

Quantum mechanical study on the kinetics and thermodynamics of O-alkyl S-methyl dithiocarbonates through α - and β -elimination pathways

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Abstract

The study of α - and β -elimination pathways through pyrolysis on the kinetics and thermodynamics of O-alkyl S-methyl Xanthates in which the alkyl groups are ethyl, n-propyl, i-propyl, n-butyl, i-butyl and t-butyl were carried out in the gas-phase using density functional theory (DFT) with B3LYP at 6-311++G** using Spartan. The mechanism proceeded through a six-centered cyclic transition state. The result obtained for the C-H, C-O and S-H bond lengthening character in a single step suggested that the reaction is a concerted and asynchronous. The energy of formation for the α -elimination pathways is lower compared to the β -elimination initiated from the hydrogen of the β -carbon. The activation parameters obtained for the β -elimination pathways ranged from ΔH^* (161.34-133.87 kJ/mol), ΔS^* (-31.18-25.65 J/mol/K), ΔG^* (180.65-149.77 kJ/mol) E_a (166.49-136.82 kJ/mol), $k = 1.14 \cdot 10^{-3}$ - $6.0 \cdot 10^{-2} S^{-2}$), A ($3.06 \cdot 10^{11}$ - $5.89 \cdot 10^{11}$). In addition, α -elimination pathway activation

parameters for isopropyl and tbutyl are in good agreement with the experimental values.

Keywords

O-alkyl S-methyl Xanthate; Pyrolysis; Dithiocarbonates; Elimination pathways; DFT Calculation

Introduction

The Chugaev elimination is broadly defined as the thermal decomposition of pyrolysis of a xanthate ester of an alcohol that contains at least hydrogen to produce an Olefin, Carbonyl sulphide and a thiol (Figure 1). This reaction is similar to the thermal decomposition of acetates, carbamates and carbonates to produces olefins.

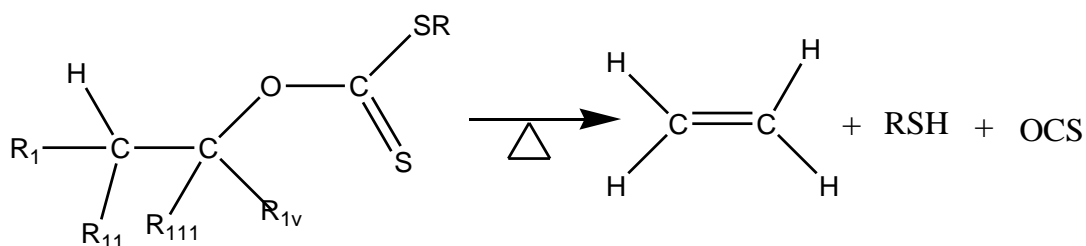


Figure 1. Chugaev Reactions [1] (where R_1 , R_{11} , R_{111} and R_{iv} are the alkyl group under consideration)

The pyrolysis of carbonate related compounds (xanthates) were valuable synthetic routes to synthesis alkenes without the rearrangement of carbon skeleton [1-11]. Their mechanisms were long debated between two possible pathways (Figure 2) [7, 8], although both pathways resulted in the same products. The pathway reported in this research proceeded through a one-step mechanism yielding an alkene, carbonyl sulphide and thiol.

Cross *et al.*, [12] and Huckel *et al.*, [13] supported the pathway reported, while Smith and Yates [5], Barton [9], and Cram [6] preferred another mechanism. Experimentally, Al-Awadi and co-worker [14] pyrolyzed a series of the esters: thiocarbonates carbamates and carbonates. The pathway of six cyclic transition state approved by the positive p-factor of Hammett correction for the pyrolysis of aryl ethyl carbonates, as well as t-butyl, N-aryl

carbonates with the reduced relativities of methyl alkyl carbonates as compared with phenyl alkyl carbonates [10, 11, 14-16]. Alexander and Mudrack also proved the other pathway, as well as the cis-elimination mechanism, by investigating the Chugaev reaction [17-19].

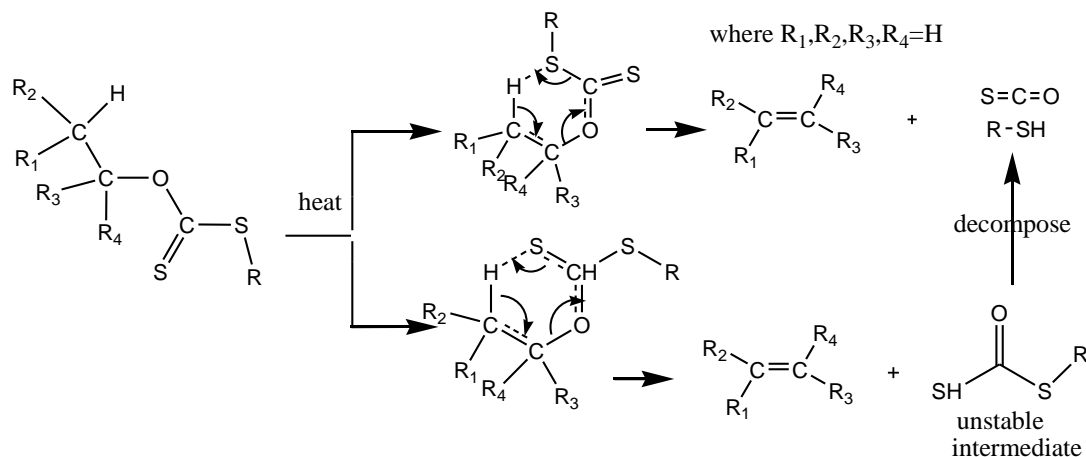


Figure 2. Mechanism of alkyl Xanthates

Bader and Borns [20] carried out isotope effect studies and found solid evidence for the pathway of six cyclic transition state. As for the theoretical studies, Lee group studied the pyrolysis of carbonate esters at AM1 level and supported the second pathway [21]. Erickson and Kahn [22] calculated the activation energies of $HSC(=S) OEt$ at MP2/6-31G(d)/ HF/6-31g(d) level in 1994. Deleuze group [23] investigated the elimination reaction (Ei) reaction of $EtSc(=S)OMe$ and its substituent effects at different theoretical levels and different basis sets and concluded that MP2 method gave comparable activation energies as CCSD(T). Harano [24] utilized B3LYP/6-31G(d) theoretical level to study the transition states of $MeSc(=S)OEt$. The regioselective pyrolysis of chugaev reaction was also investigated recently at the MP2/6-31G(d) level [25]. Consequently, this work aimed at studying the α - and β -elimination pathways (elimination of hydrogen attached to the α - carbon of the alkyl xanthate and β -carbon of the alkyl xanthate) and the effect of these elimination pathways on the kinetics and thermodynamic parameters using Spartan software with density functional theory method of calculations with Becke Lee Yang Parr number three at 6-311++G** level.

Computational Procedure

All calculations on the mechanisms, kinetics and thermodynamics of the gas- phase pyrolysis of α - and β - elimination pathways have been examined using the density functional theory (DFT) with B3LYP at the levels of 6-311++G** levels. Conformational search was done using molecular mechanics force field (MMFF) to obtain the most stable conformer [26, 27]. Geometry optimization was performed on the most stable conformer at the ground state, transition state and product to obtain the bond length, bond angle, dihedral angles and atomics charges distribution. Reaction path calculations were performed on the optimized geometry of each of α - and β -elimination path ways of the studied alkyl Xanthates using Spartan software [28]. Since these alkyl Xanthates followed the same pattern, O-ethyl S-methyl Xanthates was used as example, using H-S as the reaction coordinate. The internal coordinate varied systematically in many small steps from its initial distance in the stable reactants form to its stable product form for example, for O-ethyl, S-methyl xanthate, the initial distance between H and S is 4.8Å. This inter atomic distance is slowly altered throughout the reaction path calculation taking the value from 4.8 (initial value) to 1.2 Å its approximate value in the stable product molecule in 20 steps. Location and characterization of the transition state was done by subjecting the transition state structure to test in order to verify that this connect to true transition state and that this connect to the reactant and products. The test are: that there will be an imaginary IR value that will be in the range of 400-2000cm⁻¹ and the normal coordinate must correspond to the imaginary frequency which will connect the reactants and the product. The intrinsic reaction coordinate method was also used. kinetics and thermodynamics calculations were done using the data obtained from the geometric calculations on the reactants, transition state and products. The kinetic and thermodynamics parameters were obtained using the sum of the ground state (GSE) and the statistical mechanically calculated enthalpy to arrive at a closer approximation of the true energy of the molecule.

Theoretical calculations

The enthalpy of a species was defined as:

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

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

When Eq(1) was substituted into the initial definition of the heat of reaction we have,

$$\Delta H_{\text{Rxt}} = (\text{GSE}_{\text{prod}} + H_{\text{Prod}}^{\text{SM}}) - (\text{GSE}_{\text{React}} - H_{\text{React}}^{\text{SM}}) \quad (2)$$

Activation energy (Ea) was calculated according to the transition state theory for a unimolecular reaction at 629K [27]:

$$E_a = \Delta H^* - RT \quad (3)$$

The entropy of the reaction was calculated by taking the difference of product and reactant entropies that is:

$$\Delta S_{\text{reaction}} = S_{\text{product}} - S_{\text{reactant}} \quad (4)$$

$$\Delta S_{\text{activated}} = S_{\text{transition}} - S_{\text{reactant}} \quad (5)$$

The Gibbs free energy (ΔG) and Gibbs free energy of activation (ΔG^*) were calculated using the modified version of the heat of reaction equation, knowing that the first order coefficient $K(T)$ was calculated using transition state theory (TST) [29] as shown below:

$$G = H - TS \quad (6)$$

and

$$\Delta G^* = \Delta H^* - T\Delta S \quad (7)$$

where ΔG^* is the Gibbs free energy change between the reactant and the transition state.

The Transition State Theory (TST) [10] was used to estimate the first-order rate coefficients $k(T)$ and it was calculated assuming that the transmission coefficient is equal to 1, in the expression:

Pre-exponential factor is given as:

$$A = \frac{K_B T}{h} \exp\left(\frac{-\Delta S^\ddagger}{R}\right) \quad (8)$$

where K_B and h are the Boltzman and Planck constants respectively.

Arrhenius rate was obtained using the rate equation [29].

$$K(T) = A \exp\left[\frac{-E_a}{RT}\right] \quad (9)$$

The bond lengthening character was used to describe the extent of bond lengthening to show the rate determining step and to explain the concertedness and synchronicity of the reaction. Moyano *et al.* [30] have defined a relative variation of the bond indices at the

reactant, transition state and the product (∂B_i) for every i^{th} bond involved in a chemical reaction as:

$$\partial B_i = \frac{(B_i^{\text{Ts}} - B_i^{\text{R}})}{(B_i^{\text{P}} - B_i^{\text{R}})} \quad (10)$$

where the superscripts R, TS and P refer to reactants, transition states and products respectively.

Also (%Ev) the percentage of evolution of the bond order during the calculated mechanism can be obtained from

$$\%EV = 100\partial B_i \quad (11)$$

The dissociation of the C_{α} -O bond before C_{β} -H bond is in accordance with the experimental proposal by Taylor *et al.* [16], for the 1, 5 thermal elimination based on the fact that the Hammett P-values at the α -carbon were of larger magnitude than those observed for the β -carbon. The results also implies that, the more the C_{α} -O bond dissociate in the transition structure, the faster the rate of reaction and that the more the C_{β} -H bond dissociate, the slower is the reaction.

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

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

where n in the above equation represented the number of bonds involved in the reaction coordinates.

The synchronicity (S_y), of a chemical reaction can be calculated as follows:

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

where 'A' represents the asynchronicity. It is calculated by using the equation proposed by Moyano *et al.* [30]:

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

Synchronicities vary between zero and one. This range indicate situation when all of the bonds at the reaction coordinate have been broken or formed at exactly the same extent in the transition states.

Results and discussion

Conformational search

Conformational Search was done using molecular mechanics force field (MMFF) showed that alkyl Xanthates under studied, have different conformers with the most stable conformer having energy given below in Table 1 and (Figure 3).

Table 1. Table of Number of conformers and stable conformers with their corresponding Energy values of O-alkyl S-Methyl Xanthate

COMPOUND	NO. OF CONFORMERS	MOST STABLE CONFORMERS (kJ/mol)
O-ethyl S-methyl Xanthate	5	-48.389
O-npropyl S-methyl Xanthate	12	-34.335
O-isopropyl S-methyl Xanthate	7	-34.335
O-nbutyl S-methyl Xanthate	31	-50.926
O-isobutyl S-methyl Xanthate	10	-31.190
O-tbutyl S-methyl Xanthate	4	16.061

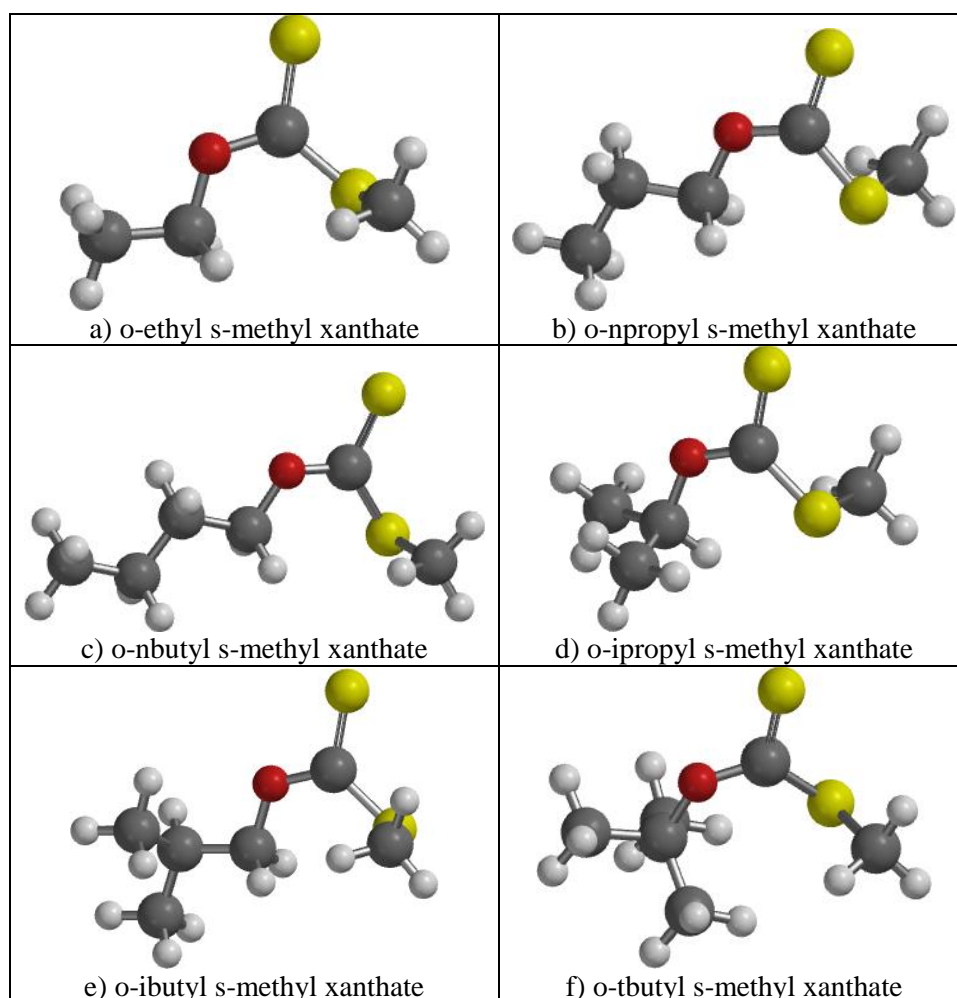


Figure 3. Structure of most stable conformers of the alkyl Xanthate

Geometry optimization

Geometry Optimization was performed on each structure of alkyl Xanthate (Figure 4) in the ground state, transition state and the product to obtain the bond length, bond angles, dihedral angles and atomic charges distribution for the α - and β - elimination series. Changes were observed in bond lengths of the ground state, transition state and the product for of α - and β - elimination series as shown in table 2. The decrease in C-C bond length in transition state(1.406) compared to that of the ground state (1.517) is as a result of the release of electron from C-O and C-H (point of cleavages) in both α - and β - elimination series thus making the carbon-carbon (C-C) single bond at the ground state attained a carbon-carbon (C=C) double bond character at the transition state for α - and β - elimination series respectively. As shown in Figure 4 and Table 2, for α -elimination series using O-isopropyl and npropyl S-methyl xanthates in the TS, the long stretch in the bond lengths between C-H (from 1.094Å to 1.248Å) and C-O (from 1.332Å to 2.291Å) are indications that cleavages occurs between C-H and C-O. Also the decrease in the inter-atomic distance of S-H from GS= 4.737Å to TS= 1.952Å and finally to Product = 1.348Å showed that a new bond is being formed.

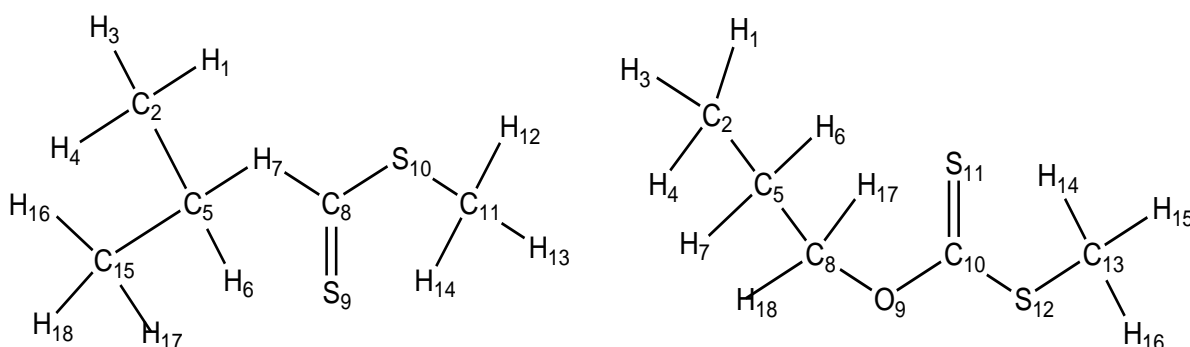


Figure 4. Geometry optimization of α - and β - O-isopropyl and O-npropyl S-methyl Xanthate

In the β - elimination series, the long stretch between C-H (from 1.0940Å to 1.2480Å) and C-O (from 1.3319Å to 2.2910Å) it shows that cleavages also occurred at these point and the change in the change in bond length between S-H from GS= 4.7370Å bond, TS=1.9520Å and product= 1.3482Å are indications that a new bond has been formed.

Table 3 also shows the bond angles for the ground state, transition state and product, the variation in the values from ground state and transition state is as a result of distortion that occurred in structures during the transition process and this kind of distortion are necessary for intramolecular transfer of protons.

Table 2. Selected bond length (Å) for the pyrolysis of o-alkyl s-methyl xanthates using B3LYP/6-311⁺⁺G^{**}

Bond (Å)	State	Ethyl Xanthate	nPropyl Xanthate	ibutyl Xanthate	iPropyl Xanthate	ibutyl Xanthate
H – C	GS	1.0940	1.0916	1.0927	1.0831	1.0832
	TS	1.2480	1.2350	1.2370	1.2470	1.2370
	PRD	-	-	-	-	-
	Δd	0.1540	0.1434	0.1443	0.1639	0.1538
C – C	GS	1.5170	1.5143	1.5134	1.5133	1.5136
	TS	1.4058	1.4066	1.4023	1.3896	1.3915
	PRD	1.3308	1.3306	1.3306	1.3171	1.3182
	Δd	-0.1112	-0.1077	-0.1111	-0.1237	-0.1221
O – C	GS	1.3364	1.3357	1.3362	1.3068	1.3162
	TS	1.2471	1.2473	1.2449	1.2163	1.2146
	PRD	-	-	-	-	-
	Δd	-0.089	-0.0884	-0.0913	-0.090	-0.1016
C = S	GS	1.6473	1.6435	1.6452	1.6385	1.6486
	TS	1.7333	1.7269	1.7220	1.7311	1.7264
	PRD	1.8142	1.8141	1.7922	1.7850	1.7345
	Δd	0.086	0.0834	0.0768	0.0926	0.0778
S – C	GS	1.8189	1.8165	1.8270	1.8053	1.8064
	TS	1.8334	1.8288	1.8362	1.8105	1.8108
	PRD	1.8284	1.8288	1.8361	1.8111	1.8107
	Δd	0.0145	0.0123	0.0092	0.0052	0.0044
H – S	GS	4.9940	4.9950	4.9962	4.910	4.9220
	TS	1.8160	1.8400	1.8260	1.8770	1.8980
	PRD	1.3480	1.3481	1.3390	1.3250	1.3242
	Δd	-3.178	-3.155	-3.1702	-3.033	-3.024

Reaction path study

Reaction path study were performed on the optimized geometry of each of the O-alkyl S-methyl Xanthate under study using α - and β -H-S from O-ethyl S-Methyl dithiocarbonates as the reaction coordinate [26] the internal coordinate was varied from its initial distance in the stable reactants form to its value in the product molecule. As reported in literature [31], instead of the energy to pass smoothly through a maximum rose to a very high value and the geometry suddenly drop to a product with a drop in the heat of formation with the values approximately the same as the sum of the expected products (ethylene and methyl dithiocarbonates) as shown in Figures 5–8. The result obtained showed that the pyrolysis of O-alkyl S-methyl Xanthate can be initiated from the hydrogen attached to α -carbon of the O-alkyl moiety to give carbonyl sulphide thiol and olefin. It can also be initiated from the hydrogen attached to the β -carbon of the O-alkyl moiety to give carbonylsulphide, thiol and olefin.

Table 3. Selected bond angle (0°) for the pyrolysis of *o*-alkyl *s*-methyl xanthates using B3LYP/6-311+G**

Bond angle (0°)	State	Ethyl Xanthate	nPropyl Xanthate	ibutyl Xanthate	iPropyl Xanthate	ibutyl Xanthate
H – C – C	GS	110.70	110.79	110.820	110.573	110.567
	TS	102.74	102.74	102.720	98.09	97.240
	PRD	-	-	-	-	-
C – C – O	GS	106.95	106.97	107.820	106.655	106.620
	TS	108.95	109.18	109.320	108.910	108.930
	PRD	-	-	-	-	-
C – O – C	GS	122.82	122.88	122.745	124.951	124.920
	TS	118.90	120.32	119.090	123.810	122.930
	PRD	-	-	-	-	-
O – C = S	GS	120.00	120.11	120.151	120.051	120.120
	TS	124.78	125.16	124.914	124.734	124.311
	PRD	124.51	123.61	124.620	123.960	124.970
O – C – S	GS	114.57	114.48	120.575	114.894	114.821
	TS	120.47	119.14	120.575	119.351	119.621
	PRD	123.97	120.06	122.720	120.060	121.240
S – C – S	GS	125.45	125.40	114.488	125.054	12.050
	TS	114.73	115.70	114.488	115.914	116.062
	PRD	111.52	112.63	114.72	116.290	116.520
C – S – C	GS	101.96	102.30	102.321	103.678	103.620
	TS	102.15	101.41	102.938	101.039	101.530
	PRD	98.140	98.120	97.620	99.330	99.440
S – C – H	GS	110.39	110.36	110.470	110.708	110.765
	TS	109.48	110.98	109.333	110.771	110.740
	PRD	110.28	111.24	112.462	110.360	111.360

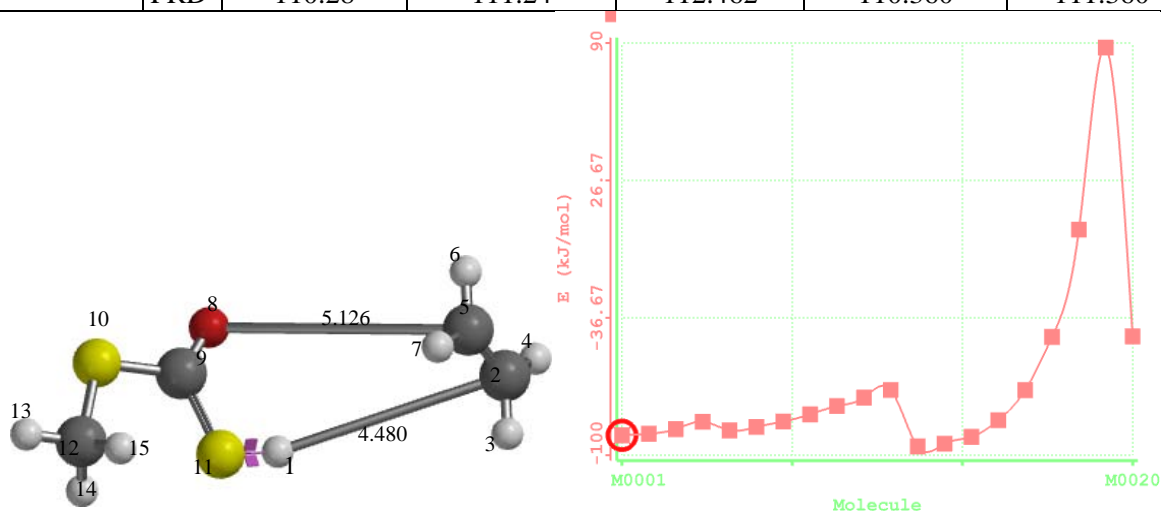


Figure 5. Reaction path study (*O*-ethyl *S*-methyl Dithiocarbonates) and a plot of energy against number of molecules to depict the reaction path study

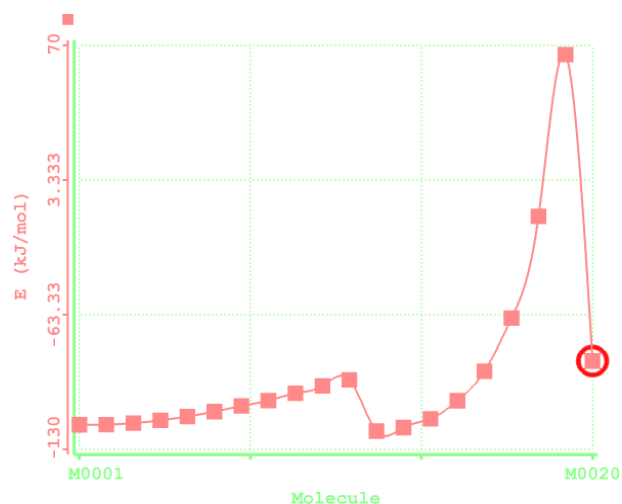
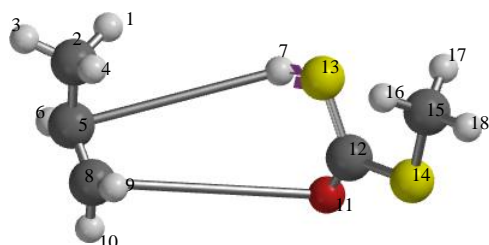


Figure 6. Reaction path study O-npropyl S-methyl Dithiocarbonates) and a plot of energy against number of molecules to depict the reaction path study

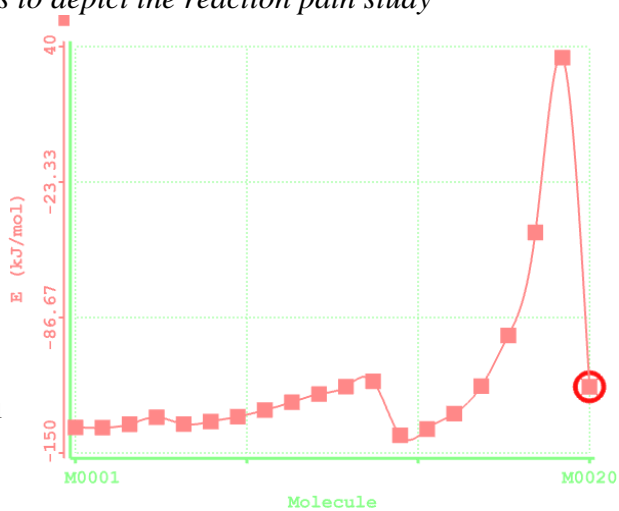
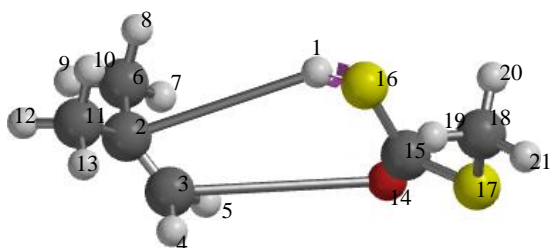


Figure 7. Reaction path study O-ipropyl S-methyl Dithiocarbonates) and a plot of energy against number of molecules to depict the reaction path study

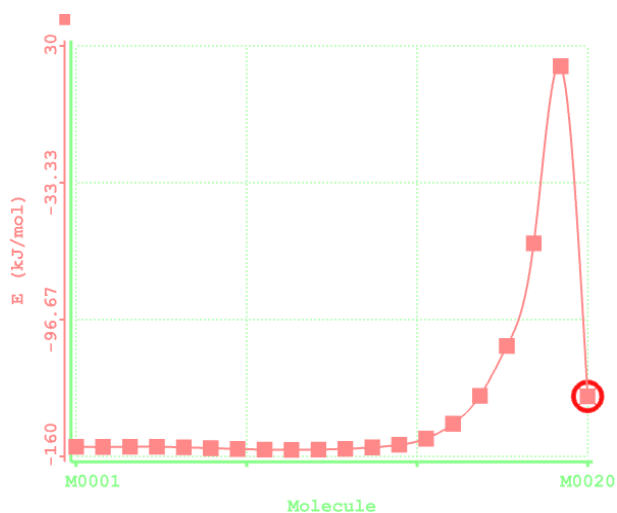
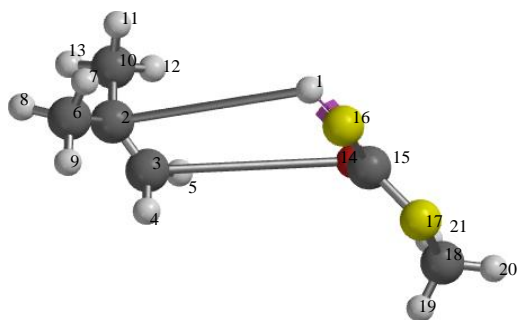


Figure 8. Reaction path study O-ibutyl S-methyl Dithiocarbonates) and a plot of energy against number of molecules to depict the reaction path study

Transition state

The transition state was characterized using two methods, the infrared (IR) values obtained for α - and β -elimination which has only one imaginary IR frequency values. The main components of these stretching are S–H. The C–O stretching is not present because the bond is virtually broken. The intrinsic reaction coordinate calculation converged, which shows that reaction is an exothermic one.

Mechanism of pyrolysis of O-alkyl S-methyl xanthate

The pyrolysis of O-alkyl S-methyl Dithiocarbonates (Xanthate) has been reported to proceeds through a concerted six-centered cyclic transition state initiated from the hydrogen that is attached to either the α - and β -carbon of the O-alkyl xanthate in which O-ethyl S-methyl xanthate is the simplest of the α - and β - studied which gives Methyl dithiocarbonates and ethylene (C₂H₄). However the result obtained for other pyrolysis of α -elimination series are O-isopropyl xanthate and O-tbutyl xanthate and the elimination series are O-npropyl xanthate, O-ibutyl xanthate and O-nbutyl xanthate are given below in Table 4.

Table 4. Reaction Mechanisms of O-alkyl Xanthate showing the α - and β -carbon elimination series

α -Elimination series		β -Elimination series	
Reactant	Products	Reactant	Products
O-isopropyl Xanthate	Propene, thiol and Carbonylsulphide	O-npropyl Xanthate	Propene, thiol and Carbonylsulphide
O-tbutyl Xanthate	2-methyl prop-1-ene, thiol carbonylsulphide	O-isobutyl Xanthate	2-methylprop-1-ene, thiol carbonylsulphide
		O-nbutyl Xanthate	2-methylprop-1-ene, thiol carbonylsulphide

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 [13]. The Chugaev reaction is analogous to the thermal decomposition of carboxylic ester of alcohols and of other related derivatives of alcohols such as carbamates and carbonates. The mechanism of xanthate pyrolysis is a concerted fragmentation but products could conceivably arise from α - and β -hydrogen abstraction through a six-membered Cyclic transition State in which the β -H atom attacking the terminal thiol, or the thion [13]. Sulphur atom attack the β -hydrogen which was obtained by Bader and Bourns [20], both the thiol and thion were part of

the six membered cyclic transition State which involves an S–H bond making, C–H and C–O bond breaking and according to experimental evidence, the C–O bond breaking is the rate determining step [32].

Atomic charges

The charges (Table 5) showed that α -H and β -H has positive charge development (+0.191 and +0.155) while S has negative charges (-0.492 and -0.550) using isopropyl and npropyl xanthate (Figure 9). The polarization of C–O and S–H bonds causes positive charges on carbon-carbon bonds (+0.138 and +0.410) respectively and causes C to become negatively charged (-0.127) for α -elimination series and the polarization of the S–H and C–O causes positive charges on carbon-carbon to increase respectively.

Table 5. Atomic charges (Mulliken) of o-alkyl s-methyl xanthates using MP2/B3LYP/6-311+G**

Atoms	State	Ethyl Xanthate	nPropyl Xanthate	ibutyl Xanthate	iPropyl Xanthate	tbutyl Xanthate
H	GS	+0.174	+0.155	+0.191	+0.191	+0.193
	TS	+0.141	+0.176	+0.116	+0.238	+0.195
	PRD	+0.273	+0.210	+0.221	+0.096	+0.095
	$\Delta q(\text{TS-GS})$	-0.033	0.021	-0.075	0.047	0.002
C	GS	-0.458	-0.550	-0.560	-0.492	-0.462
	TS	-0.480	-0.351	-0.285	-0.619	-0.391
	PRD	-0.285	-0.295	-0.321	-0.353	-0.299
	$\Delta q(\text{TS-GS})$	-0.022	-0.199	0.275	-0.127	0.071
C	GS	-0.071	-0.256	-0.242	+0.043	+0.044
	TS	-0.123	-0.198	-0.047	-0.052	-0.062
	PRD	-0.285	-0.296	-0.286	-0.353	-0.362
	$\Delta q(\text{TS-GS})$	-0.052	0.058	0.195	0.095	-0.106
O	GS	-0.387	+0.120	+0.140	-0.537	-0.620
	TS	-0.437	-0.126	-0.330	-0.614	-0.243
	PRD	-0.389	-0.426	-0.520	-0.362	-0.426
	$\Delta q(\text{TS-GS})$	-0.050	-0.246	-0.470	-0.077	0.377
C	GS	+0.064	-0.009	-0.016	-0.151	+0.162
	TS	+0.082	-0.011	+0.156	+0.190	+0.171
	PRD	+0.098	+0.068	+0.727	+0.177	+0.182
	$\Delta q(\text{TS-GS})$	0.018	0.002	0.172	0.341	0.009
S	GS	+0.162	-0.094	-0.093	+0.192	+0.182
	TS	+0.164	+0.061	+0.002	+0.171	-0.017
	PRD	+0.158	+0.168	+0.268	+0.041	+0.042
	$\Delta q(\text{TS-GS})$	-0.021	-0.155	0.095	-0.021	-0.199
S	GS	-0.186	-0.310	-0.326	-0.230	-0.241
	TS	-0.116	-0.244	-0.256	-0.263	-0.417
	PRD	-0.011	-0.012	-0.014	+0.152	+0.156
	$\Delta q(\text{TS-GS})$	0.07	0.066	0.070	-0.033	-0.176

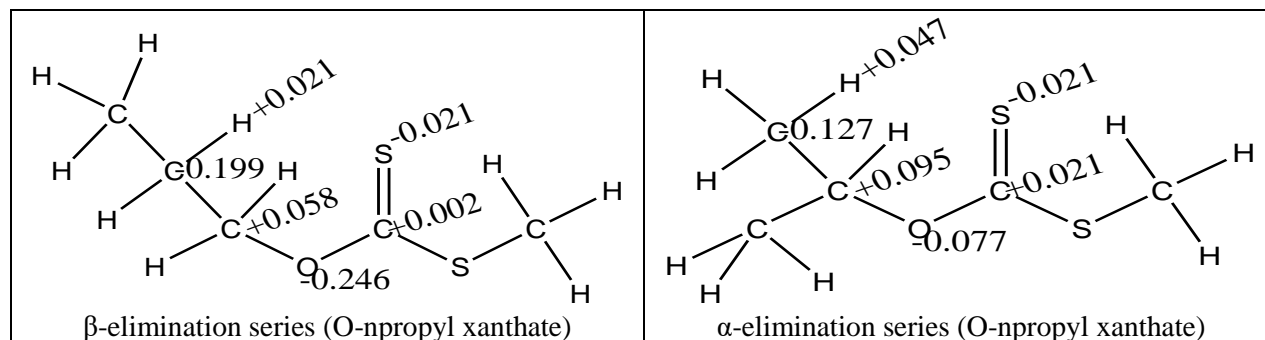


Figure 9. The distribution of atomic charges for α - and β - elimination series

Kinetics and thermodynamics parameters calculation

The result obtained for the kinetics and thermodynamics parameters (Table 6) for the β - elimination pathways for ethyl, npropyl, ibutyl and nbutyl respectively ranged from 161.34-128.04kJ/mol(ΔH^*), -31.18 to -24.00 J/mol/K(ΔS^*), 180.65 to 142.92 kJ/mol(ΔG^*), 166.49-133.19 kJ/mol(Ea), 1.04×10^{-3} to 4.3 S^{-1} (K_{620}) and 3.06×10^{11} to 7.18×10^{11} (A). It was observed that the progressive methylation decreases activation and thermodynamics parameters from ethyl, propyl, isopropyl, nbutyl, ibutyl and tbutyl xanthate respectively. However, progressive methylation increases the rate constant (k), and pre-exponential factor (A) respectively. Also for α - elimination pathway kinetic and thermodynamic parameters for isopropyl and tbutyl compared favourably well with the experimental values.

Table 6. Effect of methylation on kinetic and thermodynamic parameters for α - and β - elimination series at 629K (B3LYP/6-311++G**)

CALCULATED PARAMETERS						
Compounds	ΔH^* kJ/mol	ΔS^* J/mol	ΔG^* kJ/mol	Ea kJ/mol	$A \times 10^{11}$	k_{620} (S^{-1})
O-Ethyl Xanthate	161.34	-31.16	180.65	166.49	3.06	$1.04 \cdot 10^{-3}$
O-nPropyl Xanthate	153.23	-27.18	170.08	158.38	4.90	$6.0 \cdot 10^{-2}$
O-iPropyl Xanthate	144.21	-26.98	160.94	149.36	5.00	$1.3 \cdot 10^{-1}$
O-nButyl Xanthate	133.87	-25.65	149.77	139.02	5.89	1.14
O-iButyl Xanthate	131.67	-25.78	147.65	136.82	5.81	1.70
O-tButyl Xanthate	128.04	-24.00	142.92	133.19	7.18	4.3
EXPERIMENTAL PARAMETERS						
	ΔH kJ/mol	ΔS^* J/mol	ΔG^* kJ/mol	Ea kJ/mol	$A \times 10^{11}$	k_{620} (S^{-1})
O-Ethyl Xanthate	161.00	-28.00	178.6	166.20	4.7	$1.4 \cdot 10^{-3}$
O-nPropyl Xanthate						
O-iPropyl Xanthate	-	-	-	-	-	-
O-nButyl Xanthate	144.00	-26.00	160.4	149.17	5.7	$5.6 \cdot 10^{-1}$
O-iButyl Xanthate	-	-	-	-	-	-
O-tButyl Xanthate	-	-	-	-	-	-

It was further observed that addition substituents to the β -carbon lower the activation energy slightly from ethyl xanthate to i-butyl xanthate) with a difference of about 29.67kJ/mol., while the addition of substituents to the α -carbon from ethyl xanthate to t-butyl xanthate lower the activation energy the more, with a difference of about 33.45kJ/mol.

Wiberg bond order analysis for o-alkyl s-methyl dithiocarbonates

Generally, the calculated percentage of evolution of the bonds involved in the reaction coordinates is collected in Table 7.

Table 7. Calculation using Wiberg bond indices B_i of reactants, transition and products, percentage of evolution of bonds $\%E_v$, degree of advancement of the transition states, δB_i and absolute synchronicities S_y , of O-alkyl S-methyl Xanthate (B3LYP/6-311++G**))

Compound	Wiberg bond indices	S ₁ -C ₂	C ₂ -O ₃	O ₃ -C ₄	C ₄ -C ₅	C ₅ -H ₆	H ₆ -S ₁
O-Ethyl Xanthate	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
	δB_i	0.57	0.539	0.658	0.310	0.429	0.360
	$\%E_v$	57	53.9	65.8	31	42.9	36.0
O-nPropyl Xanthate	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
	δB_i	0.317	0.408	0.716	0.582	0.560	0.317
	$\%E_v$	30.2	58.2	71.6	58.2	40.9	31.7
O-iPropyl Xanthate	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
	δB_i	0.579	0.530	0.768	0.288	0.310	0.390
	$\%E_v$	57.9	53.0	76.8	28.8	31.0	39.0
O-nButyl Xanthate	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
	δB_i	0.685	0.530	0.76	0.685	0.310	0.407
	$\%E_v$	68.5	53.0	76.0	68.5	31.0	40.7
O-iButyl Xanthate	B_i^R	1.666	1.045	0.771	1.006	0.006	0.003
	B_i^{TS}	1.321	1.419	0.179	1.273	0.299	0.492
	B_i^P	1.070	1.695	0.000	1.933	0.964	0.953
	δB_i	0.579	0.576	0.769	0.287	0.320	0.361
	$\%E_v$	57.9	57.6	77.8	28.7	32.0	51.50
O-tButyl Xanthate	B_i^R	1.666	1.045	0.771	1.007	0.921	0.005
	B_i^{TS}	1.322	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	0.390	0.31
	$\%E_v$	57.9	57.6	76.8	28.8	39.0	31.0

As it can be seen, in the case of O-alkyl S-methyl Dithiocarbonates, (1-6), in which alkyl group are ethyl, npropyl, isopropyl, nbutyl, ibutyl and tbutyl, the breaking of the bond O-C is the most advanced process (65-77)%, followed by the transformation of the S-C double bond into a single bond (58%) and of the C-O single bond into double bond of (54-58)%.

The least advanced process is the formation of the C-C double bonds (30%) followed by the formation of the H-S bond 31-36% and the breaking of the C-H bond (39-43)%. The dissociation of the C $_{\alpha}$ -O bond before C $_{\beta}$ -H bond is in accordance with the experimental proposed by Taylor and co-worker in 1962 [16], for the 1, 5 thermal elimination. The results also implies that the more the C $_{\alpha}$ -O bond is dissociated in the transition structure the faster is the rate of reaction and that the more the C $_{\beta}$ -H bond is dissociated, the slower is the reaction. This trend in bond lengthening can be mirrored in the atomic charges. In the table of atomic charges at the atoms involved in the reaction centers of mechanism for all the compound studies.

There is a buildup of negative charge on Oxygen atom in each transition structure, consistent with C-O bond dissociation that increase rate, in accordance with the above observation that the C-O bond dissociated to a larger degree in the faster reactions. The opposite trend is apparent in the buildup of positive charge on the transferred hydrogen that decreases as the rate increases, in agreement with the trends in C-H bond lengthening [22]. The calculated δB_{av} values for the first step of the mechanism of the studied reactions are shown in table 8. As it can be seen, the δB_{av} values show that there is a difference between the transition states of the first mechanism (B) of the Chugaev reaction for the Xanthate considered. In the case of the O-alkyl S-methyl dithiocarbonates B_{av} values ranges from 0.478 to 0.485, increasing from O-ethyl to O-tert-butyl, indicating that the transition states have an “early” character, nearer to the reactants than to the products.

Synchronicities vary between zero and one, which is the case when all of the bonds at the reaction coordinate have been broken or formed at exactly the same extent in the transition states. The S_y value obtained for O-alkyl S-methyl dithiocarbonates range from 0.807 to 0.860 (Table 8) for the reaction of the compounds, indicating that O-alkyl S-methyl dithiocarbonates corresponds to highly asynchronous processes. The synchronicity rapidly decreases when the size of the alkyl group attached to sulphur or oxygen atoms increases.

Table 8. Calculation using Wiberg, degree of advancement of the transition states, δB_{av} and absolute synchronicities S_v , of O-alkyl S-methyl Xanthate (B3LYP/6-311++G**))

Compound	δB_{av}	S_v
O-Ethyl Xanthate	0.478	0.860
O-nPropyl Xanthate	0.496	0.832
O-iPropyl Xanthate	0.484	0.807
O-nButyl Xanthate	0.486	0.867
O-iButyl Xanthate	0.485	0.807
O-tButyl Xanthate	0.485	0.807

Conclusions

The calculations related with the reaction path showed that the gas-phase pyrolysis could conveniently proceed through the two pathways that is elimination initiated from the hydrogen that is attached to α -carbon of the O-alkyl xanthates and from the hydrogen that is attached to the β -carbon of the O-alkyl xanthates. It is observed that *ab-initio* method could effectively predict the kinetics, mechanisms and thermodynamics of the gas-phase pyrolysis of an alkyl Xanthate. In addition, the computed Arrhenius and thermodynamic parameters obtained at 629K kelvin are in good agreement with experimental values. The calculated percentages of evolution of the bonds involved in the reaction indicate that the bond breaking for these compounds and the bond breaking for these compounds are the most advanced processes for the reactions in the transition states. However, the energy of formation and other calculated kinetic and thermodynamic parameters for the elimination pathway from the hydrogen that is attached to α -carbon of the O-alkyl xanthates is lower compared with that of the β -carbon of the O-alkyl xanthates. Useful kinetic and thermodynamics parameters can be obtained theoretically prior to their laboratory experimentations.

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