# MOLECULAR MODELLING OF THE KINETICS AND THERMODYNAMICS OF GAS-PHASE THERMAL DECOMPOSITION OF XANTHATES

**BY**

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# ABSTRACT

Pyrolysis of xanthates (organo sulphur compounds) provides valuable synthetic routes to higher yield of olefins which has become an attraction in polymer chemistry. Thermal decomposition of unsubstituted xanthates has high activation barriers but alkyl substituents provide positive inductive effects which enhances kinetics and thermodynamics of the reaction. However, there is scanty information on the gas phase thermal decomposition of substituted xanthates. Therefore, this research was designed to investigate the effect of progressive methylation on kinetics and thermodynamics of the gas-phase thermal decomposition of some α- and β- substituted alkyl xanthates.

Quantum mechanical approach (density functional theory [B3LYP/6-311++G**]) was employed to model the progressive methylation of O-alkyl S-methyl xanthates at the α- and β- carbon positions (O-ethyl, O-npropyl, O-ipropyl, O-nbutyl, O-ibutyl, O-tbutyl) at 629K. Molecular mechanics force field was used to obtain conformers and the most stable conformer of the compounds was further subjected to geometric calculations. Reaction path calculations were carried out on the most stable conformer of each compound and the progress of the reactions was followed by the Wiberg bond indices [average bond indices ($\delta B_{av}$), percentage bond evolution (%Ev) and synchronicities ($S_y$)]. The geometric parameters [bond length, bond angle, dihedral angle and atomic charge distribution] at ground state, transition state and products were calculated using standard method. The data obtained were used to calculate the kinetics [rate constant (k), pre–exponential factors (A), Activation energy (Ea)] and thermodynamic parameters [Change in enthalpy (ΔH*), change in entropy (ΔS*) and Gibbs free energy (ΔG*)] of the substituted alkyl xanthates.

The modelled alkyl xanthates revealed the formation of acetylenes, carbonylsulphide and thiol. The energy of formation of stable conformers of the different derivatives ranged from -50.93 to +16.00 kJ/mol. Reaction path showed that the reaction involved a concerted six–membered transition state with bond lengths: C-O (2.08Å, bond breaking); C-H (1.24Å, bond breaking) and S-H (1.83Å, bond making). The %Ev ranged from 65 to 77 for C-O breaking, 30 for C-C formation and 39 to 43 for S-H formation. These showed that breaking of C-O was the most advanced process hence C-O bond breaking was the rate determining step. The least advanced process was the formation of

C-C and S-H bonds. The $\delta B_{av}$ ranged from 0.478 to 0.485 indicating that the transition states have an early character, while $S_y$ ranged from 0.899 to 0.932 for O-alkyl S-methyl xanthate indicating that the mechanism corresponds to highly asynchronous process. The Ea, A and k ranged from 166.20 to 149.18 kJ/mol, (4.90 to 7.18) x$10^{11}$ and 1.04x$10^{-3}$ to 4.30 $s^{-1}$ , respectively while, the thermodynamic parameters ranged from 161.34 to 128.04 kJ/mol ($\Delta H^*$); -24.00 to -31.16 J/mol($\Delta S^*$); and 142.90 to 178.44 kJ/mol ($\Delta G^*$). These parameters decreased with progressive methylation, and with corresponding increase in rate constant of thermal decomposition.

Progressive methylation in gas phase at the α- and/or β- position of O-alkyl S-methyl xanthates lowered thermodynamic parameters and activation energy with corresponding increase in entropy change and rate of reaction.

**Keywords:** Molecular mechanics, Density functional theory, O-alkyl, S-methyl xanthate.

**Word count:** 486

# DEDICATION

This project work is dedicated to the Almighty God, and also to my loving wife.

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I give glory to God Almighty for His devine involvement in the success of this research.

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# CERTIFICATION

I certify that this work was carried out by Mr. T.O. Esan in the Department of Chemistry, University of Ibadan

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| | |
|---|---|
| B3LYP/6-311++G** | Becke 3-Parameter,Lee, Yang and Parr |
| LCACO | Linear Combination of atomic orbital |
| DFT | Density Functional Theory |
| RRK | Rice- Ramsperger Kasher |
| RRKM | Rice-Ramsperger-Kassel-Marcus |
| PPV | Polyparaphenylene vinylene |
| SMD | Spartan Molecular Database |
| SSPD | Spartan Spectra and properties Database |
| NMR | Nuclear Magnetic Resonance |
| IR | Infra Red |
| UV | Ultra Violet Light |
| QSAR | Quantitative Structure activity relationship |
| MP2 | Moller Plesset Perturbation Theory |
| MMFF | Molecular mechanics force field |
| IRC | Intrinsic Reaction coordinate |
| HF | Hatree Fork |
| PM3 | Parametization method three |
| $\Delta d = d_{(TS)} - d_{(GS)}$ | Bond length in the transition state (TS) - Bond length in the Ground State (TS) |
| $\Delta q = q_{(TS)} - q_{(GS)}$ | Atomic charge in transition state (TS) – Atomic charge in the Ground State (GS) |

# CHAPTER ONE

# INTRODUCTION

## 1.0 Background to the study

Kinetics simply means studying the rate at which a chemical reaction occurs (Bahl *et al.*, 2004) and thermal decomposition or pyrolysis is the heating of organic compounds at elevated temperature without oxygen (Ajaz *et al.*, 2014, Hurd, 1929). Thermodynamics is the study of the heat flow or any other forms of energy into or out of a system as it undergoes a physical or chemical change (Bahl et al., 2004). Kinetic and thermodynamics studies of reactions in solution and in the gas phase are of great importance for the development of the theory and control of the reaction rate.

Preparatory pathways for the production of olefins include a group of unimolecular pyrolytic reactions and intermolecular thermal elimination reactions called ($E_i$ processes). These processes are called rearrangement, addition or pericyclic reaction. Part of the reactions is the production of alkenes through alkanols by thermal decomposition of Xanthate (O-alkyl moiety dithiocarbonates) which was discovered in 1899 by Tschugaef or Chugaev in conjunction with his experiment of the optical characteristics of dithiocarbonates (Wu *et al.*, 2013). This reaction was employed in his investigation of terpenes, and he demonstrated its use as an olefin-forming reaction and its usefulness in structure determination (Grieco and Kaufman, 1999). This reaction is termed as Chugaev reaction as shown in Figure 1.1 (a).

The thermal decomposition of Chugaev elimination reaction is very important because of its synthetic value and also continues without the carbon skeletal rearrangement (Castañeda *et al*., 2008). The potentiality of Chugaev reaction to produce bonds that are double in nature through the pyrolytic reaction of Xanthate routes is currently the focus of attention of polymer chemists, because it provides Poly(pphenylenevinylene) which are used as light emitting diodes (PPV) samples with good properties that can be used in the production of light-emitting devices (Claes, 2003; Ederly *et al.,* 2008) .

The Chugaev reaction is similar to the pyrolytic reaction of carboxylic esters of alcohols and other related alcohol derivatives such as carbonates and carbamates. It is known that many compounds containing β-hydrogen molecules undergo a pyrolytic reaction with the formation of olefins (Rajakumar *et al*., 2003 ).

The Chugaev reaction has been majorly studied with Xanthates with S-methyl substituent at the position 1, or 2 by (McAlpine, 1930) who was the first to carry out a systematic study of Xanthates with different S-substituents. He suggested that the presence of electronegative groups on the thiol or sulphur reduces the thermal stability of Xanthates and this leads to decrease in the initial temperature of the pyrolysis. The order of increasing S-substituted Xanthates stability of methyl alcohol is as shown in Figure 1.1 (b): The reaction mechanism is known as $E_i$ mechanism and was first described by (Kącka and Jasiński, 2016). Examples of compounds that are thought to decompose through $E_i$ mechanism are Xanthates and esters (Murillo *et al*., 2012; Wu *et al*., 2013) as shown in Figure 1.2.

The group of thermally decomposed molecules resulting in alkenes includes alkyl phosphinates and phosphates, although the pyrolytic elimination of these molecules was not performed to the same extent as that of xanthate and ester (Velez *et al*., 2008).

Thermal decomposition of xanthates with β-hydrogen gives olefins along with thiol and carbonyl sulphide gas. The preparation of corresponding xanthate was carried out from alcohols by reacting them with carbon disulphide by the treatment of an alkali (caustic soda i.e. sodium hydroxide) and also methylation of sodium Xanthate which is in between the reacting species was carried out with methyl iodide as shown in Figure 1.3. (Laue and Plagens, 2005)

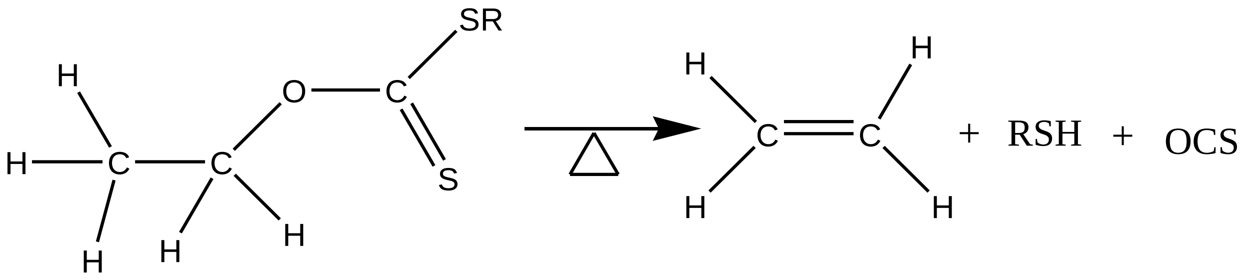


**Figure 1.1 (a) Chugaev reactions (**Tschugaeff or Chugaev 1899)

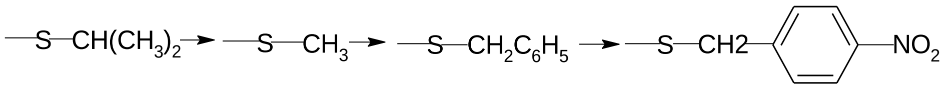


**Figure 1.1 (b) : Order of stability of S-substituted xanthates** (McAlpine, (1930)

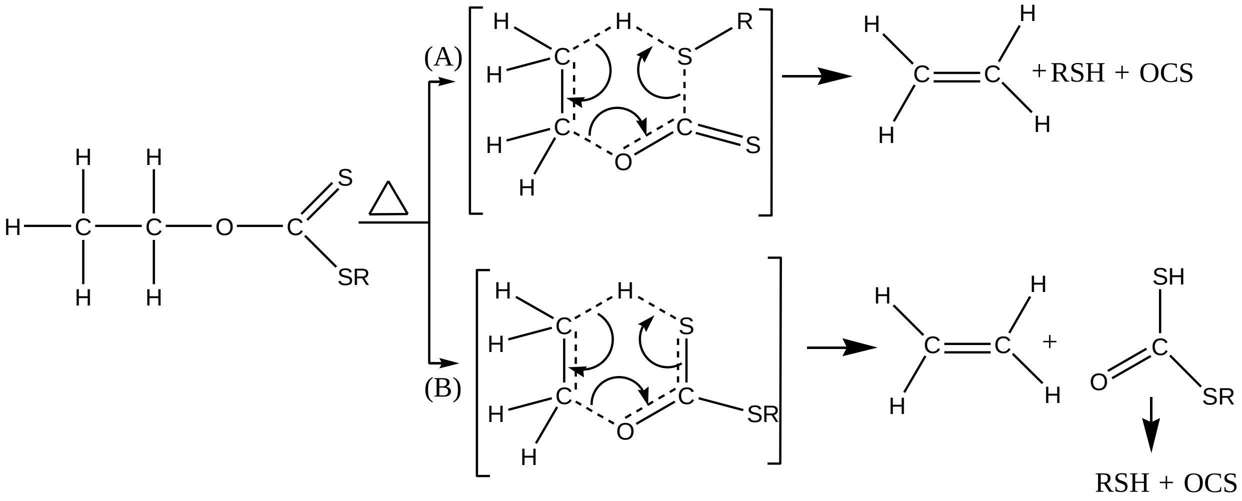


**Figure 1.2: Mechanism of the pyrolytic reaction of xanthate showing two routes in the thermal decomposition of xanthates.** (Adejoro *et al*, 2017)

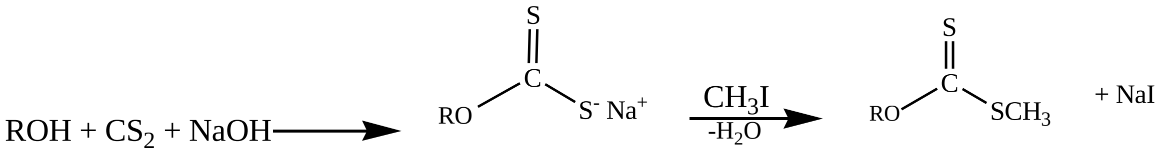


**Figure 1.3: Preparation of Xanthates** (Laue and Plagens, 2005)

The concerted nature of these pyrolytic reactions is confirmed to be first order kinetics in the thermal decomposition of esters and Xanthates (Bader and Bourns, 1961) and by observation of primary kinetic isotope effect that determine the $C_{\beta}$-H bond cleavage which is the rate determining step in these reactions (Velez *et al*., 2009).

The structure of the transition state is confirmed by observation of negative activation entropies (Wu et al., 2013) as well as by the syn stereoselectivity of the reaction that has been rigorously examined (Wu and Li, 2014)). Two mechanisms have been discovered for the thermal eliminations of phosphoester, the first is an $E_i$ type; while the other is an $E_1$ mechanism involving a carbocation processes. The $E_i$ process for the phosphoester pyrolytic elimination would involve a six membered-ring transition state and has been included in the same group as the Xanthates and esters. This group of pyrolytic elimination is classified as 1,5 thermal elimination using the sigmatropic system of naming. It is believed that the Xanthates, ester and Phosphinates move by the same mechanism during pyrolytic elimination, but their rates differ significantly.

In mechanism (A) of the pyrolysis of Xanthate, the reaction pass through one step, which gives the products as alkenes, carbonyl sulphide and a thiol, as postulated by (Leon *et al*., 2003). The second mechanisms (B) proposed by (Wu *et al*., 2013) find that reaction occur in two steps, the former results are alkenes and decomposable dithiocarbonates by product which break down and result in to a thiol and carbonyl sulphide. An experimental studied by (Bader and Bourns, 1961) showed that sulphur atom from thion (not from thiol) attacks the β-hydrogen. The pyrolysis of Xanthates has been experimentally studied several times by (Connor and Nace, 1952, Etaibi *et al.,* 2011 and Belskaya *et al.*, 2015). Everyone of the reaction investigated was in the first order, and the rates of each of them has no significant effect on the addition of a radical inhibitor or an increase of the surface. The experimental result revealed that they are homogeneous, unimolecular reactions.

Theoretical studies on xanthates have not been given much attention, few scientist conducted significant research on the thermal decomposition of xanthates. The determination of the cyclic nature transition state of pyrolysis of HSC(S)OEt at Moller pleasant 2(MP2)/6-31G*//Hatree Fork(HF)/6-31G* levels Erickson and SCOH, (1994).

The research on the gas-phase internal decomposition reaction of EtSC(S)OMe at separate levels of theories (Claes *e tal.*, 2003), another study on the transition state structure of MeSC(S)OEt at the Density functional theory (DFT)/6-31-G* level was carried out by (Harano, 2005). The purpose of caring out this research work was as result of high activation barriers attributed to studied unsubstituted alkyl xanthates by the experimental and also with few theoretical studies on the calculation of Arrhenius parameters of dithiocarbonate which prompted us to conduct a comprehensive study on the effect of progressive methylation on kinetics and thermodynamics of the gas-phase thermal decomposition of some α- and β- substituted alkyl xanthates. The considered Xanthate was the one that oxygen atom is involved in the transition state bonding (properly the Chugaev reaction) S-methyl O-alkyl xanthates.

This thesis reports the first order pyrolytic reaction with various classes of organic derivatives of alkyl xanthate under controlled conditions according to a unimolecular reaction mechanism. For centuries, nature has been explained with the help of theories of physics. The breakthrough came with Isaac Newton and his laws of motions which could only predict movement of all bodies from small particles to the planets and stars. Later, Albert Einstein, with his relativistic theory showed that Newton's laws of motion are not related to fast moving objects. At the same time quantum mechanics was designed to show that there should be other laws on the scale of atomic length. Simply put, quantum mechanics is the theories/law of physics for atoms and molecules (Prasad, 2008).

Generally, chemical reaction occurs through electronic interactions between atoms, molecules, radicals and ions. Electrons are involved in these interactions. According to de Broglie equation, electrons exhibit wave properties (Prasad, 2008).

## 1.1 Quantum Mechanics

Quantum mechanics is a science that deals with motion of atomic and subatomic particles. It interprets the physiochemical parameters for atoms and molecules, their structures, micro particles such as electrons and protons and their spectral behaviour in terms of motion. This principle leads to Schrödinger wave equation which has been successfully used to explain many chemical properties. These principles have long been used with mathematical expression to solve problems using computational methods (Prasad, 2008).

## 1.2 The Postulates of Quantum Mechanics

### The first Postulate

The state of a micro system is described in terms of a function of position coordinates and time called wave function, $\psi\ (r, R, t)$ i.e. the Schrodinger equation. The probability that the particle in volume located at (r, R) at time t exist is defined by:

$$p(r, R, t) = \psi * (r, R, t)\psi(r, R, t)dr \qquad (1.1)$$

This assumption that restrains the wave function and the total relativity must be equal to 1 that is

$$\int_{\infty}^{\infty}(\psi * (r, R, t)\psi(r, R, t)d\tau = 1 \qquad (1.2)$$

Hence, the particle must be somewhere in space. This means that the wave function must be one or single valued, continuous and limited (Prasad, 2008).

### Postulate II

For each observable quantity that can be measured experimentally, for example, position, momentum, energy, and so on, corresponds to a quantum-mechanical operator, as shown in Table 1.1.

### Postulate III

The determined values of any system in a physical quantity are given by the eigenvalues in the operational equation.

$$\tilde{A}\psi = a\psi \qquad (1.3)$$

Where Ã is the operator leading to that physical quantity and is the Eigen function. That is each single measurement of a physical quantity ‘A’ gives an Eigen value of the operator Ã. The Eigen values and Eigen function for a system can be obtained by solving the operator equation whereas its Eigen functions and the operator may be real or complex. The Eigen values must be real because they contain observable physical quantities. In addition, quantum Mechanical operators such as momentum energy, are Hamiltonian operators which have been shown at the beginning to have real Eigen Values. For instance the operator equation for momentum $P_x P_x$ in one dimension is given as

$P_x\psi(X) = \frac{h}{2\pi i}\frac{d\psi}{dx}(x) = P_x\psi(X)$ (1.4)

This is also equal to $\psi(X) = \mathrm{A}\exp\left(\pm 2\pi i P_x \frac{x}{h}\right)$ (1.5)

This Eigen value equation for the energy of a system (a single particle in three dimensions) is given as the operator energy E (KE + PE).

$\hat{\mathrm{H}} = \frac{-h^2}{8\pi^2 m}\nabla^2 + \tilde{\mathrm{V}}(\mathrm{x, y\ and\ z})$ (1.6)

This eigen value equation is given as

$\hat{\mathrm{H}}\psi(x, y\ and\ z) = E\psi\ (x, y\ and\ z)$ or simply

$\hat{\mathrm{H}}\psi = \mathrm{E}\psi$ (1.7)

That is $\frac{-h^2}{8\pi^2 m}\nabla^2\psi + \tilde{\mathrm{V}}\psi = \mathrm{E}\psi$ (1.8)

Postulate IV

The expected average values of an observable system of a physical quantity (M) whose state function is ψ .

$m = \frac{\int \psi * M\psi\ dx}{\int \psi * \psi\ dx}$ (1.9)

$\int \psi * M\psi\ d\tau$ (1.10)

If ψ is normalized where M is the operator

Postulate V

For every system, time-independent Schrödinger equation is given by the equation

$\hat{\mathrm{H}}\psi = \frac{ih\ \delta\psi}{2\pi\ \delta t}$ (1.11)

Where Ĥ is the Hamiltonian Operator, ψ is a function of position (x, y. z) as well as time (t) and V is a function of position only (Prasad, 2008) The major importance of quantum mechanics is the Schrodinger expression. The equation for standing wave is

$$\Psi= A \sin 2 \pi \frac{x}{\lambda} \quad (1.12)$$

In equation 12, ψ is a mathematical function representing the amplitude of wave function x, the displacement in a given direction, and λ, the wavelength and $A$ is a constant,

By differentiating equation (12) twice we get

$$\frac{d\psi}{dx} = A \frac{2\pi}{\lambda} cos\ 2\pi \frac{x}{y} \quad (1.13)$$

And $\frac{d^2\psi}{dx^2} = \frac{-4\pi^2}{\lambda^2} \sin 2\pi \frac{x}{\lambda}$ **(**1.14)

$$\text{A} \sin 2\pi \frac{x}{\lambda} = \psi \quad (1.15)$$

$$\frac{d^2\psi}{dx^2} = \frac{-4\pi^2}{\lambda^2} \psi \quad (1.16)$$

The kinetic energy of the particle of mass $m$ and velocity $v$ is given by the relation

$$K.E = \frac{1}{2}\, mv^2 = \frac{1}{2}\, \frac{m^2v^2}{n} \quad (1.17)$$

According to de Broglie's equation

$$\lambda = \frac{h}{mv}$$

or

$$m^2v^2 = \frac{h^2}{m^2} \quad (1.18)$$

By substituting for $m^2v^2$

$$\text{K.E} = \frac{1}{2} x \frac{h^2}{m\,\lambda^2} \quad (1.19)$$

From equation (17) we have

$$\lambda^2 = \frac{-4\pi^2\psi}{\frac{d^2\psi}{dx^2}} \tag{1.20}$$

Substituting the value of $\lambda^2$ in equation (19) we have

$$\text{K.E} = \frac{1}{2m} \cdot \frac{h^2}{4\pi^2\psi} \cdot \frac{d^2\psi}{dx^2} \tag{1.21}$$

$$= \frac{h^2}{8\pi^2 m\psi} \cdot \frac{d^2\psi}{dx^2} \tag{1.22}$$

The sum $E$ of a particle is the total of the energy of motion and the energy of position , that is

$$E = Kinetic. E + Potential. E$$

Or $$P.E = E - K.E$$

$$\frac{h^2}{8\pi^2 m\psi} \cdot \frac{d^2\psi}{dx^2} = E - P.E$$

Or

$$\frac{d^2\psi}{dX^2} = \frac{8\pi^2 m}{h^2} (E - P.E)\psi = 0 \tag{1.23}$$

This is Schrodinger equation in one dimension. For a particle in motion describe by the three space coordinate, it is given as

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2 m}{h^2} (E - P.E)\psi \tag{1.24}$$

Or, it is given as

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2} (E - P.E)\psi = 0$$

**Table 1.1 Quantum mechanical operators and corresponding physical quantities (Prasad, 2008)**

| Physical quantity | Quantum Mechanical Operator |
|---|---|
| **Position $x$** | $x$ |
| **Position $r$** | $r$ |
| **Component $(px)$** | $\frac{h}{2\pi i}\frac{\partial}{\partial x}$ |
| **Momentum $(p)$** | $\frac{h}{2\pi i}\nabla$ |
| **Kinetic energy (T)** | $\frac{-h^2}{8\pi^2 m}\nabla^2$ |
| **X-component of K.E (TX)** | $\frac{-h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2}$ |
| **Potential energy v** | $v$ |
| **Total Energy H** | $\frac{-h^2}{8\pi^2 m}\nabla^2 + \mathrm{v}$ |

Source: (Prasad, 2008).

However, experimental measurement for atomic and molecular systems show that an electron moving around the nucleus of an atom has only a discrete set of values of energy termed quantization. De Broglie equation provides a relationship between the particle and the concepts of wave as: (Bahl *et al.*, 2004).

$$\lambda = \frac{h}{p} \qquad (1.25)$$

h = Planck's constant

p = momentum

λ = wavelength

Planck's constant was postulated from the equations that explain the relationship between the magnitude of wavelength associated with mass m of a moving body and its velocity according to the planck;s theory. The photon energy, E is resulted from the equation as follows

$$E = hv \qquad (1.26)$$

From the de Brogile equation, the wave equation becomes:

$$\frac{d^2\psi}{dx^2} = \frac{4\pi^2}{h^2}\ P^2\psi \qquad (1.27)$$

Since the total energy of a particle is the addition of its kinetics energy (T) and the potential energy V.

$E = T + V$ and $E = \frac{p^2}{2m} + v$

So,

$\frac{p^2}{2m} = E - V$ and $P^2 = 2m\,(E - V)$

Thus the wave equation becomes

$$\frac{d^2\psi}{dx^2} = \left[\frac{8\pi^2 m(E-v)}{h^2}\right]\psi \qquad (1.28)$$

In a 3 dimensional system, the wave equation becomes.

$$\left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}\right)\psi = \left[\frac{-8\pi^2 m(E-v)}{h^2}\right]\psi \qquad (1.29)$$

The first three terms on the left hand side are represented by $\nabla^2\psi$

So

$$\nabla^2\psi = \left[\frac{8\pi^2 m(E-v)}{h^2}\right]\psi \qquad (1.30)$$

$$\left[\left(\frac{h^2}{8\pi^2 m}\right)\nabla^2 + v\right]\psi = E\psi \qquad (1.31)$$

$\nabla$ Is known as Laplacian operator and the above equation can be written as Hψ = Eψ where the operator $\left[\left(\frac{h^2}{8\pi^2 m}\right)\nabla^2 + v\right]$ is termed as the Hamiltonian operator. The wave function represents the amplitude of the spherical wave and it is the relativity of finding an electron in an extremely small amount in volume around a point. This happens if such function is for one particle and probably a singly electron, but in most cases this is not so. For hydrogen which is the simplest atom with only one electron moving in the field of a nucleus that contain two or more protons the problem of obtaining separate and independent one-electron Hamiltonian for each electron arises. This problem occurs because of inter electron to make up for the total energy.

## 1.3 Statement of Problems

Thermal decomposition of xanthates which are sulphur containing compounds provide preparatory or synthetic routes to higher yield of alkenes which have become an attraction and important materials in polymer production. Several experimental studies have been conducted on the pyrolysis of unsubstituted Xanthates (Mc Alpine, 1930, Connor and Nace, 1952, Anslyn and Dougherty, 2004, Wu *et al.*, 2013 and Velez *et al.*, 2014). The results of these studies showed that the reactions had high activation barriers and that alkyl substituents favourably improved the thermodynamics and increased the rate of reaction. However, few works have been done on the theoretical studies of the gas phase thermal decomposition of the substituted xanthates. (Erickson and SCOH, 1994, Claes *e tal.*, 2003, Harano, 2005, Velez *et al.*, 2008) This research focuses on the molecular modeling using systematic and consistent computational methods to study the effect of progressive methylation on the kinetics and thermodynamics of the gas-phase pyrolysis of some α- and β- substituted alkyl xanthates.

## 1.4 Aim and Objectives of the study

This research was aimed at investigating with the aid of quantum mechanical approach using density functional theory (DFT), the effect of progressive methylation on kinetics and thermodynamics of the gas-phase thermal decomposition of some α- and β-substituted alkyl xanthates.

The specific objectives or activities for this study include:

(i) Theoretical formulation of systematic and consistent procedures to predict the thermodynamics, kinetics and mechanism of the gas-phase pyrolysis of some alkyl substituted xanthates using density functional methods.

(ii) Calculation of the Arrhenius and thermodynamic parameters to be able to predict the character of the reaction in terms of rate, spontaneity and yields.

(iii) Investigation of the effect of progressive methylation, which is substitution of alkyl groups for hydrogen on kinetics and thermodynamics of the gas-phase thermal decomposition of some α- and β- substituted alkyl xanthates.

(iv) To ascertain theoretically the existing experimental reaction mechanisms

## 1.5 Justification for the Research

Pyrolysis of xanthates (organo sulphur compounds) provides valuable synthetic routes to higher yield of olefins which are very useful in polymer chemistry (Velez, *et al* 2008). Thermal decomposition of unsubstituted xanthates has high activation barriers but alkyl substituents provide positive inductive effects which enhance kinetics and thermodynamics of the reaction. Computational Chemists studying the kinetics and thermodynamics of substituted xanthates were faced with scanty information on the gas phase thermal decomposition of substituted xanthates in order to compare theoretically generated data with the existing experimental data. The use of systematic and consistent procedures was employed to calculate necessary molecular parameters from geometrical optimization of the reaction of alkyl xanthates molecules which were further used to obtain kinetic and thermodynamic parameters of the pyrolysis of alkyl acetates (Adeboye, 2013).

This research was designed to investigate with the aid of quantum mechanical approach using density functional theory (DFT), the effect of progressive methylation on kinetics and thermodynamics of the gas-phase thermal decomposition of some α- and β-substituted alkyl xanthates. The results of the study may provide a guide to the choice of alkyl substituted xanthates that would have desired properties for high yield alkenes with reduced unit cost of production of the alkenes.

## 1.6 THEORY

Theory is a logical thought that carries a lot of mathematical components. Theory is also very important that it provides a frame work in which it leads to thinking and to organize knowledge.

## 1.7 Importance of Theory to Chemistry

Theory can be used to discover the possible existence of new classes of molecules that could be of scientific value to the environment. Theory can be used to calculate molecules that are unstable or molecules with unstable conformations. The purpose of this calculation is to deduce from the calculations the factors that caused their variability. If the factors are well taken care of, we can develop a strategy to move the molecules to their lower energy. Theory provides equations that show the relationship between quantities and molecular level properties such as:

(i) In chemical kinetics

$$lnk = lnA - \frac{E_a}{R_T} \tag{1.32}$$

Where k is rate constant, A is the pre-exponential factor , Ea is the activation energy and R is the gas constant at absolute temperature.

Eryring, (1931) showed that quantum mechanics and statistical mechanics can be used to explain the rate at which reacting molecule are passing through their potential energy surface and they are also depending on the temperature as given by Arrhenius equation. The expression for activation energy Ea was given by Arrhenius equation as the height of the energy of the reacting molecular species, where $A$ is the pre-exponential factor in terms of immediate geometry and vibrational frequencies of the molecules reacting together at the level of transition state (Jones and Eryring, 1935) expressed Arrhenius equation on the theoretical level by relating the determined rate and temperature to molecular-level quantities.

Computational chemistry is simply the instruments of new experimental methodology which explains that computer with certain software which form a fundamental extension of the method can be used to obtain experimental values (Nieuwpoort, 1994).

Computational chemistry is a branch of chemistry that uses the principles of computer science to assist in solving chemical problems. It uses the result of theoretical chemistry incorporated into appropriate computer program to calculate the properties of atoms, molecules and also determine their structure. Such properties include the structures, relative energies, electronic charges distribution and reactivity of molecules using suitable computational methods. The advances of computational approach to chemical problems are remarkable.

It has been gradually shown that computer may be the instruments of new experimental methodology that is computer experiment which means computer together with appropriate software form a major fundamental extension of our means to obtain experimental information (Nieuwpoort,1994 and Schaefer,1998). Schrodinger wave equation can be used to determined exact values for atoms or molecules that have a single electron, but for atoms or molecules with more than one electron, numerical method can be used to calculate appropriate wave functions and values for observables such as energy, equilibrium, bond length, bond angles and dipole moment. This is the major focus of computational chemistry.

The computational method used in solving quantum chemistry problems covers both static and dynamic methods. The two main categories of models that have been used to calculate molecular structures and energetics are molecular and quantum chemical build up models. Quantum chemical model begins with the Schrodinger equation. It explains molecules as sets of electrons and nuclei which lead to molecular structure and energy among other observables as well as bonding information. However, the Schrodinger equation cannot be used for exact calculation for systems with more than one electron; hence approximation needs to be made.

# CHAPTER TWO

## 2.0 LITERATURE REVIEW

### 2.1 Pyrolysis

Pyrolysis is the thermal decomposition of organic compound in the absence of oxygen at elevated temperature. The process of breaking up a molecule by heat is called pyrolysis. The term pyrolysis is derived from the Greek words, (*pyros*) means “fire” and (*lysis)* means “breaking”. When alkanes are pyrolyzed, the carbon-carbon bond cleaves to produce smaller alkyl radical. (Morrison and Boyd, 2001). An increase in the temperature of an organic compound above a certain level leads to its cleavage, since chemical bonds have a limited thermal stability. This type of chemical splitting usually leads to the formation of smaller molecules, although the result of its products or fragment can interact and can form larger compounds compared to the original molecules. When the starting temperature is high, the chemical process caused by the thermal energy alone is called pyrolysis (Ajaz *et al.*, 2014; Irwin, 1979; Erricsson and Lattima, 1989 and Uden, 1995).

Pyrolysis that is frequently associated with burning is more complex. The main burning process is typically combustion. Other processes consist of volatization, distillation in steam and aerosol formations are present. Combustion is an oxidation process (commonly using oxygen), which produces heat and very small molecules, like water ($H_2O$), carbon monoxide (CO), carbon (iv) oxide ($CO_2$) and Nitrogen gas ($N_2$) from compounds that are organic in nature (Glassman, 1987). In the area that are very close to the burning zone, where heat is generated, materials around may undergo pyrolytic process leading to thermal decomposition and finally result into products. A product of pyrolysis and combustion may result from burning and the initiation of burning is caused by many factors. As a result of these, pyrolysis and burning is caused by many cases of thermal cleavage process, thermal decomposition and burning are closely related subjects and pyrolysis can be studied either without oxygen or in the presence of a certain level of oxygen mixed in an inert gas (Weber *et al.,* 2009).

The term pyrolysis is not restricted to decomposition of pure compounds alone it can be used in connection with the thermal decomposition of mixture or complex materials. In most cases, pyrolysates constituents are smaller molecules than the initial components that were subjected to pyrolysis. However in some cases, pyrolysates constituents are larger molecules than the initial ones, for example, many pyrolytic processes generate char in addition to other products and char is a complex material containing graphite, which may contain various other organic groups depending on the initial molecule that is pyrolyzed. Char can be considered to have a polymeric structure (Moldoveanu, 1998).

Besides reagents, pyrolysis method can sometimes intentionally employ a catalyst. The decomposing products that are generated due to heat further react in the presence of the catalyst to form new compound, both reagents and catalysts can combine (i.e. used at the same time) for specific experimental purpose related to pyrolysis (Tsurge, 1980; Moldoveanu, 2005). It involves the continuous change of chemical composition and its physical phase which are unchangeable. This form of pyrolysis can occur in nature, and also can be used in our surrounding in different areas (Borojovich and Aizenshtat, 2002). The thermal degradation or pyrolysis of organic materials has played a major role in the history and progress of organic chemistry. Benzene was discovered by faraday in 1825 in the condensate of a compressed illuminating gas, which had been prepared by the pyrolysis of whale oil (Badger, 2007.)

Some products from industry are produced with the help of pyrolysis and some of these products are used to produce experimental fuels and they are useful in many ways. With pyrolysis thermal decomposition occurs, breaking down of organic materials under the heat to produce gases, water, and solid as by products which can take the form of ash or char.

Pyrolysis is one of means by which different materials are produced to access useful by products of thermal degradation, for example as in pyrolysis of oil, a type of synthetic fuel, and various materials produced that are used in industrial processes. A different variety of materials can be decomposed through this process for instance products like rubber tires, which can be broken down and turned into useful byproducts with thermal degradation instead of occupying a large number of space.

Thermal decomposition of biomass is a method research in by different scientists who are interested in developing different options for fuels which involves gasification and transformation of carbon based material into a mixture of carbon monoxide and hydrogen which serve as alternative means used to fuel engines without relying on crude oil or petroleum based fuels.

Thermal decomposition is used in different ways in chemical industry, for instance to produce different types of chemicals used in industry such as methanol, activated carbon, and charcoal. Other chemicals from decomposition of wood, also conversion of ethylene dichloride to make PVC, to manufacture coke from coal, to change biomass into synthetic gas and biochar, to convert waste into safely disposable substances, and for changing medium weight hydrocarbons from petroleum into lighter one.

### 2.1.1 Chemistry of the Pyrolytic Reaction

The most common types of reaction encountered in pyrolytic processes are the pyrolytic elimination. Elimination that takes places in pyrolysis are α-elimination, β-elimination, and 1, 3 elimination depending on the atom that is involved. Reactions such as fragmentations, retro-ene reactions, retro-Diels-Alder and retro-Adol condensation and extrusion are also common reactions. Rearrangements are very common in pyrolytic reaction following elimination especially when fragmentation occurs. These are classified as 1, 2 migration rearrangements with bents bonds, electrocyclic rearrangement and sigmatropic rearrangement reaction (Winfough *et al.*, 2017).

Pyrolysis is often performed in the presence of additional reactants or catalyst such as oxygen, water and hydrogen.

### 2.1.2 Characteristics of Pyrolytic Reaction

The formation of pyrolysis products depends mainly on the structure of the starting compound and the pyrolysis conditions. Pyrolysis, when performed intentionally by choosing the exact temperature or by performing pyrolysis in the gas phase parameters such as temperature, atom, gas or solid flux in place, could be controlled (Moldoveanu, 2005).

Pyrolysis in vacuum or in the gas phase could be more than decomposition of a single molecule because the product may undergo further reaction. In pyrolysis, pyrolysate is obtained by cleaving one or more bonds from the starting compound.

Types of reactions encountered in pyrolysis are:

(i) Elimination reaction which includes: α-elimination, β-elimination, 1-3 elimination, and 1, n- eliminations.

(ii) Fragmentations reactions: Fragmentations, retro-ene reactions, retro-Diel Alder, retro – aldol condensations and extrusions

(iii) Rearrangement reactions: 1,2 – migrations, rearrangement in compounds with bent bonds, electrocyclic rearrangements, sigmatropic rearrangement reaction are pyrolysis reactions performed on purpose in the presence of catalysts.

### 2.1.3 Elimination Reactions

An elimination reaction is a type of reaction in which two substituents are removed from a molecule either in one or two step mechanism. The one step mechanism is known as $E_2$ reaction and the two step mechanism is known as $E_1$ mechanism, the number does not have to do with the step in the mechanism but rather the kinetics of the reaction, bimolecular and unimolecular respectively. Pyrolytic elimination is a type of reaction that is most common in pyrolytic reactions.

Elimination does not always take place from the 1, 2 position and depending on the atom that is to be eliminated, these reactions are grouped as α, β, and 1,3 eliminations. Pyrolytic elimination could be $E_1$ or $E_2$ and the $E_1$ mechanism involved a cyclic transition state which may be four, five or six centered.

#### 2.1.3(a) α – Elimination

This involves two leaving groups associated with the same carbon. α – carbon is the carbon attached to a functional group. They are found in some pyrolytic reactions where the most frequent elimination is impossible. For instance, in the pyrolysis of acetic acid from esters with alcohol containing a quaternary β – carbon.

### 2.1.3(b) β – Elimination

β- Elimination is another name for second-order elimination or $E_2$ where for example, hydrogen on a β-carbon and the adjacent leaving group could be eliminated to generated a π-bond. The most common reaction is the β- Elimination in which two groups from adjacent carbon atoms are lost. This reaction takes places as an $E_2$ mechanism. Lewis base pulled a proton and the X- groups from the molecule, A. $E_2$ reaction occurs (Solaka *et al.,* 2012).

The reaction is bimolecular or $E_2$. In $E_1$ mechanism, the reagent loses a X- group, from the alkyl into a solvent, to form a carbocation, and the rate determining step depends on only species. The carbocation is followed by a rapid loss of a β-proton to a Lewis base. $E_1$ mechanism are not common in pyrolysis in the gas phase. $E_2$ Mechanism is the most common in pyrolysis; it involves a cyclic transition state which may be four, five or six transition states. The intermediate is not discrete, it is concerted (Paulechka *et al.,* 2011).

## 2.2 The Chugaev Elimination

The Chugaev elimination reaction is broadly defined as the thermal decomposition of xanthate ester of an alcohol that contains at least a β–hydrogen to produce an olefin, carbonylsulphide and a thiol. This reaction is similar to the thermal decomposition of acetates, carbamates and carbonates, to produces olefins (Wu *et al*., 2013).

Chugaev discovered the reaction in 1899, in conjunction with his research on the optical characteristics of xanthates (Grieco and Kaufman, 1999), this reaction was employed in his investigation of terpenes, and he demonstrated its use as an alkenes production reaction and its usefulness in structural determination. Examination of the chugaev elimination has revealed that the reaction proceeds via the formation of a cyclic transition- state involving the syn- β- hydrogen of the alcohol moiety and the thion (double bond) sulphur atom of the xanthate.

An olefin and decomposable dithiocarbonates which accordingly disintegrates to carbonylsulphide and a thiol (Velez *et al.,* (2008) proposed that the reaction was concerted, involving a *syn*-β - hydrogen atom, and involved β- hydrogen abstraction by the less hindered thion sulphur atom rather than the thiol sulphur atom. Evidence for this assertion that the thion sulphur atom was involved in the abstraction was reported by (Wu *et al.,* 2013) based on a research of carbon and sulphur in the pyrolysis of trans-2-methyl-1-indanyl xanthate of natural isotopic abundance studying it isotope effects

Wu *et al.,* (2014) used the term "Molecular mechanism to describe the mechanism of the chugaev elimination, acetate pyrolysis and other oleifination. These eliminations proceed through a cyclic transition state involving ions nor radical but rather a redistribution of the electrons accompanied by concerted bond making and bond breaking (Wu *et al.,* 2014). He also explained the preferred *syn* cause of the chugaev reaction, thereby predicting the configurations of a numbers of elimination.

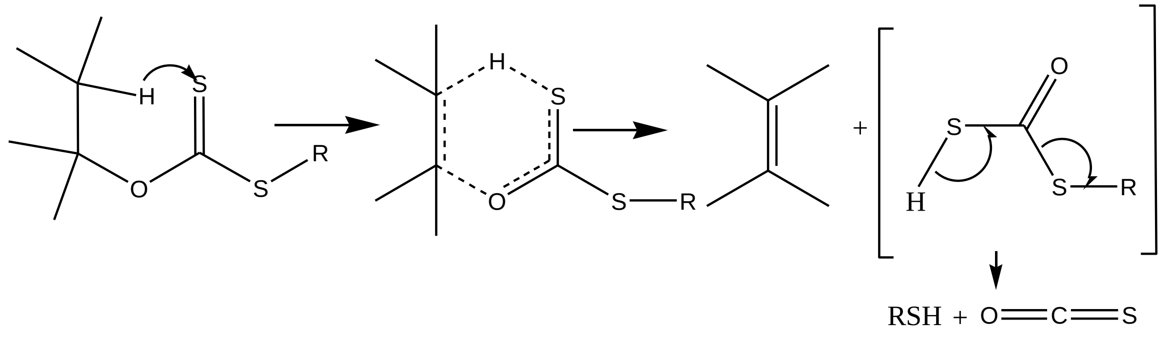


**Figure 2.1: Chugaev thermal decomposition of dithiocarbonates**

### 2.2.1 Pyrolysis of Xanthates (Dithiocarbonates)

The thermal decomposition of Xanthate esters (the Chugaev reaction) has been earlier examined with Xanthates containing the S-methyl substituents at position 1 or 2. McAlpine, (1932) who happen to be the first scientist to study dithiocarbonates with a variety of S-substituents, suggested that the presence of electronegative groups on the thiol sulphur decreases the thermal stability of dithiocarbonates and this proceeds in a lower initial temperature of pyrolysis (Chuchani *et al.*, 1980). The order of stability of S-substituted dithiocarbonates of methyl alcohol was found to be as follows in Figure 2.2: Chugaev (or tschugaeff) in 1899 discovered a preparatively useful paths to olefins from a group of unimolecular pyrolysis, the intramolecular thermal decomposition. These types of processes are termed as rearrangement or addition reactions (pericyclic). Part of them is the production of alkenes through alkanols from thermal decompositions of the dithiocarbonates (alkyl Xanthate). Thus, the reaction is called Chugaev reaction (Laue and Plagens, 2005) as shown in Figure 1.1a.

A recent research by Langlais *et al.*, (2017) showed the same trend of stability for S-substituted cholesterol of dithiocarbonates. A Study on the kinetics of the pyrolysis of these Xanthates indicated that an increase in the electronegativity of the S-alkyl group decreased the stability of the dithiocarbonates in the sequence shown below in Figure 2.2:

In other earlier studies with S-p-bromophenacyl xanthate primary alcohols, It was found evidence that another route or pathway competes with the original Chugaev elimination when the strongly electronegative S-p-bromophenacyl group is present. (Gilman and Bogdanowice, 1970).

Etaibi *et al.*, (2011) reported that all studied Xanthates: O-alkyl S-methyl xanthates and S-alkyl O-methyl dithiocarbonates, give a good kinetic report and passed the tests for homogeneity. The result of the reaction was identified (but not established) by I.R. spectroscopy of individual compounds and reliable mixtures. S-ethyl O-methyl dithiocarbonates did not give a good Kinetic report, which gave a curved on the Arrhenius plot. In order to have a primary dithiocarbonates, it needs a high temperature for thermal decomposition and thion-thiol rearrangement became evident as shown in Table 2.1(a) and Table 2.1(b) of the experimental results (Velez *et al.*, 2008).

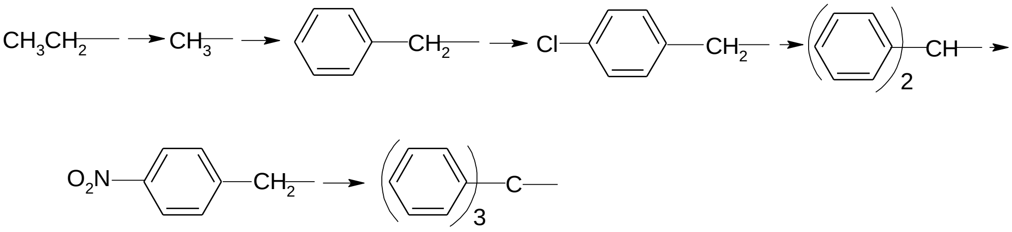


**Figure 2.2: Order of stability of S-substituted Xanthates** (Langlais et al., 2017)

**Table 2.1(a): Arrhenius parameters for the pyrolysis of O-alkyl S-methyl Dithiocarbonates**

| Alkyl | T/K | $\Delta H^{\updownarrow}$kJ/mol | $\Delta S^{\updownarrow}$J/mol/k | $k_{623}/S^{-2}$ |
|---|---|---|---|---|
| Et | 590-620 | 161 | -28 | 1.4 x $10^{-2}$ |
| $Pr^{i}$ | 500-550 | 144 | -26 | 5.6 x$10^{-1}$ |

**Table 2.1(b): Arrhenius parameters for the pyrolysis of S-alkyl O-methyl xanthates**

| Alkyl | T/K | $\Delta H^{\updownarrow}$ kJ/mol | $\Delta S^{\updownarrow}$J/mol/k | $k_{623}/S^{-2}$ |
|---|---|---|---|---|
| $Pr^{i}$ | 580-630 | 163 | -32 | 7.9 x $10^{-3}$ |
| $Bu^{t}$ | 500-550 | 144 | -26 | 4.3 x$10^{-1}$ |

The pyrolysis of dithiocarbonates (Xanthates) was studied experimentally by Langlais *et al.,* (2017); Etaibi *et al.,* (2011); Belskaya *et al., (*2015). The reaction studied by the above scientist were given to be first order, and the rates of the reactions were not mainly affected by an increase in area of the surface or the radical inhibitors addition because these are unimolecular and homogeneous in nature.

### 2.2.2 What are Xanthates (Dithiocarbonates)?

Xanthates are esters of xanthaic acid or O-esters of dithiocarbonic acid. Other names for Xanthates include carbondithioates, dithiocarbonates, xanthogenates and potassium or sodium salts of xanthanic acids(Velez**,** 2008).

Xanthates are water-soluble chemicals that are mainly used in the mining industry. Usually, they are used during the processing of metalliferous ores in mine concentrators. They are added to crush ores and grounded into a fine particulate and mixed with water.

Xanthates coat the valuable mineral particles making them water repellent, thereby facilitating their attachment to air bubbles blown out from the base of flotation cells. Xanthates precipitation is a relatively new technology compared to other methods of precipitation. Xanthates are sulphonated organic compounds thereby act as an ion exchange material, replacing heavy metals with sodium and magnesium (Tschugaeff, 1899)

Xanthates are also used in the production of cellophane and rayon. In Australia, xanthates are solely used as a collector to extract sulfide minerals. Xanthates is the common name for chemical reagents used in the flotation of base and precious metals, which is the standard method for separating valuable minerals from non-valuable minerals such as limestone or quartz. Xanthates are also used as fungicides, herbicides and insecticides in agricultural production as well as additives in the treatment and vulcanization of rubber and high pressure lubricant. New application of xanthates include inhibition of nitrogen conversion in fertilizer and the development of colour for image-recording materials (Wu *et al,* 2013).

### 2.2.3 Mechanism of Thermal Decomposition of Xanthates (Dithiocarbonates)

In the elimination of phosphoester, two mechanisms were proposed, one of which refers to $E_1$ type and the other is $E_2$ Mechanism involving a carbocation intermediate. The phosphoester thermal elimination reaction belongs to the same class as the esters and xanthates. The Ei process in which (i) can be 1 or 2 for the thermal elimination of phosphoester would involve a six membered-ring transition structure like esters and xanthates. The kinetics and mechanism of xanthates thermal decomposition is a concerted elimination but results could apparently come from β-hydrogen abstraction from either the thiol or thione sulfur atoms, mechanism A and B as in Figure 1.2 (Adejoro *et al*, 2017). In mechanism (A) , the reaction takes place in one step, giving the reaction products as in (1). In the reaction mechanism (B) ,the earlier products are alkenes and decomposable dithiocarbonates derivative that decomposed to thiol and carbonyl sulphide. The first mechanism (A) was given by (Wu *et al.,* 2013) but the second pathway was discovered (Adejoro *et al,* 2017). The data that was given by the experiment showed that thione, rather than thiol, sulfur atom attacks the β-hydrogen (Wu *et al.,* 2013; Wu *et al.,* 2014) provided additional evidence for the cis-elimination as shown in Figure 1.2.

## 2.3 The Theory of Chemical Reaction Rates

In an ideal setting, a scientific theory provides a quantitative description of some aspects of experience. Indeed, the test of any theory lies usually in the accuracy of its rationalizations and predictions. Here, the conceptual and descriptive aspects of elementary theories of reaction rates shall be discussed.

A number of factors such as the temperature, concentration of reacting molecules, pressure, etc, influence the rate of a chemical reaction. However, the effects of these factors depend on the nature of the reactants being studied. A theory of reaction rates should be able to provide a theoretical description of the dependence of the rate of any chemical reaction in terms of such measurable quantities and experimental conditions.

### 2.3.1 The Arrhenius law

Toward this direction, Arrhenius formulated one of the most important relationships in chemical kinetics, and one that provides much information about mechanism. This expression relates rate constant to an energy factor. He discovered that the plot of the logarithm of rate constant against the reciprocal of the absolute temperature of measurement was a straight line as in equation 2.1 (Gaulke *et al.,* 2016).

i.e.

$$\log k = \log A - B/2.303T \qquad (2.1)$$

Thus, $$k = A \exp(-B/T) \qquad (2.2)$$

Where k is the rate constant, A is the pre-exponential factor , Ea or B is the activation energy and R is the gas constant at absolute temperature T. Van't Hoff independently also discovered this relationship but this equation is generally referred to as the Arrhenius law. A and B are constants for the reaction. A is known as the frequency factor; while B is related to the minimum energy, E, the molecules of the reactants must acquire, and thus get activated, before reaction can occur and T is the absolute temperature.

### 2.3.2 Collision Theory in Qualitative Terms

Arrhenius suggested that for reaction to take place, the molecules of the reactant must be activated by collisions with one another, and that there exists equilibrium between normal molecules and 'active molecules'. The energy of activation represents the energy the molecules must acquire in order to be able to undergo reaction. When reactants have acquired this energy and are in the act of reacting to form products, they are referred to as activated complexes. The rapid increase in the rate of a chemical change with rising temperature is therefore caused by the shift in the equilibrium between the two kinds of molecules. The higher the temperature is, the greater is the fraction of the molecules having higher energy content. These ideas qualitatively predict the effect of varying the conditions for the determination of rate constants (Gaulke *et al.,* 2016).

Experimentally, the Arrhenius parameters, i.e. 'A', the frequency factor and 'E', the activation energy are determined by plotting the graph of the logarithm of the rate constant against the reciprocal of the absolute temperature. The slope of the line gives the energy of activation (E) while the intercept on the ‘lnk’ axis gives the frequency factor (A). For many years, theoretical kineticists have attempted to calculate the Arrhenius parameters A and E from the physical properties of the reacting molecules but so far, little success has been achieved even for very simple reactions. In practice, these parameters are generally obtained experimentally rather than theoretically.

(Wood *et al*., 2015) who suggested that, the properties of an activated complex could be calculated using the same quantum-mechanical methods that are used for calculating the energies of stable molecules, carried out the first treatment of chemical reactions from the standpoint of molecular structure. He therefore attempted to obtain the activation energies, Ea’s, of simple reactions from inter-atomic forces. This method made use of the theory, which relates the potential energy of a system of several atoms to the energies of the individual combinations of them, taken two at a time. Thus, in a system containing three atoms A, B, C, the potential energy is given by:

$$E = Q + \{1/2[(\alpha-\beta)^2 + (\alpha-\gamma)^2 + (\beta-\gamma)^2]\}^{1/2} \qquad (2.3)$$

where Q is the sum of the six coulombic energies of the six possible points and $\alpha$,$\beta$, $\gamma$ are the exchange energies (i.e. Q is the coulombic binding between three atoms- the binding energy that can be calculated using classical electrodynamics if electrons are assumed to be the diffuse clouds of quantum mechanics ( Erying, 1931). The coulombic energy is the sum of three terms: Q = A + B +C. To calculate E, it is important to know the separate values of the coulombic and the exchange energies in conjunction with the total binding energy of the diatomic molecule obtained from spectroscopic data.

At this stage, (Eyring, 1935 and Emovan, 1959) proposed an approximation, which also in very many cases has proved unreliable. They assumed that the coulombic energy constitutes about 10 to 20% of the total binding energy. By assigning a definite proportion of the total energy to be coulombic, a potential energy surface was constructed (Figure.2.3) for the reaction:

$$AB + C \rightleftharpoons A + BC \qquad (2.4)$$

based on the simplifying assumption that the most favorable condition of approach of C to AB is along the line AB.

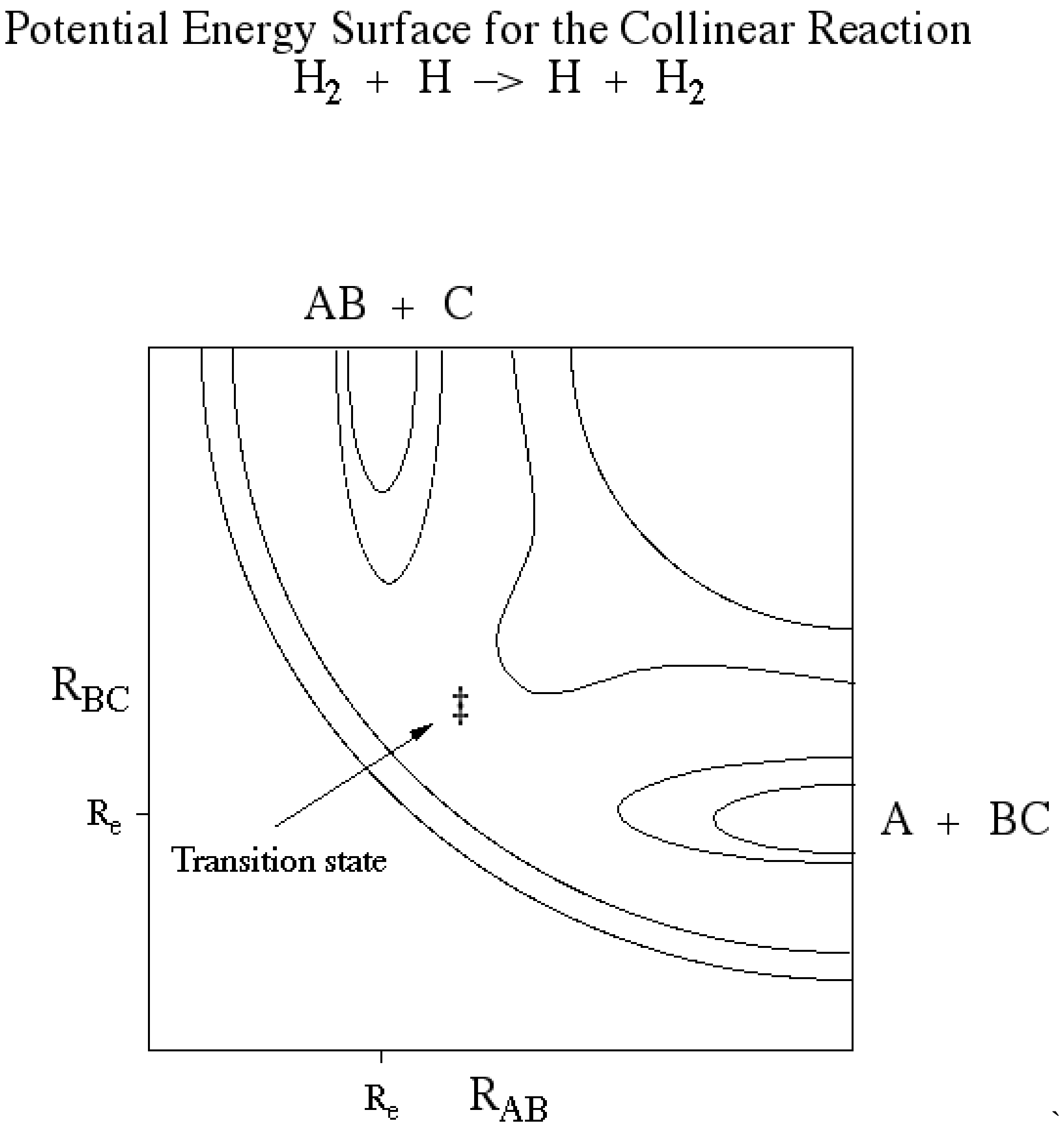


**Figure 2.3. A contour diagram showing the potential energy surface for the reaction:**

Henry Eyring, (1935) and Emovan, (1959) $AB + C \rightleftharpoons A + BC$

The energy can thus be conveniently expressed as a function of the distances between AB and BC used as coordinates and the points of equal energy joined by lines. From this surface, it is found that as C is brought to AB along the most favorable reaction path, the potential energy passes through a minimum representing the reactants to a maximum and back to a minimum as the products are formed (Figure. 2.4). The reaction activation energy is the energy difference between the highest point in the reaction path and minimum representing the reactants. This mode of calculation has been applied successfully to the reaction of a hydrogen atom with a hydrogen molecule but very wide difference occurs between the calculated and the observed activation energy for more complex reactants. To account for the rate of activation, two theories and their later modifications are of importance. These are the collision theory and the transition state theory.

### 2.3.3 Collision Theory (Quantitative Treatment)

In collision theory, the formation of the product can occur only if there are "effective" collisions between molecules of the reactant in the rate- determining step. Having the molecules of the reactant colliding is simply necessary but not enough. The collisions have to be effective and satisfy two conditions (Connors, 1990).

(i). A collision must have an impact energy that is enough to overcome the activation energy. This impact energy must be sufficient so that the bonds in the reactant molecules can be broken new bonds formed to produce the products.

(ii). The molecules must have a proper positioning for effective collision to occur. According to this theory, in any bimolecular reaction, a chemical change is a result of an encounter between molecules. Such a collision can only occur when any two molecules come within a certain critical distance, the sum of the Vander Waals radii, of each other. (Eliason and Hirschfelder, 1959) .Thus, the rate of a chemical reaction was equated to the rate of collision of the reacting species. For a bimolecular reaction between two identical gaseous molecules, Lewis suggested that the rate in molecular unit is:

$$\text{Rate} = Z_{AA}\, e^{-E/RT} \qquad (2.5)$$

The number of collisions per second in unit volume for a bimolecular reaction involving molecules A and B in $1m^3$ in one second has been obtained from the kinetic theory and it is given by:

$$Z_{AB} = N_A N_B \sigma_{AB}^2 (8\pi RT/\mu)^{½} \quad (2.6)$$

where $Z_{AB}$ is the A-B collision frequency, $N_A$ and $N_B$ are the numbers of the molecules of A and B respectively in unit volume (per $m^3$) of gas, and $\sigma_{AB}$ is the collision diameters and $\mu = m_A+m_B/m_Am_B$, the reduced mass.

According to Lewis treatment, the rate of reaction between molecules A and B is given by:

$$v = N_A N_B \sigma^2_{AB}[8\pi kT/\mu]^{1/2}\, e^{-E/RT} \quad (2.7)$$

where E is the activation energy. The significance of this equation is that the rate is the number of molecules colliding per second and having a joint energy, E in excess of the mean energy. If the concentrations are each set equal to unity, the resulting expression by ( Laider, 1935) is:

$$v' = \sigma^2_{AB}[8\pi kT/\mu]^{1/2} e^{-E/RT} \quad (2.8)$$

where the constant $\nu' = \nu/N_A N_B$, is a rate constant for the reaction in the molecular units, namely $m^3$ $molecule^{-1}$ $sec^{-1}$ which can be put into the units of $m^3$ $mole^{-1}$ $sec^{-1}$ by multiplication by N, the Avogadro number:

$$\kappa = N\sigma^2_{AB}[8\pi kT/\mu]^{1/2} e^{-E/RT}\ m^3\, mole^{-1}\, sec^{-1}. \quad (2.9)$$

Comparing this equation with the Arrhenius equation:

$$k = A\, e^{-E/RT} \quad (2.10)$$

shows that according to this theory the frequency factor A is given by:

$$A= N\sigma^2_{AB}[8\pi kT/\mu]^{1/2}\ m^3\, mole^{-1}\, sec^{-1.} \quad (2.11)$$

The expression on the right hand side is known as the collision number and usually written as Z. Lewis thus identified the frequency factor of the reaction with the collision number.

Collision number can readily be calculated using molecular diameters derived from viscosity data or other ways. If reactions were merely the result of collisions, then every chemical reaction will be instantaneous. This has been observed to be untrue. It is necessary to point out that this theory does not allow for two things:

(i). Molecules, which collide, may not lead to reaction because collision may have occurred in a geometrically unfavourable manner.

(ii). Energy requirements in more than two degrees of freedom were neglected.

Lewis tested this theory for reaction between hydrogen and iodine and for the reverse decomposition of hydrogen iodide:

$$H_2 + I_2 \rightleftharpoons 2HI \qquad (2.12)$$

The agreement between the experimental frequency factor and collision number in both cases was extremely satisfactory, but for more complex molecules, the agreement was not. Hence the collision theory was modified to incorporate an orientation or steric factor P such that:

$$k = P\, Z_{AB}\, e^{-E/RT} \qquad (2.13)$$

The P appearing in this expression is referred to as the probability, steric or orientation factor. There are several inherent fundamental difficulties in applying the simple kinetic theory of collisions to kinetic problems and these are:

(i). The correlation of the value of P with the characteristics of the reacting molecules has not always been satisfactory.

(ii). Abnormally high frequency factors have often been observed particularly in solutions and these cannot be interpreted based on the specific orientation of reactants on collision.

(ii). Another logical weakness of the simple collision theory is revealed if one considers reversible reactions. ( Laidler, 1935) such as:

$$2AB \longrightarrow A_2 + B_2 \qquad (2.14)$$

According to the kinetic theory the rate constant for the forward reaction would be given as:

$$k_1 = P_1Z_1\, e^{-E1/RT} \qquad (2.15)$$

And for the reverse reaction:

$$k_2 = P_2Z_2\, e^{-E2/RT} \qquad (2.16)$$

The equilibrium constant, $K = k_1/k_2$,

$$\text{Hence } K = k_1/k_2 = P_1Z_1\, e^{-E1/RT}/\, P_2Z_2\, e^{-E2/RT} \qquad (2.17)$$

$$\text{i.e. } K = P_1Z_1 / P_2Z_2 e^{-(E1-E2)/RT} \qquad (2.18)$$

$$K = P_1Z_1 / P_2Z_2 e^{-\Delta E/RT} \qquad (2.19)$$

where $\Delta E = E_1 – E_2$, the difference in heat contents of the products and the reactants.

From thermodynamics, the equilibrium constant must be equal to:

$$K = e^{\Delta S/R}\, e^{-\Delta H/RT} \qquad (2.20)$$

where $\Delta S$ and $\Delta H$ are the increases in the entropy and enthalpy. It is clear from the comparison of this expression for K that the terms $e^{-\Delta E/RT}$ and $e^{-\Delta H/RT}$ correspond closely; the ratio $P_1Z_1 / P_2Z_2$ must therefore be approximately equal to $e^{\Delta S/R}$.

If the molecules $A_{2,}$ $B_2$ and AB are of comparable sizes, $Z_1$ would be practically equal to $Z_{2,}$, i.e. $Z_1 /Z_2 \sim 1$; so that entropy term must be approximately equal to the ratio $P_1/ P_2$. However there is nothing in the definition of $P_1$ and $P_2$ that would cause their ratio to correspond to the entropy term. It is therefore insufficient to correlate the probability factors with the probability that certain reacting groups come together during the course of collision. These probability factors should be interpreted in terms of entropy factors. In view of the unsatisfactory features of the simple kinetic (hard sphere) collision theory, and of the fact that it is necessary for the rate equation to involve entropy terms or their equivalent, a reformulation of the rate equation is clearly necessary.

### 2.3.4 Deficiencies of Collision Theory

In order to summarize points made in the collision theory and to explain contradictions with other theories, it is useful to mention what can considered obvious shortcomings of the theory of collision.

(i). When assessing frequency of collision using the Kinetic Theory of Gases, it was assumed that the molecules include energy only through translational motion (i.e. kinetic energy). The means that as soon as sufficient kinetic energy is obtained, a reaction should occur. However, real molecules can include energy in several different ways: rotational electronic and translational as well as vibrational energy. Therefore, it is possible that a molecule with a total energy greater or equal to $E_a$ may not have this energy yet to be distributed in a way that can promote the reaction and thus may not convert to products. The only way this effect is allowed in simple collision theory is to include an undefined manner, into the steric factor, P.

(ii). Collision theory does not offer a clear method to calculate $E_a$. In fact the theory treats $E_a$ as an empirical parameter that can be determined only by experiment and is only predictive in relation to ‘ A’ factor.

(iii). Although the modified collision theory recognizes the importance of the orientation molecules by steric factor P, it again does not offer a direct way to calculate this parameter.

(iv). The simple theory of collision considers molecules as rigid spheres and therefore calculates the reaction cross-sections using simple formulae. However, the molecules can doubtlessly be distorted if they approach each other and of course, very few are truly spherical. The concept of reaction cross-section is rather poorly defined and cannot be considered as a parameter that can be easily and accurately calculated.

### 2.3.5 The Transition State Theory

Transition State or Theory of Activated Complex (also known as Theory of Absolute Rate) was developed chiefly by (Wood and Strachan, 2015; Wynne-Jones and Eyring,1935). A very similar formulation of rates was made independently at about the same time by (Hänggi *et al.,* 1990). Eyring considers reactions as taking place through the formation of a transition complex. This complex exists at the highest point of the most economical energy path, often called the reaction coordinate, as shown in figure 2.4 between reactants and products and has all the attributes of a normal molecule; except that it has a degree of vibrational freedom (corresponding to the reaction coordinate) frozen out and replaced with a translational degree of freedom. Though this theory is based on the same model of the reaction process as collision theory, it recognizes that the conversion of reactants into products requires the transfer of a high energy molecular configuration and that obtaining this energy is an important aspect of reaction. But instead of calculating the rate by considering how often molecules with the necessary activation energy can meet with each other in transition state theory, it analyses the properties of the configuration of maximum energy (transition state or activated complex) predicted by the rates. In addition, since a transition state is energy maximum, it requires a completely different approach.

The essence of transition state theory is to consider the transition state as an ordinary molecule such as reactant, with the exception of the special property that molecular vibration along the reaction coordinate does not have restoring force and cause the bond cleavage, a situation that converts reactants into products. Again, considering the transition state as a ‘normal’ molecule, the theory considered it has been effective equilibrium with the reactants, so the equilibrium constant $K^*$, can be used to relate the concentration of the observable reactant to the concentration of the unobservable transition state.

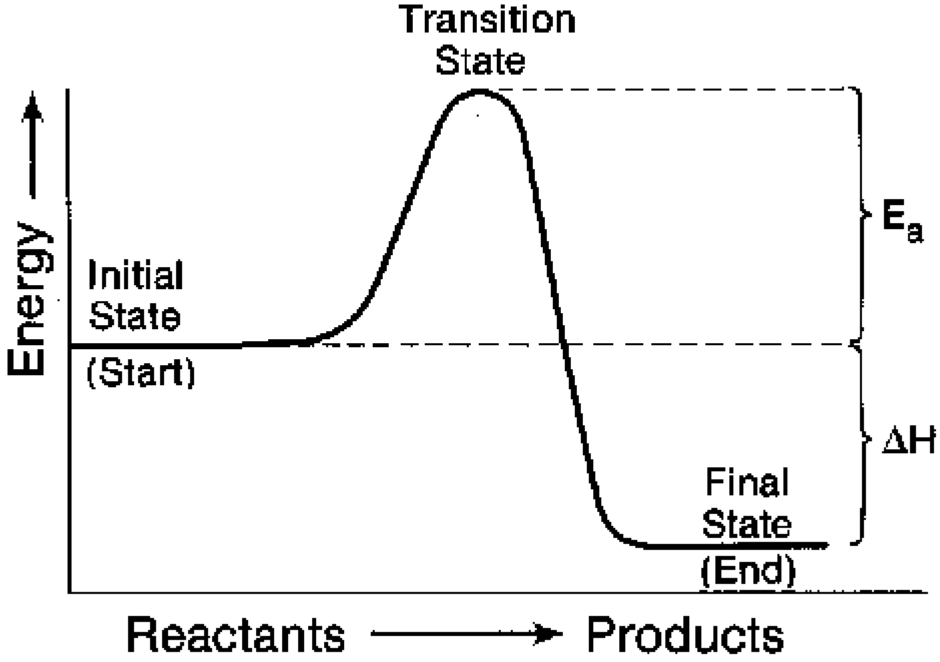


**Figure. 2.4 Energy profile of path followed by reacting complex.** Eyring, (1935)

Consider the reaction involving a molecule AB containing two univalent atoms A and B, and univalent atom C.  C may be more attracted to A or to B. Hence; the scheme may be either of the following:

$$AB + C = AC + B \tag{2.21}$$

$$AB + C = BC + A \tag{2.22}$$

This may take place in either of the following ways:

1. AB, given sufficient energy, dissociates into atoms A and B that subsequently react with C.

2. AB could be set in vibration with amplitude large enough to weaken the bond A-B as C is being brought up to it, and at the same time with sufficient energy to overcome the weakened bond. This will result in a certain position of C relative to AB where C can compete on equal terms for either A or B. With such a picture, there is a continuous change of configuration from the initial to the final one representing the products.

Initial state: AB + C

Transition state: A…B…C

Final state: A + BC or AC + B.

In the transition state, the potential energy is maximum for a given configuration of atoms A, B and C, because on either side, the potential energy decreases either towards AB + C on one hand or A + BC on the other as shown in Figure 2.3

## 2.3.6 Derivation of the Rate Equation:

The mathematical treatment of the transition state theory assumes that the activated complex has all the properties of a normal molecule except that the motion in one direction, along the reaction coordinate, results in reaction and that equilibrium exists between the initial and activated states. Suppose that the reactants A and B form the activated complex $AB^*$ in the reaction: (Gurvitz and Prager, 1996).

$$A + B \rightleftharpoons AB^{\ddagger} \longrightarrow \text{Products} \qquad (2.23)$$

The equilibrium constant for the conversion of A and B in the activated complex is given by:

$$K^{*} = [AB^{*}] / [A]\,[B] \qquad (2.24)$$

Thus, the concentration of the activated complex $AB^{*}$ is given by:

$$[AB^{*}] = K^{*}[A]\,[B] \qquad (2.25)$$

The transition complex decomposes into the products at a definite rate, and the rate of reaction according to this theory is given by the concentration of the activated complex at the top of the energy barrier multiplied by the frequency with which the barrier is crossed i.e.

$$\text{Rate} = F\,[AB^{*}] \qquad (2.26)$$

where F is the frequency with which the activated complex crosses the energy barrier and it is independent of the nature of the reactants and is given by:

$$F = k'\,T/h, \qquad (2.27)$$

where k′ is the Boltzmann constant and h is the Planck's constant.

Therefore, rate of reaction is equal to

$$K^{*}[A]\,[B]\,F \qquad (2.28)$$

$$K^{*}[A]\,[B]\,(k'\,T/h) \qquad (2.29)$$

However, for a bimolecular (2nd order) reaction between two substances A and B, the rate constant is defined by:

$$\text{Rate} = k\,[A]\,[B] \qquad (2.30)$$

It implies $k = K^*$ (k′ T/h).In order to allow for the possibility that not every activated complex is converted into the reaction product in which one is interested, it is convenient to introduce a transmission coefficient, $\alpha$, thus giving the rate constant as:

$k = \alpha K^* (k' T/h)$. (2.31)

$K^*$ represents the true equilibrium constant between the reactants and the activated complexes.

For some purposes, it is convenient to formulate the rate constant of reaction in terms of thermodynamical functions by expressing $K^*$ in terms of $\Delta G^*$, the change in Gibbs free energy in passing from the initial state to the activated state:

$\Delta G^* = -RT \ln K^*$ (2.32)

$K^* = e^{-\in \Delta G^*/RT}$ (2.33)

Therefore

$k = \alpha(k' T/h)\, e^{-\Delta G^*/RT}$ (2.34)

Expressing the free energy of activation $\Delta G^*$ in terms of entropy, $\Delta S^*$ and heat of activation $\Delta H^*$, the result is:

$k = \alpha(k' T/h)\, e^{\Delta S^*/R}\, e^{-\Delta H^*/RT}$; (2.35)

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

Wynne and Eyring (1935) gave the above equation and it shows that the rate of a chemical reaction is determined by the free energy of activation.

This equation could conveniently be expressed in a form that involves the experimental energy of activation, $E_{exp}$ in place of the heat of activation $\Delta H^{*.}$

Since $K^*$ is concentration equilibrium constant, its variation with temperature is related to the energy change $\Delta E^*$ by the equation:

$d\ln K^*/dT = \Delta E^*/RT^2$ (2.36)

Here $\Delta E^*$ is the increase in energy in passing from the initial state to the activated state. From

$k = K^* (k' T/h)$ (2.37)

Taking the logarithm and differentiating with respect ‘T’ it gives:

$d\ln k / dT = 1/T + d\ln K^*/dT$, (2.38)

it implies that,

$d\ln k / dT = 1/T + \Delta E^*/RT^2 = (RT + \Delta E^*)/RT^2$ (2.39)

Comparing this equation with the experimental value of the energy of activation, $E_a$, defined as:

$d\ln k / dT = E_a/RT^2$ (2.40)

i.e.,

$E_a/RT^2 = (RT + \Delta E^*)/RT^2$ (2.41)

Therefore,

$E_a = RT + \Delta E^*$ (2.42)

This must be expressed in an equation involving $\Delta H^*$ rather than $\Delta E^{*.}$ The relationship between the two is:

$\Delta H^* = \Delta E^* + P\Delta V^*$, (2.43)

i.e.

$\Delta E^* = \Delta H^* - P\Delta V^*$, (2.44)

where $\Delta V^*$ is the change in volume in going from the initial state to the activated state. By substitution,

$E_a = \Delta H^* - P\Delta V^* + RT$ (2.45)

For unimolecular reactions, there is no change in the number of molecules as the activated molecule is formed, and therefore $\Delta V^* = 0$.

$\Delta V^*$ is also zero for all reactions in solution. In these cases

$E_a = \Delta H^* + RT$, and the rate equation may therefore be written as

$$k = (k' T/h)\, e^{\Delta S^*/R}\, e^{-(E_a - RT)/RT}; \qquad (2.46)$$

or as

$$k = (e\, k' T/h)\, e^{\Delta S^*/R}\, e^{-E_a/RT} \qquad (2.47)$$

For reactions in the gas phase, the general relationship is

$$P\Delta V^* = \Delta n^* RT \qquad (2.48)$$

Where $\Delta n^*$ is the increase in the number of moles when the activated complex is formed from the reactants.

For example in the case of a bimolecular reaction, two molecules become one, so that $\Delta n^* = -1$, and the experimental energy of activation is related to the heat of activation $\Delta H^*$ by the relationship:

$$E_a = \Delta H^* + 2RT \qquad (2.49)$$

$$k = e^2\, k'T/h.\ e^{\Delta S^*/R} \cdot e^{-E_a/RT}. \qquad (2.50)$$

## 2.4 Description of Spartan ’10.

Molecular mechanics calculations and quantum chemical calculations play an increasing role in modern chemistry. The main functions are to provide information about structures, relative stabilities and other properties of isolated molecules. It can also be used to provide information on the mechanisms and distribution of chemical reaction product either directly through transitions state calculation or indirectly bases on the Hammond postulation, by modeling the steric and electronic demand of the reactant. Finally quantum chemical calculation can provide information to supplement existing experimental data or to completely replace it, for example, atomic charges for QSAR analyses and intermolecular potential for molecular mechanic and molecular dynamics calculation **(**Hehre and Ohlinger, 2010**).**

Spartan ’10 is a software package designed to address the increasing role that calculations play in chemistry and related fields, which is a continuous collaboration between wave function, Inc. and Quantum chemistry Inc.

Quantum chemistry codes supplement and extend the traditional strengths of Spartan as an easy to learn and use tool for molecular mechanics, Semi-empirical and Hatree-fock molecular orbital calculations, as well as a wide variety of graphical models with a full range of density functional models and a broad selection of wave function-based post-Hatree-fock models. All models have been implemented using a robust algorithms currently available, and are tuned for high performance on Intel and AMD processors including multi-core processors (Levine, 2000).

Spartan is intended to be used by chemists, not only by computational chemists who are already familiar with the possibilities of molecular mechanics and quantum chemical methods, but also by experimental chemists who have little or no prior experience, but who want to use calculations much in the same way as experimental methods such as NMR spectroscopy. Spartan’10 is a cross-platform application. Spartan comprises a series of independent modules that are closely connected by graphical user interface which is highly functional, but elementary and uncluttered. It is designed to reduce not only the grief and possibility for human error associated with the preparation of input, but also to guide the interpretation of output. The interface is best viewed as an interactive and intuitive window throughout the spectrum of modern computational techniques (Aktins and Friedman, 1997).

The interface include component for organic, inorganic and organometallic molecules, polypeptides and polynucleotide’s as well as method for guessing transition states. Access to chemdraw is provided without leaving the Spartans interface. The interface provided substructure access to the Spartans molecular database (SMD), a collection of more than 150,000 calculated structures and related molecular properties, each of which contains up to nine different theoretical models (Hatree-fock models with 3-21G, 6-31G* and 6-311+G** basis sets B3LYP and MP2 model with the 6-31G* and 6-

311+G** basis set. New in Spartan 10 is a collection of approximately 3,000 inorganic transition-metal and organometallic molecules obtained from the B3LYP/6-31G* model (Helgaker, *et al*., 2000).

The Spartan spectra and properties databases (SSPD) first appear along with Spartan 10. It consist of IR, UV and NMR spectra and various atomic and molecular properties along with QSAR. The Spartan interface provide access to variety of modern computational methods including molecular mechanic model, semi-empirical and Hatree-fock molecular orbital models as well as various correlated models, including density functional and Moller plesset model (McQuarrie, 1983).

## 2.5 Computational Chemistry

While atomic physics is concerned with the core electron in atoms, chemists are primarily interested in understanding the behavior and interaction between the valence electrons in molecules. Quantum mechanical laws describe the behavior of electron and nucleus in atom. Since it has been demonstrated that quantum mechanics adequately describes the physics governing chemical problems, the application of these laws to chemical phenomena gives rise to the non-experimental field of quantum chemistry (Kállay and Gauss, 2004).

Quantum chemistry, in principle, deal only with problems where quantum aspects are considered. It is a subfield of a wider non-experimental area of chemistry, modern theoretical chemistry. Theoretical chemistry has been traditionally associated with paper and pencil type of research, and the development of new theories and approximations. In modern research the implementation of new method in computer programs has lead to dramatic advances. Computers are used to test new methods and to investigate interesting chemical problems. The roles of computers in the development of theoretical chemistry led to the emergence of the new field of computational chemistry (Pople and Beveridge, 1970)

Computational chemistry is as wide as everything else in science, and faces challenges in science, and faces challenges in many directions e.g. reaction mechanisms and dynamics, spectroscopy and condensed phase studies. Among other things, computer-based research has provided explanation for experimental discoveries, helped calculate parameters not yet measured experimentally and develop chemical theories (e.g. Ozone depletion). Furthermore, computational chemistry has added to our understanding of bio-chemical process (e.g. enzymatic reaction, photosynthesis, assisted in the design of new drugs and chemical compounds in with specific properties and led to the discovery of structural property-reactivity relationship. (Clark, 1986).

In computational quantum chemistry, the barriers, enthalpies, and rates of a given chemical reaction, together with the geometries of the reactions products and transition structures can be calculated from first principles. It also provides access to useful related quantities such as the electron affinities, radical stabilization energies ionization energies, and singlet-triplet gaps of the reactants and the distribution of electron in a molecule of good structure (Stewart, J. J. P. 1989).

Quantum chemistry is especially useful for studying complex processes, such as free-radical polymerization. In free-radical polymerization, various competitive reactions occur and quantities available for experiment are a complex function of the rate of these individual steps. Computational chemistry is able to solve this problem by providing direct access to the rates and thermochemistry of the individual steps in the process without using such model-based assumptions. Thus computational chemistry provides a valuable tool for studying the mechanisms and kinetics of free-radical polymerization and should be considered as an important addition to experimental methods. Already quantum chemical studies have greatly contributed to our understanding of the kinetics of free radical copolymerization, where they provided direct evidence of the importance of penultimate single effects. It also helped in our understanding of the influence of substituents and chain length on the frequency factor of propagation and transfer reaction (Thiel and Voityuk, 1992).

In principle, these approximations can be extremely accurate, but in practice the most accurate methods require inordinate amounts of computing power, which are exponentially scaled depending on the size of the system. Therefore the task of quantum chemists is to develop small model reaction that can capture the basic chemical properties of the polymerization system. It is also necessary to conduct a thorough evaluation study o determine the appropriate procedures that ensured a reasonable compromise between accuracy and computational expense. However, with recent advances in computational power and the development of improved algorithms, accurate studies using reasonable chemical models of free-radical polymerization are now possible. (Dewar *et al*., 1985)

## 2.6 Overview of Molecular Modelling Techniques in Quantum Mechanics

### 2.6.1 Theoretical Models: Quantum Mechanics

(Castro-Neto, *et al.*, 2009). The name quantum mechanics (QM) originated in nature's tendency for quantization. Light and matter consist of discrete units rather than a continuum, adopting discrete energy levels. Max Planck suggested in the beginning of the last century that the energy of light emitted by a black body was quantized in elements whose energies were determined by the frequency of the light ν multiplied by a constant h: in equation (2.51).

$$E = hv = \frac{hc}{\lambda} \tag{2.51}$$

Although Planck considered the quantization as a mathematical trick, it is now known that light itself can be seen as quantized physical particles (photons). In 1905, Albert Einstein used the photon concept to explain how electrons are ejected from a material when light shines upon it, known as the photoelectric effect. This very early demonstration of the quantum nature of light is related to a phenomenon of great relevance for this thesis: the photovoltaic effect, where electrons rather than being ejected, are excited to higher energy states within the material. The exploitation of this electronic excitation energy is the basis of solar cells. Another early quantum concept of relevance for this thesis is that the electrons orbit around the atomic nuclei in quantized states, so called orbitals, each with a specific associated energy, postulated by (Niels, 1914). The last 20 years witnessed great development in the formulation, interpretation, and unification of quantum mechanical theory, including work of Planck, Einstein, Bohr, Heisenberg, Schrödinger, and many others. Being a completely fundamental theory, quantum mechanics relies on a number of postulates. These are unprovable, basic assumptions to this day have been supported by countless experiments and calculations, thus being apparently valid and certainly highly useful (Clark, 1986).

### 2.6.2 Wave Functions, Operators and Observables

One postulate of quantum mechanics states that any system of particles can be completely described by a wave function Ψ. This function of time and of the positions of each particle is generally complex. Its absolute value squared, $|\Psi|^2$, corresponds at each point in time to the probability distribution function for the particles to be found at these positions. Another postulate states that any observable is associated with an operator. Together, these two postulates imply that by acting with the appropriate operator on a system's wave function, any property of the system can be obtained, including energies, momenta, positions, *etc*. Mathematically, defining the wave function and the operators is often difficult for more complex systems, and solving the resulting equations exactly is impossible for all but the simplest cases (Helgaker, *et al*., 2000).

### 2.6.3 The Schrödinger's Wave Equation

Newton's second law of classical mechanics (f=ma) describes how a classical system evolves in time with some initial conditions. Analogously, the corresponding evolution of a quantum mechanics explains molecules or atoms in terms of interaction among electrons and nuclei while molecular geometry is described in terms of minimum energy arrangements of nuclei (Aktins and Friedman, 1997).In quantum mechanics,the state of a system is a function of the coordinates of particles called the wavefunction Ψ, which changes with time. Therefore, for one particle, one-dimensional system, the wavefunction of the system become: $\Psi = \Psi_{(x,\ t).}$ This wavefunction contains all possible information about the system. Assuming, there is a single particle possessing an electron of mass, m, moving in field of space under the influence of a potential, V. To determine the future state of a system from the knowledge of its first state, an equation that described how the wavefunction changes with time is needed (Griffiths, 2004).

#### 2.6.3(a) Schrödinger's time dependent equation

This form of Schrodinger equation depends on the physical situation. The most general form is the time-dependent Schrodinger equation, which gives a description of a system with time.

$$i\hbar\frac{\partial}{\partial t}\Psi = \hat{H}\Psi \quad (2.52)$$

Where ψ is the wave function of the quantum system, i is the imaginary unit, h is the Plank constant, t is the time and Ĥ is the Hamiltonian operator which characterizes the total energy of any given wave function and takes different forms depending on the situation.( Laloe, 2012).

The most famous example is the non-relativistic Schrodinger equation for a single particle moving in an electric field.

This particle is described by a wave-function $\Psi_{(x,\ t),}$ that satisfies the Schrödinger's time dependent equation (2.19):

$$-\frac{\hbar}{2m}\frac{\delta^2\Psi_{(x,t)}}{\delta x^2} + V_{(x)}\Psi_{(x.t)} = i\hbar\frac{\delta\Psi_{(x,t)}}{\delta t} \quad (2.53)$$

Where $\hbar = \frac{h}{2\pi}$;

h is the Planck's constant; and
$i^2 = -1$.

### 2.6.3(b) Schrödinger's time independent equation

Although, this time dependent Schrödinger's equation may be difficult, but many applications of quantum mechanics to chemistry derive their model from simpler Schrödinger's time-independent equation (2.20):

$$-\frac{\hbar^2}{2m}\frac{\delta^2\Psi_{(x)}}{\delta x^2} + V_{(x)}\Psi_{(x)} = E\Psi_{(x)} \quad (2.54)$$

The generalized Schrödinger's equation for a multi electron and multinuclear system is as shown in equation (2.21):

$$H\Psi = \mathrm{E}\Psi \quad (2.55)$$

H is the “Hamiltonian operator” which describes both kinetic energies of the electrons and nuclei that constitute the molecules, together with the electrostatic interactions felt between the electrons and nuclei. The electrons are negatively charged and nuclei are positively charged, both sides attracting each other. The quantity, E, in the above equation (2.22) is described as the energy of the system; and Ψ is termed the wave-function. The wave-function has no obvious physical meaning but the square of the wave-function multiplied by a small volume gives the probability of finding the system at a particular set of coordinates (McQuarrie, 1983). The expression for H, is given by equation (2.23):

$$H = \frac{1}{2}\sum_{i}^{es} \nabla_i^2 - \frac{1}{2}\sum_{A}^{nu} \frac{1}{M_A} \nabla_i^2 - \sum_{i}^{es} \sum_{A}^{nu} \frac{Z_A}{r_{iA}} + \sum^{e}{}_{i<} \sum_{j}^{e} \frac{1}{r_{ij}} + \sum_{A<}^{n} \sum_{B}^{n} \frac{Z_A Z_B}{R_{AB}} \qquad 2.56$$

Z is called the nuclear charge;

$M_A$ is the ratio of mass of nucleus A to the ratio of mass of an electron;

$R_{AB}$ is the distance between nuclei A and B;

$r_{ij}$ is the distance between nucleus A and electron i.

This equation yields the total energy ‘E’ of the system state; but finding the exact formulations of Ĥ and Ψ can be difficult and solving the equation exactly is impossible for most practically relevant chemical systems. Due to this complexity of the quantum mechanics equations, various approximations and simplifications of the equations are required for all but the simplest chemical systems (Levine, 2000)

### 2.6.4 Born-Oppenheimer Approximation

Formulation of the energy operator, the Hamiltonian Ĥ, varies but in general, it contains at least five contributions:

i. The attractive potential energy between the negatively charged electrons and the positive nuclei;
ii. The repulsive potential energy between nuclei;
iii. The repulsive potential energy between electrons;
iv. The kinetic energy of the electrons; and
v. The kinetic energy of the nuclei.

In reality, solving equation 2.22 must be done under simultaneous consideration of all these factors – an extremely difficult task for most chemical systems (Prasad, 2008). The commonly used Born-Oppenheimer approximation, however, separates the nuclear and electronic contributions, allowing them to be solved consecutively. Essentially, this means that the nuclei are treated classically, which is generally an acceptable approximation since the nuclei are so heavy that their movement is negligible on the time-scale of the electron movements. Thus one way of simplifying the Schrödinger's equation for multinuclei and multelectron systems is by presuming that the motion of nuclei is slow when compared with the motion at which electrons move. The Born–Oppenheimer approximation, which also involves neglecting the 5th term above: the nuclear kinetic energy, greatly reduces the complexity and increases the feasibility of quantum chemical calculations. This leads to an electronic Schrödinger's expression given in (2.24) and (2.25) where the Hamiltonian operator has been collapsed (Burkert and Allinger, 1982).

$$\hat{H}^{ei}\Psi^{ei} = E^{ei}\Psi^{ei} \qquad (2.57)$$

$$\hat{H}^{ei} = -\frac{1}{2}\sum_i^e \nabla_i^2 - \sum_i^e \sum_A^n \frac{Z_A}{r_{iA}} + \sum_{i<}^e \sum_j^e \frac{1}{r_{ij}} \qquad (2.58)$$

The nuclear kinetic energy described in equation (2.23) is missing in equation (2.25) and the nuclear coulumbic term which is constant in equation (2.22) were added to the electronic energy, $E^{ei}$, to give the total energy,E, for the system as shown in equation (2.26):

$$E = E^{ei} + \sum_{A<}^{nuclei} \sum_B^{nuclei} \frac{Z_A Z_B}{R_{AB}} \qquad (2.59)$$

### 2.6.5 Hartree-Fock Models

Hartree-Fock Models continues from electronic Schrödinger equation by introducing two approximations – the Hartree-Fork approximation and the LCAO approximation.

### 2.6.6 Hartree-Fock Approximation

Much of the difficulty in solving the Schrödinger equation stems from the necessity to determine the energy of each electron in the presence of all other electrons simultaneously. However, Hartree-Fock method, avoided this problem by assuming that electrons move independently of each other and these individual electrons are confined to functions called molecular orbitals while the energy of each electron is calculated in the averaged static field of the others. An initially guess is made of the electron energies and the energy of each electron is then calculated in the field of the initial electron configuration (Rappe and Casewit, 1997).

### 2.6.7 Linear Combination of Atomic Orbitals (LCAO) Approximation

The LCAO takes advantage of the notion that the individual one electron solutions for many-electron atoms and molecules will closely resemble the one electron solutions for the hydrogen atom. The predominant way to approximate the total many-electron wave-function Ψ, required to solve the Schrödinger equation 2.23, is by combining a number of atom-centered called basis functions Φ into molecular orbitals ψ:

$$\Psi_i = \sum_{\mu=1}^{Basisfunction} C_{\mu,i}\, \phi_\mu \qquad (2.60)$$

In equation (2.26), c is the coefficient of the molecular orbital, often named molecular orbital. The construction of N molecular orbitals from linear combination of N atomic orbitals (MO-LCAO) is a typical way of obtaining quantitative many-electron wave functions, where various quantum chemical methods are used to determine the optimal coefficients $C_i$. MO-LCAO it is also used frequently for qualitative arguments to rationalize properties of molecules, such as the nature of bond formation, reactivities, orbital hybridizations, etc. This highlights how quantum chemical method can promote a general understanding of chemistry outside the purely computational domain (Cramer, 2004)

### 2.6.8 Electron Correlation Models

Motions of individual electrons are treated as independent of one another in Hartree-fock model by replacing “instantaneous interactions” between individual electrons by interactions between electrons and the average field created by all other electrons. As a result of this, electrons get into each other’s way more than they should, leading to overestimation of the electron-electron repulsion energy and thus, a higher total energy. Electron correlation model takes into consideration the coupling of electron motions and consequently leads to reduction of electron-electron repulsion energy and to a lowering of the total energy (Woodward and Hoffmann, 1970).

### 2.6.9 Semi-Empirical Models

Correlated and Hartree-Fock models are costly in terms of computational time, a disadvantage that informed the introduction of additional approximations to significantly reduce the computational cost while still keeping the fundamental quantum mechanical formalism. This model follows directly from Hartree-Fock models by introducing the following approximations (McQuarrie, 1983).

i. Elimination of overlap between functions on different atoms (“NDDO approximation”). The implication is that atoms do not see each other ‘This is far reaching but reduces the cost computation drastically over HF models.
ii. Restriction to a “minimal valence basis set” of atomic functions. This means the remover of the inner shells functions thereby reducing the time of doing the calculations
iii. Introduction of parameters to reproduce specific experimental data, e.g heat of formation and equilibrium geometries.

### 2.6.10 Density Functional Theory (DFT) Model

Density functional models introduced an approximate explicit correlation term. They are not significantly more costly than HF models in terms of computational time. They describe the electronic states of atoms, molecules and compounds in terms of the three dimensional electronic density of the system.(Assadi and Hanaor, 2013)This is a great simplification over the wavefunction theory which involves a 3N-dimensional antisymmetric wavefunction for a system with N-electrons. The electron density unlike the wave function is a physically observable quantity. This theory was established by Kohn, Sham and Hohenberg, (Jensen, 2007) in in the mid 1960s. It states that "the energy, E, of a system is a functional of the electron density $\rho_{(r)}$ of the system which is expressed as:

$$E = F\left[\rho_{(r)}\right] \tag{2.61}$$

This theory explains further, that the functional is exact and universal, that is, it can be used for any molecular system (Kállay and Gauss, 2004).

Density functional theories are classified according to the type of approximations that are made to the $E_{xc}$, hence the approximation with the lowest level of complexity is called the Local density approximation (LDA) where $E_{xc}$ depends solely on the electron density, $\rho(r)$ at each point in space. The next level of development is the generalized gradient approximation (GGA) where the functional form of $E_{xc}$ rely on the density of the electron $\rho(r)$ and the gradient of the electron density $\nabla\rho(r)$, at each point in space. This includes P86, PW91, B95, PBE and LYP. From the previous GGA functionals, there are combinations between exchange and correlation functional (Clark, 1986). These are made in order to describe the system completely. Some of the most common combinations being BLYP, BP86 and BPW91, the exchange correlation functional ($E_{xc}$) include the exchange energy.

### 2.6.11 Hybrid Functionals

The previous functional types present a problem because the exchange part is poorly described due to the problem of electronic self-interaction. Since the exchange part is exactly defined in Hartree-Fock, an alternative approach would be to mix HF and GGA functionals to describe the exact exchange and correlation part of the hybrid functional. The Hartree-Fock theory provides the exchange energy and includes a part of the Hartree-Fock exchange energy in $E_{xc}$ has been done to improve the functionals by minimizing the artificial self-exchange of the GGA functionals. A famous example of the exchange and correlation combination is the most often used hybrid functional; B3LYP (Christoffersen, 1989; Becke, 1993; Hehre *et al.,* 1986). This functional is a mix between LDA and GGA functionals taken from the DFT and HF methods to a certain extent and is an example of a hybrid-GGA functional. The meta-GGA which includes the spin kinetic energy in the exchange correlation functional in addition to the laplacian of the density of the electron and the gradient, by including the kinetic energy density, the self-correlation is eliminated. Examples of this include M06-L and M06 (Hehre *et al.*, 1986). Density Functional theory is now the preferred method for evaluating the electronic structure of complex chemical systems, because its cost scales more favourably with system size and competes well in accuracy except for very small systems. The theory is also employed in the treatment of compounds containing metals/transition metals because of the additional advantage of static electron correlation.

### 2.6.12 Basis Sets

Basis functions are used to create the atomic orbitals (AO) or molecular orbitals (MO), and they are usually expanded as a linear combination of such functions with the coefficients to be determined. These basis functions can be classified into two main types: *(*Jensen, 2013).

(i) Slater-type orbitals, also called STOs,

(ii) Gaussian-type orbitals, also known as GTOs,

The STOs describe very closely the behaviour of hydrogen atomic orbitals because they have a good exponential decay for bigger values, of spherical coordinates. The GTOs, in contrast, decrease too rapidly for large values of spherical coordinates. Despite this problem, the GTOs are a better compromise due to the fact that the product of two GTOs centered on two different atoms is a third one situated between them. This is not the case for STOs, which are therefore very difficult to handle computationally because the four-centre-two-electron integrals are very time consuming. A number of GTOs can be combined to approximate an STO, and this often proves to be more efficient than using the STO itself. The degree of complexity, and thus precision of a basis set is defined by the number of contracted Gaussian functions (CGF) employed to represent each atomic orbital, the minimum being one contracted Gaussian function to describe a basis function. For example, the STO-3G basis set (where G indicates a combination of contracted Gaussian functions) is formed by a linear combination of three CGF for each basis function so as to resemble an STO. For more precision and better description of the system, two or more functions can be used to describe each type of orbital (Labanowski, and Andzelm, 1991).

The valence electrons are the ones that change most in chemical reactions, so it is most important to have a flexible description of these electrons. Such basis sets, where the core and valence orbitals are treated differently, are called split valence basis sets. Example of the most used split valence basis set is the 6-31G. The nomenclature of this basis set, X-YZG, is:

(i) X represents the number of primitives GTOs used to describe one single contracted Gaussian function of the core.

(ii) Y and Z (more can be added for a better precision) represent the number of primitive GTOs describing the valence orbitals. In the case of 6-31G, it is composed of two functions, one containing three primitives and the other only one.

Additions can be made to the basis sets using polarization functions and/or diffuse functions. Bonding between atoms induces a deformation of the electronic cloud around each atom, called polarization. To allow this, functions with higher angular momentum are added to the basis set. For example, the addition of a p function to H allows polarization. In the same way a d-function can be added to a basis set containing p valence orbitals, f-functions for d-valence orbitals. For more precise results, the polarization functions included can be defined better: for example for a hydrogen atom with 6-31G basis set, p and d polarization functions can be added, the basis set becoming 6-31G(p d). The diffuse functions, represented by a "+" (for example 6-31+G or 6-31++G), describe the part of atomic orbitals distant from the nuclei that can have a very important role when considering anions or diffuse electronic clouds in second or third row transition metals. Another fact to note is that for transition metals, the inner core of these atoms is very large and so the number of basis functions used to describe it would be very big. In order to resolve this problem, those basis functions can be replaced by an Effective Core Potential (ECP) (Seminario and Politzer, 1995).

The ECP will model the effects of the nucleus and the electrons from the inner shell on the valence electrons as an average effect. This allows not only the reduction of big computational calculations, but also it can include some relativistic effects on the system studied because these basis functions are generated from relativistic atomic calculations. The pople basis sets used in this work have a straight forward nomenclature scheme. The notation 6-31G means that 6 primitive gaussians are used for each core orbital and two functions containing three and one primitives are used for each of the valence orbitals. In similar fashion 6-311G means that 6 primitive gaussians are used for each core orbital and three functions containing three, one and one primitives are used for each of the valence orbitals. Most people basis sets start with 6-31G or 6-311G and then extend them by adding diffuse (+) and/or polarization functions.

## 2.7.0 Geometry Optimization

The potential energy hypersurphace (PEH) describes the energy of a molecule relative to its nuclear coordinate. Stationary points are place on the PEH with a zero gradient vector (the first derivative of the energy with respect to nuclear coordinate ). If all the eigenvalues of the Hessian Matrix are positive, the stationary point is a minimum. If there is one and only one negative curvature, the stationary point is a transition state (TS). Points with more than one negative curvature do exist but are not important in chemistry. Since vibrational frequencies are basically the square roots of the curvatures, they have a minimum of all real frequencies, and a saddle point has one Imaginary vibrational frequency. All geometry optimization require on initial guess for which the SCF equation are solved and the energy gradient is calculated (Chatzieleftheriou *et al.,*2016).

The gradient indicate the direction along the PEH where the energy decrease most rapidly from the current point as well as the steepness of that slope .The structure is then varied along the energy gradient , and the process is repeated until the gradient of each nuclear coordinate is zero or, in practice, below a pre-set threshold. At this point the geometry has converged and a stationary point has been obtained that can be characterized by a frequency analysis (Thiel and Voityuk, 1992). There are many different optimization algorithms for finding the set of coordinate corresponding to negative values of the Hessian and decrease energy where there are positive values of the Hessian. A transition structures is a maximum on the reaction pathway and a minimum in all the other coordinates. Transition state is more difficult to describe and find than equilibrium geometries. To verify that the desire Transition state has been optimized, the frequencies must be calculated (Hehre, 2003)

The Vibrational mode associated with the negative frequency should be used to describe the moving forward of reactants in one direction and product in the other direction. If after visualizing this vibrational mode it is still not clear whether the Transition state is correct, an intrinsic reaction coordinate (IRC) calculation should be performed to know if true transition state has being confirmed (Stewart, 1989).

Transition state has been computationally determined for many years. Experimentally, it has only recently become possible to examine reaction mechanisms directly using femto second pulsed laser spectroscopy. This technique cannot yet be applied to all the compound that are computationally accessible, and furthermore, they yield Vibrational information rather than an actual geometry for the Transition state. Usually after a geometry has been optimized at a certain level of theory, the energy of the molecular system is calculated at a higher level that include more electronic correlation computation that do not involve geometry optimization are called single-point calculation (Bahl et al., 2004).

### 2.7.1 Equilibrium Conformation

More than any other factors, single-bond conformation and ring conformation dictate overall molecular size and shape. Thus, proper assignment of ground-state conformation is a very important task or calculation (Li *et al.,* 2016). Equilibrium conformation function find additional equilibrium geometries by moving each atom in fairly large spatial steps and display the most energetically favourable conformation.

This aspect assesses the ability of both mechanics and quantum chemical model to correctly assign the lowest-energy conformational arrangements in flexible molecule as well as account for energy differences between alternative conformers. It also assesses the performances of different models with regard to the calculation of barriers to single- bond rotation and pyramidal inversion. Experimental data on conformational energy different derived mainly from abundance measurement on equilibrium mixtures containing different conformers (Westbrook et al., 2009). The

Obvious difficulty abundant in order to be detected, which in practice means that conformers need to be separated by no more than a few Kcal/mol.

It might be anticipated that computational model would provide good accounts of conformational energy differences and rotation/inversion barriers. Molecular mechanics model in general, and the MMFF molecular mechanics model, in particular, have been specifically parameterized to small organic molecules. Conformational changes are (extreme) example of isodesmic reaction and, aside from semi-empirical model, quantum chemical model might be expected to provide accurate energy differences. However, it need to be recognized that conformational energy differences are typically very small and even small errors might lead to incorrect assignment of lowest-energy conformer (Roger, 1991).

SYBYL molecular mechanics is completely unsatisfactory to describe conformation energy differences in acyclic system, and should not be employed for this purpose. On the other hand, the MMFF mechanics model provides a good account of all systems examined. In fact, the performances of MMFF is significantly better than any of the semi-empirical models, and in the same league as the best of the Hatree-Fock, local density, density functional and MP2 models. Except for system where the differences in energy between the conformer is very small, even the STO-3G Hatree-Fock Model property assigns ground-State conformation. However, conformation at energy differences from STO-3G calculations shows large errors in some cases (Ronald, 1974)

### 2.7.2 Unimolecular Reactions

A unimolecular gas-phase reaction can be regarded as the simplest type of elementary reaction. The theory of such processes is therefore of considerable importance, especially since many aspects of the theory have now been developed to the stage of providing a practical calculation of kinetic behavior from the fundamental properties of the reacting molecules (Truhla *et al.*, 1996).

A unimolecular reaction is in principle the simplest kind of elementary reaction, since it involves the isomerization or decomposition of a single reactant molecule (A) through an activated complex (A*), which involves no other molecule. The experimental study of gas-phase unimolecular reactions is often complicated by the simultaneous occurrence of surface processes or free-radical chain reactions. Most modern theories of unimolecular reaction rates are involving collisional energization of the reactant molecules and more specifically on Hinshelwood development of the original treatment (Baer and Hase, 1996).

The most important theory discussed is the RRKM (Marcus-Rice) theory, which has only been extensively used and tested since 1960. Its practical application raises the difficult question of the evaluation of the necessary vibrational and rotational energy level density and sums and the various procedures for the calculation are described and assessed.

The earlier theories of Lindermann, Hinshelwood, Rice Ramsperger and Kassel as well as Slater's harmonic theory are treated in sufficient depth to provide a basis for the treatment of the RRKM theory and to permit comparison of the various theories to be made.

## 2.8 Basic Theories of Unimolecular Reactions

At the beginning of the twentieth century, many gas-phase reactions were known to be first-order processes and were assumed to be unimolecular, and unimolecular reaction were thought to be first-order under all condition. Many reactions studied then, such as the pyrolysis of simple ketones, aldehydes and ethers have been subsequently found not to be unimolecular processes according to the modern definition but involve free radical chains. Despite this complexity, the early studies of these reactions were important in the development of unimolecular reaction theory (Marcus, 1993).

The focus was on how the reacting molecules acquire the activation energy needed for reaction to take place. It may be difficult to see how first-order processes could result if molecules were energized by bimolecular collisions, which would be expected to be second-order processes.

In 1919, Perrin therefore proposed the radiation hypothesis in which molecules were supposed to acquire energy by the absorption of infrared radiation from the walls of the reaction vessel. The rate constant (k) for a first-order reaction would then be given by the equation in which (v) is the frequency of the radiation absorbed.

$$K = constant\ x\ exp^{\left(-hv/_{kT}\right)} \tag{2.62}$$

In addition, experimental evidence was rapidly accumulated to show that infrared radiation is generally ineffective photochemically and indeed many molecules does not absorb in the frequency region implied by the above equation and the observed rate-constant. These facts led to the abandonment of the radiation theory and its replacement by theories in which molecular collision were involved as the means of providing the activation energy.

In the theory of Christiansen and Kramer's and overall first-order collisional energization, by supposing that product molecules were provided with an excess of energy, which could be used to re-energize reactant molecules. This theory proved to be unsatisfactory in two major respects. Firstly, most unimolecular reactions are endothermic rather than exothermic processes and so product molecules are not formed with sufficient internal energy to energize more reactant molecules. Secondly, inert gases would be expected to remove the excess energy of the product molecules and hence to reduce the overall rate or the reaction. In practice it is found that inert gases often increase the rate of unimolecular reaction. The disadvantages of earlier theories were overcome by the theory of Lindermann. The importance of molecular collision in the energization process was finally established when it was found that the first-order rate-constant for unimolecular reaction is not a true constant but does decline at low pressure.

The earlier theories of Lindermann, Hinshelwood, Rice, Ramsperger and Kassel, as well as Slater's harmonic theory are treated in sufficient depth to provide a basis for the treatment of the RRKM theory and to permit comparison of the various theories to be made.

### 2.8.1 Lindemann / Lindemann-Hinshelwood Theory

This is the simplest theory of unimolecular reaction rates, and was the first to successfully explain the observed first-order kinetics of many unimolecular reactions. The proposed mechanism actually consists of a second-order bimolecular collisional activation step, followed by a rate-determining unimolecular step (Baer and Hase, 1996).

$$A + M \, \frac{K_1}{K_{-1}} \, A^* + M \tag{2.63}$$

$$A^* \overset{K_2}{\rightarrow} P \tag{2.64}$$

Applying the steady-state approximation to the concentration of A* gives

$$[A^*] = \frac{K_1[A][M]}{K_1[M] + K_2} \tag{2.65}$$

So that the overall rate is

$$\frac{d[P]}{dT} = K_2[A^*] = \frac{K_1K_2[A][M]}{K_1[M] + K_2} \tag{2.66}$$

This is often written as

$$\frac{d[P]}{dT} = K_{eff}[A] \tag{2.67}$$

Where

$$K_{eff}[A] = \frac{K_1K_2[A][M]}{K_{-1}[M] + K_2} \tag{2.68}$$

is an effective first-order rate constant. **$k_{eff}$** is, of course, a function of pressure. At high pressures, collisional deactivation of A* is more likely than unimolecular reaction, **$k_{eff}$** reduces to **$k_1k_2/k_{-1}$** and the reaction is truly first order in **A**. At low pressures, bimolecular excitation is the rate determining step; once Formed **A*** is more likely to react than be collisionally deactivated. The rate constant reduces to **$k_{eff}$ = $k_1$[M]** and the reaction is second order.

### 2.8.2 Lindeman Theory breaks down for two main reasons:

I. The bimolecular step takes no account of the energy dependence of activation; the internal degrees of freedom of the molecule are completely neglected, and the theory consequently underestimates the rate of activation.

II. The unimolecular step fails to take into account that a unimolecular reaction specifically involves one particular form of molecular motion (e.g. rotation around a double bond for cis-trans isomerization).

Subsequent theories of unimolecular reactions have attempted to address these problems. Hinshelwood theory offers a solution to problem.

### 2.8.3 The Hinshelwood Modification

The failure of Lindermann theory in its simple form has been illustrated by the calculation of transition pressure $P_{1/2}$ which are much too high to agree with experiment. Hinshelwood developed a suggestion of Lindeman's that a more realistic model would be obtained by assuming that the required energy could be drawn in part from the internal degrees of freedom (mainly vibrational) of the reactant molecule. (Harold *et al.*, 1982)

Hinshelwood modeled the internal modes of (A) by a hypothetical molecule having (S) equivalent simple harmonic oscillators of frequency (V) and using statistical methods to determine the probability of the molecule being collisionally activated to a reactivated to a reactive state. Hinshelwwod developed a suggestion of Lindermann's that a more realistic model would be obtained by assuming that the required energy could be drawn in part from the internal degrees of freedom (mainly vibrational) of the reactant molecule.

The rate constant $K_1$ in the modified Hinshelwood – Lindermann theory is therefore given as

$$K_1 = \frac{Z_1}{(S^{-1})} \left[\frac{E_O}{kT}\right]^{S^{-1}} exp^{(-E_O/KT)} \tag{2.69}$$

which even for moderate values of S lead to much bigger values of $K^1$ than that of Lindeman's theory.

Hinshelwood now made the strong collision assumption. He assumed that the probability of deactivation of A* in any given collision is unity, so that the rate constant $^{K}1$of the Lindermann mechanism is equal to the collision frequency Z. Because the collisions promote equilibrium, the probability of forming a state V in a collision is given by the Boltzmann distribution. The rate constant for activation to state V is therefore given by (Griffiths and Nilson, 2010).

$$K_1^V = Z\,\frac{g_V\, e^{-vh/kT}}{q} \qquad (2.70)$$

The total rate of activation is found by integrating dk, over all energies greater than the critical energy.

$$K_1 = \frac{Z_1}{(S^{-1})}\left[\frac{E_0}{kT}\right]^{S^{-1}} exp^{(-E_0/KT)} \qquad (2.71)$$

This differ from the simple collision theory rate constant,

$$K_1 = Z\, exp^{(-E_0/KT)} \qquad (2.72)$$

by a factor of,

$$1/(S^{-1})\; exp^{(-E_0/KT)} \qquad (2.73)$$

Leading to an increased pronounced for large molecules, which have more oscillators and is exactly what is required to overcome the first failure of the Lindermann theory.

## 2.8.4 Rice – Ramsperger – Kasher (RRK) Theory

The Rice – Ramsperger – Kasher Theories (RRK) uses the basis Hinshelwood - Lindermann mechanism of collisional energization, but considers more realistically that the rate of conversion of an energized molecule to product is a function of its energy content (Schranz *et al.*,1982).

RRK theory can be addressed by recognizing that a minimum amount of energy must be localized in specific model of molecular motion in order for the unimolecular step to take place. A new step is added to the Lindeman mechanism in which the generally excited molecule A* is converted into the specific excited activated complex $A^{++}$ (Yao *et al.*, 2008).

$$A^{++} \xrightarrow{K_{2a}} A^{++} \xrightarrow{K^{++}} P \qquad (2.74)$$

$K^{++}$ is at the order of a vibrational frequency and $k_{2a}$ is generally much smaller. This means that Conversion of A* to $A^{++}$is rate determining and $k_{2a}A^*$ to products.

Because $k_{2a} << k^{++}$ $[A^{++}]$ is very small and small and we can use the steady state approximation to find $k_{2a}$ giving

$$K_{2a} = K^{+} \frac{[K]^{++}}{A^{*}} \tag{2.75}$$

RRK theory assumes that energy can flow one vibrational mode to another with the molecule (this is fairly reasonable assumption, since molecular vibrations are highly an harmonic at chemical energies and are therefore coupled).

### 2.8.5 RRKM (Marcus-Rice) Theory

The theory presented was developed essentially by R.A. Marcus from an earlier paper by Marcus and O.K. Rice and is known by the names of these authors or very often by the initial RRKM. Based on the result of the Hinshelwood and RRK theory, the reaction mechanism be re-written to take account of the fact that the rates of the collisional activation and unimolecular dissociation are energy dependent **(**Jacox, 1984).

In RRKM theory, the energy of the molecule is the only non fixed component can flow freely around the various model of motion of the molecule can contribute to reaction. In the high-pressure limit, RRKM theory reduces to transition state theory. In the general case, RRKM theory admits equilibrium between A* and $A^{++}$is in thermal equilibrium with the reactants. This is equivalent to assuming that the thermal Boltzmann distribution is maintained at all energies, which is true at sufficiently high pressure the RRKM model becomes the same as the transition state theory model and the results of the two theories coincide (Gu *et al.,* 2010).

$$A + M \frac{\partial K_2(E)}{K_1} A^*(E) + M \tag{2.76}$$

$$A^{*}(E)\xrightarrow{K_2(E)}P \qquad (2.77)$$

Applying the steady state approximation to (A*[E]) lead to the rate expression.

$$\frac{\partial[P(E)]}{\partial t}=\frac{K(E)\partial K_1(A)(M)}{K_1(M)+K_2(E)} \qquad (2.78)$$

From which we can identify the unimolecular rate coefficient for the energy range from E to E+ dE as

$$K[E]=\frac{K_2(E)\partial K_1(A)(M)}{K_1(M)+K_2(E)} \qquad (2.79)$$

The thermal rate coefficient is obtained by integrating over E from $E_o$ to ∞

$$K=\int\frac{K_2(E)\partial K_1(A)(M)}{K_1(M)+K_2(E)}=\int\frac{K_2(E)\partial K_1(A)(M)}{K_1(1+K_2(E)/K_1(M)} \qquad (2.80)$$

In RRKM theory, the energy of the molecule is partitioned into fixed and non-fixed components. Only the non-fixed component E*, which can flow freely around the various modes of motion of the molecule, can contribute to reaction. The various terms of the rate expression are now evaluated using statistical mechanics.

I. dk1(E*)/k-1is the equilibrium constant for energization of the A molecules into the energy range E* to E*+dE***,** and can be calculated from the partition function ratio dA*(E*)/dA.

II. $k_2$(E*) is obtained by applying the steady state treatment to the activated complex A‡ as in RRK theory, with the modification that the overall reaction is broken down into energy contributions from translation and from rotation/vibration. The rate constant $k^{\ddagger}$ and ratio of concentrations [A‡]/[A*] are evaluated using partition functions ($k^{\ddagger}$ is treated as a translation along the reaction coordinate).

In the high pressure limit, RRKM theory reduces to transition state theory. In the general case, RRKM theory admits equilibrium between A* and $A^{\ddagger}$, but not between A* and A. However, at high pressures A* and A are also in equilibrium.

Transition state theory assumes that the activated complex $A^{\ddagger}$ is in thermal equilibrium with the reactants. This is equivalent to assuming that the thermal Boltzmann distribution is maintained at all energies, which is true at sufficiently high pressures P at high pressures the RRKM model becomes the same as the transition state theory model, and the results of the two theories coincide.

### 2.8.6 The Slater’s Theory

The theory of Slater first put forward in 1939 was the first serious attempt to relate the kinetics of unimolecular reactions to our knowledge of molecular vibration (Slater, 1930).

The theory accepts the basic Hinshelwood–Lindermann mechanism of collisional energization with a more restricted definition of the energized molecule. The molecule undergoing a reaction is pictured as an assembly of harmonic oscillation of particular amplitude and phases. Reaction is said to occur when a chosen coordinate in the molecule attains a critical extension. In order to understand more fully the derivation of these equations and the assumption involved, it is necessary to consider the vibrational analysis of polyatomic molecules. Vibrational analysis is most often used in order to determine the normal mode frequencies $V_k$ for a molecule. For the application of Slater theory, we are more interested in the form of the normal mode vibration and the way in which they influence the behavior of a particular internal coordinate with time.(Robinett, 2006)

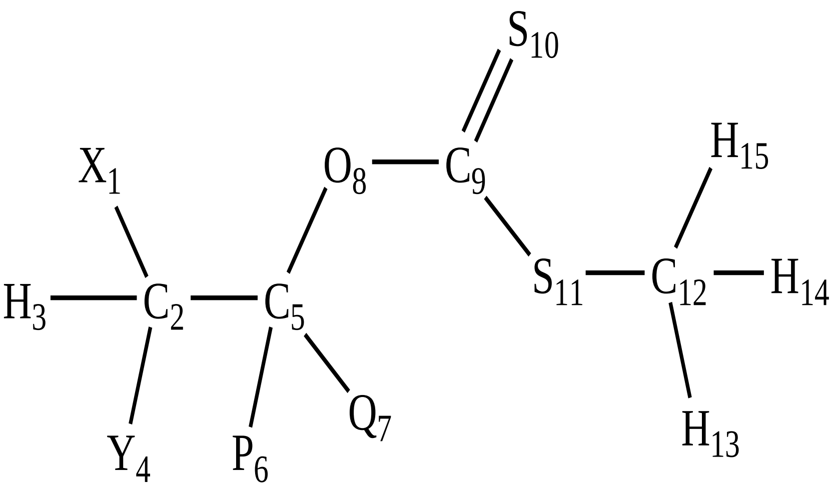
# CHAPTER THREE

## 3.0 Computational methods.

All calculations were performed using the Spartan’10 software package. The geometrical parameters for all reactants, transition states and the product of the studied reactions were fully optimized using the *ab initio* analytic gradient in the method of the density functional theory (DFT) with B3LYP Functional and 6-311++G** basis sets. The obtained data were used to estimate the Arrhenius and thermodynamics parameters such as change in enthalpy of activation $\Delta H^*$, entropy change of activation ($\Delta S^*$), Gibbs free energy of Activation ($\Delta G^*$), pre-exponential factor (A), Activation Energy (Ea) and rate constant (k). The following calculation procedures were performed, Conformational Search, Geometric Optimization, Reaction Path Study, Location of Transition State, Characterizing the Transition State, Calculation of Thermodynamics Parameters and Calculation Using Wiberg bond indices (Muyano, *et al.,* 1989, and Velez *et al.,* 2008)

## 3.1 Geometry definition

In Figure 3.1, the β-Hydrogen atom to be eliminated from the alkyl group is labeled $H_3$. P, Q, X and Y are the substituents which depend on the substrate being considered. For instance: in O-ethyl S-ethyl dithiocarbonates P, Q, X, Y will be hydrogen atom. In O-npropyl S-methyl dithiocarbonates P, Q, X will be hydrogen (H) and Y will be methyl group ($CH_3$). In O-nbutyl S-methyl dithiocarbonates P, Q and Y will be hydrogen (H) and X will be ethyl group ($-CH_2CH_3$). In O-ibutyl S-methyl dithiocarbonates P, Q, will be hydrogen (H) and X, Y will be methyl group ($CH_3$). In O-ipropyl S-methyl dithiocarbonates P, X, Y will be hydrogen (H) and Q will be methyl group ($CH_3$). In O-tbutyl S-methyl dithiocarbonates, X, Y will be hydrogen, P,Q be methyl group ($CH_3$).



O-ethyl S-methyl Xanthate

**Figure 3.1 Structure of O-alkyl S-methyl Xanthates**

P, Q, X and Y varies depending on the compound concerns;

Ethyl Xanthate P, Q, X and Y are Hydrogen

n-propyl, P, Q, X are hydrogen while Y is methyl group

i-propyl P, X and Y are hydrogen while Q is a methyl group

n-butyl, Y is ethyl and P, Q and X are hydrogen

i-butyl Q and X are methyl group, P and Y are Hydrogen

t-butyl P,Q and X are Methyl group while Y is Hydrogen.

## 3.2 Conformational search.

Conformational search for the studied molecules was performed in order to determine the structure with the lowest energy. In this way additional equilibrium geometries is found by moving each atom into fairly large spatial steps, displaying the most energetic favourable conformation and possibly, displaying a list of all conformers. The molecules were set up on the work sheet of the Spartan 10 version of the software, conformational calculation was done using molecular mechanics force field (MMFF) which is quite successful in awarding low energy conformers in providing quantitative estimates of conformational energy differences (Hehre, 2003). The lowest energy conformer is the most stable.

## 3.3 Geometry optimization

Geometry optimization was performed on the most favourable conformers of the compounds (O-ethyl S- methyl xanthates, O-npropyl S-methyl xanthates, O-isopropyl S-methyl xanthate, O-nbutyl S-methyl xanthate, O-ibutyl S-methyl xanthates, O-tbutyl S-methyl xanthates) as shown in Figure 3.1, to obtain the bond length, bond angle, dihedral angle, electronic charge distribution and other parameters of the ground state, transition state and products.

## 3.4 Reaction path study

Reaction path calculation were carried out on the optimized geometry of each of the alkyl Xanthates (O-ethyl S-methyl Xanthates, O-npropyl S-methyl Xanthates, O-isopropyl, S-methyl Xanthate, O-nbutyl, S-methyl xanthate, O-ibutyl S-methyl Xanthates, O-tbutyl, S-methyl Xanthates) under studied, using $H_3$-$S_{10}$ as their reaction coordinate. The internal coordinate was varied systematically by very small steps from the initial distance in the stable reactants form to its value in the product formed (Adejoro and Bamkole, 2005). For example, initially, distance between $H_1$ and $S_{10}$ in O-ethyl, S-methyl xanthate was 4.80 Angstroms, this inter atomic distance is slowly changed by calculating the reaction path taking the value from the initial value of 4.80 to 1.20Å, to its approximate value in the stable product form in 20 steps.

As reported by (Mclever and Kormonicki, 1971) and (Adejoro et al., 2017), in their previous work, instead of energy passing smoothly to the maximum, it increases to a very high value and the geometry suddenly fell to the product as shown in Figure 3.5 with a decrease in the heat of formation with values approximately equal to the amount of expected products (Methyl dithiocarbonates and Ethylene).

### 3.5 Transition state structures

Potential energy surface gives the basis to the understanding of the relationship between molecular structure and stability of a molecule. Molecules that are stable correspond to minimum energy along the reaction coordinate. Transition states correspond to the maximum energy. The problem is that it is impossible to build a diagram that cannot be visualized. However, the principle is that stable molecules with minimum energy will be interconnected by smooth path that pass through a well defined transition state.

The proposed transition state mechanism of the studied structures were determined by activating the guess-transition state icon in Spartan software and the proposed transition state structures were latter optimized and subjected to the following tests that verify that the practical geometry of the corresponding transition state structure connects the reactants and products. The tests are:

(i). That the Hessian matrix of second energy derivation with respect to coordinates give only one imaginary frequency ranging from 400-2000cm and the normal coordinates corresponds to the imaginary frequency that smoothly connect the reactants and the product.

(ii). The Intrinsic Reaction Coordinate (IRC) method by optimizing the studied molecules subject to a fixed position along the reaction coordinates (Hehre, 2003).

## 3.6 Intrinsic reaction coordinate

The transition state was confirmed using intrinsic reaction coordinate method (Hehre, 2003) calculated in two ways. In the first calculation, a positive perturbation was carried out using initial perturbation on the atomic coordinates in the direction of the single negative frequency while the other calculation, a negative perturbation was carried out along the same normal coordinates.

## 3.7.0 Kinetics and thermodynamics parameters calculations

The thermodynamic parameters were obtained for the studied molecules by simple calculation on the ground state (GS), Transition state (TS) and the product state (PROD) as follows.

### 3.7.1 Heat of reaction $\Delta H_{rxn}$

The enthalpy calculated using computational method is solely base 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, the ground state energy GSE can be calculated using quantum mechanics. The overall energy of the molecules or total enthalpy can be calculated as the sum of the enthalpy and the ground state energy. Thus the value of the heat of reaction can be calculated as the difference between the product and reactant overall energies (www.engin.umich.edu/cre/ webmod/quatum/topic03.htm). With this modification, the equation for the heat of reaction (The enthalpy of a species ) is given as:

$$H_i = GSE_i + H_i^{sm} \qquad (4.1)$$

Where the superscript “sm” is the statistical mechanically calculated enthalpy.

If equation 4.1 is substituted into the initial definition of the heat of reaction we have:

$$\Delta H_{rxn} = (GSE_{product} + H^{sm}_{product}) - (GSE_{reactant} + H^{sm}_{reactant}) \qquad (4.2)$$

The enthalpy of reaction was calculated at 629K.

### 3.7.2 Change in entropy of reaction (ΔS).

The change in entropy of the reaction was calculated by taking the difference between the product and the reactant entropies as shown in equation 4.3

$$\Delta S_{reaction} = S_{product} - S_{reactant} \qquad (4.3a)$$

And

$$\Delta S \text{ activated} = S_{transition} - S_{reactant} \qquad (4.3b)$$

### 3.7.3 Gibbs Free Energy (ΔG).

The Gibbs free energy was calculated using the heat of reaction equation in equation 4.1. Knowing that

$$G = H – TS$$

and

$$\Delta G = \Delta H^* - T\,\Delta S \qquad (4.4)$$

$$\boldsymbol{\Delta G_{R\times n} = G_{product} - G_{Reactant}}$$

Also Gibbs free energy was calculated

$$\Delta G_{Reaction} = (H_{product} - TS_{product}) - (H_{Reactant} - TS_{Reactant}) \qquad (4.5)$$

Where enthalpy has to be defined using the GSE and the statistical mechanically calculated enthalpy.

$$\Delta G_{R\times n} = [\, GSE_{Products} + H_{Products} - TS_{Products}] - [\, GSE_{Reactants} + H_{Reactants} - TS_{Reactant}]. \qquad (4.6)$$

### 3.7.4 Arrhenius rate constant (k)

The first order coefficient K(T) was calculated using transition State Theory (TST) (Benson and O' Neal, 1970) provided that the transmission coefficient is the same as in the following equation where G* is the Gibbs free energy change between the reactant and the transition State and K is the Boltzmann while h is the Planck Constant, respectively

$$K(T) = \frac{K_B T}{h} exp\left[\frac{-\Delta G^*}{RT}\right] \quad (4.7)$$

in addition, Arrhenius rate constant (k) was calculated using the equation (4.8), where A represent pre- exponential factor, Ea represent the activation energy, R is the gas constant and T is the temperature (Wright, 2004)

$$k = A\exp^{\frac{-Ea}{RT}} \quad (4.8)$$

### 3.7.5 Activation energy (Ea)

The activation energy was calculated in accordance with the theory of transition state for a unimolecular reaction at 629K (Bamkole, 2006). In addition, the difference of the transition state enthalpy and the reactant enthalpy with the enthalpy being defined as the sum of the ground state energy and the statistical mechanically calculated enthalpy are given below.

$$Ea = \Delta H + RT \quad (4.9)$$

$$\Delta H^{\updownarrow} = E_a = H_{transition} - H_{reactant}$$

$$Ea = [GSE_{transition} + H_{transition}] – [GSE_{reactant} + H_{reactant}] \quad (4.10)$$

### 3.7.6 Pre-exponential factor. (A)

The pre-exponential factor **A** was calculated using the equation below:

$$A = \frac{K_B T}{h}\exp^{\frac{-\Delta S^*}{R}} \quad (4.11)$$

$$\mathbf{\Delta S^* = S_{transiton} - S_{reactant}}$$

Where $K_{B} =$ Boltzmann constant J/k, T = Temperature at 623k,

h = plank constant in J/S, $\Delta S^{\updownarrow}$ = Activated Entropy change between transition state and reactant in J/mol, R = Gas constant in J/mol/k.

## 3.8 Calculation using Wiberg bond indices.

The relative variation of the bond indices at the reactant, transition state and the product ( $\partial$ Bi) for every bond, i involved in a chemical reaction is defined as: ( Moyano *et al.*, 1989),

$$\partial B_i = \frac{\left(B_i^{Ts} - B_i^R\right)}{\left(B_i^p - B_i^R\right)} \qquad 4.12$$

The superscript R, TS and P refers to reactants, transition states and products respectively.

From the bond order, the percentage of evolution of the bond order %Ev was also calculated through the chemical step (Domingo *et al.*, 1999) as shown in equation 4.13

$$\%EV = 100\partial B_i \qquad 4.13$$

The average value of the bond indices δBav is calculated as

$$\partial Bav = \frac{1}{n}\sum \partial B_i \qquad 4.14$$

the value of (n) is the number of bonds included at the reaction coordinates which gives the extent of progressiveness and advancement of the transition state structure along the reaction path way.

The synchronicity, Sy of a chemical reaction was calculated as follows,

$$Sy = 1 - A \qquad 4.15$$

Where A is the asynchronicity which calculated as: (Moyano *et al.*, 1989).

$$A = \frac{1}{(2n-2)}\sum \frac{/\partial B_i - \partial B_{av}/}{\partial B_{av}} \qquad 4.16$$

# CHAPTER FOUR

## 4.0 RESULTS AND DISCUSSION

### 4.1 Conformational search

Conformational search was performed on the molecule in order to detect the structure with the lowest energy. Figure 4.1 -4.6 shows the conformer structures of each of the studied molecules and Table 4.1 shows the numbers of conformers and stable conformers with their corresponding energy values of O-alkyl S-Methyl Xanthates. The result indicated that O-ethyl S-methyl Xanthate, O-npropyl S-methyl Xanthate, O-ipropyl S-methyl Xanthate, O-nbutyl S-methyl Xanthate, O-isobutyl S-methyl Xanthate and O-tbutyl S-methyl Xanthate have 5, 12, 7, 31, 10 and 4 conformers with the most stable conformer having energy of -48.389, -46.339, -33.608, -50.926, -31.19 and 16.06 kJ/mol respectively.

### 4.2 Reaction path study

Reaction path studies were carried out on the optimized geometry of each of the O-alkyl S-methyl under study using H–S from O-ethyl S-Methyl dithiocarbonates as the reaction coordinate. Figure 4.9 shows that the energy rose to a very high value and suddenly drop to a product instead of passing smoothly through a maximum. A decrease in heat of formation which is approximately equal to the sum of heat of formation of the products expected produced (ethylene and methyldiocarbonate) were observed. These results are consistent with the work of Mclever and koromiko (1971), Adejoro and Bamkole (2005) and Adeboye (2013).

**Table 4.1.** Numbers of conformers and stable conformers with their corresponding Energy values of O-alkyl S-Methyl Dithiocarbonates

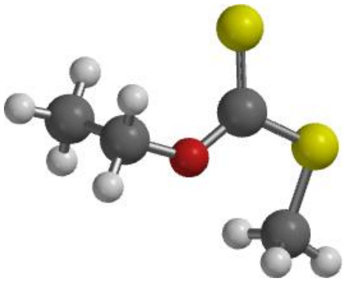
| COMPOUND | NO. OF CONFORMERS | STABLE CONFORMERS (kJ/mol) |
|---|---|---|
| O-ethyl S-methyl Xanthate | 5 | -48.389 |
| O-npropylS-methyl Xanthate | 12 | -46.339 |
| O-ipropyl S-methyl Xanthate | 7 | -33.608 |
| O-nbutyl S-methyl Xanthate | 30 | -50.926 |
| O-isobutylS-methyl Xanthate | 10 | -31.190 |
| O-tbutyl S-methyl Xanthate | 4 | 16.061 |

Energy (A) = -48.389kJ/mol

Energy(B ) = -44.778kJ/mol

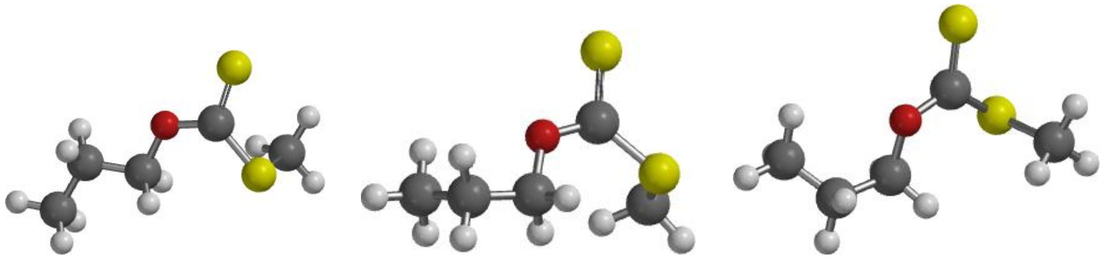
Energy(C)  = -44.000kJ/mol

Energy(D =) -44.306kJ/mol

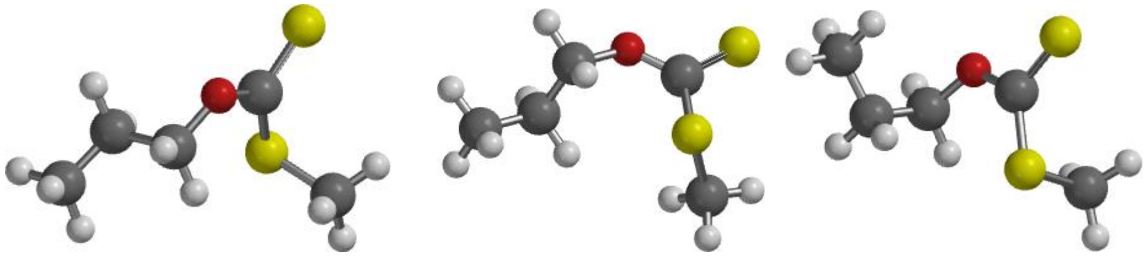


Energy (E)=  -39.506kJ/mol

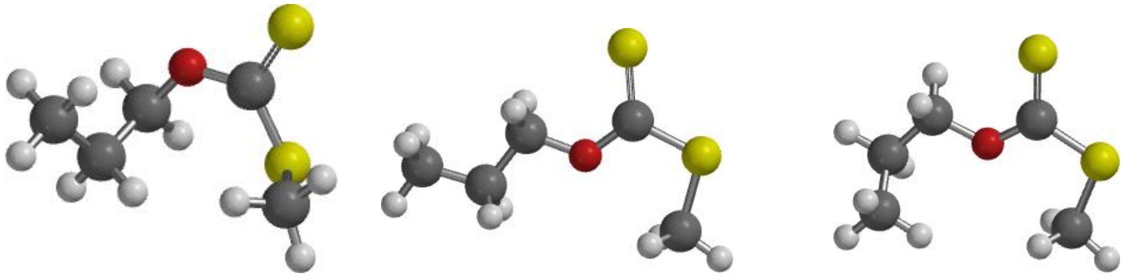
**Figure 4.1.** Conformers distribution of O-ethyl S-methyl xanthates with their corresponding energy values.



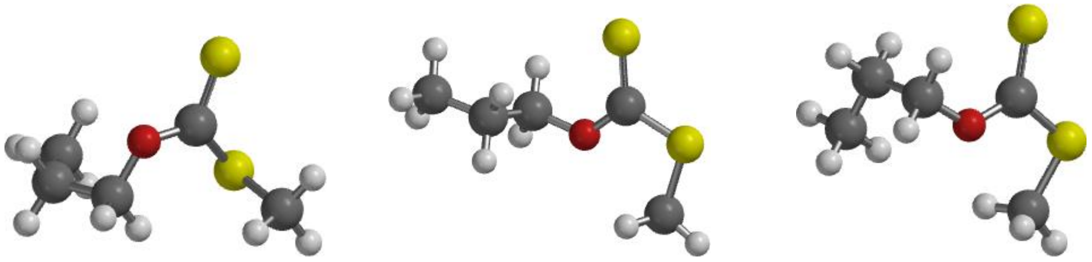
Energy(A) = -46.339kJ/mol Energy (B) = -46.238kJ/mol Energy(C) = -45.955kJ/mol



Energy(D)= -41.382kJ/mol Energy (E) = -49.950kJ/mol Energy (F) =-49.185kJ/mol

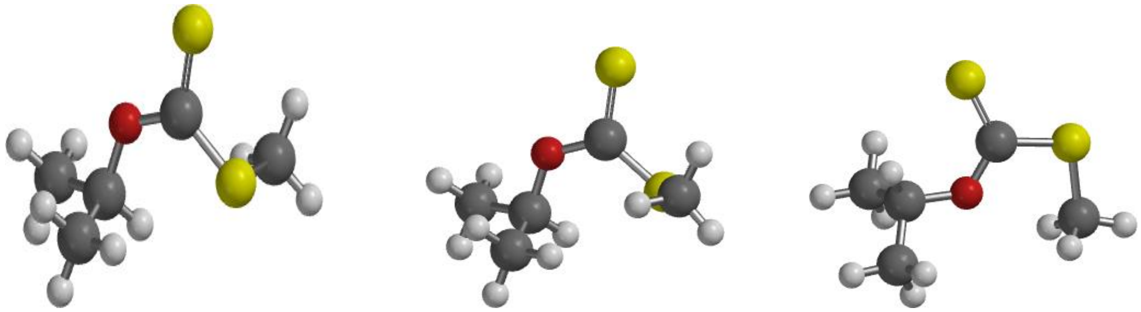


Energy (G)= -46.000kJ/mol Energy (H) = -45.490kJ/mol Energy (I) = -45.490kJ/mol



Energy (J) = -41.080kJ/mol Energy (K)= -41.902kJ/mol Energy(L) = -49.158kJ/mol

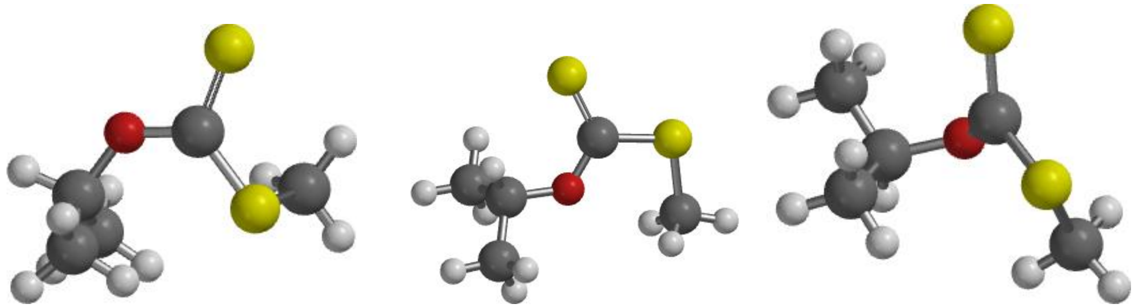
**Figure. 4.2:** Conformers distribution of O-npropyl S-methyl Xanthates with their corresponding energy values



Energy A = -33.608kJ/mol

Energy B = -33.608kJ/mol

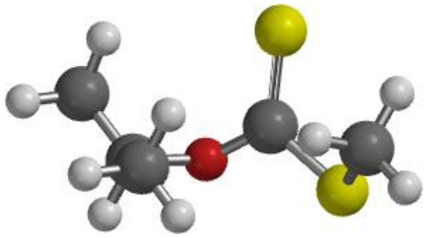
Energy C = -29.527kJ/mol



Energy D = -14.928kJ/mol

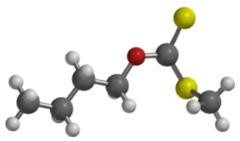
Energy E = -2.150kJ/mol

Energy F = 7.119kJ/mol

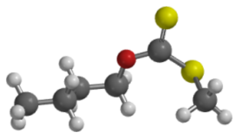


Energy G = -7.735kJ/mol

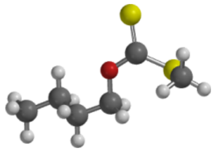
**Figure. 4.3:** Conformer distribution of O-isopropyl S-methyl Xanthates with their corresponding energy values



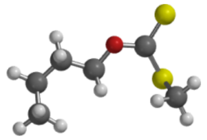
Energy 1 = -50.926kJ/mol



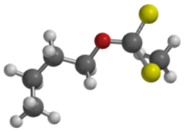
Energy 2= -50.067 kJ/mol



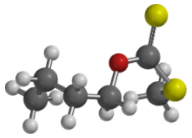
Energy 3 = -50.067 kJ/mol



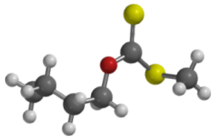
Energy 4 =  -46.982 kJ/mol



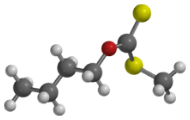
Energy 5= -44.455 kJ/mol



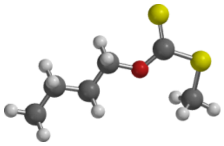
Energy 6= -47.685 kJ/mol



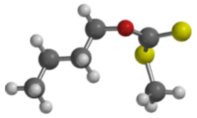
Energy 7= -39.526 kJ/mol



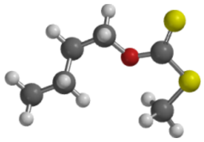
Energy 8 = -40.801 kJ/mol



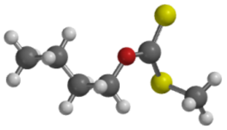
Energy 9 = -43.931 kJ/mol



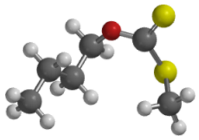
Energy10 = -43.749 kJ/mol



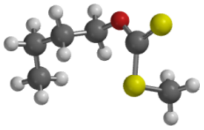
Energy 11 = -47.470 kJ/mol



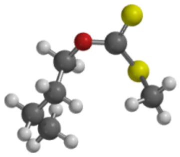
Energy 12= -47.947 kJ/mol



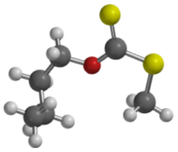
Energy13 = -44.470 kJ/mol



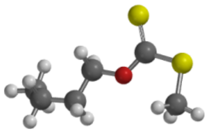
Energy 14= -47.895 kJ/mol



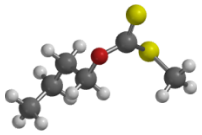
Energy 15= -47.947 kJ/mol



Energy 16 = -47.580 kJ/mol

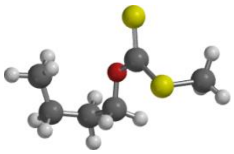


Energy 17= -43.749 kJ/mol

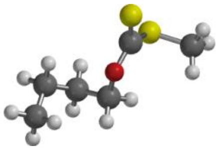


Energy 18= -40.066 kJ/mol

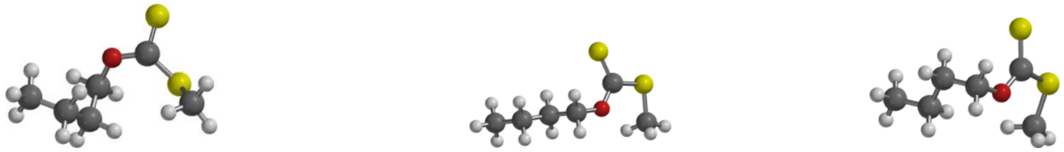
Energy 19 = -40.078 kJ/mol



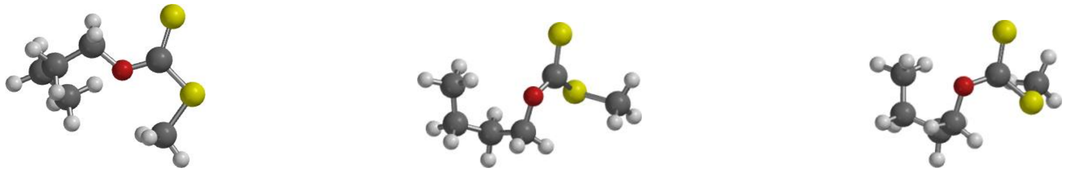
Energy 20= -47.455 kJ/mol



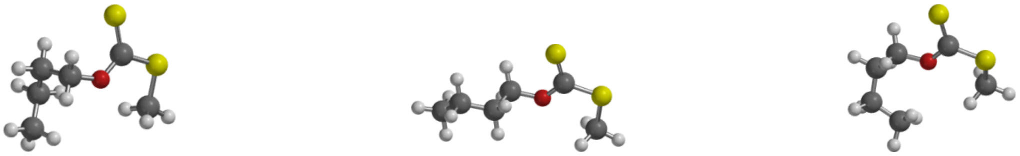
Energy21 = -47.470 kJ/mol



Energy 22= -43.580 kJ/mol Energy 23= -46.452 kJ/mol Energy 24= -47.345 kJ/mol

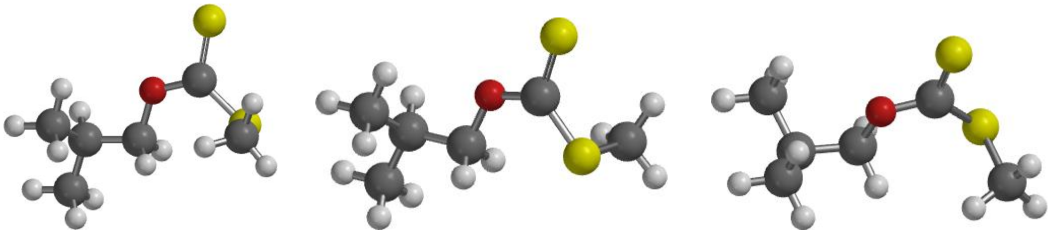


Energy 25= -42.913 kJ/mol Energy26= -46.452 kJ/mol Energy 27= -46.521 kJ/mol

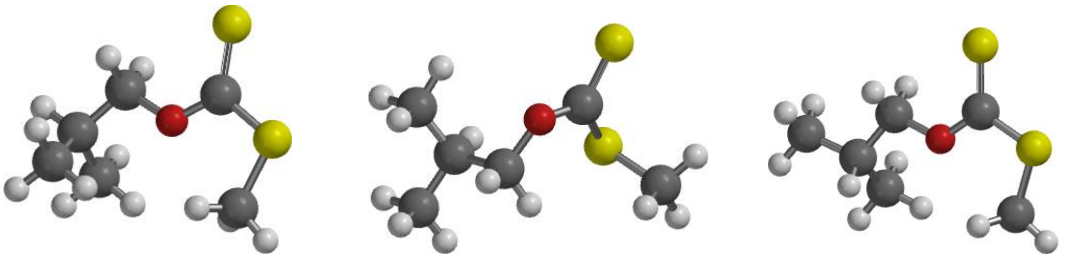


Energy28 = -43.580 kJ/mol Energy 29= -44.947kJ/mol Energy 30= -44.284kJ/mol

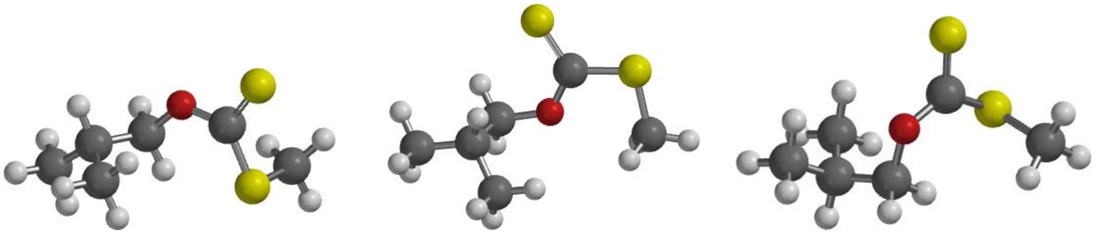
**Figure. 4.4:** Conformers distribution of O-nbutyl S-methyl Xanthates with their corresponding energy values



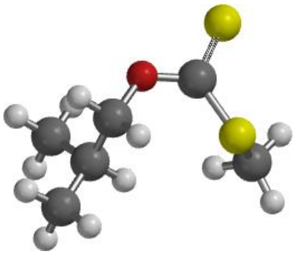
Energy = (A)-31.190kJ/mol Energy = (B)-27.999kJ/mol Energy = (C)-31.165kJ/mol



Energy D = -23.530kJ/mol EnergyE =-28.014kJ/mol Energy F = -27.845kJ/mol



Energy G = -23.779kJ/mol Energy H =- -30.887kJ/mol Energy I = -28.145kJ/mol

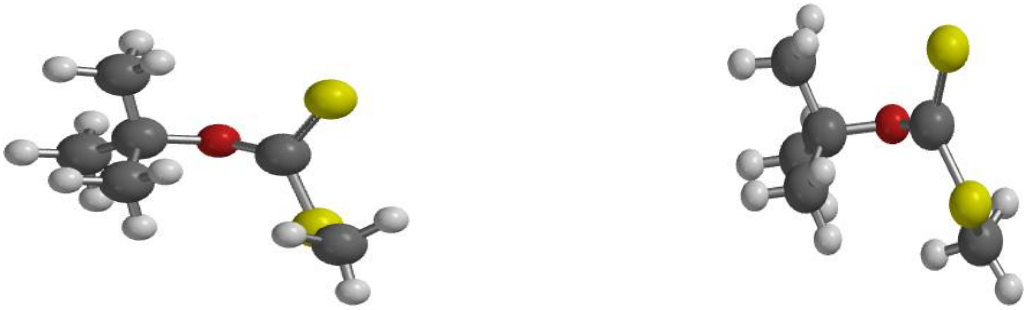


Energy J = -23.485kJ/mol

**Figure. 4.5:** Conformers distribution of O-ibutyl S-methyl Xanthates with their corresponding energy values

Energy (A)= 16.061kJ/mol

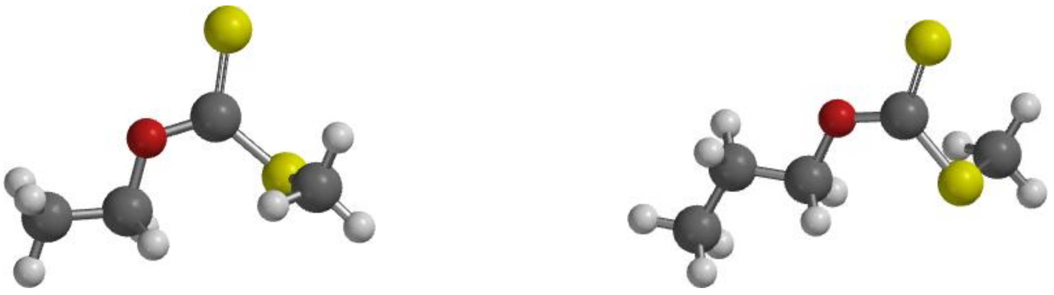
Energy (B)= 37.373kJ/mol



Energy (C) = 27.722kJ/mol ,

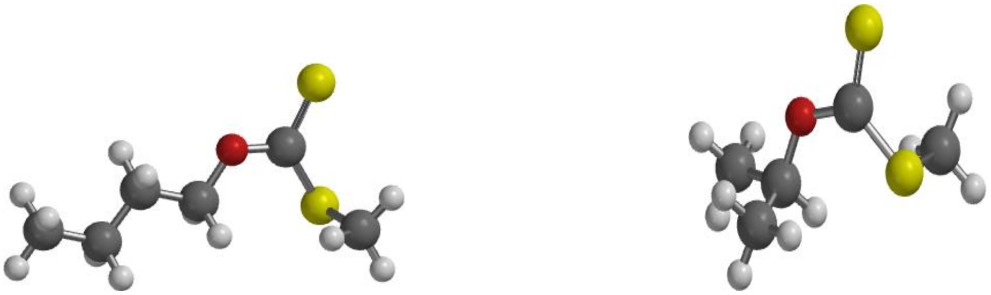
Energy (D)= 37.373kJ/mol

**Figure. 4.6:** Conformers distribution of O-tbutyl S-methyl Xanthates with their corresponding energy values



(a) O-ETHYL S-METHYL XANTHATE
Energy = -48.389kJ/mol

(b) O-nPROPYL S-METHYL XANTHATE
Energy = -46.339kJ/mol

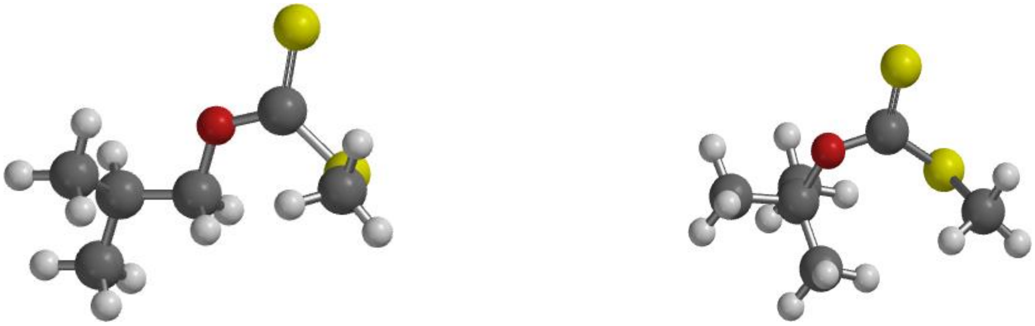


(C) O-nBUTYL S-METHYL XANTHATE

Energy = -50.926 kJ/mol

(d) O-iPROPYL S-METHYL XANTHATE

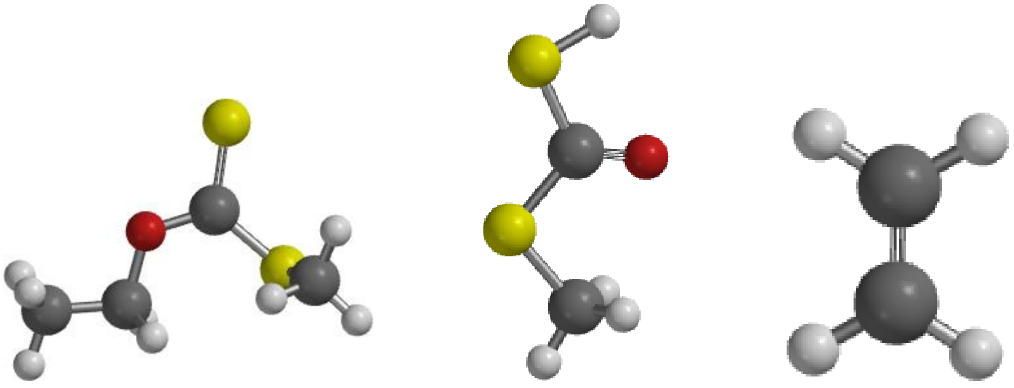
Energy = -33.608kJ/mol



(e) O-iBUTYL S-METHYL XANTHATE
Energy = -31.190kJ/mol

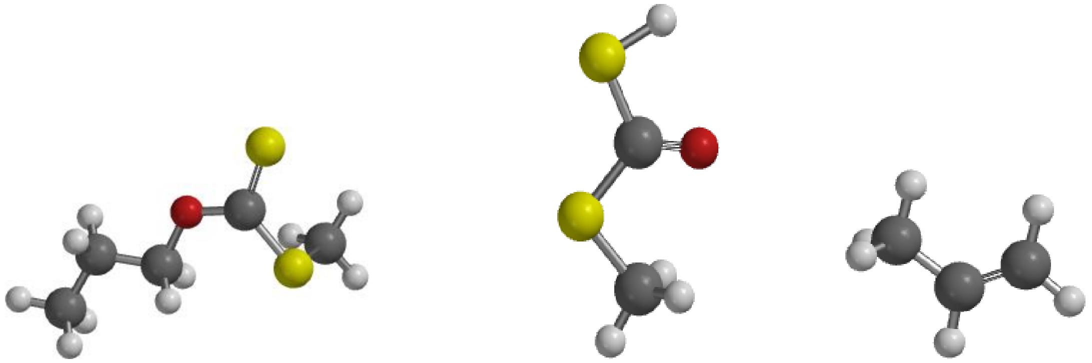
(f) O-tBUTYL S-METHYL XANTHATE
Energy = +16.061kJ/mol

**Figure 4.7:** Structure of stable conformers with their corresponding energy Values



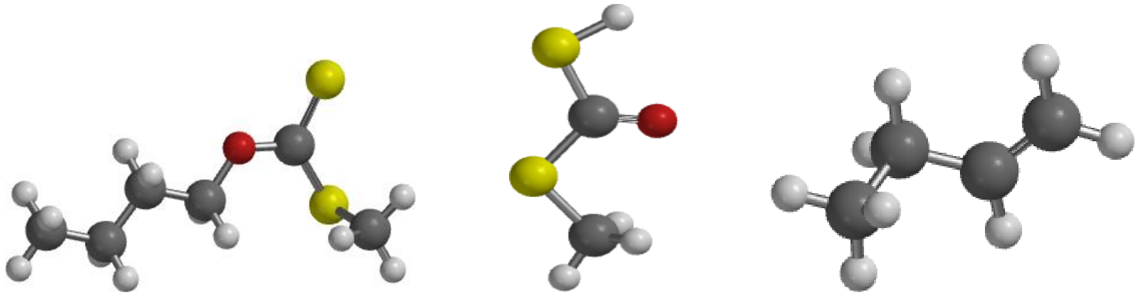
$C_4H_8S_2O \longrightarrow C_2H_4S_2O + C_2H_4$

O-ETHYL S-METHYL METHYL DITHIOCABONATES ETHYLENE



$C_5H_{10}S_2O \longrightarrow C_2H_4S_2O + C_3H_6$

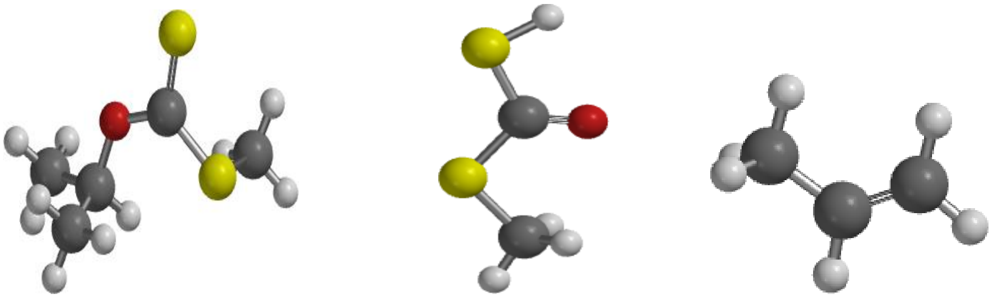
O-ETHYL S-METHYL METHYL DITHIOCARBONATES PROPYLENE



$C_6H_{12}S_2O \longrightarrow C_2H_4S_2O + C_4H_8$

O-nBUTYL S-METHYL METHYL DITHIOCARBONATES BUTYLENE

**Figure 4.8**: (a-c): Structures of reactants and products

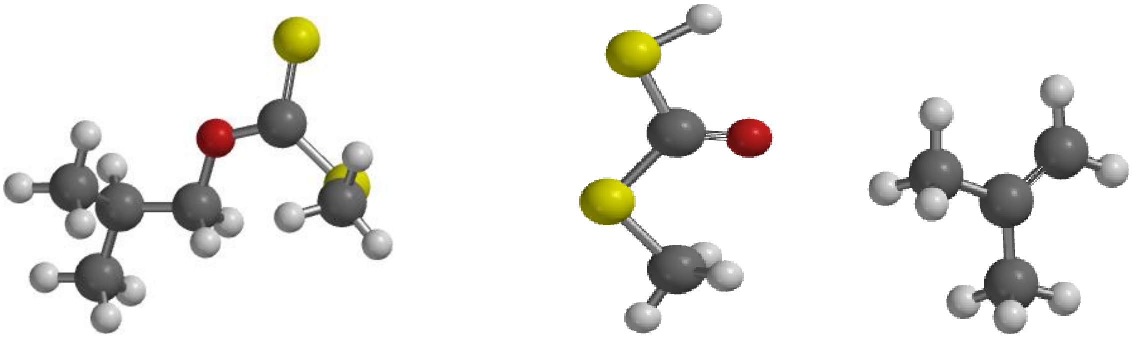


(D)

$C_5H_{10}S_2O \longrightarrow C_2H_4S_2O + C_3H_6$

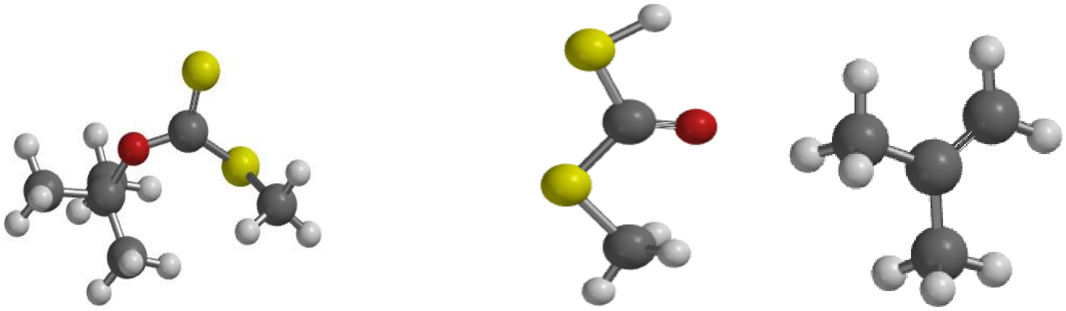
O-iPROPYL S-METHYL METHYL DITHIOCARBONATES PROPYLENE

(e)



$C_5H_{10}S_2O \longrightarrow C_2H_4S_2O + C_4H_8$

O-iBUTYL S-METHYL METHYL DITHIOCARBONATE 2-METHYLPROPYLENE



(F)

$C_6H_{12}S_2O \longrightarrow C_2H_4S_2O + C_4H_8$

O-tBUTYL S-METHYL METHYL DITHIOCARBONATES 2-METHYLPROPYLENE

**Figure 4.8** (d-f): Structures of reactants and products

### 4.3 Intrinsic reaction coordinate

Intrinsic reaction coordinate values were calculated to confirm the transition state (Hehre, 2003) for both the forward and the reverse perturbations. The Hessian second-energy derivation with respect to the normal coordinate yielded one imaginary frequency for all the studied molecules, this confirmed the saddle point. The calculated relative energy of each molecule in 40 reaction steps with their corresponding energies as shown in Table 4.2 and Figure 4.9 indicated that the pyrolysis of the O-alkyl S-methyl xanthate is endothermic.

**Table 4.2** Calculated Relative Energy Values for the Intrinsic Reaction Coordinate

| **Molecule Label** | **Relative Energy (kJ/mol)** |
|---|---|
| M1 | -102.78 |
| M2 | -93.51 |
| M3 | -84.11 |
| M4 | -75.07 |
| M5 | --65.05 |
| M6 | -57.21 |
| M7 | -48.50 |
| M8 | -41.11 |
| M9 | -31.17 |
| M10 | -25.33 |
| M11 | -18.00 |
| M12 | -10.96 |
| M13 | -4.28 |
| M14 | 2.00 |
| M15 | 7.87 |
| M16 | 13.34 |
| M17 | 18.08 |
| M18 | 22.43 |
| M19 | 24.79 |
| M20 | 28.00 |
| M21 | 24.79 |
| M22 | 16.00 |
| M23 | 0.00 |
| M24 | -21.38 |
| M25 | -46.63 |
| M26 | -73.34 |
| M27 | -99.11 |
| M28 | -122.24 |
| M29 | -142.11 |
| M30 | -159.68 |
| M31 | -175.61 |
| M32 | -191.27 |
| M33 | -203.85 |
| M34 | -216.47 |
| M35 | -228.21 |
| M36 | -239.23 |
| M37 | -249.60 |
| M38 | -258.70 |
| M39 | -267.26 |

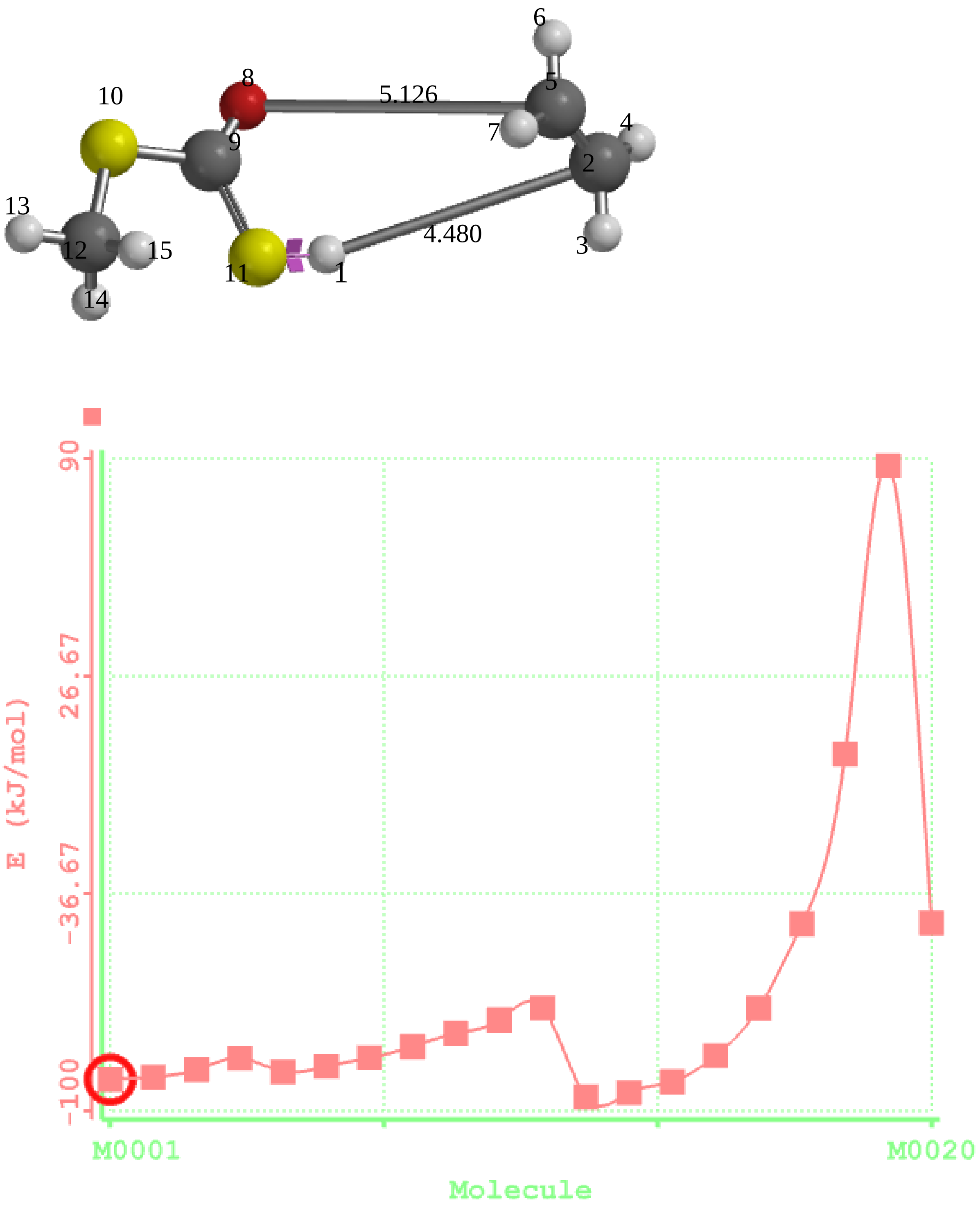
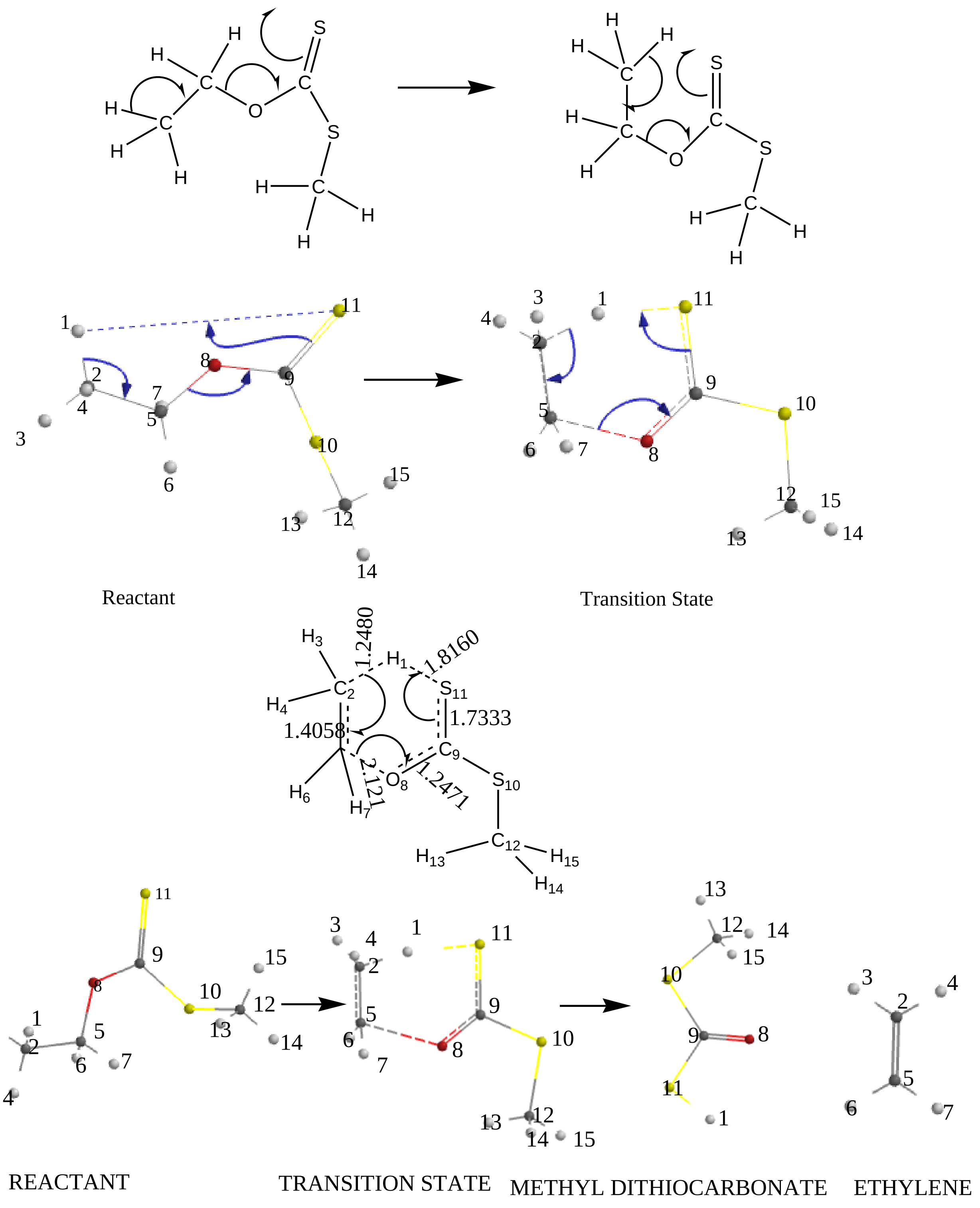


**Figure : 4.9:** Reaction Path Study (O-ethyl S-methyl Dithiocarbonates) and a plot of Energy against number of molecules to show the reaction path study.


Reactant

Transition State

REACTANT

TRANSITION STATE

METHYL DITHIOCARBONATE

ETHYLENE

**Figure.4.10:** Reaction mechanism of pyrolysis of O-ethyl S-methyl dithiocarbonates

## 4.4 Mechanism of pyrolysis of O-ethyl S-methyl Xanthate

Pyrolysis of O-ethyl S-methyl Dithiocarbonates (Xanthate) is the simplest of the O-alkyl S- methyl xanthate studied and which gives Methyl dithiocarbonates and ethylene ($C_2H_4$) as product (Al-Awadi and Bigley, 1982, Wu et al., 2014). In the optimized geometry of the ethyl xanthate $H_3$ is the hydrogen attached to β-Carbon that is to be eliminated from the alkyl group. Thermal decomposition of alkyl xanthate involves C-O, C-H bond breaking and S-H bond formation which proceeded through concerted six-centered cyclic transition state.

There are various studies on the mechanism of the thermal decomposition of xanthate. The mechanism of the Chugaev reaction was proposed to involve two possible pathways (Huckel *et al.,*1940). The pyrolysis of carboxylic ester of alcohols and other related derivatives of alkanols such as carbonates and carbamates are similar to Chugaev reaction. The pathway and mechanism of dithiocarbonates (Xanthates) thermal decomposition is a concerted disintegration but the products came as a result of β-hydrogen absorption through a transition state of six-membered ring in which the hydrogen atom at the beta position attacking the terminal thiol, or the thion (Huckel *et al.*, 1940). Sulphur atom attacks the β – hydrogen, this was shown by Bader and Bourns, (1961). Both the thiol and thion were part of the six membered cyclic transition State which involves a S – H bond making, C – H and C – O bond breaking. According to experimental evidence, the C-O bond breaking is the rate determining step (West *et al.*, 2015; Mclever and Komonicki, 1971).

The products of O-ethyl S-methyl dithiocarbonates were identified by I.R Spectroscopy of single compounds and authentic mixtures. They were from O-ethyl S-methyl dithiocarbonates, methanethiol, carbonyl Sulphide and ethylene (Al-Awadi and Bigley, 1982) in which the reaction is a concerted fragmentation through a transition state of six-membered ring in the sense that the hydrogen atom at the beta position( β-H), attracting the vinyl carbon atoms at the terminal end which is part of the transition state in the six membered ring as shown in Fig 4.10.

## 4.5. O-ethyl S-methyl Dithiocarbonate.

The decomposition of O-ethyl S-methyl dithiocarbonates proceeds through a concerted fragmentation which involves a six membered cyclic transition state (Figure 4.11)

$$C_4H_8S_2O \longrightarrow C_2H_4S_2O + C_2H_4 \quad (4.1)$$

| Ethyl Xanthate | Methyl Dithiocarbonate | Ethylene |
|---|---|---|

This involves S-H bond making (initiated from the attached hydrogen atom to β –carbon) C-O bond breaking on one part, and S-H bond formation on another part. In the transition state there is a bond stretching between $C_2$ - $H_3$ bond with bond length 1.2350 (DFT/B3LYP/6-311+G**), 1.2370 (DFT/B3LYP/CCPV-TZ), as against the bond length of 1.0916 (DFT/B3LYP 6-311+G**), 1.0927 (DFT/B3LYP/CCPV-TZ), at the ground state from Table 4.3a, 4.3b, 4.3c. Also, there is a stretch between $O_8$ – $C_5$ bonds with a bond length of 1.3364Å and 1.3362 Å while a bond is formed between $S_{11}$ – $H_3$ and also at the ground state the bond length is 4.9940Å and 4.9962 Å against the stable product bond length in the range of 1.3480 Å and 1.3390 Å. The bond angles and dihedrals are shown in Table 4.3b and 4.3c.

### 4.5.1 Atomic Charges

Atomic charges in this work are shown in Mulliken units because it gives simple and reasonable estimates of atomic charges as reported by Hehre and Ohlinger (2010). The result of atomic charge on the different atoms of the molecule shows that there is a accumulation of negative charge on the oxygen atom ($O_8$ ) in the transition structure and a positive charge buildup on the transferred hydrogen. The polarization of the $C_5$ – $O_8$ and $S_{10}$-$H_1$ bonds causes positive charges on the atoms $C_5$ and $C_9$ to increase and the $C_2$ atom to become more negatively charged (Table 4.3d). The high negative charge on $C_1$ causes much bond polarization of the $C_2$ – $S_{10}$ which places a considerable positive charge on $H_1$ atom. The negative charge on $C_2$ was used to attack the positive charge on $C_5$ to form a double bond between $C_4$ and $C_6$ this was shown in the transition state (TS) and reflecting in the bond length value for a double bond while the bond between $C_5$ and $O_8$ cleaves. It was observed that the most prominent bond length when the ground state, transition state and product bond length on comparing bond length in the ground state, transition state and the product are the bond lengths between the reaction coordinate are $C_A$- $O_B$, $C_X$- $H_Y$ and $C_Z$-$H_Y$. Where A, B, X, Y and Z are dependent of the number assign to each atom.

### 4.5.2 Wiberg bond order O-ethyl S-methyl dithiocarbonates.

The parameters calculated under bond indices of the Wiberg (Quijano *et al.,* 2002 ) (Moyano *et al.,* 1989 ) make use of all the atoms in the bonds included in the reaction coordinate of the O-ethyl S-methyl dithiocarbonates. The percentage evolution values of the bonds included in the reaction coordinate in the Wiberg bond of O-ethyl S-methyl dithiocarbonates are shown in Table 4.3(e). It was observed that the cleaving of $O_8$-$C_5$ bond is the most leading process (66.4%), the $S_{10}$-$C_9$ double bond also subsequently change into a single bond of (62.6%) and $C_9$-$O_8$ from single bond into a double bond of (58.4%). The formation of the $C_2$-$C_5$ double bond is the least progressive process with (31.7%) accompanied by the production of bond $H_1$-$S_{10}$ with (45.4%), and a cleavage of $C_2$-$H_1$ bond (44.4%) in agreement with the experimental evidence of (Taylor et al., 1962). The separation of the alpha carbon attached to oxygen ($C_\alpha$-O) occurs before that of the beta carbon attached to hydrogen ($C_\beta$-H). The outcome of the process also recommends that the greater the alpha carbon attached to oxygen ($C_\alpha$-O)bond dissociates in the transition state structure the greater and faster the speed of the reaction, on the contrary the more the beta carbon attached to hydrogen ($C_\beta$-H) bond dissociates, the rate of reaction would be slow. The calculated Average bond indices (δBav) values for the mechanism of the studied reactions are shown in Table 4.3(e) . The δBav values for O-ethyl S-methyl dithiocarbonates ranges from zero to (1) indicating that transition states have an early character i.e. it is nearer to reactants than the products.

Synchronicities (Sy) may vary from zero to one when all of the bonds at the reaction coordinate are broken or formed at exactly to the same degree in the transition states. The Sy values obtained for O-ethyl S-methyl dithiocarbonate are shown in Table 4.3e, is 0.899 which indicate that the O-ethyl S-methyl dithiocarbonates corresponds to high asynchronous processes. The outcome of the process also indicates that the greater the dissociation of the C-O bond in the transition state the greater and faster the speed of the reaction. This is in contrast to the observation that the greater the dissociation of C-H bond the slower the rate of the reaction.

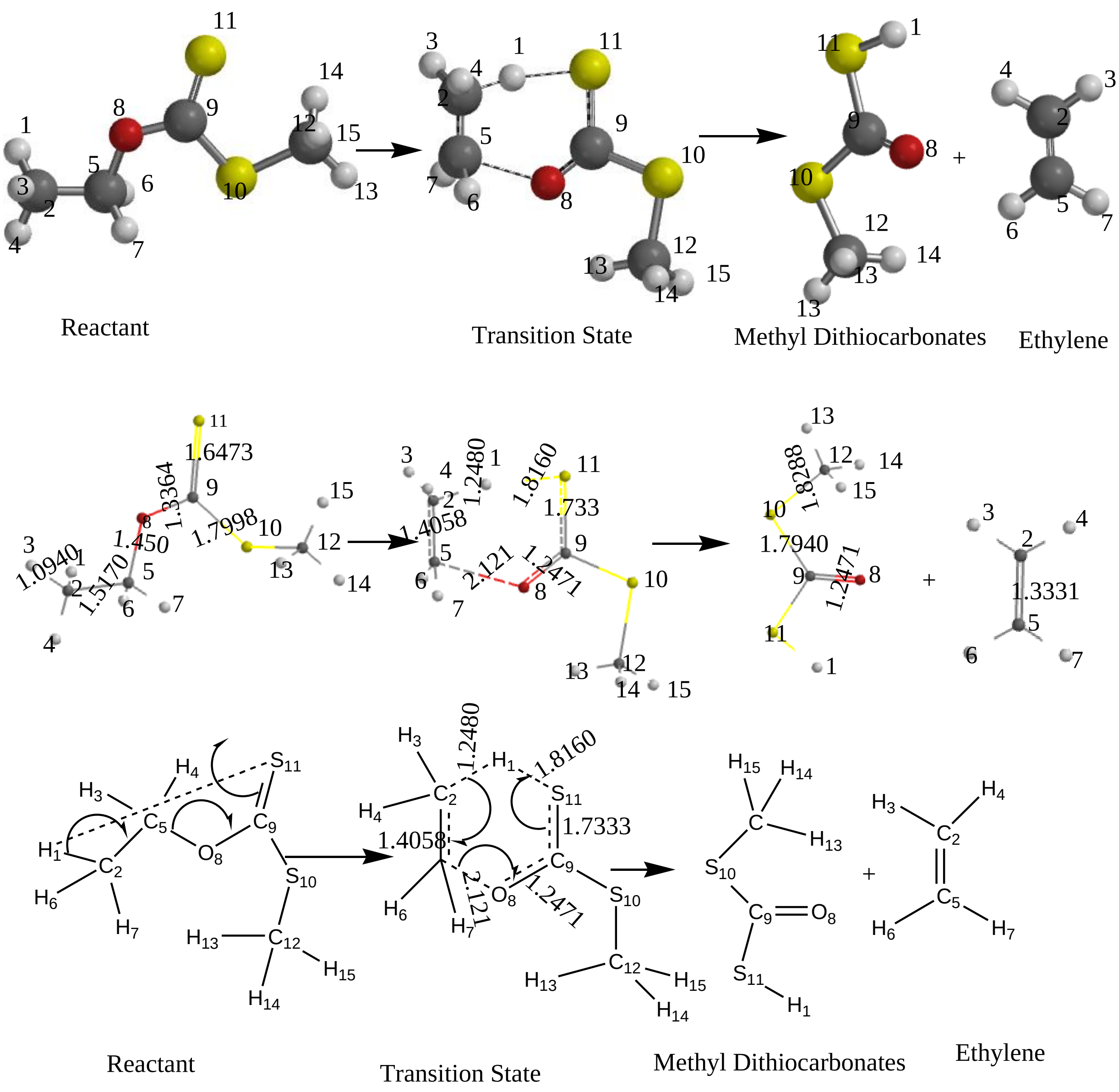


**Figure 4.11:** Reaction scheme for the gas phase thermal decomposition of O-ethyl S-methyl Dithiocarbonates

**Table 4.3a:** Selected bond length (Å) for the gas phase thermal decomposition of O-ethyl S-methyl xanthates

| **BOND (Å)** | **STATE** | **B3LYP/ 6-311+G**** | **CC-PVTZ** |
|---|---|---|---|
| **$C_2 – H_3$** | GS | 1.0916 | 1.0927 |
| | TS | 1.2350 | 1.2370 |
| | PRD | - | - |
| | Δd | 0.1540 | 0.1443 |
| **$C_2 – C_5$** | GS | 1.5170 | 1.5134 |
| | TS | 1.4058 | 1.4023 |
| | PRD | 1.3308 | 1.3306 |
| | Δd | - 0.1112 | - 0.1111 |
| **$O_8 – C_5$** | GS | 1.3364 | 1.3362 |
| | TS | 1.2471 | 1.2449 |
| | PRD | - | - |
| | Δd | -0.089 | -0.0913 |
| **$C_9 = S_{11}$** | GS | 1.6473 | 1.6452 |
| | TS | 1.7333 | 1.7220 |
| | PRD | 1.8142 | 1.7922 |
| | Δd | 0.086 | 0.0768 |
| **$C_9 – S_{10}$** | GS | 1.7883 | 1.7884 |
| | TS | 1.7998 | 1.7891 |
| | PRD | 1.7940 | 1.7892 |
| | Δd | 0.0115 | 0.0007 |
| **$S_{10} – C_{12}$** | GS | 1.8189 | 1.8270 |
| | TS | 1.8334 | 1.8362 |
| | PRD | 1.8284 | 1.8361 |
| | Δd | 0.0145 | 0.0092 |
| **$S_{11} – H_3$** | GS | 4.9940 | 4.9962 |
| | TS | 1.8160 | 1.8260 |
| | PRD | 1.3480 | 1.3390 |
| | Δd | - 3.178 | - 3.1702 |

**Note:** Δd = d(TS) – d(GS)

Bond length in the transition state (TS) - Bond length in the Ground State (TS)

PRD = Product

**Table 4.3b:** Selected bond angle (0°) for the pyrolysis of O-ethyl S-methyl xanthates

| **BOND** | **STATE** | **DFT/B3LYP/ 6-311+ G**** | **DFT/B3LYP CC-PVPZ** |
|---|---|---|---|
| $H_3 – C_2 – C_5$ | GS | 110.792 | 110.820 |
| | TS | 102.74 | 102.720 |
| | PRD | - | - |
| $C_2 – C_5 – O_8$ | GS | 106.967 | 107.820 |
| | TS | 109.180 | 109.320 |
| | PRD | - | - |
| $C_5 – O_8 – C_9$ | GS | 122.881 | 122.745 |
| | TS | 120.320 | 119.090 |
| | PRD | - | - |
| $O_8 - C_9 = S_{11}$ | GS | 120.113 | 120.151 |
| | TS | 125.156 | 124.914 |
| | PRD | 123.61 | 124.620 |
| $O_8 - C_9 - S_{10}$ | GS | 114.478 | 120.575 |
| | TS | 119.138 | 120.575 |
| | PRD | 120.060 | 122.720 |
| $S_{10} – C_9 – S_{11}$ | GS | 125.409 | 114.488 |
| | TS | 115.699 | 114.488 |
| | PRD | 112.630 | 114.72 |
| $C_9 – S_{10} – C_{12}$ | GS | 102.302 | 102.321 |
| | TS | 101.409 | 102.938 |
| | PRD | 98.120 | 97.620 |
| $S_{10} – C_{12} – H_{13}$ | GS | 110.362 | 110.470 |
| | TS | 110.982 | 109.333 |
| | PRD | 111.240 | 112.462 |

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

**Table 4.3c:** Selected dihedrals angles (0º) for the gas phase pyrolysis of O-ethyl S-methyl xanthates

| **BOND** | **STATE** | **B3LYP/ 6-311+G**** | **CC-PVTZ** |
|---|---|---|---|
| $H_1$-$C_2$-$C_5$-$H_6$ | GS | -58.861 | -60.261 |
| | TS | 103.580 | 103.970 |
| | PRD | - | - |
| $H_1$-$C_2$-$C_5$-$O_8$ | GS | 60.062 | 59.072 |
| | TS | 7.580 | 7.39 |
| | PRD | - | - |
| $C_2$-$C_5$-$O_8$-$C_9$ | GS | 179.439 | 179.462 |
| | TS | 12.230 | 14.50 |
| | PRD | - | - |
| $C_5$-$O_8$-$C_9$-$S_{10}$ | GS | 0.016 | 0.026 |
| | TS | 139.080 | 134.11 |
| | PRD | - | - |
| $C_5$-$O_8$-$C_9$-$S_{11}$ | GS | -179.976 | 178.261 |
| | TS | -39.900 | -44.04 |
| | PRD | - | - |
| $S_{11}$-$C_9$-$S_{10}$-$C_{12}$ | GS | 0.090 | 0.092 |
| | TS | -176.357 | -176.836 |
| | PRD | 180 | 180 |

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

**Table 4.3d:** Atomic charges (Mulliken) of O-ethyl S-methyl dithiocarbonates

| ATOMS | STATE | DFT/B3LYP/ 6-31G* | DFT/B3LYP/ CC-PVTZ |
|---|---|---|---|
| $H_3$ | GS | +0.174 | +0.191 |
| | TS | +0.141 | +0.116 |
| | PRD | +0.273 | +0.221 |
| | Δq | -0.033 | -0.075 |
| $C_2$ | GS | -0.458 | -0.560 |
| | TS | -0.480 | -0.285 |
| | PRD | -0.285 | -0.321 |
| | Δq | -0.022 | 0.275 |
| $C_5$ | GS | -0.071 | -0.242 |
| | TS | -0.123 | -0.047 |
| | PRD | -0.285 | -0.286 |
| | Δq | -0.052 | 0.195 |
| $O_{8}$` | GS | -0.387 | +0.140 |
| | TS | -0.437 | -0.330 |
| | PRD | -0.389 | -0.520 |
| | Δq | -0.050 | -0.470 |
| $C_9$ | GS | +0.064 | -0.016 |
| | TS | +0.082 | +0.156 |
| | PRD | +0.098 | +0.727 |
| | Δq | 0.018 | 0.172 |
| $S_{10}$ | GS | +0.162 | -0.093 |
| | TS | +0.164 | +0.002 |
| | PRD | +0.158 | +0.268 |
| | Δq | -0.021 | 0.095 |
| $S_{11}$ | GS | -0.186 | -0.326 |
| | TS | -0.116 | -0.256 |
| | PRD | -0.011 | -0.014 |
| | Δq | 0.07 | 0.070 |
| $C_{12}$ | GS | -0.594 | -0.282 |
| | TS | -0.186 | -0.300 |
| | PRD | -0.587 | -0.629 |
| | Δq | 0.408 | -0.018 |

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

PRD = Product

**Table 4.3(e).** Calculated Wiberg bond Indices of O-ethyl S-methyl Xanthate in the gas phase.

| **Compound** | **State** | **$C_2$-$C_5$** | **$C_2$-$H_1$** | **$H_1$-$S_{10}$** | **$S_{10}$-$C_5$** | **$C_9$-$O_8$** | **$O_8$-$C_5$** |
|---|---|---|---|---|---|---|---|
| **Ethyl** | $B_i^R$ | 1.026 | 0.944 | 0.000 | 1.663 | 1.081 | 0.830 |
| **Xanthate** | $B_i^{TS}$ | 1.348 | 0.534 | 0.422 | 1.258 | 1.505 | 0.279 |
| | $B_i^P$ | 2.042 | 0.000 | 0.928 | 1.006 | 1.807 | 0.000 |
| | **$\delta B_i$** | 0.317 | 0.444 | 0.454 | 0.616 | 0.584 | 0.664 |
| | **%Ev** | 31.7 | 44.4 | 45.4 | 62.6 | 58.4 | 66.4 |
| | **δBav** | 0.513 | | | | | |
| | **Sy** | 0.860 | | | | | |

## 4.6 O-npropyl S-methyl xanthate. (npropyl Xanthate)

In O-npropyl S-methyl dithiocarbonate, the products are Propylene $C_3H_6$ and methyl xanthate that decompose subsequently to carbonyl Sulphide and thiol. The decomposition occurs through a concerted fragmentation through a six membered cyclic transition State as shown in Figure 4.12 which also involves $C_8$ –$O_{11}$ and $C_5$ – $H_7$ bond breaking and a $S_{13}$ – $H_7$ bond formation. The bond length are shown in Table 4.4a noting the stretching in the bond length between $C_8$ – $O_{11}$ in the ground state to transition state respectively from 1.4689Å to 2.1830 Å (B3LYP/6-31+G**) and 1.4625Å to 2.1930Å (CCPVTZ) and also in $C_5$ – $H_7$ 1.0925 to 1.2050Å from the ground state to transition state and 1.0926 Å to 1.2151 Å. The $S_{13}$ – $H_7$ bond length from 4.9710Å and 4.8840 Å in the ground state to 1.8680Å and 1.9190Å are indications that a new bond is to be formed for B3LYP/6-31+G** and CCPVTZ methods respectively. The bond angles, dihedrals and atomic charges are shown in Table 4.4b, 4.4c and 4.4d

$$\mathbf{C_5H_{10}S_2O \longrightarrow C_2H_4S_2O + C_3H_6} \qquad (4.2)$$

**npropyl Xanthate** **Methyl Dithiocarbonate** **Propylene**

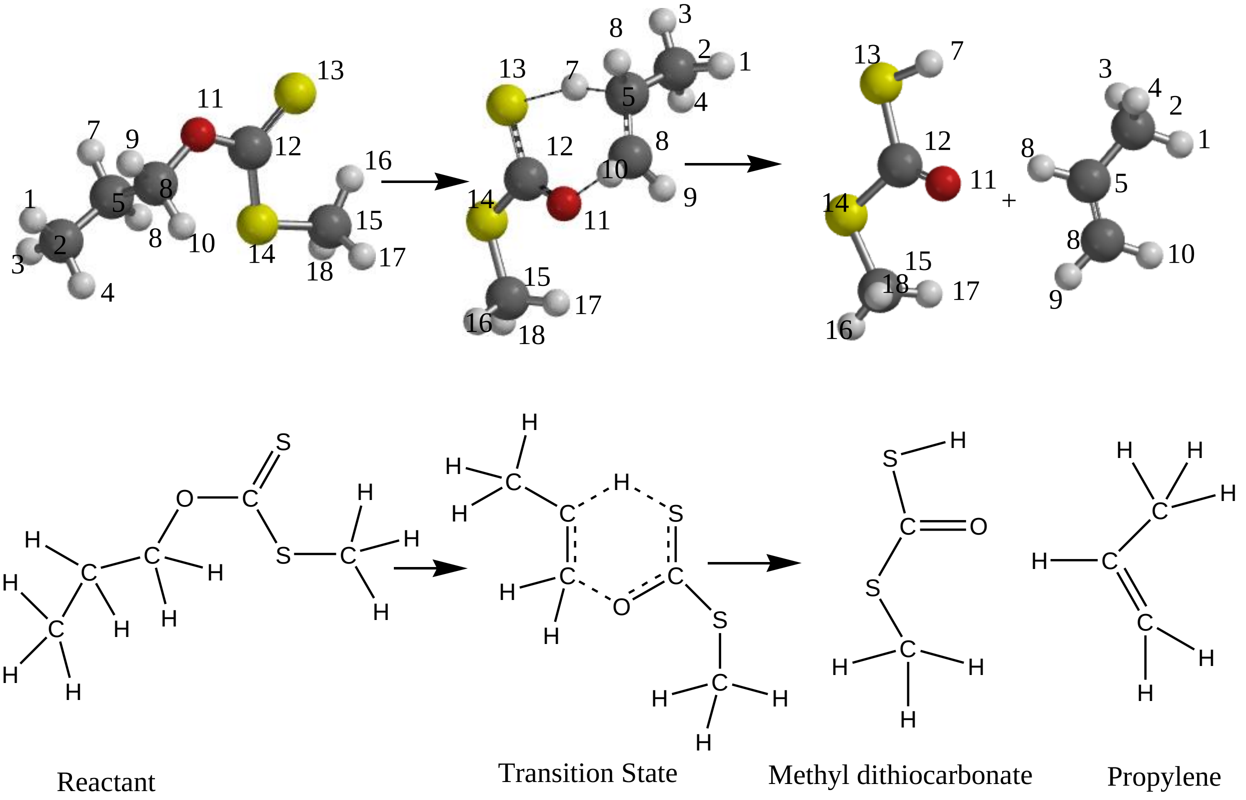


**Figure 4.12**: Reaction Scheme for Pyrolysis of O-npropyl S-methyl Dithiocarbonates.

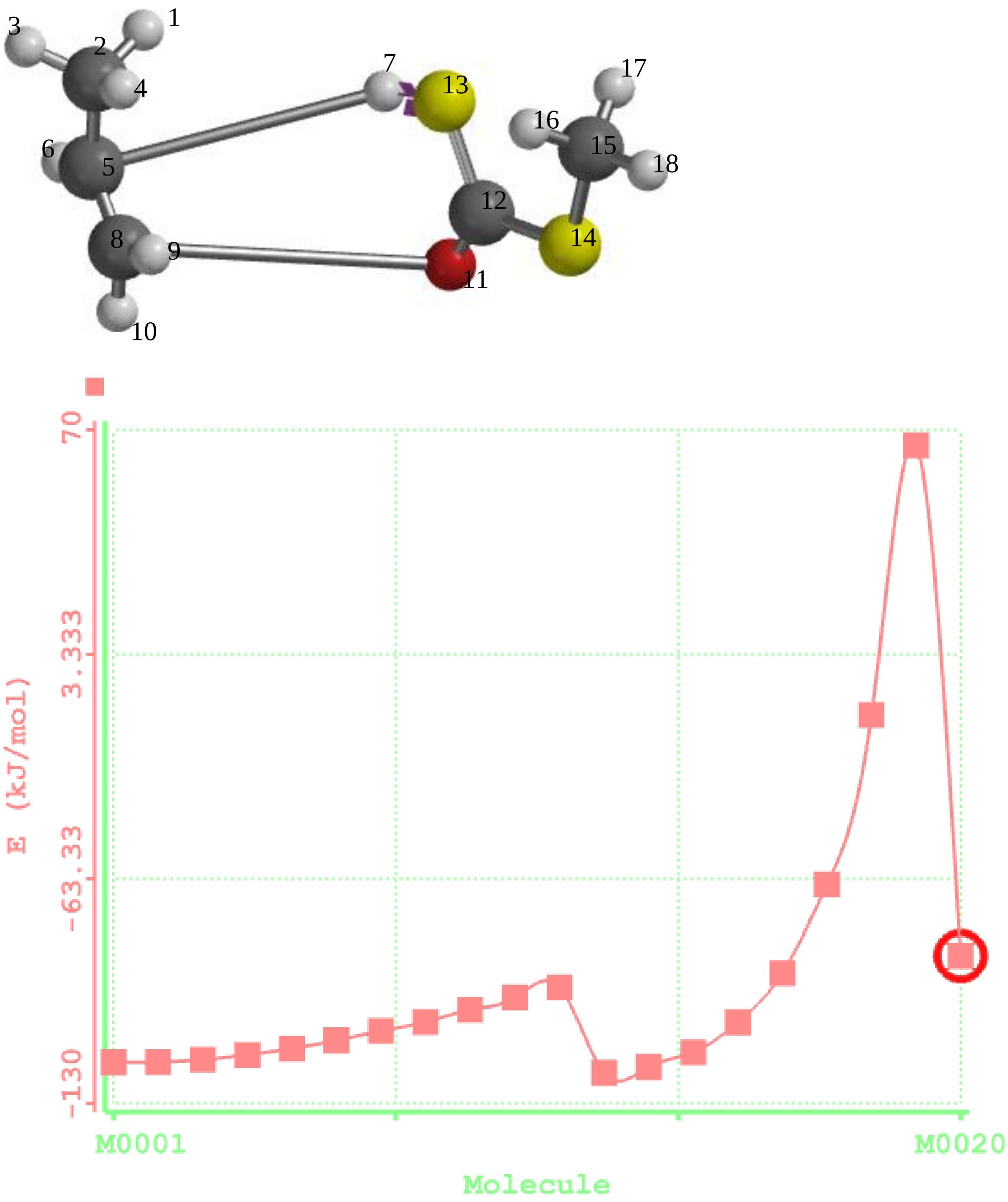


**Figure : 4.13:** Reaction path study O-npropyl S-methyl dithiocarbonates) and a plot of Energy against number of molecules to depict the reaction path study.

**Table 4.4a:** Selected bond length for the gas phase thermal decomposition of O-npropyl S-methyl dithiocarbonates

| BOND (Å) | STATE | B3LYP/6 311+G** | CC-PVTZ |
|---|---|---|---|
| $C_5$-$H_6$ | GS | 1.0925 | 1.0926 |
| | TS | 1.2050 | 1.2151 |
| | PRD | - | - |
| | Δd | 0.1125 | 0.1225 |
| $C_2$– $C_5$ | GS | 1.5200 | 1.5210 |
| | TS | 1.4169 | 1.4163 |
| | PRD | 1.3334 | 1.3425 |
| | Δd | - 0.1031 | - 0.1047 |
| $C_8$ – $O_{11}$ | GS | 1.4689 | 1.4625 |
| | TS | 2.1830 | 2.1930 |
| | PRD | - | - |
| | Δd | 0.7141 | 0.7305 |
| $O_{11}$- $C_{12}$ | GS | 1.3330 | 1.3334 |
| | TS | 1.2449 | 1.2460 |
| | PRD | 1.2003 | 1.2004 |
| | Δd | -0.0881 | -0.0874 |
| $C_{12}$= $S_{13}$ | GS | 1.6454 | 1.6451 |
| | TS | 1.7255 | 1.7252 |
| | PRD | 1.8258 | 1.8256 |
| | Δd | 0.0801 | 0.0801 |
| $C_{12}$– $S_{14}$ | GS | 1.7875 | 1.7876 |
| | TS | 1.7948 | 1.7951 |
| | PRD | 1.7904 | 1.7905 |
| | Δd | 0.0073 | 0.0075 |
| $S_{14}$– $C_{15}$ | GS | 1.8183 | 1.8182 |
| | TS | 1.8285 | 1.8235 |
| | PRD | 1.8258 | 1.8219 |
| | Δd | 0.010 | 0.0053 |
| $S_{13}$ – $H_6$ | GS | 4.980 | 4.975 |
| | TS | 1.9090 | 1.9215 |
| | PRD | 1.3475 | 1.3404 |
| | Δd | -3.071 | -3.0535 |

**Note:** Δq = d(TS) – d(GS)

Bond length in the transition state (TS) - Bond length in the Ground State (TS), PRD =Product

**Table 4.4b:** Selected bond angles for the pyrolysis of O-npropyl S-methyl xanthates

| **BOND** | **STATE** | **B3LYP/<br>6-311+ G**** | **CC-PVTZ** |
|---|---|---|---|
| $H_6– C_5– C_8$ | GS | 110.504 | 110.437 |
| | TS | 103.820 | 103.52 |
| | PRD | - | - |
| $C_5– C_8– O_{11}$ | GS | 105.196 | 105.720 |
| | TS | 105.840 | 105.730 |
| | PRD | - | - |
| $C_8– O_{11}– C_{12}$ | GS | 124.755 | 124.721 |
| | TS | 121.580 | 121.620 |
| | PRD | - | - |
| $O_{11}\text{-} C_{12} =S_{13}$ | GS | 129.905 | 119.921 |
| | TS | 125.280 | 125.560 |
| | PRD | 123.678 | 123.421 |
| $O_{11}\text{-} C_{12}\text{-} S_{14}$ | GS | 115.214 | 115.521 |
| | TS | 119.297 | 119.282 |
| | PRD | 124.567 | 124.621 |
| $S_{13} =C_{12}– S_{14}$ | GS | 124.878 | 124.820 |
| | TS | 115.415 | 115.270 |
| | PRD | 111.682 | 111.782 |
| $C_{12}– S_{14}– C_{15}$ | GS | 102.390 | 102.392 |
| | TS | 101.420 | 102.430 |
| | PRD | 98.136 | 97.146 |
| $S_{14}– C_{15}– H_{18}$ | GS | 113.630 | 114.720 |
| | TS | 122.880 | 122.860 |
| | PRD | 125.250 | 125.260 |

**Note :** GS = Ground State ,

TS = Transition State,

PRD = Product

**Table 4.4c:** Selected dihedral for the pyrolysis O-npropyl S-methyl manthates

| BOND | STATE | DFT/B3LYP/ 6-311+ G** | DFT/B3LYP/ CC-PVTZ |
|---|---|---|---|
| $O_{11}– C_8 – C_5– H_6$ | GS | 60.628 | -60.728 |
| | TS | -12.59$^0$ | -13.08 |
| | PRD | - | - |
| $C_8– O_{11}– C_{12} = S_{12}$ | GS | -176.833 | -177.657 |
| | TS | 37.420 | 35.810 |
| | PRD | - | - |
| $O_{11}$- $C_{12}$- $S_{14}$- $C_{15}$ | GS | 178.781 | 178.781 |
| | TS | -4.260 | -4.261 |
| | PRD | -0.000 | -0.000 |
| $S_{13}$= $C_{12}$- $S_{14}$- $C_{15}$ | GS | -0.571 | -0.571 |
| | TS | 176.71 | 176.71 |
| | PRD | 180.000 | 180.000 |
| $H_6$- $C_5$- $C_8$- $O_{11}$ | GS | 58.781 | 58.781 |
| | TS | 93.09 | 93.011 |
| | PRD | - | - |
| $C_{12}$- $O_{11}$- $C_8$- $C_5$ | GS | -149.948 | -149.123 |
| | TS | -5.320 | -5.420 |
| | PRD | - | - |

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

**Table 4.4d:** Atomic charges (Mulliken) Of O-npropyl S-methyl dithiocarbonates

| ATOM | STATE | DFT/B3LYP/ 6-311+G** | DFT/B3LYP CC-PVTZ |
|---|---|---|---|
| $H_6$ | GS | +0.159 | +0.167 |
| | TS | +0.120 | +0.155 |
| | PRD | +0.093 | +0.094 |
| | Δq | -0.039 | -0.167 |
| $C_5$ | GS | -0.417 | -0.447 |
| | TS | -0.358 | -0.467 |
| | PRD | -0.547 | -0.367 |
| | Δq | +0.155 | -0.02 |
| $C_8$ | GS | -0.185 | +0.091 |
| | TS | +0.030 | +0.083 |
| | PRD | -0.043 | -0.046 |
| | Δq | +0.215 | -0.008 |
| $O_{11}$ | GS | +0.205 | -0.395 |
| | TS | -0.089 | -0.462 |
| | PRD | -0.207 | -0.208 |
| | Δq | -0.294 | -0.067 |
| $C_{12}$ | GS | -0.074 | +0.063 |
| | TS | +0.054 | +0.087 |
| | PRD | +0.079 | +0.078 |
| | Δq | +0.128 | +0.128 |
| $S_{13}$ | GS | -0.291 | -0.195 |
| | TS | -0.302 | -0.159 |
| | PRD | -0.112 | -0.142 |
| | Δq | -0.011 | 0.036 |
| $S_{14}$ | GS | -0.009 | -0.158 |
| | TS | -0.011 | +0.150 |
| | PRD | +0.084 | +0.086 |
| | Δq | -0.002 | +0.300 |
| $C_{15}$ | GS | -0.459 | -0.596 |
| | TS | -0.515 | -0.587 |
| | PRD | -0.511 | -0.562 |
| | Δq | -0.056 | +0.009 |

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

PRD = Product

**Table 4.4(e).** Calculated Wiberg bond indices of O-npropyl S-methyl xanthate**.**

| **Compound** | **State** | **$C_5$-$C_8$** | **$C_5$-$H_7$** | **$H_7$-$S_{13}$** | **$S_{13}$-$C_{12}$** | **$C_{12}$-$O_{11}$** | **$O_8$-$C_{11}$** |
|---|---|---|---|---|---|---|---|
| **O-npropyl** | $B_i^R$ | 1.018 | 0.928 | 0.002 | 1.666 | 1.041 | 0.790 |
| **Xanthate** | $B_i^{TS}$ | 1.310 | 0.549 | 0.325 | 1.319 | 1.407 | 0.225 |
| | $B_i^P$ | 1.985 | 0.000 | 0.962 | 1.070 | 1.695 | 0.000 |
| | $\delta B_i$ | 0.317 | 0.408 | 0.337 | 0.582 | 0.560 | 0.716 |
| | %Ev | 30.2 | 40.8 | 33.7 | 58.2 | 56.0 | 71.6 |
| | $\delta$Bav | 0.487 | | | | | |
| | Sy | 0.832 | | | | | |

### 4.6.1 Wiberg Bond Order For O-npropyl Xanthates

The calculated percentage evolution of bond involved in the reaction coordinate for O-npropyl S-methyl dithiocarbonates is shown in Table 4.4(e). The percentage evolution of ($O_8$-$C_{11}$ ) bond cleavage is 71.6% which is the most advanced process followed by a subsequent double transformation of $S_{13}$-$C_{12}$ bond into a single bond at 58.2% evolution and also conversion of $C_{12}$-$O_{11}$ single bond to double bond of 56% evolution. The least progressive process is the changing of $C_5$-$C_8$ single bond to double bond at 30.2% evolution. This is accompany by the formation of $H_6$-$S_{13}$ bond formation at 33.7% evolution and the $C_5$-$H_7$ of bond breaking at 40.8% evolution The conversion of $C_5$-$C_8$ single bond to double bond is the least progressive process probably because of the change in hybridization from sp3 to sp2 involve in the conversion process. The average value of bond indices ($\delta$Bav) which measures the degree of advancement of the transition state along the reaction path for O-npropyl S-methyl Xanthate is 0.487 indicating that the transition state has an early character nearer to the reactants than the products. The synchronicity value of the reaction (Sy) for O-npropyl S-methyl Xanthate was 0.832 which indicate that the O- npropyl S-methyl dithiocarbonate corresponds to high asynchronous processes.

### 4.7 O– ipropyl S- methyl Dithiocarbonates.

The decomposition of O–ipropyl S–methyl dithiocarbonates also gives propylene and methyl xanthates which are then decompose to carbonyl sulphide and a thiol. This decomposition also occurs through a concerted fragmentation via an E1 mechanism which includes a cyclic transition state with six member ring as shown in Figure 4.14 that also involving $C_5 – O_7$ and $C_{15} – H_{16}$ bond cleavages and a $S_9 – H_{16}$ bond making. The bond lengths are shown in Table 4.5a. noting the stretching in the bond length between $C_5 – O_7$ in the ground state from 1.4689Å and 1.4625Å to 2.1830 Å and 2.1930Å in the transition state, for $C_{15} – H_{16}$ for 1.0925Å and 1.0925Å in the ground state, and 1.2050Å and 1.2151Å in the transition state. The $S_9 – H_{16}$ bond length from 4.980 Å and 4.9750Å in the ground state to 1.3475 Å and 1.3404 Å are the indications that a new bond is to be formed for B3LYP/6-31+G** and CCPVTZ methods respectively. The bond angles and the dihedrals and atomic charges were are reported in Tables 4.5a, 4.45, 4.5c and 4.5d.

$$\mathbf{C_5H_{10}S_2O} \longrightarrow \mathbf{C_2H_4S_2O} + \mathbf{C_3H_6} \tag{4.3}$$

**Isopropyl Xanthate** **Methyl Dithiocarbonate** **Propylene**

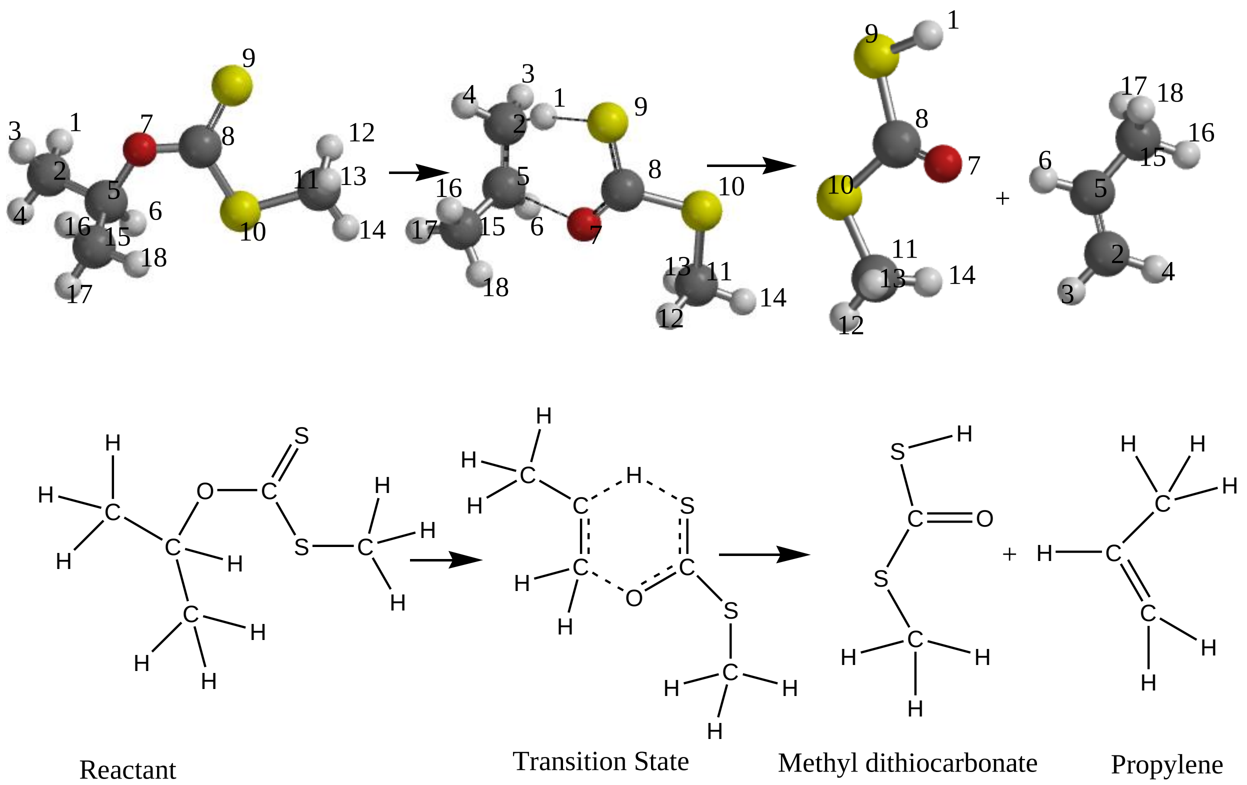


**Figure. 4.14**: Reaction scheme for pyrolysis of O-ipropyl S-methyl Dithiocarbonates

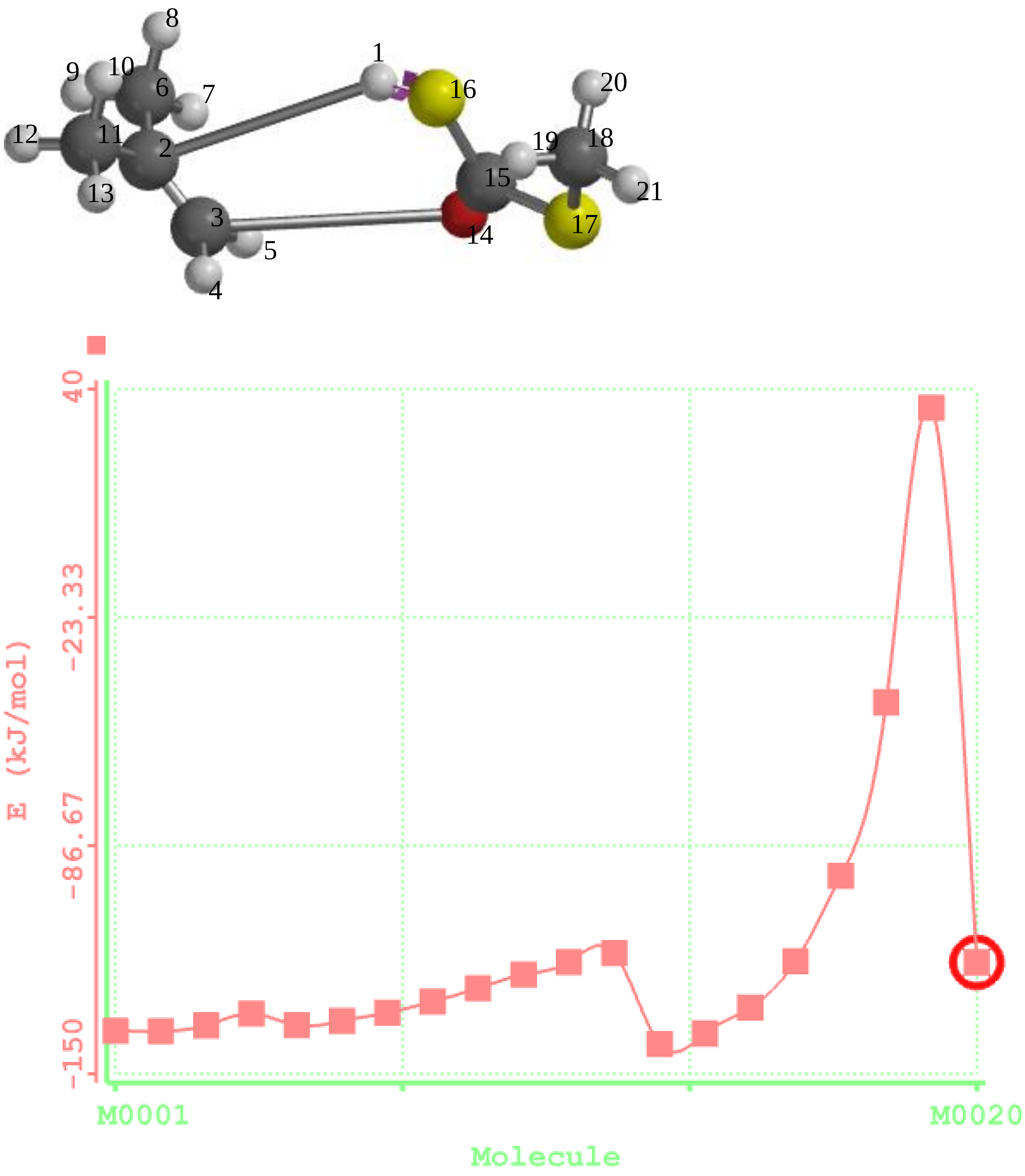


**Figure : 4.15:** Reaction path study O-ipropyl S-methyl dithiocarbonates) and a plot of Energy against number of molecules to determine the reaction path study.

**Table 4.5a:** Selected bond length for the pyrolysis of O-ipropyl S-methyl dithiocarbonates

| BOND (Å) | STATE | B3LYP/6-311+G** | CC – PVTZ |
|---|---|---|---|
| $C_{15}$-$H_{16}$ | GS | 1.0925 | 1.0926 |
| | TS | 1.2050 | 1.2151 |
| | PRD | - | - |
| | Δd | 0.1125 | 0.1225 |
| $C_5$– $C_{15}$ | GS | 1.5200 | 1.5210 |
| | TS | 1.4169 | 1.4163 |
| | PRD | 1.3334 | 1.3425 |
| | Δd | - 0.1031 | - 0.1047 |
| $C_5$ – $O_7$ | GS | 1.4689 | 1.4625 |
| | TS | 2.1830 | 2.1930 |
| | PRD | - | - |
| | Δd | 0.7141 | 0.7305 |
| $O_7$- $C_8$ | GS | 1.3330 | 1.3334 |
| | TS | 1.2449 | 1.2460 |
| | PRD | 1.2003 | 1.2004 |
| | Δd | -0.0881 | -0.0874 |
| $C_8$= $S_9$ | GS | 1.6454 | 1.6451 |
| | TS | 1.7255 | 1.7252 |
| | PRD | 1.8258 | 1.8256 |
| | Δd | 0.0801 | 0.0801 |
| $C_8$– $S_{10}$ | GS | 1.7875 | 1.7876 |
| | TS | 1.7948 | 1.7951 |
| | PRD | 1.7904 | 1.7905 |
| | Δd | 0.0073 | 0.0075 |
| $S_{10}$– $C_{11}$ | GS | 1.8183 | 1.8182 |
| | TS | 1.8285 | 1.8235 |
| | PRD | 1.8258 | 1.8219 |
| | Δd | 0.010 | 0.0053 |
| $S_9$ - $H_{16}$ | GS | 4.980 | 4.975 |
| | TS | 1.9090 | 1.9215 |
| | PRD | 1.3475 | 1.3404 |
| | Δd | -3.071 | -3.0535 |

**Note:** Δd = d(TS) – d(GS)

Bond length in the transition state (TS) - Bond length in the Ground State (TS)

PRD =Product

**TABLE 4.5b:** Selected bond angle for the gas phase thermal decomposition Of O-ipropyl S-methyl dithiocarbonates

| **BOND ($^0$)** | **STATE** | **DFT/B3LYP/ 6-311+ G**** | **DFT/B3LYP/ CC-PVTZ** |
|---|---|---|---|
| $H_{16}$– $C_{15}$– $C_1$ | GS | 110.504 | 110.437 |
| | TS | 103.820 | 103.52 |
| | PRD | - | - |
| $C_{15}$– $C_1$– $O_3$ | GS | 105.196 | 105.720 |
| | TS | 105.840 | 105.730 |
| | PRD | - | - |
| $C_1$– $O_3$– $C_4$ | GS | 124.755 | 124.721 |
| | TS | 121.580 | 121.620 |
| | PRD | - | - |
| $O_3$- $C_4$ =$S_5$ | GS | 129.905 | 119.921 |
| | TS | 125.280 | 125.560 |
| | PRD | 123.678 | 123.421 |
| $O_3$- $C_4$- $S_6$ | GS | 115.214 | 115.521 |
| | TS | 119.297 | 119.282 |
| | PRD | 124.567 | 124.621 |
| $S_5$ = $C_4$– $S_6$ | GS | 124.878 | 124.820 |
| | TS | 115.415 | 115.270 |
| | PRD | 111.682 | 111.782 |
| $C_4$– $S_6$– $C_7$ | GS | 102.390 | 102.392 |
| | TS | 101.420 | 102.430 |
| | PRD | 98.136 | 97.146 |
| $S_{11}$– $C_1$– $C_{15}$ | GS | 113.630 | 114.720 |
| | TS | 122.880 | 122.860 |
| | PRD | 125.250 | 125.260 |

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

**TABLE 4.5c**: Selected dihedral for the gas phase thermal decomposition of O-ipropyl S-methyl dithiocarbonates

| **BOND($^0$)** | **STATE** | **B3LYP/ 6-311+ G**** | **CC-PVTZ** |
|---|---|---|---|
| $O_3– C_1 - C_{15}– H_{16}$ | GS | 60.628 | -60.728 |
| | TS | -12.59$^0$ | -13.08 |
| | PRD | - | - |
| $C_1– O_3– C_4 = S_5$ | GS | -176.833 | -177.657 |
| | TS | 37.420 | 35.810 |
| | PRD | - | - |
| $O_3- C_4- S_6- C_7$ | GS | 178.781 | 178.781 |
| | TS | -4.260 | -4.261 |
| | PRD | -0.000 | -0.000 |
| $S_5= C_4- S_6- C_7$ | GS | -0.571 | -0.571 |
| | TS | 176.71 | 176.71 |
| | PRD | 180.000 | 180.000 |
| $H_{13}- C_{15}- C_1- C_{11}$ | GS | 58.781 | 58.781 |
| | TS | 93.09 | 93.011 |
| | PRD | - | - |
| $C_4- O_3- C_1- C_{15}$ | GS | -149.948 | -149.123 |
| | TS | -5.320 | -5.420 |
| | PRD | - | - |

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

**TABLE 4.5d:** Atomic charges (Mulliken) of O-ipropyl S-methyl dithiocarbonates

| ATOM | STATE | B3LYP 6-311+G* | CC-PVTZ |
|---|---|---|---|
| $H_{16}$ | GS | +0.159 | +0.167 |
| | TS | +0.120 | +0.155 |
| | PRD | +0.093 | +0.094 |
| | Δq | -0.039 | -0.167 |
| $C_{15}$ | GS | -0.417 | -0.447 |
| | TS | -0.358 | -0.467 |
| | PRD | -0.547 | -0.367 |
| | Δq | +0.155 | -0.02 |
| $C_5$ | GS | -0.185 | +0.091 |
| | TS | +0.030 | +0.083 |
| | PRD | -0.043 | -0.046 |
| | Δq | +0.215 | -0.008 |
| $O_7$ | GS | +0.205 | -0.395 |
| | TS | -0.089 | -0.462 |
| | PRD | -0.207 | -0.208 |
| | Δq | -0.294 | -0.067 |
| $C_4$ | GS | -0.074 | +0.063 |
| | TS | +0.054 | +0.087 |
| | PRD | +0.079 | +0.078 |
| | Δq | +0.128 | +0.128 |
| $S_9$ | GS | -0.291 | -0.195 |
| | TS | -0.302 | -0.159 |
| | PRD | -0.112 | -0.142 |
| | Δq | -0.011 | 0.036 |
| $S_6$ | GS | -0.009 | -0.158 |
| | TS | -0.011 | +0.150 |
| | PRD | +0.084 | +0.086 |
| | Δq | -0.002 | +0.300 |
| $C_8$ | GS | -0.459 | -0.596 |
| | TS | -0.515 | -0.587 |
| | PRD | -0.511 | -0.562 |
| | Δq | -0.056 | +0.009 |

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

**Table 4.5e:** Wiberg bond indices of O-isopropyl S-methyl Xanthate.

| Compound | State | $C_5$-$C_{15}$ | $C_{15}$-$H_{16}$ | $S_5$-$H_{16}$ | $S_9$-$C_8$ | $O_8$-$C_5$ | $C_5$-$O_7$ |
|---|---|---|---|---|---|---|---|
| **O-ipropyl** | $B_i^R$ | 1.018 | 0.928 | 0.002 | 1.666 | 1.041 | 0.790 |
| **S-methyl** | $B_i^{TS}$ | 1.310 | 0.549 | 0.325 | 1.319 | 1.407 | 0.225 |
| **Xanthate** | $B_i^P$ | 1.985 | 0.000 | 0.962 | 1.070 | 1.695 | 0.000 |
|  | $\delta B_i$ | 0.317 | 0.408 | 0.337 | 0.582 | 0.560 | 0.716 |
|  | %Ev | 30.2 | 40.8 | 33.7 | 58.2 | 56.0 | 71.6 |
|  | δBav | 0.487 |  |  |  |  |  |
|  | Sy | 0.832 |  |  |  |  |  |

### 4.7.1 Wiberg Bond Order For O-isopropyl Xanthate

Using Wiberg bond equations (Moyano *et al.,* 1989 and Quijano *et al.,* 2002) variation of bond indices $\delta B_i$ have been calculated and the percentage evolution of each bond has been obtained. The calculated percentage evolution of bond involved in the reaction coordinate is summarized in Table 4.5(e). The result obtained for the O-ipropyl xanthates, the breaking of the bond $C_5$-$O_7$ with 71.6% is the most leading process accompanied by the changing of the bond ($S_9$-$C_8$) from double bond to single bond with a percentage evolution 58.2% and also conversion of $C_9$-$O_8$ single bond of 56% to double bond. The least advanced process is the formation of the $C_5$-$C_{15}$ double bond of 30.2% accompanied by the formation of $S_9$-$H_{16}$ bond at 33.7% evolution and the breaking at bond $C_{15}$-$H_{16}$ of 40.8% evolution.

The average value of bond indices ($\delta Bav$) which measures the degree of advancement of the transition state along the reaction path for O-ipropyl S-methyl Xanthate is 0.487 indicating that the transition state has an early character nearer to the reactants than the products. The synchronicity (Sy) value of the reaction for the O-ipropyl S-methyl Xanthate was 0.832, which indicate that the O- ipropyl S-methyl dithiocarbonate corresponds to high asynchronous processes.

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### 4.8. O –nbutyl S-methyl Dithiocarbonates.

The pyrolysis of O-nbutyl S-methyl xanthates also gives butylene and unstable S-methyl xanthates which then decompose to a thiol and carbonyl sulphide. This decomposition also occurs through a concerted fragmentation via an E1 mechanism which includes a cyclic transition state with six member ring as shown in figure 4.16. The reaction coordinate involved the breaking of bond $C_{11} – O_{14}$ and $C_8 –H_9$ and $S_{17} – H_9$ bond formation. The bond lengths are given in density functional theory and are shown in Table 4.5a where the transition State bond length of $C_{11}–O_{14}$ and $C_8 – H_9$ bond cleavage ranges between 2.267 to 2.717Å and the bond length of the ground state ranges between 1.1770 to 1.2530Å and for $S_{17} – H_9$, the bond length that ranges between 1.8910 to 1.9970Å. Bond angles, dihedral and atomic charges are shown in Tables 4.5b, 4.5c and 4.5d.

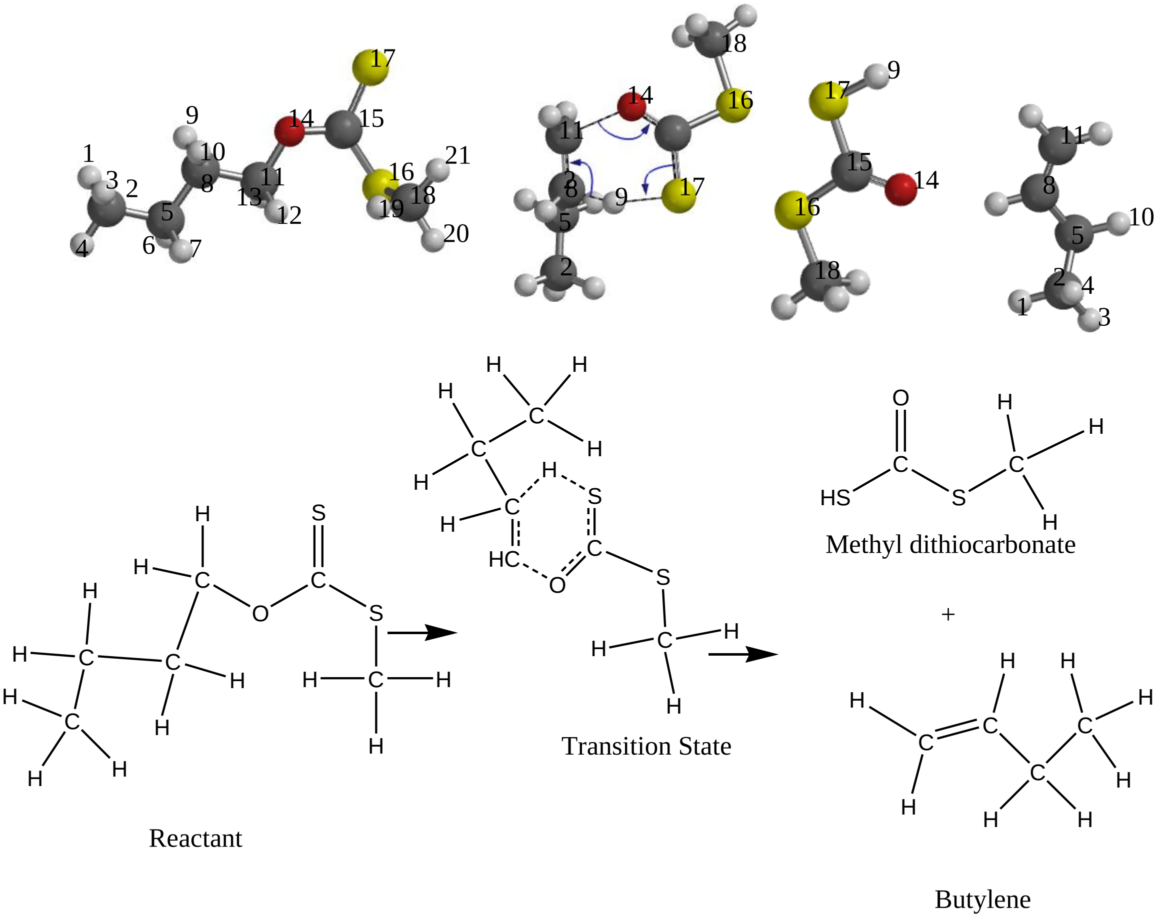


**Figure. 4.16:** Reaction scheme for thermal decomposition of O-nbutyl S-methyl Xanthates

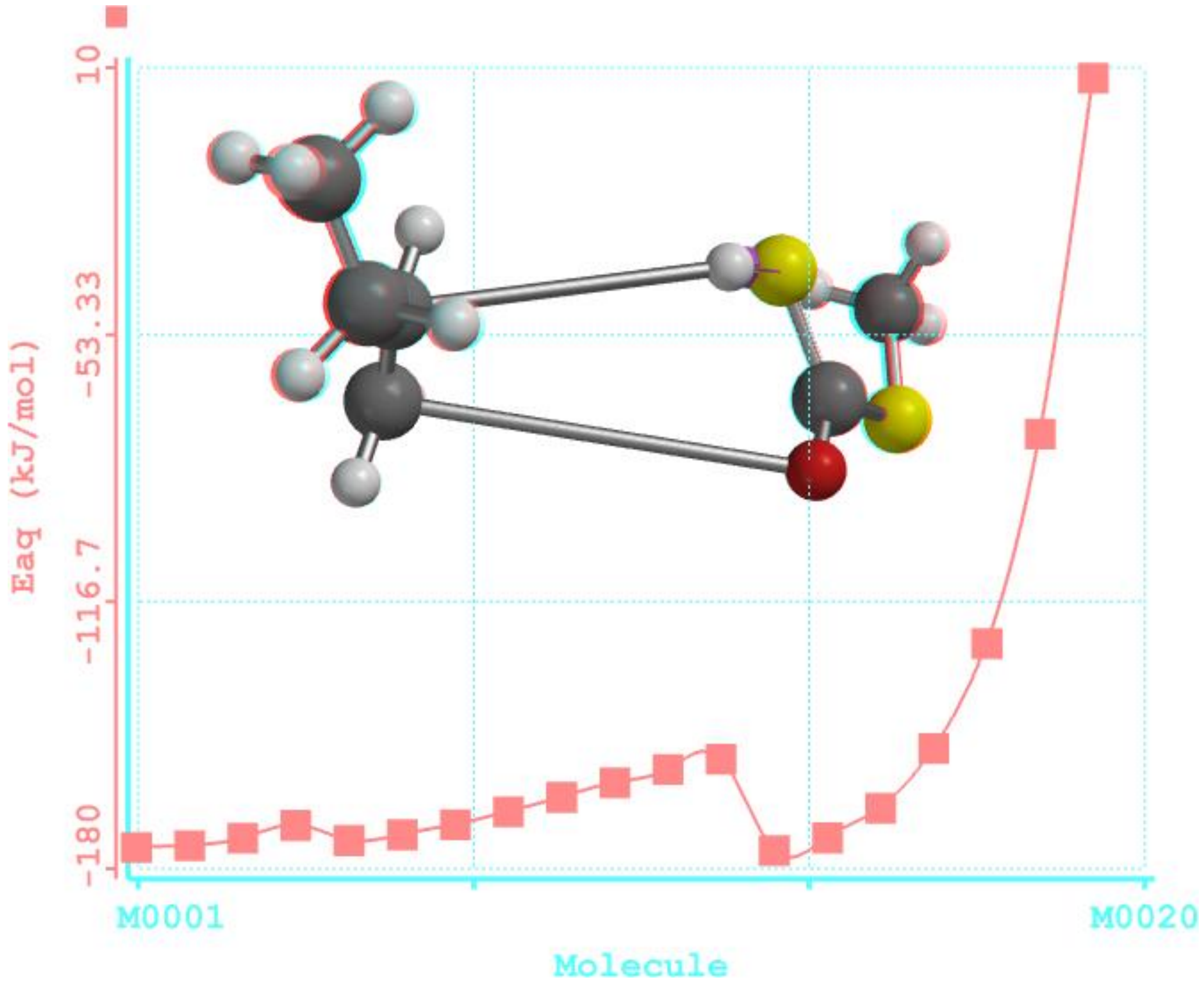


**Figure : 4.17:** Reaction path study O-nbutyl S-methyl dithiocarbonates) and a plot of energy against number of  molecules to determine the reaction path study.

**Table 4.6a** Bond length (Å) for the gas phase thermal decomposition of O-nbutyl S-methyl dithiocarbonates

| Bond (Å) | STATE | DFT/ B3LYP /6-311+G** | DFT/B3LYP /CC-PVTZ |
|---|---|---|---|
| $C_8$ -$H_9$ | GS | 1.0916 | 1.0916 |
| | TS | 1.1770 | 1.1950 |
| | PRD | - | - |
| | Δd | 0.0854 | 0.1034 |
| $C_8$-$C_{11}$ | GS | 1.5292 | 1.5294 |
| | TS | 1.4314 | 1.4288 |
| | PRD | 1.3347 | 1.3352 |
| | Δd | -0.0964 | -0.1066 |
| $C_{11}$-$O_{14}$ | GS | 1.4955 | 1.4967 |
| | TS | 2.2690 | 2.2670 |
| | PRD | - | - |
| | Δd | 0.7735 | 0.7703 |
| $O_{14}$-$C_{15}$ | GS | 1.3308 | 1.3309 |
| | TS | 1.2433 | 1.2433 |
| | PRD | 1.2186 | 1.2188 |
| | Δd | -0.0875 | -0.0863 |
| $C_{15}$=$S_{16}$ | GS | 1.7853 | 1.7867 |
| | TS | 1.7998 | 1.8048 |
| | PRD | 1.8187 | 1.80851 |
| | Δd | 0.0145 | 0.0181 |
| $C_{15}$-$S_{17}$ | GS | 1.6497 | 1.6499 |
| | TS | 1.7236 | 1.7292 |
| | PRD | 1.7932 | 1.7834 |
| | Δd | 0.0739 | 0.0793 |
| $S_{17}$-$C_{18}$ | GS | 1.8184 | 1.8184 |
| | TS | 1.8287 | 1.8299 |
| | PRD | 1.8377 | 1.8352 |
| | Δd | 0.0103 | 0.0115 |
| $C_2$-$C_5$ | GS | 1.5288 | 1.8284 |
| | TS | 1.4882 | 1.4919 |
| | PRD | 1.5070 | 1.5272 |
| | Δd | -0.0406 | -0.3365 |
| $H_9$-$S_{17}$ | GS | 4.8040 | 4.8050 |
| | TS | 1.9970 | 1.9970 |
| | PRD | 1.3492 | 1.3462 |
| | Δd | -2.8070 | -2.808 |

**Note:** Δd = d(TS) – d(GS)

Bond length in the transition state (TS) - Bond length in the Ground State (TS)

PRD =Product

**Table 4.6b**: Selected bond angle (0º) for the gas phase thermal decomposition Of O-nbutyl S-methyl dithiocarbonates

| **BOND** | **STATE** | **DFT/B3LYP / 6-311+G**** | **DFT/B3LYP/ CCPV-TS** |
|---|---|---|---|
| $H_9$-$C_8$-$C_{11}$ | GS | 110.589 | 110.678 |
| | TS | 105.060 | 105.070 |
| | PRD | - | - |
| $C_8$-$C_{11}$-$O_{14}$ | GS | 101.007 | 101.002 |
| | TS | 103.110 | 103.390 |
| | PRD | - | - |
| $C_{11}$-$O_{14}$-$C_{15}$ | GS | 131.235 | 131.242 |
| | TS | 124.57 | 124.560 |
| | PRD | - | - |
| $O_{14}$-$C_{15}$=$S_{16}$ | GS | 118.996 | 118.926 |
| | TS | 125.927 | 126.120 |
| | PRD | 124.053 | 124.556 |
| $O_{14}$-$C_{15}$-$S_{17}$ | GS | 117.158 | 117.159 |
| | TS | 118.876 | 118.820 |
| | PRD | 124.615 | 124.662 |
| $C_{15}$-$S_{17}$-$C_{18}$ | GS | 102.874 | 102.624 |
| | TS | 101.251 | 101.261 |
| | PRD | 98.930 | 98.945 |
| $S_{16}$=$C_{15}$-$S_{17}$ | GS | 123.818 | 123.428 |
| | TS | 115.193 | 115.194 |
| | PRD | 111.332 | 115.211 |
| $S_{17}$-$C_{18}$-$H_{19}$ | GS | 110.411 | 110.412 |
| | TS | 106.183 | 106.195 |
| | PRD | 110.476 | 111.420 |

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

**Table 4.6c :** Selected dihedral angle (0º) for the gas phase thermal decomposition of O-nbutyl S-methyl dithiocarbonates

| DIHEDRAL | STATE | DFT/B3LYP/ 6-311+G** | DFT/B3LYP/ CC-PVTZ |
|---|---|---|---|
| $H_9$-$C_8$-$C_{11}$-$O_{14}$ | GS | 60.106 | 60.256 |
| | TS | -9.74 | -7.76 |
| | PRD | - | - |
| $C_8$-$C_{11}$-$O_{14}$-$C_{15}$ | GS | 174.174 | 174.286 |
| | TS | -3.79 | -4.79 |
| | PRD | - | - |
| $C_2$-$C_5$-$C_8$-$H_9$ | GS | 61.276 | 61.921 |
| | TS | 30.709 | 31.762 |
| | PRD | 0.133 | 0.142 |
| $C_{11}$-$O_{14}$-$C_{15}$=$S_{16}$ | GS | -167.024 | -169.251 |
| | TS | 30.52 | 30.57 |
| | PRD | - | - |
| $C_{11}$-$O_{14}$-$C_{15}$-$S_{17}$ | GS | 14.834 | 14.846 |
| | TS | -148.72 | -148.720 |
| | PRD | - | - |
| $O_{14}$-$C_{15}$-$S_{17}$-$C_{18}$ | GS | -178.765 | -179.761 |
| | TS | -3.286 | -3.462 |
| | PRD | -0.000 | -0.000 |
| $S_{16}$=$C_{15}$-$S_{17}$-$C_{18}$ | GS | 3.192 | 3.194 |
| | TS | 177.386 | 179.251 |
| | PRD | 180.000 | 180.000 |

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

**Table 4.6d:** Atomic charges of (Mulliken) for the gas phase thermal decomposition of O-nbutyl S-methyl dithiocarbonate

| **ATOM** | **STATE** | **DFT/B3LYP/ 6-311+G**** | **DFT/B3LYP/ CC-PVTZ** |
|---|---|---|---|
| $H_9$ | GS | +0.163 | +0.164 |
| | TS | +0.126 | +0.142 |
| | PRD | +0.093 | +0.042 |
| | Δq | -0.037 | -0.022 |
| $C_8$ | GS | -0.355 | -0.356 |
| | TS | -0.281 | -0.291 |
| | PRD | -0.392 | -0.420 |
| | Δq | 0.074 | 0.065 |
| $C_{11}$ | GS | -0.279 | -0.280 |
| | TS | +0.253 | +0.252 |
| | PRD | +0.756 | +0.761 |
| | Δq | 0.532 | 0.580 |
| $O_{14}$ | GS | +0.231 | +0.232 |
| | TS | -0.062 | -0.072 |
| | PRD | -0.207 | -0.302 |
| | Δq | -0.293 | -0.304 |
| $C_{15}$ | GS | -0.109 | -0.109 |
| | TS | +0.114 | +0.121 |
| | PRD | +0.079 | +0.079 |
| | Δq | 0.223 | 0.230 |
| $S_{16}$ | GS | +0.072 | +0.073 |
| | TS | -0.032 | +0.081 |
| | PRD | +0.112 | -0.125 |
| | Δq | -0.104 | 0.008 |
| $S_{17}$ | GS | -0.295 | -0.296 |
| | TS | -0.393 | -0.297 |
| | PRD | +0.084 | +0.084 |
| | Δq | -0.098 | -0.001 |
| $C_{18}$ | GS | -0.463 | -0.465 |
| | TS | -0.517 | -0.519 |
| | PRD | -0.501 | -0.561 |
| | Δq | -0.054 | -0.054 |

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

**Table 4.6(e):** Wiberg bond indices for O-nbutyl S-Methyl Xanthate**.**

| **Compound** | **State** | **$C_8$-$C_{11}$** | **$C_8$-$H_9$** | **$H_9$-$S_{17}$** | **$S_{17}$-$C_{15}$** | **$C_{15}$-$O_{14}$** | **$O_{14}$-$C_{11}$** |
|---|---|---|---|---|---|---|---|
| **O-nbutyl** | $B_i^R$ | 1.016 | 0.926 | 0.004 | 0.980 | 1.034 | 0.771 |
| **S-methyl** | $B_i^{TS}$ | 1.411 | 0.435 | 0.472 | 0.309 | 1.390 | 0.357 |
| **Xanthate** | $B_i^P$ | 1.983 | 0.000 | 0.955 | 0.000 | 1.695 | 0.000 |
| | $\delta B_i$ | 0.407 | 0.530 | 0.494 | 0.685 | 0.539 | 0.76 |
| | %Ev | 40.7 | 53.0 | 32.0 | 68.5 | 53.9 | 76.0 |
| | δBav | 0.569 | | | | | |
| | Sy | 0.867 | | | | | |

### 4.8.1 Wiberg Bond Order For O-nbutyl S-methyl Dithiocarbonates

The percentage of evolution of bonds calculated at the centre of the reaction coordinate is summarized in table 4.6(e). The result obtained for O-nbutyl xanthates indicates that, the breaking of the bond $O_{14}$-$C_{11}$ with 76% is the most leading process accompany by the changing of the double bond $S_{17}$-$C_{15}$ with a percentage evolution of bonds of 68.5% into a single bond and the conversion of bond $C_{15}$-$O_{14}$ single bond of 63.9% to double bond. The formation of double ($C_8$-$C_{11}$) bond with 40.7% is the least progressive process accompany by the formation of $H_9$-$S_{17}$ bond of 53% and the breaking of bond $C_8$-$H_9$ of 32%. The average bond index $\delta B_{av}$ of O-nbutyl S-methyl xanthates was also calculated as 0.569 which shows that the early character display by the transition state closer to the reactant than that of the products.

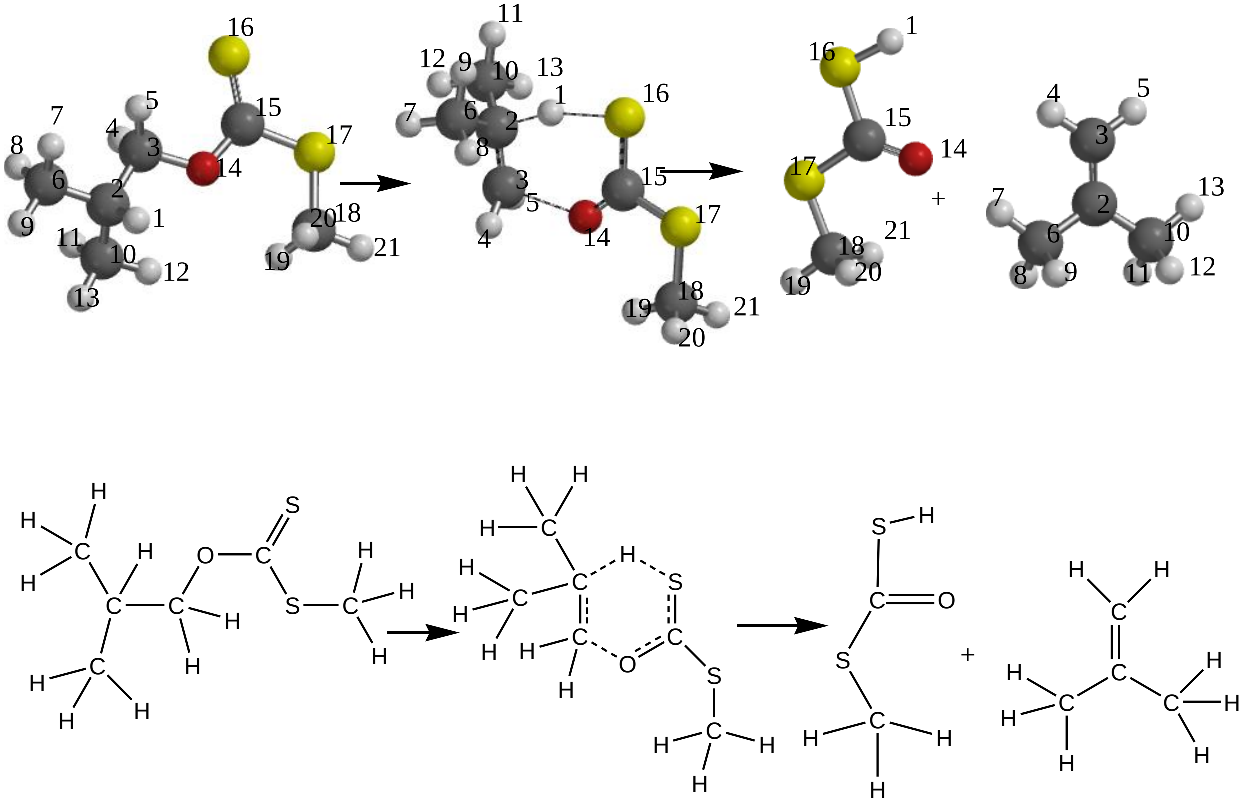
Synchronicity, (Sy) of the reaction was also calculated. Synchronicities vary from zero to one which is the case when all bonds involved in the reaction centers are broken or formed to the same extent in the transition state. The mechanism of O-nbutyl S-methyl Xanthates corresponds to highly asynchronous processes because the calculated value of the synchronicity Sy of the compound is 0.867 which is less than one.

Another area that should be taken into account is the relative asychronicity of the bond cleavage and bond-formation which measure the bond deficiency within the reaction path. In the O-nbutyl S-methyl Xanthate reaction, the bond cleavage processes are more advanced with 76% than the bond forming processes showing a bond deficiency of 31% in the transition state.

The confirmation of asychronicity was also done by using the asymmetrical charge distribution between of the transition structure of the alpha carbon and beta carbon ($C_\alpha$ and $C_\beta$) atoms (positively charged on the alpha carbon ($C_\alpha$ ) and negatively charged the beta carbon ($C_\beta$) The more polarity of the alpha carbon and beta carbon ($C_\alpha$ and $C_\beta$) atoms bond, the faster is the rate of the reaction.

## 4.9. O-ibutyl S-methyl Dithiocarbonates.

The products of decomposition of O-ibutyl S-methyl dithiocarbonates are 2-methyl propylene $CH_3C_2H_6CH_3$ and unstable S-methyl xanthates which subsequently break down to thiol and carbonyl sulphide. The reaction involves the breaking of $C_5 – O_{14}$ and $C_2 – H_1$ bonds and the making of the $S_{16} – H_1$ bond bonds as shown in Fig 4:18. The bond length were given in density functional and as shown in Table 4.7a. The values for transition states of $O_{14} – C_5$ ranges between 2.2690Å and 2.2670Å and the ground state value range between 1.4955 and 1.4962Å, for $C_2 – H_1$ the bond length for transition state ranges between1.1770 to 1.1950Å and the ground state value ranges between1.0916Å and 1.1950Å, also for the formation of bond $S_{16} – H_1$, the bond length ranges for transition state 4.8040 and 4.8050Å and ground state is 1.9970Å bond length bond angles dihedrals and atomic charges are as shown in Table 4:7b, 4.7c and 4.7d and 4.7e



Reactant

Transition State

Methyl dithiocarbonate

2-MethylPropene

**Figure. 4.18:** Reaction scheme for pyrolysis of O-ibutyl S-methyl Dithiocarbonates

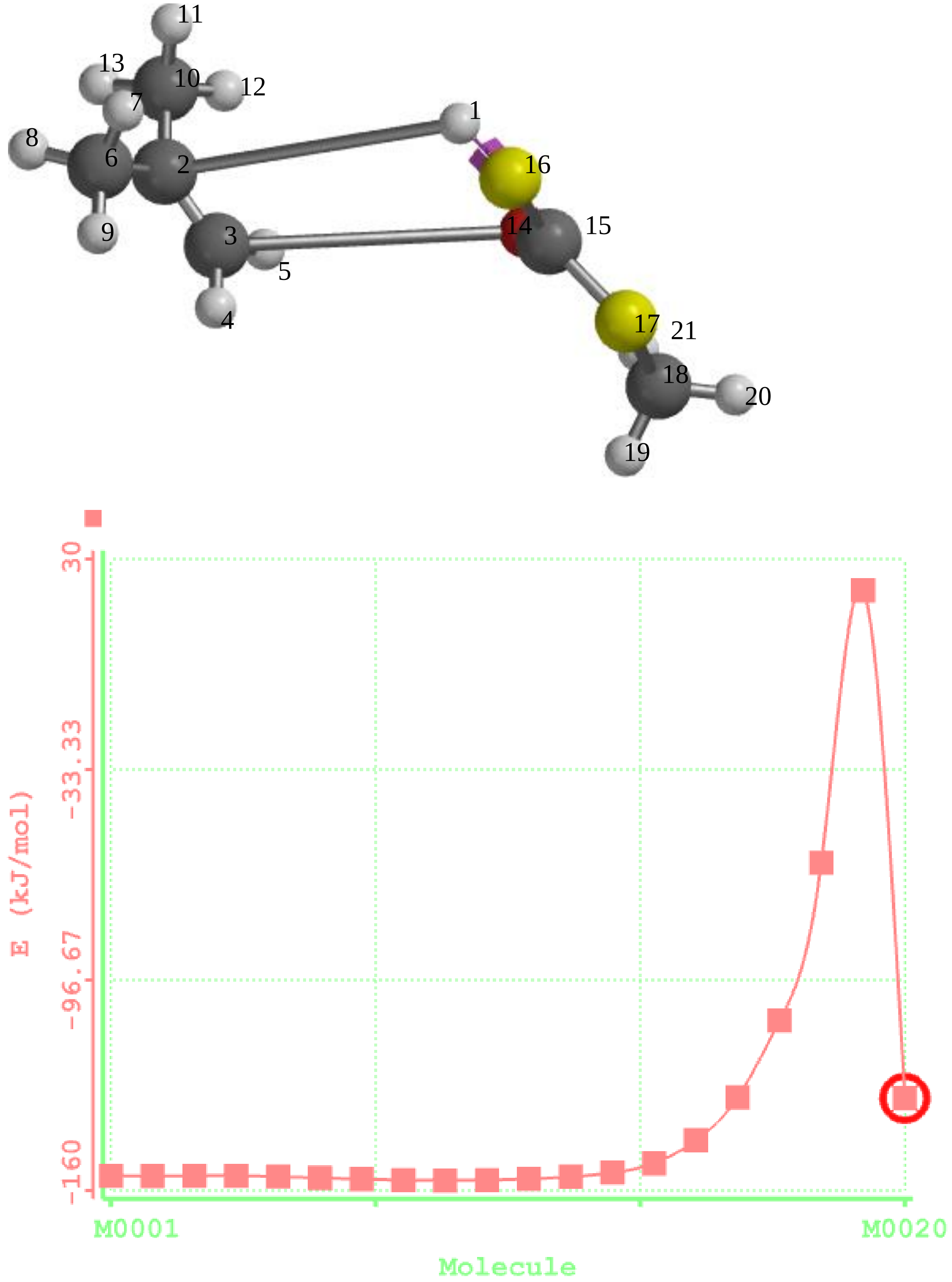


**Figure : 4.19:** Reaction path study O-ibutyl S-methyl Dithiocarbonates) and a plot of energy against number of molecules to depict the reaction path study.

**Table 4.7a** Selected bond length (Å) for the gas phase thermal decomposition Of O-ibutyl S-methyl xanthates

| **Bond (Å)** | **STATE** | **B3LYP /6-311+G**** | **CC-PVTZ** |
|---|---|---|---|
| $C_2$ -$H_1$ | GS | 1.0916 | 1.0916 |
| | TS | 1.1770 | 1.1950 |
| | PRD | - | - |
| | Δd | 0.0854 | 0.1034 |
| $C_2$-$C_3$ | GS | 1.5292 | 1.5294 |
| | TS | 1.4314 | 1.4288 |
| | PRD | 1.3347 | 1.3352 |
| | Δd | -0.0964 | -0.1066 |
| $C_5$-$O_{14}$ | GS | 1.4955 | 1.4967 |
| | TS | 2.2690 | 2.2670 |
| | PRD | - | - |
| | Δd | 0.7735 | 0.7703 |
| $O_{14}$-$C_{15}$ | GS | 1.3308 | 1.3309 |
| | TS | 1.2433 | 1.2433 |
| | PRD | 1.2186 | 1.2188 |
| | Δd | -0.0875 | -0.0863 |
| $C_{15}$-$S_{16}$ | GS | 1.7853 | 1.7867 |
| | TS | 1.7998 | 1.8048 |
| | PRD | 1.8187 | 1.80851 |
| | Δd | 0.0145 | 0.0181 |
| $C_{15}$-$S_{17}$ | GS | 1.6497 | 1.6499 |
| | TS | 1.7236 | 1.7292 |
| | PRD | 1.7932 | 1.7834 |
| | Δd | 0.0739 | 0.0793 |
| $S_{17}$-$C_{18}$ | GS | 1.8184 | 1.8184 |
| | TS | 1.8287 | 1.8299 |
| | PRD | 1.8377 | 1.8352 |
| | Δd | 0.0103 | 0.0115 |
| $C_2$-$C_6$ | GS | 1.5288 | 1.8284 |
| | TS | 1.4882 | 1.4919 |
| | PRD | 1.5070 | 1.5272 |
| | Δd | -0.0406 | -0.3365 |
| $H_1$-$S_{16}$ | GS | 4.8040 | 4.8050 |
| | TS | 1.9970 | 1.9970 |
| | PRD | 1.3492 | 1.3462 |
| | Δd | -2.8070 | -2.808 |

**Note:** Δd = d(TS) – d(GS)

Bond length in the transition state (TS) - Bond length in the Ground State (TS)

PRD =Product

**Table 4.7b :** Selected bond angle (0°) of gas phase thermal decomposition of O-ibutyl S-methyl xanthates

| **BOND** | **STATE** | **B3LYP/ 6-311+G**** | **CCPV-TZ** |
|---|---|---|---|
| $H_1$-$C_2$-$C_3$ | GS | 110.589 | 110.678 |
| | TS | 105.060 | 105.070 |
| | PRD | - | - |
| $C_2$-$C_3$-$O_{14}$ | GS | 101.007 | 101.002 |
| | TS | 103.110 | 103.390 |
| | PRD | - | - |
| $C_3$-$O_{14}$-$C_{15}$ | GS | 131.235 | 131.242 |
| | TS | 124.57 | 124.560 |
| | PRD | - | - |
| $O_{14}$-$C_{15}$-$S_{16}$ | GS | 118.996 | 118.926 |
| | TS | 125.927 | 126.120 |
| | PRD | 124.053 | 124.556 |
| $O_{14}$-$C_{15}$-$S_{17}$ | GS | 117.158 | 117.159 |
| | TS | 118.876 | 118.820 |
| | PRD | 124.615 | 124.662 |
| $C_{15}$-$S_{17}$-$C_{18}$ | GS | 102.874 | 102.624 |
| | TS | 101.251 | 101.261 |
| | PRD | 98.930 | 98.945 |
| $S_{16}$=$C_{15}$-$S_{17}$ | GS | 123.818 | 123.428 |
| | TS | 115.193 | 115.194 |
| | PRD | 111.332 | 115.211 |
| $S_{17}$-$C_{18}$-$H_{19}$ | GS | 110.411 | 110.412 |
| | TS | 106.183 | 106.195 |
| | PRD | 110.476 | 111.420 |

**Note :** GS = Ground State ,

TS = Transition State,

PRD = Product

**Table 4.7c:** Selected dihedral angle (0º) of O-ibutyl S-methyl xanthates.

| DIHEDRAL | STATE | B3LYP/ 6-311+G** | CC-PVTZ |
|---|---|---|---|
| $H_1$-$C_2$-$C_3$-$O_{14}$ | GS | 60.106 | 60.256 |
| | TS | -9.74 | -7.76 |
| | PRD | - | - |
| $C_2$-$C_3$-$O_{14}$-$C_{15}$ | GS | 174.174 | 174.286 |
| | TS | -3.79 | -4.79 |
| | PRD | - | - |
| $C_6$-$C_2$-$C_3$-$H_4$ | GS | 61.276 | 61.921 |
| | TS | 30.709 | 31.762 |
| | PRD | 0.133 | 0.142 |
| $C_3$-$O_{14}$-$C_{15}$=$S_{16}$ | GS | -167.024 | -169.251 |
| | TS | 30.52 | 30.57 |
| | PRD | - | - |
| $C_3$-$O_{14}$-$C_{15}$-$S_{17}$ | GS | 14.834 | 14.846 |
| | TS | -148.72 | -148.720 |
| | PRD | - | - |
| $O_{14}$-$C_{15}$-$S_{17}$-$C_{18}$ | GS | -178.765 | -179.761 |
| | TS | -3.286 | -3.462 |
| | PRD | -0.000 | -0.000 |
| $S_{16}$=$C_{15}$-$S_{17}$-$C_{18}$ | GS | 3.192 | 3.194 |
| | TS | 177.386 | 179.251 |
| | PRD | 180.000 | 180.000 |

**Note :** GS = Ground State ,

TS = Transition State,

PRD = Product

**Table 4.7d:** Atomic charges of (Mulliken) of the gas phase thermal decomposition of O-ibutyl S-methyl xanthates

| ATOM | STATE | DFT/B3LYP/ 6-311+G** | CC-PVTZ |
|---|---|---|---|
| $H_1$ | GS | +0.163 | +0.164 |
| | TS | +0.126 | +0.142 |
| | PRD | +0.093 | +0.042 |
| | Δq | -0.037 | -0.022 |
| $C_2$ | GS | -0.355 | -0.356 |
| | TS | -0.281 | -0.291 |
| | PRD | -0.392 | -0.420 |
| | Δq | 0.074 | 0.065 |
| $C_3$ | GS | -0.279 | -0.280 |
| | TS | +0.253 | +0.252 |
| | PRD | +0.756 | +0.761 |
| | Δq | 0.532 | 0.580 |
| $O_{14}$ | GS | +0.231 | +0.232 |
| | TS | -0.062 | -0.072 |
| | PRD | -0.207 | -0.302 |
| | Δq | -0.293 | -0.304 |
| $C_{15}$ | GS | -0.109 | -0.109 |
| | TS | +0.114 | +0.121 |
| | PRD | +0.079 | +0.079 |
| | Δq | 0.223 | 0.230 |
| $S_{16}$ | GS | +0.072 | +0.073 |
| | TS | -0.032 | +0.081 |
| | PRD | +0.112 | -0.125 |
| | Δq | -0.104 | 0.008 |
| $S_{17}$ | GS | -0.295 | -0.296 |
| | TS | -0.393 | -0.297 |
| | PRD | +0.084 | +0.084 |
| | Δq | -0.098 | -0.001 |
| $C_{18}$ | GS | -0.463 | -0.465 |
| | TS | -0.517 | -0.519 |
| | PRD | -0.501 | -0.561 |
| | Δq | -0.054 | -0.054 |

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

**Table 4.7e:** Wiberg bond indices for O-isobutyl S-methyl xanthate**.**

| **Compound** | **State** | **$C_2$-$C_3$** | **$C_2$-$H_1$** | **$H_1$-$S_{16}$** | **$S_{16}$-$C_8$** | **$C_{15}$-$O_{14}$** | **$O_{14}$-$C_5$** |
|---|---|---|---|---|---|---|---|
| **O-ibutyl** | $B_i^R$ | 1.007 | 0.921 | 0.005 | 1.666 | 1.045 | 0.771 |
| **S-methyl** | $B_i^{TS}$ | 1.274 | 0.570 | 0.298 | 1.321 | 1.419 | 0.179 |
| **Xanthate** | $B_i^P$ | 1.934 | 0.000 | 0.962 | 1.070 | 1.695 | 0.000 |
|  | $\delta B_i$ | 0.288 | 0.390 | 0.310 | 0.579 | 0.576 | 0.768 |
|  | %Ev | 28.8 | 39.0 | 31.0 | 57.9 | 57.6 | 76.8 |
|  | δBav | 0.485 |  |  |  |  |  |
|  | Sy | 0.807 |  |  |  |  |  |

### 4.9.1 Wiberg Bond Order For O-ibutyl S-methyl Dithiocarbonates

Variation of relative bond indices ($\delta B_i$) for the transition states of O-ibutyl S-methyl xanthate was calculated and percentage of evolution (%Ev) of each bond involved at the reaction coordinate of the bond order during the process was obtained. The estimated value for the percentage of evolution was shown in table 4.6(e). The most leading process is the cleavage of bond ($O_{14}$-$C_5$) which is 76.8%, accompany by the double bond conversion of $S_{16}$-$C_{15}$ to single bond with 57.9% and also changing of single bond ($C_{15}$-$O_{14}$) into double bonds of 57.6%. The least progressive process is the double bond production of the $C_2$-$C_3$ which is 28.8% accompany by the formation $H_1$-$S_{16}$ bond of 31% and the breaking of $C_2$-$H_1$ bond 39%. The average bond index $\delta B_{av}$ was also calculated as listed in Table 4.6(e). The value of $\delta B_{av}$ is 0.485 indicating that the transition state has an “early” character closer to reactant than products.

Synchronicity (Sy), of the reaction was also calculated and discovered to be greatly asynchronous because synchronization varies from zero to one(Moyano *et al.,* 1989 Quiyano *et al.*,2002), which was shown in the case all the bond involved in the reaction centers have broken or formed at exactly the same extent in the transition state. The calculated value of Sy for O-ibutyl S-methyl Xanthates is 0.807.

Another aspect should be taken into account is the relative asychronicity of the bond-forming and bond-breaking processes that measure the deficiency of bonds along the reaction path. In the reaction of O-ibutyl S-methyl Xanthate, the bond cleavage processes are more advanced with 76.8% than the bond forming processes of 31% which indicates a bond deficiency in the transition state. The charge asymmetrical distribution between the alpha carbon and beta carbon ($C_\alpha$ and $C_\beta$) atoms in the transition state indicate positively charged $C_\alpha$ and negatively charged $C_\beta$) also represents the character of the compound in the reaction to be asynchronous. The more polarity of the alpha carbon and beta carbon ($C_\alpha$ and $C_\beta$) atoms bond, the faster is the rate of the reaction.

### 4.10. O –tbutyl S-methyl Dithiocarbonates.

The pyrolysis of O-tbutyl S-methyl xanthates also gives 2-methyl propylene and unstable S-methyl dithiocarbonates which then decompose to carbonyl sulphide and a thiol. The decomposition also occurs through a concerted fragmentation via an $E_1$ mechanism involving a cyclic transition state of six membered ring as shown in Fig 4.20. The reaction coordinate involved $C_5$ – $O_6$ and $C_2$ –$H_1$ bond cleavages and $S_{17}$ – $H_1$ bond formation. The bond lengths are shown in Table 4.8a nothing the stretch in the bond length between $C_5$ – $O_6$ in the ground state from 1.4955 and 1.4967 to 2.2690 and 2.2670 in the transition State. The $C_2$ –$H_1$ bond length from 1.0916 and 1.0916 to 1.1770 and 1.1950 of $O_6$ – $C_5$ ranges between 2.2690 to 2.2670Å and the ground state is 1.4955 and 1.4967, the formation of $S_{17}$ – $H_1$ the bond length ranges between 1.1770 to 1.2530Å and for $S_{17}$ – H1, the bond length that ranges between 4.8040 to 4.8050Å and ground state are 1.9970 and 1.9970Å. The bond angles, dihedral and atomic charges are as shown in Tables 4.8b, 4.8c and 4.8d.

### 4.10.1 Wiberg Bond Order For O-tbutyl Xanthates

Relative variation of bond index for the transition states $\delta B_i$ and percentage of evolution (%Ev) in the pyrolytic reaction of O-methyl S-methyl xanthate was obtained as defined by (Moyano *et al.*, 1989) and Quijano *et al.*, 2008), was listed in table 4.8(e). The extent of breaking of bonds $O_6$-$C_5$ is the most advanced process of 77.8%, accompany the changing of double bond of ($S_{17}$-$C_{15}$) to single bond with 57.9% and the conversion of single bond of ($C_{15}$-$O_{14}$) into double bonds with 57.6%. The formation of the $C_2$-$C_3$ double bond with 28.7% is the least progressive process followed by the formation $H_1$-$S_{16}$ bond of 32% and the breaking of $C_2$-$H_1$ bond 39%. The average bond index $\delta B_{av}$ was also calculated as listed in Table 4.8(e) . As it is clearly seen the value of $\delta B_{av}$ is 0.486 which indicates that the transition state have an "early" characters closer to the reactant than the products.

Synchronicity "Sy" of a chemical reaction of all the bonds included in the reaction coordinates was also calculated. The variation of synchronization is between zero and one which is the case when we have bond broken or formed exactly at the same extent in the transition state. The calculation of synchronicity "Sy" for O-ibutyl S-methyl Xanthates is

0.865 which indicates that the mechanism of the compound corresponds to greatly asynchronous processes.

The relative asychronicity of the bond cleavage and bond formation process which measure the shortage of bond along the reaction path were also accounted for. In the pyrolysis of O-ibutyl S-methyl the bond cleavage is the leading advance process with 77.8% compared with formation of bond the percentage of 31% which indicate the shortage of bond at the transition state. The charge distribution between alpha carbon and beta carbon ($C_\alpha$ and $C_\beta$) atoms in the transition state are positively charged for carbon at the alpha position ($C_\alpha$ ) and negatively charged for carbon at the beta position ( $C_\beta$) which also represents that the character of the compound is greatly asynchronous in the reaction. The polarity of the bond between $C_\alpha$ and $C_\beta$ depend on the rate of reaction.

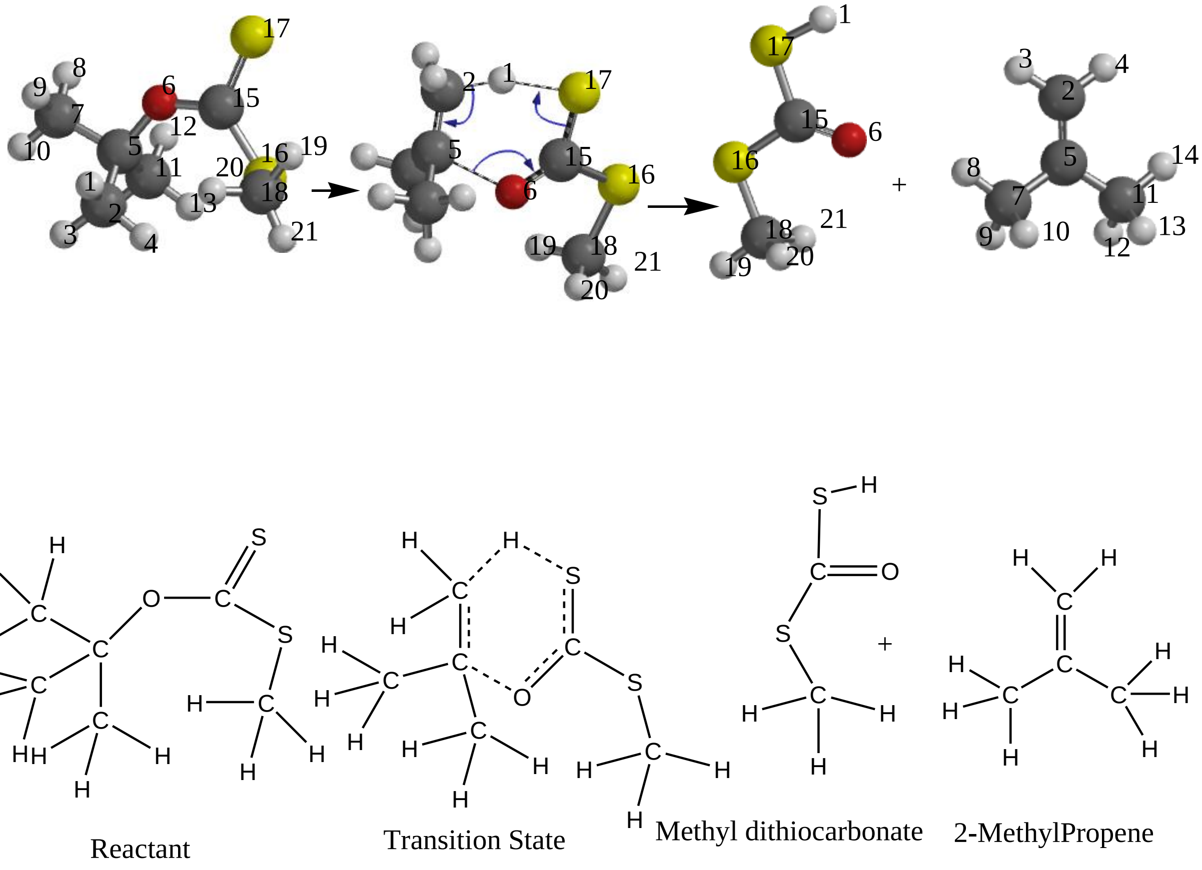


**Figure. 4.20:** Reaction scheme for thermal decomposition of O-tbutyl S-methyl xanthates

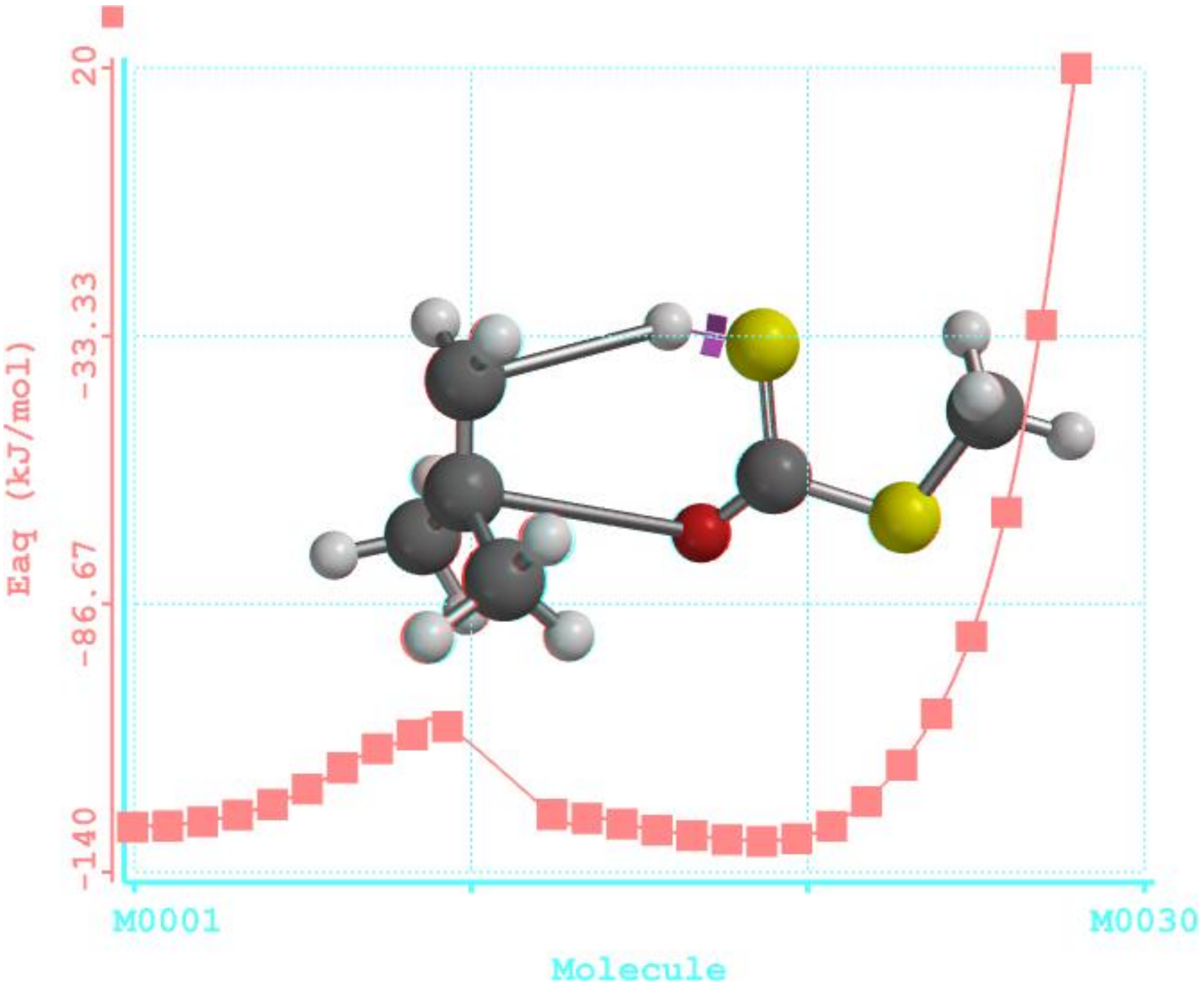


**Figure : 4.21:** Reaction path study O-tbutyl S-methyl dithiocarbonates) and a plot of energy against number of molecules to depict the reaction path study.

**Table 4.8a** Bond length (Å) for the thermal decomposition of O-tbutyl S-methyl xanthates

| Bond (Å) | STATE | B3LYP /6-311+G** | CC-PVTZ |
|---|---|---|---|
| $H_1$-$C_2$ | GS | 1.0916 | 1.0916 |
| | TS | 1.1772 | 1.1950 |
| | PRD | - | - |
| | Δd | 0.0854 | 0.1034 |
| $C_2$-$C_5$ | GS | 1.5292 | 1.5294 |
| | TS | 1.4314 | 1.4288 |
| | PRD | 1.3347 | 1.3352 |
| | Δd | -0.0964 | -0.1066 |
| $C_5$-$O_6$ | GS | 1.4955 | 1.4967 |
| | TS | 2.2690 | 2.2670 |
| | PRD | - | - |
| | Δd | 0.7735 | 0.7703 |
| $O_6$-$C_{15}$ | GS | 1.3308 | 1.3309 |
| | TS | 1.2433 | 1.2433 |
| | PRD | 1.2186 | 1.2188 |
| | Δd | -0.0875 | -0.0863 |
| $0_{15}$-$S_{16}$ | GS | 1.7853 | 1.7867 |
| | TS | 1.7998 | 1.8048 |
| | PRD | 1.8187 | 1.80851 |
| | Δd | 0.0145 | 0.0181 |
| $C_{15}$-$S_{17}$ | GS | 1.6497 | 1.6499 |
| | TS | 1.7236 | 1.7292 |
| | PRD | 1.7932 | 1.7834 |
| | Δd | 0.0739 | 0.0793 |
| $S_{16}$-$C_{18}$ | GS | 1.8184 | 1.8184 |
| | TS | 1.8287 | 1.8299 |
| | PRD | 1.8377 | 1.8352 |
| | Δd | 0.0103 | 0.0115 |
| $C_5$-$C_7$ | GS | 1.5288 | 1.8284 |
| | TS | 1.4882 | 1.4919 |
| | PRD | 1.5070 | 1.5272 |
| | Δd | -0.0406 | -0.3365 |
| $H_1$-$S_{17}$ | GS | 4.8040 | 4.8050 |
| | TS | 1.9970 | 1.9970 |
| | PRD | 1.3492 | 1.3462 |
| | Δd | -2.8070 | -2.8080 |

**Note:** Δq = d(TS) – d(GS)

Bond length in the transition state (TS) - Bond length in the Ground State (TS)

PRD = Product

**Table 4.8b :** Selected bond angle (0º) for the thermal decomposition of O-tbutyl S-methyl xanthates

| **BOND** | **STATE** | **B3LYP/ 6-311+G**** | **CCPV-TS** |
|---|---|---|---|
| $H_1$-$C_2$-$C_5$ | GS | 110.589 | 110.678 |
| | TS | 105.060 | 105.070 |
| | PRD | - | - |
| $C_2$-$C_5$-$O_6$ | GS | 101.007 | 101.002 |
| | TS | 103.110 | 103.390 |
| | PRD | - | - |
| $C_5$-$O_6$-$C_{15}$ | GS | 131.235 | 131.242 |
| | TS | 124.57 | 124.560 |
| | PRD | - | - |
| $O_6$-$C_{15}$-$S_{17}$ | GS | 118.996 | 118.926 |
| | TS | 125.927 | 126.120 |
| | PRD | 124.053 | 124.556 |
| $O_6$-$C_{15}$-$S_{16}$ | GS | 117.158 | 117.159 |
| | TS | 118.876 | 118.820 |
| | PRD | 124.615 | 124.662 |
| $C_{15}$-$S_{16}$-$C_{18}$ | GS | 102.874 | 102.624 |
| | TS | 101.251 | 101.261 |
| | PRD | 98.930 | 98.945 |
| $S_{16}$-$C_{15}$-$S_{17}$ | GS | 123.818 | 123.428 |
| | TS | 115.193 | 115.194 |
| | PRD | 111.332 | 115.211 |
| $S_{16}$-$C_{18}$-$H_{19}$ | GS | 110.411 | 110.412 |
| | TS | 106.183 | 106.195 |
| | PRD | 110.476 | 111.420 |

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

**Table 4.8c :** Selected bond dihedral angle (0°) for pyrolysis of O-tbutyl S-methyl dithiocarbonates

| **DIHEDRAL** | **STATE** | **B3LYP/ 6-311+G**** | **CC-PVTZ** |
|---|---|---|---|
| $H_1$-$C_2$-$C_3$-$O_6$ | GS | 60.106 | 60.256 |
| | TS | -9.74 | -7.76 |
| | PRD | - | - |
| $C_2$-$C_5$-$O_6$-$C_{15}$ | GS | 174.174 | 174.286 |
| | TS | -3.79 | -4.79 |
| | PRD | - | - |
| $C_2$-$C_5$-$C_{11}$-$H_2$ | GS | 61.276 | 61.921 |
| | TS | 30.709 | 31.762 |
| | PRD | 0.133 | 0.142 |
| $C_5$-$O_6$-$C_{15}$=$S_{17}$ | GS | -167.024 | -169.251 |
| | TS | 30.52 | 30.57 |
| | PRD | - | - |
| $C_5$-$O_6$-$C_{15}$-$S_{16}$ | GS | 14.834 | 14.846 |
| | TS | -148.72 | -148.720 |
| | PRD | - | - |
| $O_6$-$C_{15}$-$S_{16}$-$C_{18}$ | GS | -178.765 | -179.761 |
| | TS | -3.286 | -3.462 |
| | PRD | -0.000 | -0.000 |
| $S_{17}$=$C_{15}$-$S_{16}$-$C_{18}$ | GS | 3.192 | 3.194 |
| | TS | 177.386 | 179.251 |
| | PRD | 180.000 | 180.000 |

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

**Table 4.8d :** Atomic charges of (Mulliken) for the thermal decomposition of O-tbutyl S-methyl dithiocarbonate

| **ATOM** | **STATE** | **B3LYP/ 6-311+G**** | **CC-PVTZ** |
|---|---|---|---|
| $H_1$ | GS | +0.163 | +0.164 |
| | TS | +0.126 | +0.142 |
| | PRD | +0.093 | +0.042 |
| | Δq | -0.037 | -0.022 |
| $C_2$ | GS | -0.355 | -0.356 |
| | TS | -0.281 | -0.291 |
| | PRD | -0.392 | -0.420 |
| | Δq | 0.074 | 0.065 |
| $C_5$ | GS | -0.279 | -0.280 |
| | TS | +0.253 | +0.252 |
| | PRD | +0.756 | +0.761 |
| | Δq | 0.532 | 0.580 |
| $O_6$ | GS | +0.231 | +0.232 |
| | TS | -0.062 | -0.072 |
| | PRD | -0.207 | -0.302 |
| | Δq | -0.293 | -0.304 |
| $C_{15}$ | GS | -0.109 | -0.109 |
| | TS | +0.114 | +0.121 |
| | PRD | +0.079 | +0.079 |
| | Δq | 0.223 | 0.230 |
| $S_{16}$ | GS | +0.072 | +0.073 |
| | TS | -0.032 | +0.081 |
| | PRD | +0.112 | -0.125 |
| | Δq | -0.104 | 0.008 |
| $S_{17}$ | GS | -0.295 | -0.296 |
| | TS | -0.393 | -0.297 |
| | PRD | +0.084 | +0.084 |
| | Δq | -0.098 | -0.001 |
| $C_{18}$ | GS | -0.463 | -0.465 |
| | TS | -0.517 | -0.519 |
| | PRD | -0.501 | -0.561 |
| | Δq | -0.054 | -0.054 |

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

Table 4.8(e): Calculation using Wiberg bond indices of O-tbutyl S-methyl Xanthate.

| **Compound** | **State** | **$C_2$-$C_5$** | **$C_2$-$H_1$** | **$H_1$-$S_{17}$** | **$S_{17}$-$C_{15}$** | **$C_{15}$-$O_6$** | **$O_6$-$C_5$** |
|---|---|---|---|---|---|---|---|
| **O-tbutyl** | $B_i^R$ | 1.006 | 0.920 | 0.006 | 1.666 | 1.045 | 0.771 |
| **S-methyl** | $B_i^{TS}$ | 1.273 | 0.571 | 0.299 | 1.321 | 1.419 | 0.179 |
| **Xanthate** | $B_i^P$ | 1.933 | 0.000 | 0.964 | 1.070 | 1.695 | 0.000 |
|  | $\delta B_i$ | 0.287 | 0.390 | 0.320 | 0.579 | 0.576 | 0.769 |
|  | %Ev | 28.7 | 39.0 | 32.0 | 57.9 | 57.6 | 77.8 |
|  | $\delta B_{av}$ | 0.487 |  |  |  |  |  |
|  | Sy | 0.867 |  |  |  |  |  |

**Table 4.9 :** Calculation using Wiberg bond indices of O-alkyl S-methyl Xanthate**.**

| Compound | | $S_1$-$C_2$ | $C_2$-$O_3$ | $O_3$-$C_4$ | $C_4$-$C_5$ | $C_5$-$H_6$ | $H_6$-$S_1$ |
|---|---|---|---|---|---|---|---|
| (i) | $B_i^R$ | 1.678 | 1.034 | 0.813 | 1.030 | 0.935 | 0.000 |
| | $B_i^{TS}$ | 1.332 | 1.390 | 0.279 | 1.341 | 0.534 | 0.347 |
| | $B_i^P$ | 1.070 | 1.695 | 0.000 | 2.034 | 0.000 | 0.962 |
| | $\delta B_i$ | 0.57 | 0.539 | 0.658 | 0.310 | 0.429 | 0.360 |
| | %Ev | 57 | 53.9 | 65.8 | 31 | 42.9 | 36.0 |
| | **δBav**=0.478 | | | | **Sy**=0.860 | | |
| (ii) | $B_i^R$ | 1.018 | 0.928 | 0.002 | 1.666 | 1.041 | 0.790 |
| | $B_i^{TS}$ | 1.310 | 0.549 | 0.325 | 1.319 | 1.407 | 0.225 |
| | $B_i^P$ | 1.985 | 0.000 | 0.962 | 1.070 | 1.695 | 0.000 |
| | $\delta B_i$ | 0.317 | 0.408 | 0.716 | 0.582 | 0.560 | 0.317 |
| | %Ev | 30.2 | 58.2 | 71.6 | 58.2 | 40.9 | 31.7 |
| | **δBav**= | 0.496 | | **Sy**=0.832 | | | |
| (iii) | $B_i^R$ | 1.666 | 0.926 | 0.771 | 1.007 | 0.005 | 0.921 |
| | $B_i^{TS}$ | 1.321 | 0.435 | 0.179 | 1.274 | 0.298 | 0.570 |
| | $B_i^P$ | 1.070 | 0.000 | 0.000 | 1.934 | 0.962 | 0.000 |
| | $\delta B_i$ | 0.579 | 0.530 | 0.768 | 0.288 | 0.310 | 0.390 |
| | %Ev | 57.9 | 53.0 | 76.8 | 28.8 | 31.0 | 39.0 |
| | **δBav**= | 0.484 | | **Sy**=0.807 | | | |
| (iv) | $B_i^R$ | 0.980 | 0.926 | 0.771 | 0.980 | 0.005 | 1.016 |
| | $B_i^{TS}$ | 0.309 | 0.435 | 0.357 | 0.309 | 0.298 | 1.411 |
| | $B_i^P$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.962 | 1.983 |
| | $\delta B_i$ | 0.685 | 0.530 | 0.76 | 0.685 | 0.310 | 0.407 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | %Ev | 68.5 | 53.0 | 76.0 | 68.5 | 31.0 | 40.7 |
| | **δBa**v= | 0.569 | | **Sy**= | 0.867 | | |
| (v) | $B_i^R$ | 1.666 | 1.045 | 0.771 | 1.006 | 0.006 | 1.666 |
| | $B_i^{TS}$ | 1.321 | 1.419 | 0.179 | 1.273 | 0.299 | 1.321 |
| | $B_i^P$ | 1.070 | 1.695 | 0.000 | 1.933 | 0.964 | 1.070 |
| | δB$_i$ | 0.579 | 0.576 | 0.769 | 0.287 | 0.320 | 0.579 |
| | %Ev | 57.9 | 57.6 | 77.8 | 28.7 | 32.0 | 57.9 |
| | **δBav**=0.485 | | | **Sy**=0.807 | | | |
| (vi) | $B_i^R$ | 1.666 | 1.045 | 0.771 | 1.007 | 0.921 | 0.005 |
| | $B_i^{TS}$ | 1.321 | 1.419 | 0.179 | 1.274 | 0.570 | 0.298 |
| | $B_i^P$ | 1.070 | 1.695 | 0.000 | 1.934 | 0.000 | 0.962 |
| | δB$_i$ | 0.579 | 0.576 | 0.768 | 0.288 | 0.39 | 0.31 |
| | %Ev | 57.9 | 57.6 | 76.8 | 28.8 | 39 | 31 |
| | **δBav**= | 0.487 | | | **Sy**=0.867 | | |

## 4.11 General explanation of Wiberg Bond Order for O-alkyl S-methyl Xanthates

The percentages of evolution of the bonds included at the centre of reaction coordinates is summarized in table 4.9. It was discovered in all the alkyl Xanthates considered above, ( i ,ii iii, iv, v and vi), where the alkyl groups are ethyl, npropyl, isopropyl, nbutyl, ibutyl and tbutyl, that the breaking of the C-O bond is the most leading process with 65% to 77)% bond evolution, accompanied with the C=S double bond into a C-S single bond with 58% evolution and the conversion C-O bond into C=O bond with bond evolution of 54% to 58%. The formation of C=C bond is the least progressive process with 30% evolution, accompanied by the formation of S-H bond with 31-36 % and the C-H bond cleavage with (39-43) % evolution.

The breaking of alpha carbon to oxygen ($C_\alpha$-O) bond before that of beta carbon to hydrogen ($C_\beta$-H) bond is in agreement with the work of ( Quijano et al., 2002 and Taylor *et al.*, 1962) on thermal elimination of 1,5 abstraction of hydrogen. This is based on the fact that the Hammelt P-value for α–carbon was bigger than the value for β–carbon in , the result of Comparing the breaking of alpha carbon to oxygen ($C_\alpha$-O) bond and beta carbon to hydrogen ($C_\beta$-H) bond suggest that the more the $C_\beta$-H bond is broken the slower the reaction while the more alpha carbon to oxygen ($C_\alpha$-O) bond cleaved in the reaction, the faster was the rate of reaction.

The charges on the atom can also be used to explain strengthening of bond. In the tables of calculated atomic charges on the atom involved in the reaction coordinates of all the compound studies in each transition structure, a negative charge accumulated on the oxygen atom in accordance with dissociation of the C-O bond which cause an increases in the rate of the reaction. The reverse is case in the accumulation of positive charge on the hydrogen transferred which causes a decreases which resulted in rate increasing in accordance which follows the same trends in strengthening of bond (C – H) (Erickson and Scoh, 1994).

The values of calculated average bond indices ($\delta B_{av}$) ranged from 0.478 to 0.496. The average bond indices ($\delta B_{av}$) increased in the ethyl, propyl and butyl substituted xanthate. However all the values of ($\delta B_{av}$) indicate that all the transition states have an early character which is nearer to the reactants than the products.

Synchronicities Sy normally varies from zero to one. Sy takes the value of one, when all of the bonds in the reaction coordinates have been broken or formed at exactly the same extent in the transition state. The Sy values obtained for alkyl xanthates where in the range of 0.807 to 0.860 (Table 4.9), which indicated that the thermal decomposition of alkyl xanthates corresponded to highly asynchronous processes. The increases in the size of the alkyl group (ethyl, propyl, isopropyl, and butyl) attached to sulphur or oxygen atoms leads to the decrease in Synchronicity.

Table 4.10 shows the effect of methylation on some bond lengths in the ground state of the reactant, the transition state and of the product. The results in Table 4.10 reflect the effect of the substitution of alkyl group on $C_2$ and $C_5$ especially the increase in bond lengthening of the bond joined to the site of substitution. Substitution of alkyl group at α- carbon position causes an increase in $C_5 – O_8$ bond which leads to cleavage of the bond and causes a bond tightening and double bond formation between $C_2 – C_5$ bond while β – methyl substitution on $C_2$ reflect on the increase in bond length at the transition state, in $C_2 – H_x$ which leads to increase in bond length and finally cleavage of the bond.

Alkyl group (methyl, ethyl, propyl, isopropyl, nbutyl, ibutyl and tbutyl) has a positive inductive effect because they release electron because the carbon of the methyl group is partially negative. Therefore, α-methyl substitution facilitate the movement of electron from $C_5 – O_8$ to $O_8 – C_9$ leading to the increase in bond length of 1.8693($C_5 – O_8$) in the transition state. This means that the stretching in the $C_5 – O_8$ is more important than the development of double bond in $O_8 – C_9$. Considering the β– alkyl substitution, the bond between $C_2 – C_5$ has a dipole moment because of the negative end of $C_2$. Therefore the carbon (C) of the methyl that bears the negative charge is joined to $C_5$ which is also partially positive charge, from Table 3d of the atomic charges. It is observed that with β – substitution, the $C_2$ - $C_5$ bond length in transition state increases which causes a decrease in bond length at a product state resulted into double bond character of $C_2$–$C_5$. The electron released through β– methyl substitution into $C_2 – H_x$, enhances the bond tightening of $S_{11} – H_x$ bond formation.

The distance between the atoms in the reaction Coordinates for geometry optimized of the reactant (GS), transition state (TS), during thermal decomposition, the bond length of $C_2 – H_1$, $C_5 – O_8$ are increased while $H_1$- $S_{10}$ decreased in the transition state(TS), the transition state structure of $S_{10} – C_9$ showed the character of a single bond. The hybridization of carbon changed from $Sp^3$ to $Sp^2$ when the $C_2 – C_5$ single bond changed into changes which means that $C_2= C_5$ , double bond.

Looking at the $C_α – O$ lengthening in the reaction, it can be see that the more $C_α –$ O bond was increased in the transition state, the faster was the rate of reaction. The bond lengthening was also reflected in the atomic charge. The overall result of the geometry calculation shows that α-methyl substitution was more rate enhancing than β–methyl substitution. It can therefore be concluded that the increase in rate due to $C_5 – O_8$ bond lengthening in the transition state was more important than the β– hydrogen elimination and hence was the rate determinant.

## 4.12 Explanation of thermodynamics and Arrhenius parameters

The result obtained for the thermodynamics and Arrhenius parameters for all the compound studied were given in Table 4.12(a-h) from ethyl to tbutyl xanthates. In Table (4.12a), the calculated and experimental values for ethyl xanthate thermodynamics and Arrhenius parameters were given, enthalpy of activation ΔH*= (161.344 and 161.000kJ/mol), Gibbs free energy of activation (ΔG* = 180.65 and 178.60kJ/mol) , activation energy Ea = 166.49 and 166.20kJ/mol), Entropy of activation (ΔS* = -31.00 and -28.00J/mol/K) and rate of reaction k = $1.4 \times 10^{-2}$ and $1.4 \times 10^{-1}$).

Also the calculated thermodynamics and Arrhenius values for npropyl xanthates were give in Table (4.13b), ΔH*= (153.23kJ/mol), (ΔG* = 170.08kJ/mol), Ea = 158.38kJ/mol), (ΔS* = -27.18J/mol/K) and k = $0.006S^{-2}$). For isopropyl xanthates, ΔH* = (144.27 and 144.000kJ/mol), ΔG* = (160.94 and 160.40kJ/mol), Ea = 149.36 and 149.17kJ/mol), (ΔS* = -26.98 and -26.00J/mol/K) and k = 0.13 and $0.56S^{-2}$). For nbutyl xanthate the values were, ΔH* = (133.87kJ/mol), (ΔG* = 149.36kJ/mol) , Ea = 139.62kJ/mol), (ΔS* = -27.78J/mol/K) and k = $1.14S^{-2}$). For ibutyl xanthates the value are ΔH* = (136.820kJ/mol), (ΔG* = 147.650kJ/mol), Ea = 146.82kJ/mol), (ΔS* = -25.78J/mol/K) and k = 1.70). For tbutyl xanthates the values are ΔH* = (128.04kJ/mol), (ΔG* = 142.92kJ/mol) , Ea = 133.19kJ/mol), (ΔS* = -24.00J/mol/K) and k = $4.3S^{-2}$).

The calculated thermodynamics and Arrhenius values obtained for ethyl xanthate and isopropyl xanthate with their experimental values compared favourably well and they are in good agreement with the experimental result (Al-Awadi and Bigley, 1982, Velez *et al.*, 2008). The positive values obtained for enthalpy of activation of reaction from ethyl to ibutyl xanthates was indication that the reaction was an endothermic reaction. Also the positive value obtained for Gibbs free energy of activation was an indication that the reaction was not spontaneous but needed much heat to be completed.

It was revealed from the study that addition of alkyl substituents to the xanthate reduces the following parameters from ethyl, npropyl, ipropyl, nbutyl to ibutyl xanthates; for enthalpy of activation (ΔH* 161.34> 153.23 >144.27 >133.87 >136.82)kJ/mol, for Gibbs free energy of activation ΔG* (180.65> 170.08> 160.40> 149.36> 147.67> 142.92)kJ/mol and activation energy Ea, (166.49 >158.38 >149.36 >139.62 >146.60)kJ/mol. The opposite trend occur in the rate of reaction (k) and pre exponential factor (A), as the alkyl group were being substituted activation barrier were reducing and the rate of reaction $1.04x\ 10^{-2}$, $2.74x10^{-1}$, $1.37x10^{-1}$, $4.25x10^{-1}$, 4.678 and 4.479 and pre exponential factor A 3.6, 4.94, 5.53, 5.86, 6.52 and 6.62 were increasing.

The value of entropy of activation (ΔS*) obtained from ethyl xanthate to tbutyl xanthate are negative ;( -31.16, -27.18, -26.98, -25.78,-26.65 and -24.00) suggesting high activation barrier. This is in line with the discussion that substitution of alkyl group reduces activation complex structures (Anslyn and Dougherty, 2004).

It was observed that progressive methylation of O-alkyl S-methyl xanthates in gas phase decreases the value of enthalpy of activation, the Gibbs free energy (ΔG, and the activation energy from ethyl, npropyl, ipropyl, nbutyl, ibutyl to tbutyl progressively. The decrease in the parameters mention above leads to an increase in the rate of the reaction and pre-exponential factor resulting in high yield of olefin (ethylene).

## 4.13 Variation of Rate Constant (k) with Temperature (T).

Table 4.11(a-f) shows the variation of the rate k, Arrhenius constant, pre-exponential factors A, with temperature. These were obtained from temperature at 373K to 623K using temperature interval of 25 Kelvin. It was observed that as the temperature increases the rate of reaction also increases.

**TABLE 4.10: Effect of Methylation on Bond Lengths of the Ground State, Transition State And Product.**

| BONDS | | β-METHYLATION | | α-METHYLATION | |
|---|---|---|---|---|---|
| | ETHYL XANTHATE | n-PROPYL XANTHATE | i-BUTYL XANTHATE | i-PROPYL XANTHATE | t-BUTYL XANTHATE |
| **$S_{11}$ - $H_x$ (GS)** | 4.9480 | 4.9340 | 4.8120 | 4.4840 | 4.7880 |
| **$S_{11}$-$H_x$ (TS)** | 1.7320 | 1.6670 | 1.6520 | 1.7060 | 1.7280 |
| **$S_{11}$ -$H_x$ (PRD)** | 1.3280 | 1.3107 | 1.3167 | 1.3107 | 1.3108 |
| **$C_5$-$O_8$ (GS)** | 1.4333 | 1.4323 | 1.4401 | 1.4469 | 1.4552 |
| **$C_5$-$O_8$ (TS)** | 1.8693 | 1.8420 | 1.8210 | 1.8980 | 1.9270 |
| **$C_5$-$O_8$ (PRD)** | - | - | - | - | - |
| **$C_2$-$C_5$ (GS)** | 1.5148 | 1.5119 | 1.5256 | 1.5236 | 1.5359 |
| **$C_2$-$C_5$ (TS)** | 1.4080 | 1.5002 | 1.4233 | 1.4221 | 1.4354 |
| **$C_2$-$C_5$ (PRD)** | 1.3220 | 1.4200 | 1.3328 | 1.3279 | 1.3329 |
| **$C_2$-$H_x$ (GS)** | 1.0979 | 1.0982 | 1.1271 | 1.0978 | 1.0983 |
| **$C_2$-$H_x$ (TS)** | 1.3390 | 1.3390 | 1.4290 | 1.2940 | 1.2620 |
| **$C_2$-$H_x$ (PRD)** | - | - | - | - | - |

**Note :** GS = Ground State

TS = Transition State

PRD = Product

Where x is the number on each alkyl group in **$H_x$**

**Table 4.11a: Variation of rate ($S^{-1}$) with temperature (K) for O-ethyl S-methyl xanthates.**

| **Temp(K)** | **DFT/6-311+G**** | **CC-PVTS** |
|---|---|---|
| **373** | $1.06X10^{-2}$ | $1.56X10^{-2}$ |
| **398** | $1.08X10^{-2}$ | $2.37X10^{-2}$ |
| **423** | $1.09X10^{-2}$ | $2.11X10^{-2}$ |
| **448** | $1.12X10^{-2}$ | $2.11X10^{-2}$ |
| **498** | $1.28X10^{-2}$ | $2.16X10^{-2}$ |
| **523** | $1.39X10^{-2}$ | $3.24X10^{-2}$ |
| **548** | $1.40X10^{-2}$ | $3.54X10^{-2}$ |
| **573** | $1.53X10^{-2}$ | $3.74X10^{-2}$ |
| **598** | $1.61X10^{-2}$ | $3.87X10^{-2}$ |
| **623** | $1.64X10^{-2}$ | $3.93X10^{-2}$ |

**Table 4.11b: Variation of rate ($S^{-1}$) with temperature (K) for O-npropyl S-methyl xanthates.**

| **Temp (K)** | **DFT/6-311+G**** | **CCPVZ** |
|---|---|---|
| **373** | $2.74X10^{-2}$ | $1.56X10^{-2}$ |
| **398** | $2.87X10^{-2}$ | $2.22X10^{-2}$ |
| **423** | $2.97X10^{-2}$ | $2.39X10^{-2}$ |
| **448** | $2.98X10^{-2}$ | $2.67X10^{-2}$ |
| **498** | $3.39X10^{-2}$ | $2.64X10^{-2}$ |
| **523** | $3.42X10^{-2}$ | $3.89X10^{-2}$ |
| **548** | $3.56X10^{-2}$ | $3.14X10^{-2}$ |
| **573** | $3.79X10^{-2}$ | $3.73X10^{-2}$ |
| **598** | $3.88X10^{-2}$ | $3.64X10^{-2}$ |
| **623** | $3.93X10^{-2}$ | $3.04X10^{-2}$ |

**Table 4.11c: Variation of Rate ($S^{-1}$) with Temperature (K) for O-ipropyl S-methyl Dithiocarbonates.**

| Temp(K) | DFT/6-311+G** | CC-PVTZ |
|---|---|---|
| **373** | 1.56X$10^{-1}$ | 1.56X$10^{-1}$ |
| **398** | 2.22X$10^{-1}$ | 2.37X$10^{-1}$ |
| **423** | 2.79X$10^{-1}$ | 3.11X$10^{-1}$ |
| **448** | 2.67X$10^{-1}$ | 3.21X$10^{-1}$ |
| **498** | 2.68X$10^{-1}$ | 3.46X$10^{-1}$ |
| **523** | 2.89X$10^{-1}$ | 3.48X$10^{-1}$ |
| **548** | 3.14X$10^{-1}$ | 3.54X$10^{-1}$ |
| **573** | 5.73X$10^{-1}$ | 3.74X$10^{-1}$ |
| **598** | 5.64X$10^{-1}$ | 4.57X$10^{-1}$ |
| **623** | 5.60X$10^{-1}$ | 5.93X$10^{-1}$ |

**Table 4.11d: Variation of Rate ($S^{-1}$) with Temperature (K) For O-nbutyl S-Methyl Dithiocarbonates.**

| Temp(K) | DFT/6-311+G** | CC-PVTZ |
|---|---|---|
| **373** | 1.50 | 1.50 |
| **398** | 2.20 | 2.37 |
| **423** | 2.39 | 2.11 |
| **448** | 2.67 | 2.11 |
| **498** | 2.69 | 2.16 |
| **523** | 3.89 | 3.24 |
| **548** | 4.14 | 3.54 |
| **573** | 4.43 | 3.74 |
| **598** | 4.64 | 4.57 |
| **623** | 4.67 | 4.93 |

**Table 4.11e : Variation of Rate ($S^{-1}$) with Temperature (K) For O-tbutyl S-Methyl Dithiocarbonates.**

| **Temp(K)** | **DFT/6-31G*** | **DFT/6-31+G**** |
|---|---|---|
| **373** | 2.40 | 1.50 |
| **398** | 2.50 | 2.20 |
| **423** | 2.70 | 2.79 |
| **448** | 3.00 | 3.47 |
| **498** | 3.30 | 3.64 |
| **523** | 3.60 | 3.89 |
| **548** | 3.90 | 4.14 |
| **573** | 4.00 | 4.33 |
| **598** | 4.60 | 4.64 |
| **623** | 4.67 | 4.80 |

**TABLE 4.12a: THERMODYNAMICS AND ARRHENINS PARAMETERS (O-ETHYL S-METHYL XANTHATE (DITHIOCABONATES)**

| **PARMETERS** | **ΔS J/mol/k** | **ΔG kJ/mol** | **ΔH kJ/mol** | **Ea kJ/mol** | **A** X$10^{11}$ | **k ($S^{-1}$)** |
|---|---|---|---|---|---|---|
| **EXPTAL** | -28.000 | 178.60 | 161.000 | 166.200 | 4.70 | $1.4x10^{-2}$ |
| **DFT/6-311+G**** | -31.16 | 180.65 | 161.344 | 166.49 | 3.06 | $1.04x10^{-2}$ |
| **CC-PVTZ** | -29.842 | 181.491 | 162.808 | 167.988 | 3.56 | 2.93 |

**TABLE 4.12b: Thermodynamics and Arrhenius parameters Of (O-npropyl S-methyl dithiocarbonates**

| **PARMETERS** | **ΔS J/mol/k** | **ΔG kJ/mol** | **ΔH kJ/mol** | **Ea kJ/mol** | **A** X$10^{11}$ | **k ($S^{-1}$)** |
|---|---|---|---|---|---|---|
| **EXPTAL** | - | - | - | - | - | - |
| **DFT/6-311+G**** | -27.18 | 170.08 | 153.23 | 158.38 | 4.90 | $2.7x10^{-1}$ |

**TABLE 4.12c: Thermodynamics and Arrhenius parameters (O-ipropyl S-methyl dithiocarbonates)**

| **PARMETERS** | **ΔS J/mol/k** | **ΔG kJ/mol** | **ΔH kJ/mol** | **Ea kJ/mol** | **A** X$10^{11}$ | **k ($S^{-1}$)** |
|---|---|---|---|---|---|---|
| **EXPTAL** | -26.00 | -160.40 | 144.00 | -149.17 | 5.6 | $5.6 x 10^{-1}$ |
| **DFT/6-311+G**** | -26.98 | -160.94 | 144.27 | 149.36 | 5.5 | $1.3 x 10^{-1}$ |

**TABLE 4.12d: Thermodynamics and Arrhenius parameters( O-nbutyl S-methyl dithiocarbonates)**

| **PARMETERS** | **ΔS J/mol/k** | **ΔG kJ/mol** | **ΔH kJ/mol** | **Ea kJ/mol** | **A** X$10^{11}$ | **k ($S^{-1}$)** |
|---|---|---|---|---|---|---|
| **EXPTAL** | - | - | - | - | - | - |
| **DFT/6-311+G**** | -26.65 | 149.36 | 133.87 | 139.62 | 5.86 | 4.678 |

**TABLE 4.12e: Thermodynamics and Arrhenius parameters (O-ibutyl S-methyl dithiocarbonates)**

| **PARMETERS** | **ΔS J/mol/k** | **ΔG kJ/mol** | **ΔH kJ/mol** | **Ea kJ/mol** | **A** X$10^{11}$ | **k ($S^{-1}$)** |
|---|---|---|---|---|---|---|
| **EXPTAL** | - | - | - | - | - | - |
| **DFT/6-311+G**** | -25.78 | 147.65 | 136.82 | 136.82 | 6.52 | $4.25x10^{-1}$ |

**TABLE 4.12f: Thermodynamics and Arrhenius parameters (O-tbutyl S-methyl Dithiocarbonates)**

| **PARMETERS** | **ΔS J/mol/k** | **ΔG kJ/mol** | **ΔH kJ/mol** | **Ea kJ/mol** | **A** X$10^{11}$ | **k ($S^{-1}$)** |
|---|---|---|---|---|---|---|
| **EXPTAL** | - | - | - | - | - | - |
| **DFT/6-311+G**** | -24.00 | 142.92 | 128.04 | 133.19 | 6.62 | 4.479 |

## Table: 4.13: COMPARISM OF COMPUTED ARRHENIUS PARAMETERS WITH THE EXPERIMENTAL RESULTS.

| | | | | **CALCULATED** | | | | | **EXPERIMENTAL** | |
|---|---|---|---|---|---|---|---|---|---|---|
| | **$\Delta H$ (kJ/mol)** | **$\Delta S$ J/mol/k** | **$\Delta G$ kJ/mol** | **Ea (kJ/mol)** | **A** $10^{11}$ | **$k_{623}$ ($S^{-1}$)** | **$\Delta H$ kJ/mol** | **$\Delta S$ J/mol/ k** | **$k_{623}$ ($S^{-1}$)** | **Ea kJ/mol** |
| **Ethyl xanthate** | 161.344 | -31.16 | 178.68 | 166.520 | 3.62 | $1.04X10^{-2}$ | 161.00 | -28.00 | $1.4x10^{-2}$ | 166.20 |
| **n-Propyl Xanthate** | 128.123 | -27.18 | 170.08 | 146.089 | 4.94 | $2.74X10^{-1}$ | - | | | - |
| **i-Propyl Xanthate** | 133.873 | -26.98 | 160.94 | 139.050 | 5.53 | $1.37X10^{-1}$ | 141.00 | -26.00 | $5.6x10^{-1}$ | 149.178 |
| **i-Butyl Xanthate** | 141.596 | -25.78 | 147.65 | 146.012 | 6.53 | $4.25X10^{-1}$ | - | | | - |
| **n-Butyl Xanthate** | 130.781 | -26.65 | 149.36 | 136.231 | 5.86 | 4.678 | | | | |
| **t-Butyl Xanthate** | 128.039 | -24.00 | 142.92 | 133.218 | 6.62 | 4.479 | - | | | - |

# CHAPTER FIVE

## 5.1 CONCLUSION AND RECOMMENDATION

In the present study, theoretical calculations were done to study the kinetics and mechanism as well as thermodynamics of the thermal decomposition of six O-alkyl dithiocarbonates in the gas phase. Geometric parameters such as bond length, bond angle, dihedral angle and atomic charges in the ground state, transition state and the products have been systematically studied using Ab-initio quantum mechanical theory using at B3LYP/6-311+G** and CC-PVTZ basis sets. It was discovered that the difference in the geometric features is more than an order of magnitude.

It was also discovered that all these calculation methods could effectively be used to study the kinetics, mechanism and thermodynamics of thermal decomposition of O-ethyl S-methyl xanthates and O-isopropyl S-methyl xanthates in the gas phases because the result obtained at B3LYP/6-311+G** and CC-PVTZ basis sets for the enthalpy of activation ΔH* (161.344 and 144.27kJ/mol ) , Gibbs free energy of activation ΔG* (180.65 and 160.94 ), change in entropy ΔS* (-31.16 and -26.98J/mol) and activation energy, Ea (166.49 and 149.36kJ/mol) rate of reaction k (0.014 and 0.13$S^{-2}$) are in good agreement with the experimental values (Velez *et al.*, 2008). The result of this study showed that progressive methylation at the α-carbon was more rate enhancing than at the progressive methylation at the β-carbon position which is similar to the report on ethyl acetate (Adejoro and Eke, 2010).

It was also observed that progressive methylation in gas phase at the α- and/or β-position of O-alkyl S-methyl xanthates lowered thermodynamic parameters ΔG*, ΔH* and activation energy Ea with corresponding increase in entropy change ΔS* and rate of reaction k, when compare to the unsubstituted xanthates.

This research formulated a consistent and systematic procedure to calculate the Arrhenius and Thermodynamic parameters of the gas phase thermal decomposition of some O-alkyl S-methyl dithiocarbonates using ab-initio methods of calculations in computational chemistry, which may assists in the design and optimization of new and existing processes and products, reduce cost of experimental researches, improve energy efficiency, environmental performance and increase productivity and profitability.

Computational chemistry compliments the organic and physical laboratory experiments in Universities and consequently makes chemistry more interesting for prospective candidates, thus virtual laboratory engendered by computation chemistry should be embraced. This will cut cost of building laboratories as well as chemical wastage as a result of experiment.

It is here by recommended that:

(i) University Education Curriculum should include computational chemistry in theory and practice.

(ii) Science Researchers in our Universities should give more consideration to computational methods as it may be a less expensive means of inventions and publication of findings.

(iii)Government and Industries should focus on this direction and release funds in form of grants to sponsor researches based on computational chemistry.

Going forward we, intend to use the formulated systematic and consistent computational procedures to study the kinetics and thermodynamics of the gas-phase thermal decomposition of multipath reaction systems.

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# APPENDIX A

## STRUCTURE OF REACTANT, TRANSITION AND PRODUCT TOGETHER WITH THERE IR SPECROSCOPIC GRAPH OF ALKYL XANTHATES

Figure 1: Ground State (GS) AM1 IR Spectrum of O-ethyl, S-methyl Xanthates

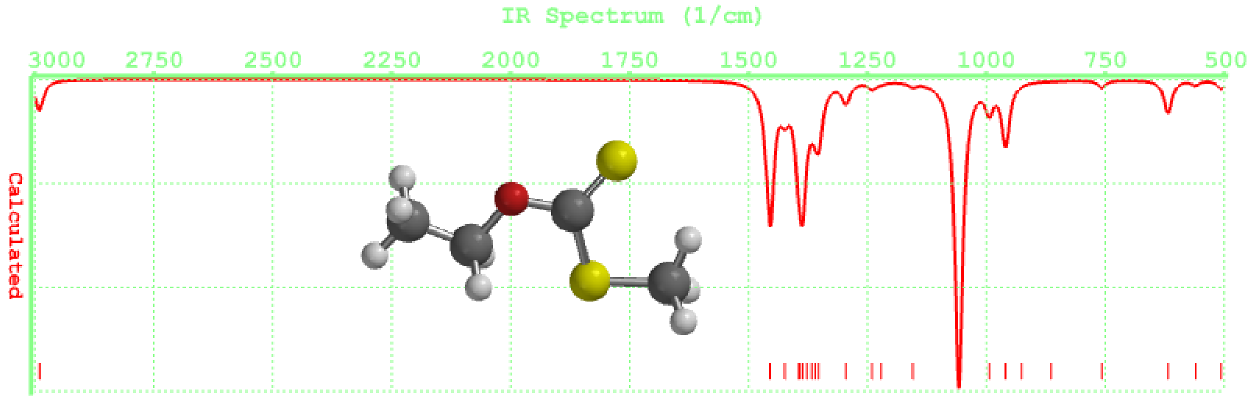


Figure 2: Transition State (TS) AM1 IR Spectrum of O-ethyl, S-methyl Xanthates

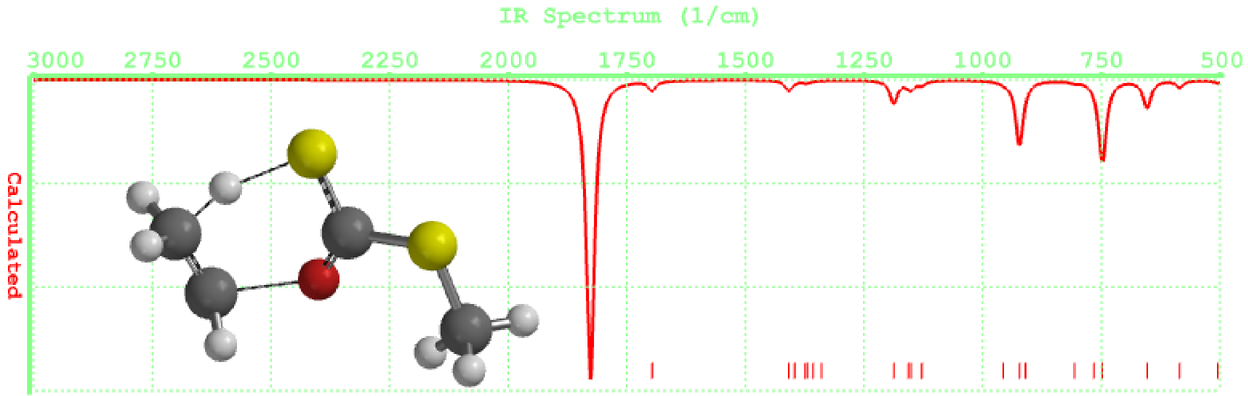


Figure 3: Product State (1)Ethene AM1 IR Spectrum of O-ethyl, S-methyl Xanthates

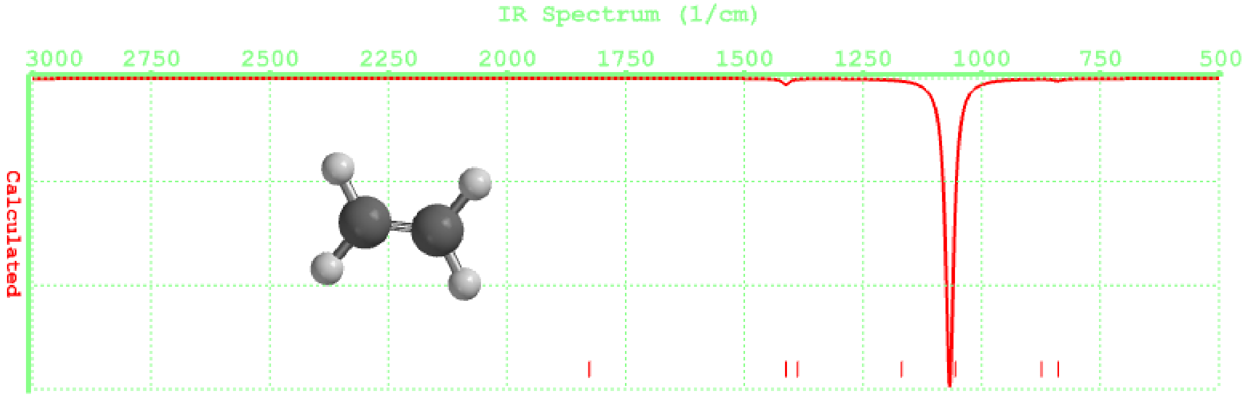


Figure 4: Product 2 Methyl Dithiocarbonate AM1 IR Spectrum of O-ethyl, S-methyl Xanthates

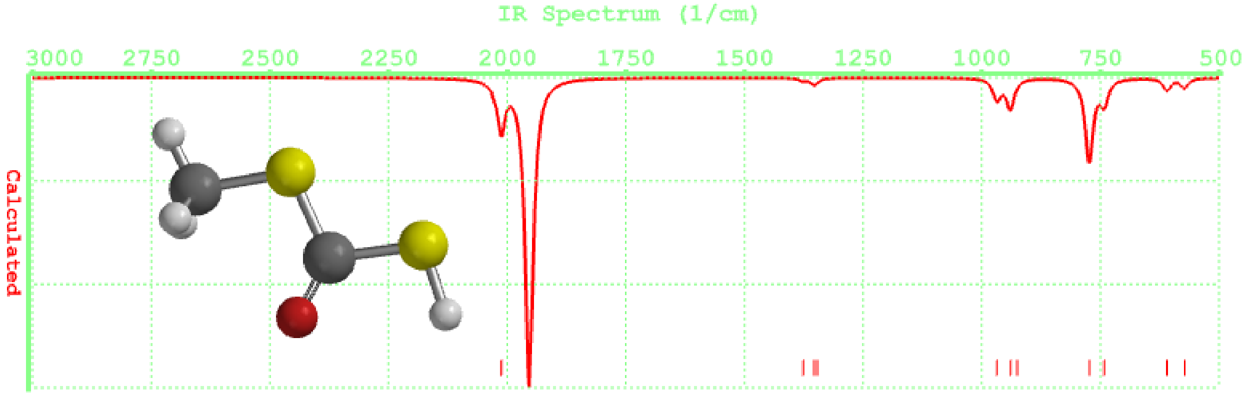


Figure 5:  Ground State (GS) PM3 IR Spectrum of O-ethyl, S-methyl Xanthates

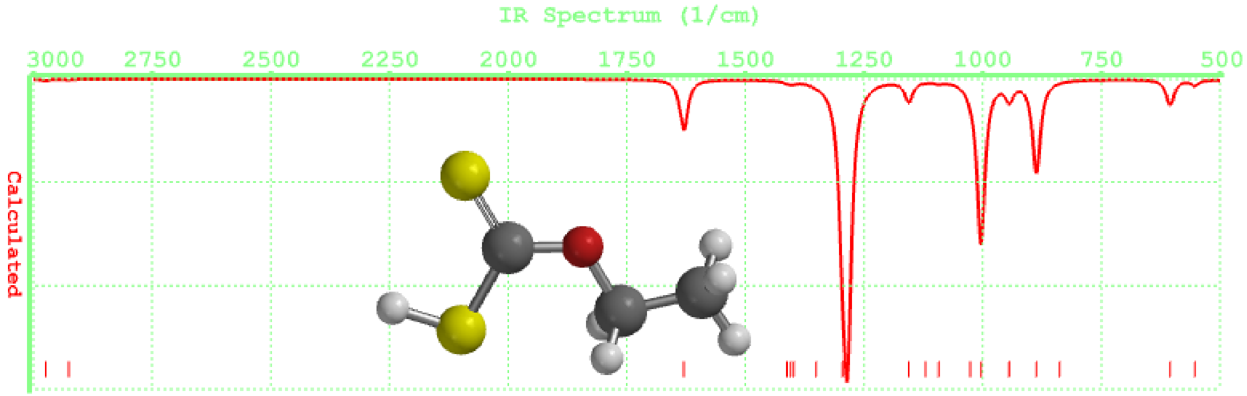


Figure 6:  Transition State (TS) PM3 IR Spectrum of O-ethyl, S-methyl Xanthates

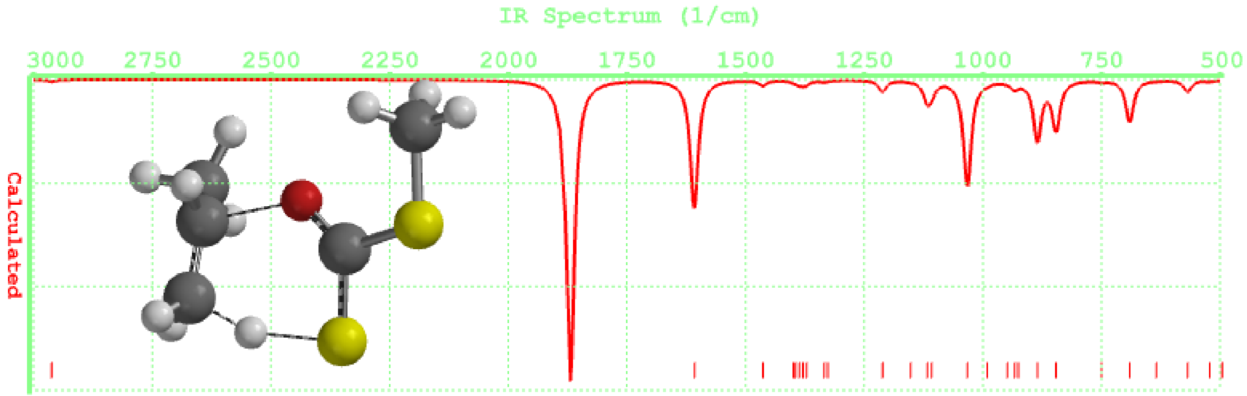


Figure 7: Product State (1)Ethene PM3 IR Spectrum of O-ethyl, S-methyl Xanthates

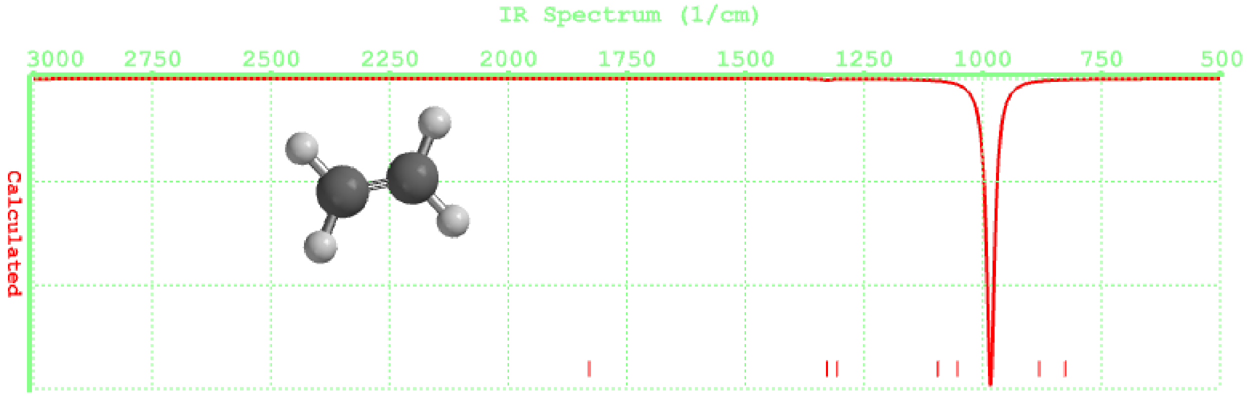


Figure 8: Product 2 Methyl Dithiocarbonate PM3 IR spectrum of O-ethyl, S-methyl Xanthates

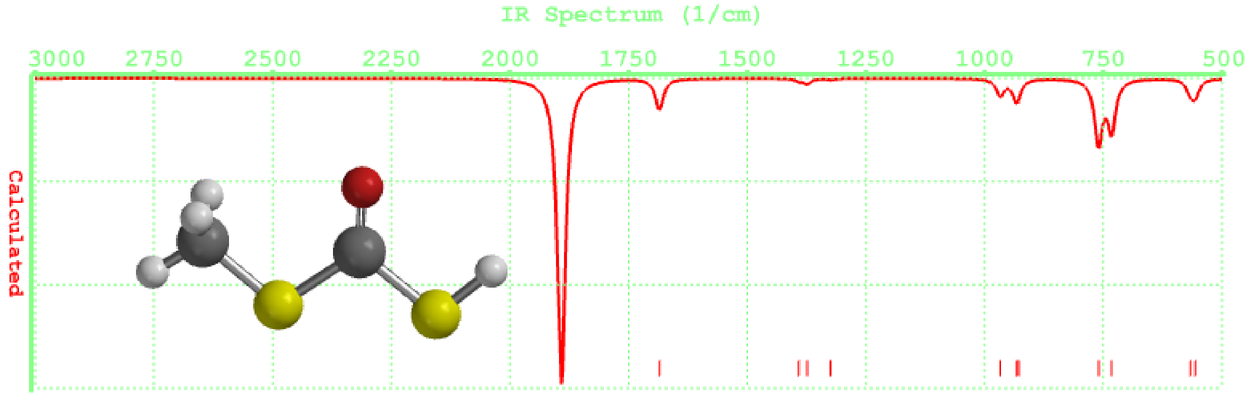


Figure 9: Ground State (GS) DFT/6-31G* IR Spectrum of O-ethyl, S-methyl Xanthates

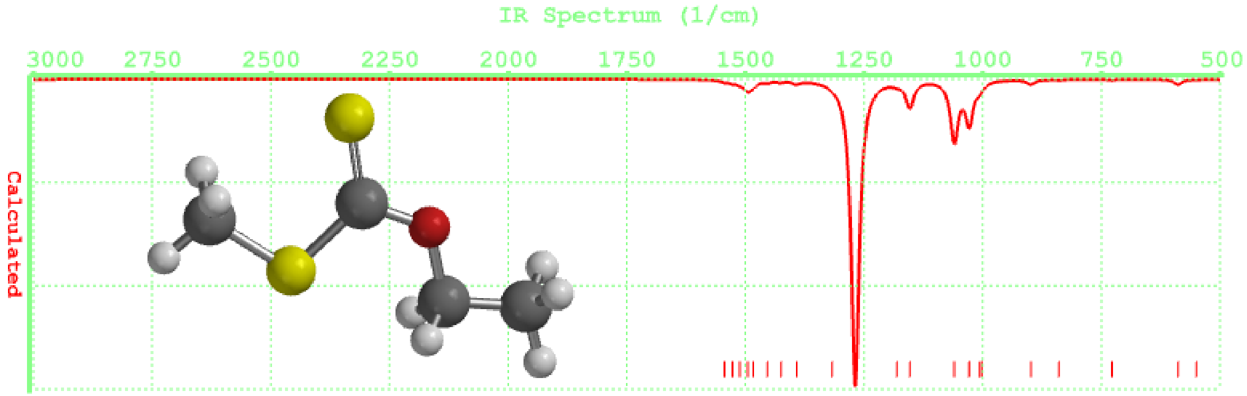


Figure 10: Transition State (TS) DFT/6-31G* IR Spectrum of O-ethyl, S-methyl Xanthates

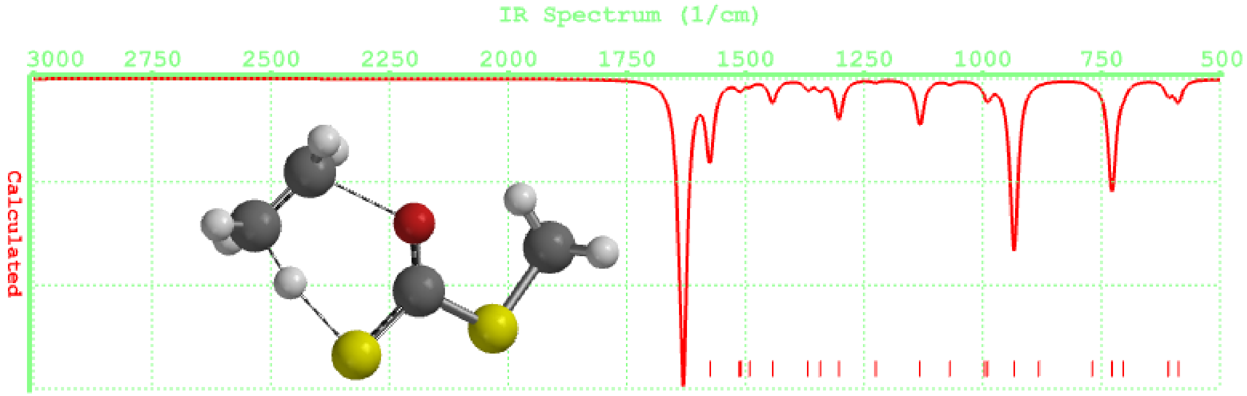


Figure 11: Product 1 Ethene DFT/6-31G* IR Spectrum of O-ethyl, S-methyl Xanthates

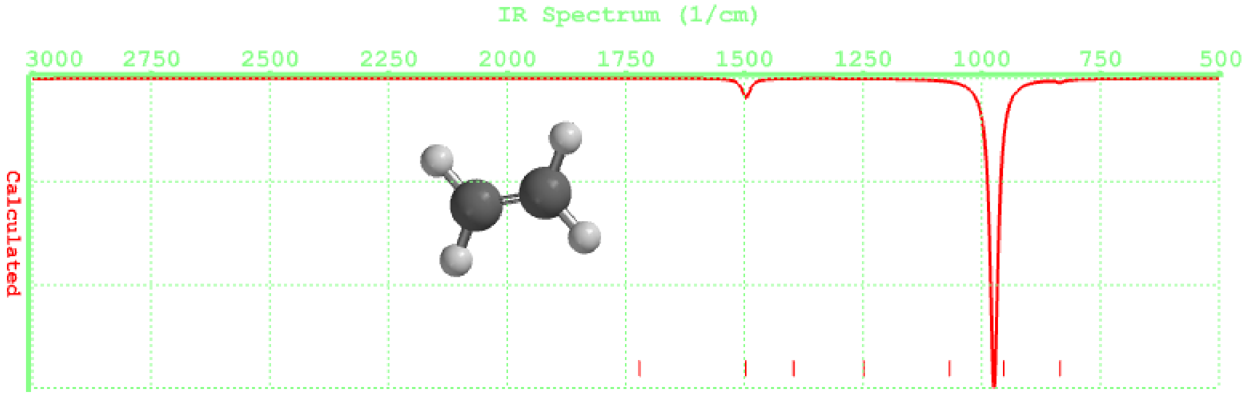


Figure 12: Product2 Methyl dithiocarbonates DFT/6-31G* IR spectrum of O-ethyl, S-methyl Xanthates

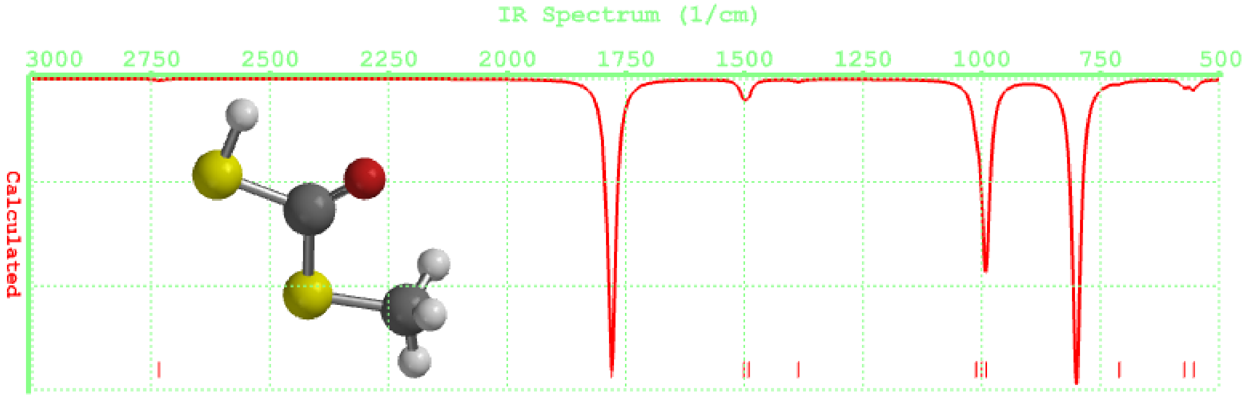


Figure 13: Ground State (GS) DFT/6-31G** IR Spectrum of O-ethyl, S-methyl Xanthates

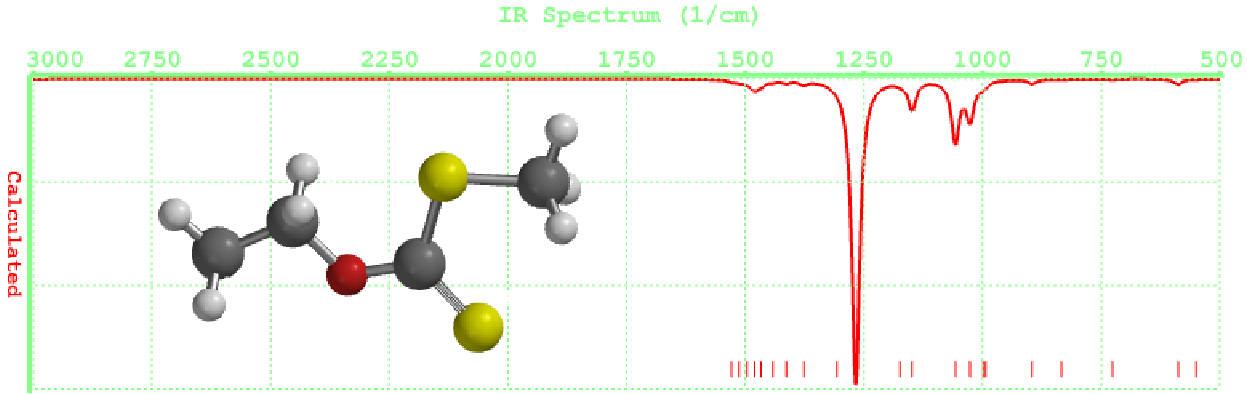


Figure 14: Transition State (TS) DFT/6-31G** IR Spectrum of O-ethyl, S-methyl Xanthates

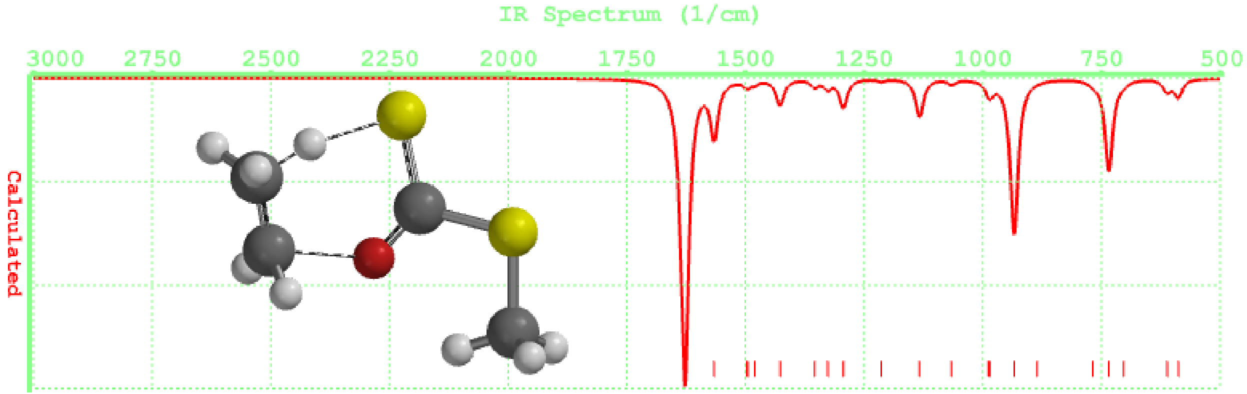


Figure 15: Product 1 Ethene DFT/6-31G** IR Spectrum of O-ethyl, S-methyl Xanthates

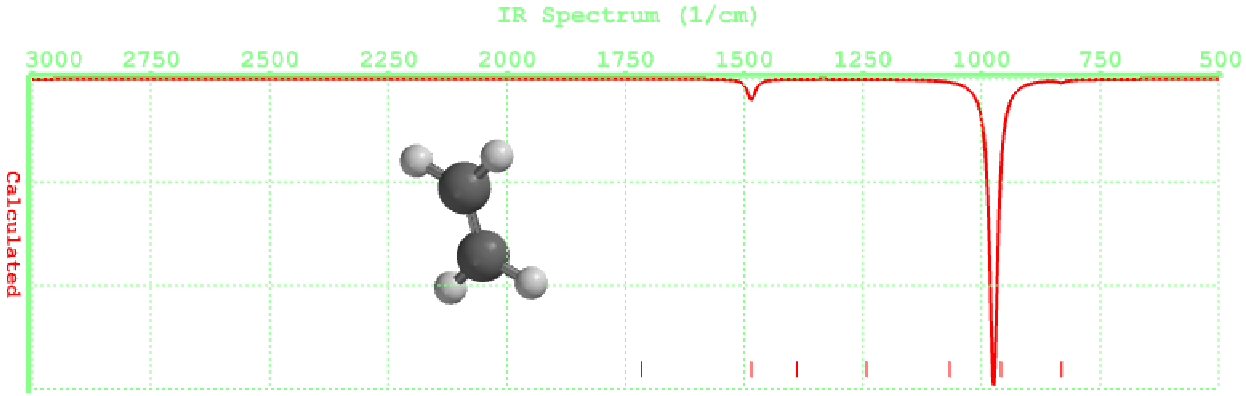


Figure 16: Product2 Methyl dithiocarbonate DFT/6-31G** IR spectrum of O-ethyl, S-methyl Xanthates

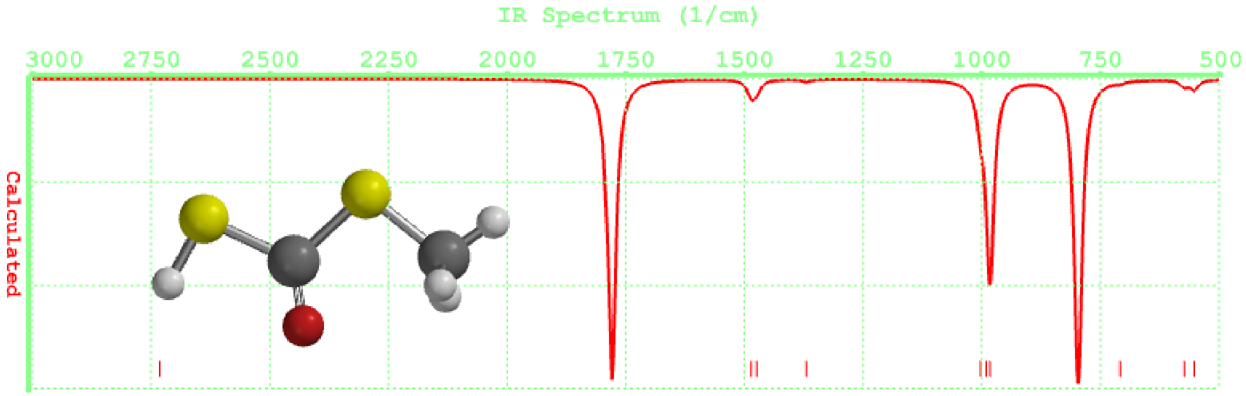
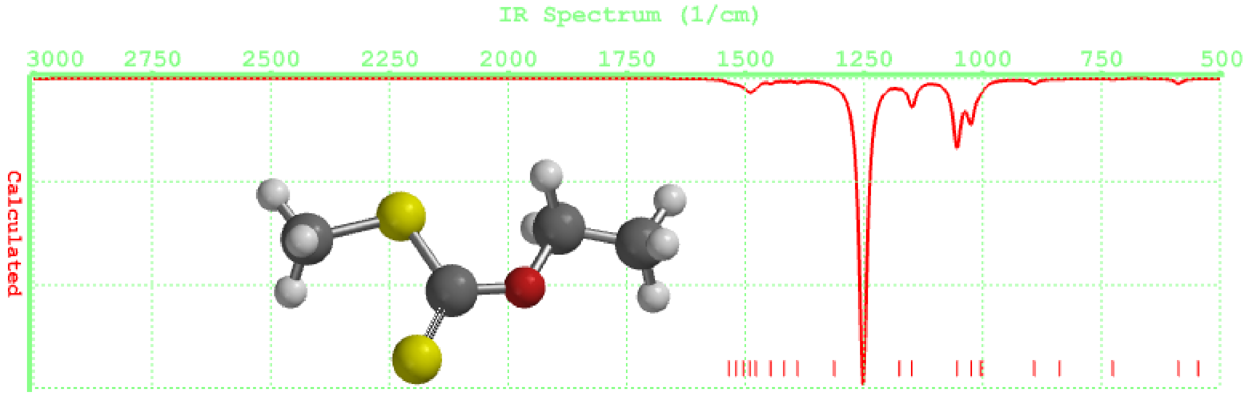


Figure 17: Ground State (GS) DFT/6-31+G* IR Spectrum of O-ethyl, S-methyl Xanthates



# APPENDIX B

## GEOMETRIC PARAMETERS WITH DIFFERENT BASIS SETS

### 6.4.0 TABLE 1: BOND LENGTH ($A^O$) OF O-ETHYL, S-METHYL XANTHATE (DITHIOCARBONATE) $\Delta d = (d_{TS} - d_{GS})$

| BOND LENTGH($A^O$) | STATE | AM1 | PM3 | DFT/ 631G* | DFT/ 6-31G** | DFT/ 6-31+G* | HF/ 3-21G* |
|---|---|---|---|---|---|---|---|
| **$H_1$-$C_2$** | GS | 1.1162 | 1.0979 | 1.0941 | 1.0930 | 1.0947 | 1.0812 |
| | TS | 1.2970 | 1.3390 | 1.2490 | 1.1960 | 1.1980 | 1.5860 |
| | PROD | - | - | - | - | - | - |
| | Δd | +0.2391 | +0.2391 | +0.7869 | +0.103 | +0.103 | +0.504 |
| **$C_2$-$H_3$** | GS | 1.1165 | 1.0979 | 1.0940 | 1.0929 | 1.0946 | 1.0811 |
| | TS | 1.1109 | 1.0919 | 1.0900 | 1.0887 | 1.0904 | 1.0890 |
| | PROD | 1.0982 | 1.0861 | 1.0876 | 1.8670 | 1.0879 | 1.0737 |
| | Δd | -0.0056 | -0.006 | -0.004 | -0.004 | -0.004 | +0.008 |
| **$C_2$-$H_4$** | GS | 1.1159 | 1.0975 | 1.0953 | 1.0941 | 1.0961 | 1.0833 |
| | TS | 1.1118 | 1.0929 | 1.0920 | 1.0907 | 1.0925 | 1.1010 |
| | PROD | 1.0982 | 1.0861 | 1.0876 | 1.0867 | 1.0879 | 1.0737 |
| | Δd | -0.0041 | -0.0046 | -0.0033 | -0.0039 | -0.004 | +0.0181 |
| **$C_2$-$H_5$** | GS | 1.5097 | 1.5148 | 1.5170 | 1.5162 | 1.5172 | 1.5208 |
| | TS | 1.4039 | 1.4080 | 1.4190 | 1.4196 | 1.4216 | 1.3140 |
| | PROD | 1.3260 | 1.3220 | 1.3308 | 1.3300 | 1.3348 | 1.3151 |
| | Δd | -0.1058 | -0.1068 | -0.0980 | -0.0967 | -0.096 | -0.2068 |
| **$C_5$-$H_6$** | GS | 1.1233 | 1.1081 | 1.0961 | 1.0958 | 1.0960 | 1.0804 |
| | TS | 1.1034 | 1.0946 | 1.0830 | 1.0820 | 1.0829 | 1.067 |
| | PROD | 1.0982 | 1.0861 | 1.0876 | 1.0867 | 1.0879 | 1.0737 |
| | Δd | -0.0199 | -0.0135 | -0.0131 | -0.014 | -0.013 | -0.013 |
| **$C_5$-$O_8$** | GS | 1.1233 | 1.1074 | 1.0961 | 1.0958 | 1.0960 | 1.0804 |
| | TS | 1.1029 | 1.0948 | 1.0820 | 1.0822 | 1.0833 | 1.068 |
| | PROD | 1.0982 | 1.0861 | 1.0876 | 1.0867 | 1.0879 | 1.0737 |
| | Δd | -0.0201 | -0.0126 | -0.0141 | -0.014 | -0.013 | -0.012 |
| **$C_5$-$O_8$** | GS | 1.4404 | 1.4333 | 1.4495 | 1.4500 | 1.4523 | 1.4646 |
| | TS | 1.9720 | 1.8693 | 2.0950 | 2.0770 | 2.0970 | 2.4150 |
| | PROD | - | - | - | - | - | - |

|  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
|  | Δd | +0.5316 | +0.4360 | +0.6455 | +0.627 | +0.64 | +0.9504 |
| **$O_8$-$C_9$** | GS | 1.3681 | 1.3584 | 1.3364 | 1.3363 | 1.3391 | 1.3395 |
|  | TS | 1.2767 | 1.2673 | 1.2560 | 1.2576 | 1.2590 | 1.2070 |
|  | PROD | 1.2349 | 1.2111 | 1.2047 | 1.2048 | 1.2086 | 1.2053 |
|  | Δd | -0.0914 | -0.09110 | -0.0804 | -0.079 | -0.080 | -0.133 |
| **$C_9$-$S_{10}$** | GS | 1.5567 | 1.6167 | 1.6473 | 1.6472 | 1.6467 | 1.6295 |
|  | TS | 1.6507 | 1.7186 | 1.7250 | 1.7224 | 1.7225 | 1.7760 |
|  | PROD | 1.7212 | 1.8025 | 1.7940 | 1.7941 | 1.7901 | 1.7644 |
|  | Δd | +0.094 | +0.1019 | +0.0777 | +0.075 | +0.076 | +0.147 |
| **$C_9$-$S_{11}$** | GS | 1.7228 | 1.7997 | 1.7883 | 1.7884 | 1.7861 | 1.7599 |
|  | TS | 1.7028 | 1.7884 | 1.8020 | 1.8016 | 1.7979 | 1.7560 |
|  | PROD | 1.7127 | 1.8031 | 1.7940 | 1,7940 | 18087 | 1.7789 |
|  | Δd | -0.020 | -0.0113 | +0.0137 | +0.013 | +0.0012 | -0.004 |
| **$S_{11}$-$C_{12}$** | GS | 1.7518 | 1.8014 | 1.8189 | 1.8182 | 1.8190 | 1.8060 |
|  | TS | 1.7494 | 1.7993 | 1.8340 | 1.8332 | 1.8344 | 1.8200 |
|  | PROD | 1.7127 | 1.8012 | 1.8280 | 1.8280 | 1.8276 | 1.8141 |
|  | Δd | -0.0024` | -0.0021 | 0.0151 | +0.015 | +0.075 | +0.014 |
| **$C_{12}$-$H_{13}$** | GS | 1.1225 | 1.1050 | 1.0910 | 1.0900 | 1.0916 | 1.0783 |
|  | TS | 1.1133 | 1.0955 | 1.0920 | 1.0911 | 1.0927 | 1.0790 |
|  | PROD | 1.096 | 1.0956 | 1.092 | 1.0899 | 1.0915 | 1.0785 |
|  | Δd | -0.0092 | -0.0095 | +0.0010 | +0.001 | +0.001 | +0.001 |
| **$C_{12}$-$H_{14}$** | GS | 1.1131 | 1.0955 | 1.0938 | 1.0927 | 1.0942 | 1.0822 |
|  | TS | 1.1139 | 1.0974 | 1.0920 | 1.0913 | 1.0931 | 1.0790 |
|  | PROD | 1.096 | 1.0975 | 1.0910 | 1.0912 | 1.0930 | 1.0806 |
|  | Δd | +0.0008 | 0.0019 | -0.0018 | -0.001 | -0.001 | -0003 |
| **$C_{12}$-$H_{15}$** | GS | 1.1131 | 1.0955 | 1.0910 | 1.0900 | 1.0916 | 1.0783 |
|  | TS | 1.1144 | 1.0958 | 1.0920 | 1.0908 | 1.0923 | 1.0780 |
|  | PROD | 1.0956 | 1.0956 | 1.0910 | 1.0899 | 1.0915 | 1.0785 |
|  | Δd | +0.0013 | +0.0003 | +0.0010 | +0.001 | +0.001 | -0.003 |
| **$S_{10}$ – $H_1$** | GS | 4.9480 | 4.9730 | 4.9930 | 4.9950 | 5.0020 | 4.9010 |
|  | TS | 1.7320 | 1.6780 | 1.8810 | 1.8800 | 1.8920 | 1.309 |
|  | PROD | 1.3280 | 1.3107 | 1.3480 | 1.3466 | 1.3482 | 1.3258 |
|  | Δd | -3.2160 | -3.2950 | -3.1120 | -3.115 | -3.110 | -3.592 |

### 6.4.1 TABLE 2: BOND ANGLES IN (DEGREES) OF O-ETHYL, S-METHYL XANTHATE (DITHIOCARBONATES)

| BOND ANGLE ($^0$) | STATE | AM1 | PM3 | DFT/ 6-31G* | DFT/ 6-31+G* | DFT/ 6-31G** | HF/ 3-12G* |
|---|---|---|---|---|---|---|---|
| **$H_1$-$C_2$-$H_3$** | GS | 108.369 | 107.356 | 108.514 | 108.539 | 108.519 | 108.672 |
| | TS | 101.350 | 99.650 | 104.72 | 103.52 | 104.910 | 93.940 |
| | PROD | - | - | - | - | - | - |
| **$H_1$-$C_2$-$H_4$** | GS | 109.232 | 107.654 | 108.577 | 108.520 | 108.563 | 109.281 |
| | TS | 100.120 | 97.500 | 101.860 | 102.520 | 101.860 | 77.810 |
| | PROD | - | - | - | - | - | - |
| **$H_1$-$C_2$-$C_5$** | GS | 110.479 | 112.094 | 110.738 | 110.868 | 110.752 | 109.743 |
| | TS | 107.210 | 109.750 | 109.750 | 103.980 | 103.980 | 99.94 |
| | PROD | - | - | - | - | - | - |
| **$C_2$-$C_5$-$C_6$** | GS | 111.545 | 111.761 | 111.626 | 111.616 | 111.616 | 1110.829 |
| | TS | 120.761 | 119.830 | 119.830 | 121.046 | 120.963 | 122.260 |
| | PROD | 122.720 | 123.098 | 121.933 | 121.791 | 121.871 | 121.896 |
| **$C_2$-$C_5$-$H_7$** | GS | 111.561 | 111.800 | 121.536 | 111.517 | 111.526 | 111.832 |
| | TS | 120.761 | 119.911 | 120.450 | 121.450 | 121.390 | 122.020 |
| | PROD | 122.720 | 123.098 | 121.933 | 121.791 | 121.871 | 121.896 |
| **$C_2$-$C_5$-$O_8$** | GS | 105.960 | 106.155 | 106.806 | 106.951 | 106.823 | 105.017 |
| | TS | 110.320 | 111.550 | 111.550 | 109.830 | 109.830 | 110.750 |
| | PROD | - | - | - | - | - | - |
| **$H_3$-$C_2$-$H_4$** | GS | 109.2760 | 107.629 | 108.588 | 108.532 | 108.575 | 109.281 |
| | TS | 112.837 | 111.748 | 117.480 | 113.608 | 113.626 | 116.180 |
| | PROD | 122.720 | 113.805 | 116.134 | 121.791 | 116.258 | 122.138 |
| **$H_3$-$C_2$-$C_5$** | GS | 110.465 | 112.126 | 110.705 | 1110.820 | 110.722 | 109.736 |
| | TS | 116.361 | 117.448 | 116.465 | 115.465 | 115.512 | 122.130 |
| | PROD | 122.720 | 123.098 | 121.933 | 121.791 | 121.871 | 121.896 |
| **$H_4$-$C_2$-$H_3$** | GS | 109.260 | 107.629 | 108.588 | 108.532 | 108.575 | 109.281 |
| | TS | 112.837 | 111.748 | 113.600 | 113.608 | 113.626 | 116.180 |
| | PROD | 114.560 | 113.805 | 116.134 | 116.418 | 116.258 | 116.208 |
| **$H_4$-$C_2$-$C_5$** | GS | 109.013 | 109.775 | 109.660 | 109.650 | 109.650 | 110.103 |
| | TS | 116.148 | 117.142 | 116.142 | 114.824 | 114.824 | 121.640 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | PROD | 122.720 | 123.098 | 121.933 | 121.871 | 121.801 | 121.896 |
| | GS | 110.465 | 112.126 | 110.705 | 110.820 | 110.722 | 109.736 |
| **$C_5$-$C_2$-$H_3$** | TS | 116.553 | 117.448 | 116.553 | 115.465 | 115.512 | 121.640 |
| | PROD | 121.900 | 121.933 | 121.933 | 121.791 | 121.871 | 121.896 |
| | GS | 109.013 | 109.629 | 109.660 | 109.497 | 109.650 | 110.103 |
| **$C_5$-$C_2$-$H_4$** | TS | 116.148 | 117.142 | 114.804 | 114.804 | 114.824 | 121.640 |
| | PROD | 122.720 | 123.098 | 121.933 | 121.791 | 121.871 | 121.396 |
| | GS | 117.320 | 119.425 | 122.828 | 123.054 | 122.770 | 125.709 |
| **$C_5$-$O_8$-$C_9$** | TS | 121.150 | 121.290 | 118.060 | 119.080 | 119.080 | 118.030 |
| | PROD | - | - | - | - | - | - |
| | GS | 109.690 | 112.126 | 108.714 | 109.002 | 108.647 | 109.546 |
| **$H_6$-$C_5$-$H_7$** | TS | 116.553 | 114.070 | 115.749 | 115.537 | 115.537 | 115.720 |
| | PROD | 113.805 | 113.805 | 116.134 | 116.418 | 116.260 | 116.208 |
| | GS | 108.985 | 109.940 | 109.073 | 108.804 | 109.049 | 109.530 |
| **$H_6$-$C_5$-$O_8$** | TS | 86.440 | 91.250 | 86.130 | 86.110 | 86.110 | 80.530 |
| | PROD | - | - | - | - | - | - |
| | GS | 109.690 | 107.940 | 108.714 | 109.002 | 108.647 | 109.546 |
| **$H_7$-$C_5$-$H_6$** | TS | 116.553 | 114.070 | 115.749 | 115.749 | 115.531 | 115.720 |
| | PROD | 114.560 | 113.80 5 | 116.134 | 114.560 | 115.530 | 116.208 |
| | GS | 108.978 | 109.324 | 109.081 | 108.870 | 109.118 | 109.238 |
| **$H_7$-$C_5$-$O_8$** | TS | 85.900 | 91.14 | 86.110 | 87.110 | 86.110 | 77.310 |
| | PROD | - | - | - | - | - | - |
| | GS | 108.985 | 109.839 | 109.013 | 108.804 | 109.049 | 109.244 |
| **$O_8$-$C_5$-$H_6$** | TS | 86.440 | 91.25 | 87.720 | 86.113 | 87.620 | 80.530 |
| | PROD | - | - | - | - | - | - |
| | GS | 108.978 | 109.324 | 109.870 | 108.870 | 109.118 | 109.238 |
| **$O_8$-$C_5$-$H_7$** | TS | 85.900 | 91.400 | 87.650 | 87.650 | 87.62 | 77.310 |
| | PROD | - | - | - | - | - | - |
| | GS | 118.372 | 118.022 | 119.999 | 119.933 | 120.013 | 120.270 |
| **$O_8$-$C_9$=$S_{10}$** | TS | 126.995 | 126.018 | 124.530 | 124.530 | 125.018 | 124.230 |
| | PROD | 125.398 | 126.490 | 124.506 | 124.526 | 124.474 | 123.611 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **O$_8$-C$_9$-S$_{11}$** | GS | 113.945 | 117.367 | 114.554 | 114.453 | 114.547 | 114.097 |
| | TS | 122.470 | 121.566 | 120.221 | 120.221 | 119.949 | 122.180 |
| | PROD | 127.028 | 127.273 | 123.974 | 123.818 | 123.987 | 123.468 |
| **C$_9$-S$_{11}$-C$_{12}$** | GS | 103.852 | 104.461 | 101.962 | 102.198 | 101.938 | 103.143 |
| | TS | 107.388 | 107.396 | 102.913 | 102.913 | 102.517 | 99.160 |
| | PROD | 104.481 | 105.300 | 106.207 | 93.218 | 98.140 | 93.937 |
| **S$_{10}$=C$_9$ -S$_{11}$** | GS | 127.683 | 124.611 | 125.447 | 125.613 | 125.440 | 125.639 |
| | TS | 110.532 | 112.416 | 115.219 | 115.219 | 115.015 | 113.590 |
| | PROD | 107.074 | 106.237 | 111.520 | 111.656 | 111.539 | 112.921 |
| **S$_{11}$=C$_9$-S$_{10}$** | GS | 127.683 | 124.611 | 125.447 | 125.613 | 125.440 | 125.639 |
| | TS | 110.532 | 112.416 | 115.219 | 115.219 | 115.015 | 113.590 |
| | PROD | 107.074 | 106.237 | 111.520 | 111.656 | 111.539 | 112.921 |
| **S$_{11}$=C$_{12}$–H$_{13}$** | GS | 111.344 | 112.376 | 110.381 | 110.519 | 110.289 | 110.607 |
| | TS | 109.967 | 113.224 | 109.251 | 109.251 | 109.390 | 109.250 |
| | PRD | 111.719 | 113.081 | 110.282 | 109.945 | 111.539 | 110.073 |
| | | | | | | 105.422 | |
| **S$_{11}$=C$_{12}$ – H$_{14}$** | GS | 108.926 | 109.561 | 105.507 | 105.422 | 109.190 | 105.817 |
| | TS | 108.727 | 107.276 | 109.675 | 109.675 | 110.198 | 109.640 |
| | PROD | 105.960 | 106.936 | 106.207 | 109.913 | 110.311 | 107.123 |
| **S$_{13}$=C$_{12}$ – H$_{15}$** | GS | 108.971 | 110.042 | 110.406 | 110.538 | 108.113 | 110.605 |
| | TS | 111.630 | 112.997 | 108.687 | 108.687 | 106.123 | 107.490 |
| | PRD | 111.719 | 113.081 | 110.282 | 109.945 | 110.548 | 110.073 |
| **H$_{13}$=C$_{12}$ – H$_{14}$** | GS | 109.123 | 108.296 | 110.447 | 110.334 | 109.936 | 110.077 |
| | TS | 108.758 | 107.836 | 109.780 | 109.780 | 109.930 | 110.080 |
| | PRD | 109.495 | 107.958 | 109.852 | 109.945 | 110.165 | 110.052 |
| **H$_{13}$=C$_{12}$- H$_{15}$** | GS | 109.034 | 108.039 | 109.631 | 109.667 | 109.930 | 109.602 |
| | TS | 108.920 | 107.486 | 109.690 | 109.690 | 110.548 | 110.110 |
| | PROD | 108.412 | 107.605 | 109.825 | 109.913 | | 109.442 |
| **H$_{14}$=C$_{12}$- H$_{13}$** | GS | 109.123 | 108.296 | 110.447 | 110.334 | 109.936 | 110.077 |
| | TS | 108.758 | 107.836 | 109.780 | 109.780 | 110.165 | 110.080 |
| | PROD | 109.495 | 107.958 | 110.081 | 109.945 | 110.512 | 110.052 |
| **H$_{13}$=C$_{12}$– H$_{15}$** | GS | 109.416 | 108.427 | 110.409 | 110.296 | 109.953 | 110.070 |
| | TS | 108.918 | 107.785 | 109.945 | 109.925 | 110.165 | 110.220 |
| | PRD | 108.412 | 107.958 | 110.081 | 109.913 | 109.953 | 110.052 |

### 6.4.2 TABLE 3: DIHEDRAL ANGLES IN DEGREE OF O- ETHYL S- METHYL XANTHATE (DITHIOCARBONATE)

| DIHEDRAL ANGLE($^O$) | STATE | AM1 | PM3 | DFT/ 6-31G* | DFT/ 6-31G** | HF/ 3-21G* | DFT/ 6-31+G* |
|---|---|---|---|---|---|---|---|
| **$H_1$- $C_2$ -$C_5$- $H_6$** | GS | -58.153 | -58.990 | -59.148 | -59.167 | -58.688 | -58.832 |
| | TS | 99.620 | 107.540 | -93.16 | -93.300 | -78.730 | -92.360 |
| | PROD | - | - | - | - | - | - |
| **$H_1$-$C_2$-$C_5$-$H_7$** | GS | 178.788 | 179.887 | 179.016 | 179.096 | 178.033 | 178.984 |
| | TS | -96.24 | -101.740 | 103.060 | 103.970 | 100.75 | 103.390 |
| | PROD | - | - | - | - | - | - |
| **$H_1$-$C_2$-$C_5$-$O_8$** | GS | 60.318 | 60.750 | 59.918 | 59.948 | 59.675 | 60.063 |
| | TS | 1.330 | 2.810 | 5.770 | 6.180 | 13.050 | 6.200 |
| | PROD | - | - | - | - | - | - |
| **$C_2$-$C_5$-$O_8$-$C_9$** | GS | 179.828 | -176.717 | 179.026 | 178.960 | -179.957 | 178.908 |
| | TS | 16.490 | 17.150 | 15.600 | 15.110 | 13.050 | 15.880 |
| | PROD | - | - | - | - | - | - |
| **$H_3$-$C_2$-$C_5$-$H_6$** | GS | -178.078 | -179.827 | -179.551 | -179.597 | -178.037 | -179.430 |
| | TS | 151.217 | 145.488 | 152.660 | 152.327 | -179.820 | 153.191 |
| | PROD | 180.000 | 180.000 | 180.000 | 180.00 | 180.00 | 180.000 |
| **$H_3$-$C_2$-$C_5$-$H_7$** | GS | 58.892 | 59.051 | 58.613 | 58.666 | 58.683 | 58.386 |
| | TS | -12.922 | -5.235 | -11.130 | -10.395 | -0.340 | -11.075 |
| | PROD | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | 60.877 |
| **$H_4$-$C_2$-$C_5$-$H_6$** | GS | 61.887 | +60.597 | 60.654 | 60.619 | 61.639 | 60.877 |
| | TS | 14.679 | 8.470 | -146.420 | 17.090 | 3.010 | 18.059 |
| | PROD | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 |
| **$H_4$-$C_2$-$C_5$-$H_7$** | GS | -61.173 | -60.525 | -61.182 | -61.117 | -61.640 | -61.307 |
| | TS | -149.460 | -142.582 | -146.420 | -145.632 | -177.510 | 146.207 |
| | PROD | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 |
| **$H_5$-$O_8$-$C_9$-$S_{10}$** | GS | -179.961 | 179.663 | 179.817 | 179.827 | 179.949 | 179.898 |
| | TS | -32.43 | 112.690 | -42.990 | -43.140 | -101.30 | -45.160 |
| | PROD | - | - | - | - | - | - |
| **$C_5$-$O_8$-$C_9$-$S_{11}$** | GS | 0.066 | -0.124 | -60.226 | -0.211 | -0.062 | -0.136 |
| | TS | 148.190 | 143.380 | -106.380 | 135.270 | 139.460 | 132.730 |
| | PROD | - | - | - | | - | - |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **$H_6$-$C_5$-$O_8$-$C_9$** | GS | -60.018 | -55.730 | -60.226 | -60.272 | -59.863 | -60.392 |
| | TS | -105.190 | -105.860 | -106.380 | -106.920 | -101.300 | -106.070 |
| | PROD | - | - | - | - | - | - |
| **$H_7$-$C_5$-$O_8$-$C_9$** | GS | 59.659 | 62.533 | 58.347 | 58.262 | 59.949 | 58.285 |
| | TS | 137.840 | 140.030 | 137.700 | 137.280 | 139.460 | 137.86 |
| | PROD | - | - | - | - | - | - |
| **$O_8$-$C_9$-$S_{11}$-$C_{12}$** | GS | -179.850 | 179.816 | -179.899 | -179.912 | 180.000 | -179.859 |
| | TS | -0.365 | 0.688 | 5.150 | 5.141 | 1.600 | 6.487 |
| | PROD | -0.000 | 0.000 | -0.000 | -0.000 | -0.000 | -0.000 |
| **$C_9$-$S_{11}$-$C_{12}$-$H_{13}$** | GS | -0.426 | -3.564 | -61.093 | -61.078 | -60.771 | -60.209 |
| | TS | -112.292 | -59.175 | -122.220 | -122.766 | -119.51 | -125.035 |
| | PROD | -60.821 | -61.307 | -60.751 | -60.781 | -60.561 | -61.307 |
| **$C_9$-$S_{11}$-$C_{12}$-$H_{14}$** | GS | -120.812 | -123.999 | 179.577 | 179.570 | -179.960 | 179.573 |
| | TS | 128.733 | -178.023 | 117.170 | 116.641 | 119.780 | 114.598 |
| | PROD | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 |
| **$C_9$-$S_{11}$-$C_{12}$-$H_{15}$** | GS | 119.882 | 116.877 | 60.279 | 60.249 | 60.850 | 60.390 |
| | TS | 8.554 | 63.325 | -2.640 | -3.194 | -0.040 | -5.373 |
| | PROD | 60.821 | 60.307 | 60.751 | 60.521 | 60.234 | 61.307 |
| **$S_{10}$=$C_9$-$S_{11}$-$C_{12}$** | GS | 0.180 | -0.137 | 0.056 | 0.047 | -0.011 | 0.104 |
| | TS | -179.103 | -179.366 | -176.270 | -176.294 | -177.910 | -175.430 |
| | PROD | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 |
| **$H_3$-$C_2$-$C_5$-$O_8$** | GS | -59.578 | -179.66 | -60.485 | -60.482 | -59.674 | -60.535 |
| | TS | -111.220 | 111.220 | -108.420 | -108.190 | -88.040 | -108.260 |
| | PROD | - | - | - | - | - | - |
| **$H_4$-$C_2$-$C_5$-$O_8$** | GS | -178.643 | -179.663 | 179.720 | 179.735 | -179.997 | 179.771 |
| | TS | 112.240 | 112.69 | 116.290 | 116.580 | 94.790 | 116.610 |
| | PROD | - | - | - | - | - | - |
| **$O_8$=$C_9$-$S_{10}$-$H_1$** | GS | - | - | - | - | - | - |
| | TS | - | - | - | - | - | - |
| | PROD | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 |
| **$H_1$-$S_{10}$-$C_9$-$S_{11}$** | GS | - | - | - | - | - | - |
| | TS | - | - | - | - | - | - |
| | PROD | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 |

### 6.4.3 TABLE 4: ATOMIC CHARGES (MULLIKEN) Δq = ($q_{ts}$ - $q_{gs}$) OF O-ETHYL-S-METHYL XANTHATE

| MOLECULE | STATE | AM1 | PM3 | DFT/ 6-3IG* | DFT/ 6-3IG** | DFT/ 6-3I+G* | HF/ 3-2IG* |
|---|---|---|---|---|---|---|---|
| **H$_1$** | GS | +0.095 | +0.056 | +0.174 | +0.221 | +0.221 | +0.237 |
| | TS | +0.247 | +0.247 | +0.140 | +0.207 | +0.207 | +0.168 |
| | PROD | +0.109 | +0.015 | +0.129 | +0.134 | +0.134 | +0.1669 |
| | Δq | +0.182 | +0.191 | -0.034 | -0.014 | -0.014 | -0.069 |
| **C$_1$** | GS | -0.215 | -0.121 | -0.458 | -0.785 | -0.785 | -0.600 |
| | TS | -0.421 | -0.415 | -0.480 | -0.524 | -0.524 | -0.429 |
| | PROD | -0.218 | -0.153 | -0.285 | -0.395 | -0.395 | -0.425 |
| | Δq | -0.206 | -0.294 | -0.938 | +0.261 | +0.261 | +0.171 |
| **H$_2$** | GS | +0.095 | +0.057 | +0.174 | +0.220 | +0.220 | +0.237 |
| | TS | +0.129 | +0.102 | +0.192 | +0.245 | +0.245 | +0.207 |
| | PRD | +o.109 | +0.076 | +0.143 | +0.197 | +0.197 | +0.213 |
| | Δq | +0.034 | +0.045 | +0.018 | +0.041 | +0.041 | -0.030 |
| **H$_4$** | GS | +0.089 | +0.053 | +0.157 | +0.211 | +0.211 | +0.207 |
| | TS | +0.134 | +0.108 | +0.197 | +0.252 | +0.252 | +0.210 |
| | PROD | +0.109 | +0.076 | +0.143 | +0.197 | +0.197 | +0.213 |
| | Δq | +0.045 | 0.055 | +0.040 | +0.041 | +0.041 | +0.003 |
| **C$_2$** | GS | -0.058 | +0.026 | -0.071 | -0.031 | -0.031 | -0.124 |
| | TS | +0.134 | +0.224 | -0.123 | -0.194 | -0.194 | -0.454 |
| | PROD | -0.218 | -0.153 | -0.285 | -0.395 | -0.395 | -0.425 |
| | Δq | +0.045 | +0.198 | -0.011 | -0.163 | -0.163 | -0.328 |
| **H$_5$** | GS | +0.096 | +0.063 | +0.176 | +0.219 | +0.219 | +0.238 |
| | TS | +0.135 | +0.071 | +0.208 | +0.267 | +0.267 | -0.246 |
| | PROD | +0.109 | +0.076 | +0.143 | +0.197 | +0.197 | +0.213 |
| | Δq | +0.039 | +0.008 | +0.032 | +0.048 | +0.048 | -0.484 |
| **H$_6$** | GS | +0.096 | +0.061 | +0.176 | +0.218 | +0.218 | +0.238 |
| | TS | +0.128 | +0.065 | +0.204 | +0.263 | +0.263 | +0.200 |
| | PROD | +0.109 | +0.076 | +0.143 | +0.197 | +0.197 | +0.213 |
| | Δq | -0.0832 | +0.004 | +0.028 | +0.045 | +0.045 | -0.038 |
| **O$_1$** | GS | -0.176 | -0.132 | -0.387 | -0.267 | -0.267 | -0.664 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | TS | -0.382 | -0.346 | -0.437 | -0.498 | -0.498 | -0.564 |
| | PROD | -0.284 | -0.280 | +0.389 | -0.432 | -0.432 | -0.561 |
| | Δq | -0.558 | -0.214 | -0.050 | -0.231 | -0.281 | +0.100 |
| **C$_3$** | GS | -0.163 | -0.040 | +0.064 | +0.159 | -0.100 | +0.124 |
| | TS | -0.021 | +0.094 | +0.082 | +0.184 | +0.217 | +0.172 |
| | PRD | -0.019 | +0.134 | +0.098 | +0.179 | +0.167 | +0.167 |
| | Δq | -0.184 | +0.054 | +0.018 | +0.025 | +0.317 | +0.048 |
| **S$_1$** | GS | -0.060 | -0.160 | -0.186 | -0.216 | -0.193 | -0.132 |
| | TS | -0.271 | -0.245 | -0.116 | -0.245 | -0.369 | +0.024 |
| | PROD | +0.057 | +0.038 | +0.158 | +0.167 | +0.190 | +0.229 |
| | Δq | -0.211 | -0.085 | +0.07 | -0.229 | -0.1759 | +0.156 |
| **S$_2$** | GS | +0.183 | +0.062 | +0.162 | +0.191 | +0.346 | +0.251 |
| | TS | +0.224 | +0.072 | +0.164 | +0.186 | +0.164 | +0.236 |
| | PRD | +0.185 | +0.044 | -0.011 | +0.046 | -0.071 | +0.017 |
| | Δq | +0.041 | +0.010 | +0.002 | -0.005 | -0.182 | -0.015 |
| **C$_4$** | GS | -0.374 | -0.217 | -0.594 | -0.505 | -0.810 | -0.789 |
| | TS | -0.390 | +0.271 | -0.618 | -0.526 | -0.734 | -0.779 |
| | PROD | -0.355 | -0.196 | -0.587 | -0.492 | -0.718 | -0.778 |
| | Δq | -0.016 | -0.054 | -0.024 | -0.021 | -0.076 | -0.010 |
| **H$_7$** | GS | +0.117 | +0.086 | +0.185 | +0.154 | +0.226 | +0.240 |
| | TS | +0.113 | +0.088 | +0.190 | +0.154 | +0.226 | +0.261 |
| | PROD | +0.126 | +0.090 | +0.189 | +0.155 | +0.228 | +0.240 |
| | Δq | -0.004 | +0.002 | +0.005 | +0.000 | +0.000 | +0.021 |
| **H$_8$** | GS | +0.117 | +0.085 | +0.214 | +0.182 | +0.263 | +0.268 |
| | TS | +0.123 | +0.075 | +0.212 | +0.185 | +0.260 | +0.262 |
| | PROD | +0.116 | +0.076 | +0.207 | +0.175 | +0.251 | +0.260 |
| | Δq | +O.006 | -0.010 | -0.002 | +0.003 | -0.003 | -0.006 |
| **H$_3$** | GS | +0.153 | +0.122 | +0.214 | +0.182 | +0.263 | +0.010 |
| | TS | +0.105 | +0.070 | +0.186 | +0.148 | +0.229 | +0.268 |
| | PROD | +0.116 | +0.076 | +0.209 | +0.175 | +0.251 | +0.242 |
| | Δq | -0.048 | -0.052 | -0.027 | -0.032 | -0.042 | +0.260 |

### 6.4.4 TABLE 5: HEAT OF FORMATION OF O – ETHYL, S-METHYL XANTHATE (DITHIOCARBONATES)

| | **GS (kJ/mol)** | **TS (kJ/mol** | **PROD (kJ/mol)** |
|---|---|---|---|
| **AM1** | -90.834 | 68.915 | -70.846 |
| **PM3** | -15.215 | 96.875 | -57.756 |
| **DFT/6-31G*** | -2700810.370 | -2700530.990 | -2700634.640 |
| **DFT/6-31G**** | -2700797.560 | -2700564.825 | -2700670.875 |
| **DFT/6-31+G*** | -2700804.320 | -2700560.625 | -2700676.125 |
| **HF/3-21G*** | -2690184.325 | -2680127.321 | -2680117.094 |

## 6.4.6 TABLE 7: VARIATION OF RATE OF REACTION ($S^{-1}$) WITH TEMPERATURE (K) OF O-ETHYL S-METHYL XANTHATES

| **Temp(K)** | **AM1** | **PM3** | **DFT/6-31G*** | **DFT/6-31G**** | **DFT/6-31+G**** | **HF/3-21G*** |
|---|---|---|---|---|---|---|
| **373** | $2.74X10^{-12}$ | $1.56X10^{-11}$ | $1.56X10^{-10}$ | $1.23X10^{-6}$ | $4.56X10^{-7}$ | $6.78X10^{-10}$ |
| **398** | $3.27X10^{-11}$ | $2.22X10^{-10}$ | $2.37X10^{-9}$ | $3.45X10^{-5}$ | $3.56X10^{-6}$ | $4.34X10^{-9}$ |
| **423** | $6.97X10^{-10}$ | $1.79X10^{-9}$ | $8.11X10^{-9}$ | $4.51X10^{-4}$ | $9.57X10^{-4}$ | $8.23X10^{-9}$ |
| **448** | $1.01X10^{-8}$ | $2.67X10^{-8}$ | $1.11X10^{-8}$ | $2.99X10^{-3}$ | $6.167X10^{-3}$ | $6.56X10^{-8}$ |
| **498** | $9.39X10^{-7}$ | $2.64X10^{-6}$ | $9.16X10^{-7}$ | $7.39X10^{-2}$ | $1.46X10^{-1}$ | $2.46X10^{-7}$ |
| **523** | $6.62X10^{-6}$ | $1.89X10^{-5}$ | $6.24X10^{-6}$ | $2.93X10^{-1}$ | $5.72X10^{-1}$ | $6.00X10^{-6}$ |
| **548** | $3.92X10^{-5}$ | $1.14X10^{-4}$ | $3.54X10^{-5}$ | 1.034 | 1.966 | $1.23X10^{-5}$ |
| **573** | $2.09X10^{-4}$ | $5.73X10^{-4}$ | $1.74X10^{-4}$ | 3.257 | 6.130 | $3.17X10^{-4}$ |
| **598** | $8.88X10^{-4}$ | $2.64X10^{-3}$ | $7.57X10^{-4}$ | 9.371 | 17.400 | $2.15X10^{-3}$ |
| **623** | $3.49X10^{-3}$ | $1.04X10^{-2}$ | $2.93X10^{-3}$ | 24.30 | 44.5 | $3.46X10^{-2}$ |

## 6.5.0 TABLE 1 : BONDLENGTH ($A^O$) OF O-NPROPYL, S- METHYL) XANTHATE (DITHIOCARBONATE$\Delta d = (d_{TS} - d_{GS})$

| **BOND LENGTH($A^O$)** | **STATE** | **AM1** | **PM3** | **DFT/ 6-31G*** | **DFT/6-31G**** | **DFT/6-31+G*** | **HF/3-21G*** |
|---|---|---|---|---|---|---|---|
| **$H_1$-$C_2$** | GS | 1.1170 | 1.0982 | 1.0967 | 1.0956 | 1.0973 | 1.0848 |
| | TS | 1.1176 | 1.0985 | 1.0967 | 1.0948 | 1.0963 | 1.0844 |
| | PROD | 1.1191 | 1.0981 | 1.0986 | 1.0942 | 1.0860 | 1.0860 |
| | $\Delta d$ | 0.0006 | 0.0003 | -0.0003 | -0.0008 | -0.0010 | -0.004 |
| **$C_2$-$H_3$** | GS | 1.1173 | 1.0981 | 1.0966 | 1.0955 | 1.0972 | 1.0848 |
| | TS | 1.1182 | 1.0980 | 1.0958 | 1.0954 | 1.0968 | 1.0846 |
| | PROD | 1.1176 | 1.0983 | 1.0950 | 1.0974 | 1.0834 | 1.0834 |
| | $\Delta d$ | 0.0009 | -0.0001 | -0.0008 | -0.0001 | -0.0004 | -0.0002 |
| **$C_2$-$H_4$** | GS | 1.1170 | 1.0975 | 1.0946 | 1.0934 | 1.0953 | 1.0831 |
| | TS | 1.1174 | 1.0974 | 1.0947 | 1.0937 | 1.0952 | 1.0831 |
| | PROD | 1.1191 | 1.0983 | 1.0986 | 1.0974 | 1.0860 | 1.0860 |
| | $\Delta d$ | 0.0004 | -0.0001 | 0.0001 | 0.0003 | -0.0001 | 0.0000 |
| **$C_2$-$C_5$** | GS | 1.5061 | 1.5119 | 1.5325 | 1.5319 | 1.5340 | 1.5398 |
| | TS | 1.4974 | 1.5002 | 1.5267 | 1.5259 | 1.5284 | 1.5300 |
| | PROD | 1.4764 | 1.4800 | 1.5021 | 1.5013 | 1.5096 | 1.5096 |
| | $\Delta d$ | -0.0087 | -0.0117 | -0.0058 | -0.0060 | -0.0056 | -0.0098 |
| **$C_5$-$H_6$** | GS | 1.1213 | 1.1081 | 1.0961 | 1.0953 | 1.0966 | 1.0821 |
| | TS | 1.1177 | 1.1041 | 1.0951 | 1.0955 | 1.0967 | 1.0967 |
| | PROD | - | - | - | - | - | - |
| | $\Delta d$ | -0.0036 | -0.0040 | -0.0007 | 0.0002 | -0.0001 | 0.0146 |
| **$C_5$-$H_7$** | GS | 1.1213 | 1.1083 | 1.0964 | 1.0956 | 1.0969 | 1.0821 |
| | TS | 1.0964 | 1.0965 | 1.0945 | 1.0945 | 1.0965 | 1.0804 |
| | PROD | 1.1034 | 1.0981 | 1.0914 | 1.0908 | 1.0763 | 1.0763 |
| | $\Delta d$ | -0.0249 | -0.0118 | -0.0019 | -0.0011 | -0.0004 | -0.0017 |
| **$C_5$-$C_8$** | GS | 1.5176 | 1.5251 | 1.5213 | 1.5208 | 1.5215 | 1.5223 |
| | TS | 1.4103 | 1.4155 | 1.4085 | 1.4087 | 1.4116 | 1.3836 |
| | PROD | 1.3310 | 1.3279 | 1.3332 | 1.3326 | 1.3161 | 1.3161 |
| | $\Delta d$ | -0.1073 | -0.1096 | -0.1128 | -0.1121 | -0.1099 | -0.1387 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **$C_8$-$H_9$** | GS | 1.1228 | 1.1078 | 1.0968 | 1.0964 | 1.0967 | 1.0811 |
| | TS | 1.1034 | 1.0951 | 1.0846 | 1.0831 | 1.0839 | 1.0681 |
| | PROD | 1.0978 | 1.0855 | 1.0886 | 1.0859 | 1.0735 | 1.0747 |
| | Δd | -0.0194 | -0.0127 | -0.0122 | -0.0133 | -0.0128 | -0.0130 |
| **$C_8$-$H_{10}$** | GS | 1.1230 | 1.1084 | 1.0969 | 1.0966 | 1.0968 | 1.0811 |
| | TS | 1.1033 | 1.0969 | 1.0830 | 1.0842 | 1.0853 | 1.0693 |
| | PROD | 1.0975 | 1.0866 | 1.0886 | 1.0878 | 1.0735 | 1.0735 |
| | Δd | -0.0197 | -0.0115 | -0.0139 | -0.0124 | -0.0115 | -0.0118 |
| **$C_8$-$O_{11}$** | GS | 1.4396 | 1.4323 | 1.4484 | 1.4488 | 1.4510 | 1.4634 |
| | TS | 1.9640 | 1.8420 | 2.1160 | 2.1200 | 2.120 | 2.154 |
| | PROD | - | - | - | - | - | - |
| | Δd | 0.5244 | 0.4097 | 0.6676 | 0.6712 | 0.6690 | 0.6906 |
| **$O_{11}$-$C_{12}$** | GS | 1.3683 | 1.3587 | 1.3364 | 1.3364 | 1.3391 | 1.3393 |
| | TS | 1.2767 | 1.2688 | 1.2488 | 1.2501 | 1.2526 | 1.2418 |
| | PROD | 1.2349 | 1.2111 | 1.2047 | 1.2048 | 1.2086 | 1.2053 |
| | Δd | -0.0916 | -0.0899 | -0.0876 | -0.0863 | -0.0865 | -0.0975 |
| **$C_{12}$-$S_{13}$** | GS | 1.5567 | 1.6167 | 1.6476 | 1.6477 | 1.6471 | 1.6296 |
| | TS | 1.6510 | 1.7187 | 1.7318 | 1.7297 | 1.7292 | 1.7229 |
| | PROD | 1.7212 | 1.8025 | 1.8142 | 1.8144 | 1.8087 | 1.7789 |
| | Δd | 0.0943 | 0.102 | 0.0842 | 0.0820 | 0.821 | 0.0933 |
| **$C_{12}$-$S_{14}$** | GS | 1.7227 | 1.7993 | 1,7874 | 1.7874 | 1.7854 | 1.7600 |
| | TS | 1.7025 | 1.7872 | 1.7964 | 1.7960 | 1.7929 | 1.7649 |
| | PROD | 1.7127 | 1.8031 | 1.7940 | 1.7941 | 1.7901 | 1.7644 |
| | Δd | -0.0202 | -0.0121 | 0.0090 | 0.0086 | 0.0075 | 0.0049 |
| **$S_{14}$-$C_{15}$** | GS | 1.7516 | 1.8015 | 1.8200 | 1.8191 | 1.8200 | 1.8060 |
| | TS | 1.7490 | 1.7991 | 1.8305 | 1.8299 | 1.8301 | 1.8130 |
| | PROD | 1.7537 | 1.8012 | 1.8284 | 1.8277 | 1.8276 | 1.8141 |
| | Δd | -0.0026 | -0.0024 | 0.0105 | 0.0108 | 0.0101 | 0.0070 |
| **$C_{15}$-$H_{16}$** | GS | 1.1133 | 1.0955 | 1.0910 | 1.0900 | 1.0916 | 1.0783 |
| | TS | 1.1131 | 1.0956 | 1.0916 | 1.0904 | 1.0922 | 1.0790 |
| | PROD | 1.1129 | 1.0956 | 1.0909 | 1.0899 | 1.0915 | 1.0785 |
| | Δd | -0.0002 | 0.0001 | 0.0006 | 0.0004 | 0.0006 | 0.0007 |
| **$C_{15}$-$H_{17}$** | GS | 1.1134 | 1.0956 | 1.0938 | 1.0927 | 1.0942 | 1.0822 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | TS | 1.1141 | 1.0957 | 1.0916 | 1.0904 | 1.0921 | 1.0791 |
| | PROD | 1.1149 | 1.0956 | 1.0923 | 1.0912 | 1.0930 | 1.0806 |
| | Δd | 0.0007 | 0.0001 | -0.0022 | -0.0023 | -0.0021 | -0.0031 |
| **$C_{15}$-$H_{18}$** | GS | 1.1230 | 1.1050 | 1.0910 | 1.0900 | 1.0915 | 1.0783 |
| | TS | 1.1135 | 1.0976 | 1.0929 | 1.0918 | 1.0937 | 1.0815 |
| | PROD | 1.1129 | 1.0956 | 1.0909 | 1.0899 | 1.0915 | 1.0785 |
| | Δd | -0.0095 | -0.0074 | 0.0029 | 0.0018 | 0.0022 | 0.0032 |
| **$H_6$-$S_{13}$** | GS | 4.9090 | 4.9340 | 4.9450 | 4.9430 | 4.9520 | 4.8780 |
| | TS | 1.7300 | 1.6670 | 1.8350 | 1.8550 | 1.8550 | 1.7590 |
| | PROD | 1.3275 | 1.3107 | 1.3479 | 1.3466 | 1.3482 | 1.3258 |
| | Δd | -3.1790 | -3.2670 | -3.1080 | -3.0880 | -3.0970 | -3.1190 |

## 6.5.1 TABLE2: SELECTED BOND ANGLE IN (DEGREE) OF O-n PROPYL, S-METHYL XANTHATE (DITHIOCARBONATES)

| BOND ANGLE($^{O}$) | STATE | AM1 | PM3 | DFT/6-31G* | DFT/6-31G** | DFT/ 6-31+G* | HF/3-21G* |
|---|---|---|---|---|---|---|---|
| **$H_1$-$C_2$-$H_3$** | GS | 108.358 | 107.352 | 107.765 | 107.745 | 107.801 | 108.350 |
| | TS | 108.132 | 107.453 | 108.162 | 108.133 | 108.220 | 108.632 |
| | PROD | 108.328 | 107.583 | 108.476 | 108.113 | 108.411 | 108.411 |
| **$H_1$-$C_2$-$H_4$** | GS | 108.435 | 107.383 | 107.638 | 107.616 | 107.603 | 107.984 |
| | TS | 108.334 | 107.339 | 107.966 | 107.539 | 107.549 | 107.712 |
| | PROD | 108.063 | 107.583 | 106.489 | 108.113 | 107.465 | 107.465 |
| **$H_1$-$C_2$-$C_5$** | GS | 110.824 | 111.745 | 111.507 | 111.523 | 111.538 | 110.993 |
| | TS | 110.214 | 111.317 | 111.467 | 110.923 | 110.994 | 110.629 |
| | PROD | 110.076 | 112.870 | 111.198 | 111.595 | 110.644 | 110.646 |
| **$C_2$-$C_5$-$H_6$** | GS | 110.380 | 110.162 | 110.373 | 110.397 | 110.303 | 110.646 |
| | TS | 113.086 | 113.858 | 115.024 | 115.116 | 114.889 | 115.754 |
| | PROD | 114.866 | 115.790 | 115.904 | 115.936 | 115.684 | 115.684 |
| **$C_2$-$C_5$-$C_8$** | GS | 110.365 | 110.125 | 111.702 | 111.728 | 111.547 | 115.754 |
| | TS | 117.488 | 116.929 | 119.596 | 119.629 | 119.462 | 110.864 |
| | PROD | 124.266 | 123.389 | 125.257 | 125.268 | 124.753 | 119.949 |
| **$H_3$-$C_2$-$H_4$** | GS | 108.395 | 107.384 | 107.633 | 107.618 | 107.604 | 124.753 |
| | TS | 108.405 | 107.497 | 107.578 | 107.944 | 107.916 | 107.984 |
| | PROD | 108.328 | 107.498 | 108.085 | 106.455 | 108.411 | 108.234 |
| **$H_3$-$C_2$-$C_5$** | GS | 110.828 | 111.755 | 111.495 | 111.489 | 111.507 | 108.411 |
| | TS | 110.451 | 111.942 | 110.921 | 111.508 | 111.425 | 110.997 |
| | PROD | 111.867 | 110.547 | 111.575 | 111.176 | 111.144 | 111.307 |
| **$H_4$-$C_2$-$H_3$** | GS | 108.395 | 107.384 | 107.633 | 107.618 | 107.604 | 111.144 |
| | TS | 108.405 | 107.497 | 107.578 | 107.944 | 107.961 | 107.984 |
| | PROD | 108.328 | 107.498 | 108.085 | 106.455 | 108.411 | 108.234 |
| **$H_4$-$C_2$-$C_5$** | GS | 109.920 | 110.986 | 110.625 | 110.666 | 110.606 | 108.411 |
| | TS | 111.215 | 111.067 | 110.601 | 110.643 | 110.548 | 110.419 |
| | PROD | 110.076 | 110.547 | 111.198 | 111.176 | 110.686 | 110.218 |
| **$C_5$-$C_2$-$H_3$** | GS | 110.828 | 111.755 | 111.954 | 111.489 | 111.507 | 110.646 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | TS | 110.851 | 111.942 | 110.921 | 111.503 | 111.425 | 110.997 |
| | PROD | 111.867 | 110.547 | 111.575 | 111.176 | 111.144 | 111.307 |
| **$C_5$-$C_2$-$H_4$** | GS | 109.920 | 110.986 | 110.625 | 110.666 | 110.606 | 111.144 |
| | TS | 110.215 | 111.067 | 110.601 | 110.643 | 110.548 | 110.419 |
| | PROD | 110.076 | 110.547 | 111.198 | 111.176 | 110.646 | 110.081 |
| **$C_5$-$C_8$-$H_9$** | GS | 111.444 | 111.619 | 111.365 | 111.367 | 111.336 | 110.646 |
| | TS | 120.772 | 119.716 | 121.598 | 121.087 | 121.152 | 111.506 |
| | PROD | 122.795 | 122.667 | 121.698 | 121.765 | 121.854 | 121.403 |
| **$C_5$-$C_8$-$H_{10}$** | GS | 111.341 | 111.615 | 111.329 | 111.296 | 111.299 | 121.854 |
| | TS | 120.338 | 119.232 | 121.205 | 21.560 | 121.629 | 111.508 |
| | PROD | 122.280 | 123.212 | 121.825 | 121.635 | 121.790 | 121.865 |
| **$H_6$-$C_5$-$C_8$** | GS | 109.191 | 110.351 | 108.700 | 108.685 | 108.821 | 121.790 |
| | TS | 114.762 | 115.145 | 113.708 | 113.630 | 113.505 | 108.401 |
| | PROD | 120.868 | 120.821 | 118.838 | 118.795 | 119.563 | 115.609 |
| **$C_8$-$C_5$-$H_6$** | GS | 109.191 | 110.351 | 108.700 | 108.685 | 108.787 | 119.563 |
| | TS | 114.762 | 115.145 | 113.708 | 113.630 | 113.505 | 108.401 |
| | PROD | 120.868 | 120.821 | 118.838 | 118.795 | 119.563 | 115.609 |
| **$H_9$-$C_8$-$H_{10}$** | GS | 109.784 | 107.923 | 108.615 | 108.552 | 108.898 | 119.563 |
| | TS | 116.929 | 114.230 | 115.882 | 115.870 | 115.988 | 109.572 |
| | PROD | 114.925 | 114.121 | 116.486 | 116.602 | 116.356 | 116.179 |
| **$H_{10}$-$C_8$-$H_9$** | GS | 109.784 | 107.923 | 108.615 | 108.552 | 108.898 | 116.356 |
| | TS | 116.929 | 114.230 | 115.880 | 115.870 | 115.988 | 109.572 |
| | PROD | 114.925 | 114.121 | 116.476 | 116.602 | 116.356 | 116.356 |
| **$O_{11}$-$C_{12}$-$S_{13}$** | GS | 118.365 | 117.969 | 119.940 | 119.948 | 119.889 | 120.303 |
| | TS | 127.027 | 126.060 | 125.305 | 125.361 | 124.867 | 123.908 |
| | PROD | 125.898 | 126.490 | 123.974 | 123.937 | 123.818 | 123.468 |
| **$O_{11}$-$C_{12}$-$S_{14}$** | GS | 113.932 | 117.387 | 114.524 | 114.524 | 114.408 | 114.055 |
| | TS | 122.296 | 121.357 | 118.909 | 118.747 | 119.194 | 119.516 |
| | PROD | 127.028 | 127.273 | 124.506 | 124.474 | 124.526 | 123.611 |
| **$C_{12}$-$S_{14}$-$C_{15}$** | GS | 103.856 | 104.470 | 102.009 | 102.000 | 102.244 | 103.134 |
| | TS | 107.305 | 107.417 | 100.740 | 100.791 | 101.344 | 99.349 |
| | PROD | 104.481 | 105.300 | 98.139 | 98.140 | 98.911 | 97.724 |
| **$S_{13}$-$C_{12}$-$S_{14}$** | GS | 127.702 | 124.644 | 125.836 | 125.528 | 125.703 | 125.642 |
| | TS | 110.675 | 112.582 | 115.779 | 115.886 | 115.930 | 116.553 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | PROD | 107.074 | 106.237 | 111.520 | 111.539 | 111.656 | 112.921 |
| **$S_{14}$-$C_{12}$-$S_{13}$** | GS | 127.702 | 124.644 | 125.536 | 125.528 | 125.703 | 125.642 |
| | TS | 110.675 | 112.582 | 115.779 | 115.886 | 115.865 | 116.553 |
| | PROD | 107.074 | 106.237 | 111.520 | 111.539 | 111.656 | 112.921 |
| **$S_{14}$-$C_{15}$-$H_{16}$** | GS | 109.146 | 109.849 | 110.422 | 110.336 | 110.553 | 110.627 |
| | TS | 110.639 | 113.185 | 110.905 | 110.464 | 110.664 | 110.229 |
| | PROD | 111.719 | 113.081 | 110.282 | 110.198 | 110.493 | 110.073 |
| **$S_{14}$-$C_{15}$-$H_{17}$** | GS | 108.732 | 109.766 | 105.456 | 105.366 | 105.380 | 105.821 |
| | TS | 111.666 | 113.089 | 110.570 | 110.853 | 111.158 | 110.564 |
| | PROD | 105.960 | 106.936 | 106.207 | 106.123 | 105.984 | 107.123 |
| **$S_{14}$-$C_{15}$-$H_{18}$** | GS | 111.376 | 112.386 | 110.362 | 110.262 | 110.497 | 110.593 |
| | TS | 108.010 | 107.213 | 106.279 | 106.194 | 106.130 | 107.192 |
| | PROD | 111.719 | 113.081 | 110.282 | 110.198 | 110.493 | 110.073 |
| **$H_{16}$-$C_{15}$-$H_{17}$** | GS | 109.370 | 108.400 | 110.434 | 110.526 | 110.328 | 110.074 |
| | TS | 108.526 | 107.480 | 109.622 | 109.706 | 109.681 | 109.240 |
| | PROD | 109.495 | 107.958 | 110.081 | 110.165 | 109.945 | 110.052 |
| **$H_{16}$-$C_{15}$-$H_{18}$** | GS | 109.006 | 108.139 | 109.634 | 109.702 | 109.665 | 109.598 |
| | TS | 108.796 | 107.831 | 109.681 | 109.823 | 109.602 | 109.877 |
| | PROD | 108.412 | 107.605 | 109.852 | 109.930 | 109.913 | 109.442 |
| **$H_{17}$-$C_{15}$-$H_{16}$** | GS | 109.370 | 108.400 | 110.434 | 110.526 | 110.328 | 110.074 |
| | TS | 108.526 | 107.480 | 109.622 | 109.706 | 109.681 | 109.240 |
| | PROD | 109.495 | 107.958 | 110.081 | 110.165 | 109.945 | 110.052 |
| **$H_{17}$-$C_{15}$-$H_{18}$** | GS | 109.187 | 108.199 | 110.473 | 110.581 | 110.353 | 100.073 |
| | TS | 109.153 | 107.804 | 109.728 | 109.744 | 109.538 | 109.717 |
| | PROD | 109.495 | 107.958 | 110.081 | 110.165 | 109.945 | 110.052 |
| **$H_{18}$-$C_{15}$-$H_{16}$** | GS | 109.006 | 108.139 | 109.634 | 109.702 | 109.665 | 109.598 |
| | TS | 108.796 | 107.831 | 109.681 | 109.823 | 109.602 | 109.877 |
| | PROD | 108.412 | 107.605 | 109.852 | 109.930 | 109.913 | 109.442 |
| **$H_{18}$-$C_{15}$-$H_{17}$** | GS | 109.187 | 108.199 | 110.473 | 110.581 | 110.353 | 110.073 |
| | TS | 109.153 | 107.804 | 109.728 | 109.744 | 109.538 | 109.717 |
| | PROD | 109.495 | 107.958 | 110.081 | 110.165 | 109.945 | 110.052 |

## 6.5.2 TABLE 3: SELECTED DIHEDRAL ANGLE ($^0$) OF O –nPROPYL, S-METHYL XANTHATE (DITHIOCARBONATE)

| **DIHEDRAL ANGLE ($^0$)** | **STATE** | **AM 1** | **PM 3** | **6-31G** | **6-31G** | **6-31+G** | **HF 3-21G** |
|---|---|---|---|---|---|---|---|
| **$H_1$-$C_2$-$C_5$-$H_6$** | GS | -60.695 | -61.200 | -60.476 | -60.563 | -60.372 | -60.025 |
| | TS | 57.152 | -67.796 | -63.904 | -175.586 | -174.382 | -174.164 |
| | PROD | -59.508 | -59.509 | -61.509 | -59.609 | -59.802 | -60.603 |
| **$H_1$-$C_2$-$C_5$-$C_8$** | GS | 60.539 | 60.745 | 60.581 | 60.509 | 60.687 | 60.281 |
| | TS | -165.539 | 70.430 | 76.942 | 43.527 | 45.529 | 39.552 |
| | PROD | 120.492 | 120.492 | 120.520 | 120.123 | 120.123 | 119.123 |
| **$C_2$-$C_5$-$C_8$-$H_9$** | GS | 60.732 | 60.810 | 60.328 | 60.080 | 60.356 | 61.415 |
| | TS | 9.732 | 0.788 | 8.332 | 158.126 | 158.273 | 162.178 |
| | PROD | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 |
| **$C_2$-$C_5$-$C_8$-$H_{10}$** | GS | -62.245 | -60.060 | -61.052 | -61.198 | -61.346 | -61.424 |
| | TS | -153.845 | -148.631 | -158.010 | -7.410 | -8.541 | -8.965 |
| | PROD | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 |
| **$H_3$-$C_2$-$C_5$-$H_6$** | GS | 178.950 | 178.477 | 179.018 | 178.948 | 179.045 | 179.413 |
| | TS | -62.271 | 171.920 | 175.505 | 63.830 | 64.932 | 64.955 |
| | PROD | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 |
| **$H_3$-$C_2$-$C_5$-$C_8$** | GS | -60.239 | -59.578 | -59.925 | -59.979 | -59.896 | -60.281 |
| | TS | 75.039 | -49.854 | -43.650 | -77.057 | -75.157 | -81.329 |
| | PROD | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 |
| **$H_4$-$C_2$-$C_5$-$H_6$** | GS | 59.155 | 58.635 | 59.278 | 59.202 | 59.346 | 59.693 |
| | TS | 177.317 | 51.752 | 56.223 | -56.325 | -55.125 | -55.148 |
| | PROD | 59.508 | 59.508 | 60.018 | 61.502 | 59.508 | 61.502 |
| **$H_4$-$C_2$-$C_5$-$C_8$** | GS | 179.947 | -179.420 | -179.664 | -179.725 | -179.595 | 179.999 |
| | TS | -45.374 | -170.022 | -162.931 | 162.789 | 164.786 | 158.568 |
| | PROD | -120.492 | -120.492 | 120.567 | -120.623 | -120.767 | -119.656 |
| **$H_6$-$C_5$-$C_8$-$H_9$** | GS | 177.808 | -177.357 | -177.648 | -177.859 | -177.726 | -176.952 |
| | TS | 146.347 | 138.485 | 149.658 | 16.698 | 17.669 | 15.848 |
| | PROD | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 |
| **$H_6$-$C_5$-$C_8$-$H_{10}$** | GS | 59.243 | 61.774 | 60.972 | 60.864 | 60.573 | 60.209 |

|  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
|  | TS | 17.230 | -10.933 | -16.683 | -148.839 | -149.145 | -155.295 |
|  | PROD | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 |
| **O$_{11}$-C$_{12}$-S$_{14}$-C$_{15}$** | GS | -179.966 | -179.872 | -179.750 | 179.730 | 179.787 | -179.998 |
|  | TS | 0.269 | -0.938 | -4.047 | 3.868 | 5.056 | 3.587 |
|  | PROD | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 |
| **C$_{12}$-S$_{14}$-C$_{15}$-H$_{16}$** | GS | -177.817 | -119.694 | -61.650 | -61.780 | -61.620 | -60.745 |
|  | TS | 99.643 | 60.945 | 64.752 | 56.470 | 55.860 | 57.086 |
|  | PROD | -60.821 | -60.821 | -59.821 | -60.856 | -61.865 | -60.865 |
| **C$_{12}$-S$_{14}$-C$_{15}$-H$_{17}$** | GS | -122.954 | 121.207 | 179.045 | 178.902 | 179.176 | -179.944 |
|  | TS | -21.352 | -61.589 | -57.072 | -65.351 | -66.275 | -63.799 |
|  | PROD | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 |
| **C$_{12}$-S$_{14}$-C$_{15}$-H$_{18}$** | GS | 2.586 | 0.747 | 59.724 | 59.558 | 59.972 | 60.875 |
|  | TS | -141.378 | 179.723 | -176.097 | 175.501 | 174.697 | 176.645 |
|  | PROD | 60.821 | 60.523 | 60.456 | 59.767 | 58.786 | 59.768 |
| **S$_{13}$-C$_{12}$-S$_{14}$-C$_{15}$** | GS | -0.030 | 0.084 | -0.235 | -0.291 | -0.186. | 0.011 |
|  | TS | 179.686 | 179.010 | 179.890 | -177.031 | -175.977 | -178.072 |
|  | PROD | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 |

## 6.5.3 TABLE 4: ATOMIC CHARGES (MULLIKEN) OF O-nPROPHYL, S-METHYL XANTHATE $\Delta q=(q_{TS}-q_{GS})$

| ATOM | STATE | AM1 | PM3 | DFT/ 6-31G* | DFT/ 6-31G** | DFT/ 6-31+G* | HF/ 3-21G* |
|---|---|---|---|---|---|---|---|
| **$H_1$** | GS | +0.076 | +0.041 | +0.151 | +0.120 | +0.198 | +0.205 |
| | TS | +0.090 | +0.033 | +0.159 | +0.122 | +0.217 | +0.215 |
| | PROD | +0.082 | +0.042 | +0.156 | +0.121 | +0.215 | +0.215 |
| | Δq | +0.014 | -0.008 | +0.008 | +0.002 | +0.019 | +0.010 |
| **$C_1$** | GS | -0.212 | -0.108 | -0.457 | -0.359 | -0.692 | -0.606 |
| | TS | -0.185 | -0.062 | -0.443 | -0.320 | -0.768 | -0.567 |
| | PROD | -0.189 | -0.078 | -0.484 | -0.359 | -0.627 | -0.627 |
| | Δq | +0.027 | +0.046 | +0.014 | +0.039 | -0.076 | +0.039 |
| **$H_2$** | GS | +0.076 | +0.041 | +0.151 | +0.120 | +0.198 | +0.205 |
| | TS | +0.071 | +0.040 | +0.163 | +0.119 | +0.215 | +0.214 |
| | PROD | +0.077 | +0.044 | +0.153 | +0.123 | +0.212 | +0.212 |
| | Δq | -0.005 | -0.001 | +0.012 | -0.001 | +0.017 | 0.009 |
| **$H_4$** | GS | +0.083 | +0.046 | +0.160 | +0.134 | +0.211 | +0.221 |
| | TS | +0.080 | +0.047 | +0.168 | +0.127 | +0.221 | +0.230 |
| | PROD | +0.082 | +0.044 | +0.156 | +0.123 | +0.215 | +0.215 |
| | Δq | -0.003 | +0.001 | +0.008 | -0.007 | +0.010 | 0.009 |
| **$C_2$** | GS | -0.161 | -0.107 | -0.272 | -0.241 | -0.268 | -0.449 |
| | TS | -0.368 | -0.405 | -0.297 | -0.217 | -0.035 | -0.646 |
| | PROD | -0.162 | -0.136 | -0.041 | -0.088 | -0.227 | -0.227 |
| | Δq | -0.207 | -0.298 | +0.256 | +0.024 | +0.233 | -0.197 |
| **$H_5$** | GS | +0.099 | +0.066 | +0.162 | +0.142 | +0.218 | +0.242 |
| | TS | +0.143 | +0.123 | +0.186 | +0.112 | +0.125 | +0.310 |
| | PROD | +0.059 | +0.015 | +0.129 | +0.092 | +0.134 | +0.136 |
| | Δq | +0.044 | +0.057 | +0.024 | -0.03 | -0.093 | +0.068 |
| **$H_6$** | GS | +0.100 | +0.066 | +0.162 | +0.143 | +0.218 | +0.241 |
| | TS | +0.280 | +0.249 | +0.139 | +0.141 | +0.242 | +0.279 |
| | PROD | +0.117 | +0.094 | +0.125 | +0.125 | +0.220 | +0.220 |
| | Δq | +0180 | +0.183 | -0.023 | -0.002 | +0.024 | +0.038 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **$C_3$** | GS | -0.054 | +0.020 | -0.065 | +0.067 | -0.256 | -0.089 |
| | TS | +0.118 | +0.213 | -0.128 | -0.043 | -0.338 | -0.133 |
| | PROD | -0.226 | -0.170 | -0.333 | -0.288 | -0.420 | +0.220 |
| | Δq | +0.172 | +0.193 | -0.063 | -0.110 | -0.082 | -0.044 |
| **$H_3$** | GS | +0.097 | +0.063 | +0.172 | +0.147 | +0.219 | +0.235 |
| | TS | +0.131 | +0.071 | +0.197 | +0.162 | +0.244 | +0.289 |
| | PROD | +0.110 | +0.079 | +0.132 | +0.124 | +0.204 | +0.204 |
| | Δq | +0.034 | +0.008 | +0.025 | +0.015 | +0.025 | 0.054 |
| **$H_7$** | GS | +0.097 | +0.065 | +0.172 | +0.147 | +0.218 | +0.235 |
| | TS | +0.134 | +0.070 | +0.204 | +0.156 | +0.240 | +0.278 |
| | PROD | +0.110 | +0.081 | +0.132 | +0.118 | +0.209 | +0.209 |
| | Δq | +0.037 | +0.005 | +0.032 | +0.009 | +0.022 | +0.043 |
| **$O_1$** | GS | -0.175 | -0.131 | -0.393 | -0.557 | -0.263 | -0.668 |
| | TS | -0.380 | -0.336 | -0.441 | -0.447 | -0.329 | -0.643 |
| | PROD | -0.284 | -0.280 | -0.389 | -0.499 | -0.432 | -0.561 |
| | Δq | -0.205 | -0.205 | -0.048 | +0.110 | -0.066 | +0.025 |
| **$C_4$** | GS | -0.163 | -0.041 | +0.064 | +0.093 | -0.085 | +0.124 |
| | TS | -0.020 | +0.090 | +0.087 | +0.086 | -0.144 | +0.164 |
| | PROD | -0.019 | +0.137 | +0.098 | +0.179 | +0.167 | +0.167 |
| | Δq | +0.143 | +0.131 | +0.023 | -0.007 | -0.059 | +0.040 |
| **$S_1$** | GS | -0.061 | -0.160 | -0.187 | -0.174 | -0.195 | -0.133 |
| | TS | -0.274 | -0.235 | -0.131 | -0.137 | -0.136 | -0.177 |
| | PROD | +0.057 | +0.038 | -0.011 | +0.046 | -0.071 | +0.017 |
| | Δq | -0.213 | -0.075 | +0.056 | +0.037 | +0.059 | -0.044 |
| **$S_2$** | GS | +0.184 | +0.064 | +0.163 | +0.204 | +0.344 | +0.252 |
| | TS | +0.228 | +0.079 | +0.157 | +0.156 | +0.348 | +o.247 |
| | PROD | +0.185 | +0.044 | +0.158 | +0.167 | +0.190 | +0.229 |
| | Δq | +0.044 | +0.015 | -0.006 | -0.048 | +0.004 | -0.005 |
| **$C_5$** | GS | -0.375 | -0.217 | -0.594 | -0.510 | -0.818 | -0.789 |
| | TS | -0.389 | -0.212 | -0.588 | -0.464 | -0.830 | -0.778 |
| | PROD | -0.355 | -0.196 | -0.587 | -0.492 | -0.718 | -0.778 |
| | Δq | -0.014 | +0.005 | +0.006 | +0.046 | -0.012 | +0.011 |
| **$H_8$** | GS | +0.117 | +0.085 | +0.217 | +0.182 | +0.262 | +0.268 |
| | TS | +0.103 | +0.071 | +0.183 | +0.158 | +0.254 | +0.251 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | PROD | +0.116 | +0.076 | +0.207 | +0.175 | +0.251 | +0.260 |
| | Δq | -0.014 | -0.014 | -0.030 | -0.024 | -0.008 | -0.017 |
| **H$_9$** | GS | +0.118 | +0.086 | +0.200 | +0.157 | +0.226 | +0.240 |
| | TS | +0.121 | +0.075 | +0.197 | +0.147 | +0.244 | +0.236 |
| | PROD | +0.126 | +0.090 | +0.189 | +0.155 | +0.228 | +0.240 |
| | Δq | +0.003 | -0.011 | -0.003 | -0.010 | +0.018 | -0.004 |
| **H$_{10}$** | GS | +0.153 | +0.122 | +0.196 | +0.184 | +0.263 | +0.268 |
| | TS | +0.116 | +0.089 | +0.182 | +0.142 | +0.231 | +0.231 |
| | PROD | +0.116 | +0.076 | +0.207 | +0.175 | +0.251 | +0.260 |
| | Δq | -0.037 | -0.033 | -0.014 | -0.042 | -0.032 | -0.037 |

### 6.5.4 TABLE 5: HEAT OF FORMATION OF O-nPROPYL, S-METHYL XANTHATE (DITHIOCARBONATE)

| | **GS(kJ/mol)** | **TS (kJ/mol)** | **PROD(kJ/mol)** |
|---|---|---|---|
| **AM1** | -119.309 | 39.823 | -112.270 |
| **PM3** | -37.190 | 68.809 | -100.556 |
| **DFT/6-31G*** | -2803891.125 | -2803733.625 | -2803851.750 |
| **DFT/6-31G**** | -2803927.300 | -2803774.425 | -2803892.516 |
| **DFT/6-31+G*** | -2803918.472 | -2803766.963 | -2803882.159 |
| **HF/3-21G*** | -2782096.643 | -2781867.903 | -2782028.532 |

## 6.6.0 TABLE 1: BONDLENGTH ($A^0$) OF O- ISOPROPHL, S- METHYL $\Delta d = (d_{TS} - d_{GS})$ XANTHATE (DITHIOCARBONATE)

| BOND LENGTH ($A^0$) | STATE | AM1 | PM3 | DFT/ 6-31G* | DFT/ 6-31G** | DFT/ 6-31+G* | HF/ 3-21G* |
|---|---|---|---|---|---|---|---|
| **$H_1$-$C_2$** | GS | 1.1159 | 1.0978 | 1.0939 | 1.0927 | 1.0945 | 1.0816 |
| | TS | 1.1222 | 1.2940 | 1.2240 | 1.2210 | 1.2230 | 1.3020 |
| | PROD | - | - | - | - | - | - |
| | Δd | 0.0063 | 0.1962 | 0.1301 | 0.1283 | 0.1285 | 0.2204 |
| **$C_2$-$H_3$** | GS | 1.1162 | 1.0984 | 1.0948 | 1.0938 | 1.0954 | 1.0833 |
| | TS | 1.1184 | 1.0945 | 1.0931 | 1.0920 | 1.0940 | 1.0790 |
| | PROD | 1.0978 | 1.0855 | 1.0868 | 1.08590 | 1.0892 | 1.0747 |
| | Δd | 0.0022 | -0.0039 | -0.0017 | -0.0018 | -0.0014 | -0.0043 |
| **$C_2$-$H_4$** | GS | 1.1156 | 1.0986 | 1.0953 | 1.0942 | 1.0960 | 1.0817 |
| | TS | 1.2410 | 1.0925 | 1.0905 | 1.0896 | 1.0917 | 1.0767 |
| | PROD | 1.0975 | 1.0866 | 1.0886 | 1.0878 | 1.0873 | 1.0873 |
| | Δd | 0.1254 | -0.0061 | -0.0048 | -0.0046 | -0.0043 | -0.005 |
| **$C_2$-$C_5$** | GS | 1.5178 | 1.5236 | 1.5225 | 1.5219 | 1.5227 | 1.5227 |
| | TS | 1.4744 | 1.4221 | 1.4144 | 1.4141 | 1.4188 | 1.3860 |
| | PROD | 1.3310 | 1.3279 | 1.3332 | 1.3326 | 1.3369 | 1.3161 |
| | Δd | -0.040 | -0.1015 | -0.1081 | -0.1078 | -0.1039 | -0.1367 |
| **$C_5$-$H_6$** | GS | 1.1277 | 1.1214 | 1.0953 | 1.0952 | 1.0953 | 1.0795 |
| | TS | 1.1080 | 1.1055 | 1.0855 | 1.0853 | 1.0862 | 1.0693 |
| | PROD | 1.1034 | 1.0965 | 1.0914 | 1.0908 | 1.0918 | 1.0763 |
| | Δd | 0.0197 | -0.0159 | -0.0098 | -0.010 | -0.0091 | -0.0102 |
| **$C_5$-$O_7$** | GS | 1.4477 | 1.4469 | 1.4649 | 1.4654 | 1.4677 | 1.4746 |
| | TS | 2.0120 | 1.8980 | 2.2130 | 2.1960 | 2.2140 | 2.2590 |
| | PROD | - | - | - | - | - | - |
| | Δd | 0.5643 | 0.4511 | 0.7481 | 0.7306 | 0.7463 | 0.7844 |
| **$C_5$-$C_{15}$** | GS | 1.5148 | 1.5238 | 1.5249 | 1.5243 | 1.5253 | 1.5263 |
| | TS | 1.4213 | 1.4865 | 1.4855 | 1.4852 | 1.4188 | 1.4910 |
| | PROD | 1.4760 | 1.4800 | 1.5021 | 1.5013 | 1.5033 | 1.5096 |
| | Δd | -0.0935 | -0.0373 | -0.0394 | -0.0391 | -0.1065 | -0.0353 |
| **$O_7$-$C_8$** | GS | 1.3651 | 1.3551 | 1.3338 | 1.3337 | 1.3363 | 1.3368 |
| | TS | 1.2765 | 1.2657 | 1.2453 | 1.2465 | 1.2500 | 1.2380 |
| | PROD | 1.2349 | 1.2111 | 1.2047 | 1.2048 | 1.2086 | 1.2053 |
| | Δd | 0.0886 | -0.0894 | -0.0885 | -0.0872 | -0.0863 | -0.0988 |
| **$C_8$-$S_9$** | GS | 1.5603 | 1.6167 | 1.6491 | 1.6490 | 1.6487 | 1.6313 |
| | TS | 1.6426 | 1.7146 | 1.7339 | 1.7323 | 1.7300 | 1.7270 |
| | PROD | 1.7212 | 1.8025 | 1.8142 | 1.8140 | 1.8210 | 1.7789 |
| | Δd | 0.0823 | 0.0979 | 0.0848 | 0.0833 | 0.0813 | 0.0957 |
| **$C_8$-$S_{10}$** | GS | 1.7237 | 1.8026 | 1.7911 | 1.7911 | 1.7885 | 1.7627 |
| | TS | 1.7071 | 1.7920 | 1.7989 | 1.7987 | 1.7950 | 1.7670 |
| | PROD | 1.7127 | 1.8031 | 1.7940 | 1.7941 | 1.7901 | 1.7644 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | Δd | 0.0166 | -0.0106 | 0.0078 | 0.0076 | 0.0065 | 0.0043 |
| **S$_{10}$-C$_{11}$** | GS | 1.7520 | 1.8017 | 1.8203 | 1.8195 | 1.8204 | 1.8065 |
| | TS | 1.7483 | 1.7991 | 1.8301 | 1.8297 | 1.8300 | 1.8129 |
| | PROD | 1.7537 | 1.8012 | 1.8284 | 1.8277 | 1.8276 | 1.8141 |
| | Δd | -0.003 | -0.0026 | 0.0098 | 0.0102 | 0.0096 | 0.0064 |
| **C$_{11}$-H$_{12}$** | GS | 1.1130 | 1.0958 | 1.0909 | 1.0899 | 1.0914 | 1.0782 |
| | TS | 1.1127 | 1.0954 | 1.0919 | 1.0906 | 1.0922 | 1.813 |
| | PROD | 1.1129 | 1.0956 | 1.0909 | 1.0899 | 1.0915 | 1.0785 |
| | Δd | 0.0003 | -0.0004 | 0.0010 | 0.0007 | 0.0008 | 0.0031 |
| **C$_{11}$-H$_{13}$** | GS | 1.1132 | 1.0956 | 1.0939 | 1.0928 | 1.0943 | 1.0823 |
| | TS | 1.1139 | 1.0955 | 1.0932 | 1.0920 | 1.0923 | 1.0813 |
| | PROD | 1.1149 | 1.0975 | 1.0923 | 1.0912 | 1.0930 | 1.0806 |
| | Δd | 0.0007 | -0.0001 | -0.007 | -0.0008 | -0.002 | -0.001 |
| **C$_{11}$-H$_{14}$** | GS | 1.1227 | 1.1053 | 1.0909 | 1.0899 | 1.0914 | 1.0782 |
| | TS | 1.1145 | 1.0973 | 1.0917 | 1.0907 | 1.0939 | 1.0790 |
| | PROD | 1.1129 | 1.0956 | 1.0909 | 1.0899 | 1.0955 | 1.0785 |
| | Δd | 0.0082 | -0.008 | 0.0008 | 0.0008 | 0.0025 | 0.0050 |
| **C$_{15}$-H$_{16}$** | GS | 1.1166 | 1.0986 | 1.0942 | 1.0939 | 1.0955 | 1.0834 |
| | TS | 1.1130 | 1.0991 | 1.0986 | 1.0934 | 1.1029 | 1.0884 |
| | PROD | 1.1191 | 1.0981 | 0.0981 | 1.0942 | 1.0988 | 1.0860 |
| | Δd | 0.0036 | 0.0005 | -0.007 | -0.0005 | 0.0074 | 0.005 |
| **C$_{15}$-H$_{17}$** | GS | 1.1180 | 1.0976 | 1.0936 | 1.0925 | 1.0941 | 1.0821 |
| | TS | 1.1176 | 1.0989 | 1.0922 | 1.0913 | 1.0950 | 1.0820 |
| | PROD | -0.005 | 1.0983 | 1.0954 | 1.0974 | 1.0988 | 1.0834 |
| | Δd | 1.1160 | 0.0013 | -0.0014 | -0.0012 | 0.0009 | -0.0001 |
| **C$_{15}$-H$_{18}$** | GS | 1.1138 | 1.0976 | 1.0957 | 1.0946 | 1.0965 | 1.0821 |
| | TS | 1.1191 | 1.1000 | 1.1018 | 1.1007 | 1.0939 | 1.0784 |
| | PROD | -0.002 | 1.0983 | 1.0986 | 1.0974 | 1.0988 | 1.0860 |
| | Δd | 4.7500 | 0.0024 | 0.0061 | 0.0061 | -0.0026 | 0.0037 |
| **S$_{9}$-H$_{1}$** | GS | 1.7970 | 4.4840 | 4.8190 | 4.8180 | 4.8390 | 4.872 |
| | TS | 1.1227 | 1.7060 | 1.8690 | 1.8660 | 1.8980 | 1.775 |
| | PROD | 1.3275 | 1.3107 | 1.3479 | 1.3470 | 1.3482 | 1.3258 |
| | Δd | 0.4695 | -2.778 | -2.950 | -2.952 | -2.941 | -3.097 |

## 6.6.1 TABLE 2: SELECTED BOND ANGLE [DEGREE] OFO-ISOPROPYL, S-METHYL XANTHATE [DITHIOCARBONATE].

| **BOND ANGLE($^{O}$)** | **STATE** | **AM 1** | **PM3** | **DFT/ 6-31G*** | **DFT/ 6-31G**** | **DFT/ 6-31+G*** | **HF/ 3-21G*** |
|---|---|---|---|---|---|---|---|
| **$H_1$-$C_2$-$H_3$** | GS | 108.505 | 107.611 | 108.471 | 108.479 | 108.461 | 109.358 |
| | TS | 108.468 | 108.468 | 108.560 | 103.390 | 101.111 | 101.95 |
| | PROD | - | - | - | - | - | - |
| **$H_1$-$C_2$-$H_4$** | GS | 109.371 | 107.629 | 108.612 | 108.608 | 108.561 | 108.623 |
| | TS | 108.260 | 108.576 | 108.760 | 104.210 | 104.070 | 98.35 |
| | PROD | - | - | - | - | - | - |
| **$H_1$-$C_2$-$C_5$** | GS | 110.257 | 111.730 | 110.798 | 110.812 | 110.875 | 109.311 |
| | TS | 110.488 | 110.560 | 111.123 | 100.580 | 103.990 | 101.070 |
| | PROD | - | - | - | - | - | - |
| **$C_2$-$C_5$-$H_6$** | GS | 110.117 | 110.469 | 109.591 | 109.603 | 109.538 | 110.750 |
| | TS | 117.093 | 118.668 | 118.977 | 118.957 | 118.869 | 119.830 |
| | PROD | 114.866 | 116.838 | 118.838 | 118.795 | 118.723 | 119.563 |
| **$C_2$-$C_5$-$O_7$** | GS | 104.750 | 109.367 | 105.056 | 105.084 | 105.183 | 103.970 |
| | TS | 108.060 | 108.060 | 108.060 | 106.130 | 105.490 | 106.280 |
| | PROD | - | - | - | - | - | - |
| **$C_2$-$C_5$-$C_{15}$** | GS | 111.747 | 111.204 | 113.481 | 113.532 | 113.474 | 112.860 |
| | TS | 121.266 | 118.760 | 123.053 | 122.909 | 123.070 | 122.770 |
| | PROD | 124.266 | 123.389 | 125.257 | 125.258 | 125.297 | 124.753 |
| **$H_3$-$C_2$-$H_4$** | GS | 109.261 | 107.588 | 108.561 | 108.577 | 108.547 | 109.200 |
| | TS | 108.858 | 111.248 | 113.883 | 114.044 | 113.830 | 115.390 |
| | PROD | 144.925 | 114.121 | 116.476 | 116.602 | 116.601 | 116.356 |
| **$H_3$-$C_2$-$C_5$** | GS | 110.357 | 111.920 | 110.452 | 110.443 | 110.556 | 110.060 |
| | TS | 111.816 | 116.359 | 115.554 | 115.448 | 115.270 | 115.390 |
| | PROD | 121.850 | 122.100 | 121.700 | 121.630 | 121.621 | 121.854 |
| **$H_4$-$C_2$-$H_3$** | GS | 109.261 | 107.588 | 108.562 | 108.557 | 108.547 | 109.200 |
| | TS | 108.858 | 111.248 | 113.883 | 114.044 | 113.830 | 115.390 |
| | PROD | 114.925 | 114.121 | 116.476 | 121.760 | 116.601 | 116.356 |
| **$H_4$-$C_2$-$C_5$** | GS | 109.071 | 110.167 | 109.866 | 109.844 | 109.779 | 110.260 |
| | TS | 108.858 | 116.283 | 116.308 | 116.344 | 116.020 | 117.860 |
| | PROD | 122.280 | 121.930 | 121.830 | 121.760 | 121.701 | 121.702 |
| **$C_5$-$C_2$-$H_3$** | GS | 110.357 | 111.920 | 110.452 | 110.443 | 110.556 | 110.060 |
| | TS | 111.816 | 116.359 | 115.554 | 115.448 | 115.270 | 117.070 |
| | PROD | 122.795 | 123.212 | 121.698 | 121.763 | 121.698 | 121.854 |
| **$C_5$-$C_2$-$H_4$** | GS | 109.071 | 110.167 | 109.886 | 109.884 | 109.779 | 110.260 |
| | TS | 108.872 | 116.283 | 116.308 | 116.344 | 116.020 | 117.86 |
| | PROD | 111.867 | 122.667 | 121.825 | 121.635 | 121.701 | 121.854 |
| **$C_5$-$O_7$-$C_8$** | GS | 119.340 | 121.055 | 124.897 | 124.758 | 125.039 | 127.680 |
| | TS | 124.100 | 124.100 | 125.900 | 120.960 | 121.120 | 122.050 |
| | PROD | - | - | - | - | - | - |
| **$C_5$-$C_{15}$-$H_{16}$** | GS | 110.355 | 112.039 | 110.248 | 110.252 | 110.326 | 111.210 |
| | TS | 110.490 | 112.473 | 111.376 | 111.307 | 111.590 | 110.450 |
| | PROD | 110.076 | 115.790 | 111.198 | 111.595 | 111.106 | 110.646 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **C$_5$-C$_{15}$-H$_{17}$** | GS | 110.314 | 111.853 | 111.367 | 111.342 | 111.478 | 109.700 |
| | TS | 114.765 | 112.491 | 111.364 | 111.495 | 111.430 | 110.830 |
| | PROD | 111.867 | 110.547 | 111.575 | 111.176 | 111.570 | 111.144 |
| **C$_5$-C$_{15}$-H$_{18}$** | GS | 109.484 | 109.991 | 109.791 | 109.791 | 109.692 | 109.270 |
| | TS | 115.012 | 109.125 | 108.263 | 108.168 | 108.110 | 108.190 |
| | PROD | 110.076 | 112.870 | 111.198 | 111.176 | 111.106 | 110.646 |
| **H$_6$-C$_5$-O$_7$** | GS | 109.226 | 110.555 | 108.536 | 108.542 | 108.378 | 109.240 |
| | TS | 82.900 | 83.900 | 84.900 | 80.540 | 80.660 | 78.330 |
| | PROD | - | - | - | - | - | - |
| **H$_6$-C$_5$-C$_{15}$** | GS | 110.829 | 109.849 | 110.727 | 110.681 | 110.755 | 111.330 |
| | TS | 119.416 | 116.538 | 116.919 | 116.944 | 116.980 | 115.684 |
| | PROD | 114.866 | 115.790 | 115.906 | 115.936 | 115.980 | 117.040 |
| **O$_7$-C$_5$-H$_6$** | GS | 109.226 | 110.555 | 108.536 | 108.542 | 108.378 | 109.240 |
| | TS | 82.900 | 84.900 | 85.600 | 85.6700 | 80.660 | 78.33 |
| | PROD | - | - | - | - | - | - |
| **O$_7$-C$_5$-C$_{15}$** | GS | 109.982 | 105.284 | 109.200 | 109.151 | 109.259 | 108.360 |
| | TS | 93.120 | 94.000 | 95.100 | 80.540 | 93.240 | 90.450 |
| | PROD | - | - | - | - | - | - |
| **O$_7$-C$_8$-=S$_9$** | GS | 117.575 | 117.470 | 119.721 | 119.755 | 119.682 | 120.130 |
| | TS | 128.336 | 126.755 | 125.374 | 125.504 | 124.980 | 124.270 |
| | PROD | 125.898 | 126.490 | 123.974 | 123.987 | 123.818 | 123.456 |
| **O$_7$-C$_8$-S$_{10}$** | GS | 115.558 | 118.555 | 115.359 | 115.314 | 115.243 | 114.730 |
| | TS | 121.871 | 121.148 | 119.175 | 119.024 | 119.480 | 119.670 |
| | PROD | 127.028 | 127.273 | 124.506 | 124.474 | 124.526 | 124.789 |
| **C$_8$-S$_{10}$-C$_{11}$** | GS | 103.906 | 104.478 | 102.094 | 102.067 | 102.319 | 103.170 |
| | TS | 107.771 | 107.619 | 100.651 | 100.716 | 101.400 | 99.30 |
| | PROD | 104.481 | 105.300 | 98.139 | 98.140 | 98.911 | 97.724 |
| **S$_9$-C$_8$-S$_{10}$** | GS | 126.867 | 123.974 | 124.917 | 124.929 | 125.071 | 125.130 |
| | TS | 109.796 | 112.096 | 115.443 | 115.465 | 115.530 | 116.050 |
| | PROD | 107.074 | 106.237 | 111.520 | 111.539 | 111.656 | 112.921 |
| **S$_{10}$-C$_8$-S$_9$** | GS | 126.867 | 123.974 | 124.917 | 124.929 | 125.071 | 125.130 |
| | TS | 109.793 | 112.096 | 115.443 | 115.465 | 115.530 | 116.050 |
| | PROD | 107.074 | 106.237 | 111.520 | 111.539 | 111.656 | 112.921 |
| **S$_{10}$-C$_{11}$-H$_{12}$** | GS | 109.210 | 109.442 | 110.506 | 110.414 | 110.632 | 110.672 |
| | | 111.243 | 113.179 | 110.733 | 110.503 | 111.160 | 110.110 |
| | PROD | 111.719 | 113.081 | 110.282 | 110.198 | 110.493 | 110.073 |
| **S$_{10}$-C$_{11}$-H$_{13}$** | GS | 108.505 | 109.993 | 105.323 | 105.239 | 105.236 | 105.680 |
| | TS | 111.634 | 113.056 | 106.359 | 106.266 | 106.150 | 110.580 |
| | PROD | 105.960 | 106.936 | 106.207 | 106.123 | 105.984 | 107.123 |
| **S$_{10}$-C$_{11}$-H$_{14}$** | GS | 111.485 | 112.435 | 110.400 | 110.300 | 110.540 | 110.680 |
| | TS | 107.370 | 107.325 | 110.765 | 110.833 | 110.730 | 107.290 |
| | PROD | 111.719 | 113.081 | 110.282 | 110.198 | 110.493 | 110.073 |
| **H$_{12}$-C$_{11}$-H$_{13}$** | GS | 109.453 | 108.491 | 110.423 | 110.522 | 110.329 | 110.080 |
| | TS | 108.326 | 107.471 | 109.679 | 109.725 | 109.590 | 109.910 |
| | PROD | 109.495 | 107.958 | 109.852 | 110.165 | 109.913 | 110.052 |
| **H$_{12}$-C$_{11}$-H$_{14}$** | GS | 109.062 | 108.231 | 109.642 | 109.701 | 109.676 | 110.070 |
| | TS | 109.310 | 107.800 | 109.583 | 109.662 | 109.490 | 109.690 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | PROD | 108.412 | 107.605 | 110.081 | 109.930 | 109.945 | 109.442 |
| **$H_{13}$-$C_{11}$-$H_{12}$** | GS | 109.102 | 108.153 | 110.423 | 110.522 | 110.329 | 110.08 |
| | TS | 108.910 | 107.471 | 109.679 | 109.302 | 109.490 | 109.910 |
| | PROD | 109.495 | 107.958 | 110.081 | 110.165 | 109.945 | 110.052 |
| **$H_{13}$-$C_{11}$-$H_{14}$** | GS | 109.102 | 108.153 | 110.482 | 110.594 | 110.360 | 110.080 |
| | TS | 109.314 | 107.769 | 109.670 | 109.725 | 109.590 | 109.240 |
| | PROD | 109.495 | 107.958 | 110.081 | 110.165 | 109.945 | 109.610 |
| **$H_{14}$-$C_{11}$-$H_{12}$** | GS | 109.062 | 108.231 | 109.642 | 109.701 | 109.676 | 109.610 |
| | TS | 108.907 | 107.800 | 109.583 | 109.662 | 109.590 | 109.610 |
| | PROD | 109.495 | 107.958 | 110.081 | 109.930 | 109.913 | 109.442 |

### 6.6.3 TABLE 3: DIHEDRAL ANGLE IN (DEGREES) OF O-ISOPROPYL S-METHYL XANTHATE (DITHIOCARBONATE).

| DIHEDRAL ANGLE($^O$) | STATE | AM1 | PM3 | DFT/ 6-31G* | DFT/ 6-31G** | DFT/ 6-31+G* | HF/ 3-21G* |
|---|---|---|---|---|---|---|---|
| **$H_1$-$C_2$-$C_5$-$H_6$** | GS | -57.829 | -57.517 | -56.715 | -56.724 | -56.565 | -176.010 |
| | TS | -52.114 | -100.360 | -100.260 | -99.840 | -98.570 | -96.820 |
| | PROD | - | - | - | - | - | - |
| **$H_1$- $C_2$-$C_5$-$O_7$** | GS | 59.499 | 64.384 | 59.718 | 59.738 | 59.727 | -58.790 |
| | TS | 120.580 | -11.890 | -11.870 | -11.870 | -10.830 | -11.150 |
| | PROD | - | - | - | - | - | - |
| **$H_1$-$C_2$-$C_5$-$C_{15}$** | GS | 178.542 | -178.703 | 178.938 | 178.944 | 179.098 | 58.400 |
| | TS | 144.935 | 93.980 | 93.980 | 93.010 | 93.670 | 90.260 |
| | PROD | - | - | - | - | - | - |
| **$C_2$-$C_5$-$O_7$-$C_8$** | GS | -157.965 | -94.926 | -150.968 | -150.580 | -151.117 | -152.880 |
| | TS | 1.740 | -5.790 | -5.790 | -5.740 | -7.880 | -3.420 |
| | PROD | - | - | - | - | - | - |
| **$C_2$-$C_5$-$C_{15}$-$H_{16}$** | GS | -59.844 | -59.365 | -57.386 | -57.407 | -57.309 | -57.840 |
| | TS | 144.940 | -39.865 | -28.209 | -30.027 | -31.40 | -26.770 |
| | PROD | -59.508 | 120.546 | -152.990 | 120.790 | -59.247 | 121.620 |
| **$C_2$-$C_5$-$C_{15}$-$H_{17}$** | GS | -179.965 | 179.869 | 179.869 | -178.160 | -178.159 | -178.040 |
| | TS | 147.562 | -161.717 | -151.089 | -153.930 | -154.43 | -148.450 |
| | PROD | 180.000 | -0.000 | -178.115 | 0.000 | -0.000 | -0.000 |
| **$C_2$-$C_5$-$C_{15}$-$H_{18}$** | GS | 60.122 | 60.230 | 62.114 | 62.095 | 62.166 | 61.790 |
| | TS | 15.224 | 79.395 | 90.215 | 87.219 | 86.890 | 92.060 |
| | PROD | 59.508 | -120.546 | -120.757 | -120.790 | -120.753 | -120.753 |
| **$H_3$-$C_2$-$C_5$-$H_6$** | GS | -177.682 | -178.278 | -176.938 | -176.958 | -176.893 | 63.870 |
| | TS | -173.033 | 141.825 | 151.620 | 151.362 | 151.720 | 157.740 |
| | PROD | - | - | - | - | - | - |
| **$H_3$-$C_2$-$C_5$-$C_{15}$** | GS | 58.689 | 59.447 | 58.116 | 58.710 | 58.770 | -61.720 |
| | TS | 24.016 | -9.932 | -15.280 | -15.786 | -16.040 | -15.180 |
| | PROD | -0.000 | -0.000 | -0.000 | 0.000 | -0.000 | -0.000 |
| **$H_4$-$C_2$-$C_5$-$H_6$** | GS | 62.281 | 62.067 | 63.314 | 63.308 | 63.380 | -59 .45 |
| | TS | 66.651 | 7.734 | 14.143 | 13.703 | 15.05 | 13.180 |
| | PROD | 180.000 | 180.000 | 180.000 | 180.000 | 180.00 | 180.00 |
| **$H_4$-$C_2$-$C_5$-$O_7$** | GS | 179.609 | -176.033 | 179.748 | 179.769 | 179.673 | -178.920 |
| | TS | -107.080 | 104.700 | -123.000 | -120.670 | 102.780 | 98.850 |
| | PROD | - | - | - | - | - | - |
| **$H_4$-$C_2$-$C_5$-$C_{15}$** | GS | -61.347 | -60.179 | -61.032 | -61.024 | -60.957 | 58.400 |
| | TS | -96.300 | -144.023 | -153.757 | -153.445 | -152.710 | -159.740 |
| | PROD | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 |
| **$C_5$-$O_7$-$C_8$-$S_9$** | GS | 178.202 | 179.622 | -177.657 | -177.721 | -176.311 | 175.890 |
| | TS | -16.370 | 28.34 | 36.18 | 35.530 | 38.100 | 28.74 |
| | PROD | - | - | - | - | - | - |
| **$C_5$-$O_7$-$C_8$-$S_{10}$** | GS | -1.859 | -0.690 | 2.887 | 2.7920 | 4.360 | 4.670 |
| | TS | 163.770 | -151.470 | -142.80 | -143.49 | -140.730 | -150.250 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | PROD | - | - | - | - | - | - |
| **$H_6$-$C_5$-$C_{15}$-$H_{17}$** | GS | 56.809 | 57.265 | 58.157 | 58.094 | 58.165 | 56.690 |
| | TS | -15.010 | 45.935 | 40.780 | 38.681 | 37.600 | 38.450 |
| | PROD | 180.000 | -59.220 | 180.000 | 59.208 | 180.000 | 59.208 |
| **$H_6$-$C_5$-$C_{15}$-$H_{18}$** | GS | -63.105 | -62.373 | -61.615 | -61.652 | -61.510 | -63.490 |
| | TS | -52.110 | -72.953 | -77.916 | -80.169 | -81.080 | -81.050 |
| | PROD | -0.000 | 180.000 | 59.24.3 | 59.208 | 59.247 | 59.670 |
| **$O_7$-$C_8$-$S_{10}$-$C_{11}$** | GS | 176.644 | -177.437 | 178.224 | 178.202 | 178.551 | 179.003 |
| | TS | 0.908 | -0.624 | -3.699 | -3.617 | -4.550 | -2.310 |
| | PROD | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 |
| **$O_7$-$C_5$-$C_{15}$-$H_{16}$** | GS | 56.051 | 58.979 | 59.434 | 59.446 | 59.704 | 56.730 |
| | TS | 150.350 | -162.670 | -40.700 | -161.20 | -162.250 | -158.160 |
| | PROD | - | - | - | - | - | - |
| **$O_7$-$C_5$-$C_{15}$-$H_{17}$** | GS | -64.070 | -61.787 | -61.220 | -61.307 | -61.146 | -63.460 |
| | TS | -89.330 | -43.800 | -159.280 | -42.34 | -43.570 | -38.660 |
| | PROD | - | - | - | - | - | - |
| **$O_7$-$C_5$-$C_{15}$-$H_{18}$** | GS | 176.017 | 178.574 | 178.933 | 178.948 | 179.179 | 176.360 |
| | TS | 31.590 | 78.060 | 82.470 | 80.560 | 79.460 | 83.01 |
| | PROD | - | - | - | - | - | - |
| **$C_8$-$S_{10}$-$C_{11}$-$H_{12}$** | GS | -116.491 | -123.553 | -61.220 | -61.363 | -61.395 | -60.990 |
| | TS | 87.635 | 59.568 | -59.421 | -56.998 | -56.960 | -53.500 |
| | PROD | -60.821 | 60.810 | -60.751 | -60.745 | -60.931 | -60.931 |
| **$C_8$-$S_{10}$-$C_{11}$-$H_{13}$** | GS | 124.266 | 117.347 | 179.521 | 179.357 | 179.443 | 179.880 |
| | TS | -33.502 | -62.924 | -178.523 | -176.062 | -175.830 | -173.090 |
| | PROD | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 |

## 6.6.4 TABLE 4: ATOMIC CHARGES OF O-ISOPROPYL S- METHYL Δq= ($q_{TS}$-$q_{GS}$ ) XANTHATE (DITHIOCARBONATE)

| ATOM | STATE | AM1 | PM3 | DFT/6-31G* | DFT/ 6-31G** | DFT/ 6-31+G* | HF/ 3-21G* |
|---|---|---|---|---|---|---|---|
| **$H_1$** | GS | +0.093 | +0.057 | +0.169 | +0.142 | +0.220 | +0.234 |
| | TS | +0.133 | +0.251 | +0.157 | +0.126 | +0.209 | +0.314 |
| | PROD | +0.059 | +0.015 | +0.129 | +0.093 | +0.059 | +0.166 |
| | Δq | +0.040 | +0.194 | -0.012 | -0.016 | -0.011 | +0.080 |
| **$C_1$** | GS | _0.214 | _0.144 | -0.448 | -0.331 | -0.591 | -0.562 |
| | TS | _0.250 | _0.419 | -0.500 | -0.354 | -0.539 | -0.766 |
| | PROD | _0.226 | _0.136 | -0.333 | -0.288 | -0.467 | -0.420 |
| | Δq | _0.036 | _0.275 | -0.436 | -0.023 | +0.052 | -0.204 |
| **$H_2$** | GS | +0.095 | +0.060 | +0.168 | +0.141 | +0.223 | +0.204 |
| | TS | +0.111 | +0.107 | +0.1880 | +0.142 | +0.248 | +0.265 |
| | PROD | +0.110 | +0.081 | +0.132 | +0.124 | +0.194 | +0.204 |
| | Δq | +0.016 | +0.047 | 0.020 | +0.001 | +0.025 | +0.061 |
| **$H_4$** | GS | +0.088 | +0.055 | +0.153 | +0.123 | +0.207 | +0.232 |
| | TS | +0.113 | +0.101 | +0.187 | +0.142 | +0.247 | +0.262 |
| | PROD | +0.110 | +0.079 | +0.136 | +0.118 | +0.198 | +0.209 |
| | Δq | +0.025 | +0.046 | +0.034 | +0.019 | +0.040 | +0.030 |
| **$C_2$** | GS | +0.003 | +0.043 | +0.090 | +0.131 | +0.024 | +0.008 |
| | TS | +0.203 | +0.264 | +0.086 | +0.098 | +0.154 | +0.030 |
| | PROD | -O.162 | -0.136 | -0.041 | -0.088 | +0.059 | -0.227 |
| | Δq | +O.200 | +0.221 | -0.004 | -0.033 | +0.130 | +0.022 |
| **$H_5$** | GS | +0.105 | +0.085 | +0.172 | +0.153 | +0.210 | +0.250 |
| | TS | +0.141 | +0.084 | +0.195 | +0.154 | +0.273 | +0.297 |
| | PROD | +0.117 | +0.094 | +0.125 | +0.125 | +0.204 | +0.220 |
| | Δq | +0.036 | -0.001 | 0.023 | +0.125 | +0.063 | +0.047 |
| **$O_1$** | GS | -0.177 | -0.133 | -0.394 | -0.357 | -0.211 | -0.567 |
| | TS | -0.404 | -0.361 | -0.452 | -0.455 | -0.455 | -0.655 |
| | PROD | -0.019 | -0.280 | -0.389 | -0.499 | -0.432 | -0.561 |
| | Δq | -0.227 | -0.228 | -0.058 | -0.098 | -0.244 | -0.088 |
| **$C_3$** | GS | -0.153 | -0.031 | +0.065 | +0.094 | -0.151 | +0.130 |
| | TS | -0.000 | +0.109 | +0.088 | +0.087 | +0.136 | +0.173 |
| | PROD | +0.128 | +0.137 | +0.098 | +0.179 | +0.167 | +0.67 |
| | Δq | +0.153 | +0.140 | +0.023 | -0.007 | +0.287 | +0.043 |
| **$S_1$** | GS | -0.011 | -0.167 | -0.191 | -0.178 | -0.179 | -0.138 |
| | TS | -O.321 | -0.285 | -0.158 | -0.163 | -0.381 | -0.207 |
| | PROD | +0.057 | +0.038 | +0.158 | +0.161 | -0.071 | +0.229 |
| | Δq | -0.31 | -0.118 | +0.033 | +0.015 | -0.202 | -0.069 |
| **$S_2$** | GS | +0.182 | +0.058 | +0.156 | +0.198 | +0.330 | +0.244 |
| | TS | +0.210 | +0.064 | +0.150 | +0.149 | +0.180 | +0.241 |
| | PROD | +0.185 | +0.044 | -0.011 | +0.167 | +0.190 | +0.017 |
| | Δq | +0.028 | +0.006 | -0.006 | -0.049 | -0.150 | -0.003 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **$C_4$** | GS | -0.375 | -0.217 | -0.593 | -0.509 | -0.826 | -0.789 |
| | TS | -0.385 | -0.213 | -0.586 | -0.462 | -0.725 | -0.778 |
| | PROD | -0.355 | -0.196 | -0.587 | -0.492 | -0.718 | -0.627 |
| | Δq | -O.O1 | +0.004 | -0.001 | +0.047 | +0.101 | +0.011 |
| **$H_3$** | GS | +0.116 | +0.086 | +0.213 | +0.182 | +0.263 | +0.267 |
| | TS | +0.102 | +0.069 | +0.193 | +0.154 | +0.226 | +0.249 |
| | PROD | +0.116 | +0.076 | +0.207 | +0.175 | +0.251 | +0.215 |
| | Δq | -0.014 | -0.017 | -0.020 | -0.028 | -0.037 | -0.018 |
| **$H_7$** | GS | +0.118 | +0.084 | +0.184 | +0.156 | +0.226 | +0.239 |
| | TS | +0.111 | +0.073 | +0.180 | +0.139 | +0.238 | +0.229 |
| | PROD | +O.126 | +0.090 | +0.189 | +0.155 | +0.228 | +0.212 |
| | Δq | -0.007 | -0.011 | -0.004 | -0.017 | +0.012 | -0.010 |
| **$H_8$** | GS | +0.154 | +0.123 | +0.214 | +0.183 | +0.263 | +0.267 |
| | TS | +0.115 | +0.087 | +0.185 | +0.145 | +0.222 | +0.236 |
| | PROD | +0.116 | +0.076 | +0.207 | +0.175 | +0.251 | +0.215 |
| | Δq | -0.039 | -0.036 | -0.029 | -0.040 | -0.041 | -0.031 |
| **$C_5$** | GS | -0.243 | -0.127 | -0.452 | -0.339 | -0.657 | -0.594 |
| | TS | -0.410 | -0.150 | -0.475 | -0.338 | -0.774 | -0.648 |
| | PROD | -0.189 | -0.078 | -0.484 | -0.359 | -0.784 | -0.778 |
| | Δq | -0.167 | -0.023 | -0.023 | +0.001 | -0.117 | -0.054 |
| **$H_6$** | GS | +0.095 | +0.059 | +0.167 | +0.140 | +0.226 | +0.209 |
| | TS | +0.276 | +0.073 | +0.190 | +0.149 | +0.235 | +0.236 |
| | PROD | +0.082 | +0.044 | +0.156 | +0.121 | +0.200 | +0.260 |
| | Δq | 0.181 | +0.014 | +0.023 | +0.009 | +0.009 | +0.027 |
| **$H_9$** | GS | +0.094 | +0.055 | +0.176 | +0.144 | +0.218 | +0.234 |
| | TS | +0.127 | +0.073 | +0.196 | +0.152 | +0.251 | +0.255 |
| | PROD | +0.77 | +0.042 | +0.153 | +0.123 | +0.198 | +0.240 |
| | Δq | +0.033 | +0.018 | +0.020 | +0.008 | +0.033 | +0.021 |
| **$H_{10}$** | GS | +0.090 | +0.053 | +0.154 | +0.126 | +0.207 | +0.234 |
| | TS | +0.129 | +0.070 | +0.176 | +0.135 | +0.254 | +0.272 |
| | PROD | +0.082 | +0.044 | +0.156 | +0.123 | +0.200 | +0.260 |
| | Δq | -0.0771 | +0.017 | +0.022 | +0.009 | +0.047 | +0.038 |

**4.23**

### 6.6.5 TABLE 5 : HEAT OF FORMATION OF O-ISOPROPYL,S-METHYL XANTHATE (DITHIOCARBONATE)

| | GS(KJ/MOL) | TS (KJ/MOL) | PROD(KJ/MOL) |
|---|---|---|---|
| **AM1** | -105.781 | 57.404 | -112.270 |
| **PM3** | -38.092 | 57.404 | -100.556 |
| **DFT/6-31G*** | -2803899.525 | -2803763.550 | -2803851.750 |
| **DFT/6-31G**** | -2803939.800 | -2803804.185 | -2803892.438 |
| **DFT/6-31+G*** | -2803796.625 | -2803796.625 | -2803892.963 |
| **HF/3-21G*** | -2782106.250 | -2781896.250 | -2782028.288 |

### 6.6.6 TABLE 6 : ARRHENIUS PARAMETERS OF THE PYROLYSIS O-ISOPROPYL, S-METHYL XANTHATE (DITHIOCARBONATE)

| | ∆S J/MOL/K | ∆G KJ/MOL | ∆H KJ/MOL | Ea KJ/MOL | LOG A | k ($S^{-1}$) |
|---|---|---|---|---|---|---|
| **EXPERIMENTAL** | -26.000 | 160.198 | 144.000 | 149.178 | $5.65x10^{11}$ | $5.6x10^{-1}$ |
| **AM1** | -25.957 | 149.485 | 133.289 | 138.466 | $5.68x10^{11}$ | $13.7x10^{-1}$ |
| **PM3** | -26.176 | 150.196 | 133.873 | 139.050 | $5.53x10^{11}$ | 1.196 |
| **DFT/6-31G*** | -26.988 | 152.907 | 136.086 | 141.263 | $5.02x10^{11}$ | $7.08x10^{-1}$ |
| **DFT/6-31G**** | -27.250 | 146.749 | 129.300 | 134.482 | $4.87x10^{11}$ | 2.543 |
| **DFT/6-31+G*** | -29.008 | 151.828 | 133.761 | 138.936 | $3.94x10^{11}$ | $8.78x10^{-1}$ |
| **HF/3-21G*** | -29.515 | 185.419 | 166.739 | 171.916 | $3.71x10^{11}$ | $1.4x10^{-3}$ |

## 6.7.0 TABLE : 1 BONDLENGTH [A$^0$] OF O-iBUTYL, S-METHYL XANTHATE [DITHIOCARBONATE]

| BONDLENTH[A$^0$] | STATE | AM1 | PM3 | RM1 | DFT/6-31G* | DFT/6-31G** | DFT/6-31+6* | HF/321-G* |
|---|---|---|---|---|---|---|---|---|
| **$C_1$-$H_2$** | GS | 1.1270 | 1.1271 | 1.1213 | 1.0984 | 1.0978 | 1.0990 | 1.0990 |
| | TS | 1.3280 | 1.4290 | 1.2750 | 1.2260 | 1.1990 | 1.2980 | 1.2970 |
| | PROD | - | - | - | - | - | - | - |
| | Δd | +O.201 | 0.3019 | 0.1537 | 0.1276 | 0.1012 | 0.1990 | 0.1980 |
| **$C_1$-$C_3$** | GS | 1.5256 | 1.5256 | 1.5377 | 1.5276 | 1.5271 | 1.5372 | 1.5420 |
| | TS | 1.4168 | 1.4233 | 1.4343 | 1.4150 | 1.4237 | 1.4276 | 1.4286 |
| | PROD | 1.3361 | 1.3328 | 1.3291 | 1.3366 | 1.3363 | 1.3400 | 1.3179 |
| | Δd | -0.1088 | -0.1023 | -0.1034 | -0.1126 | -0.1034 | -0.1096 | -0.1134 |
| **$C_1$-$C_{14}$** | GS | 1.5130 | 1.5130 | 1.5229 | 1.5344 | 1.5340 | 1.5420 | 1.5420 |
| | TS | 1.5052 | 1.5083 | 1.5185 | 1.5349 | 1.5350 | 1.5340 | 1.5520 |
| | PROD | 1.4836 | 1.4867 | 1.4878 | 1.5087 | 1.5083 | 1.5079 | 1.5143 |
| | Δd | -0.0078 | -0.0047 | -0.0044 | 0.0005 | 0.0010 | -0.0080 | 0.0100 |
| **$C_1$-$C_{18}$** | GS | 1.5134 | 1.5134 | 1.5244 | 1.5363 | 1.5358 | 1.5358 | 1.5450 |
| | TS | 1.5045 | 1.5077 | 1.5167 | 1.5327 | 1.5321 | 1.5321 | 1.5430 |
| | PROD | 1.4836 | 1.4867 | 1.4878 | 1.5087 | 1.5083 | 1.5097 | 1.5143 |
| | Δd | -0.0089 | -0.0057 | -0.0077 | -0.0036 | -0.0037 | -0.0037 | -0.0020 |
| **$C_3$-$H_4$** | GS | 1.1230 | 1.1230 | 1.1136 | 1.0964 | 1.0961 | 1.0971 | 1.0971 |
| | TS | 1.1032 | 1.0963 | 1.0963 | 1.0844 | 1.0833 | 1.0833 | 1.0833 |
| | PROD | 1.0973 | 1.0862 | 1.0849 | 1.0875 | 1.0866 | 1.0880 | 1.0739 |
| | Δd | -0.0198 | -0.0267 | -0.0173 | -0.0120 | -0.0128 | -0.0138 | -0.0138 |
| **$C_3$-$H_5$** | GS | 1.1224 | 1.1225 | 1.1133 | 1.0974 | 1.0972 | 1.0972 | 1.0973 |
| | TS | 1.035 | 1.0959 | 1.0961 | 1.0875 | 1.0831 | 1.0831 | 1.0832 |
| | PROD | 1.0973 | 1.0862 | 1.0849 | 1.0875 | 1.0866 | 1.0880 | 1.0739 |
| | Δd | -0.0189 | -0.0266 | -0.0172 | -0.0099 | -0.0141 | -0.0141 | -0.0141 |
| **$C_3$-$0_6$** | GS | 1.4400 | 1.4401 | 1.4222 | 1.4487 | 1.4489 | 1.4972 | 1.4982 |
| | TS | 1.9530 | 1.8210 | 1.9270 | 2.0950 | 2.0590 | 2.0950 | 2.0960 |
| | PROD | - | - | - | - | - | - | - |
| | Δd | +0.513 | 0.3889 | 0.5048 | 0.6463 | 0.6101 | 0.5978 | 0.5978 |
| **$O_6$-$C_7$** | GS | 1.3682 | 1.3681 | 1.3393 | 1.3359 | 1.3358 | 1.3359 | 1.3359 |
| | TS | 1.2781 | 1.2717 | 1.2598 | 1.2510 | 1.2575 | 1.2717 | 1.2718 |
| | PROD | 1.2349 | 1.2111 | 1.2047 | 1.2048 | 1.286 | 1.2053 | 1.2053 |
| | Δd | -0.0901 | -0.0964 | -0.0795 | -0.0849 | -0.0783 | 0.0642 | -0.0641 |
| **$C_7$=$S_8$** | GS | 1.5573 | 1.5571 | 1.5875 | 1.6477 | 1.6477 | 1.6476 | 1.6576 |
| | TS | 1.6495 | 1.7157 | 1.6717 | 1.7291 | 1.7216 | 1.7217 | 1.7237 |
| | PROD | 1.7212 | 1.8025 | 1.8940 | 1.8941 | 1.8087 | 1.7789 | 1.7790 |
| | Δd | 0.0922 | 0.1579 | 0.0842 | 0.0814 | 0.0739 | 0.0741 | 0.0661 |
| **$C_7$-$S_9$** | GS | 1.7225 | 1.7225 | 1.7630 | 1.7879 | 1.7878 | 1.7878 | 1.7878 |
| | TS | 1.7020 | 1.7859 | 1.7563 | 1.7953 | 1.7971 | 1.7981 | 1.7981 |
| | **PROD** | 1.7127 | 1.7107 | 1.7940 | 1.7941 | 1.7901 | 1.7644 | 1.7644 |
| | **Δd** | -0.0205 | 0.0634 | -0.0067 | 0.0074 | 0.0093 | 0.0103 | 0.0103 |
| **$S_9$-$C_{10}$** | **GS** | 1.7518 | 1.7517 | 1.7968 | 1.8192 | 1.8183 | 1.8188 | 1.8188 |
| | **TS** | 1.7488 | 1.7992 | 1.7899 | 1.8306 | 1.8305 | 1.8402 | 1.8402 |
| | **PROD** | 1.7537 | 1.8012 | 1.8284 | 1.8277 | 1.8276 | 1.8141 | 1.8142 |
| | **Δd** | -0.0030 | 0.0475 | -0.0069 | 0.0114 | 0.0122 | 0.0214 | 0.0214 |
| **$C_{10}$-$H_{11}$** | **GS** | 1,1227 | 1.1226 | 1.0956 | 1.0910 | 1.0899 | 1.0898 | 1.0899 |
| | **TS** | 1.1140 | 1.0961 | 1.0946 | 1.0918 | 1.0905 | 1.0904 | 1.0905 |
| | **PROD** | 1.1129 | 1.0956 | 1.0909 | 1.899 | 1.0915 | 1.0785 | 1.0786 |
| | **Δd** | -0.0087 | -0.0265 | -0.0010 | 0.0008 | 0.0006 | 0.00060 | 0.0006 |
| **$C_{10}$-$H_{12}$** | **GS** | 1.1133 | 1.1131 | 1.0965 | 1.0938 | 1.0927 | 1.0927 | 1.0927 |
| | **TS** | 1.1144 | 1.0977 | 1.0961 | 1.0930 | 1.0920 | 1.0921 | 1.0923 |
| | **PROD** | 1.1149 | 1.0975 | 1.0923 | 1.0912 | 1.0930 | 1.0806 | 1.0807 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | **Δd** | 0.0011 | -0.0154 | -0.0004 | -0.0008 | -0.0007 | -0.0006 | -0.0004 |
| **$C_{10}$-$H_{13}$** | **GS** | 1.1133 | 1.1131 | 1.0956 | 1.0911 | 1.0900 | 1.0900 | 1.0901 |
| | **TS** | 1.1133 | 1.0954 | 1.954 | 1.0916 | 1.0901 | 1.0902 | 1.0903 |
| | **PROD** | 1.1129 | 1.0956 | 1.0909 | 1.0899 | 1.0915 | 1.0785 | 1.0786 |
| | **Δd** | -0.0179 | 0.0821 | -0.0002 | 0.0005 | 0.0001 | 0.0002 | 0.0002 |
| **$C_{14}$-$H_{15}$** | **GS** | 1.1167 | 1.1166 | 1.0993 | 1.0981 | 1.0970 | 1.0944 | 1.0945 |
| | **TS** | 1.1177 | 1.0988 | 1.1000 | 1.0969 | 1.0944 | 1.0944 | 1.0945 |
| | **PROD** | 1.1172 | 1.0978 | 1.0998 | 1.0999 | 1.0987 | 1.0945 | 1.0945 |
| | **Δd** | 0.0010 | -0.0178 | 0.0007 | -0.0012 | -0.0026 | 0.0000 | 0.0000 |
| **$C_{14}$-$H_{16}$** | **GS** | 1.1172 | 1.11170 | 1.0996 | 1.0938 | 1.0927 | 1.0928 | 1.0929 |
| | **TS** | 1.1168 | 1.0979 | 1.0998 | 1.0948 | 1.0937 | 1.0938 | 1.0939 |
| | **PROD** | 1.1186 | 1.0984 | 1.1006 | 1.0944 | 1.0931 | 1.0993 | 1.0999 |
| | **Δd** | -0.0004 | -0.0138 | 0.0002 | 0.0010 | 0.0010 | 0.0010 | 0.0010 |
| **$C_{14}$-$H_{17}$** | **GS** | 1.1164 | 1.1163 | 1.0996 | 1.0958 | 1.0964 | 1.0947 | 1.0956 |
| | **TS** | 1.1172 | 1.0978 | 1.0998 | 1.0950 | 1.0952 | 1.0953 | 1.0962 |
| | **PROD** | 1.1186 | 1.0984 | 1.1006 | 1.0991 | 1.0980 | 1.0963 | 1.0864 |
| | **Δd** | 0.0008 | -0.0139 | 0.00002 | -0.0008 | -0.0012 | 0.0006 | 0.0006 |
| **$C_{18}$-$H_{19}$** | **GS** | 1.1168 | 1.1168 | 1.0997 | 1.0973 | 1.0963 | 1.0968 | 1.0968 |
| | **TS** | 1.1178 | 1.0989 | 1.1000 | 1.0974 | 1.0945 | 1.0951 | 1.0951 |
| | **PROD** | 1.1186 | 1.0984 | 1.1006 | 1.0991 | 1.0980 | 1.0996 | 1.0864 |
| | **Δd** | 0.0010 | -0.0179 | 0.0003 | 0.0001 | -0.0018 | -0.0017 | -0.0017 |
| **$C_{18}$-$H_{20}$** | **GS** | 1.1166 | 1.1166 | 1.0998 | 1.0965 | 1.0953 | 1.0953 | 1.0954 |
| | **TS** | 1.1167 | 1.0978 | 1.0997 | 1.0954 | 1.0940 | 1.0941 | 1.0941 |
| | **PROD** | 1.1172 | 1.0978 | 1.0998 | 1.0944 | 1.0931 | 1.0934 | 1.0827 |
| | **Δd** | 0.0001 | -0.0188 | -0.0001 | -0.0011 | -0.0013 | -0.0012 | -0.0013 |
| **$C_{18}$-$H_{21}$** | **GS** | 1.1167 | 1.1167 | 1.0999 | 1.0951 | 1.0939 | 1.0940 | 1.0943 |
| | **TS** | 1.1173 | 1.0980 | 1.0998 | 1.0951 | 1.0951 | 1.0949 | 1.0949 |
| | **PROD** | 1.1186 | 1.0984 | 1.1006 | 1.0991 | 1.0980 | 1.0990 | 1.0864 |
| | **Δd** | 0.0006 | -0.0167 | -0.0001 | 0.0000 | 0.0012 | 0.0009 | 0.0006 |
| **$H_2$-$S_8$** | **GS** | 4.7850 | 4.8120 | 4.8000 | 4.9630 | 4.9660 | 4.9550 | 4.8880 |
| | **TS** | 1.7240 | 1.6520 | 1.6470 | 1.8550 | 1.8800 | 1.8890 | 1.7800 |
| | **PROD** | 1.3275 | 1.3107 | 1.3479 | 1.3679 | 1.346 | 1.3482 | 1.3258 |
| | **Δd** | -3.061 | -3.160 | -3.153 | -3.103 | -3.086 | -3.066 | -3.108 |

## 6.7.1 TABLE 2 : SELECTED BOND ANGLE $(^{O})$ OF O- IBUTYL, S – METHYL XANTHATE(DITHIOCARBONATE)

| BOND ANGLE$(^{O})$ | STATE | AM1 | PM3 | RM1 | DFT/ 6-31G* | DFT/6-31G** | DFT/ 6-31+G* | HF/ 321-G* |
|---|---|---|---|---|---|---|---|---|
| **$C_1 - C_3 - H_4$** | **GS** | 111.066 | 111.391 | 111.482 | 111.192 | 111.182 | 111.236 | 111.256 |
| | **TS** | 120.342 | 119.110 | 120.687 | 121.505 | 121.285 | 121.285 | 120.620 |
| | **PROD** | 122.415 | 122.877 | 122.200 | 122.456 | 122.450 | 122.420 | 122.320 |
| **$C_1 – C_3 – H_5$** | **GS** | 111.369 | 111.652 | 111.719 | 110.866 | 110.807 | 1109.807 | 111.920 |
| | **TS** | 120.226 | 119.107 | 120.395 | 121.131 | 120.792 | 120.792 | 120.792 |
| | **PROD** | 122,415 | 122.827 | 122.826 | 122.726 | 122.562 | 122.760 | 122.700 |
| **$C_1 – C_{14} – H_{15}$** | **GS** | 110.741 | 111.726 | 112.512 | 110.739 | 110.722 | 110.722 | 110.723 |
| | **TS** | 110.245 | 111.164 | 111.807 | 111.023 | 111.055 | 111.055 | 112.056 |
| | **PROD** | 111.581 | 112.499 | 111.730 | 112.720 | 112.860 | 111.820 | 111.560 |
| **$C_1 – C_{14} – H_{16}$** | **GS** | 109.921 | 111.522 | 112.199 | 111.285 | 111.247 | 111.247 | 111.267 |
| | **TS** | 110.949 | 111.757 | 112.516 | 111.202 | 111.197 | 111.197 | 111.198 |
| | **PROD** | 110.082 | 110.665 | 110.626 | 110.320 | 110.360 | 110.625 | 110.726 |
| **$C_1 – C_{14} – H_{17}$** | **GS** | 110.177 | 110.992 | 111.647 | 110.629 | 110.663 | 110.673 | 110.682 |
| | **TS** | 110.081 | 111.086 | 111.603 | 110.238 | 110.226 | 110.226 | 110.236 |
| | **PROD** | 110.082 | 110.665 | 110.620 | 110.000 | 110.001 | 110.002 | 110.030 |
| **$C_1 – C_{18} – H_{19}$** | **GS** | 110.681 | 111.657 | 112.495 | 111.069 | 111.037 | 111.037 | 112.037 |
| | **TS** | 110.291 | 111.196 | 111.936 | 111.081 | 111.176 | 111.176 | 111.186 |
| | **PROD** | 110.082 | 110.665 | 110.230 | 110.320 | 110.322 | 111.362 | 110.376 |
| **$C_1 – C_{18} – H_{20}$** | **GS** | 110.675 | 111.688 | 112.400 | 111.858 | 111.876 | 111.920 | 111.930 |
| | **TS** | 111.035 | 111.826 | 112.442 | 111.425 | 111.418 | 111.620 | 111.360 |
| | **PROD** | 111.581 | 112.499 | 111.720 | 112.260 | 111.120 | 112.516 | 111.157 |
| **$C_1 – C_{18} – H_{21}$** | **GS** | 109.841 | 110.937 | 111.547 | 110.468 | 110.501 | 110.620 | 110.630 |
| | **TS** | 110.104 | 111.085 | 111.656 | 110.396 | 110.414 | 110.520 | 111.203 |
| | **PROD** | 110.082 | 110.665 | 110.000 | 111.606 | 112.203 | 112.401 | 111.200 |
| **$C_3 – C_1 – C_{14}$** | **GS** | 110.718 | 111.120 | 110.488 | 111.559 | 111.529 | 111.529 | 111.523 |
| | **TS** | 115.967 | 115.481 | 113.343 | 111.559 | 116.617 | 116.620 | 116.230 |
| | **PROD** | 122.426 | 122.144 | 112.426 | 116.786 | 115.302 | 116.630 | 116.300 |
| **$C_3 –C_1-C_{18}$** | **GS** | 109.266 | 108.966 | 109.220 | 109.110 | 109.092 | 109.092 | 109.023 |
| | **TS** | 116.102 | 115.666 | 113.710 | 117.066 | 116.987 | 116.987 | 116.920 |
| | **PROD** | 122.426 | 122.144 | 122.163 | 122.132 | 122.721 | 122.721 | 122.601 |
| **$H_4-C_3-H_5$** | **GS** | 117.209 | 108.027 | 107.121 | 108.856 | 108.804 | 108.806 | 107.108 |
| | **TS** | 115.172 | 114.215 | 114.339 | 115.913 | 115.546 | 116.547 | 116.620 |
| | **PROD** | 114.346 | 114.346 | 114.200 | 114.720 | 114.620 | 114.720 | 114.726 |
| **$H_5 – C_3- H_4$** | **GS** | 109.984 | 108.027 | 107.121 | 108.856 | 108.804 | 108.256 | 108.257 |
| | **TS** | 117.209 | 114.215 | 114.331 | 115.721 | 115.546 | 114.290 | 114.580 |
| | **PROD** | 115.170 | 114.346 | 114.320 | 114.220 | 114.620 | 114.720 | 115.650 |
| **$O_6 – C_7 – S_8$** | **GS** | 118.322 | 117.979 | 117.737 | 120.020 | 120.035 | 120.856 | 121.820 |
| | **TS** | 126.677 | 125.678 | 126.551 | 125.381 | 125.599 | 124.836 | 124.820 |
| | **PROD** | 125.898 | 126.490 | 126.560 | 123.979 | 123.987 | 123.818 | 123.768 |
| **$O_6 – C_7 –S_9$** | **GS** | 113.990 | 117.423 | 117.995 | 114.480 | 114.455 | 115.128 | 115.156 |
| | **TS** | 122.212 | 121.443 | 119.205 | 118.698 | 118.347 | 118.347 | 118.320 |
| | **PROD** | 127.028 | 127.273 | 126.205 | 124.976 | 124.474 | 124.526 | 123.611 |
| **$C_7 – S_9 – C_{10}$** | **GS** | 103.850 | 104.478 | 102.556 | 102.036 | 102.001 | 102.001 | 102.676 |
| | **TS** | 107.212 | 107.389 | 103.601 | 100.888 | 101.127 | 108.001 | 107.620 |
| | **PROD** | 104.481 | 105.300 | 108.139 | 98.139 | 98.104 | 98.991 | 97.724 |
| **$S_8- C_7 – S_9$** | **GS** | 127.689 | 124.600 | 124.268 | 125.500 | 125.510 | 125.510 | 124.820 |
| | **TS** | 111.107 | 112.879 | 114.238 | 115.913 | 116.-047 | 116.047 | 115.620 |
| | **PROD** | 107.074 | 106.237 | 105.257 | 111.520 | 111.539 | 111.656 | 112.921 |
| **$S_9 – C_7 – S_8$** | **GS** | 127.689 | 124.000 | 124.268 | 125.500 | 125.510 | 125.510 | 125.620 |
| | **TS** | 111.107 | 112.879 | 114.238 | 115.913 | 116.047 | 117.047 | 118.047 |
| | **PROD** | 107.074 | 106.237 | 111.520 | 111.620 | 111.539 | 111.656 | 112.921 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **$S_9 – C_{10} – H_{11}$** | **GS** | 111.357 | 112.387 | 112.115 | 110.470 | 110.378 | 110.420 | 110.820 |
| | TS | 111.636 | 113.089 | 112.205 | 110.657 | 110.640 | 110.720 | 110.720 |
| | **PROD** | 111.719 | 113.081 | 111.267 | 110.282 | 110.198 | 110.493 | 110.073 |
| **$S_9 – C_{10} – H_{12}$** | **GS** | 108.816 | 109.789 | 106.554 | 505.464 | 105.370 | 505.371 | 505.382 |
| | **TS** | 107.474 | 107.196 | 107.890 | 106.244 | 107.101 | 106.101 | 106.102 |
| | **PROD** | 105.960 | 106.936 | 106.234 | 106.207 | 106.123 | 105,984 | 107.123 |
| **$S_9 – C_{10} – H_{13}$** | **GS** | 109.013 | 109.799 | 112.047 | 110.412 | 110.311 | 110.312 | 110.420 |
| | **TS** | 111.107 | 113.154 | 112.227 | 110.922 | 110.938 | 110.100 | 110.200 |
| | **PROD** | 111.718 | 113.081 | 111.820 | 110.282 | 110.198 | 110.493 | 110.073 |
| **$H_{11} – C_{10} – H_{12}$** | **GS** | 109.438 | 108.161 | 108.897 | 110.388 | 110.495 | 110.495 | 110.820 |
| | **TS** | 109.224 | 107.798 | 108.367 | 109.595 | 109.671 | 109.671 | 109.820 |
| | **PROD** | 109.495 | 107.958 | 109.852 | 110.081 | 110.168 | 109.945 | 110.055 |
| **$H_{11} – C_{10}- H_{13}$** | **GS** | 109.049 | 108.170 | 108.198 | 109.642 | 109.708 | 109.708 | 109.820 |
| | **TS** | 1098.479 | 107.513 | 107.894 | 109.595 | 109.638 | 109.920 | 108.200 |
| | **PROD** | 108.412 | 107.605 | 108.852 | 109.852 | 109.930 | 109.913 | 109.442 |

## 6.7.2 TABLE 3: SELECTED DIHEDRAL ANGLE ($^0$)OF 0-IBUTYL, S-METHYL XANTHATE (DITHIOCARBONATES)

| **DIHERAL ANGEL ($^0$)** | **STATE** | **AM1** | **PM3** | **RM1** | **DFT/ 6-31G*** | **DFT/ 6-31G**** | **DFT/ 6-31+G*** | **HF/321-G*** |
|---|---|---|---|---|---|---|---|---|
| **$C_3$-$C_1$-$C_{14}$-$H_{15}$** | **GS** | -63.504 | -60.710 | -60.376 | -62.937 | -63.098 | -62.098 | -62.021 |
| | **TS** | -74.076 | -71.300 | -66.415 | -80.203 | -79.559 | -79.559 | -79.620 |
| | **PROD** | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 |
| **$C_3$-$C_1$-$C_{14}$-$H_{16}$** | **GS** | 56.559 | 59.698 | 60.189 | 57.334 | 57.135 | 56.135 | 56.134 |
| | **TS** | 46.460 | 49.072 | 54.475 | 40.747 | 41.367 | 42.367 | 42.367 |
| | **PROD** | -120.439 | -120.449 | -120.500 | -120.567 | -120.670 | -120.700 | -120.800 |
| **$C_3$-$C_1$-$C_{14}$-$H_{17}$** | **GS** | 176.475 | 179.480 | 179.671 | 177.693 | 177.519 | 176.619 | 176.619 |
| | **TS** | 166.617 | 169.324 | 174.162 | 160.251 | 160.832 | 160.832 | 160.820 |
| | **PROD** | -59.561 | -59.551 | -59.000 | -59.020 | -59.032 | -59.300 | -59.400 |
| **$C_3$-$C_1$-$C_{18}$-$H_{19}$** | **GS** | 59.340 | 59.513 | 59.106 | 61.669 | 61.657 | 61.657 | 61.240 |
| | **TS** | 74.546 | 72.131 | 66.722 | 80.757 | 80.147 | 80.148 | 81.230 |
| | **PROD** | 120.439 | 120.449 | 120.002 | 120.320 | 120.420 | 120.520 | 121.536 |
| **$C_3$-$C_1$-$C_{18}$-$H_{20}$** | **GS** | -61.093 | -60.952 | -61.671 | -59.025 | -59.015 | -59.019 | -59.019 |
| | **TS** | -45.959 | -48.221 | -54.091 | -40.059 | -40.553 | -42.561 | -42.571 |
| | **PROD** | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 |
| **$C_3$-$C_1$-$C_{18}$-$H_{21}$** | **GS** | 179.052 | 179.231 | 178.845 | -179.072 | -179.095 | -179.021 | -179.022 |
| | **TS** | -166.144 | -168.497 | -173.746 | -159.743 | -159.208 | -160.208 | -160.320 |
| | **PROD** | -120.439 | -120.449 | -120.622 | -120.621 | -120.725 | -120.640 | -120.720 |
| **$H_4$-$C_3$-$C_1$-$C_{14}$** | **GS** | 168.419 | 164.114 | 172.641 | 179.989 | -179.946 | -178.946 | -178.920 |
| | **TS** | 148.871 | 140.888 | 138.168 | 150.604 | 148.418 | 147.418 | 146.420 |
| | **PROD** | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 |
| **$H_4$-$C_3$-$C_1$-$C_{18}$** | **GS** | 45.736 | 42.247 | 51.732 | 56.127 | 56.167 | 54.167 | 55.120 |
| | **TS** | 12.335 | 5.095 | 8.408 | 8.535 | 6.678 | 5.095 | 5.092 |
| | **PROD** | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 |
| **$H_5$-$C_3$-$C_1$-$C_{14}$** | **GS** | 45.464 | 43.244 | 52.818 | 58.740 | 58.918 | 58.100 | 59.200 |
| | **TS** | -13.653 | -7.033 | -16.460 | -14.159 | -13.304 | -13.921 | -14.292 |
| | **PROD** | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 |
| **$H_5$-$C_3$-$C_1$-$C_{18}$** | **GS** | -77.219 | -78.624 | -68.090 | -65.122 | -64.969 | -64.300 | -68.520 |
| | **TS** | -150.299 | -142.826 | -146.221 | -156.228 | -155.044 | -158.044 | -159.001 |
| | **PROD** | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 |
| **$O_6$-$C_7$-$S_9$-$C_{10}$** | **GS** | -179.954 | -179.936 | -179.773 | -179.975 | -179.919 | -179.000 | -179.001 |
| | **TS** | -0.013 | -0.513 | -0.416 | -3.798 | -3.780 | -4.008 | -4.002 |
| | **PROD** | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 |
| **$C_7$-$S_9$-$C_{10}$-$H_{11}$** | **GS** | -1.441 | 0.048 | -60.176 | -61.457 | -61.528 | -61.628 | -61.700 |
| | **TS** | -28.816 | -58.720 | -59.720 | -57.702 | -57.657 | -58.657 | -59.600 |
| | **PROD** | -60.821 | -61.707 | -61.407 | -60.676 | -62.723 | -61.823 | -61.820 |
| **$C_7$-$S_9$-$C_{10}$-$H_{12}$** | **GS** | -121.781 | -120.375 | -179.221 | 179.262 | 179.166 | 179.166 | 179.200 |
| | **TS** | -148.566 | -178.840 | -178.840 | -176.733 | -176.635 | -176.626 | -176.620 |
| | **PROD** | 180.000 | 180.000 | 180.000 | 180.00 | 180.000 | 180.000 | 180.000 |
| **$C_7$-$S_9$-$C_{10}$-$H_{13}$** | **GS** | 118.917 | 120.490 | 61.713 | 59.994 | 59.877 | 59.877 | 59.001 |
| | **TS** | 92.438 | 60.969 | 61.969 | 64.157 | 64.314 | 64.314 | 60.420 |
| | **PROD** | 60.821 | 61.307 | 60.832 | 62.402 | 61.307 | 60.926 | 61.128 |
| **$S_8$=$C_7$-$S_9$-$C_{10}$** | **GS** | 0.103 | 0.139 | 0.358 | 0.118 | 0.174 | 0.312 | 0.128 |
| | **TS** | 179.311 | 178.788 | 178.799 | 177.165 | 177.105 | 179.102 | 179.200 |
| | **PROD** | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 |
| **$C_{14}$-$C_1$-$C_{18}$-$H_{19}$** | **GS** | -63.111 | 176.747 | -61.963 | -62.123 | -62.116 | -63.117 | -63.117 |
| | **TS** | -63.260 | -63.600 | -63.594 | -61.994 | -62.212 | -62.212 | -62.212 |
| | **PROD** | -59.561 | -59.561 | -59.600 | -59.000 | -59.000 | -59.000 | -59.3000 |
| **$C_{14}$-$C_1$-$C_{18}$-$H_{20}$** | **GS** | 176.455 | 176.747 | 177.261 | 177.182 | 177.212 | 177.314 | 177.322 |
| | **TS** | 176.235 | 175.500 | 175.592 | 177.190 | 177.089 | 177.089 | 177.089 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | **PROD** | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 |
| **$C_{14}$-$C_1$-$C_{18}$-$H_{21}$** | **GS** | 56.601 | 56.931 | 57.777 | 57.135 | 57.132 | 58.132 | 58.133 |
| | **TS** | 56.051 | 55.930 | 55.938 | 57.506 | 57.434 | 57.434 | 57.434 |
| | **PROD** | 59.561 | 59.600 | 59.703 | 59.765 | 59.765 | 59.726 | 59.820 |
| **$H_{15}$-$C_{14}$-$C_1$-$C_{18}$** | **GS** | 58.104 | 60.316 | 59.460 | 59.463 | 59.290 | 59.300 | 59.400 |
| | **TS** | 63.789 | 63.008 | 64.089 | 62.656 | 62.944 | 59.912 | 59.820 |
| | **PROD** | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 |
| **$H_{16}$-$C_{14}$-$C_1$-$C_{18}$** | **GS** | 178.166 | -179.277 | -179.976 | 179.735 | 179.524 | 179.600 | 179.600 |
| | **TS** | -175.675 | -179.021 | -175.021 | -176.394 | -176.131 | -176.131 | 131.920 |
| | **PROD** | 59.561 | 59.641 | 59.620 | 59.678 | 59.420 | 59.261 | 59.321 |
| **$H_{17}$-$C_{14}$-$C_1$-$C_{18}$** | **GS** | -61.917 | -59.494 | -60.494 | -59.907 | -60.092 | -60.023 | -60.920 |
| | **TS** | -55.518 | -54.333 | -55.333 | -56.891 | -56.666 | -56.668 | -56.720 |
| | **PROD** | -59.561 | -59.621 | -59.320 | -59.621 | -59.672 | -59.820 | -59.650 |

# 6.7.3 TABLE 4 : ATOMIC CHARGES OF 0-ISOBUTYL, S-METHYL XANTHATE (DITHIOCARBONATE)

| ATOM | STATE | AM1 | PM3 | RM1 | 6-31G* | 6-31G** | 6-31+G* | 321G* |
|---|---|---|---|---|---|---|---|---|
| **$C_1$** | **GS** | -0.105 | -0.081 | -0.048 | -0.099 | -0.162 | -0.163 | -0.168 |
| | **TS** | -0.315 | -0.376 | -0.325 | -0.106 | -0.259 | -0.259 | -0.260 |
| | **PROD** | -0.107 | -0.108 | -0.041 | +0.233 | +0.045 | +0.603 | +0.708 |
| | **Δq** | -0.210 | -0.295 | -0.277 | -0.007 | -0.097 | -0.096 | -0.092 |
| **$H_4$** | **GS** | +0.110 | +0.082 | +0.090 | +0.150 | +0.143 | +0.143 | +0.146 |
| | **TS** | +0.281 | +0.246 | +0.267 | +0.135 | +0.164 | +0.065 | +0.166 |
| | **PROD** | +0.059 | +0.015 | +0.016 | +0.129 | +0.093 | +0.166 | +0.166 |
| | **Δq** | +0.171 | +0.164 | +0.177 | -0.015 | +0.021 | -0.078 | +0.020 |
| **$C_2$** | **GS** | -0.053 | +0.016 | +0.002 | -0.063 | +0.079 | +0.079 | +0.080 |
| | **TS** | +0.120 | +0.205 | +0.264 | -0.134 | +0.052 | +0.054 | +0.054 |
| | **PROD** | -0.228 | -0.229 | -0.220 | -0.392 | -0.308 | -0.574 | -0.567 |
| | **Δq** | +0.173 | +0.189 | +0.262 | -0.071 | -0.027 | -0.025 | -0.026 |
| **$H_5$** | **GS** | +0.097 | +0.064 | +0.075 | +0.171 | +0.150 | +0.151 | +0.152 |
| | **TS** | +0.129 | +0.069 | +0.090 | +0.196 | +0.200 | +0.200 | +0.201 |
| | **PROD** | +0.111 | +0.112 | +0.092 | +0.129 | +0.118 | +0.196 | +0.198 |
| | **Δq** | +0.032 | +0.005 | +0.015 | +0.025 | +0.050 | +0.049 | +0.049 |
| **$H_6$** | **GS** | +0.099 | +0.068 | +O.078 | +0.169 | +0.146 | +0.146 | +0.147 |
| | **TS** | +0.136 | +0.075 | +0.094 | +0.199 | +0.204 | +0.204 | +0.205 |
| | **PROD** | -0.111 | -0.112 | +0.092 | +0.129 | +0.118 | +0.196 | +0.178 |
| | **Δq** | +0.037 | +0.007 | +0.016 | +0.030 | +0.058 | +0.204 | +0.058 |
| **$O_1$** | **GS** | -0.174 | -0.129 | -0.178 | -0.395 | -0.560 | -0.560 | -0.561 |
| | **TS** | -0.378 | -0.331 | -0.388 | -0.433 | -0.605 | -0.432 | -0.451 |
| | **PROD** | -0.019 | -0.280 | -0.389 | -0.401 | -0.402 | -0.432 | -0.561 |
| | **Δq** | -0.204 | -0.202 | -0.210 | -0.039 | -0.045 | +0.128 | -0.110 |
| **$C_3$** | **GS** | -0.162 | -0.041 | -0.046 | +0.064 | +0.093 | +0.093 | +0.094 |
| | **TS** | -0.027 | +0.077 | +0.093 | +0.086 | +0.128 | +0.129 | +0.128 |
| | **PROD** | -0.284 | +0.137 | +0.098 | +0.099 | +0.099 | +0.167 | +0.167 |
| | **Δq** | +0.135 | +0.118 | +0.139 | +0.022 | +0.035 | +0.036 | +0.034 |
| **$S_1$** | **GS** | -0.063 | -0.162 | -0.154 | -0.188 | -0.175 | -0.176 | -0.176 |
| | **TS** | -0.259 | -0.204 | -0.352 | -0.136 | -0.204 | -0.205 | -0.206 |
| | **PROD** | +0.057 | +0.038 | -0.011 | -0.012 | -0.013 | -0.071 | +0.229 |
| | **Δq** | -0.196 | -0.042 | -0.198 | +0.052 | -0.029 | -0.029 | -0.030 |
| **$S_2$** | **GS** | +0.185 | +0.063 | +0.110 | +0.164 | +0.205 | +0.206 | +0.207 |
| | **TS** | +0.229 | +0.081 | +0.161 | +0.159 | +0.184 | +0.195 | +0.198 |
| | **PROD** | +0.185 | +0.015 | +0.158 | +0.158 | +0.159 | +0.190 | +0.229 |
| | **Δq** | +0.044 | +0.018 | +0.051 | -0.005 | -0.021 | -0.005 | -0009 |
| **$C_4$** | **GS** | -0.375 | -0.217 | -0.271 | 0.594 | -0.511 | -0.527 | -0.582 |
| | **TS** | -0.386 | -0.211 | -0.314 | -0.588 | -0.502 | -0.503 | -0.504 |
| | **PROD** | -0.355 | -0.196 | -0.587 | -0.588 | -0.599 | -0.718 | -0.778 |
| | **Δq** | -0.011 | +0.006 | -0.043 | -1.182 | +0.009 | +0.024 | +0.078 |
| **H3** | **GS** | +0.153 | +0.122 | +0.110 | -0.594 | +0.183 | +0.188 | +0.189 |
| | **TS** | +0.120 | +0.076 | +0.098 | +0.197 | +0.166 | +0.166 | +0.167 |
| | **PROD** | +0.226 | +0.076 | +0.207 | +0.208 | +0.209 | +0.251 | +0.260 |
| | **Δq** | -0.033 | -0.046 | -0.012 | +0.791 | -0.017 | -0.022 | -0.022 |
| **H7** | **GS** | +0.118 | +0.085 | +0.103 | +0.185 | +0.157 | +0.186 | +0.189 |
| | **TS** | +0.118 | +0.089 | +0.103 | +0.182 | +0.151 | +0.151 | +0.152 |
| | **PROD** | +0.126 | +0.090 | +0.189 | +0.189 | +0.188 | +0.228 | +0.240 |
| | **Δq** | 0.000 | +0.004 | +0.000 | -0.003 | -0.006 | -0.035 | -0.037 |
| **H8** | **GS** | +0.117 | +0.085 | +0.109 | +0.214 | +0.183 | +0.184 | +0.185 |
| | **TS** | +0.102 | +0.071 | +0.094 | +0.187 | +0.152 | +0.153 | +0.155 |
| | **PROD** | +0.116 | +0.076 | +0.207 | +0.208 | +0.209 | +0.251 | +0.260 |
| | **Δq** | -0.219 | -0.014 | -0.015 | -0.027 | +0.031 | -0.031 | -0.030 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **C5** | **GS** | -0.212 | -0.116 | -0.186 | -0.450 | -0.338 | -0.339 | -0.339 |
| | **TS** | -0.175 | -0.053 | -0.126 | -0.444 | -0.314 | -0.315 | -0.617 |
| | **PROD** | -0.184 | -0.187 | -0.157 | -0.505 | -0.356 | -0.818 | -0.856 |
| | **Δq** | +0.037 | -0.063 | +0.060 | +0.006 | +0.024 | +0.024 | -0.279 |
| **H1** | **GS** | +0.072 | +0.041 | +0.060 | +0.139 | +0.108 | +0.109 | +0.108 |
| | **TS** | +0.070 | +0.033 | +0.050 | +0.155 | +0.121 | +0.120 | +0.122 |
| | **PROD** | +0.078 | +0.278 | +0.064 | +0.152 | +0.125 | +0.204 | +0.245 |
| | **Δq** | -0.650 | -0008 | -0.010 | +0.003 | +0.013 | +0.011 | +0.014 |
| **H9** | **GS** | +0.091 | +0.053 | +0.078 | +0.177 | +0.153 | +0.154 | +0.155 |
| | **TS** | +0.083 | +0.044 | +0.065 | +0.164 | +0.135 | +0.136 | +0.160 |
| | **PROD** | +0.081 | +0.091 | +0.066 | +0.152 | +0.122 | +0.202 | +0.203 |
| | **Δq** | -0.008 | -0.009 | -0.013 | -0.013 | -0.018 | -0.018 | +0.005 |
| **$H_{10}$** | **GS** | +0.079 | +0.045 | +0.063 | +0.147 | +0.121 | +0.122 | +0.124 |
| | **TS** | +0.089 | +0.046 | +0.074 | +0.164 | +0.141 | +0.143 | +0.142 |
| | **PROD** | +0.081 | +0.067 | +0.066 | +0.152 | +0.122 | +0.202 | +0.018 |
| | **Δq** | +0.010 | +0.001 | +0.111 | +0.017 | +0.020 | +0.021 | +0.018 |
| **$C_6$** | **GS** | -0.211 | -0.113 | -0.190 | -0.453 | -0.344 | -0.345 | -0.346 |
| | **TS** | -0.178 | -0.058 | -0.131 | -0.446 | -0.317 | -0.318 | -0.319 |
| | **PROD** | -0.184 | -0.158 | -0.157 | -0.505 | -0.356 | -0.818 | -0.498 |
| | **Δq** | +0.033 | +0.055 | +0.059 | +0.007 | +0.027 | +0.013 | +0.027 |
| **H2** | **GS** | +0.076 | +0.042 | +0.064 | +0.147 | +0.117 | +0.118 | +0.119 |
| | **TS** | +0.071 | +0.034 | +0.051 | +0.155 | +0.122 | +0.123 | +0.124 |
| | **PROD** | +0.081 | +0.068 | +0.064 | +0.152 | +0.122 | +0.202 | 0.212 |
| | **Δq** | -0.005 | -0.008 | -0.013 | +0.008 | +0.005 | +0.005 | +0.005 |
| **H11** | **GS** | +0.076 | +0.043 | +0.062 | +0.147 | +0.120 | +0.122 | +0.123 |
| | **TS** | +0.079 | +0.039 | +0.061 | +0.158 | +0.128 | +0.128 | +0.127 |
| | **PROD** | +0.078 | +0.065 | +0.064 | +0.152 | +0.125 | +0.204 | +0.124 |
| | **Δq** | +0.003 | -0.004 | -0.001 | +0.011 | +0.008 | +0006 | +0.004 |
| **H12** | **GS** | +0.084 | +0.048 | +0.069 | +0.156 | +0.131 | +0.132 | +0.133 |
| | **TS** | +0.090 | +0.048 | +0.074 | +0.165 | +0.142 | +0.165 | +0.143 |
| | **PROD** | +0.081 | +0.068 | +0.066 | +0.152 | +0.122 | +0.202 | +0.267 |
| | **Δq** | +0.006 | +0.000 | +0005 | +0.009 | +0.011 | +0.033 | +0.010 |

### 6.7.4 TABLE 5 : HEAT OF FORMATION OF i-BUTYL XANTHATE

| **H.O.F(KJ/mol)** | **GS** | **TS** | **PROD** |
|---|---|---|---|
| **AM1** | -138.311 | 20.609 | -144.599 |
| **PM3** | -58.648 | 44.650 | -141.250 |
| **RM1** | -130.589 | 13.826 | 150.178 |
| **DFT/6-31G*** | -2907217.000 | -2906935.500 | -2907064.125 |
| **DFT/6-31G**** | -2907135.000 | -2906982.750 | -2907114.000 |
| **DFT/6-31+G*** | -2907397.500 | -2907213.750 | -2907108.750 |
| **HF/321-G*** | -2884006.125 | -2883772.500 | -28883772.500 |

### 6.7.5 Table 6 : Variation of rate of reaction ($S^{-1}$) with Temperature (K) for O- ibutyl S-methyl xanthate

| Temp(K) | AM1 | PM3 | DFT/6-31G* | DFT/6-31G** | DFT/6-31+G** | HF/3-21G* |
|---|---|---|---|---|---|---|
| **373** | $2.74X10^{-12}$ | $1.56X10^{-11}$ | $1.56X10^{-10}$ | $1.23X10^{-6}$ | $4.56X10^{-7}$ | $6.78X10^{-10}$ |
| **398** | $3.27X10^{-11}$ | $2.22X10^{-10}$ | $2.37X10^{-9}$ | $3.45X10^{-5}$ | $3.56X10^{-6}$ | $4.34X10^{-9}$ |
| **423** | $6.97X10^{-10}$ | $1.79X10^{-9}$ | $8.11X10^{-9}$ | $4.51X10^{-4}$ | $9.57X10^{-4}$ | $8.23X10^{-9}$ |
| **448** | $1.01X10^{-8}$ | $2.67X10^{-8}$ | $1.11X10^{-8}$ | $2.99X10^{-3}$ | $6.167X10^{-3}$ | $6.56X10^{-8}$ |
| **498** | $9.39X10^{-7}$ | $2.64X10^{-6}$ | $9.16X10^{-7}$ | $7.39X10^{-2}$ | $1.46X10^{-1}$ | $2.46X10^{-7}$ |
| **523** | $6.62X10^{-6}$ | $1.89X10^{-5}$ | $6.24X10^{-6}$ | $2.93X10^{-1}$ | $5.72X10^{-1}$ | $6.00X10^{-6}$ |
| **548** | $3.92X10^{-5}$ | $1.14X10^{-4}$ | $3.54X10^{-5}$ | 1.034 | 1.966 | $1.23X10^{-5}$ |
| **573** | $2.09X10^{-4}$ | $5.73X10^{-4}$ | $1.74X10^{-4}$ | 3.257 | 6.130 | $3.17X10^{-4}$ |
| **598** | $8.88X10^{-4}$ | $2.64X10^{-3}$ | $7.57X10^{-4}$ | 9.371 | 17.400 | $2.15X10^{-3}$ |
| **623** | $3.49X10^{-3}$ | $1.04X10^{-2}$ | $2.93X10^{-3}$ | 24.30 | 44.5 | $3.46X10^{-2}$ |

## 6.7.6 TABLE 7: ARRHENIUS PARAMETERS OF PYROLYSIS OF i-BUTYL XANTHATE (DITHIOCARBONATE)

| | ∆H (KJ/mol) | ∆S(J/mol) | Ea(KJ/mol) | A | k(S-1) |
|---|---|---|---|---|---|
| **EXPERIMENTAL** | | - | | | |
| **AM1** | 137.412 | -30.000 | 142.596 | $3.49X10^{11}$ | $3.86X10^{-1}$ |
| **PM3** | 141.596 | -22.483 | 146.778 | $8.63X10^{11}$ | $4.25X10^{-1}$ |
| **RM1** | 140.083 | -26.852 | 145.263 | $5.10X10^{11}$ | $3.37X10^{-1}$ |
| **DFT/6-31G*** | 141.695 | -30.193 | 146.875 | $3.42X10^{11}$ | $1.65X10^{-1}$ |
| **DFT/6-31G**** | 141.761 | -31.371 | 146.938 | $2.75X10^{11}$ | $1.32X10^{-1}$ |
| **DFT/6-31+G*** | 140.261 | -26.976 | 145.438 | $4.68X10^{11}$ | $2.98X10^{-1}$ |
| **HF/321-G*** | 140.261 | -30.976 | 145.441 | $2.65X10^{11}$ | $1.69X10^{-1}$ |

## 6.8.0 TABLE : 1 BONDLENGTH [$A^0$] OF O-t BUTYL, S-METHYL XANTHATE [DITHIOCARBONATE]

| BONDLENTH[$A^0$] | STATE | AM1 | PM3 | RM1 | DFT/6-31G* | DFT/6-31G** | DFT/6-31+6* | HF/321-G* |
|---|---|---|---|---|---|---|---|---|
| **$H_1$-$C_2$** | GS | 1.1155 | 1.0983 | 1.1000 | 1.0940 | 1.0929 | 1.0944 | 1.0990 |
| | TS | 1.2150 | 1.2620 | 1.1970 | 1.1930 | 1.1990 | 1.1990 | 1.2970 |
| | PROD | - | - | - | - | - | - | - |
| | Δd | +O.0995 | 0.1637 | 0.0970 | 0.0990 | 0.1061 | 0.1085 | 0.1980 |
| **$C_2$-$H_3$** | GS | 1.1157 | 1.0983 | 1.0997 | 1.0940 | 1.0929 | 1.0929 | 1.0929 |
| | TS | 1.1143 | 1.0949 | 1.0977 | 1.0933 | 1.0921 | 1.0908 | 1.0907 |
| | PROD | 1.0961 | 1.0928 | 1.0970 | 1.0966 | 1.0963 | 1.0900 | 1.0951 |
| | Δd | -0.0014 | -0.0034 | -0.002 | -0.0007 | -0.0008 | -0.0005 | -0.1134 |
| **$C_2$-$H_4$** | GS | 1.1150 | 1.0978 | 1.0988 | 1.0920 | 1.0939 | 1.0956 | 1.0957 |
| | TS | 1.1149 | 1.0943 | 1.0977 | 1.0920 | 1.0908 | 1.0926 | 1.0927 |
| | PROD | 1.4836 | 1.0967 | 1.0956 | 1.0967 | 1.0956 | 1.0965 | 1.0963 |
| | Δd | -0.0001 | -0.0035 | -0.001 | 0.0005 | -0.003 | -0.0030 | 0.0100 |
| **$C_2$-$C_5$** | GS | 1.5305 | 1.5359 | 1.5374 | 1.5322 | 1.5316 | 1.5321 | 1.5450 |
| | TS | 1.4383 | 1.4354 | 1.4438 | 1.4279 | 1.4280 | 1.4926 | 1.5430 |
| | PROD | 1.4836 | 1.4867 | 1.4878 | 1.5087 | 1.5083 | 1.5097 | 1.5143 |
| | Δd | -0.0922 | -0.1005 | -0.094 | -0.1043 | -0.1036 | -0.0982 | -0.0020 |
| **$C_5$-$O_6$** | GS | 1.4514 | 1.4552 | 1.4245 | 1.4886 | 1.4892 | 1.4926 | 1.4927 |
| | TS | 2.0340 | 1.9297 | 1.9590 | 1.2930 | 2.2730 | 2.293 | 2.2940 |
| | PROD | - | - | - | - | - | - | - |
| | Δd | +0.5826 | 0.4718 | 0.5345 | 0.804 | 0.7838 | -0.0138 | -0.0138 |
| **$C_5$-$C_{14}$** | GS | 1.5188 | 1.5279 | 1.5245 | 1.5312 | 1.5308 | 1.5311 | 1.5312 |
| | TS | 1.4813 | 1.4938 | 1.4883 | 1.4923 | 1.4919 | 1.4908 | 1.4909 |
| | PROD | 1.3361 | 1.3328 | 1.3229 | 1.3366 | 1.3363 | 1.3400 | 1.3179 |
| | Δd | -0.0375 | -0.0341 | -0.036 | -0.0395 | -0.0393 | -0.041 | -0.0141 |
| **$C_5$-$C_{18}$** | GS | 1.5187 | 1.5279 | 1.5244 | 1.5312 | 1.5307 | 1.5311 | 1.4982 |
| | TS | 1.4811 | 1.4943 | 1.4888 | 1.4923 | 1.4919 | 1.4919 | 2.0960 |
| | PROD | 1.3362 | 1.3329 | 1.3339 | 1.3367 | 1.3368 | 1.3456 | 1.3267 |
| | Δd | -0.0376 | -0.0336 | -0.035 | -0.0389 | -0.0388 | -0.0401 | 0.5978 |
| **$O_6$-$C_7$** | GS | 1.3616 | 1.3516 | 1.3331 | 1.3312 | 1.3310 | 1.3339 | 1.3359 |
| | TS | 1.2775 | 1.2648 | 1.2648 | 1.2445 | 1.2575 | 1.2490 | 1.2718 |
| | PROD | 1.2349 | 1.2111 | 1.2047 | 1.2048 | 1.286 | 1.2053 | 1.2053 |
| | Δd | -0.0841 | -0.0868 | -0.075 | -0.0867 | -0.0854 | -0.0849 | -0.0641 |
| **$C_7$=$S_8$** | GS | 1.5674 | 1.6267 | 1.5960 | 1.6535 | 1.6535 | 1.6530 | 1.6576 |
| | TS | 1.6338 | 1.7087 | 1.6633 | 1.7301 | 1.7284 | 1.7269 | 1.7237 |
| | PROD | 1.7212 | 1.8025 | 1.8940 | 1.8941 | 1.8087 | 1.7789 | 1.7790 |
| | Δd | 0.0664 | 0.0.082 | 0.0673 | 0.0766 | 0.0749 | 0.0739 | 0.0661 |
| **$C_7$-$S_9$** | GS | 1.7190 | 1.8004 | 1.7598 | 1.7884 | 1.7888 | 1.7857 | 1.7878 |
| | TS | 1.7114 | 1.7968 | 1.7572 | 1.8048 | 1.8044 | 1.8013 | 1.7981 |
| | **PROD** | 1.7127 | 1.7107 | 1.7940 | 1.7941 | 1.7901 | 1.7644 | 1.7644 |
| | **Δd** | -0.0076 | -0.0036 | 0.0074 | 0.0164 | 0.0156 | 0.0156 | 0.0103 |
| **$S_9$-$C_{10}$** | **GS** | 1.7515 | 1.8019 | 1.7973 | 1.8203 | 1.8196 | 1.8204 | 1.8188 |
| | **TS** | 1.7487 | 1.7968 | 1.7902 | 1.8299 | 1.8293 | 1.8299 | 1.8402 |
| | **PROD** | 1.7537 | 1.8012 | 1.8284 | 1.8277 | 1.8276 | 1.8141 | 1.8142 |
| | **Δd** | -0.0028 | -0.0028 | -0.007 | 0.010 | 0.0097 | 0.0095 | 0.0214 |
| **$C_{10}$-$H_{11}$** | **GS** | 1.1133 | 1.0957 | 1.0955 | 1.0909 | 1.0899 | 1.0916 | 1.0899 |
| | **TS** | 1.1139 | 1.0974 | 1.0943 | 1.0918 | 1.0910 | 1.0926 | 1.0905 |
| | **PROD** | 1.1129 | 1.0956 | 1.0909 | 1.899 | 1.0915 | 1.0785 | 1.0786 |
| | **Δd** | 0.0005 | -0.0001 | -0.002 | 0.0009 | 0.0011 | 0.001 | 0.0006 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **$C_{10}$-$H_{12}$** | **GS** | 1.1131 | 1.0955 | 1.0965 | 1.0942 | 1.0932 | 1.0945 | 1.0927 |
| | **TS** | 1.1131 | 1.0974 | 1.0943 | 1.0931 | 1.0908 | 1.0925 | 1.0923 |
| | **PROD** | 1.1149 | 1.0975 | 1.0923 | 1.0912 | 1.0930 | 1.0806 | 1.0807 |
| | **Δd** | 0.0000 | 0.0001 | -0.012 | -0.0011 | -0.0024 | -0.0020 | -0.0004 |
| **$C_{10}$-$H_{13}$** | **GS** | 1.1226 | 1.1054 | 1.0965 | 1.0907 | 1.0897 | 1.0912 | 1.0901 |
| | **TS** | 1.1138 | 1.0955 | 1.0965 | 1.0920 | 1.0921 | 1.0940 | 1.0903 |
| | **PROD** | 1.1129 | 1.0956 | 1.0957 | 1.0899 | 1.0915 | 1.0785 | 1.0786 |
| | **Δd** | 0.0042 | -0.0099 | -0.008 | 0.0013 | 0.0024 | 0.0028 | 0.0002 |
| **$C_{14}$-$H_{15}$** | **GS** | 1.1165 | 1.0979 | 1.0999 | 1.0957 | 1.0946 | 1.0964 | 1.0945 |
| | **TS** | 1.1207 | 1.0997 | 1.1019 | 1.1017 | 1.1006 | 1.0927 | 1.0945 |
| | **PROD** | 1.1172 | 1.0978 | 1.0998 | 1.0999 | 1.0987 | 1.0945 | 1.0945 |
| | **Δd** | 0.0042 | 0.0018 | 0.0020 | -0.0016 | 0.006 | -0.0037 | 0.0000 |
| **$C_{14}$-$H_{16}$** | **GS** | 1.1166 | 1.0980 | 1.0999 | 1.0946 | 1.0935 | 1.0951 | 1.0929 |
| | **TS** | 1.1183 | 1.0989 | 1.1019 | 1.0930 | 1.0920 | 1.1028 | 1.0939 |
| | **PROD** | 1.1186 | 1.0984 | 1.1006 | 1.0944 | 1.0931 | 1.0951 | 1.0999 |
| | **Δd** | 0.0017 | 0.0009 | 0.0020 | -0.0016 | -0.002 | -0.0015 | 0.0010 |
| **$C_{14}$-$H_{17}$** | **GS** | 1.1184 | 1.0980 | 1.0990 | 1.0916 | 1.0906 | 1.0919 | 1.0956 |
| | **TS** | 1.1201 | 1.0989 | 1.1013 | 1.0922 | 1.0912 | 1.0935 | 1.0962 |
| | **PROD** | 1.1186 | 1.0984 | 1.1006 | 1.0991 | 1.0980 | 1.0963 | 1.0864 |
| | **Δd** | 0.0017 | -0.002 | 0.0023 | 0.0006 | 0.0006 | 0.0016 | 0.0006 |
| **$C_{18}$-$H_{19}$** | **GS** | 1.1166 | 1.1012 | 1.0999 | 1.0957 | 1.0934 | 1.0951 | 1.0968 |
| | **TS** | 1.1186 | 1.0992 | 1.1019 | 1.0933 | 1.0926 | 1.0938 | 1.0951 |
| | **PROD** | 1.1186 | 1.0984 | 1.1006 | 1.0991 | 1.0980 | 1.0996 | 1.0864 |
| | **Δd** | 0.0020 | -0.002 | 0.0020 | -0.002 | -0.0008 | -0.0013 | -0.0017 |
| **$C_{18}$-$H_{20}$** | **GS** | 1.1167 | 1.0978 | 1.0999 | 1.0957 | 1.0946 | 1.0963 | 1.0954 |
| | **TS** | 1.1205 | 1.0999 | 1.1025 | 1.1022 | 1.1013 | 1.1034 | 1.0941 |
| | **PROD** | 1.1172 | 1.0978 | 1.0998 | 1.0944 | 1.0931 | 1.0934 | 1.0827 |
| | **Δd** | 0.0038 | 0.0021 | -0.003 | 0.007 | 0.0067 | 0.0071 | -0.0013 |
| **$C_{18}$-$H_{21}$** | **GS** | 1.1186 | 1.1011 | 1.0988 | 1.0917 | 1.0907 | 1.0923 | 1.0943 |
| | **TS** | 1.1200 | 1.0992 | 1.1013 | 1.0921 | 1.0913 | 1.0926 | 1.0949 |
| | **PROD** | 1.1186 | 1.0984 | 1.1006 | 1.0991 | 1.0980 | 1.0990 | 1.0864 |
| | **Δd** | 0.0814 | -0.0019 | 0.0142 | 0.0004 | 0.0006 | 0.0003 | 0.0006 |
| **$H_1$-$S_8$** | **GS** | 4.7640 | 4.7880 | 4.7140 | 4.7160 | 4.7210 | 4.6530 | 4.8880 |
| | **TS** | 1.8570 | 1.7280 | 1.7550 | 1.9540 | 1.9490 | 1.9490 | 1.7800 |
| | **PROD** | 1.3275 | 1.3107 | 1.3479 | 1.3679 | 1.346 | 1.3482 | 1.3258 |
| | **Δd** | -2.9070 | -3.060 | -2.959 | -2.762 | -2.772 | -2.772 | -3.108 |

## 6.8.1 TABLE 2 : SELECTED BOND ANGLE ($^O$) OF O- t BUTYL, S – METHYL XANTHATE(DITHIOCARBONATE)

| BOND ANGLE($^O$) | STATE | AM1 | PM3 | RM1 | DFT/ 6-31G* | DFT/6-31G** | DFT/ 6-31+G* | HF/ 321-G* |
|---|---|---|---|---|---|---|---|---|
| **$C_2$– $C_5$- $C_{14}$** | **GS** | 111.066 | 111.391 | 111.482 | 111.192 | 111.182 | 111.236 | 111.256 |
| | **TS** | 120.342 | 119.110 | 120.687 | 121.505 | 121.285 | 121.285 | 120.620 |
| | **PROD** | 122.415 | 122.877 | 122.200 | 122.456 | 122.450 | 122.420 | 122.320 |
| **$C_2$ – $C_5$ – $C_{18}$** | **GS** | 111.369 | 111.652 | 111.719 | 110.866 | 110.807 | 1109.807 | 111.920 |
| | **TS** | 120.226 | 119.107 | 120.395 | 121.131 | 120.792 | 120.792 | 120.792 |
| | **PROD** | 122,415 | 122.827 | 122.826 | 122.726 | 122.562 | 122.760 | 122.700 |
| **$H_3$ – $C_2$– $H_4$** | **GS** | 110.741 | 111.726 | 112.512 | 110.739 | 110.722 | 110.722 | 110.723 |
| | **TS** | 110.245 | 111.164 | 111.807 | 111.023 | 111.055 | 111.055 | 112.056 |
| | **PROD** | 111.581 | 112.499 | 111.730 | 112.720 | 112.860 | 111.820 | 111.560 |
| **$H_3$ – $C_2$– C5** | **GS** | 109.921 | 111.522 | 112.199 | 111.285 | 111.247 | 111.247 | 111.267 |
| | **TS** | 110.949 | 111.757 | 112.516 | 111.202 | 111.197 | 111.197 | 111.198 |
| | **PROD** | 110.082 | 110.665 | 110.626 | 110.320 | 110.360 | 110.625 | 110.726 |
| **$H_4$ – $C_2$ – $H_3$** | **GS** | 110.177 | 110.992 | 111.647 | 110.629 | 110.663 | 110.673 | 110.682 |
| | **TS** | 110.081 | 111.086 | 111.603 | 110.238 | 110.226 | 110.226 | 110.236 |
| | **PROD** | 110.082 | 110.665 | 110.620 | 110.000 | 110.001 | 110.002 | 110.030 |
| **$H_4$ – $C_2$ – $C_5$** | **GS** | 110.681 | 111.657 | 112.495 | 111.069 | 111.037 | 111.037 | 112.037 |
| | **TS** | 110.291 | 111.196 | 111.936 | 111.081 | 111.176 | 111.176 | 111.186 |
| | **PROD** | 110.082 | 110.665 | 110.230 | 110.320 | 110.322 | 111.362 | 110.376 |
| **$C_5$ – $C_2$ – $H_3$** | **GS** | 110.675 | 111.688 | 112.400 | 111.858 | 111.876 | 111.920 | 111.930 |
| | **TS** | 111.035 | 111.826 | 112.442 | 111.425 | 111.418 | 111.620 | 111.360 |
| | **PROD** | 111.581 | 112.499 | 111.720 | 112.260 | 111.120 | 112.516 | 111.157 |
| **$C_5$ – $C_2$ – $H_4$** | **GS** | 109.841 | 110.937 | 111.547 | 110.468 | 110.501 | 110.620 | 110.630 |
| | **TS** | 110.104 | 111.085 | 111.656 | 110.396 | 110.414 | 110.520 | 111.203 |
| | **PROD** | 110.082 | 110.665 | 110.000 | 111.606 | 112.203 | 112.401 | 111.200 |
| **$C_5$ – $C_{14}$ – $H_{15}$** | **GS** | 110.718 | 111.120 | 110.488 | 111.559 | 111.529 | 111.529 | 111.523 |
| | **TS** | 115.967 | 115.481 | 113.343 | 111.559 | 116.617 | 116.620 | 116.230 |
| | **PROD** | 122.426 | 122.144 | 112.426 | 116.786 | 115.302 | 116.630 | 116.300 |
| **$C_3$ –$C_{14}$-$H_{16}$** | **GS** | 109.266 | 108.966 | 109.220 | 109.110 | 109.092 | 109.092 | 109.023 |
| | **TS** | 116.102 | 115.666 | 113.710 | 117.066 | 116.987 | 116.987 | 116.920 |
| | **PROD** | 122.426 | 122.144 | 122.163 | 122.132 | 122.721 | 122.721 | 122.601 |
| **$C_5$-$C_{14}$-$H_{17}$** | **GS** | 117.209 | 108.027 | 107.121 | 108.856 | 108.804 | 108.806 | 107.108 |
| | **TS** | 115.172 | 114.215 | 114.339 | 115.913 | 115.546 | 116.547 | 116.620 |
| | **PROD** | 114.346 | 114.346 | 114.200 | 114.720 | 114.620 | 114.720 | 114.726 |
| **$C_5$ – $C_{18}$- $H_{19}$** | **GS** | 109.984 | 108.027 | 107.121 | 108.856 | 108.804 | 108.256 | 108.257 |
| | **TS** | 117.209 | 114.215 | 114.331 | 115.721 | 115.546 | 114.290 | 114.580 |
| | **PROD** | 115.170 | 114.346 | 114.320 | 114.220 | 114.620 | 114.720 | 115.650 |
| **$C_5$ – $C_{18}$ – $H_{20}$** | **GS** | 118.322 | 117.979 | 117.737 | 120.020 | 120.035 | 120.856 | 121.820 |
| | **TS** | 126.677 | 125.678 | 126.551 | 125.381 | 125.599 | 124.836 | 124.820 |
| | **PROD** | 125.898 | 126.490 | 126.560 | 123.979 | 123.987 | 123.818 | 123.768 |
| **$C_5$ – $C_{18}$ –$H_{21}$** | **GS** | 113.990 | 117.423 | 117.995 | 114.480 | 114.455 | 115.128 | 115.156 |
| | **TS** | 122.212 | 121.443 | 119.205 | 118.698 | 118.347 | 118.347 | 118.320 |
| | **PROD** | 127.028 | 127.273 | 126.205 | 124.976 | 124.474 | 124.526 | 123.611 |
| **$O_6$– $C_7$ – $S_8$** | **GS** | 103.850 | 104.478 | 102.556 | 102.036 | 102.001 | 102.001 | 102.676 |
| | **TS** | 107.212 | 107.389 | 103.601 | 100.888 | 101.127 | 108.001 | 107.620 |
| | **PROD** | 104.481 | 105.300 | 108.139 | 98.139 | 98.104 | 98.991 | 97.724 |
| **$O_6$- $C_7$ – $S_9$** | **GS** | 127.689 | 124.600 | 124.268 | 125.500 | 125.510 | 125.510 | 124.820 |
| | **TS** | 111.107 | 112.879 | 114.238 | 115.913 | 116.-047 | 116.047 | 115.620 |
| | **PROD** | 107.074 | 106.237 | 105.257 | 111.520 | 111.539 | 111.656 | 112.921 |
| **$C_7$ – $S_9$ – $C_{10}$** | **GS** | 127.689 | 124.000 | 124.268 | 125.500 | 125.510 | 125.510 | 125.620 |
| | **TS** | 111.107 | 112.879 | 114.238 | 115.913 | 116.047 | 117.047 | 118.047 |
| | **PROD** | 107.074 | 106.237 | 111.520 | 111.620 | 111.539 | 111.656 | 112.921 |

|  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|
| **$S_8 = C_7 - S_9$** | **GS** | 111.357 | 112.387 | 112.115 | 110.470 | 110.378 | 110.420 | 110.820 |
|  | TS | 111.636 | 113.089 | 112.205 | 110.657 | 110.640 | 110.720 | 110.720 |
|  | **PROD** | 111.719 | 113.081 | 111.267 | 110.282 | 110.198 | 110.493 | 110.073 |
| **$S_9 - C_7 - S_8$** | **GS** | 108.816 | 109.789 | 106.554 | 505.464 | 105.370 | 505.371 | 505.382 |
|  | **TS** | 107.474 | 107.196 | 107.890 | 106.244 | 107.101 | 106.101 | 106.102 |
|  | **PROD** | 105.960 | 106.936 | 106.234 | 106.207 | 106.123 | 105,984 | 107.123 |
| **$S_9 - C_{10} - H_{11}$** | **GS** | 109.013 | 109.799 | 112.047 | 110.412 | 110.311 | 110.312 | 110.420 |
|  | **TS** | 111.107 | 113.154 | 112.227 | 110.922 | 110.938 | 110.100 | 110.200 |
|  | **PROD** | 111.718 | 113.081 | 111.820 | 110.282 | 110.198 | 110.493 | 110.073 |
| **$S_9 - C_{10} - H_{12}$** | **GS** | 109.438 | 108.161 | 108.897 | 110.388 | 110.495 | 110.495 | 110.820 |
|  | **TS** | 109.224 | 107.798 | 108.367 | 109.595 | 109.671 | 109.671 | 109.820 |
|  | **PROD** | 109.495 | 107.958 | 109.852 | 110.081 | 110.168 | 109.945 | 110.055 |
| **$S_9 - C_{10}$- $H_{13}$** | **GS** | 109.049 | 108.170 | 108.198 | 109.642 | 109.708 | 109.708 | 109.820 |
|  | **TS** | 1098.479 | 107.513 | 107.894 | 109.595 | 109.638 | 109.920 | 108.200 |
|  | **PROD** | 108.412 | 107.605 | 108.852 | 109.852 | 109.930 | 109.913 | 109.442 |

## 6.8.2 TABLE 3: SELECTED DIHEDRAL ANGLE $(^0)$OF 0-t BUTYL, S-METHYL XANTHATE (DITHIOCARBONATES)

| DIHERAL ANGEL $(^0)$ | STATE | AM1 | PM3 | RM1 | DFT/ 6-31G* | DFT/ 6-31G** | DFT/ 6-31+G* | HF/ 321-G* |
|---|---|---|---|---|---|---|---|---|
| **$C_2$-$C_5$-$C_{14}$-$H_{15}$** | **GS** | -63.504 | -60.710 | -60.376 | -62.937 | -63.098 | -62.098 | -62.021 |
|  | **TS** | -74.076 | -71.300 | -66.415 | -80.203 | -79.559 | -79.559 | -79.620 |
|  | **PROD** | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 |
| **$C_2$-$C_5$-$C_{14}$-$H_{16}$** | **GS** | 56.559 | 59.698 | 60.189 | 57.334 | 57.135 | 56.135 | 56.134 |
|  | **TS** | 46.460 | 49.072 | 54.475 | 40.747 | 41.367 | 42.367 | 42.367 |
|  | **PROD** | -120.439 | -120.449 | -120.500 | -120.567 | -120.670 | -120.700 | -120.800 |
| **$C_2$-$C_5$-$C_{14}$-$H_{17}$** | **GS** | 176.475 | 179.480 | 179.671 | 177.693 | 177.519 | 176.619 | 176.619 |
|  | **TS** | 166.617 | 169.324 | 174.162 | 160.251 | 160.832 | 160.832 | 160.820 |
|  | **PROD** | -59.561 | -59.551 | -59.000 | -59.020 | -59.032 | -59.300 | -59.400 |
| **$C_2$-$C_5$-$C_{18}$-$H_{19}$** | **GS** | 59.340 | 59.513 | 59.106 | 61.669 | 61.657 | 61.657 | 61.240 |
|  | **TS** | 74.546 | 72.131 | 66.722 | 80.757 | 80.147 | 80.148 | 81.230 |
|  | **PROD** | 120.439 | 120.449 | 120.002 | 120.320 | 120.420 | 120.520 | 121.536 |
| **$C_2$-$C_5$-$C_{18}$-$H_{20}$** | **GS** | -61.093 | -60.952 | -61.671 | -59.025 | -59.015 | -59.019 | -59.019 |
|  | **TS** | -45.959 | -48.221 | -54.091 | -40.059 | -40.553 | -42.561 | -42.571 |
|  | **PROD** | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 |
| **$C_2$-$C_5$-$C_{18}$-$H_{21}$** | **GS** | 179.052 | 179.231 | 178.845 | -179.072 | -179.095 | -179.021 | -179.022 |
|  | **TS** | -166.144 | -168.497 | -173.746 | -159.743 | -159.208 | -160.208 | -160.320 |
|  | **PROD** | -120.439 | -120.449 | -120.622 | -120.621 | -120.725 | -120.640 | -120.720 |
| **$H_3$-$C_2$-$C_1$-$C_{14}$** | **GS** | 168.419 | 164.114 | 172.641 | 179.989 | -179.946 | -178.946 | -178.920 |
|  | **TS** | 148.871 | 140.888 | 138.168 | 150.604 | 148.418 | 147.418 | 146.420 |
|  | **PROD** | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 |
| **$H_3$-$C_2$-$C_5$-$C_{18}$** | **GS** | 45.736 | 42.247 | 51.732 | 56.127 | 56.167 | 54.167 | 55.120 |
|  | **TS** | 12.335 | 5.095 | 8.408 | 8.535 | 6.678 | 5.095 | 5.092 |
|  | **PROD** | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 |
| **$H_4$-$C_2$-$C_5$-$C_{14}$** | **GS** | 45.464 | 43.244 | 52.818 | 58.740 | 58.918 | 58.100 | 59.200 |
|  | **TS** | -13.653 | -7.033 | -16.460 | -14.159 | -13.304 | -13.921 | -14.292 |
|  | **PROD** | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **$H_4$-$C_2$-$C_5$-$C_{18}$** | **GS** | -77.219 | -78.624 | -68.090 | -65.122 | -64.969 | -64.300 | -68.520 |
| | **TS** | -150.299 | -142.826 | -146.221 | -156.228 | -155.044 | -158.044 | -159.001 |
| | **PROD** | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 |
| **$O_6$-$C_7$-$S_9$-$C_{10}$** | **GS** | -179.954 | -179.936 | -179.773 | -179.975 | -179.919 | -179.000 | -179.001 |
| | **TS** | -0.013 | -0.513 | -0.416 | -3.798 | -3.780 | -4.008 | -4.002 |
| | **PROD** | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 |
| **$C_7$-$S_9$-$C_{10}$-$H_{11}$** | **GS** | -1.441 | 0.048 | -60.176 | -61.457 | -61.528 | -61.628 | -61.700 |
| | **TS** | -28.816 | -58.720 | -59.720 | -57.702 | -57.657 | -58.657 | -59.600 |
| | **PROD** | -60.821 | -61.707 | -61.407 | -60.676 | -62.723 | -61.823 | -61.820 |
| **$C_7$-$S_9$-$C_{10}$-$H_{12}$** | **GS** | -121.781 | -120.375 | -179.221 | 179.262 | 179.166 | 179.166 | 179.200 |
| | **TS** | -148.566 | -178.840 | -178.840 | -176.733 | -176.635 | -176.626 | -176.620 |
| | **PROD** | 180.000 | 180.000 | 180.000 | 180.00 | 180.000 | 180.000 | 180.000 |
| **$C_7$-$S_9$-$C_{10}$-$H_{13}$** | **GS** | 118.917 | 120.490 | 61.713 | 59.994 | 59.877 | 59.877 | 59.001 |
| | **TS** | 92.438 | 60.969 | 61.969 | 64.157 | 64.314 | 64.314 | 60.420 |
| | **PROD** | 60.821 | 61.307 | 60.832 | 62.402 | 61.307 | 60.926 | 61.128 |
| **$S_8$=$C_7$-$S_9$-$C_{10}$** | **GS** | 0.103 | 0.139 | 0.358 | 0.118 | 0.174 | 0.312 | 0.128 |
| | **TS** | 179.311 | 178.788 | 178.799 | 177.165 | 177.105 | 179.102 | 179.200 |
| | **PROD** | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 |
| **$C_{14}$-$C_5$-$C_{18}$-$H_{19}$** | **GS** | -63.111 | 176.747 | -61.963 | -62.123 | -62.116 | -63.117 | -63.117 |
| | **TS** | -63.260 | -63.600 | -63.594 | -61.994 | -62.212 | -62.212 | -62.212 |
| | **PROD** | -59.561 | -59.561 | -59.600 | -59.000 | -59.000 | -59.000 | -59.3000 |
| **$C_{14}$-$C_5$-$C_{18}$-$H_{20}$** | **GS** | 176.455 | 176.747 | 177.261 | 177.182 | 177.212 | 177.314 | 177.322 |
| | **TS** | 176.235 | 175.500 | 175.592 | 177.190 | 177.089 | 177.089 | 177.089 |
| | **PROD** | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 |
| **$C_{14}$-$C_5$-$C_{18}$-$H_{21}$** | **GS** | 56.601 | 56.931 | 57.777 | 57.135 | 57.132 | 58.132 | 58.133 |
| | **TS** | 56.051 | 55.930 | 55.938 | 57.506 | 57.434 | 57.434 | 57.434 |
| | **PROD** | 59.561 | 59.600 | 59.703 | 59.765 | 59.765 | 59.726 | 59.820 |
| **$H_{15}$-$C_{14}$-$C_5$-$C_{18}$** | **GS** | 58.104 | 60.316 | 59.460 | 59.463 | 59.290 | 59.300 | 59.400 |
| | **TS** | 63.789 | 63.008 | 64.089 | 62.656 | 62.944 | 59.912 | 59.820 |
| | **PROD** | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 |
| **$H_{16}$-$C_{14}$-$C_5$-$C_{18}$** | **GS** | 178.166 | -179.277 | -179.976 | 179.735 | 179.524 | 179.600 | 179.600 |
| | **TS** | -175.675 | -179.021 | -175.021 | -176.394 | -176.131 | -176.131 | 131.920 |
| | **PROD** | 59.561 | 59.641 | 59.620 | 59.678 | 59.420 | 59.261 | 59.321 |
| **$H_{17}$-$C_{14}$-$C_5$-$C_{18}$** | **GS** | -61.917 | -59.494 | -60.494 | -59.907 | -60.092 | -60.023 | -60.920 |
| | **TS** | -55.518 | -54.333 | -55.333 | -56.891 | -56.666 | -56.668 | -56.720 |
| | **PROD** | -59.561 | -59.621 | -59.320 | -59.621 | -59.672 | -59.820 | -59.650 |

### 6.8.3 TABLE 4: ATOMIC CHARGES OF 0-tBUTYL, S-METHYL XANTHATE (DITHIOCARBONATE)

| ATOM | STATE | AM1 | PM3 | RM1 | DFT/ 6-31G* | DFT/ 6-31G** | DFT/ 6-31+G* | HF/321G* |
|---|---|---|---|---|---|---|---|---|
| **$H_1$** | **GS** | +0.094 | +0.059 | +0.083 | +0.166 | +0.141 | +0.228 | +0.176 |
| | **TS** | +0.268 | +0.255 | +0.267 | +0.185 | +0.147 | +0.195 | +0.167 |
| | **PROD** | +0.107 | +0.108 | +0.041 | +0.233 | +0.045 | +0.603 | +0.708 |
| | **Δq** | +0.174 | +0.196 | +0.184 | +0.019 | +0.006 | +0.033 | -0.009 |
| **$C_1$** | **GS** | -0.207 | -0.126 | -0.198 | -0.443 | -0.311 | -0.472 | -0.476 |
| | **TS** | -0.390 | -0.421 | -0.468 | -0.429 | -0.366 | -0.484 | -0.494 |
| | **PROD** | +0.059 | +0.015 | +0.016 | +0.129 | +0.093 | +0.166 | +0.166 |
| | **Δq** | -0.183 | -0.295 | -0.270 | +0.014 | -0.055 | -0.012 | -0.018 |
| **$H_2$** | **GS** | +0.095 | +0.059 | +0.082 | +0.166 | +0.443 | +0.311 | +0.141 |
| | **TS** | +0.122 | +0.104 | +0.125 | +0.185 | +0.529 | +0.366 | +0.139 |
| | **PROD** | -0.228 | -0.229 | -0.220 | -0.392 | -0.308 | -0.574 | -0.567 |
| | **Δq** | +0.027 | +0.045 | +0.043 | +0.019 | +0.086 | +0.055 | -0.002 |
| **$H_4$** | **GS** | +0.086 | +0.054 | +0.082 | +0.166 | +0.141 | +0.227 | +0.238 |
| | **TS** | +0.125 | +0.104 | +0.125 | +0.185 | +0.139 | +0.238 | +0.456 |
| | **PROD** | +0.111 | +0.112 | +0.092 | +0.129 | +0.118 | +0.196 | +0.198 |
| | **Δq** | +0.039 | +0.050 | +0.043 | +0.019 | -0.002 | +0.011 | +0.218 |
| **$C_2$** | **GS** | +0.065 | +0.094 | +0.171 | +0.281 | +0.223 | -0.223 | +0.213 |
| | **TS** | +0.277 | +0.312 | +0.440 | +0.309 | +0.243 | +0.287 | +0.253 |
| | **PROD** | -0.111 | -0.112 | +0.092 | +0.129 | +0.118 | +0.196 | +0.178 |
| | **Δq** | +0.037 | +0.007 | +0.016 | +0.030 | +0.058 | +0.204 | +0.058 |
| **$O_1$** | **GS** | -0.174 | -0.129 | -0.178 | -0.395 | -0.560 | -0.560 | -0.561 |
| | **TS** | -0.378 | -0.331 | -0.388 | -0.433 | -0.605 | -0.432 | -0.451 |
| | **PROD** | -0.019 | -0.280 | -0.389 | -0.401 | -0.402 | -0.432 | -0.561 |
| | **Δq** | -0.204 | -0.202 | -0.210 | -0.039 | -0.045 | +0.128 | -0.110 |
| **$C_3$** | **GS** | -0.162 | -0.041 | -0.046 | +0.064 | +0.093 | +0.093 | +0.094 |
| | **TS** | -0.027 | +0.077 | +0.093 | +0.086 | +0.128 | +0.129 | +0.128 |
| | **PROD** | -0.284 | +0.137 | +0.098 | +0.099 | +0.099 | +0.167 | +0.167 |
| | **Δq** | +0.135 | +0.118 | +0.139 | +0.022 | +0.035 | +0.036 | +0.034 |
| **$S_1$** | **GS** | -0.063 | -0.162 | -0.154 | -0.188 | -0.175 | -0.176 | -0.176 |
| | **TS** | -0.259 | -0.204 | -0.352 | -0.136 | -0.204 | -0.205 | -0.206 |
| | **PROD** | +0.057 | +0.038 | -0.011 | -0.012 | -0.013 | -0.071 | +0.229 |
| | **Δq** | -0.196 | -0.042 | -0.198 | +0.052 | -0.029 | -0.029 | -0.030 |
| **$S_2$** | **GS** | +0.185 | +0.063 | +0.110 | +0.164 | +0.205 | +0.206 | +0.207 |
| | **TS** | +0.229 | +0.081 | +0.161 | +0.159 | +0.184 | +0.195 | +0.198 |
| | **PROD** | +0.185 | +0.015 | +0.158 | +0.158 | +0.159 | +0.190 | +0.229 |
| | **Δq** | +0.044 | +0.018 | +0.051 | -0.005 | -0.021 | -0.005 | -0009 |
| **$C_4$** | **GS** | -0.375 | -0.217 | -0.271 | 0.594 | -0.511 | -0.527 | -0.582 |
| | **TS** | -0.386 | -0.211 | -0.314 | -0.588 | -0.502 | -0.503 | -0.504 |
| | **PROD** | -0.355 | -0.196 | -0.587 | -0.588 | -0.599 | -0.718 | -0.778 |
| | **Δq** | -0.011 | +0.006 | -0.043 | -1.182 | +0.009 | +0.024 | +0.078 |
| **$H_3$** | **GS** | +0.153 | +0.122 | +0.110 | -0.594 | +0.183 | +0.188 | +0.189 |
| | **TS** | +0.120 | +0.076 | +0.098 | +0.197 | +0.166 | +0.166 | +0.167 |
| | **PROD** | +0.226 | +0.076 | +0.207 | +0.208 | +0.209 | +0.251 | +0.260 |
| | **Δq** | -0.033 | -0.046 | -0.012 | +0.791 | -0.017 | -0.022 | -0.022 |
| **$H_7$** | **GS** | +0.118 | +0.085 | +0.103 | +0.185 | +0.157 | +0.186 | +0.189 |
| | **TS** | +0.118 | +0.089 | +0.103 | +0.182 | +0.151 | +0.151 | +0.152 |
| | **PROD** | +0.126 | +0.090 | +0.189 | +0.189 | +0.188 | +0.228 | +0.240 |
| | **Δq** | 0.000 | +0.004 | +0.000 | -0.003 | -0.006 | -0.035 | -0.037 |
| **$H_8$** | **GS** | +0.117 | +0.085 | +0.109 | +0.214 | +0.183 | +0.184 | +0.185 |
| | **TS** | +0.102 | +0.071 | +0.094 | +0.187 | +0.152 | +0.153 | +0.155 |
| | **PROD** | +0.116 | +0.076 | +0.207 | +0.208 | +0.209 | +0.251 | +0.260 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | **Δq** | -0.219 | -0.014 | -0.015 | -0.027 | +0.031 | -0.031 | -0.030 |
| **$C_5$** | **GS** | -0.212 | -0.116 | -0.186 | -0.450 | -0.338 | -0.339 | -0.339 |
| | **TS** | -0.175 | -0.053 | -0.126 | -0.444 | -0.314 | -0.315 | -0.617 |
| | **PROD** | -0.184 | -0.187 | -0.157 | -0.505 | -0.356 | -0.818 | -0.856 |
| | **Δq** | +0.037 | -0.063 | +0.060 | +0.006 | +0.024 | +0.024 | -0.279 |
| **$H_6$** | **GS** | +0.072 | +0.041 | +0.060 | +0.139 | +0.108 | +0.109 | +0.108 |
| | **TS** | +0.070 | +0.033 | +0.050 | +0.155 | +0.121 | +0.120 | +0.122 |
| | **PROD** | +0.078 | +0.278 | +0.064 | +0.152 | +0.125 | +0.204 | +0.245 |
| | **Δq** | -0.650 | -0008 | -0.010 | +0.003 | +0.013 | +0.011 | +0.014 |
| **$H_9$** | **GS** | +0.091 | +0.053 | +0.078 | +0.177 | +0.153 | +0.154 | +0.155 |
| | **TS** | +0.083 | +0.044 | +0.065 | +0.164 | +0.135 | +0.136 | +0.160 |
| | **PROD** | +0.081 | +0.091 | +0.066 | +0.152 | +0.122 | +0.202 | +0.203 |
| | **Δq** | -0.008 | -0.009 | -0.013 | -0.013 | -0.018 | -0.018 | +0.005 |
| **$H_{10}$** | **GS** | +0.079 | +0.045 | +0.063 | +0.147 | +0.121 | +0.122 | +0.124 |
| | **TS** | +0.089 | +0.046 | +0.074 | +0.164 | +0.141 | +0.143 | +0.142 |
| | **PROD** | +0.081 | +0.067 | +0.066 | +0.152 | +0.122 | +0.202 | +0.018 |
| | **Δq** | +0.010 | +0.001 | +0.111 | +0.017 | +0.020 | +0.021 | +0.018 |
| **$C_6$** | **GS** | -0.211 | -0.113 | -0.190 | -0.453 | -0.344 | -0.345 | -0.346 |
| | **TS** | -0.178 | -0.058 | -0.131 | -0.446 | -0.317 | -0.318 | -0.319 |
| | **PROD** | -0.184 | -0.158 | -0.157 | -0.505 | -0.356 | -0.818 | -0.498 |
| | **Δq** | +0.033 | +0.055 | +0.059 | +0.007 | +0.027 | +0.013 | +0.027 |
| **$H_5$** | **GS** | +0.076 | +0.042 | +0.064 | +0.147 | +0.117 | +0.118 | +0.119 |
| | **TS** | +0.071 | +0.034 | +0.051 | +0.155 | +0.122 | +0.123 | +0.124 |
| | **PROD** | +0.081 | +0.068 | +0.064 | +0.152 | +0.122 | +0.202 | 0.212 |
| | **Δq** | -0.005 | -0.008 | -0.013 | +0.008 | +0.005 | +0.005 | +0.005 |
| **$H_{11}$** | **GS** | +0.076 | +0.043 | +0.062 | +0.147 | +0.120 | +0.122 | +0.123 |
| | **TS** | +0.079 | +0.039 | +0.061 | +0.158 | +0.128 | +0.128 | +0.127 |
| | **PROD** | +0.078 | +0.065 | +0.064 | +0.152 | +0.125 | +0.204 | +0.124 |
| | **Δq** | +0.003 | -0.004 | -0.001 | +0.011 | +0.008 | +0006 | +0.004 |
| **$H_{12}$** | **GS** | +0.084 | +0.048 | +0.069 | +0.156 | +0.131 | +0.132 | +0.133 |
| | **TS** | +0.090 | +0.048 | +0.074 | +0.165 | +0.142 | +0.165 | +0.143 |
| | **PROD** | +0.081 | +0.068 | +0.066 | +0.152 | +0.122 | +0.202 | +0.267 |
| | **Δq** | +0.006 | +0.000 | +0005 | +0.009 | +0.011 | +0.033 | +0.010 |

## 6.8.4 TABLE 5 : HEAT OF FORMATION OF t-BUTYL XANTHATE

| **H.O.F(KJ/mol)** | **GS** | **TS** | **PROD** |
|---|---|---|---|
| **AM1** | -106.434 | 0.620 | -144.599 |
| **PM3** | -51.064 | 22.711 | -141.250 |
| **RM1** | -140.398 | -36.081 | 150.178 |
| **DFT/6-31G*** | -2907205.875 | -2906992.625 | -2907064.125 |
| **DFT/6-31G**** | -2907129.750 | -2907037.875 | -2907114.000 |
| **DFT/6-31+G*** | -2907114.000 | -2907024.750 | -2907108.750 |
| **HF/321-G*** | -2884163.625 | -2883893.250 | -28883772.500 |