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The Regioselective Pyrolysis of (Trithio)carbonate: A Computational Study[1]

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Abstract—The regioselective pyrolysis of *sec*-butyl methyl (trithio)carbonate was calculated at the MP2/6-31G(d) level in the Gaussian program. Twelve possible pathways were calculated. Nine of them gave the desired alkene products, 1-butene, *E*-butene, and *Z*-butene, and the other three, the rearrangement products, *sec*-butyl methyl ether and butanone for *sec*-butyl methyl carbonate and *sec*-butyl methyl thioether and butane-2-thione for *sec*-butyl methyl trithiocarbonate. It was shown that the two-step mechanism, including the carbonyl oxygen- or thion sulfur atom-involved six-membered ring transition state, as rate-determining step, is a preferred mechanism of the pyrolysis. The calculated product distribution is consistent with the experimental data on the pyrolysis of *sec*-butyl methyl carbonate. The product distribution for *sec*-butyl methyl trithiocarbonate was also predicted by the MP2/6-31G(d) method.

Keywords: MP2/6-31G(d), pyrolysis, regioselectivity, (trithio)carbonate

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INTRODUCTION

Versatile synthetic methodologies, such as Cope rearrangement, Burgess dehydration, Wittig olefination, Chugaev pyrolysis, Grob fragmentation, and other methods are used for alkene synthesis. Among them, the Chugaev elimination is the advantageous reaction, since it does not lead to carbon skeleton rearrangement [1–11]. Two mechanisms of the pyrolysis are suggested, resulting in the formation of the same products and each having its own support [7, 8]. The first one-step mechanism involves a six-membered ring transition state to generate the desired alkenes and two by-products. The second two-step mechanism also involves the six-membered ring, whereas the desired alkenes and an unstable intermediate formed in the process are rapidly decompose onto the same two by-products, which are formed by the first mechanism. The first mechanism was confirmed experimentally in a Hückel's study [12] in 1940 and was further corroborated by the Stimson's data on the thermolysis of carbonate esters in 1976 [13].

At the same time, in a number of studies, the opposite results are reported [5, 6, 9]. The second mechanism was confirmed by the positive ρ-factor of the Hammett correlations in comprehensive experimental studies on the thermolysis of esters, thiocarbonates, thiocarbamates, amides, and other compounds [10, 11, 14–16]. Further, the isotope effect and the *cis*-elimination mechanism of the second pathway were determined elsewhere [17, 18–20].

The pyrolysis mechanism was also studied by the theoretical methods. An AM1 semi-empirical method was used to calculate the thermolysis of carbonate esters by Lee et al. [21] to support the second mechanism. Later, calculations were performed at the higher levels: Erickson et al. [22] employed the MP2/6-31G(d)//HF/6-31G(d) level, and Vélez et al. [23–28], the M05-2X/6-31G(d,p), MP2/6-31G(d), MP2/6-31++G(d,p), MP2/6-311++G(2d,p)//MP2/6-31G(d), and QCISD(T)/6-311+G(3df,2p)//MP2(full)/6-31G(d) methods. The thermolysis of EtSC(=S)OMe

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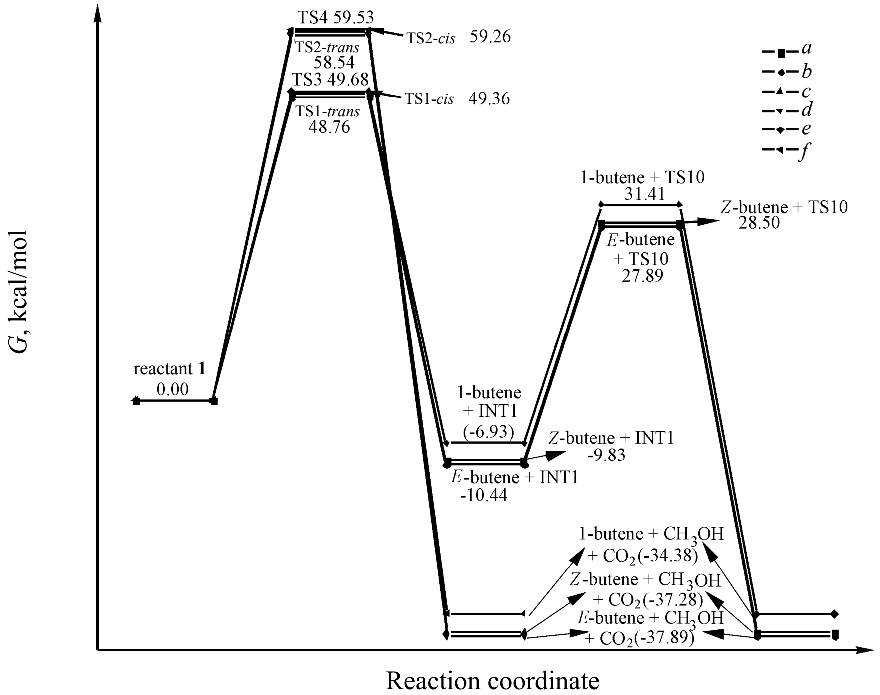


Fig. 1. Gibbs energy profile of the roots *a*–*f* for the pyrolysis of *sec*-butyl methyl carbonate.

was considered at different theoretical levels by Deleuze et al. [29]. The above calculations show that the MP2 and CCSD(T) methods give the same results. In our previous studies, the regioselective pyrolysis of thiocarbonates and (thion)carbonates was calculated by the MP2/6-3 1G(d) method [30–32]. In this study, we calculate the regioselective pyrolysis of *sec*-butyl methyl (trithio)carbonate.

Calculation methods. Gaussian 03 software was used to calculate reactants, transition states, intermediates, and products [33]. In continuation of our calculations [30–32], the MP2/6-31G(d) method was also employed in this study. The experimental temperature of 723.15 K was used for frequency calculations to obtain the corresponding thermodynamic data [34–36]. The zero-point vibrational energies were corrected based on the applied method with a scaling factor of 0.9670 [37]. All structures were determined by the vibrational analysis. It was found that the reactants, intermediates, and products have no imaginary frequencies, whereas the transition-state structures have only one imaginary frequency, which was further corroborated by calculating the intrinsic reaction coordinate (IRC) [38].

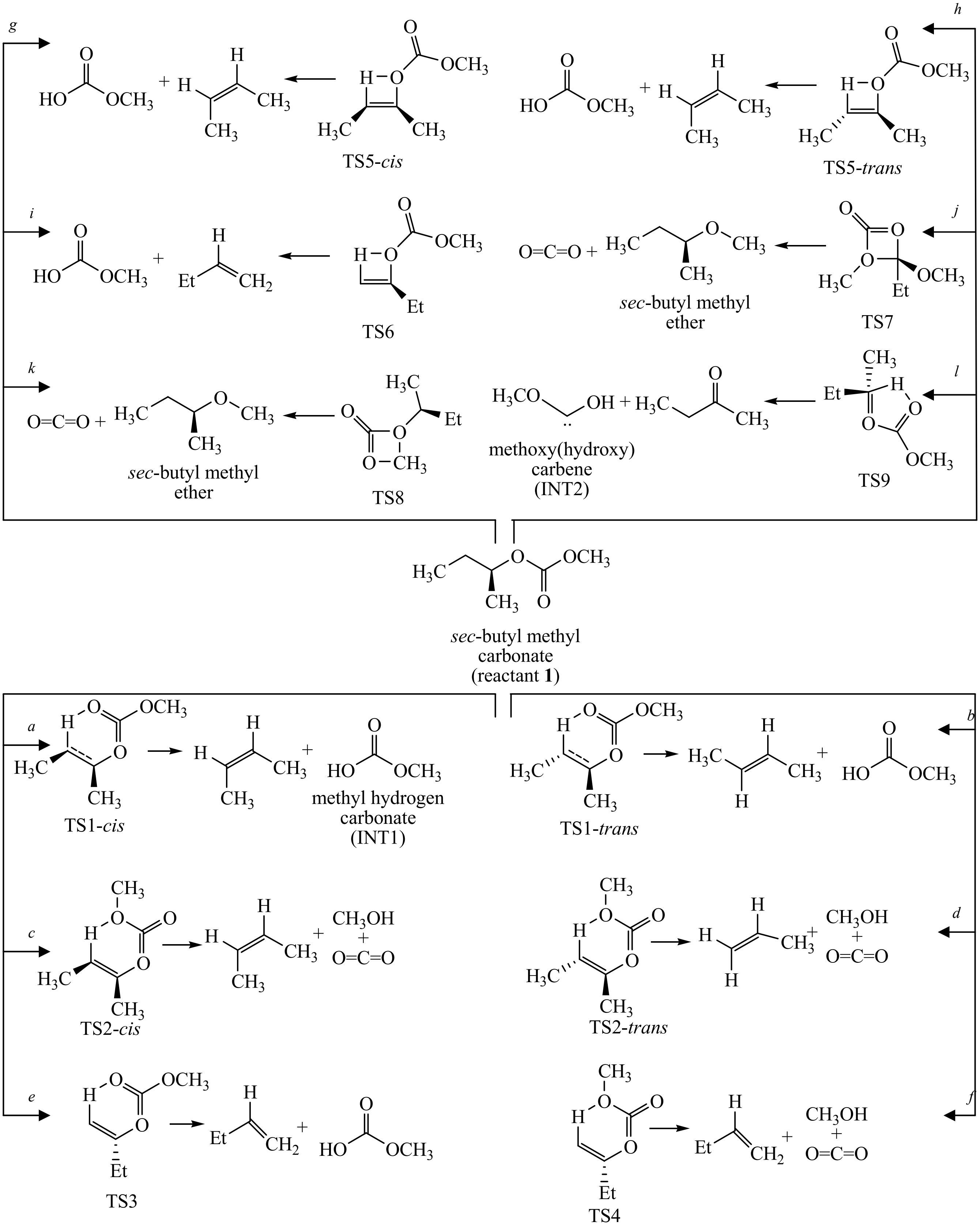
RESULTS AND DISCUSSION

As was reported previously [30], the theoretical product distribution calculated by the MP2-6-31G(d) method for pyrolysis of *O*-*sec*-butyl *S*-methyl xanthate and *S*-*sec*-butyl *O*-methyl xanthate is consistent with the experimental results [34]. Therefore, the same method was employed in our present calculation for the thermal decomposition of *sec*-butyl methyl (trithio)-carbonate.

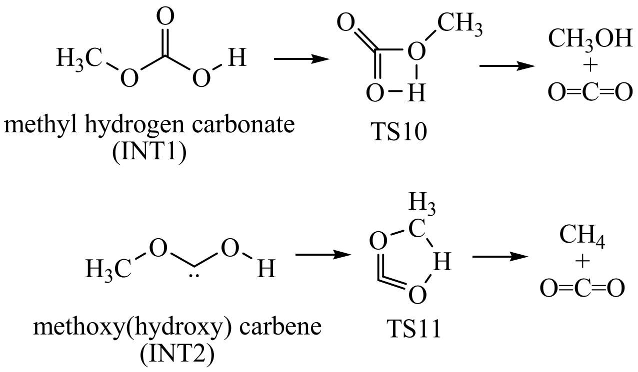
Pyrolysis of *sec*-butyl methyl carbonate. Schemes 1 and 2 present twelve possible pathways for the pyrolysis of *sec*-butyl methyl carbonate in the gas phase at the MP2/6-31G(d) level.

Nine of them can give the desired alkene products, in agreement with the experimental results. Roots *a*, *b*, and *e* are the second mechanism involving the attack of an sp^2 oxygen atom to a β-hydrogen to generate *Z*-butene, *E*-butene, and 1-butene, as well as an unstable intermediate, methyl hydrogen carbonate (INT1), which would convert to carbon dioxide and methanol via a four-membered ring transition state (TS10). The first mechanism is illustrated by roots *c, d*, and *f*, including an oxygen attack in one step. The other

Scheme 1. Twelve possible pathways for the pyrolysis of *sec*-butyl methyl carbonate.



Scheme 2. Thermal decomposition of INT1 and INT2.



possible pyrolysis roots include the four-membered ring transition states (roots *g*, *h*, and *i*) to alkene products, roots *j* and *k* of ether generation, and the five-membered ring root *l* to produce a butanone and a methoxy(hydroxy) carbene (INT2).

The zero-point vibrational energies, Gibbs free energies, and the corrected Gibbs free energies for all species are collected in Table 1. The relative free energy profiles for twelve possible roots are plotted in Figs. 1, 2.

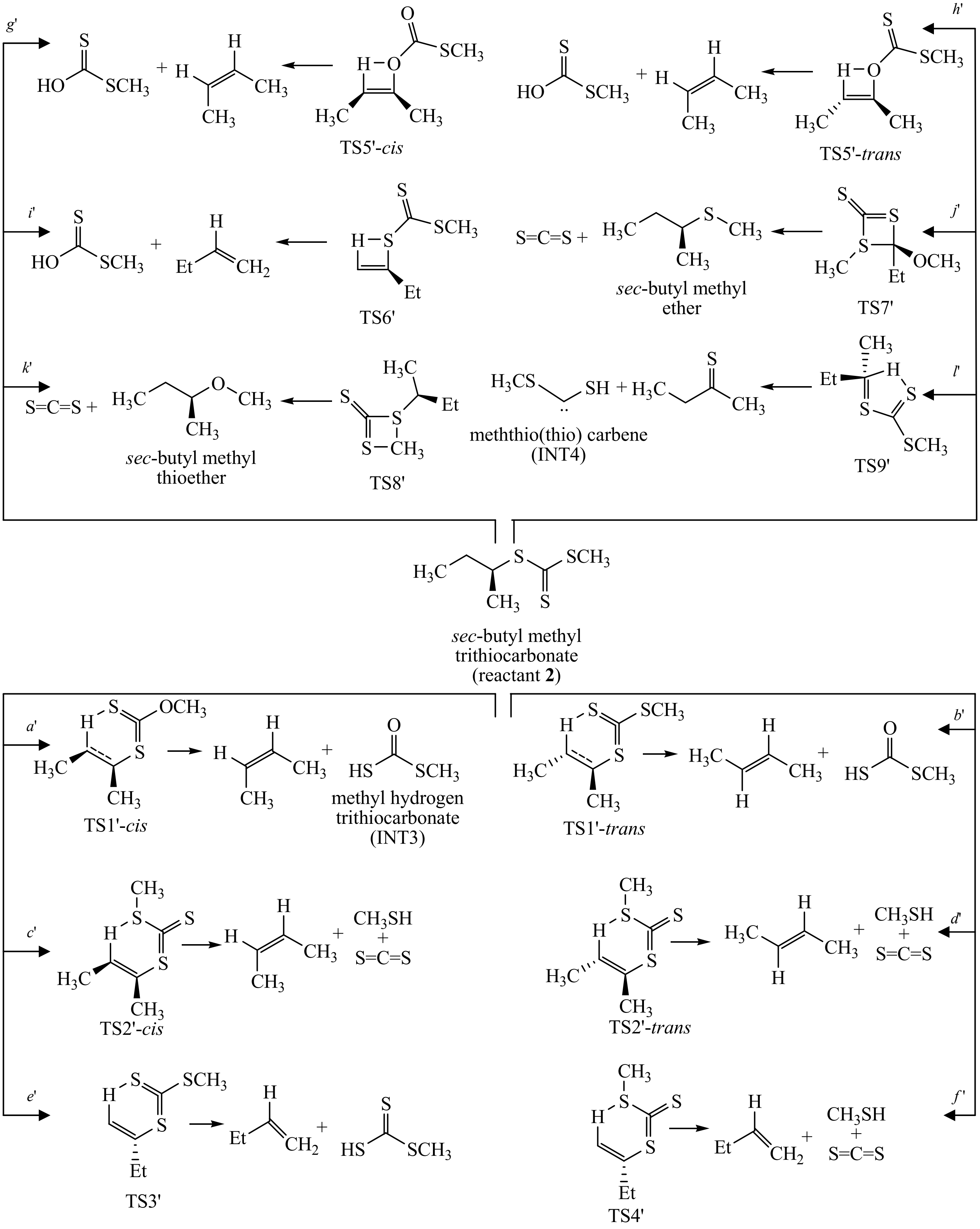
As seen from Figs. 1, 2, the roots *a*, *b*, and *e* of the two-step mechanism are the lowest three roots (activation energies are 48.76, 49.36, and 49.68 kcal/mol for TS1-*trans*, TS1-*cis*, and TS3, respectively), which would give corresponding products, *E*-butene, *Z*-butene, and 1-butene. Our calculated energies are consistent with the experimental data on the alkene product distribution (about 28 : 19 : 15 after normalization) for *E*-butene, *Z*-butene, and 1-butene [34–36]. An unstable intermediate, methyl hydrogen carbonate (INT1), also obtained for the above roots, decomposes onto methanol and carbon dioxide with an activation energy of 38.33 kcal/mol. The overall reaction process was exothermic (–37.89, –37.28, and –34.38 kcal/mol, respectively).

As for the roots *c*, *d*, and *f* of the one-step mechanism, TS2-*trans*, TS2-*cis*, and TS4 have the higher activation energies (58.54, 59.26, and 59.53 kcal/mol) than the corresponding compounds (at least 8.86 kcal/mol for TS1-*trans*, TS1-*cis*, and TS3). This clearly demonstrates a preference for two-step mechanism relative to one-step one. For other three alkene-generation roots *g*, *h*, and *i*, the activation energies are even higher 62.31, 62.50, and 63.14 kcal/mol, respectively, for

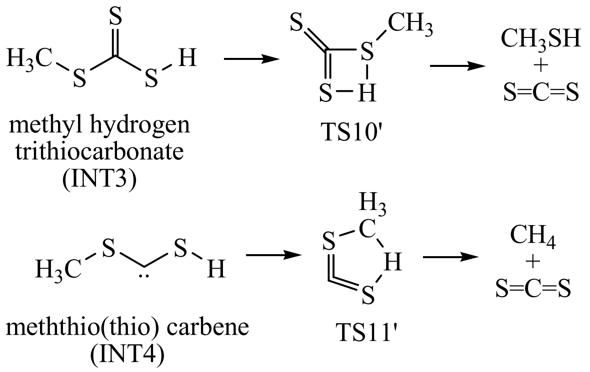
Table 1. Zero-point vibrational energies and Gibbs free energies, in Hartrees, and the calculated Gibbs free energies for the reactants, transition states and products involved in the pyrolysis of *sec*-butyl methyl carbonate (Scheme 2 and 3)

Species	ZPE	*G*	Corrected *G*	Species	ZPE	*G*	Corrected *G*
Reactant **1**	0.185265	–460.053182	–460.0592957	TS10	0.0627260	–303.4093540	–303.4114240
TS1-*cis*	0.177666	–459.974765	–459.9806280	TS11	0.0561780	–228.2867530	–228.2886069
TS1-*trans*	0.177572	–459.975734	–459.9815939	1-Butene	0.1111760	–156.5941540	–156.5978228
TS2-*cis*	0.176204	–459.959043	–459.9648577	*Z*-Butene	0.1107970	–156.5987920	–156.6024483
TS2-*trans*	0.176091	–459.96019	–459.9660010	*E*-Butene	0.1107120	–156.5997650	–156.6034185
TS3	0.177797	–459.974264	–459.9801313	INT1	0.0689780	–303.4702440	–303.4725203
TS4	0.176346	–459.958602	–459.9644214	INT2	0.0626620	–228.3319750	–228.3340428
TS5-*cis*	0.177274	–459.953839	–459.9596890	Ether	0.1695230	–271.9444000	–271.9499943
TS5-*trans*	0.177694	–459.95414	–459.9600039	Butanone	0.1155190	–231.6698910	–231.6737031
TS6	0.177314	–459.952826	–459.9586774	CH_3OH	0.0526030	–115.3590270	–115.3607629
TS7	0.180803	–459.948016	–459.9539825	CH_4	0.0463600	–40.3369190	–40.3384489
TS8	0.181008	–459.939523	–459.9454963	O=C=O	0.0115110	–188.1551180	–188.1554979
TS9	0.175785	–459.892692	–459.8984929				

Scheme 3. Twelve possible pathways for the pyrolysis of *sec*-butyl methyl trithiocarbonate.



Scheme 4. Thermal decomposition of INT3 and INT4.



TS5-*trans*, TS5-*cis* and TS6). TS7 and TS8 would release carbon dioxide to generate *sec*-butyl methyl ether with corresponding activation energies of 66.09 and 71.41 kcal/mol. Finally, butanone and methoxy(hydroxy) carbene (INT2) can be obtained via a TS9 with an activation energy of 100.91 kcal/mol. This step was endothermic (32.35 kcal/mol). However, the decomposition of INT2 was highly exothermic process (the released energy is 100.34 kcal/mol).

Pyrolysis of *sec*-butyl methyl trithiocarbonate. Scheme 3 and 4 illustrate twelve pathways for the pyrolysis of *sec*-butyl methyl trithiocarbonate. The corresponding zero-point vibrational energies, Gibbs free energies, and corrected Gibbs free energies are collected in Table 2 for all species. The free energy profiles are plotted in Figs. 3, 4 for all pathways.

Twelve roots were also considered for the pyrolysis of *sec*-butyl methyl trithiocarbonate, of which *Z*-butene can be obtained from roots *a*', *c*', and *g*', *E*-butene, from roots *b*', *d*', and *h*', and 1-butene, from roots *c*', *f*', and *i*'. Roots *j*' and *k*' gave the same products, *sec*-butyl methyl thioether and carbon disulfide. The only five-membered ring transition state was found for root *l*' to generate butane-2-thione and meththio(thio) carbene (INT4), which changed to gaseous carbon disulfide and methane *a*' TS11', another five-membered ring transition state.

For the pyrolysis of *sec*-butyl methyl trithiocarbonate, the energy profiles were the same. TS1'-*trans* (43.43 kcal/mol), TS1'-*cis* (44.37 kcal/mol) and TS3' (46.82 kcal/mol) corresponding to roots *a*', *b*,' and *e*', are the lowest transition states, indicating that *E*-butene is major product and *Z*-butene and 1-butene, minor products. This result differs from our previous data on the pyrolysis of *S*-*sec*-butyl *O*-methyl xanthate, in which the activation energies of two four-membered ring transition states (TS5'-*cis* and TS5'-*trans*) were lower than the energy of a six-membered ring transition state (TS3'), which was explained by the larger atomic size of sulfur in comparison with oxygen [30]. In addition to the alkene products, an unstable

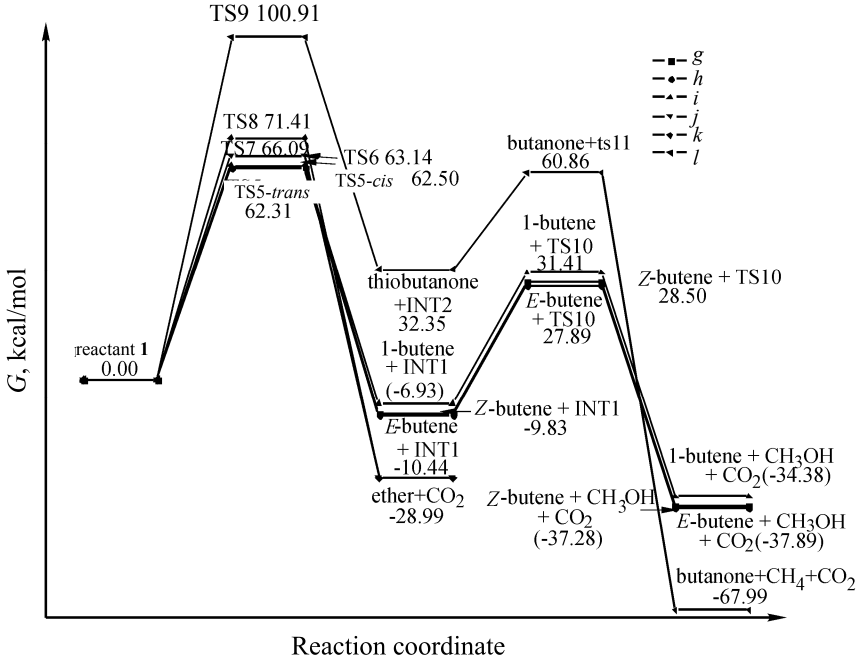


Fig. 2. Gibbs energy profile of the roots *g*–*l* for the pyrolysis of *sec*-butyl methyl carbonate.

Table 2. Zero-point vibrational energies and Gibbs free energies, in Hartrees, and the calculated Gibbs free energies for the reactants, transition states and products involved in the pyrolysis of *sec*-butyl methyl trithiocarbonate (Scheme 4 and 5)

Species	ZPE	*G*	Corrected *G*	Species	ZPE	*G*	Corrected *G*
reactant **2**	0.1755010	–1427.8407900	–1427.8465815	TS10'	0.0530170	–1271.1849400	–1271.1866896
TS1'-*cis*	0.1680320	–1427.7703260	–1427.7758711	TS11'	0.0496070	–873.4784910	–873.4801280
TS1'-*trans*	0.1677690	–1427.7718330	–1427.7773694	INT3	0.0572810	–1271.2484320	–1271.2503223
TS2'-*cis*	0.1667360	–1427.7461680	–1427.7516703	INT4	0.0542060	–873.5264160	–873.5282048
TS2'-*trans*	0.1665330	–1427.7481490	–1427.7536446	CH_3SH	0.0477860	–437.9747690	–437.9763459
TS3'	0.1679540	–1427.7664220	–1427.7719645	S=C=S	0.0071080	–833.3230600	–833.3232946
TS4'	0.1667420	–1427.7429480	–1427.7484505	Thioether	0.1662770	–594.5640030	–594.5694901
TS5'-*cis*	0.1683740	–1427.7369190	–1427.7424753	Z-Butene	0.1107970	–156.5987920	–156.6024483
TS5'-*trans*	0.1682960	–1427.7367180	–1427.7422718	*E*-Butene	0.1107120	–156.5997650	–156.6034185
TS6'	0.1679360	–1427.7348950	–1427.7404369	1-Butene	0.1111760	–156.5941540	–156.5978228
TS7'	0.1721760	–1427.7252800	–1427.7309618	Thiobutanone	0.1136950	–554.2545770	–554.2583289
TS8'	0.1721530	–1427.7181510	–1427.7238320	CH_4	0.0463600	–40.3369190	–40.3384489
TS9'	0.1686120	–1427.7379740	–1427.7435382				

intermediate, methyl hydrogen trithiocarbonate (INT3), was also obtained to rapidly decompose onto methanethiol and carbon disulfide via a four-membered ring transition state (TS10') with an energy barrier of 39.93 kcal/mol. The one-step mechanisms were also considered as roots *c*', *d*', and *f*', with their activation energies however higher (59.56 kcal/mol for TS2'-*cis*, 58.32 kcal/mol for TS2'-*trans*, and 61.58 kcal/mol for TS4'). Three other alkene-generation roots, *g*', *h*', and *i*' had even higher activation energies (65.33, 65.46, and

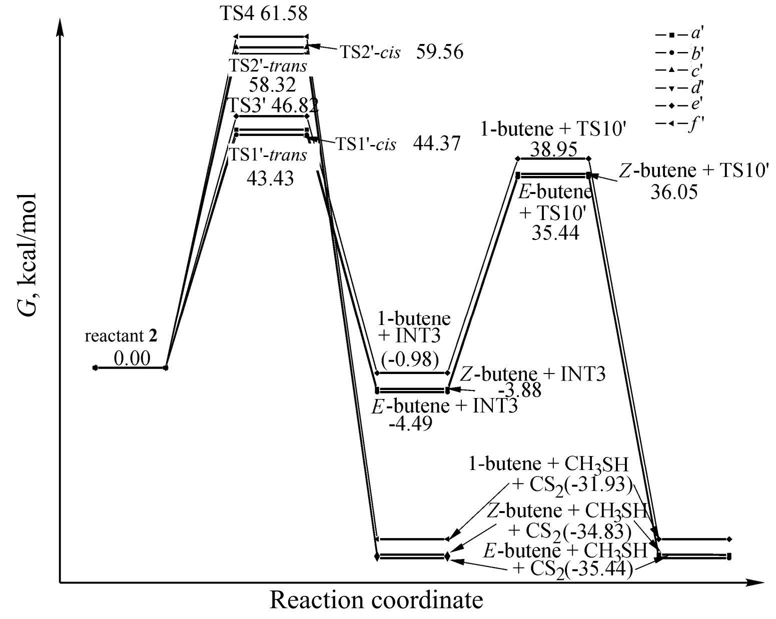


Fig. 3. Gibbs energy profile of the pathways *a*'–*f*' for the pyrolysis of *sec*-butyl methyl trithiocarbonate.

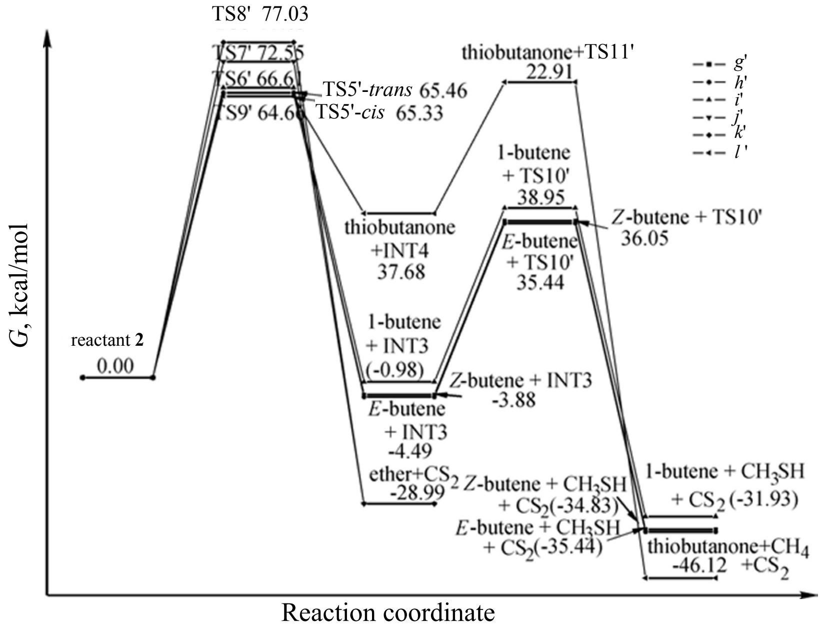


Fig. 4. Gibbs energy profile of the pathways *g'*–*l'* for the pyrolysis of *sec*-butyl methyl trithiocarbonate.

66.61 kcal/mol for TS5'-*cis*, TS5'-*trans*, and TS6', respectively). For roots *j*' and *k*', products were *sec*-butyl methyl thioether and carbon disulfide (activation energies 72.55 and 77.03 kcal/mol corresponding TS7' and TS8'). The overall processes are exothermic (–28.99 kcal/mol). Finally, the first transition state (TS9') for the five-membered ring root *l*' had the activation energy 64.66 kcal/mol to generate butane-2-thione and meththio(thio) carbene (INT4). INT4 rearranged to methane and carbon disulfide (TS11'), with activation energy 30.17 kcal/mol and released energy 113.97 kcal/mol. The overall energy of products on the energy profile diagram was lesser by 46.12 kcal/mol than the energy of reactants.

CONCLUSIONS

The theoretical calculation at the MP2/6-31G(d) level was performed to investigate the mechanisms of regioselective pyrolysis of *sec*-butyl methyl (trithio) carbonate. For one- and two-step mechanisms, twelve possible roots were found and a preference of the two-step mechanism was demonstrated. For the pyrolysis of *sec*-butyl methyl carbonate, a two-step mechanism of roots *a*, *b*, and *e* has three lowest activation energies, corresponding to generation of *E*-butene, *Z*-butene, and 1-butene. The result of this calculation is consistent with the experimental data on the product distribution. In the case of *sec*-butyl methyl trithiocarbonate, the products are distributed in the same order: TS1'-*trans* < TS1'-*cis* < TS3', i.e., *E*-butene is major product and *Z*-butene and 1-butene, minor products.

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