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Theoretical studies on the pyrolysis of (Thion)carbonates

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MP2/6-31G(d) was employed to investigate the theoretical calculations on the pyrolysis of alkyl methyl (thion)carbonates, where alkyl groups referred to ethyl, isopropyl and *t*-butyl groups. Nine possible pathways were considered for the pyrolysis of alkyl methyl thioncarbonates, while only seven possible pathways were found to pyrolyze alkyl methyl carbonates. Both of them had three pathways to generate the desired alkene products. Not only thermal elimination pathways were calculated, other possible mechanisms, such as rearrangements and nucleophilic substitutions, were also considered. The progress of the reactions was also investigated by the calculation of Wiberg bond indices at MP2/6-31G(d) level.

Keywords: MP2/6-31G(d); alkyl methyl (thion)carbonate; pyrolysis.

1. Introduction

As a valuable synthetic route to synthesize alkenes without rearrangement of the carbon skeleton, the pyrolysis of carbonate related compounds have been extensively investigated.[1–15]

As for the pyrolysis mechanism, although the same products can be obtained, two possible pathways had been long debated, as shown in Scheme 1.[7,8,16–18] A one-step mechanism was involved in the first pathway, yielding an alkene, a (thio) ether and a gas of carbon dioxide, carbon disulfide or carbonyl sulfide. The second pathway proceeded through a two-step mechanism, of which the first step generated the desired alkene product, as well as an unstable intermediate. The unstable
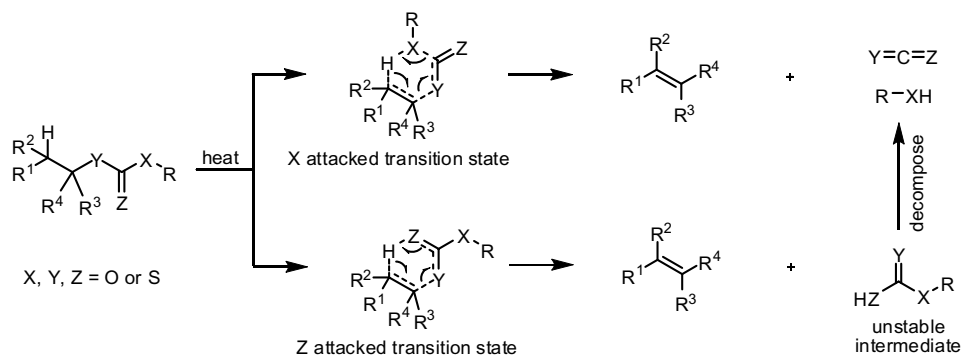
Scheme 1.   Two possible pathways for the pyrolysis of the carbonate related compounds.

intermediate would rapidly decompose to a (thio) ether and a gas of carbon dioxide, carbon disulfide or carbonyl sulfide, resulting in the same products as the first pathway.

The first pathway was supported by Stimson and Hückel,[19,20] while the second pathway was preferred by Smith,[5] Barton[9] and Cram.[6] Al-Awadi and Taylor group carried out a series pyrolysis of the esters, (thio) carbonates, carbamates, etc. They also approved the second pathway with their experimental evidences: the positive ρ-factor of Hammett correlation for the pyrolysis of aryl ethyl carbonate, as well as *t*-butyl *N*-aryl carbamates and the reduced reactivities of methyl alkyl carbonates as compared with phenyl alkyl carbonates.[10,11,21–23] The *cis*-elimination mechanism of the second pathway was further proven by Alexander and Mudrak in the pyrolysis of the Chugeave reaction.[24–26] Isotope effect was also carried out with solid evidences to prove the second pathway.[27]

The theoretical studies were also involved in the debate of the pyrolysis pathways.[28–31] The pyrolysis of carbonate esters at AM1 level was calculated by Lee group to support the second pathway.[32] In 1994, the pyrolysis activation energies of HSC(=S)OEt was calculated by Erickson and Kahn[33] at MP2/6-31G (d)//HF/6-31G(d) level. Recently, Vélez group did an extensive investigation on the pyrolysis of carbonate esters, carbamates and dithiocarbonates at higher level methods.[34–39] All these calculations supported the second pathways. Different theoretical levels and different basis sets were compared by Deleuze group[40] in the pyrolysis of EtSC(=S)OMe and its substituent effects with the conclusion that MP2 method gave comparable activation energies as CCSD(T). Harano[41] also utilized B3LYP/6-31G(d) theoretical level to study the transition states of MeSC(=S)OEt. We also performed the regioselective pyrolysis of Chugeav reaction and the pyrolysis of thiocarbonates recently at the MP2/6-31G(d) level.[42,43] As a continuous interest in the pyrolysis of carbonate related compounds, herein, we present our calculation result for the pyrolysis of alkyl methyl (thion)carbonates, where alkyl groups were ethyl, *i*-propyl and *t*-butyl groups, at the level of MP2/6-31G(d).

2. Computational Details

Gaussian-03 package were employed to calculate the pyrolysis of (thion)carbonates.[44] As mentioned by Deleuze group[40] that the MP2 level gave nice activation barriers as the CCSD(T) method, as well as the recent applications on the regioselective pyrolysis of Chugeav reaction and the pyrolysis of thiocarbonates[42,43] with the basis set of 6-31G(d),[45] the same computational level was also selected for the structural optimization. For the transition state calculations, force constants were also calculated with MP2/6-31G(d) method and noeigen test was applied to facilitate the transition state optimization. The frequency calculations were evaluated at 629 K, the same as the experimental temperature. A scaling factor of 0.9670 for the zero-point vibrational energies was used for correction.[46] All zero-gradient structures were characterized by a vibrational analysis with no imaginary frequency. All of the transition-state structures had only one imaginary frequency and the intrinsic reaction coordinates (IRC)[47] were followed to make sure that all transition states connected to the expected reactants and products.

The natural bond orbital (NBO) analysis[48,49] was utilized to investigate the bonding characteristics of all the reactants, transition states and products, which provided the atomic natural total charges and the Wiberg bond indices for the pyrolysis procedures.

Classic transition-state theory (TST)[50,51] was selected to calculate the rate constant, $k(T)$, for the rate-determining steps, as shown in Eq. (1), which assumes that the transmission coefficient is equal to unity:

$$k(T) = \frac{k_B T}{h} e^{\frac{-\Delta G^{\neq}(T)}{RT}}, \tag{1}$$

where k_B, h and R are the Boltzmann constant, Planck's constant and the universal gas constant, respectively, and $\Delta G^{\neq}(T)$ is the standard free energy of activation at the absolute temperature T.

Derived from TST, the activation energy, E_a, and the Arrhenius factor, A, could also be obtained from Eqs. (2) and (3):

$$E_a = \Delta H^{\neq}(T) + RT, \tag{2}$$

$$A = \frac{e k_B T}{h} e^{\frac{-\Delta S^{\neq}(T)}{R}}. \tag{3}$$

3. Results and Discussion

For alkyl methyl thioncarbonates **I** to **III**, nine possible pathways were proposed, of which pathways A to C, including two six-membered ring and one four-membered ring transition states, resulted in the desired alkene products, as observed by the experimental results. Four-membered ring rearrangements (pathways D to G) and five-membered ring transition states (pathways H and I) were also considered, giving
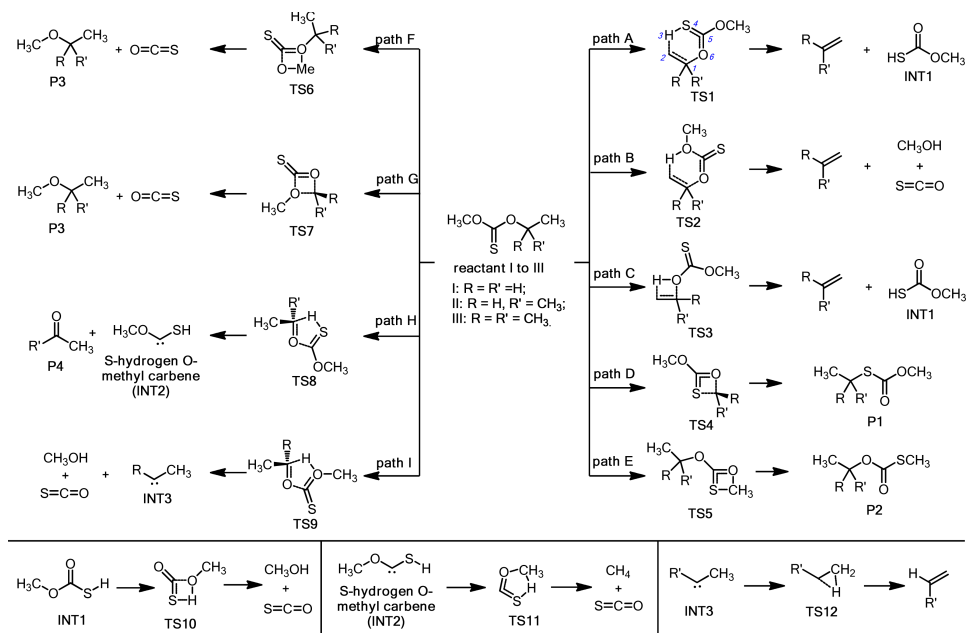
Scheme 2.   Nine possible pathways for the pyrolysis of alkyl methyl thioncarbonates **I** to **III**.

thiocarbonates, ethers, carbenes and aldehyde or ketone. The detailed results were listed in Scheme 2 as calculated at MP2/6-31G(d) level.

Scheme 2 listed all nine possible pathways. Pathways A to C resulted in the experimental products of an alkene, methanol and carbonyl sulfide. In pathway A, a thionyl sulfur atom attacked a β-hydrogen *via* a six-membered ring transition state, giving the desired alkene product, together with an unstable intermediate, O-methyl thiocarbonate (INT1), which rapidly decomposed into carbonyl sulfide and methanol. For pathway B, a methoxy oxygen atom was participated in the six-membered ring transition state to generate the same products as pathway A, but in a one-step process. An alkoxy oxygen atom can also attack a β-hydrogen via four-membered ring transition state to produce an alkene and O-methyl thiocarbonate intermediate (INT1). Pathways D and E underwent thionyl-to carbonyl rearrangements to O-methyl S-alkyl or S-methyl O-alkyl thiocarbonates (P1 and P2). Four-membered transition states were also observed for pathways F and G to release carbonyl sulfide, giving an ether product (P3). Pathways H and I proceeded with five-membered transition states by the attack of α-hydrogen atoms to give an aldehyde or ketone, methanol, carbonyl sulfide, and two carbene intermediates (INT2 and INT3). INT2 decomposed into methane and carbonyl sulfide, while INT3 underwent a H-transfer to generate an alkene product. However, due to the steric hindrance and an α-hydrogen lack, pathways C, H and I were not available for the pyrolysis of *t*-butyl methyl thioncarbonate **III**.
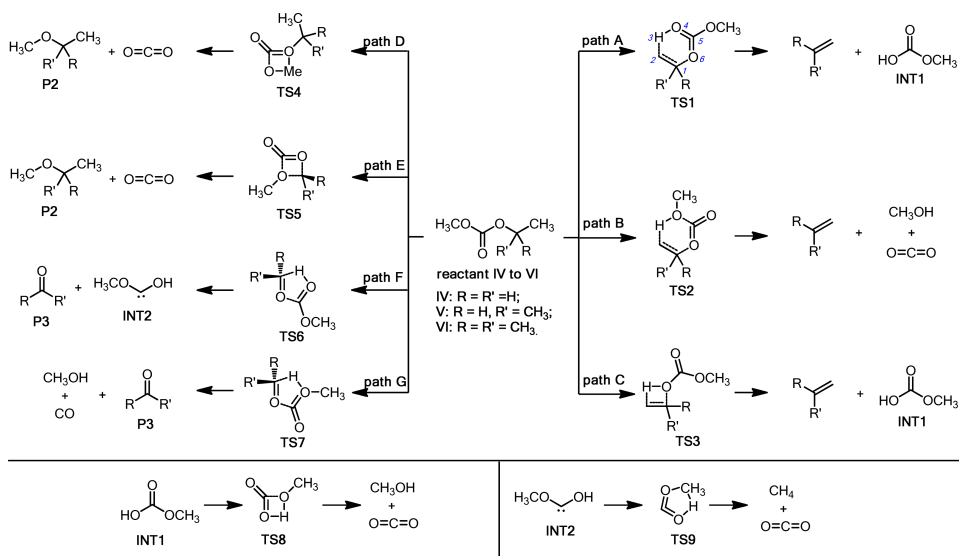
Scheme 3.   Seven possible pathways for the pyrolysis of alkyl methyl carbonates **IV** to **VI**.

Scheme 3 collected the proposed pathways for the pyrolysis of alkyl methyl carbonates **IV** to **VI**. For pathway A, a carbonyl oxygen atom attacks a β-hydrogen *via* a six-membered ring transition state to produce the desired alkene product and an unstable intermediate, methyl carbonate (INT1). INT1 decomposed into methanol and carbon dioxide. Pathway B took a one-step mechanism via a six-membered transition states. A four-membered decomposition transition state was also found via pathway C to give the same products as Pathway A. Pathways D to G had the similar transitional states and generated similar products as alkyl methyl thiocarbonates **I** to **III**. For the pyrolysis of *t*-butyl methyl carbonate **VI**, pathways C, F and G were not found due to the steric hindrance and an α-hydrogen lack.

The detailed electronic energies, zero-point vibrational energies, thermal corrections to enthalpies, entropies, and the calculated free energies for the reactants, transition states and products involved in the pyrolysis of alkyl methyl (thion)carbonates were collected in Tables S1 and S2 in the supplementary data at MP2/6-31G(d) level. Figures 1(a), 1(b) and 1(c) depicted the relative Gibbs free energy profiles for pathways A to E of alkyl methyl thioncarbonate **I**, **II** and **III**, respectively. The pathways A to C for alkyl methyl carbonate **IV** and **V**, as well as all pathways for *t*-butyl methyl carbonate **VI** were depicted in Figs. 1(d)–1(f). The remaining pathways were all collected in Fig. S1.

Pathway A was preferred among all the possible pathways, as observed from the energy profiles. The other six-membered transition states, pathway B, were about $14\,\text{kcal} \cdot \text{mol}^{-1}$ higher for alkyl methyl thioncarbonates, and about $10\,\text{kcal} \cdot \text{mol}^{-1}$ higher for alkyl methyl carbonates. These observations strongly indicated that

(a)

(b)

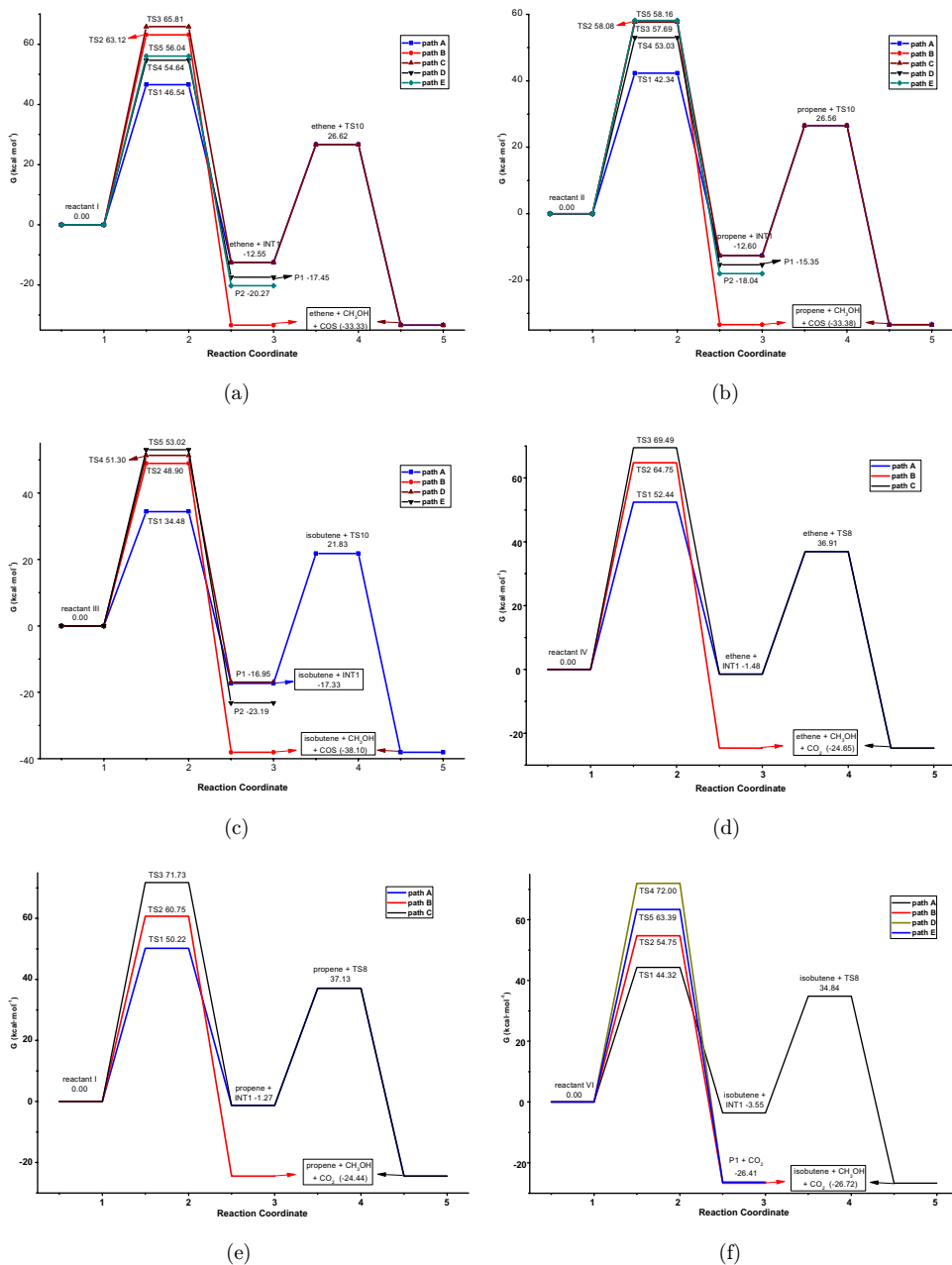(c)

(d)

(e)

(f)

Fig. 1.   Relative Gibbs energy profiles of pathways A to E for the pyrolysis of (a) ethyl methyl thion-
carbonate **I**; (b) *i*-propyl methyl thioncarbonate **II**; (c) *t*-butyl methyl thioncarbonate **III**; pathways A to
C for (d) ethyl methyl carbonate **IV**; (e) *i*-propyl methyl carbonate **V**; and all four pathways for (f) *t*-butyl
methyl carbonate **VI**.

pathway A, a two-step mechanism, is preferred for the pyrolysis of alkyl methyl (thion)carbonates. The overall processes for all pathways A were exergonic with reaction free energies of $-33 \, \text{kcal} \cdot \text{mol}^{-1}$–$38 \, \text{kcal} \cdot \text{mol}^{-1}$ and $-24 \, \text{kcal} \cdot \text{mol}^{-1}$–$26 \, \text{kcal} \cdot \text{mol}^{-1}$ for alkyl methyl thioncarbonates **I** to **III** and alkyl methyl carbonates **IV** to **VI**, respectively. Besides, by comparing the two steps involved in pathways A, the relative Gibbs free energies for the first step decreased as the sizes of the alkyl groups increased, which should be attributed to the Thorpe–Ingold effect.[52]

A comparison between the calculated kinetic and activation parameters and the experimental values for pathway A was collected in Table 1. The calculated activation enthalpies and entropies did not correlate with the experimental results well, in particularly for entropies. The entropies increased with the increasing alkyl group sizes, which were opposite to the experimental results. However, the relative Gibbs free energies and relative kinetic constants agreed better, which might be ascribed to the enthalpy–entropy compensations. For all (thion)carbonates, the rate constants, k-values, increased when the size of the alkyl groups increased due to the Thorpe–Ingold effect.[52]

As an objective tool to understand and interpret the results of the studied mechanism, NBO analysis[48,49] was carried out in the pyrolysis of alkyl methyl (thion) carbonates by means of the Wiberg bond indices, B_i, to avoid any subjective understanding involved in the geometrical analysis of the transition states.[53] The bond index, B_i, measures the bond order and the bond strength between two atoms, which can give a precise understanding toward the timing and the extent of the new forming or breaking bonds during the reaction process. Table 2 collected the Wiberg bond indices of all the bonds involved in pathways A for all the reactants, transition states and products.

As defined by Moyano and Pericas,[54] a relative variation of the bond index for the transition state, δB_i, for every bond, i, involved in the reaction is defined as Eq. (4):

$$\delta B_i = \frac{(B_i^{\text{TS}} - B_i^R)}{(B_i^P - B_i^R)}, \tag{4}$$

where the superscripts R, TS and P refer to reactants, transition state and products, respectively. With δB_i, the percentage of evolution, %EV, of the bond order during the calculated mechanism can be obtained from Eq. (5):

$$\%\text{EV} = 100\delta B_i. \tag{5}$$

Table 2 listed the calculated values for the percentage of bond evolution. The extent of the breaking bonds O6—C1 and the new forming bonds H3—S4 were found to be 64%–75% and 36%–31% for alkyl methyl thioncarbonates **I** to **III**. Similar results were observed for alkyl methyl carbonates **IV** to **VI**, with the breaking extent of O6—C1 bonds and the forming extent of H3—O4 bonds to be 63%–75% and 38%–33%, respectively. The slightly decreased extent of H3—S4 versus H3—O4 bonds might be attributed to the larger atomic size of sulfur than oxygen. As the alkyl groups increased from ethyl to *t*-butyl, the extent of O6—C1

Table 1. Experimental and theoretical calculated activation parameters and rate constants for the pyrolysis of alkyl methyl (thion)carbonates[a].

Compound	$\Delta H^{\neq}$/kcal·mol⁻¹		$\Delta S^{\neq}$/J·mol⁻¹·K⁻¹		$\Delta G^{\neq}$/kcal·mol⁻¹		E_a/kcal·mol⁻¹		$\log(A/s^{-1})$		k/s⁻¹	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
I	34.45	46.26	−59	−1.86	43.33	46.54	—	47.51	—	30.98	1.30×10^{-2}	9.13×10^{-4}
II	30.14	42.86	−48	3.46	37.36	42.34	—	44.12	—	31.62	1.5	2.62×10^{-2}
III	—	35.68	—	8.59	—	34.38	—	36.93	—	32.24	—	15.19
IV	—	52.73	—	1.99	—	52.44	44.84	53.98	12.20	31.44	7.60×10^{-5}	8.18×10^{-6}
V	—	50.67	—	3.16	—	50.22	43.10	51.92	13.04	31.58	2.23×10^{-3}	4.84×10^{-5}
VI	—	46.41	—	14.59	—	44.32	37.33	47.66	12.94	32.96	0.22	5.40×10^{-3}

[a]Values for alkyl methyl thioncarbonates and carbonates were taken from references 11 and 23, respectively.

Table 2. MP2/6-31G(d) calculated Wiberg bond indices, B_i, for the 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, S_y, for pathways A for the pyrolysis of alkyl methyl (thion)carbonates. The atom numbers can be obtained from Schemes 2 and 3.

Compound		C1—C2	C2—H3	H3—S4	S4—C5	C5—O6	O6—C1
I	B_i^R	1.029	0.935	0.000	1.647	1.040	0.821
	B_i^{TS}	1.321	0.533	0.349	1.323	1.372	0.292
	B_i^P	2.034	0.000	0.964	1.067	1.688	0.000
	%EV	29.1	43.0	36.2	56.0	51.2	64.4
	δB_{av}			0.466			
	S_y			0.864			
II	B_i^R	1.018	0.935	0.000	1.633	1.048	0.798
	B_i^{TS}	1.290	0.554	0.323	1.316	1.389	0.239
	B_i^P	1.985	0.000	0.964	1.067	1.688	0.000
	%EV	28.2	40.8	33.5	56.1	53.2	70.0
	δB_{av}			0.470			
	S_y			0.836			
III	B_i^R	1.004	0.934	0.000	1.629	1.052	0.781
	B_i^{TS}	1.254	0.575	0.296	1.316	1.399	0.196
	B_i^P	1.934	0.000	0.964	1.067	1.688	0.000
	%EV	26.9	38.4	30.7	55.8	54.6	74.9
	δB_{av}			0.469			
	S_y			0.810			
IV	B_i^R	1.031	0.936	0.000	1.643	0.997	0.831
	B_i^{TS}	1.350	0.445	0.271	1.313	1.312	0.310
	B_i^P	2.034	0.000	0.711	1.001	1.650	0.000
	%EV	31.8	52.5	38.0	51.4	48.3	62.7
	δB_{av}			0.475			
	S_y			0.894			
V	B_i^R	1.018	0.937	0.000	1.634	1.004	0.811
	B_i^{TS}	1.337	0.460	0.254	1.278	1.364	0.247
	B_i^P	1.985	0.000	0.711	1.001	1.650	0.000
	% EV	33.0	50.9	35.7	56.3	55.7	69.6
	δB_{av}			0.502			
	S_y			0.874			
VI	B_i^R	1.005	0.937	0.000	1.628	1.009	0.795
	B_i^{TS}	1.302	0.484	0.233	1.288	1.371	0.199
	B_i^P	1.934	0.000	0.711	1.001	1.650	0.000
	% EV	32.0	48.3	32.8	54.3	56.5	74.9
	δB_{av}			0.498			
	S_y			0.854			

bonds increased, indicating easier breaking procedures, while the forming extent of H3—S4 or H3—O4 bonds decreased, making them harder to be formed.

The average relative bond indices, δB_{av},[54] were also calculated as a measurement of the degree of advancement of the transition states along the reaction path, i.e. the

"early" or "advanced" nature of the transition states, as calculated from Eq. (6):

$$\delta B_{\mathrm{av}} = \frac{1}{n} \Sigma \delta B_i, \tag{6}$$

where n is the number of bonds involved in the reaction. The δB_{av} values for alkyl methyl thioncarbonates **I** to **III** were slightly lower than 0.500, indicating "early" characters for the transition states. However, nearly equal characters (0.475, 0.502 and 0.498) were found for alkyl methyl carbonates **IV** to **VI**, indicating reversible first steps.

The synchronous or asynchronous nature of the concerted mechanism was also considered by the synchronicity, Sy, as calculated from Eq. (7):

$$Sy = 1 - A, \tag{7}$$

where A is the asychronicity defined from Eq. (8) by Moyano and Pericas[54]:

$$A = \frac{1}{2(n-1)} \Sigma \frac{|\delta B_i - \delta B_{\mathrm{av}}|}{\delta B_{\mathrm{av}}}. \tag{8}$$

The synchronicity values varied from zero to one, indicating complete asynchronous and synchronous processes, respectively. As stated by Moyano and Pericas,[43] the synchronicity values obtained were, in principle, independent from the degree of advancement of the transition states. The calculated Sy values for alkyl methyl (thion)carbonates were also collected in Table 2. The values ranged from 0.864 to 0.810 for alkyl methyl thioncarbonates **I** to **III**, and 0.894 to 0.854 for alkyl methyl carbonates **IV** to **VI**. This result clearly indicated that all the transition states were slightly asynchronous process. As the alkyl groups increased, the synchronicity values decreased, which might be attributed to the increased steric hindrances.

NBO analysis were also performed to calculate the charge distributions of the reactants and the transition states involved in pathway A, as listed in Table 3. For

Table 3. MP2/6-31G(d) calculated NBO charges for the atoms involved in the first pathway of the mechanism for the studied reactions. The atom numbers can be obtained from Schemes 2 and 3.

Compound	C1	C2	H3	S4	C5	O6
I	−0.016	−0.496	0.171	−0.279	0.595	−0.573
I-TS1	−0.038	−0.626	0.182	−0.184	0.608	−0.666
II	0.128	−0.481	0.167	−0.285	0.596	−0.585
II-TS1	0.147	−0.627	0.192	−0.220	0.609	−0.674
III	0.292	−0.468	0.163	−0.294	0.606	−0.612
III-TS1	0.331	−0.633	0.208	−0.255	0.610	−0.680
IV	−0.009	−0.497	0.168	−0.611	1.075	−0.625
IV-TS1	−0.021	−0.726	0.479	−0.729	1.083	−0.726
V	0.138	−0.483	0.165	−0.615	1.076	−0.636
V-TS1	0.150	−0.724	0.474	−0.758	1.071	−0.711
VI	0.299	−0.470	0.161	−0.620	1.087	−0.663
VI-TS1	0.333	−0.726	0.467	−0.763	1.067	−0.723

alkyl methyl thioncarbonates **I** to **III**, C1, H3 and S4 were observed with slightly increased positive charges, while C2 and S6 were more negatively charged. A reversed charge distribution was found between C1 and C2, indicating the formation of a new C1—C2 double bond. Negatively charged S6 was used to attack the positively charged H3, and O6 was ready to form a new double bond with C5. As for alkyl methyl carbonates **IV** to **VI**, the positive charges on H3 increased from 0.16 for reactants to 0.47 for TSs, while O4 increased its nucleophilicity by increasing its negative charges (-0.61 to -0.62 for reactants versus -0.73 to -0.76 for TSs). This clearly indicated that H3 was ready to be attacked by O4. Two new double bonds, C1=C2 and C5=O6, were also formed during the transition states.

4. Conclusion

The pyrolysis of alkyl methyl (thion)carbonates were considered with nine and seven possible pathways, respectively, where alkyl groups were ethyl, *i*-propyl and *t*-butyl groups. Of all the possible pathways, the two-step six-membered transition state pathways A were more favored than any other pathways for at least $10 \, \text{kcal} \cdot \text{mol}^{-1}$. As the size of the alkyl group increased, the enthalpies, activation energies and the Gibbs free energies decreased. These calculation results were consistent with the experimental observations, and can be interpreted as the Thorpe–Ingold effect. Relatively, the pyrolysis of alkyl methyl carbonates **IV** to **VI** was more synchronous than the corresponding alkyl methyl thioncarbonates **I** to **III**, as indicated by NBO analysis.

Acknowledgment

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