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Computational study of the mechanism of thermal decomposition of xanthates in the gas phase (the Chugaev reaction)[†]

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A theoretical study on the mechanism of the thermal decomposition of a series of xanthates, O-alkyl S-methyl and S-alkyl O-methyl dithiocarbonates, has been carried out, and the alkyl groups being ethyl, isopropyl, and *tert*-butyl. Kinetically, these xanthates can be classified in two groups: those where the oxygen atom is involved in the bonding changes of the transition state (properly the Chugaev reaction), and those where it is not, O-alkyl S-methyl and S-alkyl O-methyl dithiocarbonates, respectively. We have studied not only the thermal elimination reactions but also the other possible reactions such as the thione-to-thiol rearrangement and the nucleophilic substitution to give ethers or thioethers. Two possible mechanisms for the thermal elimination reactions, in one and in two steps, respectively, have been studied. Calculations were made at the MP2/6-31G(d) level of theory, and the progress of the reactions has been followed by means of the Wiberg bond indices. Copyright © 2008 John Wiley & Sons, Ltd.

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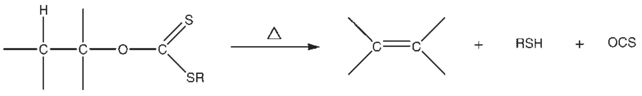
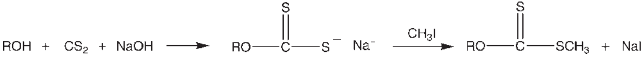
INTRODUCTION

Preparatively useful routes to alkenes include a family of unimolecular thermal decompositions, the intramolecular pyrolytic eliminations (E_i reactions). These reactions are classed as pericyclic processes. Among them is the formation of olefins from alcohols through pyrolysis of the corresponding xanthates (O-alkyl S-alkyl dithiocarbonates), which was discovered in 1899 by Chugaev (or Tschugaeff)[1] in connection with his studies on the optical properties of xanthates.[2] So, the reaction is named as Chugaev reaction.[3–6]



(1)

Under thermolysis of xanthates having one β-hydrogen, olefins can be obtained, together with gaseous carbonyl sulfide and a thiol. The corresponding xanthates can be prepared from alcohols by reaction with carbon disulfide in the presence of sodium hydroxide and subsequent alkylation of the intermediate sodium xanthate, usually with methyl iodide.[6]



$$\mathrm{ROH} + \mathrm{CS_2} + \mathrm{NaOH} \longrightarrow \mathrm{RO{-}\overset{\overset{\displaystyle S}{\|}}{C}{-}S^{-}\ Na^{-}} \xrightarrow{\mathrm{CH_3I}} \mathrm{RO{-}\overset{\overset{\displaystyle S}{\|}}{C}{-}SCH_3} + \mathrm{NaI} \qquad (2)$$

Xanthates having no β-hydrogens undergo thione-to-thiol rearrangement to give S,S-dialkyl dithiocarbonates (thiolcarbonates).

$$\mathrm{RO{-}\overset{\overset{\displaystyle S}{\|}}{C}{-}SR'} \longrightarrow \mathrm{O{=}\overset{\overset{\displaystyle SR}{|}}{C}{-}SR'} \qquad (3)$$

The Chugaev elimination is of synthetic value because it proceeds without the rearrangement of the carbon skeleton.[4] The ability to form double bonds via thermal elimination of xanthate precursors, the so-called xanthate route, is currently attracting considerable interest among polymer chemists because it enables the synthesis of poly-paraphenylene-vinylene (PPV) samples with promising characteristics for the fabrication of light-emitting devices.[7] However, applicability of the Chugaev reaction is limited if the elimination is possible in more than one direction and if a β-carbon has more than one hydrogen.

The Chugaev reaction is analogous to the thermal decomposition of carboxylic esters 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 β-hydrogen abstraction by

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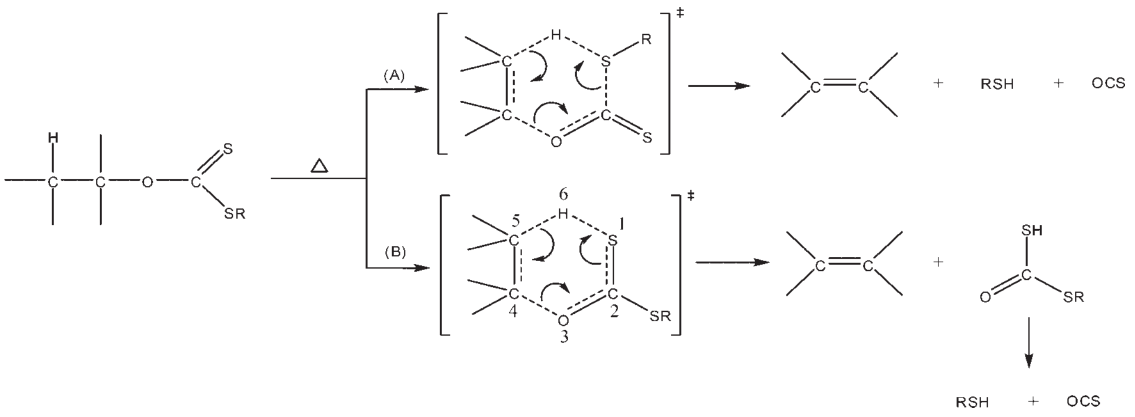


Figure 1. The two possible pathways in the pyrolysis of xanthates

either the thiol or thione sulfur atoms, mechanisms A and B, respectively, in Fig. 1.

In mechanism (A), the reaction occurs in one step, giving the products of reaction (1). In mechanism (B), the initial products are the alkene and an unstable dithiocarbonate derivative which subsequently decomposes to carbonyl sulfide and a thiol. Hückel *et al.*[8] postulated first mechanism (A), but Barton[9] and Cram[10] proposed the second mechanism. Experimental evidence that the thion, rather than the thiol, sulfur atom attacks the β-hydrogen was obtained by Bader and Bourns[11] who made a study of ^{34}S and ^{13}C isotope effects for the pyrolysis of *trans*-2-methyl-1-indanyl xanthate of natural isotopic abundance. Alexander and Mudrak[12–14] provided further convincing evidence for the *cis*-elimination course.

The thermal decomposition of xanthates has been experimentally investigated a number of times.[15–18] All the reactions studied were of first order, and their rates were largely unaffected by an increase of surface or by the addition of radical inhibitors. They are homogeneous, unimolecular reactions.

To our knowledge there have been only three previous theoretical studies on these type of reactions. Erickson and Kahn[19] studied the transition structure of the thermal elimination of HSC(S)OEt at MP2/6-31G(d)//HF/6-31G(d) level, Claes *et al.*[7] studied the gas-phase internal elimination reaction of EtSC(S)OMe at different levels of theory, and more recently Harano[20] studied the transition structure of the Chugaev reaction of MeSC(S)OEt at the B3LYP/6-31G(d) level of theory.

The shortage of theoretical studies on the reactions of xanthates have prompted us to carry out a detailed study of the mechanism of the thermal decomposition of a series of xanthates, O-alkyl S-methyl and S-alkyl O-methyl dithiocarbonates, and the alkyl groups being ethyl, isopropyl, and *tert*-butyl. Kinetically, these xanthates can be classified in two groups: those where the oxygen atom is involved in the bonding changes of the transition state (properly the Chugaev reaction), and those where it is not, O-alkyl S-methyl and S-alkyl O-methyl dithiocarbonates, respectively. We have studied not only the thermal elimination reactions but also the other possible reactions such as the thione-to-thiol rearrangement (reaction (3)) and the nucleophilic substitution to give ethers or thioethers (reaction (4)).

$$RX-\overset{\overset{S}{\|}}{C}-YR' \longrightarrow CXS + RYR' \qquad (4)$$

COMPUTATIONAL DETAILS

All calculations were carried out using the Gaussian 03 computational package.[21] The geometric parameters for all the reactants, transition states and products of the reactions studied were fully optimized using *ab initio* analytical gradients at the MP2 level[22] with the 6-31G(d) basis set.[23] Each structure was characterized as a minimum or a saddle point of first order by analytical frequency calculations. A scaling factor[24] of 0.9670 for the zero-point vibrational energies has been used. Thermal corrections to enthalpy and entropy values have been evaluated at the experimental temperature of 629.0 K. To calculate enthalpy and entropy values at a temperature *T*, the difference between the values at that temperature and 0 K has been evaluated according to standard thermodynamics.[25]

Intrinsic reaction coordinate (IRC) calculations[26] have been performed in all cases to verify that the localized transition state structures connect with the corresponding minimum stationary points associated with reactants and products.

The bonding characteristics of the different reactants, transition states, and products have been investigated using a population partition technique, the natural bond orbital (NBO) analysis of Reed and Weinhold.[27,28] The NBO formalism provides values for the atomic natural total charges and also provides the Wiberg bond indices[29] used to follow the progress of the reactions. The NBO analysis has been performed using the NBO program,[30] implemented in the Gaussian 03 package,[21] and has been carried out on the MP2 charge densities in order to explicitly include electron correlation effects.

We have selected the classical transition state theory (TST)[31,32] to calculate the kinetic parameters.

RESULTS AND DISCUSSION

Experimental and calculated values of the activation parameters and rate constants for the thermal decomposition of the compounds studied here are collected in Table 1.

Theoretical calculations at the MP2/6-31G(d) level of theory have been carried out in order to explore the nature of the mechanisms of all the reactions studied for S-alkyl O-methyl and O-alkyl S-methyl dithiocarbonates in the gas phase, as they are shown in Schemes 1 and 2.

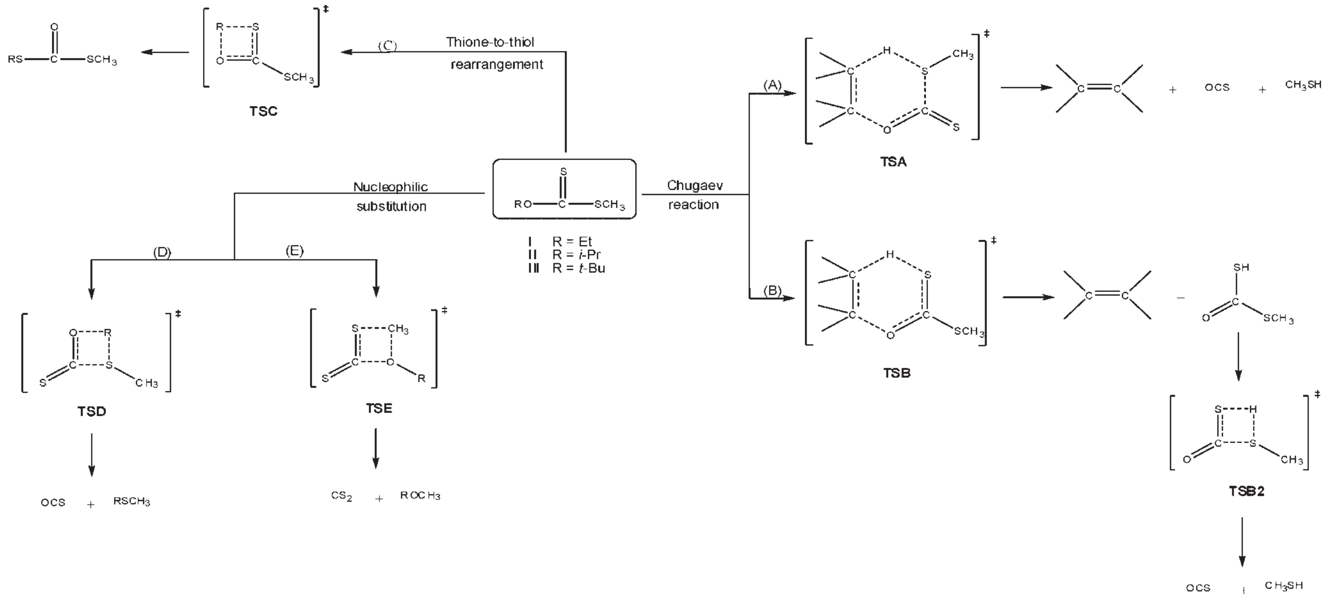
For O-alkyl S-methyl dithiocarbonates, **I, II,** and **III** (Scheme 1), five pathways have been investigated. Mechanisms (A) and (B) correspond to the Chugaev reaction. Mechanism (A) is a one-step

Table 1. Experimental[a] and calculated[b] activation parameters and rate constants for the thermal decomposition of xanthates

		$\Delta H^{\neq}$/ kJ mol^{-1}		$\Delta S^{\neq}$/ J mol^{-1}		$\Delta G^{\neq}$/ kJ mol^{-1}		$k_{629\,K}$/s^{-1}	
Compound		Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
O-alkyl	O-Et (I)	161	197.4	−28	−0.3	178.6	197.6	1.4×10^{-2}	5.1×10^{-4}
S-methyl	O-Pr^{i} (II)	144	182.9	−26	5.1	160.4	179.7	5.6×10^{-1}	1.6×10^{-2}
dithiocarbonates	O-Bu^{t} (III)	—	152.6	—	0.9	—	152.1	—	3.1
S-alkyl	S-Et (IV)	—	184.2		−8.6	—	189.4	—	2.4×10^{-3}
O-methyl	S-Pr^{i} (V)	163	175.6	−32	−6.0	183.1	179.4	7.9×10^{-3}	1.7×10^{-2}
dithiocarbonates	S-Bu^{t} (VI)	135	155.9	−44	−1.1	162.7	156.6	4.3×10^{-1}	1.3

[a] Values taken from Reference [17]

[b] Values calculated at the MP2/6-31G(d) level of theory at 629.0 K.



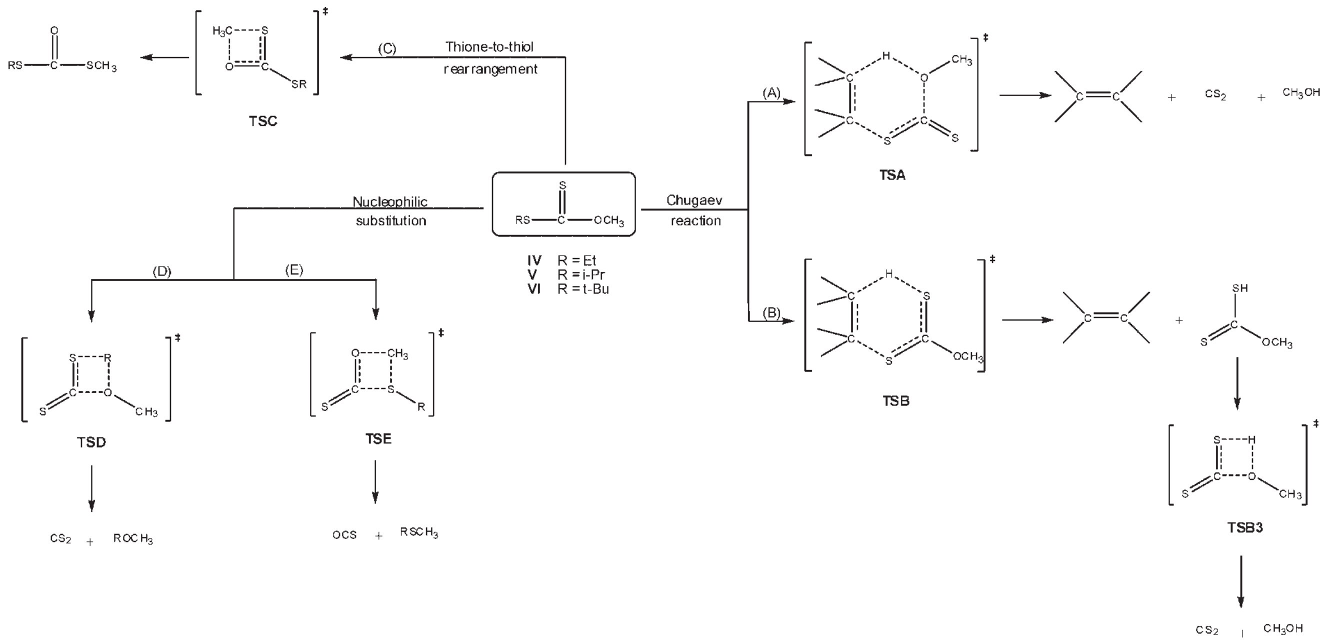
Scheme 1.

process proceeding through six-membered cyclic transition state, in which the thioether sulfur atom and the ether oxygen participate. Mechanism (B) is a two-step process, with an initial rate-determining step via a six-membered cyclic transition state in which the thiocarbonyl sulfur and the ether oxygen participate, followed by a rapid decomposition of the intermediate. In both mechanisms the final products are the same: alkene, methanethiol, and carbonyl sulfide.

Mechanism (C) corresponds to thione-to-thiol rearrangement giving the corresponding S-alkyl S-methyl dithiocarbonates, and mechanisms (D) and (E) correspond to the two possibilities of nucleophilic substitution, transferring R or a methyl group, and giving a thioether and carbonyl sulfide, or an ether and carbon disulfide, respectively.

For S-alkyl O-methyl dithiocarbonates, **IV**, **V**, and **VI** (Scheme 2), we have investigated five pathways, similar to those described above for O-alkyl S-methyl dithiocarbonates. The only difference between both types of dithiocarbonates is that in mechanism (B) the thiocarbonyl and the thioether sulfur atoms participate, whereas the oxygen ether does not participate in the transition state. The products are alkene, methanol, and carbon disulfide. The thermal decomposition of dithiocarbonates **IV**, **V,** and **VI** is not strictly a Chugaev reaction because in the Chugaev reaction xanthates are obtained from alcohols, alkylating the intermediate sodium xanthates with methyl iodide, and so the products are O-alkyl S-methyl dithiocarbonates (see reaction (2)). But the mechanism is very similar and we are going to use the name ‘Chugaev reactions’ for the thermal eliminations of xanthates, in general.

Electronic energies, zero-point vibrational energies, thermal corrections to enthalpies, and entropies, for the reactants, transition states, and products involved in all the reactions studied (see Schemes 1 and 2) are collected in Tables S1 and S2 in the Supporting Information. The transition state corresponding



Scheme 2.

to the nucleophilic substitution of dithiocarbonate **VI** through mechanism (D) (see Scheme 2) was not possible to obtain at the level of theory used in this work.

Gibbs energy profiles for the thermal decomposition processes of the six xanthates studied are presented in Figs 2 and 3. As it can be observed in the Figures, the lowest barrier in all the cases corresponds to the first step of the mechanism (B) of the Chugaev reaction. Transition states corresponding to mechanism (A) of this reaction, in only one step, are much higher in Gibbs energy, *ca.* 50 kJ mol^{-1} in the case of O-alkyl S-methyl dithiocarbonates, and higher by 75 kJ mol^{-1} in the case of S-alkyl O-methyl dithiocarbonates. This result is in accord with the experimental evidence[11] that the thion, rather than the thiol, sulfur atom attacks the β-hydrogen in O-alkyl S-methyl dithiocarbonates. The activation Gibbs energies of the processes following the mechanisms (C), (D), and (E), are all higher than the corresponding values for the first step of mechanism (B). These results confirm that the thermolysis of xanthates is a *cis*-concerted elimination (Chugaev reaction), which occurs via a mechanism in two steps, the first one being the rate-limiting step. The overall processes are highly exergonic. Between the other two reactions studied, thione-to-thiol rearrangement to give S-alkyl S-methyl dithiolcarbonates presents lower activation Gibbs energies than nucleophilic substitution to give ethers or thioethers.

It is interesting to point out that, in the case of compound **IV**, S-ethyl O-methyl dithiocarbonate, the activation Gibbs energy of mechanism (C) is only slightly higher (2.5 kJ mol^{-1}) than the value corresponding to mechanism (B). Al-Awadi and Bigley[17] observed that this compound gave curved Arrhenius plots and gave ethyl methyl dithiolcarbonate in competition with the Chugaev products. This experimental fact agrees with our theoretical results.

Comparing the barriers of the two steps in mechanism (B), when the alkyl group attached to O or S atoms increases its size, the activation Gibbs energy of the first step decreases, and in the case of the reaction of compound **III**, the height of the barriers of the two steps is similar.

Optimized geometries for the transition states of the first step in mechanism (B) for all the reactions studied in this work are shown in Figs 4 and 5. In general, the transition structures consist of a near-planar six-membered ring, in which the hydrogen transfer is close to linear (angles S_1—H_6—C_5 of 168–173°).

There is one and only one imaginary vibrational frequency in the transition states corresponding to the first step of the mechanism (B) for all the studied reactions (1310.9i, 813.5i, 646.9i, 959.3i, 925.0i, and 878.8i cm^{-1} for TSB-I, TSB-II, TSB-III, TSB-IV, TSB-V and TSB-VI, respectively, evaluated at the MP2/6–31G(d) level of theory).

Table 2 shows the distances between the atoms involved in the reaction center for each optimized reactant and TS. During the thermolysis process, when the reactant is being transformed into its TS, the S_1—C_2, $O_3(S_3)$—C_4, and C_5—H_6 distances are increasing, whereas the C_2—$O_3(S_3)$, C_4—C_5, and H_6—S_1 distances are decreasing. S_1—C_2 has single bond character in the transition state, whereas C_2—O_3 bond has double bond character. In all cases, C_4—C_5 changes from single to double bond, that is, C_4 and C_5 change their hybridization from sp^3 to sp^2.

The fundamental feature of the process is the H_6—S_1 distance in the reactants; the corresponding distances in the transition states are similar for the O-alkyl S-methyl dithiocarbonates (~1.49 Å) and for the S-alkyl O-methyl dithiocarbonates (~1.63 Å).

Calculated kinetic and activation parameters for the first step of mechanism (B) for all the reactions studied are shown in Table 1. As can be seen, calculated activation enthalpies and entropies are very different from the experimental ones, but there is likely to be an enthalpy–entropy compensation, and the Gibbs energies and kinetic constants agree better, while the relative experimental *k*-values are pretty well reproduced. In both series of dithiocarbonates studied, *k*-values increase when the size of the alkyl group attached to O or S atoms increases.

As NBO is a powerful tool for understanding and interpreting results from mechanistic studies, the progress of the Chugaev reactions has been followed, like in other theoretical studies on reaction mechanisms carried out by us,[33–36] by means of the Wiberg bond indices,[29] B_i. The bond index between two atoms is

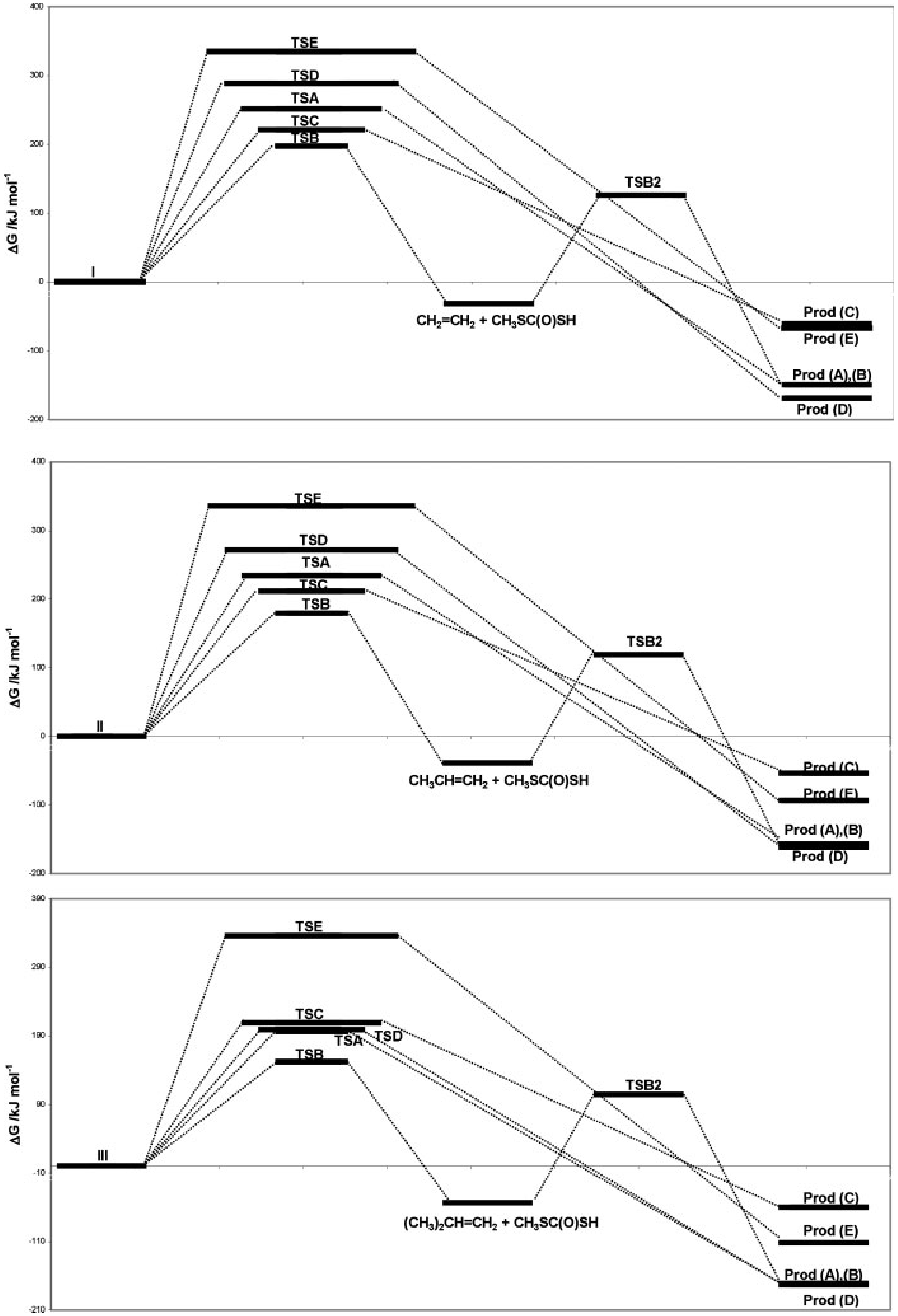


Figure 2. Gibbs energy profile at 629.15 K, evaluated at the MP2/6-31G(d) level, for the pyrolysis process of O-alkyl S-methyl dithiocarbonates. Relative free energy values (to reactants, in kJ mol^{-1}) of the transition states found are as follows: TSA-I, 251.1; TSB-I, 197.6; TSC-I, 221.2; TSD-I, 288.7; TSE-I, 335.0; TSA-II, 234.4; TSB-II, 179.7; TSC-II, 211.8; TSD-II, 271.3; TSE-II, 336.0; TSA-III, 196.3; TSB-III, 152.3; TSC-III, 209.1; TSD-III, 199.3; TSE-III, 352.0

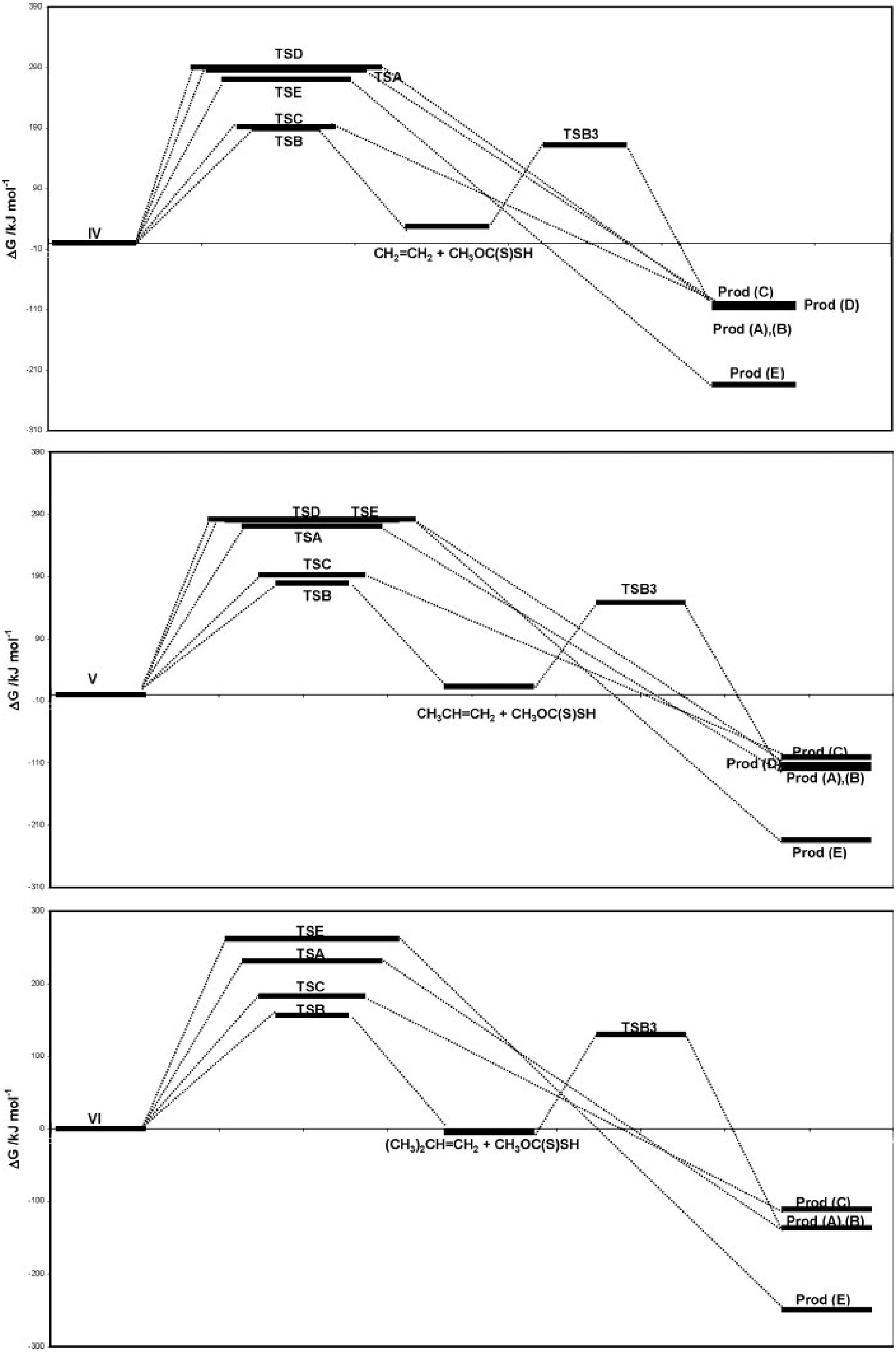


Figure 3. Gibbs energy profile at 629.15 K, evaluated at the MP2/6-31G(d) level, for the pyrolysis process of S-alkyl O-methyl dithiocarbonates. Relative free energy values (to reactants, in kJ mol^{-1}) of the transition states found are as follows: TSA-IV, 286.2; TSB-IV, 189.6; TSC-IV, 192.1; TSD-IV, 290.7; TSE-IV, 270.5; TSA-V, 271.2; TSB-V, 179.4; TSC-V, 192.6; TSD-V, 281.8; TSE-V, 280.5; TSA-VI, 231.3; TSB-VI, 156.6; TSC-VI, 182.6; TSE-VI, 261.8

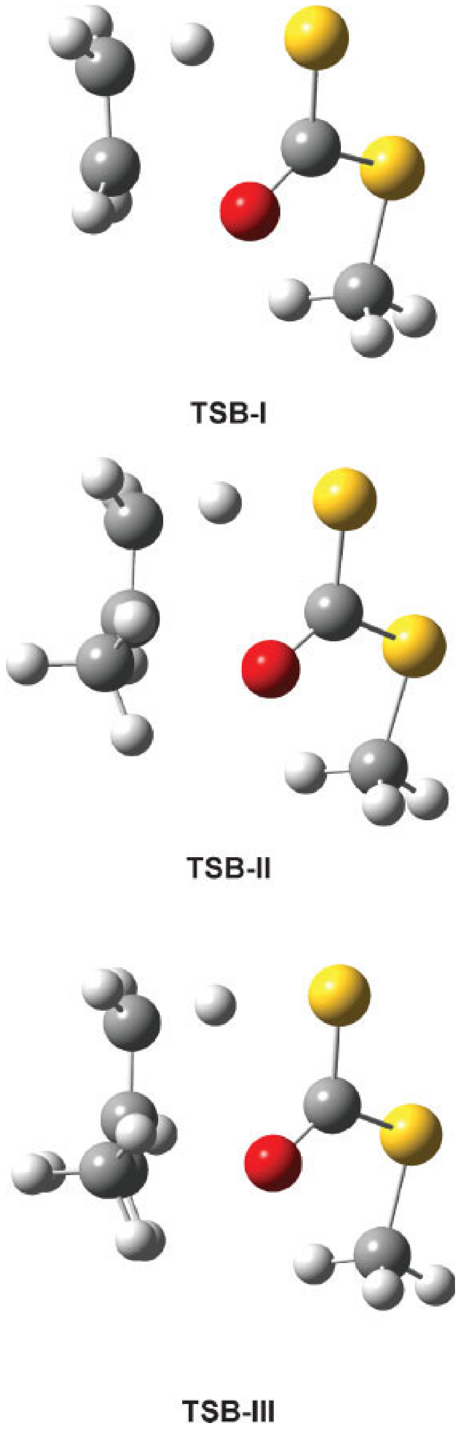


Figure 4. Structures of the transition states, TSB for each reaction, corresponding to the first step of mechanism (B) in the thermolysis of O-alkyl S-methyl dithiocarbonates, optimized at the MP2/6-31G(d) level of theory.

a measure of the bond order and, hence, of the bond strength between these two atoms, thus, if the evolution of the bond indices corresponding to the bonds being made or broken in a chemical reaction is analyzed along the reaction path, a very precise image of the timing and extent of the bond-breaking and bond-forming processes at every point can be achieved.[37]

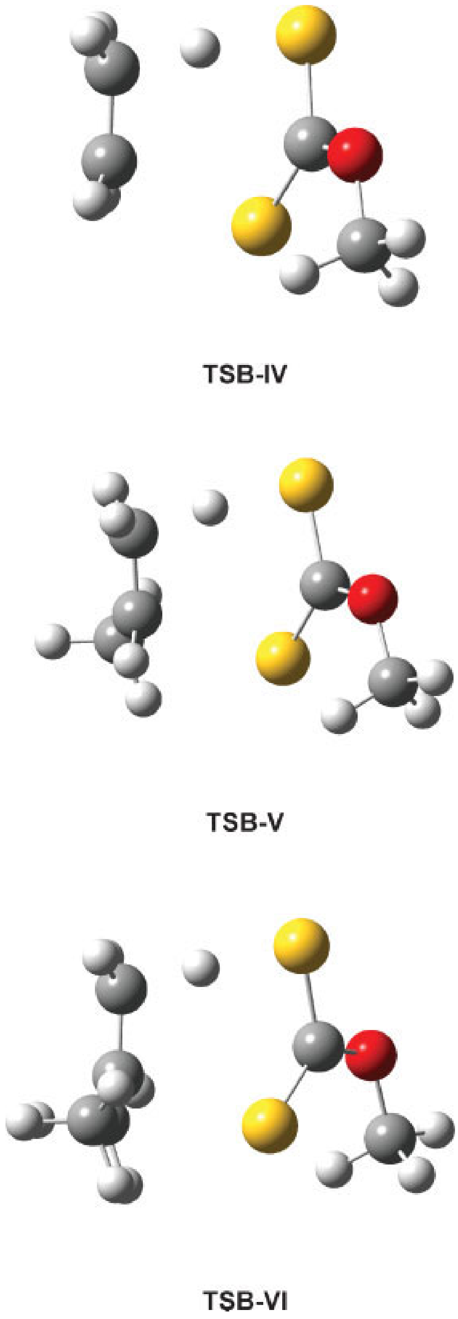


Figure 5. Structures of the transition states, TSB for each reaction, corresponding to the first step of mechanism (B) in the thermolysis of S-alkyl O-methyl dithiocarbonates, optimized at the MP2/6-31G(d) level of theory.

The Wiberg bond indices corresponding to the bonds involved in the reaction center of the first step of the mechanism (B) for all the reactants, transition states, and products are collected in Table 3.

Moyano *et al.*[37] have defined a relative variation of the bond index at the transition state, δB_i, for every bond, i, involved in a chemical reaction as:

$$\delta B_i = \frac{(B_i^{\mathrm{TS}} - B_i^{\mathrm{R}})}{(B_i^{\mathrm{P}} - B_i^{\mathrm{R}})} \qquad (5)$$

Table 2. MP2/6-31G(d)-calculated main distances, in Ångstroms, in the reactants and transition states corresponding to the first step of mechanism (B) for all the studied reactions

	Distance, Å					
	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	1.632	1.336	1.466	1.521	1.084	5.193
TSB-I	1.720	1.261	1.893	1.393	1.453	1.485
II	1.637	1.345	1.463	1.516	1.092	3.006
TSB-II	1.720	1.261	1.893	1.393	1.453	1.485
III	1.637	1.342	1.480	1.521	1.089	2.726
TSB-III	1.720	1.258	1.926	1.400	1.430	1.495
	S_1–C_2	C_2–S_3	S_3–C_4	C_4–C_5	C_5–H_6	H_6–S_1
IV	1.634	1.773	1.812	1.522	1.091	2.976
TSB-IV	1.702	1.668	2.467	1.394	1.349	1.614
V	1.635	1.770	1.825	1.523	1.091	2.948
TSB-V	1.703	1.667	2.510	1.395	1.335	1.631
VI	1.635	1.768	1.849	1.525	1.090	2.692
TSB-VI	1.702	1.666	2.566	1.398	1.318	1.653

View Fig. 1 to atom labels.

where the superscripts R, TS, and P refer to reactants, transition sates, and products, respectively. So, it is possible to calculate the percentage of evolution of the bond order through the chemical step by means of[38]

$$\%EV = 100\delta B_i \tag{6}$$

The calculated percentages of evolution of the bonds involved in the reaction center are collected in Table 3. As it can be seen, in the case of O-alkyl S-methyl dithiocarbonates, **I**, **II**, and **III**, the breaking of the O_3—C_4 bond is the most advanced process (65–77%), followed by the transformation of the S_1—C_2 double bond into a single one (*ca.* 58%) and of the C_2—O_3 single bond into a double one (54–58%). The least advanced process is the formation of the C_4—C_5 double bond (only *ca.* 30%), followed by the formation of the H_6—S_1 bond (31–36%), and the breaking of the C_5—H_6 bond (39–43%). In the case of S-alkyl O-methyl dithiocarbonates, the behavior is similar but the percentages of evolution of each type of bond are different. The most advanced process is the breaking of the S_3—C_4 bond (65–72%), followed by the transformation of the S_1—C_2 double bond into a single one (61–63%) and of the C_2—S_3 single bond into a double one (*ca.* 57%). The least advanced process is the formation of the C_4—C_5 double bond (39–42%), followed by the formation of the H_6—S_1 bond (46–51%) and the breaking of the C_5—H_6 bond (50–55%). The dissociation of the C_α—X bond before the C_β—H bond is in accordance with the proposal by Taylor *et al.*[39,40] for the 1,5 thermal eliminations, based on the fact that the Hammett ρ-values at the α-carbon were of larger magnitude than those observed for the β-carbon.

The results also imply that the more the C_α—X bond is dissociated in the transition structure, the faster is the rate of reaction; and that the more the C_β—H bond is dissociated, the slower is the reaction. This trend in bond lengthening can be mirrored in the NBO atomic charges. In Table 4, we have collected the natural atomic charges (the nuclear charges minus summed natural populations of the natural atomic orbitals on the atoms) at the atoms involved in the first step of the mechanism (B) for all the studied reactions.

There is a buildup of negative charge on X_3 atom in each transition structure, consistent with C_α—X bond dissociation that increases with the increasing rate, in accordance with the above observation that the C_α—X bond is 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 trend in C_β—H bond lengthening.[19]The average value, δB_{av}, is calculated as[37]

$$\delta B_{av} = \frac{1}{n}\sum \delta B_i \tag{7}$$

with *n* being the number of bonds involved in the reaction, measures the degree of advancement of the transition state along the reaction path.

The calculated δB_{av} values for the first step of the mechanism (B) of the studied reactions are shown in Table 3. As it can be seen, the δB_{av} values show that there is a difference between the transition states of the first step of mechanism (B) of the Chugaev reaction for both type of dithiocarbonates. In the case of O-alkyl S-methyl dithiocarbonates, δB_{av} values range from 0.478 to 0.485, increasing from O-ethyl to O-*tert*-butyl, indicating that transition states have an 'early' character, nearer to the reactants than to the products. In the case of S-alkyl O-methyl dithiocarbonates, δB_{av} values range from 0.543 to 0.556, decreasing from S-ethyl to S-*tert*-butyl, indicating that transition states have a 'late' character, nearer to the products than to the reactants. The synchronicity, *Sy*, of a chemical reaction can be calculated as follows:

$$Sy = 1 - A \tag{8}$$

Table 3. Wiberg bond indices, B_i, of reactants, transition states, and products; percentage of evolution through the chemical process of the bond indices at the transition states, %EV; degree of advancement of the transition states, δB_{av}, and absolute synchronicities, *Sy*, for the first step of mechanism (B) of the studied reactions

		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
	%EV	57.0	53.9	65.8	31.0	42.9	36.0
			$\delta B_{av} = 0.478$			$Sy = 0.860$	
II	B_i^R	1.666	1.041	0.790	1.018	0.928	0.002
	B_i^{TS}	1.319	1.407	0.225	1.310	0.549	0.325
	B_i^P	1.070	1.695	0.000	1.985	0.000	0.962
	%EV	58.2	56.0	71.6	30.2	40.8	33.7
			$\delta B_{av} = 0.484$			$Sy = 0.832$	
III	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
	%EV	57.9	57.6	76.8	28.8	39.0	31.0
			$\delta B_{av} = 0.485$			$Sy = 0.807$	
		S_1–C_2	C_2–S_3	S_3–C_4	C_4–C_5	C_5–H_6	H_6–S_1
IV	B_i^R	1.688	1.108	1.001	1.027	0.927	0.003
	B_i^{TS}	1.312	1.466	0.350	1.447	0.420	0.492
	B_i^P	1.091	1.726	0.000	2.034	0.000	0.953
	%EV	63.0	57.9	65.0	41.7	54.7	51.5
			$\delta B_{av} = 0.556$			$Sy = 0.932$	
V	B_i^R	1.684	1.115	0.980	1.016	0.926	0.004
	B_i^{TS}	1.311	1.470	0.309	1.411	0.435	0.472
	B_i^P	1.091	1.726	0.000	1.985	0.000	0.953
	%EV	62.9	58.1	68.5	40.7	53.0	49.4
			$\delta B_{av} = 0.554$			$Sy = 0.916$	
VI	B_i^R	1.680	1.120	0.960	1.004	0.915	0.009
	B_i^{TS}	1.319	1.465	0.269	1.369	0.457	0.446
	B_i^P	1.091	1.726	0.000	1.934	0.000	0.953
	%EV	61.4	56.9	72.0	39.3	50.1	46.2
			$\delta B_{av} = 0.543$			$Sy = 0.899$	

Values calculated at the MP2/6-31G(d) level. View Fig. 1 to atom labels.

A being the asynchronicity, which is calculated by using the expression proposed by Moyano *et al.*[37]

$$A = \frac{1}{(2n-2)} \sum \frac{|\delta B_i - \delta B_{av}|}{\delta B_{av}} \qquad (9)$$

Synchronicities vary between zero and one, which is the case when all of the bonds implicated in the reaction center have broken or formed at exactly the same extent in the TS. The *Sy* values obtained in this way are, in principle, independent of the degree of advancement of the transition state. The *Sy* values calculated for the reactions studied are shown in Table 3. The synchronicities range from 0.807 to 0.860 for the reactions of compounds **I**, **II**, and **III**, and from 0.899 to 0.932 for the reactions of compounds **IV**, **V**, and **VI**, indicating that there is a big difference between the processes for both type of dithiocarbonates. For O-alkyl S-methyl dithiocarbonates the mechanism corresponds to highly asynchronous processes, whereas for S-alkyl O-methyl dithiocarbonates the *Sy* values indicate that the mechanism corresponds to slightly asynchronous processes. In both cases, the synchronicity rapidly decreases when the size of the alkyl group attached to S or O atoms increases.

Asymmetrical charge distribution between C_α and C_β atoms in the transition structures (positively charged C_α and negatively charged C_β) also suggests asynchronous character in these reactions. The more polar the C_α—C_β bond, the faster is the reaction.

Another aspect to be taken into account is the relative asynchronicity of the bond-breaking and the bond-forming processes that measures the 'bond deficiency' along the reaction path. In the reactions of O-alkyl S-methyl dithiocarbonates, the bond-breaking processes are more advanced (55–58%) than the bond-forming ones (39–40%) indicating a bond deficiency in the transition states. The same behavior is observed in the reactions of S-alkyl O-methyl dithiocarbonates where the bond-breaking processes are more advanced (61–62%) than

Table 4. MP2/6–31G(d)-calculated NBO charges, at the atoms involved in the first step of the mechanism (B) for the studied reactions

	S_1	C_2	O_3	C_4	C_5	H_6
I	−0.171	0.110	−0.625	−0.048	−0.665	0.226
TSB—I	−0.173	0.207	−0.726	0.018	−0.808	0.266
II	−0.181	0.118	−0.634	0.139	−0.667	0.240
TSB—II	−0.212	0.236	−0.751	0.232	−0.799	0.275
III	−0.182	0.132	−0.645	0.303	−0.668	0.248
TSB-III	−0.239	0.240	−0.767	0.433	−0.790	0.287
	S_1	C_2	S_3	C_4	C_5	H_6
IV	−0.142	0.113	0.275	−0.577	−0.650	0.239
TSB-IV	−0.014	0.105	−0.112	−0.222	−0.744	0.216
V	−0.145	0.117	0.270	−0.371	−0.647	0.243
TSB-V	−0.039	0.110	−0.149	0.015	−0.749	0.266
VI	−0.146	0.122	0.266	−0.160	−0.649	0.252
TSB-VI	−0.061	0.117	−0.180	0.239	−0.751	0.239

View Fig. 1 to atom labels.

the bond-forming ones (48–50%), but the smaller difference indicates that the deficiency is minor.

CONCLUSIONS

Among all the pathways for the different processes studied for O-alkyl S-methyl and S-alkyl O-methyl dithiocarbonates, the lowest barriers correspond to the first step in the mechanism in two steps of the thermal elimination reaction (the Chugaev reaction). Theoretical results confirm that the thermolysis of xanthates is a *cis*-concerted elimination that occurs via a mechanism in two steps, the first one being the rate-limiting step.

In the case of S-ethyl O-methyl dithiocarbonate, the activation Gibbs energy of the mechanism of the thion-to-thiol rearrangement is only 2.5 kJ mol^{-1} higher than the value corresponding to the process of thermal elimination. This result could explain the experimental fact that the thermal elimination of this compound could not be studied because the compound did not well behaved kinetically, giving a curved Arrhenius plot.

The breaking of the C_α—X bond is the most advanced process in all the reactions studied. This dissociation in advance of the C_α—X bond before than the C_β—H bond is in accordance with a previous proposal in the literature based on the fact that the Hammett ρ-values at the α-carbon were of larger magnitude than those observed for the β-carbon. The more the C_α—X bond is dissociated in the transition structure, the faster is the rate of reaction.

The calculated δB_{av} values for the first step of the mechanism (B) of the studied reactions show a difference between the transition states for both type of dithiocarbonates. In the case of O-alkyl S-methyl dithiocarbonates, δB_{av} values range from 0.478 to 0.485, increasing from O-ethyl to O-*tert*-butyl, indicating that transition states have an 'early' character, nearer to the reactants than to the products. In the case of S-alkyl O-methyl dithiocarbonates, δB_{av} values range from 0.543 to 0.556, decreasing from S-ethyl to S-*tert*-butyl, indicating that transition states have a 'late' character, nearer to the products than to the reactants.

Calculated synchronicities range from 0.807 to 0.860 for the reactions of compounds **I**, **II**, and **III**, and from 0.899 to 0.932 for the reactions of compounds **IV**, **V**, and **VI**, indicating that there is a big difference between the processes for both types of dithiocarbonates. For O-alkyl S-methyl dithiocarbonates the mechanism corresponds to highly asynchronous processes, whereas for S-alkyl O-methyl dithiocarbonates the *Sy* values indicate that the mechanism corresponds to slightly asynchronous processes. In both cases, the synchronicity rapidly decreases when the size of the alkyl group attached to S or O atoms increases.

Supplementary Material

Tables S1 and S2 with the MP2/6-31G(d)-calculated electronic energies, zero-point vibrational energies, thermal corrections to enthalpies, and entropies, for the reactants, transition states and products involved in all the reactions studied; and Table S3 with the MP2/6-31G(d)-optimized Cartesian coordinates for all the studied transition states.

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