

process with the yield not exceeding 5% with respect to chlorobenzene (**Ia**) introduced into the reaction.

Thermal thiylation of chloroarenes was studied in a flow system. A mixture of chloroarene and methanol (10, 15, 25, 40, 50, and 75 mol % of methanol with respect to chloroarene) was brought into the reaction zone in a flow of hydrogen sulfide. The mixture of chloroarene with methanol and diethyl disulfide was brought into the reactor in a nitrogen flow. The reactions in the presence of methanol were compared with the processes without it. The reaction conditions and the yields of the products in reactions with compounds **Ia** and **Ib** are presented in Tables 1 and 2.

The reactions of chloroarenes with hydrogen sulfide (or diethyl disulfide) in the presence of methanol start at higher temperature. This phenomenon is caused by capturing of radicals initiating thermal reactions by methanol as efficient hydrogen donor.



R is any radical formed at the thermal degradation of molecules.

However when the concentration of the initiating radicals reaches a sufficient level begin thermal reactions of chloroarenes thiylation. Therewith the methanol addition in some cases significantly affects the selectivity of thiols **IIa** and **IIb** formation.

In the absence of methanol chlorobenzene (**Ia**) the most efficiently reacted with the hydrogen sulfide at 620 and 650°C. At 620°C thiophenol (**IIa**) and diphenyl sulfide (**IIIa**) formed in equal amount [30.8% calculated on the reacted chlorobenzene (**Ia**)], and at 650°C the yield of thiol **IIa** exceeded that of sulfide **IIIa** (27.1 and 7.4% respectively), but a considerable quantity of side products arose under these conditions: benzene (**IVa**) (yield up to 39%) and dibenzothiophene (**V**) (3–4%) resulting in a high conversion of chlorobenzene (**Ia**) (Table 1). Bringing into the system methanol in amount of 15 mol % resulted in a sharp increase in the selectivity of thiol **IIa** formation at 650°C: the yield of thiol **IIa** was 55.4%, and sulfide **IIIa** 19.2% with respect to the reacted chlorobenzene (**Ia**). Therewith the yield of benzene (**IVa**) fell to 5%, and dibenzothiophene (**V**) did not form at all. At 620°C the selectivity of thiol **IIa** formation is also high, but the conversion of chlorobenzene remained low. The other methanol concentrations are less efficient.

The reaction of chlorobenzene (**Ia**) with the diethyl disulfide also afforded thiol **IIa** and sulfide **IIIa**, and the

selectivity of thiol **IIa** at 600–650°C was high (Table 1). The side products in this reaction are thiophene, benzothiophene, and thienothiophene. Bringing methanol into this system also increased the selectivity of thiol **IIa** formation. The best results were obtained at the use of 15 (600–630°C) and 25 mol % of methanol (600°C). Therewith the yield of the side products was reduced. Applying 50–75 mol% of methanol raised the selectivity of thiophenol (**IIa**) formation at 630–650°C, but here the yield of the side reaction products grew.

4-Methylchlorobenzene (**Ib**) reacted with the hydrogen sulfide at 620–640°C providing 4-methylthiophenol (**IIb**) and bis(4-methylphenyl) sulfide (**IIIb**). Therewith the yield of thiol **IIb** was less or equal to that of sulfide **IIIb** [17.6/29.6 (620°C) and 18.1/15.3% (640°C)] (Table 2). Thus the reaction was not selective with respect to thiol. Introduction of methanol favors the increase in selectivity of thiol **IIb** formation: at the methanol concentration 20 mol % **IIb/IIIb** = 47.3/18.0 (630°C), at 25 mol% 48.5/31.6 (620°C), and at 50 mol% 45.7/22.9% (640°C). Simultaneously the yield of toluene (**IVb**) decreased, and the other side products did not form at all.

Thiol **IIb** formed selectively in reaction of 4-methylchlorobenzene (**Ib**) with diethyl disulfide. The yield of thiol **IIb** at 600–640°C is approximately two times larger than the yield of sulfide **IIIb** (50 and 30% respectively) (Table 2). Therewith the yield of toluene (**IVb**) did not exceed 19%, but the other side products appeared (thiophene and thienothiophene). The reaction of 4-methylchlorobenzene (**Ib**) with diethyl disulfide in the presence of methanol in amount of 15, 25, or 50 mol% occurred with greater selectivity with respect to thiol **IIb**. The best results were obtained at the use of 50 mol% of methanol. At 620°C the yields of compounds **IIb** and **IIIb** equal to 68.3 and 14.6%, and at 630°C to 64.0 and 17.7% respectively. Simultaneously the yield of side products toluene (**IVb**) and thiophene decreased, and the others did not form.

4-Hydroxythiophenol (**IIc**) is an interesting monomer and semiproduct of the organic synthesis. The direct gas-phase reaction of 4-chlorophenol (**Ic**) with the hydrogen sulfide at 540–560°C did not yield thiol **IIc** selectively for it involved considerable reduction of the initial compound into phenol (**IVc**). The yield of phenol (**IVc**) was always than that of thiol **IIc** (58/21 at 540°C and 49/43% at 560°C). Therewith the conversion of initial compound **Ic** was relatively low (up to 32%). The introduction of methanol into this reaction in amount of 25 mol% provided a slight effect at 580°C. Simultaneous-

Table 1. Gas-phase reaction of chlorobenzene (**Ia**) with hydrogen sulfide (runs nos. 1–20) and diethyl disulfide Et₂S₂ (runs nos. 21–40) in the presence of methanol. Molar ratio (**Ia**) : H₂S = 1:2.5; reagents contact time 35–40 s. Molar ratio (**Ia**) : Et₂S₂ = 1:2; reagents contact time 50–55 s

Run no.	MeOH (mol)	Temperature, °C	Conversion of compound (Ia), %	Yield of reaction products, % calculated on the taken (reacted) chlorobenzene (Ia)			
				IIa	IIIa	IVa	V
1	–	620	64	19.8(30.8)	19.2(30.7)	13.0(20.0)	0.7(1.2)
2	–	650	83	22.6(27.1)	6.2(7.4)	33.1(39.7)	3.1(3.8)
3	10	600	16	6.5(39.3)	5.7(34.9)	–	–
4	10	620	34	11.9(35.0)	9.4(27.4)	2.0(8.5)	1.4(4.2)
5	10	650	59	26.6(49.7)	16.7(29.2)	4.8(8.3)	–
6	10	670	89	3.2(3.6)	4.0(4.5)	47.5(52.7)	12.5(13.8)
7	15	620	19	11.3(60.4)	2.0(10.8)	–	–
8	15	650	59	32.7(55.4)	11.4(19.2)	3.1(5.2)	–
9	15	670	88	28.6(32.4)	6.0(6.7)	44.0(49.3)	4.0(4.5)
10	20	620	16	6.5(43.0)	5.2(33.2)	–	–
11	20	650	50	18.1(35.9)	20.8(41.3)	5.6(11.1)	–
12	20	670	73	21.9(30.1)	16.9(23.1)	20.0(27.5)	1.2(1.7)
13	20	690	98	2.9(3.0)	1.5(1.6)	66.2(67.5)	3.2(3.3)
14	25	620	13	5.2(30.5)	7.0(46.2)	–	–
15	25	650	34	14.6(39.7)	11.1(30.6)	3.2(7.9)	–
16	25	670	54	29.6(43.7)	14.8(24.7)	11.5(19.5)	–
17	25	690	90	3.3(3.6)	2.7(3.0)	71.8(80.3)	1.9(2.1)
18	50	650	37	11.6(30.0)	11.4(29.6)	4.6(11.7)	–
19	50	670	50	14.9(29.6)	16.4(32.7)	8.2(16.4)	–
20	50	690	78	26.7(34.2)	13.3(17.1)	23.9(30.4)	–
21	–	600	34	15.5(46.7)	4.8(14.4)	0.8(2.5)	–
22	–	630	50	21.1(32.2)	10.5(21.6)	2.4(4.7)	–
23	–	650	64	24.6(38.9)	15.4(23.9)	8.4(13.1)	–
24	–	680	72	18.7(27.3)	11.0(15.7)	17.6(26.1)	–
25	15	600	31	15.9(50.6)	3.6(11.5)	0.4(1.3)	–
26	15	630	44	21.1(53.3)	6.4(14.6)	1.1(2.6)	–
27	15	650	55	24.5(44.3)	7.4(13.5)	7.1(12.8)	–
28	15	670	73	14.5(19.5)	13.0(17.3)	20.1(26.8)	–
29	25	600	30	15.2(51.6)	3.8(12.9)	–	–
30	25	630	45	19.9(44.5)	9.4(21.1)	1.5(3.4)	–
31	25	650	50	22.7(47.2)	7.0(14.6)	4.6(9.6)	–
32	25	670	58	21.1(36.5)	10.2(17.7)	11.5(19.9)	–
33	50	600	37	18.0(48.3)	5.0(13.3)	–	–
34	50	630	48	25.3(52.4)	7.1(14.8)	1.1(2.3)	–
35	50	650	54	30.0(52.2)	8.1(15.6)	4.9(10.0)	–
36	50	670	68	33.2(47.5)	13.6(18.8)	11.0(16.1)	–
37	75	600	29	12.6(43.1)	3.6(12.4)	–	–
38	75	630	32	14.6(50.5)	2.9(9.6)	–	–
39	75	650	38	22.9(59.7)	6.8(17.5)	0.7(1.8)	–
40	75	670	53	29.8(47.9)	12.9(23.2)	3.7(6.7)	–

Table 2. Gas-phase reaction of 4-methylchlorobenzene (**Ib**) with hydrogen sulfide (runs nos. 1–17) and diethyl disulfide Et₂S₂ (runs nos. 18–40) in the presence of methanol. Molar ratio (**Ib**): H₂S = 1:2.5; reagents contact time 40–45 s. Molar ratio (**Ib**): Et₂S₂ = 1:2; reagents contact time 45–50 s

Run no.	MeOH (mol%)	Temperature, °C	Conversion of compound (Ib), %	Yield of reaction products, % calculated on the taken (reacted) 4-methylchlorobenzene (Ib)		
				IIb	IIIb	IVb
1	–	620	61	12.8(17.6)	21.2(29.6)	9.1(12.6)
2	–	640	75	14.3(18.1)	12.2(15.3)	26.6(32.2)
3	20	620	45	12.8(44.6)	9.8(27.5)	8.3(17.6)
4	20	630	62	28.6(47.3)	10.2(18.0)	11.9(24.0)
5	20	640	78	27.4(33.7)	9.9(13.5)	32.5(39.0)
6	20	650	85	24.8(29.0)	9.4(11.2)	39.7(43.8)
7	25	620	41	21.8(48.5)	14.9(31.6)	6.0(13.3)
8	25	630	65	34.0(47.2)	17.8(24.2)	16.9(22.9)
9	25	640	88	28.2(31.5)	11.5(13.0)	40.3(46.5)
10	40	630	51	20.6(36.6)	22.3(38.3)	9.5(19.4)
11	40	640	72	27.8(38.0)	22.6(30.3)	20.0(27.0)
12	40	650	83	30.7(37.1)	15.8(18.3)	30.2(36.1)
13	40	660	88	18.4(21.3)	14.4(18.9)	42.0(47.7)
14	50	630	45	14.4(30.6)	19.4(40.8)	10.7(22.8)
15	50	640	70	32.0 (45.7)	16.3 (22.9)	18.9(26.9)
16	50	650	76	33.8 (42.8)	13.2(16.4)	27.5(35.2)
17	50	660	87	30.9 (34.6)	9.8(11.3)	42.0(47.3)
18	–	600	23	11.8 (58.0)	7.6 (33.3)	1.1(4.6)
19	–	620	37	17.3 (50.0)	11.0 (29.3)	3.5(9.3)
20	–	630	41	16.9 (44.6)	13.7 (33.4)	4.0(9.9)
21	–	640	45	20.6 (46.2)	11.9 (25.4)	9.0(19.5)
22	15	600	23	11.8(55.0)	5.0(21.4)	–
23	15	620	40	22.3(54.3)	6.8(16.8)	3.3(7.9)
24	15	630	44	20.5(46.7)	11.4(26.7)	5.3(12.3)
25	15	640	50	27.4(51.8)	11.6(22.6)	7.6(15.3)
26	15	650	54	28.8(50.0)	11.7(21.9)	12.3(22.8)
27	15	660	61	23.8(43.3)	10.0(16.6)	21.9(36.8)
28	15	670	68	20.5(29.8)	8.7(12.7)	24.3(35.4)
29	25	600	25	16.7(65.7)	5.4(21.5)	–
30	25	620	37	18.6(52.4)	9.6(26.0)	3.3(8.9)
31	25	630	49	32.2(58.4)	10.8(23.8)	5.9(12.6)
32	25	640	54	29.3(53.3)	19.0(24.8)	8.2(17.0)
33	25	650	60	23.4(39.1)	14.7(24.5)	17.3(28.9)
34	25	660	66	22.9(34.6)	9.0(13.6)	27.9(42.2)
35	50	600	30	15.7(52.4)	8.5(28.3)	–
36	50	620	34	21.3(68.3)	4.5(14.4)	1.5(4.7)
37	50	630	46	26.7(64.0)	7.4(17.7)	2.5(5.8)
38	50	640	55	30.7(52.2)	11.8(21.5)	6.9(12.0)
39	50	650	59	30.2(48.5)	8.3(14.1)	12.6(20.1)
40	50	660	67	26.3(39.3)	8.1(12.2)	22.7(35.7)

ly the conversion of 4-chlorophenol (**Ic**) grew (37%), the yield of thiol **Ic** increased (58.3%), and the yield of phenol (**Ivc**) decreased (32%). The corresponding bis(4-hydroxyphenyl) sulfide (**IIIc**) formed in neither case. The effect from methanol addition in amount of 15 and 50 mol% is even less pronounced.

The reaction of 1,4-dichlorobenzene (**Id**) with hydrogen sulfide occurred at 560–580°C to a low conversion (25–30%). Yields of 4-chlorothiophenol (**IId**) are somewhat lower or equal to the yields of bis(4-chlorophenyl) sulfide (**IIId**) (32–42.3/45–37.5%). The addition of methanol at any concentration practically did not favor increasing the conversion of initial compound **Id** and selectivity with respect to thiol **IId**. The best result was obtained at 590°C using 25 mol% of methanol (**IIId/IIId** = 45.3/38.3%, conversion of compound **Id** 34%).

For the sake of comparison we studied the gas-phase reaction of 2,5-dichlorothiophene with hydrogen sulfide. This reaction proceeded to a low conversion with strong tarring at 490–510°C giving as the main product of sulfurization bis(5-chlorothiophenyl) sulfide, and the expected 5-chloro-2-thiophenethiol did not form at all. 2,5-Dichlorothiophene to a large extent was reduced into 2-chlorothiophene that was converted into 2-thiophenethiol and bis(2-thienyl)sulfide. The introduction of methanol into this reaction did not favor formation of 5-chloro-2-thiophenethiol but accelerated the process as a whole. Therewith grew the yields of all reaction products, both the main one and the side compounds.

4-Trifluoromethylchlorobenzene in the absence of methanol efficiently reacted with hydrogen sulfide (conversion up to 70%) in a narrow temperature range (610–620°C). The yield of 4-trifluoromethylthiophenol (**IIe**) is greater than that of bis(4-trifluoromethylphenyl) sulfide (**IIIe**) [25.8/14.3 (610°C) and 17.6/10.1% (620°C)]. However the process gave rise to a considerable amount of the reduction product, trifluoromethylbenzene (**Ive**) (29.6–45.2%). The decrease in the reaction temperature by 10°C resulted in a significant reduction in conversion (to 20%). Interestingly, at this temperature no thiol **IIe** was obtained, and the yield of

sulfide **IIIe** was 14%. Bringing the methanol into the system in amount of 25 mol% only slightly improved the selectivity of thiol **IIe** formation at 640°C (yield of compound **IIe** 31.4, that of **IIIe** 15.1%) and reduced the yield of the reduction product **Ive** to 19.4%.

The results obtained are in agreement with the stability of arenethiyl radicals whose stability we have quantitatively estimated before [2]. The formation of thiols **II** and diaryl sulfides **III** by reactions (1) and (2) occurs involving thiyl radicals HS \cdot and RC $_6$ H $_4$ S \cdot in substitution of the chlorine in the aromatic ring [1].

The rate of reaction (7) and consequently the selectivity of thiols **II** formation depend on the concentration of the radicals RC $_6$ H $_4$ S \cdot . When the only H-donor in the system is the hydrogen sulfide the less stable arenethiyl radicals generated from the chloro derivative and the hydrogen sulfide further react with it faster than with the initial chloro derivative, and with the more stable radicals the opposite is valid. In the presence of stronger H-donors than the hydrogen sulfide the thiyl radicals are faster converted into the hydrogen sulfide and the corresponding thiol.

The high concentration of the hydrogen sulfide in the reaction zone (the ratio chloroarene: H $_2$ S = 1:2–2.5) ensures sufficiently high concentration of HS \cdot radicals notwithstanding their consumption by reaction (8). However at the high methanol amount reaction (8) leads to decrease in the concentration of HS \cdot radicals, and the selectivity of thiol formation diminishes. Therefore an optimum range of methanol addition exists where the selectivity of thiol formation increases (15–25 mol% with respect to chloroarene).



The improvement of the process selectivity for thiols **IIa** and **IIb** originates apparently from the fact that the methanol, being more efficient H-donor than the hydrogen sulfide, considerably reduces the concentration of radicals RC $_6$ H $_4$ S \cdot by reaction (9) and decelerates reaction (7). Arenethiyl radicals destabilized by the acceptor substituents (X = OH, Cl, CF $_3$) react with chloroarene along scheme (7) at a high rate [2], and therefore here the methanol addition virtually does not affect the selectivity of the process.



It was established that methanol addition did not considerably increase the rate of reduction of initial chloroarenes into arenes **IV**. This fact suggests that reaction (3) apparently occurs due to the halophilic attack of thiyl radicals on the chlorine atom.



Inasmuch as the presence of methanol decreases the thiyl radicals concentration, reaction (10) should not significantly accelerate.

The results obtained permit making an improvement in the preparative procedure of thiophenol and 4-methylthiophenol synthesis from the corresponding chloroarenes and hydrogen sulfide.

EXPERIMENTAL

Initial reagents and condensates formed in the course of reaction were analyzed by GLC on a chromatograph LKhM 80-MD-2, column 2000×3 mm, liquid phase XE 60 (5%), oven temperature linearly programmed at a rate 12 deg/min, carrier gas helium.

Thermal reactions were carried out in a flow system at atmospheric pressure in a hollow quartz pipe of 19 mm diameter. The length of the reaction zone was 250 mm. The quartz pipe was placed into a pipe electric heater where the temperature was automatically controlled. The initial liquid and crystalline reagents were charged into the reaction zone with an automatic syringe batcher; therewith the crystalline reagents were preliminary melted in the batcher heated with a nichrome coil. The velocity of gas (nitrogen or hydrogen sulfide) flow was manually controlled with the help of rheometers. Reagents contact time was estimated from the volume of the reaction zone and supply rate of all reagents in gas state at the reaction temperature.

Reaction of chlorobenzene (Ia) with hydrogen sulfide in the presence of methanol (Table 1, run no. 8). Into a reactor preliminary flushed with nitrogen was charged at 650°C a mixture of 1.60 g (14 mmol) of chlorobenzene (**Ia**) and 0.067 g (2 mmol) of methanol at a rate of 3 ml/h in a flow of hydrogen sulfide (1.6 l/h). Contact time 35 s. In 29 min we obtained at the output of the reactor 1.37 g of liquid condensate containing according to GLC 0.51 g of thiophenol (**IIa**), 0.15 g of diphenyl sulfide (**IIIa**), 0.05 g of benzene (**IVa**), and 0.66 g of unreacted initial chlorobenzene (**Ia**).

Reaction of chlorobenzene (Ia) with diethyl disulfide in the presence of methanol (Table 1, run no. 26). Into a reactor at 630°C was charged a mixture of 0.97 g (8.5 mmol) of chlorobenzene (**Ia**), 2.11 g (17 mmol) of diethyl disulfide, and 0.041 g (1.3 mmol) of methanol at a rate of 2 ml/h in a flow of nitrogen (1.2 l/h). Contact time 52 s. In 90 min we obtained at the output of the reactor 0.9 g of liquid condensate containing according to GLC 0.28 g of thiophenol (**IIa**), 0.078 g of diphenyl sulfide (**IIIa**), 0.06 g of benzene (**IVa**), 0.018 g of benzothiophene, 0.001 g of carbon disulfide, 0.02 g of thiophene, 0.013 g of thienothiophene, and 0.43 g of unreacted initial chlorobenzene (**Ia**).

Reaction of 4-methylchlorobenzene (Ib) with hydrogen sulfide in the presence of methanol (Table 2, run no. 4). Into a reactor at 630°C was charged a mixture of 1.12 g (8.9 mmol) of 4-methylchlorobenzene (**Ib**) and 0.057 g (1.8 mmol) of methanol at a rate of 3 ml/h in a flow of hydrogen sulfide (1.4 l/h). Contact time 42 s. In 21 min we obtained at the output of the reactor 0.99 g of liquid condensate containing according to GLC 0.31 g of 4-methylthiophenol (**IIb**), 0.11 g of bis(4-methylphenyl) sulfide (**IIIb**), 0.14 g of toluene (**IVb**), and 0.43 g of unreacted 4-methylchlorobenzene (**Ib**).

Reaction of 4-methylchlorobenzene (Ib) with diethyl disulfide in the presence of methanol (Table 2, run no. 37). Into a reactor at 630°C was charged a mixture of 0.37 g (2.9 mmol) of 4-methylchlorobenzene (**Ib**), 0.7 g (5.7 mmol) of diethyl disulfide, and 0.046 g (1.4 mmol) of methanol at a rate of 3 ml/h in a flow of nitrogen (1.2 l/h). Contact time 48 s. In 21 min we obtained at the output of the reactor 0.36 g of liquid condensate containing according to GLC 0.09 g of 4-methylthiophenol (**IIb**), 0.022 g of bis(4-methylphenyl) sulfide (**IIIb**), 0.013 g of toluene (**IVb**), 0.013 g of carbon disulfide, 0.022 g of thiophene, and 0.2 g of unreacted 4-methylchlorobenzene (**Ib**).

Gas-phase reactions of chloroarenes **Ic–Ie** in the absence and in the presence of methanol were carried out in a similar way.

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