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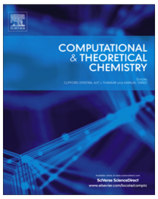

Theoretical studies on the pyrolysis of thiocarbonates

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ABSTRACT

Theoretical studies were carried out to investigate the pyrolysis of O-methyl S-alkyl and S-methyl O-alkyl thiocarbonates, where alkyl groups referred to ethyl, isopropyl and *t*-butyl groups. Eight possible pathways were found, of which three pathways would generate the alkene products. Not only thermal elimination pathways were calculated, other possible mechanisms, such as rearrangements and nucleophilic substitutions, were also considered. MP2/6-31G(d) level was employed to carry out the calculation and the progress of the reactions was followed by the Wiberg bond indices.

1. Introduction

The pyrolysis of carbonate related compounds were valuable synthetic routes to synthesize alkenes without the rearrangement of carbon skeleton [1–11]. Their mechanisms were long debated between two possible pathways (Scheme 1) [7,8], although both pathways resulted in the same products. The first pathway proceeded through a one-step mechanism, yielding an alkene, a (thio)ether and a gas of carbon dioxide, carbon disulfide or carbonyl sulfide. The second pathway involved a two-step mechanism. The first step generated the desired alkene product, as well as an unstable intermediate, which rapidly decomposed to a (thio)ether and a gas of carbon dioxide, carbon disulfide or carbonyl sulfide, the same products as the first pathway.

Cross et al. [12] and Hückel et al. [13] supported the first pathway, Smith and Yates [5], Barton [9] and Cram [6] preferred the second mechanism. Experimentally, Al-Awadi and Taylor group pyrolyzed a series of the esters, (thio)carbonates, carbamates, and etc. They approved the second pathway with the following evidences: the positive ρ-factor of Hammett correlation for the pyrolysis of aryl ethyl carbonate, as well as *t*-butyl *N*-aryl carbamates; the reduced reactivities of methyl alkyl carbonates as compared with phenyl alkyl carbonates [10,11,14–16]. Alexander and Mudrak also proved the second pathway, as well as the *cis*-elimination mechanism, by investigating the Chugeave reaction [17–19]. Bader and Bourns [20] carried out isotope effect studies and found solid evidence for the second pathway.

As for the theoretical studies, Lee group studied the pyrolysis of carbonate esters at AM1 level and supported the second pathway [21]. Velez group recalculated the pyrolysis of carbonate esters, as well as carbonates, carbamates, dithiocarbonates, etc., at higher computational levels [22–27], Erickson and Kahn [28] calculated the activation energies of HSC(=S)OEt at MP2/6-31G(d)//HF/6-31G(d) level in 1994. Deleuze group [29] investigated the E_i 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 [30] utilized B3LYP/6-31G(d) theoretical level to study the transition states of MeSC(=S)OEt. The regioselective pyrolysis of Chugeav reaction was also investigated recently at the MP2/6-31G(d) level [31]. However, the theoretical calculations for the pyrolysis of thiocarbonates were not reported yet. In this paper, we present our calculation result for the pyrolysis of O-methyl S-alkyl and S-methyl O-alkyl thiocarbonates, where alkyl groups were ethyl, *i*-propyl and *t*-butyl groups, at the level of MP2/6-31G(d).

2. Computational details

All calculations were performed with the help of Gaussian 03 package [32]. As mentioned by Deleuze group [29] that the MP2 level gave nice activation barriers as the CCSD(T) method, which was also applied by the recent calculation on the regioselective pyrolysis of Chugeav reaction [31] with the basis set of 6-31G(d) [33], the same computational level was also selected for the structural optimization. For the transition state calculations, force constants were

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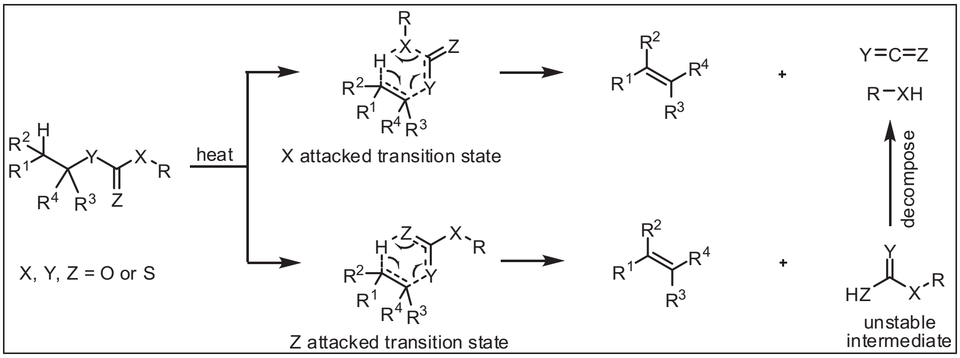

Scheme 1. Two debated pathways for the pyrolysis of the carbonate related compounds.

also calculated with MP2/6-31G(d) method and noeigentest 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 [34]. 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) [35] were followed to make sure that all transition states connected to the expected reactants and products.

The Natural Bond Orbital (NBO) analysis [36,37] 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 progress.

Classic transition-state theory (TST) [38,39] 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

Eight possible mechanisms were proposed for the pyrolysis of O-methyl S-alkyl and S-methyl O-alkyl thiocarbonates, where alkyl groups were ethyl, *i*-propyl and *t*-butyl groups. Among the eight mechanisms, the first three mechanisms, which included 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 and five-membered ring transition states were also found, giving (thio)ethers, carbenes, and (thio)aldehyde or (thio)ketones.

The MP2/6-31G(d) calculated results for the pyrolysis of O-methyl S-alkyl thiocarbonates **I**–**III** were shown in Scheme 2.

Scheme 2 listed all eight possible pathways, of which pathways A–C ended up with the experimental products. In pathway A, a carbonyl oxygen atom attacked a β-hydrogen *via* a six-membered ring transition state, giving the desired alkene product, together with an unstable intermediate, O-methyl thionocarbonate (INT1), which rapidly decomposed into carbonyl sulfide and methanol. For pathway B, the same products were obtained, but in a one-step process. An ether oxygen atom was participated in the six-membered ring transition state. A sulfur atom could also act as a nucleophile, as shown in pathway C, to extract a β-hydrogen atom through a four-membered ring transition state, generating an alkene and O-methyl thiocarbonate (INT2) as an intermediate, which also pyrolyzed into methanol and carbonyl sulfide. Pathway D resulted in a carbonyl-to-thiocarbonyl rearrangement product, O-methyl O-alkyl thionocarbonate (P1). Pathways E and F released carbon dioxide and carbonyl sulfide, giving thioether (P2) and ether (P3), respectively. Pathways G and H proceeded with five-membered ring transition states by the attack of α-hydrogen atoms to give a thial or thioketone, as well as methanol, carbon monoxide, and O-hydrogen O-methyl carbene (INT3), which was unstable and easily decomposed into methane and carbon dioxide. However, due to the steric hindrance and an α-hydrogen lackage, pathways C, G and H were not available for the pyrolysis of O-methyl S-*t*-butyl thiocarbonate **III**.

Similar mechanisms for S-methyl O-alkyl thiocarbonates **IV**–**VI** were collected in Scheme 3. For pathway A, both oxygen atoms were participated in the six-membered ring transition state to generate the desired alkene, as well as an unstable intermediate INT1, which decomposed to carbon dioxide and methanethiol. A one-step mechanism was also found for Pathway B, but a sulfur atom was utilized as a nucleophile. Pathway C preceded via a four-membered ring transition state to give the same products as Pathway A. Pathways D–H had the same transitional states and generated the same products as thiocarbonates **I**–**III**. For the pyrolysis of S-methyl O-*t*-butyl thiocarbonate **VI**, pathways C, G and H were not found due to the steric hindrance and an α-hydrogen lackage.

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 O-methyl S-alkyl thiocarbonates **I**–**III** and S-methyl O-alkyl thiocarbonates **IV**–**VI** were collected in Tables S1 and S2 in the Supplementary data at MP2/6-31G(d) level. For thiocarbonates **I**, **II**, **VI** and **V**, the relative Gibbs free energy profiles for the pathways A–D were depicted in Fig. 1a–d, while Fig. 1e and f illustrated all the five pathways for thiocarbonates **III** and **VI**. Pathways E–H for thiocarbonates **I**, **II**, **VI** and **V** were collected in Fig. S1.

Among all the possible pathways, pathway A had the lowest barrier, as observed from the energy profiles. The other six-membered ring transition states, pathway B, were about 10 kcal mol^{-1} higher than pathway A. This result clearly indicated that the pyrolysis of all thiocarbonates preferred to go through pathway A, a two-step mechanism with a rate-determining first step. The overall processes for all pathways A were exergonic with reaction free