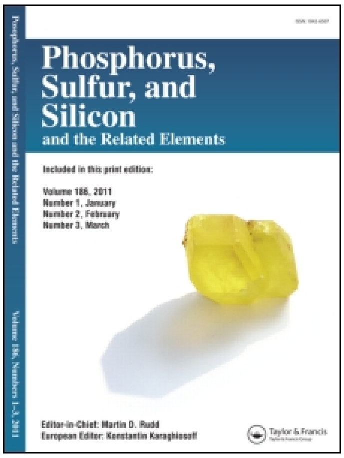

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GAS-PHASE THERMOLYSIS OF SULFUR COMPOUNDS. PART VII. 4,6-DITHIA-1-OCTENE, 4,6-DITHIA-1,8-NONADIENE AND 4,6-DITHIA-6-PHENYL-1-HEXENE

Gonzalo Martín[a]; Henry Martínez[a]; Heriberto Ortega[b]; José Salazar[b]
[a] Centro de Química, Instituto Venezolano de Investigaciones Científicas, I.V.I.C., Caracas, Venezuela [b] Departamento de Química, Universidad Simón Bolívar, Caracas, Venezuela

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GAS-PHASE THERMOLYSIS OF SULFUR COMPOUNDS. PART VII. 4,6-DITHIA-1-OCTENE, 4,6-DITHIA-1,8-NONADIENE AND 4,6-DITHIA-6-PHENYL-1-HEXENE

GONZALO MARTÍN* and HENRY MARTÍNEZ

Centro de Química, Instituto Venezolano de Investigaciones Científicas,
I.V.I.C., Apartado 1827, Caracas 1010-A, Venezuela

HERIBERTO ORTEGA and JOSÉ SALAZAR

Departamento de Química, Universidad Simón Bolívar, Caracas, Venezuela

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Under stirred-flow conditions, the title compounds pyrolyze to yield propene and the ethyl, allyl and benzyl dithioformates, respectively, as reaction products.

The first order rate coefficients of these unimolecular decompositions followed the Arrhenius equations

4,6-dithia-1-octene

$$k\ (\mathrm{sec}^{-1}) = 10^{10.85 \pm 0.18} \exp(-142 \pm 2\ \mathrm{kJ/mol}\quad RT)$$

4,6-dithia-1,8-nonadiene

$$k\ (\mathrm{sec}^{-1}) = 10^{10.45 \pm 034} \exp(-132 \pm 4\ \mathrm{kJ/mol}\quad RT)$$

4,6-dithia-6-phenyl-1-hexene

$$k\ (\mathrm{sec}^{-1}) = 10^{10.09 \pm 0.43} \exp(-130 \pm 5\ \mathrm{kJ/mol}\quad RT)$$

The activation parameters are discussed in relation to those of other allyl sulfides. These suggest that a sulfur atom can stabilize the transition state to the same extent as a π-electron system.

INTRODUCTION

It has been previously proposed[1,2] that the retro-ene mechanism of pyrolysis of allyl sulfides proceeds via a non-synchronous process. The 1–5 hydrogen shift in the six-centered cyclic transition state is facilitated by the acidic character of the α-H atoms, which provides assistance to the rate-determining C—H bond breaking step. This scheme implies the development of a partial negative charge on the α-C atom, stabilized by the high polarizability of the sulfur atom as has been established for the α-S carbanions.[3,4] The higher reactivity of benzyl allyl,[1] and propargyl allyl[2] sulfides, when compared with that of the alkyl allyl sulfides[5,6] can be explained considering that in the former, the negative charge developed in the transition state can be further stabilized over the π-electron system. In the present work, the

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*Author to whom all correspondence should be addressed.

pyrolyses of 4,6-dithia-1-octene, 4,6-dithia-1,8-nonadiene and 4,6-dithia-6-phenyl-1-hexene have been studied in order to observe the effect of a second sulfur atom on the reactivity, and hence on the stabilization of the transition state of these reactions.

RESULTS

In Tables I, II and III are shown the experimental conditions for the pyrolyses of 4,6-dithia-1-octene, 4,6-dithia-1,8-nonadiene and 4,6-dithia-6-phenyl-1-hexene, respectively. In each case, the observed reaction products were propene and a viscous polymer. The latter was identified by NMR and mass spectrometry as 2,4,6-triethylthio-1,3,5-trithiane, 2,4,6-(2-propenylthio)-1,3,5-trithiane and 2,4,6-phenylthio-1,3,5-trithiane, respectively. The reaction stoichiometry is represented in Figure 1.

In computing the products outflow, it was assumed that the primary reaction products were propene and the corresponding ethyl, allyl and phenyl dithioformate monomers, each formed in the same proportion as propene.

The order of consumption of the 4,6-dithia-1-octene, obtained from flow data by the usual procedure[1,6] had the value of 1.11 ± 0.04 at 362°C. For the other two reactants studied an order one was assumed for their consumption. The measured order, as well as the rate coefficients for the three reactants over each temperature range, was based on the percent decomposition estimated from the amount of

TABLE I

Stirred flow pyrolysis of 4,6-dithia-1-octene

T °C	$k \times 10^3$ sec^{-1}	a θ sec	b $\%r_{C_3}$	P Torr	c f_s^0	d fc/f_s^0
354.8	139	4.609	39.0	9.84	180.8	5.5
355.1	131	4.657	37.9	10.3	189.0	5.4
354.7	132	4.593	37.8	10.1	179.1	5.8
354.5	128	3.510	31.0	6.12	326.3	1.8
354.5	128	3.534	31.2	6.06	275.2	2.3
361.5	165	4.018	39.9	5.21	72.90	8.8
361.6	184	1.395	20.4	9.98	116.6	34
361.7	169	1.464	19.8	7.78	255.2	11
362.1	172	1.248	17.7	6.75	299.2	9.2
370.9	250	1.176	22.5	7.24	253.9	13
370.9	248	1.144	22.1	8.18	217.7	17
371.5	242	0.6273	13.2	6.50	286.5	19
381.6	394	0.5840	18.7	6.84	314.2	20
381.9	424	1.161	33.0	7.30	218.3	15
382.3	398	1.086	30.2	10.5	146.2	36
381.3	401	1.080	30.2	9.38	157.1	30
392.4	649	0.4707	23.4	4.73	291.2	18
392.6	571	0.5287	23.2	6.63	322.1	20
392.4	613	0.5999	26.9	6.43	306.2	18
392.9	606	0.6707	28.9	6.74	313.0	16
393.0	595	0.6570	28.1	6.36	294.6	17

[a] Residence time.

[b] Percent reaction from propene measurement.

[c] Reactant inflow in mol · sec^{-1} × 10^8.

[d] Toluene to reactant flow ratio.

TABLE II

Stirred flow pyrolysis of 4,6-dithia-1,8-nonadiene

T °C	$k \times 10^3$ sec^{-1}	θ sec	$\%r_{C_3}$	P Torr	f_s^0	fc/f_s^0
329.0	112	5.169	36.7	8.87	161.5	4.4
328.9	97.2	1.529	12.9	7.72	331.5	8.6
340.3	159	0.7195	10.2	6.27	1204	4.3
340.6	173	1.407	19.6	8.92	252.5	15
340.3	183	1.446	20.9	7.35	312.1	9.0
349.0	249	1.126	21.9	7.94	430.4	8.9
349.5	261	1.152	23.1	7.48	411.1	8.5
359.8	416	0.8438	26.0	6.94	111.3	44
359.5	348	0.9063	24.0	9.11	555.5	9.8
359.5	368	0.9090	25.1	8.15	148.9	35
370.5	570	0.8940	33.8	7.20	352.6	13
370.1	559	0.9294	34.2	6.13	257.0	14

Headings as in Table I.

propene volumetrically measured. The least square fits of the rate coefficients given in Tables I, II and III yielded the following Arrhenius equations:

4,6-dithia-1-octene

$$k\ (\text{sec}^{-1}) = 10^{10.85 \pm 0.18} \exp(-142 \pm 2\ \text{kJ/mol} \quad RT)$$

4,6-dithia-1,8-nonadiene:

$$k\ (\text{sec}^{-1}) = 10^{10.45 \pm 0.34} \exp(-132 \pm 4\ \text{kJ/mol} \quad RT)$$

4,6-dithia-6-phenyl-1-hexene:

$$k\ (\text{sec}^{-1}) = 10^{10.09 \pm 0.43} \exp(-130 \pm 5\ \text{kJ/mol} \quad RT)$$

The corresponding plots are shown in Figure 2.

TABLE III

Stirred flow pyrolysis of 4,6-dithia-6-phenyl-1-hexene

T °C	$k \times 10^3$ sec^{-1}	θ sec	$\%r_{C_3}$	P Torr	f_s^0	fc/f_s^0
361.0	228	1.200	21.48	7.29	57.27	57.7
360.6	252	1.101	22.03	9.17	102.0	47.1
360.5	237	1.119	20.99	12.4	140.1	45.8
360.0	240	0.5764	12.17	8.49	196.8	43.2
375.4	371	0.5813	17.73	11.2	236.8	45.9
375.2	409	0.5277	17.76	11.9	278.0	45.9
375.5	446	0.5609	20.02	10.0	235.5	42.6
385.9	653	0.5619	26.83	9.81	215.8	44.8
385.8	611	0.5518	25.21	12.0	269.8	44.8
384.4	538	0.5208	21.87	9.98	207.2	51.5
395.8	942	0.5708	34.96	9.15	190.3	45.9
395.4	831	0.5544	31.54	9.35	196.5	46.9

Headings as in Table I.

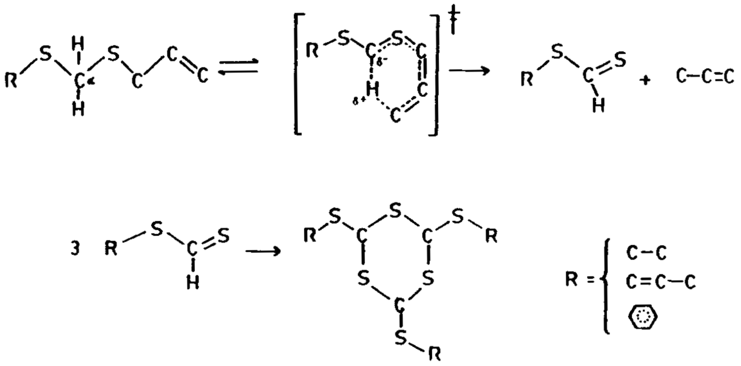


FIGURE 1 Reaction stoichiometry.

DISCUSSION

Within experimental error, and after allowance for the statistical factor, both 4,6-dithia-1,8-nonadiene and 4,6-dithia-1-octene pyrolyze at nearly the same reaction rate whereas the 4,6-dithia-6-phenyl-1-hexene is at least 25% more reactive than the latter. The rate coefficients listed in Table IV show that the benzyl allyl and diallyl

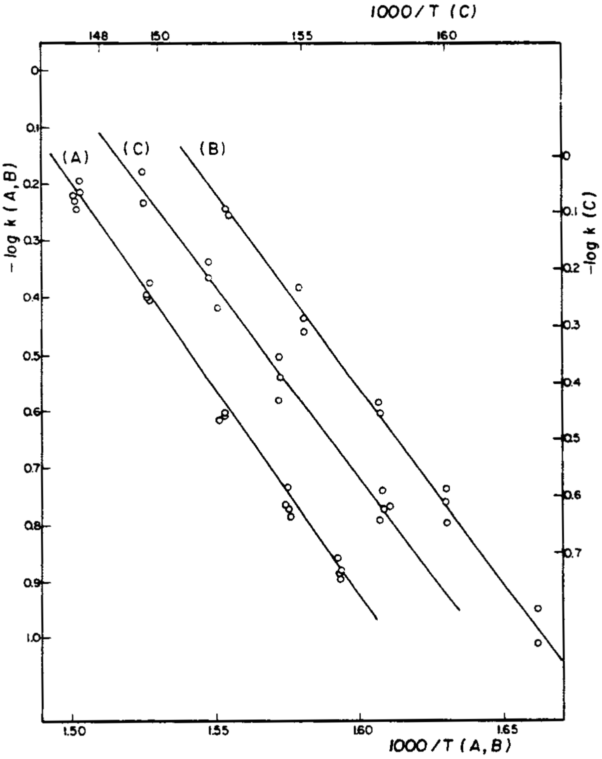


FIGURE 2 Arrhenius Plots, (A) 4,6-dithia-1-octene; (B) 4,6-dithia-1,8-nonadiene; (C) 4,6-dithia-6-phenyl-1-hexene.

sulfides react about 20% faster than 4,6-dithia-1-octene, whereas the latter is about four times more reactive than n-butyl allyl sulfide. This suggests that when the partial negative charge in the transition state is stabilized on a π-electron system plus a sulfur atom, the reactivity is higher than when the stabilization is produced by two sulfur atoms. The increased reactivity of 4,6-dithia-6-phenyl-1-hexene further supports this assumption. Considering that in a π-electron system the charge is delocalized through a number of resonance structures whereas in the molecule with two sulfur atoms it is only dispersed in a volume of space, it can be concluded that the magnitude of the stabilization by a sulfur atom is considerable.

In Figure 3 are represented the activation energies and frequency factors for the series of related allyl sulfides[1,2,5,6] and the present dithia compounds. As can be observed, the activation energies for the alkyl allyl sulfides are higher than those for the systems having benzyl, allyl and propargyl substituents by a magnitude beyond the standard deviation of the values. The figures $\overline{\mathrm{Ea}}(\mathrm{R}) = 156.5 \pm 6$ and $\overline{\mathrm{Ea}}(\mathrm{R}\pi) = 139 \pm 6$ kJ · mol^{-1} can be calculated as mean values for each group of compounds, respectively. The frequency factors are spread about the value $10^{11.05 \pm 0.32}$ in accordance with a common structure for the transition states. The above mean values and standard deviations are represented in Figure 2 by solid and dotted lines, respectively.

The following relationships can be used to quantify approximately the extent of transition state stabilization by a π-electron system $\Delta\mathrm{Ea}(\pi)$ and by sulfur atom $\Delta\mathrm{Ea}(\mathrm{S})$.

$$\Delta\mathrm{Ea}(\pi) = \overline{\mathrm{Ea}}(\mathrm{R}) - \overline{\mathrm{E}}(\mathrm{R}\pi)$$

$$\Delta\mathrm{Ea}(\mathrm{S}) = \overline{\mathrm{Ea}}(\mathrm{R}) - \mathrm{Ea}(\mathrm{RS})$$

Using $\mathrm{Ea}(\mathrm{RS}) = 142 \pm 2$ kJ · mol^{-1}, the activation energy for 4,6-dithia-1-octene, the relationships yield $\Delta\mathrm{Ea}(\pi) = 17.5$ kJ · mol^{-1}; $\Delta\mathrm{Ea}(\mathrm{S}) = 14.3$ kJ · mol^{-1}. These values suggest that a sulfur atom should be nearly as effective as a π-electron system in stabilizing the transition state of these retro-ene elimination reactions.

In Table V are collected some literature[7,3a] values of absolute equilibrium acidity of carbon acids in solution. According to these, substitution of *n*-propylthio for phenyl in di-*n*-propylthio phenylmethane, decreases the acidity in 2.1 pK units.

TABLE IV

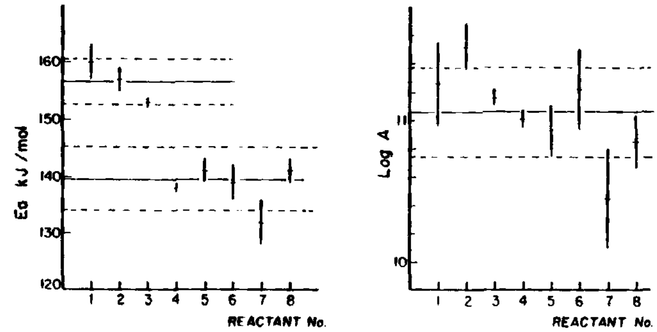
Relative reactivities of allyl sulfides

R—C—S—C—C=C

R	k/ka[a]	$k \times 10^4$ (sec^{-1})[b]
C—C—S	1	1581 ± 69
C—C	0.23 ± 0.01	370 ± 2
C—C—C	0.28 ± 0.04	440 ± 39
C=C—C—S	1.03 ± 0.09	1629 ± 66
C=C	1.21 ± 0.06	1918 ± 16
ϕ	1.2 ± 0.1	1899 ± 83
ϕS	1.3 ± 0.1	2020 ± 71
C≡C	1.6 ± 0.2	2617 ± 231

[a] ka = Rate coefficient for C—C—S—C—S—C—C=C.

[b] Calculated at 375°C, statistically corrected.

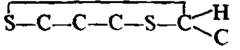
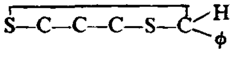


1 C—S—C—C=C
2 C—C—C—S—C—C=C
3 C—C—C—C—S—C—C=C
4 C=C—C—S—C—C=C
5 φ—C—S—C—C=C
6 C≡C—C—S—C—C=C
7 C=C—C—S—C—S—C—C=C
8 C—C—S—C—S—C—C=C

FIGURE 3 Activation energies and frequency factors for allyl sulfides and dithianes.

TABLE V

Acidity of carbon acids

Compound	pK	Ref.
$(C—C—C—S)_2CH\phi$	29.2	7
$(C—C—C—S)_3CH$	31.3	7
ϕ_3CH	30.6	7
ϕ_2CHSO	26.7	7
$\phi CH(S\phi)_2$	23.0	7
$(\phi S)_3CH$	22.8	7
	38.3	3
	29.6	3

Similarly, substitution of phenylthio for phenyl in triphenylmethane increases the acidity in 8.1 pK units, while substitution of phenyl for alkyl in the cyclic 1,3-dithianes increases acidity by 7.6 pK units. This behavior agrees with the results about the relative reactivities of the allyl sulfides in gas phase as discussed above.

EXPERIMENTAL

4,6-dithia-1-octene. This compound was obtained by reaction of allyl thiol[8] with chloromethyl ethyl sulfide. The latter was synthesized using an improved version of Schobert and Wagner's[9] technique. Paraformaldehyde (2.2 mol) and ethyl thiol (1.5 mol) (Aldrich) in 80 mL of dry dichloromethane were treated for 90 min at −30°C with a stream of hydrogen chloride, in the presence of 20 g anhydrous magnesium sulfate. The mixture was then passed by suction through a column containing successive layers of anhydrous magnesium sulfate, 4A molecular sieve and phosphorus pentoxide, followed by 50 mL of dichloromethane. It was collected in a three necked flask at 0°C and treated with dry allyl thiol under a stream of nitrogen. The solvent and other volatile compounds were separated in a vacuum line. The product was first distilled in a 100 cm spinning band column. A 4th fraction collected overnight consisted of 50 mL 80% (by gas chromatography) 4,6-dithia-1-octene. This fraction was redistilled in a 50 cm spinning band column. A fraction collected at 2.5 torr between 40 and 60°C consisted of 32 g 96.2% 4,6-dithia-1-octene plus 2.9% 3,5-dithiaheptane. It was experimentally established that 3,5-dithiaheptane did not pyrolyze over the temperature range used in the study of the 4,6-dithia-1-octene. Since further attempts to purify the latter by distillation were unsuccessful, it was decided to do the study with the mixture, including the impurity in the calculation as another inert carrier gas flow.

4,6-dithia-1,8-nonadiene. This reactant was not obtained by direct synthesis. During the distillation of the crude 4,6-dithia-1-octene (see above) in the 100 cm spinning band column, a 5th fraction was collected at 0.5 torr, between 62 and 74°C which consisted of 18 g, 99.7% pure 4,6-dithia-1,8-nonadiene. The latter was probably formed, quite unexpectedly, by a thermal rearrangement during the distillation.

4,6-dithia-6-phenyl-1-hexene. This compound was obtained by reaction of potassium thiophenoxide dissolved in methanol with chloromethyl allyl sulfide. The latter compound was synthesized by the same technique described above for chlorometyl ethyl sulfide, using paraformaldehyde and allyl thiol. The chloromethyl allyl sulfide was separated from the dichloromethane solvent by distillation in a vacuum line and purified by distillation at reduced pressure in a 30 cm Vigreux column packed with glass beads (b.p. 48–50°C at 5 torr, yield 22%). The 4,6-dithia-6-phenyl-1-hexene was purified by eluting the crude product, after evaporation the methanol solvent, through a column packed with Alumina Merck 90, activity II–III, 0.063–0.2 mm, using hexane as eluent. The yield of 98% pure product was 66%. The identity and purity of the reactants and products was confirmed by NMR and gas chromatography-mass spectrometry in the instruments previously described.[5] The columns used were 1.5 m × 3.2 mm outside diameter packed with 3% SE30 on 100/120 mesh Varaport and 2 m × 3.2 mm outside diameter packed with 10% Carbowax 20M on chromosorb 60/80 mesh.

Kinetic Measurements. The stirred-flow technique has been previously described in detail.[1,10,11] Due to its low volatility, the 4,6-dithia-6-phenyl-1-hexene was introduced into the stirred-flow system as a 0.2 molar solution in toluene, by means of a peristaltic pump. The pump injected the solution at flow rates in the range 0.5–0.9 mL · min^{-1} into an evaporator heated to 200°C, placed just before the reactor.

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