Substituent effects on the gas phase reactivity of alkyl allyl sulfides, a theoretical study

M. Izadyar a,*, M.R. Gholami b

a Department of Chemistry, University of Payam-e-Nour, Gonabad, Khorasan-e-Razavi, Iran
b Department of chemistry, Sharif University of Technology, Tehran, Iran

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Abstract

The potential energy surface of the reaction C3H5SCH2X → C3H6 + XCH=S was studied for the various X substitutions (X = CH3, H, Cl, F) at the high level of the theory (G3MP2 method) using the 6-31G(d) basis set. It was demonstrated that CH3, H, Cl and F substitution, respectively, accelerates the reaction (This order for the substitutions will be called X = CH3-to-F throughout this paper). Barrier height changes from ΔE‡ = 167.76 to 148.63 kJ mol⁻¹, because of the electronic effects introduced upon the substitution. It was shown that the X = CH3-to-F substitution in the C6-position posses two types of contribution to the calculated energy barriers and bond lengths at the transition state (TS). First, it facilitates the TS complex formation, consequently reduces the barrier height. Second, it reduces the H1–C2 bond length, the major component of the reaction coordinate at the TS, and increases the rate of the reaction. Charge analysis shows that the acceptor substituent (F) induces more positive character on C6 atom at the Transition state (TS), while donor substituent (CH3) induces the less positive one, therefore, the reactivity decreases. HOMO–LUMO energy differences confirmed the activation energy and reactivity order. The G3MP2 results show the capability of this level of calculation to predict the reactivity of the intramolecular retro-ene reaction correctly.

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1. Introduction

The mechanism of the retro-ene reaction has been the subject of the interesting controversies [1–8]. Both experimental and theoretical studies indicate that this type of reaction proceeds through a concerted mechanism, although in some cases, stepwise mechanism involving diradical intermediate is less favorable [1–3,6,9–19].

Gas phase pyrolysis of organo-sulfur compounds has a special place among the great variety of chemical reactions, because of the generation of labile sulfur containing intermediates, which are difficult to obtain alternatively.

The most important molecular mechanisms that are involved in the gas phase pyrolysis of organosulfur compounds include the radical and concerted mechanisms. The kind of molecular mechanism depends on different factors. The most important factors are; temperature, C–S bond strength, electron donating and electron withdrawing properties of the substituents and intramolecular parameters.

Many experimental and theoretical investigations have been carried out to determine the kinetics and mechanism of organosulfur compounds pyrolysis in both gas and liquid phases [10–21].

Martin et al. studied the gas phase thermolysis of alkyl and cycloalkyl allyl sulfides at 673–773 K [22]. A molecular rearrangement (Retro-ene reaction) involving either four or six-member cyclic TS has been suggested.

Upon pyrolysis reaction, alkyl allyl sulfides eliminate propene and corresponding thiocarbonyl compounds via an intramolecular γ-hydrogen transfer (Scheme 1).

The objective of this study is to provide a theoretical prediction of the kinetic and activation parameters. It is also important to elucidate the molecular mechanism associated with this retro-ene reaction in order to find out a precise idea of the reaction pathway. Another aim of this survey is to obtain a more complete understanding of the electronic effects role on the reactivity order of alkyl allyl sulfides.

This paper is organized as follows: Section 2 shows the theoretical methods which were adopted. Section 3 presents the results and discussion of the calculations including
the geometrical parameters, reaction path, charge analysis and activation energy. Section 4 provides a summary of the present paper.

2. Computational procedures

The structures corresponding to the reactant, transition state and products for the studied reaction were optimized using the GAUSSIAN 98 computational package [23] with DFT method. Optimized geometries of the stationary points on the potential energy surfaces (PES) were obtained using the Becke’s-three parameter hybrid exchange functional with the correlation functional of Lee–Yang–Parr (B3LYP) [24,25]. In these calculations we used the 6-31G* basis set. The corresponding TSs were calculated using the synchronous transit-guided quasi-Newton (STQN) method as implemented by Schlegel et al. [26]. The intrinsic reaction coordinate (IRC) method was also used to check the profiles connecting the TSs to the associated minima of the concerted mechanism [27].

Thermodynamic parameters (total energy, enthalpy, Gibbs free energy and entropy) for the stationary points along the pyrolysis reaction were calculated from a very high level computation, the G3MP2 method.

In order to determine the atomic charges at the stationary points along the reaction paths, population analysis at the Merz-Kollman-Singh (MKS) level was applied [28] using the B3LYP/6-31 G(d) method.

3. Results and discussion

Optimized structures for the reactants and the TSs are shown in Fig. 1 and geometrical parameters for the stationary points along the reaction are given in Table 1. From Table 1 it can be concluded the lengths of H1–C2 and C4–S5 bonds at

![Fig. 1. Optimized structures for the reactants and the TSs at the B3LYP/6-31G(d) level.](image-url)
the TSs fell well within the usual range for the retro-ene reactions and agree with a concerted mechanism [10–15].

The concerted mechanism is an intramolecular transfer of H1 atom to an unsaturated allylic center via six-centered cyclic TS, yielding propene and alkyl thioaldehyde. This can proceed through the H1–C2 bond formation and C4–S5 bond cleavage (See Fig. 1 for atom labeling).

During the pyrolysis reaction of alkyl allyl sulfide, H1–C2, C3–C4 and S5–C6 bond lengths are decreased, while H1–C6, C4–S5 and C2–C3 bond lengths are increased.

Comparison between H1–C2 and C4–S5 bond lengths at the TSs with the same one in the reactants indicates that H1–C2 bond formation occurs faster than the C4–S5 bond splitting. Therefore, the new bond formation occurs by a slightly asynchronous nature in the concerted mechanism.

The most important feature of the transition structures is that the X substitution leads to the sizable changes in the geometry. For the TSs, changes in the calculated H1–C2 and C4–S5 bond lengths are important; the electron donating substituent (X=CH3) makes the H1–C2 distance 0.12 Å shorter, but C4–S5 lengths are important; the electron donating substituent (X=CH3) makes the H1–C2 distance 0.12 Å shorter, but C4–S5 lengths are important; the electron donating substituent (X=CH3) makes the H1–C2 distance 0.12 Å shorter, but C4–S5 lengths are important; the electron donating substituent (X=CH3) makes the H1–C2 distance 0.12 Å shorter, but C4–S5 lengths are important; the electron donating substituent (X=CH3) makes the H1–C2 distance 0.12 Å shorter, but C4–S5 lengths are important; the electron donating substituent (X=CH3) makes the H1–C2 distance 0.12 Å shorter, but C4–S5 lengths are important; the electron donating substituent (X=CH3) makes the H1–C2 distance 0.12 Å shorter, but C4–S5 lengths are important; the electron donating substituent (X=CH3) makes the H1–C2 distance 0.12 Å shorter, but C4–S5 lengths are important; the electron donating substituent (X=CH3) makes the H1–C2 distance 0.12 Å shorter, but C4–S5 lengths are important; the electron donating substituent (X=CH3) makes the H1–C2 distance 0.12 Å shorter, but C4–S5 lengths are important; the electron donating substituent (X=CH3) makes the H1–C2 distance 0.12 Å shorter, but C4–S5 lengths are important; the electron donating substituent (X=CH3) makes the H1–C2 distance 0.12 Å shorter, but C4–S5 lengths are important; the electron donating substituent (X=CH3) makes the H1–C2 distance 0.12 Å shorter, but C4–S5 lengths are important; the electron donating substituent (X=CH3) makes the H1–C2 distance 0.12 Å shorter, but C4–S5 lengths are important; the electron donating substituent (X=CH3) makes the H1–C2 distance 0.12 Å shorter, but C4–S5 lengths are important; the electron donating substituent (X=CH3) makes the H1–C2 distance 0.12 Å shorter, but C4–S5 lengths are important; the electron donating substituent (X=CH3) makes the H1–C2 distance 0.12 Å shorter, but C4–S5 lengths are important; the electron donating substituent (X=CH3) makes the H1–C2 distance 0.12 Å shorter, but C4–S5 lengths are important; the electron donating substituent (X=CH3) makes the H1–C2 distance 0.12 Å shorter, but C4–S5 lengths are important; the electron donating substituent (X=CH3) makes the H1–C2 distance 0.12 Å shorter, but C4–S5 lengths are important; the electron donating substituent (X=CH3) makes the H1–C2 distance 0.12 Å shorter, but C4–S5 lengths are important; the electron donating substituent (X=CH3) makes the H1–C2 distance 0.12 Å shorter, but C4–S5 lengths are important; the electron donating substituent (X=CH3) makes the H1–C2 distance 0.12 Å shorter, but C4–S5 lengths are important; the electron donating substituent (X=CH3) makes the H1–C2 distance 0.12 Å shorter, but C4–S5 lengths are important; the electron donating substituent (X=CH3) makes the H1–C2 distance 0.12 Å shorter, but C4–S5 lengths are important; the electron donating substituent (X=CH3) makes the H1–C2 distance 0.12 Å shorter, but C4–S5 lengths are important; the electron donating substituent (X=CH3) makes the H1–C2 distance 0.12 Å shorter, but C4–S5 lengths are important; the electron donating substituent (X=CH3) makes the H1–C2 distance 0.12 Å shorter, but C4–S5 lengths are important; the electron donating substituent (X=CH3) makes the H1–C2 distance 0.12 Å shorter, but C4–S5 lengths are important; the electron donating substituent (X=CH3) makes the H1–C2 distance 0.12 Å shorter, but C4–S5 lengths are important; the electron donating substituent (X=CH3) makes the H1–C2 distance 0.12 Å shorter, but C4–S5 lengths are important; the electron donating substituent (X=CH3) makes the H1–C2 distance 0.12 Å shorter, but C4–S5 lengths are important; the electron donating substituent (X=CH3) makes the H1–C2 distance 0.12 Å shorter, but C4–S5 lengths are important; the electron donating substi...
Table 4
Experimental kinetic parameters for some pyrolysis reactions in the gas phase

<table>
<thead>
<tr>
<th>Reactant</th>
<th>( E_a (kJ \text{ mol}^{-1}) )</th>
<th>( \Delta S^* (J \text{ mol}^{-1} \text{ K}^{-1}) )</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allyl methyl sulfide</td>
<td>160±3</td>
<td>-44.7</td>
<td>[29]</td>
</tr>
<tr>
<td>Diallyl sulfide</td>
<td>122.8±1</td>
<td>-53.9</td>
<td>[11]</td>
</tr>
<tr>
<td>Allyl benzyl sulfide</td>
<td>141±2</td>
<td>-50.1</td>
<td>[29]</td>
</tr>
<tr>
<td>Allyl methyl ether</td>
<td>174.1</td>
<td>-47.44</td>
<td>[30]</td>
</tr>
<tr>
<td>Allyl ethyl ether</td>
<td>182.4</td>
<td>-33.0</td>
<td>[31]</td>
</tr>
</tbody>
</table>

4. Conclusions

From the above-presented results we can make the following conclusions:

1. The X=CH\text{3}-to-F substitutions (upon going from the reactant 2 to reactant 3) dramatically accelerate the pyrolysis reaction. The G3MP2 studies beautifully demonstrate that this acceleration, mainly, is the result of the electronic effects introduced upon the substitutions.

2. It was shown that the X=CH\text{3}-to-F substitution in the C6-position has two contributions to the calculated energy barriers and bond evolution at the TSs. First, it destabilizes the transition state complex. The 'geometry destabilisation' is shown to be one of the large contributors to the calculated energetic of the reaction. Second, it reduces the H1–C2 distance, the major component of the reaction coordinate at the TSs.

3. Different electronic effects due to X substitutions, makes the acidic character of the H1 atom to change. Electron-negative substituents (F, Cl) increase the acidic character of the H1 atom and reduce the activation energy, while electropositive group (CH\text{3}) reduces it and increase the activation energy.

4. Calculated trend in the HOMO-LUMO energy difference qualitatively correlates with the trend in the barrier heights; \( R_2 > R_1 > R_4 > R_3 \).

5. The application of a high level of the theory (G3MP2) generates a good energetic barriers and reactivity order according to the experimental evidences.

6. Experimental verification for some of these predictions would be interesting and a test of the computational results.

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References


