

## High-Temperature Synthesis of Thiophene from Bis(2-chloroethyl) Sulfide

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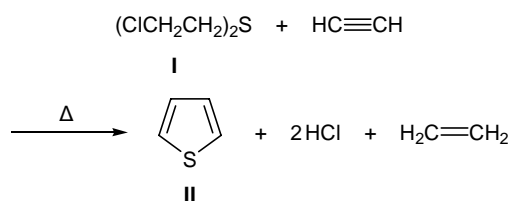
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**Abstract**—Gas-phase reaction of bis(2-chloroethyl) sulfide (Yperite) with acetylene at 550–700°C leads to formation of thiophene in 45% yield, the conversion of the initial sulfide being complete. The yield of thiophene reaches 63–68% in the thermolysis of a mixture of acetylene, bis(2-chloroethyl) sulfide, and lower organic disulfides.

Thiophene is a thermodynamically stable aromatic compound. It is formed as a result of thermal transformations of a number of sulfur-containing compounds, e.g., dimethyl and diethyl sulfides and disulfides [1, 2], dibutyl polysulfides [3, 4], divinyl sulfide [5], bis(2-chloroethyl) sulfide, etc., and their joint thermolysis with acetylene [6–8]. Taking into account that thiophene is widely used in organic synthesis [9], development of new practical and economic methods for preparation of thiophene is an important problem. For this purpose, convenient starting materials may be bis(2-chloroethyl) sulfide (Yperite) and “disulfide oil” (a mixture of lower dialkyl disulfides). Therefore, we examined in detail gas-phase thermolysis of bis(2-chloroethyl) sulfide (**I**) and found that thiophene can be obtained therefrom in a high yield. Yperite is a chemical weapon [10], and utilization of its reserves is important from the ecological viewpoint.

Thermolysis of sulfide **I** was not studied in detail previously. It was shown that bis(2-chloroethyl) sulfide (**I**) completely decomposes above 500°C; however, the structure of the decomposition products was not discussed [6, 10]. We found that thermolysis of sulfide **I** in a flow reactor at 400–600°C (contact time 20–30 s) is characterized by a conversion of no more than 30% and that thiophene (**II**) is thus formed in 5–10% yield (calculated on the initial sulfide). The process is accompanied by strong tarring (see table, run nos. 1–5).

We also showed (cf. [6]) that the conversion of sulfide **I** and the yield of thiophene considerably increase when the thermolysis of **I** is performed in the presence of acetylene at 550–700°C. Here, the conversion of sulfide **I** and the yield of thiophene depend not only on the temperature but also on the sulfide-to-acetylene ratio (run nos. 6–11). The optimal conditions for the synthesis of thiophene (**II**) are as follows: temperature 650–700°C, sulfide **I**-to-acetylene ratio 1:2. The yield of thiophene reaches 45%, the conversion of **I** being 100% (run nos. 8, 9). According to the GLC and GC–MS data, bithienyls (a mixture of isomers), thienothiophenes (a mixture of isomers), benzothiophene, benzene, toluene, and carbon disulfide are formed as by-products. The overall yield of sulfur-containing compounds does not exceed 10%. The gas phase contains hydrogen chloride, C<sub>1</sub>–C<sub>4</sub> hydrocarbons, and hydrogen sulfide.



The mechanism of formation of thiophene by thermolysis of organosulfur compounds and their joint thermolysis with acetylene was thoroughly discussed in [1, 5–8, 11]. It includes initial generation of vinyl-

High-temperature reactions of bis(2-chloroethyl) sulfide (**I**) and yields of thiophene

Run no.	Molar ratio <b>I</b> : C <sub>2</sub> H <sub>2</sub> : R <sub>2</sub> S <sub>2</sub>	Temperature, °C	Conversion of <b>I</b> , %	Yield of <b>II</b> , <sup>a</sup> %
1	<sup>b</sup>	400	6	5
2	<sup>b</sup>	450	13	6
3	<sup>b</sup>	500	19	6
4	<sup>b</sup>	550	25	10
5	<sup>b</sup>	600	30	8
6	1 : 2 <sup>c</sup>	550	83	53
7	1 : 2 <sup>c</sup>	600	98	48
8	1 : 2 <sup>c</sup>	650	100	45
9	1 : 2 <sup>c</sup>	700	100	43
10	1 : 1 <sup>c</sup>	700	84	38
11	1 : 3 <sup>c</sup>	650	96	47
12	1 : 3 : 1 <sup>d</sup>	650	100	63
13	1 : 3 : 1 <sup>e</sup>	650	100	68
14	1 : 3 : 1 <sup>e</sup>	700	100	65

<sup>a</sup> Calculated on the initial sulfide **I**.

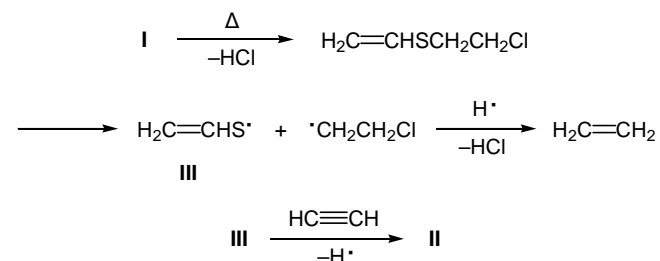
<sup>b</sup> Neither acetylene nor polysulfides were added.

<sup>c</sup> Joint pyrolysis of sulfide **I** with acetylene.

<sup>d</sup> R = Me.

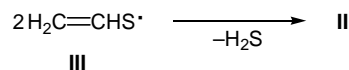
<sup>e</sup> R<sub>2</sub>S<sub>2</sub> was a 1:1 mixture of dimethyl and diethyl disulfide ("disulfide oil").

sulfanyl radicals (**III**) from sulfur-containing substrates. In the absence of chemical traps, radicals **III** undergo mainly profound decomposition. Acetylene binds vinylsulfanyl radicals to produce thiophene, thus preventing their decomposition [11]. Sulfide **I** is capable of yielding radicals **III** via elimination of hydrogen chloride and subsequent decomposition of divinyl sulfide.



In the absence of acetylene, the concentration of radicals **III** is low; therefore, their condensation contributes little to the formation of thiophene. Thermolysis of sulfide **I** produces mainly a considerable

amount of tars. Acetylene effectively binds vinylsulfanyl radicals, thus accelerating thermal decomposition of sulfide **I** with formation of thermodynamically stable thiophene. When the concentration of acetylene in the system decreases, the conversion of **I** does not attain 100% even at 700°C (run no. 10).



The yield of thiophene appreciably increases when the thermolysis of sulfide **I** and acetylene is performed in the presence of lower organic disulfides, dimethyl disulfide or a mixture of dimethyl and diethyl disulfides (disulfide oil) which is a waste product in the processing of sulfur-rich natural gases [8]. In these experiments (run nos. 12–14), the yield of thiophene reaches 68% (650–700°C, 100% conversion of **I**) provided that one molecule of **I** and one disulfide molecule react with acetylene to form two thiophene molecules. Among by-products, only the yields of carbon disulfide and thienothiophenes increase.

The larger yield of thiophene in the reaction of sulfide **I** with acetylene in the presence of disulfide is favored by both additional generation of vinylsulfanyl radicals and increase in their stability in the presence of hydrogen sulfide arising from thermolysis of disulfides.

Thus, joint thermolysis of bis(2-chloroethyl) sulfide (**I**) with acetylene gives 45% of thiophene, whereas in the presence of disulfides the yield of thiophene increases to 68%. Thiophene is readily separated from the condensed products by distillation. It is isolated in a sufficiently pure form and can be brought into further syntheses. The proposed procedures for the synthesis of thiophene attract practical interest from the viewpoint of utilization of bis(2-chloroethyl) sulfide and disulfide oil as large-scale waste product.

## EXPERIMENTAL

Liquid initial compounds and thermolysis products were analyzed by gas–liquid chromatography on an LKhM 8MD-2 instrument equipped with a 2000×3-mm column (stationary phase 5% XE-60, linear oven temperature programming at a rate of 12 deg/min, carrier gas helium). The liquid products were additionally analyzed by GC–MS using an LKB-2091-152 instrument (SE-54 capillary column, injector temperature 300°C, oven temperature programming at 8 deg/min, energy of ionizing electrons 70 eV, carrier gas helium). The gaseous products were analyzed on

a KhL-6 chromatograph (7.5-m column packed with molecular sieves, carrier gas argon).

The thermolysis was carried out in a flow system under atmospheric pressure; the reactor was a hollow quartz tube (19 mm in diameter) with a 3-mm ring gap between the tube wall and thermocouple pocket. The length of the reaction zone was 250 mm. The quartz tube was placed into a tube furnace with automatic temperature control. Liquid reactants were supplied with the aid of an automatic syringe sampler. The flow rate of gases (nitrogen or acetylene) was controlled manually using a rheometer. The thermolysis products were trapped into cooled receivers. The contact time was calculated from the volume of the reaction zone and volume rate of the reactants in the gas phase at the reaction temperature.

The thermolysis of sulfide **I** alone was carried out in a stream of nitrogen (1.2 l/h); compound **I** was supplied at a volume rate of 3.2 ml/h.

**Joint thermolysis of sulfide I with acetylene** (see table, run no. 8). The reactor was preliminarily purged with nitrogen and heated to 650°C. Sulfide **I**, 7.28 g (0.046 mol), was supplied at a rate of 3.2 ml/h, and acetylene was supplied at a rate of 1.2 l/h (reactant ratio 1:2, contact time 21.5 s). After 105 min, 2.9 g of a liquid product mixture was collected. It contained 1.73 g of thiophene, 0.12 g of benzothiophene, 0.22 g of thienothiophenes, 0.09 g of isomeric bithienyls, 0.09 g of carbon disulfide, 0.25 g of benzene, and 0.4 g of other aromatic hydrocarbons (GLC). Thiophene was isolated by distillation. A fraction with bp 80–82°C contained more than 98% of thiophene,  $n_D^{20} = 1.5240$  (1.5246 [11]). Joint thermolysis of sulfide **I**, disulfides, and acetylene was carried out in a similar way.

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