

DFT Calculations on the Retro-ene Reactions, Part III: Allyl Benzyl Sulfide Pyrolysis in the Gas Phase

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Abstract

Theoretical study on the pyrolysis of allyl benzyl sulfide was carried out in the gas phase using the DFT method at the B3LYP/6-31G(d) level of the theory. Two possible mechanisms were studied, one of them includes a six-centered cyclic transition state and the other one is a multi steps process (Free radical mechanism). Theoretical results show that propene and thiobenzaldehyde formation are accordance to a concerted mechanism. The reaction progress was followed by means of natural bond analysis. Calculated kinetic parameters for the studied reaction agree with the available experimental results.

Key-Words: Allyl benzyl sulfide, Pyrolysis, Gas phase, Concerted mechanism, DFT, Kinetic Parameters.

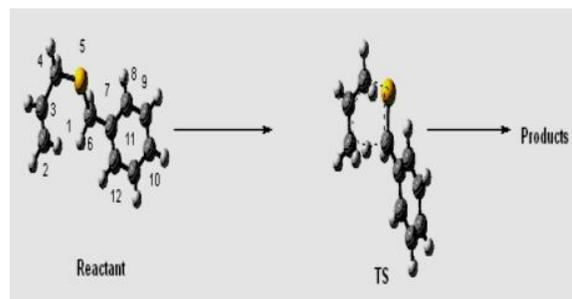
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1 Introduction

Since they are powerful tools for the synthesis of hetero unsaturated compounds, the interest on the synthesis and theoretical studies of the retro-ene reactions have increased considerably [1,2]. Studies on the retro-ene reactions have shown that the interaction of S, O, and N atoms on the H atom migration toward an unsaturated system can exert a strong chemical control [3,4]. The mechanisms of these reactions have been the subject of the most controversies in the recent years [3-7]. However it is not straight forward to be sure which mechanism is favored in different conditions.

The most important mechanism that are involved in the gas phase pyrolysis of organosulfur compounds include radical and concerted pathways. In a previous study we reported the thermal decomposition of diallyl disulfide at 603.4 K experimentally and theoretically [8]. Based on experimental and theoretical results a free radical mechanism was proposed. But in the other works on the kinetics and mechanism of diallyl and alkyl allyl sulfides, a molecular rearrangement involving a six-centered cyclic TS have been suggested [3-7].

G. Martin and coworkers studied the kinetics of ABZS experimentally at 606-647 K. Owing to the low volatility all runs were made in a flow system in the presence of toluene as a carrier gas [9]. They showed that there was no difference in the presence or absence of free radical inhibitor on the rate coefficients and a concerted mechanism was proposed for ABZS pyrolysis. This retro-ene reaction leads to the formation of propene and thiobenzaldehyde through six-centered TS (Scheme1).



Scheme 1

The empirical rate coefficients for ABZS have been reported to be satisfied by the following equation (1):

$$\log k = (10.93 \pm 0.18) - (141 \pm 2 \text{ kJmol}^{-1}) / (2.303RT)^{-1}$$

$$R = 8.314 \text{ Jmol}^{-1}\text{K}^{-1}$$

The size of a molecule is a key parameter on selecting a computational method in theoretical kinetics. As we reported that the density functional methods (DFT) are useful for the study of nearly large system, the B3LYP/6-31G(d) method has been applied to investigate the kinetic and mechanism of allyl benzyl sulfide (ABZS) pyrolysis in the gas phase.

With the aim of elucidation the reaction mechanism and understanding the performance of DFT methods on the kinetics, the retro-ene reaction of ABZS pyrolysis has been studied in the gas phase.

2 Problem Formulation

The structures corresponding to the reactant, transition state and products for the studied reaction were optimized using the GAUSSIAN 98 computational package with DFT method [10]. 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) [11]. 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. [12].

Vibrational frequencies for the points along the reaction paths were determined to provide an estimation of the zero point vibrational energies (ZPVE).

Activation parameters were calculated in the temperature range of the pyrolysis reaction (626 K). Activation energy, E_a , and the Arrhenius factor were computed using the equations (2) and (3), respectively. These equations have been derived from the transition state theory [13,14]:

$$E_a = \Delta H^\ddagger(T) + RT \quad (2)$$

$$A = (eK_B T/h) \exp(\Delta S^\ddagger(T)/R) \quad (3)$$

The natural bond orbital (NBO) analysis, suggested by Reed et al. [15], was applied to determine the charges at the stationary points through the pyrolysis reaction.

3 Problem Solution

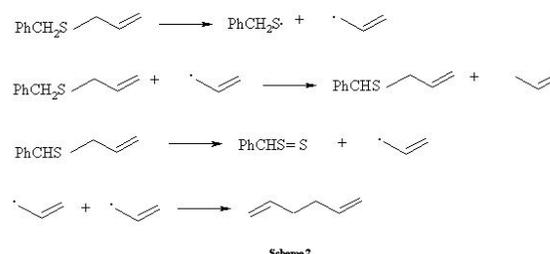
Propene elimination from the ABZS may occur through the two probable mechanisms. The first one may be started by the cleavage of the C4-S5 bond (for atom numbering see Scheme 1), followed by a step-wise mechanism.

The second possibility is the intermolecular transfer of H-atom to an unsaturated center via six-centered cyclic TS, yielding propene and thiobenzaldehyde. This can proceed through the H1-C2 bond formation and C4-S5 bond cleavage.

The C4-S5 bond breaking is the rate-determining step in the former mechanism. Bond dissociation energy of the C4-S5 would be mainly the

activation barrier of this process from the energy point of view (Scheme 2).

It has been reported that the unrestricted B3LYP remains fairly parallel to full configuration interaction potential energy curves for breaking bonds [16]. Therefore, the energies of the probable radicals were calculated



after full geometry optimization at the UB3LYP level of the theory using the 6-31G(d) basis set. The results are shown in table 1. It is obvious that the calculated activation energy is 664.85 kJ mol⁻¹ for the ABZS pyrolysis. The calculated Activation energy is much greater than the experimental one; hence the radical mechanism is rejected. So, we should focus on the later one and consequently, the concerted mechanism was fully investigated.

During the reaction, the H1-C2, C3-C4 and S5-C6 bond lengths are decreased, while the H1-C6, C4-S5 and C2-C3 bond lengths are increased.

Geometric parameters for the reactant and the TS are reported in table 2. Comparison between the H1-C2 and C4-S5 bond lengths in the TS with the same one in the reactant indicates that the H1-C2 bond formation occurs faster than the C4-S5 bond splitting. Therefore the new bond formation occurs by a slightly asynchronous mechanism in the concerted reaction.

Table 1. Calculated total energies in hartree for some probable radicals at the B3LYP/6-31G(d) level.

C ₆ H ₅	C ₃ H ₅	C ₃ H ₅ S
-231.43	-117.09	-515.45
C ₆ H ₅ CHSC ₃ H ₅	C ₆ H ₅ CH ₂ S	C ₆ H ₅ CH ₂
-785.78	-669.11	-270.79

Table 2. Main geometric parameters for the ABZS (R) and the TS in the gas phase, using the B3LYP/6-31G(d) method (Distances in angstrom and dihedrals in degree).

	R	TS
H1-C2	2.99	1.31
C2-C3	1.33	1.41
C3-C4	1.51	1.39
C4-S5	1.83	2.24
S5-C6	1.85	1.71
C6-C7	1.50	1.48
C8-C9	1.40	1.40
C9-C10	1.39	1.39
H1-C2-C3	79.02	99.09
C2-C3-C4	127.22	119.06
C4-S5-C6	99.77	101.10
H1-C2-C3-C4	-52.61	-60.52
C4-S5-C6-C7	-178.44	-89.43

Table 3. Distributed NBO charges on the ABS and the TS at the B3LYP/6-31G(d) level.

	H1	C2	C3	C4	S5	C6	C7	C8	C9
R	0.25	0.44	-	-	0.21	-	-	-	-
			0.24	0.63		0.59	0.06	0.22	0.23
TS	0.27	-	-0.2	-	0.12	-	-	-	-
		0.62		0.49		0.56	0.07	0.22	0.23

Table 4. Calculated kinetic and activation parameters for the pyrolysis of ABZS at 626.65 K, using the B3LYP/6-31G(d) methods (E_a, ΔH[‡] in kJ mol⁻¹ and ΔS[‡] in J mol⁻¹K⁻¹).

E _a	ΔH [‡]	log A	-ΔS [‡]
134.96	129.75	13.08	8.93

Table 3 shows the charge distribution of the reactant and the TS in

the gas phase using the NBO analysis. Calculated values for the TS indicate that a small positive charge developed on the H1 atom, while the C2 atom supported the electronic excess. The positive character of the H1 atom allows it to be attracted by negative character of C2 atom. On the other hand the positive characters of the C3 and C4 atoms demonstrate that the H1-C2 bond formation is faster than the C4-S5 bond cleavage for the retro-ene reaction.

Imaginary vibrational frequencies for the TS were also obtained. High magnitude of this frequency (1060 icm⁻¹) shows that these points are associated with the light atom movement of H1 in the TS. Also dipole moments changes through the retro-ene reactions justify the greater polarity of the TS compared to the reactant (2.18, 1.53), and it confirmed the cyclic structures for the TS.

Calculated kinetic and activation parameters for the reaction at 626.65K are listed in tables 4 using the equations 2 and 3.

The calculated activation energy is good in comparison with the experimental value for the pyrolysis of ABZS and expected values for other allylic organosulfur compounds[3-7], suggesting that the reaction is concerted.

The negative calculated activation entropies show that ABZS pyrolysis proceeds through concerted cyclic TS, which have been confirmed experimentally.

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