ISSN 1070-4280, Russian Journal of Organic Chemistry, 2018, Vol. 54, No. 12, pp. 1794–1797. © Pleiades Publishing, Ltd., 2018.
Original Russian Text © A.V. Mashkina, L.N. Khairulina, 2018, published in Zhurnal Organicheskoi Khimii, 2018, Vol. 54, No. 12, pp. 1780–1783.

Catalytic Synthesis of Methylthiophenes

A. V. Mashkina[a]* and L. N. Khairulina[a]

[a] *Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences,*
pr. Akad. Lavrent'eva 5, Novosibirsk, 630090 Russia
**e-mail: amash@catalysis.ru*

Received January 12, 2018; revised October 10, 2018; accepted October 19, 2018

Abstract—The gas-phase reaction of dimethyl disulfide with thiophene over Co/HZSM-5 catalyst in a helium medium under atmospheric pressure at 250–350°C gave a mixture of mono-, di-, tri-, and tetramethylthiophenes with an overall selectivity of 94–96%.

DOI: 10.1134/S1070428018120096

Methylthiophenes are used as starting materials for the preparation of fuel additives, antioxidants, rubber vulcanization accelerators, monomers, medicines, herbicides, and insectofungicides. Methylthiophene has found application as an animal hair growth stimulator, hair care agent, and weight-gain supplement. Methylthiophenes can be synthesized by dehydrocyclization of diene hydrocarbons with hydrogen sulfide, from 1,4-dicarbonyl compounds and phosphorus heptasulfide, from furans and hydrogen sulfide [1–4]. Accessibility of starting materials is an important factor for the choice of a method for the preparation of methylthiophenes. Accessible and cheap starting compounds are lower dialkyl disulfides [mostly dimethyl disulfide (**1**)] that are isolated in large amounts from oxidative desulfurization products of petroleum, natural gas, and gas condensate [5].

In this work we studied the formation of methylthiophenes in the reaction of dimethyl disulfide with thiophene in the presence of cobalt-containing HZSM-5 high-silica zeolite. This catalyst possesses active surface protonic and Lewis acid sites, as well as moderate-strength basic sites [6], which activate the reactants and favor the reaction.

The reaction of thiophene with dimethyl disulfide (**1**) was carried out at a reactant molar ratio of 1 : (4–5) over Co/HZSM-5 catalyst in the gas phase (helium, atmospheric pressure) at different temperatures and contact times. Preliminarily, the behavior of pure thiophene (initial concentration ~0.8 vol %) was studied under these conditions. Almost no decomposition of thiophene was observed at 200–250°C. At 300°C, the conversion of thiophene was 3–10% with the formation of hydrocarbons, hydrogen sulfide, and high-boiling compounds which were not identified.

Pure dimethyl disulfide (**1**) (initial concentration ~3.5 vol %) over Co/HZSM-5 at 200–350°C decomposed to produce methanethiol, dimethyl sulfide, hydrogen sulfide, dimethyl trisulfide, ethylene, and "coke" (Scheme 1). At 200°C, the transformation of dimethyl disulfide occurred even in a short contact time; subsequently, the conversion of **1** and the yields of dimethyl sulfide and hydrogen sulfide increased; the yield of methanethiol increased up to a certain limiting value and then decreased, whereas the yield of dimethyl trisulfide decreased as the contact time increased (Table 1). Raising the temperature accelerated the reaction. Presumably, increased yield of dimethyl sulfide at elevated temperature and longer contact time is related to preferential formation of methyl fragments on the catalyst surface. As shown in [7], disulfide **1** in the presence of solid acid catalysts decomposed to methanethiol which was then converted to dimethyl sulfide and hydrogen sulfide; in addition, partial cracking of initial disulfide **1**, methanethiol, and dimethyl sulfide occurred.

Dimethyl disulfide (**1**) in the presence of thiophene decomposed in the same manner as in the absence of it, but at a lower rate (Table 1). Thiophene reacted with disulfide **1** at 160–200°C to give mainly sulfonyl-

Scheme 1.

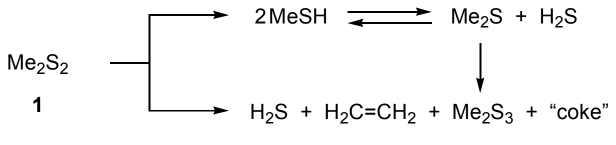


Table 1. Transformation of dimethyl disulfide (**1**) over Co/HZSM-5 at 300°C at different contact times[a]

Contact time, s	Conversion of Me_2S_2, %	Yield (mol %) calculated on the initial dimethyl disulfide (**1**)			
		MeSH	Me_2S	H_2S	Me_2S_3
Pure dimethyl disulfide (**1**)					
0.3	42	8.0	17.1	12.1	4.0
0.5	62	15.1	28.0	15.1	3.5
0.6	75	16.0	34.6	19.4	3.0
0.7	85	17.2	40.0	26.3	2.1
1.1	100	18.0	46.1	30.2	0.8
3.5	100	13.1	58.2	25.0	0.2
Dimethyl disulfide (**1**) + thiophene					
0.3	17	5.0	3.0	3.0	4.1
0.6	30	8.1	7.2	7.1	3.3
1.1	51	12.2	20.0	17.3	2.8
2.2	73	17.3	23.1	27.7	0.9
3.5	100	19.2	37.7	36.5	0.5
4.5	100				

[a] Minor amounts of Me_2S_4, COS, and sulfur-containing coke were also formed.

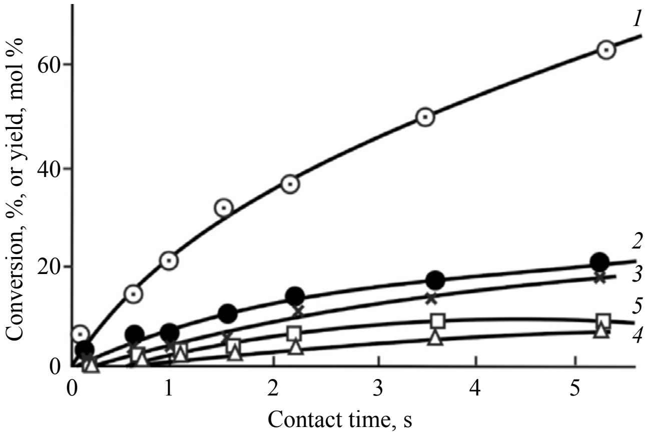


Fig. 1. Plots of the (*1*) conversion of thiophene and yields of (*2*) methylthiophenes, (*3*) dimethylthiophenes, (*4*) trimethylthiophenes, and (*5*) tetramethylthiophene versus contact time; catalyst Co/HZSM-5, temperature 300°C; the yields were calculated on the initial thiophene.

thiophenes, whereas the yield of methylthiophenes did not exceed 0.4–2 mol %. The yield of the latter increased when the temperature was raised to 250–300°C. Further raising the temperature accelerated cracking of initial disulfide **1**, as well as of methanethiol and dimethyl sulfide generated therefrom, which reduced the yield of methylthiophenes. Increased contact time at a constant temperature favored the formation of methylthiophenes (Fig. 1). The best results were obtained at 300°C. As a result, mono-, di-, tri-, and tetramethylthiophenes **2**–**5** were formed (Scheme 2). At 300°C, the yield of 2-methylthiophene was ~3.3 times as high as that of 3-methylthiophene; isomeric dimethylthiophenes were formed in similar yields differing by no more than a factor of 1.1–1.2; the yield of 2,3,4-trimethylthiophene was higher that the yield of 2,3,5-trimethylthiophene by almost an order of magnitude; and tetramethylthiophene was formed in a fairly high yield. The yields of methylthiophenes calculated on the reacted thiophene rank as follows: monomethylthiophenes >> dimethylthiophenes > tetramethylthiophene > trimethylthiophenes.

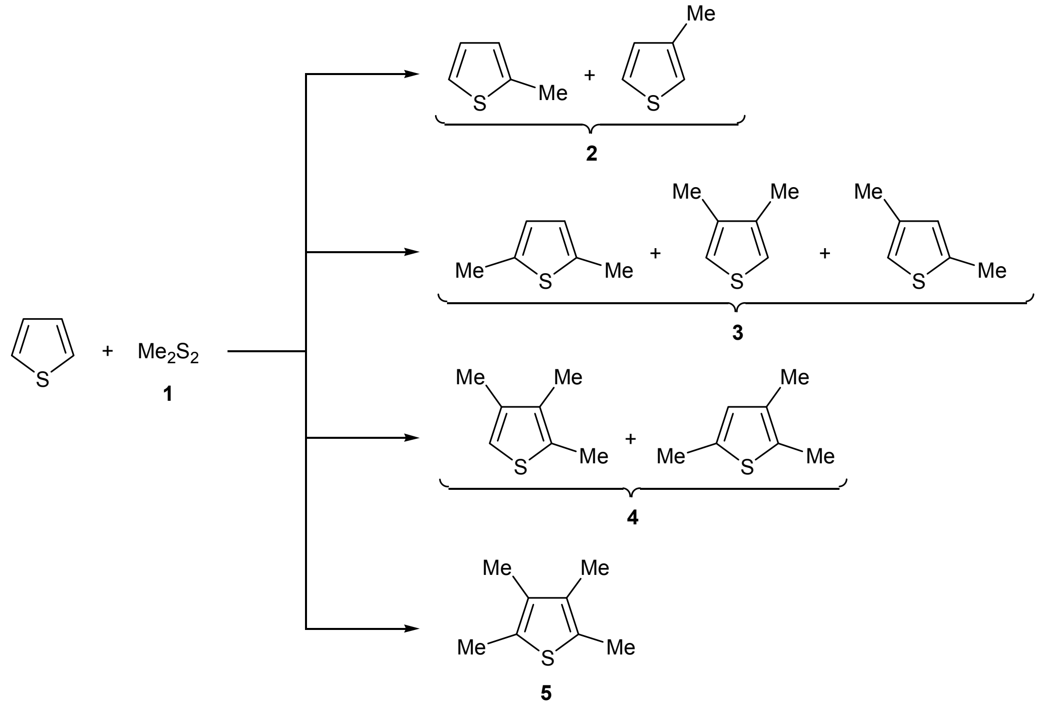
Taking into account the properties of the initial reactants and data on their chemisorption on acid–base catalysts [7], we presumed that disulfide **1** is sorbed on the catalyst surface through coordination of one sulfur atom of **1** to a Lewis acid site and of methyl carbon atom to a basic site. Decomposition of the resulting

Table 2. Yields[a] of methylthiophenes in the reaction of dimethyl disulfide (**1**) with thiophene over Co/HZSM-5 catalyst at 300°C

Conversion of thiophene, %	Methylthiophenes **2**		Dimethylthiophenes **3**		Trimethylthiophenes **4**			Tetramethyl-thiophene (**5**)
	2-Me	3-Me	2,5-Me_2	3,4-Me_2	2,4-Me_2	2,3,4-Me_3	2,3,5-Me_3	2,3,4,5-Me_4
8	20.0	9.1	11.7	10.8	10.2	9.2	0.9	19.0
15	26.8	9.3	12.0	11 2	10.1	9.0	0.9	18.1
22	25.7	8.2	12.2	11.8	10.5	8.2	0.8	17.5
32	26.2	9.0	11.6	11.3	9.4	7.7	0.8	19.1
36	30.0	9.0	12.4	11.6	11.2	7.2	0.7	15.0
49	26.9	8.3	13.7	12.2	10.0	8.1	0.9	16.2
60	27.0	8.1	11.8	10.7	9.5	10.8	1.1	17.0

[a] Calculated on the reacted thiophene, mol %.

Scheme 2.



surface complex involves cleavage of the S–S and C–S bonds in disulfide **1** with the formation of CH_3S and CH_3 surface species. Contact of thiophene with an active protonic site generates thiophenium ion [8] which reacts with surface CH_3 groups to give methyl-substituted thiophene. The conversion of thiophene is not related to the yields of methylthiophenes (Table 2). This means that methylthiophenes are formed directly from thiophene along independent paths (Scheme 2).

Thus, our results showed that the overall yield of methylthiophenes in the reaction of dimethyl disulfide (**1**) with thiophene in the presence of a cobalt-containing zeolite catalyst can attain 94–96% (calculated on the reacted thiophene).

EXPERIMENTAL

The catalyst was cobalt-modified HZSM-5 high-silica zeolite (SiO_2/Al_2O_3 = 39, S_{sp} = 500 m^2/g; Co, 5 wt %) which was prepared as described in [6] and was calcined for 5 h at 530°C in a stream of dry air. The other reagents used were of pure grade.

The reactions were carried out under atmospheric pressure in a flow setup with a fixed bed of catalyst (grain size 0.25–0.5 mm). A fresh portion of the catalyst was used in each run. The system was maintained at a constant temperature. Helium was passed from a cylinder to saturators filled with dimethyl disulfide and thiophene and maintained at a required temperature. The gas mixture was fed into the reactor heated to a required temperature. Samples of the gas mixture were withdrawn intermittently for analysis. High-boiling products were trapped in a cold receiver. The products were identified by GC/MS using an Agilent 7000 gas chromatograph coupled with a Triple Quad mass-selective detector (HP-5MS capillary column, 30 m × 0.25 mm). Quantitative analysis of the product mixtures was performed with an LKhM-8MD chromatograph equipped with a thermal conductivity detector and a 2-m × 3-mm column packed with XE-60 on Chromaton AW-LMCS; carrier gas helium. The contact time was equal to the ratio of the catalyst volume (cm^3) to the gas mixture flow rate (cm^3/s) at room temperature under atmospheric pressure. The conversions of thiophene and dimethyl disulfide and the yields were calculated with respect to the initial reactants and reacted substrate.

REFERENCES

1. Sharipov, A.Kh., *Chem. Technol. Fuels Oils*, 2002, vol. 38, no. 5, p. 340.
2. Belen’kii, L.I., Zakharov, E.P., Kalik, M.A., Litvinov, V.P., Stoyanovich, F.M., Taits, S.Z., and Fabrichnyi, V.P., *Novye napravleniya khimii tiofenov* (New Trends in the Chemistry of Thiophenes), Gol’dfarb, Ya.L., Ed., Moscow: Nauka, 1976.

3. Kulakov, V.N. and Abramovich, V.B., *Khimiya seroorganicheskikh soedinenii, soderzhashchikhsya v neftyakh i nefteproduktakh* (Chemistry of Organosulfur Compounds of Oils and Oil Products), Moscow: Vysshaya Shkola, 1968, vol. 8, p. 28.
4. Lyapina, N.K., *Khimiya i fizikokhimiya seroorganicheskikh soedinenii neftyanykh distillatov* (Chemistry and Physical Chemistry of Organosulfur Compounds from Oil Distillates), Moscow: Nauka, 1984.
5. Mazgarov, A.M. and Vil'danov, A.F., *Pet. Chem.*, 1999, vol. 39, p. 331.
6. Krivoruchko, O.P., Anufrienko, V.F., Paukshtis, E.A., Lyapina, T.V., Burgina, E.B., Yashnik, S.A., Ismagilov, Z.I., and Parmon, V.N., *Dokl. Phys. Chem.*, 2004, vol. 398, nos. 1–3, p. 226.
7. Mashkina, A.V., *Russ. Chem. Rev.*, 2014, vol. 83, p. 733.
8. Belen'kii, L.I., *Chem. Heterocycl. Compd.*, 1992, vol. 28, p. 610.