



A joint experimental and computational study on the kinetic and mechanism of diallyl disulfide pyrolysis in the gas phase

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Abstract

A combined theoretical and experimental kinetic and mechanism of diallyl disulfide pyrolysis reaction in the gas phase was studied in a static system over the temperature range of 586.7–621.2 K and a total pressure of 72 Torr in the presence of cyclohexene as radicals inhibitor. The experimental results show that the reaction is homogeneous, unimolecular and proceeds through a radical mechanism. Theoretical calculations at the B3LYP level using the 6-31G*, 6-31++G** and 6-311++G** basis sets confirm the radical mechanism for the diallyl disulfide pyrolysis. The calculated kinetic and activation parameters especially at the B3LYP/6-31G* level are in good agreement with the experimental data.

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1. Introduction

Organic disulfides are less stable than the corresponding sulfides and therefore readily undergo diverse transformations and react with organic compounds under the liquid and gas phase thermolysis conditions.

Very few examples of the gas phase kinetics for disulfides compounds have been reported. Coope and Bryce [1] have studied thermal decomposition of dimethyl disulfide. They proposed a stepwise mechanism with methyl mercaptan and thioformaldehydes polymer as the main products.



Di-tert-butyl disulfide was found to pyrolyse yielding hydrogen disulfide and isobutene [2]. A consecutive unimolecular elimination of two molecules of isobutene via a four-center cyclic transition state (TS) and C–S bond splitting attributed to the product formation.

A radical mechanism involving thioalkyl radicals for the hydrogen sulfide, alkenes and free sulfur formation

has been proposed by Bock and Mohmand [3] for the gas phase pyrolysis of alkyl disulfide. This mechanism proceeds by an initial S–S bond cleavage followed by hydrogen abstraction to form alkanethiol products which is decomposed latter on.

The C–S and S–S bond fission are favorable in the gas phase photolysis of disulfides [4,5].

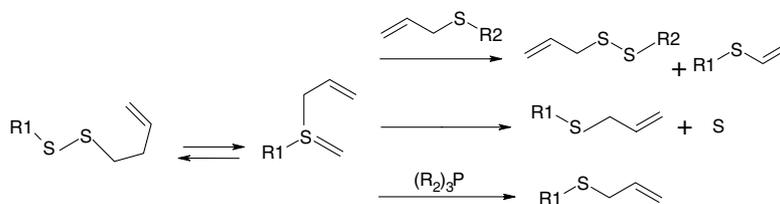
Gas phase thermolyses of aryl tert-butyl disulfide were studied by Martin and Ascanio [6] at 390–450 °C and 7–15 Torr pressure. The reaction products were 95% isobutene, 5% isobutane and the corresponding RC₆H₄SSH disulphanes. A four-center cyclic transition state mechanism was suggested for the formation of isobutene and aryl disulphane products.

The pioneering research on the pyrolysis of allylic disulfides and trisulfide, Barnard et al. [7] have demonstrated the existence of an equilibrium at the room temperature between these compounds and thiosulfoxides, which formed by facile [2,3]-sigmatropic process (Scheme 1).

At high temperatures and in the presence of phosphines, sulfur atom can be transferred from allylic disulfides (AlI₂S₂) to allylic sulfides. Loss of sulfur from allylic disulfides and trisulfides is a particularly a favorable process [8].

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Scheme 1.

In addition to [2,3]-sigmatropic rearrangement, a second parallel process likely accompany with All_2S_2 homolytic bond cleavage. In the pyrolysis of All_2S_2 homolytic process is as important as intermolecular processes involving sulfur exchange from thiosulfoxides.

The existence of the allyl radical has been confirmed by Maier et al. [9] using the flash pyrolysis of diallyl disulfide with the UV, IR and EPR spectroscopy techniques at 750 °C.

A combined theoretical and experimental study of the gas phase pyrolysis of diallyl disulfide was carried out to obtain the kinetic parameters for diallyl disulfide, which has not been reported so far. A complementary study with the aim of elucidation the molecular mechanism associated with this pyrolysis process is important in order to have a precise idea of the reaction pathway.

2. Experimental

Commercial diallyl disulfide was freed from diallyl sulfide and other impurities by pumping at room temperature and pressure of 1 Torr for one hour. Further purification was done by trap to trap distillation at high vacuum ($\sim 10^{-3}$ Torr).

Cyclohexene was synthesized as reported in the literature [10]. Commercial absolute ethanol was used as internal standard.

The reactant structure (All_2S_2) was confirmed by gas chromatography mass spectroscopy using a HP-5793 instrument fitted with a 30 m \times 0.25 mm i.d. and HP-5 capillary column.

The analysis indicates a purity better than 97% for All_2S_2 . NMR spectra were obtained on the Bruker 500-Ultrashield instrument. An 8- μL volume of the net reactant in ethanol as internal standard was injected directly into the reaction vessel, using a microsyringe (HP, Agilent 5181-1267).

The pyrolysis experiments were performed in a static system using a glass reaction vessel over 10 half-lives in the presence of cyclohexene as a free radicals inhibitor. The reaction mixture was injected into the GC instrument (HP, Agilent serie 6890), equipped with a flame ionization detector in each kinetic run.

Gaseous mixture at the definite interval times by a gas-tight syringe (PS, A-2) was injected into the GC capillary column (HP-5, 30 m \times 0.32 mm i.d.). The experimental technique and the rate coefficient calculations have been described elsewhere [11].

3. Computational details

The structures corresponding to the reactant, intermediate, TS and the products for the pyrolysis reaction were optimized, using the Gaussian 98 computational package [12] with the DFT method as implemented in the computational program.

Lee et al. [13] have previously reported that the B3LYP hybrid functional gives structures and vibrational frequencies in good agreement with the coupled-cluster theory. Therefore, the optimized geometries of the stationary points on the potential energy surface (PES) were performed using the Becke's three parameter hybrid exchanges functional with the correlation functional of Lee, Yang and Parr (B3LYP) level of the theory [14,15] with the 6-31G* basis set [16].

The synchronous transit-guided quasi-Newton (STQN) method as implemented by Schlegel et al. [17] was used to locate the TS for the concerted mechanism.

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

The enthalpy, entropy and Gibbs free energy of the reaction (ΔH , ΔS , ΔG) were calculated from the B3LYP data, using the 6-31++G** basis set at 298.15 K.

The activation parameters were also determined in the temperature range of the pyrolysis reaction. The activation energy, E_a , and the Arrhenius factor were computed using the Eqs. (1) and (2), respectively. These equations have been derived from the transition state theory [18,19]:

$$E_a = \Delta H^\ddagger(T) + RT, \quad (1)$$

$$A = (eK_B T/h) \exp(\Delta S^\ddagger(T)/R). \quad (2)$$

The natural bond orbital (NBO) analysis, which suggested by Reed et al. [20,21] was applied to determine the charge changes through the reaction.

4. Results and discussion

4.1. Experimental results

Gas phase pyrolysis of diallyl disulfide was investigated in the temperature range of 586.7–621.2 K and a total pressure of 72 Torr. The main products of the reaction are accordance to Scheme 2. However the minor products such as All_2S and All_2S_3 were detected. The experimental stoichiometry as described in Scheme 2 implies that for long reaction times $P_f = 2P_0$, where P_f and P_0 are the final and initial pressures, respectively. The average experimental P_f/P_0 values at the temperature range of the reaction and 10 half-lives was 1.73. The stoichiometry results are reported in Table 1. The departure from the theoretical stoichiometry was due to the secondary reactions that led to polymerization.

The products were identified using the mass spectrometry method. Kinetic studies of the reaction were performed by measurements of the All_2S_2 decomposition percentage, which obtained from the chromatographic analysis. The variation of the first order rate coefficient with the temperature are given in Table 2.

The homogeneity of this process was studied using the vessels with a surface-to-volume ratio of 2.5 and 5 times greater than the unpacked vessel. No important differences in the rate coefficient were obtained which indicates the homogeneity of the reaction (Table 3).

Several kinetic runs at 621.2 K with different ratios of cyclohexene as a free radical scavenger were carried out. Table 4 shows the presence of a free-radical mechanism.

A least square fit of the rate coefficients in the form of the Arrhenius equation produced the following relationship:



Scheme 2.

Table 1
Final to initial pressure ratio in the gas phase

T (K)	P_0	P_f	P_f/P_0	Average
585.7	62	107	1.73	
600.2	65	112	1.72	1.73
605.2	59	101	1.71	
621.2	69	120	1.74	

Table 2
Variation of the rate coefficients with the temperature for the pyrolysis process in the gas phase

T (K)	$10^3 k$ (S^{-1})	$-\ln k$	σ (%)
585.7	3.12	5.77	4.31
600.2	5.98	5.12	1.53
605.2	7.91	4.84	3.78
621.2	22.15	3.81	4.12

Table 3
Homogeneity of the pyrolysis reaction at 600.2 K

S/V (cm^{-1})	$10^3 k$ (S^{-1})	Differences (%)
1.0	5.98	0.00
2.5	5.66	-5.21
5.0	6.18	3.43

Table 4
Effects of cyclohexene on the rate coefficients at 621.2 K

$P_{\text{inhibitor}}/P_{\text{All}_2\text{S}_2}$	$10^3 k$ (S^{-1})	Differences (%)
0	22.15	0.00
1	23.97	8.11
3	25.47	15.07

$$\log k = (11.85 \pm 0.21) - (38.54 \pm 0.16)/(2.303RT),$$

$$R = 1.987 \times 10^{-3} \text{ kcal mol}^{-1} \text{ K}^{-1},$$

$$1 \text{ kcal} = 4.185 \text{ kJ}.$$

The corresponding plot is shown in Fig. 1. Activation parameter values for some sulfide and disulfide organic compounds are listed in Table 5. The activation energy for All_2S is smaller than the other organodisulfur compounds. This value and the negative activation entropy suggest that the mechanism for All_2S is certainly highly concerted as was proposed previously [11].

The highest activation energy of pyrolysis is reported for organodisulfur compounds. This could be explained with much less concerted bond breaking and bond making in the TS for these compounds with the radical development. Although the activation entropy for All_2S_2 pyrolysis is negative, it is smaller than for All_2S . Comparison between the activation energies in Table 5 indicates the presence of free radical chain decomposition for All_2S_2 pyrolysis.

4.2. Theoretical results

Two possible mechanisms have been suggested for the pyrolysis of diallyl disulfide in the gas phase: a [2,3]-

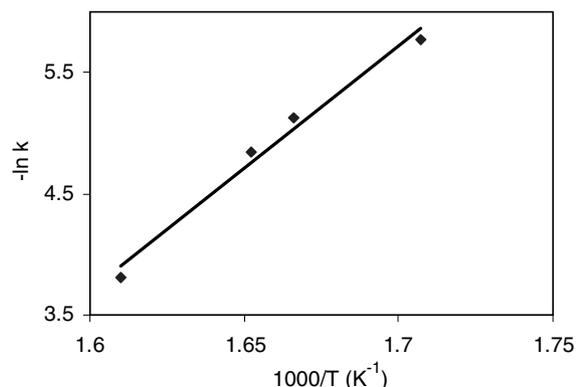


Fig. 1. Plot of $\ln k$ vs. $1000/T$ for the pyrolysis reaction in the gas phase.

Table 5

The experimental kinetic parameters for some organosulfur and organodisulfur compounds in the gas phase

Compound	E_a (kcal mol ⁻¹)	log A	$-\Delta S^\ddagger$ (cal mol ⁻¹ K ⁻¹)	Ref.
All-S-All	29.34	10.6	12.85	[11]
Ph-SS- <i>t</i> -Butyl	43.50	13.5	0.55	[2]
P-NO ₂ -Ph-SS- <i>t</i> -Butyl	44.21	13.5	0.69	[2]
<i>t</i> -Butyl-SS- <i>t</i> -Butyl	42.3	13.6	0.19	[2]
All-SS-All	38.54	11.85	7.69	This work

sigmatropic process, intermolecular sulfurization–desulfurization, and free-radical reaction (Scheme 3).

The first one may be started by thiosulfoxide formation due to facile [2,3]-sigmatropic process follows by a direct unimolecular splitting through six-center TS [22,23]. The concerted mechanism is initiated with the H1–C2 bond formation and C4–S5 bond cleavage yielding propene and thioacrolein S-sulfide according to Fig. 2. When the intermediate is transformed to the TS, during the retro-ene process, the H1–C2, S5–C6 and C3–C4 bond lengths decrease, whereas the H1–C6, C4–S5 and C2–C3 bond lengths increase.

Table 6 shows the geometric parameters for the reactant, intermediate and the TS according to atom numbering on the Fig. 2.

The thermochemical parameters for the reaction (ΔH , ΔS and ΔG) obtained from the thermochemistry calculations and reported in Table 7. The pyrolysis of diallyl disulfide is an endothermic process ($\Delta H > 0$) and the global process is spontaneous ($\Delta G < 0$). The entropy changes during the reaction are positive.

In order to obtain more reliable kinetic and activation parameters for the reaction, frequency calculations using the 6-31++G** and 6-311++G** basis sets were carried out on the optimized structures at the B3LYP/6-31G* level. All the theoretical kinetic and activation parameters were calculated at 603.2 K. The comparison of the calculated with the experimental one is listed in Table 8. It is obvious that the calculated activation energy for concerted mechanism is much less than the experimental one. Therefore the concerted mechanism is

Table 6

Main geometric parameters for the All₂S₂, intermediate and the TS at the B3LYP/6-31G* level for the concerted/radical mechanisms

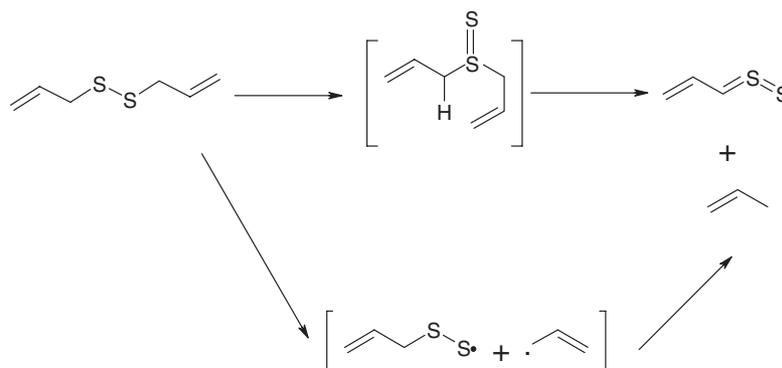
Parameter	All ₂ S ₂	Intermediate	TS
H1–C2	6.88	2.93	1.45/8.231
C2–C3	1.33	1.33	1.41/1.33
C3–C4	1.49	1.49	1.37/1.38
C4–S5	1.85	1.88	2.76/3.49
S5–S6	2.09	2.01	2.00/2.09
S6–C7	1.85	3.14	3.03/1.85
S5–C7	2.97	1.88	1.75/2.97
C7–C8	1.49	1.49	1.48/1.49
C8–C9	1.33	1.33	1.33/1.33
H1–C2–C3	31.92	69.62	97.01/37.01
C2–C3–C4	124.01	124.21	121.98/124.01
C3–C4–S5	108.31	112.42	97.69/108.31
C4–S5–S6	97.91	106.34	98.48/97.91
H1–C2–C3–C4	–54.70	–66.31	–72.13/63.30
C2–C3–C4–S5	110.31	115.46	59.47/–110.31
C3–C4–S5–S6	160.31	176.39	–116.17/166.31

rejected. This brought our attention to the latter mechanism and the radical mechanism was fully investigated.

Since the allylic C–S_n bonds are common in vulcanized rubber, homolytic cleavage of C–S bonds may represent an important role of initiation for the thermal degradation of these materials at the temperatures above 100 °C.

Let us assume that upon thermolysis of All₂S₂ homolytic cleavage of the C–S bond predominates according to step 1 in Scheme 4. Other sources for All₂S₃ and All₂S formation can be regarded as the following:

- Bimolecular reaction of thioacrolein S-sulfide with diallyl disulfide according to Scheme 5.



Scheme 3.

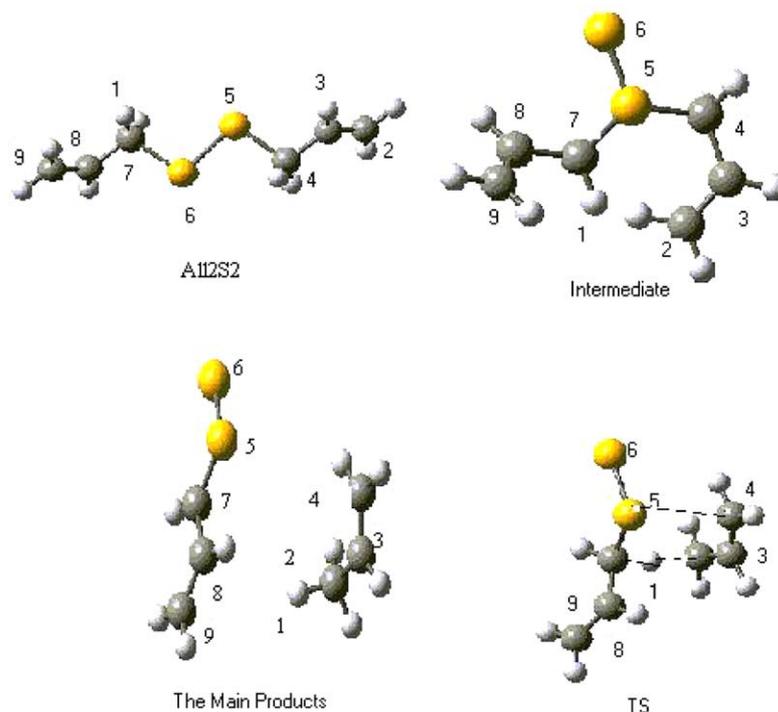


Fig. 2. Atom numbering for the reactant, intermediate, TS and products in the concerted mechanism.

Table 7

Calculated thermodynamic parameters for the pyrolysis reaction at the B3LYP/6-31++G** level and 298.15 K

Parameter	Value
ΔH (kcal mol ⁻¹)	13.22
ΔG (kcal mol ⁻¹)	-7.27
ΔS (cal mol ⁻¹ K ⁻¹)	30.00

Table 8

Calculated kinetic and activation parameters at 603.4 K for the concerted/radical mechanism in the gas phase (rate coefficients at 621.2 K)

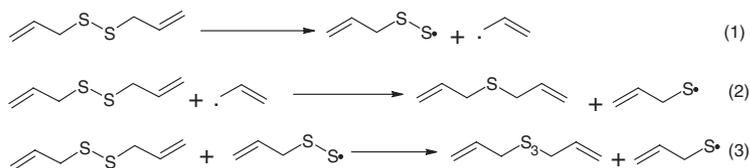
Parameter	6-31G*	6-31++G**	6-311++G**
E_a (kcal mol ⁻¹)	27.44/40.30	26.80/38.46	26.50/40.12
$\log A$	12.88/13.79	12.79/13.76	13.07/13.80
ΔH^\ddagger (kcal mol ⁻¹)	26.24/39.10	25.60/37.26	25.30/38.92
ΔS^\ddagger (cal mol ⁻¹ K ⁻¹)	-3.01/1.17	-3.40/1.05	-2.10/1.21

- Bimolecular reaction of thiosulfoxide with diallyl disulfide according to Scheme 6.

Since the mass spectrometry of the products did not detect the thioacrolein mass, All₂S₃ formation process through the Scheme 6 was ignored.

In addition to the reaction molecularity, another important difference between the Schemes 4 and 5, is the rate-determining step, i.e., C–S and S–S bond cleavage. Therefore the pyrolysis process can be investigated through the C–S bond and S–S bond dissociation energy.

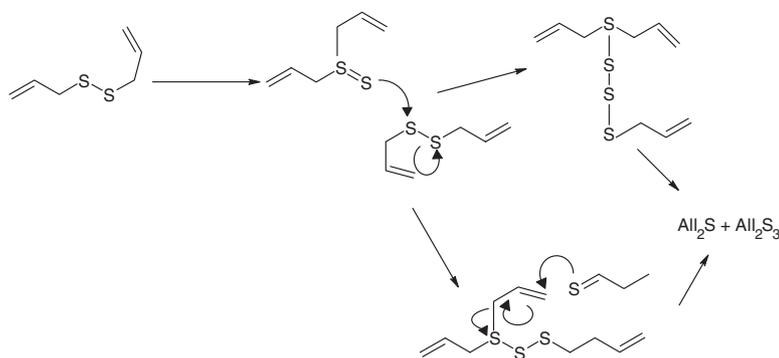
Bond dissociation energy for the C–S bond and S–S bonds have been previously calculated using the electron impact method [24]. The reported bond dissociation energies are 46 and 62 kcal mol⁻¹ for *D*(allyl-SS-allyl) and *D*(allyl-S–S-allyl), respectively [25].



Scheme 4.



Scheme 5.



Scheme 6.

Table 9

Calculated energies in hartrees for some probable radicals and neutral compounds including ZPVE and thermal correction

Basis set	AllS ₂	All	AllS	All ₂ S	All ₂ S ₂	All ₂ S ₃
6-31G*	-913.50	-117.09	-515.29	-632.48	-1030.66	-1428.85
6-31++G**	-913.52	-117.11	-515.31	-632.51	-1030.69	-1428.89
6-311++G**	-913.59	-117.13	-515.36	-632.58	-1030.78	-1428.89

These results show that the allylic C–S bond is weaker than the S–S bond by 16 kcal mol⁻¹, hence this difference should be decisive for the mode of thermal dissociation.

According to the bond dissociation energy, C–S bond cleavage is the most probable step in the radical mechanism, thus the All₂S₂ formation through the Scheme 6 was rejected.

After full geometry optimization of the most probable radicals in Scheme 4, frequency calculations were performed to estimate the ZPVEs, thermal corrections and the SCF energies.

The results with unrestricted B3LYP method using the 6-31G*, 6-31++G** and 6-311++G** are reported in Table 9. Calculated kinetic and activation parameters for the second mechanism are listed in Table 8. Calculated parameters for the radical mechanism especially at the 6-31G* level are in good agreement with the experimental one as well as the previous studies [11,26–28]. So, we conclude that the pyrolysis reaction of All₂S₂ proceeds through a radical mechanism introducing the C–S bond cleavage at the TS.

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