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# GAS-PHASE REACTION OF 2-CHLOROTHIOPHENE WITH HYDROGEN SULFIDE IN THE PRESENCE OF ALCOHOLS*

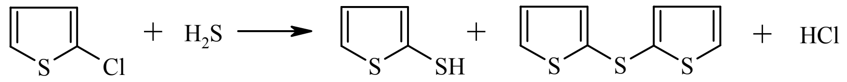
**E. N. Deryagina, E. N Sukhomazova, and E. P. Levanova**

*The effect of methanol and ethanol on the route of the gas-phase reaction of 2-chlorothiophene with hydrogen sulfide, leading to 2-thiophenethiol and to bis(2-thienyl) sulfide, has been investigated. It was found that methanol significantly enhances this reaction and increases its selectivity for the thiol at higher temperatures than without the initiator. The optimal conditions were achieved at 570°C in the presence of 10 mole % of methanol when the conversion of the 2-chlorothiophene in the reaction with hydrogen sulfide reaches 98% and the yield of the thiophenethiol (43%) exceeds that of the bis(2-thienyl)sulfide (31%). In the absence of methanol the 2-thiophenethiol is formed only at 510-540°C in just 17% yield, the basic reaction product being the indicated sulfide (52% yield); the conversion of the 2-chlorothiophene does not exceed 54%.*

**Keywords:** bis(2-thienyl) sulfide, thiophene, 2-thiophenethiol, 2-chlorothiophene, initiation, gas-phase synthesis.

The direct gas-phase synthesis of 2-thiophenethiol (**1**) is based on the reaction of hydrogen sulfide with 2-chlorothiophene at 510-540°C [1-2].

Scheme 1



**1** **2**

However, under these conditions, thiol **1** is formed in only 17% yield and the basic reaction product is the bis(2-thienyl) sulfide (**2**) in 52% yield. Moreover, the conversion of the 2-chlorothiophene does not exceed 54%. At 540°C and above the yield of sulfide **2** increases and there is an acceleration in the side reactions of the reduction of 2-chlorothiophene to thiophene and the formation of bithiophenes. In the presence of 0.5 mole % of

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* Dedicated to Academician M. G. Voronkov on his 80th Birthday.

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TABLE 1. Gas-phase Reaction of 2-Chlorothiophene with Hydrogen Sulfide in the Presence of Methanol*

| Experiment | MeOH, mole % | Temperature, °C | Conversion of 2-chlorothiophene, % | Yield of reaction products, % based on the amount taken in the reaction of 2-chlorothiophene*[2] | | | | | |
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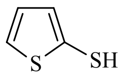
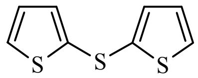
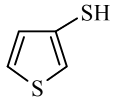
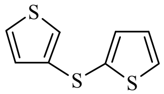
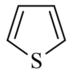
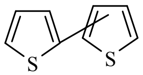
| | | | |  |  |  |  |  |  |
| 1 | — | 510 | 54.0 | (16.0) | (52.0) | — | — | (10.0) | — |
| 2 | — | 540 | 85.0 | (10.3) | (63.5) | — | — | (13.0) | — |
| 3 | $Me_2Se$ (0.5%) | 500 | 100 | (10.0) | (1.8) | (3.0) | (3.8) | (46.0) | (4.2) |
| 4 | 5.0 | 490 | 44.6 | 1.9 (4.2) | 35.9 (82.3) | — | — | — | — |
| 5 | 5.0 | 510 | 47.5 | 3.4 (7.1) | 39.4 (84.5) | — | — | — | — |
| 6 | 5.0 | 530 | 54.0 | 11.1 (20.5) | 37.8 (70.8) | — | — | — | — |
| 7 | 5.0 | 550 | 83.3 | 24.5 (29.3) | 50.0 (60.8) | — | 2.0 (2.5) | 2.7 (3.2) | — |
| 8 | 5.0 | 570 | 97.9 | 32.4 (33.6) | 25.2 (26.0) | — | 2.5 (3.1) | 19.2 (24.3) | 2.3 (3.0) |
| 9 | 10.0 | 490 | 25.0 | — | 2.5 (89.5) | — | — | — | — |
| 10 | 10.0 | 510 | 32.1 | 6.4 (20.0) | 27.3 (64.5) | — | — | — | — |
| 11 | 10.0 | 530 | 53.4 | 13.1 (24.5) | 30.0 (55.9) | — | — | — | — |
| 12 | 10.0 | 550 | 82.88 | 19.2 (25.2) | 43.3 (54.3) | — | — | — | — |
| 13 | 10.0 | 570 | 97.9 | 42.1 (43.0) | 31.1 (31.8) | 2.6 (2.7) | 3.0 (3.1) | 14.9 (15.2) | — |
| 14 | 10.0 | 590 | 100.0 | 22.6 | 12.6 | 8.0 | 3.8 | 22.6 | 4.4 |
| 15 | 25.0 | 490 | 19.6 | — | 16.0 (81.8) | — | — | — | — |
| 16 | 25.0 | 510 | 36.6 | 5.3 (14.5) | 24.2 (66.1) | — | — | — | — |
| 17 | 25.0 | 530 | 52.5 | 11.4 (21.9) | 29.9 (56.0) | — | — | 0.9 (1.9) | — |
| 18 | 25.0 | 550 | 59.6 | 16.2 (27.4) | 31.1 (52.8) | — | — | 2.9 (3.4) | — |
| 19 | 25.0 | 570 | 96.6 | 38.4 (38.9) | 40.0 (40.7) | 1.8 (1.9) | 2.4 (2.5) | 7.4 (7.7) | 1.2 (1.3) |
| 20 | 50.0 | 570 | 68.3 | 23.8 (35.0) | 33.5 (48.9) | — | — | 6.5 (9.5) | — |
| 21 | 50.0 | 590 | 94.5 | 37.3 (40.5) | 26.5 (28.3) | 1.5 (1.6) | 2.8 (3.0) | 15.4 (16.6) | — |
| 22 | 50.0 | 610 | 99.2 | 25.5 (26.8) | 17.7 (18.8) | 10.2 (10.7) | 7.1 (7.6) | 21.1 (22.4) | 1.0 (1.0) |

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* Ratio of 2-chlorothiophene:$H_2S$ 1:2.5, reagent contact time 60-70 s.

*[2] In experiments 2 and 3 there are also formed 2.4 and 11.4% of dithienothiophene respectively.

TABLE 2. Gas-phase Reaction of 2-Chlorothiophene with Hydrogen Sulfide in the Presence of Ethanol*

| Experiment | EtOH, mole % | Temperature, °C | Conversion of 2-chlorothiophene, % | Yield of reaction products, % based on the amount taken in the reaction of 2-chlorothiophene*[2] | | | | | |
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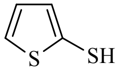
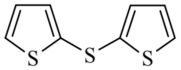
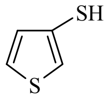
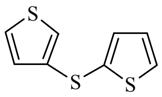
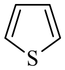
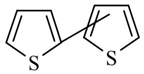
| | | | |  |  |  |  |  |  |
| 1 | 10 | 550 | 92.4 | 22.9 (24.4) | 52.9 (57.4) | — | 0.8 (0.8) | 4.1 (4.2) | 0.8 (0.9) |
| 2 | 10 | 570 | 98.0 | 28.4 (28.7) | 39.3 (40.0) | — | 3.7 (3.7) | 13.4 (13.7) | 2.4 (2.4) |
| 3 | 10 | 590 | 100.0 | 16.3 | 8.6 | 2.6 | 6.4 | 37.2 | 7.1 |
| 4 | 25 | 550 | 67.4 | 13.4 (19.8) | 40.0 (59.1) | 0.6 (0.8) | 0.9 (1.4) | 2.6 (2.7) | 3.2 (5.6) |
| 5 | 25 | 570 | 88.0 | 21.6 (24.5) | 48.1 (55.1) | 0.8 (0.9) | 1.1 (1.1) | 6.1 (7.0) | 1.6 (1.7) |
| 6 | 25 | 590 | 97.8 | 31.1 (31.6) | 26.9 (27.4) | 1.6 (1.7) | 4.9 (5.0) | 19.6 (20.2) | 1.5 (1.8) |

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* Ratio of 2-chlorothiophene:$H_2S$ 1:2.5, reagent contact time 60-70 s.

*[2] In experiments 2 and 3 there are also formed 2.4 and 11.4% of dithienothiophene respectively.

dimethylselenide the selectivity of formation of 2-thiophenethiol can be improved with 100% conversion of the 2-chlorothiophene. However, the yield of the thiol **1** obtained does not exceed 10% (with a 1% yield of sulfide **2**) due to the marked reduction of the 2-chlorothiophene to thiophene (yield 46%).

With the aim of increasing the selectivity of formation of the 2-thiophenethiol in the reaction of 2-chlorothiophene with hydrogen sulfide we have introduced methanol into the reaction, since it is a more powerful hydrogen atom donor than is hydrogen sulfide. This is related to the greater stability of alkoxyl radicals which are readily converted to carbonyl compounds [3]. For comparison, the effect of ethanol on the course of the reaction of 2-chlorothiophene with hydrogen sulfide has been studied (Tables 1 and 2).

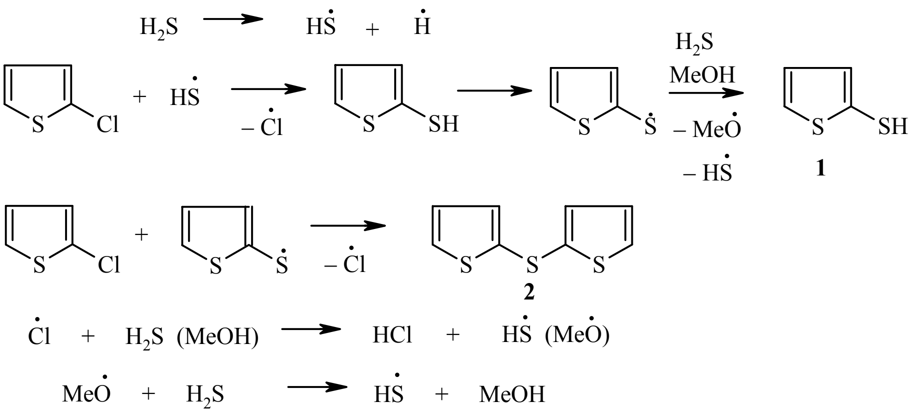
The reaction was carried out in a hollow quartz tube at a feed velocity of 2-chlorothiophene in the mixture with the alcohols of 10 ml/h and of hydrogen sulfide of 6 l/h. The methanol was added in amounts of 5, 10, 25, and 50 mole % and ethanol 10 and 25 mole %. Methanol at the 5 mole % level had virtually no effect on the course of the reaction of 2-chlorothiophene with hydrogen sulfide at 490-530°C and resulted in the principal formation of the bis(2-thienyl) sulfide (**2**) with a low conversion of the 2-chlorothiophene. However, at 550-570°C there is a sharp increase in the conversion of the chloro derivative (to 98%) and the 2-thiophenethiol **1** at 570°C becomes the main reaction product (the yield of the thiol **1** was 34% and the sulfide **2** 26%). At the same time, side products of the reaction are formed and these include thiophene (24%).

In the presence of 10 mole % of methanol a marked conversion of the 2-chlorothiophene (25%) is seen even at 490°C but at this temperature only the sulfide (**2**) is produced. With an increase in temperature to 590°C the conversion of the 2-chlorothiophene increases to 100%, increasing the yield of the thiol **1** and the sulfide **2** reaction products; moreover the yield of the thiol now exceeds that of the sulfide at 570-590°C. The optimum conditions were achieved in the presence of 10 mole % methanol at 570°C when the conversion of the 2-chlorothiophene in reaction with hydrogen sulfide was 98% with a 43% yield of thiol **1** and 31% yield of sulfide **2**. At a temperature above 550°C the conversion of the 2-chlorothiophene to thiophene is significantly increased (15% at 570°C and 22.6% at 590°C). There appeared in small amounts the side products of the reaction like 3-thiophenethiol, 2,3'-dithienyl sulfide, and isomeric bithiophenes and dithienothiophenes. Their overall yield was 7-12%.

In the presence of 25 mole % methanol, the reaction according to Scheme 1 at 490°C occurs with selective formation of only the one sulfide **2**. Moreover, the conversion of the 2-chlorothiophene (19.6%) and the yield of the sulfide (16.0%) were somewhat lower than in the presence of 10 mole % methanol. However, at 570°C the yield of the thiol **1** and sulfide **2** become approximately the same (38.9 and 40.7% respectively) with a high conversion of the 2-chlorothiophene (96.0%). The positive effect of using 25 mole % methanol in the reaction is the lowering at 570°C of the yield of thiophene to 7% and other side products to 5%. Using 50 mole % methanol inhibits the Scheme 1 reaction at 570-610°C since the yield of the main thiylation products are decreased and, at 570°C, there is a reduction in the conversion of the chloride. At higher temperatures a significant amount of side products are observed, as a result of which the yields of the basic thiylation products **1** and **2** are reduced to 26.7 and 18.8% respectively (Table 1).

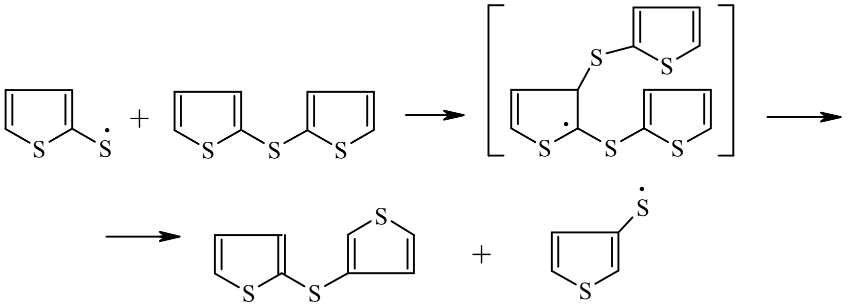
The presence of ethanol (10 or 25 mole %, 550-590°C) increases the conversion of the 2-chlorothiophene in the Scheme 1 reaction to 100% but it lowers the selectivity since the rate of side process decomposition of starting materials and final reaction products is increased. The yield of thiol **1** and sulfide **2** at 570°C are only 28 and 39% respectively (Table 2). The high selectivity of the reaction for 2-thiophenethiol in the presence of methanol (Scheme 1) is evidently related to the higher H-donor property than for hydrogen sulfide, hindering the formation of 2-thienylthiyl radicals from the thiol **1** and thus slowing the second stage of the reaction involving formation of sulfide **2** according to Scheme 2.

Scheme 2

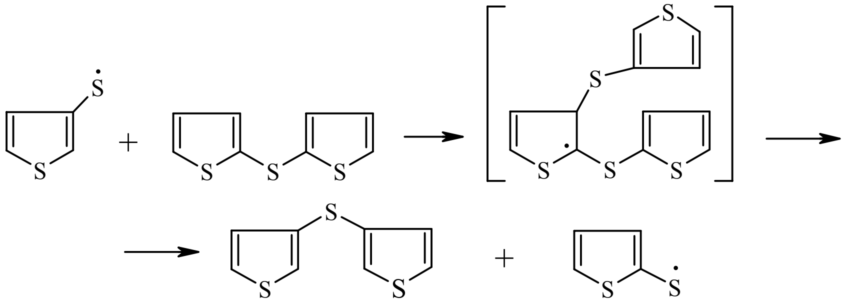


The 2- and 3- thienylthiyl radicals participate in the formation of side reaction products such as the isomeric bis(thienyl) sulfides according to Schemes 3 and 4:

Scheme 3

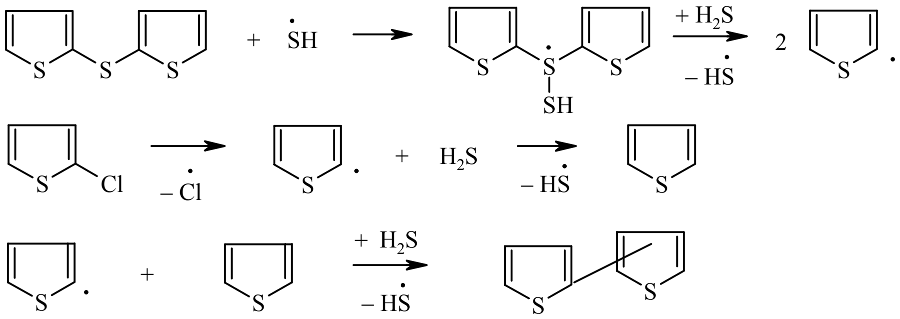


Scheme 4



Hence the removal of the thienylthiyl radicals from the reaction *via* Schemes 3 and 4 using methanol (Scheme 2) hinders the formation of the side products in Scheme 1. Under these conditions thiophene is formed via the partial thermal degradation of sulfide **2** by sulfhydryl radicals. The thienyl radical formed is readily reduced by hydrogen sulfide to thiophene and it also takes part in the formation of dithienyl molecules as in Scheme 5:

Scheme 5



In addition, thiophene can be a thermolysis product of 2-chlorothiophene through dissociation of the C–Cl bond. Upon increasing the amount of methanol in the reaction of the 2-chlorothiophene with hydrogen sulfide from 10 to 25 mole % the conversions according to Scheme 5 are suppressed by a factor of about two. This may be due to the ability of methanol to remove sulfhydryl radicals causing the decomposition of sulfide **2** (as shown in Scheme 6).

Scheme 6

$$H\dot{S} + MeOH \longrightarrow H_2S + Me\dot{O}$$

Ethanol is a less selective initiator of the reaction according to Scheme 1 since it is evidently decomposed under the reaction conditions via fission of a C–C bond. It only partially fulfils the role of a hydrogen atom donor, hence it should not be used to increase the efficiency and selectivity of the reaction.

The results of our investigation of the effect of methanol on the direction of the gas phase reaction of 2-chlorothiophene with hydrogen sulfide lead to the development of a technically straight forward and efficient synthesis of 2-thiophenethiol. Work is continuing in this area since it is connected with the manufacture of a catalyst for calophonium purification. In addition, the effect found can be extended to many other thermal reactions involving thiyl radicals and their analogs.

## EXPERIMENTAL

Reaction mixtures were analyzed chromatographically by comparison with known samples. LKM-80-1 Chromatograph (3 × 2000 mm column, liquid phase silicon XE-60 and DC 550 on Chromaton N-AW-HMDS carrier, 5%), column linear temperature program 12 deg/min with helium carrier gas.

The reactions were carried out in a flow through system using an electric furnace with a hollow quartz tube (30 × 650 mm). At the given reactor temperature an automatic dispenser delivered the starting reagents at a velocity of 10 ml/h in a stream of hydrogen sulfide (6 l/h). The ratio of 2-chlorothiophene to hydrogen sulfide was 1: 2.5. The reaction conditions and products yields are given in Tables 1 and 2.

## REFERENCES

1. M. G. Voronkov, E. N. Deryagina, A. S. Nakhmanovich, and L. G. Klochkova, *Khim. Geterotsikl. Soedin.*, 712 (1974).
2. M. G. Voronkov, E. N. Deryagina, L. G. Klochkova, and A. S. Nakhmanovich, *Zh. Org. Khim.* **12**, 1515 (1976).
3. M. G. Voronkov and E. N. Deryagina, *Usp. Khim.*, **59**, 1338 (1990)