



Original Research Article

Molecular Modeling of the Kinetics, Mechanisms and Thermodynamics of the Gas-Phase Thermal Decomposition of O-Isopropyl S-Methyldithiocarbonate

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ARTICLE INFO

Article history

Submitted: 2020-06-24

Revised: 2020-08-20

Accepted: 2020-08-22

Available online: 2020-10-17

Manuscript ID: [AJCB-2006-1051](#)DOI: [10.33945/SAMI/AJCB/ajcb.2020.236591.1051](#)

KEYWORDS

Kinetics

Ethyldithiocarbonate

Semi-empirical

Ab-initio transition state

Xanthates

ABSTRACT

The gas-phase elimination reaction of O-isopropyl S-methyl dithiocarbonate was studied using density functional theory with a hybrid B3LYP correlation with large 6-31G*, 6-311+G** basis sets. Calculated values of the activation and thermodynamics parameters for the thermal breakdown were estimated at 623.0K at interval of 25K. The entropy change was $\Delta S = (-29.842)$ and (-28.48) J/mol/K; free energy change $\Delta G = 181.491$ and 131.164 kJ/mol and enthalpy change $\Delta H_{\text{reaction}} = 162.808$ and 113.720 kJ/mol; activation energy $E_a = 167.988$ and 118.897 kJ/mol; Arrhenius factor $A = 3.56 \times 10^{11}$ and 4.20×10^{11} and rate constant $k = 1.4 \times 10^{-2}$ and 2.9×10^{-3} , $4.45 \times 10^{-1} \text{ s}^{-1}$ compared well with the experimental results at 623K $\Delta S(-29.842 \text{ J/mol/K})$ $\Delta G = (181.491 \text{ kJ/mol})$, $\Delta H = (162.808 \text{ kJ/mol})$, $E_a = (167.988 \text{ kJ/mol})$, $A = (3.56 \times 10^{11})$ rate constant $k = (1.4 \times 10^{-2})$. The results showed the influence of electron donating group on the kinetics and thermodynamics parameters of xanthates. It affirms concertedness of the elimination mechanism via a two-step reaction. The first being the liberation of ethylene an intermediate (methyl dithiocarbonate) through a 6-membered transition state (TS). The second step involves decomposing the intermediate through 4-membered cyclic TS to produce carbonylsulphide and thiol which involves a C-H and C-O bond breaking and S-H bond formation. Intrinsic reaction coordinate (IRC) calculation was done on each of the TS structures to verify that they each connect to their respective minima. Wilberg bond index was employed to monitor the reaction progress and it shows that the TS possess 'an early' character closer to the reactant than the products.

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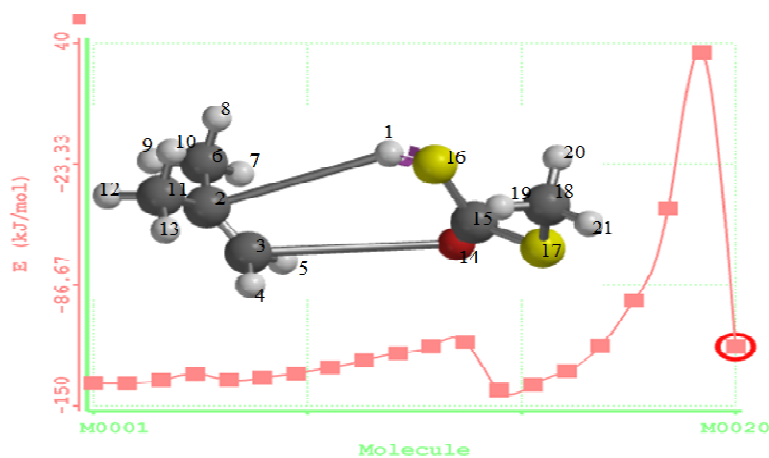
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GRAPHICAL ABSTRACT

**Introduction**

Ab initio chemistry methods are computational chemistry methods based on quantum chemistry [1,2]. Ab initio quantum chemistry methods attempt to solve the electronic Schrödinger equation given the positions of the nuclei and the number of electrons in order to yield useful information such as electron densities, energies and other properties of the system [3]. Computational chemistry aimed at solving Schrodinger equations for electronic and nuclear motions using different functional such as Hartree Fock, Density Functional theory (DFT) and semi-empirical methods. It is a method that generates data to complement experimental data on structures, properties and reactions of substances [4].

Advancement in computational chemistry has allowed quantum mechanical calculations to support research in green chemistry and it has contributed immensely to the green nature of chemical practices [3]. The ability to run these calculations has enabled theoretical chemists to solve a range of problems and their importance [5].

The gas phase thermal decomposition of O-isopropyl, S-methyl Xanthates has been reported to give propene and methylthiocarbonates which then decomposes to carbonyl sulphide and a thiol. 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. [6-9].

According to experimental reports [10], the mechanism of the reaction follows a concerted 6-membered cyclic transition state. Kinetically, the dithiocarbonates (Xanthates) can be categorized to the group where oxygen atom is involved in bonding i.e. *O-alkyl*, and where oxygen is not involved which is *S-alkyl*, [6,11] reported that all studied Xanthates: O-alkyl xanthates and S-alkyl dithiocarbonates gives a good kinetic report and passed the tests for homogeneity [11]. The first reporter of systematic observation on xanthates having several *S-substituents* came up with suggestion that thermal stability decreases with the attachment of electronegative groups to the thiol Sulphur; which eventually results in temperature decreased of the pyrolysis [12].

Many of the unimolecular reactions in gas-phase which have been studied appeared to occur through 4-center and 6-center cyclic process [13].

A study by Connor and Nace [14] indicated the same stability order for the alternative cholesterol component in S-substituted Xanthates. Although, there are numbers of experimental researches on the gas phase thermal decomposition of alkyl Xanthate in which few works have been reported on the theoretical studies on the kinetics, thermodynamics and mechanism using computational approach [15].

The gas-phase thermal decomposition of alkyl Xanthates takes place through an intensive fragmentation and product could be conceived through hydrogen atom abstraction from a terminal carbon and the transfer β -hydrogen atom is part of the six-member cyclic transition state which involves a hydrogen-sulphur (H-S) bond making; carbon-hydrogen (C-H) and carbon-oxygen (C-O) bonds breaking [16]. The thermal decomposition of alkyl Xanthate gives Olefins together with gaseous carbonyl sulphide and a thiol [17].

In recent work, the effects of the attachment on pericyclic process like alkyl xanthate determining the nature of substituent which influences the feasibility of the reaction relating with the work that has been carried out recently on the thermodynamics and kinetics thermodynamics of ethyl xanthates [18], it is evident that there is paucity of information on the effect of alkyl or attachment attached to the O-alkyl moiety on the kinetics and thermodynamic parameters of xanthate. Therefore, the aim of this work is to use computational approach to study the influence of electron donating groups attached to the O-alkyl moiety of the xanthates on the thermodynamic and kinetics parameters to show the effect on activation and kinetics parameters [19].

Computational procedure

Conformational Search

The molecules were set up for pre-optimization by search for conformers with the least possible energy value. The molecular mechanics force field (MMFF), a model that has shown good ability for determining lowest conformer energy, was employed. MMFF has also proven to be efficient in quantifying estimated conformer energy differences [20]. Seven conformers were obtained, and their heats of formations are shown in **Fig. 1**.

Fig. 2 shows the stoichiometry of the reaction. A β -hydrogen is to be removed from the isopropyl moiety and transferred to the other side of the -O- part to form a -S-H group of the methyl dithiocarbonate product. This was evident by the acute negative dihedral angle that results.

Reaction path study

The optimized structures of O-isopropyl (dithiocarbonates) Xanthates were subjected to reaction path study. This was achieved by taking the H₁-S₁₆ bond length as the typical coordinate for the reaction. The value of the initial internal coordinate in the steady reactants was adjusted gradually to the fair accurate length in the product. O-isopropyl xanthates, for instance, was studied by setting the H₁-C₂ bond length gradually from 4.723Å in about 20 steps to 1.200Å, being the estimated value in the product. McIver and Kormonicki [21] in their work reported that rather than the reaction path energy rising to a very a high potential through a maximum, it abruptly falls to product. This is accompanied by a decrease in the enthalpy of formation, though relatively close to that of the products, i.e. Methyl dithiocarbonates and Propene. This is presented in **Fig. 3**.

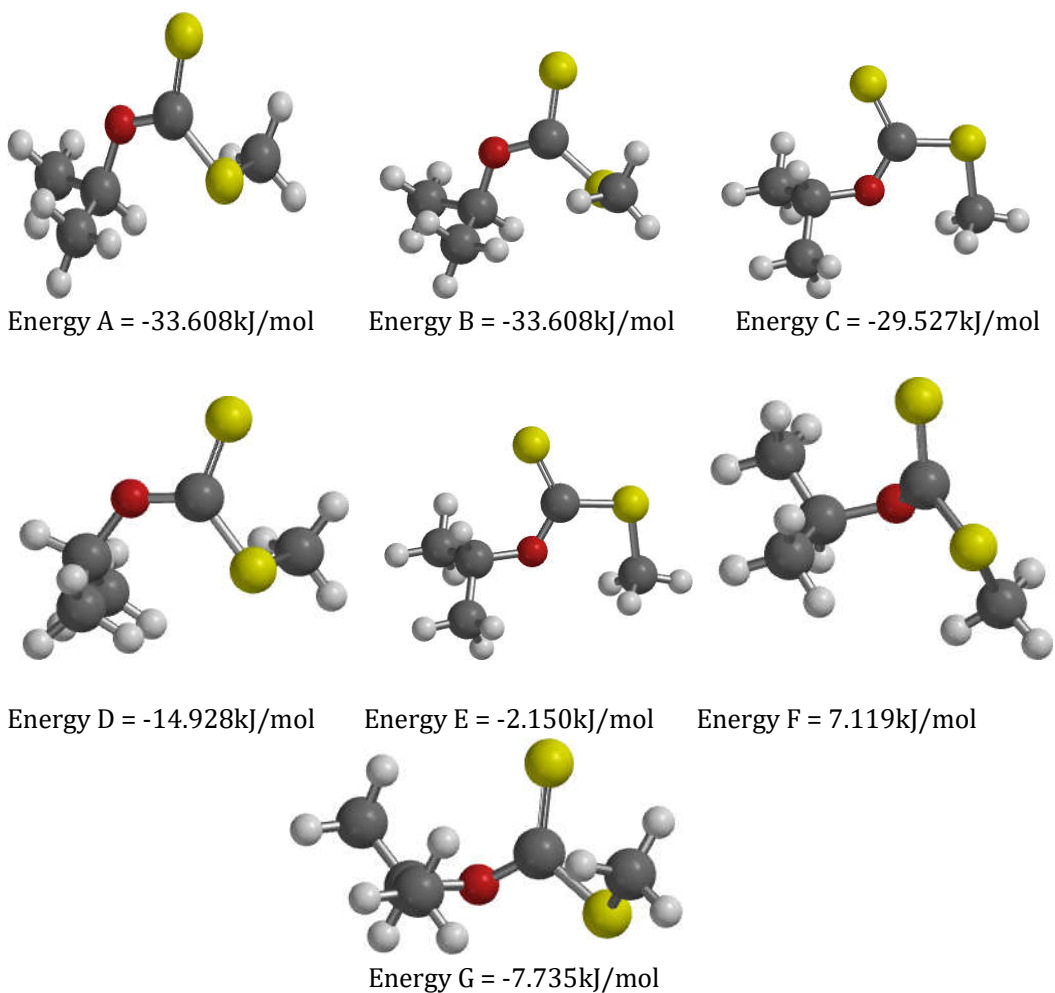
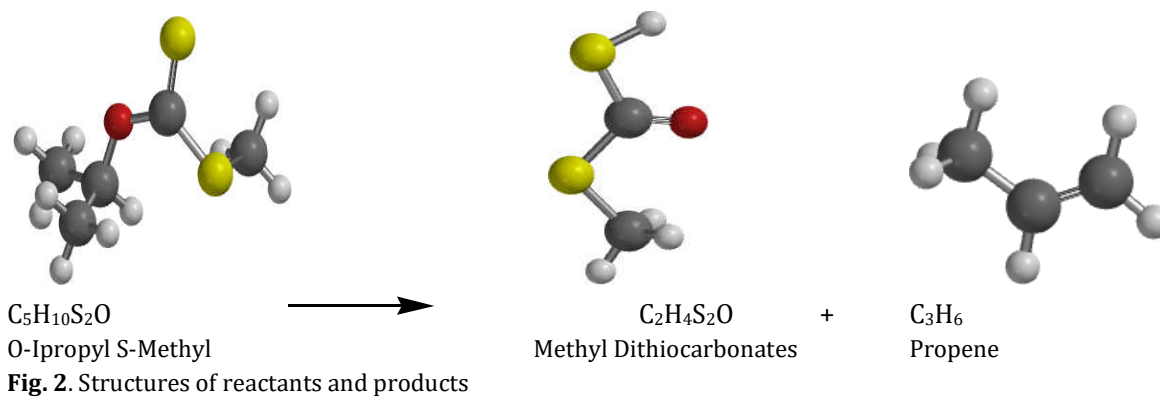


Fig. 1. Conformer distribution of O-isopropyl S-methyl Xanthates with their corresponding energy values



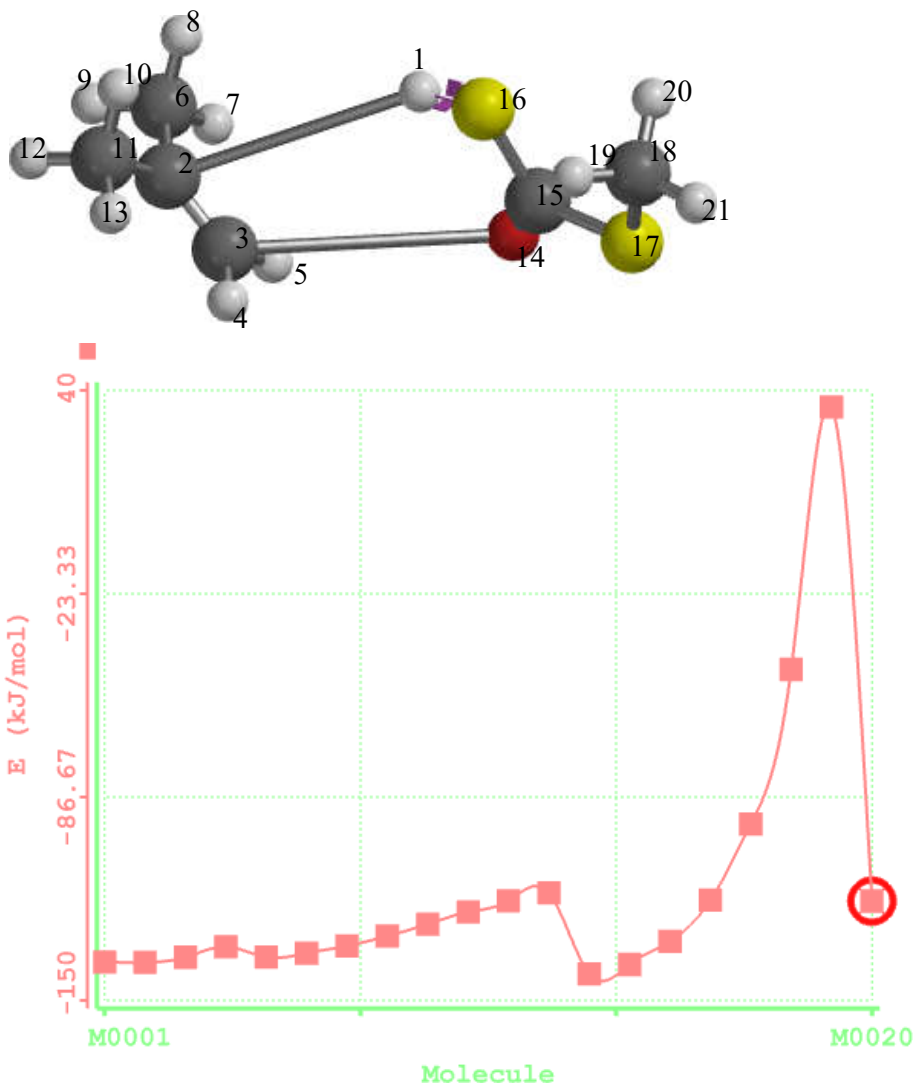


Fig. 3. Reaction path study O-isopropyl S-methyl dithio

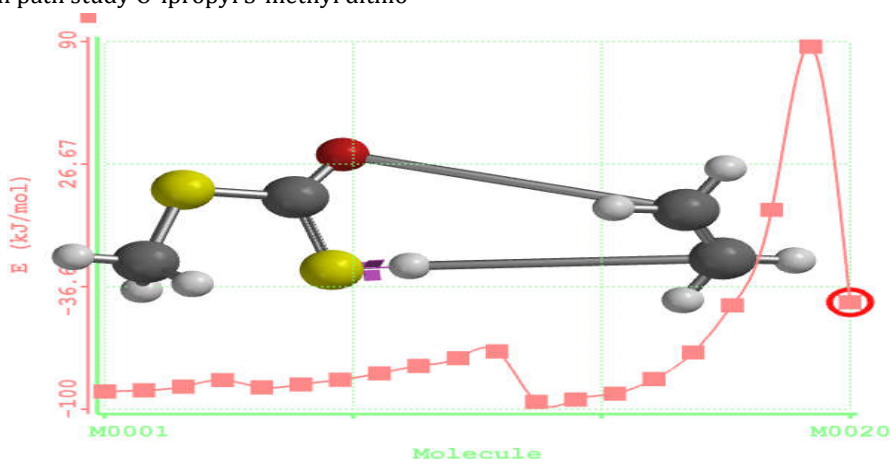


Fig. 4. A plot of energy against the number of molecules to depict the reaction path studies.
Transition State Structure

The potential energy surface (PES) provides a fundamental knowledge of the relation between structures and stability of stable molecules to the minimal enthalpy the length side of the reaction path. In this case, the transition state (TS) geometry corresponds to energy maxima. The basic idea is that steady molecules unified by an even pathway which goes through sharp transition state. In order to overcome the challenge of locating the TS structure, the guess-TS structure provided by the suggested mechanism was optimized and put through the two-test needs. This is resourceful and pivotal in locating the saddle-point i.e. transition state. It also helps to show that the TSs connect the reactants as well as the products.

The tests are that:

- (i) the Hessian matrix of second-order energy derivatives when compared to coordinates gives only a single imaginary frequency within the range of 400-2000 cm^{-1} , and
- (ii) Normal coordinates match up to the imaginary frequency slickly connects both reactants and products. This is obtained when the regular coordinate is animated.

Intrinsic Reaction Coordinate

Each molecule was optimized by being subjected to a fixed point on the reaction path with the aid of intrinsic reaction coordinate (IRC) [20]. This method helps to affirm the transition states. The first IRC calculation, known as positive perturbation, was based on atomic coordinate directed towards a single negative frequency. The second, being negative perturbation, is done on the same typical coordinate.

Mechanism of decomposition of Alkyl Dithiocarbonates (Xanthates)

The Chugaev reaction [22] is comparable to thermolysis of alcoholic carboxylic esters as well

as other alcohol derivatives including carbamates and carbonates. The xanthates reaction mechanism is a fragment of concertedness. However, the product formation may result from abstraction of β -hydrogen through the thiol or thione sulphur atom in the reaction route. This is shown in **Fig. 5**.

Mechanism A is a one-step reaction wherein the products were formed at a goal. On the other hand, mechanism B is a complex reaction giving intermediate products alkene and an unstable dithiocarbonate derivative. The unstable intermediate then breaks down to give carbonyl sulphide and a thiol, i.e. the desired products. Huckel *et al.*, [23] hypothesized mechanism A while Barton [24] projected the mechanism B. The research work of Bader and Bouns [25] on the effects of ^{14}C and ^{13}C isotope on the pyrolysis of trans-2-methyl-1-indanyl Xanthate with normal isotopic loads reveals the experimental indication of thio posing an attack on the β -hydrogen rather than usual thiol nor sulphur atoms.

Kinetics and thermodynamic parameters

The thermodynamic parameters achieved for isopropyl xanthate was from calculations of the ground state (GS), transition state (TS) and the products structures. The statistically mechanistic premeditated enthalpy and the ground state energy (GSE) were summed up to obtain the approximate molecular energy. This was necessitated by the fact that high percentage of molecule's energy is domiciled in the bonds and physical geometry. The energy of a molecular entity is defined as;

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

SM denotes statistical mechanistically determined energy.

When substituted into initial description of enthalpy of reaction gives equation 2.

$$\Delta H_{rxn} = (GSE_p + H_p^{sm}) - (GSE_r + H_r^{sm}) \quad 2$$

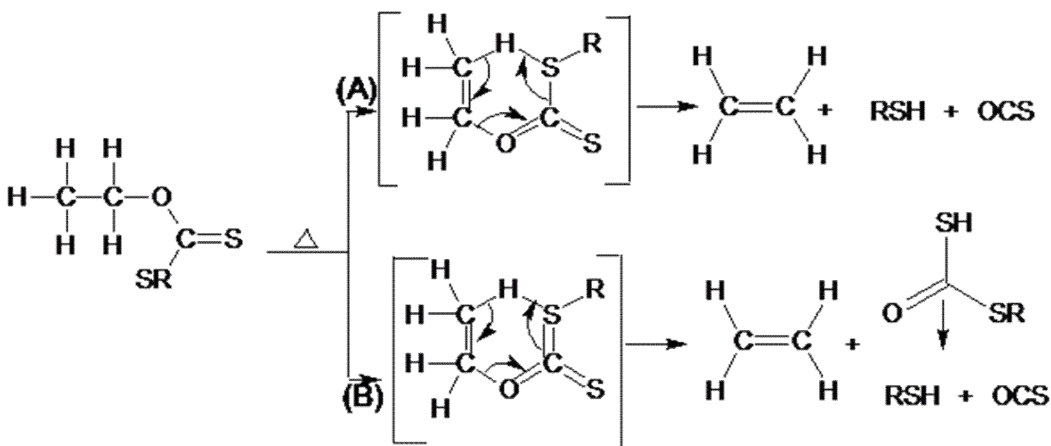


Fig. 5: Reaction Mechanism

The activation barrier, E_a , was determined in line with the transition state model for reaction involving one molecule at 623K;

$$E_a = \Delta H + RT \quad 3$$

The reaction entropy was evaluated by finding the difference between entropies of the products and that of the reactants.

$$\Delta S_{rxn} = S_p - S_r \quad 4$$

$$\Delta S_{activated} = S_{ts} - S_r \quad 5$$

The Gibb's free energy was determined by modifying the equation for heat of reaction i.e.

$$G = H - TS; \quad \Delta G^* = \Delta H^* - T\Delta S \quad 6$$

The transition state theory, [26] which proposes that the co-efficient of transition is unity, was employed to determine the first-order co-efficient k_T .

$$k_T = K \frac{T}{h} e^{-G^*/RT} \quad 7$$

ΔG^* represents change in Gibb's free energy between reactants and transition state; K is the Boltzmann constant and h is the Planck's constant.

The Arrhenius factor is expressed as;

$$A = K_B \frac{T}{h} e^{-\Delta S/R} \quad 8$$

By the use of the rate equation, Arrhenius rate is given as;

$$k_T = A e^{-E_a/RT} \quad 9$$

Wiberg bond indices

Moyano *et al.*, [23] termed the comparative disparity of the bond indices of the reactant, transition state and the product (∂B_i) for each bond i , associated with a chemical reaction as

$$\partial B_i = \frac{B_i^{ts} - B_i^r}{B_i^p - B_i^r} \quad 10$$

Terms r , ts and p in equation (10) refers to the reactant, transition state and product respectively. Hence, percentage of evolution ($\%E_v$) of the order of the bonds can be evaluated by given chemical steps.

$$\%E_v = 100\partial B_i \quad 11$$

As hypothesized by Taylor, [27] C_{α} -O bond breaking ahead of C_{β} -H bond agrees with information available from experimental study for 1,5 thermolysis. This relies on the evidence that Hammett P-values of the α -carbon are higher than those for β -carbon. It can also be inferred that greater dissociation potential of C_{α} -O bond account for increased reaction rate. On the other hand, greater dissociation potential of C_{β} -H bond accounts for reduced rate of reaction.

The average value of the bond indices δB_{av} is calculated as

$$\delta B_{av} = \frac{1}{n} \sum \partial B_i \quad 12$$

Where n represents number of bonds engaged in the reaction coordinate. It is a measure of the

level of progression of the transition state the length of the reaction coordinate. As it can be shown, the δB_{av} values show that there is difference between the two pathways of the Chugaev reaction.

The measure of how synchronous a chemical reaction is expressed as:

$$S_y = 1 - A \quad 13$$

A represents asynchronicity evaluated by using the proposal of Moyano *et al.*, [23].

$$A = \frac{1}{(2n-2)} \sum \frac{|\partial B_i - \partial B_{av}|}{\partial B_{av}} \quad 14$$

Synchronicity ranges from 0 to 1, being the limit where all bonds along the reaction path are broken or formed at closely the same level in the transition states.

Result and discussion

The pyrolysis of O-isopropyl S-methyl Xanthates (dithiocarbonates) initiated from hydrogen (H) atom that is attached to β -carbon which is removed from alkyl moiety of the Xanthate which first gives propene (C_3H_6) and methyl dithiocarbonates (CH_3SCOSH), the methyl dithiocarbonate decomposes further to yield methyl sulphide and thiol from the reaction path as shown in **Fig. 5**.



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 **Fig. 3** that also involving $C_1 - O_3$ and $C_{15} - H_{16}$ bond cleavages and a $S_5 - H_{16}$ bond making. The bond lengths are shown in **Table 1**. We observed a long stretching in the bond length between $C_1 - O_3$ in the ground state from 1.4689Å and 1.4625Å to 2.1830 Å and 2.1930Å in the transition state, for $C_{15} - H_{16}$ from

1.0925Å and 1.0925Å in the ground state, to 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 using **B3LYP/6-31+G*** and **DFT/B3LYP/6-311+G**** methods respectively. The bond angles and dihedrals are shown in **Table 2** and **3** below. The Mulliken charges represent the atomic charges and they provide simple and logical estimates of the atomic charges. From **Table 1** below showing the bond length, the two dotted lines in the bonds of $C_1 - O_3$ and $C_{15} - H_{16}$ shows the point where cleavage occurs with a lengthy stretch in the bond length at the transition state, which leads to a bond is formation between $S_9 - H_{16}$. The variation observed in the bond angle (**Table 2**) and in the dihedral angle (**Table 3**) is as a result of the distortion that occurs during the breaking and the formation of new bonds [16]. Atomic charge (**Table 4**) calculation is very important to molecular systems because it affect molecular properties like polarizability, dipole moment and electronic structures. Atomic charge was calculated in Mulliken charge distribution for the reactant, transition and product state, as given in **Table 4** at the transition state (TS), shows that H_{16} has the leading charge population while C_1 has the least charge population [25]. The reason for the increase in positive charge development on C_1 and C_{15} carbon atoms from **Table 4**, is as a result of charge polarization of the bonds between $C_1 - O_3$ and $C_{15} - H_{16}$ which also causes the sulphur atom (S_5) atom to become more negative. The intermediate formation of methyl dithiocarbonates in the mechanism of the reaction in (**Fig. 5**) is caused by the positive charge cloud on the β -hydrogen H_{16} atom which attack ethyl vinyl carbon C_{15} which is negatively charged shown in **Table 4** [25].

Table 1. Bond length for the pyrolysis of o-isopropyl s-methyl dithiocarbonates

BOND (Å)	STATE	DFT/B3LYP/6-31G*	DFT/B3LYP/6-311+G**
C ₁₅ -H ₁₆	GS	1.10	1.09
	TS	1.22	1.23
	PRD	-	-
	$\Delta d(\text{TS-GS})$	0.13	0.11
C ₁ - C ₁₅	GS	1.52	1.52
	TS	1.41	1.41
	PRD	1.33	1.33
	Δd	-0.11	-0.10
C ₁ - O ₃	GS	1.47	1.47
	TS	2.22	2.18
	PRD	-	-
	Δd	0.75	0.71
O ₃ - C ₄	GS	1.33	1.33
	TS	1.24	1.24
	PRD	1.20	1.20
	Δd	-0.09	-0.08
C ₄ = S ₅	GS	1.65	1.65
	TS	1.73	1.73
	PRD	1.81	1.83
	Δd	0.09	0.08
C ₄ - S ₆	GS	1.79	1.79
	TS	1.80	1.79
	PRD	1.79	1.79
	Δd	0.01	0.01
S ₆ - C ₇	GS	1.82	1.82
	TS	1.83	1.83
	PRD	1.83	1.83
	Δd	0.01	0.01
S ₅ - H ₁₆	GS	4.97	3.00
	TS	1.87	4.98
	PRD	1.35	1.90
	Δd	-3.10	1.35
			-3.07

Note: $\Delta d = d(\text{TS}) - d(\text{GS})$

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

Table 2: selected bond angle for the pyrolysis of o-isopropyl s-methyl dithiocarbonates

BOND (°)	STATE	DFT/B3LYP/6-31G*	DFT/B3LYP/6-311+G**
H ₁₆ - C ₁₅ - C ₁	GS	110.452	110.504
	TS	103.610	103.820
	PRD	-	-
C ₁₅ - C ₁ - O ₃	GS	105.056	105.196
	TS	103.780	105.840
	PRD	-	-
C ₁ - O ₃ - C ₄	GS	124.897	124.755
	TS	120.89	121.580
	PRD	-	-
O ₃ - C ₄ =S ₅	GS	119.721	129.905
	TS	125.441	125.280
	PRD	123.974	123.678
O ₃ - C ₄ - S ₆	GS	115.359	115.214
	TS	119.206	119.297
	PRD	124.506	124.567
S ₅ = C ₄ - S ₆	GS	124.917	124.878
	TS	115.345	115.415
	PRD	111.520	111.682
C ₄ - S ₆ - C ₇	GS	102.094	102.390
	TS	100.695	101.420
	PRD	98.139	98.136
S ₁₁ - C ₁ - C ₁₅	GS	113.482	113.630
	TS	123.025	122.880
	PRD	125.257	125.250

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

Table 3. Selected bond dihedral for the pyrolysis of o-isopropyl s-methyl dithiocarbonates

BOND (°)	STATE	DFT/B3LYP/6-31G*	DFT/B3LYP/6-311+ G**
O ₃ - C ₁ - C ₁₅ - H ₁₆	GS	-60.504	60.628
	TS	-11.35	-12.59 ⁰
	PRD	-	-
C ₁ - O ₃ - C ₄ = S ₅	GS	-177.657	-176.833
	TS	35.810	37.420
	PRD	-	-
O ₃ - C ₄ - S ₆ - C ₇	GS	178.224	178.781
	TS	-3.82	-4.260
	PRD	-0.000	-0.000
S ₅ = C ₄ - S ₆ - C ₇	GS	-1.200	-0.571
	TS	177.148	176.71
	PRD	180.000	180.000
H ₁₃ - C ₁₅ - C ₁ - C ₁₁	GS	58.716	58.781
	TS	91.21	93.09
	PRD	-	-
C ₄ - O ₃ - C ₁ - C ₁₅	GS	-150.967	-149.948
	TS	-4.62	-5.320
	PRD	-	-

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

Table 4. Atomic charges (mulliken) of o-isopropyl s-methyl dithiocarbonates

ATOM	STATE	DFT/B3LYP/6-31G*	DFT/B3LYP 6-311+G*
H ₁₆	GS	+0.168	+0.159
	TS	+0.157	+0.120
	PRD	+0.129	+0.093
	$\Delta q(TS-GS)$	-0.011	-0.039
C ₁₅	GS	-0.448	-0.417
	TS	-0.499	-0.358
	PRD	-0.333	-0.547
	Δq	-0.051	+0.155
C ₁	GS	+0.090	-0.185
	TS	+0.085	+0.030
	PRD	-0.041	-0.043
	Δq	-0.005	+0.215
O ₃	GS	-0.394	+0.205
	TS	-0.452	-0.089
	PRD	-0.389	-0.207
	Δq	-0.058	-0.294
C ₄	GS	+0.065	-0.074
	TS	+0.088	+0.054
	PRD	+0.098	+0.079
	Δq	+0.023	+0.128
S ₅	GS	-0.191	-0.291
	TS	-0.158	-0.302
	PRD	-0.011	-0.112
	Δq	0.033	-0.011
S ₆	GS	+0.156	-0.009
	TS	+0.150	-0.011
	PRD	+0.158	+0.084
	Δq	-0.006	-0.002
C ₇	GS	-0.593	-0.459
	TS	-0.586	-0.515
	PRD	-0.587	-0.511
	Δq	0.007	-0.056

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

Wiberg Bond Order for O-isopropyl Xanthate

Using Wiberg bond equations [23] variation of bond indices δB_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 5**. The result obtained for

the O-isopropyl xanthates, the breaking of the bond C₅-O₇ with 71.6% is the most leading process accompanied by the changing of the bond (S₉-C₈) from double bond to single bond with a percentage evolution 58.2% and also conversion of C₉-O₈ single bond of 56% to double bond. The simplest of the process is the formation of the C₅-

C₁₅ double bond of 30.2% accompanied by the formation of S₉-H₁₆ bond at 33.7% evolution and the breaking at bond C₁₅-H₁₆ of 40.8% evolution. The average value of bond indices (δB_{av}) is a measure of the degree of progression of the transition state through the reaction path for O-isopropyl S-methyl Xanthate is 0.487 indicating that the transition state formed closer to the

reactants than to the products. The synchronicity (Sy) value of the reaction for the O-isopropyl S-methyl Xanthate was 0.832, which indicate that the O-isopropyl S-methyl dithiocarbonate corresponds to high asynchronous processes. The determined Arrhenius parameters are in good order with the experimentally determined values.

Table 5. Wiberg bond indices derived parameters

Compound	State	C ₂ -C ₅	C ₂ -H ₁	H ₁ -S ₉	S ₉ -C ₈	O ₃ -C ₁	C ₁₅ -O ₃
O-isopropyl	E_i^R	1.018	0.928	0.002	1.666	1.041	0.790
S-methyl	E_i^{TS}	1.310	0.549	0.325	1.319	1.407	0.225
Xanthate	E_i^P	1.985	0.000	0.962	1.070	1.695	0.000
	δB_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
	δB_{av}	0.484					
	A	0.168					
	Sy	0.832					

Table 6. Heat of formation of the pyrolysis of o – ethyl, s-methyl x anthate (dithiocarbonates)

Methods	O-isopropyl	S-methyl	Xanthate
DFT/6-31G**	-2700797.560	-2700564.825	-2700670.875
DFT/6-31+G*	-2700804.320	-2700560.625	-2700676.125

Table 7. Arrhenius Parameters O-Isopropyl S-Methyl Xanthate (Dithiocarbonates)

	ΔS (J/mol. K)	ΔG (kJ/mol)	ΔH (kJ/mol)	Ea (kJ/mol)	A	k (S ⁻¹)
EXPERIMENTAL	-28.000	143.560	161.000	166.200	4.70X10 ¹¹	1.4x10 ⁻²
DFT/6-31G*	-29.842	181.491	162.808	167.988	3.56x10 ¹¹	2.93x10 ⁻²
DFT/6-3+1G**	-28.480	131.164	113.720	118.897	4.20x10 ¹¹	4.45x10 ¹

Table 8. Variation of rate of reaction (sec⁻¹) with Temperature (K)

Temp(K)	DFT/6-31G*	DFT/6-31+G**
373	1.56X10 ⁻¹⁰	4.56X10 ⁻⁷
398	2.37X10 ⁻⁹	3.56X10 ⁻⁶
423	8.11X10 ⁻⁹	9.57X10 ⁻⁴
448	1.11X10 ⁻⁸	6.167X10 ⁻³
498	9.16X10 ⁻⁷	1.46X10 ⁻¹
523	6.24X10 ⁻⁶	5.72X10 ⁻¹
548	3.54X10 ⁻⁵	1.966
573	1.74X10 ⁻⁴	6.130
598	7.57X10 ⁻⁴	17.400
623	2.93X10 ⁻³	44.5

Spectra of O-Isopropyl, S-Methyl Xanthate

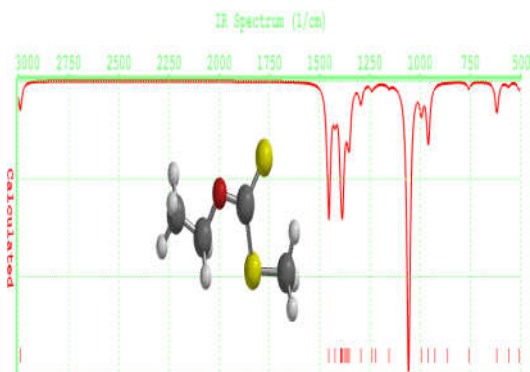


Fig. 6: Ground State (GS) of O-ethyl, S-methyl Xanthates

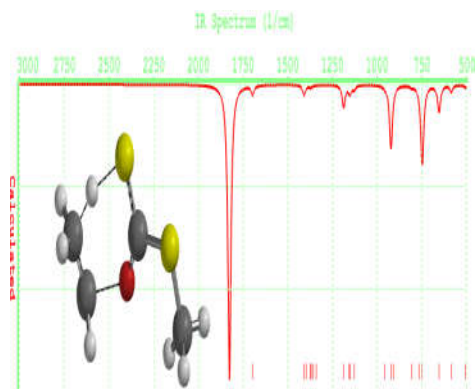


Fig. 7: Transition State (TS) of O-ethyl, S-methyl Xanthates

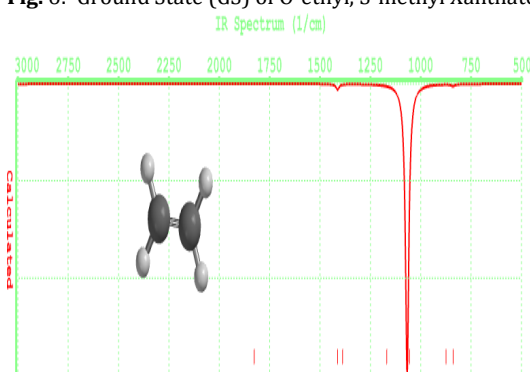


Fig. 8: Product1 Ethene of O-ethyl S-methyl Xanthates

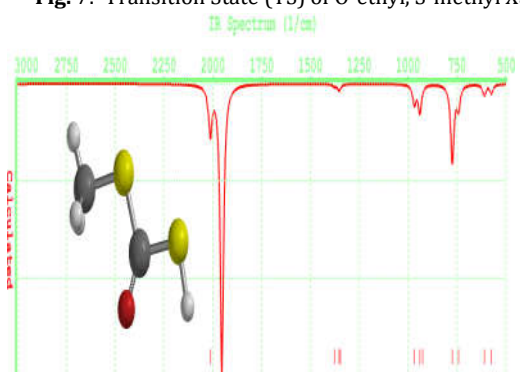


Fig. 9: Product 2 Methyl Dithiocarbonate of O-ethyl, S-methyl Xanthates

Conclusion

This study presented the theoretical calculations of the kinetics and mechanism as well as thermodynamics of the thermal decomposition of O-isopropyl, S-methyl 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 at B3LYP/6-31G* and 6-31+G** basis sets. It was discovered that the difference in the geometric features is more than an order of magnitude.

It was also discovered that these calculation methods could effectively be used to study the kinetics, mechanism and thermodynamics of thermal decomposition of O-isopropyl S-methyl xanthates in the gas phases because the result

obtained at B3LYP/6-31G* and 6-31+G** basis sets for the enthalpy of activation ΔH^* (162.808 and 113.702kJ/mol), Gibbs free energy of activation ΔG^* (181.49 and 131.164kJ/mol), change in entropy ΔS^* (-29.842 and -28.480J/mol) and activation energy, E_a (167.988 and 118.897kJ/mol) rate of reaction k (2.93×10^{-2} and 4.45×10^{-2}) are in good agreement with the experimental values $\Delta S = -28.00$ J/mol/K, $\Delta G = 143.560$ kJ/mol, $\Delta H = 161$ kJ/mol, $\Delta E_a = 166.2$ kJ/mol, $A = 4.70 \times 10^{11}$ and $k = 1.4 \times 10^{-2}$ (S⁻¹) [9]. 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 [16,28]. This is an indication that computational modeling is an environmentally friendly

methodology because it helps researchers to get insight into the reaction mechanism, rate of reactions, quantity of heat required etc. This fore knowledge helps to reduce cost, time of laboratory experiments and most importantly the level of exposure to release of hazardous chemicals.

References

- [1] N. Levine, Ira Quantum Chemistry. Englewood Cliffs, New jersey: Prentice Hall. (1991). 455–544. ISBN 978-0-205-12770-2.
- [2] G. Parr., D. P. Robert; I. G. Craig; Ross, "Molecular Orbital Calculations of the Lower Excited Electronic Levels of Benzene, Configuration Interaction included". *Journal of Chemical Physics*. 18 (1950) 1561–1563.
- [3] Leach, Dr Andrew. Molecular Modelling: Principles and Applications (2 ed.). Harlow: Prentice Hall. (2001).
- [4] P. Schlexer. Computational Modeling in Heterogenous Catalysis. *Elsevier*. (2017). DOI: 10.1016/B978-0-12-409547-2.14273-8
- [5] R.G. Parr. "On the genesis of a theory". *Int. J. Quantum Chem*. 37 (1990) 327–347.
- [6] A. Al. Etaibi., E John., M. R Ibrahim., N. A. Al-Awadi., Stereoselective synthesis of dihydrothiadiazinoazines and dihydrothiadiazinoazoles and their pyrolytic desulfurization ring contraction *Tetrahedron* Vol. 67 (2011) 6259-6274.
- [7] E.V. Anslyn, D. A. Dougherty. Mordern physical organic chemistry-University Science books. (2004) 1-1952.
- [8] P. Wu., J. Truong., Y .Huang., J.Li, Regioselectivity Investigation For The Pyrolysis Of Xanthates: Computational study. *Journal of theoretical and computational chemistry*. Vol. 12 (2013) 1350064.
- [9] E. Velez, J. Quijano, R. Notario, E. Pabon, J. Murillo, J. Leal, E. Zapata, G. Alarcon. A computational study of stereospecificity in the thermal elimination reaction of methyl benzoate in the gas phase, *Journal of Physical Organic Chemistry* 22 (2009) 971.
- [10] N. AL-Awadi, D.B. Bigley. Carbonate Pyrolysis. Part 6. The kinetics and mechanism of the pyrolysis of Thion and Dithio-carbonates implications for the Transition state in carbonate pyrolysis. *J. Chem. Soc. Perkin Trans. 2* (1982) 773-775.
- [11] O.O. Adeboye., The kinetics and thermodynamics of the Diels-Alder reaction of acrolein and 1, 3-butadiene to produce 3-cyclohexenecarboxaldehyde (1, 2, 3, 6Tetrahydrobenzaldehyde), a fragrance and masking ingredient used in many skin care products was modelled in the gas-phase. *Journal of Chemical Society of Nigeria* 44 (2019) 1095 -1105.
- [12] I.M. Mc-Aplpine. Name Reactions of functional group Transformation *Journal of Chemical Society* 906 (1930) 15114-15123.
- [13] H.E. O'Neal, S.W. Benson. A Method for Estimating the Arrhenius A factors for Four- and Six-centre Unimolecular Reactions, *J. Phys. Chem*. 71 (1967) 2903 - 2921.
- [14] N. Al-Awadi. The mechanism of Thermal Elimination. Part 24. Elimination From Mono Di and Trithiocarbonates. The Dependence of the Transition State polarity, Thione to Thiol Rearrangement and Ether Formation via Nucleophilic Substitutions. *J. Chem. Soc. Perkin Trans. 2*, (1988) 197-182.
- [15] I. A. Adejoro, T. O. Bamkole. Semi-empirical quantum mechanical, molecular orbital method using MOPAC, calculation of the Arrhenius parameters for the pyrolysis of some alkyl acetates. *J. Appl. Sci.*, 5 (2005). 1559-1563.

- [16] O.O. Adeboye, I.A. Adejoro, A. M. Olatunde. Computational Modelling of the Kinetics and Thermodynamics of Diels-Alder reaction: 1,3-cyclohexadiene and substituted ethene. *Leonardo Electronic Journal of Practices and Technologies*. (2018). 33, July-December 207-218.
- [17] A.C West, M.W Schmidt, M.S Gordon, K. Ruedenberg. A Comprehensive Analysis in Terms of Molecule-Intrinsic Quasi-Atomic Orbitals. IV. Bond Breaking and Bond Forming along the Dissociative Reaction Path of Dioxetane. *The Journal of Physical Chemistry A*. 119 (2015)10376–10389.
- [18] I. A. Adejoro, T. O. Esan., O. O Adeboye, B. B Adeleke. Quantum mechanical studies of the kinetics, mechanisms and thermodynamics of gas-phase thermal decomposition of ethyl dithiocarbonate (xanthate). *Journal of Taibah University for Science*, 11 (2017) 700–709.
- [19] G. Sudhakar, B. Rajakumar. Thermal decomposition of 1-chloropropane behind the reflected shock waves in the temperature range of 1015–1220 K: Single pulse shock tube and computational studies. *Journal of Chemical Sciences*, 126 (2014) 897–909.
- [20] W.J. Hehre. Guide to Molecular Mechanics and Quantum Chemical Calculations Hardcover. (2003).
- [21] J.W. McIver Jr, A. Kormonicki. Rapid Geometry optimization for Semi- Empirical molecular Orbital Methods. *Chem. Phys. Letts*. 10 (1971) 303.
- [22] S.W. Benson. The foundations of chemical kinetics, Mcgraw-Hill, New York 1-30 of 79 (1960).
- [23] A. Moyano, M.A. Pericas, E. Valenti. A theoretical study on the mechanism of the thermal and the acid-catalysed decarboxylation of 2-oxetanones (beta lactones) *J. Org. Chem.* 54 (1989) 573-582
- [24] R. Taylor. The mechanism of thermal elimination. *Journal of Chemical Society, Perkin Transaction*. 2 (1983) 291-296.
- [25] V.M. Lee, M. J. Carden, W.W. Schlaepfer, J. O. Trojanowski. Monoclonal antibodies distinguish several differentially phosphorylated states of the two largest rat neurofilament subunits (NF-H and NF-M) and demonstrate their existence in the normal nervous system of adult rats. *J. Neurosci.*, 7 (1987) 3474-3488.
- [26] R.F.W. Bader, A.N. Bourns. A kinetic isotope effect study of the Tschugaeff reaction, *Canadian Journal Chemistry* 3 (1961) 348-358.
- [27] W. Huckel, W. Tappe, G. Legutke. Abspaltungsreaktionen und ihr sterischer verlauf, *Ann.* 543 (1940) 191.
- [28] O.O. Adeboye. Computational Modelling of the Mechanisms, Kinetics and Thermodynamics of Pyrolysis of Isobutyl Bromide in the Gas-Phase. *Chemical Science International Journal* 18 (2017) 1-9

HOW TO CITE THIS ARTICLE

Timothy Oluwaseun Esan, Oluwatoba Emmanuel Oyeneyin, Eric Oluwafisayo Akintemi, Isaiah Ajibade Adejoro, Babatunde Benjamin Adeleke, Molecular Modeling of the Kinetics, Mechanisms and Thermodynamics of the Gas-Phase Thermal Decomposition of O-Isopropyl S-Methyldithiocarbonate, Ad. J. Chem. B, 3 (2021) 1-15
DOI: 10.33945/SAMI/AJCB/ajcb.2020.236591.1051
URL: http://www.ajchem-b.com/article_118051.html

