

CATALYTIC SYNTHESIS OF SOME SULFUR-CONTAINING HETEROCYCLIC COMPOUNDS. (REVIEW)

A. V. Mashkina

Researches on the synthesis of sulfur-containing heterocyclic compounds at the G. K. Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, are reviewed. They include the synthesis of thiolane by the recyclization of THF in hydrogen sulfide; the synthesis thiacycloalkanes by the hydrogenation of thiophenes; the synthesis of 4-methylthiazole by the reaction of SO₂ with methylisopropylideneamine; the synthesis of thiophenes by the heterocyclization of aliphatic compounds of sulfur and dehydrogenation of thiacycloalkanes; the synthesis of thiolane 1,1-dioxide by the hydrogenation of 2- and 3-thiolene 1,1-dioxides and 3-alkoxythiolane 1,1-dioxides; the synthesis of sulfoxides by the oxidation of thiacycloalkanes with atmospheric oxygen.

Keywords: 3-alkoxythiolane 1,1-dioxides, catalysts, hydrogen sulfide, 4-methylthiazole, sulfoxides, thiacycloalkanes, thiolane, thiolane 1,1-dioxide, thiophenes, synthesis.

Sulfur-containing heterocycles represent an important group of sulfur compounds that are promising for use in practical applications. For instance thiacycloalkanes (extractants for noble metals) are starting materials for the synthesis of physiologically active substances [1]; unsubstituted thiolane is used as an odorant for gas [2]; thiophenes can be used as physiologically active substances, dyes, oil additives, and polyorganosiloxanes [3]; the so-called "petroleum sulfoxides", produced from sulfur compounds present in petroleum products, can be used in hydrometallurgy and nonferrous metallurgy as extractants and flotation reagents [4]; thiolane 1,1-dioxide is used for the extraction of aromatic hydrocarbons from reformed petroleum products and as a solvent in various processes, including the purification of gas from acidic impurities [5].

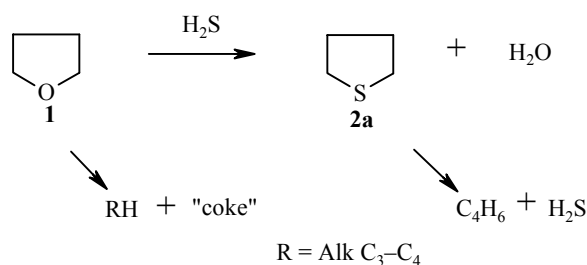
Various noncatalytic methods for the synthesis of sulfur-containing heterocycles are known, but in a number of cases they involve multistage processes and the use of difficultly obtainable and expensive raw materials. More effective are catalytic methods, which are more productive and more viable technologically. At the Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, systematic investigations were carried out on the development of catalysts and processes for the catalytic synthesis of sulfur-containing heterocyclic compounds. The main results of these investigations are reviewed here.

G. K. Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Novosibirsk; e-mail: A.V.Mashkina@catalysis.nsk.su. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 5, pp. 579-602, May, 2002. Original article submitted May 12, 2000. Revision submitted March 1, 2002.

1. SYNTHESIS OF THIACYCLOALKANES

Synthesis of Thiolane from Tetrahydrofuran and Hydrogen Sulfide

Thiacycloalkanes can be obtained by the Yur'ev reaction by exchanging an oxygen atom in the ring with sulfur under the influence of hydrogen sulfide in the presence of solid catalysts. Thus, the thiolane (**2a**) is obtained by the recyclization of tetrahydrofuran (**1**). By Yur'ev [6] this reaction was carried out at $\leq 400^\circ\text{C}$ in the presence of aluminum oxide. As a result of detailed investigation [7-13] we found that at solid catalysts with protic centers (PC) [SiO_2 , $\text{H}_3\text{PO}_4/\text{SiO}_2$, phosphotungstic acid (HSiW) deposited on SiO_2 , aluminosilicate (AlSi), zeolites HZSM-5 and HNaY] the formation of thiolane from THF becomes appreciable above 300°C . The products contain water, thiolane, and C_3 - C_4 hydrocarbons. The yield of the product **2a** calculated on the amount of THF used was 1-25 mol. %, while the selectivity of its formation (s) did not exceed 30% (at HNaY $s = 50\%$) and remained constant with variation of the degree of transformation from 1 to 95%. The degree of conversion (x) of THF and the yield of the hydrocarbons increased with increase in the temperature, while the yield of the thiolane **2a** changed little. The reaction takes place according to the following scheme:



The rate of transformation of the THF depends on the strength of PC on the surface. Thus, on SiO_2 , which has only weak PC, the rate of formation of the product **2a** is low. The addition of acids (phosphoric and silicotungstic) to the SiO_2 and also the use of aluminosilicate or zeolite in the H-form, which contain strong PC, lead to an increase in the reaction rate (Table 1). Resins formed during the decomposition of the THF condense on the surface of catalysts with PC, and as a result the initial activity of the catalysts decreases in the course of time. At aluminum oxide catalysts (γ - and η - Al_2O_3 without additives and with the addition of HF or Mo, Cr, and B oxides) at 200 - 400°C with an excess of hydrogen sulfide in relation to the THF practically the only products are the thiolane **2a** and water, and the rate of the reaction is significantly higher than at the catalysts with PC (Table 1) [7, 10]. At aluminum oxide catalysts increase in the contact time leads to an increase in the yield of compound **2a**, which at $x = 100\%$ amounts to 95-100 mol %, i.e., path **1** \rightarrow **2** of the scheme presented above for the reaction at the PC is mainly realized. Above 400°C the selectivity of the process decreases with increase in the conversion of the THF on account, probably, of decomposition of the product **2a** that forms. In this temperature range the aluminum oxide catalysts perform quite consistently, but their initial activity decreases as a result of the accumulation of carbon deposits and resins, mainly formed during the decomposition of the THF, on the surface.

In the recyclization of THF to the thiolane **2a** the activity of the aluminum oxide catalysts and zeolite NaX is due largely to the presence of Lewis acid centers (L centers), which participate in complexation with the THF, on their surface. It was established by IR spectroscopy (from the frequency of the CO bond) that the adsorption of compound **1** on Al_2O_3 leads to a decrease in the concentration of L centers, and with large degrees of surface coverage they are completely blocked [9]. During investigation of this adsorption by high-resolution NMR in the solid it was found that the ^1H NMR spectrum contains signals belonging to structure **1** with an open C-O bond ($\delta = 0.6$ ppm), firmly attached to the surface, and a signal at $\delta = 4.0$ - 4.5 ppm for a more reactive structure (probably alkoxy-containing fragments, attached associatively to L centers of moderate strength). In

TABLE 1. The Formation Rate of the Thiolane **2a** and the Selectivity during the Recyclization of THF in Hydrogen Sulfide in the Presence of Acidic Catalysts*

Catalyst	Strength of PC PA ^c , kJ/mol* ²	Strength of L centers, Q_{CO} , kJ/mol* ³	Formation rate of thiolane 2a , mmol/h·g of Ct.	Selectivity of formation of 2a , %
SiO ₂	1390	—	0.14	20
H ₃ PO ₄ /SiO ₂	1390	—	0.10	8
HSiW/SiO ₂	<1180	—	0.4	26
AlSi	<1300	53	3.3	22
HNaY	<1200	45-55	10.5	47
γ -Al ₂ O ₃	1420	34-41	500	100
Cr/Al ₂ O ₃	<1300	36	569	96
B/Al ₂ O ₃	<1400	34-41	730	100
η -Al ₂ O ₃	1420	34-56	853	100
HF/Al ₂ O ₃	1310	42	683	100
0.03% Na/Al ₂ O ₃	—	29	500	100
0.6% Na/Al ₂ O ₃	—	28	128	100

* $T = 360^\circ\text{C}$, H₂S:1, 5:1, x 50% [7, 9, 10]

*² PA^c is the proton affinity (according to the adsorption of pyridine).

*³ Q_{CO} is the heat of adsorption of CO.

the presence of hydrogen sulfide the intensity of the last signal decreases, and signals belonging to adsorbed H₂S appear ($\delta = 1.60$ and 2.13 ppm). In the ¹³C NMR spectra there is a signal ($\delta = 29.90$ ppm) belonging to the product **2a** attached to the surface [9].

With the addition of sodium oxide to γ -Al₂O₃ the strength of the L centers is reduced, and this affects the activity of the catalyst [11]. Here the rate of formation of the product **2a**, related to one L center, is higher the higher the strength of the L center. However, the formation of the product is favored by the presence of L centers with moderate strength on the surface, since the THF decomposes at the very strong centers. Very strong L centers ($\delta = 71.5$ ppm) were found in γ -Al₂O₃ by the ¹⁵N NMR method from the adsorption of nitrogen [12]. According to the IR spectra their strength, estimated from the heat of adsorption of CO, is $Q_{CO} = 39 \pm 2$ kJ/mol, while the concentration is 10-15 $\mu\text{mol/g}$ of Ct. They are suppressed with the addition of sodium oxide to the γ -Al₂O₃ up to 0.03 wt.%, calculated on the Na, but the formation rate of the thiolane (**2a**) at this catalyst is the same as at pure Al₂O₃ (Table 1). The suppression of the very strong acid centers, which accelerate the decomposition of THF with the formation of resins and coke, stabilizes the catalyst, and it performs more consistently. If the concentration of sodium in the Al₂O₃ is increased the less strong L centers, determined by NMR from the adsorption of N₂O ($\delta = 22.3$ ppm), are affected. According to IR spectroscopy these centers have strength $Q_{CO} \sim 34$ kJ/mol, and their concentration amounts to ~ 60 $\mu\text{mol/g}$ of Ct [12].

The transformation rate of THF in H₂S at the various catalysts is described by the same equation [13]:

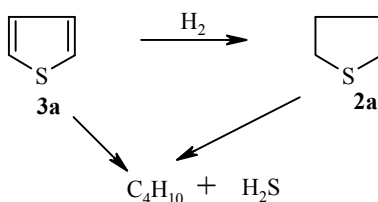
$$w = k P_1^{0.3} P_2^{0.7},$$

where k is the rate constant of the reaction, and P_1 and P_2 are the partial pressures of THF and H₂S respectively. It was assumed [8, 13] that the reaction is identical at catalysts with PC and L centers. During the chemisorption of THF at the acidic centers on the surface an oxonium complex is formed initially and then undergoes cleavage

at the C–O bond with the formation of alkoxy-containing structures and hydrocarbon structures. In the case where the reactivity of the H₂S is insufficient (this occurs at catalysts with PC) these surface structures decompose with the release of hydrocarbons, and "coke" is deposited on the surface of the catalyst. During the reaction of the alkoxy groups with activated hydrogen sulfide the thiolane **2a** is formed. The participation of SH groups, formed during the dissociative chemisorption of hydrogen sulfide on catalysts with L centers, in the process leads to a higher rate of formation of the product **2a** at aluminum oxide catalysts than at proton-donating catalysts, which are incapable of activating the hydrogen sulfide to a sufficient degree. Thus, in the recyclization of THF to the thiolane **2a** it is not advisable to use solid catalysts having mostly PC on the surface. Catalysts with L centers of moderate strength conjugated with the basic centers have a substantial advantage. At such catalysts with $T = 360^{\circ}\text{C}$, $P = 1 \text{ MPa}$, molar ratio H₂S:THF = 5:1, and $x = 85\%$, the product **2a** is formed with 100% selectivity [9, 10].

Synthesis of Thiacycloalkanes by Hydrogenation of Thiophenes

In the gas phase in the presence of transition metal sulfides at elevated temperature hydrogenation of the thiophene ring to thiolane is possible, but this reaction is complicated by hydrogenolysis [14-19]. At various sulfide catalysts the conversion of the unsubstituted thiophene **3a** and the yields of the hydrogenolysis products increase with increase in the contact time, while the yield of the product **2a** calculated on the initial thiophene increases up to a certain limit, after which it decreases [15-17]. The hydrogenation of the thiophene takes place according to the parallel-consecutive scheme:



Similar results were obtained during the hydrogenation of 2-methylthiophene **3b** [14]. The rate of overall transformation of the unsubstituted thiophene **3a** is described by the equation:

$$w = k P_1 P_2^{0.7} P_3^{-1},$$

where k is the rate constant of the reaction, and P_1 , P_2 , and P_3 are the partial pressures of the initial **3a**, hydrogen, and the product **2a** respectively [16, 17].

The activity and selectivity of the catalysts depend on their composition. In the presence of the AlNiMo, AlCoMo, and AlNiW sulfide catalysts usually employed in desulfurization processes the hydrogenation of the thiophene **3a** to the thiolane **2a** takes place at a low rate with $s = 10\text{-}34\%$, and hydrogenolysis of the initial **3a** with the release of hydrogen sulfide and C₄ hydrocarbons mainly occurs. Monometallic sulfide catalysts accelerate hydrogenation. Among the massive sulfides Pd and W sulfides are the most active in this reaction at $T = 300^{\circ}\text{C}$ ($T = 240^{\circ}\text{C}$ for PdS) with $P = 0.5 \text{ MPa}$ and $x = 30\%$, while Ni sulfide is least active [17]:

	PdS	WS ₂	CoS	MoS ₂	FeS	NiS
$w, \mu\text{mol}/\text{m}^2\cdot\text{h}$ of Ct	34.0	5.1	9.0	3.0	2.7	2.3
$s, \%$	64	35	16	30	17	6

TABLE 2. The Dependence of the Formation Rate of Thiolane **2a** from Thiophene **3a** and the Selectivity on the Nature of the Metal Sulfides on Various Supports*

Sulfide* ²	Carbon		SiO ₂		Al ₂ O ₃		AlSi	
	w, mmol 2a/h·g Me	s, %	w, mmol 2a/h·g Me	s, %	w, mmol 2a/h·g Me	s, %	w, mmol 2a/h·g Me	s, %
Ni	0	0	0.1	4	0	0	0	0
Co	1.2	30	0.5	26	0.5	22	1.7	55
Mo	6	78	4.3	70	2.5	72	2.5	86
W	1.0	90			0.5	60		
Rh	0.6	0	10.8	54	11.0	34	1.5	40
Ru	9.2	48	1.3	32	1.8	40	0.7	30
Pd	3.5	44	88	88	4.9	30	216	90

* $T = 240^{\circ}\text{C}$, $P = 3 \text{ MPa}$, concentration of **3a** = 1 vol. %, $x = 20\%$ [15, 17].

*² Content of metal in catalyst: Mo 10%, W 18%, others 5 wt. %.

The activity and selectivity of the latter is increased little by deposition on Al₂O₃, SiO₂, AlSi, and carbon (Table 2) [15, 17]. The catalytic characteristics of NiS are improved significantly by incorporating it into zeolite NaX and particularly NaY. Increase in the acidity of the zeolite leads to an increase in the activity of the Ni-zeolite catalyst. For example, the formation rate of the thiolane **2a** at the NiS/HNaY catalyst with high acidity is twice the rate observed at the nonacidic NiS/NaY. The highest yield of compound **2a** obtained at NiS/HNaY amounts to 80 mol % with $s = 86\%$, and its formation rate is 1.3 g/h·g of Ct. The activity of this catalyst decreases with time, and its deactivation occurs mainly on account of the deposition of coke, formed as a result of hydrocracking and condensation at the acid centers of the zeolite, on the surface. The NiS/HNaY can be regenerated by oxidizing treatment at an elevated temperature [18, 19]. The sulfides of Co, Rh, and Ru on Al₂O₃, SiO₂, AlSi, and carbon as supports accelerate the hydrogenation of the thiophene **3a** to the thiolane **2a**, but the selectivity of the formation of the latter is not greater than 55% (Table 2) [15, 17]. The sulfides of Mo and W deposited on supports are more selective, and the formation rate of the product (**2a**) at these catalysts is higher, the greater the degree of dispersion of the metal sulfide, which varies with the supports in the order: carbon > SiO₂ > Al₂O₃ > NaY. Palladium sulfide catalysts, and PdS/AlSi and PdS/SiO₂ in particular, deposited on a support are highly active and selective in the hydrogenation of thiophene **3a** and methylthiophene **3b** (Table 2).

In their specific activity in the hydrogenation of thiophenes **3a,b** the palladium sulfide catalysts based on SiO₂, AlSi, and HNaY surpass PdS without a support and PdS on other supports by an order of magnitude and have enhanced selectivity in the formation of the thiolane **2a** and 2-methylthiolane **2b**. According to the specific rate of formation of the product **2b** from methylthiophene **3b** at PdS/support ($T = 240^{\circ}\text{C}$, $P = 0.8 \text{ MPa}$, $x = 50\%$) the catalysts can be arranged in the following order [14]:

Supports	SiO ₂	HNaY	AlSi	C	Al ₂ O ₃	TiO ₂	Without support
w, mmol/h·m ² Pd	3.80	3.30	2.46	0.45	0.22	0.18	0.16
s, %	85	83	82	38	56	60	64

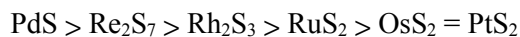
The difference in the activity of the catalysts is not due to the degree of dispersion of the PdS on the supports. The acidity of the surface is very important for the catalytic characteristics of palladium sulfide catalysts [16, 17]. The activity of aluminopalladium sulfide catalysts depends on the nature of the precursor [14, 15]. Thus, the catalyst PdS/Al₂O₃ produced by the deposition of palladium from a hydrochloric acid

solution of PdCl₂ is approximately four times more active than the catalyst produced from a solution of palladium acetate in toluene. During preparation of the catalyst with PdCl₂ the released HCl can be adsorbed on the support, forming strong acid centers. In samples of PdS/Al₂O₃ and PdS/SiO₂ produced by impregnating the support with a hydrochloric acid solution of PdCl₂ PC of moderate strength are found ($PA^k \leq 1300$ kJ/mol). Their amount in the case of PdS/SiO₂ is 25 times larger than at PdS/Al₂O₃ (0.25 and 0.01 $\mu\text{mol}/\text{m}^2$ respectively). There are stronger PC in samples of PdS on AlSi or HNaY ($PA = 1180\text{-}1200$ kJ/mol, at the rate of 0.2-0.4 $\mu\text{mol}/\text{m}^2$ [14, 15]. As shown by experiment, the most active in the hydrogenation of 2-methylthiophene (**3b**) are catalysts containing PdS deposited on SiO₂, AlSi, and zeolite HNaY, which have a surface with increased protic activity. It is most likely that the PC take part in the activation of the thiophene ring. During the adsorption of compound **3a** on the hydroxylated surface there is a reaction involving the π -system of the thiophene ring. In the ¹H NMR spectra of samples of PdS/SiO₂ and Pd⁰/SiO₂ after the admission of thiophene **3a** a decrease is observed in the intensity of the signals of the OH groups on the surface, and a narrow singlet with $\delta = 6.7$ ppm, belonging to the hydrogen-bonded compound **3a**, appears. The small width of this signal is explained by the high mobility of the adsorbed molecule. Hydrogen adsorbed on the palladium sulfide can undergo heterolytic dissociation with the formation of hydride ion. The thiophene **3a** protonated at the α -carbon atom presumably reacts with the hydride ion to form the thiolane ring [14, 15]. A further argument in favor of such a reaction mechanism may be the fact that under identical conditions the rate of formation of the thiolane **2a** during hydrogenation of the thiophene **3a** is lower than the rate of formation of methylthiolane during hydrogenation of methylthiophene **3b**, which has increased electron density at the α -carbon atom and is therefore protonated more easily than unsubstituted thiophene. Some of the thiophene molecules are adsorbed at the active centers, forming an S-Pd bond. The disruption of aromatic conjugation that occurs here facilitates decomposition of the thiophene ring with the formation of hydrogenolysis products in the hydrogen medium. Chemisorption involving the sulfur atom of the products from hydrogenation of the thiophenes, i.e., the thiolanes, also promotes their hydrogenolysis.

During gas-phase hydrogenation of the thiophenes **3a,b** in the presence of palladium sulfide catalyst (200-300°C, $P = 2\text{-}3$ MPa) the yield of the thiolanes **2a,b** amounts to 40-65%, while the selectivity of their formation is 80-90% with degrees of conversion $x = 50\%$ and 40-80% with $x = 80\%$ [14-17].

The liquid-phase low-temperature hydrogenation of various organic compounds is often realized in the presence of group VIII metals. However, these catalysts are unsuitable for selective hydrogenation of the thiophene ring [20, 21]. Catalysts containing 1-10 wt. % of Pd on aluminum oxide, activated carbon, and barium sulfate at $T = 20\text{-}80^\circ\text{C}$ and $P = 0.1\text{-}5$ MPa in solutions in alcohols, hydrocarbons, and DMFA accelerate the hydrogenation of various thiophenes with initial thiolane yields of up to 100%. However, they are quickly and irreversibly deactivated on account of the formation of a Pd←S< bond and also the formation of surface compounds of the PdSR and PdS_x type. Irrespective of the nature of the support, its Pd content, and the hydrogenation conditions (the nature of the solvent, the acidity of the medium, the pressure, the contact time, the thiophene content of the initial solution) during the hydrogenation of the thiophene (**3a**) total deactivation of the catalyst occurs after the formation of ~0.1 g of thiolane to 1 g of catalyst. An attempt to protect the metallic palladium from poisoning by complexation was unsuccessful [22-23]. Although the activity of the metal complexes during the hydrogenation of thiophene in solution **3a** is higher than for the metals, they are also not stable during the process. It was shown by XPES and UV methods that during the hydrogenation of thiophene the Pd complex attached to SiO₂ is deactivated as a result of the fact that the thiolane formed enters the coordination sphere of the palladium, displacing the outer ligand and forming a Pd-S bond; under certain conditions the structure of the complex is fully destroyed.

At sulfides of the platinum group and rhenium in the individual state or deposited on Al₂O₃, SiO₂, AlSi, and carbon the hydrogenation of thiophene in hydrocarbon solvents (150-250°C, $P = 3\text{-}25$ MPa) leads to the thiolane with yields of up to 60% with $s = 70\text{-}90\%$ [24, 25]. Metal sulfides deposited on Al₂O₃ can be arranged in the following order according to their activity:

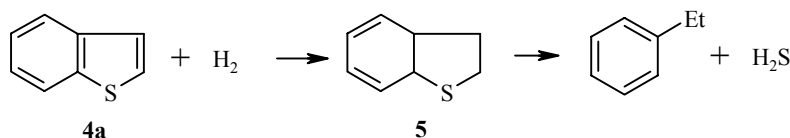


During liquid-phase hydrogenation the same kinetic relationships are observed as during gas-phase hydrogenation [25-27]. The rate of accumulation of methylthiolane **2b** during the hydrogenation of methylthiophene **3b** ($T = 220\text{-}300^\circ\text{C}$, $P = 3.3\text{-}3.5$ MPa) in the presence of Pd/Al₂O₃ and Pd/AlSi is described by the equation:

$$w = k_1 c_1 P / c_2 - k_2 P,$$

where k_1 and k_2 are the rate constants of the overall transformation of compound **3c** and its hydrogenolysis respectively, c_1 and c_2 are the concentrations of compounds **3b** and **2b** respectively, and P is the hydrogen pressure [26].

The liquid-phase hydrogenation of benzothiophene **4a** with the formation of 2,3-dihydrobenzothiophene **5**, ethylbenzene, and hydrogen sulfide takes place according to the same scheme as the hydrogenation of the thiophenes **3a,b**, but the stage involving hydrogenolysis of the initial compound **4a** is absent [28, 29]:



With less than 60% conversion the selectivity of formation of **5** is close to 100%. It decreases with increase in the degree of conversion, and with $x = 100\%$ it amounts to 50%. Hydrogenolysis probably occurs to a small degree in the case of alkyl-substituted benzothiophenes. Thiophenes with various structures (thiophene, 2-methyl-, 2-propyl-, 2-hexyl-, 2-octyl-, and 2,5-dimethylthiophenes, benzothiophene, and 3-methylbenzothiophene) have high reactivity. For example, at the PdS/Al₂O₃ catalyst (200°C, $P = 5$ MPa, solvent cyclohexane, time 0.25-1 h) the yield of the thiolanes and 2,3-dihydrobenzothiophenes amounts to 23-55 mol %; their formation rate with $x = 35\text{-}40\%$ is 1.5-2.8 mmol/h·g of Ct, and $s = 85\text{-}98\%$ [30].

An aluminopalladium sulfide catalyst was used to produce up to 80% yields of thiacycloalkanes by reduction of the alkyl- and cycloalkylthiophenes and benzothiophenes present in the middle fractions of Samotlor and Arlansk oils and in the concentrates isolated from them with hydrogen. It was also used to produce thiabicyclo- and thiatricycloalkanes by the reduction of benzothiophenes, dibenzothiophenes, and naphthalenothiophenes from the concentrates of vacuum gasoil from Mangyshlak and West-Siberian oils [31].

In its specific activity in the liquid-phase hydrogenation of thiophenes [30] the PdS/AlSi catalyst surpasses PdS without a support and PdS deposited on aluminum oxide and carbon supports by an order of magnitude and exhibits higher selectivity. For example, at $T = 260^\circ\text{C}$, $P = 5$ MPa, and $x = 50\text{-}60\%$ in the presence of catalysts containing 2 wt. % of Pd on a support the mean values of the selectivity and formation rate of methylthiolane **2b** from 3-methylthiophene **3b** calculated for 1 g of palladium are [30]:

	PdS/AlSi	PdS/C	PdS/Al ₂ O ₃	PdS
w , mmol/h·g Pd	2.7	0.25	0.15	0.08
s , %	91	82	77	84

The yields of the thiolanes **2a,b** in the liquid-phase hydrogenation of the thiophenes **3a,b** at an aluminopalladium sulfide catalyst ($T = 200\text{-}300^\circ\text{C}$, $P = 2\text{-}5$ MPa) amounted to 50-75 mole.% respectively with $s = 80\text{-}90\%$. The catalyst performs consistently but is nevertheless deactivated with time as a result of the

accumulation of coke on the surface with a low degree of condensation (ESR data) [30]. Thus, there are no fundamental differences between the processes for selective hydrogenation of thiophenes in the gas and liquid phases [15, 30].

2. SYNTHESIS OF THIOPHENES

Dehydrocyclization of Aliphatic Compounds of Sulfur

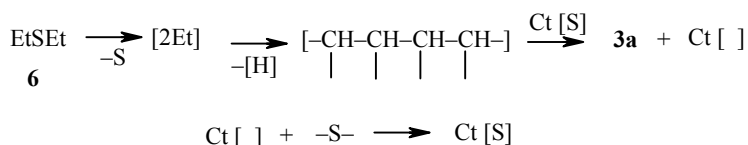
One method for the synthesis of thiophenes is heterocyclization of alkanethiols RSH, dialkyl disulfides R^1SSR^2 , dialkyl sulfides R^1SR^2 , and their oxides R^1SOR^2 (frequently $R^1 = R^2$) in the presence of catalysts. The reactions leading to the formation of the thiophenes are complicated by cracking of the initial compounds with the release of hydrocarbons and hydrogen sulfide or sulfur dioxide [32-34]. The absence of a maximum on the curves for the dependence of the conversion of the various compounds on the contact time and the constancy of the selectivity among the products for various degrees of conversion indicate that these reactions take place along individual paths. The thiophene **3a** is formed from aliphatic compounds with R^1 or $R^1, R^2 = C_2$ and C_4 , while its homologs are formed from the higher compounds. For example, in the presence of a chromium catalyst at 500°C thiophene is mainly formed from the compounds with R^1 or $R^1 = R^2 = C_2$ [methyl ethyl sulfide, diethyl sulfide (**6**), divinyl sulfide, diethyl disulfide, diethyl sulfoxide) and with R^1 or $R^1 = R^2 = C_4$ [butanethiol (**7**), ethyl butyl sulfide, dibutyl sulfide (**8**), diisobutyl sulfide, di-*sec*-butyl sulfide, dibutyl sulfoxide], and the content of thiophene in the mixture with its homologs is 90-95%. 2-Methylthiophene **3b** or 3-methylthiophene **3c** respectively are obtained from compounds with $R^1 = R^2 = C_5$ (diamyl and diisoamyl sulfides), and their contents in the mixture are 87-91 mol %. From the compounds with R^1 or $R^1 = R^2 = C_3$ (ethyl propyl sulfide, dipropyl sulfide, diisopropyl sulfide) a mixture of thiophene **3a**, methylthiophenes **3b,c**, 2-ethylthiophene, and 2,4- and 2,5-dimethylthiophenes is formed. The composition of the products is consistent with the idea that their formation is preceded by dissociation of the initial compounds at the C-S bonds [32-34]. The transformation into thiophenes in the reaction of H_2S with C_4 and C_5 hydrocarbons [divinyl, butylene **9**, isoprene, piperylene] takes place similarly to the aliphatic sulfur compounds. The kinetic relationships of these reactions are close to those observed in the case of the heterocyclization of organic compounds of sulfur [33].

TABLE 3. The Dependence of the Rate Constants for the Formation of Thiophene from Various Compounds at 500°C on the Mobility of the Sulfur on the Surface of the Catalyst [33]

Sulfide	q_s	$k, ml/m^2 \cdot sec$				
		BuSH (7)	Bu ₂ S (8)	Et ₂ S (6)	Thiolane 2a	Butylene 9
Re	34	270	250	32	274	152
Mo	23	140	127	51	144	92
Co	22	224	91	33	80	14
Cr	19	60	104	26	60	68
W	19	82	60	10	35	18
Mg	15	26	4	1	9	1
Si	14	7	5	1	2	0.3
Al	13	8	7	0.7	1.4	0.03

* The mobility of the sulfur (q_s) was estimated from the reciprocal of the temperature ($1/T, K \cdot 10^4$) at which a certain specific rate of release of H_2S is reached during treatment of the catalyst with hydrogen.

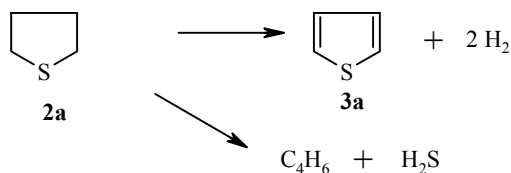
Only the sulfides of transition metals are active in the formation of thiophenes, and the sulfur present on the surface of the catalyst plays a significant role in their catalytic activity. It was established that the thiophenes from the various organosulfur compounds and from the mixtures of hydrocarbons with hydrogen sulfide are formed at higher rates, the lower the energy of the bond between the sulfur and the surface (Table 3) [33-35]. The thiophene is formed by a stage mechanism [35]. Aliphatic compounds of sulfur are thermally unstable (the dissociation energy of the first C-S bond is 70-73, and that of the second is 25-30 kcal/mol), and their adsorption at elevated temperature is accompanied by decomposition with the release of sulfur and hydrocarbon fragments. The latter undergo a series of transformations and, in particular, dehydrogenation, sometimes isomerization, and condensation to fragments with not less than four carbon atoms, which then react with the surface sulfur atoms, leading to the thiophene **3a** or its homologs. By reacting with the sulfur-depleted catalyst the sulfur compounds restore a steady content of sulfur on the surface. The stages of adsorption and desorption, cracking, isomerization, condensation, dehydrogenation of the hydrocarbon fragments, and resulfurization of the catalyst take place at a high rate. The slow stage is the reaction of the dehydrogenated fragments with the sulfur atoms on the surface of the catalyst. The formation of thiophene from diethyl sulfide **6**, for example, can be described by the following scheme [35]:



The most active of the various sulfur compounds in heterocyclization are the sulfides of Re, Mo, Cr, and Co, deposited on nonacidic Al₂O₃ and AlSi. Depending on the substrate and on the employed catalyst, the yield of the thiophenes at $T = 450\text{-}500^\circ\text{C}$ varies in the range of 25-50 mol % [33].

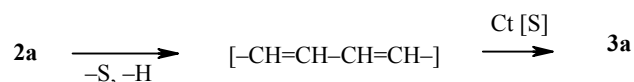
Dehydrogenation of Thiacycloalkanes

Above 400°C ($P = 0.1$ MPa) in an inert medium sulfide catalysts accelerate the formation of thiophenes from thiolanes. The sulfides of metals without a support or deposited on Al₂O₃, SiO₂, AlSi, MgO, and activated carbon are active, for example, in the transformation of thiolane into thiophene. The formation of the thiophene **3a** is accompanied by parallel decomposition of the initial thiolane **2a**:



The product yield increases with increase in temperature and contact time and does not depend on the concentration. At 450-500°C thiophene is formed with a yield of up to 75 mol % and selectivity up to 80% [36-38].

The mechanism of formation of thiophene from thiolane at elevated temperature at sulfide catalysts is the same as in the case of the dehydrocyclization of aliphatic compounds of sulfur. The thiolane **2a**, chemisorbed on the surface of the catalyst, decomposes at elevated temperature at both C-S bonds with the release of sulfur and the C₄ hydrocarbon fragment. The latter undergoes dehydrogenation to $\text{-}\underset{|}{\text{CH}}\text{-}\underset{|}{\text{CH}}\text{-}\underset{|}{\text{CH}}\text{-}\underset{|}{\text{CH}}\text{-}$ particles, the condensation of which with the surface sulfur atoms leads to the thiophene **3a**:



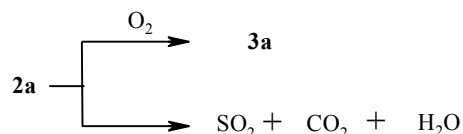
The rate of formation of the product **3a** depends on the reactivity of the sulfur on the surface of the catalyst (Table 3) [35].

The formation of the thiophene **3a** is also possible during the catalytic transformation of thiolane 1,1-dioxide (**10**) by the same mechanism as in the transformation **2a** → **3a**. At sulfidized catalysts AlMo, AlCr, and AlCoMo at 400-500°C and $P = 0.1$ MPa thiophene is obtained from compound **10** with a yield of up to 46 mol %, and hydrogen sulfide and sulfur dioxide are also released [39].

In the process of formation of thiophenes from the various sulfur compounds the sulfide catalysts are deactivated after the formation of 0.05-0.1 mmol of the products for 1 m² of surface. It was found that the deactivation takes place as a result of coke formation and the consequent decrease in the reactivity of the surface sulfur. Oxidizing treatment of the deactivated catalyst leads to its regeneration [21, 37].

Oxide catalysts containing Mo, Cr, Ni, Co, and W in an inert medium at $T = 290-300^\circ\text{C}$ and $P = 0.1$ MPa also exhibit activity in the transformation of the thiolane **2a** and its homologs into thiophene and its alkyl derivatives, and the aluminomolybdenum catalysts are particularly active [36]. The initial yield of the thiophenes amounts to 70-95%, but it soon decreases as a result of the reaction of the oxide catalyst with the sulfur-containing reaction medium, and here only 0.02 g of the product **3a** is obtained to 1 g of catalyst. Presumably, in the oxide catalysts the oxygen ions attached to the metal take part in the dehydrogenation of the thiolane ring, e.g., in the aluminum-molybdenum catalyst these are the oxygen ions attached to the molybdenum.

The introduction of oxygen into the reaction mixture [40, 41] stabilizes the activity of the MoO₃ catalysts without a support and the MoO₃/Al₂O₃ catalysts, which operate at 200-400°C. The products of the catalytic transformation of the thiolane **2a** are the thiophene **3a**, water, sulfur dioxide, and carbon dioxide. Increase in temperature above 350°C leads to a marked increase in the degree of oxidation of compound **2a** and a decrease of the selectivity with respect to the product **3a**. In the presence of air the transformation of thiolane takes place in two independent directions, i.e., dehydrogenation to thiophene and the formation of the products from deeper oxidation:

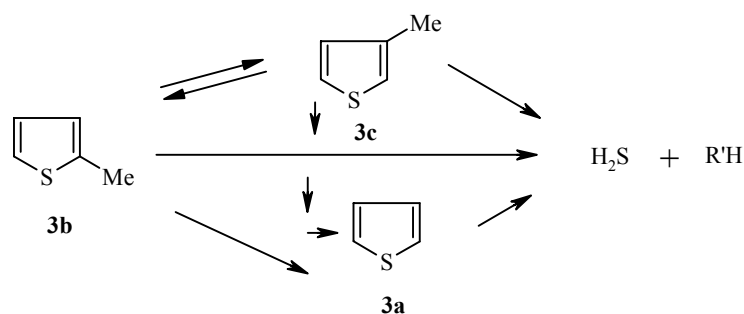


The overall rate of the reaction is given by the equation $w = kP_1P_2n$, where P_1 and P_2 are the partial pressures of thiolane and oxygen respectively; $n = 0$ and 1 with $[\text{O}_2]:2\mathbf{a} > 3$ and < 1 respectively. With a deficiency of oxygen in relation to the thiolane **2a** the yield of the product **3a** is lower than with an excess of oxygen. In the last case, however, reduced selectivity is observed in the formation of the thiophene **3a**, since the deep oxidation rate of the initial **2a** is increased. At the MoO₃/Al₂O₃ catalyst at 300-350°C, $P = 1$ MPa, $\tau = 0.3-0.7$ sec, and $[\text{O}_2]:2\mathbf{a} > 1$ the yield of thiophene during the oxidative dehydrogenation of thiolane amounts to 67%, $s = 75\%$. The durability of the catalyst is increased by 50 times compared with the aluminomolybdenum catalyst in the absence of oxygen, and it is possible to obtain ~4 g of the product for 1 g of catalyst.

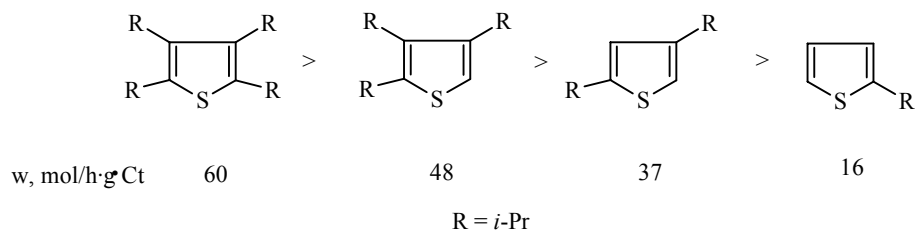
The oxidative dehydrogenation **2a** → **3a** is also accelerated by metal sulfides, e.g., by the sulfides of Mo and W (360-380°C), and the reaction rate here is an order of magnitude greater in the presence of MoS₂ than with WS₂. The active component of the catalyst is evidently the oxysulfides of Mo and W. At these catalysts the relationships governing the variation of the yield of thiophene in relation to the reaction conditions are completely analogous with those for the oxide catalysts. In the presence of oxygen, however, the product **3a** is obtained with greater selectivity, which with a yield of 77 mol % amounts to 90-100%. Thiophene with a high degree of purity (99.99%), not containing benzene and other hydrocarbons as impurities, was obtained by this method. The catalysts are stable during prolonged use [40, 41].

Dealkylation of Thiophenes

Substituted thiophenes can be converted into the thiophene **3a** and its lower homologs [42-46]. Dealkylation is possible in the presence of sulfide and oxide catalysts. At Mo, W, V, Cr, Fe, and Co sulfides dehydrogenation of the side chain with the formation of alkenylthiophenes is observed in addition to the dealkylation of thiophenes with normal alkyl radicals [36]. More selective in dealkylation are the acidic oxide catalysts and in particular the amorphous silicates and zeolites [42-46]. However, at these catalysts at 450-500°C with $P = 0.1$ MPa migration to a different position of the ring and elimination of the sulfur occur in addition to the removal of alkyl groups from the thiophene ring. The products from the transformation of 2-methylthiophene **3b** are the thiophene **3a**, 3-methylthiophene **3c**, hydrogen sulfide, methane, a small amount of C_2 and C_4 hydrocarbons, "coke," and also hydrogen, which participates in demethylation. The process takes place according to the following scheme:

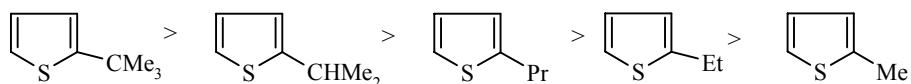


The higher homologs of thiophene **3a** with normal alkyl groups at position 2 are converted at acid oxide catalysts mainly into the product **3a**, 3-alkylthiophene, and hydrocarbons with the same number of carbon atoms as in the alkyl group. The amount of hydrocarbon released here is close to the amount of thiophene **3a** formed. Thiophenes with substituents having *iso* structures undergo dealkylation preferentially; the rate of migration of R from position 2 to position 3 and back in this case is significantly lower than the rate of dealkylation to the thiophene **3a**. During the dealkylation of tetrasubstituted thiophenes with identical radicals, such as *i*-Pr, at $x = 40-70\%$ one alkyl residue, and then the second, third, and fourth, is easily removed from the thiophene ring. The isopropylthiophenes can be arranged in the following order according to the rate of dealkylation at the catalyst AlSi at 450°C with $x = 30\%$ [46]:



With $x > 70\%$ the alkylthiophenes that form undergo further transformations. Not only the individual alkylthiophenes but also mixtures of thiophenes present in natural products can be subjected to dealkylation [46].

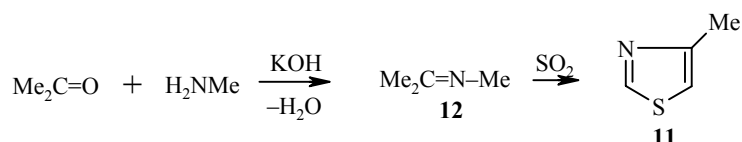
The dealkylation of 2-alkylthiophenes takes place by a carbonium ion mechanism; in reactivity they can be arranged in an order coinciding with the order of stability of the alkyl cations [45]:



The activity of the catalysts depends on the acidity of the surface. Thus, a linear relationship is observed between the acidity function of the various catalysts and the logarithm of the dealkylation rate referred to one acid center. For catalysts of one type the reaction rate increases with increase in the number of acid centers on the surface. Depending on the structure of the initial alkylthiophene, the yield of the unsubstituted thiophene and its lower homologs amounts to 40-90 mol % with 60-98% selectivity.

3. SYNTHESIS OF 4-METHYLTHIAZOLE

4-Methylthiazole (**11**) was obtained by the reaction of sulfur dioxide with N-methylisopropylideneimine (**12**), which is easily formed from acetone and methylamine in the presence of alkali [47, 48].



Without a catalyst with a mixture of the vapor of the imine **12** and sulfur dioxide in a stream of inert gas (350-450°C, SO₂:**12** = 1.3-1.5, gas flow rate 4 l/h) the yield of the product (**11**) does not exceed 7 mol %, but it is increased significantly in the presence of the oxides and sulfides of Fe, Cr, Mo, W, Al, and Si. The degree of conversion of compound **12** under the various conditions was 100%. The main products of the catalytic reaction are methylthiazole **11** and water. The side products are acetone, carbon disulfide, acetonitrile, carbon monoxide, carbon dioxide, hydrogen, hydrogen sulfide, elemental sulfur, and tar. The yield of the product **11** increases with increase in temperature and contact time and does not depend on the concentration of the initial imine **12**. The yield of the methylthiazole calculated on the imine at 440°C and τ = 1.8 sec at oxide catalysts amounts to 30-67 mol %.

The investigated massive catalysts can be arranged in the following order according to their specific activity [47, 48]:



$w, \mu\text{mol}/\text{m}^2 \cdot \text{h}$	480	193	190	170	90	28	14	4	3
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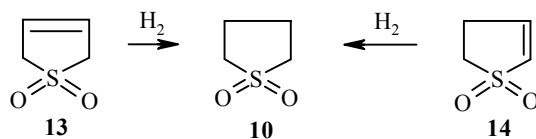
If the oxides are deposited on Al₂O₃, SiO₂, and the carbon support "Sibunit," the rate calculated for 1 m² of metal remains constant.

The activity of the catalyst varies in relation to the acid-base characteristics of its surface. In the presence of catalysts containing PC (SiO₂, H₂SO₄/SiO₂) or strong L centers (Al₂O₃, B₂O₃/Al₂O₃) the reaction rate for the formation of the product **11** does not exceed 0.5 mg/h·m². It is increased substantially (by 40-100 times) in the presence of strong basic centers conjugate with the weak L centers (e.g., CaO, MgO, potassium oxide deposited on SiO₂ and Al₂O₃) in the catalyst. It is assumed that during contact with the catalyst the imine **12** is chemisorbed at the basic centers with the participation of a hydrogen atom of the CH₃ group and of SO₂ at the L centers. The reaction between these surface forms leads to the methylthiazole **11**. Strong basic centers favor activation of the initial compound **12**. The L centers at which the SO₂ is activated must not possess great strength, since otherwise concurrent chemisorption of the initial imine **12** with participation of a nitrogen

atom will occur at these centers, leading to destruction of the N–C bond. Reaction of the catalyst with the SO₂ is accompanied by the formation of surface sulfonates and sulfates, which are not active in the synthesis of the product **11**. The maximum yield of compound **11** at 440°C with SO₂:**12** = 1.5 amounts to 64 mol % (90 wt. %). On 1 g of catalyst it is possible to obtain 3 g of the methylthiazole **11**, after which the catalyst is deactivated, but it can be regenerated by heating at 450-500°C in a stream of air [47, 48].

4. SYNTHESIS OF THIOLANE 1,1-DIOXIDE

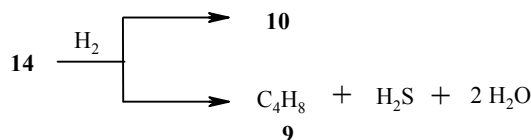
A convenient method for the synthesis of thiolane 1,1-dioxide (**10**) is catalytic liquid-phase hydrogenation of 3-thiolenene 1,1-dioxide (**13**) and 2-thiolenene 1,1-dioxide (**14**) [5].



In this process the sulfides of transition metals exhibit activity at increased temperature and hydrogen pressure [24, 49]. During the hydrogenation of thiolene dioxide **13** (100°C, *P* = 25 MPa) at the sulfides of Os, Pt, Rh, and Ru the yield of the product **10** is not greater than 1 mol %. At the sulfides of Pd and Re it is increased to 50%. The formation of the thiolane dioxide **10** is complicated by decomposition of the thermally unstable compound **13**. During hydrogenation of its more thermally stable isomer **14** (150°C, *P* = 11 MPa) at the sulfides of W, Ni, and Co the product **10** is obtained with a yield of up to 6 mol %, while at the sulfides of Re, Pt, Os, Rh, and Pd it is increased to 50-90 mol %. The specific rate of formation of the thiolane dioxide **10** from the thiolene dioxide **14** at the sulfides of Pd, Rh, and Re is significantly higher than at the sulfides of other metals [49]:

	PdS	Rh ₂ S ₃	Re ₂ S ₇	OsS ₂	PtS ₂	CoS	WS ₂	NiS
<i>w</i> , mmol/m ² ·h	3.5	2.5	1.3	0.6	0.2	0.2	0.14	0.004
<i>s</i> , %	88	90	72	88	68	86	39	46

The hydrogenation of compound **14** in the presence of metal sulfides deposited on γ-Al₂O₃ or SiO₂ takes place according to the following scheme:



The reaction rate increases in direct proportion to increase in the concentration of the initial dioxide **14** and the partial pressure of hydrogen (up to *P* = 12 MPa) but does not change at higher pressures. The reaction is limited by the reaction of the dissolved dioxide **14** with hydrogen adsorbed on the catalyst. The sulfide catalysts are stable during the hydrogenation of this compound. For example, the rate of the reaction at 1 g of catalyst PdS/Al₂O₃ does not change up to the formation of ~50 g of the product **10** [49].

Metals of group VIII are very active in the hydrogenation of the dioxides **13** and **14** (solvent alcohol, sulfolane, benzene) under mild conditions (10-30°C and *P* > 1 MPa), and the product **10** is obtained with a yield of up to 100% [50-57]. In the case of compound **13** the highest specific activity (20°C, *P* = 5 MPa) with *s* = 100% is given by rhodium and palladium and the lowest by nickel [50]:

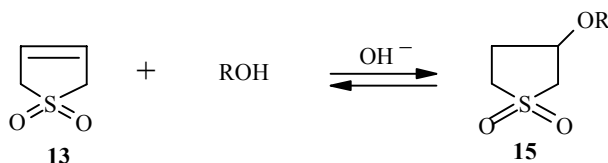
	Rh	Pd	Pt	Ir	Ru	Ni
w, mmol/h·m ²	306	92	19	2	1	0.1

If metals of group VIII are deposited on a support, their degree of dispersion is increased, and this leads to an increase in the rate of formation of thiolane 1,1-dioxide **10**. It is possible to control the degree of dispersion by changing the nature of the support (greatest dispersion is observed with deposition of the metal on γ -Al₂O₃, SiO₂, AlSi and carbon), by reducing the surface concentration of the metal, by varying the nature of the precursor, by additional chemical treatment of the sample before reduction, and by changing the heat treatment conditions. In a number of cases the degree of dispersion of the metals can be increased by adding other elements to it. It is convenient to use deposited metallic catalysts for the preparative synthesis of compound **10** [50-54]. Although the degree of dispersion of the metal decreases with increase of its content in the catalyst, up to a certain limit the total surface area of the metal increases, and the hydrogenation rate calculated on unit mass of catalyst therefore increases. The specific activity of the catalyst, i.e., the rate referred to 1 m² of metal surface, remains approximately constant with change in the degree of dispersion and hardly differs at all from the activity of the metal without a support.

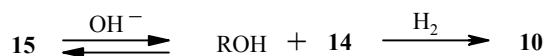
The mechanism of hydrogenation of the thiolene dioxide **13** at various metals of group VIII is similar, and identical kinetic relationships are therefore observed [53, 55]. The rate of formation of the product **10** increases in direct proportion with increase in the hydrogen pressure from 0.1 to 2 MPa and in the concentration of the oxide **13** to 0.1 M but remains unchanged with further increase of these parameters. The observed change of the reaction orders from first to zero is due to difference in the limiting stages of the reaction, which depend on the degree of coverage of the catalyst surface with the reactants with variation of the hydrogenation conditions.

Metallic catalysts are fairly stable in the hydrogenation of thiolene oxides **13** and **14**, but in a very prolonged process their initial activity is reduced. The deactivation of the catalyst is due to poisoning of the metal by the compounds of divalent and tetravalent sulfur (H₂S, SO₂, thiolane **2a**) formed in the process [21, 51, 56, 57]. Full deactivation occurs when less than 0.14 mmol of SO₂ or H₂S calculated for 1 m² of metal is added to the solution. In their specific stability, determined from the amount of the product **10** formed on 1 m² of metal (in the massive or deposited catalyst) up to its total deactivation, the metals of group VIII can be arranged in the same order according to their specific catalytic activity, i.e., the more active the catalyst in the hydrogenation of compound **13** the more consistently it functions. In this process the stability of the catalysts increases not only with increase in the accessible surface of the metal, which is achieved in various ways, but also with decrease in the hydrogenation temperature, which promotes decrease in the decomposition rate of the thiolene dioxide **13** with the release of sulfur dioxide and, consequently, decrease in the rate of formation of the toxic divalent sulfur compounds. The process is also favored by thorough purification of compound **13** from SO₂ impurities, for which purpose alkali is added to the solution for hydrogenation [58, 59]. Here the stability of the catalyst is somewhat increased, but in the presence of alkali, such as potassium hydroxide, the rate of formation of the product **10** at a palladium catalyst compared with the rate observed in a neutral medium decreases in proportion to [KOH]^{0.5}.

One of the reasons for the decrease in the activity of metallic palladium during the hydrogenation of the oxide **13** in an alkaline medium is the increase in the strength of the bond between the hydrogen and the palladium, which hinders its reaction with the oxide. The isomerization **13** → **14** takes place under the influence of a base at room temperature. However, the rate of formation of the thiolene dioxide **10** during hydrogenation of the thiolene dioxide **14** in neutral and alkaline media is close to that observed during the hydrogenation of its isomer **13**, i.e., the decrease in the rate of hydrogenation of the latter in an alkaline alcohol solution is not due to its isomerization. In addition to isomerization in an alkaline alcohol medium the alcohol adds to the double bond of compound **13** with the formation of 3-alkoxythiolane 1,1-dioxide **15**.



When the alkaline solution is heated the product **15** decomposes to the dioxide **14** and alcohol, and this process is reversible. In hydrogen in the presence of a catalyst compound **14** is hydrogenated, and the equilibrium is displaced toward the formation of the product from the elimination of alcohol.



The complete transformation **13** \rightarrow **10** takes place as a result of the reactions [60, 61]. Under the conditions of hydrogenation in an aqueous alkaline solution at 20-85°C with $P = 0.1\text{-}5$ MPa in the presence of Pd/Al₂O₃ ethers **15** substituted at position 3, such as 3-butoxythiolane 1,1-dioxide (**15a**), and higher (C₇-C₁₂) 3-alkoxythiolane 1,1-dioxides are converted into the thiolane dioxide **10**. The yield of the latter from the ether **15a** amounts to 100% after 15-42 min, while the yield from the other ethers after 2 h amounts to 18-34%. This transformation also takes place in the presence of PdS/Al₂O₃. The process is affected by the conditions under which it is conducted. Thus, the yield of the product **10** is reduced by ~10 times if the concentration of the initial **15a** in the solution is increased from 0.1 to 1.5 M. Increase in the partial pressure of hydrogen from 0.1 to 5 MPa increases the yield a little, and the process is accelerated with increase in the concentration of potassium hydroxide. The transformation rate of compound **15a** is described by the equation:

$$w = k c_1^n P^{0.2} c_2^{0.5},$$

where c_1 and c_2 are the concentrations of **15a** and KOH respectively, and P is the hydrogen pressure [59, 60]. The limiting stage in the formation of the thiolane dioxide **10** is the elimination of the alcohol and not reduction of the thiolene dioxide **14** that forms. Since both the catalytic transformation of the ether **15a** and the addition of the alcohol to the thiolene dioxide **13** occur in the presence of alkali, the two processes can be combined: Compound **15a** is first produced from the dioxide **13** and butanol and is then converted under the hydrogenation conditions, without isolation in the pure form, into the product **10** with a yield of up to 100% (100°C, $P = 5$ MPa). Under these conditions without the alkali decomposition of compound **13** mostly occurs. Compared with hydrogenation of the thiolene dioxides **13** and **14** at metals in a neutral medium the transformation of the ether **15a** in aqueous alcohol solutions takes place under harsher conditions (elevated temperature, long reaction time) and at a lower rate. In the aqueous alcohol medium the rates of formation of thiolane dioxide **10** from compounds **13**, **14**, and **15a** at Pd/Al₂O₃ and PdS/Al₂O₃ catalysts are close (Table 4), since an identical catalyst state, in which the active component is PdS, is established under these conditions [59].

During prolonged hydrogenation of the ethers **15** the employed catalysts are deactivated. Irrespective of the concentration of the substrate, with 1 g of the catalyst 0.2-0.5 g of the product **10** can be obtained at $P = 0.1$ MPa, and 50 g at $P = 5$ MPa. These differences are due to the increase of the hydrogenation rate of compound **14** compared with the isomerization rate **14** \rightarrow **13** at high pressure [59]. The presented data show that the hydrogenation of compound **13** at a palladium catalyst in the presence of additions of alkali does not have advantages over hydrogenation at metals in a neutral medium at low temperature. Combination of the metal into a complex also does not protect it from poisoning by sulfur compounds [62]. At a series of complexes of group VIII metals, for example, homogeneous and heterogeneous complexes of palladium with S- and N-containing ligands, at room temperature and atmospheric pressure the thiolene dioxides **13** and **14** are readily hydrogenated, and the yields of the thiolane amount to 100%. These complexes are not inferior to the metals in

TABLE 4. Hydrogenation of Thiolenes Oxides **13** and **14** and Transformation of the Ether **15a** at Aluminopalladium Catalysts at $P = 5$ MPa [59]

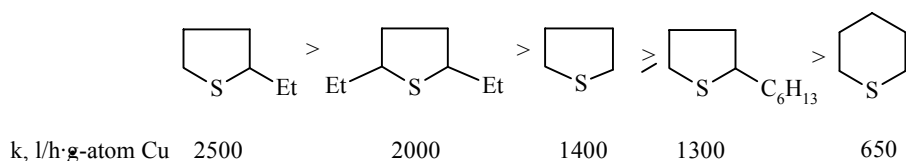
Catalyst	Solvent	Substrate	Content in initial mixture, M		$T, ^\circ\text{C}$	Rate at $x = 65\text{-}70\%$, mmol/h·g Ct
			substrate	KOH		
Pd /Al ₂ O ₃	<i>i</i> -PrOH	13	0.4	0	20	11670
		13	0.13	0	20	3750
		13	0.04	0	20	1250
		14	0.4	0	20	12840
		14	0.13	0	20	4500
		14	0.04	0	20	1500
	BuOH	13	0.53	0	85	8.3
		13	0.53	0.45	87	12.0
		14	0.60	0.45	87	12.5
		15a	0.60	0.45	87	123.3
PdS /Al ₂ O ₃	BuOH	13	0.04	0	100	0.67
		13	0.04	0.45	100	1.0
		14	0.04	0	100	0.83
		14	0.04	0.45	100	1.5
		15a	0.04	0.45	100	1.5

specific activity or even surpass them and have increased stability in the process. However, it is still not possible to prevent completely the poisoning of the metal complexes by di- and tetravalent sulfur compounds, and the rate of formation of the product **10** decreases in the course of the hydrogenation of compounds **13** and **14**. As established by investigation using UV, NMR, and XPES, the reason for the deactivation of the palladium complexes is that the sulphur poison, entering the coordination sphere of the metal, displaces the outer ligand and forms a bond between the palladium and the sulfur, and in certain cases the complex is completely destroyed.

The thiolane dioxide **10** is therefore synthesized preparatively by hydrogenation of the thiolene dioxide **13** in a neutral medium in the presence of metals of group VIII deposited on a support, which exhibit high activity and 100% selectivity under mild conditions. At the created catalyst IK-7-1 [63] the synthesis of compound **10** is realized in the liquid phase at 17-25°C at $P = 2\text{-}5$ MPa with a product yield of 100% and productivity in the kinetic region of up to 3000 g/h·g Ct. The amount of the thiolane dioxide **10** produced after complete deactivation of the catalyst amounts to 120-140 g/g of Ct. In continuously operating apparatus with a fixed layer of catalyst the yield decreases from 100 to 97% after continuous operation for 600 h, and the catalyst is then regenerated.

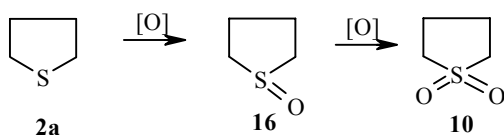
5. SYNTHESIS OF SULFOXIDES

Thiacycloalkanes, having a sulfur atom with unshared electron pairs, are activated in reaction with catalysts based on compounds of transition metals as a result of the formation of a donor–acceptor complex, which facilitates their reaction with molecular oxygen to form compounds activated at the sulfur atom [64, 65]. The most active catalysts of this reaction are compounds of divalent copper. During the oxidation of thiacycloalkane in the presence of copper chloride or *o*-aminophenolate in acetone solution with the addition 3.3 M of acetic acid at 100-130°C and $P = 5\text{-}6$ MPa after 5-30 min the sulfoxides are obtained with yields of up to 95 mol %. According to their reactivity, determined from the rate constant of the first-order reaction, the compounds can be arranged in the following order [65]:



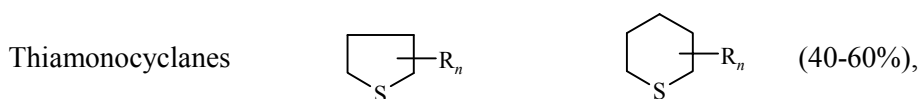
Depending on the catalyst and the compound being oxidized, the productivity with respect to the sulfoxides amounts to 350-600 mol/h·g Ct.


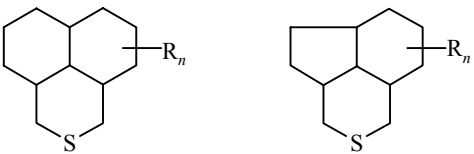
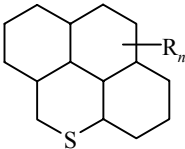
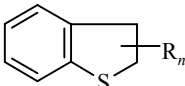
The yield of the thiolane 1-oxide (**16**) during the oxidation of the thiolane **2a** does not depend on the pressure of hydrogen in the range of 2.5-5.0 MPa; an acidic medium is favorable for the reaction. With increase in the amount of the catalyst and the duration of the reaction the yield of the product **16** increases up to a certain limit, after it decreases. The selectivity of its formation with up to 80% conversion of the initial **2a** is 100%. With higher degrees of conversion it decreases, and the sulfone **10** is found in the oxidation product. The sulfone is formed during oxidation of the pure oxide **16**. It follows from its kinetic data that the process takes place according to a consecutive scheme [65]:



In all cases the overall selectivity of the formation of compounds **16** and **10** is 100%. The high selectivity with respect to the sulfoxides and sulfones is due to the fact that oxidation takes place through the stage of single-electron transfer without cleavage of the C-S bond. During contact with the copper catalyst the radical-cation $(\text{CH}_2)_4\text{S}^+$ is formed. This is transformed in the oxidizing medium into the peroxide $(\text{CH}_2)_4\text{S}^+\text{OO}^-$, which reacts with the initial thiolane **2a** with the formation of the sulfoxide **16**. The latter is then oxidized to the sulfone **10** by an analogous mechanism. The copper ion, reduced as a result of complex formation, is reoxidized by oxygen. By the action of thiolanes the divalent copper ion can be reduced to Cu^+ and Cu^0 , and the Cu^0 is reoxidized by oxygen with difficulty. The acetone used as solvent prevents strong reduction of the copper. It forms a $\text{Cu}^{2+}-\text{Cu}^+$ cluster, and the presence of the Cu^{2+} ion (which is required for the activation of the sulfide sulfur) and the Cu^+ ion (which activates the molecular oxygen) and also the total homogenization of the system on account of the dissolution of the copper complex with the substrate and the reaction products in acetone secure a high rate of formation of the sulfoxide **16** and sulfone **10**. The lower rate of formation of the sulfone is explained by the more difficult activation of the sulfoxide as a result of the reduced donor capacity of the sulfur atom and also on account of the fact that the sulfoxide molecule is partly coordinated with the catalyst at the oxygen atom of the SO_2 group and not at the sulfur atom. Increase in the acidity of the reaction medium reduces the rate of oxidation of the sulfoxide to the sulfone on account of the formation of the stable complex $(\text{CH}_2)_4\text{SO}-\text{H}$. This hinders the coordination of the sulfoxide with the Cu^{2+} , and this is essential for its oxidation to the sulfone [66].

Compounds of copper(II) in acetone solution also accelerate the partial oxidation of a natural mixture of thiacyclanes by atmospheric oxygen [67, 68]. In the middle-distillate fractions of a series of Siberian and Volga oils (e.g., Arlansk, Zapadno-Surgutsk, Samotlor) the main fraction of the sulfur compounds (80-90%) consists of the so-called "petroleum sulfides" (PS):



Thiabicyclanes		(10-20%),
Thiatriacyclanes		(4-8%),
Thiatetracyclanes		(0-1.5%),
Thiaindanes		(1.5-2.5%),

where R = C₁-C₇ alkyl, located at various carbon atoms; the average degree of substitution (*n*) is close to 3.

Various compounds of divalent sulfur (the chloride, phenolate, *p*-cresolate, α -naphtholate, *o*- and *p*-aminophenolates, acetate, phthalate, benzoate) are active in the oxidation of petroleum sulfides to sulfoxides. The most active are CuCl₂ and copper-phenolate catalysts. The reaction takes place at 120-150°C and *P* = 5-6 MPa with the addition of 0.4 M of acetic acid and sulfur concentrations of 0.25-0.40 M. The yield of the sulfoxides here reaches 95 mol %. The kinetic relationships for the oxidation of the petroleum sulfides are completely analogous with those established for the oxidation of the individual thiacycloalkanes. Irrespective of the nature of the catalyst and the oxidation conditions (temperature, reaction time, concentrations of catalyst and acid) with up to 80% conversion of the petroleum sulfides the selectivity of formation of the sulfoxides is close to 100%. With higher degrees of conversion it decreases, since the sulfoxides undergo further transformation to sulfones and sulfonic acids. The petroleum sulfides of various oils have similar reactivity in partial oxidation. Thus, at 130°C with *P* = 5 MPa, reaction time 20 min, and [Ct] = 7-7.9 mg-atom Cu/l the yield of the sulfoxides amounted to 90-100% during the oxidation of diesel fuel from the Arlansk oil and the concentrates isolated from it (bp 190-260, 260-360, 190-360°C) and also the concentrates of the petroleum sulfides produced from the West-Siberian and Samotlor oils. The reaction rate constant, determined with less than 70% conversion of the petroleum sulfide, varies in the range of 900-1100 l/h·g-atom Cu, and the productivity in the petroleum sulfoxides amounts to about 250±60 mol/h·g-atom Cu [67, 68]. Since the presence of thiophenes and hydrocarbons in the raw material has little effect on the oxidizability of the petroleum sulfides [69], it is possible to obtain petroleum sulfoxides by direct oxidation of the fuel without extracting the sulfur compounds from it.

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