

Reaction Path for C₃H₅SCH₂F Pyrolysis, A Theoretical Study

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Abstract

The potential energy surface of the reaction $\text{C}_3\text{H}_5\text{SCH}_2\text{F} \longrightarrow \text{C}_3\text{H}_6 + \text{FCH}=\text{S}$ was studied at the high level of the theory (G3MP2 method) using the 6-31G(d) basis set. Barrier height is $148.63 \text{ kJ mol}^{-1}$, because of the electronic effects introduced upon the F-substitution. It was shown F substitution in the C6-position possess two types of contribution to the calculated energy barriers and bond lengths at the transition state (TS). The first, it facilitates the TS complex formation, consequently reduces the barrier height. Secondly it reduces the H1-C2 bond length, the major component of the reaction coordinate at the TS, and increases the rate of the reaction. The G3MP2 results show the capability of this level of calculation to predict the reactivity of the intramolecular retro-ene reaction correctly.

Keywords: Fluoromethyl allyl sulfide; Retro-ene reaction; Pyrolysis; Concerted mechanism; Gas-phase kinetics; G3MP2.

1. Introduction

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 [1-3].

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. 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.

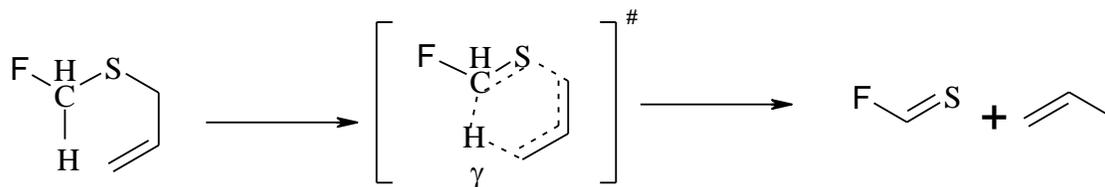
2. Computational procedures

The structures corresponding to the reactant, transition state and products for the studied reaction were optimized using the Gaussian 09 computational package [4] with DFT method. The corresponding TS was calculated using the synchronous transit-guided quasi-Newton (STQN) method as implemented by Schlegel et. al.[5]. The intrinsic reaction coordinate (IRC) method was also used to check the profiles connecting the TSs to the associated minima of the concerted mechanism [6].

3. Results and discussion

Optimized structures for the reactants and the TSs are shown in figure 1 and geometrical parameters for the stationary points along the reaction were calculated. These

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Scheme 1

data show that lengths of H1-C2 and C4-S5 bonds at the TSs fell well within the usual range for the retro-ene reactions and agree with a concerted mechanism [7-9].

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 figure 1 for atom labeling).

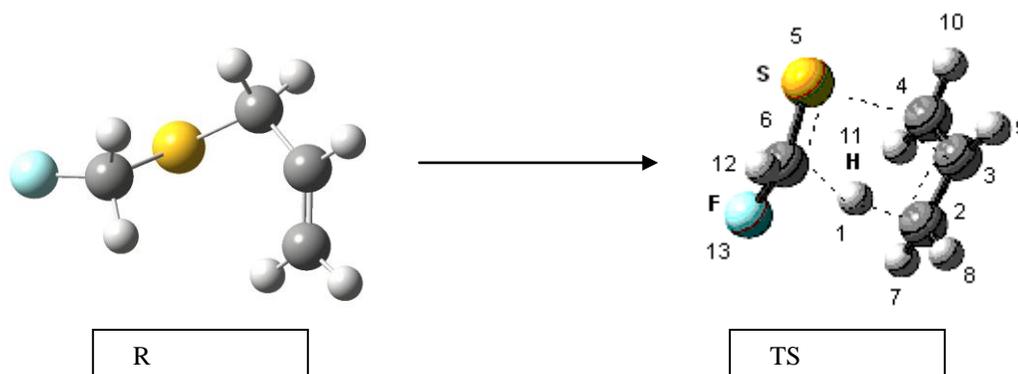


Fig. 1. Optimized structures for the reactants and the TSs at the B3LYP/6-31G(d) level.

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.

Calculated activation energies, free energies and entropies for the pyrolysis reactions at the G3MP2 level of the theory are given in Table 1. From table 1 we can see that the calculated potential energy barrier for the reaction is 154 kJmol^{-1} , the usual range for the experimental activation energies of alkyl allyl sulfides. Negative values for the activation entropy confirmed the concerted mechanism for the studied reactions (Table1).

Table 1

Calculated activation parameters, using the G3MP2/6-31G(d) method

ΔE^\ddagger (kJmol ⁻¹)	144.74
ΔG^\ddagger (kJmol ⁻¹)	152.72
$-\Delta S^\ddagger$ (Jmol ⁻¹ K ⁻¹)	26.77

The reactivity of alkyl allyl sulfides can be explained in terms of the acidic character of the H1 atom and HOMO-LUMO energy difference. Charge distribution on the atoms for the reactants and the TSs was calculated using the Merz-Kollman-Singh (MKS) electrostatic properties at the B3LYP/6-31G(d) level. We can notice that the positive charge on C6 and H1 atoms increases from X= CH₃-to-F. This positive character shows that acidic character for H1 atom increases from X=CH₃-to-F according to activation energy depletion and reactivity order.

The acidic character of the H1 atom depends on the electronic effects of substituents on C6-position. F substituent possess an electron with-drawing effect (-I), therefore it makes the electron density on C6 atom to decrease and the acidic character of the H1 atom to increase.

5. Acknowledgement

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