# Computational Study of Mechanism of Esterification under Different Catalytic Conditions

*A*

*Thesis submitted*

*In the partial fulfillment of the requirement of degree*

**MASTERS OF SCIENCE**

**IN**

**CHEMISTRY**


*Submitted By*

**SABRINA**

**(301602037)**

UNDER THE SUPERVISION OF

**Dr. AMJAD ALI**

(Associate Professor and Head)

**Dr. DIBYENDU MALLICK**

(Assistant Professor)

**SCHOOL OF CHEMISTRY AND BIOCHEMISTRY,**

**THAPAR INSTITUTE OF ENGINEERING & TECHNOLOGY,**

**PATIALA-147004**

**2018**

## CERTIFICATE

This is to certify that the thesis entitled **"Computational Study of Mechanism of Esterification under Different Catalytic Conditions"** submitted by **Ms. Sabrina** in the partial fulfillment of the requirements for the degree of **Masters of Science in Chemistry** from **Thapar Institute of Engineering and Technology, Patiala** is a bonafied piece of work carried out under the guidance and supervision of **Dr. Amjad Ali,** Associate Professor and Head, and **Dr. Dibyendu Mallick,** Assistant Professor, School of Chemistry and Biochemistry, Thapar Institute of Engineering and Technology, Patiala and no part of project has been submitted for award of any other degree in this or any other university.

Sabrina

**(SABRINA)**

This is to certify above statement made by student concerned is correct and true to the best of my knowledge.

Amjad

Dr. Amjad Ali
Supervisor
Associate Professor and Head,
School of Chemistry and Biochemistry,
Thapar Institute of Engineering and Technology,
Patiala

Dibyendu Mallick 6/8/18

Dr. Dibyendu Mallick,
Supervisor
Assistant Professor,
School of Chemistry and Biochemistry,
Thapar Institute of Engineering and Technology,
Patiala

## SELF DECLARATION

The work embodied in the project entitled **" Computational Study of Mechanism of Esterification under Different Catalytic Conditions"** has been done by me in the partial fulfillment of the requirement of the Award of degree of **Masters of Science in Chemistry,** submitted in the **School of Chemistry and Biochemistry, Thapar Institute of Engineering And Technology, Patiala,** is an authentic record of my own carried under the supervision and guidance of **Dr. Amjad Ali,** Associate Professor and Head, and **Dr. Dibyendu Mallick,** Assistant Professor, School of Chemistry and Biochemistry, Thapar Institute of Engineering and Technology, Patiala. All the ideas and references have been duly acknowledged.

**( SABRINA)**

Place: Patiala

Date:

This is to certify above statement made by student concerned is correct and true to the best of my knowledge.

Dr. Amjad Ali
Supervisor
Associate Professor and Head,
School of Chemistry and Biochemistry,
Thapar Institute of Engineering and Technology,
Patiala

Dibyendu Mallick 6/8/18

Dr. Dibyendu Mallick,
Supervisor
Assistant Professor,
School of Chemistry and Biochemistry
Thapar Institute of Engineering and Technology,
Patiala

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Sabrina

Place: Patiala

# TABLE OF CONTENT

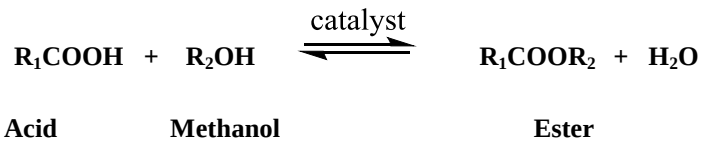
## Abstract

The reaction mechanism of homogeneous and heterogeneous catalyzed esterification reaction was examined by means of Density functional theory (DFT). The mechanistic investigation showed that the reaction was a two-step process which involved the formation of cyclic transition structures. The theoretical results provide crucial guide to understand the mechanism of acid-catalysed esterification reactions in presence of both homogeneous and heterogeneous catalysts. The structures of catalysts were modeled and their activation energies were determined. A comparison of the activation energies between the homogeneous and heterogeneous catalyzed reactions were done at M06-2X/ 6-31+G* level of theory. The energy diagrams demonstrate the activation energy required decreases in presence of both homo- and heterogeneous catalyzed reactions as compared to the uncatalyzed pathway. The activation energy barrier for the homogeneous catalyzed reaction has the lowest value among all the pathways studied.

# Chapter 1
# Introduction and Literature Review

## 1.1 Introduction

The reaction of a carboxylic acid and an alcohol in the presence of an acid catalyst is known as Fischer esterification.[1–3] Emil Fischer and Arthur Speier described this reaction in 1895.[4]




**Scheme 1:** Esterification of carboxylic acid with alcohol.

In the above reaction, $R_1$ and $R_2$ are general hydrocarbon groups.[5,6] Esters have great applications in the living world as well as in the industries. The esters with the lower molecular mass carry stronger odor than those with the higher molecular mass. The lower molecular mass esters improve the flavor and smell of the processed food items, so they are used as food additives. These esters are listed as "artificial flavors" on the labels of the various processed food items. Small esters like methyl acetate, ethyl ethanoate are outstanding solvents for organic compounds, nail paint removers, sunburn lotions, plasticizers,[3] glues etc. Besides, large esters (>C9) are used in the production of various soaps and detergents, as a biodiesel, solvent in paint industry. The long chain ester molecules are very unreactive and have good tensile strength. In industry, the hydrocarbon chain having length C18-C22 (that is, oleic acid and erucic acid) have wide applications as lubricant.

Mechanism and kinetics of esterification reactions by using homogeneous[7] and heterogeneous catalysts[8] are studied widely by experimental groups.[9] However, the theoretical aspect of these mechanisms has been less extensively studied, specially when heterogeneous catalyst is used.[10] Earlier, homogeneous catalysts like $H_2SO_4$, HCl, HI, HCOOH were mainly used in the industries because of their ease and lesser reaction time needed. Although they provide very higher conversions but their neutralization and separation from the reaction mixture is a very tedious, time consuming task and also one have to deal with the waste that contains acid.[11,12]

Heterogeneous catalysts are used to avoid these limitations as they can easily be separated and purified and its few examples are ion-exchange resins,[13] zeolites,[14] acid clay catalysts,[15] solid acids and bases.[16,17] Presently, mesoporous catalysts are used extensively because of their large surface area and desirable thermal stability.

Density Functional Theory (DFT) techniques have been utilized for the examination of mechanism of a variety of organic reactions.[18,19] The theoretical results provide a vital guide to illustrate the classical acid-catalyzed reaction mechanisms for esterification reaction. It is reported that the esterification takes place through the cyclic four membered TS structures in two steps mechanism.[10] Here, we are going to compare the esterification mechanisms for the reaction of methanol with acetic acid in presence of homogeneous acid catalyst,[20] heterogeneous acid catalyst[21] and in the absence of any catalyst by using DFT calculations. $H_2SO_4$ has been used as homogeneous catalyst whereas silica supported sulfuric acid as heterogeneous catalyst has been used for the esterification reaction[22] and their relative activation energies are compared. Modeling of the surface in the form of cage-like cluster consisting of Si-O-Si sequence is a promising technique for the judgment of the structure of the silica gel. However, for the systems having large number of atoms the calculation becomes quite time-consuming for obtaining accurate and consistent results.[23]

## 1.2 Literature Review

Wiliamson and Pickles examined the kinetics of estrification reaction between acetic acid and methanol in the alcoholic and non-hydroxylic media.[24] The kinetic model was proposed by them was based on the esterification reaction by utilizing HCl as a catalyst. Miao and Shanks studied the kinetics of esterification reaction between the acetic acid and methanol by using propyl sulfonic acid fuctionized SBA-3 catalyst.[25] They utilized propane sulfonic acid as homogeneous catalyst (has same structure as fuctional group grafted on silica). They examined that pre-adsorption of the acetic acid slowed down the reaction while the pre-adsorption of methanol or acetic acid along with methanol enhanced the rate of the reaction and concluded that heterogeneous and homogeneous catalysis followed different mechanisms. Liu and his co-workers studied the kinetics between acetic acid and methanol using Nafion/silica nanocomposite SAC-13 and $H_2SO_4$ to study the similarities between the heterogeneous and

homogeneous catalysed reaction[26] and they found that SAC-13 (Nafion resin was supported on a permeable silica matrix) has equivalent site activity as $H_2SO_4$. They also exhibit comparable reaction inhibition due to the presence of water. They observed that the catalytic activity of $H_2SO_4$ was greater by a factor of three than that of SAC-13 on per site basis. They have also done the experiments to study the effect of the carboxylic acid carbon chain length for both homogeneous (using $H_2SO_4$) and heterogeneous acid (Nafion SAC-13) catalysed esterification reactions.[27] The reactivity for small carboxylic acids (HAc and HBu) is similar for both homogeneous and heterogeneous acid catalyst. For larger carboxylic acids (HBu to HCp) little impact on the reactivity was observed when the chain length of carboxylic acid was increased for homogeneous catalysed reactions. On the other hand, for the heterogeneous catalysed reactions the inhibitory effect on the reactivity is observed by increasing the chain length.

Mekala and Goli investigated the kinetics of esterification of acetic acid with methanol by using mineral homogeneous acid as catalyst.[28] Acetic acid to methanol molar proportion was varied from 1:1 to 1:4 and the effect of temperature, reactant concentration and catalyst concentration on the rate of the reaction was studied. The kinetic model based on concentration and also on the activity was developed and its predictions were compared with that of the experimental data as well as with the models in literature. Mekala and Goli also investigated the comparative kinetics of esterification between acetic acid and methanol by using both homogeneous and heterogeneous catalysts.[9] $H_2SO_4$ was used as liquid catalyst and ion exchange resins, such as Indion-180, Indion-190 and Amberlyst-16 wet were used as solid catalysts. They found that Indion-180 is better than other two solid catalysts. The liquid catalyst (that is $H_2SO_4$) was observed to be better than the other three solid catalysts.

Vafaeezadeh and Fattahi used computational modeling technique to study the Fischer esterification reaction between the acetic acid and ethanol over silica functionized propylsulfonic acid (silica-propyl-$SO_3H$) .[23] They found that the mechanism is comprised of two transition states with the concerted transformations. A very low difference in free energies is observed between the esterification (forward reaction) and ester hydrolysis (backward reaction) that is 0.3 Kcal/mol which means that it is a reversible reaction. Shi and his co-workers investigated the mechanism of acid-catalysed carboxylic acid esterification and hydrolysis using DFT and concluded that it is a two step reaction.[19] In the first step, the carboxylic acid hydroxyl-oxygen is

protonated, which generated the highly active acylium ion and it was the rate determining step of the reaction. In the second step, the acylium ion instinctively reacted with the two alcohol molecules and lead to the formation of a neutral product molecule. The highly active intermediate acylium ion was generated in the esterification and hydrolysis reaction and it was confirmed by ESI-MS (Electrospray Ionization- Mass Spectroscopy). Lawal and his co-workers applied DFT to study the esterification reaction mechanism of methanol with carboxylic acid as well as its halide derivative by using acid-catalyst.[10] Single-step concerted reaction is modeled and it included 6-membered cyclic pre-complex and transition structures. They observed that the free activation energy that is calculated theoretically in solution phase is in reasonable agreement with that of experimental for the esterification reaction of acetic acid with methanol. It was concluded that the acid-catalysed esterification of acid halides (that is I, Br and Cl) with methanol is a spontaneous process.

Shagufta and co-workers discussed that various recyclable sulfonic acid functioanized solid acids are active and environmentally friendly catalysts for esterification and transesterification between carboxylic acids and alcohols for making various commercial chemicals like esters and biodiesels respectively.[29] Ronnback and co-workers studied the kinetics of the esterification of acetic acid and methanol by using hydrogen iodide as homogeneous catalyst.[5] They examined that the rate initiating step in the reaction mechanism was the protonation of carboxylic acid. Hydrogen iodide was esterified by methanol and methyl iodide and a by-product was produced.

# Chapter 2

## Objectives

- To demonstrate a mechanistic model for homogeneous and heterogeneous catalysed esterification reaction.
- To compare the activation energy required for esterification reaction in presence and absence of catalyst.

# Chapter 3

# Computational Details

All the theoretical calculations were performed by utilizing the Gaussian 09 program[30] at M06-2X/6-31G* level of theory.[31,32] Guass view 5.0.8 and chemcraft are used as the visual interface for this study. M06-2X functional and 6-31G* basis set was observed to be adequate and accurate for anticipating the energy parameters for this required esterification reaction.[10] Full geometry optimization and frequency calculations were performed for each reactions in gas phase as well as in presence of implicit solvent. Solvent effects were included by using Polarized continum model (PCM)[33] and methanol was used as solvent. Free energy profiles were constructed for the reactions based on the optimized structures. The reaction free energy and enthalpy for all the states were evaluated.[31] By DFT calculations, we found that esterification reaction of acid-catalysed carboxylic acid is a two-step reaction.[19] Two transition states were observed, TS1 and TS2 and the presence of one imaginary frequency for each TSs confirms their nature. The energy values reported are stated in kcal/mol.

Vienna ab initio simulation package (VASP)[35–37] is used for computing the surface of $SiO_2$-$H_2SO_4$. The electron exchange correlation is included by using Generalized Gradient Approximation (GGA)[38] with Perdew Burke Ernzerhof (PBE) functional and PAW pseudopotentials[39] is used to treat the electron ion interactions. 400 eV energy is required to cutoff for the plane wave basis set and equivalent set of k point grid is taken for all the calculations ehich has spacing of around $2\pi$ x $0.04 Å^{-1}$. The energy of $10^{-6}$ eV and force of $10^{-3}$ eV/Å is set for electronic energy convergence threshold .

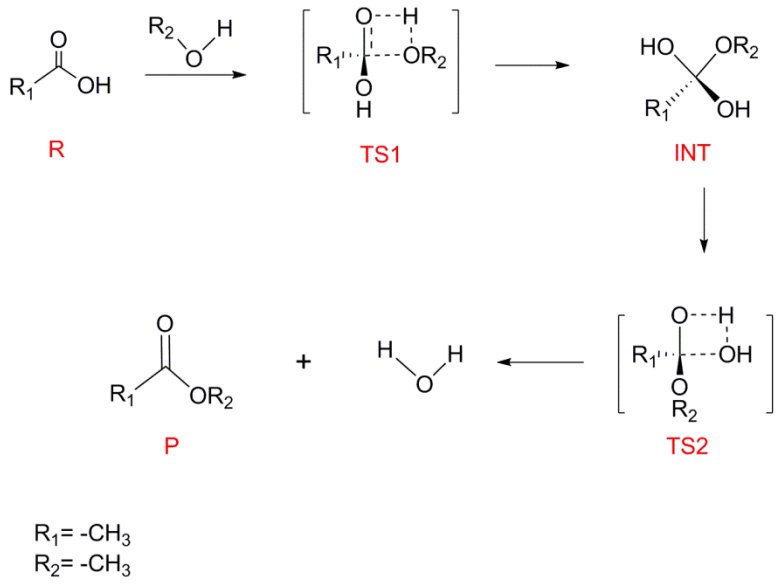
# Chapter 4

## Results and Discussions

The esterification reaction of acetic acid (HOAC) with methanol (MeOH) has been done in three different ways. First, the esterification reaction is done without using any catalyst, then it is done by using $H_2SO_4$ as a homogenous catalyst and finally it is done by using silica-$H_2SO_4$ as a heterogeneous catalyst. Different activation energy barriers are obtained for these reactions. Detailed mechanism and its energy barriers are discussed below.

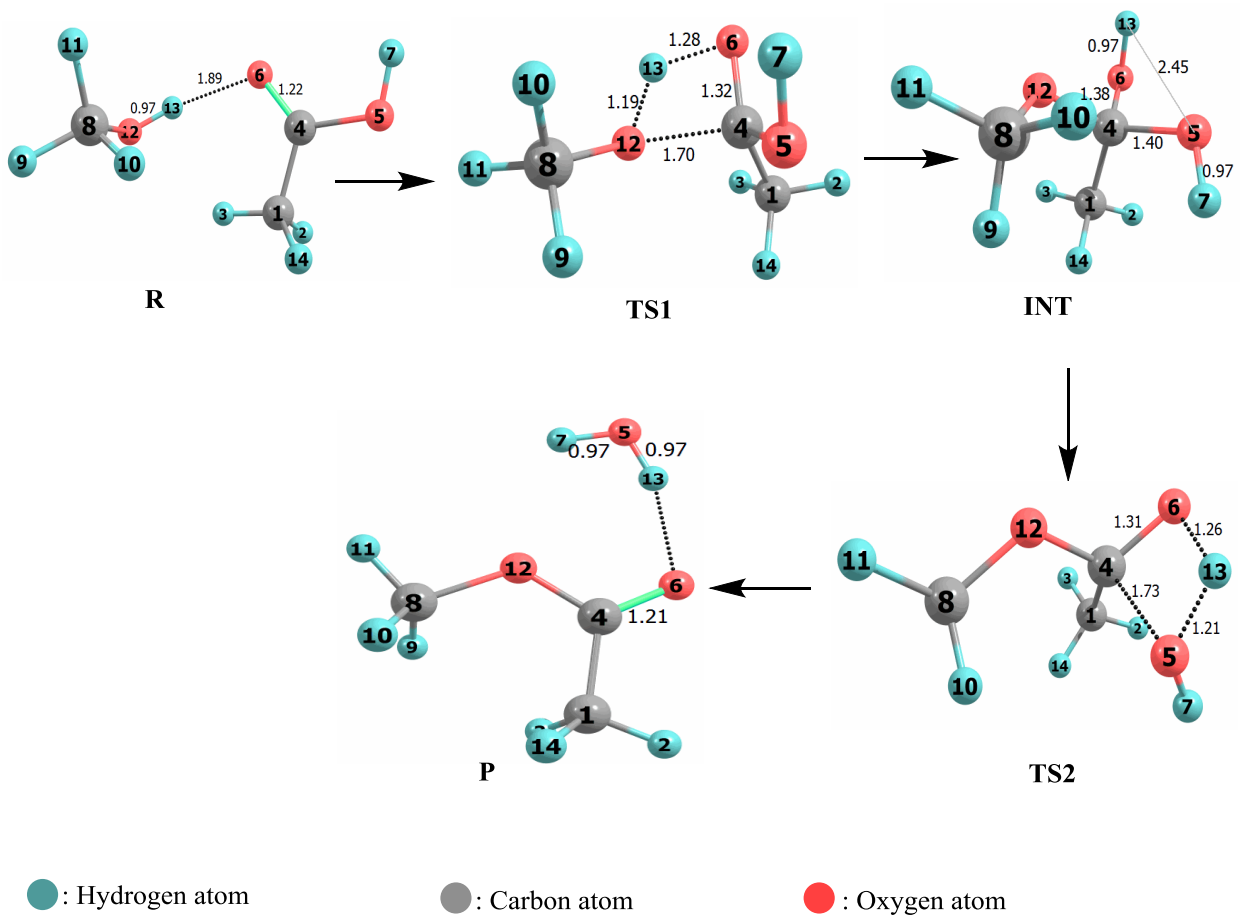
### 4.1 Without using catalyst

**4.1.1 With solvation (MeOH):** According to the mechanism made by Fischer-Speier, the transition state without catalyst was defined as tetra atomic geometry containing C-O-H-O moiety. In the first step of the mechanism, the proton is transferred from the alcohol to the oxygen of the carboxyl carbon and also oxygen of the alcohol attacked the carboxyl carbon. In the next step, the condensation between the two hydroxyl groups leads to the removal of water and ester is formed. It means, this reaction is a nucleophilic acyl substitution in which, the carbon atom acts as electrophile and alcohol as nucleophile.




**Scheme 2:** Proposed mechanism for esterification between acetic acid and methanol in absence of any catalyst[37]

Scheme 3 describes the esterification mechanism in the absence of catalyst along with the optimized structures of reactant complex (R), transition states (TS1 and TS2), intermediate (INT) and product (P).




**Scheme 3:** The optimized geometries of R, TS1, INT, TS2 and P and their important geometrical parameters (given in angstrom) at M06-2X/6-31G* level of theory.

In the above mechanism, the distances between the atoms in R are $O_{(12)}$-$H_{(13)}$ = 0.97 Å, $H_{(13)}$-$O_{(6)}$ = 1.89 Å and $O_{(6)}$-$C_{(4)}$ = 1.32 Å . TS1 shows the four membered transition state structure having the distance between $O_{(12)}$-$H_{(13)}$ = 1.19Å and $H_{(13)}$-$O_{(6)}$ = 1.28Å which indicates that H from methanolic O-H has started to shift from $O_{(12)}$ of methanol to $O_{(6)}$ of carboxyl carbon. The intermediate formed in the first step (INT) contains two hydroxyl groups which undergoes condensation to form the ester by eliminating a water molecule. This step involves a four membered TS (TS2) as shown in Scheme 3.

The relative free energy profile obtained from the optimized structures of various species along the reaction coordinate is shown in figure 1. According to this profile, the free energy barrier for the conversion of reactant to intermediate for this esterification is 41.7 kcal/mol and it is the rate determining step. The free energy barrier for the conversion of intermediate to product is 36.3 kcal/mol.

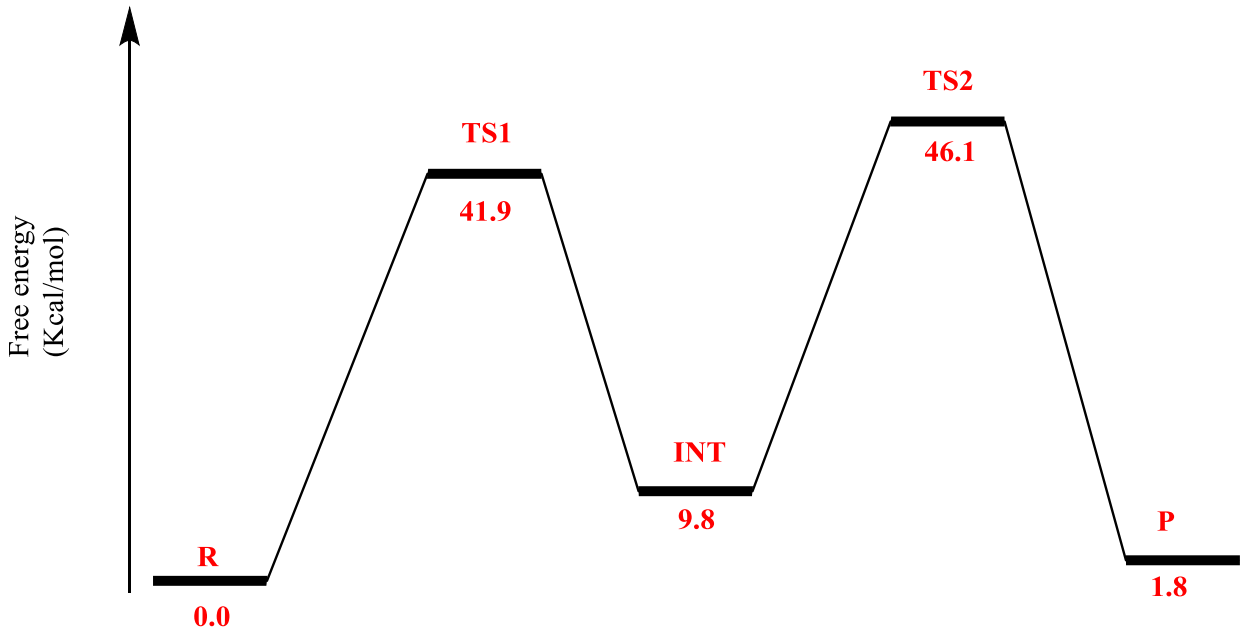



**Figure 1.** The relative free energy diagram derived by optimizing the structures for esterification reaction between acetic acid and methanol at M06-2X/6-31G* level of theory. PCM solvent model with solvent parameters of MeOH is used.

**4.1.2 In gas phase:** Same mechanism was followed as observed in scheme 3 only the bond lengths are different in this case. Its reaction pathway diagram for relative free energy obtained from the computational modeling is shown in figure 2. The highest energy barrier was observed to be 41.1 kcal/mol for TS1.

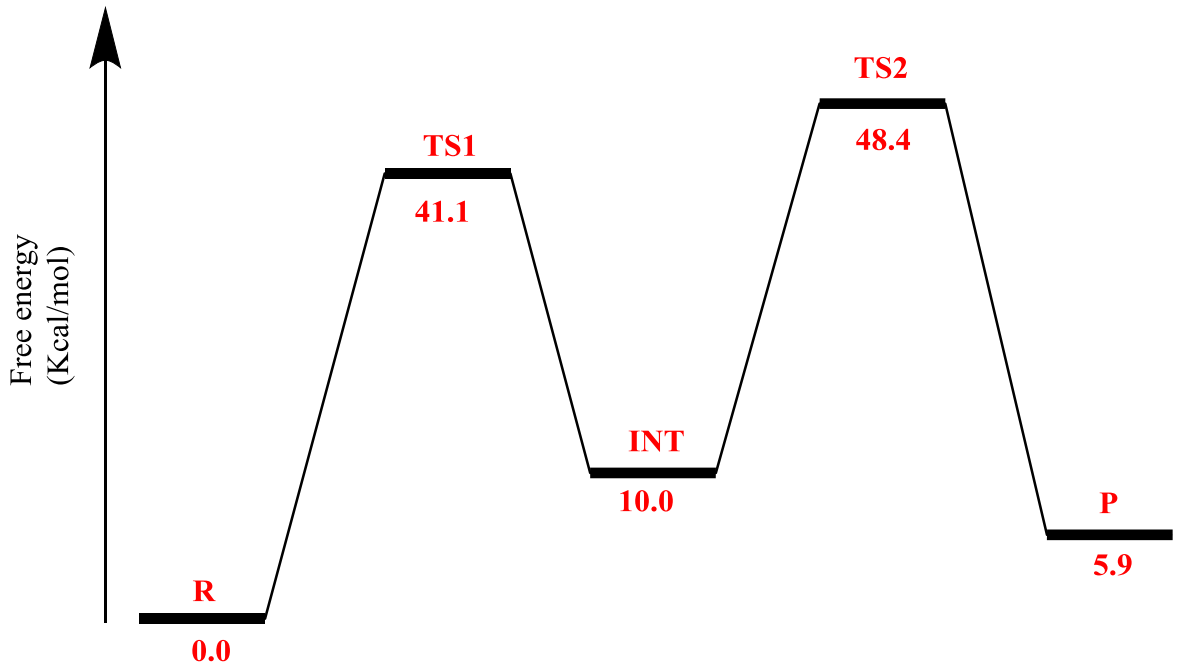
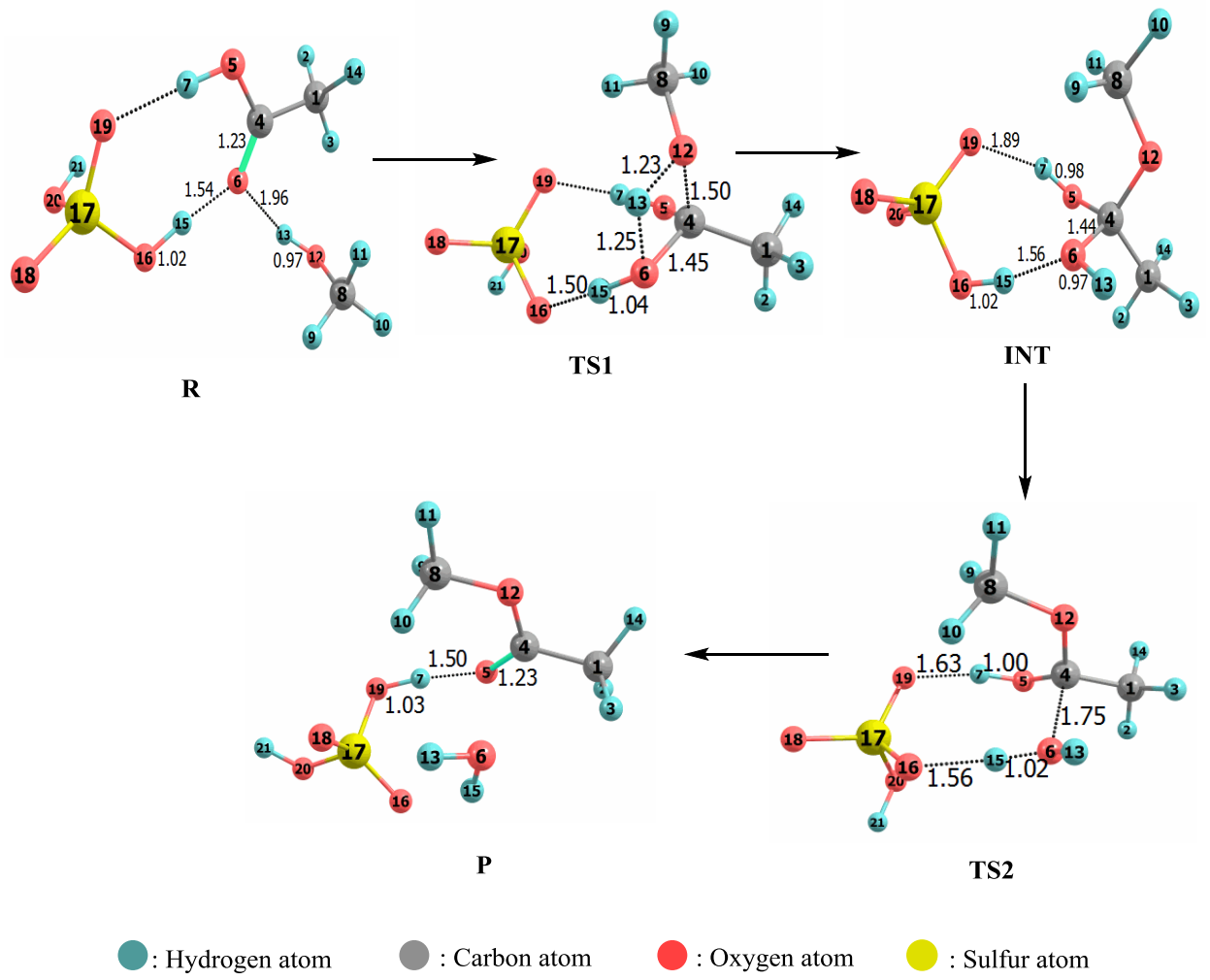



**Figure 2.** The relative free energy diagram derived by optimizing the structures for esterification reaction between acetic acid and methanol at M06-2X/6-31G* level of theory (calculations are done in gas phase).

### 4.2 Using $H_2SO_4$ as homogeneous catalyst

**4.2.1 With solvation (MeOH):** In literature $H_2SO_4$ has been employed for the esterification of acetic acid with methanol to produce methyl acetate. Here, $H_2SO_4$ is used as homogeneous catalyst and the acetic acid and methanol makes strong hydrogen bonding with the catalyst. Initial attack of the oxygen atom of methanol to the carboxyl carbon of acetic acid is mediated through first transition structure, TS1. In TS1, the double bond between $C_{(4)}$-$O_{(6)}$ gets elongated and oxygen from the hydroxyl group of the alcohol (that is $O_{(12)}$ ) has started making bond with the carboxyl carbon ($C_{(4)}$). In the intermediate state (INT), $O_{(12)}$-$C_{(4)}$ bond gets formed and $H_{(13)}$ is shifted to $O_{(6)}$. In the second transition state (TS2), $C_{(4)}$-$O_{(6)}$ bond gets elongated and 8-membered TS is formed . Finally, the product is formed by the elimination of water as shown in Scheme 4. To prove the role of the proton during acetic acid esterification with methanol an experiment was performed in presence of $K_2SO_4$ as a catalyst in place of $H_2SO_4$. However, during the reaction no methyl acetate formation was observed as supported by the proton NMR analysis of the reaction mixture (Appendix -1).




**Scheme 4:** The optimized geometries of R, TS1, INT, TS2 and P and their important geometrical parameters (given in angstrom) at M06-2X/6-31G* level of theory.

To examine the pathway of reaction, a diagram with relative free energies which are obtained by optimizing the structures using computational calculations is shown in figure 3. According to the diagram, the highest energy barrier is 33.3 kcal/mol that is for the conversion of reactant to intermediate. It is very less as compared to the energy barrier without using any catalyst, which shows that by using catalyst the recation becomes more feasible and as the catalyst lowers the activation energy. The activation energy required to convert intermediate into product is also comparatively very less and is 5.0 kcal/mol.

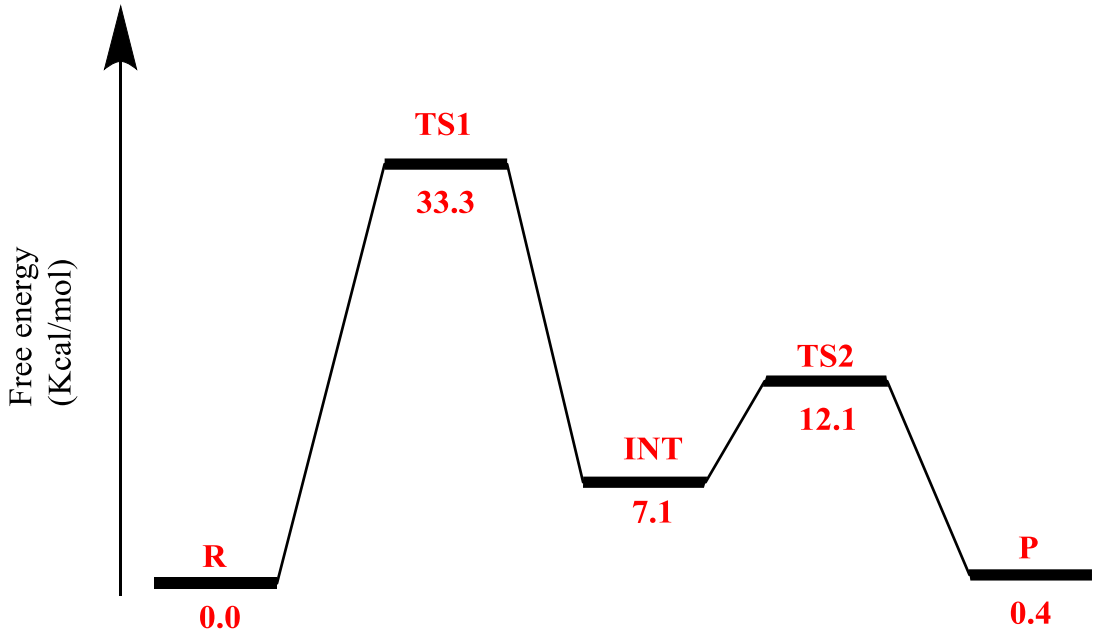



**Figure 3.** The relative free energy diagram derived by optimizing the structures for esterification reaction between acetic acid and methanol by using $H_2SO_4$ as homogeneous catalyst at M06-2X/6-31G* level of theory. PCM solvent model with solvent parameters of MeOH is used.

**4.2.2 In gas phase:** Same mechanism was followed as observed in scheme 4 only the bond lengths are different in this case. Its reaction pathway diagram with relative energies gained from the theoretical modeling is shown in figure 4. The relative energy barriers for this reaction were almost comparable with that of the esterification reaction with $H_2SO_4$ as homogeneous catalyst in presence of implicit solvent (see section 4.2.1). The barrier for the rate determining step is found to be 33.1 kcal/mol via TS1. In this case, the reaction is found to be slightly exothermic as compared to the solvent phase calculation.

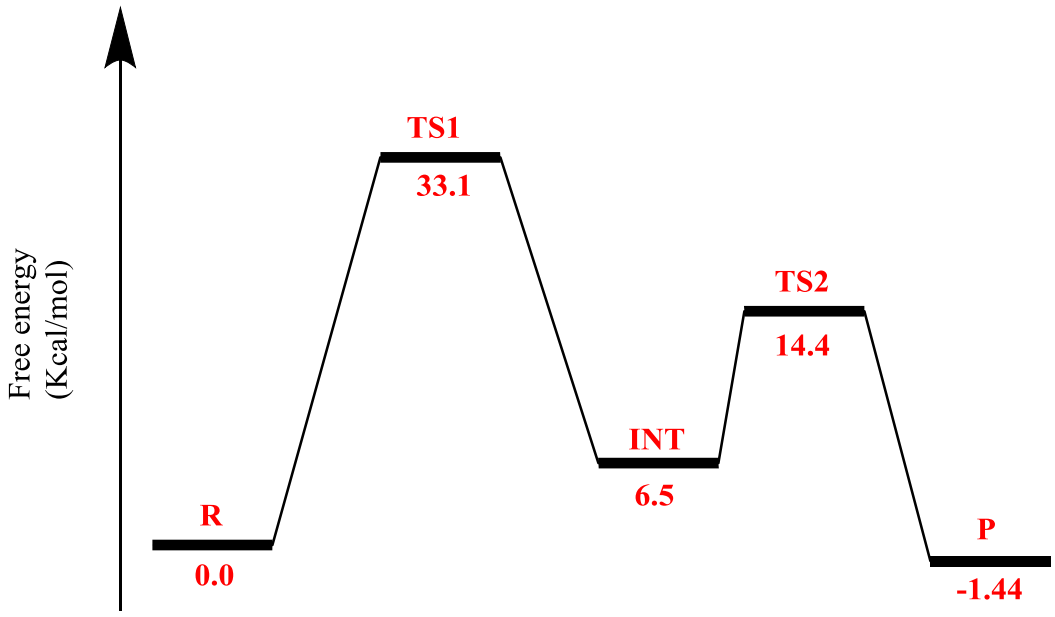



**Figure 4.** The relative free energy diagram derived by optimizing the structures for esterification reaction between acetic acid and methanol by using $H_2SO_4$ as homogeneous catalyst at M06-2X/6-31G* level of theory (calculations are done in gas phase).

### 4.3 Using $SiO_2$-$H_2SO_4$ surface as heterogeneous catalyst

**4.3.1 Modeling of the surface ($SiO_2$-$H_2SO_4$):** Several studies showed that the (111) surface is the most stable facet of β-crystobalite lattice of $SiO_2$.[41–43] Thus, the $SiO_2$ surface is modeled by taking a 2x2 supercell with four layers of $SiO_2$ (111) surfaces cleaved from the β-crystobalite lattice of $SiO_2$. Each layer contains eight Si atoms and sixteen O atoms. A vacuum space of around 20 Å is added to prevent the interaction between adjacent periodic images. The Si-terminated surface shows two distinct possibilities, namely sulphated-silica-A and sulphated-silica-B (Figure 5(a) and 5(b)) for the adsorption of $H_2SO_4$ depending upon the orientation of the molecule. The upper two layers of the surface are allowed to relax along with the $H_2SO_4$ molecule while the last two layers of the surface were fixed. The van der Waals interaction between the $H_2SO_4$ and the $SiO_2$ (111) surface has been built-in by using vDW correction (DFT-D3 method)[44]. The sulphated-silica-B surface is more stable (~93 kcal/mol) as compared to sulphated-silica-A and thus will be used for reactivity study. In the sulphated-silica-B surface, the O-H groups of the $H_2SO_4$ detach themselves and get attached to the nearest Si atoms on the (111) surface.

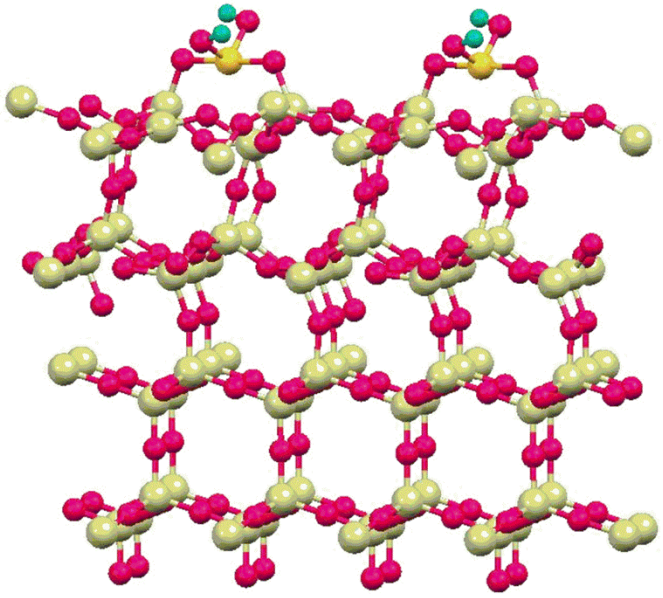


Figure 5(a)

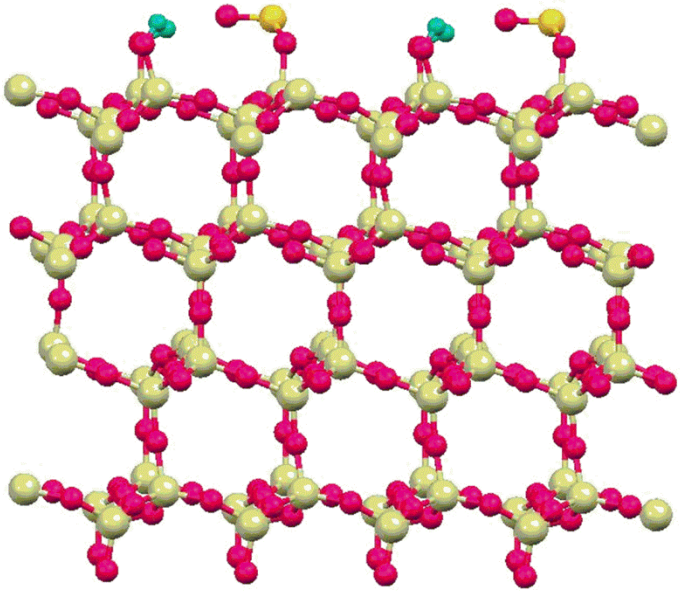


Figure 5(b)

: Silicon atom :Oxygen atom : Sulfur atom :Hydrogen atom

**Figure 5:** Modeled structure of $SiO_2$-$H_2SO_4$ surfaces

**4.3.2 Mechanism of Esterification in presence of heterogeneous catalyst:** Here, Sulphated-silica-B is used as heterogeneous catalyst owing to its lowest energy between the two surfaces considered. The acetic acid and methanol are strongly held to the $SiO_2$ surface through strong hydrogen bonding with the newly formed O-H and Si-O bonds, respectively as shown in Figure 6. Here we have taken only one unit of $SiO_2$ cluster for mechanistic study and the dangling Si-O bonds of the cluster were terminated by protonating them. Scheme 4 depicts the mechanism of esterification by $SiO_2$-$H_2SO_4$ catalyst. Initial attack of the oxygen atom of methanol to the carboxyl carbon of acetic acid is mediated through first transition structure, TS1. In TS1, the double bond between $C_{(55)}$-$O_{(54)}$ gets elongated and oxygen from the hydroxyl group of the alcohol (that is $O_{(61)}$ ) has started making bond with the carboxyl carbon ($C_{(55)}$). The bond distance between $C_{(55)}$ and $O_{(61)}$ in TS1 is 1.61Å. In the intermediate state (INT), $O_{(61)}$-$C_{(55)}$ bond gets formed with the bond distance of 1.40Å and $H_{(60)}$ is shifted to $O_{(54)}$. Finally, the product is formed by the elimination of water via a six membered cyclic transition state (TS2) as shown in Scheme 5.

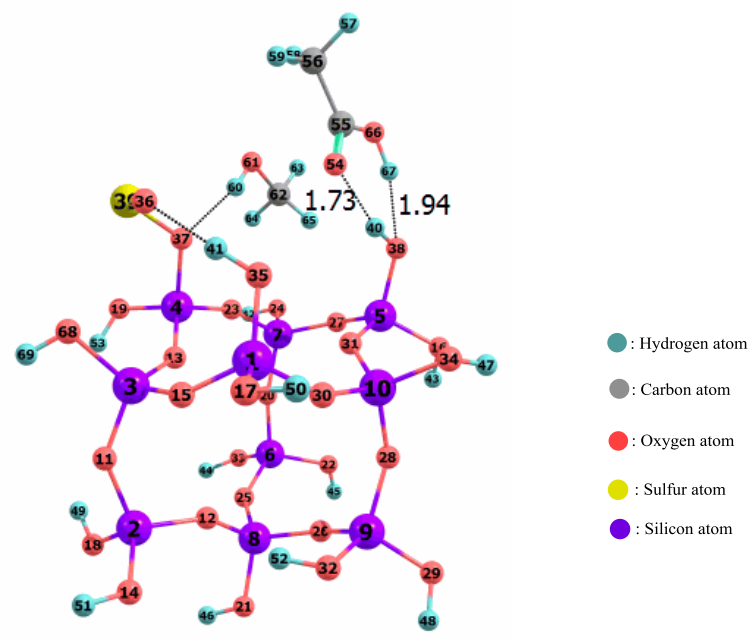
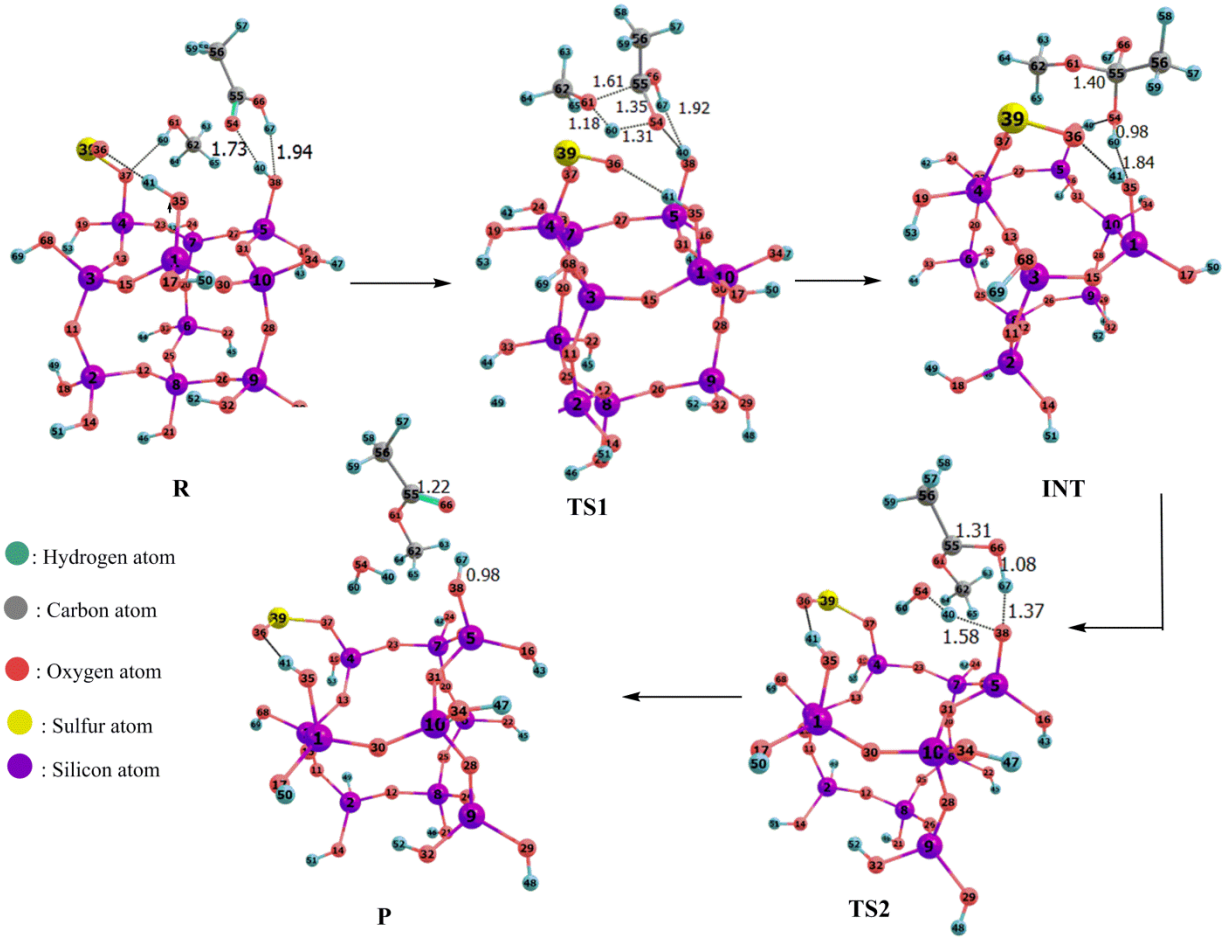



**Figure 6.** Optimized structure of reactant for $SiO_2$-$H_2SO_4$ heterogeneous catalysed reaction at M06-2X/6-31G*.




**Scheme 5:** The optimized structures of R, TS1, INT, TS2 and P and important geometrical parameters (given in angstrom) at M06-2X/6-31G* level of theory.

To examine the pathway of reaction, a diagram with relative energies which are obtained from optimizing the structures by the computational calculations is shown in Figure 7. Here, the the rate determining step is the attack of methanol to the carboxylic carbon of acid which has a barrier of 37.6 kcal/mol. This barrier is slightly greater (4.3 kcal/mol) than that for the homogeneous catalysed reaction. It is still significantly lower as compared to the energy barrier for the above step (41.9 kcal/mol) while no catalyst is used. The activation energy required to convert the intermediate into product is 20.1 kcal/mol and the free energy of reaction is -4.2 kcal/mol. Thus the product formation is spontaneous in this case.

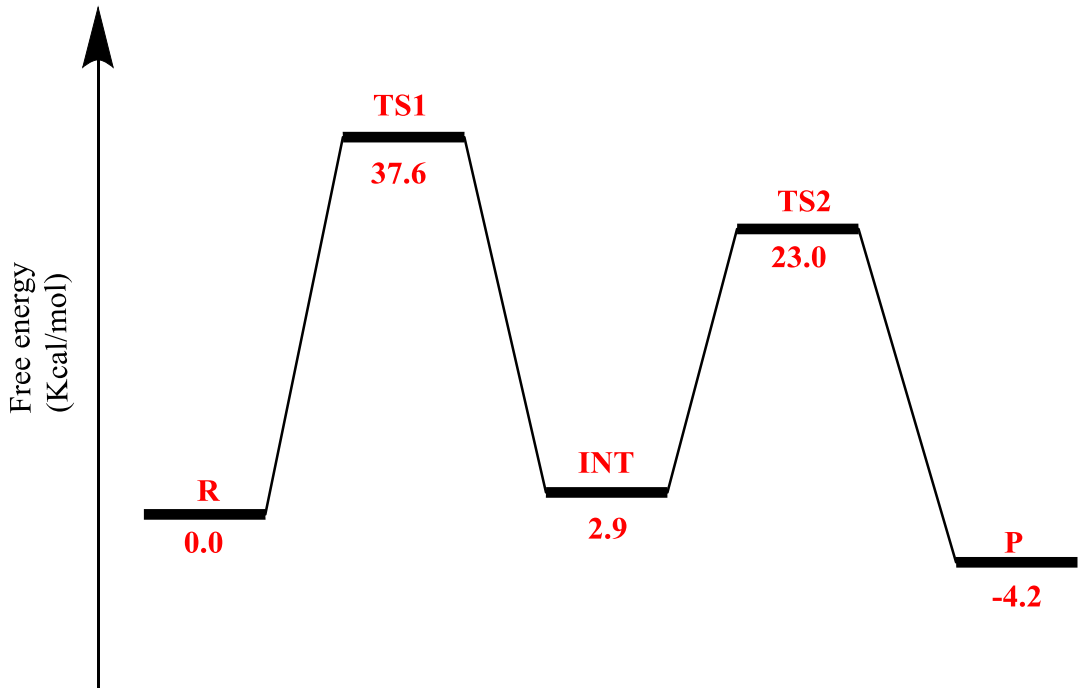



**Figure 7.** The relative free energy diagram derived by optimizing the structures for esterification reaction between acetic acid and methanol by using $SiO_2$-$H_2SO_4$ as heterogeneous catalyst at M06-2X/6-31G* level of theory. PCM solvent model with solvent parameters of MeOH is used.

# Chapter 5

# Conclusion

Mechanistic investigation of esterification reaction has been carried out in presence and absence of catalyst by using DFT. Two different types of catalyst, homogeneous and heterogeneous, have been used. The energy barrier for uncatalyzed reaction came out to be very high as compared to catalyzed reaction. The lowest energy barrier was obtained for the homogeneous catalyzed esterification reaction (using $H_2SO_4$ as catalyst). Though the energy barrier for the heterogeneous catalyzed reaction (using $SiO_2$-$H_2SO_4$ as catalyst) is higher than that for homogeneous catalyzed reaction, heterogeneous catalyst can easily be separated from the product and purified.[11,12] On the other hand, the homogeneous catalyst separation is a tedious task. Thus heterogeneous catalysts are preferred over homogeneous catalysts. Here, $H_2SO_4$ adsorbed on silica is used while various other catalysts such as sulfated zirconia,[45] mixed metal oxides, ion-exchange resins,[13] zeolites,[14] acid clay catalysts[15] can also be used as heterogeneous catalysts.

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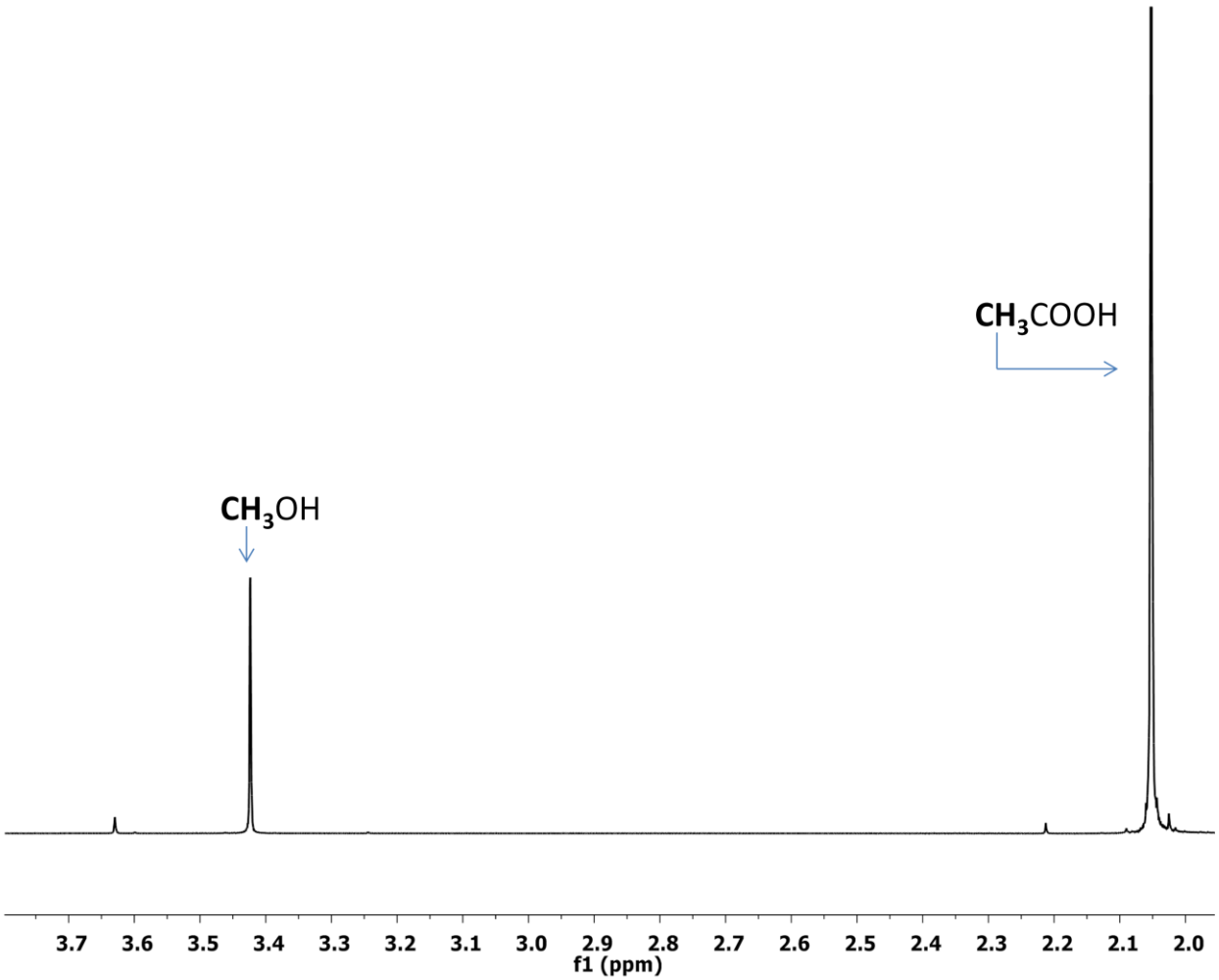
## Appendix - 1




Proton NMR of esterification of acetic acid with methanol in the presence of $K_2SO_4$ (FT-NMR recorded on JEOL ECS-400 (400MHz) spectrophotometer)