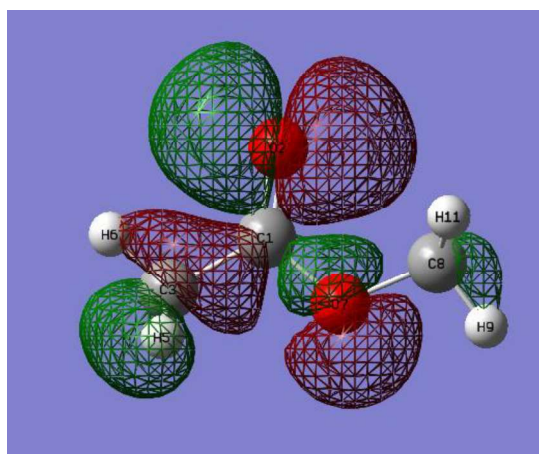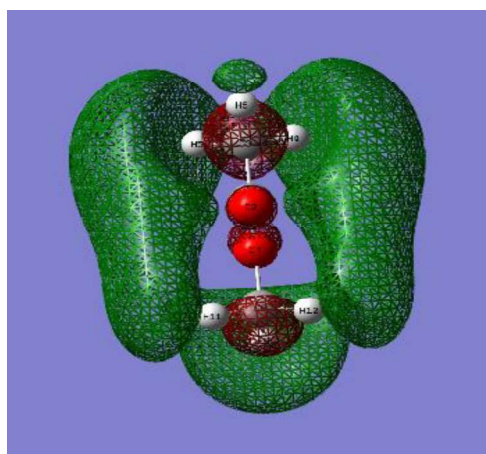

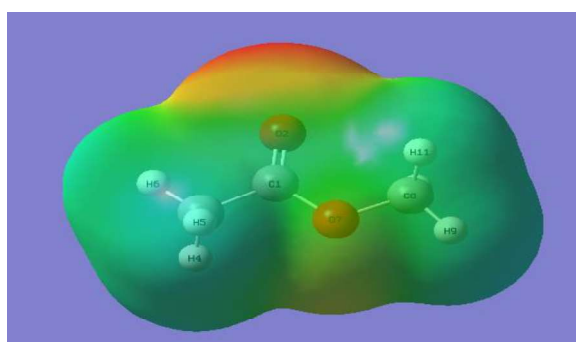Fig.2 HOMO   Fig. 3 LUMO

Fig. 4 MEP of ISM Methyl acetate

RESONANCE STRUCTURE
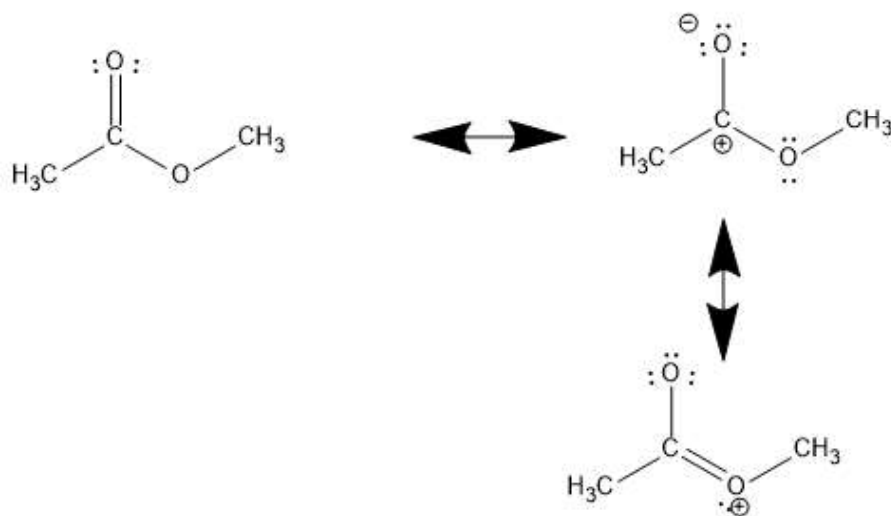
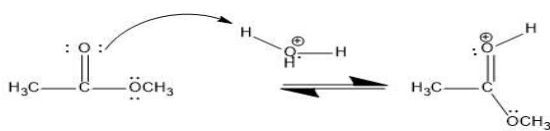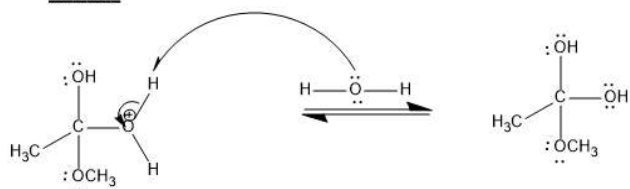**Fig. 5 Resonance structure of methyl acetate**
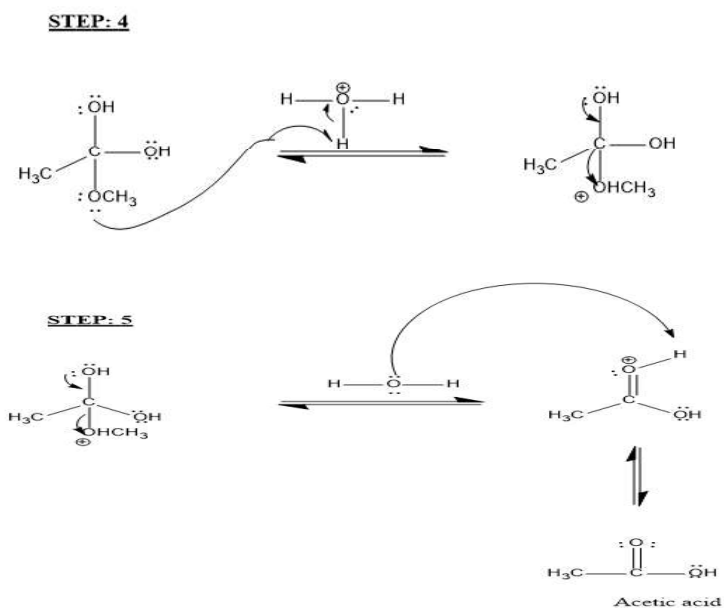
Fig.6 Mechanism of Hydrolysis
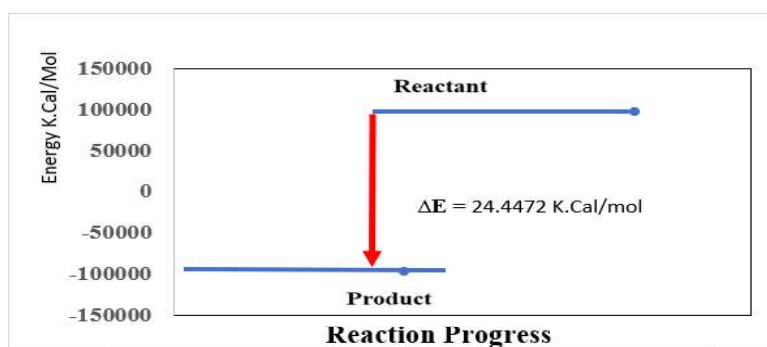
Fig. 7 Reaction Progress for hydrolysis of methyl acetate

Tables:

Table 1. Reactivity Parameters Derived from Frontier Molecular Orbitals

Molecular Properties	B3LYP/6-311d(d,p)
HOMO	-0.28625
LUMO	-0.01010
Energy Gap	-0.27615
I	0.28625
A	0.01010
χ	0.148175
μ	-0.148175
η	0.138075
S	7.2424
ω	0.07952
N	12.5755

Table 2. Fukui functions Derived from Mulliken charges

	q_n	q_{n-1}	q_{n+1}	f^{k+}(nucleophilic attack	f^{k-}(Electrophilic attack)
C	0.167931	0.267923	-0.594776	-0.762707	-0.099992
O	-0.295953	0.133449	-0.347765	-0.051812	-0.429402
C	-0.527905	-0.528272	2.160853	**2.688758**	0.000367
H	0.174718	0.254283	-0.692777	-0.867495	-0.079565
H	0.174774	0.227328	-0.798313	-0.973087	-0.052554
H	0.168069	0.254261	-0.798238	-0.966307	-0.086192
O	-0.109705	-0.009021	-0.284471	-0.174766	-0.100684
C	-0.247867	-0.270777	1.618567	1.866434	**0.022910**
H	0.150258	0.219972	-0.562577	-0.712835	-0.069714
H	0.172842	0.230956	-0.562545	-0.735387	-0.058114
H	0.172837	0.219899	-0.137957	-0.310794	-0.047062

Table 3. Second Order Perturbation Analysis of Fock Matrix in NBO Basis of ISM Methyl acetate [21]

Donor NBO(i)	Acceptor NBO(j)	E_2 kcal/mol	E(j)-E(i) a.u	F(i,j) a.u
1. $\sigma\ C_1\text{-}O_2$	145. $\sigma^*C_1\text{-}C_4$	1.12	1.45	0.036
	146. $\sigma^*O_3\text{-}C_8$	1.78	1.35	0.044
2. $\pi\ C_1\text{-}O_2$	143. $\pi^*C_1\text{-}O_2$	0.68	0.40	0.015
	147. $\sigma^*C_4\text{-}H_5$	1.54	0.77	0.031
	148. $\sigma^*C_4\text{-}H_6$	1.54	0.77	0.031
4.$\sigma\ C_1\text{-}C_4$	142.$\sigma^*C_1\text{-}O_2$	1.09	1.30	0.034
5. $\sigma O_3\text{-}C_8$	142.$\sigma^*C_1\text{-}O_2$	2.70	1.48	0.056
6.$\sigma\ C_4\text{-}H_5$	142.$\sigma^*C_1\text{-}O_2$	1.91	1.17	0.042
	143.$\pi^*C_1\text{-}O_2$	4.28	0.55	0.045
7.$\sigma C_4\text{-}H_6$	142.$\sigma^*C_1\text{-}O_2$	1.91	1.17	0.042
	143.$\pi^*C_1\text{-}O_2$	4.29	0.55	0.045
8.$\sigma C_4\text{-}H_7$	142.$\sigma^*C_1\text{-}O_2$	0.56	1.16	0.023
	144.$\pi^*C_1\text{-}O_3$	4.91	0.88	0.060
9.$\sigma C_8\text{-}H_9$	144.$\sigma^*C_1\text{-}O_3$	3.19	0.89	0.049
10.$\sigma C_8\text{-}H_{10}$	146.$\sigma^*O_3\text{-}C_8$	0.56	0.81	0.019
11.$\sigma C_8\text{-}H_{11}$	146.$\sigma^*O_3\text{-}C_8$	0.56	0.81	0.019
17.$n1O_2$	144.$\sigma^*C_1\text{-}O_3$	0.85	1.04	0.027
	145.$\sigma^*C_1\text{-}C_4$	2.57	1.05	0.047
18.$n2\ O_2$	144.$\sigma^*C_1\text{-}O_3$	33.13	0.61	0.129
	145.$\sigma^*C_1\text{-}C_4$	18.25	0.62	0.097

19.$n1O_3$	142.σ^*C_1-O_2	2.01	1.19	0.044
	145.σ^*C_1-C_4	5.88	0.91	0.066
	150.σ^*C_8-H_9	2.80	0.94	0.046
	151.σ^*C_8-H_{10}	0.77	0.92	0.024
	152. σ^*C_8-H_{11}	0.77	0.92	0.024
20.$n2$ O_3	143.π^*C_1-O_2	42.41	0.34	0.108
	151.σ^*C_8-H_{10}	5.24	0.69	0.056
	152. σ^*C_8-H_{11}	5.24	0.69	0.056
143.π^*C_1-O_2	147.π^*C_4-H_5	0.89	0.37	0.050
	148.π^*C_4-H_6	0.89	0.37	0.050
144.σ^*C_1-O_3	147.σ^*C_4-H_5	1.29	0.03	0.023
	148.σ^*C_4-H_6	1.28	0.03	0.023
	149.σ^*C_4-H_7	2.47	0.06	0.044
	150.σ^*C_8-H_9	1.75	0.03	0.029
	151.σ^*C_8-H_{10}	1.16	0.01	0.015
	152.σ^*C_8-H_{11}	1.16	0.01	0.015

Table 4. Kinetic data calculated theoretically

Species	Name	Free energy
CH_3COOCH_3	**Methyl acetate**	-268.386377
H_2O	**Water**	-76.437562
CH_3COOH	**Acetic acid**	-229.104027
CH_3OH	**Methanol**	-115.714538

Table 5. Experimental Results for Rate constants

S.No	Time/min	Titre value Vt	$(V_\infty-V_t)$	$Log((V_\infty-V_t))$	Rate constant $K=2.303/t \times log(V_\infty-V_0)/(V_\infty-V_t)$
1	0	24.5			
2	10	26.4	14	1.1461	0.0127
3	20	29.2	11.2	1.0492	0.0175
4	30	32.1	8.3	0.9191	0.0217
5	40	34.8	5.6	0.7482	0.0261
6	50	37.9	2.5	0.3979	0.0370
7	∞	40.4			
Rate constant			$K=0.023=2.3 \times 10^{-2}$ s^{-1}		

Table 6. Hydrolysis of ISM methyl acetate

Energy	Reactant		Total	Product		Total
	CH_3COOCH_3	H_2O		CH_3COOH	CH_3OH	
E (a.u)	-268.478175	-76.458532	-344.936707	-229.132718	-115.764998	-344.897716
E(K. Cal/mol)	-168472.6054	-47978.43510	-216451.0405	-143782.9573	-72643.63601	-216426.59331
a.u $E_{reaction}=E_{product} - E_{reactant}$ $\qquad = 0.038807$ a. u			**kcal/mol** $E_{reaction}=E_{product} - E_{reactant}$ $\qquad = 24.4472$ kcal/mol			

Table 7. Enthalpies and Free energies of reaction (Hydrolysis of methyl acetate)

	Reactant		Product	
	CH$_3$COOCH$_3$	H$_2$O	CH$_3$COOH	CH$_3$OH
ε_0	-268.478175	-76.458532	-229.132718	-115.764998
E_{zpe}	0.089216	0.02129	0.061526	0.051025
E_{tot}	0.089362	0.021432	0.061669	0.051167
H_{corr}	0.089410	0.02148	0.061716	0.051215
G_{corr}	0.088440	0.02097	0.060801	0.050460
ε_0+E_{zpe}	-268.385601	-76.437242	-229.103302	-115.713973
ε_0+E_{tot}	-268.385455	-76.4371	-229.103159	-115.713831
ε_0+H_{corr}	-268385408	-76.437052	-229.103112	-115.713783
ε_0+G_{corr}	-268.386377	-76.437562	-229.104027	-115.714538
Δ_rH^0	3.48895 kcal/mol			
Δ_rG^0	3.48205 kcal/mol			

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