



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

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## Abstract

The potential energy surface of the reaction  $C_3H_5SCH_2X \rightarrow C_3H_6 + XCH=S$  was studied for the various X substitutions (X = CH<sub>3</sub>, H, Cl, F) at the high level of the theory (G3MP2 method) using the 6-31G(d) basis set. It was demonstrated that CH<sub>3</sub>, H, Cl and F substitution, respectively, accelerates the reaction (This order for the substitutions will be called X = CH<sub>3</sub>-to-F throughout this paper). Barrier height changes from  $\Delta E^\ddagger = 167.76$  to  $148.63 \text{ kJ mol}^{-1}$ , because of the electronic effects introduced upon the substitution. It was shown that the X = CH<sub>3</sub>-to-F substitution in the C6-position possesses 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 (CH<sub>3</sub>) 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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**Keywords:** Alkyl allyl sulfides; Retro-ene reaction; Pyrolysis; Concerted mechanism; Gas-phase kinetics; G3MP2

## 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.

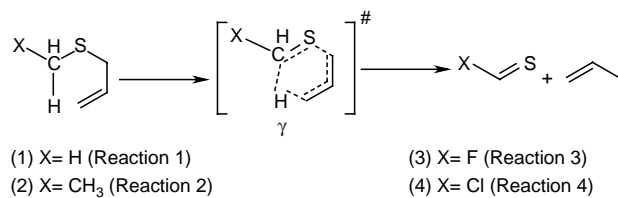
Upon pyrolysis reaction, alkyl allyl sulfides eliminate propene and corresponding thiocarbonyl compounds via an intramolecular  $\gamma$ -hydrogen transfer (Scheme 1).

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

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Scheme 1.

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

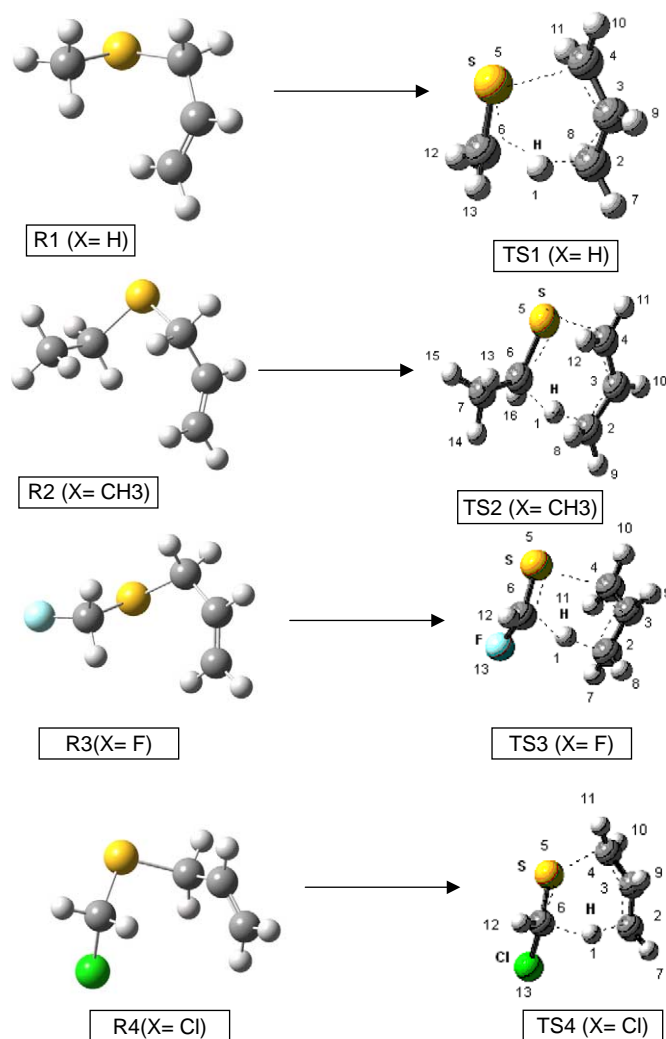


Fig. 1. Optimized structures for the reactants and the TSs at the B3LYP/6-31G(d) level.

Table 1

Optimized geometric parameters (bond lengths in angstrom, angles in degree) for the reactants (R) and the transition states (TSs) using the B3LYP/6-31G(d) method in the gas phase

Parameter <sup>a</sup>	R1/TS1 (X=H)	R2/TS2 (X=CH <sub>3</sub> )	R3/TS3 (X=F)	R4/TS4 (X=Cl)
H1–C2	2.87/1.24	2.94/1.36	3.15/1.27	2.92/1.24
C2–C3	1.33/1.42	1.33/1.40	1.33/1.42	1.33/1.42
C3–C4	1.50/1.38	1.49/1.37	1.51/1.39	1.51/1.39
C4–S5	1.80/2.24	1.82/2.41	1.83/2.23	1.83/2.19
S5–C6	1.80/1.68	1.81/1.68	1.83/1.66	1.83/1.67
C6–X13	1.09/1.08	1.52/1.51	1.37/1.38	1.80/1.76
H1–C2–C3	81.07/100.96	67.14/97.88	87.77/99.79	78.19/100.89
C2–C3–C4	126.52/118.58	123.78/119.70	127.32/117.95	127.22/117.94
C4–S5–C6	116.80/102.06	100.26/99.84	117.47/98.76	98.06/99.94
H1–C2–C3–C4	–53.36/–62.35	76.22/65.51	–45.22/–62.07	–53.48/–59.86
C2–C3–C4–S5	13.29/71.52	–114.33/–69.45	9.95/68.97	11.84/70.78
C3–C4–S5–C6	70.32/–47.53	–26.15/40.17	71.96/–50.35	72.35/–53.58

<sup>a</sup> See Fig. 1 for the labeling of atoms.

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=CH<sub>3</sub>) makes the H1–C2 distance 0.12 Å shorter, but C4–S5 distance 0.17 longer than unsubstituted (X=H) molecule, while the electron with-drawing substituents (X=F, Cl) significantly reduce H1–C2 bond length at the TSs relative to the same one in the reactant. Since the H1–C2 bond formation can be considered as a driving force for the concerted pathway, the electron with-drawing groups (X=F, Cl) noticeably affect the calculated barrier height. Other geometrical parameter's changes for the reactants and the TSs are relatively small.

Calculated activation energies, free energies and entropies for the pyrolysis reactions at the G3MP2 level of the theory are

Table 2

Calculated activation energies, free energies and entropies for alkyl allyl sulfides pyrolysis with different X substitutions, using the G3MP2/6-31G(d) method

Parameter	X=H	X=CH <sub>3</sub>	X=F	X=Cl
$\Delta E^\ddagger$ (kJ mol <sup>-1</sup> )	154.56	167.76	144.74	148.63
$\Delta G^\ddagger$ (kJ mol <sup>-1</sup> )	160.49	172.13	152.72	154.15
$-\Delta S^\ddagger$ (J mol <sup>-1</sup> K <sup>-1</sup> )	19.90	21.32	26.77	48.59

given in Table 2. From Table 2 we can see that the calculated potential energy barriers for the reactions are around (average) 154 kJ mol<sup>-1</sup>, the usual range for the experimental activation energies of alkyl allyl sulfides. TS3 (X=F) is more stable than TS4 (X=Cl) by 3.89 kJ mol<sup>-1</sup>, TS4 is more stable than TS1 (X=H) by 5.39 kJ mol<sup>-1</sup> and TS1 is more stable than TS2 (X=CH<sub>3</sub>) by 13.2 kJ mol<sup>-1</sup>, according to acidic character of H1 atom. The overall reactivity for the alkyl allyl sulfides is found to decrease in the order of R3>R4>R1>R2.

Negative values for the activation entropy confirmed the concerted mechanism for the studied reactions (Table 2).

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. In Table 3 we can notice that the positive charge on C6 and H1 atoms increases from X=CH<sub>3</sub>-to-F. This positive character shows that acidic character for H1 atom increases from X=CH<sub>3</sub>-to-F according to activation energy depletion and reactivity order.

Increasing the positive character of the H1 and C6 atoms for R3, R4 and R1 at the TSs shows that the acidic character increases for H1 atom. This makes the H1–C6 bond to break faster at the TS3 and TS4 relative to TS1 and TS2. The acidic character of the H1 atom depends on the electronic effects of substituents on C6-position. F and Cl substituents possess an electron withdrawing effect (–I), therefore, they make the

Table 3

Calculated atomic charges for the reactants (R) and the TSs at the Merz–Kollman–Singh level in the gas phase using the B3LYP/6-31G(d) method

	H1	C2	C3	C4	S5	C6	X13
R1 (X=H)	0.12	–0.46	+0.04	–0.16	–0.22	–0.31	0.17
TS1 (X=H)	0.13	–0.39	–0.06	–0.43	–0.28	–0.19	0.11
R2 (X=CH <sub>3</sub> )	0.20	–0.40	–0.11	–0.51	0.10	–0.47	–0.47
TS2 (X=CH <sub>3</sub> )	0.08	–0.30	–0.11	–0.41	–0.36	–0.15	–0.36
R3 (X=F)	0.09	–0.48	0.02	–0.16	–0.22	0.18	–0.23
TS3 (X=F)	0.19	–0.28	–0.09	–0.41	–0.29	0.09	–0.20
R4 (X=Cl)	0.08	–0.37	–0.12	–0.22	–0.17	–0.23	–0.16
TS4 (X=Cl)	0.19	–0.33	–0.01	–0.49	–0.19	–0.11	–0.15

Table 4  
Experimental kinetic parameters for some pyrolysis reactions in the gas phase

Reactant	Ea(kJ mol <sup>-1</sup> )	ΔS <sup>‡</sup> (J mol <sup>-1</sup> K <sup>-1</sup> )	Refs.
Allyl methyl sulfide	160 ± 3	-44.7	[29]
Diallyl sulfide	122.8 ± 1	-53.9	[11]
Allyl benzyl sulfide	141 ± 2	-50.1	[29]
Allyl methyl ether	174.1	-47.44	[30]
Allyl ethyl ether	182.4	-33.0	[31]

electron density on C6 atom to decrease and the acidic character of the H1 atom to increase. On the other hand CH<sub>3</sub> substituent has an electron-donating effect (+I), therefore it makes the electron density on C6 atom to increase and the acidic character of the H1 atom to reduce.

It may be concluded that the electronic effects of the substituents significantly affect the potential energy barrier and reactivity order. Since this finding is also consistent with the changes in energy difference of the frontier orbital, in the next stages of our studies we calculated the HOMO–LUMO energy difference.

The reactivity order found; ΔE3 = 171.45 kJ mol<sup>-1</sup>, ΔE4 = 189.11 kJ mol<sup>-1</sup>, ΔE1 = 197.54 kJ mol<sup>-1</sup> and ΔE2 = 213.87 kJ mol<sup>-1</sup>. These calculations demonstrate that the frontier orbital energies in qualitative agreement with the computed activation energies and experimental evidence (Table 4).

In Table 4 we can notice that allyl and benzyl substituents possess a greater acidic character for H1 atom, therefore their corresponding activation energies is smaller than allyl methyl sulfide pyrolysis. There is no experimental value for the activation energy of allyl ethyl sulfide pyrolysis, but according to the different values of the activation energy for the corresponding ethers, one can predict that the activation energy for allyl ethyl sulfide must be greater than allyl methyl sulfide which is consistent with the G3MP2 results.

#### 4. Conclusions

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

1. The X=CH<sub>3</sub>-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<sub>3</sub>-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 destabilization' 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. Electro-negative substituents (F, Cl) increase the acidic character of

the H1 atom and reduce the activation energy, while electropositive group (CH<sub>3</sub>) 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; R2 > R1 > R4 > R3.
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

- [1] H.M.R. Hoffmann, *Angew. Chem.* 81 (1969) 597.
- [2] W. Oppolzer, V. Snieckus, *Angew. Chem.* 90 (1978) 506.
- [3] J. Dubac, A. Laporterie, *Chem. Rev.* 87 (1987) 319.
- [4] R.F.C. Brown, in: R.H. Wasserman (Ed.), *Pyrolytic Methods in Organic Chemistry*, Academic Press, New York, 1980, p. 229.
- [5] M. Karpf, *Angew. Chem.* 98 (1986) 413.
- [6] A. Viola, J.J. Collins, N. Phillip, *Tetrahedron* 37 (1981) 3765.
- [7] L.E. Guesnikov, N.S. Nametkin, *Chem. Rev.* 79 (1979) 529.
- [8] G. Raable, J. Michle, *Chem. Rev.* 85 (1985) 419.
- [9] M. Izadyar, A.H. Jahangir, M.R. Gholami, *J. Chem. Res.* 11 (2004) 585.
- [10] M.R. Gholami, M. Izadyar, *J. Mol. Struct. (Theochem)*. 672 (2004) 61.
- [11] M.R. Gholami, M. Izadyar, *J. Phys. Org. Chem.* 16 (2003) 153.
- [12] M.R. Gholami, M. Izadyar, *Proceeding of the Sixth Iranian Physical Chemistry Seminar, Urmia University, Iran, 2002*, pp. 31.
- [13] M. Izadyar, M.R. Gholami, M. Haghgu, *J. Mol. Struct. (Theochem)* 686 (2004) 37.
- [14] M. Izadyar, M.R. Gholami, M. Haghgu, 14<sup>th</sup> Iranian Chemistry & Chemical Engineering Congress, 2004, pp. 754.
- [15] M.R. Gholami, M. Izadyar, *Chem. Phys.* 301 (2004) 45.
- [16] C.H. Deputy, C.A. Bishop, C.N. Goeders, *J. Am. Chem. Soc.* 83 (1961) 2151.
- [17] M.J. Molera, J.A. Lopez, *J. Am. Chem. Soc.* 54 (1958) 127.
- [18] A.T. Blades, *Can. J. Chem.* 31 (1953) 418.
- [19] J.A.L. Quiros, M.J. Molera, *J. Am. Chem. Soc.* 50 (1954) 851.
- [20] G. Martin, J. Ascanio, *J. Phys. Org. Chem.* 4 (1991) 579.
- [21] L.J. Rodriguez, R. Anez, E. Ocando-Mavarez, *J. Mol. Struct. (Theochem)* 536 (2001) 53.
- [22] G. Martin, M. Roperio, R. Avila, 10<sup>th</sup> International Symposium on Organic Chemistry of Sulfur, Bangor, 1974, pp. 409.
- [23] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, R.E. Stratmann, J.C.

- Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Chterski, G.A. Petersson, P.Y. Ayala, Q. Morokuma, K. Cui, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Ciolowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, J.L. Martin, D.J. Fox, T. Kieth, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gills, B. Jonhson, W. Chen, M.W. Wong, J.L. Andres, M. Head-Gordon, E.S. Replogle, J.A. Pople, GAUSSIAN 98 Revision A9, Gaussian, Inc.: Pittsburgh, PA, 1998.
- [24] A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648.
- [25] C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B* 371 (1988) 785.
- [26] H.B. Schlegel, C. Peng, P.Y. Ayala, M.J. Frisch, *J. Comput. Chem.* 17 (1996) 49.
- [27] A.E. Reed, R.B. Weinstock, F. Weinhold, *J. Chem. Phys.* 78 (1983) 4066.
- [28] B.H. Besler, K.M. Merz, P.A. Kollman, *J. Comput. Chem.* 11 (1990) 431.
- [29] G. Martin, M. Roper, R. Avila, *Phosphorus Sulfur* 13 (1982) 213.
- [30] H. Kwart, S.F. Sarnar, J. Slutsky, *J. Am. Chem. Soc.* 96 (1973) 5234.
- [31] K.W. Eggar, P. Vittins, *Int. J. Chem. Kinet.* 6 (1974) 429.