ISSN 1070-4280, *Russian Journal of Organic Chemistry, 2011, Vol. 47, No. 5, pp. 678–681.* © *Pleiades Publishing, Ltd., 2011.*
Original Russian Text © A.V. Mashkina, 2011, published in Zhurnal Organicheskoi Khimii, 2011, Vol. 47, No. 5, pp. 677–679.

New Method of Dimethyl Sulfide Synthesis

A. V. Mashkina

Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences
Novosibirsk, 630090 Russia; e-mail: amash@catalysis.ru

Received December 2, 2009

Abstract—The synthesis of dimethyl sulfide consists in the reaction of dimethyl disulfide with methanol in the presence of solid catalyst, aluminum γ-oxide. The yield of dimethyl sulfide grows with growing temperature, contact time, and content of methanol in the reaction mixture. At 350–400°C, molar ratio methanol–dimethyldisulfide 2.0–2.5, and total conversion of the reagents the yield of dimethyl sulfide reached 95 mol%.

DOI: 10.1134/S1070428011050046

Dimethyl sulfide is used as extraction reagent, odorant for gases, and as initial raw material for production of dimethyl sulfoxide [1].

A promising source of raw material for preparation of dimethyl sulfide may be dimethyl disulfide, manufactured at the purification of sulfur-containing hydrocarbon mixtures [2]. It was found earlier [3] that in the presence of a series of solid catalysts at the atmospheric pressure and 190–350°C the decomposition of dimethyl disulfide in an inert medium resulted in dimethylsulfide but the process was accompanied with the formation of side products: methanethiol, hydrogen sulfide, carbon disulfide, methane, ethane, and other substances. Consequently the selectivity of dimethyl sulfide formation from dimethyl disulfide does not exceed 56%, and it is not possible to improve it by varying the catalyst composition and the reaction conditions.

In this study with the goal to increase the selectivity with respect to dimethyl sulfide the decomposition of dimethyl disulfide was carried out on a solid catalyst (γ-Al_2O_3) in the presence of methanol that methoxylated the surface of the catalyst easier than dimethyl disulfide [4].

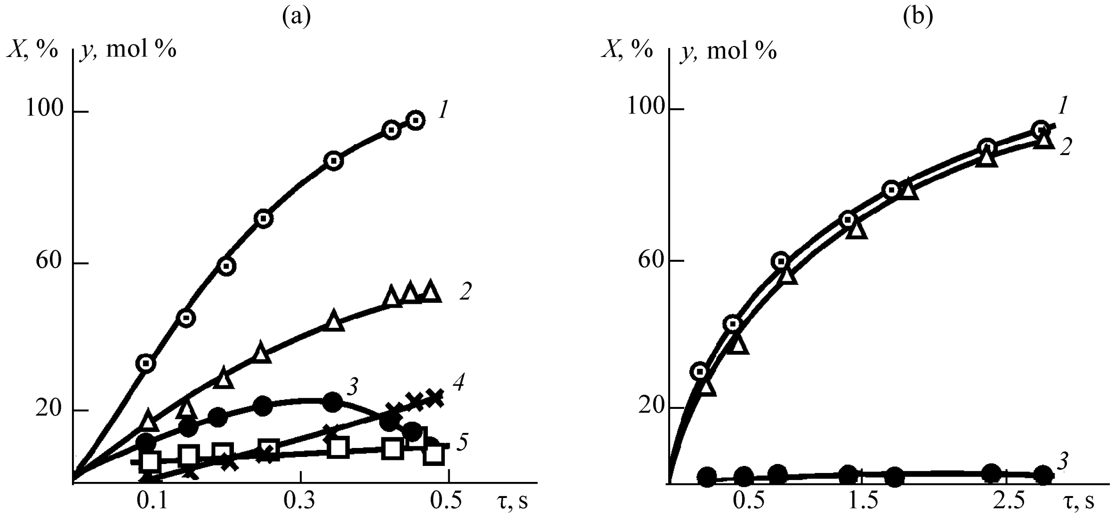
The conversion of dimethyl disulfide with addition of various amounts of methanol was investigated at the contact time providing the dimethyl disulfide conversion in the range 30–98%. For example the figure illustrates the effect of the contact time on the conversion of dimethyl disulfide and on the yields of the main sulfur-containing products at 350°C and molar ratio methanol–dimethyldisulfide 0.5 and 2.6.

At low content of methanol in the reaction mixture alongside the dimethyl sulfide formed the other sulfur-containing products: methanethiol, hydrogen sulfide, carbon disulfide, and also traces of carbon oxysulfide; among the reaction products also methane, ethylene, and carbon oxides were found. The increase in the contact time resulted in the growth of dimethyl disulfide conversion and of the yield of dimethyl sulfide and hydrogen sulfide, but virtually did not affect the yields of the other reaction products.

At excess methanol with respect to dimethyl disulfide its decomposition proceeded giving mainly dimethyl sulfide, and as the side product methanethiol formed in a small yield. The yield of dimethyl sulfide grew with the increase in the contact time and at the total conversion of methanol and dimethyl disulfide the yield attained 95%. At varying contact time the yield of dimethyl sulfide was close to the conversion of dimethyl disulfide. The variation of the degree f conversion of dimethyl disulfide virtually did not affect the selectivity of the dimethylsulfide formation.

Conversion, %	34	41	60	70	82	94	97
Selectivity, %	93	95	94	95	96	93	95

From the kinetic curves of the runs at 350°C and different molar ratios methanol– dimethyl disulfide we



The effect of contact time on dimethyl disulfide conversion (*X*, %) (*1*), yields of sulfur-containing products (*y*, %): dimethyl sulfide (*2*), methanethiol (*3*), hydrogen sulfide (*4*), carbon disulfide (*5*) in the presence of aluminum oxide at 350°C and molar ratio methanol–dimethyl disulfide 0.5 (a) and 2.6 (b).

selected the contact time corresponding to the dimethyl disulfide conversion of 70–73% and determined the yield of reaction products in this point (see the table). At the molar ratio methanol–dimethyl disulfide 0.1–0.2 the composition of sulfur-containing reaction products was the same as at the decomposition of pure dimethyl disulfide, but the yield of dimethyl sulfide and the selectivity of its formation were a little better. With the growing ratio methanol– dimethyl disulfide up to 0.5–1.0 the yield of dimethyl sulfide and the selectivity of its formation notably increased, and at the double and larger methanol excess the main product was dimethyl sulfide, namely, the reaction proceeded as follows:

$$(CH_3)_2S_2 + 2CH_3OH \xrightarrow{[H^+]} 2(CH_3)_2S + 2H_2O,$$

where $[H^+]$ were the protons on the catalyst surface.

The effect of the temperature of the experiment on the parameters of the process was examined at the molar ratio methanol–dimethyl disulfide 2 : 1. At different temperature the contact time required to obtain the dimethyl

Decomposition of dimethyl disulfide in the presence of various content of methanol. Catalyst γ-Al_2O_3, 350°C, dimethyl disulfide conversion 70–73%

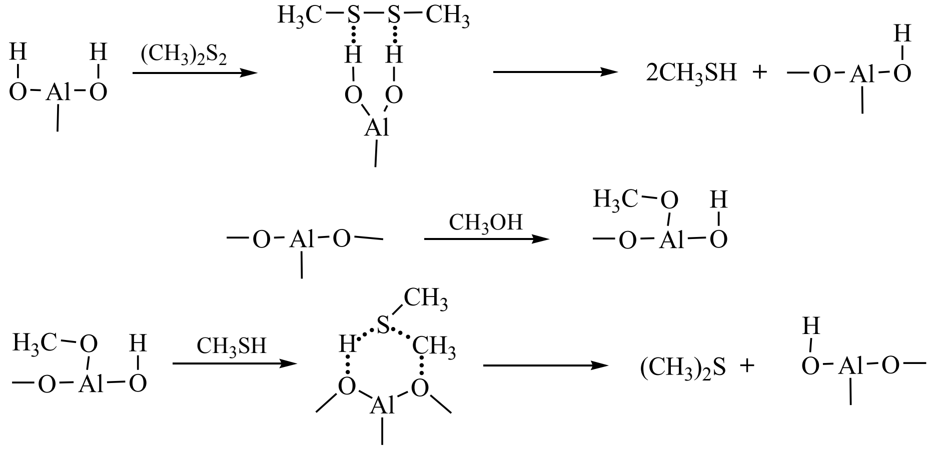
Molar ratio methanol–dimethyl disulfide	Contact time, s	Yield, %				Selectivity with respect to dimethyl sulfide , %
		dimethyl sulfide	metanethiol	hydrogen sulfide	carbon disulfide	
0	0.04	25	23	11	12	36
0.12	0.14	27	16	17	11	38
0.24	0.16	28	18	11	13	40
0.50	0.24	34	19	9	9	47
1.0	0.62	46	11	4	8	66
1.4	0.75	60	7	3	1	85
2.0	1.10	64	5	0	0	91
2.5	1.15	65	5	0	0	95
2.8	1.2	66	4	0	0	94

disulfide conversion of 70–73% was different.

Temperature, °C	250	300	325	350	375	390	400	420	450
Contact time, s	9.0	3.5	1.7	1.1	0.6	0.3	0.25	0.16	0.06
Selectivity with respect to dimethyl sulfide, %	70	78	82	90	93	94	95	93	86

The formation of dimethyl sulfide was observed already at 250°C, but the reaction required a long contact. With growing temperature the process accelerated, and the required contact time decreased: At the temperature growth from 250 to 450°C the contact time decreased 150 times. At the constant temperature the variation in the contact time and consequently in the dimethyl disulfide conversion virtually did not affect the selectivity with respect to dimethyl sulfide, but it grew with temperature from 250 to 400°C and somewhat decreased at higher temperature due to the partial decomposition of dimethyl sulfide [5].

Taking into consideration the data on adsorption of reagents and the results of their transformations on catalysts with diverse acid-base properties of the surface [3, 4, 6–9] it is presumable that the reaction proceeds through the stages of the decomposition of dimethyl disulfide to methanethiol and the dehydration of methanol resulting in the formation of surface CH_3 groups that further react with the formation of dimethyl sulfide. The mechanism of this reaction is evidently similar to that described in [6] for the formation of dimethyl ether from methanol.



The prevailing formation of methoxy groups from methanol impedes the proceeding of the side processes of dimethyl disulfide decomposition thus increasing the selectivity with respect to dimethylsulfide.

As showed the study of the effect of the reaction conditions on the parameters of the process, the preparative synthesis of dimethyl sulfide from dimethyl disulfide and methanol should be carried out at the atmospheric pressure, temperature of 350–400°C, molar ratio methanol–dimethyl disulfide 2.0–2.5, and contact time 2.5–4.0 s. Under these conditions at the total conversion of reagents dimethyl sulfide forms in 95 mol% yield.

EXPERIMENTAL

Methanol and dimethyl disulfide used in the study were of “pure” grade. A ready sample of γ-Al_2O_3 with the specific surface 275 m^2/g was used as the catalyst. The catalyst was dispersed till the size of grains 0.25–0.5 mm and before use it was calcined in the flow of dry air for 5 h at 500°C. The experiments were performed in an installation of flow type at the atmospheric pressure. The glass reactor was filled with catalyst and placed into a tubular electric oven. Methanol and dimethyl disulfide were poured into two different saturators that were at temperature control. At a desired velocity the helium flow was passed through the saturators, then the gas was passed into a mixer and afterwards into the reactor. The initial mixture and reaction products were sampled intermittently for chromatographic analysis. The GLC was performed on a chromatograph LKhM-8MD equipped with the katharometer, column 2 m × 3 mm packed with Paropack R+Q (1 : 1), carrier gas helium.

The contact time was calculated as the ratio of the catalyst volume to the velocity of the gas flow (cm^3/s at the room temperature and the atmospheric pressure. The conversion of dimethyl disulfide, yield of the products, and the selectivity of dimethyl sulfide formation equal to the ratio of its yield to the conversion of dimethyl disulfide were calculated.

REFERENCES

1. Mashkina, A.V., *Kataliz reaktsii organicheskikh soedinenii sery* (Catalysis of Reaction of Organic Compounds of Sulfur), Novosibirsk: Izd. SO RAN, 2005, p. 86.
2. Mazgarov, A.M. and Vil'danov, A.F., *Neftekhimiya*, 1999, vol. 39, p. 371.
3. Mashkina, A.V. and Khairulina, L.N., *Kinetika, Kataliz*, 2009, vol. 50, p. 434.
4. Krylov, O.V. and Matyshak, V.A. *Usp. Khim.*, 1994, vol. 63, p. 585.
5. Koshelev, S.N., Mashkina, A.V., and Kalinina, N.G., *React. Kinet. Catal. Lett.*, 1989, vol. 39, p. 367.
6. Kazanskii, V.B., *Usp. Khim.*, 1988, vol. 57, p. 1237.
7. Lyapina, N.K., Lygin, V.I., and Ulendeeva, L.D., *Usp. Khim.*, 1980, vol. 49, p. 998.
8. Halevi, B. and Vohs, J.M., *J. Phys. Chem. B*, 2005, vol. 109, p. 23976.
9. King, D.H. and Friend, C.M., *Langmuir*, 2004, vol. 20, p. 11443.