INVESTIGATION IN THE SERIES OF CONDENSED HETEROAROMATIC SYSTEMS, INCLUDING A THIOPHENE RING

COMMUNICATION 16.* CATALYTIC SYNTHESIS OF BENZO-[b]-THIOPHENE AND THIENO-[3,2-b]-THIOPHENE

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The substantial growth of the number of investigations in the field of the chemistry of organosulfur compounds observed in recent years, in particular, for condensed heteroaromatic systems including a thiophene ring, has been due to a substantial degree to an expansion of the scales of utilization of sulfur and high-sulfur petroleums in the oil refining industry. One of the compounds of the indicated type, benzo-[b]-thiophene, is an important intermediate product in the industry of thioindigoid dyes [2], complex-forming compounds [3], and in organic synthesis. The syntheses of benzothiophene described in the literature chiefly include vapor phase catalytic conversion of ethylbenzene or styrene and a sulfur donor (H_2S, SO_2, S) over dehydrogenation catalysts [4-9]. Close to these are a number of other studies on the catalytic synthesis of benzothiophene [10-13]. Another compound of a similar type is thieno-[3,2-b]-thiophene. The methods of production both of unsubstituted thieno-[3,2-b]-thiophene by intramolecular cyclization of esters of (2-formyl-3-thienylmercapto)-acetic acid [14], and of alkyl-substituted thieno-[3,2-b]-thiophene by the cyclization of acetonylmercaptothiophenes [14, 15] or alkyl-substituted esters of (2-formyl- or 2-acetyl-3-thienylmercapto)-acetic acid [16, 17], which we described, as well as others, known from the literature (see, for example, [18]), while permitting the production of products in pure form and with an acceptable yield, usually include several steps. Insofar as we know, up to the present time there have been no data on a catalytic method of producing thieno-[3,2-b]-thiophene.

In connection with the development of investigations in the field of condensed heteroaromatic systems in our laboratory, we were interested in investigating reactions of ethyl benzene and styrene, as well as 2-ethylthiophene, with SO_2 and H_2S in the presence of catalysts of the type of Al_2O_3, Fe/Al_2O_3, Fe_2O_3/Al_2O_3, and Cr_2O_3/Al_2O_3 at atmospheric pressure and various temperatures for the production of benzothiophene and thieno-[3,2-b]-thiophene. Let us note that only a limited number of data have been cited in the literature [5, 8], pertaining to the interaction of ethylbenzene with SO_2, and there are no data at all on the interaction of 2-ethylthiophene with SO_2.

EXPERIMENTAL METHOD

Ethylbenzene and styrene were preliminarily redistilled, chromatographically pure, bp 136 and 146°, n_D^{20} 1.4960 and 1.5465, respectively; 2-ethylthiophene was produced by reducing 2-acetothienone, bp 133-134°, n_D^{20} 1.5128; SO_2 was from a cylinder (preliminarily passed through conc. H_2SO_4); H_2S was from a Kipp apparatus (Fe_2S, 17% HCl), preliminarily passed through Tishchenko bottles with water. The velocity of SO_2 was measured with a rheometer.

A laboratory flow-type catalytic apparatus with automatic delivery of the substances with a syringe, connected to an electric motor, was used. The reactor was a quartz tube (inner diameter 20 mm, length

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*For Communication 15 see [1].

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1000 mm). The apparent volume of the catalyst in the reactor was 100 ml. Catalyst: 1) Al_2O_3; 2) 6 mole % Fe_2O_3/94 mole % Al_2O_3; 3) Fe/Al_2O_3 (prepared by reducing Fe_2O_3/Al_2O_3 in a stream of H_2 at 550-600°); 4) 6 mole % Cr_2O_3/94 mole % Al_2O_3. Catalysts 2-4 were prepared by impregnating Al_2O_3 with an aqueous solution of ferric or chromium nitrate, followed by drying and calcination at 500° for 6 h.

In the experiment we took 10 g of 2-ethylthiophene, ethylbenzene, or styrene. The products of catalysis were collected in a cooled trap and analyzed by the method of gas–liquid chromatography on an LKhM-7A chromatograph of the Special Design Office of the Institute of Organic Chemistry of the Academy of Sciences of the USSR with programming of the temperature from 75 to 220° at a rate of temperature change of 15 deg/min. Stainless steel columns (length 190 mm, inner diameter 3 mm), filled with chromosorb-W 80/100, impregnated with polyethylene glycol adipate (10%) were used; the carrier gas was helium, velocity 20 ml/min. Benzene, toluene, ethylbenzene, styrene, phenylacetylene, acetophenone, and benzothiophene were used as standard substances for determining the composition of the reaction products in the case of the use of ethylbenzene and styrene; the standards were thiophene, 2-methylthiophene, 2-ethylthiophene, 2-vinylthiophene, 2-acetothienone, thieno-[2,3-b]-thiophene, and thieno-[3,2-b]-thiophene when 2-ethylthiophene was used. The specific surface of the catalyst was determined by the method of gas –liquid chromatography [19] according to the change in the volume of retention of toluene as a function of the surface of the catalyst. A weighed sample of the catalyst (0.3-1 g) with grain size 0.25-0.5 mm was loaded into a stainless steel tube (length 20 mm, inner diameter 3 mm), which served as the chromatographic column. Temperature 40°, carrier gas helium, velocity 40 ml/min, amount of toluene introduced 0.7 mg.

The reaction products obtained with various catalysts were treated by the same method. The data on the treatment of the catalyzate obtained by passing a mixture of ethylbenzene (volume velocity 0.1 h^{-1}) and SO_2 (in a 4 : 1 molar ratio) over Fe_2O_3/Al_2O_3 at 550° and atmospheric pressure can serve as an example. From 100 ml (86.7 g) ethylbenzene we obtained 88 ml of the organic portion of the catalyzate, which, after washing with water, a 10% solution of NaOH, and water, was dried for 24 h over KOH. The dried catalyzate (84 ml, 76 g), according to the data of gas–liquid chromatography, had the following composition: 12.5% benzothiophene, 33% styrene, 47.1% ethylbenzene, 0.7% acetophenone, 1% benzene and toluene, and 5.7% condensation products. When it was redistilled under vacuum, the following fractions were obtained: I) 57-90° (65 mm), 61.2 g; II) 90-136° (65 mm), 10.5 g; III) residue, 4.3 g. Fraction II was redistilled on a fractional distillation column with an efficiency of 30 theoretical plates at 12 mm. The following fractions were obtained: I) up to 80°, 0.3 g; II) 80-92°, 0.5 g; III) 92-110°, 9 g; IV) residue, 0.7 g. Fraction II consisted primarily of acetophenone with an impurity of benzothiophene, while fraction III consisted of benzothiophene with a small impurity of acetophenone. The benzothiophene obtained (~95% purity) was subjected to repeated sublimation under vacuum at 0.5-1 mm. After this, the purity of benzothiophene was 99% (mp 32°). To confirm the data of gas–liquid chromatography on the presence of acetophenone from the fraction 80-92° (12 mm), we produced the semicarbazone with mp 196-198° (after recrystallization from 50% alcohol). A mixed sample with known acetophenone semicarbazone gave no depression of the melting point.

The residues remaining after redistillation of the organic portion of the catalyzate were extracted with alcohol to isolate 2,5-diphenylthiophene, which, as was shown in [9], is formed under analogous conditions in the interaction of acetophenone with H_2S. After recrystallization of the isolated crystalline product from n-heptane, benzene, and acetone, we obtained 2,5-diphenylthiophene with mp 149-150°. According to the data of [9]: mp 149.2-149.7°.

The catalyzates obtained in the interaction of 100 g 2-ethylthiophene with SO_2 over Cr_2O_3/Al_2O_3 (rate of delivery of 2-ethylthiophene 0.2 h^{-1}, ratio of 2-ethylthiophene : SO_2 = 4 : 1, temperature 450°) were treated analogously. When 75.7 g of the washed and dried catalyzate, containing, according to the data of gas –liquid chromatography, 5.3% thiophene, 3.1% 2-methylthiophene, 51.2% 2-ethylthiophene, 28.5% 2-vinylthiophene, 2.7% 2-acetothiophene, and 9.2% thieno-[3,2-b]-thiophene, was redistilled, the following fractions were obtained: I) 40-105° (60 mm), 63.9 g; II) 95-130° (15 mm), 6.6 g; III) residue, 3 g. The catalyst was regenerated in a stream of air at 700° for 6 h, then activated by passing through SO_2 (400°, 1 h), and fraction I was subjected to repeated catalysis. After treatment and redistillation of the catalyzate, the following fractions were obtained: I) 47.3 g 40-105° (60 mm); II) 4.2 g 95-130° (15 mm); III) 2 g residue. The second fractions were combined, and 10.5 g of the product was redistilled on a column; a thienothiophene fraction with bp 98-110° (15 mm), 9.5 g, was isolated in this case, with a content of thieno-[3,2-b]-thiophene fluctuating from 75 to 90% in different experiments. Thieno-[3,2-b]-thiophene was purified by the method of zone melting. Found: C 51.29, 51.39; H 2.63, 2.75; S 45.56, 45.87%. $C_6H_4S_2$. Calculated: C 51.40; H 2.87; S 45.75%.

TABLE 1. Composition of the Reaction Products of Ethylbenzene and Styrene with SO_2 and H_2S

Initial hydrocarbon	Ratio of hydrocarbon to SO_2 or H_2S, M	Yield of organic part of catalyzate, %	Composition, %					Yield of benzothiophene, % of hydrocarbon passed through	Catalyst
			benzene and toluene	ethylbenzene	styrene	acetophenone	benzothiophene		
Ethylbenzene	SO_2 1 : 4	99	—	91,0	8,4	—	0,6	0,6	—
Ethylbenzene	SO_2 1 : 4	95	3,9	26,2	51,0	2,6	16,3	15,5	Cr_2O_3/Al_2O_3
Styrene	SO_2 1 : 4	80	13,0	34,2	34,6	—	18,2	14,5	Cr_2O_3/Al_2O_3
Styrene	H_2S Excess	95	12,3	47,6	26,3	—	13,8	13,1	Cr_2O_3/Al_2O_3
Ethylbenzene	SO_2 1 : 4	90	5,0	42,7	42,1	0,2	10,0	9,0	Al_2O_3
Styrene	SO_2 1 : 4	80	9,6	36,2	32,4	—	21,8	17,5	Al_2O_3
Styrene	H_2S Excess	90	6,5	47,0	41,4	—	5,1	4,6	Al_2O_3

Note: Temperature 500°C, volume velocity 0.2 h^{-1}.

TABLE 2. Composition of the Reaction Products of Ethylbenzene and SO_2 over Cr_2O_3/Al_2O_3 at 400-550°

T, °C	Ratio of ethylbenzene to SO_2, M	Yield of organic part of catalyzate, %	Composition, %*							Content of condensation products, %†	Conversion, %	Yield of benzothiophene, % of ethylbenzene	
			benzene	toluene	ethylbenzene	styrene	acetophenone	benzothiophene	unidentified products			passed through	decomposed
400	1 : 1	45	4,6	4,6	47,7	30,9	2,7	8,6	0,9	—	79	3,9	4,9
450	4 : 1	90	0,8	1,3	27,3	56,9	4,3	6,6	2,8	—	74	5,9	8,0
450	2 : 1	95	1,2	0,4	13,2	60,6	3,7	9,9	11,0	22	90	7,3	8,1
450	1 : 1	95	1,9	1,2	21,0	58,4	1,2	9,9	6,4	22	86	7,3	8,5
500	6 : 1	97	0,8	0,8	35,4	52,5	1,0	9,5	—	15	71	7,8	11,0
500	4 : 1	95	2,4	1,5	27,2	51,0	1,6	16,3	—	27	82	11,3	13,8
500	2 : 1	90	1,6	1,0	13,2	59,7	1,1	23,4	—	40	93	12,4	13,3
500	1 : 1	85	0,9	0,7	6,8	64,0	0,6	27,0	—	54	97	13,5	13,9
550	4 : 1	80	0,5	0,2	20,5	56,0	1,6	21,2	—	40	90	10,1	11,2
550	2 : 1	75	—	—	—	59,8	3,5	37,3	—	73	100	10,1	10,1

* Without considering condensation products.

†Established by the method of gas–liquid chromatography with an accuracy of ± 5%.

DISCUSSION OF RESULTS

The data that we obtained in experiments on the reaction of ethylbenzene and styrene with SO_2 and H_2S over Al_2O_3 and Cr_2O_3/Al_2O_3, as well as in the absence of the catalyst (by passing the reagents through a tube filled with quartz fragments) at 500° and a volume velocity of 0.2 h^{-1}, are evidence that the yield of benzothiophene is greater when styrene is used than in the case of ethylbenzene (Table 1). Moreover, the formation of benzene and toluene evidently occurs chiefly after the stage of transformation of ethylbenzene to styrene, since in experiments with the latter their amount in the catalyzates increases 2-3-fold. The use of chromium oxide is not necessary in this case, since the reaction proceeds almost in the same way on aluminum oxide alone. When styrene and H_2S are used, the addition of chromium oxide leads to a 3-fold increase in the yield of benzothiophene. Since acetophenone was not detected in the reaction products of styrene with H_2S, while in the reaction of styrene with SO_2 only traces of it are observed, it may be assumed that this ketone is formed directly in the interaction of ethylbenzene and SO_2: in this case its yield reaches 3%.

The data on an investigation of the conversion of ethylbenzene and SO_2 at various ratios of the reagents and temperatures over Cr_2O_3/Al_2O_3 (Table 2 and Fig. 1) permit us to draw the following conclusions: the benzothiophene content varies parallel with the styrene content in the organic portion of the catalyzate, increasing with increasing temperature and ratio of SO_2 and ethylbenzene; however, increasing the mole ratio of SO_2 to ethylbenzene above 1 : 4 leads to a rapid increase in the content of condensation products. At

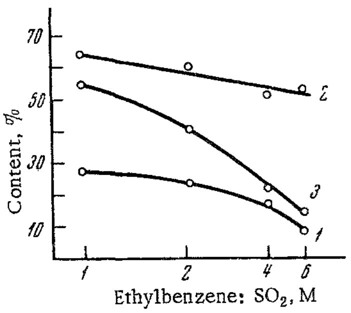

Fig. 1

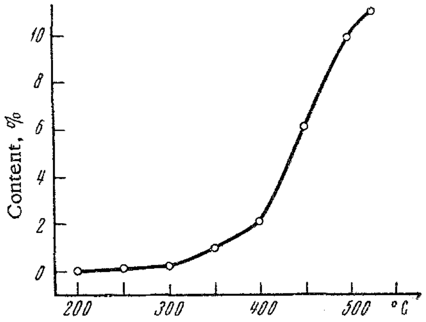

Fig. 2

Fig. 1. Dependence of the content of benzothiophene (1), styrene (2), and condensation products (3) on the ratio of ethylbenzene to SO_2 (Cr_2O_3/Al_2O_3, 500°, $v = 0.2\ h^{-1}$).

Fig. 2. Content in the catalyzate of benzothiophene, produced by the reaction of ethylbenzene and SO_2, as a function of the temperature.

a temperature of 500-550°, the yield of benzothiophene varies little with changing ratios of SO_2 and ethylbenzene. The conversion increases with increasing temperature and relative content of SO_2 in the mixture passed through. When Fe/Al_2O_3 and Fe_2O_3/Al_2O_3 were used as the catalysts, the same products of catalysis were obtained. The difference in the behavior of these catalysts lies in the fact that in the presence of Fe/Al_2O_3, the yield of the catalyzate and, correspondingly, of benzothiophene is reduced; Fe_2O_3/Al_2O_3 behaves analogously to Cr_2O_3/Al_2O_3 in this process.

Figure 2 graphically depicts the change in the content of benzothiophene as a function of the temperature of the reaction of ethylbenzene (volume velocity $0.2\ h^{-1}$) and SO_2 over Fe/Al_2O_3 (ratio of SO_2 to ethylbenzene 1 : 2); The formation of benzothiophene becomes appreciable above 250°, and when the temperature is raised to 550°, an increase in the content of benzothiophene in the catalyzate is observed. In this case there is also a proportional increase in the styrene content in the catalyzate as well.

The data that we obtained on the influence of the change in the specific surface of the catalyst, with the conversion of ethylbenzene to styrene and benzothiophene as an example (ethylbenzene : SO_2 = 4 : 1, 500°, $V = 0.2\ h^{-1}$, Cr_2O_3/Al_2O_3) are evidence that the yield of the catalyzate increases regularly with decreasing specific surface, while the content of styrene and benzothiophene reaches a maximum under these conditions at a specific surface of the catalyst equal to $\sim 120\ m^2/g$. It is advisable to regenerate the catalyst after 6 h of work. Longer work of the catalyst leads to a further decrease in the specific surface of the catalyst and a reduction of the yield of benzothiophene (Figs. 3 and 4). 2-Ethylthiophene interacts with SO_2 in the presence of Cr_2O_3/Al_2O_3 and Fe_2O_3/Al_2O_3 analogously to ethylbenzene, forming thieno-[3,2-b]-thiophene instead of benzothiophene.

Both the intermediate and the side products of the conversion of ethylbenzene and 2-ethylthiophene are analogous: in the case of ethylbenzene, chiefly benzene, toluene, styrene, acetophenone, and benzothiophene

TABLE 3. Composition of the Reaction Products of 2-Ethylthiophene with SO_2 over Cr_2O_3/Al_2O_3

T, °C	Yield of organic part of catalyzate, %	Composition, %							Conversion, %	Yield of thieno-[3,2-b]-thiophene, % of 2-ethylthiophene	
		thiophene	2-methylthiophene	2-ethylthiophene	2-vinylthiophene	2-acetothienone	thieno-[3,2,-b]-thiophene	condensation products		passed through	decomposed
300	70	8,9	—	83,9	4,0	0,8	2,4	—	39,6	1,7	4,3
350	70	1,2	0,4	80,4	9,5	5,8	2,7	—	33,7	1,9	5,7
400	80	5,1	4,9	46,4	34,1	2,3	7,2	—	42,9	3,5	12,9
450	75	5,3	3,1	51,2	26,5	2,7	11,2	—	62,0	8,4	13,5
500	80	2,5	1,6	50,2	29,5	0,9	6,3	9,0	60,0	5,0	8,3
550	95	2,1	1,2	45,2	29,6	1,0	6,9	14,0	57,0	5,5	9,6
600	98	0,5	0,3	39,0	20,0	0,5	4,0	35,7	61,0	3,9	6,4

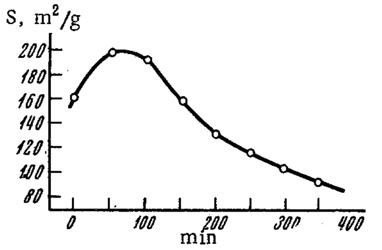

Fig. 3

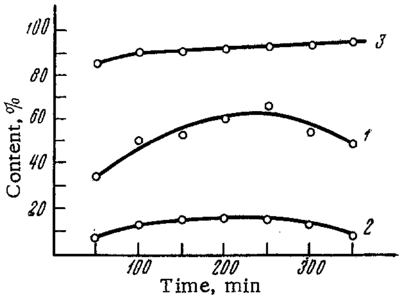

Fig. 4

Fig. 3. Change in the specific surface of a Cr_2O_3/Al_2O_3 catalyst as a function of the time of work of the catalyst.

Fig. 4. Change in the content of styrene (1) and benzothiophene (2) and yield of the catalyzate (3) as a function of the time of work of the catalyst (Cr_2O_3/Al_2O_3, ethylbenzene : SO_2 ≐ 4 : 1, v = $0.2\ h^{-1}$).

are formed, while in the case of 2-ethylthiophene, the main products are thiophene, 2-methylthiophene, 2-vinylthiophene, 2-acetothienone, and thieno-[3,2-b]-thiophene. We should mention that the reaction products of 2-ethylthiophene with SO_2 do not contain the second isomer of thienothiophene – thieno-[2,3-b]-thiophene. Together with the analogy in the behavior of ethylbenzene and 2-ethylthiophene in the interaction with SO_2 over oxide catalysts, a substantial difference is also manifested. The data cited in Table 3 show that when the temperature is raised above 450°, the content in the catalyzate of substances to be subjected to chromatographic analysis – thiophene, 2-methylthiophene, 2-ethylthiophene, 2-vinylthiophene, 2-acetothienone, and thieno-[3,2-b]-thiophene – begins to decrease and reaches a minimum at a temperature of 600° (the yield of the catalyzate in this case reaches a maximum). The maximum yield of thieno-[3,2-b]-thiophene is reached at a temperature of 450°, and that of benzothiophene at 500°.

CONCLUSIONS

1. The conversions of ethylbenzene, styrene, and 2-ethylthiophene in the stream of sulfur dioxide and hydrogen sulfide over aluminum oxide, aluminochromium and aluminoiron oxides, and metallic catalysts were investigated in the temperature range 200-600°.

2. 2-Ethylthiophene is converted to thieno-[3,2-b]-thiophene in the reaction with H_2S over aluminochromium and aluminoiron oxide catalysts, analogously to the conversion of ethylbenzene to benzothiophene.

3. Within the limits of the investigated conditions, the yields of thieno-[3,2-b]-thiophene and benzothiophene reach 13.5 and 13.9%, respectively, at 450 and 500°, on the basis of the reacted 2-ethylthiophene or ethylbenzene.

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