THERMAL HYDROTHIOLYSIS OF DI(2-THIENYL)SULFIDE IN THE GASEOUS AND LIQUID PHASE*

M. G. Voronkov, E. N. Deryagina, L. K. Papernaya,
E. N. Sukhomazova, N. A. Korchevin, and G. G. Efremova

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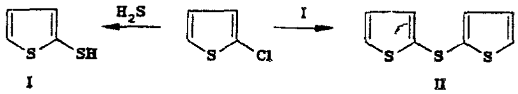
At 500-600°, di(2-thienyl)sulfide is converted to thiophene, thiophene thiols, dithienyls, and dithienothiophenes, and isomerized to 2,3-dithienylsulfide. Hydrogen sulfide accelerates these reactions significantly. In the liquid phase the thermal conversion of di(2-thienyl)sulfide takes place only with the participation of elemental sulfur or in the system sulfur—hydrogen sulfide. Thiophene and diethienothiophenes are not formed in this case, while isomerization occurs to a large degree. The observed thermal conversions of di(2-thienyl)-sulfide are based on the addition of thiyl radicals to the double bonds of the thiophene ring and to the sulfide sulfur atom.

The main products of the high-temperature reaction of 2-chlorothiophene with hydrogen sulfide are 2-thiophenethiol (I) and di(2-thienyl)sulfide (II) [2]:



(1)

The synthesis of the thiol I by the traditional methods [3] is difficult; the reaction (1) is therefore of considerable practical interest. The selectivity of the formation of the thiol I according to scheme (1) apparently depends significantly on the thermal stability of the thiol I as well as of the sulfide II which has not been studied so far. Only the high thermal stability of diarylsulfides has been pointed out [4, 5]. For instance, under the conditions of pulsed (flash) pyrolysis in vacuum diphenyl sulfide is stable up to 900° [6].

We have studied the thermal stability and hydrothiolysis of the sulfide II and the thiol I in the gas phase under the conditions of the reaction (1) and in the liquid phase. The sulfide II is thermally less stable than diphenyl sulfide. It begins to decompose at 500°; at 550° and above its thermolysis is rapid (Table 1). Hydrogen sulfide accelerates the thermal decomposition of the sulfide II, which in its presence starts at 400° and reaches 100% at 600°.

The products of thermolysis and hydrothiolysis of sulfide II in the gas phase are qualitatively identical: thiophene (III), 2-thiophenethiol (I), 3-thiophenethiol (IV), dithienyls (V) [mixture of isomers with 2,2'-dithienyl (Va) predominating], 2,3'-dithienylsulfide (VI), isomeric to the sulfide II, and diethienothiophenes VII (mixture of isomers: dithieny[3,2-b; 2,3-d]thiophene (VIIa) and dithieno-[2,3-b; 2,3-d]thiophene (VIIb)) (Table 1). The ratio of the products of thermolysis and hydrothiolysis of sulfide II depends on the temperature. The yield of thiophene, dithienyls, and dithienothiophenes increases with increasing temperature. The content of thiol I in the mixture decreases and the yield of thiol IV increases slightly. In the presence of H_2S and with increasing temperature from 500 to 600°, the sulfide VI is consumed together with the original isomer II. The thermolysis and hydrothiolysis of the sulfide II are always accompanied by slight resin formation. According to the

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TABLE 1. Gas-Phase Thermolysis (tests 1-3) and Hydrothiolysis (tests 4-7) of Sulfide II (gas supply rate 3 liters/h)

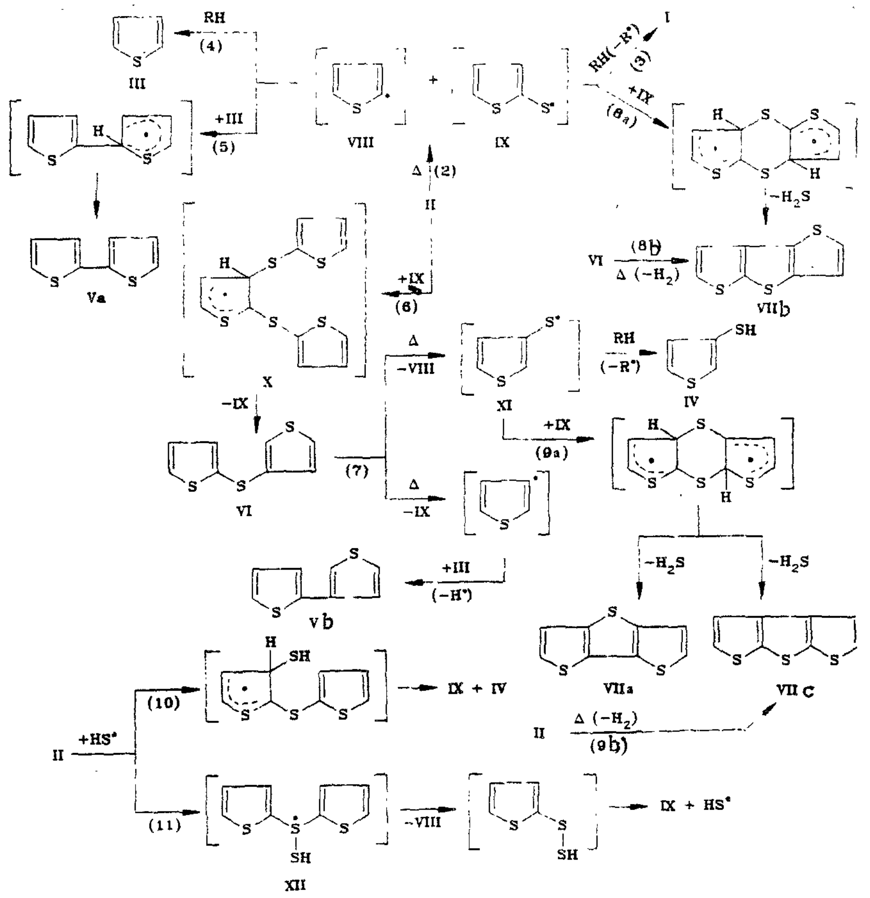
Test No.	T, °C	Composition of condensate, %							
		III	I	IV	V	Va	II	VI	VII
1	500	1,0	6,0	—	1,0	1,0	92,0	—	—
2	550	17,6	13,1	1,4	3,2	3,0	56,6	0,5	7,5
3	600	16,9	8,4	4,9	9,1	7,4	45,4	4,0	16,5
4	450	4,3	10,6	—	2,0	2,0	83,1	—	—
5	500	31,8	6,0	5,0	16,4	15,2	15,7	4,7	20,4
6	550	20,2	2,9	7,6	12,2	9,4	3,5	3,6	40,9
7	600	35,1	1,4	5,8	20,7	14,2	Traces	Traces	37,0

material balance the resin yield increases with increasing temperature; however, it does not exceed 5-15%.

In the liquid phase the sulfide II is stable up to 180° in an inert gas as well as in an H_2S atmosphere. However, in the presence of an equivalent amount of sulfur (1/8 S_8) the sulfide is converted (slowly in an inert atmosphere and rapidly in the presence of H_2S) to the thiols I and IV, the sulfide VI, and the dithienyls Va-c (at an approximately equal isomer ratio). Thiophene and dithienothiophenes are not formed in the reaction. An excess of sulfur promotes the formation of thiols I and IV.

Sulfide bonds usually undergo homolytic rupture at 500-600°; this initiates chain reactions of sulfide decomposition [7]. Apparently the thermal decomposition of the dithienylsulfide II in the gas phase also starts with the dissociation of the C—S bond [general scheme reaction (2)]. The radicals VIII and IX formed are capable of splitting off hydrogen atoms from any hydrogen-containing particles (chain propagation stages in radical reactions [8]), leading to the formation of the thiophene III and the 2-thiophenethiol (I).

Scheme of Thermal Conversions of Di(2-thienyl)sulfide in the Gas Phase



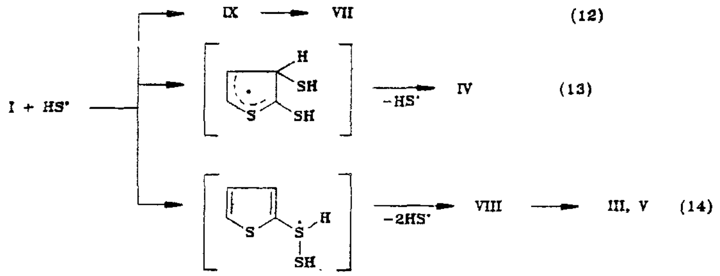
(2)-(11)

The dithienyl Va is the product of the reaction of radical VIII with thiophene [reaction (5)]; diphenyl is formed from benzene in the same way [9]. When the temperature is increased to 600°, the reaction (5) is accelerated; as a result of this, the yield of the dithienyls V increases and the yield of thiophene becomes stabilized. The fraction of isomer Vb in the mixture of dithienyls increases. We have shown in [10] that at 750-850° the radical VIII attacks predominantly the position 3 in the thiophene ring.

In the isomerizing transformations of the sulfide II which are presented by reactions (6) and (7), radical IX apparently plays a significant role. The isomerization II → VI is probably initiated by the addition of the radical IX to the double bond of the thiophene ring, whereby it is known [11, 12] that the reactivity of the position 3 of the thiophene ring increases in radical reactions with increasing temperature. Decomposition of the radica adduct X leads to the formation of the isomeric sulfide VI and the radical IX is regenerated. Thermal decomposition of sulfide VI according to reaction (7) leads to 3-thiophenethiol (IV) and the isomeric dithienyl Vb. The yield of the isomerization products Vb, IV, and VI in the thermolysis products increases with increasing temperature. The intramolecular isomerization of the radical IX can also take place in the gas phase [13].

The dithienothiophenes VII are formed from the dithienylsulfide II only in the gas phase. The transformation II → VII is possible only in two routes: by condensation of radicals IX and XI [reactions (8a) and (9a)] or by intramolecular cyclization of sulfides II and VI [reactions (8b) and (9b)]. According to PMR (see Experimental), a mixture of dithienothiophenes VIIa and VIIb is formed in the thermolysis of sulfide II in the ratio 1:2; the isomer VIIc has not been detected, the formation of the dithienothiophenes VIIa, b by condensation of radicals IX and XI is therefore more probable.

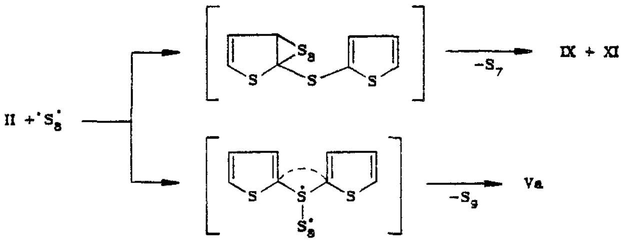
The thermolysis of sulfide II is accelerated by hydrogen sulfide, which initiates the formation of thiophene, dithienyls (again with the 2,2'-isomer predominating), dithienothiophenes, and the isomeric transformations of sulfide II (Table 1). This is apparently due to the fact that the radicals VIII and IX formed in the reaction (2) react with H_2S to form HS radicals. The latter can attach themselves to the thiophene ring [reaction (10)] as well as to the sulfide sulfur atom of the sulfide II [reaction (11)]. It is well known that the thiyl radicals are inclined to the formation of so-called perthiyl radicals with sulfides [14, 15], analogous to XII. Reactions (10) and (11) lead to additional regeneration of radicals VIII and IX, as well as to the formation of 3-thiophenethiol (IV). An increase in the concentration of radicals VIII and IX increases the yield of thiophene [reaction (4)], the isomeric sulfide [reaction (6)], and the dithienothiophenes VII [reactions (8) and (9)].



(12)-(14)

The low yield of the thiol I in the hydrothiolysis of sulfide II can be due to its thermal lability. In fact, at 500-550° in a nitrogen as well as in a H_2S atmosphere the thiol I is rapidly converted to a mixture of products of the thermolysis and hydrothiolysis of sulfide II. Hydrogen sulfide also accelerates the thermal conversions of the thiol I (Table 3), which lead to the formation of significant amounts of thiophene, dithienyls, dithienothiophenes, and isomerization products IV and VI, apparently according to schemes analogous to the conversions of the sulfide II. In the hydrothiolysis of the thiol (I) the reaction (14) is probably the most important one, since thiophene and the dithienyl Va are formed with the highest yields.

Thermal conversions of sulfide II in the liquid phase take place only with the participation of elemental sulfur or in the system sulfur–H_2S (more rapidly) (Table 2). Recently it has been shown convincingly that cyclic S_8 molecules are ruptured at temperatures above 160° with the formation of linear biradicals [16]. The products obtained can be formed in the reaction of the latter with the sulfide II according to the schemes



(15)

(16)

Isomerization of the sulfide II to the sulfide VI and further to di(3-thienyl)sulfide takes place according to reaction (6) with the participation of radicals IX and XI. In the reaction with sulfur according to scheme (16) the above products are converted to dithienyls Vb, c. The yield of the dithienyls increases with reaction time, the ratio between the isomers remaining the same.

Negligible amounts of di(3-thienyl)sulfide in the reaction mixture, indicate a higher rate of its reaction with sulfur according to Eq. (16) (evidently due to the more favorable steric location of sulfide sulfur).

The initiating effect of H_2S in the system sulfur—H_2S is related to the activation of elemental sulfur [17]. An excess of sulfur increases the concentration of HS radicals which together with the radicals IX participate in the decomposition and isomerization of the sulfide II according to the schemes (6), (10), and (11).

$$S_8 + H_2S \longrightarrow HS^{\bullet} + HS_8^{\bullet\bullet} \longrightarrow HS^{\bullet} + S_7 \qquad (17)$$

Thus, the observed thermal conversions of the sulfide II and thiol I in the gaseous and liquid phase are based on the attachment of thiyl radicals to the polarized bond in the thiophene ring and on the formation of perthiyl radicals. The formation of the thiol I and the sulfide II as the main products in reaction (1) is due to the fact that chlorothiophene (like chlorobenzene [18]) represents a highly efficient trap for thiyl radicals; this prevents the latter from taking part in the thermal decomposition of products I and II according to the schemes discussed above. It is evidently expedient in order to improve the selectivity of thiol I formation according to scheme (1) not to permit a sharp increase in the concentration of radicals HS and IX at the end of the process.

EXPERIMENTAL

The IR spectra were taken on a Specord 75 IR spectrometer [solids as KBr tablets, liquid as a thin layer or in CCl_4 (2 M)]. The PMR spectra were recorded on a Tesla BS 567A spectrometer (100 MHz), using 20% solutions in $CDCl_3$ (with HMDS as internal standard). The mass spectra were obtained on a MAT-212 gas chromatograph—mass spectrometer at an ionizing voltage of 70 eV (liquid phase SE-54). The condensates were analyzed by GLC on a LKhM-8MD-5 chromatograph, liquid phase OV-17, 5% on Chromaton and XE-60 on Chesasorb, with linear temperature programming of the column (3 × 2000 mm; 30-230°, 12 deg/min).

The 2-thiophenethiol I and sulfide II were synthesized by the procedure given in [2]. The thermolysis of the sulfide II was performed in a quartz tube (650 × 30 mm) by passage

TABLE 2. Conditions for the Liquid-Phase Thiolysis of Sulfide II and Composition of the Reaction Mixture*

Test No.	Reaction time, h	Ratio II:1/8S_8, mole	Composition of reaction mixture, %							Conversion of II, %
			I	II	IV	Va	V6	Vв	VI	
1	10	1,0	1,6	26,8	0,8	8,2	10,6	8,6	40,7**	74,3
2	8	0,5	29,9	20,0	12,6	7,7	4,4	5,7	16,6**	80,5
3	10	1,0	3,2	92,0	3,0	—	—	—	1,8	9,5
4	14	1,0	2,4	79,4	0,9	1,8	Traces	—	15,5	22,0
5	20	1,0	1,2	67,4	0,7	1,8	1,2	0,4	27,3	33,6
6	26	1,0	1,7	63,2	1,0	2,1	1,8	1,8	28,1**	39,0
7	32	1,0	1,9	45,7	1,1	4,4	4,0	3,4	38,8**	55,9

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*Temperature 180°; in tests 1 and 2, H_2S supply rate 3 liters/h.
†Di(3-thienyl)sulfide also present in the reaction mixture.

TABLE 3. Thermolysis (tests 1 and 2) and Hydrothiolysis (test 3) of 2-Thiophenethiol (I) (flow rate: N_2, 0.3 liter/h, H_2S, 0.4 liter/h)

Test No.	T, °C	Composition of condensate, %							
		III	I	IV	V	Va	II	VI	VII
1	500	8,1	30,2	6,7	6,1	6,1	29,0	9,0	10,7
2	550	39,1	14,9	2,6	7,2	7,0	16,2	5,0	14,8
3	500	62,3	1,9	4,2	11,8	9,3	Traces	Traces	19,8

through a reaction zone, preheated to the required temperature, in a stream of dry nitrogen or hydrogen sulfide in an experimental setup [2] at 15 ml/h. The condensate was collected in receivers and traps cooled to −50°, and analyzed by GLC. The conditions used for thermolysis and hydrothiolysis and the composition of the condensates are given in Table 1.

The thermolysis of 2-thiophenethiol was performed in a quartz tube (250 × 19 mm) by passage at a rate of 1.1 ml/h. The conditions of the reactions and the composition of the condensates are given in Table 3. The thiolysis of di(2-thienyl)sulfide in the liquid phase was performed in a four-neck flask equipped with a stirrer, a thermometer, and a reflux condenser. H_2S (or nitrogen) was bubbled through the sulfide II (or its mixture with sulfur) with stirring. The reaction conditions and the composition of the reaction mixture are given in Table 2. Thiophene was stripped from the condensates and identified by GLC and refractometry.

Identification of 3-Thiophenethiol (IV). The thiol IV was isolated together with the thiol I by vacuum fractionation of the condensate from test 7 (Table 1); 23 g sulfide II was taken for the reaction. The mass of the condensate was 19.5 g. The fraction 70-75° consisted according to GLC of a mixture of thiols I and IV in the ratio 1:3. According to GLC–mass spectrometry, both substances had a molecular mass of 116. The PMR spectrum represented a superposition of the spectra of thiols I and IV with a signal intensity that corresponded to the isomer ratio. Thiol I, δ: 6.90 (4-H), 7.05 (3-H), 7.22 (5-H), 3.35 ppm (SH); J_{34} = 3.5, J_{45} = 5.4, J_{35} = 1.4 Hz. Thiol IV, δ: 6.94 (4-H), 7.12 (2-H), 7.30 (5-H), 3.35 ppm (SH); J_{45} = 5.0, J_{25} = 3.5, J_{24} = 1.6 Hz. For the pure thiol I, obtained by the procedure [2], δ: 6.86 (4-H), 7.03 (3-H), 7.20 (5-H), 3.46 ppm (SH); J_{45} = 5.4, J_{34} = 3.5, J_{35} = 1.4 Hz. The IR spectrum of the mixture (thin film) contains a band at 2560 cm^{-1} (νS-H in IV) and a shoulder at 2525 cm^{-1} which corresponds to a band observed for the pure thiol I [19]. A fraction was isolated from the reaction mixture of test 2 (Table 2) corresponding to the composition I:IV = 1:1. The IR spectrum of such a mixture contains in the region of S–H vibrations two maxima at 2525 and 2560 cm^{-1} (shoulder). In CCl_4 solution these two bands approach each other (2530 and 2545 cm^{-1}, respectively).

The dithienyls V were isolated by vacuum fractionation of the condensates from tests 5-7 (Table 1), fraction 135-140° (12 mm). They were identified by comparison with samples of known composition, obtained according to [10].

Identification of Isomeric Dithienylsulfides. The mixture of dithienyl sulfides obtained under the conditions of test 7 (Table 2) (fraction 144-148°, 5 mm) was separated by preparative GLC on a PAKhV-07 chromatograph, using a stainless-steel column (1000 × 8 mm) packed with 20% polyphenyl ether on Chromaton N-AW-DMCS. The separation temperature was 190°. The IR spectra of the isolated isomers agree fully with the data in [20]. PMR spectra: sulfide II, δ: 6.88 (4-H), 7.15 (3-H), 7.26 ppm (5-H), J_{45} = 5.3, J_{34} = 3.5, J_{35} = 1.3 Hz; sulfide VI, δ: 6.94 (4-H), 7.06 (3-H), 7.31 (5-H), 6.92 (4'-H), 7.19 (2'-H), 7.24 ppm (5'-H); J_{45} = 5.3, J_{34} = 3.5, J_{35} = 1.5, $J_{4'5'}$ = 5.1, $J_{2',4'}$ = 1.3, $J_{2'5'}$ = 3.0 Hz; di(3-thienyl)sulfide, δ: 6.96 (4-H), 7.15 (2-H), 7.29 ppm (5-H); J_{45} = 5.0, J_{25} = 2.9, J_{24} = 1.2 Hz.

Diethienothiophenes VII were obtained by vacuum fractionation of the condensate from test 7 (Table 1). The fraction 190-200° (15 mm) representing a pale yellow liquid produced colorless needle-shaped crystals when ethanol was added to it, mass 8.5 g (yield 37%), mp 41-44° (literature data: VIIa 66-67° [21], VIIb 53-54° [22]). Found, %: C 49.0, H 2.3, S 48.8. M 196 (by mass spectrometry). $C_8H_4S_3$. Calculated, %: C 49.0, H 2.0, S 49.0; M 196. PMR spectrum (acetone), δ, ppm: VIIa 7.43d, 7.61d, J = 5.0 Hz (see [21]); VIIb 7.42d, 7.43d, 7.57d, 7.61d, J = 5.0 Hz (see [22]). Ratio VIIa:VIIb = 1:2.

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