

Gas-phase kinetics and mechanism of diallyl sulfide thermal decomposition

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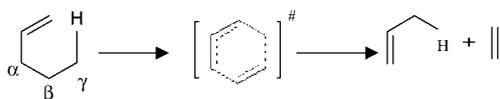
ABSTRACT: The gas-phase kinetics of diallyl sulfide pyrolysis were studied experimentally and theoretically in a static system over the temperature range 433–463 K and a total pressure of 80 Torr in a glass vessel with the free radical inhibitor cyclohexene. The experimental results show that this reaction is homogeneous, unimolecular and follows a first-order rate law. Theoretical studies at the B3LYP/6–31G* computational level indicate that the elimination reaction proceeds through a six-centered cyclic transition state and the reaction mechanism is concerted and non-synchronous. Copyright © 2003 John Wiley & Sons, Ltd.

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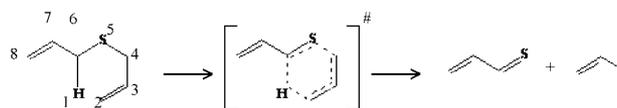
KEYWORDS: diallyl sulfide; unimolecular reaction; thermal decomposition; non-synchronous, concerted reaction; radical mechanism; homogeneity

INTRODUCTION

The formal reverse of an ene reaction, intramolecular transfer of a γ -hydrogen atom to an unsaturated center via a six-electron cyclic transition state (TS), can occur thermally (Scheme 1). Although the concerted nature of this process has received experimental support,^{1–3} some suggestions to the effect that the reaction has a free-radical intermediate have been advanced.^{4–9} Reactive π -bonds for retro-ene fragmentation include olefinic,^{1–3} acetylenic,⁷ allenic,¹⁰ cyclopropyl,¹¹ carbon-hetero^{12–14} and hetero-hetero¹⁵ bonds. Since the thermolysis of allyl ethers has been shown to lead to the formation of carbonyl compounds,^{16–18} together with an olefin, it seemed probable that a similar reaction should be available to allyl sulfides. Allyl sulfide is present in garlic oil and possesses anticarcinogenic properties.^{19,20} The flash vacuum thermolysis (FVT) of alkenyl sulfides, namely allyl sulfide derivatives, has been widely used to synthesize a variety of thiocarbonyl compounds, including thioaldehydes. In pioneering work, de Mayo and co-



Scheme 1



Scheme 2

workers²¹ investigated the retro-ene reaction of allyl sulfide under FVT conditions. The thiocarbonyls obtained were characterized by mass and low-temperature infrared spectrometry (Scheme 2).

A complementary study with the aim of elucidating the molecular mechanism associated with this thermal decomposition process is of importance in order to have a precise idea of the reaction pathway. This work involved theoretical and experimental studies, and here we report on combined experimental and theoretical kinetics. We are interested in investigating the heteroatom (S) effect on the rate of thermal decomposition and in characterizing the potential energy surface (PES) to elucidate the nature of the molecular mechanism of the reaction.

COMPUTATIONAL METHODS

Theoretical studies were performed with the Gaussian 98 suite of programs²² with the *ab initio* method as implemented in the computational package. Since Lee *et al.*²³ previously reported that the B3LYP hybrid functional^{24,25} gives structures and vibrational frequencies that are in good agreement with coupled-cluster

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theory, optimized geometries and frequencies for the reactant, products and the TS were calculated using density functional theory (DFT), the B3LYP method and the 6-31G* basis set.²⁶ The intrinsic reaction coordinate (IRC) method²⁷ was applied in order to check and obtain the profiles connecting the TS to the two associated minima of the proposed mechanism, using the B3LYP method.

Vibrational frequencies were determined for the points along the reaction path and to provide an estimation of the zero point energy (ZPE). These calculations verified the nature of the stationary points as minima with real frequencies and the TS with one imaginary frequency. Thermodynamic properties were evaluated from DFT data for enthalpy, entropy and Gibbs free energy at 298 K. Activation parameters were also determined in the temperature range of the pyrolysis reaction. Bond orders were calculated with the natural bond orbital method (NBO).^{28,29} The atoms in molecule method (AIM)³⁰ was used to characterize the electron density in the stationary points of the reaction.

RESULTS AND DISCUSSION

Experimental Results

The unimolecular elimination of allyl sulfide was examined in the temperature range 433–463 K and at a total pressure of 80 Torr (1 Torr = 133.3 Pa). The stoichiometry of the reaction is in accordance with Scheme 2. The small departure from the theoretical stoichiometry was due to a small extent of polymerization of the product thioacrolein. The products were identified by comparing their retention times with those known for propene and thioacrolein. The rate coefficients in the temperature range 433–463 K are given in Table 1.

The homogeneity of this pyrolytic elimination was examined by using a vessel with surface-to-volume ratios of 1.5 and 3.0 times greater than that of the unpacked vessel. No important differences in the rate coefficients were observed (Table 2). Several kinetic runs at 463 K with different ratios of cyclohexene as a free radical inhibitor to allyl sulfide were carried out. The pyrolysis experiment results show the absence of free-radical chain decomposition (Table 3).

A least-squares fit of the rate coefficients in the form of

Table 1. First-order rate coefficients

<i>T</i> (K)	$10^4 k$ (s ⁻¹)	σ (%)
433	0.538	3.4
443	1.553	1.5
453	3.005	2.6
463	5.054	3.7

Table 2. Rate coefficients of the reaction in reactors with various surface-to-volume ratios

<i>T</i> (K)	<i>S/V</i> (cm ⁻¹)	$10^4 k$ (s ⁻¹)	Difference (%)
453	1.5	3.217	7.05
453	3.0	2.891	3.79
463	1.5	4.854	3.96
463	3.0	5.261	4.09

Table 3. Rate coefficients in the presence of cyclohexene as a free radical inhibitor at 463 K

$P_{\text{inhibitor}}/P_{\text{reactant}}$	$10^4 k$ (s ⁻¹)	Difference (%)
1.26	5.173	2.35
2.50	4.903	2.90

the Arrhenius equation produced the relationship

$$k \text{ (s}^{-1}\text{)} = (4.0 \pm 0.12) \times 10^{10} \exp[-29.34 \pm 0.23 \text{ kcal mol}^{-1} (RT)^{-1}]$$

(1 kcal = 4.184 kJ). The corresponding plot is shown in Fig. 1. Values of the activation parameters for several allyl compounds are listed in Table 4. Allyl sulfide shows the lowest activation energy and the highest rate of decomposition. This indicates that hydrogen atoms on the α -carbon of the allyl group have a more acidic character than those in allylamines and allyl ethers. This may be due to higher polarizability of the S atom than N and O atoms. The negative activation entropy for the compounds (Table 4) suggests a similar TS geometry, that is proposed as a six-centered cyclic structure. As shown in Table 4, the activation entropy decreased from allyl ether to allyl sulfide, probably owing to a progressively smaller internal rotation barrier in the ground state.

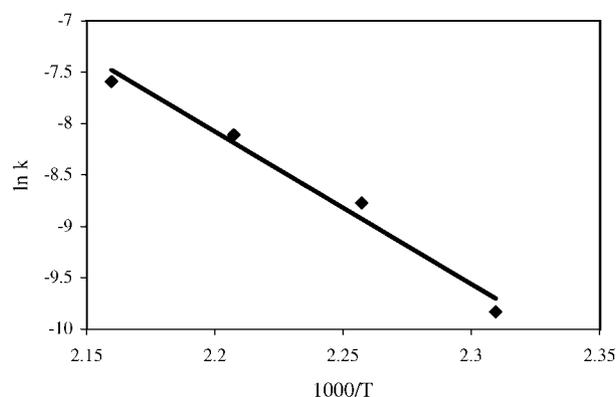


Figure 1. Plot of $\ln k$ vs $1000/T$ for allyl sulfide pyrolysis

Table 4. Kinetic parameters for some allyl compounds

Reactant	E_a (kcal mol ⁻¹)	Log A	$-\Delta S^\ddagger$ (cal mol ⁻¹ K ⁻¹)	Ref.
C ₆ H ₁₀ O ^a	42.30	11.9	8.9	18
C ₆ H ₁₀ N ^a	37.10	11.0	11.5	31
C ₆ H ₁₀ S	29.34	10.6	12.85	This work

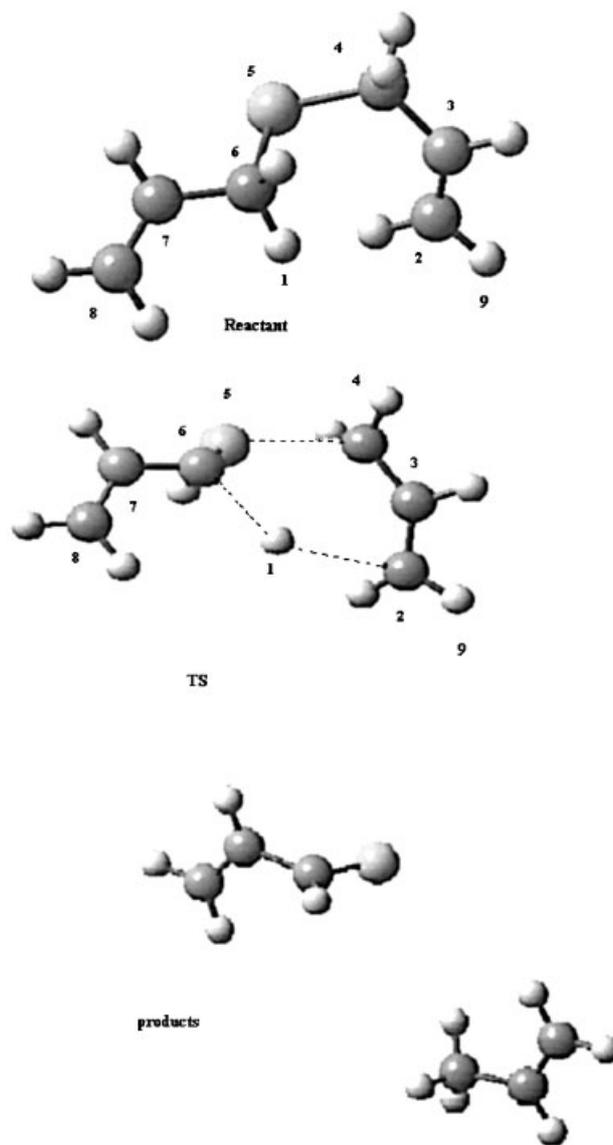
^a Calculated at 375 °C.

Theoretical results

Theoretical studies of these types of chemical reactions suggest that the elimination occurs through a cyclic process. The TS is described by a six-centered ring with the H1—C2 bond formation and C4—S5 bond cleavage (see Scheme 2), yielding propene and thioacrolein.

The geometric parameters for the reactant and the TS are given in Table 5 (see Scheme 3). During the pyrolysis process, when the reactant is converted to the TS; the C2—C3, C4—S5 and H1—C6 distances increase, whereas the C3—C4, C6—S5 and H1—C2 distances decrease. The reaction path for the pyrolysis is evaluated as IRC. The B3LYP/6-31G* results are shown in Fig. 2. This figure shows energy as a function of the reaction coordinate, C—H, and represents the minimum energy path that connects the reactant to the products passing through the saddle point.

An analysis of NBO charges in the TS shows a positive charge developing on H1 (+0.38) and fairly high negative charges on C3 (-0.53) and C2 (-0.50), while C4 and C6 support charges more positive with respect to the reactant. From an electronic point of view, the relative positive charges on C6 and C4 move to S5 and

**Scheme 3****Table 5.** Calculated geometric parameters in the gas phase at the B3LYP/6-31G* level

Parameter ^a	Reactant	TS
H1—C2	3.97	2.02
C3—C2	1.33	1.42
C4—C3	1.51	1.46
S5—C4	1.83	2.41
C6—S5	1.85	1.64
C7—C6	1.50	1.44
C8—C7	1.33	1.35
C3—C2—H1	60.04	34.55
C4—C3—C2	127.24	135.90
S5—C4—C3	117.49	120.15
C6—S5—C4	100.26	121.71
C7—C6—S5	109.65	120.55
C8—H9—C6	124.27	118.92
C4—C3—C2—H1	-48.85	-76.64
S5—C4—C3—C2	10.68	44.97
C6—S5—C4—C3	72.15	52.76
C7—C6—S5—C4	164.58	-181.90
C8—C7—C6—S5	114.63	122.45

^a Distances in Å, angles in degrees; for numbering of atoms, see Scheme 3.

C3 on the TS, respectively. These results show the C4—S5 bond cleavage and C6—S5 bond formation (Table 6).

The thermochemical data for the reaction, ΔH , ΔS and

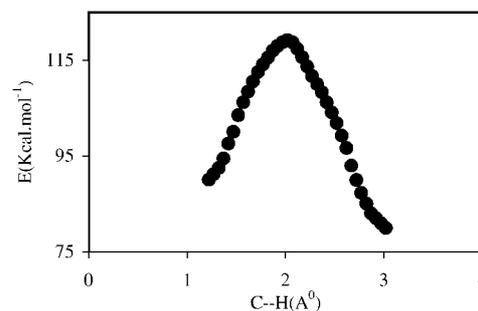
**Figure 2.** Schematic energy profile of the potential energy surface for the pyrolysis reaction at the B3LYP/6-31G* level

Table 6. Charge distribution on atoms

Atom	Reactant	TS
H1	+0.25	+0.38
C2	-0.43	-0.50
C3	-0.24	-0.53
C4	-0.63	-0.49
S5	+0.21	+0.12
C6	-0.61	-0.37
C7	-0.24	-0.28
C8	-0.41	-0.41

Table 7. Calculated thermodynamic parameters

Parameter	Value
ΔH (kcal mol ⁻¹)	8.21
ΔS (cal mol ⁻¹ K ⁻¹)	37.49
ΔG (kcal mol ⁻¹)	-9.15

Table 8. Calculated and experimental kinetic parameters

	E_a (kcal mol ⁻¹)	Log A	$-\Delta S^\ddagger$ (cal mol ⁻¹ K ⁻¹)
Calc.	29.11	9.5	22.53
Exp.	29.34	10.6	12.85

ΔG , are reported in Table 7. As can be seen, the decomposition of allyl sulfide is an endothermic process, the ΔH value being positive. The overall process is spontaneous; the ΔG value is negative. The entropy of the products is higher than those of the reactants and through the elimination reaction the entropy is increased ($\Delta S > 0$).

The theoretical and experimental activation parameters ΔS^\ddagger , E_a and $\log A$ are given in Table 8. These values show discrepancies; e.g., as the theoretical ΔS^\ddagger is nearly double the experimental value, it confirms the proposed six-centered cyclic TS. However, the theoretical and experimental E_a values show good agreement.

The calculated frequency at the B3LYP/6-31G* level for the TS is 1081 cm⁻¹, indicating that this point is associated with the light atom movement. For the investigation of the non-synchronous character of the TS, an analysis of the bond order evaluation is needed.³²⁻³⁴ An atoms in molecule analysis was used to calculate

the bond orders of the reactant and products. For the TS, the commonly used Pauling bond order,³⁵ n_p , is defined as

$$n_p = n_0 \exp[(R_0 - R)/0.3] \quad (1)$$

where n_0 is the bond order of the fully formed bond of length R_0 and R is the length of a bond with bond order n_p .

It is more appropriate to use the Gajewski, Davidson and Shiner equation (J. J. Gajewski, personal communication; based upon work with E. R. Davidson and V. J. Shiner):

$$n_p = n_0 \exp[(R_0 - R)/0.6] \quad (2)$$

where, since the Pauling bond order using a factor of 0.3 does not give reasonable values of the bond orders for very long bonds, for the region of bond orders smaller than 1, the factor of 0.3 is changed to 0.6.³⁶

A better description of the extent of bond formation and bond cleavage is shown in Table 9. One can see a moderate increase in n_p (H1—C2) from the reactant to the TS and a large decrease in n_p (C4—S5). An analysis of the geometric parameter values also shows a non-synchronous character for the TS: the H1—C2 bond distance is 2.02 Å, whereas the C4—S5 distance is longer (2.41 Å). This indicates that the C4—S5 bond cleavage is faster than H1—C2 bond formation. Again, an analysis of the synchronicity values³⁷ in Table 9 indicates that when the C4—S5 bond rupture proceeds by nearly 65%, the H1—C2 bond formation is only 22%. The synchronicity value (syn%) of 0.725 shows that the allyl sulfide pyrolysis reaction pathway can be described as concerted but nearly moderate non-synchronous.

EXPERIMENTAL

Materials. Allyl sulfide was synthesized according to the literature,³⁸ purified and collected at 68–70 °C and a pressure of 1 Torr. A purity of better than 99% of the allyl sulfide was confirmed by gas–liquid chromatography (GLC) (OV-1, 80–100 mesh). Cyclohexene was synthesized according to the literature.³⁹ n-Octane was obtained from Merck.

Kinetics. The pyrolysis experiments were performed in a

Table 9. Bond order and percentage of evaluation (Ev %) through the chemical process

	H1—C2	C2—C3	C3—C4	C4—S5	S5—C6	C6—H1
Reactant	—	1.92	1.05	1.10	1.10	0.96
TS	0.21	1.49	1.31	0.38	1.87	0.16
Products	0.97	1.07	1.94	—	2.03	—
Ev (%)	22	51	13	65	83	83
Syn (%)	72.5					

static system with a glass reaction vessel and in the presence of the free radical inhibitor cyclohexene. The system was evacuated by a rotary and diffusion pump (Leybold) down to 10^{-3} Torr. A 5 μ l volume of the net reactant in n-octane as internal standard was injected directly into the reaction vessel, using a microsyringe (Thermo, Model UMS-10). The temperature was controlled maintained within ± 0.3 K using a Beckman thermometer. In each kinetic run, the reaction mixture was injected into the GLC system equipped with a flame ionization detector (Perkin-Elmer) with a gas-tight syringe (PS Model A-2), using a 3 m column of OV-1 (80–100 mesh). The initial rate plot of $\ln(S_0/S)$, where S_0 and S are the initial and the subsequent reactant concentration, respectively, against time, t , were satisfactory over at least three half-lives in pyrolysis. Since P_0/P , the initial to final pressure ratio, is equal to the S_0/S ratio, the GC response factor was assumed. The first kinetic runs were carried out with a relative standard deviation of $<4\%$ at a given temperature.

Supplementary material

Two table of data (Z-matrix for allyl sulfide and the TS) are available at the epoc website (<http://www.wiley.com/epoc>).

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