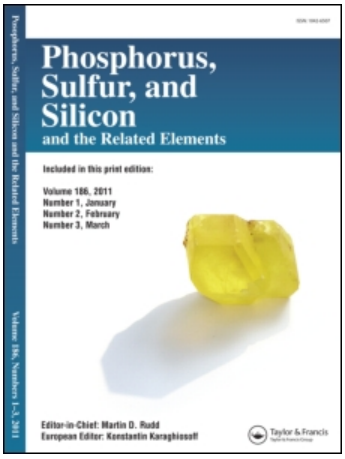

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GAS-PHASE THERMOLYSIS OF SULFUR COMPOUNDS. PART V. METHYL ALLYL, DIALLYL AND BENZYL ALLYL SULFIDES

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GAS-PHASE THERMOLYSIS OF SULFUR COMPOUNDS. PART V. METHYL ALLYL, DIALLYL AND BENZYL ALLYL SULFIDES

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The title compounds have been pyrolyzed in a stirred-flow system, at temperatures within the range 315–418°C and pressures between 2 and 15 torr. Under these conditions, the products observed were propene and the polymers of thiomethanal, allyl thioaldehyde and benzyl thioaldehyde. Diallyl sulfide was further studied in a static system, over the temperature range of 227–256°C and initial pressures between 90 and 255 torr.

The reactions showed first-order kinetics and the rate coefficients yielded the following Arrhenius equations

Methyl Allyl Sulfide:

$$k\ (sec^{-1}) = 10^{11.23\pm0.25} \exp(-160 \pm 3\ kJ/mol.\ RT)$$

Diallyl Sulfide:

$$k\ (sec^{-1}) = 10^{11.01\pm0.06} \exp(-138.2 \pm 0.7\ kJ/mol.\ RT)$$

Benzyl Allyl Sulfide:

$$k\ (sec^{-1}) = 10^{10.93\pm0.18} \exp(-141 \pm 2\ kJ/mol.\ RT)$$

The Arrhenius parameters are consistent with a unimolecular mechanism involving six-centered cyclic transition states yielding propene and thioaldehyde. The results are discussed in relation to allyl ethers and amines reported in the literature.

INTRODUCTION

Previous work[1,2] has established that alkyl allyl sulfides pyrolyze homogeneously in the gas phase through a molecular mechanism involving a six-centered transition state. The formation of the products, propene and thioaldehyde, via a 1–5 hydrogen shift, has been confirmed by using deuterated sulfides.

Other systems such as alkyl and aryl allyl ethers[3] and amines[4–7] have been reported to decompose thermally by a similar mechanism. As a continuation of our work on the pyrolysis of sulfur compounds, we have studied the pyrolysis of sulfur homologues of allyl amine and ether systems in order to compare their reactivities and kinetic parameters.

RESULTS

The orders of consumption of the methyl allyl sulfide and diallyl sulfide were found to be 0.996 ± 0.048 at 398°C and 1.08 ± 0.05 at 333°C, respectively. They were ob-

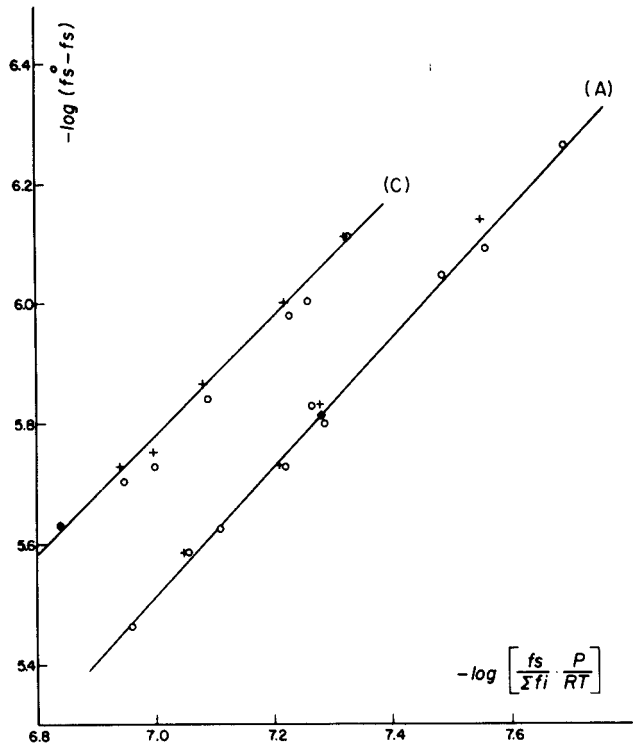

FIGURE 1 Reaction order plots. (A) Diallyl sulfide; (C) Benzyl allyl sulfide: ⊙ Propene measurement; + Reactant measurement.

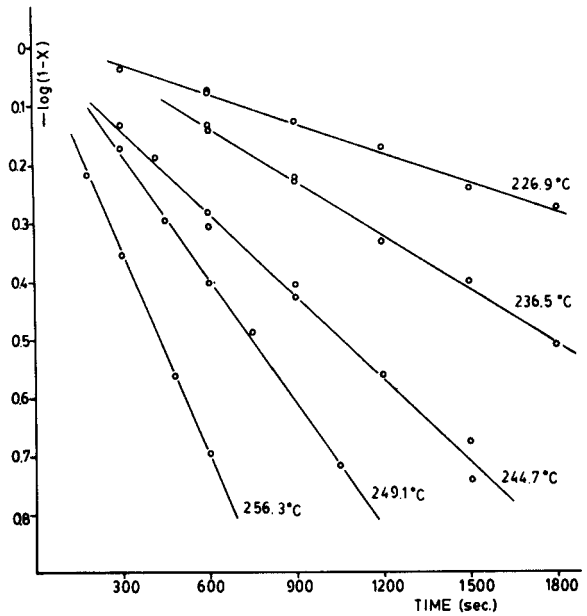

FIGURE 2 First order plots for diallyl sulfide. (Static system).

tained from the least-square linear fits shown in Figure 1. The symbols ⊙ and + in this figure denote measurements of the outflow of reactant (f_S) from the amount of propene formed and from gas chromatographic measurement of the undecomposed reactant, respectively. The order thus obtained corresponds to the initial reaction since the conversions examined ranged between 9 and 32%. First order was assumed for the pyrolysis of benzyl allyl sulfide.

Figure 2 shows the first-order plots for diallyl sulfide obtained in the static experiments for initial pressures in the range 90–255 torr and conversions between 8 and 80%. The conversions in these experiments were obtained from volumetric measurement of the amount of propene formed at appropriate reaction times at each temperature.

In Tables I, II and III are listed the experimental and kinetic data of representative runs for methyl allyl, diallyl and benzyl allyl sulfide, respectively. The agreement between the conversion estimated from gas chromatographic measurement of the unreacted sulfide ($\%r_{glc}$) and from volumetric measurement of propene ($\%r_{C_3}$) indicates that the amount of C_3 hydrocarbon is representative of the amount of reactant consumed. On experimental grounds, the conversion based on the amount of propene is more accurate, particularly in the case of the benzyl allyl sulfide, and it was used in calculating the rate coefficients shown in the tables.

TABLE I

Stirred-Flow Pyrolysis of Methyl Allyl Sulfide Kinetic Parameters and Experimental Conditioning

T °C	$k \cdot 10^4 \cdot sec^{-1}$	(a) θ sec	(b) $\%r_{C_3}$	(c) $\%r_{glc}$	P Torr	(d) f_S^0
376.5	236	4.89	10.35	—	3.62	439.4
377.3	233	5.16	10.67	11.5	2.69	308.5
376.7	261	4.27	10.03	9.2	5.81	808.5
386.9	400	4.62	15.60	16.4	3.83	461.1
387.2	395	5.02	16.54	18.3	2.65	291.4
386.9*	407	3.86	13.58	—	9.50	254.1
397.8	634	4.72	23.02	23.9	3.99	436.2
397.4	577	8.49	32.89	—	5.09	285.8
398.0	644	3.27	17.38	19.2	2.76	456.2
397.5	657	2.76	15.36	16.3	5.79	1153.0
398.1	613	1.51	8.50	9.0	5.66	2203.6
397.6	648	3.27	17.50	16.5	3.28	540.2
397.2	619	3.15	16.34	17.4	4.82	832.9
397.4	617	3.05	15.84	15.9	8.26	1482.0
407.7	955	2.46	19.03	18.2	3.21	684.3
407.3	907	2.08	15.90	17.6	3.38	873.2
407.1	914	1.68	13.26	14.2	4.89	1606.3
407.9*	1009	1.31	11.70	10.0	9.80	903.4
407.8	876	1.60	12.30	11.8	4.60	1595.7
417.3	1399	1.33	15.66	17.9	9.34	3746.0
417.1	1359	1.10	13.01	13.4	14.92	7381.8
418.0	1473	2.23	24.70	22.9	4.25	940.1
417.7	1409	1.39	16.43	18.7	11.38	867.0
417.9*	1396	1.45	16.89	14.9	13.70	1595.5

* Cyclohexene as carrier gas.
(a) Residence time.
(b) Percent reaction from propene measurement.
(c) Percent reaction from reactant measurement.
(d) Reactant inflow in mol. $sec^{-1} \cdot 10^8$.

TABLE II

Stirred-Flow Pyrolysis of Diallyl Sulfide

T °C	$k \cdot 10^4 \cdot sec^{-1}$	(a) θ sec	(b) $\%r_{C_3}$	(c) $\%r_{glc}$	P Torr	(d) f_3^3	(e) fc/f_3^3
312.6	488	4.45	17.82	—	4.66	555.2	—
312.8	496	3.51	14.41	—	14.53	809.2	—
315.3	522	4.77	19.93	—	3.68	427.4	—
323.2	854	3.85	24.72	24.4	4.19	535.2	—
323.7	815	3.38	21.62	22.4	14.19	741.3	2.3
324.0	831	3.66	23.30	23.1	14.42	665.1	2.4
333.6	1292	1.32	14.54	12.9	11.01	559.2	8.0
332.4	1342	0.921	11.00	10.6	2.86	1704.2	—
333.1	1287	0.976	11.16	11.3	2.49	1382.8	—
331.4	1200	3.17	27.56	29.3	14.12	538.9	3.7
332.3	1347	3.37	31.15	33.6	13.47	508.7	3.4
332.9	1308	1.65	17.78	17.6	4.77	1476.5	—
343.4	2073	1.29	21.17	22.8	11.01	812.2	5.1
343.9	2056	1.24	20.35	22.5	11.36	841.4	5.2
343.7	1879	1.21	18.56	16.8	1.61	664.8	—
353.6	2902	1.02	22.80	—	1.64	768.6	—
352.0	2945	0.470	12.17	11.2	10.41	1299.0	8.8
352.6	3094	0.620	16.09	—	4.71	3825.0	—
352.9	3127	0.732	18.62	—	3.56	2396.8	—
362.2	4546	0.946	30.06	—	2.77	1294.9	—
364.2	4711	1.59	42.85	—	1.49	374.9	—
364.1	5313	1.41	42.81	—	1.43	408.6	—

Static System Pyrolysis of Diallyl Sulfide

T °C	$k \cdot 10^4 \cdot sec^{-1}$	(f) $\sigma(\%)$	(g) N
266.9	3.851	3.7	7
236.5	7.078	2.6	7
244.7	10.93	3.6	9
249.1	16.44	2.6	5
256.3	26.30	0.2	4

(a), (b), (c) and (d) as in Table I.
(e) Cyclohexene to reactant flow ratio.
(f) Standard deviation; (g) number of measurements.

A least-square fit of the rate coefficients in the form of the Arrhenius equation produced the relationships

Methyl allyl sulfide (376–418°C, flow)

$$k\ (sec^{-1}) = 10^{11.23\pm0.25} \exp(-160 \pm 3\ kJ/mol.\ RT)$$

Diallyl sulfide (227–364°C, static plus flow)

$$k\ (sec^{-1}) = 10^{11.01\pm0.06} \exp(-138.2 \pm 0.7\ kJ/mol.\ RT)$$

Benzyl allyl sulfide (333–374°C, flow)

$$k\ (sec^{-1}) = 10^{10.93\pm0.18} \exp(-141 \pm 2\ kJ/mol.\ RT)$$

The corresponding plots are shown in Figure 3.

The kinetic studies which afforded the above Arrhenius equations are limited to the experimental conditions at which these reactions behave as "clean systems"

TABLE III

Stirred-Flow Pyrolysis of Benzyl Allyl Sulfide

T °C	$k \cdot 10^4 \cdot sec^{-1}$	(a) θ sec	(b) $\%r_C$,	P Torr	(d) f_S^0	(e) f_C/f_S^0
332.8	616	3.22	16.55	6.98	205.4	6.2
333.5	600	3.63	17.90	7.17	272.1	3.9
343.5	1035	3.53	26.72	6.56	189.5	5.5
343.1	1010	3.09	23.81	5.79	585.8	1.0
353.1	1498	2.60	28.01	6.36	496.4	2.1
353.0	1420	1.39	16.48	4.21	983.1	1.0
364.0	2548	1.35	25.53	8.63	254.1	15.6
363.6	2307	1.49	25.56	5.51	630.9	2.7
364.7	2445	1.27	23.70	9.66	1097.7	3.4
364.1	2479	1.34	24.90	9.24	360.7	11.5
372.7	3572	1.34	32.29	8.41	324.6	11.4
374.2	3695	1.35	33.20	9.75	689.2	5.6
372.5	3409	0.826	16.37	9.35	730.5	9.0
382.0	4699	0.786	26.98	9.16	558.8	12.3
382.9	4705	0.764	26.45	9.04	729.4	9.2

(a), (b) and (d) as in Tables I and II.
(e) Toluene to reactant flow ratio.

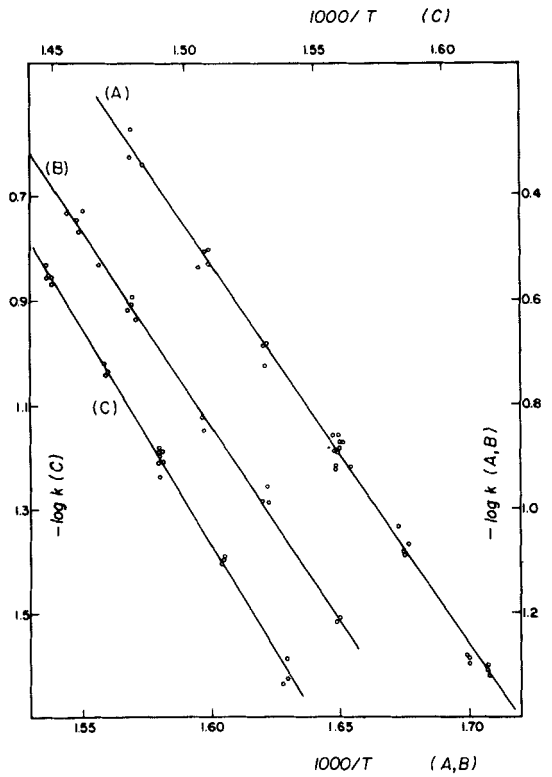

FIGURE 3 Arrhenius plots. (A) Diallyl sulfide; (B) Benzyl allyl sulfide; (C) Methyl allyl sulfide.

yielding only propene and thioaldehyde polymer as the reaction products. In calculating the total outflow from the reactor, it was assumed that the thioaldehyde leaves the reactor as a monomer and polymerizes in the cold trap.

Diallyl sulfide pyrolyzed with the above "clean system" behavior over a wide range of experimental conditions. However, methyl allyl sulfide and benzyl allyl sulfide, when pyrolyzed at conversions higher than about 35% (or at residence times longer than about 8 seconds), yield free sulfur and ethylene for the former, and diphenylethylene, hydrogen sulfide and benzyl thiol for the latter, as minor reaction products. This observation was assumed to be an indication of the onset of secondary reactions under such conditions.

Owing to the low volatility of the benzyl allyl sulfide, all runs were made with the vapor of the reactant diluted in toluene as carrier gas. A few runs were made with diallyl and methyl allyl sulfides using cyclohexene as carrier gas and free-radical inhibitor. These showed no difference either in product distribution or in the magnitude of the rate coefficient with respect to the runs made with the pure sulfides. This fact indicates an absence of free-radical chain decomposition.

1,3,5-Trithiane was collected in the cold trap as a white crystalline solid of melting point 235–237°C (reported[8] 220°C). Its IR spectrum in nujol was identical to that reported.[9] It was quite insoluble in both polar and non-polar solvents. The polymer of allyl thioaldehyde had the consistency of a film which could be peeled from the cold-trap wall whereas that of benzyl thioaldehyde was obtained as an amorphous solid. Attempts to recrystallize it in benzene-ethanol mixtures were unsuccessful.

DISCUSSION

Table IV lists the literature values of activation parameters and the statistically corrected rate coefficients calculated at 375°C for several alkyl allyl ethers and amines. It also includes the data for *n*-propyl and *n*-butyl allyl sulfides previously obtained in this laboratory.[1,2]

The common features of these homogeneous, first-order reactions are their negative entropy of activation $\Delta S^{\ddagger}_{648}$, and activation energies considerably lower than the estimated homolytic bond dissociation energy D(Allyl-XR). These features suggest a similar transition-state geometry for all these systems; that is, the proposed six-centered cyclic structure. The reactivities and substituent effects on reaction rates suggests that there are important differences in the degree of concertedness of the various transition states.

The ratios of rate coefficient k (diallyl)/k (methyl allyl) for the sulfides, amines and ethers have the values 25, 32 and 8.5, respectively. Similarly, the ratios k (benzyl allyl)/k (methyl allyl) for the sulfides and ethers are 26 and 5.6, respectively. The value for k (benzyl allyl sulfide)/k (benzyl allyl ether) is 87. These ratios suggest that the mechanism for the ethers is certainly highly concerted as proposed previously[3] without partial charges or radicals being developed that might conjugate with the substituents. The temperature dependence of the deuterium kinetic isotope effect and the lack of substituent effect on rates were also used to propose[10] a nonplanar structure for the transition state with the 1–5 hydrogen shift taking place through a linear three-centered configuration.

Diallyl amine[5], triallyl amine[6] and diallyl sulfide decompose 2.5, 3.5 and 57 times faster, respectively, than diallyl ether.[3,4] They also decompose 23, 31 and 507 times

TABLE IV

Kinetic Parameters for Allyl Compounds

	log A	Ea kJ·mol^{-1}	$\Delta S^{\ddagger}$ (a) J·mol^{-1}K^{-1}	k·10^4 (b) sec^{-1}	BDE (c) kJ·mol^{-1}	Ref.
Amines						
methyl allyl	11.4	181.6	−41.4	2.67	305	4
N-cyclohexyl allyl	11.4	176.6	−34.9	3.73		7
diallyl	11.0	155.3	−48.3	84.5		5
triallyl	11.7	160.1	−34.9	114.8		6
Ethers						
methyl allyl	11.1	174.1	−47.4	3.87	285	3
ethyl allyl	11.8	182.4	−33.0	6.90		4,3
benzyl allyl	11.5	172.4	−33.0	21.8		3
diallyl	11.9	171.1	−37.4	33.0		3
Sulfides						
methyl allyl	11.2	159.7	−44.7	75.0	247	•
n-propyl allyl	11.4	155.8	−40.9	370.0		2
n-butyl allyl	11.4	155.0	−41.1	428.5		1
benzyl allyl	10.9	141.0	−50.1	1891		•
diallyl	11.0	138.2	−48.6	1891		•

(a) Calculated at 375°C.
(b) Rate coefficient at 375°C per α-hydrogen atom.
(c) ΔH°_{298} for the process $CH_3X—C_3H_5 \rightarrow CH_3X^{\cdot} + C_3H_5^{\cdot}$
ΔH°_{298} for the radicals from Refs. 17 and 18.
ΔH°_{298} for the molecules from group additivities, Ref. 17.
• Values from this work.

faster, respectively, than *N*-allylcyclohexylamine.[7] These relative reactivities could be explained with less concerted bond-making and bond-breaking in the transition state for these amines, with the vinyl group stabilizing a partial charge or radical developing on the carbon atom transferring the hydrogen atom. This stabilization is reflected also in the lower activation energy of diallylamine as compared with diallyl ether.

The allyl sulfides show the highest rate of decomposition. Our interpretation of the greater reactivity in the sulfides is that the hydrogen atoms on the α-carbon of the alkyl group possess an enhanced acidic character. This can be expected owing to the greater polarizability of the sulfur atom (3.48 Å^3 as compared with 1.04 Å^3 for N and 0.73 Å^3 for O)[11] which would allow a better stabilization of the negative charge developed on the α-carbon atom. This charge stabilization resembles that of the α-S anions discussed in the literature on the basis of molecular orbital calculations.[12] The term reactivity umpolung is used[13,14] to describe this behavior as opposed to the normal reactivity of a carbon atom possessing a positive charge and bonded to an electronegative atom.

As previously reported,[1,2] the kinetic deuterium isotope effect in 1,1-dideutero *n*-propyl and *n*-butyl allyl sulfides has a magnitude of 2.7 ± 0.2 over the temperature range 281–387°C. This has suggested[2] that the 1-5 hydrogen shift occurs via a nonlinear configuration.[15] The geometry of the transition state for the alkyl allyl sulfides would thus differ from that of the alkyl allyl ethers in being more like a regular hexagon with bond angles of about 120°.

EXPERIMENTAL

Methyl allyl and diallyl sulfides were purchased from Aldrich. Benzyl allyl sulfide was synthesized by a standard technique[19] from allyl bromide and benzyl thiol (Aldrich). They were purified by distillation (≥99% by gas chromatography), and used after being thoroughly degassed under vacuum. The pyrolyses were carried out in two stirred-flow systems[16] fitted with reactors of 265 and 228 ml capacity, respectively. The total pressure in the reactors was measured with type 315BHS-100 pressure transducers from MKS Instruments.

Products and reactant were quantitatively measured and analyzed by gas chromatography and mass spectrometry using the same instruments and methods previously described.[1,2]

The order of the reactions was examined from flow data using the equation $f_i^0 - f_s = kV(f_s P/\Sigma f_i RT)^a$; f_i^0 and f_s are the inflow and outflow of reactant in mol. sec^{-1}; Σf_i the total outflow from the reactor in mol. sec^{-1}; V,P and T are the volume, pressure and absolute temperature of the reactor, respectively; R is the universal gas constant; and a gives the order of the reaction with respect to the concentration of the reactant. A plot of log $(f_i^0 - f_s)$ vs log $(f_s P/\Sigma f_i RT)$ should give a straight line of slope a and intercept log kV,k being the rate coefficient at temperature T. The first-order rate coefficients were calculated using the expression $k = F/\theta(1\text{-}F)$ where F is fraction reacted and θ is the residence time given by $\theta = PV/RT\Sigma f_i$.

The static experiments with diallyl sulfide were done in a 273 ml capacity Pyrex glass reactor fitted with a 315BHS-1000 MKS pressure transducer. The rate coefficients were obtained from plots of log (1-X) vs t, where X is the fraction of reactant decomposed at time t. The technique has been described previously.[1]

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