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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Development of Technique for Synthesis of Methyl(β-oxyethyl) Sulfide by the Reaction of Ethylene Oxide with Methyl Mercaptan

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Abstract—Reaction of ethylene oxide with methyl mercaptan in the presence of a catalyst, a solution of potassium hydroxide in methyl(β-oxyethyl) sulfide, was studied. Various technological procedures for synthesis of methyl(β-oxyethyl) sulfide were analyzed. The process conditions providing a 98–99% conversion of the starting reagents at a selectivity of 97–98% were suggested.

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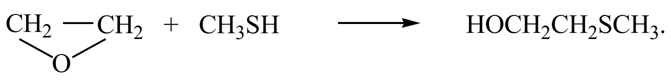
Manufacture of alkyl(β-oxyethyl) sulfides is a topical task because compounds of this class have found wide application as starting products for production of plant-protecting agents (Tinox, methyl mercaptophos) [1], stimulants of fructification and fruit ripening [2], and medicinal preparations [3]. For example methyl(β-oxyethyl) sulfide is a starting product for synthesis of Sulfet, a preparation raising the mass of cereal crops from unit area and stimulating plant growth [2], which is of no small importance for most of climactic zones of the country.

Various methods for synthesis of methyl(β-oxyethyl) sulfide are known [4–14]. An analysis of these methods demonstrated that the most technologically convenient is that based on the reaction of ethylene oxide with alkyl mercaptans with a yield of 75–81%. In this study, we examined this reaction using technical-grade ethylene oxide (**I**) and methyl mercaptan (**II**) manufactured by Volga plant of organic synthesis and used to obtain methionine accroding to Scheme 1.

It should be noted that technical-grade methyl mercaptan contains, in addition to dimethyl sulfide and dimethyl sulfoxide (which are inert under the reaction conditions), reactive impurities, hydrogen sulfide and moisture. Therefore, the main process may be accompanied by side reactions (Scheme 2).

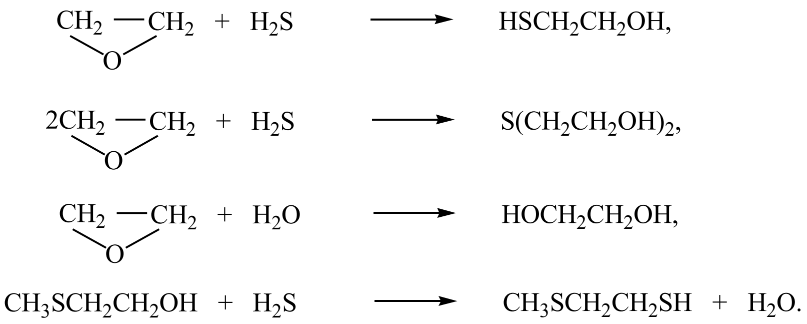
The reaction of α-oxides with alkyl mercaptans has autocatalytic nature, which is favored by the final products of the reaction [15]. It is known that reactions of α-oxides are accelerated by catalysts of acid and base types. We studied the effect of catalysts of these different types on the reaction of methyl mercaptan with ethylene oxide, including such catalysts as potassium hydroxide, sulfuric acid, and titanium tetrachloride (Table 1). It can be seen from the data in the table that acid catalysts provide only a 50–55% conversion under the conditions specified. With a 10% solution of potassium hydroxide in ethanol, the conversion of the reactants was 99%. Use of ethanol, water, and the final product as the catalysts of the reactions was inefficient in the condition under

Scheme 1.



I **II** **III**

Scheme 2.



study. There, we first performed further study with a 10% solution of potassium hydroxide in ethanol as the catalyst. However, in doing so, we found that ethanol can be replaced in the catalyst with methyl(β-oxyethyl) sulfide. This compound easily provided dissolution of KOH in a concentration of 10%. At a temperature of 80°C (recommended in the patent [14]), equimolar ratio between the reactants, and a catalyst content of 0.1 wt % relative to the mass of raw materials, the conversion of the reactants reached a value of 99% in 30 min (Fig. 1).

It was found that a nearly quantitative yield is provided in 30 min even at lower temperatures in the range 30–40°C (Fig. 2).

Replacement of ethanol with methanol in the catalyst at its same content in the reaction mixture at a temperature of 30–40°C and equimolar ratio between the reactants has no effect on the reaction duration and yield of methyl(β-oxyethyl) sulfide. In this case, the content of the main substance in the technical-grade product is no less than 98%. Taking into account that there is no significant effect of methanol on the reaction parameters and on the quality and quantity of the product obtained and application of this alcohol under industrial conditions is considerably more dangerous, we recommend to use a 10% solution of potassium hydroxide in methyl(β-oxyethyl) sulfide as the catalyst. The exclusion of the alcoholic component from the catalyst composition (be it ethanol or methanol) and its replacement with the target product can markedly simplify the subsequent stage of evaporation of low-boiling impurities.

Raw methyl(β-oxyethyl) sulfide obtained in the synthesis stage contains both unreacted starting substances, together with their components, and by-products of the reaction. For the most part, these impurities have low boiling points and can be easily separated from the main mass of the target product. A light fraction can be evaporated from the reaction mass both under atmospheric pressure and in a low vacuum (residual pressure ~200 mm Hg) at a comparatively low temperature (58–60°C). The last variant is preferable because it does not lead to any increase in

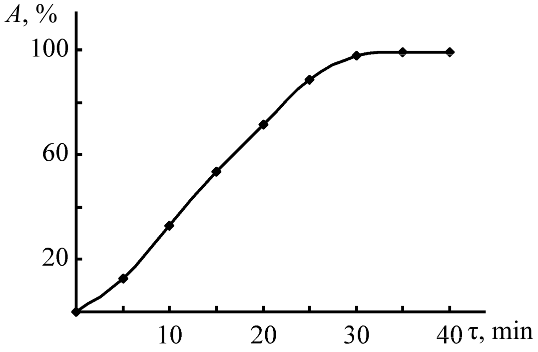


Fig. 1. Yield A of methyl(β-oxyethyl) sulfide vs. the reaction duration τ. Temperature 80°C, 1 : 1 molar ratio between ethylene oxide and methyl mercaptan, catalyst content 0.1% relative to the mass of raw materials (10% solution of KOH in ethanol).

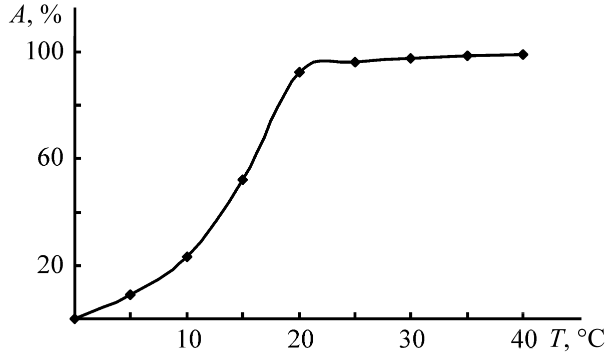
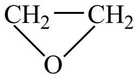


Fig. 2. Effect of the reaction temperature T on the yield A of methyl(β-oxyethyl) sulfide. Molar ratio between ethylene oxide and methyl mercaptan 1 : 1, KOH catalyst content 0.1 wt %, reaction duration 30 min.

Table 1. Influence of catalysts on the reaction between ethylene oxide and methyl mercaptan. Temperature 80°C, reaction duration 180 min

Reagent mass, g		Catalyst	Catalyst content, % relative to the reagent mass	Conversion of the starting reagents, %	Content of $HOCH_2CH_2SCH_3$ in the raw product, %
	CH_3SH				
0.44	0.48	KOH	1	99.0	97.9
0.44	0.48	H_2SO_4	1	55.1	97.1
0.44	0.48	$TiCl_4$	1	50.3	96.8
0.44	0.48	C_2H_5OH	1	0	–
0.44	0.48	H_2O	1	0	–
0.44	0.48	$HOCH_2CH_2SCH_3$	1	0	–
0.66	0.72	KOH	0.1	99.8	98.3

the content of high-boiling impurities, various products of condensation of the target product, and provides exhaustive evaporation of low-boiling impurities during 2 h.

The composition and structure of the products obtained was confirmed by IR and ^{1}H NMR spectroscopic data, as well as by the results of thin-layer and gas-liquid chromatography.

Although methyl(β-oxyethyl) sulfide has not been manufactured in the Soviet Union and Russia, it should be noted that its analog, ethyl(β-oxyethyl) sulfide, was industrially produced in an amount of 1.5–2 thousand tons in the 1960s in manufacture of methyl mercaptophos. The technological process comprised two stages: synthesis of raw ethyl(β-oxyethyl) sulfide and evaporation of the light fraction from the reaction mass. The process was performed in the batch mode in a reactor with a jacket, stirrer, and bubblers for delivery of components in the obligatory presence of a "seed," technical-grade ethyl(β-oxyethyl) sulfide in an amount of 10–15% relative to the working volume of the reactor. A 10% solution of potassium hydroxide in ethanol served as the catalyst. The process occurring at 50–80°C was monitored by the decrease in the reactor pressure. After the synthesis was complete, the residual pressure was relieved to the system for purification of exhaust gases and the reaction mixture was kept at the synthesis temperature in a low vacuum (residual pressure 200–300 mm Hg). The content of the main substances in the resulting target product was no less than 98% at a nearly quantitative yield.

An important disadvantage of the process is that is performed at an elevated pressure, which poses additional industrial and technological difficulties when explosive, readily inflammable, and combustible liquids are used {even methyl(β-oxyethyl) sulfide is a combustible liquid: flash point 76°C, ignition point 78°C, self-ignition point 215°C; lower concentration limit of flame propagation, 2 vol % (calculation); upper and lower temperature limits of flame propagation: 72 and 97°C, respectively [18]}. The process can be performed under atmospheric pressure via reaction in the medium of the target product only in the case when the height of the product layer provides not only solubility of the delivered raw material in this layer, but also the residence time of the reagents required for their interaction. These conditions can be satisfied if the reaction of ethylene oxide with methyl mercaptan is performed in babble and packed columns. The optimal synthesis mode of methyl(β-oxyethyl) sulfide was sought for both columns by the mathematical experiment design method. In doing so, it was necessary to evaluate the effect (significance) of technological factors [19].

It was found that the process in which methyl(β-oxyethyl) sulfide is synthesized in a bubble column is described by a regression equation that is adequate to the experiment:

$$y = 2.30 + 0.26X_1 - 0.083X_2 + 350.22X_3 + 9.13X_4,$$

where y is the yield of the product (%); X_1, temperature (°C); X_2, delivery rate of reagents (ml min^{-1}); X_3, mass fraction of the catalyst (wt %); and X_4, level of the reaction mass in the reactor, related to the column diameter.

As follows from the mathematical model, the strongest influence on the conversion of the reagents and on the yield of the product is exerted by the catalyst concentration and by the level of the reaction mass in the reactor, related to the column diameter. The process temperature in the range under study and the delivery rate of the reagents affect the conversion only slightly.

Depending on the synthesis conditions, the conversion of the starting reagents is 25–99%, and the yield of methyl(β-oxyethyl) sulfide, 24.3–97.2% (Table 2). Using the data in the Table 2, we developed a mathematical model and found modes providing the maximum yield of the product: equimolar ratio between ethylene oxide and methyl mercaptan; catalyst content 0.05 wt %; delivery rate of ethylene oxide and methyl mercaptan, 16.8 l h^{-1}; reaction temperature 30°C, ratio between the reaction mass layer and column diameter, ≥8.

The process in which methyl(β-oxyethyl) sulfide is obtained in the packed column is described by a regression equation adequate to the experiment:

$$y = 96.1 - 0.17X_1 - 0.05X_2 + 0.76X_3 + 73.4X_4 + 2.79X_5$$

where y is the yield of the product (%); X_1, temperature (°C); X_3, rate of column reflux (ml min^{-1}); X_4, mass fraction of the catalyst (wt %); and X_5, ratio between the packing height and column diameter.

All the coefficients in the equation are statistically significant. It can be seen that, in the factor variation range under study, raising the temperature and the delivery rate adversely affects the conversion. An increase in the rate of column reflux, catalyst concentration, and packing layer height is accompanied by a rise in the conversion and in the yield of the target product. The dependence of the reaction rate on the amount of the catalyst indicates that the reaction occurs under kinetic control. A decrease in the packing height and an increase in the reagent delivery rate results in that the contact time of reagents in the reaction zone becomes shorter and, as a consequence, the conversion decreases and

Table 2. Synthesis of raw methyl(β-oxyethyl) sulfide in a bubble column

Run no.	Delivery rate of ethylene oxide	Delivery rate of methyl mercaptan	Delivery rate of 10% solution of KOH in methyl(β-oxyethyl) sulfide, ml h^{-1}	T, °C	Ratio between the fluid layer height and the column diameter	Catalyst content, %	Conversion of starting reagents, %	Raw methyl(β-oxyethyl) sulfide				
	l h^{-1}							amount of product in unit time, g h^{-1}	content of the main substance, %	yield, %	d_4^{20}, g cm^{-3}	n_D^{20}
1	4.2	4.2	0.08	30	2.0	0.005	25	4.3	97.1	24.3	1.061	1.4910
2	4.2	4.2	0.81	30	8.0	0.05	99	17.1	97.8	96.8	1.063	1.4924
3	16.8	16.8	3.24	30	2.0	0.05	48	33.1	98.2	47.1	1.062	1.4920
4	16.8	16.8	0.32	30	8.0	0.005	84	57.9	97.9	82.2	1.062	1.4916
5	4.2	4.2	0.08	50	8.0	0.005	94	16.2	98.0	92.1	1.064	1.4924
6	4.2	4.2	0.81	50	2.0	0.05	52	8.9	97.8	50.9	1.063	1.4918
7	16.8	16.8	0.32	50	2.0	0.005	32	22.1	98.3	31.4	1.061	1.4913
8	14.8	14.8	3.24	50	8.0	0.05	99	68.4	98.2	97.2	1.064	1.4924

a breakthrough of the reagents occurs. In contrast to the case of the bubble column, raising the reaction temperature in the packed column with a sprinkling leads to a decrease in the conversion of the reagents. According to the data in Table 3, a 97.9–99% content of the target product in raw methyl(β-oxyethyl) sulfide can be provided by maintaining the optimal technological parameters (equimolar ratio between ethylene oxide and methyl mercaptan; catalyst content 0.005 wt %; delivery rate of ethylene oxide and methyl mercaptan, 16.8 l h^{-1}; reaction temperature 25°C, ratio between the reaction mass layer and column diameter, ≥1).

After volatile products are removed in a vacuum, the content of methyl(β-oxyethyl) sulfide is no less than 98.8% (Table 4, run nos. 5 and 8). In vacuum distillation of the raw product, the yield of the target product is 80.5 wt %, and the amount of still bottoms, 17.2 wt %. A chromatographic analysis demonstrated that methyl(β-oxyethyl) sulfide constitutes 94% of the still bottoms. In this context, a conclusion can be made that there is no need to purify the product by vacuum distillation because the resulting technical-grade methyl(β-oxyethyl) sulfide is a high-quality product (Table 4) which contains no less than 99% main substance and can be industrially processed into required commercial products. Comparative analysis of the parameters of the process under study in the bubble and packed columns (Tables 2 and 3) indicates that the conversion of the starting reagents is higher in the packed column. For example, a 98–99% conversion can be reached at lower temperatures and smaller catalyst contents, which predetermines the higher output capacity of this technique.

Table 3. Synthesis of raw methyl(β-oxyethyl) sulfide in a packed column

Run no.	Delivery rate of ethylene oxide	Delivery rate of methyl mercaptan	Rate of column sprinkling	T, °C	Ratio between the packing bed height and the column diameter	Catalyst content, %	Conversion of starting reagents, %	Raw methyl(β-oxyethyl) sulfide				
	l h^{-1}							amount of product in unit time, g h^{-1}	content of the main substance, %	yield, %	d_4^{20}, g cm^{-3}	n_D^{20}
1	39.6	39.6	1.2	50	4.0	0.05	90	146.5	98.5	88.7	1.062	1.4920
2	39.6	39.6	1.2	50	1.0	0.005	63	102.6	98.8	62.2	1.063	1.4923
3	39.6	39.6	0.6	50	4.0	0.005	78	126.9	99.0	77.2	1.064	1.4924
4	16.8	16.8	0.6	50	1.0	0.005	88	60.7	98.7	86.9	1.061	1.4921
5	16.8	16.8	0.6	25	4.0	0.005	98	67.6	98.4	96.4	1.063	1.4924
6	16.8	16.8	0.6	25	1.0	0.05	99	68.3	98.8	97.8	1.062	1.4924
7	16.8	16.8	1.2	25	4.0	0.05	96	66.2	98.0	94.1	1.062	1.4923
8	39.6	39.6	1.2	50	1.0	0.05	95	154.7	97.9	93.0	1.063	1.4919
9	39.6	39.6	0.6	25	1.0	0.005	70	113.9	99.0	69.3	1.062	1.4918
10	39.6	39.6	1.2	50	4.0	0.005	90	146.5	99.1	89.1	1.062	1.4922
11	16.8	16.8	1.2	25	1.0	0.05	98	67.6	98.3	96.3	1.062	1.4917
12	16.8	16.8	1.2	50	1.0	0.005	98	67.6	99.2	97.2	1.064	1.4924
13	39.6	39.6	0.6	50	1.0	0.05	57	92.8	98.9	52.9	1.062	1.4919
14	16.8	16.8	0.6	50	4.0	0.05	99	68.3	99.0	98.0	1.065	1.4924
15	16.8	16.8	1.2	25	4.0	0.005	99	68.3	99.1	98.1	1.064	1.4924
16	39.6	39.6	0.6	25	4.0	0.05	82	133.5	98.1	80.4	1.063	1.4923

Thus, on performing a study of the process in which methyl(β-oxyethyl) sulfide is synthesized, we developed optimal conditions of synthesis and isolation of a high-quality technical-grade product. In these conditions, the synthesis can be carried out under atmospheric pressure at lower temperatures (30–40°C) in a short time (0.5–1 h) in nearly quantitative yield.

EXPERIMENTAL

We used technical-grade ethylene oxide, GOST (State Standard) 7568–88 (main substance 99.9%, water ≤0.01%). In conformity with manufacture regulations, methyl mercaptan produced at Volga plant of organic synthesis had the following composition (%): main substance not less than 97.0, water ≤0.20, hydrogen sulfide ≤0.10, methanol 0.5–2.0, dimethyl sulfide ≤0.05, dimethyl sulfoxide ≤0.10, light fractions ≤1.01.

^{1}H NMR spectra were measured on a Bruker IC-200 spectrometer with a working frequency of 200 MHz and DMFA-d_6 as a solvent and reference substance; IR spectra were obtained on a UR-20 spectrometer. The chromatographic analysis was made on a Khrom 3 laboratory chromatograph (flame-ionization detector, 5% polymethylsiloxane supported by Chromaton of the 0.025–0.30-mm fraction as a sorbent, carrier-gas hydrogen, column length 2.5 mm, inner diameter 3.0 mm; operation mode: evaporator temperature 275°C, column temperature 250°C, carrier gas flow rate 40–50 cm^3 min^{-1}, 1-μl sample introduced.

Synthesis of methyl(β-oxyethyl) sulfide from ethylene oxide and methyl mercaptan in sealed ampules. We preliminarily cooled a calibrated ampule to –10°C and then, without removing the ampule from the Dewar vessel, condensed into it 0.51 ml of ethylene oxide and 0.54 ml of methyl mercaptan from cylinders. A 0.02-ml portion of a 10% solution of potassium hydroxide in ethanol was introduced with a microsyringe. The ampule was sealed and kept at 80°C for 3 h. Then it was cooled to –20°C, opened, and kept at 30°C for 30 min to remove volatile impurities and its content was analyzed. The reaction product was a colorless fluid, bp 76 ± 0.4°C (24 mm Hg), n_D^{20} 1.4924, d_4^{20} 1.064 g cm^{-3}. Yield 0.916 g (99%), content of methyl(β-oxyethyl) sulfide is 97.9%, technical-grade methyl(β-oxyethyl) sulfide has R_f = 0.36 (2 : 1 mixture

Table 4. Isolation of methyl(β-oxyethyl) sulfide

Run no.[a]	Yield of methyl-(β-oxyethyl) sulfide, %	Content of methyl-(β-oxyethyl) sulfide, %	bp, °C (*P*, mm Hg)	d_4^{20}, g cm^{-3}	n_D^{20}
Process in a bubble column					
Evaporation of low-boiling fractions of raw methyl(β-oxyethyl) sulfide					
2	99.2	99.4	58±2 (200)	1.064	1.4924
8	98.8	99.3	58±2 (200)	1.064	1.4923
Vacuum distillation of technical-grade methyl(β-oxyethyl) sulfide ческого					
2	84.5	99.6	70±2 (20)	1.064	1.4924
8	83.6	99.4	71±2 (20)	1.064	1.4924
Process in a packed column					
Evaporation of low-boiling fractions of raw methyl(β-oxyethyl) sulfide					
5	98.9	99.2	58±2 (200)	1.064	1.4923
15	99.4	99.0	58±2 (200)	1.064	1.4924
Vacuum distillation of technical-grade methyl(β-oxyethyl) sulfide					
5	81.8	99.3	78±1 (23)	1.064	1.4924
15	80.7	99.1	79±1 (23)	1.064	1.4924

[a] Run no. corresponds to the data in Tables 2 and 3.

of hexane and acetone as eluent). Published data [18]: bp 180°C, n_D^{20} 1.4924, d_4^{20} 1.064 g cm^{-3}.

IR spectrum, ν, cm^{-1}: 1325 (CH_3–), 2850 (–CH_2–), 2962 (CH_3–S–), 3420 (–OH). ^{1}H NMR spectrum (DMFA-d_6), δ, ppm: 2.09 s (CH_3–), 2.63 t (–CH_2–S–, J = 6 Hz), 3.90 t (HO–$\underline{CH_2}$–, J = 6 Hz), 4.78 m ($\underline{HO}$–CH_2–). Found (%): C 39.10, H 8.75, S 34.79. C_3H_8OS. Calculated (%): C 39.02, H 8.52, S 34.23.

The results of the study are presented in Table 1 and Fig. 1.

Reaction of ethylene oxide with methyl mercaptan in the bubble column. The synthesis reactor had the form of a glass column with a diameter of 15 mm and height of 250 mm, equipped with a jacket and a reflux condenser. The lower part of the column, with a sealed-in porous plate, was charged to a height of 135 mm with methyl(β-oxyethyl) sulfide containing 0.05 wt % potassium hydroxide. The reactor temperature was raised to 30°C by delivering warm water into the jacket. The starting reagents, ethylene oxide and methyl mercaptan, were batched from cylinders into the lower part of the reactor at a rate of 16.8 l h^{-1}. The catalyst, 10% solution of potassium hydroxide in methyl(β-oxyethyl) sulfide, was delivered with a syringe-type metering device at a rate of 0.35 g h–1. After the temperature of 40°C was reached, cold water was delivered into the jacket to maintain the reactor temperature at 30–40°C. Unreacted gases were transferred through the reflux condenser into a Tishchenko flask filled with an alkali, to be absorbed there. The process was monitored by readings of rotameters at the reactor inlet and outlet, and also by the amount and composition of the resulting reaction mass, which was analyzed by chromatography. The reaction product was a colorless fluid. We obtained 136.8 g of raw methyl(β-oxyethyl) sulfide (yield 99%), with the content of the main substance being 97.4% (n_D^{20} 1.4922, d_4^{20} 1.062 g cm^{-3}).

Table 2 lists the results of our study of the reaction between ethylene oxide and methyl mercaptan in the bubble column.

Reaction of ethylene oxide with methyl mercaptan in the packed column. Ethylene oxide and methyl mercaptan were delivered at a rate of 30 l h^{-1} into the lower part of the packed column with a diameter of 20 mm, height of 350 mm, and packing bed height of 80 mm, equipped with a jacket and a reflux condenser. Methyl(β-oxyethyl) sulfide containing 0.05 wt % potassium hydroxide was delivered with a batching pump into the upper part of the column in an amount of 1.2 l h^{-1}. The reaction temperature was maintained in the range 25–35°C by passing cold water through the jacket. Unreacted substances were condensed in the reflux condenser and returned into the reactor. The exhaust gases were delivered into a Tishchenko flask filled with a solid alkali, to be absorbed there. The reaction product was collected in the still of the column. The reaction course was monitored by the difference between the readings of rotameters at the reactor inlet and outlet, as well as by the amount of the resulting liquid phase and its composition, determined by chromatography. The reaction product was a colorless fluid. We obtained 236.8 g of raw methyl(β-oxyethyl) sulfide (yield 96%, content of the main substance 97.7%, n_D^{20} 1.4918, d_4^{20} 1.061 g cm^{-3}).

Table 3 lists the results of our study of the reaction between ethylene oxide and methyl mercaptan in the packed column.

Isolation of methyl(β-oxyethyl) sulfide. To remove low-boiling by-products from raw methyl(β-oxyethyl) sulfide, we placed 200 g of raw methyl(β-oxyethyl) sulfide in a distillation flask and kept the flask at 58–60°C and a residual pressure of 200 mm Hg for 2 h. The weight of the residue, technical-grade methyl-(β-oxyethyl) sulfide, was 197.2 g (yield 98.6%). The content of the main substance was no less than 99.0%. Then the residue was distilled at 80–82°C and a residual pressure of 32 mm Hg. We obtained 158.7 g of methyl(β-oxyethyl) sulfide (80.5%), n_D^{20} 1.4924, d_4^{20} 1.064 g cm^{-3}.

CONCLUSIONS

(1) It was demonstrated that the reaction of ethylene oxide with methyl mercaptan in the presence of potassium hydroxide enables synthesis of methyl-(β-oxyethyl) sulfide in 98–99% yield.

(2) The process in which methyl(β-oxyethyl) sulfide is synthesized in bubble and packed columns was optimized. The mathematical experiment design method was employed to determine the optimal parameters with which the reaction can be performed under atmospheric pressure in comparatively mild conditions to give a technical-grade product with the content of the main substance no less than 99%.

(3) It was shown that synthesis in a bubble column is more technologically convenient than that in a packed column because of the unnecessary sprinkling. At the

same time, it was found that the packed column has a higher output capacity. Thus, it is recommended that a particular column should be chosen depending on the production purpose.

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